Alfred Bader

Aldrich

Aldrichimica Acta

Volume 12, Number 1, 1979

Boranes for Organic Reductions. **See Page 3.**
Trialkylborohydrides in Organometallic Syntheses. **See Page 13.**

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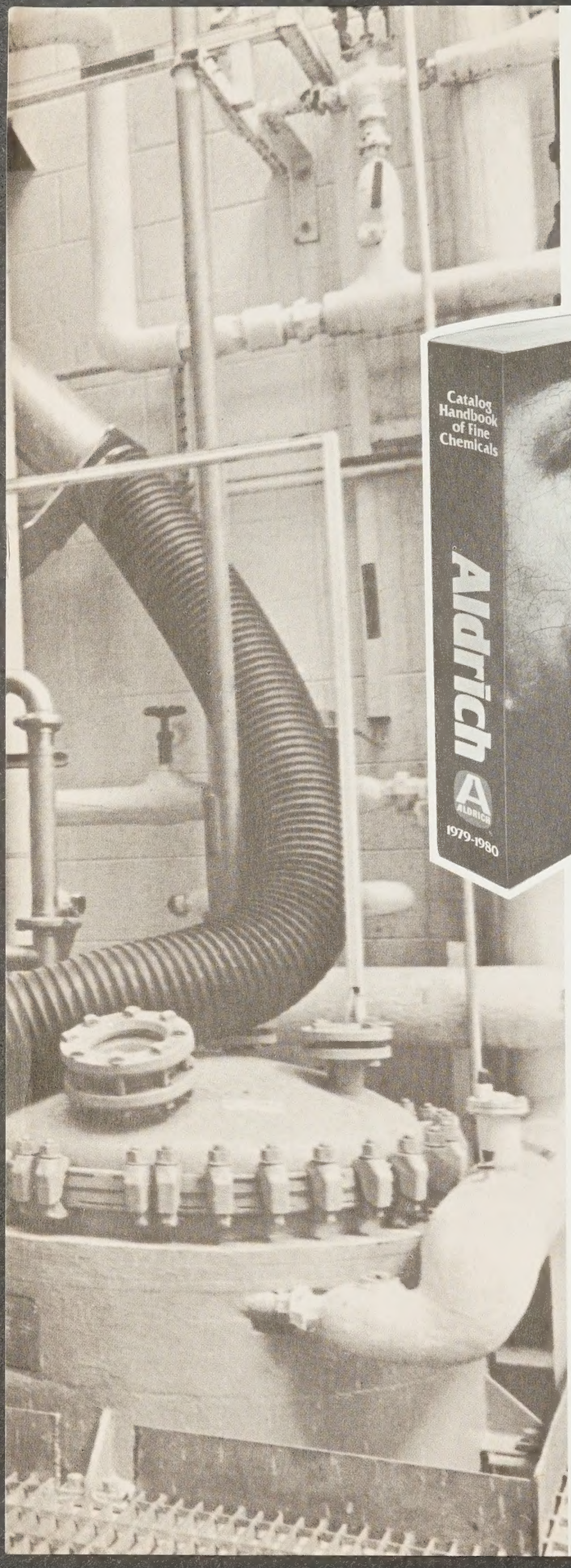

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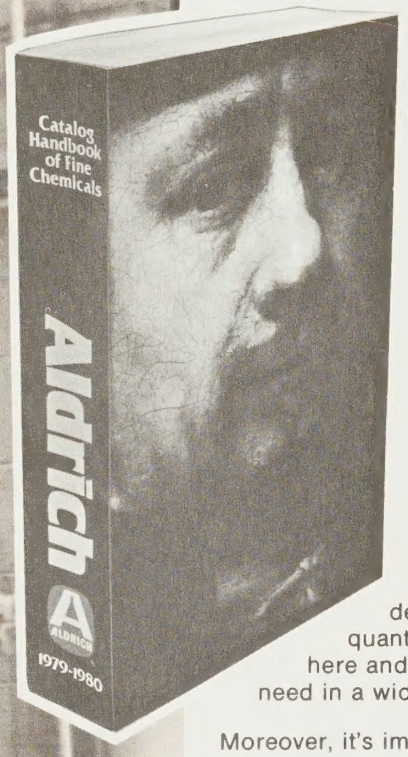
...when you think of Aldrich



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Aldrichimica Acta

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About Our Cover:

When our chemist-collector first saw this interesting study (oil on paper, mounted on wood, 14-$^1/_4$ x 15-$^1/_2$ inches), it was attributed to Jacob Jordaens, a Flemish contemporary of Rubens. Our chemist doubts this attribution, and even doubts that it is by an artist from Northern Europe. Rather, he thinks it is Bolognese, *ca.* 1600, by Annibale Caracci or an artist closely associated with him.

To us, this work seemed particularly fitting for the cover of the Acta which bears a summary of the work of Professor Herbert C. Brown and shows Aldrich's contribution to teaching the art and the science of hydroboration. For obviously, here is a young and dedicated teacher explaining an intriguing problem to his alert student. One of Professor Brown's great strengths is his ability as a teacher. As one of his associates put it, "Professor Brown inspires confidence in his students that they can solve problems systematically." We can almost hear Professor Brown say, "It's very simple," and proceed with a clear explanation. His counselling is best on an individual basis — teacher to student — just as depicted in our painting.

This is also how we envisioned our role when we created Aldrich-Boranes. The brilliance of Professor Brown's work in hydroboration had been recognized for many years, but the application of the process was not widespread. It was considered dangerous, and many of the requisite reagents and specialized equipment were not readily available. Aldrich takes pride in its role as teacher and supplier of the tools of the hydroboration technique. And we do our best to treat each of our customers on an individual basis. We are chemists helping chemists.

Are you interested in our Acta Covers? *Selections from the Bader Collection*, with 30 duotone reproductions, many of previous Acta covers, and an introduction by Professor Wolfgang Stechow is available to all chemist art-lovers.

Z10,118-4 $6.00

Also, many paintings reproduced on our Acta covers were shown at the Milwaukee Art Center in an exhibition, "The Bible Through Dutch Eyes," arranged by Dr. Bader in 1976. The fully illustrated catalog with 66 black-and-white and 4 full-color reproductions contains many art historical and Biblical comments.

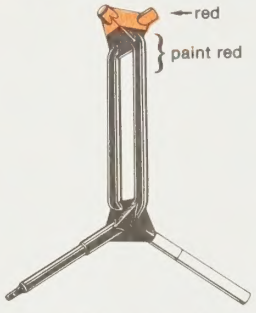
Z10,374-8 $10.00

Many of the early issues of the *Aldrichimica Acta* have become very rare. Please do not throw your issues away. In time, we believe that complete sets will become valuable, and — if you do not want to keep them — there probably are chemists near you who would be interested.

Lab Notes

For years I used the Fieser Molecular Models now supplied by you. I feel they are probably the best models for class demonstration. However, there is one feature that I have had to change to meet my needs: no carbonyl.

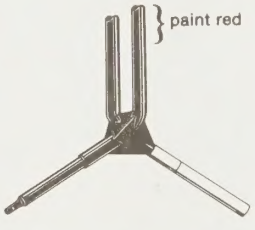
I make a carbonyl by breaking apart a C=C at a "joint" then gluing on the red oxygen piece. I remove the aluminum bonding tube and cut off the long, red bonding projection. This piece is dissolved



in methylene chloride to paint over some of the black of my new carbonyl to enhance the red color on that end.

James W. Hill
Professor of Chemistry
Panhandle State University
Goodwell, OK 73939

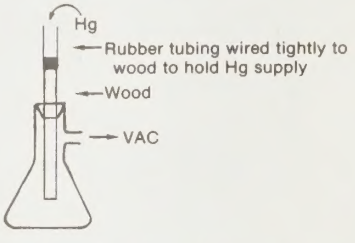
Editor's Note: Various modifications of the Fieser molecular models to give other functional groups are discussed by Prof. Fieser in *J. Chem Educ.*, **42**, 408 (1965). Prof. Fieser recommended cutting a double bond into two to produce two carbonyl groups.



A carbonyl model may also be contructed by following Fieser's directions for a carbonium ion. The resulting planar structure resembles a Dreiding carbonyl model if one arm is painted red.

Frequently a laboratory worker wishes to clean some mercury for purposes such as filling manometers, McLeod gauges, etc. Although a preliminary cleaning may be achieved by allowing the mercury to trickle through a pin hole in a piece of filter paper shaped into a cone, this method is often time-consuming and does not remove all impurities.

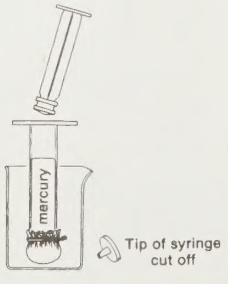
A preferable technique with respect to both speed and cleanliness is to draw the mercury through the pores of a piece of wood (a 6-in. section of a broomstick works well) using an arrangement similar to that shown in the diagram.



The mercury cleaned in this manner can be used for all purposes except those requiring the purity achieved with triple distillation.

Arden P. Zipp
Chairman & Professor
Chemistry Department
State University of New York
College at Cortland
Cortland, New York 13045

Mercury may be cleaned and dried by forcing it through a piece of chamois. Cut off the end of a 10- or 20-cc plastic hypodermic syringe and slightly flare the end of the barrel. Firmly tie a small piece of chamois over the barrel, using Nichrome or Chromel wire. Remove the plunger, pour in the mercury, replace the plunger and force the mercury slowly through the chamois. Hold the syringe near the bottom of a small beaker, as extremely fine jets of mercury squirt in all directions. The residue can be shaken out of the syringe. This device is inexpensive, very effective, and will last for years.



William D. Murray
Environmental Engineer
AMP Inc.
Harrisburg, PA 17105

Any interesting shortcut or laboratory hint you'd like to share with ACTA readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome red and white ceramic Aldrich coffee mug as well as a copy of **Selections from the Bader Collection** *(see "About Our Cover"). We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Ayesha Bader.

Dr. Dieter M. Kramsch of the Boston University School of Medicine called me recently to ask whether we could lower our price substantially for 5-methyl-2-thiophenecarboxylic acid in large quantities. Dr. Kramsch and his associates have found[1] that this acid prevents hardening of the arteries in rabbits. They now want to study this effect in monkeys and, of course, need larger amounts. We had been making small quantities only, but our preparation could be scaled up. Naturally, we wanted to help, particularly in an application that might become so important. Hence we quoted much lower prices for kilo quantities, received the order and filled it rapidly.

It was no bother at all, just a pleasure to be able to help.

1) C.T. Chan, H. Wells, and D.M. Kramsch, *Circulation Res.*, **43**, 115 (1978).

M8,442-9 5-Methyl-2-thiophenecarboxylic acid, 99% **10g $25.35**
Kilo: Inquire

Diels-Alder Chemistry

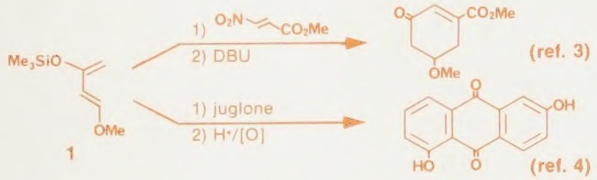
Four Dienes and Two Dienophiles

It has been about fifty years[1] since O. Diels and K. Alder described the reaction of cyclopentadiene with *p*-benzoquinone and elucidated the structure of the resulting 1:1 adduct. Since that time, the Diels-Alder reaction has become an indispensable part of the organic chemist's repertoire of synthetic methodology.[2]

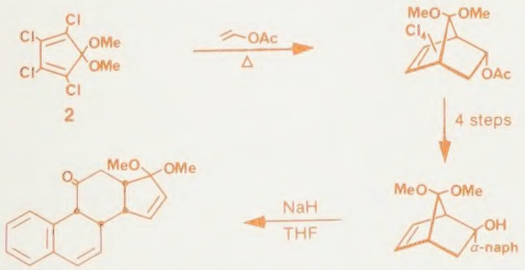
Aldrich offers a wide variety of new and classical Diels-Alder reagents, a few of which are described below:

Dienes

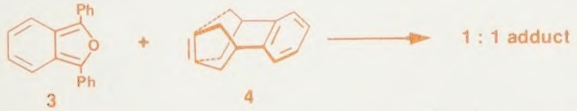
The regiospecific nature of cycloadditions involving **1-methoxy-3-trimethylsilyloxy-1,3-butadiene** (**1**, "Danishefsky's diene"[5]) has made it useful for the construction of highly functionalized cyclohexenones. Recently, **1**, has been employed for the synthesis of the natural products prephenic acid (disodium salt)[6] and *dl*-pentalenolactone.[7]



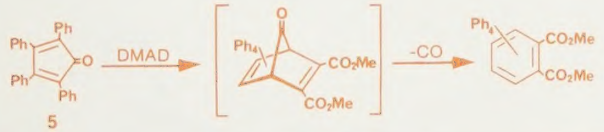
5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (**2**) has figured recently in an interesting steroid synthesis[8] (shown) and in a useful three-carbon annulation process.[9]



1,3-Diphenylisobenzofuran (**3**) has been used to trap the highly distorted olefin **4**.[10]

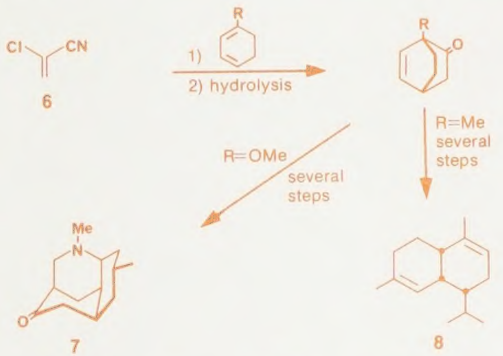


Fieser has employed the reaction of **tetraphenylcyclopentadienone** (**5**, "tetracyclone") with dimethyl acetylenedicarboxylate (DMAD) in an extensive study[11] of the suitability of various solvents for the Diels-Alder reaction.

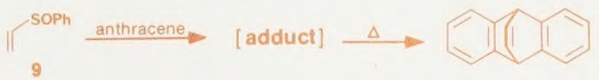


Dienophiles

2-Chloroacrylonitrile (**6**) serves as a Diels-Alder *ketene equivalent* for the construction of carbocyclic frameworks in natural product synthesis. The syntheses of (±)-luciduline (**7**)[12] and (±)-α-amorphene (**8**)[13] are shown as examples.



The use of **phenyl vinyl sulfoxide** (**9**) as an *acetylene equivalent* in Diels-Alder cycloadditions has been reported recently.[14]



Four dienes and two dienophiles from Aldrich; [4+2] from Diels and Alder. An unbeatable combination!

References:

1) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **460**, 98 (1928).
2) For a list of reviews of various aspects of the Diels-Alder reaction, see J. March, "Advanced Organic Chemistry," 2nd edition, 1977, McGraw-Hill, Inc., New York, N.Y., pp 761-765, refs. 581-607 cited therein.
3) S. Danishefsky, M.P. Prisbylla, and S. Hiner, *J. Am. Chem. Soc.*, **100**, 2918 (1978).
4) R.K. Boeckman, Jr., T.M. Dolak, and K.O. Culos, *ibid.*, **100**, 7098 (1978).
5) S. Danishefsky and T. Kitahara, *ibid.*, **96**, 7807 (1974).
6) S. Danishefsky and M. Hirama, *ibid.*, **99**, 7740 (1977).
7) S. Danishefsky, *et al.*, *ibid.*, **100**, 6536 (1978).
8) M.E. Jung and J.P. Hudspeth, *ibid.*, **100**, 4309 (1978).
9) M.E. Jung and J.P. Hudspeth, *ibid.*, **99**, 5508 (1977).
10) R. Greenhouse, *et al.*, *ibid.*, **99**, 1664 (1977).
11) L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, 1967, John Wiley & Sons, Inc., New York, N.Y., pp 236-241.
12) W.L. Scott and D.A. Evans, *J. Am. Chem. Soc.*, **94**, 4779 (1972).
13) R.P. Gregson and R.N. Mirrington, *Chem. Commun.*, 598 (1973).
14) L.A. Paquette, *et al.*, *J. Am. Chem. Soc.*, **100**, 1597 (1978).

21,283-0	**1-Methoxy-3-trimethylsilyloxy-1,3-butadiene,** 90% (Danishefsky's diene)	**1g $4.50; 5g $14.00**
20,098-0	**5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene**	**25g $20.00**
10,548-1	**1,3-Diphenylisobenzofuran**	**1g $7.50; 5g $21.00**
T2,580-1	**Tetraphenylcyclopentadienone** (tetracyclone)	**25g $14.15; 100g $47.00**
C2,236-9	**2-Chloroacrylonitrile**	**100g $7.00; 500g $28.00**
21,330-6	**Phenyl vinyl sulfoxide**	**5g $6.00; 25g $20.00**

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Our reputation as chemists helping chemists in research and industry has grown, we think, because of our sensitivity to new needs. For example, we have learned that quality inorganic reagents, such as those described by Fieser and Fieser in *Reagents for Organic Synthesis,* are often critical to organic applications. Consequently you can expect to find more and more inorganic chemicals in the Aldrich Catalog/-Handbook.

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Volume 12, Number 2, 1979

Spin Trapping. See page 23.
A Businessman's Look at PMN. See page 35.

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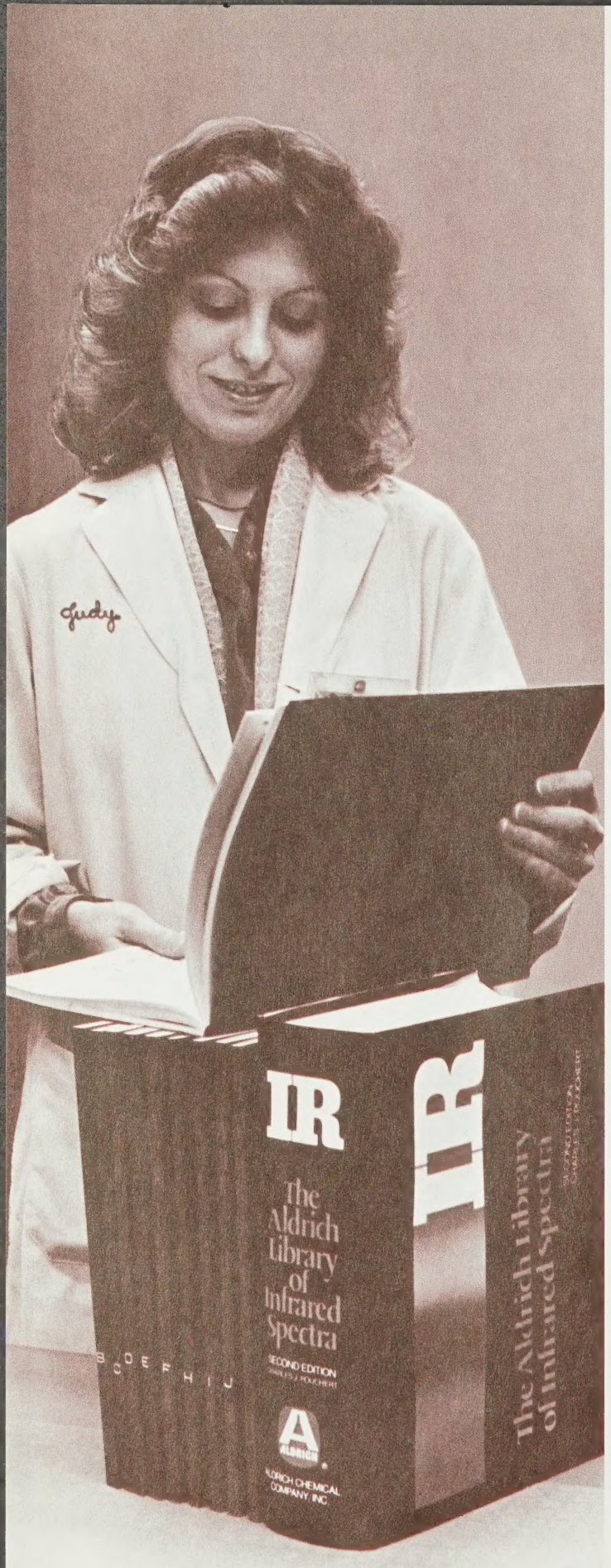

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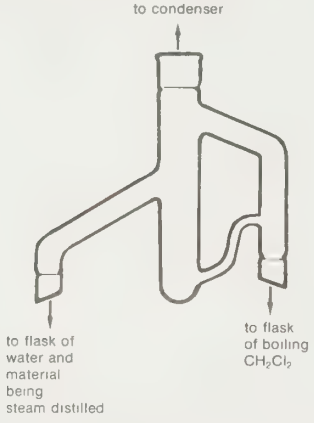
About Our Cover:

Unlike many works bought by our chemist-collector, this painting (oil on canvas, 40 x 50 inches) poses no problems of authorship or iconography; it was signed and dated 1629 by Jan Pynas, and the subject is not in doubt: 'Potiphar's Wife Accusing Joseph.' Jan Pynas was one of a group of artists known as the 'Pre-Rembrandtist' and his works are rare; only about fifteen works are known for certain, and of these only one other is in the United States.

What surprised us was that our chemist bought another work depicting Joseph, one of his least likeable heroes in the Bible. Our chemist is fond of quoting Maurice Samuel who wrote that Joseph's only good *personal* deed ever was to resist the advances of Potiphar's wife, and to be undersexed is not sufficient to be considered a truly good person. Why then, we asked our chemist, did he buy this work? Only because of its quality. It is beautiful in color — light pinks and greens and a sheer white in Joseph's robe — and so telling in its psychological insights: Potiphar is obviously in doubt, and so is his wife!

Lab Notes

Steam distillation of a compound of low volatility requires condensation of a large volume of water; this normally makes isolation of the desired compound, by extraction or filtration, tedious.



The arrangement shown[1] obviates the need to collect a large volume of water. The compound steam-distills into the condenser where it undergoes continuous extraction by dichloromethane.[2] A progressively more concentrated solution of the compound accumulates in the CH_2Cl_2 flask; this solution is simply run through a small cotton-wool plug and evaporated[3] leaving the desired material.

With this device we concentrated into about 200ml of CH_2Cl_2 a quantity of 1,5-dibenzocyclooctadiene that would have required filtration from tens of liters of water.[4]

References:

1) This device was designed by Dr. A.C. Mackey, then a graduate student at the University of Toronto.
2) CH_2Cl_2 is the only common heavier-than-water organic solvent that seems to be noncarcinogenic and nontoxic: *Chemical and Engineering News*, July 24, 1978, p 7.
3) E. Lewars, *Aldrichimica Acta*, **8**, 38 (1975).
4) P. Yates, E.G. Lewars, and P.H. McCabe, *Can. J. Chem.*, **48**, 788 (1970).

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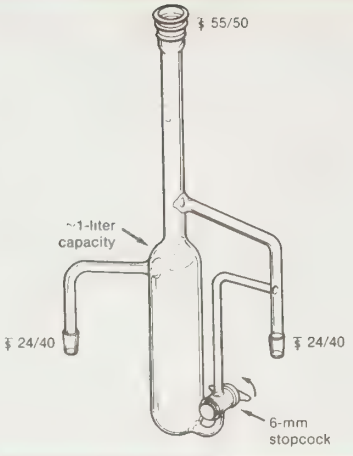
Peterborough, Ontario K9J 7B8
Canada

Editor's note:

We have found this continuous steam distillation/extraction apparatus quite useful, so as a service to chemists who may have need for it, we offer the device shown below, accompanied by an instruction sheet.

Z10,408-6
Continuous steam distillation/extraction apparatus **$155.00**

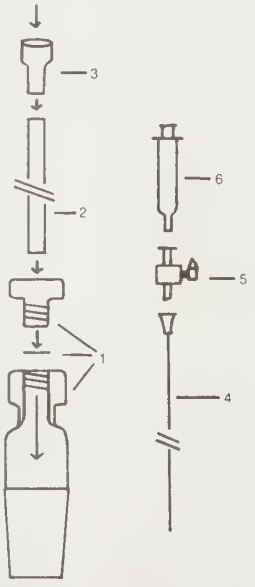


The accompanying drawing details an apparatus which we use to sample a reaction in progress without interruption of the reaction, or if run under inert atmosphere, without introduction of air.

The arrangement is particularly suitable for use with high-temperature reactions where hot organic solvents would attack a septum cap attached directly to the flask *via* a sidearm or adapter.

By attaching the septum cap to a Pyrex glass tube and inserting this into the adapter (as one would a thermometer), the tube, which now extends out from the pot, acts as an air-cooled condenser, protecting the septum.

The needle is then inserted through the septum cap and manipulated to allow sample removal. After a sample has been taken the needle is withdrawn from the solution and the luer-lock is closed to allow syringe removal without admitting air to the pot.



(1) Thermometer adapter assembly
(2) Pyrex glass tube of appropriate length and diameter
(3) Septum cap
(4) Heavy-gauge needle of appropriate length
(5) Luer-lock
(6) Syringe of appropriate volume

In taking successive samples, the syringe must be "pumped" several times to flush traces of the previous sample from the syringe and needle.

Michael D. Tufano
Corporate Research Laboratories
UOP Incorporated
Des Plaines, IL 60016

Editor's note:

This sampling assembly is easily constructed from materials normally available in the laboratory. To chemists who would make use of the described assembly frequently, we recommend Aldrich's septum-inlet adapter with Teflon stopcock.

Cat. No.	⅘	Price
Z10,228-8	14/20	$21.60
Z10,136-2	19/22	23.40
Z10,137-0	24/40	25.80

Cont'd on page 36

"Please Bother Us."

by

Recently Dr. Colin F. Chignell, the chief of the Laboratory of Environmental Biophysics at the N.I.H. suggested that we offer α-(4-pyridyl 1-oxide)-*N*-*tert*-butylnitrone (4-POBN), a new spin trap uniquely useful for the identification of hydroxyl radicals in solution, reported by Janzen *et al.*, *J. Am. Chem. Soc.*, **100**, 2923 (1978). Unfortunately, Professor Janzen's method of preparation given in a footnote of that communication to the editor, is very sketchy. Well, when a compound as interesting as 4-POBN is suggested to us, we don't let lack of experimental details deter us — and we have now made it.

It was no bother at all, just a pleasure to be able to help.

21,543-0 **α-(4-Pyridyl 1-oxide)-*N*-*tert*-butylnitrone** (4-POBN)
100mg $6.00; 1g $30.00

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Low-cost Molecular Models — designed by Professor Louis F. Fieser.[1-4] The models consist of sturdy, color-coded plastic and aluminum parts which snap together to form bonds. They are easily assembled and handled, and may be disassembled for repeated use.

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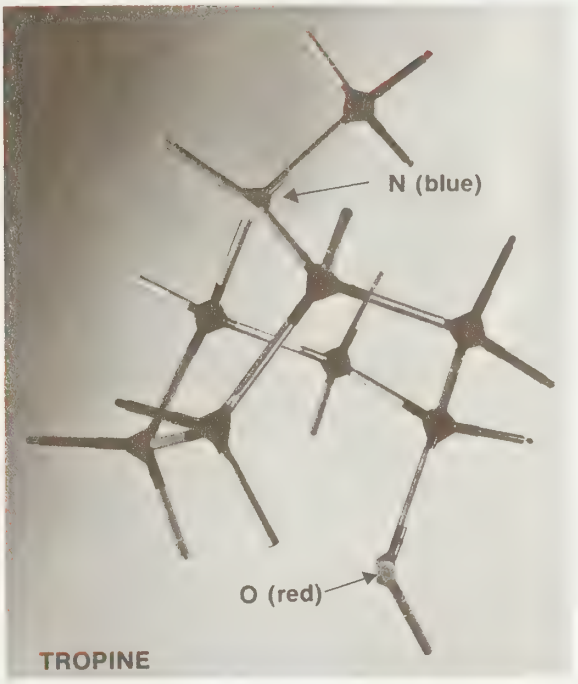
References:

(1) L.F. Fieser, *J. Chem. Ed.*, **40**, 62 (1963).
(2) L.F. Fieser, *ibid.*, **40**, 457 (1963).
(3) L.F. Fieser, *ibid.*, **42**, 408 (1965).
(4) L.F. Fieser, "Chemistry in Three Dimensions," Aldrich Catalog Number Z10,160-5.



Each kit consists of the following pieces:

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Chemistry Departments may wish to purchase quantities of atomic models to sell individually where the research kit proves too small. Hence, we also offer each atomic model in lots of 100.

Z10,401-9 100 carbon atoms (black) **$37.95**

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Z10,403-5 100 oxygen (or sulfur) atoms (red) **$19.35**

Z10,404-3 100 nitrogen atoms (blue) **$29.25**

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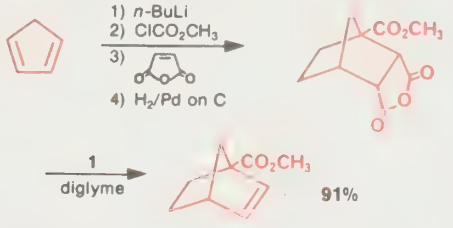
Homogeneous Catalysts

Organometallic catalysts have become important tools in synthetic organic chemistry. Aldrich offers several exciting catalysts at competitive prices.

Dicarbonylbis(triphenylphosphine)nickel(0) $[(Ph_3P)_2Ni(CO)_2]$, **1**, has been used extensively for a wide variety of synthetic transformations. The novel oxidative bisdecarboxylation technique of Trost and Chen[1] was extended recently by Grunewald and Davis to provide a convenient synthesis of bridgehead-substituted norbornenes:[2]



91%

Symmetrical alkyl ketones have been prepared in modest yields using **1**.[3]

40%

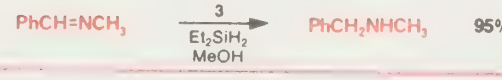
Other uses include hydrosilylation of dienes,[4] amination of aryl halides,[5] and cycloaddition.[6]

A wealth of literature dealing with Wilkinson's catalyst, **chlorotris(triphenylphosphine)rhodium(I)** $[(Ph_3P)_3RhCl]$, **2**, has been generated in recent years, including studies of stereospecific hydrogenation of allenes[7] and the effects of Lewis acids on rates of hydrogenation.[8] Many references recommend purification of "commercial $(Ph_3P)_3RhCl$";[8] therefore, Aldrich offers, at 99.99% purity, Wilkinson's catalyst as well as Vaska's catalyst $[(Ph_3P)_2Ir(CO)Cl]$ and its rhodium analog, $(Ph_3P)_2Rh(CO)Cl$, **3**.

Oxidations of 3-(trimethylsilyl)cycloalkenes have been catalyzed by **2** in good yields;[9] for example:

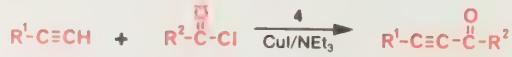
83%

Both **2** and **3** catalyze the reduction of Schiff bases by hydrosilylation.[10]

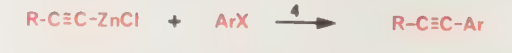


95%

Dichlorobis(triphenylphosphine)palladium(II) $[(Ph_3P)_2PdCl_2]$, **4**, was used recently for a general synthesis of α-alkynyl ketones and α-alkynamides.[11]



Arylalkynes have been prepared by the reaction of alkynylzinc reagents with aryl halides, catalyzed by **4**.[12]



In view of the wide application of rhodium(I) catalysts, Aldrich has included, among recent listings, 99% (min.) grades of $[Rh(CO)_2Cl]_2$, $[Rh(C_2H_4)_2Cl]_2$ and $(Ph_3P)_2Rh(CO)Cl$.

For new catalysts and reagents, it pays to think Aldrich first!

References:

1) B.M. Trost and F. Chen, *Tetrahedron Lett.*, 2603 (1971).
2) G.L. Grunewald and D.P. Davis, *J. Org. Chem.*, **43**, 3074 (1978).
3) T.C. Flood and A. Sarhangi, *Tetrahedron Lett.*, 3861 (1977).
4) M. Capka, P. Svoboda, J. Hetflejs, V. Bazant, P. Bazant, V. Bazantova, and J. Bazant, U.S. Patent 3,907,850; *Chem. Abstr.*, **84**, 44344d (1976).
5) R. Cramer and D.R. Coulsen, *J. Org. Chem.*, **40**, 2267 (1975).
6) P.W. Jennings, G.E. Voecks, and D.G. Pillsbury, *ibid.*, **40**, 260 (1975).
7) S. Siegel and G. Perot, *Chem. Commun.*, 114 (1978).
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9) J.M. Reuter, A. Sinha, and R.G. Salomon, *J. Org. Chem.*, **43**, 2438 (1978).
10) I. Ojima, T. Kogure, and Y. Nagai, *Tetrahedron Lett.*, 2475 (1973).
11) Y.Tohda, K. Sonogashira, and N. Hagihara, *Synthesis*, 777 (1977).
12) A.O. King, E. Negishi, F.J. Villani, Jr., and A. Silveira, Jr., *J. Org. Chem.*, **43**, 358 (1978).

21,393-4	**$(Ph_3P)_2Ni(CO)_2$**	**10g $16.00; 50g $59.00**
19,998-2	**$(Ph_3P)_3RhCl$ (Wilkinson's catalyst)**	**1g $15.00; 5g $63.00**
20,503-6	**$(Ph_3P)_3RhCl$, 99.99%**	**1g $27.50; 5g $110.00**
20,348-3	**$(Ph_3P)_2Ir(CO)Cl$, 99.99% (Vaska's catalyst)**	**1g $35.00**
21,464-7	**$(Ph_3P)_2Rh(CO)Cl$**	**1g $23.00; 5g $80.00**
20,424-2	**$(Ph_3P)_2Rh(CO)Cl$, 99.99%**	**1g $27.50 5g $110.00**
20,867-1	**$(Ph_3P)_2PdCl_2$**	**1g $16.50; 5g $61.00**
20,903-1	**$[Rh(CO)_2Cl]_2$**	**1g $42.00**
20,902-3	**$[Rh(C_2H_4)_2Cl]_2$**	**1g $41.00**
20,554-0	**Copper(I) iodide, 98%**	**250g $17.50; 1kg $54.00**

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Aldrichimica Acta

Volume 12, Number 3, 1979

New Synthetic Reagents and Reactions. **See page 43.**

Choosing and Using Noble Metal Hydrogenation Catalysts. **See page 53.**

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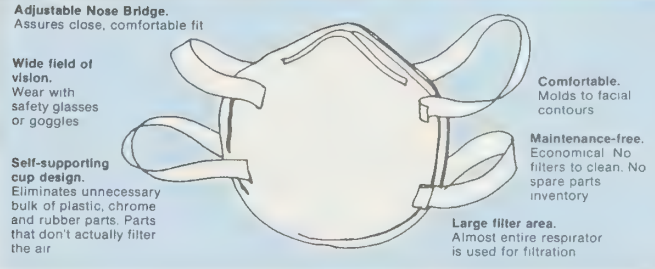

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About Our Cover:

When we first looked at the painting reproduced on our cover, we were reminded of what we had written about another Acta cover (Volume 8, Number 4, 1975) and we were happy that our chemist-collector did not limit himself to one painting per subject.

"The Bible is the book of dreams, par excellence: dreams of individuals, dreams of a people, dreams of all mankind. It is surely no accident that the very first well known dream in the Bible is not that of a king or of a general but of a man at the lowest point in his life — homeless and hunted, yearning for God's promise that He would return him to his country.

The vision of a ladder with angels going up and down on it is unique in Biblical imagery, and so *Jacob's Dream* has aroused artists' imagination for centuries." This depiction (oil on canvas, 29 x 33$^1/_2$ inches) by Abraham Bloemaert, *ca.* 1620, was purchased in an antique store in The Hague where it was thought to be of a mythological subject, and painted in the nineteenth century. In fact, much of the extensive overpaint was nineteenth century, and it took careful restoration to bring out its original beauty. If only our chemist could find a good many more such dreams of paintings.

This painting and those on five other Acta covers are among twenty-four Dutch and Flemish paintings in an exhibition in honor of Professor Anna Harrison, past-president of the American Chemical Society, held at the Art Museum, Mount Holyoke College this autumn. If you would like the fully illustrated catalog please send your check for $3.00 to the Art Museum, Mount Holyoke College, South Hadley, MA 01075, and you will receive the catalog postpaid.

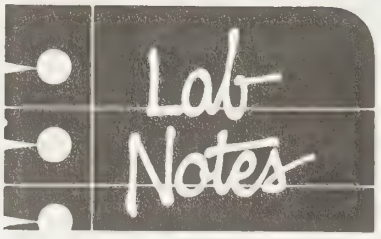
Are you interested in our Acta covers? *Selections from the Bader Collection*, with 30 duotone reproductions, many of previous Acta covers, and an introduction by Professor Wolfgang Stechow is available to all chemist art-lovers.

Z10,118-4 $6.00

Also, many paintings reproduced on our Acta covers were shown at the Milwaukee Art Center in an exhibition, "The Bible Through Dutch Eyes," arranged by Dr. Bader in 1976. The fully illustrated catalog with 66 black-and-white and 4 full-color reproductions contains many art historical and Biblical comments.

Z10,374-8 $10.00

Many of the early issues of the *Aldrichimica Acta* have become very rare. Please do not throw your issues away. In time, we believe that complete sets will become valuable, and — if you do not want to keep them — there probably are chemists near you who would be interested.



There are many instances where it is difficult to prevent charcoal from passing through a filter bed prepared from many of the commonly used filter aids. This is particularly true, for example, when DMF is used as a solvent for a catalytic reduction with Pt or Pd on charcoal. In such cases, the use of a bed of magnesium sulfate (anhydrous reagent powder) helps overcome this difficulty.

Jules Freedman, Ph.D.
Organic Chemistry Department
Merrell Research Center
110 Amity Road
Cincinnati, Ohio 45215

A common problem is the vacuum filtration of products from hot, highly acidic solutions. It always seems that the filtration is 90% complete and then the filter paper disintegrates. Hot, highly caustic solutions and/or slurries are equally hard to handle. A convenient solution to this problem is to use polypropylene filter cloth. Impervious to most mineral acids and strong bases, it is easily cut with a pair of scissors into any size using the appropriate-size filter paper as a model. It is insoluble in almost all organic solvents, and therefore can be used again and again. A bed of Filter-Cel® or Dicalite® on the cloth works beautifully in clarifying solutions with activated charcoal. The cloth can be easily cleaned by washing or even boiling in a solvent like acetone.

Henry C. Koppel
Vice President, Production
Aldrich Chemical Company

Editor's Note:
For the convenience of our customers, Aldrich offers this filter cloth.

Z10,425-6 Polypropylene filter cloth, 94cm wide 1 meter $5.25
5 meters $21.00

The Kuderna-Danish concentrator suffers from the disadvantage that the ground-glass joint between the evaporator flask and receiver tube represents a potential contamination site. Unless grease, a chemical spray coating (*e.g.*, Teflon®) or a Teflon sleeve is used to render the joint watertight, water vapor seeps in depositing chlorides and other salts. Both grease and chemical coatings themselves represent contaminants since they dissolve in certain organic solvents, and Teflon sleeves often leak and collect contaminants. This note describes a modification to the Kuderna-Danish concentrator which does away with the outside ground-glass joint between receiver tube and flask.

The modified apparatus is illustrated in Figure 1. Instead of being detachable the receiver tube is now physically joined to the evaporator flask and contains a ground-glass joint inside the tube using a Quickfit socket and cup piece. When the solution has been concentrated to a small enough volume to be contained in the receiver tube (usually about 4ml) the Snyder column is removed and a micro-Snyder column with an extension tube if necessary, is lowered through the top of the evaporator flask and inserted into the ground-glass joint leading to the receiver tube. Concentration of the solution is continued until the desired volume is obtained. Alternatively, the final concentration can be performed under reduced pressure or using a stream of nitrogen. The final concentrate is removed by pipette and either injected directly into the gas chromatograph or transferred for the next step, *e.g.*, the clean-up stage in pesticide residue analysis.

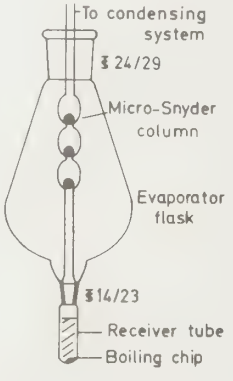


Fig. 1. Modified Kuderna-Danish concentrator showing the position of the micro-Snyder column for the final stage of the concentration process.

Apart from obviating the need for an outside joint between the receiver tube and evaporator flask the modification has another advantage. The micro-Snyder column, being enclosed completely by the evaporator flask, can operate more efficiently especially if the flask is evacuated by use of an adapter with vacuum take-off and outlet (*e.g.*, Quickfit plastic screwcap-type) for the top of the Snyder column placed at the outlet from the flask. Improving the efficiency of fractional distillation at this stage is vital if pesticides are not to be lost in the process.

R.D. Davies
Fuel Research Institute
P.O. Box 217
Pretoria, South Africa

The reciprocating motor supplied as part of the Aldrich Kugelrohr Distillation Apparatus (Cat. No. Z10,046-3) makes an extremely useful substitute for a conventional rotary motor used to drive the paddle stirrer in a reaction flask. Since the oscillating motor is either air- or vacuum-driven, there is little danger from electrical sparking and the motor will not burn out if the stirrer should stall.

Cont'd on page 49

"Please Bother Us."

by Cyrus Baaer.

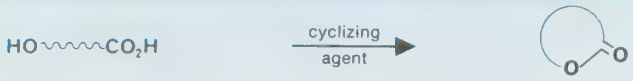
Earlier this year I received a very interesting letter from Dr. J.A. Cotruvo, Director, Criteria and Standards Division of the Office of Drinking Water of the EPA in Washington, expressing his deep concern about the unavailability of Basic Fuchsin. Dr. Cotruvo explained that "this dye is used as an ingredient in the bacteriological medium m-Endo agar, which is used by most water treatment facilities on a regular basis for the enumeration of certain bacterial indicators of fecal pollution. National drinking water regulations allow for only one other alternative procedure (the Most Probable Number test), but this test is less precise and more expensive than that using m-Endo agar." I replied that the problem might have seemed funny if it wasn't so sad and serious. Basic Fuchsin used to be made by two large American companies which have discontinued its production (and that of many other low-volume stains and dyes) because of regulatory pressures!

In this case we were able to help. We are now manufacturing Basic Fuchsin on a modest scale, and will continue unless the EPA stops us.

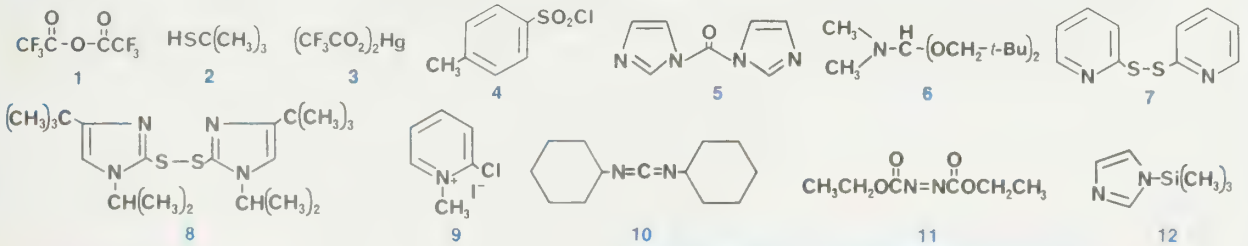
85,734-3 Basic Fuchsin, certified **25g $18.00; 100g $50.00**
86,108-1 Basic Fuchsin, special for flagella, certified **5g $6.00**
25g $20.00

It was no bother at all, just a pleasure to be able to help.

Macrolide Reagents



The construction of macrocyclic lactones has become a challenging task for the synthetic organic chemist. Recent work by a number of groups has extended the frontiers of this exciting area of organic synthesis.[1] Aldrich offers many of the "cyclizing" agents used in preparing macrolides. Below are selected examples of these reagents.



Applications:

1) Trifluoroacetic anhydride: Synthesis of zearalenone,[2] the related macrolide (±)-di-*O*-methylcurvularin,[3] the total synthesis of the macrolide antibiotic methymycin[4] as well as other macrocyclizations.[5,6]
10,623-2 25g $5.90; 100g $15.70

2) 2-Methyl-2-propanethiol: Its thallium salt in the synthesis of the antibiotic methymycin[4a] and (±)-dimethylzearalenone secoacid ketal.[4b]
10,920-7 (free thiol) 100g $4.40; 500g $8.25; 3kg $23.10

3) Mercuric trifluoroacetate: Synthesis of the macrolide antibiotic methymycin[4b] and (±)-dimethylzearalenone secoacid ketal.[4c]
15,648-5 10g $10.95; 50g $36.55

4) *p*-Toluenesulfonyl chloride: Synthesis of the macrolides curvularin[6] and erythronolide B.[7a]
T3,595-5 1kg $12.10; 3kg $24.20

5) 1,1′-Carbonyldiimidazole: Synthesis of the antibiotic (±)-pyrenophorin,[7a] a model of the antibiotic erythromycin B,[7b] and the macrolide nonactin.[7c]
11,553-3 5g $13.55; 10g $22.55; 25g $37.40; 100g $105.60

6) *N,N*-Dimethylformamide dineopentyl acetal: Synthesis of a number of macrocyclic lactones.[8]
14,024-4 10g $18.45; 50g $65.90

7) Aldrithiol-2 (2,2′-dipyridyl disulfide): Synthesis of (±)-11-hydroxy-*trans*-8-dodecenoic acid lactone,[9] the conversion of a series of ω-hydroxy acids to lactones,[10] a number of macrocyclic lactones of the prostaglandin and polyether series,[11] the naturally occuring macrolides brefeldin A, carpaine, vertaline and erythronolide B,[12] and the synthesis of the steroid hydroxylase inhibitor (±)-diplodialide A.[13]
14,304-9 5g $11.95; 25g $39.65

8) 2,2′-Dithiobis(4-*t*-butyl-1-isopropylimidazole): Synthesis of a number of macrocyclic lactones from the corresponding ω-hydroxy acids.[14]
19,598-7 2.5g $12.40; 10g $35.40

9) 2-Chloro-1-methylpyridinium iodide: Synthesis of a number of macrocyclic lactones from the corresponding ω-hydroxy acids.[15]
19,800-5 25g $21.95; 100g $62.70

10) Dicyclohexylcarbodiimide: Synthesis of curvularin[6] and other macrocyclic lactones.[16]
D8,000-2 25g $5.50; 100g $10.45; 1kg $79.20

11) Diethyl azodicarboxylate: Synthesis of nonactin,[17] a number of macrocyclic lactones from the corresponding ω-hydroxy acids,[18] and the cytotoxic antibiotic vermiculine.[19]
D9,000-8 25g $20.30; 100g $57.20

12) *N*-(Trimethylsilyl)imidazole: Synthesis of a number of macrocyclic lactones.[20]
15,358-3 5g $3.30; 25g $14.10; 100g $50.60

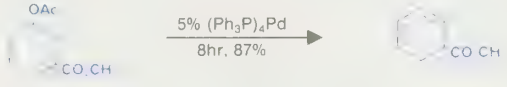
References: **(1)**For recent reviews on the synthesis of macrocyclic lactones, see: S. Masamune, *Aldrichimica Acta*, **11**, 23 (1978); T. Back, *Tetrahedron*, **33**, 2041 (1977); S. Masamune, G. Bates, and J. Corcoran, *Angew. Chem., Int. Ed. Engl.*, **16**, 585 (1977). **(2)** D. Taub, N.N. Girotra, R.D. Hoffsommor, C.H. Kuo, H.I. Slates, S. Weber, and N.L. Wendler, *Chem. Commun.*, 225 (1967). **(3)** P.M. Baker, B. Bycroft, and J. Roberts, *J. Chem. Soc. (C)*, 1913 (1967). **(4a)** S. Masamune, C. Kim, K. Wilson, G. Spessard, P. Georghiou, and G. Bates, *J. Am. Chem. Soc.*, **97**, 3512 (1975); **(4b)** S. Masamune, H. Yamamoto, S. Kamata, and A. Fukuzawa, *ibid.*, **97**, 3513 (1975); **(4c)** S. Masamune, S. Kamata, and W. Schilling, *ibid.*, **97**, 3515 (1975). **(5)** P.M. Baker, W.D. Ollis, and T.S. Zealley, *J. Chem. Soc.*, 1447 (1952). **(6)** O.C. Musgrave, R. Templeton, and H.D. Munro, *J. Chem. Soc. (C)*, 250 (1968). **(7a)** E. Colvin, T. Purcell, and R. Raphael, *J. Chem. Soc., Perkin Trans. 1*, 1718 (1976); **(7b)** J.D. White, S.N. Lodwig, G.L. Trammel, and M.P. Flemming, *Tetrahedron Lett.*, 3263 (1974); **(7c)** J. Gombos, E. Haslinger, A. Nikiforov, H. Zak, and U. Schmidt, *Monatsh. Chem.*, **106**, 1043 (1975). **(8)** H. Vorbrüggen and K. Krolikiewicz, *Angew. Chem., Int. Ed. Engl.*, **16**, 876 (1977). **(9)** E.J. Corey, P. Ulrich, and J. Fitzpatrick, *J. Am. Chem. Soc.*, **98**, 222 (1976). **(10)** E.J. Corey and K. Nicolaou, *ibid.*, **96**, 5614 (1974). **(11)** E.J. Corey, K. Nicolaou, and L. Melvin, Jr., *ibid.*, **97**, 653 (1975). **(12)** *Idem, ibid.*, **97**, 654 (1975). **(13)** T. Ishida and K. Wada, *J. Chem. Soc., Perkin Trans. 1*, 323 (1979). **(14)** E.J. Corey and D.S. Brunelle, *Tetrahedron Lett.*, 3409 (1976). **(15)** T. Mukaiyama, M. Usui, and K. Saigo, *Chem. Lett.*, 49 (1976). **(16)** Y. Kasai, T. Tanimura, and Z. Tamura, *Anal. Chem.*, **47**, 34 (1975). **(17)** U. Schmidt, J. Gombos, E. Haslinger, and H. Zak, *Chem. Ber.*, **109**, 2628 (1976). **(18)** T. Kurihara, Y. Nakajima, and O. Mitsunobu, *Tetrahedron Lett.*, 2455 (1976). **(19)** Y. Fukuyama, C. Kirkemo, and J. White, *J. Am. Chem. Soc.*, **99**, 646 (1977). **(20)** G. Bates, J. Diakur, and S. Masamune, *Tetrahedron Lett.*, 4423 (1976).

$(Ph_3P)_4Pd$, $(Ph_3P)_2PdCl_2$, $(Ph_3P)_2Ni(CO)_2$

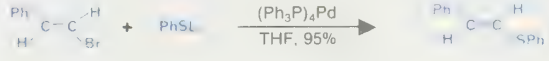
Homogeneous Catalysis – The Triphenylphosphine Connection

Many precious metal salts are more efficient catalysts when used with excess **triphenylphosphine**,[1,2] and a survey of the current literature can easily demonstrate the versatility of phosphine-rich catalysts. The best example may be **tetrakis(triphenylphosphine)palladium(0)**.[3-7]

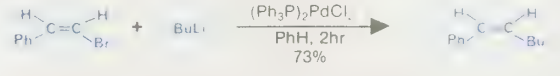
One recent application of **$(Ph_3P)_4Pd$** involved the positional and stereochemical isomerization of allylic acetates.[8] Evaluation of this activity led to a useful synthetic procedure for the conversion of allyl acetates to 1,3-dienes:



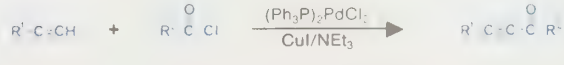
Also of great synthetic utility are the cross-coupling reactions of alkenyl halides with RLi, RMgX, and lithium thiolates, catalyzed by **$(Ph_3P)_4Pd$**.[9] These are high-yield, stereoselective reactions. For example, isomeric purities over 99.5% were obtained from the reaction



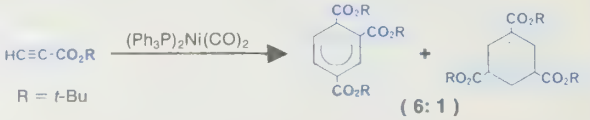
In the same study, **$(Ph_3P)_2PdCl_2$** catalyzed a similar conversion of (*Z*)-β-bromostyrene to (*Z*)-1-phenyl-1-hexene.



Dichlorobis(triphenylphosphine)palladium(II) has also been used in the general synthesis of α-alkynyl ketones and α-alkynamides.[10]



Phosphine complexes of Ni(0) and Ni(II) have also been shown to be versatile synthetic tools.[11] For example, **$(Ph_3P)_2Ni(CO)_2$** has been compared to $Fe_2(CO)_9$ as a catalyst in the dimerization of acid chlorides,[12] and has also been proven effective in the cyclotrimerization of bulky acetylenic esters.[13]



In an extension of the oxidative bisdecarboxylation technique of Trost and Chen,[14] Grunewald and Davis used this catalyst to synthesize bridgehead-substituted norbornenes.[15]

These three complexes are only a few from the diverse collection of homogenenous catalysts now available from Aldrich at very attractive prices.

References:

1) D.M. Fenton, *J. Org. Chem.*, **38**, 3192 (1973).
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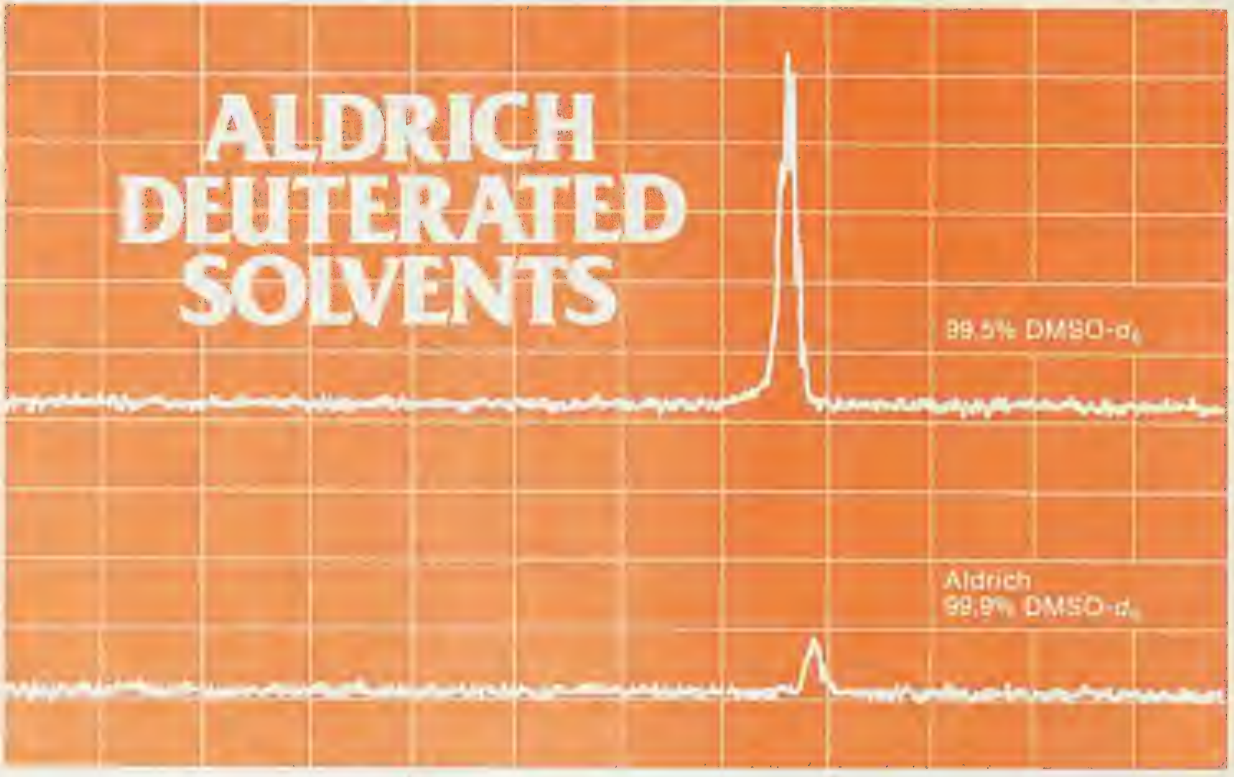

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Our chemist-collector's favorite paintings are works by Rembrandt and his students. Hence we can understand his pleasure at acquiring a portrait of Rembrandt by Rembrandt's first student, Gerard Dou. Rembrandt loved fancy costumes, and here he himself is dressed as an oriental. This work (oil on panel, 16 x $13^1/_4$ inches) is so influenced by one of Rembrandt's famous works, the so-called "Noble Slav" now at the Metropolitan Museum, that we can conjecture the date of Dou's work. It must be close to that of Rembrandt's — 1632, when Rembrandt was 26.

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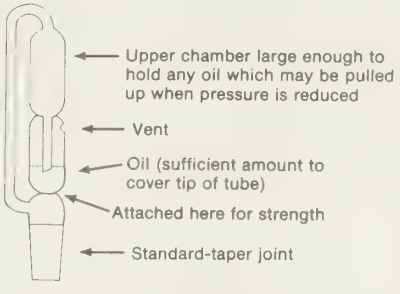
Many of the early issues of the *Aldrichimica Acta* have become very rare. Please do not throw your issues away. In time, we believe that complete sets will become valuable, and — if you do not want to keep them — there probably are chemists near you who would be interested.

Congratulations:

Just as we were about to go to press we received the wonderful news that Professors Herbert C. Brown and George Wittig are sharing this year's Nobel prize in chemistry. We do not believe that there can be many companies in the world that have benefited as much by the inventions of these two great scientists as has Aldrich. We have made many Wittig reagents, and have formed a company, Aldrich-Boranes, to utilize Professor Brown's inventions in the field of hydroboration. Thus, we are delighted to be able to share in their happiness.

Lab Notes

Oil bubblers are frequently used in the chemistry laboratory to monitor the evolution of a gas produced in a reaction, the rate of flow of an inert or reacting gas through a reaction vessel, or simply as a means of closing off a reaction vessel from the atmosphere. Because of problems associated with bubblers made from pipettes and test tubes connected to the reaction vessel with flexible tubing, I asked our glassblower to make a bubbler of the following design which can simply be fitted into the top of a condenser or addition funnel equipped with a standard-taper glass joint. The lower chamber is filled to



the proper level with an appropriate oil or other liquid through the vent. When not in use the bubbler can be stored by simply hanging it on a convenient hook. If desired, the bubbler could be fitted with a sidearm and stopcock for introduction of a gas.

Robert F. Boswell
Research Chemist
A.H. Robins Company
Research Laboratories
1211 Sherwood Ave.
Richmond, Virginia 23220

Editors note:
For the convenience of our customers, Aldrich offers the bubbler shown below.

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Also available from Aldrich is the bubbler shown below whose use has been described in C.F. Lane, *Aldrichimica Acta*, **10**, 11 (1977).

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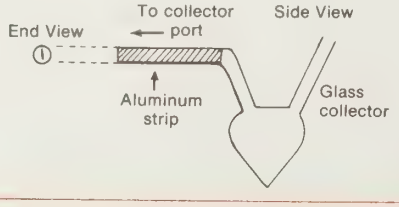
A recent note on the removal of small amounts of water and ethanol from chloroform [*Aldrichimica Acta*, **11**, 42 (1978)] prompts me to report a procedure, which is more rapid and easy.

Water and ethanol present in commercial chloroform or carbon tetrachloride can be eliminated simply by addition of zeolite NaA (pellets) just prior to use. After swirling for some minutes the amounts of water and ethanol are reduced to less than 5 ppm and less than 1 ppm, respectively (as determined by ^{1}H FT-NMR). Generally, 50g zeolite pellets/liter solvent is sufficient for effective elimination of water and ethanol. The zeolite can be recovered *via* filtration or after decantation of the solvent. As known, zeolite can be reused after drying in air at room temperature, at 120° (2 hrs) and at 400° (4 hrs).

J.A. Peters
Laboratory of Organic Chemistry
Delft University of Technology
Julianalaan 136
2628 BL Delft
The Netherlands

During preparative VPC collection, many high-boiling compounds often form troublesome aerosols instead of completely condensing in the collector. Aerosol (smoke) formation can be greatly reduced by decreasing the rate of cooling of the gaseous compound as it leaves the collector port. Accordingly, a thin strip of aluminum approximately 2.5-3cm long is cut with scissors from an aluminum can or the backing of a used, washed TLC plate. The width of the strip should equal the inside diameter of the collector tube. The strip is inserted into the collector as shown. The strip, being heated by the effluent gases at one end, provides a shallower cooling gradient for the compound to be collected.



When used with a cooling bath in the usual manner, collection efficiency of both high- and low-boiling compounds is improved.

K.L. Smouse
Chemistry Department
University of Utah
Salt Lake City, Utah 84112

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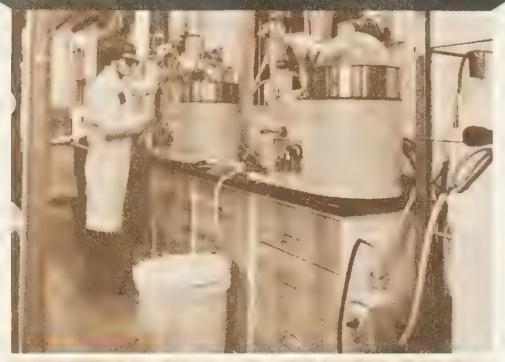

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2) M. Lauwers, B. Regnier, M. Van Eenoo, J.N. Denis, and A. Krief, *Tetrahedron Lett.*, 1801 (1979)
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About Our Cover:

This is a most unusual painting, in subject, in color and in its history.

It depicts Sarah bringing Hagar to the aged Abraham (Genesis *16*, 1-3), a subject rarely used by baroque artists. It is a small panel ($12\,^1/_2 \times 9\,^3/_4$ inches) of unusual color - delicate greens and reds. It was painted by Salomon de Bray in 1650. It is interesting to trace the model of the naked Hagar through the ages. De Bray probably copied the main figure of the *Allegory of Fertility* by Jacob Jordaens (Fig. 1), who had copied it from a figure by Moeyaert (Fig. 2), who must have taken his idea from a figure of Aphrodite by Praxiteles. Transmissions of visual ideas, such as this one from the antique through a pre-Rembrandtist and Jacob Jordaens to our Hagar, are probably quite common, but seldom so obvious and well documented.

Fig. 1

Fig. 2

Our chemist-collector had known this painting for many years, as it had belonged to one of the great private collectors in England, Dr. E.S. Schapiro, who had loaned it and ten other Biblical works to an exhibition, "The Bible through Dutch Eyes" in Milwaukee, of which our chemist had been the guest curator. Dr. Schapiro passed away recently and left his entire collection to the Hermitage in Leningrad. However, the Hermitage was not willing to pay the high estate taxes due, and so the executors had to sell some of the paintings, this one among them.

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Also, many paintings reproduced on our Acta covers were shown at the Milwaukee Art Center in an exhibition, "The Bible Through Dutch Eyes," arranged by Dr. Bader in 1976. The fully illustrated catalog with 66 black-and-white and 4 full-color reproductions contains many art historical and Biblical comments.

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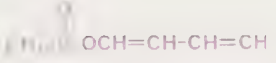
Potpourri

Diels-Alder Diene



1-Acetoxy-1,3-butadiene is a Diels-Alder diene useful in regiospecific synthesis. Recent applications include the synthesis of the antibiotics thienamycin[1] and rhodomycinon,[2] its photoaddition to steroids,[3,4] and several regiospecific Diels-Alder additions.[5-7]

1) D. Johnston, S. Schmitt, F. Bouffard, and B.G Christensen, *J. Am. Chem. Soc.*, **100**, 313 (1978)
2) K. Krohn and A. Rösner, *Tetrahedron Lett.*, 353 (1978)
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5) K. Okado, H. Sakuma, M. Kondo, and S. Inoue, *Chem. Lett.*, 213 (1979)
6) C. Shin, M. Yamamura, E. Inui, Y. Ishida, and J Yoshimura, *Bull. Chem. Soc. Jpn.*, **51**, 2618 (1978)
7) M. Hirama, Y. Koyama, Y. Shoji, and S. Ito, *Tetrahedron Lett.*, 2289 (1978)

22,086-8 1-Acetoxy-1,3-butadiene 10g $19.10

Useful Reagent for the Detection of Specific RNA's

1-(*m*-Nitrobenzyloxymethyl)pyridinium chloride is used to prepare diazobenzyloxymethyl (DBA) paper.[1] DBA paper is useful in the detection of specific RNA's on agarose gels.[1-10] More recently, it has been used in the detection of proteins after separation on polyacrylamide/agarose gels.[11]

1) J.C. Alwine, D.J. Kemp, and G.R. Stark, *Proc Nat. Acad. Sci. U.S.A.*, **74**, 5350 (1977)
2) H.A. Erlich, S.N. Cohen, and H.O. McDevitt, *Cell*, **13**, 681 (1978)
3) G.S. Martin and F. Radke, *Virology*, **96**, 530 (1979)
4) B.A. Parker and G.R. Stark, *J. Virol.*, **31**, 360 (1979)
5) D.L. Robertson and H.E. Varmus, *ibid.*, **30**, 576 (1979)
6) J.R. Broach, J.F. Atkins, C. McGill, and L. Chow, *Cell*, **16**, 827 (1979)
7) D.H. Hamer, K.D. Smith, S.H. Boyer, and P. Leder, *ibid.*, **17**, 725 (1979).
8) J.G. Williams, M.M. Lloyd, and J.M. Devine, *ibid.*, **17**, 903 (1979).
9) M.R. Green, R.M. Lebovitz, and R.G. Roeder, *ibid.*, **17**, 967 (1979)
10) J.S. Lee, H.E. Varmus, and J.M. Bishop, *J. Biol Chem.*, **254**, 8015 (1979)
11) J. Renart, J. Reiser, and G.R. Stark, *Proc. Nat Acad. Sci. U.S.A.*, **76**, 3116 (1979).

22,031-0 1-(*m*-Nitrobenzyloxymethyl)-pyridinium chloride 10g $26.50

Resolving Agents: Optically Active Isocyanates

Optically active isocyanates are becoming increasingly useful for the resolution of racemic mixtures of alcohols, α-hydroxy esters and thiols *via* fractional crystallization and, more recently, chromatography.[1] Subsequent hydrolysis of the carbamate derivative by the trichlorosilane method[2] affords the pure, optically active product in high yield **as well as recovery** of the optically active isocyanate reagent in >90% yield. The utility of the reagents is further enhanced by a recent study involving the NMR spectral determination of the diasteriomeric carbamates.[3]

1) W.H. Pirkle and M.S. Hoekstra, *J. Org. Chem.*, **39**, 3904 (1974)
2) W.H. Pirkle and J.R. Hauske, *ibid.*, **42**, 2781 (1977).
3) W.H. Pirkle, K.A. Simmons, and C.W. Boeder, *ibid.*, **44**, 4891 (1979).

22,044-2 *R*-(-)-1-(1-Naphthyl)ethyl isocyanate 1g $19.50

22,056-6 *R*-(-)-α-Methylbenzyl isocyanate 1g $10.75

22,057-4 *S*-(+)-α-Methylbenzyl isocyanate 1g $10.75

Reagent for Macrolide Synthesis

Cesium carbonate has been used recently in the synthesis of crown ethers and macrocyclic lactones.[1-3]

1) B.J. van Keulen, R.M. Kellogg, and O. Piepers, *Chem. Commun.*, 285 (1979).
2) O. Piepers and R.M. Kellogg, *ibid.*, 383 (1978).
3) W.H. Kruizinga and R.M. Kellogg, *ibid.*, 286 (1979).

20,212-6 Cesium carbonate 25g $19.75; 100g $59.40

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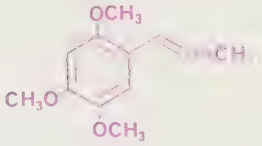
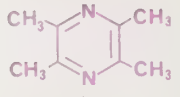


Aldrich's 2,4,5-trimethoxypropenylbenzene, 97%, contains *ca.* 70% of the *cis* compound, β-asarone (the remainder is the *trans* isomer, α-asarone). β-Asarone causes regression of the ovaries in many gravid insects,[1] and is a constituent of Oil of Calamus, which has been shown to cause malignant duodenal tumors and growth depression in rats.[2]

1) *Chem. Eng. News*, April 16, 1979, p 24; M.T.S. Hsia, American Chemical Society Meeting, Honolulu, 1979, Abstract PEST-98.
2) J.M. Taylor, *et al.*, 6th Annual Meeting, American Association for Cancer Research, 1967, Abstract 72.

22,107-4 2,4,5-Trimethoxypropenylbenzene 5g $19.50

Tetramethylpyrazine



Tetramethylpyrazine, a metabolic product of *Bacillus subtilis*, has been reported as an ingredient in a flavoring composition,[1] and a sweetness enhancer for beverages.[2] The compound is a powerful photographic sensitizer,[3] as well as an effective buffer in the acid-catalyzed hydrolysis of epoxides.[4]

Pharmacological studies[5] of its effects on the cardiovascular system reveal that tetramethylpyrazine inhibits the vasoconstrictor-induced contraction of rabbit aorta strip, raises hypoxia tolerance of mice, reduces petrissen-potentiated hypoxemia and improves circulation in rabbit mesenteries. Not only did tetramethylpyrazine inhibit ADP-caused platelet aggregation *in vitro*, it also dispersed aggregated platelets.

1) I. Flament, Fr. Demande 2,128,744 (1972).
2) J. Kaneko, T. Nakao, and T. Kosuge, Japan. Kokai 73 17,073 (1973).
3) W.E. Nixon and J.W. Mitchell, *Photogr. Sci. Eng.*, **22**, 111 (1978).
4) J.G. Pritchard and I.A. Siddiqui, *J. Chem. Soc., Perkin Trans. 2*, 1309 (1972).
5) Peking Pharmaceutical Industries Laboratory, *Chinese Med. J.*, **4**, 319 (1978).

18,393-8 Tetramethylpyrazine 25g $15.20; 100g $40.85

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to give oxindole in 32% yield (eq. 69).[74]

MISCELLANEOUS

Most of the preceding reactions described have involved the incorporation of the nitrogen of the HOSA in the reaction product. One reaction which differs from all of these is that between aromatic ethers and HOSA in polyphosphoric acid. Here, sulfur is incorporated and the product is a diaryl sulfone (eq. 70).[75] It is suggested that HOSA is cleaved to give H_2SO_4 and it is further reaction of this that gives rise to the sulfone.

CONCLUSIONS

HOSA has proved to be a reagent of diverse synthetic utility, its multifarious uses having been amply illustrated in the foregoing paragraphs. Such versatility is a consequence of the inherent ability of HOSA to act as both a nucleophile and electrophile and also to provide an *in situ* source of other chemical entities, factors referred to at the beginning of this article. These properties have led to its exploitation in such a variety of situations.

Clearly there is scope for its application in further organic transformations, and in particular, it must have a further part to play in new heterocyclic syntheses.

ACKNOWLEDGMENT

I wish to thank the Cancer Research Campaign for financial support.

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4) R. Gösl and A. Meuwsen, *Chem. Ber.*, **92**, 2521 (1959)
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About the Author

Dr. Wallace is a research scientist working for the Cancer Research Campaign. He obtained his B.Sc. degree from Southampton University in 1968 and subsequently carried out his Ph.D. research at the School of Pharmacy, Portsmouth Polytechnic. His main interests lie in the area of heterocyclic chemistry and in particular he is concerned with the synthesis of hypoxic cell radiosensitizers for use in cancer therapy. He holds a Visiting Research Fellowship at Brunel University.

New Listings

Interesting Bicyclic Diketone

Two recent reports[1,2] on the synthesis of (±)-gymnomitrol starting with *cis*-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione have prompted us to offer this interesting bicyclic diketone as a potential starting material for sesquiterpenes such as α-barbatene,[3] pinguisone and deoxopinguisone.[4]

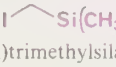
1) Y.K. Han and L.A. Paquette, *J. Org. Chem.*, **44**, 3731 (1979)
2) R.M. Coates, S.K. Shah, and R.W. Mason, *J. Am Chem. Soc.*, **101**, 6765 (1979)
3) N.H. Anderson and S. Huneck, *Phytochemistry*, **12**, 1818, 2709 (1973)
4) S.M. Krutov, Z. Samek, V. Benesova, and V Herout, *ibid.*, **12**, 1405 (1973).

22,084-1 *cis*-1,5-Dimethylbicyclo[3.3.0]-octane-3,7-dione 1g $19.75

Also available:

19,210-4 *cis*-Bicyclo[3.3.0]octane-3,7-dione 1g $23.00; 5g $100.70

Reagent for Olefin Synthesis

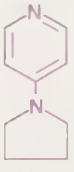


(Iodomethyl)trimethylsilane is used to make 2-(trimethylsilyl)ethyl phosphonium iodide, a useful intermediate in the preparation of allylsilanes, which may be converted to olefins.[1,2] The reagent is also used to synthesize β-silyl sulfones which yield terminal olefins upon elimination.[3]

1) D. Seyferth, K.R. Wursthorn, and R.E. Mammarella, *J. Org. Chem.*, **42**, 3104 (1977)
2) I. Fleming and I. Paterson, *Synthesis*, 446 (1979)
3) P. Kocienski, *Tetrahedron Lett.*, 2649 (1979)

22,030-2 (Iodomethyl)trimethylsilane 5g $18.50; 25g $61.00

Esterification Catalyst

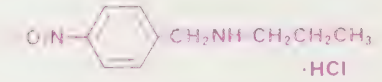


4-Pyrrolidinopyridine has been shown to be an effective catalyst for room-temperature esterification.[1,2] The reagent allows the mild, one-pot esterification of a number of carboxylic acids in good yields,[1] as well as the preparation of the cholesteryl esters of fatty acids.[2]

1) A. Hassner and V. Alexanian, *Tetrahedron Lett.*, 4475 (1978)
2) K.M. Patel, *et al.*, *Lipids*, **14**, 816 (1979).

21,337-3 4-Pyrrolidinopyridine 5g $9.15; 25g $30.35

Reagent for Isocyanates



4-Nitro-*N*-propylbenzylamine has been shown recently to be a very useful reagent in a rapid and sensitive method for the qualitative and quantitative determination of aliphatic and aromatic isocyanates in working environments.[1-5] The procedure is based on the formation of the stable urea derivative (from the reagent and the isocyanate) and its determination by TLC or HPLC. The method is applicable to isocyanate monomers as well as resins.

1) K.L. Dunlap and R.L. Sandridge, *Anal. Chem.*, **46**, 1845 (1974)
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4) S.P. Levine, J.H. Haggat, E. Chalaclek, G. Jungclaus, and J.L. Gerlack, *ibid.*, **51**, 1106 (1979).
5) C. Sango, *J. Liq. Chromatogr.*, **2**, 763 (1979).

22,191-0 4-Nitro-*N*-propylbenzylamine hydrochloride 1g $7.50; 5g $25.00

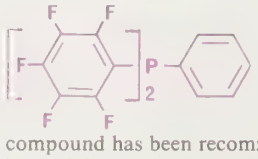
Mild Chlorinating Agent

Hakimelahi and Just[1] have reported a mild, effective method of chlorinating carbon acids in the pK_a range of dimethyl malonate, using trifluoromethanesulfonyl chloride with triethylamine or DBU. The reaction takes place in the presence of alcohols and has been used to produce 2,2-disubstituted tetrahydropyrans and -furans.

1) G.H. Hakimelahi and G. Just, *Tetrahedron Lett.*, 3643 (1979).

16,479-8 Trifluoromethanesulfonyl chloride 5g $13.45; 25g $50.05

Bis(pentafluorophenyl)phenyl-phosphine

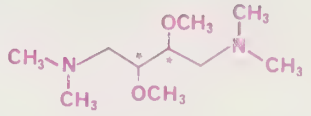


This compound has been recommended by workers of the Environmental Protection Agency as a calibration standard for the ion-abundance scales and performance evaluations of GC/MS instruments.

J.W. Eichelberger, L.E. Harris, and W.L. Budde, *Anal. Chem.*, **47**, 995 (1975).

22,196-1 Bis(pentafluorophenyl)phenyl-phosphine 500mg $19.75

(+)- and (-)-DDB: Versatile Chiral Solvents



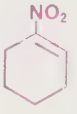
(*R,R*)-(-)- and (*S,S*)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane [(+)- and (-)-DDB] can be used as chiral solvents in organic syntheses.[1,2] DDB can be recovered easily, is miscible with cosolvents whose polarities vary from that of water to that of pentane, and has a low crystallization tendency enabling it to be used in low-temperature solvent mixtures. DDB is especially effective in organometallic reactions, processes involving H-bonding, and base-catalyzed transformations.

1) D. Seebach, H. Dörr, B. Bastani, and V. Ehrig, *Angew. Chem., Int. Ed. Engl.*, **8**, 982 (1969).
2) D. Seebach, *et al.*, *Helv. Chim. Acta*, **59**, 301 (1977).

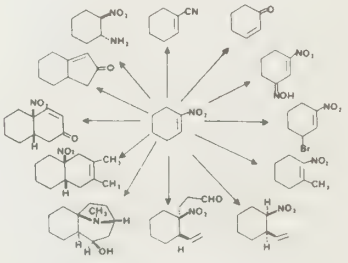
19,548-0 (*S,S*)-(+)-2,3-Dimethoxy-1,4-bis(dimethylamino)butane 10g $32.25

21,296-2 (*R,R*)-(-)-2,3-Dimethoxy-1,4-bis(dimethylamino)butane 10g $41.35

1-Nitro-1-cyclohexene



1-Nitro-1-cyclohexene is a versatile intermediate recently shown by Corey to be useful in a wide variety of synthetic transformations, as summarized below.[1]



1) E.J. Corey and H. Estreicher, *J. Am. Chem. Soc.*, **100**, 6294 (1978).
2) E.J. Corey and H. Estreicher, *Tetrahedron Lett.*, **21**, 1113 (1980).
3) E.J. Corey and H. Estreicher, *Ibid.*, **21**, 1117 (1980).

21,953-3 1-Nitro-1-cyclohexene 5g $20.00

Biochemical Tools

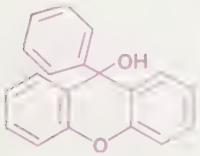
Potent Inhibitor of Nucleoside Transport - Cancer Research Tool

S-(*p*-Nitrobenzyl)-6-thioinosine (NBMPR) is a potent inhibitor of nucleoside transport in a number of animal cells.[1-5] The compound was found to bind tightly and reversibly to nucleoside transport sites of tumor cells in culture, with inhibition of uptake of adenosine,[6-11] cytidine,[7] guanosine,[7,8] inosine,[7] thymidine,[4,7,8,12] and uridine[3,4,7,8,13] by replicating cells. Thus, NBMPR is a very useful high-affinity probe for the nucleoside transport system and a useful tool in cancer research involving the implication of nucleoside uptake in tumor-cell replication.

1) C.T. Warnick, H. Muzik, and A.R.P. Paterson, *Cancer Res.*, **32**, 2017 (1972)
2) M.A. Pickard, R.R. Brown, B. Paul, and A.R.P Paterson, *Can. J. Biochem.*, **51**, 666 (1973).
3) C.E. Cass and A.R.P. Paterson, *Biochim. Biophys. Acta*, **419**, 285 (1976)
4) G.J. Lauzon and A.R.P. Paterson, *Mol. Pharmacol.*, **13**, 883 (1977).
5) S.M. Jarvis and J.D. Young, *J. Physiol. (London)*, **284**, 96P (1978).
6) J.D. Pearson, J.S. Carleton, A. Hutchings, and J.L. Gordon, *Biochem. J.*, **170**, 265 (1978).
7) C.E. Cass, E. Dahlig, E.T. Law, T.P. Lynch, and A.R.P. Paterson, *Cancer Res.*, **39**, 1245 (1979).
8) T.P. Lynch, G.J. Lauzon, S.R. Naik, C.E. Cass, and A.R.P. Paterson, *Biochem. Pharmacol.*, **27**, 1303 (1978)
9) R.M. Wohlhueter, R. Marz, and P.G.W Plagemann, *J. Membr. Biol.*, **42**, 247 (1978)
10) A.R.P. Paterson, L.R. Babb, J.H. Paran, and C.E. Cass, *Mol. Pharmacol.*, **13**, 1147 (1977).
11) C.E. Cass and A.R.P. Paterson, *Biochem. Pharmacol.*, **24**, 1989 (1975)
12) C.E. Cass and A.R.P. Paterson, *Exp. Cell Res.*, **105**, 427 (1977).
13) Y. Eilam and Z.I. Cabantchik, *J. Cell Physiol.*, **92**, 185 (1977).

86,149-9 *S*-(*p*-Nitrobenzyl)-6-thioinosine 100mg $26.50

Nucleoside-protecting Reagent

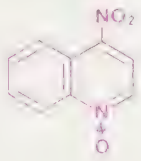


This reagent is converted to the chloride, which is used to derivatize the 5′-hydroxy groups of 2′-deoxyribonucleosides. These "pixyl" derivatives can be deblocked under very mild, acidic conditions (80% acetic acid, 20°C, 8-15 min).

J.B. Chattopadhyaya and C.B. Reese, *Chem. Commun.*, 639 (1978).

21,886-3 9-Phenylxanthen-9-ol 5g $10.60; 25g $31.80

DNA-complexing Agent

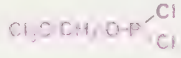


4-Nitroquinoline-*N*-oxide is a potent mutagen and carcinogen which forms charge-transfer complexes with 5′-deoxynucleotides[1] and deoxydinucleotides.[2]

1) S.A. Winkle and I. Tonoco, Jr., *Biochemistry*, **17**, 1352 (1978)
2) *Idem, ibid.*, **18**, 3833 (1979).

21,844-8 4-Nitroquinoline-*N*-oxide 100mg $9.80; 1g $57.75

Reagent for Oligonucleotide Synthesis

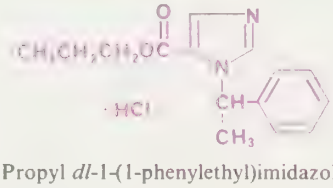


2,2,2-Trichloroethyl phosphorodichloridite is a useful reagent in the synthesis of oligonucleotides *via* phosphite triester intermediates.[1-3]

1) R.L. Letsinger and W.B. Lunsford, *J. Am. Chem Soc.*, **98**, 3655 (1976).
2) K.K. Ogilvie, N. Theriault, and K.L. Sadana, *ibid.*, **99**, 7741 (1977).
3) K.K. Ogilvie, S.L. Beaucage, A.L. Schifman, N. Theriault, and K.L. Sadana, *Can. J. Chem.*, **56**, 2768 (1978).

21,954-1 2,2,2-Trichloroethyl phosphorodichloridite 10g $10.35 50g $34.45

Fish Anesthetic

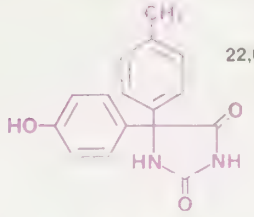


Propyl *dl*-1-(1-phenylethyl)imidazole-5-carboxylate hydrochloride is a potent, safe anesthetic agent for cold-blood invertebrates, about 100 times as potent as tricaine methanesulfonate (E1052-1). The compound is very soluble in both fresh and salt water.

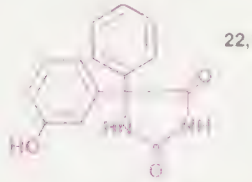
D. Thienpont and C.J.E. Niemegeers, *Nature*, **205**, 1018 (1965)

22,082-5 Propyl *dl*-1-(phenylethyl)-imidazole-5-carboxylate hydrochloride 100mg $11.15; 500mg $37.10

Anticonvulsant Drug Standards



22,083-3

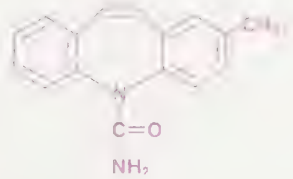


22,158-9

m-Hydroxyphenyl-5-phenylhydantoin (*m*-HPPH) as the glucuronide is a minor metabolite[1] of 5,5-diphenylhydantoin (DPH), while 5-(*p*-hydroxyphenyl)-5-(*p*-tolyl)hydantoin (HMPPH) is a useful standard[1] in the GC analysis of DPH.

1) K.M. Witkin, D.L. Bius, B.L. Teague, L.S. Weise L.W. Boyles, and K.H. Dudley, *Therapeutic Drug Monitoring*, **1**, 11 (1979)

22,083-3 5-(*p*-Hydroxyphenyl)-5-(*p*-tolyl)hydantoin 100mg $11.50
22,158-9 5-(*m*-Hydroxyphenyl)-5-phenylhydantoin 100mg $20.00

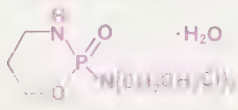


2-Methyl-5*H*-dibenz[*b,f*]azepine-5-carboxamide (2-methylcarbamazepine) is a new and very useful internal standard for the assay of carbamazepine.

J.R. Patton and K.H. Dudley *J. Heterocycl. Chem* **16**, 257 (1979)

22,042-6 2-Methyl-5*H*-dibenz[*b,f*]-azepine-5-carboxamide 5mg $23.85

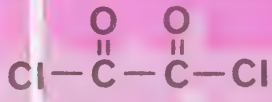
Cancer Research Tool



The antineoplastic activity of cyclophosphamide monohydrate is well documented.

21,870-7 Cyclophosphamide monohydrate 5g $20.00; 25g $65.00

OXALYL CHLORIDE



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Oxalyl chloride is also finding many industrial applications, often as surprising as they are intriguing. These include: stabilizer for color photographic material, formation of monomers of thermally stable polymers, formation of polyamides useful as UV absorbers, polymerization catalyst, polymer crosslinking agent, production of resins for affinity chromatography, production of photopolymerizable printing materials, and chemiluminescent formulations.

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Aldrichimica Acta

Volume 13, Number 2, 1980

Recent Developments in the Chemistry of Natural Products. **See page 23.**

Hydrazine - Rocket Fuel to Synthetic Tool. **See page 33.**

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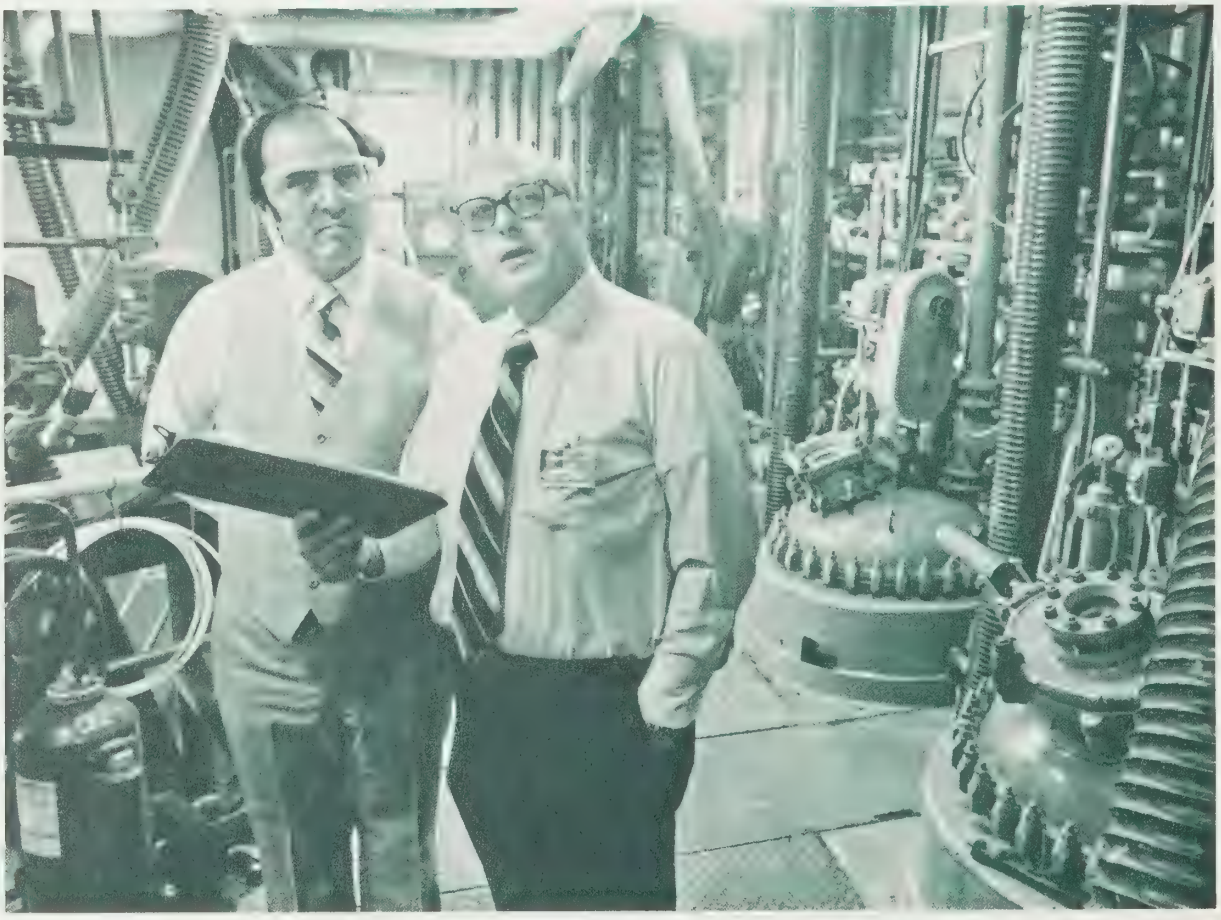

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About Our Cover:

Our chemist-collector prefers paintings by Rembrandt and his students to all others. That he concerned himself far more with the agonies of King Saul and the vicissitudes of King David than with the splendor of King Solomon is surely indicative of Rembrandt's understanding of the Bible. Yet other artists of 17th-century Holland loved to depict scenes from the life of King Solomon: the judgment of Solomon, Solomon and the Queen of Sheba and, as depicted here in this large canvas (160 x 205 cm.), Solomon's Idolatry, painted by Jan de Bray (1627-1697).

History has been kind, perhaps too kind, to King Solomon. Can a man who used slave labor and lavished his affection on so many "wives" have been really wise? What makes biblical history so different from the history of most nations is that Biblical heroes are shown to us with all their blemishes — and Solomon's were many.

Lab Notes

Suction filtration of certain solids frequently results in the inconvenience of plugged filter-paper pores.

A dependable and inexpensive solution to this problem involves placing a circular piece of wire gauze (approx. 17 mesh, composed of 0.016-in. wire) between the Buchner funnel and the filter paper. The diameter of the wire gauze should be such that the outer ring of funnel holes is in direct contact with the filter paper, enabling the paper to be seated properly.

The wire gauze serves to distribute the suction more evenly over the filter paper, allowing ease of filtration without embedding the solid in the filter paper and plugging the pores.

Diane Grob Schmidt
Graduate Student
University of Cincinnati
Cincinnati, Ohio 45221

Editor's note:

In an earlier issue of *Aldrichimica Acta* (Vol. 11, Number 4, 1979, p 62) J.A. Peter's lab note suggested the use of zeolite NaA pellets for eliminating water and ethanol in commercial chloroform or carbon tetrachloride. Aldrich offers 4A molecular sieves which can be used for this purpose.

20,859-0 4A Molecular sieves, 4- to 8-mesh ($^1/_8$-inch beads) 1kg $21.30
5kg $75.00

I always read your "Lab Notes" column for ideas and suggestions that I might use in the Chemistry Department stockroom or laboratories. There have been many very good and useful letters over the years. Now I would like to submit an idea that is right in step with the growing trend of conservation or "putting everything to full use."

Since DOT regulations have forced you to make beautiful, sturdy boxes to ship chemicals in, our custodian, Nicholas Szymanski, decided these boxes were much too nice to be thrown away. He makes attractive bird houses out of them at a minimum of cost and effort. (We also save all of the vermiculite packing material for oil spills, insulation and other shipping uses.) Thus we utilize everything we receive from Aldrich.

Aldrich Wooden Shipping Box
Bird House

1. Cut slant from front of box to back so rain will run off roof.
2. Drill a $1^1/_4$-in. hole 3 in. from top (any bigger will allow undesirable birds to enter). Place wooden peg 1 in. below hole.
3. Cut roof from scrap lumber 1 in. larger than box, nail guides on inner surface to secure roof.
4. Cut scrap lumber to fasten house to tree or pole and nail to back of box.
5. Leave natural or use stain.

Sylvia M. Clarke
Chemistry Stores Manager
Chemistry Department
State University College
Fredonia, New York 14063

Single crystals for X-ray diffraction studies are often grown by vapor diffusion of a poorer solvent into a solution of the compound of interest, however the choice of a solvent system is often elusive. In order to minimize the amount of sample (and shelf space) necessary to find a suitable system, I have found that sealed disposable pipettes placed in snap-cap one-dram vials work well. In more detail, a Pasteur pipette is broken at the wide end, at a length slightly less than the height of the vial to be used. The sharp edge of the soft glass is easily sealed with a Bunsen burner, leaving a sample well with a polished opening. This is placed in the one-dram vial which contains the volatile solvent (approx. $^1/_3$ full). The sample solution is added to the well and the vial is capped and placed aside where it will not be disturbed. This system is so small that many vapor diffusion chambers can be simultaneously set up.

If a larger diffusion chamber is desired, I have found that a 200-ml Berzelius beaker and a small (70 x 50mm) crystallization dish (or a #11 rubber stopper) work well. In this case a small (30ml) beaker containing the sample solution is placed inside the Berzelius beaker which is charged with the second solvent. The lip of the Berzelius beaker is smeared with vacuum grease and the inverted crystallization dish is placed on top (or it can be stopped with the rubber stopper). This chamber is advantageous in that it is narrow and doesn't take up much shelf space and at least one other chamber can be stacked on top of it. It is also a very good solvent chamber for TLC.

Robert Nathan Katz
Postdoctoral Research Associate
Department of Chemistry
Columbia University
New York, N.Y. 10027

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome red-and-white ceramic Aldrich coffee mug as well as a copy of **Selections from the Bader Collection** *(see "About Our Cover"). We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Ayira Bader.

After the last catalog, #19, was published in 1978, hundreds of chemists wrote and talked to me about our apparent thoughtlessness in deleting the "Classes of Compounds" section which had been in our catalogs for many years.

We had made a study and had found that only a small proportion of our customers use that section, and so we had taken it out of our catalog and printed it separately, to send to every chemist requesting it. We included a postpaid card in the front of the catalog, for our customers' convenience in ordering the separate supplement, but who looks at postcards?

In our new catalog, just published, we placed that postcard in the very center of the catalog, in the hope that *now* it just couldn't be missed, but again, a number of chemists have wondered why we have not included that section. Just send us the postcard — or any postcard requesting it — and we will send you that supplement.

However, remember that this supplement lists only the compounds in our Catalog/Handbook, not those in our Library of over 23,000 compounds. If you would like a computer printout of *all* compounds of a given class in both the Catalog/Handbook and the Library, we will be happy to send you that specific printout at no charge.

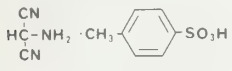
Answering those many chemists was no bother at all, just a pleasure to be able to help.

Methotrexate

Isomers and Intermediates for the Synthesis of Analogs and Folic Acid Metabolites

Methotrexate [L-(+)-amethopterin, L-(+)-4-amino-N^{10}-methylpteroylglutamic acid, MTX], a high-affinity pseudosubstrate of the enzyme dihydrofolate reductase (DFR),[1] is one of the first folic acid (pteroylglutamic acid) analogs to show antineoplastic activity.[2] Methotrexate inhibits DFR, thereby depleting tetrahydrofolic acid, resulting in a decrease of thymidylate synthetase and inhibition of DNA synthesis.[3] Thus, few compounds have been as exciting in cancer research as methotrexate which is proving increasingly important in the treatment of leukemias, lymphomas, psoriasis and various other malignancies.

Since methotrexate is a folic acid antagonist, continuing research in this area will involve possible DFR inhibitors, folic acid metabolites, and other analogs of methotrexate. We offer a number of intermediates with structures bearing the benzoyl-L-glutamic acid or the pteridinyl moiety. D-(-)- and DL-amethopterin are also available.



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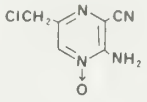

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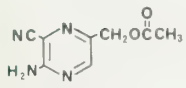

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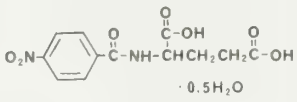

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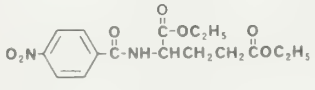

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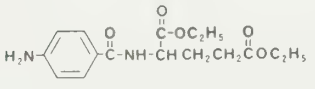

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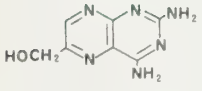

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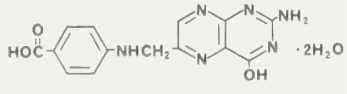

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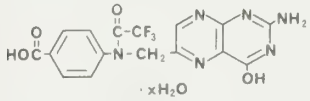

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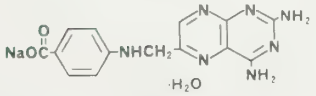

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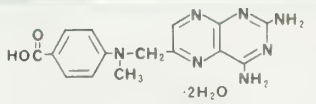

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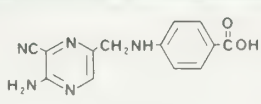

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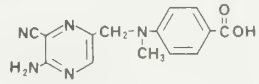

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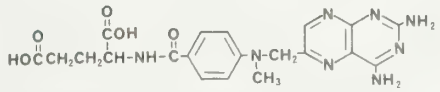

22,394-8 22,395-6 19,469-7

References:

1) J.W. Williams, J.F. Morrison, and R.G. Duggleby, *Biochemistry*, **18**, 2567 (1979).
2) R.L. Blakely, "The Biochemistry of Folic Acid and Related Pteridines," North-Holland Publishing Co., Amsterdam, 1969, pp 157-176.
3) A.A. Kumar, D.T. Blankenship, B.T. Kaufman, and J.H. Freisheim, *Biochemistry*, **19**, 667 (1980).

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86,153-7	Pteroic acid dihydrate	25mg $12.00
86,154-5	N^{10}-(Trifluoroacetyl)pteroic acid hydrate	25mg $15.00
86,158-8	4-[*N*-(2,4-Diamino-6-pteridinylmethyl)amino]-benzoic acid, sodium salt monohydrate	100mg $19.00
86,155-3	4-[*N*-(2,4-Diamino-6-pteridinylmethyl)-*N*-methylamino]benzoic acid hemihydrochloride dihydrate	25mg $10.00
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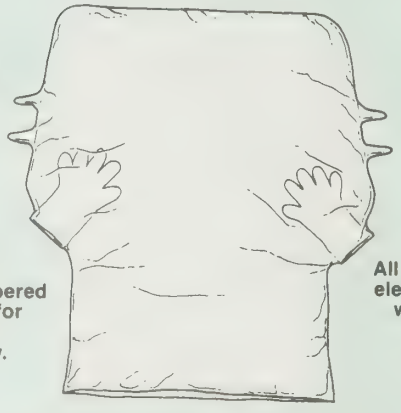
An optional floor base of high-density polyethylene (0.5 x 22.5 x 32 inches) fits into the AtmosBag to provide a rigid, inert work surface.

In addition to the various general uses of the AtmosBag for handling air- and moisture-sensitive and toxic reagents and reactions, its versatility may be extended to applications in other scientific fields. For example, the AtmosBag may be used to create a controlled atmosphere habitat for animals or plants, and as a protective chamber for using sensitive scientific equipment outdoors. Use your imagination to extend the usefulness of your AtmosBag. The AtmosBag may be disposed of if contaminated or may be reused.

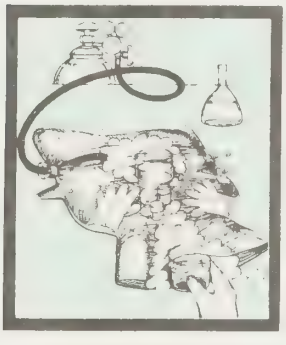
To order the AtmosBag, call 800 558-9160, or mail order directly to Aldrich Chemical Company, P.O. Box 355, Milwaukee, WI 53201.

AtmosBag	Cat. No. Z10,608-9 1 ea/$18.50; 4 ea/$60.00; 12 ea/$165.00 (Free pair cotton gloves with each order of 12 AtmosBags)
Floor Base	Cat. No. Z10,691-7 $40.00
Sealing Tape	Cat. No. Z10,692-5 3 in. wide, 60-yd. roll $7.50

Made entirely of polished polyethylene, a highly inert, flexible material. Inflated size: 38 x 37 x 26 inches.

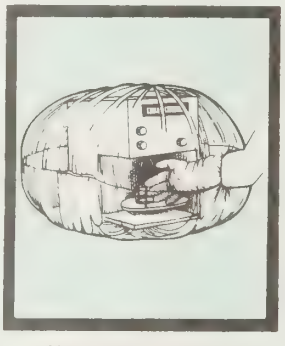


Open end is easily sealed with strip of removable tape. Tape strips included.

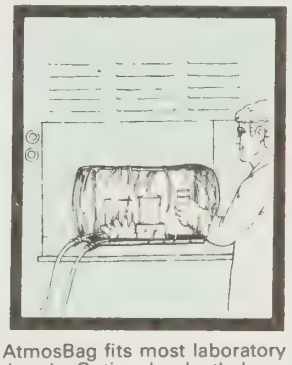


Load AtmosBag with necessary equipment, purge through inlets on either side.

AtmosBag is a convenient chamber for experiments requiring a controlled atmosphere.



New tapered glove design provides snugger fit, greater dexterity.



AtmosBag fits most laboratory hoods. Optional polyethylene internal work surface available.

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Aldrichimica Acta

Volume 13, Number 3, 1980
(Last issue in 1980)

Organosilicon Reagents for Carbon-Carbon Bond-Forming Reactions. **See page 43.**

PTC in PracTiCe. **See page 55.**

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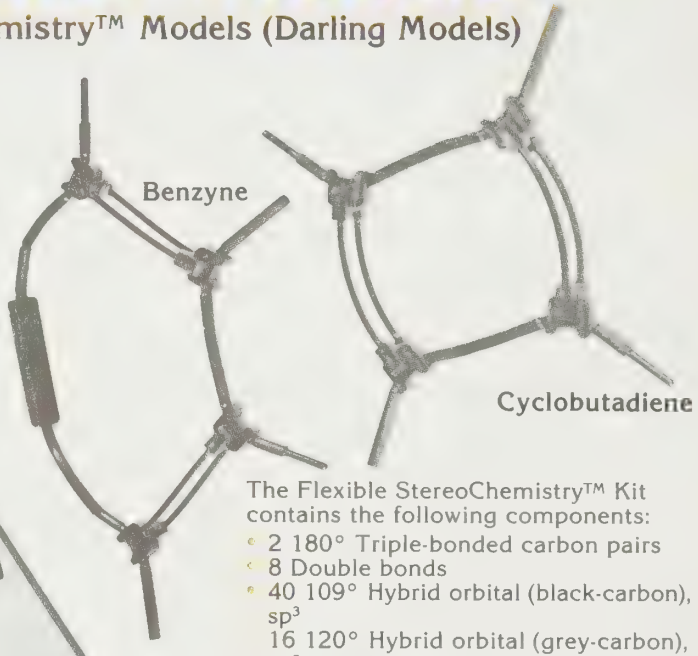
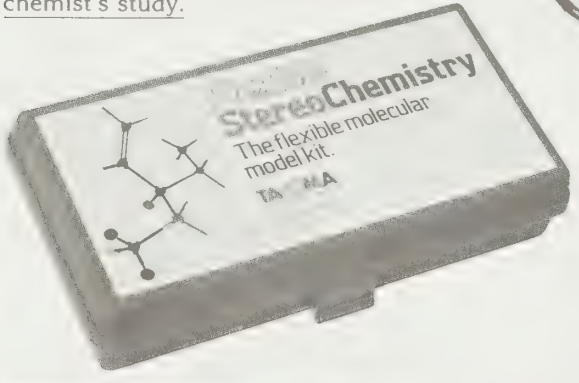
Molecular Models

Flexible StereoChemistry™ Models (Darling Models)

Newly developed by Professor Stephen D. Darling, the models bring a new dimension to the visualization of molecules in space. The special feature of flexibility permits one to "see" whether there is strain in a molecule due to angle distortion or torsional stress and whether two atoms in a molecule can "approach" each other.This unique feature in the Flexible StereoChemistry™ kit permits a more realistic study of spatial relationships and accurate relative interatomic distances for making comparisons. They are approximately the same size as the Fieser models. We believe the Darling models are best suited for the individual chemist's study.





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- 4 109° Hybrid orbital (blue-nitrogen), sp^3
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- 2 trivalent nitrogen atoms (blue)

Z10,400-0 Fieser Molecular Model Research Kit $24.00

See page 1102 of the Aldrich catalog for large quantities of individual atomic models.

References

(1) L.F. Fieser, J. Chem. Ed., **40,** 62 (1963).
(2) L.F. Fieser, ibid., **40,** 457 (1963).
(3) L.F. Fieser, ibid., **42,** 408 (1965)
(4) L.F. Fieser, 'Chemistry in Three Dimensions,' Aldrich Catalog Number Z10,160-5 $4.00.

Aldrichimica Acta

Volume 13, Number 3, 1980
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About Our Cover:

Our chemist-collector loves puzzles of iconography and authorship of paintings.

There is no iconographic problem, of course, with this moving depiction of *The Good Samaritan*, but who painted this fine, large (oil on canvas, 41″ x 58″) work? Our chemist believes it is Dutch, *circa* 1630-1640, by an artist strongly influenced both by Italian art and pre-Rembrandtists. In time, the right name will be known, as happens to most works of such competence.

The story of the Good Samaritan (St. Luke *10*, 25-37) has excited artists' imaginations throughout the ages, for it raises that most important question about the greatest of all the Biblical commandments, in Leviticus *19*, "Love thy neighbor as thyself." For who is your neighbor? Almost always, when we say — as did the priest and the Levite — "It's none of my business," we are mistaken. If only we understood the lesson truly, that our neighbor is all mankind, we would try harder to give the best possible service, to all who need help.

Are you interested in our Acta covers? *Selections from the Bader Collection*, with 30 duotone reproductions, many of previous Acta covers, and an introduction by Professor Wolfgang Stechow is available to all chemist art-lovers.

Z10,118-4 $6.00

Also, many paintings reproduced on our Acta covers were shown at the Milwaukee Art Center in an exhibition, "The Bible Through Dutch Eyes," arranged by Dr. Bader in 1976. The fully illustrated catalog with 66 black-and-white and 4 full-color reproductions contains many art historical and Biblical comments.

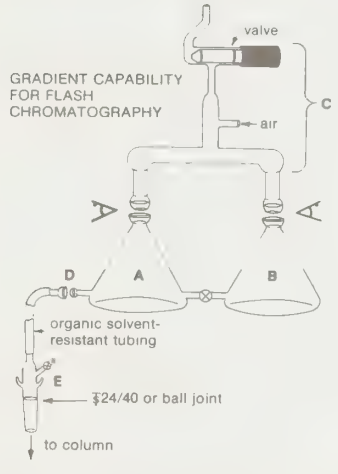
Z10,374-8 $10.00

Eight paintings that have been depicted on Acta covers and four that have been on catalog covers were among 18 Old Master paintings in an exhibition in honor of Professor Herbert C. Brown at Purdue University in October. If you would like the fully illustrated catalog of the exhibition entitled "Old Students and Old Masters: The School of Rembrandt," please send your check for $4.00 to the Department of Creative Arts, Purdue University, West Lafayette, IN 47907, and you will receive the catalog postpaid.

Many of the early issues of the *Aldrichimica Acta* have become very rare. Please do not throw your issues away. In time, we believe that complete sets will become valuable, and — if you do not want to keep them — there probably are chemists near you who would be interested.

Lab Notes

Flash chromatography reported by Still *et al.*, [*J. Org. Chem.*, **43**, 2923 (1978)] is rapidly replacing gravity flow chromatography because of the quickness and the better resolution it affords. As originally introduced, the system is isocratic. We have designed an apparatus which allows one to perform this and other types of chromatography in the gradient mode. The modification basically consists of two 1-L



flasks with ball joints, connected by a stopcock and an upper segment C for introduction of air pressure. Solvent of low polarity is contained in flask A while that of higher polarity is in flask B. After the flasks are filled to the same level, the stopcock is opened and the solutions are stirred (magnetic stirring bars). The solvent is introduced into the column through outlet D. Air is forced through the system using part C as shown in the diagram. To obtain an air-free system, unit E which fits on top of the column is necessary. If outlet D is sealed and the upper portion C removed, this apparatus also can be used for medium- and high-pressure gradient LC work.

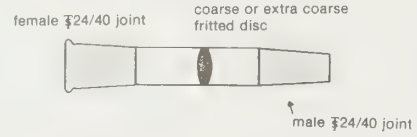
Bruce B. Jarvis
Professor of Chemistry

and

Jacob O. Midiwo
Research Assistant
Department of Chemistry
University of Maryland
College Park, Maryland 20742

A common problem encountered when adsorbing a sample on a chromatography support, especially when the adsorption solvent is much too polar for elution of the column, is the fast and complete removal of the adsorption solvent before the sample-support mixture is placed on the chromatography column.

We have found that a glass adapter made by having our glass blower place one male ⅐24/40 ground glass joint on a cylindrical sealing tube with a sealed-in fritted disc (extra-coarse- or coarse-porosity disc) to be convenient for this purpose. The insertion of this adapter between the round-bottom



flask containing the solvent-adsorbent-sample mixture and the vapor duct of any rotary evaporator allows the *in vacuo* removal of solvent without the sample-adsorbent mixture being sucked into the condenser of the rotary evaporator.

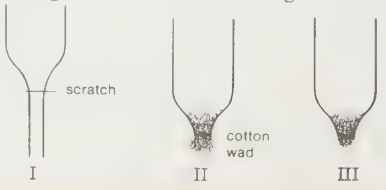
Similarly, this adapter prevents any solid from being sucked into the condenser when it is necessary to remove all solvent from a solid-solvent mixture.

Aldean J. Kolar, Ph.D.
Research Associate
Department of Medicinal Chemistry
School of Pharmacy
The University of Kansas
Lawrence, Kansas 66045

Editor's Note: For our customers' convenience, we now offer the adapter described above.

Z10,747-6 $25.00

An applicator for preparative TLC can be made conveniently from a Pasteur pipet. The narrow end of the pipet is scratched and broken off leaving a small constriction (I). A small wad of absorbent cotton is pushed from the wider end of the pipet and tapped into the constriction (II) (another Pasteur pipet may be used to put the wad into place). The end of the cotton is pulled until the wad is securely in place. Scissors are then used to trim the end of the wad to the desired shape (III). The sample, dissolved in a suitable solvent, is sucked up through the cotton wad using a rubber



bulb. The sample can be added in a controlled fashion to the TLC plate by applying slight pressure to the rubber bulb.

Gerald W. Kutney
Erindale College
University of Toronto
Mississauga, Ontario, Canada

Many laboratories keep solvents handy by storing them in polyethylene squeeze bottles. Unfortunately, the labels often wash off these bottles very readily. I have found that by marking the bottle with a felt tip pen and then carefully heating the bottle with a heat gun, the label will become permanently affixed. This makes the wash bottle easier to find and much safer to use.

Z10,319-5 Flameless heat gun $67.35
Z10,320-9 Flameless heat gun $71.65

Scott Stoltzmann
Laboratory Technician
Aldrich-Boranes, Inc.

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome red-and-white ceramic Aldrich coffee mug as well as a copy of **Selections from the Bader Collection** *(see "About Our Cover"). We reserve the right to retain all entries for consideration for future publication.*

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by Ofra Bader.

When I visited the Converse Labs at Harvard the other day, Dr. Leo Letendre indicated that our deuterochloroform has too much TMS (1%) to be useful for Fourier Transform NMR; 0.02 mole % would be much more useful. When working with very small samples, the intensity of the TMS peak might mask small peaks, yet some TMS is necessary.

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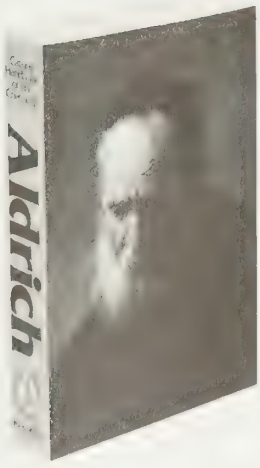
22,578-9 500g $65.00

It was no bother at all, just a pleasure to be able to help.



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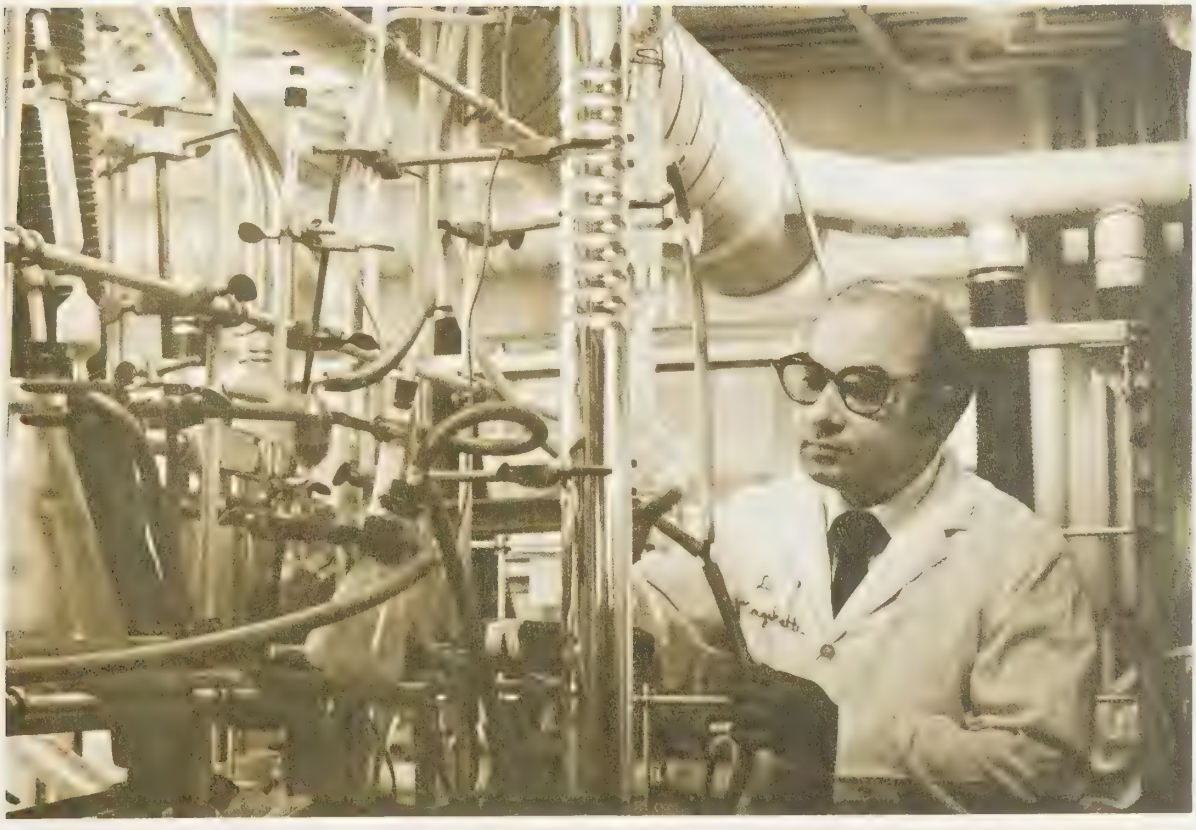

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Volume 14, Number 1, 1981

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By CHARLES J. POUCHERT, Vice President, Quality Control, Aldrich Chemical Company

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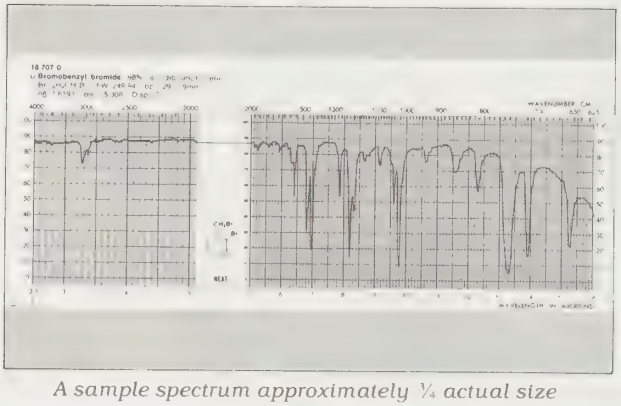

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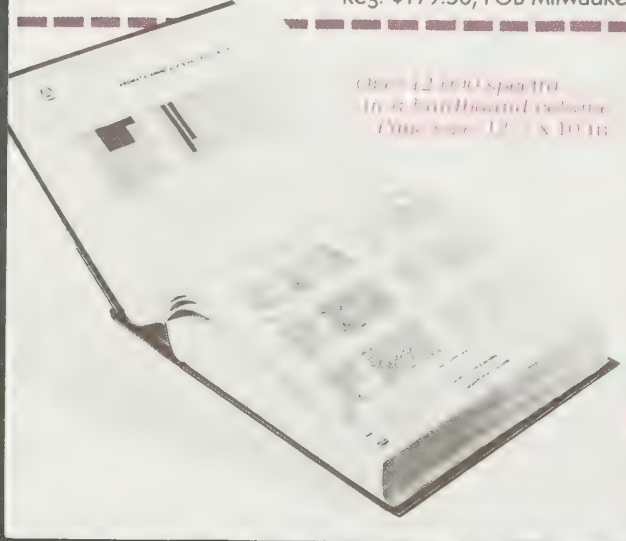

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About Our Cover:

This moving depiction of *Jesus and the Samaritan Woman at the Well* (John *4*) is one of the great puzzles in our chemist's collection. The subject was a favorite of Rembrandt and several of his students have been suggested as the artist, for instance, Carel Fabritius, probably Rembrandt's ablest and most inventive student, and Gerbrand van den Eeckhout who became Rembrandt's great friend. Our chemist believes it is by neither but has, as yet, no plausible solution—beauty in search of its creator is no less beautiful because of our ignorance.

The painting is a symphony of colors and shadows. The dominant colors are very unusual—violets and blues, and the concentration on shadow dominates the work: her shadow and the shadow of Jesus' hand, the focus of the whole.

This large work (oil on canvas, 43-1/4 x 33-1/2") was probably painted in the 1640's. It is unusual not only for its color, composition and the breathtaking psychological relationship—Jesus' great care for the woman—but also its execution: part of the foliage was painted with the brush handle cutting into the paint film. This technique was used by Rembrandt and his last student, Aert de Gelder, in the second half of the 17th century and may, in time, provide a clue to the artist of this masterpiece.

Lab Notes

We have found that one of the frequent causes of poor resolution in routine NMR work is the presence of paramagnetic particles adhering to the inside of the tube from the washing process. If a cotton plug is placed in the bottom of the inlet of a tube washer (such as your Z10,724-7) and samples are always filtered through a cotton plug, the tubes never come in contact with unfiltered solvent and remain free of these particles.

Douglas A. Livingston
Department of Chemistry
Columbia University
New York, NY 10027

Did you ever leave a water-cooled condenser on overnight then find water all over the floor the next morning because the latex tubing popped off the joint of the condenser? A cable tie, a piece of plastic approximately 1/8″ x 3-1/2″ used to tie electrical wires together, can prevent this occurence. To install, place latex tubing over inlet/outlet to condenser. Pull cable tie tightly around tubing and joint. To remove cable tie, slit the tie with a razor blade.

Becky Eubank
Commercial Lab Application
POLAROID
Assonet, MA 02702

Editor's Note: Aldrich offers a tie for this application.

Z10,595-3 Wrap-it tie, self-locking, nylon, 4-3/16" long $6.75/250

For applications requiring a longer tie:

Z10,596-1 Wrap-it tie, self-locking, nylon, 7-1/2″ long $10.00/250

Z10,598-8 Wrap-it tie adjustable installing tool $69.50

A common problem inherent with the daily usage of gas chromatographs is the eventual breakage or deactivation of the ignition filament incorporated within its self-contained detector unit. Replacement usually necessitates the inconvenience and expense of a service call by a factory representative. Alternatively, flame ignition may be brought about directly by using a match — a dangerous procedure which usually contaminates the detector — or by implementing a commercially available "Electric Match" or other portable spark source.

However, in our laboratory, a simple, inexpensive and readily available soldering gun has been employed effectively and safely over the past several years to ignite various self-contained flame-ionization detectors. The soldering gun is a "pistol" type, Model 199 manufactured by Wen with replaceable tips and is available at a very nominal price. Detector ignition is accomplished in the usual manner except for the external placement of the hot probe over the detector port. The tip geometry of this soldering gun is easily modified to adapt to various detector designs.

This type of external flame ignitor offers several advantages. Its construction is extremely durable and safe as well as simple and convenient to operate. The physical thickness of the ignition probe effectively eliminates the need for frequent tip replacements while clean ignitions are achieved without imparting contaminating residues to the detector. Most significantly, this approach appears to be independent of detector design and can be used without causing electrical damage to the internal circuitry of the detector unit.

Peter D. Frade, Ph.D.
Annetta R. Kelly, Ph.D.
Department of Pathology
Division of Pharmacology and Toxicology
Henry Ford Hospital
Detroit, Michigan 48202

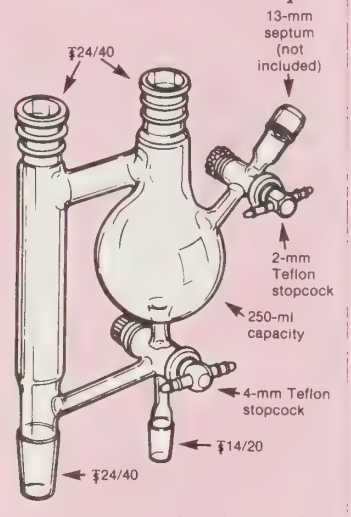
The violent "bumping" of certain liquids during vacuum distillation may be effectively prevented by merely packing the distillation flask with glass wool and distilling as usual. This method is effective even when the addition of boiling stones has proven useless.

David J. Eickhoff
Laboratory Technician
Procter & Gamble Co.
Miami Valley Labs
Cincinnati, Ohio 45247

P.S. Credit for this technique goes to Dr. E.D. Mihelich who first showed it to me.

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome red-and-white ceramic Aldrich coffee mug as well as a copy of **Selections from the Bader Collection** *(see "About Our Cover"). We reserve the right to retain all entries for consideration for future publication.*

From the Aldrich Glass Shop



Solvent still head. Designed by Paul F. Hudrlik for drying and distilling solvents. May be used for continuous distillation.

Z10,748-4 $140.00

"Please Bother Us."

by Aldrich Bader.

Mr. John Fulmer of the General Electric Company Plastics Division wrote to me recently to suggest that we synthesize 2-methylbenzofuran as an analytical standard. Mr. Fulmer explained that this "is a byproduct impurity in the commercial synthesis of phenol from cumene. Almost three billion pounds of phenol is produced annually in the U.S. All of the major industrial phenol producers (Monsanto, Allied, Dow, General Electric, Georgia Pacific, USS Chemicals, Shell Chemical) require gram quantities of 2-methylbenzofuran on a continuing basis for gas chromatograph and UV standardizations. No one in the *world* offers it."

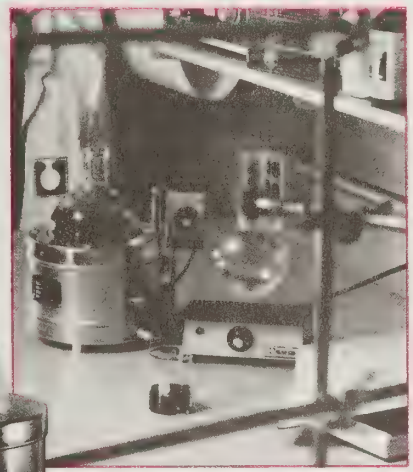
Naturally, we made it.

22,434-0 2-Methylbenzofuran 1g $15.00

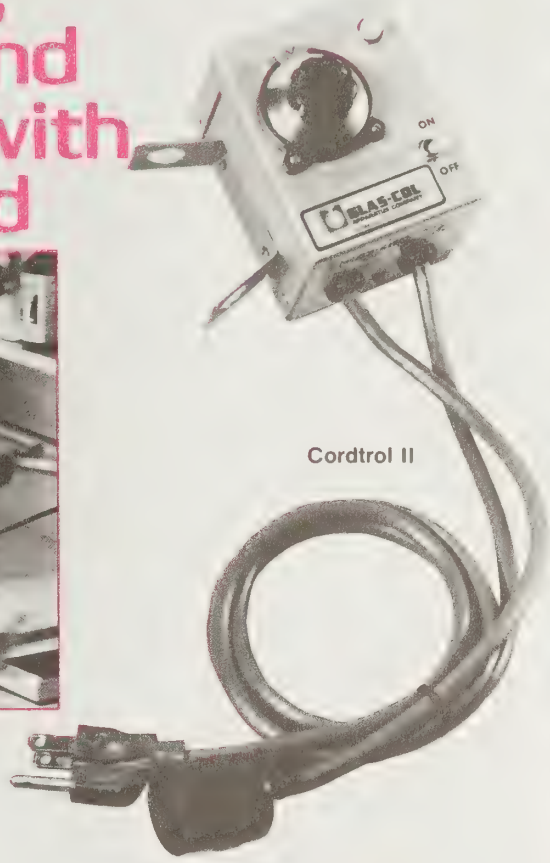
It was no bother at all, just a pleasure to be able to help.

New! Only through Aldrich.*

Non-arcing circuitry, greater accuracy, and more convenience with Glas-Col mantles and solid-state heating controls.



Mantle with Accutrol



Cordtrol II

*The best chemicals deserve the best processing equipment. Aldrich offers both. So, for the finest electric heating, we look to the Glas-Col Apparatus Company, inventors of the electric heating mantle and leaders in the chemical process industries for more than 40 years. Our teamwork with Glas-Col has led to the development and marketing of two new products: 1) Cordtrol II, a detachable, solid-state control; and, 2) Accutrol, an integral, solid-state control. Both of these new Glas-Col products work with the most popular heating mantles and are now available only through Aldrich Chemical Company. We hope you'll take advantage of this special offer.

Non-arcing circuitry.

To complement its electric heating mantles, Glas-Col has marketed both solid-state controls and variable transformers for several years and knows their strengths and weaknesses. For example, while the variable transformer's brush arcs as it crosses the coil, solid-state controls offer non-arcing circuitry. Neither Cordtrol II nor Accutrol cause arcing, and that means added operating safety.

Greater accuracy.

Both Cordtrol II and Accutrol feature high-ratio vernier dials for precise setting and exacting repeatability on subsequent settings. The shafts of non-vernier potentiometers generally rotate from 270 to 330 degrees to span a range of zero to 115 volts. And since the voltage curve usually flattens at the upper and lower ends, the useful range is perhaps only 180 to 240 degrees. But Glas-Col's vernier dial expands this range and provides more accuracy in both initial and repeat settings.

More convenience.

Both Cordtroll II and Accutrol solid-state controls have attractive features of convenience.

Cordtrol II's compact size (2¼" x 3⅜" x 1⅝"), no-mar feet (rubber), attachment bracket (stainless steel for ½" diameter rods), and durable case (anodized aluminum) allow for handy mounting on a lab bench, a distillation rack, in or outside fume hood, and on the mantle itself. It's easy to move and store. Cordtrol II may be purchased as part of a mantle-control package or by itself.

Accutrol's integral mounting on the mantle conveniently eliminates meandering cords and puts an end to equipment piracy among your departments or labs. It is durable, properly sized for the mantle it's mounted on, and always within the operator's reach.

Mantles with Cordtrol II:

Aldrich Number	For Flask Cap. (ml)	Wattage	Price
Z10,763-8	250	180W-115V	$110.00
Z10,764-6	500	270W-115V	$111.00
Z10,765-4	1000	380W-115V	$117.00
Z10,766-2	2000	500W-115V	$120.00
Z10,767-0	3000	500W-115V	$126.00
Z10,768-9	5000	600W-115V	$136.00

Cordtrol II (separate; use with existing mantles):

Aldrich Number	Volts	Amps	Price
Z10,769-7	120	5	$51.00

Mantles with Accutrol:

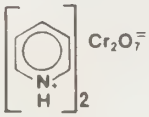
Aldrich Number	For Flask Cap. (ml)	Wattage	Price
Z10,770-0	12000	(2)-650W-115V	$425.00
Z10,771-9	22000	(2)-770W-115V	$459.00
Z10,772-7	50000	(2)-1500W-230V	$630.00
Z10,773-5	72000	(2)-2000W-230V	$700.00

More control.

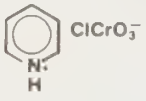
Cordtrol II and Accutrol are solid-state variations on a team—the Glas-Col and Aldrich team. For the best chemicals and processing equipment and for more heating control, call us.

PDC&PCC

Mild, Selective Oxidizing Agents Now Available in Bulk



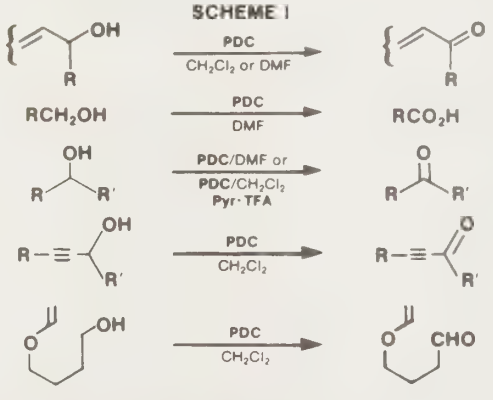
PDC



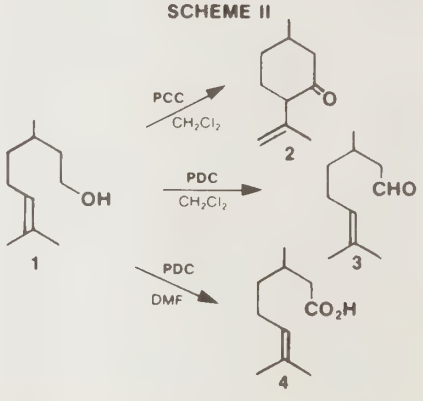
PCC

The search for mild, versatile, selective reagents for the operationally simple oxidation of alcohols to carbonyl compounds has long been the objective of many synthetic organic laboratories. Several years ago, Aldrich introduced **pyridinium chlorochromate (PCC).** With this reagent a variety of alcohols can be oxidized to the corresponding carbonyl compounds in methylene chloride. The mild acidity of **PCC** has been used to advantage in several unique oxidative transformations. For cases in which a more neutral reagent is necessary, Aldrich offers **pyridinium dichromate (PDC),** which has been shown recently to be of wide applicability for the oxidation of alcohols to aldehydes, ketones, and, in some cases, carboxylic acids. Some applications of **PDC** appear in Scheme I. It should be noted that **PDC** may be used in DMF (aqueous workup with extraction) or CH_2Cl_2 (nonaqueous workup; experimental procedure similar to that used with **PCC**). The results of a given oxidation may be different in the two solvents. For rapid oxidations of secondary alcohols with

SCHEME I



SCHEME II



PDC/CH_2Cl_2 catalytic amounts of **pyridinium trifluoroacetate** (also available from Aldrich) are used.

The more neutral character of **PDC** compared to **PCC** is contrasted in Scheme II for the oxidation of citronellol **(1).** In the reactions yielding **3** and **4,** no isopulegone **(2)** was detected.

On the other hand, the mildly acidic nature of **PCC** has been used to advantage in oxidative cationic cyclizations such as **1** → **2** and in oxidative 1,3-allylic oxygen transpositions.

Another interesting application of **PCC** is the synthesis of dihydropyranone derivatives from 2-furyl carbinols. **PCC** has also been used for the conversion of oximes to ketones and the direct oxidation of alcohol THP ethers to aldehydes. A study of the kinetics of the **PCC** oxidation of alcohols has been reported.

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Aldrichimica Acta

Volume 14, Number 2, 1981

Polymeric Dyes

Bromotrimethylsilane and Iodotrimethylsilane — Versatile Reagents for Organic Synthesis

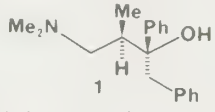
chemists helping chemists in research & industry

aldrich chemical co.

Chirald™

Reduce Your Problems With A Simple Complex

One of the most avidly explored areas of contemporary synthetic organic chemistry is the use of chiral reagents for the construction of optically active molecules.[1] A very useful reagent — which, to date, has not been readily available — is the amino alcohol **1** [(2*S*,3*R*)-(+)-4-dimethylamino-1,2-diphenyl-3-methyl-



≡ R*OH

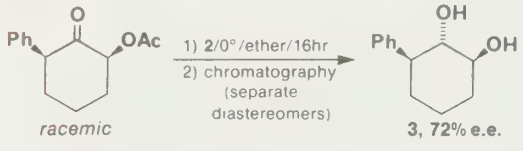
2-butanol].[2] It is now available from Aldrich at very reasonable prices. We call it **Chirald™**!

When used as a complex (**2**,[3] eq. 1) with **lithium aluminum hydride**, this reagent effects the enantioselective reduction of

$$n\ \underset{\mathbf{1}}{\text{R*OH}} + \text{LiAlH}_4 \xrightarrow[0°/N_2]{Et_2O} \underset{\mathbf{2}}{\text{"LiAl(OR*)}_n\text{H}_{4-n}\text{"}} + n\,H_2 \qquad n=1\text{-}3 \qquad (1)$$

prochiral ketones.[4] Complex **2** is prepared *in situ*, and **Chirald™** can be recovered and reused.[4]

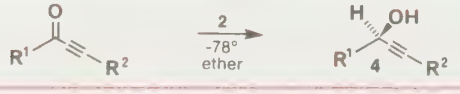
For example, a method for the synthesis of optically active *vic*-diols employs a freshly prepared, 2:1 complex of **Chirald™** and $\mathbf{LiAlH_4}$ (eq. 2).[5]

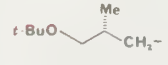
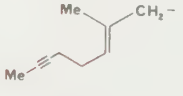
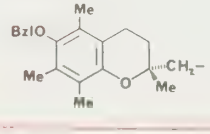


(2)

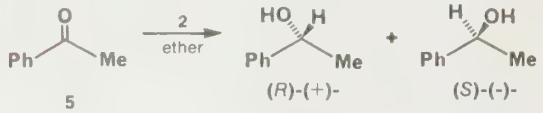
In addition, a wide variety of *R*-propargyl alcohols (**4**) have been synthesized by the reduction of α,β-acetylenic ketones with freshly prepared complex **2**.[6-8] Examples are given in the Table.

TABLE



R¹	R²	% e.e.	ref(s)
Me_2CHCH_2-	-Me	82	6,7
C_5H_{11}-	-H	72	7
	-Me	86	6
	-H	82	7,8
	-Me	90	6

It is interesting that the absolute stereochemistry of the reduction products is often a function of the *age* of the **Chirald™-$\mathbf{LiAlH_4}$** complex (**2**).[4] As shown in eq. 3,[4b] reduction of acetophenone (**5**) with *freshly prepared* **2** produces predominantly the *R* alcohol. However, if the complex is allowed to stand overnight,

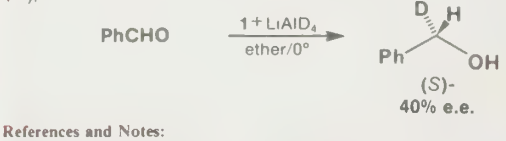


(3)

freshly prepared **2** (0°):	**MAJOR** (68% e.e.)	**MINOR**
"aged" **2** (r.t.):	**MINOR**	**MAJOR** (66% e.e.)

the *S* alcohol is the major product![4] Although there might appear to be a correlation between the solubilities[9] of the fresh *vs.* aged complexes and the stereochemical outcome of the reduction, exceptions have been reported.[4b] A generally accepted transition-state model for this phenomenon is yet to be published.

If $\mathbf{LiAlH_4}$ is replaced by **lithium aluminum deuteride** in eq. 1, the resulting **Chirald™** complex enables the synthesis of enantiomerically enriched α-deuterio alcohols (see, for example, eq. 4[4b]).



(4)

References and Notes:

1) See, for example, Szabo, W.A.; Lee, H.T. *Aldrichimica Acta* **1980**, *13*, 13 and ref. 1 cited therein. Copies of this review are available from Aldrich upon request.
2) Although this compound has been referred to in the chemical literature as "Darvon alcohol", the term is not only technically incorrect, its use is strictly unauthorized by Eli Lilly and Company (for whom the trademark Darvon® is registered).
3) This formula is simply meant to indicate the stoichiometry of the reagents used for the preparation of the **Chirald™-$\mathbf{LiAlH_4}$** complex; see ref.4.
4) (a) Yamaguchi, S.; Mosher, H.S.; Pohland, A. *J. Am. Chem. Soc.* **1972**, *94*, 9254. (b) Yamaguchi, S.; Mosher, H.S. *J. Org. Chem.* **1973**, *38*, 1870.
5) Kabuto, K.; Ziffer, K. *J. Org. Chem.* **1975**, *40*, 3467. Kabuto, K.; Shindo, H.; Ziffer, H. *ibid.* **1977**, *42*, 1742. There appears to be a discrepancy in these papers in that the enantiomer 3 is described in the texts as having the 1*R*, 2*R*, 3*R* configuration but it is drawn as shown in eq. 2 (1*S*, 2*S*, 3*S*).
6) Cohen, N.; Lopresti, R.J.; Neukom, C.; Saucy, G. *J. Org. Chem.* **1980**, *45*, 582.
7) Brinkmeyer, R.S.; Kapoor, V.M. *J. Am. Chem. Soc.* **1977**, *99*, 8339.
8) Johnson, W.S.; Brinkmeyer, R.S.; Kapoor, V.M.; Yarnell, T.M. *ibid.* **1977**, *99*, 8341.
9) Freshly prepared **2** is insoluble in ether; the aged reagent is soluble.

22,740-4	**Chirald™** [(2*S*,3*R*)-(+)-4-dimethylamino-1,2-diphenyl-3-methyl-2-butanol]	**10g $7.00; 50g $28.00**
19,987-7	**Lithium aluminum hydride**	**10g $6.70; 25g $11.90 100g $30.90; 1kg $179.00**
21,279-2	**Lithium aluminum hydride,** 1*M* solution in diethyl ether	**100ml $11.30; 800ml $50.25**
19,310-0	**Lithium aluminum deuteride**	**1g $12.00 5g $49.75**

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About Our Cover:

We have asked our chemist-collector about his criteria for including a given painting in his collection, and he has told us that he prefers Dutch 17th century portraits and "histories", especially Biblical and of the school of Rembrandt, well-drawn and strong in color. He had first seen this large (oil on canvas, 41 × 46-1/2 inches) *Baptism of the Eunuch* (Acts 8) many years ago in the living room of a great collector in England, Dr. Efim Schapiro, who had simply called it "Rembrandt School." The most stunning feature of this "history" is its contrast of colors, the cherry red of the little boy's dress and the shining gold of the eunuch's coat. Charming, also, is the blue Delft dish held by the little boy, a charm enhanced by the incongruity of a Delft dish in a New Testament story.

Our chemist believes that this was painted by Jacob Backer, generally thought to have been a Rembrandt student in Amsterdam in the early 1630's. There is no definite proof, although Backer and Rembrandt occasionally used the same models. For instance, the head of Democritus in Backer's painting of *Democritus Visited by Hippocrates* (Fig. 1) which we used on the cover of our biochemical catalog is of the same model used by Rembrandt for St. Paul in his painting of *St. Peter and St. Paul in Discussion* (Fig. 2) of 1628, now in Melbourne.

This *Baptism of the Eunuch* is not particularly "Rembrandtesque" and so may be an early work, before Backer became influenced by Rembrandt. The fourth figure from the right, the young man who looks so out of place in this New Testament story, may be a self-portrait.

Fig. 1

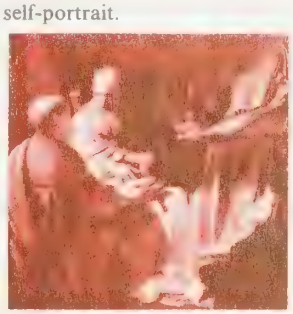


Fig. 2

Are you interested in our Acta covers? *Selections from the Bader Collection*, with 30 duotone reproductions, many of previous Acta covers, and an introduction by Professor Wolfgang Stechow is available to all chemist art-lovers. **Z10,118-4 $6.00**

Also, many paintings reproduced on our Acta covers were shown at the Milwaukee Art Center in an exhibition, "The Bible Through Dutch Eyes," arranged by Dr. Bader in 1976. The fully illustrated catalog with 66 black-and-white and 4 full-color reproductions contains many art historical and Biblical comments. **Z10,374-8 $10.00**

Lab Notes

When the seal (vacuum gasket) in our Büchi Rotavapor R recently developed a leak necessitating a seal replacement, we learned that the current (mid-1980) cost of the required tool for seal removal was $85. We wished to avoid this expense, if possible. A new-style fluorocarbon seal does not require use of such a tool, but the removal of the original piece still posed a problem. The following comments are applicable to the models R and RE.

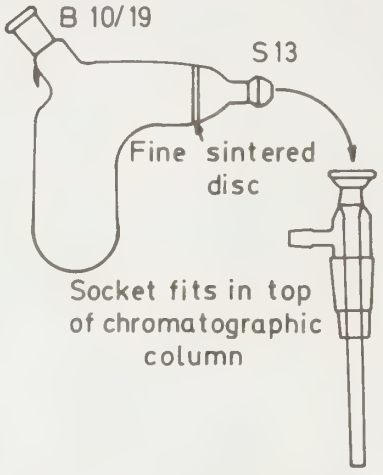
An easy solution was obtained by first removing the large coil spring and plastic screw coupling from the outside of the condenser and then carving away all the exposed rubber from the old seal. This exposed the metal washer which is responsible for the very tight pressfit of the original seal. The base of the condenser was immersed in aqua regia overnight. This resulted in complete solution of the washer and permitted easy removal of the residue the next day. Thorough cleaning should precede installation of the newer fluorocarbon seal.

Robert Rothchild
Assistant Professor, Science Department
John Jay College of Criminal Justice
City University of New York
445 West 59th St., New York, NY 10019

It is always convenient to eliminate as many steps in experimental procedures as possible, especially when dealing with difficult samples. The following apparatus has proved useful for loading dissolved asphaltene derived from coal-to-oil conversion processes onto chromatographic columns.

Powdered asphaltene is accurately weighed into the apparatus *via* the B10/19 socket and a known volume of solvent is introduced (*e.g.*, by pipette) as shown in the figure. When as much of the sample as possible has dissolved (the lower bulb of the apparatus can be immersed in hot water to aid dissolution, if necessary) the apparatus is turned 90°, seated on the suction column, and the solution is sucked through gently, directly onto the chromatographic support. In dealing with solvents having low boiling points (*e.g.*, diethyl ether) suction causes the solvent to bubble up from the column, in which case the application of slight pressure to the sample holder is preferred.

When the solution has been drained off, the apparatus is dried and weighed. The concentration of the solution added to the chromatographic column can then be calculated.



The apparatus eliminates some transfer steps and therefore cuts down on sample loss, for example, that remaining on glassware surfaces, sockets, taps, etc.

Dr. R. D. Davies
Fuel Research Institute
P.O. Box 217
Pretoria, South Africa 0001

It is often advantageous to have an airflow monitor in a fume hood. A simple monitor consists of a model airplane propeller (from a hobby shop) mounted on a needle stuck in a cork, with a short length of plastic tubing between the cork and the

propeller. Three nails can provide the legs of the airflow monitor which, when placed at the back of the hood, spins for years, unless airflow is interrupted.

Charles E. Gragg
Research Scientist
Burroughs Wellcome Co.
3030 Cornwallis Rd.
Research Triangle Park, NC 27709

One of life's minor irritations is the weighing of small quantities of statically charged peptide/protein material from lyophilization. Under normal circumstances, the light, fluffy, material flies everywhere.

We have found that using a commercial laundry antistatic cloth (Bounce) to wipe the outside of the receiving vessel, the glass balance doors, the containing vessel and the balance knobs, eliminates this problem.

Lucila Licate
Larry Taylor
Lafayette Clinic
951 East Lafayette
Detroit, Michigan 48207

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome red-and-white ceramic Aldrich coffee mug as well as a copy of **Selections from the Bader Collection** *(see "About Our Cover"). We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Alfred Bader.

Recently Professor J. C. Stowell at the University of New Orleans suggested that we offer dicinnamalacetone, an indicator for detecting excess hydrogen halides in many organic solvents (acetic acid, acetone, chloroform, dichloromethane, toluene, but not alcohols). It turns from yellow to a brilliant red. It is a very useful indicator, because so often, when a product is in contact with HCl or HBr for any length of time, yields decline. For example, Professor Stowell uses it in the addition of HBr to acrolein. Naturally, we made dicinnamalacetone right away.

22,906-7 Dicinnamalacetone
(1,9-diphenyl-1,3,6,8-nonatetraen-5-one)
5g $7.00

It was no bother at all, just a pleasure to be able to help.

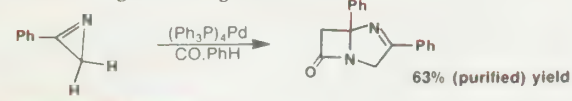
Homogeneous Catalysts

Easy Answers To Tough Problems

The increasing popularity of precious metal-mediated homogeneous reactions is evidenced by the appearance of numerous reviews and books[1] in addition to hundreds of research papers. The facility with which many of these transformations occur is amazing when one considers more traditional synthetic alternatives. The following recent examples illustrate this point.

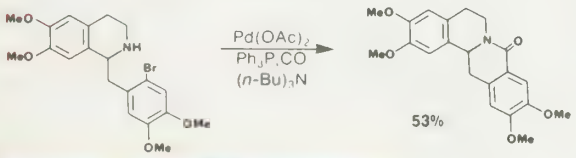
Tetrakis(triphenylphosphine)palladium(0)[2]

21,666-6 1g $15.00; 5g $59.00



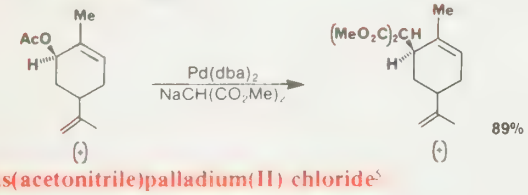
Palladium(II) acetate[3]

20,586-9 2g $29.00; 10g $119.00



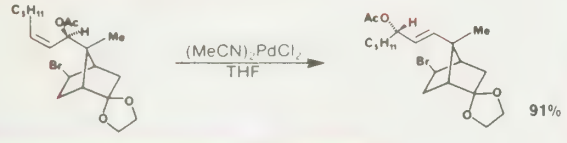
Palladium(0) bis(dibenzylideneacetone)[4]

22,799-4 500mg $16.25



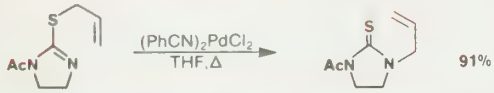
Bis(acetonitrile)palladium(II) chloride[5]

22,565-7 500mg $15.00; 5g $99.00



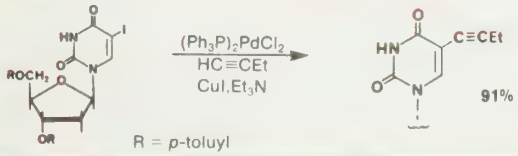
Bis(benzonitrile)palladium(II) chloride[6]

22,368-9 1g $14.00; 10g $99.00



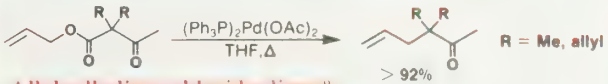
Bis(triphenylphosphine)palladium(II) chloride[7]

20,867-1 1g $13.75; 5g $55.00



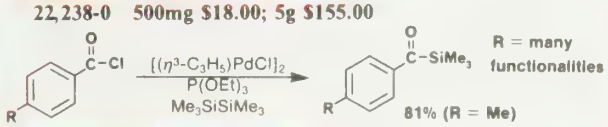
Bis(triphenylphosphine)palladium(II) acetate[8]

22,545-2 1g $7.95; 10g $57.50



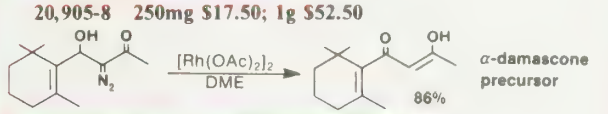
Allylpalladium chloride dimer[9]

22,238-0 500mg $18.00; 5g $155.00



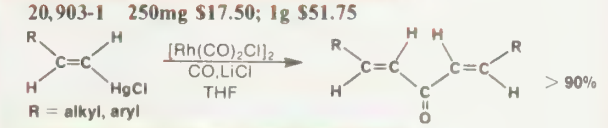
Rhodium(II) acetate dimer[10]

20,905-8 250mg $17.50; 1g $52.50



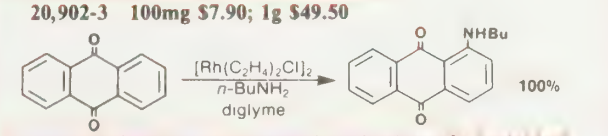
Tetracarbonyldi-μ-chlorodirhodium(I)[11]

20,903-1 250mg $17.50; 1g $51.75



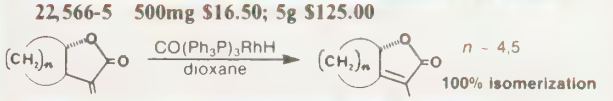
μ-Dichlorotetraethylenedirhodium(I)[12]

20,902-3 100mg $7.90; 1g $49.50



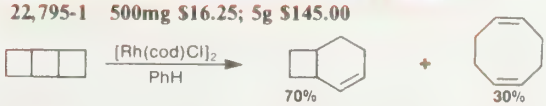
Carbonyltris(triphenylphosphine)rhodium(I) hydride[13]

22,566-5 500mg $16.50; 5g $125.00



Chloro(1,5-cyclooctadiene)rhodium(I) dimer[14]

22,795-1 500mg $16.25; 5g $145.00



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1) For example, see Tsuji, J. "Organic Synthesis with Palladium Compounds;" Springer-Verlag: New York, 1980; Trost, B.M. *Accts. Chem. Res.* **1980**, *13*, 385; Baker, R. *Chem. Ind.* **1980**, 816.
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MCPBA

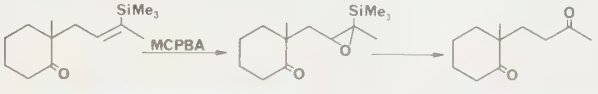
(m-Chloroperoxybenzoic acid)

MCPBA has long been the reagent of choice for the epoxidation of alkenes. It is superior to other peroxyacids and hydrogen peroxide in reactivity, stereoselectivity, and in purity and yield of products. Isolated double bonds, α,β-unsaturated ketones and esters, and acid-sensitive olefins are epoxidized in high yields.

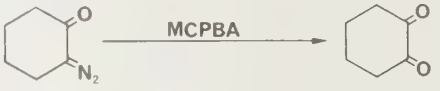
75%

Epoxides are very versatile intermediates, and recent reports indicate their utility in many hitherto difficult synthetic manipulations.

Vinyltrimethylsilanes are easily converted to trimethylsilyl epoxides, latent precursors to carbonyl groups.



MCPBA is an excellent reagent for the Baeyer-Villiger oxidation of ketones to esters, acid chlorides to alcohols, and ketals to ortho esters. Secondary alcohols are oxidized to ketones in the presence of catalytic amounts of nitroxides. α-Diketones are obtained in excellent yield from α-diazo ketones.



MCPBA oxidizes primary alkylamines to nitroalkanes, primary aromatic amines to nitroso compounds, secondary amines to nitroxides, and tertiary amines to N-oxides. MCPBA also enables the direct oxidation of amino-substituted nitrogen heterocycles to N-oxides without amino protection.

MCPBA is an excellent reagent for the oxidation of sulfides to sulfoxides and sulfones, intermediates with diverse applications.

For details of the chemistry of MCPBA send for our technical bulletin no. AL-116. MCPBA is also available in bulk quantities; call our toll-free number 800-558-9160 and ask for a bulk quotation.

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Aldrichimica Acta

Volume 14, Number 3, 1981

Transition-Metal Templates for Selectivity in Organic Synthesis
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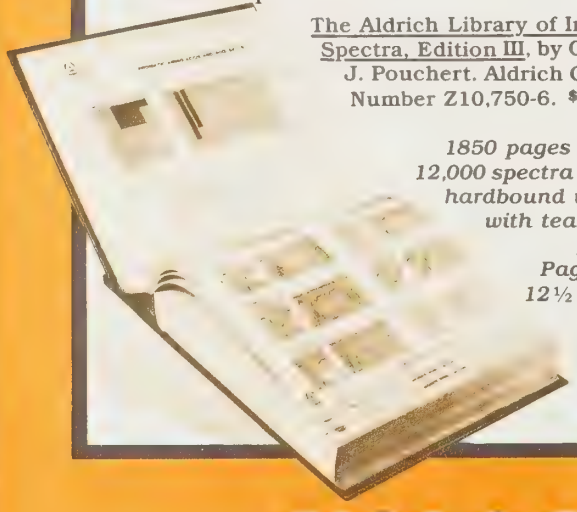

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About Our Cover:

Our chemist-collector first saw this almost mystical landscape (oil on panel, 27-$^1/_2$ × 41 inches) after giving a talk on Chemistry in Art at an A.C.S. meeting in Rochester, New York some time ago. A collector there inquired whether he might be interested in purchasing it, which he did. The painting appears to be by a mid-seventeenth-century painter strongly influenced by two of the greatest Dutch painters, Hercules Seghers and Rembrandt. Our chemist knows of several similar works by the same hand, generally misattributed to other Rembrandt students such as Govaert Flinck and Roland Roghman.

Fig. 1

This painting is signed (Fig. 1), but the signature is hard to decipher. Could it be that of the artist, van Terlee, born in Dordrecht in 1636 and died there in 1687, who is reported to have been a Rembrandt student? If so, this would be the first known signed work of van Terlee, and the other very similar works could then be attributed to him. What a pleasure to resurrect an able artist from oblivion.

Many of the early issues of the *Aldrichimica Acta* have become very rare. Please do not throw your issues away. In time, we believe that complete sets will become valuable, and — if you do not want to keep them — there probably are chemists near you who would be interested.

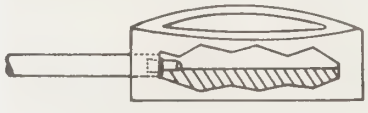
Lab Notes

In our laboratory we occasionally need to protect our vacuum pumps from volatile acid gases such as HCl or HBr. We have found that these gases are effectively removed by bubbling through a mixture of approximately 10% triethylenetetramine and 90% ethylene glycol. At pressures as low as 0.1mm Hg, very little ethylene glycol boils away, and is easily collected in the usual cold trap (-78°C).

Lauren R. Brown, Ph.D.
JBL Chemical Company
825 Capitolio Way
San Luis Obispo, CA 93401

In many small-scale chemical reactions it is necessary to maintain the temperature of the reaction mixture at 0°C (usually by means of an ice bath) for several hours. Pyrex recrystallization dishes are often used as containers for such baths. These dishes are inefficient insulators, requiring painstaking siphoning of water from the ice bath in order to add more ice.

Styrofoam containers are quite efficient insulators and can usually be obtained by modification of styrofoam crates used for shipping one-gallon bottles of mineral acids. A styrofoam crate is dissected diagonally and the edges smoothened with a sharp knife. The resulting 5.5-inch-diameter container (itself a good storage chamber for ice or Dry Ice) can be shortened to the desired height. A drain is easily added by boring a hole through one side using a 0.25-inch-diameter cork borer. Tygon



tubing (0.25 inch) is forced through the opening and is secured with a tubing "quick disconnect." The ice bath is now ready for use and will generally maintain 0°C for seven to eight hours with one filling of ice.

Dale E. O'Dell
J.S. Sawyer
D.R. Reagan
Department of Chemistry
Vanderbilt University
Nashville, TN 37235

Recovering mercury from the bulb end of a broken thermometer is a frequently encountered problem. Since it is usually difficult to break the bulb without scattering mercury droplets, the following procedure is offered as a solution.

Slowly immerse the bulb of the thermometer in a Dry Ice/acetone slush to contract all the mercury into the bulb. Freeze the mercury completely by keeping it in the bath for approximately 1 min., then rapidly plunge the bulb end into a warm-water bath. The thermal shock will crack the glass and the mercury will fall neatly to the bottom. Mercury thus obtained can be stored under water in a closed jar until needed for a manometer, etc.

This procedure can also be used to coalesce a broken mercury column in a thermometer. After freezing all the mercury into the bulb, allowing the thermometer to reach room temperature slowly will give a column of mercury with no separations.

Jim Sarafin
Aldrich-Boranes, Inc.

It is often very handy to have solvents in polyethylene squeeze bottles, but these tend to drip if the solvents are volatile and the temperature fluctuates. We overcome this problem by punching a small vent hole near the top of the bottle by means of a hot glass rod. Simply place a finger over the hole to use the bottle.

We often use Parafilm® to cover the mouths of flasks and test tubes. Unfortunately, it is sometimes difficult to separate the film from the backing. Pulling on a corner of a piece of film and backing stretches the film but not the paper backing, making it easy to separate film from paper.

George Chang
Department of Nutritional Sciences
Agricultural Experiment Station
College of Natural Resources
University of California, Berkeley
Berkeley, CA 94720

**Editor's note:*

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Ronald J. Mattson
College of Pharmacy
University of South Carolina
Columbia, SC 29208

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Selections from the Bader Collection** *(see "About our Cover"). We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Alfred Bader.

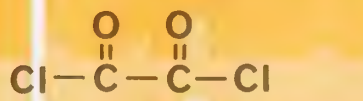
Recently, Dr. Malcolm R. Bell at the Sterling-Winthrop Research Institute suggested that we offer tris(4-bromophenyl)aminium hexachloroantimonate. Nathan L. Bauld and coworkers at the University of Texas at Austin have shown (*J. Am. Chem. Soc.* **1981,** *103,* 718) that this radical cation effectively catalyzes Diels-Alder reactions involving neutral or electron-rich dienophiles, precisely those cases in which Lewis-acid catalysis is not very effective.

Naturally, we made it.

23,022-7 Tris(4-bromophenyl)aminium hexachloroantimonate 5g $14.50
25g $45.00

It was no bother at all, just a pleasure to be able to help.

OXALYL CHLORIDE



Now Available In Bulk!

We ran our first ad on **oxalyl chloride** some twelve years ago and have filled much of the world's research needs for it ever since. It was made in 50-L flasks from anhydrous oxalic acid and PCl_5, a method that is difficult to scale up. Now we use a much better method and can supply ton lots quickly. Our product is much purer, higher than 99% with practically no heavy metal impurities.

Most uses of oxalyl chloride are well known (*cf.* Fieser and Fieser, *Reagents for Organic Synthesis*, **1**,767 **2**,301 **3**,216 **4**,361 **5**,481 **6**,424 **7**,257 and *Merck Index*, **9**,6745).

Oxalyl chloride is also finding many industrial applications, often as surprising as they are intriguing. These include: stabilizer for color photographic material, formation of monomers of thermally stable polymers, formation of polyamides useful as UV absorbers, polymerization catalyst, polymer crosslinking agent, production of resins for affinity chromatography, production of photopolymerizable printing materials, and chemiluminescent formulations.

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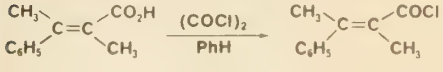
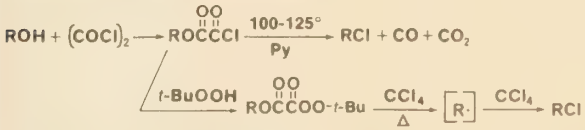
Some recent applications are:

Formation of very reactive acid chlorides:

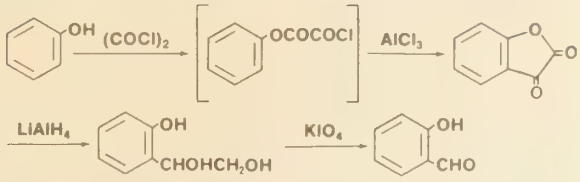


Formation of alkyl chlorides:

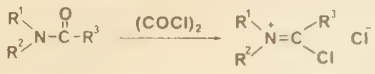


Conversion of amides to isocyanates:

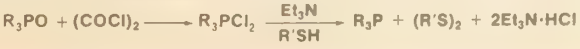
***o*-Formylation of phenols:**



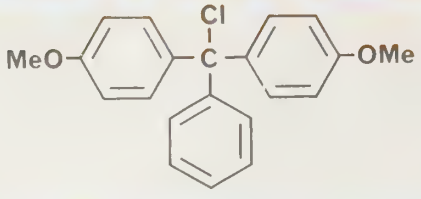
Preparation of chloroiminium chloride intermediates:



Reduction of phosphine oxides to phosphines *via* the dichlorides:



DMTCl



(4,4′-Dimethoxytrityl chloride)

For nearly 20 years, the dimethoxytrityl (DMT) function has enjoyed widespread use as a protecting group for the primary hydroxyl function of sugars.[1] It is easily attached by reaction of the substrate with **DMTCl** in pyridine solution, and its bulkiness ensures attachment only to primary alcohols. Moreover, it is readily removed by treatment with either dilute aqueous acid (to which it is even more labile than a tetrahydropyranyl ether) or with zinc bromide.

During the late 1960's, two approaches to solid-phase polynucleotide synthesis were developed[2] which now nearly always utilize **DMTCl** as the 5′-protecting reagent. A 5′-DMT-protected nucleoside is coupled to a solid support through its 3′-hydroxyl group, whereupon removal of the DMT group allows reaction with a 5′-protected nucleotide to form the usual phosphate linkage. This sequence is repeated until the chain is complete. In this way, 10-15-fragment polynucleotide chains have been prepared and successfully spliced together to form an artificial gene.[3]

Most exciting is the current research and development of mechanized polynucleotide synthesis.[4] The chemistry is the same, and again, the choice of the 5′-protecting group is nearly always **dimethoxytrityl**. Two firms already have automated the process and now market the instrument, and several others are likely to do so in the near future.[5] Obviously, **dimethoxytrityl chloride** is fast becoming a staple of polynucleotide and DNA research.

Aldrich also offers **4-methoxytrityl chloride (MTCl)**, another popular hydroxyl-protecting reagent in nucleotide chemistry.[6] Since aqueous-acid removal of the MT group is ten times slower than that of the DMT group,[1] **MTCl** is ideal for applications requiring greater acid stability.

To fill the expanding demand for **DMTCl** and **MTCl**, Aldrich now offers these reagents in bulk quantities. For a quotation, call our toll-free number 800-558-9160.

References:

1) Smith, M.; Rammer, O.H.; Goldberg, I.H.; Khorana, H.G. *J. Am. Chem. Soc.* **1962**, *84*, 430.
2) Letsinger, R.L.; Caruthers, M.H.; Jerina, D.M. *Biochemistry* **1967**, *6*, 1379; Letsinger, R.L.; Ogilvie, K.K.; Miller, P.S. *J. Am. Chem. Soc.* **1969**, *91*, 3360, and other papers in this Nucleotide series.
3) *Chem. Brit.* **1981**, *17*, 267.
4) *Chem. Eng. News* **1981**, *59*, 17.
5) *Ind. Chem. News* **1981**, *2*(7), 1.
6) See, for example, Gregor, I.; Sequin, U.; Tamm, C. *Helv. Chim. Acta* **1975**, *58*, 712.

10,001-3 4,4′-Dimethoxytrityl chloride **5g $16.00**
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Aldrichimica Acta

Volume 14, Number 4, 1981

The Role of Silver Salts in Organic Processes
A Compilation of References on Formyl and Acyl Anion Synthons

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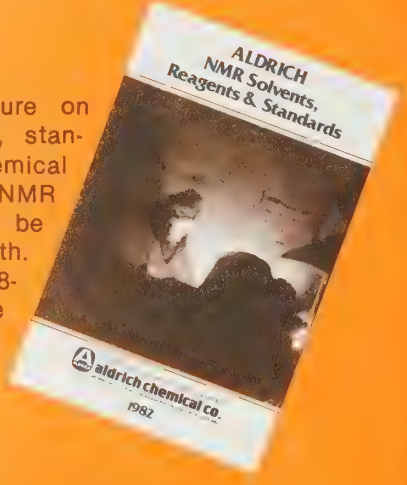

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About Our Cover:

Sometimes we wonder whether our chemist-collector buys old master paintings more because of their quality or for the problems of authorship and iconography they present. In the case of the large (44 × 55 inches) painting on our cover, surely it was both. When he was offered this painting by a dealer in London last summer, it was called "Christ Disputing with the Doctors" by Jan Lievens. Some years earlier, Christie's in London had sold it under the same title, as by Gerrit Willemsz. Horst, a Rembrandt student.

Our chemist-collector is certain that it depicts Joseph explaining his dreams, and believes it is a work of Jan Victors, influenced more by Lievens than Rembrandt, although Victors was a Rembrandt student. Compare it, for instance, with Lievens' "Feast of Esther" (Fig. 1). That painting, in the North Carolina Museum of Art in Raleigh, is so similar to this work that our chemist has wondered whether that famous work might possibly be by Victors, rather than by Lievens.

Jesus' disputation with the Pharisees is always depicted in the Temple — not in a bedroom as in the painting on our cover. Victors may have intended the old woman to be Rachel, but, if so, simply overlooked that Rachel, in the Biblical account, had died years earlier. Rembrandt made the same mistake in his representation of this subject (Fig. 2), now in the Rijksmuseum.

Victors painted a great many Biblical subjects; none depicts an episode from the life of Jesus. The rich colors make this painting one of his most beautiful.

Fig. 1

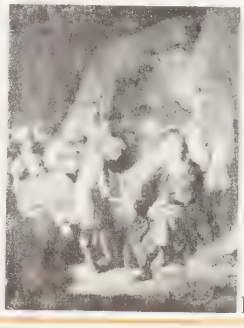

Fig. 2

Are you interested in our Acta covers? *Selections from the Bader Collection,* with 30 duotone reproductions, many of previous Acta covers, and an introduction by Professor Wolfgang Stechow is available to all chemist art-lovers.

Z10,118-4 $6.00

Also, many paintings reproduced on our Acta covers were shown at the Milwaukee Art Center in an exhibition, "The Bible Through Dutch Eyes," arranged by Dr. Bader in 1976. The fully illustrated catalog with 66 black-and-white and 4 full-color reproductions contains many art historical and Biblical comments.

Z10,374-8 $10.00

Lab Notes

I was prompted to write by the Lab Note in Vol. 14, No. 2 of *Aldrichimica Acta* which described a method for eliminating the problem of statically charged peptides.

We, too, have long suffered this problem. The commercially available anti-static devices that contain a radioactive strip have been marginally successful in our hands. Several years ago we bought an anti-static pistol (*ca.* $20) from the local stereo store. The unit operates on the piezoelectric effect to emit a stream of charged ions which completely neutralizes all surface static over a 30-cm area. This unit has worked extremely well and the only trouble that we have experienced is trying to keep track of it as many co-workers borrow it.

Paul D. Gesellchen, Ph.D.
Biochemistry Research Department
Lilly Research Laboratories
307 East McCarty St.
Indianapolis, Indiana 46285

Editor's note: We believe that such an anti-static device will be very useful in many laboratories, so, for the convenience of our customers, we now offer the Zerostat anti-static pistol.

Z10,881-2 $23.00

The following three shortcuts have proven useful in our laboratory:

1) A discarded square plastic bottle (of the type several chemical manufacturers use to distribute their products), after being cut down to size and notched at opposite ends, is very convenient for cooling the receiver flasks in Kugelrohr distillations. This device stands up well to both wet ice and Dry-Ice/acetone.

2) A polyethylene squeeze bottle with a pinhole in its side is an excellent container for running anhydrous HF reactions. After adding the substrate to the bottle, HF is introduced from an inverted precooled lecture cylinder. Upon capping the squeeze bottle, the HF which boils off displaces any remaining air. From 10-25ml of HF (a suitable volume for typical-scale Friedel-Crafts reactions involving 0.1-5g of substrate) can be handled in a 100-ml bottle without danger of bursting. The HF will evaporate overnight allowing the reaction mixture to be worked up in the usual fashion.

3) A simple procedure for the purification of tosyl chloride consists of placing the crude material in an extraction thimble for overnight extraction with reagent-grade hexane in a Soxhlet extraction apparatus. Seeding of the cooled hexane solution results in a beautiful snow-like crystallization. Decantation of the hexane under a dry atmosphere followed by pumping at high vacuum affords tosyl chloride of excellent purity.

John L. Belletire
Assistant Professor of Chemistry
University of Cincinnati
Cincinnati, Ohio 45221

Dissolving hard clumps of crude solid in a minimal amount of solvent, such as in sample preparation for NMR analysis or MPLC, is often difficult and time-consuming.

This problem can often be overcome easily by placing the tube, flask or vial containing the undissolved solid in the water bath of an ultrasonic cleaner for a few seconds.

Peter K. Trumper
Department of Chemistry
University of Minnesota
207 SE Pleasant St.
Minneapolis, Minnesota 55455

A frequent problem with gas chromatographs used for routine analysis is septum failure. The down time for this is usually at least an hour, particularly if an electron-capture detector or other gas-flow-sensitive detector is being used.

We have found that two things can be done to prevent this. First of all, be sure that there are no microscopic burrs on the syringe needle point. These can usually be felt by drawing the needle point between the nails of your thumb and forefinger. If a burr is found, remove it with a very fine-grit crocus cloth. Secondly, daily cleaning and lubrication of the syringe needle greatly reduces septum wear and also makes insertion and withdrawal of the needle easier. This is accomplished by wiping the needle with a 10% solution of SE30 (a GLC liquid phase) in toluene. The excess is removed with a clean dry tissue. We have been using SE30 as a needle lubricant for at least four years on various kinds of GLC columns and have never encountered any interference or column degradation that

Cont'd. on page 77.

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Selections from the Bader Collection** *(see "About our Cover"). We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Ayesha Bader.

Recently, Dr. James W. Miles of the Center for Infectious Diseases in Atlanta called us with an interesting problem. *m*-Diphenoxybenzene is used worldwide as an internal standard in the GLC analysis of malathion. The only supplier known to Dr. Miles was a laboratory supply house whose smallest package was 25 grams priced at more than a hundred dollars. That may not seem excessive to some U.S. laboratories, but it does to us. Also, 25 grams is such a large quantity for that application. Would Aldrich help?

Of course, we would. Some years ago, we perfected an elegant preparation of *m*-phenoxybenzaldehyde, of great importance in the synthesis of pyrethroids, and that technology was applicable here. We made a small batch of *m*-diphenoxybenzene and were able to cut the price by more than half. And, of course, we offer a 5-gram unit. For bulk quantities, we could lower the price much further.

23,263-7 ***m*-Diphenoxybenzene, 99+%, GOLD LABEL** **5g $12.00**
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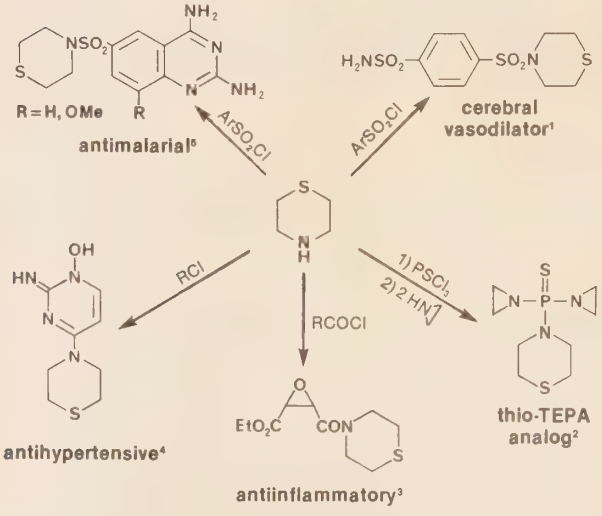
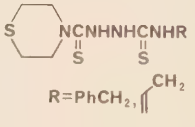
THIOMORPHOLINE

The functionally simple structure of **thiomorpholine** belies its proven versatility in medicinal chemistry as well as in other branches of chemistry.

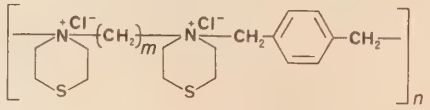


Hydrazine derivatives of **thiomorpholine** were found to inhibit the secretion of pituitary gonadotrophins and were useful in control of the ovarian cycle of domestic animals.[6]



Thiomorpholine, together with phosphoric acid derivatives, acts as a catalyst in the conversion of certain substituted penicillins to the corresponding cephalosporins.[7]

When condensed with α,ω-dibromoalkanes, **thiomorpholine** forms the corresponding bis-thiomorpholinealkanes, which afford polymers of the type shown, when heated with *p*-xylylene dichloride.



$m = 3,6$

Thiomorpholine has been N-aminated and the resulting N-amino heterocycles condensed with aldehydes or ketones to afford azomethines. Acid halides gave the corresponding N-acyl derivatives and oxidation with yellow HgO afforded tetracenes.[8]

A comparative study of the relative donor ability of nitrogen and sulfur atoms in a series of complexes between **thiomorpholine** and Pt(II) and Pd(II) halides has been made.[9]

Thiomorpholine is now available from Aldrich in bulk quantities! For a quotation, call our toll-free number, 800-558-9160.

References:

1) Holland, G.F. U.S. Patent 3 932 647, 1976; *Chem. Abstr.* **1976**, *84*, 121463w.
2) Hillers, S. *et al. Imifos* **1968**, 11.
3) Goi, M. *et al.* German Patent 2 938 571, 1980; *Chem. Abstr.* **1980**, *93*, 95117a.
4) Morrison, G.C. *et al.* U.S. Patent 3 973 016, 1976; *Chem. Abstr.* **1976**, *85*, 192759d.
5) Egli, C. *et al.* German Patent 2 441 959, 1975; *Chem. Abstr.* **1975**, *83*, 28274e.
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7) Ishimaru, T. *et al.* German Patent 2 344 130, 1974; *Chem. Abstr.* **1974**, *80*, 133460y.
8) Asinger, F. *et al. Monatsh. Chem.* **1980**, *111*, 385.
9) Allen, E.A. *et al. J. Chem. Soc. A* **1970**, 2137.

19,627-4 Thiomorpholine **2.5g $14.35; 10g $37.80**
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About Our Cover:

When we asked our chemist-collector to allow us to reproduce his finest recent acquisition in the *Acta* dedicated to Professor Stork, he pointed to the painting (oil on panel, 23½ × 17½ inches) reproduced on our cover. "Not *another* Jacob's Dream!" Our first reaction subsided quickly when we saw the quality of the painting — truly a dream in every sense of the word.

When it came up for sale in April of 1980, it was so covered by layers of dirty varnish (Fig. 1) that Christie's in London, who operate two auction galleries — one on King Street for better works and the other in Kensington for minor works — put it into the Kensington sale. It was attributed to one of the Carraccis, an artist family in Bologna early in the 17th century. Cleaning revealed that the painting is in excellent condition and is by Domenico Fetti, an artist who also worked early in that century in Rome, Mantua and Venice. Fetti often produced several versions of his compositions, and his best-known of this subject (Fig. 2) is in Vienna.

The painting had been sent to Christie's by its former owner in Weymouth, Dorset, who had inherited it from his grandfather. Nothing is known of its previous history, although it must have belonged to a collector whose seal (Fig. 3) is burnt three times into the back of the panel. Our collector has not yet determined the identity of the seal, and would be most grateful for help from any reader who recognizes it.

Fig. 1 (far left)

Fig. 2

Fig. 3

We are reminded of what we have written about this wonderful subject, in Vol. 8, No. 4 and Vol. 12, No. 3, of the *Acta*: "The Bible is the book of dreams, par excellence: dreams of individuals, dreams of a people, dreams of all mankind. It is surely no accident that the very first well known dream in the Bible is not that of a king or of a general but of a man at the lowest point in his life — homeless and hunted, yearning for God's promise that He would return him to his country.

"The vision of a ladder with angels going up and down on it is unique in Biblical imagery, and so *Jacob's Dream* has aroused artists' imaginations for centuries."

It seems a particularly fitting subject for the cover of this *Acta*, because Professor Stork — like Jacob — escaped from his homeland. We, in America, are lucky that Professor Stork did not return to France, but stayed with us and became one of our greatest chemists and teachers.

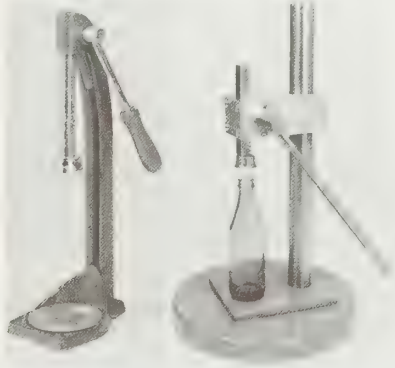
Lab Notes

The Aldrich Sure/Seal™ system of packaging sensitive reagents is so effective that we wanted to use it on our own samples. We saved the bottles, obtained a set of teflon septa and steel crown caps, Aldrich Cat. Nos. Z10,215-6 and Z10,214-8, and then discovered that there was no way of applying a cap to a bottle without using a capping device, available, for example, from Sears. Since it was not immediately apparent in our laboratory that such devices are available, we'd like to share this knowledge with other chemists to facilitate their use of this excellent system.

Jeanne Hoftiezer Marvin J. Hoard
Warner Lambert Co.
Pharmaceutical Research Division
Ann Arbor, MI 48105

Editor's note:
Aldrich now offers the following capping devices:

Z11,296-8	Crown-cap crimper	$44.00
Z11,297-6	Heavy-duty crown-cap crimper	$295.00



Z11,296-8 *Z11,297-6*

Ethyl acetimidate hydrochloride, prepared by the method of Dox (*Org. Syn. Col. Vol. 1*, p 5) is a solid mass which must be broken up for removal from the flask. Since it is hygroscopic and readily hydrolyzed, atmospheric moisture must be excluded. This could be accomplished conveniently by attaching a drying tube to the sidearm of the reaction flask and placing a glass rod or spatula in the flask with the handle protruding into the finger of a rubber glove secured around the neck of the flask with a rubber band. The rod or spatula may be manipulated almost as easily as if the glove were not present, and the arrangement, besides excluding moisture, protects the manipulator from HCl fumes.

This technique may be applied conveniently in many operations requiring manual stirring or crushing under anhydrous conditions. It is equally useful with multi-neck round-bottom flasks, and, by the attachment of an appropriate nitrogen inlet in place of the drying tube, may be applied in operations requiring an inert atmosphere.

John F. Hansen
Department of Chemistry
Illinois State University
Normal, IL 61761

A recent *Lab Note* described a qualitative air-flow monitor for a fume hood (*Aldrichimica Acta* **1981**, *14*, 22). In our laboratory the same function has been fulfilled for many years by what we believe is a much simpler and more convenient device. Thus, a disposable paper wiper was clamped by its narrow side, with a metal clip, to the lower edge of the hood window. In an efficient hood, when the window is half-way down, the free end of the tissue is sucked inside reaching an almost horizontal position. Obviously, in the absence of airflow the tissue hangs in a vertical position.

Magdi M. Mossoba
Laboratory of Pathophysiology
National Cancer Institute
Bldg. 10 B1B50
Bethesda, MD 20205

In trace-level analytical methods, it is necessary to minimize background levels. When quenching fluorinated acid anhydride derivatization reactions using aqueous phosphate buffer solutions, we have found that pre-extracting the buffer with a suitable immiscible solvent, *e.g.*, benzene, removes residues that could interfere with subsequent electron-capture gas-chromatographic assays. Also, the traces of benzene that remain in the buffer solution prevent the growth of mold. This treatment can also be applied to deionized water and NaOH solutions (inhibits carbonate formation) not only to minimize background, but to enhance stability on storage.

Charles Nony
Division of Chemistry
National Center for Toxicological Research
Jefferson, AR 72079

Preparation of dilute polymer solutions in 100-ml volumetric flasks is a routine task in our lab and wet resin invariably forms lumps, sometimes sticking to the wall of the flask.

While the use of a tiny magnetic stirring bar is common practice, we have found that its efficiency is notably increased when the flask is placed *on its side*. With the flask in this position the speed of mixing can be increased greatly without having the bar fly all over the flask. The vortex is deep and smooth. Finally, the liquid moves vigorously through the neck of the flask where stray resin often adheres.

When a large number of samples are involved this technique can speed up the entire process appreciably.

H. Russell Flanagan
Vice President,
Research and Development
Ruskat, Inc.
P.O. Box 43
Townsend, TN 37882

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Selections from the Bader Collection**. *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Ofira Bader.

Last December Dr. John Frost at Harvard suggested that solid tetrabutylammonium fluoride trihydrate would be even more useful than the THF solution we have been selling, simply because a solid is so much more convenient to handle. The solution can corrode syringes, and sometimes solvents other than THF are needed. We had thought that the solution would be more convenient, but of course we are happy to offer the solid also.

24,151-2 Tetrabutylammonium fluoride trihydrate 10g $12.00; 100g $80.00
21,614-3 Tetrabutylammonium fluoride, 1*M* in THF **100ml $28.25; 500ml $105.80**

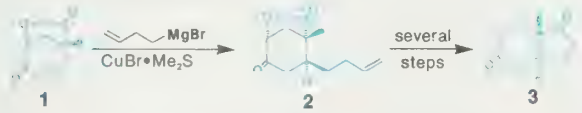
It was no bother at all, just a pleasure to be able to help.

Inspired by Gilbert Stork

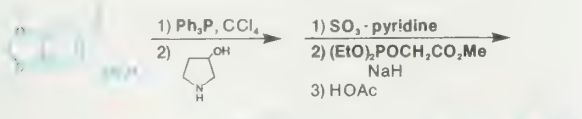
Selected Synthetic Transformations {1971-1981}

In his long and distinguished career, Professor Gilbert Stork has pioneered some of the most creative synthetic methods to appear in the chemical literature.[1] Aldrich salutes Professor Stork on his 35th anniversary! Below are some highlights of important synthetic methodologies developed by Professor Stork and his group during the last decade.

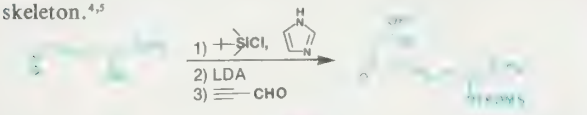
In a new, general construction of *trans*-hydrindanediones, the stereochemically crucial step in the synthesis of **3** is the 1,4-addition of 1-butene-4-magnesium bromide (prepared from **4-bromo-1-butene**) to **1**, promoted by **copper bromide-dimethyl sulfide complex**.[2]

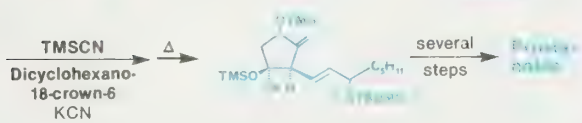


A simple stereospecific construction of the basic ring skeleton of the lycorine alkaloids was provided by application of the intramolecular Diels-Alder reaction.[3]

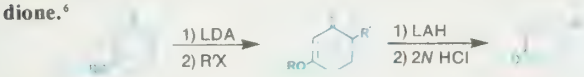


The thermal ene reaction of an appropriately substituted acyclic enyne afforded an efficient entry into the prostanoid ring skeleton.[4,5]

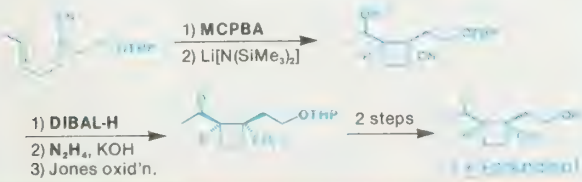




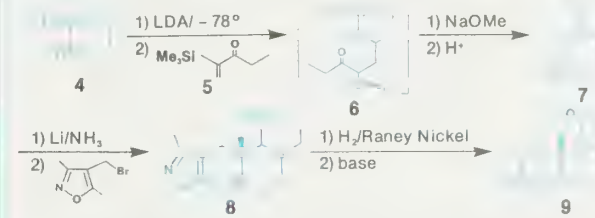
A general synthesis of 4-alkyl-2-cyclohexenones was provided by a regiospecific alkylation of the enol ether of **1,3-cyclohexanedione.**[6]



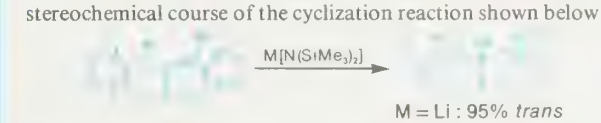
Perhaps the most general nonphotochemical synthesis of substituted cyclobutanes, the epoxy nitrile cyclization,[7] is illustrated by the pivotal step in a total synthesis of (±)-grandisol.[8]



A recent paper introducing the regiospecific and stereoselective reductive alkylation of enediones (*i.e.*, **7→8**) demonstrates several other important Stork synthetic techniques, namely, formation of the kinetic enolate of **4**, the α-silyl vinyl ketone annulation reaction (**4 + 5→6→7**), and the isoxazole annulation reaction (**7→8→9**). Reagent **5** is prepared from **vinyltrimethylsilane.**[9]



An application of the α-haloketal cyclization demonstrates a profound effect of the choice of metal counterion on the stereochemical course of the cyclization reaction shown below.[10]



M = Li : 95% *trans*
M = K : 95% *cis*

References:

1) An outline of Prof. Stork's achievements appears on p 7 of this issue of *Aldrichimica Acta.*
2) Stork, G.; Logush, E.W. *Tetrahedron Lett.* **1979**, 3361.
3) Stork, G.; Morgans, Jr., D.J. *J. Am. Chem. Soc.* **1979**, *101*, 7110.
4) Stork, G.; Kraus, G. *ibid.* **1976**, *98*, 6747.
5) Stork, G.; Isobe, M. *ibid.* **1975**, *97*, 4745, 6260.
6) Stork, G.; Danheiser, R.L. *J. Org. Chem.* **1973**, *38*, 1775.
7) Stork, G. *et al. J. Am. Chem. Soc.* **1974**, *96*, 5268.
8) Stork, G.; Cohen, J.F. *ibid.* **1974**, *96*, 5270.
9) Stork, G.; Ganem, B. *ibid.* **1973**, *95*, 6152; Stork, G.; Singh, J. *ibid.* **1974**, *96*, 6181. See also Boeckman, Jr., R.K. *ibid.* **1974**, *96*, 6179; Boeckman, Jr., R.K. *et al. Org. Syn.* **1978**, *58*, 152.
10) Stork, G.; Boeckman, Jr., R.K. *J. Am. Chem. Soc.* **1973**, *95*, 2016.

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P7,435-4	**3-Pyrrolidinol**	**1g $22.50; 5g $70.00**
S755-6	**Sulfur trioxide-pyridine complex**	**25g $9.65; 100g $24.95**
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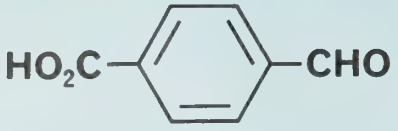
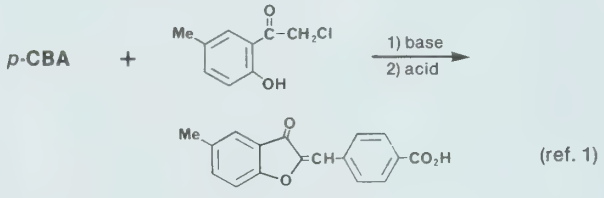
19,050-0	***t*-Butyldimethylsilyl chloride**	**5g $12.85; 25g $42.50; 100g $117.90**
21,284-9	**Trimethylsilyl cyanide**	**5g $13.85; 25g $46.20**
15,840-2	**Dicyclohexano-18-crown-6**	**2.5g $7.15; 10g $21.00; 100g $150.00**
C10,160-5	**1,3-Cyclohexanedione**	**100g $19.80**
C6,270-0	***m*-Chloroperoxybenzoic acid**	**25g $10.00; 100g $29.20; 500g $122.90; 1kg $196.60**
22,577-0	**Lithium bis(trimethylsilylamide),** 1*M* in THF	**100ml $9.00; 800ml $49.00**
21,500-7	**DIBAL-H,** 1.0*M* in toluene	**100ml $11.95; 800ml $37.25**
21,515-5	**Hydrazine,** anhydrous	**100g $12.00; 500g $45.00**
21,395-0	**Vinyltrimethylsilane**	**5g $12.10; 25g $32.50**

p-Carboxybenzaldehyde



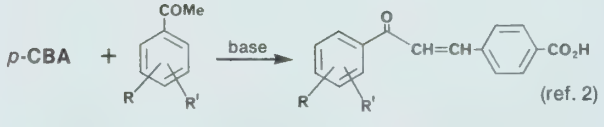
Since the first report seventy years ago, ***p*-carboxybenzaldehyde** (***p*-CBA**, terephthalaldehydic acid) has been employed in an increasing number of applications requiring an exceptionally reactive aromatic aldehyde. The aldehyde function can be manipulated under a variety of reaction conditions with no interference from (and thus no need for protection of) the carboxylic acid group.

During the past decade, the use of ***p*-CBA** in industrial processes has increased tremendously. Usually, ***p*-CBA** is condensed with an amine, enolate, or other nucleophile to afford a *p*-carboxybenzylidene moiety in excellent yield. A few recent syntheses of biologically active molecules illustrate this diversity.



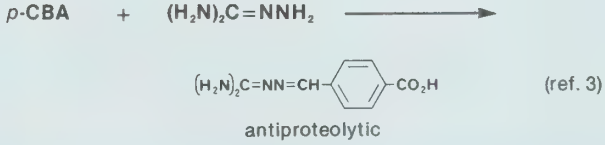
(ref. 1)

antiasthmatic



(ref. 2)

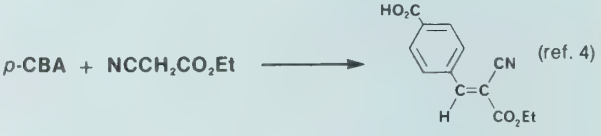
antiinflammatory



(ref. 3)

antiproteolytic

In addition, ***p*-CBA** has found wide use in the polymer industry. The previously mentioned high reactivity of the formyl group makes ***p*-CBA** ideally suited for large-scale processes requiring high yields. As shown below, both monomers and polymers have been prepared from ***p*-CBA**.



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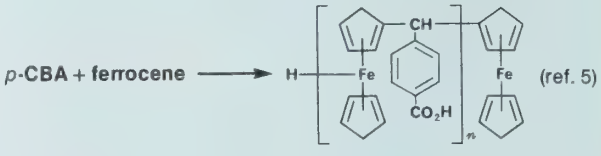

(ref. 5)

***p*-CBA** has also been employed as a sensitizer in photochromic systems[6] and when incorporated into polyolefins, initiates UV-photodegradation of the polymer.[7]

In response to the expanding demand for large quantities of ***p*-CBA**, Aldrich now offers ***p*-carboxybenzaldehyde** in bulk quantities. For a quotation, call our toll-free number, 800-558-9160.

References:

1) Baker, S.R. *et al.* Ger. Offen. 2 936 730, 1980; *Chem. Abstr.* **1981**, *94*, 15550u.
2) Biorex Laboratories Ltd. Fr. Demande 2 383 157, 1978; *Chem. Abstr.* **1979**, *91*, 39136c.
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6) Newland, G. *et al.* U.S. Patent 3 501 410, 1970; *Chem. Abstr.* **1970**, *73*, 40503e.
7) Tokuzumi, T. *et al.* Japan 72 11 654, 1972; *Chem. Abstr.* **1972**, *77*, 153122f.

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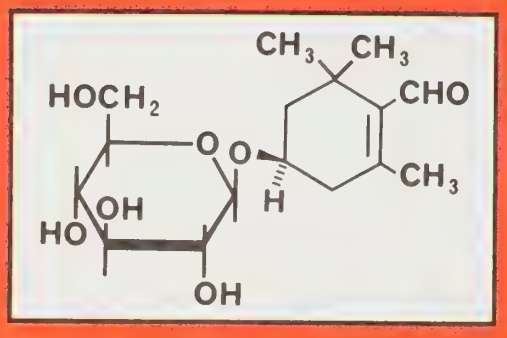

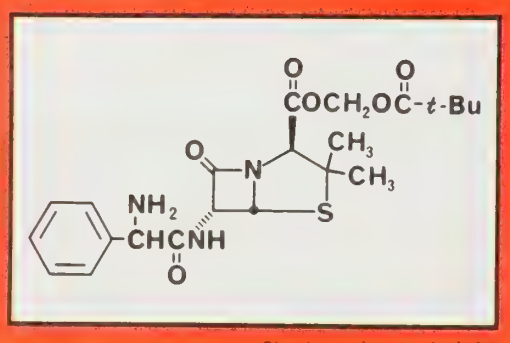

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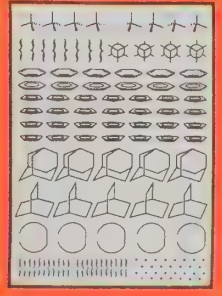
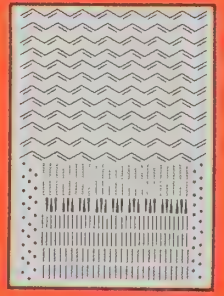
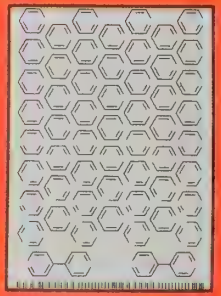
Since we first offered these dry-transfer symbols in 1980, we have received a number of requests to add other symbols, and to offer a smaller size compatible with typewritten copy. Although the larger structures are easier to work with, the use of smaller symbols avoids camera reduction for manuscript copy.

The latest additions to the collection are shown below. In all, there are 22 different sheets. Except for the two sheets of lines and arrows, all are available in large and small sizes. A tool kit consisting of a burnisher, knife, blades and eraser is available. See pages 1349-1351 of the 1982-1983 Aldrich Catalog/-Handbook for the complete listing.







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About Our Cover:

The painting (oil on canvas, 44½ × 35½ inches) reproduced on our cover has been auctioned twice at Christie's — once in London in 1969, then believed to be by Barent Fabritius, and again last year in New York as by Jan Victors, both Rembrandt students. It is, in fact, an early work by one of Rembrandt's ablest students, Nicolaes Maes. Several drawings for it exist; the best known (Fig. 1) is in the Victoria and Albert Museum.

The very human face of the angel portrays one of Nicolaes Maes' friends, probably the artist Barent Fabritius, whose face we meet again on the far left of Maes' most famous work, *Jesus Blessing the Children* (Fig. 2, detail in Fig. 3), now in the National Gallery in London.

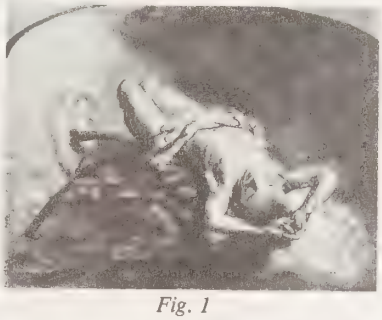

Fig. 1

Fig. 2

Fig. 3

Abraham's Sacrifice was a favorite subject among Dutch artists. To quote *The Bible Through Dutch Eyes*: "It is probably significant that, of all the many sacrifices detailed in the Five Books of Moses, this is the only one that specifically mentions the use of a knife — to heighten our revulsion toward human sacrifice. The word used here for knife in Hebrew, Maacheleth, occurs only here in the entire Five Books of Moses. Abraham's sacrifice is one of the most difficult events in the Bible to understand. Why did God demand that of Abraham? It cannot have been to show God how obedient Abraham was, because God knew what would happen. The only plausible explanation is that God wanted us to see that Abraham and Isaac were willing to do at God's command what must have been the most abhorrent act possible to them."

Maes must have been fascinated by this story which shows a trust in God we find hard to understand and could not match, and so he was challenged to portray this moment of complete obedience.

Lab Notes

The attachment of rubber tubing to glassware (condensers, etc.) is often difficult unless grease, oil, silicone or water is used. Recently, I wished to attach an air condenser to the top of a micro Snyder column; a collar of 4-mm-i.d. latex tubing would not fit over the 8.5-mm-o.d. column and it was desirable not to use the usual lubricants since contamination and hydrous conditions had to be avoided.

When silanizing glassware to reduce adsorption of a diamine, the glassware becomes "slippery". This phenomenon was used to facilitate attachment of the above latex tubing. The glassware was wiped with or dipped into the silanization reagent, dichlorodimethylsilane (99%, Aldrich D6,082-6), and air-dried.

Brian L. Worobey
Sir Frederick Banting Research Centre
Tunney's Pasture
Ottawa, Ontario K1A 0L2

To facilitate manipulations in a controlled-atmosphere bag, the gloves can be replaced by a pair of "rubber" gloves. These are easily connected to the arm openings with 4-in. embroidery hoops.

I have used Playtex gloves for several years, but use of your Viton gloves would allow safe handling of toxic materials which readily penetrate other gloves.

Robert Gotts
Research Laboratory
Muskatatuck State Hospital
and Training Center
Butlerville, IN 47223

Editor's note: Aldrich now offers a gloveless AtmosBag™ which is provided with two glove rings (3½-in. diam., 1½in. wide) made of high-density polyethylene to which desired gloves can be taped.

Z11,284-4 $27.60

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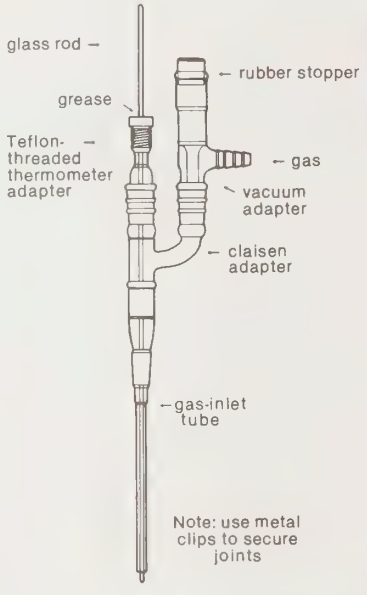
We have found a simple and inexpensive solution to the problem of large graduated cylinders with broken bases. Simply place the broken cylinder in a shallow dish made from the bottom of a plastic bottle (bleach bottles work well) and fill with clear casting resin. Upon hardening, the cylinder is equipped with a broader, more stable, shatterproof base. Careless handling of certain solvents may shorten the life of the base, but we have used this method to salvage 1- to 4-liter cylinders satisfactorily for several years.

Roger Nash and JoAnn Garner
Crown City Plating Co.
4350 Temple City Blvd.
El Monte, CA 91731

Often during reactions involving gas addition, the formation of solids causes the gas inlet tube to become plugged. It is a nuisance to have to shut off the gas and remove the tube to unplug it, especially when working with toxic or corrosive gases. Aggravation can be avoided by using the following setup which consists of common glassware.



By using the glass rod as a plunger, solids in the inlet tube can be dislodged without interrupting the gas addition. Not only is this method convenient, it is safe since the rubber-stoppered neck will serve as a pressure-relief outlet should the tube become plugged.

Jeff Reimer
Aldrich Chemical Co.

We purchase 95% and absolute ethanol in unmarked gallon bottles, which are distinguished only by the labels on the boxes in which they arrive. Occasionally someone will remove a bottle from the box without labeling it, causing a potentially time-consuming identity problem. A quick way to distinguish 95% ethanol from absolute or denatured ethanol is to mix one part (by volume) of the alcohol with two parts of petroleum ether; 95% ethanol forms a separate layer while the other alcohols are miscible.

John W. Lehman
Assoc. Professor of Chemistry
Lake Superior State College
Sault Ste. Marie, MI 49783

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Selections from the Bader Collection** *(see "About Our Cover"). We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Ryra Bader.

Recently a young chemist in San Francisco, Steven Gill, interested and very knowledgeable in chemiluminescence, expressed his surprise that we could offer TKDE so inexpensively. He inquired whether we might also be able to offer 6,13-pentacenequinone — the bis(phenylethynyl)pentacene made from it would be an interesting red fluorescer.

We do not know much about chemiluminescence but offer hundreds of quinones (mainly through our ABC Library of Rare Chemicals) and many intermediates for chemiluminescents (such as phenylacetylene). So we made the pentacenequinone.

24,688-3	**6,13-Pentacenequinone**	**1g $19.00**
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It was no bother at all, just a pleasure to be able to help.

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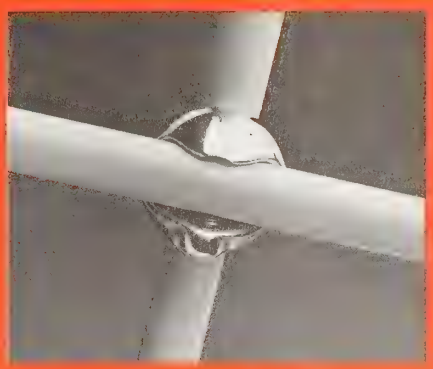

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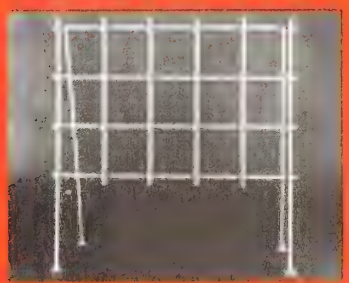
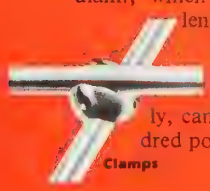


Chemists are now replacing metal supports with these new smooth, unthreaded rods, 1¼" (13mm) in diam., which can be cut to any length with a hacksaw. They are strong enough that a 4-ft. rod, held horizontally, can support over a hundred pounds from its center.



Clamps

The fiberglass lattice rod support system includes integrated components such as compact, high-strength, corrosion-resistant clamps die-cast in aluminum alloy. They come complete with Allen-head screws and are supplied in sets of twelve, with one Allen wrench. Quick-action clamps are equipped with sliding T-handle, stainless steel screws which are useful for frequent adjustments. These T-handle screws may also be purchased separately.

Base Plate

Two different base plates are available: one has a swivel-type design that permits locking a fiberglass rod in any position of up to 22.5° from the vertical.

Swivel-Type Base Plate

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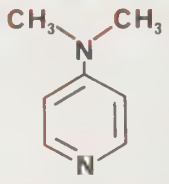
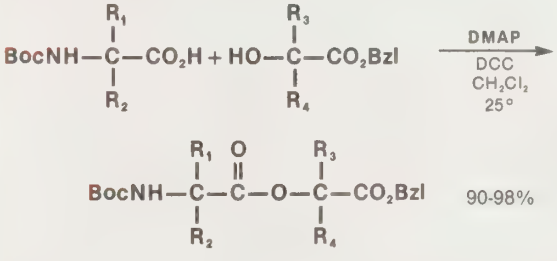
Z10,859-6	24ea.	$25.65
BASE PLATES		
Z10,718-2	Reg., ea.	$3.25
Z10,719-0	Swivel, ea.	$3.85

DMAP

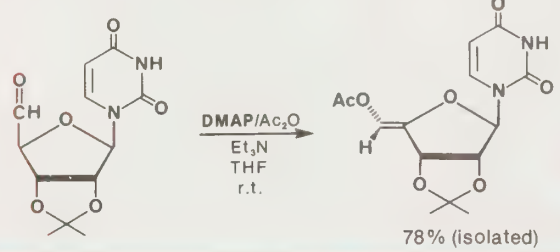


(4-Dimethylaminopyridine)

4-Dimethylaminopyridine (DMAP) has been a very popular acylation catalyst for some years, as outlined in a recent review article.[1] It is particularly effective for the acylation of sterically hindered alcohols. For instance, while neither pyridine nor triethylamine alone will effect the reaction of acetic anhydride with 1-methylcyclohexanol, the addition of 0.05 equiv. of DMAP to a mixture of the alcohol, Et_3N and Ac_2O results in the formation of the corresponding acetate in 86% isolated yield.[2] The remarkable catalytic efficiency of DMAP was demonstrated in a high-yield synthesis of depsipeptides using carbodiimide methodology, as shown below.[3]



Enol acetates of aldehydes (but not ketones) are produced in high yield under mild conditions using Ac_2O/Et_3N/DMAP (0.1 equiv.),[4] even in sensitive systems, as illustrated in the following nucleoside example:



Nucleoside chemists are using DMAP with increasing frequency for introducing protecting groups. For example, 5′-O-tritylations,[5] -monomethoxytritylations,[6–8] and -dimethoxytritylations[9] of nucleosides have been catalyzed by DMAP, as have N^4-monomethoxytritylations[8] and O^6-phosphorylations,[6,7] sulfonations,[6,7,10] and silylations[6] of guanosine and deoxyguanosine base residues. DMAP is also an effective catalyst for the **selective** *t*-butyldimethylsilylation of primary alcohols in the presence of secondary alcohols.[11]

DMAP is available in bulk quantities. For more details on the chemistry and properties of DMAP, ask for Technical Bulletin No. AL-114. For a quotation on bulk quantities, call 800-558-9160.

References:

1) Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569.
2) Hassner, A.; Krepski, L.; Alexanian, V. *Tetrahedron* **1978**, *34*, 2069.
3) Gilon, C.; Klausner, Y.; Hassner, A. *Tetrahedron Lett.* **1979**, 3811.
4) Cousineau, T.J.; Cook, S.L.; Secrist, J.A. III *Synth. Commun.* **1979**, *9*, 157.
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6) Daskalov, H.P.; Sekine, M.; Hata, T. *ibid.* **1980**, *21*, 3899.
7) Sekine, M.; Matsuzaki, J.; Satoh, M; Hata, T. *J. Org. Chem.* **1982**, *47*, 571.
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11) Chaudhary, S.K.; Hernandez, O. *ibid.* **1979**, 99.

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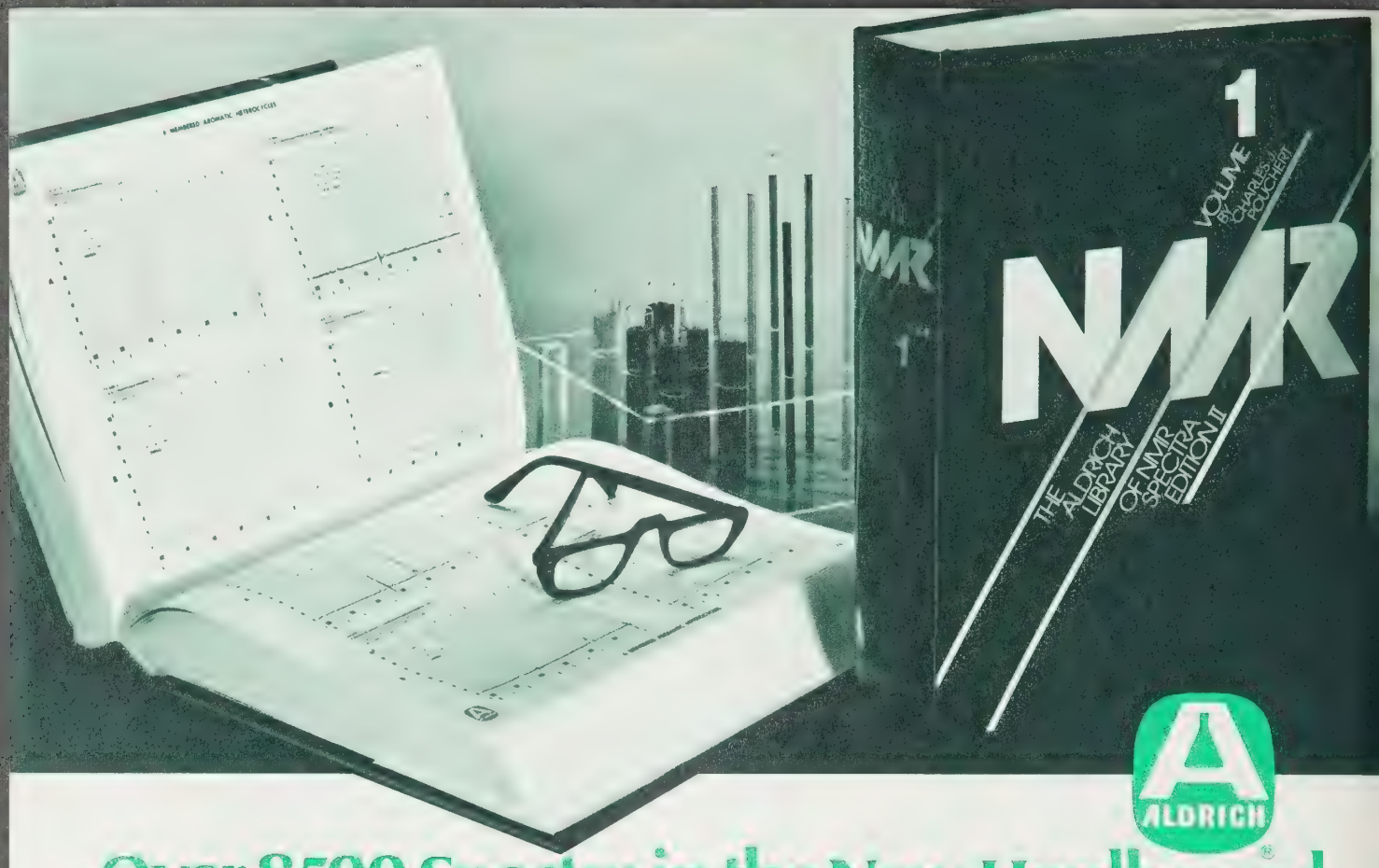
Aldrichimica Acta

Volume 15, Number 3, 1982 (Last issue in 1982)

Advances in Stereochemical Control. The 1,2- and 1,3-Diol Systems.



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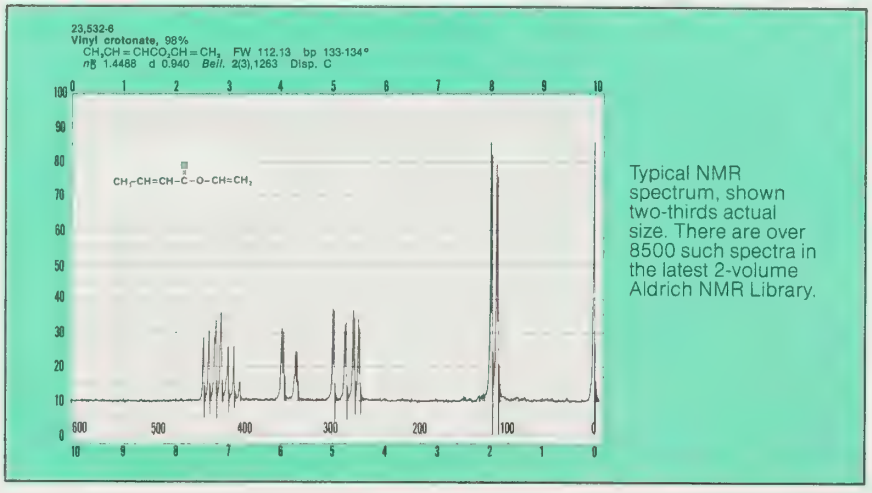

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About Our Cover:

As you know, our chemist-collector buys paintings for all sorts of reasons: puzzles of authorship or iconography, and often for the sheer beauty of the work.

We have sometimes wondered whether there were many great old masters whose names are now almost unknown. Our chemist-collector believes that Leonard Bramer is one of these little-known painters whose works are greatly undervalued.

Readers of the *Aldrichimica Acta* may remember the "Queen of Sheba Visiting King Solomon," a painting by Bramer which appears on the cover of Vol. 7, No. 1, 1974. This issue's cover, "The Presentation in the Temple" (oil on panel, 27¼ × 21½ inches) is another work of Bramer so beautiful in composition, coloring and light that it immediately appealed to our collector.

Though Bramer was 10 years older than Rembrandt, his works show the influence of both Rembrandt and the Italians, and provide an important link between Rembrandt and 18th-century Italians like Magnasco.

This painting has an interesting history. It belonged to Thomas Jefferson Bryan, one of America's first serious collectors of old master paintings. He was born in Philadelphia in 1802, graduated from Harvard in 1823, and after twenty years in Europe returned to New York. In 1867 he gave his large collection to the New York Historical Society which sold 113 of his paintings, this one among them, at auction at Sotheby Parke Bernet in New York in 1980.

Are you interested in our *Acta* covers? Selections from the Bader Collection, with 30 duotone reproductions, many of previous *Acta* covers, and an introduction by Professor Wolfgang Stechow is available to all chemist art-lovers.

Z10,118-4 $6.00

Also, many paintings reproduced on our *Acta* covers were shown at the Milwaukee Art Center in an exhibition, "The Bible Through Dutch Eyes," arranged by Dr. Bader in 1976. The fully illustrated catalog with 66 black-and-white and 4 full-color reproductions contains many art historical and Biblical comments.

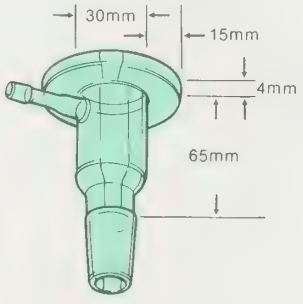
Z10,374-8 $10.00

Many of the early issues of the *Aldrichimica Acta* have become very rare. Please do not throw your issues away. In time, we believe that complete sets will become valuable, and — if you do not want to keep them — there probably are chemists near you who would be interested.

Lab Notes

The most common sequence of operations in preparative organic chemistry is probably aqueous extraction, drying over a desiccant, filtration and rotary evaporation. Generally, one filters into a filter flask and then transfers into an evaporating flask.

We have found that a simple adapter with a rubber collar is useful for filtering directly into an evaporating flask.



The dimensions given are those for a general-purpose adapter, which may be used with small Hirsch funnels or sinters. Particularly small funnels or filter columns may be mounted *via* a flat block of rubber with a hole in the middle (*e.g.*, a bung sliced in half).

Dr. David R. Kelly
Dyson Perrins Laboratory
Oxford University
England

Editor's note:

For the same purpose, Aldrich offers three sizes of the adapter shown at left. For size and price information, see page 1335 of the 1982-1983 Aldrich Catalog/Handbook.

Like most synthetic chemists, we are perpetually faced with the problem of removing small amounts of product from large reaction flasks. Scraping with spatulas usually only leads to a smearing of the product into an even finer coating on the sides of the flask.

To overcome this problem of material loss we use the following process. The product is loosened from the walls of the flask by scraping with a spatula and then a small amount of liquid nitrogen is added to the flask. The liquid nitrogen is swirled around for a few seconds and then left to settle at the bottom of the flask. The product becomes suspended in the liquid nitrogen, and as the nitrogen evaporates, it leaves a pellet of product which can be simply removed with a spatula. Water condensation is prevented by blowing a nitrogen stream through the flask during evaporation.

John R. Thornback
Department of Chemistry
Loughborough University of Technology
Loughborough, Leicestershire LE11 3TU
England

In our laboratory, heat-sensitive chemicals are stored in a regular refrigerator modified with an external thermostat, and with the internal light and defroster disconnected to prevent sparking and the possibility of an explosion.

We have found that the inevitable slow leakage from the containers causes an accumulation of obnoxious and potentially dangerous vapors. The simple solution was the installation of a vent in the refrigerator. A hole was carefully drilled through one wall just below the freezer compartment, another in the bottom of the door. The holes were fitted with two short pieces of glass tubing and a flexible sealant. A long, thin drying tube (1cm × 75cm) filled with Drierite®, to retard frost accumulation, was fastened onto the door and connected to the tube there. The other vent was attached to the house vacuum (an equivalent source of vacuum would also serve). A slow, continuous flow rate essentially eliminated the odors. The rate of consumption of the drying agent was quite slow (less than 15cm/-month).

Werner Fritz
Department of Chemistry
The University of Manitoba
Winnipeg, Manitoba R3T 2N2

Quick connectors in cooling water lines make the assembly of lab glassware fast and convenient. Unfortunately, accidental separation of quick connectors can result in lab floods — particularly in the case of unattended equipment.

A simple, lightweight retaining clip for quick connectors can be readily constructed from sheet metal. In one useful design, a 7/8″ strip of 20-gauge cold-rolled steel is formed into the shape of a "U" and slots are cut into the sides of the end pieces. For one brand of quick connector (Mallinckrodt QD Size 1), the base of the "U" is 1-1/8″ with 7/8″ square end pieces and 7/16″ × 5/8″ slots. This design yields an effective retaining clip weighing less than 9g.

Paul E. Eckler
International Minerals & Chemical Corp.
P.O. Box 207
Terre Haute, IN 47808

Editor's note:

In response to Mr. Eckler's lab note, we now offer two "lockable quick disconnects" shown in the picture below. We hope to make a retaining clip available to our customers soon.

Z11,632-7	**With check valve**	**$9.95/2**
Z11,641-6	**Without check valve**	**$9.45/2**

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Selections from the Bader Collection**. *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Alfred Bader.

When I visited Oxford University recently, I received many good suggestions for new products. One of them, from Dr. Carl Ziegler, was for 3-(phenylsulfonyl)-propionic acid, an elegant tool for 3-carbon homologation.[1]

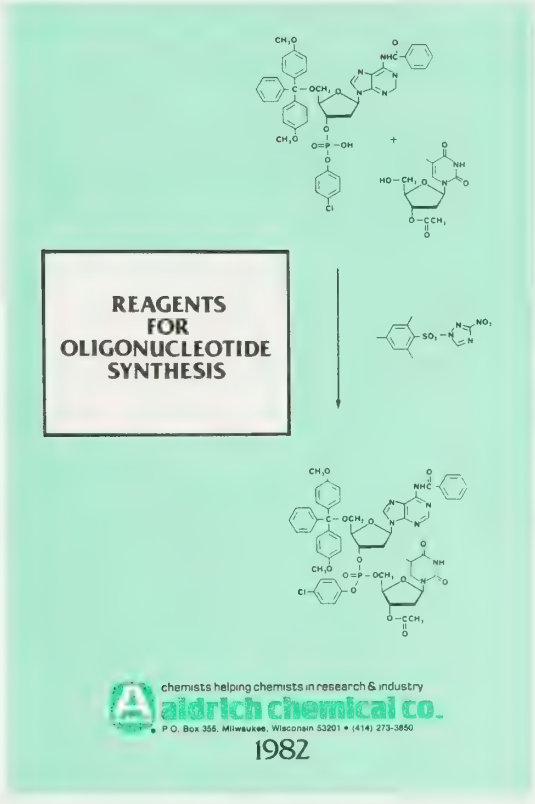
Naturally, we made it.

1) Iwai, K. *et al. Synth. Commun.* **1976**, *6*, 357.

25,157-7	**3-(Phenylsulfonyl)propionic acid**	**5g $8.00; 25g $28.00**

It was no bother at all, just a pleasure to be able to help.

Reagents for Oligonucleotide Synthesis



The chemical synthesis of defined sequences of ribo- and deoxyribonucleotides is an important source of tools for geneticists, microbiologists, and genetic engineers. Synthetic procedures have been refined significantly in recent years. Aldrich is a leading supplier of specialty reagents used in oligonucleotide synthesis, and we continue to add new important reagents to our listings as they appear in the chemical literature and gain acceptance. For the convenience of the researchers in this field, we have listed these reagents in a brochure, in which they are categorized by function (protection, deprotection, phosphorylation, condensation). Leading references are given for the applications of each reagent. For the most comprehensive listing of reagents for oligonucleotide synthesis, write or call toll-free 800-558-9160 and request a free copy of the brochure.

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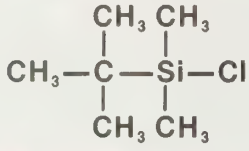
TBDMSCl



(*tert*-Butyldimethylsilyl chloride)

Ten years ago, Professor E.J. Corey and co-workers introduced *tert*-butyldimethylsilyl chloride (TBDMSCl) as a protecting reagent for alcohols which offered specific advantages over the alternatives available at the time:[1] a TBDMS ether is 10^4 times more stable than a trimethylsilyl (TMS) ether toward solvolysis in protic media, and is stable toward aqueous or alcoholic base, hydrogenolysis, and mild chemical reduction. Although these properties are shared by tetrahydropyranyl (THP) ethers, introduction of the TBDMS group does not create a new chiral center.

Since its original report, TBDMSCl has grown in popularity such that it is now considered by many to be the ideal choice for hydroxyl-group protection. TBDMS ethers are usually prepared in dimethylformamide solution employing imidazole as the acid scavenger; simple aqueous/extractive workup allows isolation of the product in high yield.

Another major benefit is that highly selective protection reactions are made possible by the steric bulk surrounding the silicon atom of TBDMSCl. Even pairs of alcohols of the same type (*e.g.*, primary[2] or secondary[3]) have been differentiated by virtue of their steric environment in the molecule.

In light of the properties outlined above, it is not surprising that the popularity of TBDMSCl continues to grow tremendously. Very recently, it figured prominently in the total syntheses of the vitamin E side chain,[4] prostaglandin E_1,[5] and the Prelog-Djerassi lactone.[6] To fill this expanding demand, Aldrich now offers TBDMSCl in bulk quantities. For a quotation, call our toll-free number 800-558-9160.

Of course, we also offer the reagents for the preparation of THP or TMS ethers, for those instances requiring the special properties of these groups.[7]

References:

1) Corey, E.J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.
2) Tanis, S.P.; Nakanishi, K. *ibid.* **1979**, *101*, 4398.
3) Hirayama, M. *et al. Tetrahedron Lett.* **1982**, *23*, 4725.
4) Heathcock, C.H.; Jarvi, E.T. *ibid.* **1982**, *23*, 2825.
5) Sato, C. *et al. ibid.* **1982**, *23*, 2099.
6) Workulich, P.M.; Uskokovic, M.R. *J. Org. Chem.* **1982**, *47*, 1600.
7) Greene, T.W. "Protective Groups in Organic Synthesis"; Wiley-Interscience: New York, 1981 (Z10,823-5 $37.50)

19,050-0 ***tert*-Butyldimethylsilyl chloride** **5g $12.85; 25g $42.50; 100g $117.90**

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Aldrichimica Acta

Volume 16, Number 1, 1983

The Preparation and Reactions of Diazomethane. Triflic Acid and its Derivatives.

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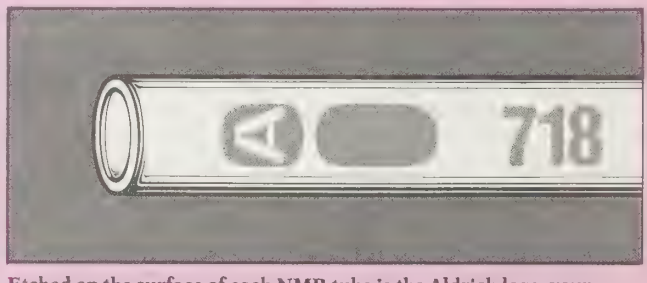

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5	Standard	0.1955 ±0.0003 0.1655 +0.0005 −0.0000	±0.0015	±0.001	Z11,718-8	19.75/5
5	Premium	0.1955 ±0.0003 0.1655 +0.0005 −0.0000	±0.0015	±0.0005	Z11,719-6	22.25/5
5	Gold Label	0.1955 ±0.0003 0.1655 +0.0005 −0.0000	±0.0005	±0.00025	Z11,721-8	59.00/5
10	Standard	0.3933 ±0.0003 0.3569 ±0.0005	±0.005	±0.001	Z11,722-6	8.80 ea.
10	Gold Label	0.3933 ±0.0003 0.3569 ±0.0005	±0.00075	±0.00025	Z11,723-4	20.40 ea.
				Pressure caps for 5-mm NMR tubes, red	Z11,807-9	2.75/100
				Pressure caps for 10-mm NMR tubes, red	Z11,808-7	6.30/100

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About Our Cover:

There are all sorts of interesting art-historical problems; the most common is the identification of the artist. In the case of the painting on our cover, the quest is rather unusual: we know some ten small paintings by the same hand, all monogrammed IS (intertwined) and usually dated in the 1640's and 50's. The best known of these, dated 1651, is a beautiful study of an old woman (Fig. 1) in the museum in Vienna. Our panel (17 x 13 inches) is monogrammed and dated 1649.

Fig. 1

Who was this Master, IS? Probably a student of Rembrandt, perhaps from Scandinavia or Poland — the costumes of the two men in earnest discussion look Polish. What is the subject of their discussion? A puzzle within a puzzle, heightened by the mysteriousness of that large room, and the subtle color accents, the cinnabar of the chair, the purple and gold of the cloak of the man with the fur hat.

When our chemist started collecting, he knew of three distinct unidentified personalities among 17th-century Netherlandish painters. They were the Master of the Winter Landscapes, now identified as Gysbrecht Leytens, the Pseudo van der Venne (see the *Aldrichimica Acta*, *7*, 1974) now identified as Jan van de Venne, an Antwerp artist of the early 1600's, and the Monogrammist IS, one of the most subtle and mysterious of the many artists influenced by Rembrandt. I.S. — a monogram in search of a name.

Are you interested in our *Acta* covers? Selections from the Bader Collection, with 30 duotone reproductions, many of previous *Acta* covers, and an introduction by Professor Wolfgang Stechow is available to all chemist art-lovers.

Z10,118-4 $6.00

Also, many paintings reproduced on our *Acta* covers were shown at the Milwaukee Art Center in an exhibition, "The Bible Through Dutch Eyes," arranged by Dr. Bader in 1976. The fully illustrated catalog with 66 black-and-white and 4 full-color reproductions contains many art historical and Biblical comments.

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Many of the early issues of the *Aldrichimica Acta* have become very rare. Please do not throw your issues away. In time, we believe that complete sets will become valuable, and — if you do not want to keep them — there probably are chemists near you who would be interested.

Lab Notes

We often find it necessary to identify parts and fittings made from Viton®, since after use, Viton may be confused with Buna-N, rubber or other elastomers. When Viton is needed, it can be dangerous or disastrous to use a substitute.

A simple identification test can be made with perchloroethylene. If the part sinks it is made of Viton, if it floats it is made of something else.

Bob McCreary
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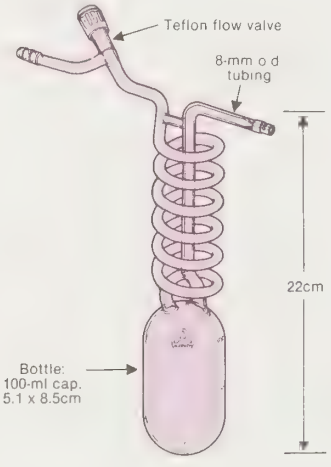
When a gas (*e.g.*, Cl_2, SO_2, CH_3Br or CH_3SH) is required for synthetic work, it is sometimes necessary to measure the amount to be added to the reaction mixture. This can be accomplished by condensing the gas in the apparatus shown below (cooled in dry-ice/acetone), and then determining its weight or volume.



The rate of gas addition to the reaction mixture can be controlled by warming/cooling the bottle. A constant flow is achieved by insulating the bottle with a cloth towel.

Of course, the material can also be dispensed as a liquid.

Kanu Parikh
Aldrich Chemical Co.

Editor's note: For our customers' convenience, we now offer the apparatus described above and the appropriate Dewar flask.

Z11,664-5 With Luer lock $115.50
Z11,665-3 With hose connection $105.50
Z10,312-8 Dewar flask, 14-cm i.d. x 28cm **$154.00**

As the importance of environmental protection and the awareness of chemical carcinogenicity increase, we wish to share our idea for the more efficient recovery of solvents from the rotary evaporator. We have connected a dry-ice trap between the water aspirator and the water-cooled rotary evaporator. This set-up allows for the efficient trapping of low-boiling solvents at the dry-ice stage, while collecting the higher-boiling solvents at the water-cooled stage. The common problem of getting solidified aromatic solvents at the dry-ice trap is thus avoided, and low-boiling chlorinated solvents no longer escape the system through the aspirator.

The Nitrone Group
277 Chemistry
Wayne State University
Detroit, MI 48202

Editor's note: Another efficient method of solvent recovery is by use of a dry-ice condenser. See page 23 for illustration.

The loss of intensity of both mounted and hand-held shortwave ultraviolet lamps used to visualize TLC plates can be traced to problems with the filter. In our experience, the lamp has a long lifetime, but the filter, through a process termed solarization, becomes less transparent over a period of a few months. A typical shortwave UV filter has a transmittance of 35-40%; a UVS-54 lamp (Ultraviolet Products) in heavy use for *ca.* 2.5 years was found to have a 254-nm transmittance of 0.8% as measured in a Cary-14 UV-Vis spectrophotometer.

Replacement filters cost between $40.00 and $60.00, but an inexpensive solution to the problem is to rejuvenate the filters by a simple annealing process as follows: The filters are dislodged from their plastic mounting with the aid of a knife and are scraped clean of adhering glue, washed with acetone, and dried. Rough side down, they are laid on smooth blocks of graphite/-ceramic cloth in an ordinary glass working oven and subjected to a typical annealing cycle of 575° C for 1-2 hours, with slow (*ca.* 1-2 hr.) cooling (a cycle used here for pyrex glass). Some flowing of the glass is normal, and some trimming may be required to fit the filters to the frame holder. A typical UV scan shows a U-shaped curve with the following % T values: 36 (254 nm), 13.2 (310) and 46 (390). For stubborn cases, two or three annealing cycles are required.

We recommend that rejuvenation of the filters be a yearly maintenance task, as the loss of intensity is gradual and is recognized only after much frustration with weak light output.

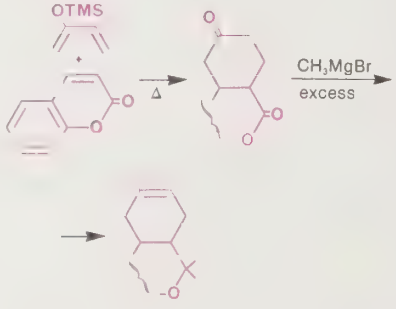
Professor David C. Baker
Merrill B. Watson, Glassblower
Department of Chemistry
The University of Alabama
University, AL 35486

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Selections from the Bader Collection** *(see "About Our Cover"). We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Ayira Bader.

Recently Professor K. Jankowski at the University of Moncton suggested that we offer 2-trimethylsilyloxy-1,3-butadiene, a reactive diene useful in Diels-Alder reactions leading, in three steps, to Δ^1-THC from

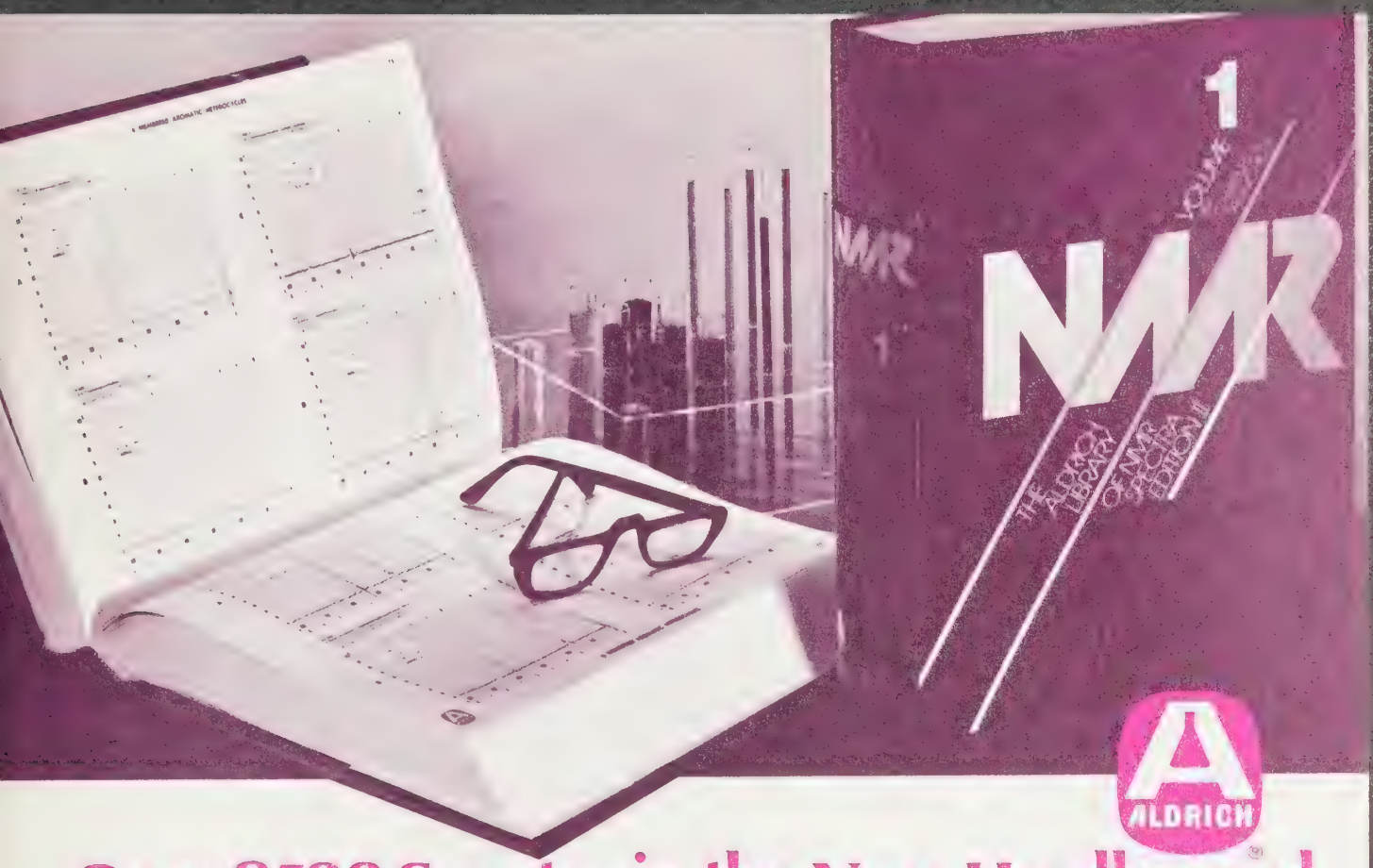


coumarin,[1] and to substituted cyclohexanones.[2,3] Naturally, we made it.

1) Jankowski, K. Unpublished results.
2) Jung, M.E.; McCombs, C.A. *Tetrahedron Lett.* **1976**, 2935.
3) Liu, H.-J.; Ngooi, T.K. *Synth. Commun.* **1982**, 715.

25,440-1 2-Trimethylsilyloxy-1,3-butadiene 1g $12.00; 5g $40.00

It was no bother at all, just a pleasure to be able to help.



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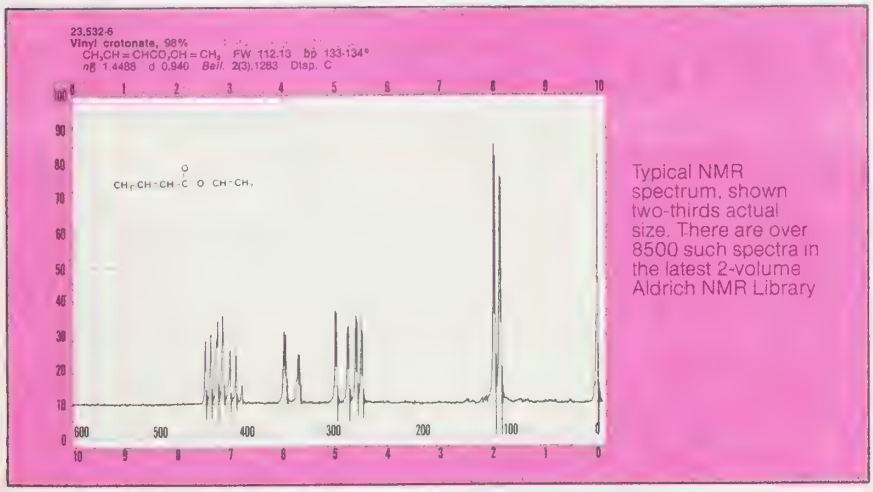

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18,620-1	**Methyllithium,** as complex with lithium bromide, 1.5*M* in diethyl ether
22,076-0	**K-Selectride,®** 1.0*M* in THF
22,449-9	***tert*-Butylmagnesium chloride,** 2.0*M* in diethyl ether
17,849-7	**L-Selectride,®** 1.0*M* in THF
17,972-8	**Super-Hydride,®** 1.0*M* in THF
22,444-8	**Phenylmagnesium chloride,** 2.0*M* in THF
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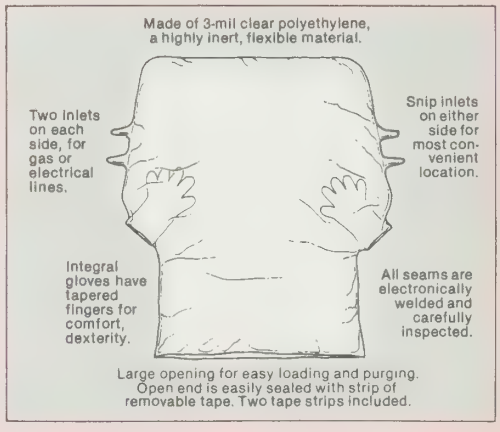
S	12	27	30	Z11,837-0	$15.80	Z11,283-6	$13.80



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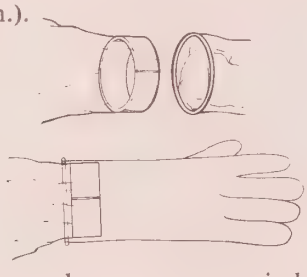

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About Our Cover:

The painting on our cover is particularly fitting for this *Acta* which highlights biochemicals offered by Aldrich and Sigma.

The subject, the visit of Hippocrates the famous physician to Democritus, one of the first biochemists, is based on the apocryphal letters of Hippocrates. The inhabitants of Abdera where Democritus lived had considered him insane because he spent so much time studying plants and dissecting animals — depicted clearly in the lower left of our painting. Hippocrates had come to examine Democritus, only to find him one of the wisest of men.

The relation of the painting to biochemistry is clear — and to those who know Sigma, so is its relation to our sister company. Many of our customers, learning about Sigma service, must at first consider Sigma crazy. How can a company stay in business and yet do so much for its customers — ship almost all orders prepaid within hours of receipt, accept collect telephone calls, offer many products at less than $3 and require no minimum purchase? Crazy!...until you realize what customer loyalty such service creates.

This painting (oil on canvas, 37 x 26 inches) is by Jacob Backer, who probably worked with Rembrandt in the early 1630's. The model for Democritus may also have been Rembrandt's model for St. Paul in *St. Peter and Paul in Discussion* (Fig. 1) now in Melbourne. Backer must have given his painting a great deal of thought: he made a chalk drawing of the head of Hippocrates (Fig. 2) and a study in oil (Fig.3) which is now in Dresden.

Fig. 1

Fig. 2

Fig. 3

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Lab Notes

A simple self-contained micro or semi-micro recrystallization apparatus has evolved from observing a vacuum coffee maker in operation. The apparatus depicted in Fig. 1 consists of three parts: two Erlenmeyer-type flasks with standard-taper joints, and a short glass tube equipped on both ends with corresponding standard-taper joints. One joint is fitted (fused) with a medium-porosity-frit plate at the narrow tip. Various sizes of standard-taper joints with frit plates attached in this manner are available from many glassware suppliers. The apparatus can be easily fabricated by conventional glassblowing techniques. In our laboratory, two sizes of the unit have been found to be particularly useful — one with 14/20 standard-taper joints and flask volumes of 15ml, and the other with 10/22 joints and flask volumes of 75ml. The procedure for operating the apparatus is as follows. Material to be recrystallized is dissolved in a hot solvent in flask B and the open-end joint of the tube is inserted into B. Concomitantly, a few milliliters of the same solvent are heated in flask A. Flask A is then connected to the other end of the

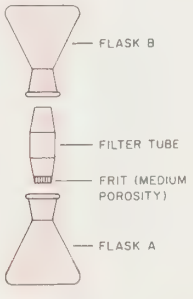

FIGURE 1

tube bearing the frit plate. The heat source is removed from the assembled device, the apparatus inverted, and flask A is cooled to a temperature lower than that of flask B. A vacuum is generated in A from the condensation of the solvent vapor causing a pull of the contents of B into A, giving a clean, filtered solution from which the solute may be crystallized. For rapid filtration, flask A is plunged into cold water or ice. If desired, a small amount of solvent may be heated in B to extract traces of mother liquor, for a quantitative transfer of solute. The procedure is then reversed. Vacuum is generated in flask B and the crystals collected on the clean side of the frit plate still connected to flask A. Cold wash solvent may be slurried with the collected crystals in A to cleanse them of mother liquor. Recrystallization can be performed within various temperature ranges provided a sufficient temperature differential (and pressure gradient) between flasks A and B is produced.

In addition to routine recrystallizations we have found many applications for this equipment. For example, small-scale radiosynthetic reactions have been carried out totally within the confines of the unit. Subsequent purification of the product, followed by vacuum drying and final weight determination are all done with no loss of valuable radioactivity and no hazardous contamination of the surroundings by spillage or volatilization of radioactive substances.

Franklyn W. Gubitz & Joseph W. Baum
Sterling-Winthrop Research Institute
Rensselaer, NY 12144

The catalytic hydrogenation of small samples (*i.e.*, 0.5-5.0g), either neat or in solvent, at pressures of 30-65 psi presents a problem in the laboratory. Use of a rocker-type Parr® hydrogenator usually leaves catalyst deposits on the vessel walls above the level of the liquid. This physical separation of catalyst and reactant causes incomplete hydrogenation and erratic results.

A simple solution involves the conversion of a glass Parr bottle to a micro reactor. Molten sealing wax, the type used for bottles and envelopes, is added to a glass Parr bottle and a standard 18mm x 150mm Pyrex® test tube is inserted into the molten wax which is then allowed to cool and congeal. The test tube is then gently removed.

The catalyst and reactants are charged into the test tube which is then inserted into the wax cavity. Hydrogenation is then carried out in the usual fashion. This apparatus can be used over and over again.

Richard E. Naipawer & Vasile Wertheimer
Givaudan Corporation
Clifton, NJ 07014

In the past we have had problems with vapors from thiols during workup of large-scale reactions. Especially problematic is the odor of *tert*-butylthiol which can be mistaken for a gas leak, a situation which has led to complacency due to repeated "leaks". The odor could be contained and the thiols quenched during most of the workup, but the contaminated water from the rotovap was a serious problem until the following procedure was discovered.

A large rubber tube is run from the aspirator to a large beaker placed in the sink. Crystals of potassium permanganate are sprinkled into the bottom of the beaker. The rotovap is then used, care being taken that sufficient permanganate remains in the beaker. The low concentration of permanganate which is in steady state in the cold water is enough to oxidize a rather large influx of thiol. This procedure presumably could also be applied to other easily oxidized materials.

Philip Hamann
Purdue University
West Lafayette, IN 47907

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Selections from the Bader Collection**. *We reserve the right to retain all entries for consideration for future publication.*

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by Ayers Bader.

Recently, Prof. Kishi at Harvard suggested that we offer benzyl trichloroacetimidate, a useful reagent for the facile benzylation of alcohols under conditions sufficiently mild that acetals are not cleaved. This reagent has been described[1,2] by researchers at the N.R.C. in Ottawa who were most helpful in guiding us in the scale-up of this new reagent. It is bound to become important, particularly to carbohydrate chemists.

1) Iversen, T.; Bundle, D.R. *Chem. Commun.* **1981**, 1240.
2) Wessel, H.-P.; Iversen, T.; Bundle, D.R. "Abstracts of Papers", XIth International Carbohydrate Symposium, Vancouver, British Columbia, August 1982; 1-46.

14,033-3 Benzyl trichloroacetimidate
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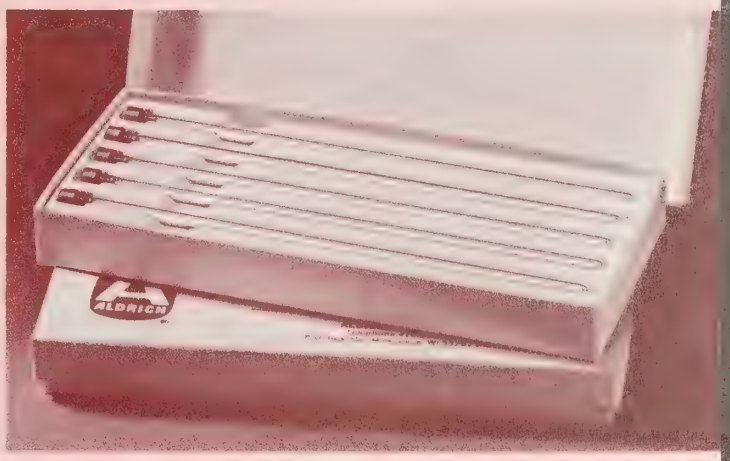

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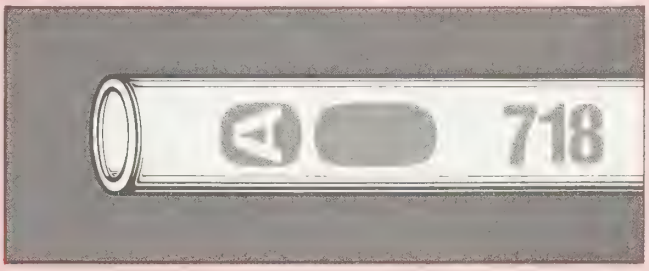

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Volume 16, Number 3, 1983

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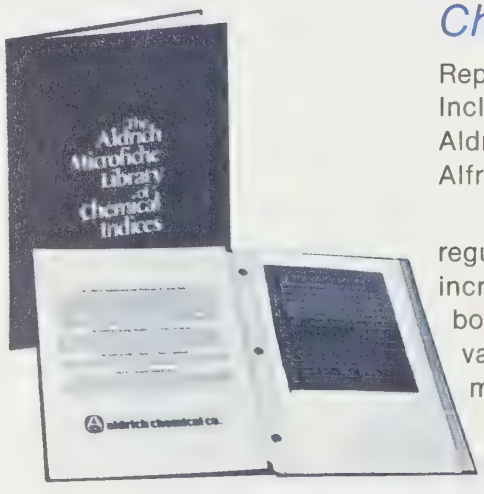

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About Our Cover:

Our chemist-collector bought the painting on our cover for the best reason we know: the sheer joy of looking at it.

Fig. 1

Fig. 2

He had never heard of Guidobono, a little known Italian artist of the 17th century, who painted this moving *Parting of Tobias from his Blind Father*. Baroque artists loved this apocryphal story, perhaps because of their concern with blindness, and this is the third Tobias to appear on an *Acta* cover.

This depiction is very different from our two previous *Acta* covers (Figs. 1 and 2), and a comparison of them shows clearly the differences between Italian, Flemish and Dutch baroque art. The Dutch painting (Fig. 1) by a Rembrandt student, Paulus de Lesire, is of subdued color, and father, mother and son — and even the angel — look like contemporary placid Dutchmen. The father in the Flemish painting by Jan van de Venne (Fig. 2) looks like an Eastern European Jew who found his way to Antwerp into a much more colorful, theatrical setting. The Italian painting, vibrant with vivid blues and reds, concentrates on the blind father's emotion-filled face and gnarled hand as he clutches his son in a last embrace. And how differently the painters saw the son! The Dutch Tobias is an experienced doctor who knows exactly how to treat his father's eyes. The Flemish son is a youth, while the Italian is merely a child about to leave home for the first time. Here are one beginning and two conclusions to the story. Baroque artists painted many different episodes in the story, and our chemist-collector hopes to find others.

Are you interested in our *Acta* covers? Selections from the Bader Collection, with 30 duotone reproductions, many of previous *Acta* covers, and an introduction by Professor Wolfgang Stechow is available to all chemist art-lovers.

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Also, many paintings reproduced on our *Acta* covers were shown at the Milwaukee Art Center in an exhibition, "The Bible Through Dutch Eyes," arranged by Dr. Bader in 1976. The fully illustrated catalog with 66 black-and-white and 4 full-color reproductions contains many art historical and Biblical comments.

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Lab Notes

Recently we encountered difficulty during small-scale ester rectification. Several esters, dried over anhydrous $MgSO_4$, foamed vigorously on vacuum rectification, sometimes with foam reaching the top of the column. We tried anti-foaming agents and filling the glass with glass wool but have now found two techniques satisfactory.

a. A blowing-over capillary — a capillary tube from which air or N_2 is blown horizontally above the liquid to destroy the foam. This method is less satisfactory because air or N_2 passing the column affects the rectification.

b. A gas-phase turbine-type stirrer — a stirrer placed directly above the liquid phase, thereby immediately destroying the foam produced. This method is preferred because the distillation is not affected at all. We had no difficulty maintaining the vacuum, using an all-glass stirrer with KPG collar, even without special devices like a nitrogen inlet. The esters probably do not dissolve the collar grease, which sometimes happens with other organic solvents.

J. Housmans
Central Laboratory DSM
Department POCP
P.O. Box 18
6160 MD Geleen, Netherlands

We had occasion to use 200-ml amounts of anhydrous liquid HF in an organic preparation. The reaction was carried out in a plastic bottle in a well ventilated hood. At the conclusion of the reaction and before work-up, the excess HF was slowly blown off under a stream of nitrogen. This caused etching and translucency of the safety glass panels of the hood door, side panel and the light fixtures. These had to be replaced at a significant cost and lost operation time in the hood. Thereafter, all inside glass panels were covered with a 4-mil polyethylene plastic sheet cut to size and fastened to the metal frames with a cloth adhesive tape. After a number of reruns of this preparation, the glass panels have remained transparent.

O.P. Goel, Ph.D.
Warner-Lambert Company
Pharmaceutical Research Division
Ann Arbor, MI 48105

In our laboratory, we have found that an efficient, low-dead-volume flow restrictor for HPLC fraction collection can be quickly fabricated from a discarded section of a fused silica capillary GC column. Simply swage several feet of column to the detector outlet using a graphite-vespel ferrule and a zero-dead-volume double female connector. This has proven absolutely trouble-free in hundreds of LC runs. It completely prevents bubble formation in the detector cell and preserves excellent resolution in the collected fractions, with minimum holdup.

Michael Alexander
Department of Pharmacology
The Ohio State University
Columbus, Ohio 43210

I wish to point out a method of cleaning nonpolar materials from glassware. Organic chemists tend to use relatively polar solvents such as acetone or alcohol for removing tars and residues from flasks. Although such solvents are quite effective for moderately polar materials, hydrocarbons and chlorinated solvents are more effective with nonpolar materials such as silicone oil. With crude oil (petroleum), acetone is indeed not the solvent of choice, so I tried one of the degreasers sold for cleaning automobile engines, machinery, garage floors, etc. The material, essentially a solution of a dispersing agent in a kerosene-type solvent, works quite well. After the organic material has dissolved (with warming if necessary), the solution can be disposed of with waste solvents. Water disperses most of the degreaser and dissolved material and washing with soap and water removes most of the rest. An advantage over the usual solvent-cleaning approach is that, unless the amount of residue in the glassware is considerable, one portion of degreaser can remove the material. At least one brand of degreaser is sold as a concentrated solution to be diluted with kerosene; presumably a somewhat more polar diluent, or one with a different boiling point, could be used.

Joseph H. Ross
Associate Professor of Chemistry
Indiana University at South Bend
South Bend, IN 46634

We have used the AtmosBag™ to sample water-sensitive and toxic reagents in the warehouse.

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We have thus sampled thionyl chloride and sodium methoxide, both of which are toxic and moisture-sensitive.

We have also sampled smaller drums, but in this case the bag is placed over the whole drum.

Luis N. Guedes
Q.A. Manager
Janssen Inc.
Gurabo, Puerto Rico 00658

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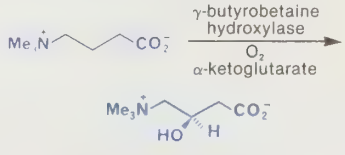
by Ansfra Bader.

γ-Butyrobetaine hydroxylase catalyzes the final reaction in the biosynthesis of *R*-carnitine.[1] This interesting enzyme is overproduced by *Pseudomonas sp. AK1* grown with γ-butyrobetaine as its sole source of carbon. Dr. Robert Pascal of Princeton University needed an inexpensive source of γ-butyrobetaine for the large-scale preparation of this hydroxylase for mechanistic studies.



Naturally, we made it.

1) Lindstedt, G.; Lindstedt, S.; Nordin, I. *Biochemistry* **1977**, *16*, 2181.

26,365-6 (3-Carboxypropyl)trimethylammonium chloride (γ-butyrobetaine hydrochloride) **5g $9.85; 25g $32.80**

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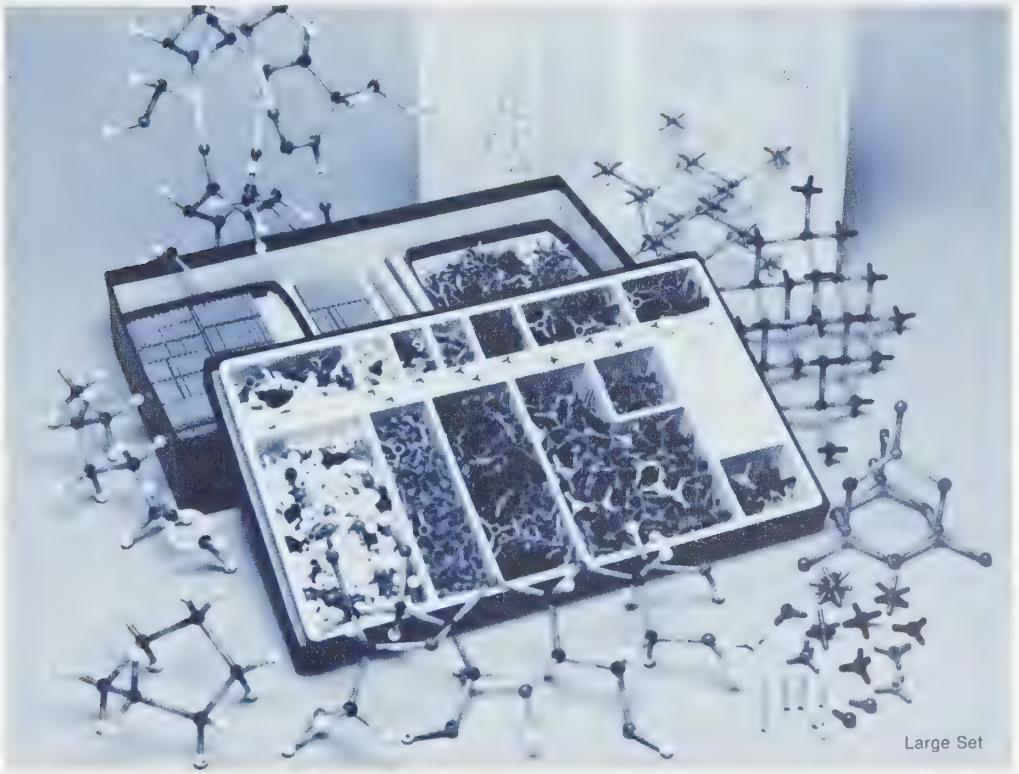

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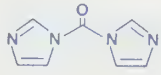

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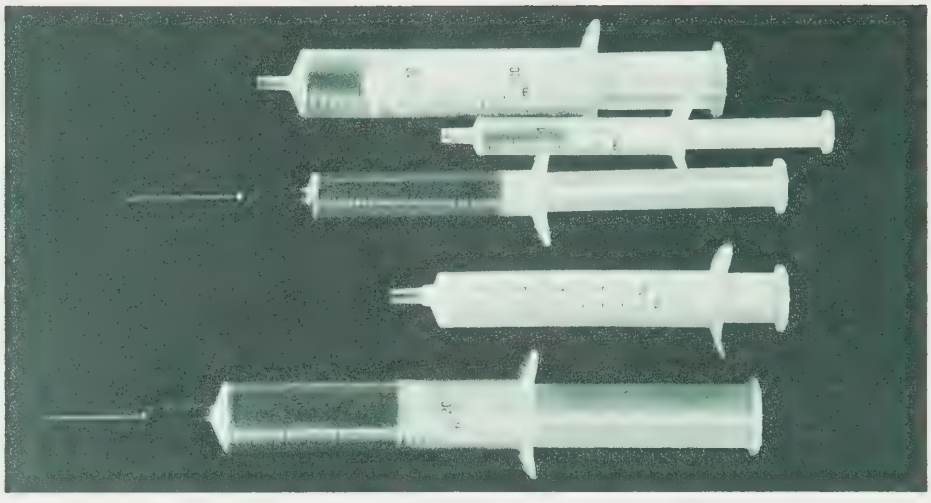

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Most disposable syringes have rubber plungers that can contaminate solutions. Our syringes consist of a polyethylene plunger and a polypropylene barrel with a tapered Luer connector; no lubricant of any kind is present. In the chemical laboratory, these syringes are useful for:

- Transferring air-sensitive reagents dissolved in organic solvents
- Weighing solutions for titrimetric or spectroscopic analysis
- Sampling liquids
- Delivering small gas samples for GC or IR analysis
- Sampling where trace-metal contamination must be avoided (use with Teflon needles; also available from Aldrich)
- Replacing breakable glass syringes.

The stainless steel needles are equipped with all-polypropylene Luer fitting hubs. Needles and syringes are sterilized and are individually packaged.

Aldrich offers sterile and non-sterile polypropylene Luer-tip pressure caps for sealing prefilled syringes. A useful, inexpensive syringe destroyer which efficiently cuts the tip of the needle as well as the Luer connector of the syringe is also available.

Syringes with needles:

2ml	22-gauge, 1¼ in.	Z11,689-0	$37.00/200
5ml	22-gauge, 1¼ in.	Z11,690-4	$24.35/125
10ml	21-gauge, 1½ in.	Z11,691-2	$36.00/100
20ml	20-gauge, 1½ in.	Z11,692-0	$35.40/60

Syringes without needles:

2ml	Z11,685-8	$19.10/200
5ml	Z11,686-6	$13.10/125
10ml	Z11,687-4	$18.50/100
20ml	Z11,688-2	$18.95/60
50ml	Z11,840-0	$22.50/30

Needles only:

22-gauge, 1 in.	Z11,806-0	$16.00/100
20-gauge, 1½ in.	Z11,805-2	$16.00/100
18-gauge, 1½ in.	Z11,804-4	$16.00/100
16-gauge, 1½ in.	Z11,803-6	$28.00/100

Luer-tip caps:

Sterile	Z12,096-0	$8.20/100
Non-sterile	Z12,097-9	$4.20/100

Syringe and needle destroyer:

Z12,497-4	$14.50

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Aldrichimica Acta

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About Our Cover:

While the subject of this beautiful landscape is clear, its author is still unknown. The Dutch dealer who sold it assured our chemist collector that it was by a little known Cologne artist, Johann Hulsmann. It reminded our chemist of the work of Rembrandt's teacher, Jacob Pynas. Both were mistaken, for the painting is monogrammed MCG and dated 1670, by which time Hulsmann and Pynas had long passed away. Who was the artist of this beautiful long view? French, Flemish, Dutch, German? He tried to write God's Hebrew name, the tetragrammaton, in the sky but certainly did not know Hebrew. Our chemist would be most grateful to hear from any reader who can identify this monogrammist MCG.

The story of Noah has a special appeal. All mankind descended from this one man, who was not a member of an identified people, just a man who listened to God. Here Noah and his family bring an offering after the flood, and the first rainbow appears as a token of God's promise never again to destroy all of mankind.

There is a particular poignancy to this story today. God promised that He would not destroy the world, but have we any assurance that we will not destroy it ourselves?

Lab Notes

Since the introduction of flash chromatography by Still *et al.*[1] in 1978, the technique has become a "standard" method of purification in many laboratories. Often, we find that the initial packing of the column is the most troublesome aspect of the technique. It takes several column volumes of solvent to degas completely the silica gel, and if excess pressure is applied to the column to force out the last air bubbles, the column is liable to crack when the pressure is released. This problem is particularly prominent with small-diameter (~2cm) columns. An easy and efficient modification of the packing procedure is as follows: The solvent is poured onto the silica gel and allowed to percolate through the column *without* external pressure until it drips from the column. (This takes 5-10 minutes.) Application of pressure then usually packs the column within 30 seconds. Columns thus packed are also less likely to crack.

J. Michael Chong & Ian D. Suckling
Department of Chemistry
University of British Columbia
Vancouver, B.C. V6T 1Y6, Canada

[1]Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Editor's note: Flash chromatography columns of various capacities are available from Aldrich. In addition to those listed on page 1352 of the 1982-1983 Catalog/Handbook, Aldrich now offers the two-liter apparatus and solvent reservoirs for all the columns. See page 80.

We have increased the usefulness of your Kugelrohr distillation apparatus by using the frame of a horizontal rotary evaporator for support. The collection bulbs replace the evaporator and condenser flasks and rest on the rollers provided. The bulbs can be cooled with water, ice, etc. The existing connections for vacuum are used. The air-driven rocker motor is connected to the evaporator-drive pulley with a belt. The modified apparatus is convenient to use and easy to operate.

Robert G. Jensen, Professor
Mark B. Fey, Graduate Assistant
Department of Nutritional Sciences
University of Connecticut
Storrs, CT 06268

I wish to point out a method of cleaning nonpolar materials from glassware. Organic chemists tend to use relatively polar solvents such as acetone or alcohol for removing tars and residues from flasks. Although such solvents are quite effective for moderately polar materials, hydrocarbons and chlorinated solvents are more effective with nonpolar materials such as silicone oil. With crude oil (petroleum), acetone is indeed not the solvent of choice, so I tried one of the degreasers sold for cleaning automobile engines, machinery, garage floors, etc. The material, essentially a solution of a dispersing agent in a kerosene-type solvent, works quite well. After the organic material has dissolved (with warming if necessary), the solution can be disposed of with waste solvents. Water disperses most of the degreaser and dissolved material and washing with soap and water removes most of the rest. An advantage over the usual solvent-cleaning approach is that, unless the amount of residue in the glassware is considerable, one portion of degreaser can remove the material. At least one brand of degreaser is sold as a concentrated solution to be diluted with kerosene; presumably a somewhat more polar diluent, or one with a different boiling point, could be used.

Joseph H. Ross
Associate Professor of Chemistry
Indiana University at South Bend
South Bend, IN 46634

We find the Aldrich AtmosBag™ Floor Base (Z10,691-7) ideal as a TLC reagent spray chamber base. Our home-made Plexiglas chamber (14" x 14" x 14") is placed on the polyethylene base (32" x 22") which is located in a fume hood. The base is very durable to the corrosive sprays and is easily cleaned.

D. DeClercq
Grain Research Laboratory Division
1404-303 Main Street
Winnipeg, Manitoba
R3C 3G8 Canada

TLC analysis of reaction mixtures in high-boiling solvents such as dimethyl sulfoxide, dimethylformamide, pyridine, etc., is beset with problems of low resolution, excessive spreading, and gross changes in mobility of appropriate spots. Overlap of a solvent spot with those of reaction products can further complicate the separation. Drying of TLC plates with hot air or infrared lamp could lead, in many instances, to decomposition of sensitive materials. These difficulties are circumvented by drying the TLC plate *in vacuo* below 0.1mm prior to development. In our laboratory, we conveniently use lyophilization flasks attached to a lyophilizer, but a vacuum desiccator connected to an ordinary oil pump may also be employed. The whole procedure can easily be monitored visually. The original "wet" spot usually becomes dry in 2-3 min.

Jiri Zemlicka, Ph.D.
Michigan Cancer Foundation
Detroit, Michigan 48201

Any interesting shortcut of laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Selections from the Bader Collection**. *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Ofira Bader.

Recently Dr. Arnold Brossi at the NIH suggested that we offer bis(tricyclohexyltin) sulfide which has been described as an elegant reagent for the conversion of carbonyls to thiocarbonyls. The authors describe our other sulfurating reagent, Lawesson's Reagent, as the "most effective sulfurating reagent to be reported to date..." but "extremely sensitive to moisture and very difficult to prepare and handle in pure form." We have sold many hundreds of bottles of Lawesson's Reagent, albeit of only 97% purity. Clearly this new tin reagent will have advantages for some reactions where Lawesson's Reagent is cumbersome to use.

Naturally we now offer both.

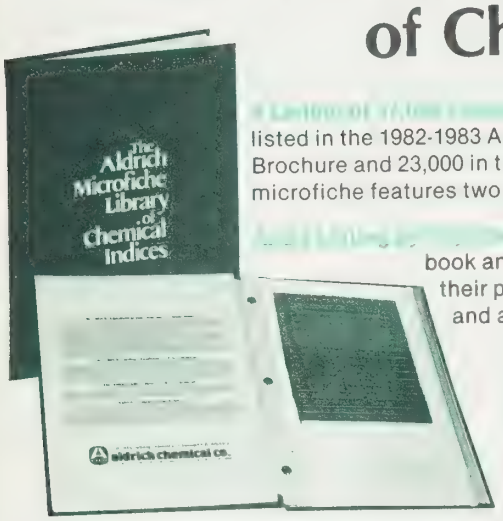
Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104.

26,885-2 Bis(tricyclohexyltin) sulfide
5g $8.00; 25g $35.00

22,743-9 Lawesson's Reagent, 97%
25g $12.15; 100g $42.15; 1kg $268.00

It was no bother at all, just a pleasure to be able to help.

The Aldrich Microfiche Library of Chemical Indices



The largest collection of chemicals in the world. Includes 14,000 listed in the 1982-1983 Aldrich Catalog/Handbook of Fine Chemicals and in the New Products Brochure and 23,000 in the Alfred Bader Collection of Rare Chemicals. This up-to-date listing on microfiche features two indices — alphabetical and molecular formula.

The 14,000 chemicals featured in the Aldrich Catalog/Handbook and in the New Products Brochure are listed alphabetically along with their physical constants. They are also computer-sorted by physical property and are indexed separately according to increasing:

- formula weight
- melting point
- boiling point
- density
- refractive index
- wavelength (μ) of maximum IR absorption.

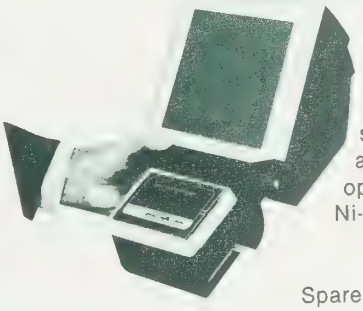
Each list also gives the other five (when appropriate) physical properties and other data such as flash point and reference numbers to the Aldrich IR and NMR libraries. These indices are valuable in determining unknowns and in locating chemicals that meet specific physical property requirements.

Microfiche Readers

Viewing screen is gray, 11 x 11in. 110v.

Spare DED lamp:

Movable linefinder:

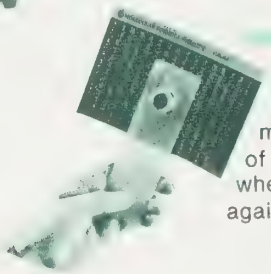


This hand-held reader folds flat for easy storage. It has a 5½ x 5½in. gray screen and is supplied with a 110-v AC adapter. It may be operated with rechargeable Ni-Cd batteries.

Spare FHZ lamp:

Leatherette carrying case:

Ni-Cd rechargeable batteries:



Economy model with plastic optics, for the occasional microfiche user. Enables viewing of a single frame through the lens when microfiche reader is held against a bright light.

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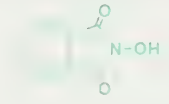
From Aldrich Production: Synthetic Reagents in Bulk

A major commitment at Aldrich is to offer as large and as diverse an array of high-quality products as possible. This versatility extends to our ever-increasing line of chemicals which we can offer in bulk quantities. The listings below are only a few of the many prepared in bulk in our production facility; please write or call our Bulk Sales Department at (800) 558-9160 for a quotation.

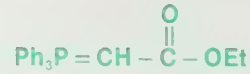
N-Hydroxyphthalimide



For the preparation of active esters in peptide synthesis.

H5,370-4 **100g $15.85; 500g $56.45**

(Carbethoxymethylene)triphenylphosphorane



Valuable Wittig reagent.

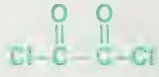
C510-6 **5g $14.35; 25g $44.90; 100g $113.60**

Dimethyl sulfite, 99.7 + %, GOLD LABEL (electronic grade)

Extremely pure electrolyte.

22,786-2 **25g $21.40; 100g $58.55**

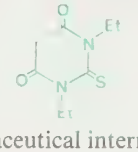
Oxalyl chloride, 99 + %, GOLD LABEL



Powerful chlorinating agent.

22,101-5 **25g $17.10; 100g $47.95**

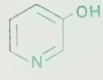
1,3-Diethyl-2-thiobarbituric acid



Pharmaceutical intermediate.

16,195-0 **50g $24.30; 250g $80.95**

3-Hydroxypyridine



Pharmaceutical and synthetic intermediate.

H5,700-9 **100g $18.90; 500g $63.00**

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Aldrichimica Acta

Volume 17, Number 1, 1984

"Our Chemist-Collector Approaches Sixty"

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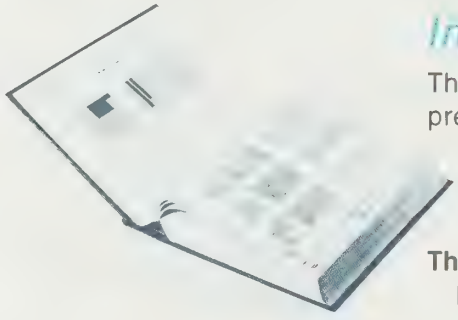


Infrared Spectra

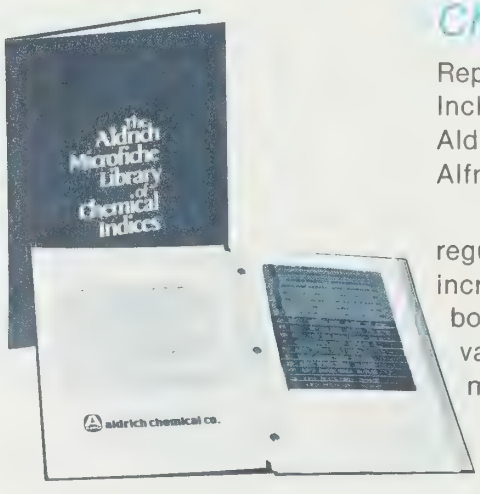
The most complete, definitive collection of IR spectra ever presented in one volume (1850 pages). This hardbound 3rd edition contains over 12,000 spectra classified by functional groups and structural variations into 50 sections, making IR spectral identification swift and easy.

The Aldrich Library of Infrared Spectra, Edition III, by Charles J. Pouchert. **Z10,750-6** **$179.50**

NMR Spectra

An indispensable resource for anyone who works with NMR instruments. The new hardbound 2-volume (2416 total pages) 2nd edition features 8,500 NMR spectra arranged by functionality and in order of increasing molecular complexity. No other collection of NMR spectra is as well organized or easy to use as this Aldrich NMR Library.

The Aldrich Library of NMR Spectra, Edition II, 2-volume set, by Charles J. Pouchert. **Z11,000-0** **$240.00**



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Represents the largest collection of chemicals in the world. Includes alphabetical and molecular-formula listings of the entire Aldrich inventory — 14,000 regular Aldrich items and 23,000 in the Alfred Bader Collection of Rare Chemicals.

It also includes seven physical property indices in which the regular Aldrich chemicals are listed alphabetically and in order of increasing formula weight, melting point, refractive index, density, boiling point and wavelength of maximum IR absorption. They are valuable in determining unknowns and in locating chemicals that meet specific physical property requirements.

The set of 19 microfiche is supplied in a convenient, hardbound holder.

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About Our Cover:

This portrait of Adriaen Brouwer by the Flemish artist Joos van Craesbeeck (1605 - 1662) was the first painting acquired by our chemist-collector, Dr. Alfred Bader, and we know it has remained one of his favorites. Consequently, we considered it appropriate for the cover of this issue which features the article "Our Chemist-Collector Approaches Sixty." Furthermore, nothing could better depict the surprise of our chemist-collector upon seeing this *Aldrichimica Acta*.

As our chemist-collector approaches sixty, all his friends and colleagues wish him many more productive years in chemistry and art.

Lab Notes

To prolong the life expectancy of a GC syringe, we trim a septum to 1/16" using a cork borer, and place it at the base of the needle to provide a small cushion that protects the barrel tip during injections. Over the past 2 years, the life expectancy of our syringes has increased from about one month to over one year.

Judith L. Vozza
State Health Laboratory
1520 West Adams Street
Phoenix, AZ 85007

I would like to report a simple solution to a laboratory annoyance.

Application of vacuum grease to ground-glass surfaces always has been a messy job. I now keep the grease in a 10-ml disposable syringe and dispense it neatly as needed. Syringes are easily filled with grease by removing the plunger and squeezing the grease straight from the tube or by using a spatula if filling from a jar. The tip that comes on the needle end of the syringe makes a good cap.

Joseph H. Saugier
Associate Radiochemist
Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

For some time it has been known that a variety of homogeneous bimolecular reactions can be accelerated at high pressures (above 2,000 atm). Recent synthetic applications of high-pressure chemistry have included Diels-Alder cycloadditions, Michael additions and enolate condensations. Often selectivities and yields of such reactions are significantly improved, while conditions involving high temperatures or the addition of Lewis acids can be avoided. Recently we began an investigation of the reduction of sterically hindered prochiral ketones with the asymmetric reducing agent Alpine-Borane (Aldrich) at elevated pressures.

Our initial explorations into high-pressure chemistry revealed that a number of groups are using a wide variety of equipment derived from both commercial and "homemade" sources. In general, the apparatus used consists of a hydraulic pump, a pressure intensifier (for pressures above 2,000 atm), a gauge, a pressure vessel and a valve to isolate the pressure vessel during reaction and release the pressure at the end of the reaction. Research pressure vessels from commercial sources have internal volumes ranging from about 5cc to more than 100cc, while fabricated vessels may cover a wider size range to meet individual needs.

One major difficulty with high-pressure work involves the design of a sample cell to isolate reactants from the hydraulic fluid during the reaction. A suitable sample cell must meet several strict requirements, especially retaining impermeability to the pumping fluid at high pressures while remaining resilient to rapid pressure changes. Additionally, the cell should be air-tight, easily filled, inexpensive, inert and readily available in a variety of sizes. Commonly, a sealed Teflon tube is used; unfortunately such tubes are often difficult to fill and seal, and become expensive if a number of sizes are stocked for use.

Fortunately an excellent cell can be easily formed from Aldrich disposable syringes. The all-poly design meets all the requirements. Other disposable syringes fail to remain closed to the pumping fluid at high pressures within the vessel while glass syringes often shatter when the pressure is released. In practice, a sample is taken up into the syringe in the normal manner. The needle is then replaced with a syringe cap. When necessary, the handle and finger holds are cut away to facilitate an easy fit of the cell into the pressure vessel.

We have used these cells for more than 30 days at 6,000 atm without mishap. When the reaction is over, the contents are emptied and the syringe is disposed of. Because the Luer and plunger seal are retained, these cells are especially suited for use with air-sensitive samples; their low cost and inertness also make them attractive for a wide range of chemistry.

Jim McLoughlin
Department of Chemistry
University of California, Riverside
Riverside, CA 92521

Editor's note: The following products cited above are available from Aldrich.

23,273-4 (*R*)-Alpine-Borane®
100ml $18.50; 800ml $98.25

23,770-1 (*S*)-Alpine-Borane®
100ml $18.50; 800ml $98.25

For disposable syringes and syringe caps, see the Equipment Section of your current Aldrich Catalog/Handbook.

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Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Selections from the Bader Collection.** *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Alfred Bader.

When the history of chemistry in our century is written, Prof. Barry Sharpless' asymmetric epoxidations will surely be among the most significant discoveries. One of Prof. Sharpless' important reagents in these epoxidations is anhydrous *tert*-butyl hydroperoxide. Some years ago Prof. Sharpless had suggested that we offer anhydrous TBHP in solutions, but the solutions in chlorinated solvents are unstable. Recently, Prof. Sharpless suggested that we offer the TBHP solution in toluene[1] which is stable.

Naturally we made it.

1) Hill, J.G.; Rossiter, B.E.; Sharpless, K.B. *J. Org. Chem.* **1983**, *48*, 3607.

27,016-4 *tert*-Butyl hydroperoxide, anhydrous, 3.0*M* solution in toluene
25g $8.90; 100g $24.75

It was no bother at all, just a pleasure to be able to help.

"OUR CHEMIST-COLLECTOR" APPROACHES SIXTY

Dr. Alfred Bader

In 1924, Vienna, so recently the flamboyant capital of the Austrian Hungarian Empire and echoing the strains of the waltzes of Johann Strauss, was hardly recovering from World War I and the effect of the Peace Treaty. The lively, bustling, self-indulgent, high-living Viennese had been forced to change their lifestyle.

This was the world into which our "Chemist-Collector," Chairman of Sigma-Aldrich and Founder of Aldrich, Dr. Alfred Robert Bader, was born. His mother was a Hungarian of noble family. His father, son of the Chief Engineer to Ferdinand de Lesseps, builder of the Suez Canal, had died shortly after his birth, and he was brought up by his dearly loved aunt and uncle. From early childhood on, he was exposed to art in his own home and to the Old Masters at the Kunsthistorisches Museum in Vienna. It should not have been totally surprising, therefore, when at age ten he used money given to him for another purpose to acquire an Old Master drawing at an auction.

By the mid-thirties, Austria was heading towards the Anschluss with Germany. When possible, Jewish youngsters were sent off to presumably friendlier and safer environments. In 1938, saying goodbye to his surrogate parents for the last time, Alfred Bader journeyed to England, a move which may well have saved him from death at the hands of the Nazis.

At fourteen, Alfred found himself at school in Brighton, Southern England, and, despite a strange language and an unfamiliar lifestyle, he was an exceptional student, whose qualities were soon recognized. He received a modest grant (supplemented by the occasional deal in stamps) to study chemistry at the Brighton Technical College. During this period his interest in art continued, and he became immersed in the study of the Bible. This combination of chemistry, art and Bible became his lifelong passion. Even at this early stage, he had begun to shape a future as scientist, businessman and collector.

This relatively settled interval in his life was soon to be disturbed by the German army advancing to the beaches of Northern France, placing England in danger. Fearful of a threatened invasion, Churchill considered that refugees from Europe could be a potential threat to the security of Great Britain. He then made his "Collar The Lot" decision to intern not only potential Nazi-sympathizers but also a great many refugees. Most were interned on the Isle of Man off Britain, but many were shipped overseas. In 1940, Alfred found himself part of a shipload of German Jewish refugees destined for a prisoner-of-war camp on the Richelieu River near Montreal, Canada. However, finding himself interned with able and learned tutors, Alfred put this most difficult period to good use, furthering his learning of the Bible and science.

Being hungry for any kind of news, he, like others in the camp, read through every line of any available newspaper. In doing so, he ran across the obituary of an elderly lady who had been his benefactor in England.

Editor's Note: Since our Chemist-Collector would never have permitted us to devote space in the *Aldrichimica Acta* to him, the references to his early days necessarily depended upon recollections of reminiscenses by him to friends and associates and could not be checked for accuracy with the "source." Hence, for any inaccuracies in history, our apologies.

The item listed her son of Montreal among her survivors. Alfred's note of condolence led to a lifelong close association with his second surrogate family, the Wolf family of Montreal. Mr. Wolf helped to arrange for Alfred's parole from the camp in November, 1941, and for his admission to Queen's University in Kingston, Ontario, notwithstanding the absence of standard, formal admission requirements and the fact that the term was well along. His gratitude to Queen's University for this special accommodation is manifested by his service on its Board of Trustees and his contributing to a major collection of Old Masters in its Agnes Etherington Art Centre.

While at Queen's, Alfred overcame the obstacles of English as a second language so well that he entered and won the McColloch speaking contest and the sorely needed prize money associated with it. Thereafter, at the urging of his professors, he became a member of the University's championship debate team. He also served as president of the Hillel House and in other campus leadership positions while earning a B.Sc. degree in Chemical Engineering (1945), a B.A. in History (1946) and a M.S. (1947). During the summer and after graduation, Alfred worked for the Murphy Paint Company of Montreal. Here he generally spent a couple of days visiting customers to discover their needs, then as quickly as possible formulated a suitable paint. Sales soon doubled. Thus Alfred was first shocked to find his job terminated until he realized the company simply wished him to further his education and was prepared to assist with funds.

Alfred attended Harvard which provided him with years of stimulation and excitement. Of course, Alfred began to pursue studies in two distinct disciplines, art history competing with research in chemistry. The contest between the two became concern enough for one chemistry professor to declare anxiously, "Alfred, you haven't made up your mind whether you want to be a chemist or an art historian." Alfred decided perhaps reluctantly for chemistry. As a doctoral research student of the famous Louis Fieser[1], he received great inspiration. Upon receiving his doctorate, Alfred intended to return to his former employer, but in the meantime, the Murphy Paint Company had been sold to Pittsburg Plate Glass, and they placed him in Milwaukee.

There, he was employed as a Research Chemist and later became Organic Group Leader in the paint division. Alfred found it wasteful of research chemists' time and talent to prepare high-purity intermediate compounds necessary to get on with the heart of the research itself. At that time, the only significant U.S. source for such products was a division of Eastman Kodak Company. He suggested to his superior to form a division to augment the list of high-quality intermediates available to research chemists. The proposal was rejected.

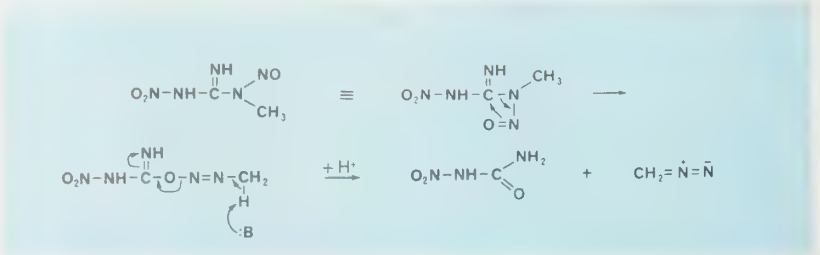
He then requested and received permission to try it on his own during his spare time. In 1951, he rented a $25.00-a-month garage, acquired some basic equipment and made MNNG, 1-methyl-3-nitro-1-nitrosoguanidine which was used as a starting material for diazomethane, and a few other compounds. Not wishing to personalize the company by using his own name he suggested to the attorney preparing the articles of incorporation that they toss a coin between "Daniels" and "Aldrich," the names of his own and the attorney's fiancée. The coin came up "Aldrich."

In 1954, Pittsburgh Glass decided to move its research division to Springdale, Pennsylvania. Although sales from his personal venture were only $15,000 per year, Alfred decided to resign his position and stay in Milwaukee, a city he had come to like. The development of Aldrich now became his full-time occupation.

Alfred began Aldrich with the idea of offering a list of organic chemicals other than those available from Eastman. But, he soon recognized the necessity for developing a complete line of organic chemicals for research. This required the establishment of a network of reliable suppliers to augment Aldrich's then limited production facilities. He also sought close ties with research chemists to enable him to know and even anticipate their needs. Accordingly, he established and developed friendships and working relationships with chemists throughout the world, giving them valuable assistance and promptly responding to their requests and suggestions. Over the years, he has personally helped many able and deserving chemists at universities with research grants underwriting their research, and helping some of them on their way to becoming leading chemists of their time.

While building Aldrich into the world's foremost supplier of high-quality fine organic chemicals, Alfred has been the first to acknowledge his debt to the countless dedicated employees, many of whom are still with the company. But his employees in turn credited him with the vision, drive and readiness to make the pragmatic decisions necessary for such an achievement.

Alfred's enthusiasm and creativity attracted other able chemists who began to cast their lot with Aldrich. Among these was the late John Biel, whose contributions to medicinal chemistry at Lakeside Laboratories, had made him an ideal Director of



Diazomethane production from MNNG

Research at Aldrich. This made possible the carrying on of contract work for governmental and pharmaceutical clients with the natural fall-out of both new products and greater insight into the needs of the research chemist.

A catalog evolved which proved to be not only a valuable sales tool but also an indispensable handbook of fine chemicals. This catalog, readily recognized by the Old Master paintings from Alfred's collection reproduced on the front cover with descriptions by "Our Chemist-Collector," soon became Aldrich's hallmark. The 1984-1985 edition will list over 16,000 products.

Alfred Bader and Professor Gilbert Stork in search of rare chemicals at Columbia University

In 1967 Alfred launched the *Aldrichimica Acta* to promote Aldrich products and also to disseminate chemical review articles by leading chemists. Today, the *Acta* is perhaps more attentively read than many a scientific journal, and there is no shortage of able prospective authors. With his customary attention to detail, Alfred still zealously guards the quality of the *Acta* which is published quarterly, although for this issue he cannot be held responsible.

Another unique development by Aldrich was the formation of the ABC (Alfred Bader Chemical) Division of Rare Chemicals. This certainly stemmed from Alfred's passion for collecting, in this case, chemicals. But again, he saw the possibilities of acquiring rare and difficult-to-obtain chemicals from universities and laboratories around the world and making them available to others in the research community. Today, over 23,000 such products are offered. The chemicals are featured now in the "Aldrich Microfiche Library of Chemical Indices."

Even in the early days, Alfred revealed that looking for a number of compounds from Aldrich's regular and ABC inventory (over 37,000 chemicals in 1984) containing a particular structural fragment was no easy task. Thus, Aldrich developed a computer-search service capable of locating the required compounds. This unique, free service is now used by scientists worldwide.

Of course, emphasis was placed on supplying quality products. From the infrared spectra taken in the laboratory during routine analyses, there developed "The Aldrich Library of Infrared Spectra" in 1970. Alfred rightly surmised that such a book of quality spectra would be welcomed by the research community. This book, currently in its third edition, and its subsequent companion, "The Aldrich Library of NMR Spectra," have established Aldrich compounds as the standard reference.

In the leading scientific journals, Aldrich advertisements were soon a regular feature on the back outside cover. The emphasis was generally on promoting new products, often those suggested by Alfred's friends and colleagues at universities.

Aldrichimica Acta Preview Issue 1967

These varied developments helped establish Aldrich as a major supplier of research chemicals. However, Alfred soon recognized the potential for supplying larger quantities and enlarged Aldrich's production capabilities to become an important source of bulk specialty chemicals. As the business expanded, so did the need for space. After intermediate moves, Aldrich acquired its present St. Paul Avenue headquarters in 1967.

Looking beyond the confines of the United States, Alfred, during the course of his travels to Europe, found a most useful German supplier - later to become known as EGA Chemie. In England, he persuaded an old friend of his war-time sojourn there, to assist with the development of sales and Ralph N. Emanuel, Ltd. was founded. In 1970, both these European companies became totally owned subsidiaries and ultimately bore the Aldrich name. From such beginnings, Aldrich was to become an international company well known on every continent.

In 1972, Aldrich acquired Diaprep, Inc., an Atlanta, Georgia firm and a small supplier of deuterated com-

pounds. Today, Aldrich is one of the world's major suppliers of such stable isotopes. The same year Alfred established Boranes, Inc., an Aldrich subsidiary, to develop entirely new chemical technology based on borane chemistry discovered by Professor H. C. Brown of Purdue University who was later to be recognized with the Nobel Prize in chemistry. Up to that point, Professor Brown had tried in vain to interest larger companies in the technology. In contrast, Alfred, with characteristic vision and decisiveness, promptly recognized and acted on the opportunity. Today, this activity is carried on at a separate plant in Sheboygan, Wisconsin.

In 1975, Aldrich merged with Sigma Chemical Company to form Sigma-Aldrich Corporation, thus combining the world's leading supplier of research biochemicals with what had become the leading supplier of organic and inorganic research chemicals. Alfred Bader, as well as two of Sigma's founders, Aaron Fischer and Dan Broida, envisioned the opportunity for interplay between the technical, service, and marketing strengths of the two companies in a way which would better serve the research community thus making the combined company greater than the sum of its parts.

Sigma Chemical, having started in a small storefront in 1948, had a similar humble beginning. Its first biochemical product was ATP (adenosine triphosphate), a major source of energy in living organisms. The growth of Sigma had been due mainly to the vision, energy and hard work of its president, Dan Broida. Upon the merger, Dan Broida became Chairman and Alfred Bader President. In 1980, Broida stepped aside, and Bader became the Chairman. Unfortunately, Sigma-Aldrich was not to have the continuing support of Broida for long, for he passed away in 1981. However, as Bader has stated, "Broida was a legend in his own lifetime and probably did more than anyone else to advance biochemistry. Sigma will remain a lasting monument to his vision and untiring work."

At the time of the merger, Sigma also had a subsidiary, B-Line, which manufactured and distributed metal components for strut and cable tray systems used in routing electrical and mechanical services in industrial installations and utilities. Emphasizing the same principles of quality product and service, B-Line has prospered over the years as part of the Sigma-Aldrich organization.

Although some relatively small companies were acquired by Sigma-Aldrich over the years — such as, Makor Chemicals, Ltd. in Jerusalem which had the unique ability to produce bacterial and fungal toxins, and Floyd Green's Dyes and Stains Company — the major growth was internal, based on the development of new products and related product lines supplied at competitive prices backed by unsurpassed service.

Today, Sigma and Aldrich products are purchased by universities, research institutions, hospitals and industry in nearly every country in the world. Over one million catalogs are distributed. Apart from the USA, Sigma-Aldrich now has warehousing and production plants in England, Germany and Israel and sales locations in Canada, Belgium, France and Japan.

Alfred, as Chairman of a company that now employs over 1,800 people, must surely reflect that this is a far cry from his garage of 1951.

Alfred Bader and Dan Broida

Over the years, Alfred has travelled extensively both in the USA and overseas visiting customers and suppliers. He is known throughout the chemical industry and at many universities. Early on, his main mode of transport was the train, usually at night, while he snatched a few hours sleep to maximize the use of time and minimize expenses. In his customary manner, he soon became an expert on train timetables. As the company grew, Alfred also had the comfort of being driven from place to place by the company's salesmen. Alfred readily adapted to this way of life having the ability to fall asleep quickly, occasionally arousing for a few minutes to comment, "what lovely countryside," without necessarily gazing out of the window. Suitably refreshed between visits to customers and suppliers, Alfred would devote the full day to business. There was hardly any time for eating. A quick sandwich generally sufficed. Even

in the evening, little thought was given to culinary delights, for then Alfred either switched his attentions to looking for objects of art or had further business meetings. At the end of such a day, it was not uncommon for Alfred to remark, "put that down to a day's holiday." The Aldrich salesmen, who perhaps had driven hundreds of miles, did not always agree with these well meant comments, but everyone admired his stamina.

The chemist-collector at his desk in 1972

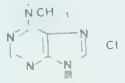
During the growth of the company, Alfred continued his intense interest in art — particularly Old Masters — and the Bible. He has assembled an important private collection of 17th-Century Dutch Masters, and found time to teach Bible at a religious school. Being unable to resist fine paintings, Dutch or otherwise, the homes of Alfred's friends and business associates, museums and universities became the beneficiaries of his remarkable eye for those acquisitions which did not fit into his private collection. Apart from Queen's University, institutions benefiting from his Old Master "finds" include The Milwaukee Art Center, the Allen Memorial Art Center, The Minneapolis Institute of Arts, Oberlin College, and the Fogg Art Museum at Harvard.

As a recognized art historian, Alfred was invited to act as guest curator of The Milwaukee Art Center in 1976 and to organize an exhibition "The Bible through Dutch Eyes." He produced a scholarly catalog reflecting his insight and knowledge of painting and the Bible. He is a much sought-after lecturer throughout the USA, Canada and Europe on subjects such as "the Bible as represented by the Dutch Masters" and "the chemistry involved in the restoring of works of art." He was selected as Fellow of the Royal Society of Arts in London in recognition of his achievements as an art collector and historian, and his research in art restorations.

Ten years ago, on the occasion of Alfred's fiftieth birthday, Professor Wolfgang Stechow wrote in the introduction to "Selections from the Bader Collection:" "Lots of art historians could learn a great many things from Alfred Bader; and all art lovers are indebted to his zeal, his perspicacity and his often proven generosity in sharing his treasures with them."

In spite of his enthusiasm for art, chemistry was never neglected. Alfred has authored or co-authored 25 scientific publications covering a wide range of topics in the field of organic chemistry with the emphasis being on practical rather than theoretical chemistry. He also holds 27 patents.

His first scientific publication dealt with the osmium tetroxide oxidation of some long-chain unsaturated fatty acids[2] while the most recent concerned some work on purin-6-yltrimethylammonium chloride.[3] It is interesting to note that Aldrich now offers all the starting materials which Alfred had to prepare for this research.



purin-6-yltrimethylammonium chloride

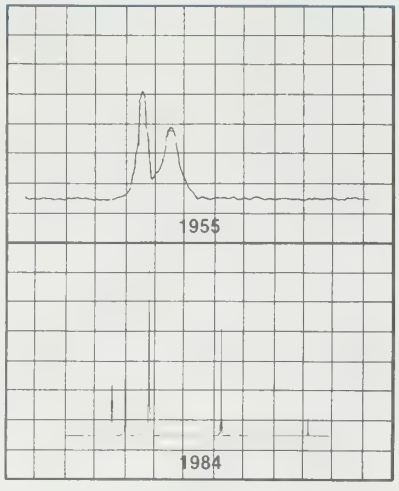
Of course, even Alfred could not completely resist the allure of elucidating structures using new techniques. His 1955 paper on "The Proton Magnetic Resonance Spectrum and Structure of Diketene"[4] confirmed that liquid diketene exists in the 3-buteno-β-lactone form. The contrast of his spectra with those recently taken on Aldrich's 300MHz (superconducting magnet) NMR equipment dramatically illustrates the strides in technology during the last decades.

While Alfred's practical nature and knowledge of chemistry provided the backbone in building Aldrich, he has also proved to be a most successful businessman. Yet, he is known to his many friends and acquaintances as a person who attaches little importance to the so-called "luxuries of life." Paintings — one of his weaknesses, although he does admit to others — are an exception. He still lives in the

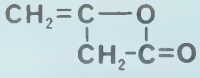
same house, which he himself describes as modest, bought in the early days of Aldrich. He generally drove a car discarded by an Aldrich salesman when it had been driven over 100,000 miles. One of Alfred's own favorite tales concerns the time he drove up to a fund-raising event. The house employee took one look at Alfred and his car and informed him that tradesmen were to use the back entrance.

Kind at heart as many friends can certainly substantiate, Alfred has never suffered fools gladly, and he would be the first to admit that patience is not one of his virtues. Indulging in few hobbies or interests outside of chemistry, the Bible, and art, Alfred's pragmatic, decisive approach and singlemindedness go far toward accounting for his success in the world of both chemistry and art.

Over the years Alfred Bader's contributions to science, industry and art have been recognized in many ways, including an Honorary Doctorate of Science degree from the University of Wisconsin-Milwaukee; the 1983 Engineer-of-the-Year Award given annually to a Milwaukee-area engineer or scientist in recognition of distinguished contributions to the profession and the community; and honorary doctorates from the University of Wisconsin-Madison and Purdue University to be awarded this year.



Diketene NMR Spectra


Diketene

As Alfred Bader approaches his 60th birthday his coworkers and associates at Sigma-Aldrich wish "Our Chemist-Collector" many more productive and fruitful years of activity as our Chairman and as a renowned art collector and historian.

References:
1) Fieser, L.F.; Bader, A.R. *J. Am. Chem. Soc.* **1951**, *73*, 681.
2) Bader, A.R. *ibid.* **1948**, *70*, 3938.
3) Klemm, R.; Schulze, H.; Ettlinger, M.G.; Bader, A.R. *J. Med. Chem.* **1966**, *9*, 981.
4) Bader, A.R.; Gutowsky, H.S.; Williams, G.A.; Yankwich, P.E. *J. Am. Chem. Soc.* **1956**, *78*, 2385.

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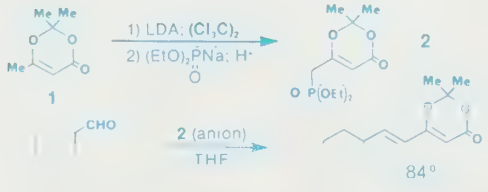
Marvin E. Klitsner, Partner, Foley and Lardner, Attorneys at Law.

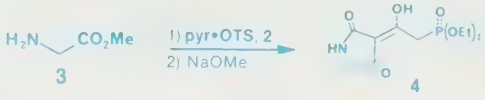
Diketene-Acetone Adduct

(2,2,6-Trimethyl-1,3-dioxen-4-one)

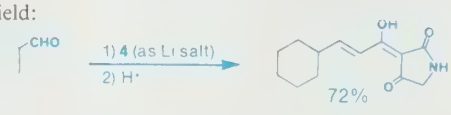
Over 30 years ago, the adduct derived from diketene and acetone, **1**, was shown to function as a convenient replacement for diketene in various reactions.[1] Recently, this interesting heterocycle has re-emerged as the precursor to a novel phosphonate β-keto ester synthon, **2**. Easily prepared from **1**, the anion of phosphonate **2** reacts with a variety of aldehydes to afford the expected Nazarov-type reagents in excellent yields, as shown below.



Even more impressive is the ease with which **2** reacts with α-amino esters to form 3-acetyltetramic acids activated toward olefin formation at the acetyl methyl group. Thus, glycine methyl ester (**3**) affords the corresponding tetramic acid **4** after two mild steps:



As expected, the anion of **4** (or similar acids) reacts with carbonyl compounds to afford the enoyl tetramic acid derivatives in high yield:



The above conversions are mild enough that acid- and heat-sensitive molecules have been constructed.

The potential utility of **1** in organic synthesis employing modern methodology is just beginning to be appreciated. The acidity of the vinyl methyl protons coupled with the latent β-keto ester function should stimulate other chemists to follow Professor Boeckman's fine start in developing adduct **1** as a useful natural product synthon.

References:
1) Carroll, M.F.; Bader, A.R. *J. Am. Chem. Soc.* **1953**, *75*, 5400.
2) Boeckman, Jr., R.K.; Thomas, A.J. *J. Org. Chem.* **1982**, *47*, 2823.

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23,223-8	**Pyridinium 4-toluenesulfonate**	**25g $19.50; 100g $71.25**

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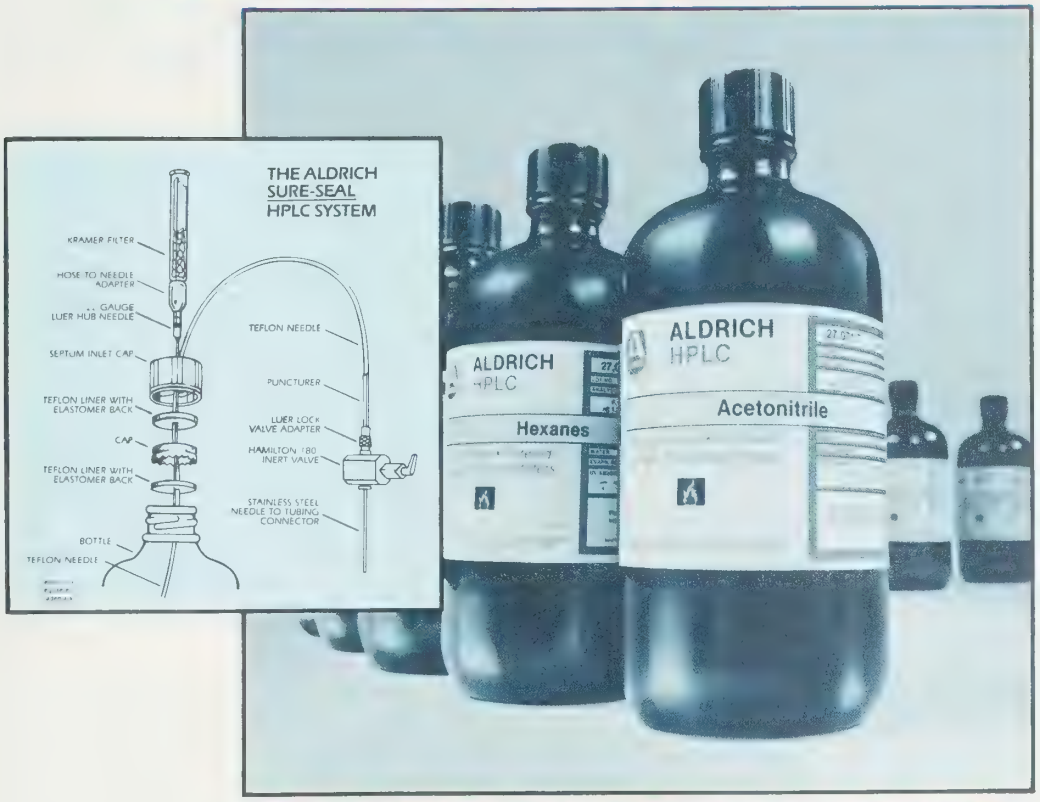

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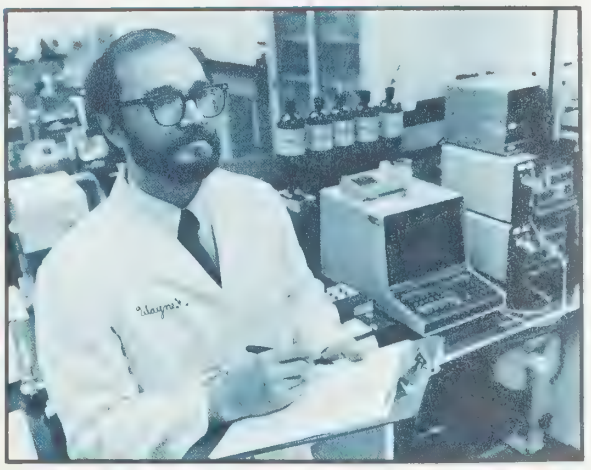

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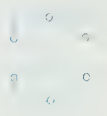

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1, R = H 2, R = OMe

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Aldrichimica Acta

Volume 17, Number 2, 1984

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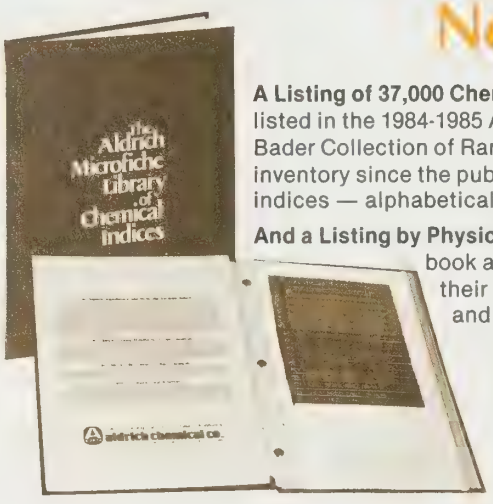

A Listing of 37,000 Chemicals. The largest collection of chemicals in the world. Includes 14,000 listed in the 1984-1985 Aldrich Catalog/Handbook of Fine Chemicals and 23,000 in the Alfred Bader Collection of Rare Chemicals. The microfiche also contains all products added to our inventory since the publication of the catalog. This up-to-date listing on microfiche features two indices — alphabetical and molecular formula.

And a Listing by Physical Property. The 14,000 chemicals featured in the Aldrich Catalog/Handbook and those added since its publication are listed alphabetically along with their physical constants. They are also computer-sorted by physical property and are indexed separately according to increasing:

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- melting point
- boiling point
- density
- refractive index
- wavelength (μ) of maximum IR absorption.

Each list also gives the other five (when appropriate) physical properties and other data such as flash point and reference numbers to the Aldrich IR and NMR libraries. These indices are valuable in determining unknowns and in locating chemicals that meet specific physical property requirements.

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Z12,213-0 $14.00
Movable linefinder:
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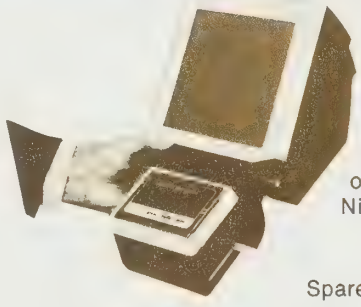

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About Our Cover:

Our chemist-collector owns several works by Gerbrand van den Eeckhout, and this is his favorite. Eeckhout, who was a student of Rembrandt and became one of his good friends, was influenced by both Rembrandt's teacher, Pieter Lastman (see *Aldrichimica Acta* Vol. 8, No. 2, Fig. 1), and by Rembrandt, as in the painting on this cover.

This painting (oil on canvas, 39-½ x 33 inches, signed and dated 1652) may be a *Rest on the Flight to Egypt* in which Baroque paintings traditionally show Joseph as an old man. Here is the essence of fatherly love and pride, and equally touching is the care with which Mary handles her baby. Can you think of a more beautiful depiction of parental love?

Aert de Gelder, one of Rembrandt's last students, dealt with this same subject 30 years later in one of his masterpieces (Fig. 2) which is now in Boston. Perhaps de Gelder was influenced by Eeckhout's work, for his painting, too, depicts the parents' great care for their child. Love is infectious: we feel good all over just looking at these paintings.

Fig. 1

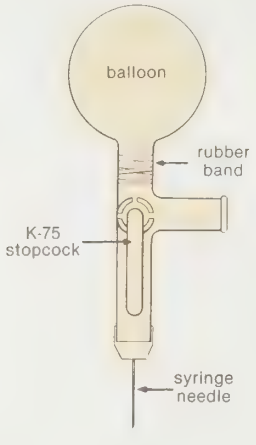
Fig. 2

Lab Notes

When conducting small- to moderate-scale hydrogenations *without elevated pressure*, it is convenient to transfer and introduce the hydrogen using an apparatus assembled from a syringe needle, a Pharmaseal® K-75 three-way stopcock, a balloon, and a rubber band (as illustrated).

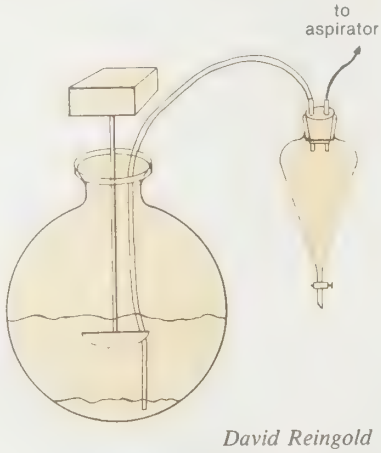
Hydrogen is introduced into the balloon (after it has been deflated completely) by attaching a piece of surgical tubing to a hydrogen tank port, inserting the needle through the tubing, then filling the balloon *under low pressure*. After the stopcock is closed, the apparatus may be easily transported to the reaction flask and connected by inserting the needle through a septum. Purging the reaction vessel and the solvent is accomplished by attaching a vacuum source to the open stopcock port with a needle-tubing connector, followed by repeated evacuation/hydrogen introduction cycles *via* the stopcock. After purging, the vacuum source may be disconnected, and the reaction left under positive pressure.

A typical balloon will hold in excess of 250cc of gas, and maintain a positive pressure overnight. Should more hydrogen be needed, the stopcock/balloon assembly is easily disconnected leaving the needle in place, and another filled unit is connected.



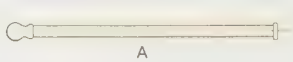
Carl Wheeler
Department of Chemistry - 4630
Washington State University
Pullman, Washington 99164

We have developed a method for thorough extraction of large volumes of aqueous solution with chloroform, which eliminates the tedious and physically exhausting use of large separatory funnels. We had 12 liters of aqueous layer which we placed in a 22-liter flask. A 300-ml portion of chloroform was added and the mixture was agitated (we used a vibromixer, but an overhead stirrer would probably work as well). Mixing was stopped and the lower layer was sucked by an aspirator into a 500-ml separatory funnel through a long plastic tube. It is not necessary to be able to see the bottom of the flask: when the aqueous layer starts coming over, stop the transfer. The chloroform layer was saved and the aqueous layer was returned to the large flask. The process can be repeated as often as necessary without ever lifting anything heavy, until it is time to deal with the chloroform layer. In our case, this amounted to a much more manageable 2 liters.



David Reingold
Eaton Group
University of Chicago
Department of Chemistry
Chicago, Illinois 60637

A simple modification of the applicator/-holder for the popular disposable TLC spotters has increased their utility. By replacing the 4 x 25-mm tubing with a longer one (A), TLC samples may be easily taken from reaction vessels.



An offshoot of this idea is the extension for use with Pasteur pipettes (B). Using this device, it is quite easy to apply samples to chromatography columns with minimal disruption of the bed. We have found this to be especially useful with partially filled columns, such as those encountered with flash chromatography.

Michael Okagaki
Bioproducts Division
Beckman Instruments
1050 Page Mill Road
Palo Alto, California 94304

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Selections from the Bader Collection**. *We reserve the right to retain all entries for consideration for future publication.*

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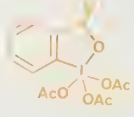
by Ayra Bader.

Recently Professor J.C. Martin suggested that we offer the periodinane,[1]



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1) Dess, D.B.; Martin, J.C. *J. Org. Chem.* **1983**, *48*, 4155.

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About Our Cover:

Most readers of the *Aldrichimica Acta* know by now that our chemist-collector looks for paintings depicting episodes from the book of Tobias. One of the most dramatic of these episodes is the actual catching of the fish which was instrumental in warding off the demon that had beset Sarah, Tobias' fiancée, and in curing Tobias' father of his blindness.

The painting has a rather strange, recent history. It belonged for many years to the Los Angeles County Museum of Art, where it was attributed to Domenico Fetti, the great early-17th-century Italian artist. Connoisseurship of Fetti's works is difficult because he repeated his own compositions and was so admired that many artists copied his work. Two other versions of this composition are known, one in Dresden (Fig. 1) and one in Verona. Perhaps thinking their painting also a copy, the Museum sold it recently at an auction in Los Angeles. Subsequent cleaning has revealed many details which are different from the other versions, so our chemist believes that it may also be autograph.

The triangular composition with the fish's head at its focal point is tremendously dramatic. You can feel Tobias straining to hold the fish, and even the dog — the first friendly dog in the Bible — shares the excitement. The drama greatly impressed other artists. Note, for instance, Giovanni Antonio Guardi's depiction, now in Cleveland (Fig. 2), clearly based on Fetti's composition.

This depiction of the exciting moment when Tobias catches the magic fish seems fitting for the cover of the *Acta* in which Prof. Deslongchamps suggests how a young researcher might well choose a project which will shape his future.

Fig. 1

The Cleveland Museum of Art,
Mr. and Mrs. William H. Marlatt Fund

Fig. 2

Pictures from the Age of Rembrandt

Twenty-five paintings that have been reproduced on our *Acta* covers, and six that have been on our catalog covers are among thirty-six paintings in an exhibition of Dutch paintings at Queen's University in Kingston, Ontario. The fully illustrated catalog written by Professor David McTavish contains a wealth of art-historical information — enough for several evenings of relaxed enjoyment — probably the best value in art-history anywhere.

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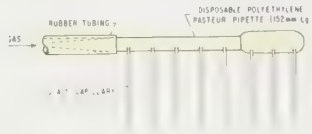
Lab Notes

An inexpensive (< $0.10) manifold for simultaneously delivering gas to a number of relatively small receptacles can be constructed in about 10 minutes from common laboratory equipment. A disposable polyethylene Pasteur pipette (length 152mm, diameter 7.5mm or length 184mm, diameter 4.5mm) is punctured along one seam with the tip of an 18-gauge hypodermic syringe needle from the bulb end to just before the tapered-end portion. The holes are then enlarged slightly by pushing the plunger from a 100-µl syringe into them. Melting-point capillaries (0.9-1.1mm i.d. x 100mm) cut to any desired length are forced into the holes to complete the manifold.



Daniel P. Schwartz
Food Safety Laboratory
USDA Northeastern Region
Eastern Regional Research Center
600 East Mermaid Lane
Philadelphia, PA 19118

Everyone, at one time or another, has had to deal with a small spillage of mercury from a manometer or a mercury seal. The normal spillage-disposal techniques have drawbacks: forming the amalgam with zinc dust or Mercurisorb is messy and the mercury is lost; sucking up the droplets with a vacuum-assisted aspirator is clumsy and requires special equipment.

I have found a quick, simple and safe way to handle such spillage. A small piece of solid carbon dioxide is placed on the surface of the mercury which very quickly freezes (m.p. -38 °C) and can then be transferred with tweezers to a suitable container for reuse.

Stephen Mann
Marconi Research Centre
Great Baddow
Chelmsford, Essex
England

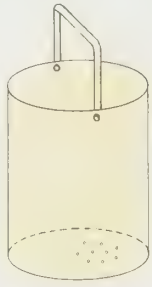
Many recorders employ pens with capillary tips and ink reservoirs. These capillary tips tend to become clogged especially after prolonged periods of non-use.

We have found that, alternatively, fiber-tipped pens can be used, attached to either the existing pen holder, or an easily made adapter. In cases where the whole length of the fiber-tipped pen cannot be used because of space considerations, the pen (the body of which is generally plastic) can be cut to fit, as long as a sufficient length of fiber wick is left. This has the advantage that ink can be added to the wick and the pen used as long as the tip remains sharp.

Mordechai Brand
Department of Chemistry
Tel Aviv University
69978 Tel Aviv
Israel

The use of highly corrosive cleaning agents, such as potassium dichromate/sulfuric acid, suffers from several drawbacks. One obvious problem is safety. If a gloved hand is used to insert and retrieve objects, there is the danger of acid burns as a result of pinhole leaks or the tearing of a glove on a sharp object. The use of tongs is less hazardous, but introduces a new problem. Have you ever attempted to retrieve a glass stopper from the bottom of a murky dichromate cleaning solution with a pair of tongs? At best it is a very frustrating endeavor.

We have devised a simple solution to this problem. Articles to be cleaned are placed in a polyethylene basket which is lowered into the dichromate cleaning solution. When cleaning is completed the basket is removed from the solution and taken to a sink where the excess cleaning solution is washed off. The entire cleaning process is accomplished without ever having to place a gloved hand in the cleaning solution, and even very small objects are readily retrievable.



A polyethylene basket can be constructed from a one-gallon micro cleaning-solution bottle. The top of the bottle is cut off about 18cm from the bottom and a number of ¼-inch holes are drilled in the bottom. A handle is fashioned from a 2 x 30cm strip of polyethylene cut from the discarded top of the bottle. A ¼-inch hole is drilled in each end of the handle and two ¼-inch holes are drilled along the top edge of the basket. The handle is riveted to the basket using 1-cm lengths of ¼-inch polyethylene tubing. The ends of the polyethylene tubing are softened with a soldering gun or other hot object and flared to rivet the handle to the basket.

The basket will fit into a 4-liter Pyrex® beaker. We have used such a basket in a potassium dichromate/sulfuric acid cleaning solution for the past six months without any noticeable deterioration of the basket.

Thomas D. Harris
Assistant Professor of Chemistry
Department of Chemistry
State University of New York at Fredonia
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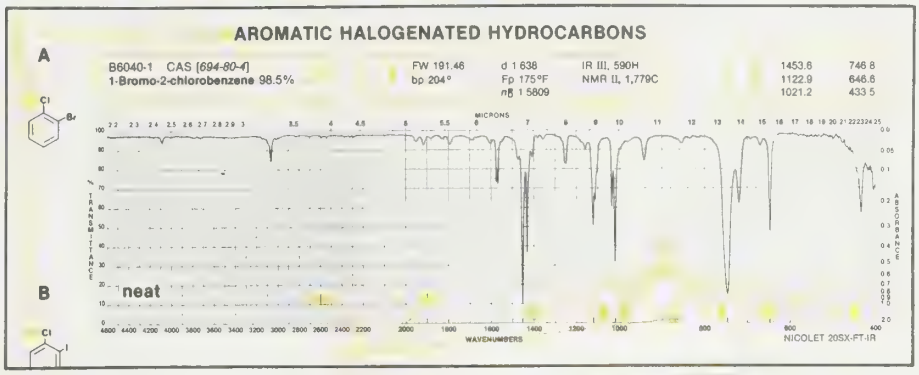

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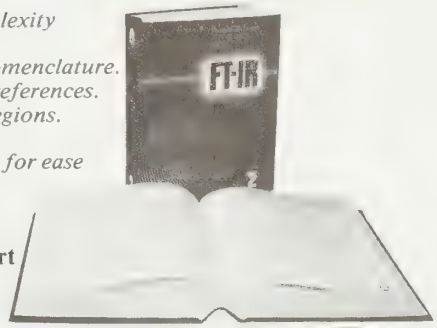

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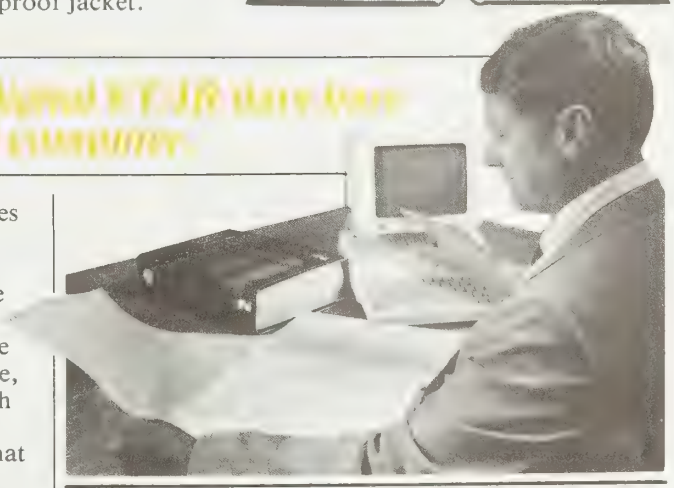

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1) Tanis, S.P. *Tetrahedron Lett.* **1982**, *23*, 3115 and references cited therein.
2) (a) Cama, L.D. *et al. Tetrahedron* **1983**, *39*, 2531. (b) Lowe, G.; Swain, S. *Chem. Commun.* **1983**, 1279.
3) Ojika, M. *et al. ibid.* **1982**, 628.
4) Hallberg, A.; Pedaja, P. *Tetrahedron* **1983**, *39*, 819.
5) Gammill, R.B.; Hyde, B.R. *J. Org. Chem.* **1983**, *48*, 3863.

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D-7924 Steinheim
West Germany
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Telex: 714838 Aldri D
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About Our Cover:

Our chemist-collector prefers Biblical paintings of the School of Rembrandt to all others, and believes that this moving landscape (oil on canvas, 33 × 50 inches) qualifies. Philips Koninck, probably a Rembrandt student in the early 1640's, became one of the greatest landscape artists ever. This painting is done with such assurance, that it must be a mature work of the artist, done around 1675. The whole world is before us in this sunset scene, and how insignificant is man. Perhaps Koninck was inspired by one of the Psalms: "The Heavens declare the glory of God, and the firmament showeth His handiwork."

The painting was sold recently at Christie's in London, and brought only a small fraction of the value of a fine Koninck landscape. The sky had been completely overpainted and most connoisseurs feared that it had been overcleaned and then overpainted. Fortunately, a subsequent cleaning proved this fear groundless: the original, beautiful sky is intact, and had just been glazed over by an inexperienced restorer.

It is our collector's finest landscape.

Lab Notes

I have devised some simple solutions to prevent refluxing solvents or splashing reaction mixtures from entering an all-glass stirrer shaft and bearing assembly.

For non-refluxing or non-heated systems, a straight glass joint *ca.* 6″ long, with male and female ends will serve as a "spacer" between the bearing and the system (see Fig. 1). (This spacer could take the form of, *e.g.*, the straight portion of a Claisen adapter if an extra neck is needed.)

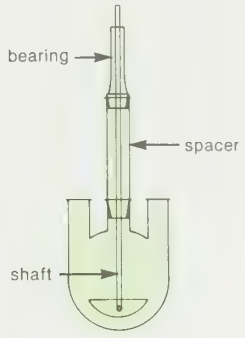


Figure 1

For refluxing systems, a short spacer-condenser, *ca.* 6″ long, with a wide internal diameter will keep the hot vapors refluxing below the bearing (see Fig. 2). (Existing water-cooled bearings do not prevent solvents from forming a plug between the rotating shaft and bearing walls.)

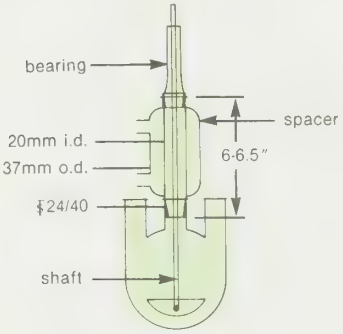


Figure 2

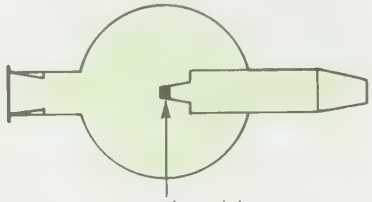
Use of these spacers prevents accumulation or escape of liquids or freeze-ups caused by either trapped solid particles or dissolving bearing lubricants.

Fred G. Schreiber, Ph.D.
Process Development
Rhone-Poulenc, Inc.
297 Jersey Avenue
New Brunswick, NJ 08903

I have found that flash chromatography tends to give broad elution bands and, therefore, decreased resolution. This is caused in part by the need to load the sample in a large volume of the solvent mixture to obtain the required R_f value for the desired product, or to load with a more polar solvent, decreasing separatory resolution by an increase in the R_f value.

These problems can be overcome and increased resolution achieved by preadsorbing the sample onto anhydrous sodium sulfate, fine powder, in a ratio by weight of *ca.* 1:5 to 1:10, respectively.

The mixture is easily eluted from the sodium sulfate and adsorbed onto the top of the silica packing in a tight band. The sodium sulfate then acts as a protective layer for the column packing when adding more solvent. Adsorbing the mixture onto the sodium sulfate is no problem if the trap shown below is used in conjunction with rotary evaporation, and a gentle take-off of solvent (CH_2Cl_2 is a good choice).



When all the solvent is removed, a "flowable" powder is obtained, easily removed from the round-bottom flask and poured directly onto the top of the silica packing, pre-eluted with the desired solvent system (it is best if the top of silica packing is slightly dry).

A small amount of solvent, *ca.* 4″ deep, is placed over the sodium sulfate layer and sucked through it. Chromatography then proceeds normally. This preadsorption technique is as quick as wet loading, and I now use it routinely.

Dr. Ian Dawson
Department of Organic Chemistry
University of Edinburgh
West Mains Road
Edinburgh, Scotland

Editor's note: We have employed this technique successfully here at Aldrich, using neutral alumina instead of sodium sulfate.

Aldrich offers an adapter with extra-coarse fritted disc, for use with rotary evaporator.

Adapter, with extra-coarse fritted disc and ⅋24/40 joints
Z10,747-6 **$30.20**

"Please Bother Us."

by Ian Dawson.

Recently Prof. John T. Gupton at the University of Central Florida suggested that we offer Gold's Reagent[1] which reacts in many ways like the DMF acetals, with some distinct advantages.[2-6]

It is an efficient β-dimethylaminomethylenating agent for ketones.[2,3] It also reacts easily with esters and lactones to yield the corresponding enamino derivatives.[4] Perhaps its greatest utility will be in the conversion of Grignard reagents to the corresponding aldehydes.[5]

Naturally we made Gold's Reagent.

1) Gold, H. *Angew. Chem.* **1960**, *72*, 956.
2) Gupton, J.T. *et al. J. Org. Chem.* **1980**, *45*, 4522.
3) Gupton, J.T.; Andrew, S.S.; Colon, C. *Synth. Commun.* **1982**, *12*, 35.
4) Gupton, J.T.; Lizzi, M.J.; Polk, D.E. *ibid.* **1982**, *12*, 939.
5) Gupton, J.T.; Polk, D.E. *ibid.* **1981**, *11*, 571.
6) Gupton, J.T.; Correia, K.F.; Hertel, G.R. *ibid.* **1984**, *14*, 1013.

28,907-8 Gold's Reagent [(dimethylaminomethyleneaminomethylene)-dimethylammonium chloride]
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It was no bother at all, just a pleasure to be able to help.

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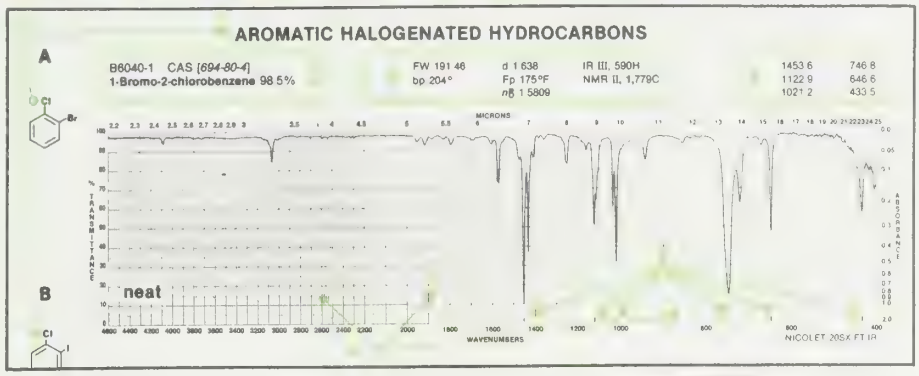

1. *Arranged in order of functionality and complexity for easy flip-through reference.*
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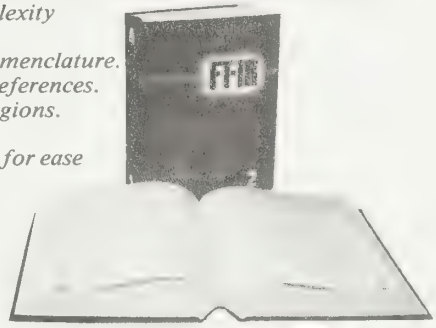

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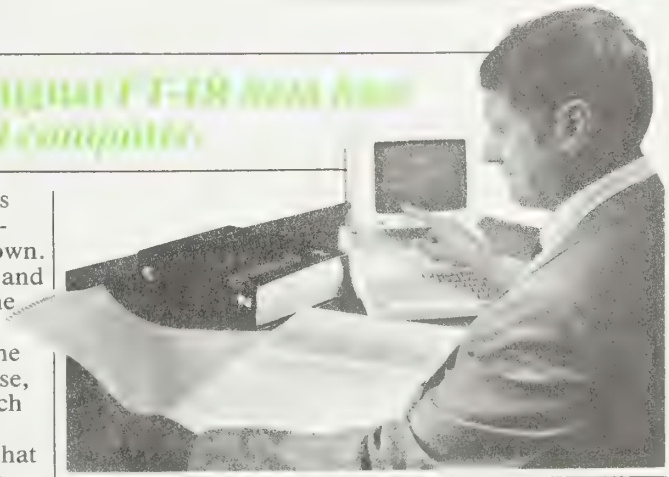

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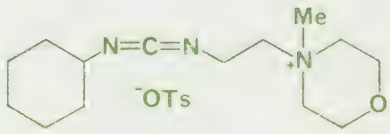

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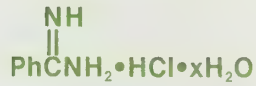

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Cl_2POMe

Phosphorylating agent for oligonucleotide synthesis.

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17,617-6

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Aldrichimica Acta

Volume 18, Number 2, 1985

Organozirconium Compounds as New Reagents and Intermediates

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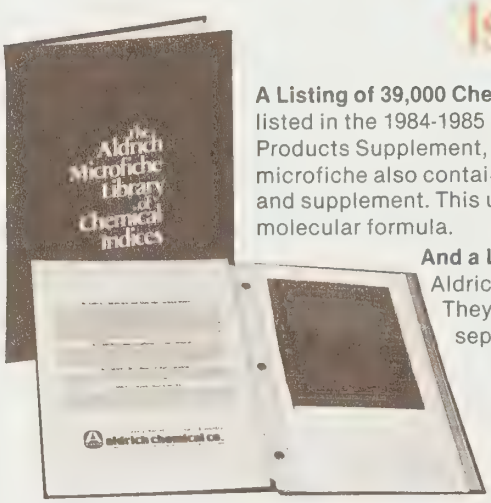
New Edition of The Aldrich Microfiche Library of Chemical Indices Is Available



A Listing of 39,000 Chemicals. The largest collection of chemicals in the world. Includes 16,000 listed in the 1984-1985 Aldrich Catalog/Handbook of Fine Chemicals and the February, 1985 New Products Supplement, as well as 23,000 in the Alfred Bader Collection of Rare Chemicals. The microfiche also contains all products added to our inventory since the publication of the catalog and supplement. This up-to-date listing on microfiche features two indices — alphabetical and molecular formula.

And a Listing by Physical Property. The 16,000 chemicals from our regular Aldrich inventory are listed alphabetically along with their physical constants. They are also computer-sorted by physical property and are indexed separately according to increasing:

- formula weight
- melting point
- boiling point
- density
- refractive index
- wavelength (μ) of maximum IR absorption.

Each list also gives the other five (when appropriate) physical properties and other data such as flash point and reference numbers to the Aldrich IR and NMR libraries. These indices are valuable in determining unknowns and in locating chemicals that meet specific physical property requirements.

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Microfiche Readers

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Movable linefinder:
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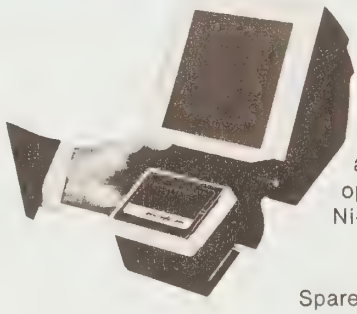
Portable, 16X magnification



This hand-held reader folds flat for easy storage. It has a 5½ x 5½in. gray screen and is supplied with a 110-v AC adapter. It may be operated with rechargeable Ni-Cd batteries.
Z12,156-8 $160.00

Spare FHZ lamp:
Z12,210-6 $14.00
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Z12,211-4 $16.95
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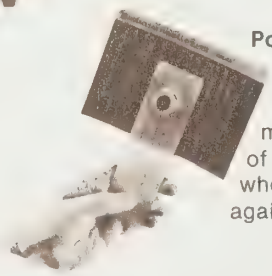

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About Our Cover:

We know relatively little about artistic practice in the 17th century, so our chemist-collector was delighted to find *The Artist in His Studio* by Aert de Gelder, one of Rembrandt's last students. De Gelder probably depicted himself in his studio, and it would be fun to be able to identify the sitter. The man in the corner is grinding pigments and, apparently, the cloth hanging from the ceiling is used to control the direction and intensity of the light.

De Gelder was a genial fellow who remained faithful to Rembrandt's style for some sixty years. By the time of de Gelder's death in 1727, Rembrandt's paintings had gone completely out of fashion, yet de Gelder never became "modern". This symphony in umber, with just a few highlights of green in the chairs, must be a sketch done late in the artist's life, probably after 1700.

Lab Notes

Drying large glassware that will not fit into desiccators can be problematic. We have found that wrapping the male joints with Teflon® tape before placing the glassware in the drying oven is a good idea.

After a suitable drying period, the apparatus can be assembled while still hot, without fear of the joints freezing. Teflon tape withstands temperatures well over 160 °C.

John Messinger II
State University of New York at Buffalo
Department of Chemistry
Acheson Hall
Buffalo, New York 14214

Editor's note: Aldrich offers Teflon sealing tape in ½" wide x 520" rolls.

Z10,438-8 **$6.95/3 rolls**

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Traditionally, inexpensive chromatography columns have been made by attaching the barrel of a disposable polypropylene syringe to a suitable length of glass tubing with epoxy, butyl rubber caulking, electrical tape, or a combination thereof. The inertness of these sealants to pH extremes and organic solvents is questionable, and the time required for hardening is unacceptable when immediate use is desired. A fast, new method is suggested:

A disposable polypropylene syringe barrel is selected to fit over the outside of the glass tubing. A *gentle* flame is applied to the syringe barrel one inch from the luer lock end (Fig. 1) until the plastic softens

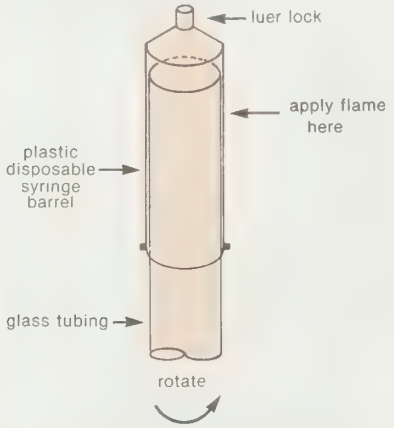


Figure 1

and becomes clear. The flame is then removed and the butt of the barrel is pulled down until the plastic separates at the point of heating (Fig. 2). The end of the barrel

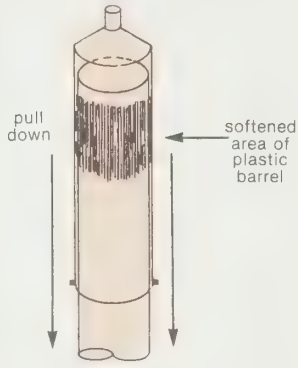


Figure 2

is removed and discarded. This leaves about one inch of the barrel with the luer lock end stuck on the glass tubing. While the plastic is still hot, two nylon wrap-it ties are tightened around the soft plastic barrel to hold it firmly against the glass (Fig. 3). As the plastic cools (water can be used

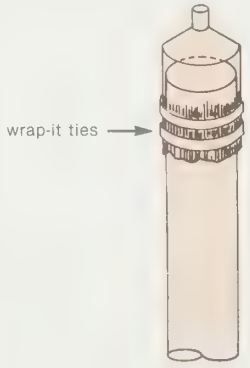


Figure 3

to speed the process) the barrel will shrink around the glass tubing creating a mechanically firm, leak-proof seal. Only polypropylene and glass are in contact with the column material. The entire process takes less than two minutes and the column can be used immediately.

Charles B. Grissom
Department of Biochemistry
Janet W. Grissom
Department of Chemistry
University of Wisconsin
420 Henry Mall
Madison, Wisconsin 53706

Editor's note: Consult the Equipment Section of the Aldrich Catalog/Handbook for a variety of disposable syringes and wrap-it ties.

I have found that a convenient NMR tube holder can be made in a cork ring by cutting a hole into (not through) the ring near the outer edge using a No. 2 cork borer. This holder facilitates transfer of flask contents into the NMR tube and provides a simple method for keeping flasks and NMR tubes matched.

Burnell Lee
University of Illinois
1209 W. California
Box 96-5 RAL
Urbana, Illinois 61801

Editor's note: Aldrich offers polyethylene NMR-tube racks.

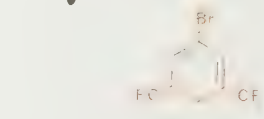
Z11,825-7 Holds 72 5-mm tubes **$14.25**

Z11,826-5 Holds 24 10-mm tubes **$13.25**

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt**. *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by



Recently Dr. Hans-Ullrich Siehl at the University of Tuebingen suggested that we offer 3,5-bis(trifluoromethyl)bromobenzene as a reagent to introduce an inductively withdrawing substituent into precursors for carbocations.

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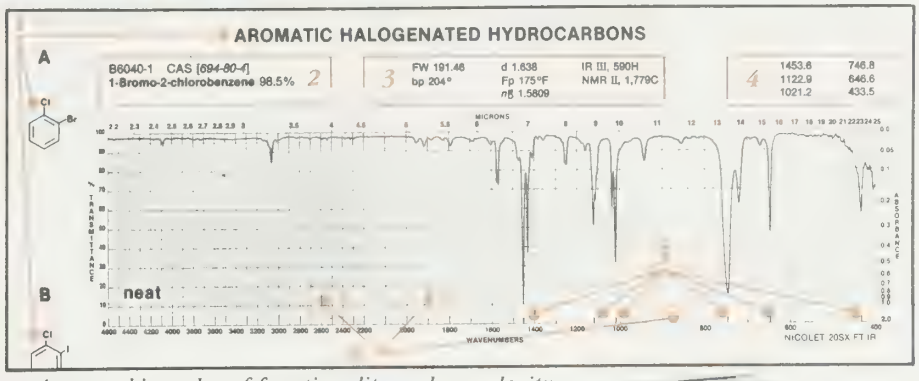

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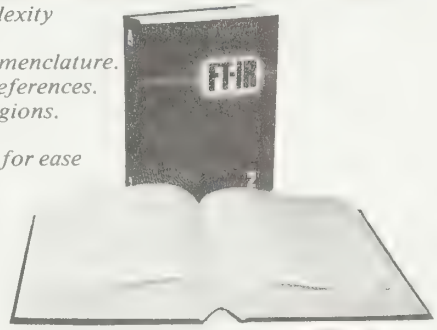

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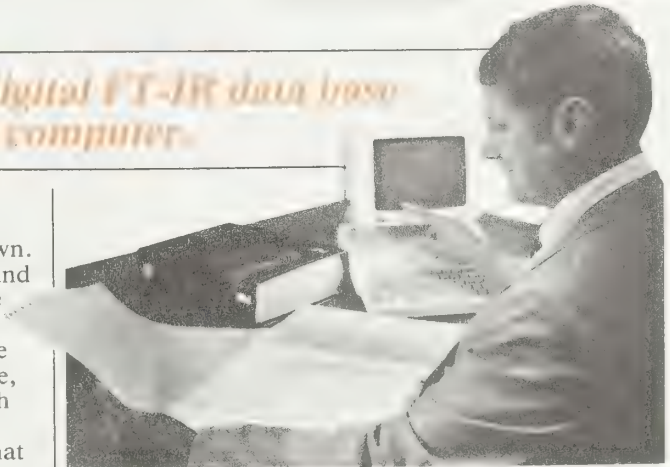

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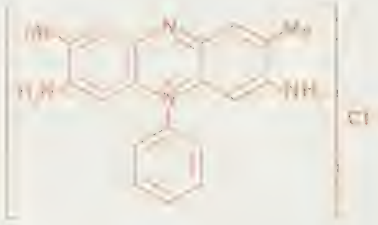

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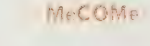

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Aldrichimica Acta

Volume 18, Number 3, 1985

Formamidines as Precursors to α-Amino Carbanions and Their Application to Asymmetric C–C Bond-Forming Reactions

Tetrathiafulvalenes (TTF) and Their Selenium and Tellurium Analogs (TSF and TTeF): Electron Donors for Organic Metals

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WIMP

Wisconsin Interactive Molecule Processor

by Professor H.W. Whitlock of the University of Wisconsin, Madison

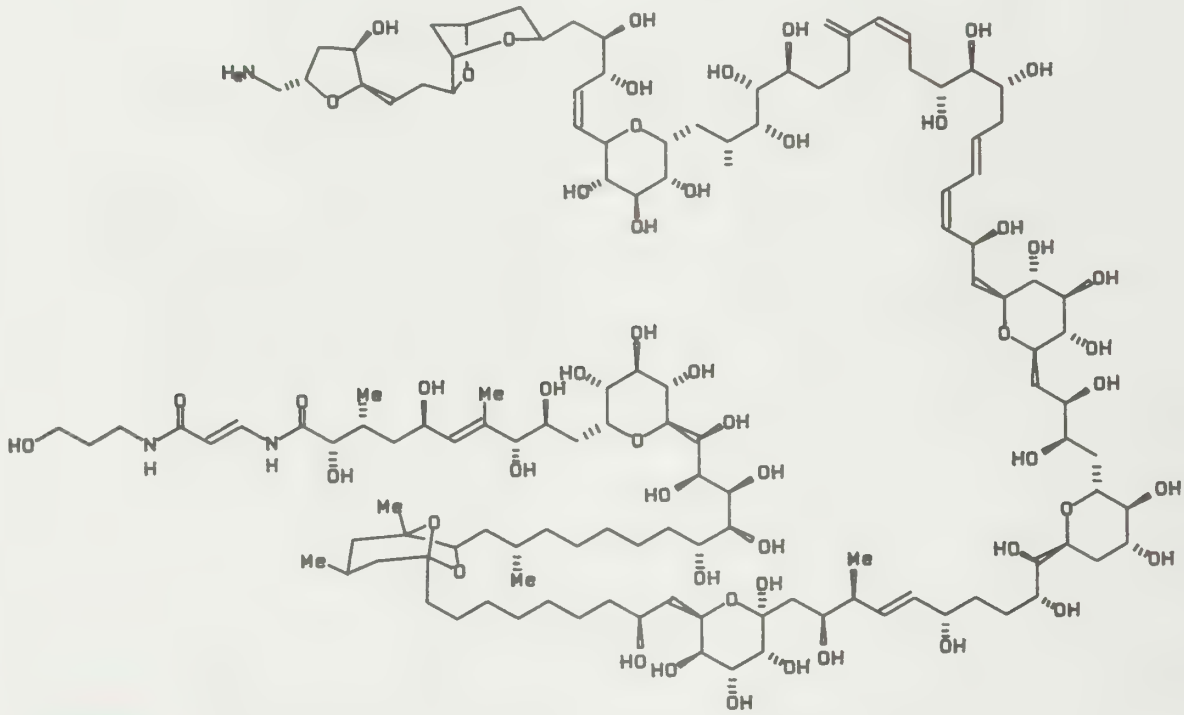

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Fig. 1

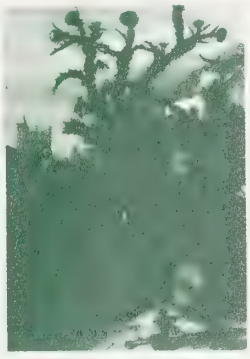

Fig. 2

There are thousands of portraits of men, women and children, and quite a few of cats, dogs and horses — but who has ever seen a real portrait of goats? Our chemist-collector loves to acquire paintings the likes of which he has never seen before — particularly by artists who were close to Rembrandt. So he tried for years to acquire this 'portrait' (oil on canvas, 27 x 36 inches) by one of Rembrandt's good friends, Lambert Doomer.

Doomer was one of the great draftsmen of the Golden Age; his many landscape drawings are superb. His paintings are rare, though one has appeared on an *Acta* (Vol. 9, No. 2, 1976). Doomer must really have been intrigued by these animals; there is a drawing (Fig. 1) of one of them in the Albertina in Vienna, and the same appears in a painting (Fig. 2) in the museum in Copenhagen. Doomer's biographer calls our collector's painting Doomer's finest animal painting;[1] Doomer thought so highly of it that he mentioned it in his will of 1677, and in 1700 it was recorded in the inventory of his estate.

1) W. Schultz, *Lambert Doomer, 1624-1700, Leben und Werke*, Berlin, 1972, pp 101-102 and p 468, G57.

Lab Notes

Everyone, at one time or another, has had to deal with a small spillage of mercury from a manometer or a mercury seal. The normal spillage-disposal techniques have drawbacks: forming the amalgam with zinc dust or Mercurisorb is messy and the mercury is lost; sucking up the droplets with a vacuum-assisted aspirator is clumsy and requires special equipment.

I have found a quick, simple and safe way to handle such spillage. A small piece of solid carbon dioxide is placed on the surface of the mercury which very quickly freezes (m.p. -38 °C) and can then be transferred with tweezers to a suitable container for reuse.

Stephen Mann
Marconi Research Centre
Great Baddow
Chelmsford, Essex
England

The mixing of small quantities of some liquids, such as endotoxin, requires extensive vortexing in order to break up the clumping molecules. Some instructions demand vigorous vortexing for as long as 30 to 60 minutes. This can be performed easily with an expensive shaker, or by manually holding the vial on a Vortex® mixer for the required time period.

We have found one way to overcome this expense and monotony. We equip our Vortex-Genie™ with a wide rubber band "girdle" used to secure the capped vial to the Vortex. One No. 62 (¼" x 2½") rubber band is tied between two No. 105 (⅛" x 5") rubber bands. The two large rubber bands are then placed around the sides of the Vortex. The smaller rubber band, placed near the top and bottom of the vial, secure the vial to the Vortex head. The pressure of the girdle maintains the action of the Vortex which can be adjusted to any speed on the variable control. Using this device now frees the technician to perform other tasks while the apparatus does the mixing.

John T. Shirtz
Microbiological Control
Bristol Laboratories
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Editor's note: We are grateful to Dr. Ronald Wolfe, Sigma Chemical Company, for helpful suggestions regarding this technique.

The sharp water peak at ~δ 1.5 in $CDCl_3$ solution is familiar to organic chemists who work with ^1H NMR samples in the microgram range (*e.g.*, ref. 1). Chemists who carry out deuterium-exchange experiments with D_2O in the milligram range are familiar with the HOD peak at ~δ 4.7 (*e.g.*, ref. 2). Since speculation failed to provide a convincing explanation of the nature of these two "water" peaks, we did the following simple experiments:

1. A 150-μl aliquot of Aldrich "100 atom % D" $CDCl_3$ was transferred from a freshly opened 0.5-ml ampule to a dry 150-μl cavity cell. This sample showed a peak at δ 1.52 of approximately the same intensity as the residual $CHCl_3$ peak. The remaining 350μl was dried over 4Å molecular sieves (activated at 350 °C); this treatment decreased the intensity of the δ 1.52 peak by about one-half.

2. Aldrich 99.8 atom % $CDCl_3$ was saturated with water by shaking, and the mixture was centrifuged. The $CDCl_3$ layer was removed by syringe and placed in a dry 150-μl cavity cell. The NMR spectrum showed a greatly increased (slightly shifted) peak at δ 1.55, which was approximately 3.4 times the intensity of the residual (0.2 atom %) $CHCl_3$ peak, and a small peak at ~δ 4.75 (~⅓ the intensity of the residual $CHCl_3$ peak). This solution was shaken *in situ* to saturation with water and centrifuged, but the $CDCl_3$ solution was not transferred to another cell; these are the usual conditions for the deuterium-exchange experiment. The δ 4.75 peak was greatly increased in intensity (~2 times that of the residual $CHCl_3$ peak). The peak at δ 1.55 was unchanged.

We draw the following conclusions:

1. The "δ 1.5" peak represents "monomeric" dissolved water in $CDCl_3$. In "dry" $CDCl_3$ it occurs at δ 1.52. Even at satura-

(*Lab Notes* continued on page 70)

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt**. *We reserve the right to retain all entries for consideration for future publication.*

Formamidines as Precursors to α-Amino Carbanions and Their Application to Asymmetric C-C Bond-Forming Reactions*

Albert I. Meyers
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

Introduction

In the past decade, organic chemists have met the challenge of uncovering useful asymmetric syntheses admirably, where virtually none existed prior to the 1970's. The monograph "Asymmetric Organic Reactions" by J.D. Morrison and H.S. Mosher,[1] published in 1971, outlines many of the frustrated attempts by earlier investigators to develop useful C-C bond-forming reactions with simultaneous enantioselectivity. This monograph was probably the major impetus for recent studies assessing the factors required to achieve useful asymmetric syntheses. It should not be construed that the earlier chemists lacked the insight and intellect to succeed, only that the current generation of synthetic chemists is able to see the problem more clearly. In the words of Sir Isaac Newton, "If (we) have seen farther than others, it is because (we) have stood on the shoulders of giants". Today, one only has to glance through current periodicals to find a steady stream of reports on useful asymmetric C-C bond-forming reactions. The five-volume treatise[2] "Asymmetric Synthesis", edited by Professor James D. Morrison (University of New Hampshire), is a tribute to the many laboratories which have successfully developed useful methodology — methodology that hardly existed in 1971. Other summaries of the successes in this field have also appeared.[3] Furthermore, it should not go unnoticed that three of the past four ACS Awards for Creative Work in Synthetic Organic Chemistry, presented to D.A. Evans (1982), K.B. Sharpless (1983), and the author (1985), have been given for work with novel approaches to asymmetric synthesis. The works of the first two are described in *Aldrichim. Acta* **1982**, *15*(2), 23 and **1983**, *16*(4), 67, respectively.

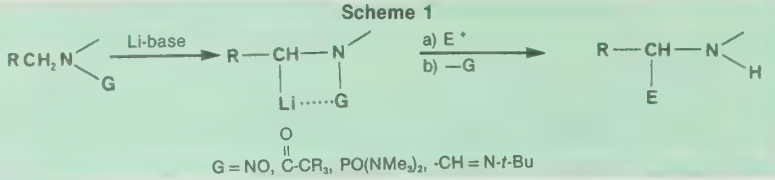
Professor Albert I. Meyers (right) receiving the A.C.S. Award for Creative Work in Synthetic Organic Chemistry, sponsored by Aldrich, from Dr. Alfred Bader, Chairman of the Board, Sigma-Aldrich Corporation.

This report describes the efforts and results of a novel C-C bond-forming process which not only leads to new chemistry, but also to a potentially powerful and unprecedented asymmetric synthesis. The following will chronicle the use of formamidines, both chiral and achiral, as precursors to α-amino carbanions and their application to a variety of natural products.

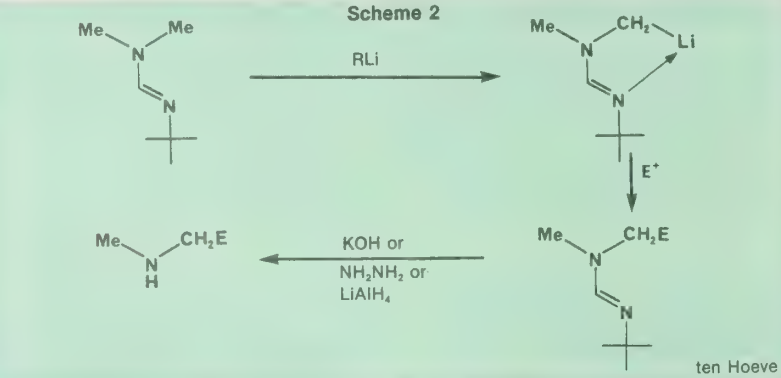
Achiral Formamidines - Synthesis, Metallation and Alkylation. The formation of a carbanion adjacent to nitrogen has been a long-sought-after process whose successful implementation would allow alkylation of a variety of amines. The generalized process (Scheme 1) depicts the manner in which an "activating" group (G) on nitrogen increases the kinetic acidity of an α-proton such that a lithio salt would result. The latter is then capable of reacting with electrophilic reagents to form a new C-C bond and, after removal of G, leads to an α-alkylated amine. Indeed, in recent years, this process has been successfully demonstrated by the elegant studies of Seebach[4] and Beak,[5] and has been reviewed by Beak[6] and Krief.[7] The activating group utilized in Scheme 1 is nitroso, phosphoryl, hindered acyl or, as this report shows, a formamidine. Our studies began in 1980 when we found[8] that formamidines (Scheme 2) readily gave α-lithio anions when treated with various organolithium compounds and that these could be alkylated efficiently to the elaborated derivatives.[3] Removal of the formamidine moiety by hydrolysis, hydrazinolysis, or reduction gave the unsymmetrically alkylated N-methyl amine. The ease with which this two-step process occurred stirred our interest in assessing its scope and utility. In view of the extensive studies by Seebach[4] and Beak,[5] it was necessary to evaluate whether the formamidines indeed provided a convenient alternative. As it turned out, formamidines derived from dimethylamine were prepared readily from dimethylformamide or its acetal according to the routes in Scheme 3. Since the dimethylamino formamidine and its resulting carbanion in Scheme 3 are of limited synthetic value, the acquisition of the formamidine made it possible to transform a number of secondary amines (Scheme 4) into their formamidines (**1-5**) by simple exchange in refluxing toluene, with or without an acid catalyst.[9] Finally, it was deemed important that the formamidine, after metallation and alkylation, be easily removed to regenerate the parent amino group. This was done routinely by adding hydrazine solution (25-50°) and stirring 12-18h, or refluxing with methanolic KOH, or treating with ethereal lithium aluminum hydride.[9] In some cases, the formamidine was removed by shaking with aluminum amalgam in moist ether, leaving an N-methyl group (Scheme 5).

With the knowledge that secondary amines could be transformed easily into their N-*tert*-butyl formamidines (TBF) and the starting amine regenerated under mild conditions, we proceeded to survey the

Scheme 1

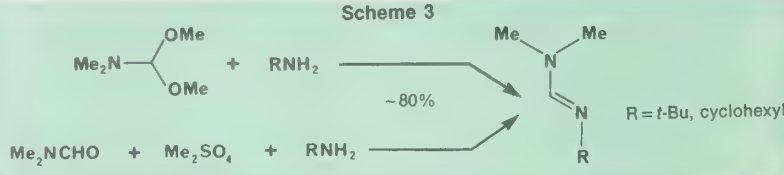


Scheme 2



ten Hoeve

Scheme 3



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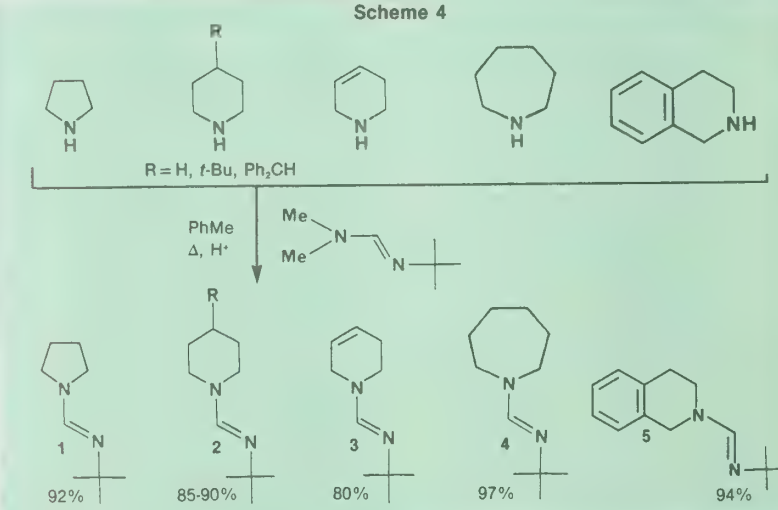
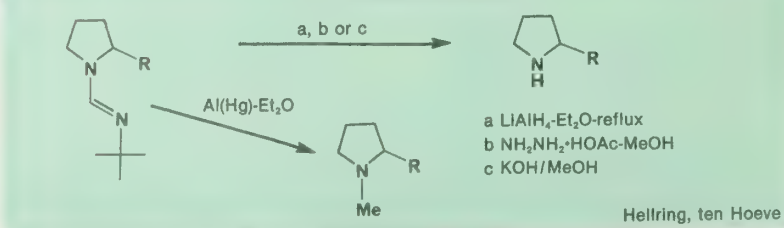
Scheme 4



Fuentes, Rieker, Bailey, Boes, Edwards

Scheme 5
Formamidine Removal



Hellring, ten Hoeve

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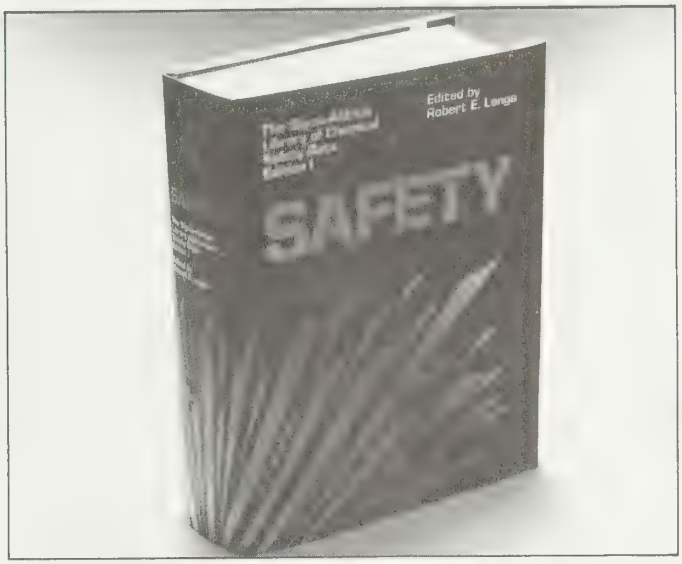

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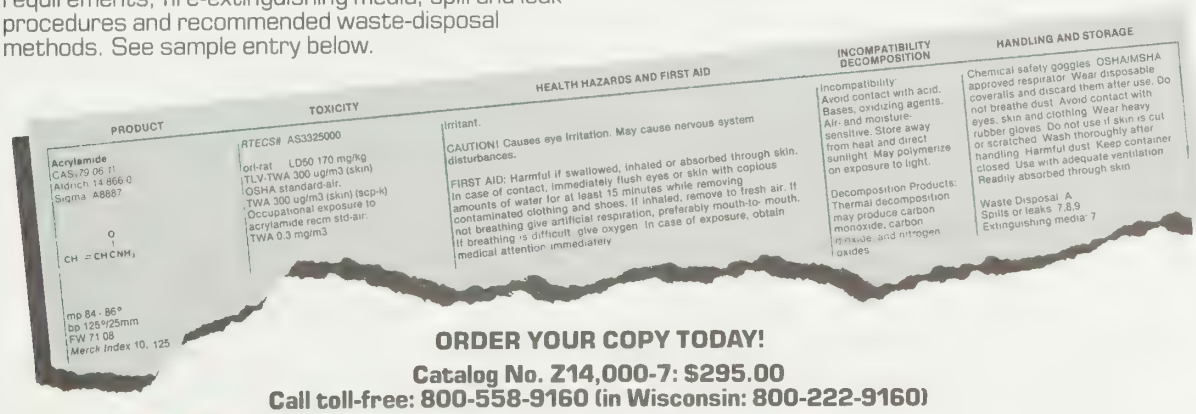
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Acrylamide
CAS: 79 06 1
Aldrich 14 866 0
Sigma A8887

O
CH =CHCNH,

mp 84 - 86°
bp 125°/25mm
FW 71 08
Merck Index 10, 125

TOXICITY

RTECS# AS3325000

orl-rat LD50 170 mg/kg
TLV-TWA 300 ug/m3 (skin)
OSHA standard-air:
TWA 300 ug/m3 (skin) (tscp-k)
Occupational exposure to
acrylamide recm std-air:
TWA 0.3 mg/m3

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$MePPh_3Br$

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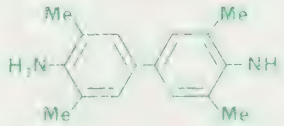
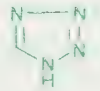
3,3′,5,5′-Tetramethylbenzidine (TMB)



Reported noncarcinogenic analog of benzidine.

86,033-6 (99 + %)
86,151-0 (•2HCl •$2H_2O$)

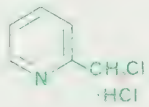
1*H*-Tetrazole



Precursor to popular condensing reagents.

24,395-7 (99 + %)
15,569-1 (98%)

2-Picolyl chloride hydrochloride



Useful heterocyclic intermediate.

16,270-1

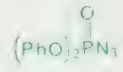
Acetone-d_6

CD_3COCD_3

Deuterated solvent.

99.5 atom % D	**15,179-3**
	23,685-3
99.5 atom% D (with 1% v/v TMS)	**18,597-3**
99 + atom % D	**17,595-1**

Diphenylphosphoryl azide



Synthesis of peptides, carbamates, thiol esters and azides.

17,875-6

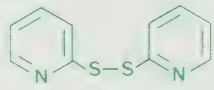
Methyl dichlorophosphite

Cl_2POMe

Phosphorylating agent for oligonucleotide synthesis.

23,522-9

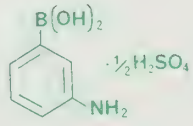
Aldrithiol-2



Versatile coupling reagent for lactone synthesis.

14,304-9

3-Aminophenylboronic acid hemisulfate



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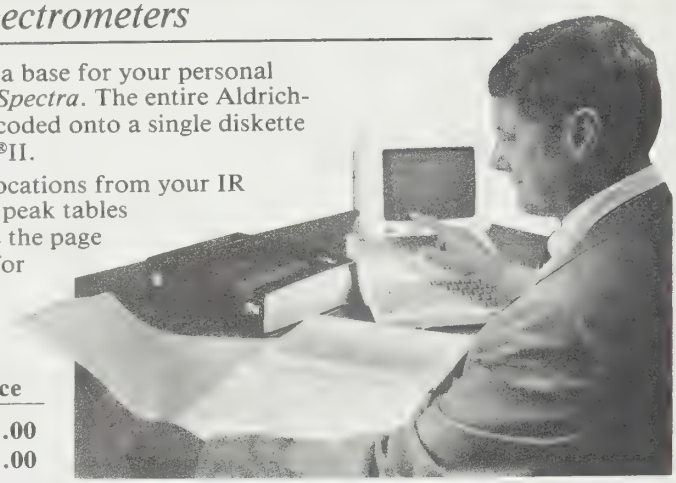

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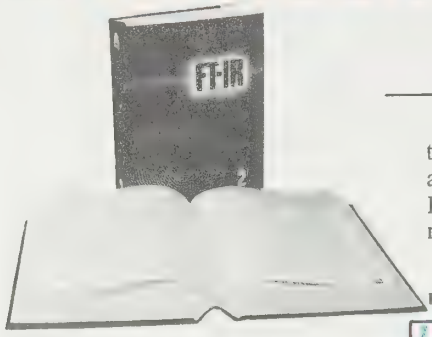
The Aldrich Library of FT-IR Spectra



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Spectra were recorded on a Nicolet 20SX FT-IR spectrometer. Each spectrum measures 18 x 4.5cm.

1. *Arranged in order of functionality and complexity for easy flip-through reference.*
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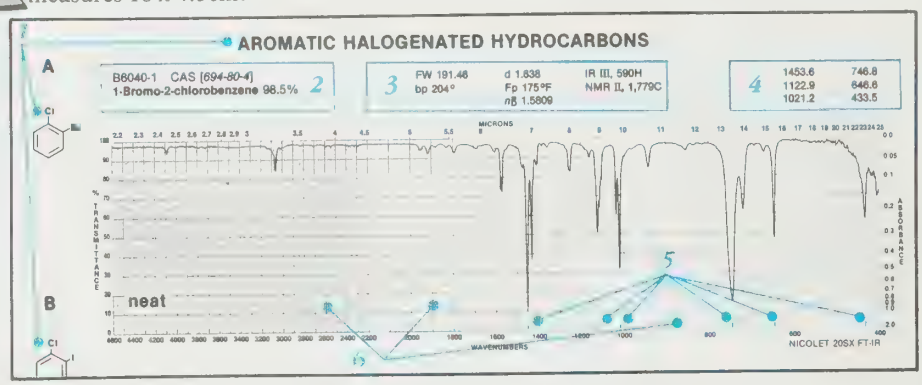

The Aldrich Library of FT-IR Spectra, Edition I, by Charles J. Pouchert
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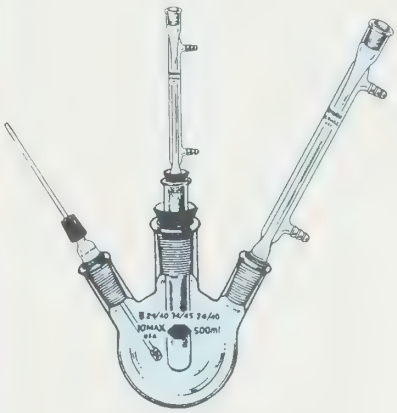
About Our Cover:

Our chemist-collector recently bought this small winter landscape (oil on canvas, 14 x 12¼ inches) by Jacob van Ruisdael in a London auction. Rather than describe it, he asked us to read what the late Wolfgang Stechow wrote about Ruisdael's winter landscapes in his treatise on *Dutch Landscape Painting of the Seventeenth Century* (Phaidon, London, 1966). Professor Stechow did not know this painting, yet his description appears so applicable:

> "...there is no trace of the traditional gaiety... It would be altogether absurd to think of skaters when looking at this picture; the real topic is the forlorn mood of a winter day... the mood is without any grandiloquence...profound, and wonderfully intimate... The 'dejected day' is now silenced by a deep, desolate grey from which some patches of sharply lit snow stand out threateningly rather than soothingly... There is nothing comparable with this in Dutch seventeenth-century landscapes; and outside of landscapes, only the deep gloom that spreads over a religious tragedy through the magic of Rembrandt's chiaroscuro comes to mind. I do not doubt that in spite of all technical and colouristic discrepancies, Rembrandt's 'synthesis of the visible and the invisible' here inspired Ruisdael: the very fact that all outward, imitative features of such an 'influence' are missing, is eloquent, for this can be expected of the fruitful relationship between two very great artists.
>
> "It is as though greatness in the interpretation of winter as a drama had been preserved for one single artist: Jacob van Ruisdael."

Lab Notes

I have found a rather simple method for heating reaction mixtures at constant temperature, which your readers may find useful.



The 25 x 200-mm test tube which contains the reaction mixture is fitted into the center neck (₹34/45) of the round-bottom flask using a No. 4 rubber filter adapter, as shown in the diagram. The test tube is then fitted with a condenser (₹19/22) using a No. 2 rubber filter adapter. The side arms of the round-bottom flask are fitted with a reflux condenser and a thermometer. A solvent having a boiling point equal to the constant temperature required is placed in the round-bottom flask and heated to reflux with a heating mantle. The refluxing solvent vapors will then maintain a constant temperature around the test tube reactor. A wide variety of solvents or solvent mixtures may be used to maintain different temperatures.

Howard L. Murray
Associate Professor of Chemistry
Northeastern Illinois University
5500 N. St. Louis Avenue
Chicago, IL 60625

Atmospheric moisture can sometimes ruin an organic or inorganic reaction. Some people go to great pains to flame glassware, dry solvents and otherwise prepare for anhydrous reaction conditions, then connect dry nitrogen or argon tanks to their flasks with tubing which might well have been used previously for condenser water. A simple solution is to maintain two sets of tubing labeled "wet" and "dry", respectively. Dry tubing can be stored closed into a loop using quick connectors, and hung over a convenient hook labeled "DRY TUBING ONLY".

Charles E. Gragg
Department of Chemistry
North Carolina State University
Box 5247
Raleigh, NC 27650

Editor's note: Aldrich carries various sizes of polyethylene tubing quick disconnects.

Cleaning a 10-microliter syringe can be time-consuming if the methodology necessitates prolonged rinsing with solvent. A disposable pipette tip (200-microliter capacity) serves as a "quick-disconnect" joint between the syringe and the water aspirator. With the syringe removed, the needle is dipped into the rinse solvent while the pipette tip is held over the barrel. (The broad end of the pipette tip is attached to the aspirator through a pressure tubing.) The syringe can be easily cleaned with a number of solvents in sequence. Thus, tedious rinsing as well as contamination due to rubber/glass connections can be avoided. An intermediate trap prevents the solvent from getting into the aspirator.

Ashok D. Deshpande
The College of William and Mary
Virginia Institute of Marine Science
School of Marine Science
Gloucester Point, VA 23062

I would like to report a simple solution to a problem that has been a constant annoyance to us and, I'm sure, many other NMR users.

The problem involves the sticking of caps to NMR tubes. Often the amount of force required to remove a cap results in a broken or chipped tube. Previously, we have cut off the offending cap with a razor blade – saving the tube and sample, but ruining the cap.

However, if the cap is warmed ***gently*** with a heat gun, it will soon soften and can be easily removed without being destroyed.

Rick M. Ede
Wood Technology Division
Forest Research Institute
Private Bag, Rotorua
New Zealand

Editor's note: For your convenience, Aldrich offers NMR caps and NMR tubes in various grades.

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt**. *We reserve the right to retain all entries for consideration for future publication.*

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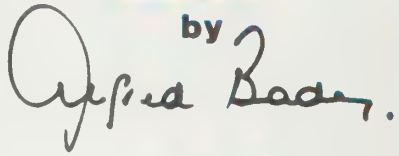
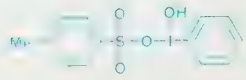
by





Professor G. F. Koser at the University of Akron suggested that we offer hydroxy(tosyloxy)iodobenzene, a useful reagent for the *cis*-ditosyloxylation of alkenes,[1] the α-tosyloxylation of ketones[2] and the phenyliodination of alkynes[3] and (trimethylsilyl)arenes.[4] This is a very versatile reagent which we would like to call "Koser's Reagent".

Naturally we made it.

1) Rebrovic, L.; Koser, G.F. *J. Org. Chem.* **1984**, *49*, 2462.
2) Koser, G.F.; Relenyi, A.G.; Kalos, A.N.; Rebrovic, L.; Wettach, R.H. *ibid.* **1982**, *47*, 2487.
3) Rebrovic, L.; Koser, G.F. *ibid.* **1984**, *49*, 4700.
4) Koser, G.F.; Wettach, R.H.; Smith, C.S. *ibid.* **1980**, *45*, 1543.

30,103-5 Hydroxy(tosyloxy)iodobenzene, 98% (Koser's Reagent)
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It was no bother at all, just a pleasure to be able to help.

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Wittig reagent.

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99.8 atom % D	**15,182-3**
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$MeNHOH \cdot HCl$

For specific cleavage of the phosphoramide bond in nucleotide peptides.

M5,040-0

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Reagent for peptide synthesis.

D12,540-7

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RSO_3Na

Ion-associating reagents for HPLC.

Sodium salts of:	
1-Butanesulfonic acid	**22,151-1**
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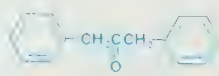
1-Hexanesulfonic acid	**22,154-6**
1-Heptanesulfonic acid	**22,155-4**
1-Octanesulfonic acid	**22,156-2**

1,3-Diphenylacetone



Useful intermediate.

D20,460-9

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Aldrichimica Acta

Volume 19, Number 1, 1986

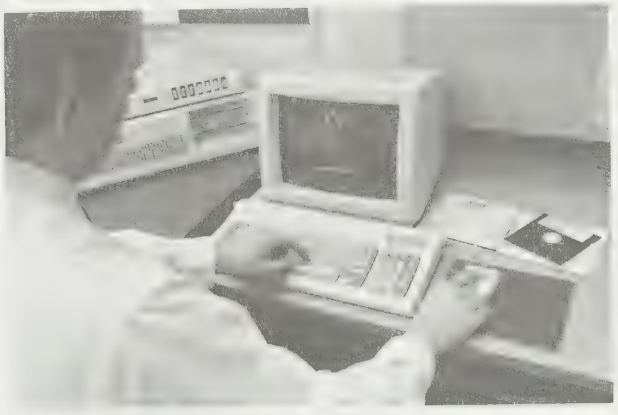
Dedicated to Professor Ralph Alexander Raphael on his sixty-fifth birthday

NEW VERSION

WIMP

Molecule – Drawing Software

by Professor H.W. Whitlock of the University of Wisconsin, Madison



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WIMP computer program, enhancement V2.00 with MOUSE adaptation
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Structures on pages 10 and 19 were drawn with the WIMP Molecule–Drawing Software

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About Our Cover:

This portrait of an old man (oil on panel, 52 × 42cm) leaves you with an unforgettable image of wisdom in old age. Our chemist-collector recently purchased this from a Hungarian nobleman; it had been in the well known Esterhazy collection where, of course, it had been attributed to Rembrandt. It is, in fact, by one of Rembrandt's students, Solomon Koninck, signed and dated 164....

In the nineteenth century such paintings were generally called "Portrait of a Rabbi," but how can you tell? Look, for instance, at Rembrandt's portrait of Johannes Uyttenbogaert. If we did not know that he was a well known Protestant preacher of the time, we might call it, too, "Portrait of a Jew" or of a rabbi.

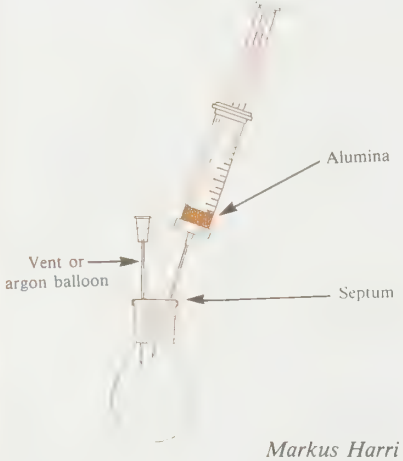
In any case, the old man depicted on our cover is almost ethereal, wise and kind, his mind as much in the world to come as in this one. What a fitting work to grace the cover of the *Acta* dedicated to Professor Ralph A. Raphael who, until age 16, had considered becoming a rabbi. Now, at age 65, he must know that he has taught, guided and helped many people even though he chose a different path.

Lab Notes

We have found a convenient improved technique to dry solvents on a small scale by filtration through alumina (or molecular sieves). Instead of glass chromatography columns, we use a 10-ml disposable plastic syringe.

A plug of cotton wool is poked into the narrow needle part of the syringe barrel followed by *ca.* 2ml of alumina (or molecular sieves). The barrel is filled with solvent. Reinsertion of the piston causes the first milliliter or two to be expelled through the needle. The needle can then be inserted through the septum and a measured amount of solvent squirted into the reaction vessel. (For large amounts of solvent, we have attached a needle to a chromatography column with an Aldrich needle-tubing connector.)

The advantage of this method is that the inert gas atmosphere of the reaction vessel is not disturbed during the procedure and there is no water condensing as the solvent evaporates from the tip of the dispenser.



Markus Harri
Ciba-Geigy Ltd.
4002 Basle
Switzerland

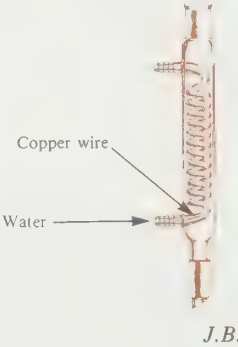
Editor's note: Aldrich carries a full line of anhydrous solvents. Check the equipment section of our Catalog/Handbook for disposable syringes and needle-tubing connectors.

The deterioration of partly used lithium reagents is a common problem, in spite of efforts to prevent hydrolysis and oxidation by means of Sure/Seal™ caps. We have found, however, that a few simple precautions can prolong the life of lithium alkyls significantly.

The bottle is secured by a clamp and the Sure/Seal pierced with a 16-gauge hypodermic needle connected to a nitrogen supply, which is maintained at a slight overpressure. The lithium alkyl solution is withdrawn by piercing the seal again with a gas-tight syringe; only little suction may be necessary if the nitrogen overpressure is high enough (*ca.* 50mm Hg). Syringe and gas supply are then removed and the holes in the cap immediately sealed by applying a small dab of silicon grease which is squeezed tight with the screw cap. (A small round piece of silicone rubber *ca.* 1mm thick may serve the same purpose.) The bottle is then stored in a freezer at -10 °C. The grease is wiped off prior to the next withdrawal to avoid contamination of the reagent. When *n*-butyllithium was handled in this way we found that the reduction in the lithium alkyl concentration was 10% or less over a period of approximately twelve months.

Manfred Bochmann
School of Chemical Sciences
University of East Anglia
Norwich NR4 7TJ

The growth of algae in the condensers of rotary evaporators or any permanent distillation set-up is greatly inhibited by copper wire (*ca.* 5cm long) placed in the coils of the condensers.



J.B. Fisher, III
Aldrich Chemical Co., Inc.

Intractable emulsions are often encountered in workup of phase-transfer reactions. We have noticed that small trapped air bubbles appear to stabilize the emulsions. Application of aspirator vacuum to the afflicted separatory funnel rapidly removes these bubbles, speeding the separation of the phases. **Naturally, a separatory funnel of appropriate strength must be selected when this technique is used.**

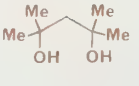
N.E.D. Jaxxon
Department of Chemistry
Princeton University
Princeton, NJ 08544

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt**. *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by

Professor E.J. Corey at Harvard University suggested that we offer 2,4-dimethyl-2,4-pentanediol. Just catalytic amounts of the Cr(VI) ester of this ditertiary 1,3-diol are needed for the high-yield peroxyacetic acid oxidation of secondary alcohols to ketones.[1] The chromate ester is easily prepared *in situ*.



As chromium reagents are environmental hazards and, also, large quantities complicate product isolation, this catalytic use of the chromium ester is clearly advantageous.

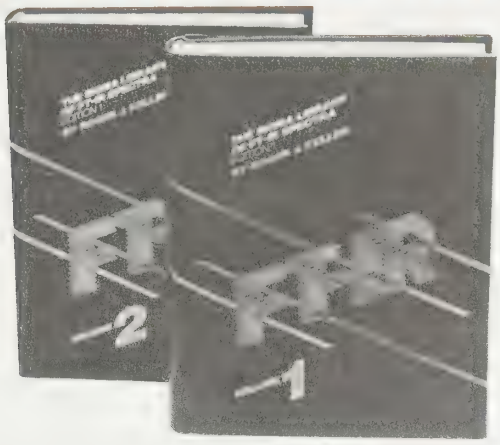
Naturally we made the diol.

1) Corey, E.J.; Barrette, E.P.; Magriotis, P.A. *Tetrahedron Lett.* **1985**, *26*, 5855.

30,538-3 2,4-Dimethyl-2,4-pentanediol
1g $5.00; 5g $20.00

It was no bother at all, just a pleasure to be able to help.

The Sigma Library of FT-IR Spectra



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In addition to the spectrum, each entry contains Sigma Product Number, physical properties, Chemical Abstracts Service registry number, and the chemical structure, as applicable.

The library is indexed alphabetically, by Chemical Abstracts Service registry number and by molecular formula.

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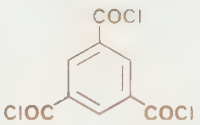
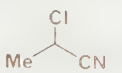
1,3,5-Benzenetricarboxylic acid chloride



Useful organic reagent.

14,753-2

2-Chloropropionitrile



Epoxide synthesis *via* Darzens condensation.

19,240-6

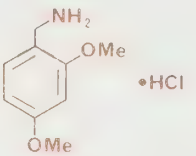
Silver carbonate

Ag_2CO_3

Selective oxidation of alcohols.

17,964-7

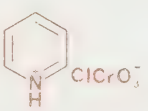
2,4-Dimethoxybenzylamine hydrochloride

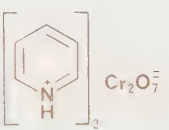


Building block for medicinal chemists.

17,860-8

Pyridinium chlorochromate (PCC)
Pyridinium dichromate (PDC)



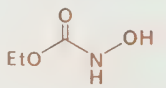


PCC **PDC**

Versatile oxidants in organic synthesis.

PCC **19,014-4**
PDC **21,469-8**

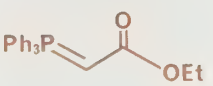
***N*-Hydroxyurethane**



Nitrene precursor.

11,947-4

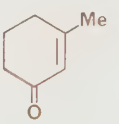
(Carbethoxymethylene)triphenylphosphorane



Valuable Wittig reagent.

C510-6

3-Methyl-2-cyclohexen-1-one



Sex-pheromone of the Douglas-fir beetle.

M3,910-5

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Aldrichimica Acta

Volume 19, Number 2, 1986

Guidelines for Handling Air-Sensitive Compounds
Some Useful Synthetic Applications of Gold's Reagent

chemists helping chemists in research & industry
aldrich chemical company, inc.

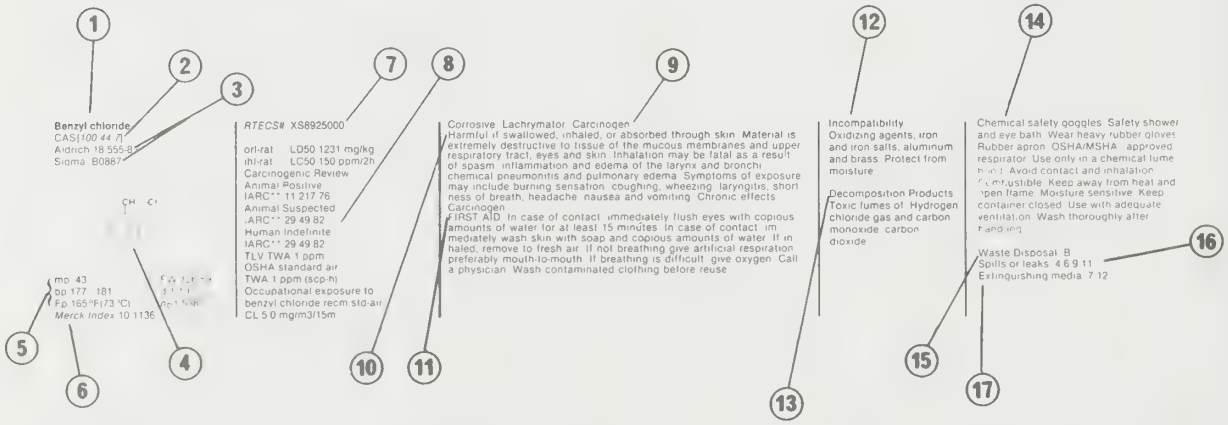
The Sigma-Aldrich Library of Chemical Safety Data

A reference for the safe handling of over 7000 chemicals

1900 pages, hardbound, with tearproof jacket. Page size 9½ × 12in.

The Sigma-Aldrich Library of Chemical Safety Data is an extensive yet compact collection of up-to-date safety information. The data were compiled through the collaboration of Sigma and Aldrich Chemical Companies.

The library will be useful to all users of chemicals who must assess the individual and composite hazards of mixtures, solutions, and reactions. It should provide employers with a basis for a sound safety program for complying with the Hazard Communication Standard and any training programs. A sample entry is shown below with explanation.



1. Name of chemical.
2. Chemical Abstracts Service Registry number.
3. Aldrich and Sigma Product numbers.
4. Structure or formula.
5. Physical data.
6. Reference to Merck Index, 10th edition.
7. Reference to the Registry of Toxic Effects of Chemical Substances.
8. Toxicity data, reviews and standards.
9. Specific health-hazard signal words.
10. Acute and chronic health effects.
11. FIRST AID measures.
12. Incompatible materials and conditions.
13. Products of decomposition.
14. Protective equipment, handling precautions and storage conditions.
15. *Suggested method of disposal.
16. *Recommended protective equipment and procedures for spill or leak clean-up.
17. *Extinguishing agents recommended for fires involving the material.

*Tables explaining the reference codes in each category will be found at the front of the book

The Sigma-Aldrich Library of Chemical Safety Data, Edition I, edited by Robert E. Lenga — **Z14,000-7** — **$295.00**

(Includes Explanation of Codes Chart, Z14,866-0)

Explanation of Codes Chart — **Z14,866-0** — **$3.00**

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Aldrichimica Acta

Volume 19, Number 2, 1986
A publication of the ALDRICH CHEMICAL COMPANY

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About Our Cover:

Readers of the *Acta* will remember that *Jacob's Dream* is one of the favorite subjects of baroque artists — "The vision of a ladder with angels going up and down on it is unique in Biblical imagery, and so *Jacob's Dream* has aroused artists' imaginations for centuries." It is also such a favorite of our chemist-collector that three have appeared on our covers: Vol. 8, No. 4; Vol. 12, No. 3 and Vol. 15, No. 1. You may also remember that Gerbrand van den Eeckhout, Rembrandt's best friend, is one of our chemist-collector's favorite artists. His works have graced two previous covers: Vol. 8, No. 2 and Vol. 17, No. 2; the latter, the *Rest on The Flight to Egypt*, is perhaps Eeckhout's finest work. We had so many requests that we had color reproductions made. And so our readers will not be surprised at yet another Eeckhout, of *Jacob's Dream* (oil on canvas, 121 x 103cm) on our cover.

Eeckhout must have thought about this subject a good deal, since he painted it several times. The earliest version (Fig. 1), of 1642, is in Warsaw and another (Fig. 2), of 1669, is in Dresden. Our version is one of Eeckhout's last works, dated 1672. Two of the preparatory drawings (Figs. 3 and 4) he made for this painting are in Schwerin and in the Albertina in Vienna.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

As we wrote previously: "The Bible is the book of dreams, par excellence: dreams of individuals, dreams of a people, dreams of all mankind. It is surely no accident that the very first well known dream in the Bible is not that of a king or of a general but of a man at the lowest point in his life — homeless and hunted, yearning for God's promise that He would return him to his country."

Lab Notes

I wish to point out that red (or clear) silicone rubber tubing possesses many advantages over common rubber or plastic tubing. Because of its self-lubricating quality, it slips easily over glass tubulations that would never permit the same size rubber tubing; thus only 2 sizes (¼in. i.d. x ⅛in. wall and 3/16in. i.d. x 3/64in. wall) accommodate most glassware. The larger size slips easily over even ⅜in. tubulation and does not collapse under vacuum. Furthermore, it will not melt on accidental contact with heating mantles nor will it lose flexibility when connected to a steam bath. From a safety standpoint, its use with glass tubing can certainly be recommended in a teaching laboratory. The higher cost of silicone rubber tubing can be offset by its longer life.

Henry M. Fales
Chief, Laboratory of Chemistry
Department of Health & Human Services
Building 10, Room 7N309
National Institutes of Health
Bethesda, MD 20205

Editor's note: Aldrich now offers silicone-rubber tubing as follows:

Z15,305-2 Silicone-rubber tubing, clear, ¼in. i.d., ½in. o.d. **15.2 meters $44.75**

Z15,306-0 Silicone-rubber tubing, clear, 3/16in. i.d., 9/32in. o.d. **15.2 meters $14.00**

We have found a solution to the problem of storing NMR samples at low temperatures and anhydrous conditions (for following reactions in NMR tubes over a number of days) by using inexpensive "Zip-Loc" bags (4 to 6mil) containing a small amount of desiccant. Capped but unsealed NMR samples stored for up to two weeks in a freezer showed no evidence of hydrolysis from atmospheric moisture. We have also found "Zip-Loc" bags to be effective miniature desiccators for short-term storage of moisture-sensitive materials.

Ricardo A. Silva
Department of Chemistry
California State University
Northridge, CA 91330

In Lab Notes, *Aldrichim. Acta,* Vol. 17, No. 2, p. 30, 1984, a hydrogenation procedure was described in which a balloon was used as a reservoir for hydrogen. A common variation is the use of an argon-filled balloon to maintain an inert atmosphere during a reaction. Thus, a good-quality rubber balloon is attached to a ~2-in. section of pressure tubing (¼in. i.d., ⅜in. o.d.) with a rubber band. The balloon is inflated and deflated 6-8 times with argon. It is inflated once more (to ~5-in. diameter for a 7-in. maximum diameter balloon) and attached to a hose-to-needle adapter (*e.g.,* Aldrich Z10,116-8) fitted with a ~1-in., 20-gauge needle. Some gas is allowed to escape *via* the needle. The needle is then used to attach the balloon to a previously argon-purged reaction vessel equipped with a rubber septum. Reagents and/or solvents can then be introduced *via* syringe or cannula. The balloon expands to accommodate the volume change.

An argon-filled balloon can also make the removal of air- or moisture-sensitive reagents from a septum-capped vessel (*e.g.,* a Sure/Seal™ bottle) more convenient. The septum is first pierced with a 20-gauge needle furnished as above with an argon-filled balloon. An oven-dried syringe is equipped with a lightly greased stainless steel syringe stopcock (*e.g.,* Aldrich Z10,235-0). A needle (20-gauge, except for viscous solutions like Red-Al® in toluene which require an 18- or even a 16-gauge needle) is attached and the needle is passed through the vessel's septum. The syringe stopcock is opened and the reagent is withdrawn. The syringe is then raised to allow withdrawal of some argon (clearing the needle of reagent and allowing accurate measurement of the volume of reagent). The stopcock is closed and the syringe needle can then be safely removed from the vessel. This procedure is recommended particularly for pyrophoric liquid reagents.

Dr. R. Thomas Swann
Department of Medicinal Chemistry
SUNY at Buffalo
Buffalo, NY 14260

Editor's note: Aldrich now lists balloons suitable for the manipulations discussed above. See page 50 of this *Acta* issue.

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Visualization of compounds on TLC plates with iodine is usually a slow process. We have found that the time for development can be shortened by blowing iodine gas directly on the surface of the plate. The device that we have used is a disposable Pasteur pipette with a few iodine crystals held between two glass-wool wads. In the hood, the iodine gas is blown gently over the dried plate by passing air through the pipette (*via* a compressed-air line or rubber bulb). The visualization is best achieved by using a movement that follows the expected path of the sample. The spots are then preserved by placing a glass plate or plastic tape on the plate.

Alberto Haces
Drug Design & Chemistry Section
Laboratory of Medicinal Chemistry & Biology
National Cancer Institute
National Institutes of Health
Bethesda, MD 20205

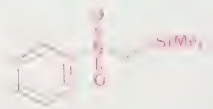
Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt**. *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Aldrich Boys.

Mr. Donald Craig and Professor Steven V. Ley at Imperial College in London suggested that we offer phenyl trimethylsilylmethyl sulfone for the conversion[1] of aldehydes and ketones to the corresponding vinyl sulfones *via* a modified Peterson olefination.[2]

Naturally, we made it.



1) Craig, D.; Ley, S.V.; Simpkins, N.S.; Whitham, G.H.; Prior, M.J. *J. Chem. Soc., Perkin Trans.1* **1985**, 1949.
2) Peterson, D.J. *J. Org. Chem.* **1968**, *33*, 780.

30,674-6 Phenyl trimethylsilylmethyl sulfone, 98% **5g $8.00; 25g $28.00**

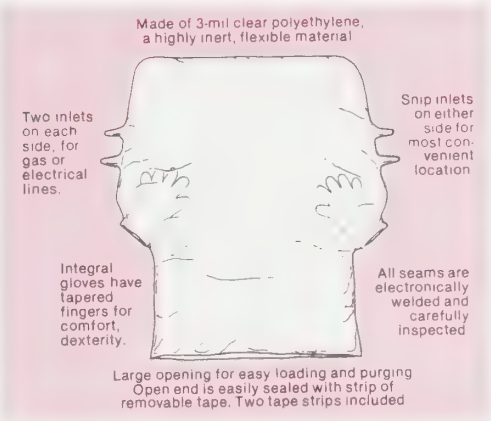
It was no bother at all, just a pleasure to be able to help.

The Aldrich AtmosBag™

controlled-atmosphere chamber with built-in gloves

The Aldrich AtmosBag™ is a polyethylene bag which can be sealed, purged, and inflated with an appropriate gas, creating a portable, convenient, and inexpensive "glove box" for handling air- and moisture-sensitive and toxic* materials. It is especially suitable for handling air-sensitive solid reagents: at Aldrich such reagents are packaged in an AtmosBag inflated with the appropriate inert gas.

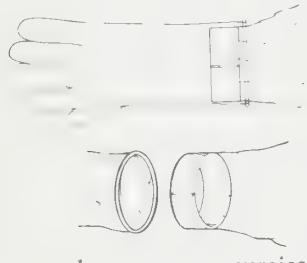
Other applications include: dust-free operations, controlled-atmosphere habitat, and, for the ethylene-oxide-treated AtmosBag, immunological and microbiological studies.



Size	Dimensions when uninflated (in) Opening	Width	Length	Volume when inflated (in^3/liters)	Cat. No.	Price	Ethylene-oxide-treated Cat. No.	Price
L	36	51	58	32,000/520	**Z10,608-9**	**$25.95**	**Z11,835-4**	**$27.25**
M	24	39	48	17,000/280	**Z11,282-8**	**$20.80**	**Z11,836-2**	**$21.95**
S	12	27	30	3,000/50	**Z11,283-6**	**$15.60**	**Z11,837-0**	**$17.00**

Select-a-glove AtmosBag

Equipped with rings instead of gloves, this AtmosBag enables one to use the gloves of choice by simply taping the gloves onto the rings (1½in wide, 3½-in diam.).



For example, one can use surgical gloves for better feel or Viton gloves for greater protection. NBR rubber, premium white rubber, and neoprene gloves may also be used.

Z11,284-4 Gloveless Two-Hand AtmosBag (L) **$31.20**

Four-Hand AtmosBag

This AtmosBag [dimensions (uninflated): 30 (opening) × 45 × 58in] has four built-in gloves and is slightly smaller than the large two-hand AtmosBag. It is completely symmetrical and is designed so that cutting off the sealed end enables attachment of AtmosBags in series, using semi-rigid ring connectors. It also enables construction of an air-lock, using the AtmosBag divider.

Z10,840-5 Four-Hand AtmosBag **$31.05; $105.40**/4

Z10,852-9 AtmosBag Connector (66 × 3 × 1/16in) **$4.30**

Z10,866-9 AtmosBag Divider **$8.05**

Accessories

Bench-top Base. Rigid polyethylene, ½in thick. Keeps AtmosBag in place.

L	22 × 32in	**Z10,691-7**	**$43.00**
M	20 × 16in	**Z11,285-2**	**$33.85**
S	11 × 15in	**Z11,286-0**	**$31.60**

Sealing Tape. 3in × 60yd **Z10,692-5** **$8.05**

Glove Liners. White cotton-knit gloves.

S – M	**Z11,833-8**	**$12.00**/12pr
M – L	**Z11,834-6**	**$12.00**/12pr

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*CAUTION. When handling toxic materials use only in a hood or other controlled system to prevent and protect against exposure in case of leakage. All products made of polyethylene may tear, break or puncture. To assure that air-sensitive materials do not become exposed to air, follow instructions on package; also test and monitor AtmosBag for leaks before and during use.

For more information on the AtmosBag chamber, see pages 1692-1693 of our 1986-1987 Catalog/Handbook.

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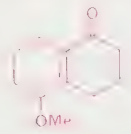
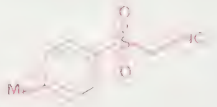
5-Methoxy-1-tetralone



Pharmaceutical intermediate.

11,311-5

Tosylmethyl isocyanide



For the synthesis of nitrogen heterocycles, ketones and nitriles.

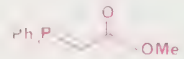
18,820-4

Phenylselenenyl chloride

For the synthesis of allylic alcohols, ethers and acetates.

18,334-2

Methyl (triphenylphosphoranylidene)acetate



Wittig reagent.

15,792-9

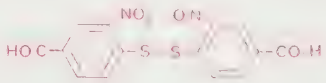
***N*-Methylhydroxylamine hydrochloride**

MeNHOH · HCl

Reagent for the cleavage of the phosphoramide bond in nucleotide peptides.

M5,040-0

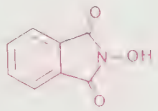
5,5′-Dithiobis(2-nitrobenzoic acid) (Ellman's Reagent)



Thiol reagent.

D21,820-0

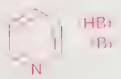
***N*-Hydroxyphthalimide**



For the preparation of active esters in peptide synthesis.

H5,370-4

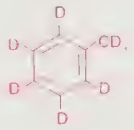
Pyridinium bromide perbromide



Brominating agent.

13,324-8

Toluene-d_8



Deuterated solvent.

99+ atom % D **15,199-8**
99+ atom % D **26,987-5**
(with 1% v/v TMS)

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Aldrichimica Acta

Volume 19, Number 3, 1986 (Last issue in 1986)

Reflections on Organic Synthesis: The Evolution of a General Strategy for the Stereoselective Construction of Polyoxygenated Natural Products

chemists helping chemists in research & industry

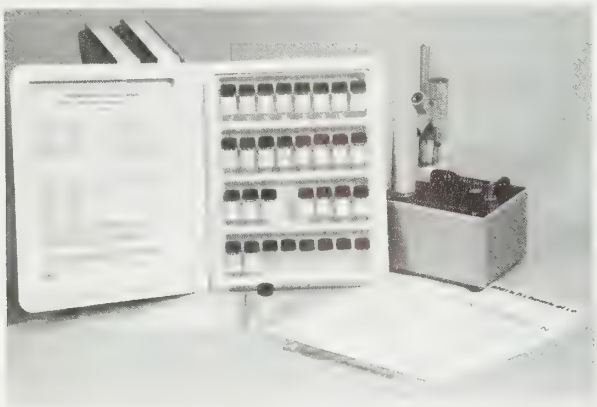
aldrich chemical company, inc.

Melting-Point Standards Kit

A Valuable Kit for Use in Education, Research and Analysis

- **reference standards**
- **product identification**
- **instrument calibration**
- **comparison with unknowns**

Kit contains 26 standards, 50-300°C, in 10-degree intervals. The standards are packaged in 250mg-1g units in 2-ml Wheaton Shorty Vials,™ and are supplied in the convenient Aldrich kitcase. Sample vials and blank labels are included for your convenience. Individual refills may be reordered.



Kit index lists all standards in tray sequence for easy location.

Kitcase is 7¼" wide, 9⁵⁄₁₆" tall and 1½" thick.

Standards snap in and out of trays.

Melting-point standards in the exclusive Aldrich kitcase and the MEL-TEMP capillary-melting-point apparatus.

Kit Contents

Acetamide
Acetylsalicylic acid
Anthraquinone
Anthraquinone-2-carboxylic acid
Benzophenone
Benzotriazole
4-Benzoylbenzoic acid
Cyclohexanone 2,4-dinitrophenylhydrazone
2,6-Di-*tert*-butyl-4-methylphenol
Dimethylglyoxime
1,3-Diphenoxybenzene
4-Fluorocinnamic acid
Formic acid, sodium salt
Imidazole
DL-Mandelic acid
Methylhydroquinone
1,8-Naphthalimide
Nitroterephthalic acid
1,4-Phenylenediacetic acid
Saccharin
Succinic acid
L-Tartaric acid
3,3-Tetramethyleneglutaric acid
m-Toluic acid
α,α,α-Trifluoro-*p*-toluic acid
L-Xylose

30,038-1 Melting-Point Standards Kit, 50-300°C **$168.00**
Technical Information Bulletin No. AL-158 with instructions on obtaining melting point and melting range is provided with each kit.

See our Catalog/Handbook for other kits available in the Aldrich Library of Chemical Standards.

Aldrich offers the following equipment for melting-point determination.

Z15,060-6 MEL-TEMP® capillary melting point apparatus, 100-125V, 200 watts **$275.40**
[see *Aldrichim. Acta* **1986**, *19*(1), 22 for more details]

Z15,061-4 Thermometer, 0-400°C **$21.00**

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Aldrichimica Acta

Volume 19, Number 3, 1986
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About Our Cover:

Our chemist-collector loves puzzles both of iconography and authorship, and is doubly delighted when these coincide in a painting. The previous owner, one of London's most sensitive and honest dealers, believed that this painting (oil on canvas, 28¾ x 23¼ inches), then filthy dirty, was by a late 17th-century Dutch artist, and that it might depict a specific cabalistic rabbi who had lived in Frankfurt and Amsterdam. Recent cleaning shows this to be untenable. It was painted about 1820, probably in England, by a most painterly artist, a great colorist who used such rich reds in the curtains — someone like Sir David Wilkie.

Is it a portrait of a rabbi, or of an actor, or of a figure from literature or history? In any case, this painting, done with such bravura, seems most fitting for the *Acta* with Professor Danishefsky's masterly essay.

Lab Notes

Independent communications by Dawson and Harwood [*Aldrichim. Acta* **1985**, *18*(1)] on improved procedures for flash column chromatography prompt me to report a method which we have been using in these laboratories for the past three years.

The procedure was developed to eliminate the loading problems encountered when the sample to be purified is not readily soluble in the eluant mixture. We call this procedure "*dry flash*" column chromatography to indicate that it is a hybrid between normal dry column and flash column chromatography as reported by Still.[1]

Selection and packing of the column are according to Still's procedure. The sample is dissolved in a low-boiling organic solvent or solvent mixture and the solution is used to prepare a slurry with silica gel (ratio of sample to adsorbent *ca.* 1:7, by weight). The solvent is allowed to evaporate at room temperature while the mixture is stirred manually with a spatula. The dry sample-containing silica gel is placed as a thin, even band at the top of the column and covered with *ca.* 2in of sand. Expulsion of the air and final packing of the column are done by passing the least polar solvent of the mixture through the column. At this point the flow rate can also be regulated. The purification is initiated by adding the chosen eluant.

We have found that mixtures of Skellysolve B/acetone, ethyl ether/Skellysolve B and benzene/acetone give best results. A further advantage in using these solvent mixtures is that often compounds crystallize upon concentration of the fractions.

Column lengths may vary from 8in for complex mixtures to 4in for simple purifications. We have used this method to purify mixtures of 3-350mg.

1) Still, W.C.; Kalin, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Luis Manuel Pena-Rodriguez
Graduate Student
Department of Chemistry
The University of Alberta
Edmonton, Alberta
Canada T6C 2G2

Traditional procedures for the purification of chlorotrimethylsilane are objectionable since the methods for removal of residual hydrogen chloride are either very tedious or provide material of varied quality. Recently we have developed a new procedure for purification of chlorotrimethylsilane. Commercial material is stirred with calcium hydride overnight and distilled under an inert atmosphere through a dry short-path distillation apparatus into a *ca.* 100-ml bottle *previously charged with a ½-inch layer of cross-linked poly(4-vinylpyridine).* The bottle is then sealed under an inert atmosphere with a septum. The material obtained is often initially very cloudy due to the fact that traces of hydrogen chloride are still being scavenged by the polymer. The material is allowed to sit 2-3 days at room temperature, after which all polymer settles to the bottom of the container and the supernatant chlorotrimethylsilane is crystal clear. The material so obtained contains very little hydrogen chloride and is completely suitable for use with lithium dimethylcuprate and other proton-sensitive organometallic reagents on a submillimole scale. The chlorotrimethylsilane purified in this manner can be stored at room temperature for at least one month prior to redistillation.

D. K. Hutchinson
Department of Chemistry
Purdue University
West Lafayette, IN 47907

Editor's note: Aldrich lists the following reagents mentioned in the above procedure.

21,326-8 Calcium hydride, 95+%, -40 mesh (fine ground powder) **100g $12.80; 500g $42.80**

20,802-7 Calcium hydride, 95+%, -4+40 mesh (coarse ground powder) **100g $12.80; 500g $42.80**

21,332-2 Calcium hydride, 95+%, -1+4 mesh (granules/lumps) **100g $12.80 500g $42.80**

C7,285-4 Chlorotrimethylsilane, 98% **100g $7.80; 500g $17.00**

22,696-3 Poly(4-vinylpyridine), cross-linked **50g $25.65; 250g $85.70**

I would like to report a simple solution to the problem of removal of volatile solvent from an organic solution contained in a small test tube or ampule.

Instead of flushing it with dry nitrogen and/or heating it with a heat gun, we placed the tube into a round-bottom flask (with ground-glass joint) of appropriate height. The tube must stand in the flask. The evaporation is then conducted under reduced pressure in a rotary film evaporator.

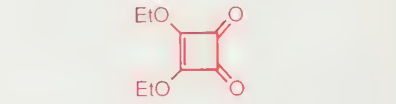
This nontedious method affords a deposit of the sample in the bottom of the ampule, making sealing it easier.

Darío Doller
Departamento de Química Orgánica y UMYMFOR
Facultad de Ciencias Exactas y Naturales
Universidad de Buenos Aires
Buenos Aires, Argentina

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt**. *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by



Professor Lanny S. Liebeskind at Emory University suggested that we offer diethyl squarate. 3,4-Disubstituted 3-cyclobutene-1,2-diones of this type have been shown recently[1,2] to be useful starting materials for the general synthesis of highly substituted quinones.

Naturally, we made diethyl squarate.

1) Liebeskind, L.S.; Iyer, S.; Jewell, C.F., Jr. *J. Org. Chem.* **1986**, *51*, 3065.
2) Perri, S.T.; Foland, L.D.; Decker, O.H.W.; Moore, H.W. *ibid.* **1986**, *51*, 3067.

31,077-8 3,4-Diethoxy-3-cyclobutene-1,2-dione, 99% (diethyl squarate) **5g $15.00; 25g $62.00**

It was no bother at all, just a pleasure to be able to help.

WIMPlates

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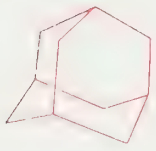

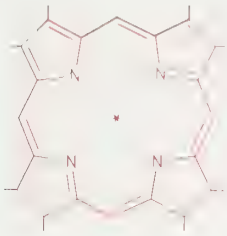

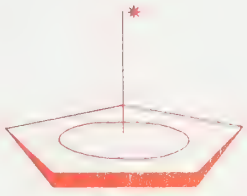

Over 450 structure backbones and functional-group fragments representing all chemical classes. Accessible at the touch of a key! A reference manual showing templates by chemical class is supplied. The manual also features important drawing tips and has blank text pages and extra indexing space to aid in the classification and storage of user-created templates.

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$Me_3SiC{\equiv}CH$

Ethynylation of aromatic compounds.

21,817-0

Tetrakis(triphenylphosphine)-palladium(0)

$(Ph_3P)_4Pd$

Useful catalyst and catalyst precursor.

21,666-6

Phenyl chlorothionocarbonate

Conversion of protected ribonucleosides to 2′-deoxyribonucleosides.

23,452-4

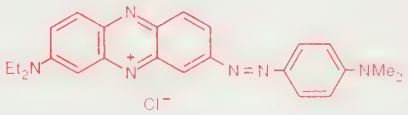
Trifluoromethanesulfonic anhydride

$(CF_3SO_2)_2O$

Synthesis of triflates.

17,617-6

Janus Green B, certified (C.I. No. 11050)



20,167-7

Hexamethylphosphorous triamide (HMPT)

$(Me_2N)_3P$

Useful aprotic solvent.

14,355-3

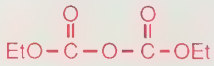
Trimethylsulfonium iodide

$(Me)_3SI$

Precursor to dimethylsulfonium methylide.

T8,048-9

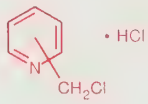
Diethyl pyrocarbonate (DEPC)



Ribonuclease inhibitor.

15,922-0

Picolyl chloride hydrochloride, 2-, 3- and 4-isomers



Useful heterocyclic intermediates.

2- 16,270-1
3- P4,360-2
4- P4,380-7

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Aldrichimica Acta

Volume 20, Number 1, 1987

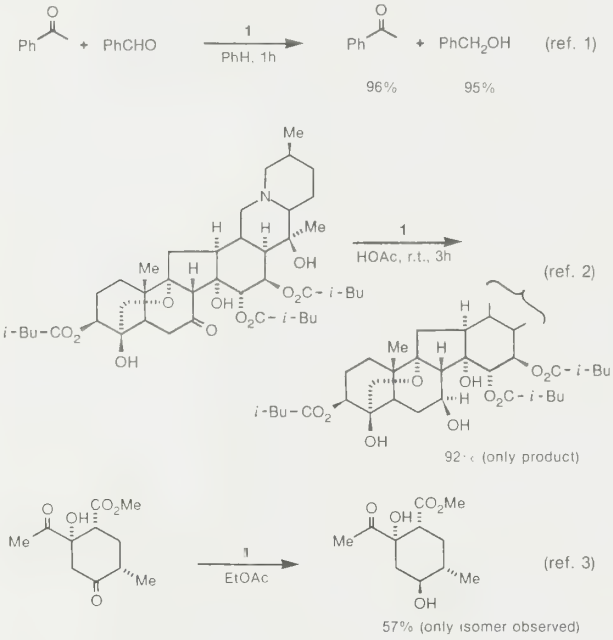
Dedicated to Professor Herbert C. Brown on his seventy-fifth birthday

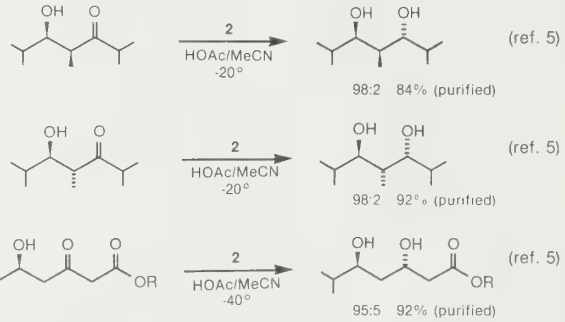
New Selective Reducing Agents

Triacetoxyborohydrides

$NaBH(OAc)_3$ **1** $Me_4NBH(OAc)_3$ **2**

Triacetoxyborohydrides are mild and selective reducing agents. Gribble has shown that aldehydes may be reduced in the presence of ketones with **sodium triacetoxyborohydride (1).**[1] Saksena and Turnbull have demonstrated this reagent's ability to reduce cyclic β-hydroxyketones stereoselectively.[2,3] Evans has reduced acyclic β-hydroxyketones with high stereoselectivity employing **sodium triacetoxyborohydride**[4] and **tetramethylammonium triacetoxyborohydride (2).**[5] The latter reagent reduces ketones only if it can be directed by a hydroxyl group. In fact, these reactions may be run in a 1:1 acetone/acetic acid solvent mixture! Many other reductions with these reagents await discovery.[6]





References:
(1) Gribble, G.W.; Ferguson, D.C. *Chem. Commun.* **1975**, 535. (2) Saksena, A.K.; Mangiaracina, P. *ibid.* **1983**, *24*, 273. (3) Turnbull, M.D.; Hatter, G.; Ledgerwood, D.E. *Tetrahedron Lett.* **1984**, *25*, 5449. (4) Evans, D.A.; DiMare, M. *J. Am. Chem. Soc.* **1986**, *108*, 2476. (5) Evans, D.A.; Chapman, K.T. *Tetrahedron Lett.* **1986**, *27*, 5939. (6) For a review of the uses of **sodium triacetoxyborohydride**, see Gribble, G.W.; Nutaitis, C.F. *Org. Prep. Proced. Int.* **1985**, *17*, 317.

31,639-3 Sodium triacetoxyborohydride (1) **25g $12.00**
100g $32.00

31,736-5 Tetramethylammonium triacetoxyborohydride (2)
10g $10.00; 50g $27.00

We also list the following related reagent:
31,068-9 Tetramethylammonium borohydride **10g $18.00**
50g $54.00

Lithium Aluminum Hydride Derivatives

$LiAl(OCEt_3)_3H$ $LiAl-t\text{-}Bu(i\text{-}Bu)_2H$ $LiAl-n\text{-}Bu(i\text{-}Bu)_2H$

Lithium tri(*tert*-butoxy)aluminohydride is a widely used selective reducing agent. The above closely related reagent offers an even milder source of hydride for the chemoselective reduction of aldehydes even in the presence of unhindered ketones.

Krishnamurthy, S. *J. Org. Chem.* **1981**, *46*, 4628.

30,550-2 Lithium tris[(3-ethyl-3-pentyl)-oxy]aluminohydride, 0.5*M* solution in tetrahydrofuran **100ml $22.00**
800ml $141.00

This reagent has been used for the reduction of cyclic and bicyclic ketones to the corresponding thermodynamically less stable alcohols. Norcamphor was reduced to the endo alcohol in >99% stereoselectivity.

Kim, S.; Ahn, K.H.; Chung, Y.W. *J. Org. Chem.* **1982**, *47*, 4581.

30,327-5 Lithium *tert*-butyldiisobutyl-aluminohydride, 1.0*M* solution in petroleum ether **100ml $17.00**
800ml $88.50

The above reagent selectively reduces enones, epoxides, disulfides and other functional groups.

Kim, S.; Ahn, K.H. *J. Org. Chem.* **1984**, *49*, 1717.

30,326-7 Lithium butyldiisobutyl-aluminohydride, 1.0*M* solution in hexanes **100ml $14.00**
800ml $75.00

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About Our Cover:

Really fine 17th-century paintings of scholars are hard to find; and so our chemist-collector was happy to acquire this work by Thomas Wyck, a mid-17th-century Haarlem artist. The first painting on an *Acta* cover, in 1968, was by Thomas Wyck (Fig. 1) — a much more involved work, with an alchemist and his assistant in a magic circle practicing, not chemistry, but some form of black art.

Here, an impressive scholar, perhaps an alchemist, sits alone in his study deep in thought. What an appropriate cover for the *Acta* dedicated to Professor Herbert C. Brown.

Fig. 1

Lab Notes

The control and monitoring of gas flow present a recurring problem in synthetic laboratories. While various valves and meters are available for these purposes, we have found that an oil bubbler fitted with a Rotaflo® or similar valve is especially convenient as a one-piece unit for both controlling and monitoring gas flow at low (< 2 psi) pressures. Using this bubbler, we have found it very easy to set up systems using polyethylene tubing and "T" valves to control the flow of N_2 or Ar independently from a single gas tank to many manifolds. We also use it when adding gaseous reagents (*e.g.*, acetylene and ammonia) to reactions.

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William D. Wombat
J. Michael Chong
The Guelph-Waterloo Centre for Graduate Work in Chemistry
University of Waterloo
Department of Chemistry
Waterloo, Ontario N2L 3G1

Editor's note: Aldrich now offers a mineral-oil bubbler fashioned after that described by the authors.

Z15,656-6
Mineral-oil bubbler, with threaded vacuum stopcock
$89.00

The value of K_2CO_3 as a base in two-phase systems often depends on its degree of division, even when a phase-transfer catalyst is employed. Hand grinding is exhausting, slow and only moderately effective, while laboratory mills can be very expensive. We have found that a blender-type coffee mill will reduce 50-g batches of granules to a fine dust in a few seconds, with minimal atmospheric contact. This powder is so well suspended, it permits magnetic stirring of mixtures even at high-solids loading, and reactivity is significantly enhanced.

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Polaroid Corporation
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Cambridge, MA 02139

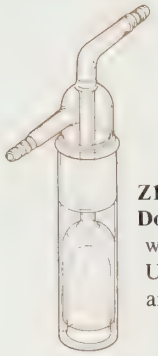
Editor's note: Aldrich offers a blender-type mill for grinding small samples (~50g), as described above. Details of this **Lab Mill** are given in *Aldrichim. Acta* **1986,** *19*(3), 80. Aldrich Technical Information Bulletin No. AL-159 is also available.

Z15,649-3 Lab Mill, with stainless steel blades **$25.00**

Enclosed is a diagram of a double-surface cold trap which we find very useful for drying large amounts of nitrogen used in reactions requiring an inert atmosphere. It completely removes the necessity for cumbersome drying trains; applying a slight positive pressure of nitrogen when the trap is immersed in liquid N_2 causes some of the nitrogen gas to liquefy inside the trap. By ensuring that enough liquid is condensed to isolate the inlet side of the trap from the outlet - only nitrogen which evaporates at -196°C enters the reaction zone - no entrainment of water vapor in a moving stream of nitrogen gas is possible and the nitrogen "blanket" is thus completely dry. For less rigorously dry nitrogen requirements, the gas may be passed without condensation through two such traps in series; we regularly use this latter set-up for the handling of organolithium reagents.

Dr. A.G. Massey
University of Technology
Department of Chemistry
Loughborough
Leicestershire
England LE11 3TU

Editor's note: We have made and listed the cold trap following Dr. Massey's recommendations.



Z16,283-3
Double-surface cold trap, with ₹55/50 joints
Useful for drying large amounts of nitrogen.
$120.00

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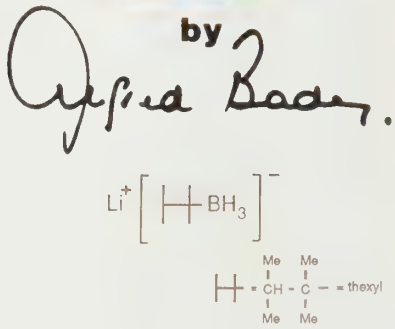


Professor Herbert C. Brown suggested that we offer lithium thexylborohydride,[1] a stable source of thexylborane, a versatile reagent for the preparation of unsymmetrical ketones.[2,3]

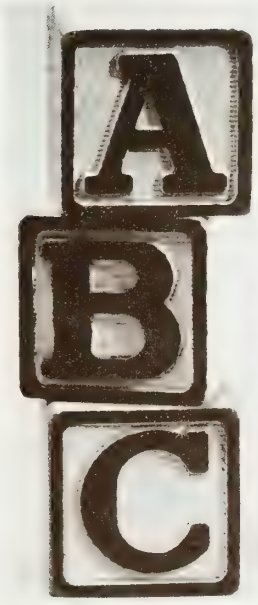
Naturally, we made lithium thexylborohydride.

1) Brown, H.C.; Singaram, B.; Mathew, C.P. *J. Org. Chem.* **1981**, *46*, 2712.
2) Brown, H.C. *Aldrichim. Acta* **1974**, *7*(3), 43.
3) Brown, H.C.; Mandal, A.K.; Kulkarni, S.U. *J. Org. Chem.* **1977**, *42*, 1392.

31,637-7 Lithium thexylborohydride, 2.0*M* solution in tetrahydrofuran
50ml $24.00; 500ml $142.50

It was no bother at all, just a pleasure to be able to help.

The Alfred Bader Library of Rare Chemicals



The **ABC** (**A**lfred **B**ader **C**hemicals) Library contains over 26,000 rare chemicals, and we add about 200 new ones each month. Many of these products have come from research laboratories all over the world and many are research samples of great chemists – Robert B. Woodward, W.S. Johnson, Melvin Newman, Louis F. Fieser, to name but a few – *what a treasure house for chemists looking for compounds for screening, testing new reactions or for comparison with unknowns!*

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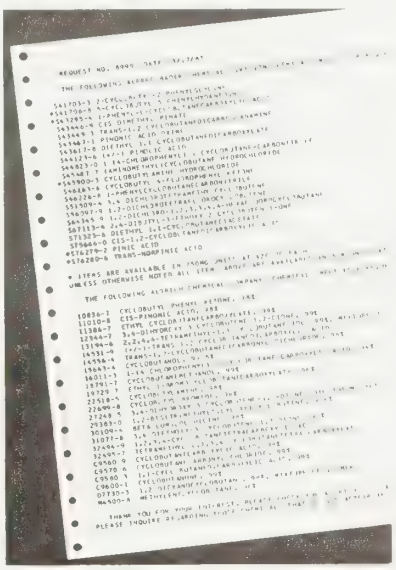

Availability, pricing and purity

The compounds in the **ABC** Library are generally sold in standard 5-gram or 250-mg packages priced at $20.00. Other package sizes can be made available and in cases of special interest we will, of course, investigate the possibility of offering larger quantities at special prices.

Unlike regular Aldrich products, **ABC** compounds are not analyzed by our Quality Control Laboratories, and are offered "as is".

NOTE: Since most of these compounds are research samples which are not commercially available, very little, if any, hazard data are available on them. As with all products of unknown toxicity, appropriate precautions should be observed when handling them.

The Aldrich Microfiche Library of Chemical Indices

Since all *Aldrich* and **ABC** compounds are computer-coded, you will find this microfiche library invaluable for quick location of a product. This library, which is updated periodically, lists the entire Aldrich inventory by both name and molecular formula, on 20 microfiche.

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Tetrabutylammonium borohydride Bu_4NBH_4 **23,017-0**	**9-BBN,** 0.5*M* solution in THF  **15,107-6**	**Lithium borohydride,** 2.0*M* solution in THF $LiBH_4$ **23,020-0**
K-Selectride® (potassium tri-*sec*-butylborohydride, 1.0*M* solution in THF) $KB(CHMeEt)_3H$ **22,076-0**	**Super-Hydride®** (lithium triethylborohydride, 1.0*M* solution in THF) $LiBEt_3H$ **17,972-8**	**L-Selectride®** (lithium tri-*sec*-butylborohydride, 1.0*M* solution in THF) $LiB(CHMeEt)_3H$ **25,704-4**

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Aldrichimica Acta

Volume 20, Number 2, 1987

O-Acyl Thiohydroxamates: New and Versatile Sources of Alkyl Radicals for Use in Organic Synthesis

Allylic Tin Compounds in Organic Synthesis

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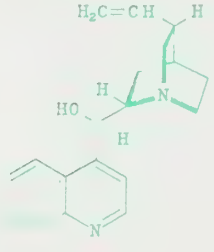

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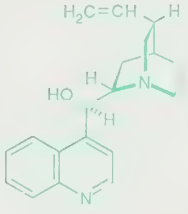

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About Our Cover:

When our chemist-collector first saw this splendidly direct portrait of a man (oil on panel, 18 x 15 inches) at a London auction, it was ill-framed and dirty, although in fact, in fine condition. This hitherto unrecorded portrait is signed and dated 1656 by one of Rembrandt's ablest students, Nicholas Maes, who was 22 years old at the time. The man's dress is so informal and his gaze so searching that one wonders whether this is a self-portrait. Maes depicted himself in one or two genre paintings, on one occasion in a mirror, but it is difficult to make comparison with such a small-scale sketch. Another self-portrait by Maes (Fig. 1), painted some 30 years later, is now in his birthplace, Dordrecht; but the wig and considerable difference in age again make comparison difficult.

Fig. 1

Lab Notes

There is often a need for pure potassium *tert*-butoxide which is one of the most commonly used bases in organic synthesis. The impurities which are usually present (*i.e.*, potassium hydroxide and potassium carbonate) may be removed by subliming the *t*-BuOK. However, the sublimation in the laboratory is limited to relatively small quantities. I have found that due to the very good solubility of *t*-BuOK in tetrahydrofuran, it may be easily purified by dissolving in dry THF, filtering off the insoluble material quickly, followed by removal of the solvent by evaporation. The solution to be filtered should not be more than 10g of *t*-BuOK/100ml of THF to prevent clogging of the filter funnel by the *t*-BuOK crystals which might form when the THF cools and evaporates during the vacuum filtration. Samples of up to 20g of potassium *tert*-butoxide have been successfully purified in this way.

Tomasz Glinka
Institute of Organic Chemistry
Polish Academy of Sciences
Warsaw, Poland

Editor's note: It has been suggested that pressure-filtering under nitrogen might eliminate crystallization caused by cooling and evaporation of the solvent.

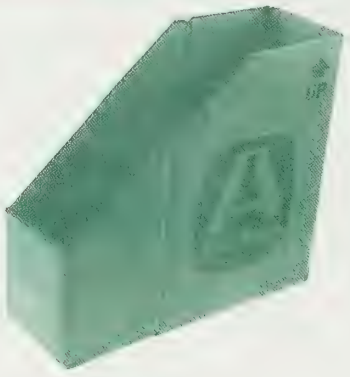
We carry the reagents used above.

15,667-1 Potassium *tert*-butoxide, 97% **100g $16.20; 500g $38.85**

18,656-2 Tetrahydrofuran, anhydrous, 99.9% **100ml $14.15; 800ml $26.10 8l $116.75; 18l $217.75**

We order many chemicals from Aldrich and have accumulated the 7½ x 7½ x 9½-inch boxes in which the chemicals are shipped. With some tape, a pair of scissors or a carton opener, these can be converted to shelf files, using the following simple instructions.

1) Cut off top flaps.
2) Slit tape on bottom and extend bottom flaps.
3) Cut flaps that are connected to the blank sides in half, vertically.
4) Fold blank sides in half.
5) Fold box into a rectangle with the Aldrich symbol facing you and in the right ⅔ of the side.



6) Fold end flaps in.
7) Fold side flaps in.
8) Tape bottom securely.
9) Draw a diagonal line on Aldrich side of the box.
10) Draw a parallel line on opposite side.
11) Draw a connecting line across the front.
12) Cut along lines.

Hugh Emerson
Supervisor of Science Stores
University of Missouri
123 Chemistry Building
Columbia, MO 65211

Unless sophisticated cooling systems are available, Dewar flasks are required for low-temperature reactions. This invariably precludes magnetic stirring if the flask is not shallow. While a totally submersible magnetic stirrer may be used (such as the model manufactured by Troemner), its placement is still a problem.

I have devised an adjustable holder for the Troemner model that can be used in a relatively large (>12cm i.d.) Dewar flask and can also be easily made in a machine shop. It consists of two concentric aluminum rings welded to a flat plate. The ring i.d.'s are 51mm and 80mm, respectively, and the height *ca.* 2cm. A wall section *ca.* 12mm is cut out of the inner ring to accommodate the stirrer shape. The outer ring has three round rubber feet mounted equidistantly and perpendicularly to the metal surface. Each foot is attached *via* a threaded screw that allows the foot to be extended by 15-20mm. The thickness of the outer-ring wall should be at least 2mm to permit threading of the holes. The feet allow the holder to be positioned firmly at any height within the flask, thus permitting stirring while the holder is partially or totally submerged. The arrangement still permits the addition of dry ice to the coolant or the inclusion of a cryogenic probe.

Dr. Stephen J. Carter
Dartco Manufacturing
P.O. Box 5867
Augusta, GA 30906

This technique was devised while at GTE Laboratories.

Editor's note: We are pleased to offer both the Troemner stirrer and a stirrer adapter as described by Dr. Carter.

Z15,423-7 Troemner submersible magnetic stirrer, with power supply **$197.00**
Z16,654-5 Stirrer-motor adapter, for use with Troemner stirrer **$38.50**

See page 58 for details.

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt**. *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Aldrich Boys.

Professor Ralph A. Raphael at Cambridge University suggested that we offer potassium trimethylsilanolate, an organic-solvent-soluble, completely anhydrous KOH equivalent. This useful reagent is appreciably soluble in a variety of organic solvents (ether, THF, toluene, methylene chloride, etc.) and has been used to convert carboxylic acid derivatives directly into their corresponding anhydrous potassium salts under mild and nonaqueous conditions.

Naturally, we made the compound.

Laganis, E.D.; Chenard, B.L. *Tetrahedron Lett.* **1984**, *25*, 5831.

32,486-8 Potassium trimethylsilanolate 25g $10.00; 100g $25.00

It was no bother at all, just a pleasure to be able to help.

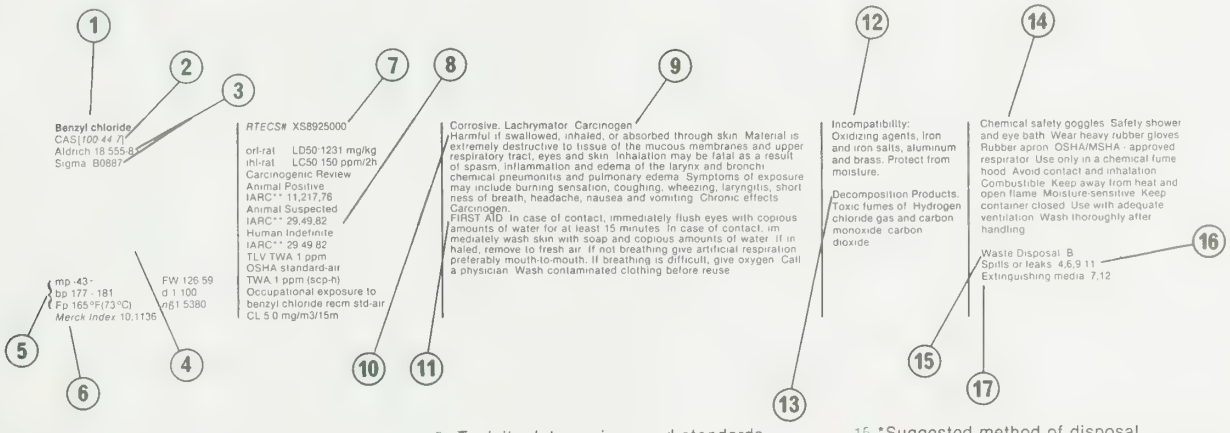
The Sigma-Aldrich Library of Chemical Safety Data

A reference for the safe handling of over 7000 chemicals

The Sigma-Aldrich Library of Chemical Safety Data is an extensive yet compact collection of up-to-date safety information. The data were compiled through the collaboration of Sigma and Aldrich Chemical Companies.

The library will be useful to all users of chemicals who must assess the individual and composite hazards of mixtures, solutions, and reactions. It should provide employers with a basis for a sound safety program for complying with the Hazard Communication Standard and any training programs. A sample entry is shown below with explanation.

1900 pages, hardbound, with tearproof jacket. Page size 9½ × 12in.



1. Name of chemical.
2. Chemical Abstracts Service Registry number.
3. Aldrich and Sigma Product numbers.
4. Structure or formula.
5. Physical data.
6. Reference to Merck Index, 10th edition.
7. Reference to the Registry of Toxic Effects of Chemical Substances.
8. Toxicity data, reviews and standards.
9. Specific health-hazard signal words.
10. Acute and chronic health effects.
11. FIRST AID measures.
12. Incompatible materials and conditions.
13. Products of decomposition.
14. Protective equipment, handling precautions and storage conditions.
15. *Suggested method of disposal.
16. *Recommended protective equipment and procedures for spill or leak clean-up
17. *Extinguishing agents recommended for fires involving the material

*Tables explaining the reference codes in each category will be found at the front of the book

The Sigma-Aldrich Library of Chemical Safety Data, Edition I, edited by Robert E. Lenga — **Z14,000-7** — **$295.00**
(Includes Explanation of Codes Chart, Z14,866-0)

Explanation of Codes Chart — **Z14,866-0** — **$3.00**

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99 atom % D **15,180-7**

Toluene-d_8

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Iodotrimethylsilane

Versatile synthetic tool.

19,552-9

***N*-Benzylglycine ethyl ester**

Synthetic intermediate.

B2,270-4

Proton Sponge®
[1,8-bis(dimethylamino)-naphthalene]

Strong base.

15,849-6

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3,5-Diaminobenzoic acid dihydrochloride

Synthetic intermediate.

11,383-2

3-Aminophenylboronic acid hemisulfate
(3-aminobenzeneboronic acid)

Chromatographic tool.

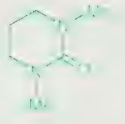
A7,175-1

Trifluoroacetic acid, 99+ %

Suitable for protein sequencing.

29,953-7

1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone



Replacement solvent for HMPA.

25,156-9

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Ion-associating reagents for HPLC.

Sodium salts of:

1-Butanesulfonic acid	**22,151-1**
1-Pentanesulfonic acid	**22,153-8**
1-Hexanesulfonic acid	**22,154-6**
1-Heptanesulfonic acid	**22,155-4**
1-Octanesulfonic acid	**22,156-2**

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Aldrichimica Acta

Volume 20, Number 3, 1987 (Last issue in 1987)

New Methods in the Formation of Macrocyclic Lactams and Lactones of Biological Interest

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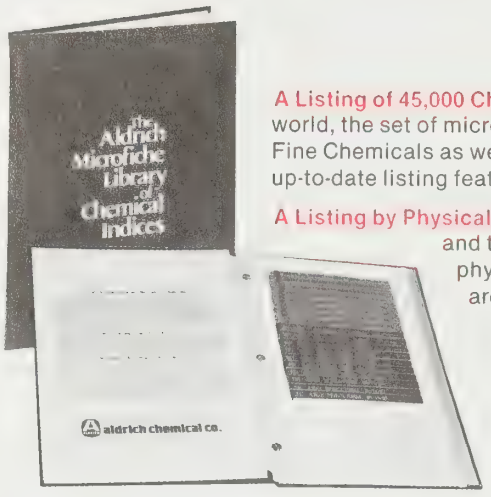
New Edition of The Aldrich Microfiche Library of Chemical Indices Is Available



A Listing of 45,000 Chemicals. The largest collection of commercially available chemicals in the world, the set of microfiche includes 18,000 listed in the 1988-1989 Aldrich Catalog/Handbook of Fine Chemicals as well as 27,000 in the ABC (Alfred Bader Collection of Rare Chemicals). This up-to-date listing features two indices — alphabetical and molecular formula.

A Listing by Physical Property. The 18,000 chemicals featured in the Aldrich Catalog/Handbook and those added since its publication are listed alphabetically along with their physical constants. They are also computer-sorted by physical property and are indexed separately according to increasing:

- formula weight
- melting point
- boiling point
- density
- refractive index
- wavelength (μ) of maximum IR absorption

Each list also gives the other five (when appropriate) physical properties and other data such as flash point and reference numbers to the Aldrich IR and NMR libraries. These indices are valuable in determining unknowns and in locating chemicals that meet specific physical-property requirements.

Z11,838-9	**The Aldrich Microfiche Library of Chemical Indices** (20 microfiche in a convenient, hardbound holder)	**$29.50**
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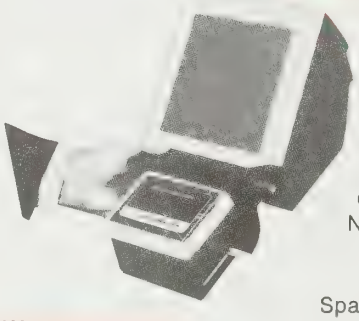
Microfiche Readers

Table-model, 32X magnification
Viewing screen is gray, 11 x 11in; 110V.

Z12,157-6 $267.00

Spare DED lamp
Z12,213-0 $15.50
Movable linefinder
Z12,214-9 $16.75



Portable, 16X magnification

This hand-held reader folds flat for easy storage. It has a 5½ x 5½-in gray screen and is supplied with a 110-V AC adapter. It may be operated with rechargeable Ni-Cd batteries.

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Pocket-size, 9X magnification

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Z12,292-0 $10.15

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About Our Cover:

Our chemist-collector loves puzzles and has never encountered a greater puzzle than that on this cover. When he bought this *Dancing Fishermen* (oil on panel, 12½ x 16¾ inches) in a small gallery in Surrey some years ago, he was told it was 18th-century Italian. Since then, various Italian, French, Flemish and Dutch artists from the 17th to the 19th century have been suggested. The panel is old and the paint film could be 17th-century; so our chemist-collector is inclined to think it is by an out-of-the-way Dutch artist of the late 17th century, one greatly influenced by the Italianate artists of Utrecht, such as Abraham Bloemaert. Now a puzzle within a puzzle: are these just dancing fishermen, or is this possibly a New Testament subject, Peter the Fisher of Men, at an Atlantic fishing port? Our chemist-collector would greatly welcome help from our readers.

Lab Notes

Prompted by Alberto Haces' lab note concerning visualization of compounds on TLC plates with iodine, [*Aldrichim. Acta* **1986**, *19*(2), 30], I am describing an alternative, even quicker method.

Almost instant visualization can be achieved by sprinkling a mixture of silica gel and iodine (*ca.* 10:1) over the TLC plate placed on a piece of paper. Tipping the powder off the plate onto the paper after a few seconds leaves the plate clearly developed. The silica gel and iodine can then be poured from the paper into a storage jar for reuse.

D. Levin
ICI Organics Division
P.O. Box A38
Leeds Road
Huddersfield HD2 IFF
England

I have designed a glass water bath which has proved very convenient over the years. It fits on a magnetic stirrer and allows easy observation of the beaker or flask contents.

Felix Friedberg
Department of Biochemistry
Howard University
Washington, D.C. 20059

Editor's note: We have made and listed the water bath following Dr. Friedberg's recommendations.

Z17,442-4 Glass water bath, accommodates up to a 400-ml flask or beaker **$75.60**

We have perfected a small-scale filtration device which allows convenient filtration into any small vessel.

The bottom of a Buchner flask (100 or 250ml) is removed and the new edge ground flat in order to form a reasonably airtight seal with a thick glass plate (6mm).

A small flask or sample tube is placed inside the Buchner flask under the funnel, and the sample is filtered in the usual way. Exchange of flasks is easy, and we have used this system for both small-scale dry flash chromatography and hot filtration during recrystallization.

Maxwell H. Muir
Robert A. Johnson
Chemistry Department
Brunel University
Uxbridge, Middlesex UB8 3PH
England

Working with surfactants in the lab, we have found that all sorts of solutions can be freed of bubbles by placing the container in an ultrasonic bath filled with tap water. Some products like sulfosuccinates trap bubbles created by mechanical agitation so well that this is one of the few methods that allows for rapid color determinations. A few seconds of exposure to the ultrasound, and *voilà* — clear bubble-free solutions ready to be checked for turbidity and color.

Raymond E. Bilbo
Alkaril Chemicals, Inc.
P.O. Box 1010
Winder, Georgia 30680

The safe sampling of hazardous solutions for analysis can be a difficult problem, especially when air-, light- or heat-sensitive compounds may decompose in the process. Moreover, the use of a syringe generally can cause the liquid to be sprayed as the needle is withdrawn from the septum.

Recently, we devised an inexpensive aliquoting device for sampling under negative pressure.

The device was made from such readily accessible materials as a ½-cc disposable syringe, a "Microcap" tube, septa (Aldrich Z10,072-2) and a 4-in. needle. By sliding a small Tygon tubing collar down the plunger against the barrel of the syringe, the plunger is locked in place and both hands are free to operate the device.

To sample, simply insert the needle through the solvent chamber, dry the needle bore with nitrogen, then penetrate the flask septum. While holding the solvent chamber firmly against the flask septum, withdraw the aliquot into the syringe. Pull the needle into the solvent chamber containing reaction solvent or quench medium. After mixing the aliquot with solvent, push the needle back through the chamber septum for chromatographic analysis. The diluted aliquot in the solvent chamber can be saved for further analysis.

Minor modifications of this method allow air-, light- and heat-sensitive materials to be sampled; for example, the chamber can be filled with inert gas, wrapped with foil, or cooled.

Steve de Keczer
Institute of Organic Chemistry
Syntex Research
Palo Alto, CA 94304

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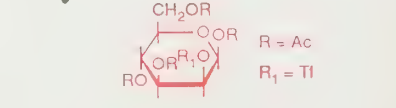
"Please Bother Us."

by



Professor Henry C. Padgett at UCLA School of Medicine suggested that we offer 1,3,4,6-tetra-*O*-acetyl-2-*O*-trifluoromethanesulfonyl-β-D-mannopyranose. As reported recently,[1] this sugar derivative, when treated with ^{18}F-fluoride ion under phase-transfer catalysis followed by acetate hydrolysis, affords high yields of 2-^{18}FDG (2-deoxy-2-fluoro-D-glucose). 2-^{18}FDG is the most widely used radiochemical in positron emission tomography diagnostic imaging.[2]

Naturally, we made the suggested triflate.

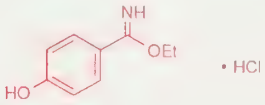
1) Hamacher, K.; Coenen, H.H.; Stöcklin, G. *J. Nucl. Med.* **1986**, *27*, 235.
2) Phelps, M.E.; Mazziotta, J.C. *Science* **1985**, *228*, 799.

31,025-5 1,3,4,6-Tetra-*O*-acetyl-2-*O*-trifluoromethanesulfonyl-β-D-mannopyranose, 99% **100mg $20.00**

It was no bother at all, just a pleasure to be able to help.

Biochemical Tools

Ethyl 4-Hydroxybenzimidate

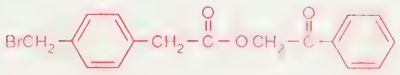


Used in the synthesis of phenol-protein conjugates[1] and nematic liquid crystal compositions containing a tetrazine subunit.[2]

(1) Wagner, G.; Briel, D. *Pharmazie* **1982**, *37*, 251; *Chem. Abstr.* **1982**, *97*, 160748f. (2) Demus, D. *et al.* Ger. (East) DD 151 950 (Nov. 11, 1981); *Chem. Abstr.* **1982**, *97*, 14855x

32,446-9 Ethyl 4-hydroxybenzimidate hydrochloride 5g $12.00

Peptide Reagent

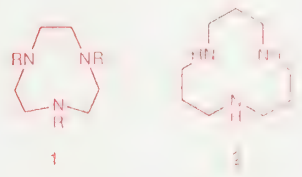


Reagent used for the preparation of aminoacylated 4-(oxymethyl)phenylacetamidomethyl-resin *(-OCH$_2$-Pam-resin)* used in solid-phase peptide synthesis.

Mitchell, A.R. *et al. J. Org. Chem.* **1978**, *43*, 2845.

31,754-3 Phenacyl 4-(bromomethyl)-phenylacetate 1g $19.50; 5g $69.50

Macrocyclic Ligands



Potentially useful as models of biological transport systems and as reagents for complexometric titrations with high cation-binding selectivity.

Yang, R.; Zompa, L.J. *Inorg. Chem.* **1976**, *15*, 1499 Geraldes, C.F.G.C. *et al. ibid.* **1985**, *24*, 3876

31,130-8 1,4,7-Triazacyclononane, 97% (**1**, R = H) **100mg $17.50; 500mg $58.00**

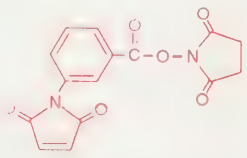
32,949-5 1,4,7-Triazacyclononane trihydrochloride (1, R = H) **250mg $13.50; 1g $37.50**

31,129-4 1,4,7-Trimethyl-1,4,7-triazacyclononane, 99% (**1**, R = Me) **100mg $19.50; 500mg $64.25**

31,979-1 1,5,9-Triazacyclododecane (2) 100mg $17.75; 500mg $58.25

32,383-7 1,5,9-Triazacyclododecane trihydrobromide (2) 250mg $18.00; 1g $50.00

Protein Cross-Linking Agent

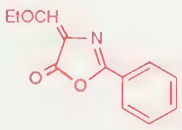


Useful heterobifunctional (sulfhydryl, amine) cross-linking agent for modification of enzymes,[1] proteins[2] and liposomes.[3]

(1) Hashida, S. *et al. J. Appl. Biochem.* **1984**, *6*, 56. (2) Madison, L.D.; Rosenzweig, S.A.; Jamieson, J.D. *J. Biol. Chem.* **1984**, *259*, 14818. (3) Hashimoto, Y.; Endoh, H.; Sugawara, M. *Liposome Technol.* **1984**, *3*, 41; *Chem. Abstr.* **1984**, *101*, 198074x.

28,653-2 3-Maleimidobenzoic acid *N*-hydroxysuccinimide ester, 98% **25mg $11.20; 100mg $29.55**

Synthetic Hapten



Used to induce cutaneous inflammatory reaction. Now available in a recrystallized grade.

Streilein, J.W.; Sullivan, S.; Thompson, S. *J. Immunol.* **1980**, *124*, 577.

86,220-7 4-Ethoxymethylene-2-phenyl-2-oxazolin-5-one, recrystallized **1g $12.00; 5g $40.00**

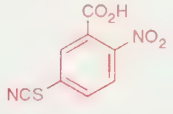
85,755-6 4-Ethoxymethylene-2-phenyl-2-oxazolin-5-one 1g $8.70; 5g $30.90 10g $50.10

Important capping ligand which binds to a wide variety of transition-metal ions.[1-9] The resulting complexes often exhibit exceptional redox and electronic properties.

(1) Setzer, W.N.; Ogle, C.A.; Wilson, G.S.; Glass, R. *Inorg. Chem.* **1983**, *22*, 266. (2) Ashby, M.T.; Lichtenberger, D.L. *ibid.* **1985**, *24*, 636. (3) Küppers, H.-J.; Wieghardt, K.; Weiss, J. *ibid.* **1985**, *24*, 3067. (4) Hartman, J.R.; Cooper, S.R. *J. Am. Chem. Soc.* **1986**, *108*, 1202. (5) Küppers, H.-J. *et al. Inorg. Chem.* **1986**, *25*, 2400. (6) Wilson, G.S.; Swanson, D.D.; Glass, R.S. *ibid.* **1986**, *25*, 3827. (7) Rawle, S.C.; Cooper, S.R *Chem. Commun.* **1987**, 308. (8) Rawle, S.C.; Yagbasan, R.; Prout, K.; Cooper, S.R. *J. Am. Chem. Soc.*, in press. (9) Clarkson, J. *Chem. Commun.*, in press

30,080-2 1,4,7-Trithiacyclononane, 98% (9S3) **500mg $19.50**

Cleavage of Proteins at Cysteine



2-Nitro-5-thiocyanatobenzoic acid can be used to cleave proteins at cysteine residues. This has been used to study the structure of nonhistone chromosomal proteins HMG1 and HMG2.[1,2]

(1) Walker, J.M.; Goodwin, G.H.; Johns, E.W. *Eur. J. Biochem.* **1976**, *62*, 461. (2) Kohlstaedt, L.A.; King, D.S.; Cole, R.D. *Biochemistry* **1986**, *25*, 4562.

28,486-6 2-Nitro-5-thiocyanatobenzoic acid, 98% **250mg $11.70; 1g $31.45**

Liquid Scintillation Mixture

A premixed liquid scintillation cocktail containing 1.25g **POPOP** [1,4-bis(5-phenyloxazol-2-yl)benzene] and 100g **PPO** (2,5-diphenyloxazole) per liter of toluene solution. This concentrated mixture which makes 25 liters of counting solution in toluene or *p*-xylene, has the advantage of being easier to store, more accurate and more economical.

32,712-3 Liquid scintillation mixture, containing POPOP and PPO in toluene **250ml $19.50; 1 liter $58.00**

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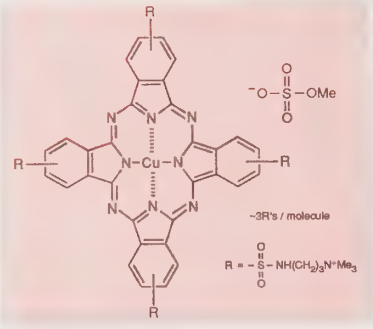
Alcec Blue™ — Biological Stain



Alcian Blue has been widely used to stain and quantify biological polyanions of all kinds,[1] particularly mucins and connective tissue glycosaminoglycans. When manufacture of the dye ceased in 1973,[2] stocks began to run out quickly. Aldrich has now resumed production of Alcian Blue. However, the dye is of limited stability, since it is an ingrain dye, designed to break down under mild conditions.

Alcec Blue™ (*Al* — from Alcian Blue, *cec* — critical electrolyte concentration[3,4]) was developed by Scott[3] to replace Alcian Blue in most of its biochemical applications. The structure of **Alcec Blue**™ is based on molecular-biological principles; it is a quaternized Astrablau* and is stable over a wider pH range than is Alcian Blue.[5]

The dye can replace Alcian Blue in acetic acid as a mucin stain, in hydrochloric acid as a connective tissue stain, in ethanol-water solutions to stain cellulose acetate, electrophoretograms and chromatograms, and in electrolyte solutions in CEC methods.[3,4] Cellulose acetate strips can be dissolved in dimethyl sulfoxide to quantify the stained bands exactly as with Alcian Blue.[6]

Alcec Blue™ has the same CEC pattern as Alcian Blue with polycarboxylates, DNA and RNA at $<0.2M$ $MgCl_2$, and with sulfated proteoglycans (*e.g.*, in cartilage) at 0.5 - 0.8M $MgCl_2$.[7–9]

References and notes:

1) Mowry, R.W. *Ann. N.Y. Acad. Sci.* **1963**, *106*, 402.
2) Scott, J.E. *Histochemie* **1973**, *37*, 379.
3) *Idem J. Microsc.* **1980**, *119*, 373.
4) Scott, J.E.; Dorling, J. *Histochemie* **1965**, *5*, 221.
5) The tetramethylisothiouronium group of Alcian Blue is unstable in alkali (pH > 8), especially on warming; the quaternary ammonium group of **Alcec Blue** is stable to at least pH 12, with no tendency to decompose on standing as the solid or in solution.
6) Newton, D.J.; Scott, J.E.; Whiteman, P. *Anal. Biochem.* **1974**, *62*, 268.
7) **Alcec Blue** chloride is slightly less soluble than Alcian Blue; therefore there may be precipitation of the dye chloride at high $MgCl_2$ (or other chloride) concentrations. This can be avoided by staining in 20% DMSO (instead of straight aqueous) solutions, with the added advantage that differentiation between polycarboxylates and polyphosphates or sulfated polyanions is improved.
8) Excellent CEC patterns are obtained using $Mg(OAc)_2$ with improved polycarboxylate-polysulfate differentiation, without dye percipitation (Scott, J.E., unpublished results).
9) Scott, J.E.; Hughes, E.W. *J. Microsc.* **1983**, *123*, 209.

™ Trademark of Professor J.E. Scott and Aldrich Chemical Co., Inc.
*Astrablau is a trademark of Hoechst.

30,903-6	**Alcec Blue™**	**5g $15.00; 25g $64.00**

We list the following:

23,655-1	**Alcian Blue 8GX**, certified (Dye content ~55%)	**25g $29.80**
19,978-8	**Alcian Blue 8GX**	**25g $15.35; 100g $51.15**

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Aldrichimica Acta

Volume 21, Number 1, 1988

Fluoroaromatic Compounds: Synthesis, Reactions and Commercial Applications

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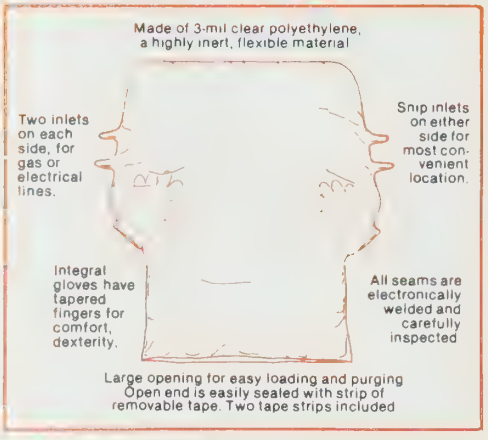
The Aldrich AtmosBag™

Controlled-Atmosphere Chamber with Built-In Gloves

The Aldrich AtmosBag is a polyethylene bag which can be sealed, purged, and inflated with an appropriate gas, creating a portable, convenient, and inexpensive "glove box" for handling air- and moisture-sensitive and toxic* materials. It is especially suitable for handling air-sensitive solid reagents; at Aldrich such reagents are packaged in an AtmosBag inflated with the appropriate inert gas.

Other applications include: dust-free operations, controlled-atmosphere habitat and, for the ethylene-oxide-treated AtmosBag, immunological and microbiological studies. Each AtmosBag is supplied with instructions for use.



Two-hand AtmosBag

Dimensions (inflated, in.)				Vol. (inflated, in.³/L)			Ethylene-oxide-treated	
Size	Opening	Width	Length		Cat. No.	Price	Cat. No.	Price
L	36	51	58	32,000/520	Z10,608-9	$25.95	Z11,835-4	$27.25
M	24	39	48	17,000/280	Z11,282-8	$20.80	Z11,836-2	$21.95
S	12	27	30	3,000/50	Z11,283-6	$15.60	Z11,837-0	$17.00

Two-Hand Select-A-Glove AtmosBag

Equipped with rings instead of gloves, this AtmosBag enables one to use the gloves of choice by simply taping them onto the rings (1½in. wide, 3½in. diam.).

For example, one can use surgical gloves for better feel or Viton® gloves for greater protection. Nitrile-rubber, premium white rubber and neoprene gloves may also be used.

Z11,284-4 Gloveless Two-Hand AtmosBag (L) **$31.20**

Four-Hand AtmosBag

This AtmosBag [dimensions (uninflated): 30 (opening) × 45 × 58in.] has four built-in gloves and is slightly smaller than the large two-hand AtmosBag. It is completely symmetrical and is designed so that cutting off the sealed end enables attachment of AtmosBags in series, using semi-rigid ring connectors (HDPE). It also enables construction of an air-lock, using the AtmosBag divider (PE film).

Z10,840-5 Four-Hand AtmosBag **$31.05; $105.40/4**

Z10,852-9 AtmosBag Connector (66 × 3 × 1/16in.) **$4.30**

Z10,866-9 AtmosBag Divider **$8.05**

Accessories

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M 20 × 16in. **Z11,285-2 $33.85**
S 11 × 15in. **Z11,286-0 $31.60**

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M/L **Z11,834-6 $12.00**/12 pairs

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For more information on the AtmosBag chamber, see pages 2003-2004 of our 1988-1989 Catalog/Handbook.

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Aldrichimica Acta

Volume 21, Number 1, 1988
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About Our Cover:

Our readers may well guess that our chemist-collector bought this painting (oil on canvas, 104 x 118cm) for its subject, rather than its attribution. He loves the story of Tobias, and perhaps some day he will be able to arrange for an exhibition of paintings which will illustrate this story of man's faith. There are hundreds of paintings of its many scenes, but this depiction of Tobias and the angel baking the fish is very unusual.

When our chemist-collector purchased this painting, he was told it was a work by Philips Koninck, for it was recorded as No. 119 in Horst Gerson's monograph of the artist. Koninck, a student of Rembrandt, was one of the greatest masters of landscape, but he occasionally also tried his hand at genre and historical paintings. For a beautiful landscape by Philips Koninck, see the cover of the *Aldrichimica Acta*, Volume 18, No. 1, 1985.

Fig. 1

But collecting has its pitfalls. Imagine the surprise when cleaning revealed the signature and date (Fig. 1) — certainly not the signature of Philips Koninck! Martin van der Fuick is almost unknown, and yet an artist who painted with such imagination must have produced other works. His only other known work is a painting of militiamen of the town of Den Briel, done in 1660. Perhaps Fuick was an artist who died young, and probably other paintings remain to be discovered.

Rembrandt and the Bible - in Japan

We are offering a limited number of a 174-page catalog of an exhibition in Japan, the first of its kind there, on Rembrandt and the Bible. The scholarly essays in Dutch, English, German and Japanese deal with works by Rembrandt and his students — 38 paintings, 7 drawings and 44 etchings, all beautifully illustrated. Thirteen of the paintings, all in full color, have appeared on covers of the *Acta*. The works are fully described in English and Japanese. An unusual and wonderful buy for lovers of art and the Bible!

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Twenty-five paintings that have been reproduced on our *Acta* covers, and six that have been on our catalog covers are among thirty-six paintings in an exhibition of Dutch paintings at Queen's University in Kingston, Ontario. The fully illustrated catalog written by Professor David McTavish contains a wealth of art-historical information — enough for several evenings of relaxed enjoyment — probably the best value in art-history anywhere.

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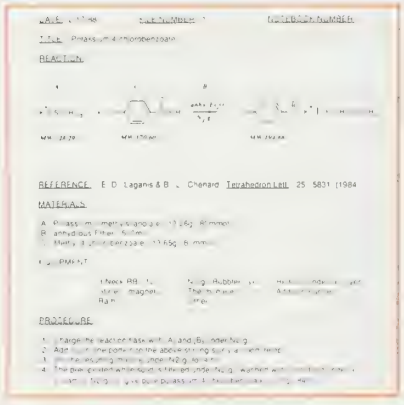

Evan D. Laganis
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Editor's note: For additional information on WIMP™ publishing software for chemists see page F26 of the 1988-1989 Aldrich Catalog/Handbook. Call or write for Technical Information Bulletin AL-162 describing the WIMP molecule-drawing software.

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Sampling a reaction mixture for GC or TLC analysis while maintaining an inert atmosphere can be inconvenient, especially when one is using a deep reaction vessel or wishes to remove only a few microliters of solution. This operation can be easily done using a short (12-24-inch) piece of fused silica capillary (0.2-0.33mm i.d.) such as is often discarded during maintenance of capillary gas chromatographs. With the reaction mixture under slightly greater than atmospheric pressure, the capillary is inserted through a slit in the septum and very briefly (1-2sec) dipped below the surface of the liquid. A few seconds later (depending on the pressure applied and viscosity of the liquid) a tiny droplet emerges from the other end of the capillary and it can be derivatized or diluted as necessary for analysis. The capillary is readily cleaned by forcing a small amount of solvent through it using the same technique. In this manner, very small samples ($\leqslant$10 microliters) can be taken conveniently without disturbing the reaction mixture. I have found that these fused-silica capillaries are quite durable and can be used indefinitely.

Charles M. Garner
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

Hot oil baths present a serious fire hazard in the laboratory, particularly when they are used for unattended experiments overnight. Wood's metal (m.p. 70 °C) is safer in that respect, but it is expensive and toxic.

Flaked graphite has advantages over both oil and Wood's metal. It is clean and inexpensive. It is a good conductor of heat and permits magnetic stirring. In addition, it is thermally stable and not flammable under normal laboratory conditions.

Professor A.G. Davies
Department of Chemistry
University College London
20 Gordon Street
London WC1H OAJ
England

Editor's note: We have recently added flaked graphite to our listings.

33,246-1 Graphite, flake **2.5kg $11.50**

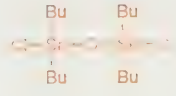
Anyone who uses silicone oil baths to heat chemical reactions can attest to the fact that, over time, the oil becomes discolored due to soluble and insoluble contaminants. Simple filtration of the bath oil will not remove the discoloration but we have found that the addition of a small amount of decolorizing carbon to the bath, followed by filtration of the mixture, yields oil that is as good as new. Water can be removed by the addition of anhydrous magnesium sulfate before stirring with decolorizing carbon. The filtration may be accomplished by using water aspirator vacuum (be sure to use filter cel to protect the glass frit) or more conveniently, by gravity filtration overnight.

Deborah A. Davis
Department of Chemistry
Dartmouth College
Hanover, NH 03755

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt**. *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Aldrich Boys.



Professor Hitosi Nozaki at Okayama University of Science in Japan suggested that we offer bis(chlorodibutyltin) oxide as a catalyst to convert ω-hydroxycarboxylic acids to macrolides. The transformation occurs under neutral and mild conditions in a variety of organic solvents including decane.

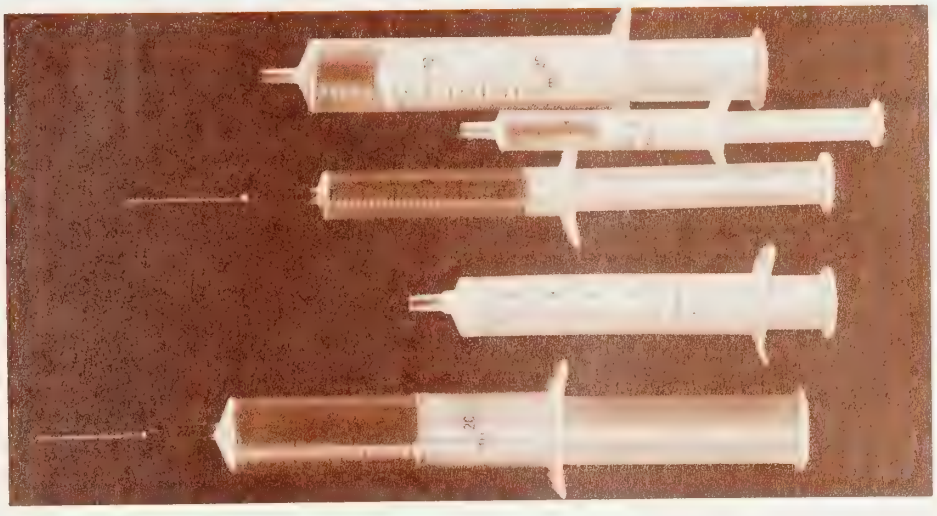
Naturally we made the compound.

Otera, J.; Yano, T.; Himeno, Y.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 4501.

33,109-0 Bis(chlorodibutyltin) oxide (1,1,3,3-tetrabutyl-1,3-dichlorostannoxane) **10g $17.00; 50g $45.00**

It was no bother at all, just a pleasure to be able to help.

All-Polypropylene/Polyethylene Disposable Syringes



Offered by Aldrich — the only all-polypropylene/polyethylene syringe available.

Most disposable syringes have rubber plungers that can contaminate solutions. Our syringes consist of a polyethylene plunger and a polypropylene barrel with a tapered Luer connector; no lubricant of any kind is present. In the chemical laboratory, these syringes are useful for:

1) Transferring air-sensitive reagents dissolved in organic solvents
2) Weighing solutions for titrimetric or spectroscopic analysis
3) Sampling liquids
4) Delivering small gas samples for GC or IR analysis
5) Sampling where trace-metal contamination must be avoided (use with Teflon® needles; also available from Aldrich)
6) Replacing breakable glass syringes.

The stainless steel needles are equipped with all-polypropylene Luer-fitting hubs.

Needles and syringes are individually packaged.

Aldrich also offers polypropylene Luer-tip pressure caps, sterile and nonsterile, for sealing prefilled syringes. A useful, inexpensive syringe destroyer which efficiently cuts the tip of the needle as well as the Luer connector of the syringe is also available.

Syringes with needle:			
2.5ml	22-gauge, 1¼in	Z11,689-0	$37.00/200
5ml	22-gauge, 1¼in	Z11,690-4	$24.35/125
10ml	21-gauge, 1½in	Z11,691-2	$36.00/100
20ml	20-gauge, 1½in	Z11,692-0	$35.40/60
Syringes without needle:			
2.5ml		Z11,685-8	$19.10/200
5ml		Z11,686-6	$13.10/125
10ml		Z11,687-4	$18.50/100
20ml		Z11,688-2	$18.95/60
50ml		Z11,840-0	$22.50/30
Needles only:			
22-gauge, 1in		Z11,806-0	$16.00/100
20-gauge, 1½in		Z11,805-2	$16.00/100
18-gauge, 1½in		Z11,804-4	$16.00/100
16-gauge, 1½in		Z11,803-6	$29.00/100
Luer-tip caps:			
Sterile		Z12,096-0	$8.20/100
Nonsterile		Z12,097-9	$4.20/100
Syringe and needle destroyer:			
		Z15,087-8	$30.50

Write or call for a discount on larger quantities.
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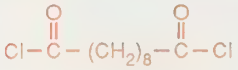
From Aldrich Production: Synthetic Reagents in Bulk

At Aldrich we offer as large and diverse an array of high-quality products as possible, many in bulk. Please write or call our Bulk Sales Department at (800) 255-3756 for a quotation on these and other products which may interest you.

Sebacoyl chloride



Useful building block.

23,636-5

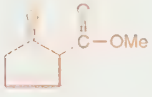
Allyltrimethylsilane

$H_2C{=}CHCH_2SiMe_3$

Silylating reagent.

20,826-4

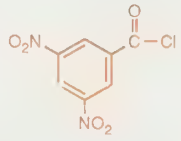
Methyl 2-oxocyclopentanecarboxylate (methyl 2-cyclopentanonecarboxylate)



Synthetic tool.

16,810-6

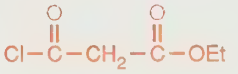
3,5-Dinitrobenzoyl chloride



Useful synthetic reagent.

15,627-2

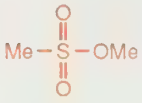
Ethyl malonyl chloride



Pharmaceutical intermediate.

16,387-2

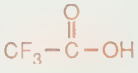
Methyl methanesulfonate



Sulfhydryl reagent.

12,992-5

Trifluoroacetic acid, 99 + %



30,203-1, spectrophotometric grade
29,953-7, suitable for protein sequencing

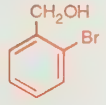
1,3-Diisopropylcarbodiimide

$Me_2CHN{=}C{=}NCHMe_2$

Peptide-coupling agent.

D12,540-7

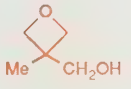
2-Bromobenzyl alcohol



O-Protecting reagent in peptide synthesis.

18,427-6

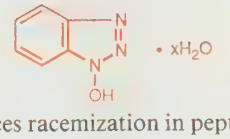
3-Methyl-3-oxetanemethanol



Synthesis of bridged carboxylic ortho esters.

27,768-1

1-Hydroxybenzotriazole hydrate



Reduces racemization in peptide synthesis.

15,726-0

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ADDRESS CORRECTION REQUESTED

Aldrichimica Acta

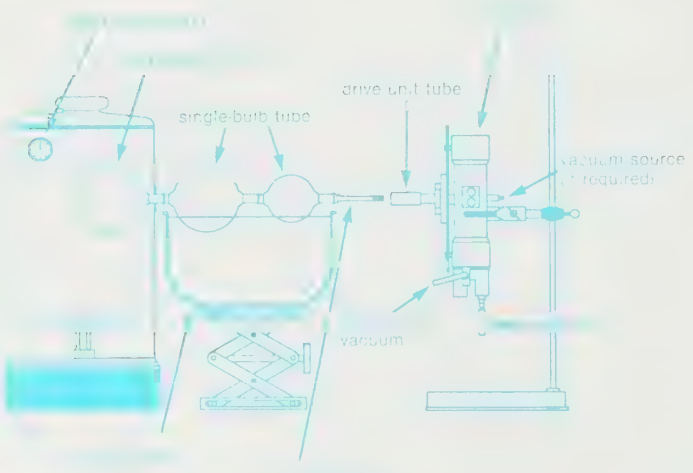
Volume 21, Number 2, 1988

Ultrasound in Organic Synthesis

The Aldrich Kugelrohr: NEW Large-Capacity Apparatus

For years, the Aldrich Kugelrohr (German: *Kugel* = bulb, *Rohr* = tube) has been used in laboratories throughout the world as a small-scale, short-path distillation apparatus. The operation is simple: the distillable product contained in a round-bottom flask is placed in the heating unit/air bath. The distillate is collected in horizontally adjacent bulb tubes which are rocked by an oscillating motor which speeds distillation.

Aldrich now carries a large-capacity Kugelrohr apparatus for use with up to a 4-liter round-bottom flask. The apparatus features a modified support mechanism to ensure smooth, trouble-free oscillation of large volumes. Specially constructed 2- and 4-liter round-bottom flasks with additional support tubes are required. The unit is available in 120 and 220 volts.



Large-Capacity Kugelrohr Distillation Apparatus

Includes:
• drive unit • heating unit — complete with dial-type thermometer, heavy-duty Teflon® bearing set and metal cover • glassware set — consists of a straight tube and round-bottom flask with special support tube and one single-bulb receiving flask.

Glassware set is available in 2- or 4-liter size with ₹24/40 ground glass joints. The 220-volt unit is supplied with UL-approved line cord only. Customers must supply plug meeting their own local electrical code requirements. Temperature controller must be purchased separately.

Z17,634-6	with 2000ml flasks; 120 volts	**$384.50**
Z17,635-4	with 2000ml flasks; 220 volts	**$394.00**
Z17,636-2	with 4000ml flasks; 120 volts	**$475.00**
Z17,637-0	with 4000ml flasks; 220 volts	**$485.00**

Temperature Controller

Thermolyne type 45500

Z15,299-4	120 volts	**$78.00**
Z15,300-1	220 volts	**$78.00**

Replacement Parts for Large-Capacity Kugelrohr

Glassware Set

Consists of a straight tube, one round-bottom flask with support tube and one single-bulb receiving flask, with ₹24/40 ground-glass joints.

Z17,429-7	2-liter flask	**$92.40**
Z17,428-9	4-liter flask	**$192.00**

Heating Unit

500-watt far-IR radiant heater for use with round-bottom flasks up to 4-liter capacity. Includes dial-type thermometer, heavy-duty Teflon® bearing set and metal cover.

Z17,426-2	120 volts	**$204.90**
Z17,427-0*	220 volts	**$214.90**

Drive Unit

An oscillating motor which operates on compressed air or vacuum; 300° turning arc.

Z10,047-1 $125.00

Round-Bottom Flask

With additional support tube and ₹24/40 ground-glass joint.

Z17,654-0	2-liter flask	**$39.00**
Z17,655-9	4-liter flask	**$89.00**

Straight Tube

Z11,908-3 ₹24/40 joint **$14.70**

Teflon® Bearing Set

Contains two heavy-duty bearings of diameter 1⅜-in.

Z17,434-3 $19.50

Dial-Type Thermometer

For use up to 200°C

Z15,302-8 $27.50

For additional information on this unit and the very popular small-capacity Kugelrohr and accessories, send for revised Technical Information Bulletin No. AL-139.

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Volume 21, Number 2, 1988
A publication of the ALDRICH CHEMICAL COMPANY

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About Our Cover:

Fig. 1

Professor Seymour Slive at Harvard voiced an interesting question in aesthetics when he saw this arresting portrait of Descartes: "Why is a portrait vastly enhanced when we know that the sitter is one of the great Western philosophers?" Perhaps because we can grasp the man's character and so understand him better — some of the toughness and "blackness" to which Descartes' contemporaries referred, in admiration bordering on fear.

René Descartes (1596-1650) was a Frenchman of many parts — soldier, philosopher, mathematician, physicist, teacher, the founder of modern rationalism. Few great thinkers have been so versatile. Cartesian philosophy complemented that of Spinoza, his mathematics that of Huygens, his physics foreshadowed that of Newton.

As Descartes lived in Holland from 1629 to 1649, and was there recognized as one of the greatest philosophers of his time, many Dutch artists — Rembrandt, Jan Lievens and Frans Hals among them — depicted Descartes, and there has been a good deal of speculation which of these is the best likeness.[1] Rembrandt's brush drawing had been in a famous collection of Rembrandt's work, that of Valerius Röver in Delft early in the 18th century, and is now lost. If only we could see it!

Our portrait (oil on canvas, 30 x 25 inches) was done in 1647 by Peter Nason, an able portraitist from The Hague. He shows Descartes with such spirit that it is likely he painted it from life.

Frans Hals' little portrait (Fig. 1), now in Copenhagen, shows Descartes with similarly fierce intensity, and was probably done a year or two later. Most of the many portraits and prints of Descartes known to us were done posthumously and were based on Hals' portrait. Nason's portrait, signed and dated 1647, corroborates Descartes' almost frightening intensity.

(1) For a detailed discussion of some of the portraits of Descartes, see S. Slive, *Frans Hals,* Phaidon 1970-74; Vol. 1, pp 164-168; Vol. 3, No. 175, pp 89-91.

Lab Notes

Some of the components of the analytical instrumentation in our laboratory require frequent cleaning for satisfactory instrument performance. The nebulizer assembly on our atomic absorption spectrometer is such a component.

A quick way to clean these components is to use a freezer-weight "ziploc" or a Whirl-pak™ bag and an ultrasonic bath.

By placing the items to be cleaned in a "ziploc" bag, you not only prevent the loss of small pieces, but you can also regulate the cleaning environment within each bag and separate delicate (and usually expensive) glassware from the nuts and bolts. We have found the use of a small amount of a nonionic detergent, such as Triton® X-100, and type II water to be an excellent cleaning medium.

Moreover, since the items to be cleaned are not placed directly in the water of the ultrasonic bath, you can keep the bath filled with tap water and you need not be too worried about the condition of the bath's water. This is truly convenient if you are "borrowing" the ultrasonic bath from the lab next door.

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™Trademark of Nasco

Jim Genes
University of California VMTRC
18830 Road 112
Tulare, CA 93274

Editor's note: We list ultrasonic cleaners and zipper-top bags. Consult the equipment section of our Catalog/Handbook.

I have found that hexanes may be substituted for benzene in preparing acetals by azeotropic removal of water, thereby eliminating exposure to benzene. However, because of the similarities in refractive index between water and hexanes, the interface between layers in the Dean-Stark trap is difficult to see. This problem may be solved by adding a drop of food color to the bottom of the Dean-Stark trap before starting the reaction. The accumulating water is colored and the interface easily seen. The enjoyment of monitoring the reaction's progress is also enhanced.

Timothy J. Wilkinson
Chemistry Department
Wheaton College
Wheaton, IL 60187-5593

One possible explanation for the general broadening of signals occasionally seen in NMR spectra is the presence of microscopic paramagnetic particles in the sample solution. This problem can be solved by filtering the sample through a plug of

cotton with a flea-size magnetic stirring bar placed at the neck of a disposable Pasteur pipette. The stirring bar is very effective for removing the interfering paramagnetic particles.

Dr. Hing Sham
Abbott Laboratories
D-74B; AP10
Abbott Park, IL 60064

Editors note: Aldrich offers stirring bars in the size suggested by the author.

Z11,536-3 Micromagnetic stirring bar assortment of six fleas $14.20

The continuous use of high-capacity drying agents such as silica gel and Drierite® in desiccators and drying columns is hampered by the long reactivation times required for these agents. Our work in the field of air-quality monitoring often requires that large amounts of these desiccants be dried for several hours. The process of reactivation can be greatly speeded up by the use of conventional microwave ovens. Silica gel or Drierite is placed in a large porcelain evaporating dish and treated at full power (500 to 1000 watts) for a period of 10 to 20 minutes. Drying agents activated in this manner are indistinguishable from material dried in a conventional oven.

We have tested the process on silica gel (both indicating and chromatographic grades) and granular Drierite and have found the method satisfactory. Furthermore, we believe the method shows potential for drying other desiccants such as calcium chloride and molecular sieves.

®Registered trademark of W.A. Hammond Drierite Co.

Adam P. Latawiec
Stan E. Macbeth
Ontario Ministry of the Environment
Air Quality Section, South-East Region
Kingston, Ontario K7K 6C2, Canada

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of* Pictures from the Age of Rembrandt. *We reserve the right to retain all entries for consideration for future publication.

"Please Bother Us."

by Gianni Bodini.

Professor G. Capozzi at the University of Florence suggested that we make methylbis(methylthio)sulfonium hexachloroantimonate, a useful reagent[1] which forms stable episulfonium[2] and thiiranium[3] salts on reaction with alkenes and alkynes. The compound is also useful for the preparation of substituted oxazolines[4] and benzofurans.[5]

Naturally, we made the compound.

(1) Weiss, R.; Schlierf, C. *Synthesis* **1976,** 323. Capozzi, G. *Pure Appl. Chem.* **1987,** *59,* 989.
(2) Capozzi, G. *et al. Tetrahedron Lett.* **1975,** 2603.
(3) *Idem Chem. Commun.* **1975,** 248.
(4) Capozzi, G. *et al. Tetrahedron Lett.* **1981,** *22,* 3325.
(5) Capozzi, G. *et al. J. Chem. Soc., Perkin Trans. 1* **1981,** *12,* 3106.

33,290-9 Methylbis(methylthio)sulfonium hexachloroantimonate 5g $18.50
25g $61.00

It was no bother at all, just a pleasure to be able to help.

Superconductivity Update

Keeping Aldrich in the mainstream of superconductivity research has called for our commitment to supply a wide range of specialty materials, including some distinctive ceramic composites.

Yttrium-Barium-Copper Composites

Product data sheets accompany all composite products.

32,862-6 Yttrium barium copper oxide, calcined, unannealed
10g $19.30; 50g $67.50; 250g $275.00

Manufactured by a proprietary molten oxide process, this fine powder is representative of the material used in many of the 1-2-3-compound demonstration kits sold regionally to high schools and colleges since mid-1987. Its high-temperature production provides a distinctive, orthorhombic material which, although unannealed, typically exhibits superconductive character. $YBa_2Cu_3O_x$ ($6.5<x<7.0$) formulation.

33,588-6 Yttrium barium copper oxide, annealed, Hi T_C powder **5g $20.00; 25g $75.00**

One of two products commercially produced by W.R. Grace, this $YBa_2Cu_3O_{7-x}$ ($x<0.1$) composite is described as a high T_C superconducting powder, 99.9% pure. The Y:Ba:Cu mole ratio is 1:2:3 ± 3%, and AC susceptibility data demonstrate >92% superconductivity at a temperature of 4K. DC resistivity experiments show onset of resistance loss at 95K, with loss of all resistance at 93K. Particle size is nominal 0.5-10μ.

33,587-8 Yttrium barium copper oxide carbonate, 99.9%
5g $17.50; 25g $69.00

Described by W.R. Grace as a precursor powder, this mixture is governed by the composition $(Y_2O_3)_{0.5}(BaCO_3)_2(CuO)_3$, with mole ratios ± 3%. The density of the brown powder is 0.75g/ml and the particle size is 1000Å crystalline units agglomerated up to 10μ. Requires heat treatment by user.

New Listings and New Grades of Ultrapure Raw Materials

The 1988-89 Aldrich Catalog/Handbook includes a variety of superconductivity raw materials which feature the best balance of special purity and economy:

32,545-7 Copper(II) oxide, 99.99 + %
10g $10.00
100g $70.00

A new, intermediate grade; our first batch exhibited less than 30 ppm total metallic impurities, with Fe = 8 ppm and Si = 9 ppm.

32,943-6 Barium carbonate, 99.98%
25g $22.00
100g $68.00

Typical strontium level by ICP <50 ppm.

32,806-5 Barium nitrate, 99.98%
25g $15.00
100g $50.00

Typical strontium level by ICP <20 ppm.

33,595-9 Bismuth(III) oxide, 99.99%
50g $22.60
250g $91.75

A recently created grade, not in the 1988-89 catalog, which complements the 3N and 5N grades listed below.

We put particular emphasis on our analysis for ppm levels of impurities by ICP spectrometry. Evaluation of samples of the highest grade of **copper(II) oxide** available from typical Aldrich stock and from another supplier revealed some striking differences:

Copper(II) oxide source	Purity	ICP analysis (ppm)
Aldrich No. **20,313-0,** lot no. 02912AV	99.999 + %	Ca = 1; Mg = 0.3 (only detectable impurities)
Competitor material (not domestically made)	99.999%	Fe > 10; Ni = 8; Si = 4; Ca = 3; Mg = 0.6

The Aldrich line of ultrapure products, developed in the late seventies, includes quality raw materials for the rapidly changing field of superconductivity research. Oxides, carbonates, nitrates and other compounds as well as elemental forms of copper, bismuth, thallium, strontium, barium, calcium, antimony, rare earths and other key elements are generally available for immediate delivery.

20,264-9 Antimony(III) oxide, 99.999%
10g $19.25
50g $69.25

20,271-1 Barium carbonate, 99.999%
5g $12.15
25g $41.25; 100g $120.25

25,414-2 Bismuth(III) chloride, 99.999%
25g $42.50
125g $169.05

20,282-7 Bismuth(III) oxide, 99.999% **10g $15.80; 50g $60.95**

22,389-1 Bismuth(III) oxide, 99.9% **100g $19.10; 500g $69.25**

25,415-0 Bismuth(III) nitrate pentahydrate, 99.999%
25g $23.45; 100g $74.75

20,293-2 Calcium carbonate, 99.995 + %
5g $15.85
25g 62.00

22,963-6 Copper(II) nitrate hydrate, 99.999%
25g $23.20
100g $75.25

20,313-0 Copper(II) oxide, 99.999 + %
5g $17.40
25g $67.05

20,445-5 Strontium carbonate, 99.995%
5g $17.65
25g $68.40

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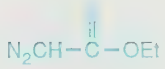

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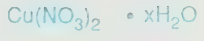

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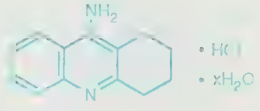

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Aldrichimica Acta

Volume 21, Number 3, 1988

Synthetic Methodology in the Context of Natural Product Total Synthesis

John D. Roberts

Dedicated to Professor John D. Roberts on his seventieth birthday

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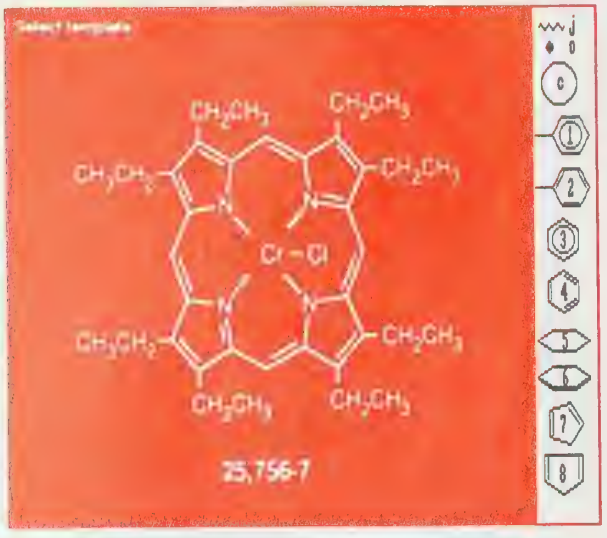

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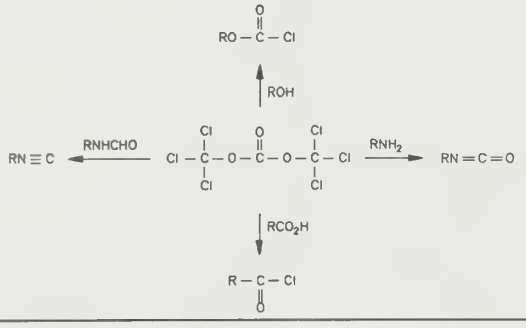

WordPerfect Report Printed on a Hewlett-Packard DeskJet® Printer

Send for Technical Information Bulletin No. **AL-162** describing WIMP and accessory WIMP database products. WIMP was created by Professor H.W. Whitlock of the University of Wisconsin, Madison.

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Volume 21, Number 3, 1988
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About Our Cover:

As readers of "About our Cover" know, our chemist-collector loves puzzles, particularly those involving Biblical paintings of the 17th century.

The painting reproduced here (oil on canvas, 41½ x 52¼ inches) was in the collection of the Earls Spencer at Althorp for more than three hundred years, attributed to the great Italian painter Domenico Fetti, whose work it is not. Our collector is not even certain that it is Italian; the landscape looks so Dutch, *ca.* 1620 — but who painted this masterpiece? Is it, per chance, by two hands — the landscape by a Dutchman in Italy and the great figures by an Italian? What luck that we do not know — were the artist(s) known, it might not have been sold.

The subject is clear: the angel appearing to Hagar (*Gen. 16,* 7-14). There were two such meetings. In the first, shown here, the angel tells Hagar to return to Abraham and Sarah. In the second, the angel helps Hagar and Ishmael after their expulsion from the patriarch's home.

The first appearance of an angel was not to a king or a general, nor even to Noah or Abraham, but to a runaway Egyptian slave. There is a lesson here, as there is in the angel's questions, which each of us should ask ourselves:

"Whence camest thou, and whither wilt thou go?"

Coloristically, this painting is a marvel, with the wonderful contrast between the rich red of Hagar's mantle and the shot silk of her gown juxtaposed with the coolness of the angel's shimmering white robe and wings. And what an angel, beautifully naive, the same angel that art lovers have met so often in annunciations to Mary. Hagar listens so attentively, her face framed by that multicolored gypsy bern — appropriate for Hagar the Egyptian, for in the 17th century, gypsies were believed — as the name implies — to be descendants of the Egyptians. Now Hagar is contrite, but the mocking face on the fountain reminds us of her previous haughtiness.

If someone had told our chemist-collector before he acquired this painting that he could not tell the difference between paintings done *ca.* 1620 in Rome and in Amsterdam, he would just have laughed. He doesn't laugh anymore, and would greatly appreciate help from readers.

This is one of our chemist-collector's finest paintings, and hence a fitting cover for the *Acta* dedicated to Professor Jack Roberts.

Lab Notes

A good example of the utility of the Flash Vacuum Thermolysis (FVT) method[1] is the preparation of ^{13}C-labeled acrylonitrile *via* elimination of acetic acid from 2-cyanoethyl acetate.[2] Pyrolysis of acetates to olefins is a classic thermal reaction[3] that proceeds essentially quantitatively under FVT conditions.[2] However, the separation of volatile olefins like acrylonitrile from acetic acid requires laborious workup techniques, such as preparative GC or flash distillation. This purification step can be omitted when a benzoate (in our case 2-cyanoethyl benzoate instead of 2-cyanoethyl acetate) is used instead of an acetate. Elimination occurs under the same experimental conditions, but the eliminated benzoic acid crystallizes directly behind the hot zone in the bend of the quartz tube at room temperature and acrylonitrile is collected in the trap in essentially pure state (see Fig. 1).

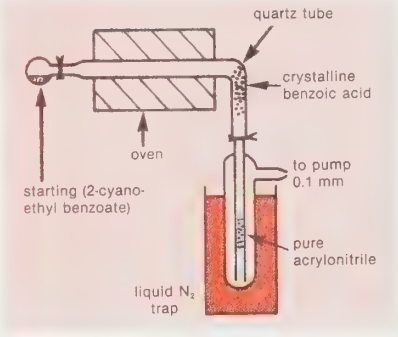

Fig. 1

We feel that the use of benzoates instead of acetates makes the preparation of simple, pure (volatile) olefins by FVT a very convenient procedure, requiring only that the benzoate be sublimed into the quartz tube.

1) Wiersum, U.E. *Aldrichim. Acta* **1984**, *17*, 31.
2) Van de Berg, E.M.M.; Richardson, E.E.; Lugtenburg, J.; Jenneskens, L.W. *Synth. Commun.* **1987**, *17*, 1189.
3) Hurd, C.D.; Blunck, F.H. *J. Am. Chem. Soc.* **1938**, *60*, 2419.

Leo W. Jenneskens
Ulfert E. Wiersum
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I wish to report that 2.8 denier white poly(propylene) staple is an outstanding replacement for glass wool in many applications. As a porous plug for packing columns, it has the following advantages: it packs densely and will hold back 30-micron particles without breakthrough of the particles. It does not produce fragments which can clog lines downstream, thus it can be applied in systems using microbore tubing. It is hydrophobic and ideal for systems where moisture must be excluded. Its flexibility allows it to be packed in very-small-diameter bores, allowing reliable plugs or filters to be made simply in 0.0625-in. i.d. columns. While poly(propylene) is relatively chemically inert, it dissolves in hot nonpolar solvents; so this is a possible limitation. Since poly(propylene) fibers are manufactured on a large scale for yarns and fabrics, the cost is potentially on the order of a few dollars per pound for large-scale chemical applications.

Douglas Jewett
The University of Michigan Medical School
Cyclotron/P.E.T. Facility
Division of Nuclear Medicine
3480 Kresge III
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Editor's note: We now offer the poly(propylene) wool recommended by Professor Jewett.

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The Editor
Aldrichimica Acta

Dear Editor:

When I prepared my paper, *Ultrasound in Organic Synthesis,* for the *Aldrichimica Acta,* Vol. 21, No. 2, 1988, I relied heavily on notes I had made for a presentation on sonochemistry at Eli Lilly in 1982. In that presentation, I had used a review on sonochemistry prepared by Dr. Charles B. Little, then at the Department of Chemistry of the University of Illinois in Urbana. That review had been presented by Dr. Little at a Chemistry Department seminar in December, 1981, and I cited the review in my presentation at Lilly. Unfortunately, my own notes of my talk at Lilly did not include the reference to Dr. Little's work, and in the years between my presentation at Lilly and my preparation of the paper for you, I had forgotten this important source and so did not cite it.

It has also been brought to my attention that my paper failed to cite some seminal work on sonochemistry, for instance:

Suslick, K.S.; Goodale, J.W.; Schubert, P.F.; Wang, H.H. *J. Am. Chem. Soc.* **1983**, *105*, 5781.

Suslick, K.S.; Johnson, R.E. *ibid.* **1984**, *106*, 6856.

Suslick, K.S. *Mod. Synth. Methods* **1986**, *4*, 1.

Suslick, K.S.; Hammerton, D.A.; Cline, R.E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5641.

Suslick, K.S.; Casadonte, D.J. *ibid.* **1987**, *109*, 3459.

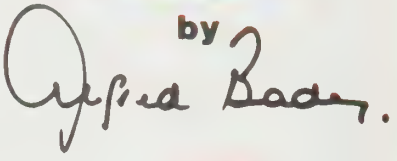
Suslick, K.S.; Flint, E.B. *Nature* **1987**, *330*, 553.

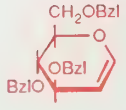
Riaz F. Abdulla, Ph.D.
Lilly Research Laboratories

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of* Pictures from the Age of Rembrandt. *We reserve the right to retain all entries for consideration for future publication.

"Please Bother Us."

by





Dr. David Crich at University College, London, suggested that we offer tri-*O*-benzyl-D-glucal, an important glycoside building block.[1-3]

Naturally we made it.

1) Ito, Y.; Ogawa, T. *Tetrahedron Lett.* **1987**, *28*, 2723.
2) Lesimple, P. *et al. Chem. Commun.* **1985**, 894.
3) Kinzy, W.; Schmidt, R.R. *Ann.* **1985**, 1537.

33,743-9 Tri-*O*-benzyl-D-glucal, 97%
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It was no bother at all, just a pleasure to be able to help.

Synthetic Methodology in the Context of Natural Product Total Synthesis*

Dedicated to John D. Roberts on his seventieth birthday

Robert E. Ireland
Thomas Jefferson Professor of Chemistry
Chemistry Department
University of Virginia
McCormick Road
Charlottesville, VA 22901

I. INTRODUCTION

The plethora of structurally fascinating natural products has for many years driven the art and science of synthetic organic chemistry. In many instances, these naturally occurring molecules are of important therapeutic value to mankind and have, therefore, stimulated much synthetic work. Nevertheless, other systems lacking this intrinsic incentive have been important substrates for the exploration of valuable synthetic methodology. The purpose of this article is to demonstrate how synthetic strategy has been the force that has led to the development of such useful methodology as well as the construction of complex natural products.

II. TERPENOID SYSTEM

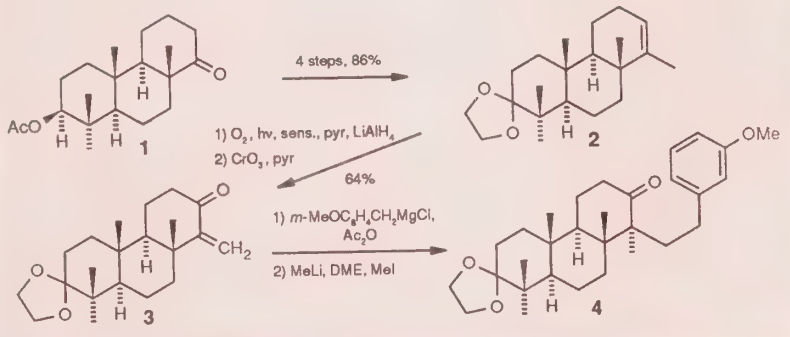
1. Germanicol synthesis

One such case is the investigation of a route for the synthesis of some terpenoid systems. In the course of the investigation of the total synthesis of the unsymmetrical triterpene germanicol,[1] the utility of the α-methylene ketone **3** became apparent. Through organometallic conjugate addition, followed by enolate trapping and then methylation, **3** led to the regioselectively and stereoselectively alkylated ketone **4** in good yield (Scheme 1). This latter ketone **4** was converted to the target molecule. The crucial structural and stereodemanding steps were accomplished through the α-methylene ketone **3** and they proved that such systems are of great synthetic value.

In this case, the preparation of the α-methylene ketone **3** was readily accomplished through photooxygenation of olefin **2** which itself was available by classical methods from ketone **1.** In order to generalize this synthetically valuable strategy, it was necessary to devise means for the construction of other less readily accessible olefins such as **5** to serve as photooxygenation substrates. Such systems could *not* be obtained by the classical methodology used for the transformation of ketone **1** to olefin **2**; a new method was necessary. The methodology devised for this process has been found to have synthetic value beyond the problem at hand.

A means for the deoxygenation of an enol was sought as a possible synthetic route. Enolization of a keto group provides for the regioselective introduction of a double bond *if* the carbon-oxygen bond can be reductively cleaved. Such a process was available through metal-amine reduction of an enol phosphate derivative.[2] For olefin **5**, this translated into reducing enone **6** with lithium/ammonia, and trapping the resulting enolate with diethyl phosphorochloridate in order to fix the location of the double bond. Subsequent reduction of the derived enol phosphate **7** gave olefin **5** in excellent yield (Scheme 2). The availability of **5** then led to further explorations into

Scheme 1



Professor Robert E. Ireland (left) receiving the A.C.S. Award for Creative Work in Synthetic Organic Chemistry, sponsored by Aldrich, from Dr. Alfred Bader, Chairman of the Board, Sigma-Aldrich Corporation.

terpene and steroid syntheses through conjugate additions to derived α-methylene ketones.

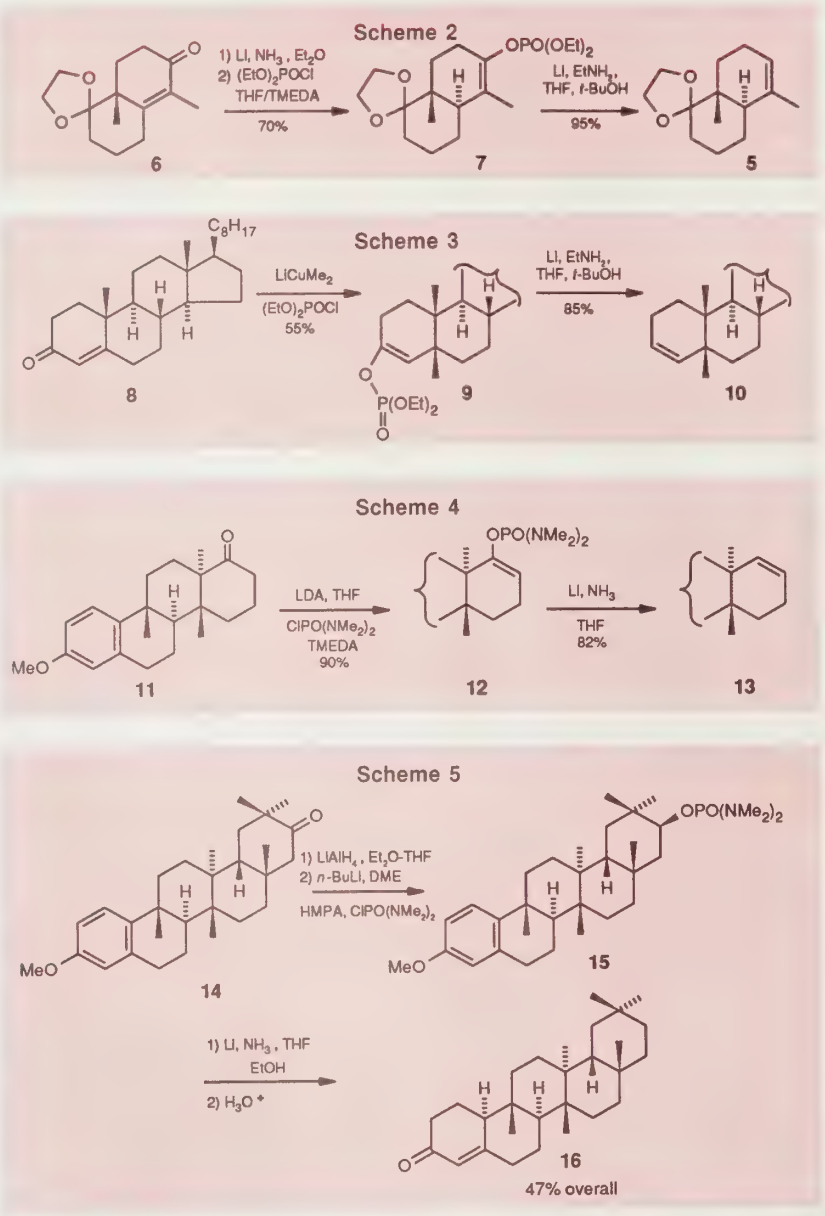
The efficiency and uniqueness of the phosphate reduction process suggested further examination of this method, and some very useful transformations have resulted. The conjugate addition/enolate-trapping process proved effective for the conversion of enone **8** to olefin **10** in good yield[3] (Scheme 3). Direct enolization and then trapping with *N,N,N′,N′*-tetramethyldiamidophosphorochloridate provided access to the phosphorodiamidate derivative **12** from the tetracyclic ketone **11**[4] (Scheme 4). The phosphorodiamidate group makes the reduction process even more facile and opens the way to effect general carbon-oxygen bond cleavage. In the case at hand, reductive deoxygenation[5] of the enol phosphorodiamidate **12** was *more facile* than anisole-ring reduction in lithium/ammonia solution with no alcohol present. When alcohol was added to the reducing medium, both phosphorodiamidate cleavage *and* anisole-ring reduction took place, *i.e.*, the conversion of the aromatic ketone **14** to enone **16**[6] occurred (Scheme 5).

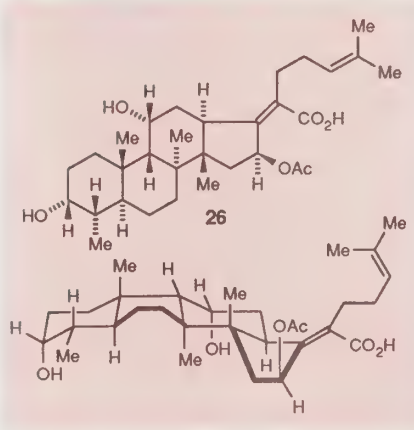
The latter process showed that the phosphorodiamidate derivative of simple alcohols can be reductively removed. This useful reduction process can be generalized for the removal of other alcohol-bearing systems. Three structurally demanding cases (Scheme 6) are the neopentyl system in alcohol **17** that gives ketal **19** in excellent yield, the tertiary axial alcohol **20** that cleanly provides hydrocarbon **22** and the hindered secondary alcohol **23** that is very effectively removed by this procedure.[5] An added feature of the phosphorodiamidate grouping is its stability under a wide range of common reaction conditions. This group is most effectively removed by metal/ammonia reduction but it can also be removed with excess *n*-butyllithium to regenerate the original alcohol.

2. Fusidic acid synthesis

During the formulation of a plan for the synthesis of the terpenoid antibiotic fusidic acid (**26**),[7] the deoxygenation process played a central role. Aside from the general logistics problems that a molecule such as **26** presents, the presence of a boat B-ring posed a severe challenge. Standard steroid and terpenoid synthetic methodology that relies on metal/ammonia reduction of enones will not produce the strained fusidic acid nucleus. This was shown[8] in a model tricyclic series when the monoketal of diketone **27** gave the *cis-syn-trans* ketone ketal **30** exclusively on metal/ammonia reduction or catalytic hydrogenation (Scheme 7). Catalytic hydrogenation or hydroboration of the C-5 - C-6 double bond of bisketal **28** also led exclusively to the same *cis-syn-trans* skeleton. The *intermolecular* reactions on these substrates take place reasonably from the less hindered β-face of the molecule and lead to the undesired *cis-syn-trans* structures.

In order to overcome this structural feature of the tricyclic model system, advantage was taken of the C-5 - C-6 double bond of **28**. This led to β-epoxide **29** wherein the C-6 hydrogen is of necessity α-oriented and intramolecular rearrangement then gave the desired *trans-syn-trans*





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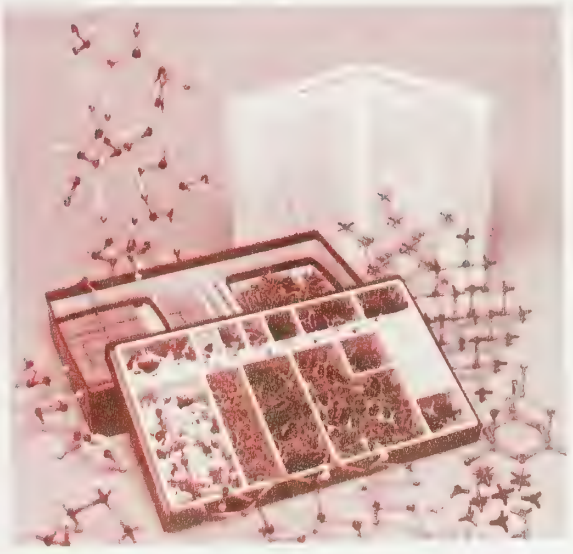

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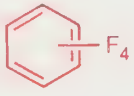

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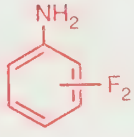
Trifluorobenzenes

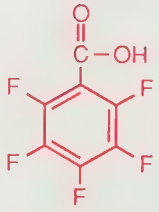
32,475-2 1,2,3-Trifluorobenzene
19,684-3 1,2,4-Trifluorobenzene
19,685-1 1,3,5-Trifluorobenzene

Difluoroanilines



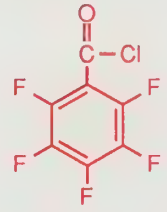
26,530-6 2,3-Difluoroaniline
19,660-6 2,5-Difluoroaniline
19,661-4 2,6-Difluoroaniline
27,023-7 3,4-Difluoroaniline
26,353-2 3,5-Difluoroaniline

Pentafluorobenzoic acid



P536-0

Pentafluorobenzoyl chloride



10,377-2

Difluorobenzenes

12,615-2 1,2-Difluorobenzene
D10,200-8 1,3-Difluorobenzene
D10,220-2 1,4-Difluorobenzene

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Aldrichimica Acta

Volume 21, Number 4, 1988

The Mechanisms of Oxygen Transfer from Acyl and Alkyl Hydroperoxides to Metal(III) Porphyrins and the Epoxidation of Alkenes by the Resultant Hypervalent Metal-Oxo Porphyrin Products

"CLAYCOP," A User-Friendly Oxidizing and Nitrating Reagent

Diazomethane Generators

Diazomethane (CH_2N_2) is the most common methylating reagent for carboxylic acids [a reprint of the review - Black, T.H. *The Preparation and Reactions of Diazomethane, Aldrichim. Acta* **1983,** *16*(1), 3 - is available upon request].

Diazomethane is an extremely toxic, highly irritating gas which has been known to explode unaccountably, both as a gas and in solution, although rough surfaces are proven initiators of detonations. The kits/apparatuses feature Clear-Seal joints (manufactured by Wheaton Scientific Co.), smooth-surface joints which do not require grease. *Ground-glass joints should not be used.*

Aldrich carries a number of apparatuses for the safe preparation of diazomethane. Technical Information Bulletins on the uses of the kits/apparatuses are available as indicated below. Also consult the equipment section of our Catalog/Handbook for details on the kits and replacement parts.

Diazald® Kit

With ₹19/22 Clear-Seal joints

For the preparation of up to 100 mmol diazomethane from Diazald® (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide).

Technical Information Bulletin No. AL-131.

Z10,025-0 $309.70

Replacement parts:

1. West condenser, 200mm	**Z10,030-7**	**$41.70**
2. Vacuum-distilling adapter	**Z10,029-3**	**31.30**
3. Claisen adapter	**Z10,026-9**	**31.80**
4. Connecting adapter	**Z10,027-7**	**22.80**
5. Distilling column, 200mm	**Z10,031-5**	**39.50**
6. Gas-inlet tube	**Z12,251-3**	**5.30**
7. Round-bottom flask, 500ml	**Z10,037-4**	**15.00**
8. Round-bottom flask, 50ml	**Z10,033-1**	**11.10**
9. Round-bottom flask, 25ml	**Z10,032-3**	**11.10**
10. Round-bottom flask, 250ml	**Z10,036-6**	**13.90**
11. Round-bottom flask, 100ml	**Z10,035-8**	**12.90**
12. Thermometer adapter with neoprene connector	**Z10,028-5**	**8.10**
13. Teflon® stopper	**Z10,039-0**	**8.00**
14. Separatory funnel with Teflon stopcock, 125ml	**Z10,038-2**	**53.00**

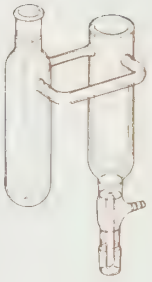
Mini Diazald Apparatus

With ₹19/22 Clear-Seal joints

A compact unit consisting of a reaction vessel and condenser, for the generation of 1-50 mmol diazomethane from Diazald. The major feature is the cold finger which, when filled with dry ice/acetone slush, efficiently prevents escape of diazomethane/ether.

Technical Information Bulletin No. AL-121.

Z10,889-8 $127.90



MNNG Diazomethane-Generation Apparatus

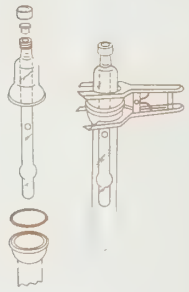
For the preparation, without distillation, of <1 mmol diazomethane from MNNG (1-methyl-3-nitro-1-nitrosoguanidine, 12,994-1). MNNG is the reagent of choice for small quantities of diazomethane, but because of its mutagenicity and skin-sensitivity, Diazald is preferred for large-scale production.

Technical Information Bulletin No. AL-132.

Z10,100-1 with "O"-ring joint **$53.90**
Z10,159-1 with Clear-Seal joint **51.50**

Replacement parts:

Rubber septum and cap	**Z10,148-6**	**$12.20/12**
"O"-ring	**Z10,151-6**	**21.10/12**



Macro Diazald Kit

With ₹24/40 Clear-Seal joints

Designed by M. Hudlicky (*J. Org. Chem.* **1980,** *45*, 5377) for the large-scale (0.2-0.3 mol) generation of diazomethane from Diazald.

A reprint of this article is available on request.

Technical Information Bulletin No. AL-180.

Z10,851-0 $450.00

Replacement parts:

1. Teflon stopper, ₹24/25	**Z11,558-4**	**$10.40**
2. Dropping funnel, 500ml	**Z11,554-1**	**119.00**
3. Round-bottom flask, 2-neck, 500ml	**Z11,557-6**	**64.90**
4. Cold-finger condenser assembly	**Z11,559-2**	**305.00**
5. Erlenmeyer flask, 500ml	**Z11,556-8**	**27.20**

Diazomethane Precursors

D2,800-0 Diazald®, 99% **25g $7.50; 100g $24.60; 500g $67.60; 1kg $116.60**

27,761-4 Diazald® -*N*-methyl-^{13}C, 99 atom % ^{13}C **250mg $106.70; 1g $294.95**

29,598-1 Diazald® -*N*-methyl-^{13}C-*N*-methyl-d_3, 99 atom % ^{13}C, 99.5 atom % D **250mg $114.45; 1g $315.55**

32,990-8 Diazald® -*N*-methyl-d_3, 98 atom % D **5g $107.50**

12,994-1 1-Methyl-3-nitro-1-nitrosoguanidine, 97% (MNNG) **10g $16.50; 25g $29.60**

19,738-6 *N*-[*N*′-Methyl-*N*′-nitroso(aminomethyl)]benzamide **25g $13.90**

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Aldrichimica Acta

Volume 21, Number 4, 1988
A publication of the ALDRICH CHEMICAL COMPANY

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About Our Cover:

You may be surprised to find a still life (oil on panel 17½ x 13½ inches) on our cover, the first in over twenty years of *Acta* covers. But it is so beautiful, apparently simple, yet subtle, a fitting work to grace the *Acta* with two very different papers, both brilliant in their innovation.

This is a "vanitas" still life, the broken brazier suggesting the vanity of material things and the transience of human life. It was painted in Amsterdam in 1664 by Evert Collier — we know this because it is signed and dated, and the seal on the jug is that of the city of Amsterdam.

This vanitas was painted on top of a portrait of a man with a white ruff; the outline is clearly visible through the thinly painted still life and more can be seen on an X-ray. You can read all about the painting in the catalog, "The Detective's Eye: Investigating the Old Masters", described below.

NEW

The Detective's Eye: Investigating the Old Masters

Twenty paintings (including the still life on this cover) that have been reproduced on our *Acta* covers and five that have been on our catalog covers are among some seventy works in an exhibit at the Milwaukee Art Museum (January 19 - March 19, 1989) for which Isabel and Alfred Bader are guest curators.

If you relish detective work and puzzles about Old Master paintings, you will find much to enjoy in this fully illustrated catalog, and you will learn something about our chemist-collector's interest in art and connoisseurship as well.

Z18,350-4 $12.00

Rembrandt and the Bible - in Japan

We are offering a limited number of a 174-page catalog of an exhibition in Japan, the first of its kind there, on Rembrandt and the Bible. The scholarly essays in Dutch, English, German and Japanese deal with works by Rembrandt and his students — 38 paintings, 7 drawings and 44 etchings, all beautifully illustrated. Thirteen of the paintings, all in full color, have appeared on covers of the *Acta*. The works are fully described in English and Japanese. An unusual and wonderful buy for lovers of art and the Bible!

Z16,235-3 $12.00

Pictures from the Age of Rembrandt

Twenty-five paintings that have been reproduced on our *Acta* covers, and six that have been on our catalog covers are among the thirty-six paintings in an exhibition of Dutch paintings at Queen's University in Kingston, Ontario. The fully illustrated catalog written by Professor David McTavish contains a wealth of art-historical information — enough for several evenings of relaxed enjoyment — probably the best value in art-history anywhere.

Z12,794-9 $8.00

Reprints of Aldrich Catalog Covers

Eight beautiful 14 x 11 inches, full-color reproductions of paintings on our catalog covers are available, ready for framing, to add beauty to your laboratory.

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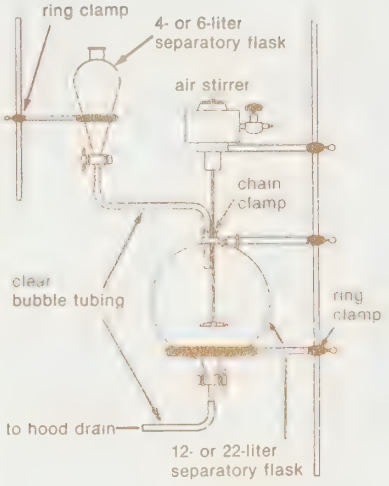
Selections from the Aldrichimica Acta, 1968-1982

Because of the ever-increasing demand for earlier issues of the *Acta*, we now offer a collection of articles from volumes 1-15: 354 pages of great review articles, in one beautiful hard-bound volume. All articles are included except those whose subject matter has been updated in later issues.

Z12,148-7 $15.00

Lab Notes

I wish to report a safe and efficient method for quenching large volumes of acids, $SOCl_2$, PCl_3 and related compounds.



For example, place a 50% NaOH/ice mixture in the lower flask. Place the material to be quenched in the upper flask. Slowly add material to the lower flask, replacing ice as necessary. When the material is quenched or the NaOH solution has been neutralized, open the bottom stopcock and run the contents down the hood drain. This method reduces close contact with the acid/base solutions, avoids the use of clumsy 5-gallon buckets and solutions can all be vacuum-transferred.

Mary Doyle
Production Department
Aldrich Chemical Co., Inc.

2-Nitro-5-thiocyanatobenzoic acid is a good cyanylating agent for protein sulfhydryl groups and for the cleavage of proteins at cysteine [*Aldrichimica Acta* **1987**, *20*(3), 87].

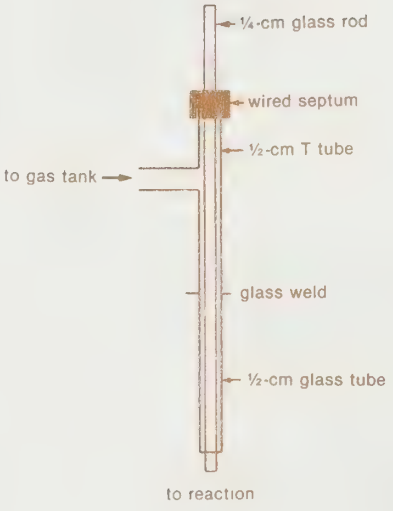
For these purposes, 1-cyano-4-(dimethylamino)pyridinium tetrafluoroborate compares favorably with this reagent (Banks, G.R. *Biochemistry* **1986**, *25*, 5882; *Chem. Commun.* **1976**, 21). Moreover, the latter reagent may be used for the covalent attachment of ligands to polysaccharide resins (Wilchek, M. *Appl. Biochem. Biotechnol.* **1984**, *9*, 285) and for the C-cyanation of imidazoles (Witten, J.P. *Synthesis* **1988**, 470).

M. Wakselman
Centre National de la Recherche Scientifique
C.E.R.C.O.A.
2 à 8 rue Henri - Dunant
B.P. 28 - 94320 Thiais, France

Editor's note: Aldrich carries the reagents mentioned by the author.

28,486-6 2-Nitro-5-thiocyanatobenzoic acid, 98% **250mg $13.40; 1g $36.10**
28,466-1 1-Cyano-4-(dimethylamino)-pyridinium tetrafluoroborate, 98% **50mg $16.00; 250mg $51.35**

We do many salt exchanges in our lab, replacing the HBr salt with the HCl salt. This is accomplished by dissolving the HBr salt in hot methanol and then adding HCl gas to the refluxing mixture. The HCl salt then precipitates out of solution and is collected. However, a problem arises in this procedure because the gas-inlet tube often becomes plugged with precipitate before the exchange is complete. The gas must then be shut off, the tube removed and cleaned, and the tube replaced before gas addition can continue. I have found a simple solution to this problem which could be applied to any system where gas-inlet tubes become plugged.



Have a glassblower attach a ½cm-diameter T-tube to a similar glass rod as shown. Stopper the top of the T-tube with a rubber septum and insert a ¼cm-diameter glass rod through the septum. The rod must be longer than the combined length of the T-tube and tube. The other opening of the T-tube goes to the gas tank and the ½-cm glass tube is inserted through a septum into the reaction. As the inlet tube becomes plugged, working the rod up and down will free the precipitate.

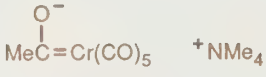
Jay B. Fell
Research Biochemicals Inc.
9 Erie Drive
Natick, MA 01760-1390

Any interesting shortcut or laboratory hint you'd like to share with the Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt.** *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by

Dr. Stéphane De Lombaert at Colorado State University suggested that we offer the tetramethylammonium salt of (1-hydroxyethylidene)pentacarbonylchromium.[1]



This particularly stable organometallic reagent is readily converted into a variety of synthetically useful heterosubstituted chromium carbene complexes[2] after activation with an acylating agent.[3]

Naturally, we made it.

1) Fischer, E.O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.
2) a) Dötz, K.H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.
b) Hegedus, L.S.; de Weck, G.; D' Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.
3) a) Fischer, E.O.; Selmayr, T.; Kreissl, F.R. *Chem. Ber.* **1977**, *110*, 2947.
b) Connor, J.A.; Jones, E.M. *J. Chem. Soc. (A)* **1971**, 3368.

34,264-5 Tetramethylammonium (1-hydroxyethylidene)pentacarbonylchromium 1g $10.00; 5g $39.00

It was no bother at all, just a pleasure to be able to help.

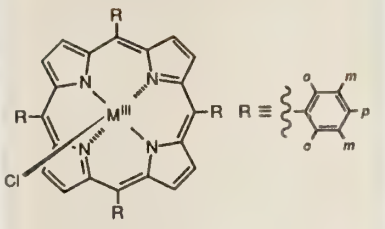
The Mechanisms of Oxygen Transfer from Acyl and Alkyl Hydroperoxides to Metal(III) Porphyrins and the Epoxidation of Alkenes by the Resultant Hypervalent Metal-Oxo Porphyrin Products

Thomas C. Bruice
Department of Chemistry
University of California at Santa Barbara
Santa Barbara, CA 93106

"Oxene equivalent" transfer to metalloporphyrins to provide hypervalent metal-oxo porphyrins and the reactions of the latter in epoxidation and oxygen insertion have received considerable attention. The following report summarizes our recent investigations. Consideration is given to two problems: (1) the mechanisms of oxidation of various porphyrin metal complexes by oxygen transfer from acyl hydroperoxides, hydrogen peroxide and alkyl hydroperoxides; and (2) the mechanism of epoxidation of metal-oxo porphyrin species two-electron-oxidized above the metal(III) porphyrin state.

Metal(III) porphyrins are easily oxidized at the four *meso*-positions of the porphyrin ring. Susceptibility to oxidation can be greatly impeded by protecting these *meso*-positions with phenyl substituents. The *meso*-tetrakis(phenyl)porphinato metal(III) salts $[(TPP)M^{III}(X)_n]$ (TPP = tetraphenylporphyrin, M = metal cation and X = axial ligand or counter anion), and analogues bearing substituents on the phenyl rings (Table I), have been used in modeling protoporphyrin-IX mixed-function oxidases (peroxidases, catalases and cytochrome P-450 enzymes).

Table I



Abbreviation	M^{III}	*o*	*m*	*p*
$(TPP)Fe^{III}(Cl)$	Fe	H	H	H
$(TPP)Cr^{III}(Cl)$	Cr	H	H	H
$(TPP)Mn^{III}(Cl)$	Mn	H	H	H
$(TPP)Co^{III}(Cl)$	Co	H	H	H
$(F_{20}TPP)Fe^{III}(Cl)$	Fe	F	F	F
$(Cl_8TPP)Fe^{III}(Cl)$	Fe	Cl	H	H
$(Cl_8TPP)Mn^{III}(Cl)$	Mn	Cl	H	H
$(Br_8TPP)Fe^{III}(Cl)$	Fe	Br	H	H

Oxidation by Oxygen-Transfer Step

The first step in the mixed-function oxidation is transfer of an "oxene equivalent" to the metal(III) porphyrin such that the oxygen becomes an axial ligand of the metal and the metal(III) porphyrin undergoes two-electron oxidation (eq. 1). It is conventional to refer to the product of the two-electron oxidation of a metal(III)-oxo porphyrin as "compound I" and the product of one-electron reduction of compound I as "compound II". This nomenclature does not specify the structure of the products of two-electron and one-electron oxidation of the metal(III)-oxo porphyrin. The structure of compound I is dependent upon the nature of the metal(III) species

$$[(\text{porphyrin})\text{Fe}]^+[X]^- \xrightarrow{[O]} [(\text{porphyrin})\text{Fe}(O)]^+[X]^- \quad \text{(eq. 1)}$$

and the presence or absence of a strongly basic axial oxo ligand. When an oxo ligand is present, compound I may have the structure of a metal(V)-oxo porphyrin, a metal(IV)-oxo porphyrin π-cation radical or a metal(III)-oxo porphyrin dication (Fig. 1).

Our initial studies of the dynamics of oxidation by oxygen transfer using acyl hydroperoxides, hydrogen peroxide and alkyl hydroperoxides (ROOH species) were carried out in various organic solvents. The following metal(III) complexes were investigated in the solvents indicated: $(EDTA)Fe^{III}$ (in MeOH)[1]; $(TPP)Cr^{III}(Cl)$ (in CH_2Cl_2)[2,3]; $(TPP)Mn^{III}(Cl)$ (in PhCN)[4]; $(TPP)Fe^{III}(Cl)$ (in MeOH)[3,5]; and

Professor Thomas C. Bruice (left) receiving the Alfred Bader Award in Bioinorganic and Bioorganic Chemistry from Dr. Alfred Bader, Chairman of the Board, Sigma-Aldrich Corporation.

$(TPP)Co^{III}(Cl)$ (in $CHCl_3$)[6]. Second-order rate constants (k_{ROOH}) for reaction of each metal(III) complex with a series of ROOH compounds were generally determined by trapping of the compound I or compound II species. Trapping was carried out by the use of one or another agent that upon one-electron oxidation provides a monitorable colored radical (eqs. 2 and 3) or by monitoring the formation of compound II species which arise by the comproportionation of compound I with remaining metal(III) porphyrin (eq. 4). Plots of log k_{ROOH} *vs.* the pK_a (in water) of the leaving ROH group establish linear relationships between the free energy of activation (ΔG^*) and the standard free energies ($\Delta G°$) of acid dissociation of ROH. The pK_a values of the leaving ROH group are an index of the polarity of the RO-OH bond. Plots of log k_{ROOH} *vs.* pK_a of ROH are shown in Figure 2.

Traylor and associates[7] used $PhCH_2CO_3H$ as oxygen donor in order to differentiate between oxygen-transfer reactions which involve heterolytic and homolytic O-O bond cleavage. A heterolytic mechanism provides $PhCO_2H$ while homolytic O-O bond cleavage gives $PhCH_2CO_2^{\bullet}$ which immediately decomposes into $PhCH_2^{\bullet}$ and CO_2. By finding $PhCH_2CO_2H$ as the product of reaction of $PhCH_2CO_3H$, we showed that oxygen transfers by percarboxylic acids to $(EDTA)Fe^{III}$, $(TPP)Cr^{III}(Cl)$, $(TPP)Mn^{III}(Cl)$, and $(TPP)Co^{III}(Cl)$ occur by heterolytic O-O bond scission. Thus, metal(III) porphyrins are oxidized by acyl hydroperoxides to the compound I oxidation state (eq. 5).

Examination of the linear free-energy plots of log k_{ROOH} *vs.* pK_a of ROH (Fig. 2) shows that a single line suffices to correlate the log k_{ROOH} values for both acyl and alkyl hydroperoxides when the species undergoing oxidation is $(EDTA)Fe^{III}$ or $(TPP)Cr^{III}(Cl)$. With the exception of the least acidic alkyl hydroperoxides, this is also true of the imidazole (ImH)-ligated manganese(III) complex $(TPP)Mn^{III}(Cl)(ImH)$ (CH_2Cl_2 solvent).[8] It is reasonable to assume that in these cases, both acyl hydroperoxide and alkyl hydroperoxide reactions involve heterolytic O-O bond scission. The linear free energy plots for $(TPP)Fe^{III}(Cl)$ and $(TPP)Co^{III}(Cl)$ exhibit a break at a pK_a of ROH of between 9 and 11. We have proposed that this is due to a change from heterolytic O-O bond scission to rate-determining homolytic O-O bond scission for the alkyl hydroperoxides. The slopes ($-\beta_{lg}$) of the linear free-energy plots for the heterolytic mechanism with $(EDTA)Fe^{III}$,

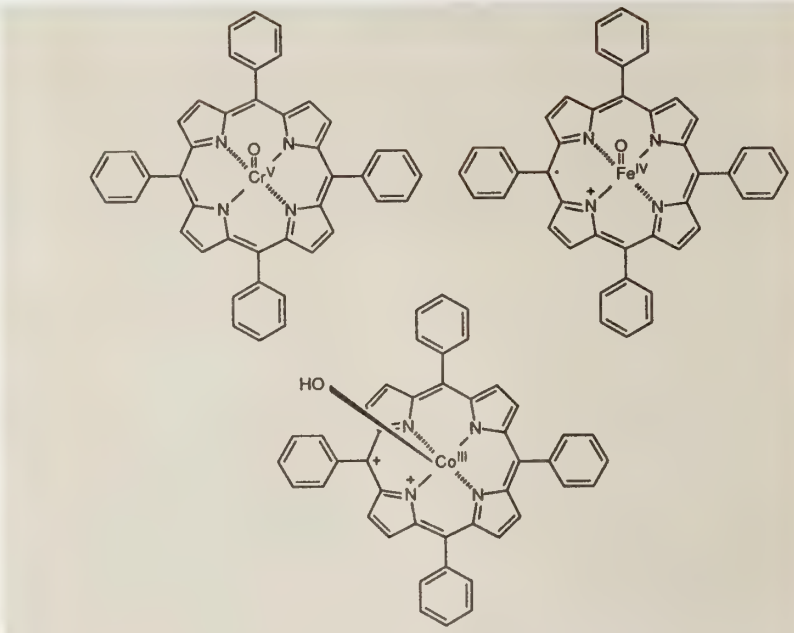


Fig. 1 - Structures formed by 2e⁻ oxidation of 5,10,15,20-tetraphenylporphinato metal(III)-oxo species are dependent upon the metal. Shown are the Cr^{V}-oxo species, the Fe^{IV}-oxo porphyrin π-cation radical and the Co^{III}-OH porphyrin dication.

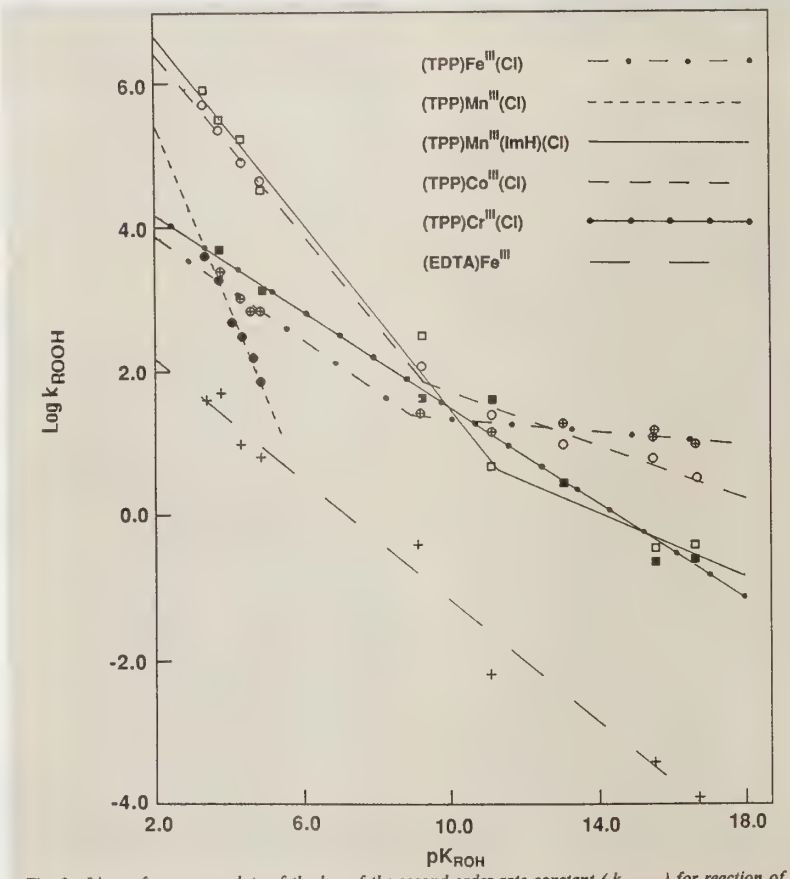


Fig. 2 - Linear free-energy plots of the log of the second-order rate constant (k_{ROOH}) for reaction of acyl and alkyl hydroperoxides with a series of metal complexes vs. the pK_a of the corresponding carboxylic acids and alcohols.

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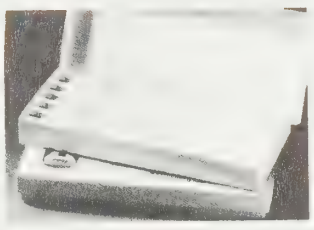
5	Premium	0.1955 ±0.0003 0.1655 +0.0005 -0.0000	±0.0015	±0.0005	Z11,719-6	39.90/5
5	Premium, extra-long*	0.1955 ±0.003 0.1655 ±0.0005 ±0.000	±0.0015	±0.0005	Z12,919-4	72.90/5
5	Gold label	0.1955 ±0.0003 0.1655 ±0.0005 -0.0000	±0.0005	±0.00025	Z11,721-8	72.50/5
10	Standard	0.3933 ±0.0003 0.3569 ±0.0005	±0.005	±0.001	Z11,722-6	11.40/1 51.80/5
10	Premium, extra-long*	0.1955 ±0.003 0.1655 ±0.0005	±0.0015	±0.0005	Z12,920-8	17.50/1
10	Gold Label	0.3933 ±0.0003 0.3569 ±0.0005 -0.000	±0.00075	±0.00025	Z11,723-4	26.50/1 120.60/5

*9in. long, for making standards and for use with tip-off manifolds.



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For 5-mm NMR tubes

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yellow	Z15,330-3	4.15
green	Z15,331-1	4.15
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Pressure caps for 10-mm NMR tubes, red **Z11,808-7** **$7.65/100**

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For use with 7-in.-long tubes only.

Z10,724-7 for 5-mm tubes **$41.90**

With ₹24/40M joint and hose barb

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Oxygenation/epoxidation reagent.

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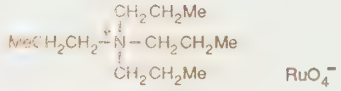
21,312-8 90% (remainder 5% water, 5% *tert*-butyl alcohol)
31,037-9 anhydrous, 3.0*M* solution in 2,2,4-trimethylpentane

33,127-9 anhydrous, 5.5*M* solution in 2,2,4-trimethylpentane

Tetrapropylammonium perruthenate (TPAP)



Catalytic oxidant for the conversion of alcohols to carbonyls.

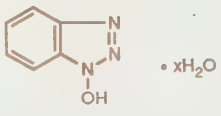
33,074-4

Trifluoromethanesulfonic anhydride

Synthesis of triflates.

17,617-6

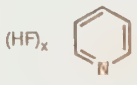
1-Hydroxybenzotriazole hydrate



Anti-racemization additive in peptide synthesis.

15,726-0

Hydrogen fluoride-pyridine



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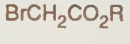

Pharmaceutical intermediates.

	15,791-0	**R = methyl**
	13,397-3	**R = ethyl**
NEW	**34,213-0**	**R = propyl**
	25,534-3	**R = isopropyl**
	12,423-0	**R = *tert*-butyl**

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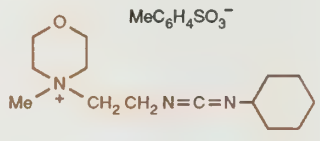

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Aldrichimica Acta

Volume 22, Number 1, 1989

Design and Implementation of Tactically Novel Strategies for Stereochemical Control Using the Chiron Approach

Johann Josef Loschmidt (1821-1895): a Forgotten Genius

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Aldrichimica Acta

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About Our Cover:

Fig. 1

When our chemist collector bought this painting (oil on canvas, 19 x 22 inches) some years ago, it was a 'wreck' (Fig. 1). Luckily, an art-historian friend had a photograph of this *Presentation in the Temple* as it looked some 100 years ago. Some time since that photograph was taken, the painting was cut down, perhaps because of water or fire damage, the figures of Simon and the baby Jesus were scraped off right down to the canvas, and that area was then overpainted. During restoration of the 'wreck', the figures of Simon and the baby had to be reconstructed. You can read more about this in the *Detective's Eye* described below.

The artist, Jan Lievens, also painted the "St. Paul" on the cover of our current Catalog-Handbook, which contains a brief discussion of the artist in the "About Our Cover". Lievens produced his best works around 1630, when this "Presentation" was painted. It is a beautiful work, and so seems a fitting cover for Professor Hanessian's paper which is also great art, of a different kind.

Jan Lievens has long been very much in the shadow of Rembrandt, even though their early works are comparable in quality. In fact many works by Lievens, such as our *St. Paul,* were long attributed to Rembrandt. Hence this painting is also a fitting cover for Dr. Wiswesser's historical eye-opener which rediscovers the brilliant work of Josef Loschmidt.

NEW

The Detective's Eye: Investigating the Old Masters

Twenty paintings (including the still life on this cover) that have been reproduced on our *Acta* covers and five that have been on our catalog covers were among some seventy works in an exhibit at the Milwaukee Art Museum (January 19 - March 19, 1989) for which Isabel and Alfred Bader were guest curators.

If you relish detective work and puzzles about Old Master paintings, you will find much to enjoy in this fully illustrated catalog, and you will learn something about our chemist-collector's interest in art and connoisseurship as well.

Z18,350-4 $12.00

Rembrandt and the Bible - in Japan

We are offering a limited number of a 174-page catalog of an exhibition in Japan, the first of its kind there, on Rembrandt and the Bible. The scholarly essays in Dutch, English, German and Japanese deal with works by Rembrandt and his students — 38 paintings, 7 drawings and 44 etchings, all beautifully illustrated. Thirteen of the paintings, all in full color, have appeared on covers of the *Acta*. The works are fully described in English and Japanese. An unusual and wonderful buy for lovers of art and the Bible!

Z16,235-3 $12.00

Pictures from the Age of Rembrandt

Twenty-five paintings that have been reproduced on our *Acta* covers, and six that have been on our catalog covers are among the thirty-six paintings in an exhibition of Dutch paintings at Queen's University in Kingston, Ontario. The fully illustrated catalog written by Professor David McTavish contains a wealth of art-historian information — enough for several evenings of relaxed enjoyment — probably the best value in art-history anywhere.

Z12,794-9 $8.00

Lab Notes

A common problem when preparing samples for thin-layer chromatography is to find a handy piece of apparatus in which to hold the vials or durum tubes in which the sample is being prepared.

We have recently discovered that Aldrich Suba•Seal septa caps, when inverted, are exactly the correct shape to support tubes of this type. Particularly useful are the 4- and 8-mm septa.

Neil S. Ringan
Dundee College of Technology
Department of Molecular and Life Sciences
Bell Street
Dundee DD1 1HG
England

Editor's note: Aldrich carries Suba•Seal septa in both white and red rubber. Please consult the Equipment Section of our Catalog/Handbook.

For some experiments, we have required a supply of air saturated with various different organic vapors at ambient temperature. When the organic liquids were fairly nonvolatile, we experienced difficulty in achieving reproducible concentrations of saturated vapor (as evidenced by glc analysis).

The traditional method of producing saturated vapors involves a gas line in which air is pumped through a series of glass vessels containing organic liquid. We were looking for a simple, rapid and effective method somewhat less cumbersome and easily organized at any point in our laboratories. The solution proved to be very simple.

A Drechsel tube was used to disperse air into an organic liquid contained in a flask immersed in a common ultrasonic laboratory cleaning bath. Sonication provided very efficient vapor production in the flask from which the vapors were passed through a second bubbler held at room temperature outside the ultrasonic bath. This second bubbler serves two purposes: (a) it helps prevent atomized liquid from being carried over and (b) it ensures saturation at ambient temperatures since ultrasonic baths normally operate a few degrees above ambient.

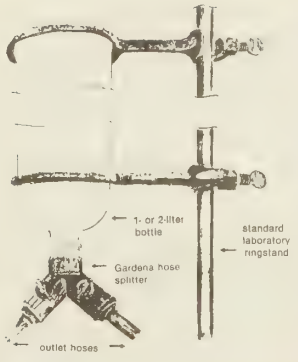
The method is clearly adaptable for the generation of saturated vapors at temperatures other than ambient.

Timothy J. Mason
Paul Sephton
The Sonochemistry Group
Coventry Lanchester Polytechnic
Coventry CV1 5FB
England

Editor's note: Aldrich lists Bransonic ultrasonic baths. Please check the Equipment Section of our Catalog/Handbook.

If you are tired of the lines at the counter when students are obtaining reagents, or of spills and the inconvenience of reagent bottles and dispensers, or of washing and storing glassware, you may wish to try this teaching tip.

Your local hardware/garden store carries a two-outlet "Y" adapter for outside faucets equipped with two, lever-type, continuous turning control valves. A suitable type of adapter is made by Gardena. The input end just fits on plastic soda (pop) bottles. Prepare your non-caustic solutions, deionized water, dilute acids (or anything that is safe when stored in a plastic container right in the soda bottle), attach the Gardena Y fitting, place a large ringstand ring over the bottle neck, up-end the entire apparatus and suspend on a ringstand with another ring at the top for security (see diagram). Two lines of students can dispense their solutions accurately and easily *without* spillage while controlling the outflow from a dribble to the full flow. If you need a larger volume-flow output, simply poke an air hole in the bottom of the soda bottle. When you are finished with the solution, simply rinse the soda bottle and recycle it. No more washing glassware!



The Gardena Y fits most plastic soda bottles, so you have .5-, 1-, 2- and even 3-liter containers. An extra hose washer has been added to the fittings to prevent leaks, and a 5-cm piece of Tygon® tubing has been connected to each end of the Y to make access easier for the students.

Bob Zafran
Abraham Lincoln High School
555 Dana Avenue
San Jose, CA 95126

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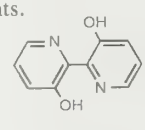
Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt.** *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Aldrich Boys.

Professor Randy Ruchti of the Department of Physics at the University of Notre Dame suggested that we offer 2,2′-bipyridine-3,3′-diol, a fluorescent dye with a large Stokes shift,[1,2] of interest as a scintillator for the superconducting super collider. Among the advantages of this dye are its photochemical stability and its solubility in many organic solvents.



Naturally, we made it.

(1) Langhals, H.; Pust, S. *Chem. Ber.* **1986,** *118,* 4674.
(2) Sepiol, J.; Bulska, H.; Grabowska, A. *Chem. Phys. Lett.* **1987,** *140,* 607.

34,008-1 2,2′-Bipyridine-3,3′-diol, 98%
50mg $18.00

It was no bother at all, just a pleasure to be able to help.

Design and Implementation of Tactically Novel Strategies for Stereochemical Control Using the Chiron Approach

As we approach the twenty-first century, the present generation of organic chemists will reflect upon this decade as the turning point in the art of stereocontrolled synthesis. While present-day accomplishments may be regarded as modest in the year 2001, those who will work in the field at that time will have the onus of doing much better. Stereochemical control is not just a requirement nowadays, but a way of life in the laboratory as we strive for the highest optical purity for those targets we choose to synthesize. Biological response is intimately related to enantiomeric purity, a situation which is well appreciated in medicinal chemistry. Stereochemistry is therefore an important link between biology and chemistry. Challenged by this need, and armed with a rapidly expanding wealth in synthetic methodology, numerous research programs dealing with "asymmetric synthesis" were initiated over the past 10 to 15 years.[1] The fruits of these intensive efforts have been in continuing harvest since then, and innovations on many fronts are steadily forthcoming. Today, enantiomeric and diastereomeric excesses for a given transformation of less than 90% are frowned upon, when only a decade ago, attaining such levels was regarded as the sought-for exception. An optical purity of *ca.* 100% is only a relative measure of the true state of affairs, depending on what standard we adopt or what method we use to reach this revered figure. Practically, an optical purity of 90% corresponds to a 95:5 ratio of isomers which may be good enough for a single reaction. A multi-step sequence, however, with each proceeding in 90% optical efficiency, will rapidly lead to a much diminished purity for the final product, unless the "other isomer" can be separated *en route*. Chemists therefore strive to get as close to 100% purity as their methods will allow. Since the dividing line between a 90%-plus optical purity and the expected "maximum" level is tenuous beyond a certain point, other factors such as practicality, efficiency, generality, and overall appeal must be considered.

Controlling the stereochemical outcome of a chemical transformation has always been a major goal for synthetic organic chemists. Nowhere are such needs more manifest than in the synthesis of natural products and molecules of biological interest. Different eras have brought forth increasingly novel targets with correspondingly challenging solutions. While the goals have not changed over the years, the criteria for innovation have. New and often misused terms (*e.g.*, chiral this or that) have become a part of our spoken and oftentimes written lexicon. Bond formation is invariably considered in terms of site and stereochemical selection. While we may never beat nature at her own game of producing a plethora of products, we are becoming increasingly adept in producing what nature normally does not need, or possibly cannot make. This in itself is a major triumph of modern-day organic synthesis, and much of it is due to innovations in stereochemical control. When we consider stereochemical control, we generally focus on a given reaction at a time. However, it is the collection of several such transformations that constitutes a synthetic scheme culminating with the production of an optically pure (or enriched) compound. General synthetic approaches and global strategies to a given target may change depending on the investigator. This shows the individuality, creativity and personal philosophies of the synthetic chemist, and it enriches the subdiscipline of total synthesis enormously. Faced with a given transformation involving stereochemical control, however, opinions and ultimate

Professor Stephen Hanessian (left) receiving the first Canadian Alfred Bader Award in Organic Chemistry from Dr. Alfred Bader.

choices may not be as divergent as in the planning of the overall blueprint. Our common ground is the repertoire of "methods" that we are taught, and will, in turn, continue to teach. However, a blueprint for a synthesis is not an unrelated set of reactions, but a chain of interdependent events.

Stereochemical control in a given reaction relies on the application or exploration of notions and concepts well known in organic chemistry (Figure 1). Depending on the type of bond to be formed, we may exploit certain "effects" that are inherent in or imposed upon the substrate, in order to gain maximum stereochemical control. Coupled with these notions and effects is the proper choice of reaction conditions and an astute power of observation. The combination of all these factors may lead to the design of new reagents, catalysts, etc., hence to what we sometimes loosely refer as "innovation". Truly genuine innovation is rare, even if at first sight it appears to be unprecedented. We are all each other's intellectual feeders, reluctantly interdependent, learning still, yet rebelling for our identities and our place in the system.

At the present time, the main strategies for stereocontrolled synthesis are reagent- or substrate-based and involve either acyclic or cyclic molecules, or combinations thereof.[2] Such templates can be interconverted either before or after the chemical event and the effects listed in Figure 1 are operative here. Thus, with the aid of an "imposed" chiral auxiliary, and implicating notions of chelation, for example, it may be possible to functionalize an acyclic molecule in order to produce a stereochemically pure or enriched product as exemplified by the aldol condensation (Figure 2).[3] Asymmetric induction may also be brought about using external reagents or catalysts as in the Sharpless epoxidation, for example.[4] Cyclic molecules may be manipulated to benefit from a privileged conformation, from steric bias and topological effects. Bond formation in such systems will usually occur with a high level of stereochemical control. Enzymatic and microbial processes, as well as modern biotechnological methods, will play increasingly important roles in the synthetic chemist's repertoire of reagents and methods. A synthetic blueprint may draw upon one or more of these strategies in order to generate optically pure products. It is the judicious choice of such methods, coupled with good "timing" in the sequence, that will determine the optical purity of the final product. As previously mentioned, such issues as efficiency, practicality and overall appeal must be factored

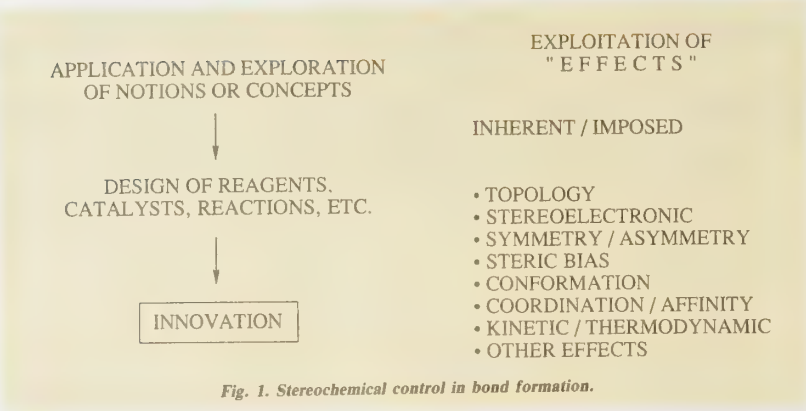


Fig. 1. Stereochemical control in bond formation.

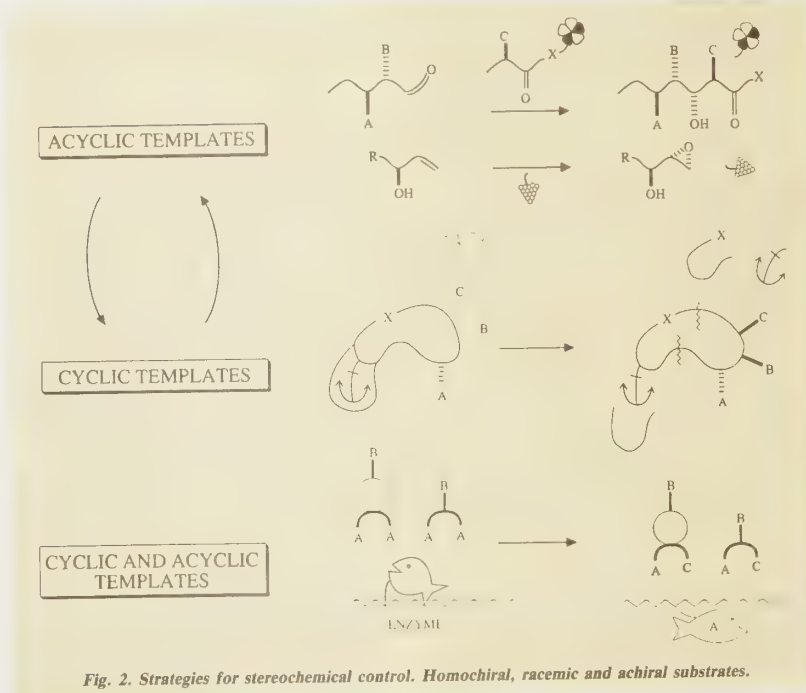


Fig. 2. Strategies for stereochemical control. Homochiral, racemic and achiral substrates.

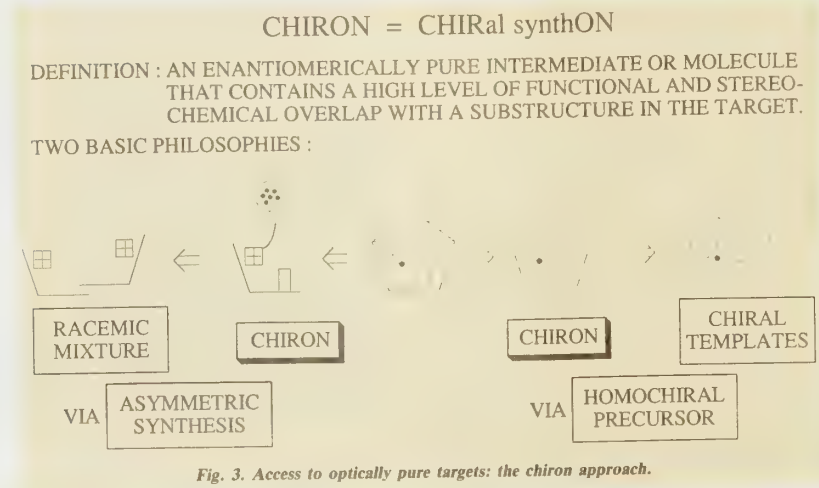


Fig. 3. Access to optically pure targets: the chiron approach.

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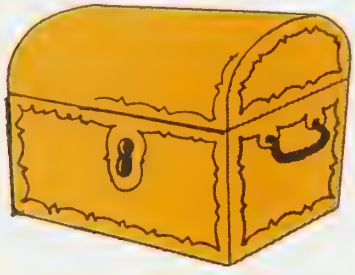

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- For compounds with a particular structural fragment or functionality, call or write us with any combination of the following parameters — *structural fragments, functional groups, ring systems, elements and molecular weight range.* We will send you a *free computer search* — a computer-generated list containing names, molecular formulas, prices and structures of all the compounds in the library that match your criteria.
- We offer **The Aldrich Microfiche Library of Chemical Indices** — a set of 24 microfiche lists all compounds in the Aldrich and the Alfred Bader Library inventories in alphabetical and molecular formula indices (see below). For details, consult our Catalog/Handbook or send for Technical Information Bulletin No. AL-179.
- Aldrich has now released the **Aldrichem Data Search**™ on CD-ROM (see insert in this issue). This invaluable database can be searched by catalog no., chemical name or name fragment, molecular formula, structure or structure fragment, etc.

We are constantly improving our information-retrieval systems to enhance our ability and increase our efficiency in helping you find compounds for your research.

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This updated version of the library includes 30,000 chemicals from the **Alfred Bader Library of Rare Chemicals**, 18,000 listed in our 1988-1989 Catalog/Handbook, and 1,800 listed since publication of the catalog. The listing features 2 indices - alphabetical and molecular formula.

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Aldrichimica Acta

Volume 22, Number 2, 1989

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	divalent	8
	tetrahedral	2
C	6-ring planar	14
	bonded planar	2 sets
	tetrahedral	24
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	tetrahedral	10
P	tetrahedral	4
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Volume 22, Number 2, 1989
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About Our Cover:

Fig. 1

Fig. 2

Readers of our *Acta* know how our chemist-collector loves puzzles. One of the greatest puzzles in Dutch 17th-century art is the identity of the Master IS, an artist active in the middle of the century, influenced by Rembrandt. Only about a dozen of his works are known, and these are usually dated about 1650. One of his masterpieces, dated 1649, graced the cover of our *Acta,* Vol. 16, No. 1.

His best known work is a moving portrait of an old woman (Fig. 1) in the Kunsthistorisches Museum in Vienna. Recently, our chemist-collector acquired the painting on our cover (oil on wood, 18½ x 14 inches), monogrammed but undated, of a woman looking up from her book—perhaps a biblical subject—possibly Hannah in the Temple (Luke 2). Did the artist depict his mother as Rembrandt depicted his in 1631, in the painting (Fig. 2) now in the Rijksmuseum in Amsterdam?

As discussed in *The Detective's Eye* described below, the artist's figures look Eastern European. Did an eastern or perhaps a Scandinavian artist come to Amsterdam to study with Rembrandt?

The Master IS: a monogram in search of a name.

NEW

The Detective's Eye: Investigating the Old Masters

Twenty-one paintings that have been reproduced on our *Acta* covers and five that have been on our catalog covers were among some seventy works in an exhibit at the Milwaukee Art Museum (January 19 - March 19, 1989) for which Isabel and Alfred Bader were guest curators.

If you relish detective work and puzzles about Old Master paintings, you will find much to enjoy in this fully illustrated catalog, and you will learn something about our chemist-collector's interest in art and connoisseurship as well.

Z18,350-4 $12.00

Rembrandt and the Bible - in Japan

We are offering a limited number of a 174-page catalog of an exhibition in Japan, the first of its kind there, on Rembrandt and the Bible. The scholarly essays in Dutch, English, German and Japanese deal with works by Rembrandt and his students — 38 paintings, 7 drawings and 44 etchings, all beautifully illustrated. Thirteen of the paintings, all in full color, have appeared on covers of the *Acta*. The works are fully described in English and Japanese. An unusual and wonderful buy for lovers of art and the Bible!

Z16,235-3 $12.00

Pictures from the Age of Rembrandt

Twenty-five paintings that have been reproduced on our *Acta* covers, and six that have been on our catalog covers are among the thirty-six paintings in an exhibition of Dutch paintings at Queen's University in Kingston, Ontario. The fully illustrated catalog written by Professor David McTavish contains a wealth of art-historian information — enough for several evenings of relaxed enjoyment — probably the best value in art-history anywhere.

Z12,794-9 $8.00

Lab Notes

I wish to direct this suggestion to chemists who do some glassblowing or to those involved in a user-friendly glassblowing shop.

There is no common, ready source of screw-thread connections for use as building blocks for glassblowing. The most common screw-thread size is 13-425. The Wheaton Micro Kit® (Z10,372-1), which has many useful applications, is a very good example of screw-thread connection utility. The 5-ml Wheaton round-bottom micro flask (Z10,667-4) has a 13-425 screw-thread, but there is another option. The 4-ml Wheaton sample vial (Z18,870-0) offers an inexpensive source of 13-425 screw-thread. These vials are borosilicate glass and can be easily connected to Pyrex® glass or other glass of similar quality.

Pavel Drasar
Institute of Organic Chemistry and Biochemistry
Flemingovo 2
CS-166 10 Praha 6
Czechoslavakia

Editor's note: We are pleased to offer the Wheaton sample vial with 13-425 screw-thread suggested by Pavel Drasar.

Z18,870-0 Wheaton sample vials, clear, 4ml, 13-425 (pkg = 200) **$40.40**

Z10,667-4 Wheaton round-bottom micro flask, 5ml, screw-thread size 13-425 **$8.90**

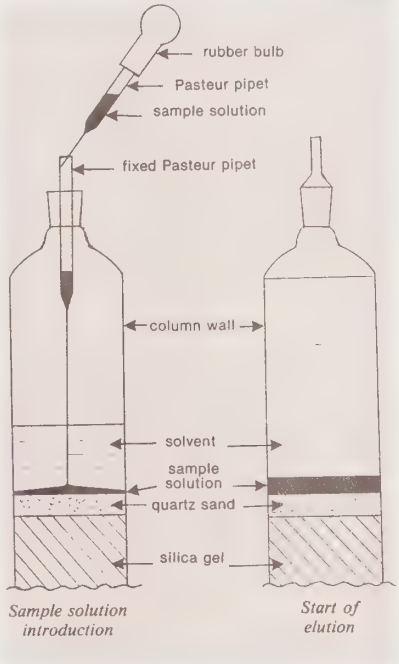
Z10,372-1 Wheaton Micro Kit $322.20

Aldrich also carries other screw-thread Wheaton glassware, as well as caps and septa to fit screw-thread size 13-425. Please check the Equipment Section of our Catalog/Handbook or contact us for more information.

® Pyrex is a registered trademark of Corning Glass Works. Micro Kit is a registered trademark of Wheaton.

Introduction of a sample on a chromatographic column is the most critical part of widely used procedures such as "flash", "filtering-column" and "vacuum" chromatography. Most often, it is recommended that the sample solution be introduced *via* a Pasteur pipet on a wet silica gel bed from which the solvent has been eluted. This method is prone to the risks of bed surface disturbance and uneven sample application with resulting decrease in column efficiency. For several years our lab has used a simple method which does not carry these risks.

Fix a Pasteur pipet with a long capillary with narrow end (to reduce flow) above the prepared chromatographic column. The column must contain a 2-10cm layer of solvent on top of the silica gel bed, preferably covered with a 1-2cm layer of quartz sand (see Figure). The pipet tip should end just above (1-2mm) the surface of the column bed. Dissolve the sample in a solvent (mixture) of high specific gravity but low elution power. CCl_4, $CHCl_3$, benzene and cyclohexane are recommended. The specific gravity of the solvent for sample dissolution should exceed that of the eluting solvent system by at least 0.1. Rapidly transfer the sample solution using a shortended Pasteur pipet, into the one fixed on the column. In several seconds the sample solution will form an even layer between the top of the column bed and the solvent layer. Remove the Pasteur pipet, add (if necessary) additional solvent and start chromatography (vacuum, gravity, low-pressure). The sample will automatically and very efficiently load onto the chromatographic sorbent at the beginning of elution. According to measurements, the procedure results in approximate doubling of the effectiveness of flash chromatography in terms of theoretical plate number.



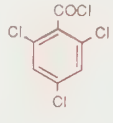
Kasimir K. Pivnitsky
Institute of Experimental Endocrinology and Hormone Chemistry
AMS USSR, 1 ul. Moskvorechje
115522 Moscow, USSR

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt.** *We reserve the right to retain all entries for consideration for future publication.*

"Please Bother Us."

by Cyrus Bader.

Professor K.C. Nicolaou of the University of Pennsylvania suggested that we offer ***2,4,6-trichlorobenzoyl chloride*** used in Yamaguchi's efficient method of converting long-chain hydroxy acids to large-ring lactones.[1] This macrolactonization procedure involves initial formation of a mixed anhydride between the substrate hydroxy acid and ***2,4,6-trichlorobenzoyl chloride***, followed by ring closure (lactonization) on treatment with DMAP in toluene solution. Yamaguchi's method has been used in the syntheses of macrocyclic lactones such as elaiophylin,[2] (-)-cladospolide A,[3] neomethynolide,[4] (+)-conglobatin,[5] and 6-*epi*-colletodiol.[6]



Naturally, we made it.

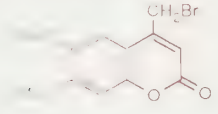
(1) Yamaguchi, M. *et al. Bull. Chem. Soc. Jpn.* **1979,** *52,* 1989. (2) Kinoshita, M. *et al. ibid.* **1988,** *61,* 2369. (3) Mori, K.; Maemoto, S. *Liebigs Ann. Chem.* **1987,** 863. (4) Inanaga, J.; Kawanami, Y.; Yamaguchi, M. *Bull. Chem. Soc. Jpn.* **1986,** *59,* 1521. (5) Schregenberger, C.; Seebach, D. *Liebigs Ann. Chem.* **1986,** 2081. (6) Tsutsui, H.; Mitsunobu, O. *Tetrahedron Lett.* **1984,** *25,* 2163.

34,550-4 2,4,6-Trichlorobenzoyl chloride, 97% **5g $11.00; 25g $29.00**

It was no bother at all, just a pleasure to be able to help.

COUMARINS

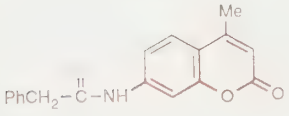
Coumarins, chromones and chromanones comprise an important class of heterocyclic compounds which finds varied applications in chemistry. Coumarins have been used as fluorescent labels over the past several decades[1-5] for such substrates as carboxylic acids,[6] surfactants[7] and enzymes.[8,9] They have also found utility in the synthesis of medicinally important compounds[10-12] and in organic synthesis.[13] Listed below are some of these important compounds which are available from Aldrich. For a complete listing of these products, by class, please contact our Technical Services Department at 800-231-8327.



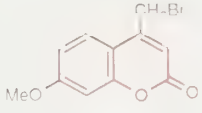
30,145-0
4-(Bromomethyl)-6,7-dimethoxycoumarin, 97%
1g $37.05

19,564-2
7-Ethoxycoumarin, 99.5%
100mg $18.05; 1g $74.80

23,519-9
7-Methoxycoumarin-4-acetic acid, 99%
500mg $25.70

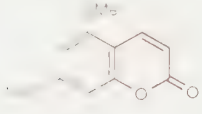


33,146-5
4-Methyl-7-(phenylacetamido)coumarin, 98%
500mg $15.00; 1g $25.00

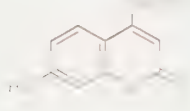


23,520-2
4-(Bromomethyl)-7-methoxycoumarin, 97%
1g $22.60; 5g $92.00

33,147-3
7-(Phenylacetamido)-4-(trifluoromethyl)-coumarin, 98%
250mg $10.00; 1g $28.00

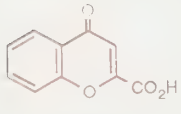


11,623-8
5,7-Dimethoxycoumarin
1g $20.40; 5g $79.10

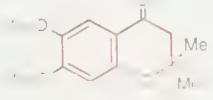


33,566-5
7-Hydroxycoumarin-4-acetic acid, 98%
1g $9.00; 5g $36.00

12,235-1
4-Chromanone, 97%
5g $26.10; 10g $38.55



18,978-2
4-Oxo-4*H*-1-benzopyran-2-carboxylic acid, 97% (chromone-2-carboxylic acid)
97%
5g $18.70



30,063-2
6,7-Dimethoxy-2,2-dimethyl-4-chromanone, 98%
1g $20.40; 5g $66.85

31,640-7
6,7-Dimethoxy-4-methylcoumarin, 99%
1g $14.50; 5g $48.00

For bulk quotes on these catalog items and for custom synthesis requests for coumarins, chromones and chromanones that are not currently listed, please contact our Bulk Sales Department at 800-255-3756.

References:

(1) Yoshida, S.; Adachi, T.; Hirose, S. *J. Chromatogr.* **1988**, *430*, 156. (2) Small, J.V.; Zobeley, S.; Rinnerthaler, G.; Faulstich, H. *J. Cell Sci.* **1988**, *89*, 21. (3) Grayeski, M.L.; DeVasto, J.K. *Anal. Chem.* **1987**, *59*, 1203. (4) Yoshida, S.; Hirose, S.; Iwamoto, M. *J. Chromatogr.* **1986**, *383*, 61; Bousquet, E.; Romeo, G.; Giannola, L. *ibid.* **1985**, *344*, 325. (5) Scheper, T.; Weiss, M.; Schuegerl, K. *Anal. Chim. Acta* **1986**, *182*, 203. (6) Farinotti, R. *et al. J. Chromatogr.* **1983**, *269*, 81; Crozier, A. *et al ibid.* **1982**, *249*, 323; Voelter, W. *et al. ibid.* **1981**, *217*, 491; Desbene, D.L. *et al. Anal. Biochem.* **1983**, *128*, 359. (7) Kondoh, Y; Takano, S. *Anal. Sci.* **1986**, *2*, 467. (8) Reinke, L.A.; Tupper, J.S.; Smith, P.R.; Sweeny, D.J. *Mol. Pharmacol.* **1987**, *31*, 631. (9) Murakami, H. *et al. DNA* **1987**, *6*, 189. (10) Hanmantgad, S.S. *et al. Indian J. Chem.* **1986**, *25B*, 779. (11) Hanmantgad, S.S.; Kulkarni, M.V.; Patil, V.D. *Rev. Roum. Chim.* **1985**, *30*, 735. (12) Thakur, R.S.; Bagadia, S.C.; Sharma, M.L. *Experientia* **1978**, *34*, 158. (13) Cho, T.H.; Shim, H.K.; Shim, S.C. *Bull. Korean Chem. Soc.* **1987**, *8*, 206; Shim, S.C. *et al. J. Photochem.* **1987**, *37*, 125; Primo Millo, J. *et al. Rev. Agroquim. Tecnol. Aliment.* **1980**, *20*, 489; Waykole, P.; Usgaonkar, R.N. *Indian J. Chem.* **1984**, *23B*, 478.

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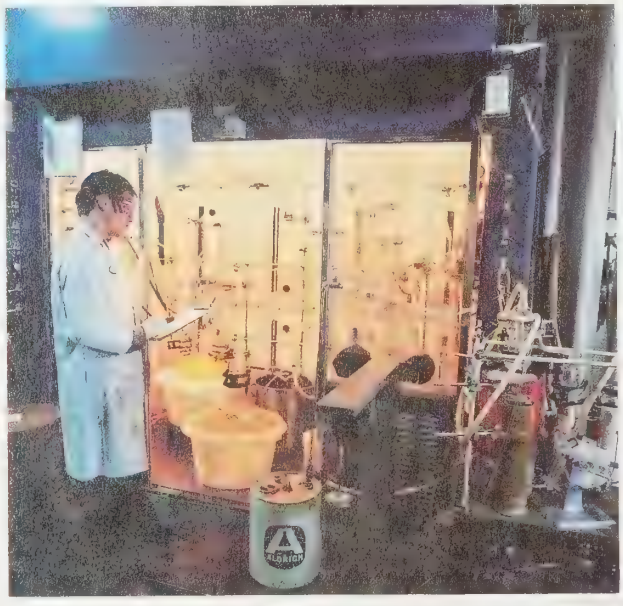

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Aldrichimica Acta

Volume 22, Number 3, 1989 (Last issue in 1989)

Mechanistic Ingenuity in Enzyme Catalysis: Dehydroquinate Synthase

At the Organic Chemistry/Bioscience Interface: Rate Processes in Complex Systems

chemists helping chemists in research & industry

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New Products
from our Stable Isotopes Department

Aldrich's Stable Isotopes Department is diligently working to provide high-quality products to the scientific community. Part of this effort is directed towards producing new products in response to customer suggestions and inquiries. Listed below are just a few of the new products we have added since our last Catalog/Handbook was published. For bulk quotations on any of these products, as well as requests for custom syntheses, please contact our Bulk Sales Department at 800-255-3756.

Please contact our Technical Services Department to suggest new additions to our Stable Isotopes product line.

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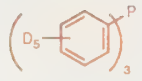

Useful ligand for NMR spectroscopy and mechanistic studies.

Siedle, A.R.; Newmark, R.A. *J. Am. Chem. Soc.* **1989**, *111*, 2058. Baldwin, J.E. *et al. J. Org. Chem.* **1987**, *52*, 3303.

33,876-1 1g $78.75

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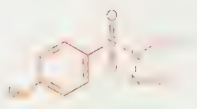

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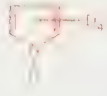

Used in spectroscopic studies and for preparing deuterium-labeled porphyrins.

Groves, J.T. *et al. J. Am. Chem. Soc.* **1985**, *107*, 354.

34,438-9 1g $120.00; 5g $400.00

Lithium-6, 95 atom % ^6Li

^6Li

Used to prepare lithium-6 reagents for ^6Li NMR studies.

Berta, S.H.; Dabbagh, G. *J. Am. Chem. Soc.* **1988**, *110*, 3668. Bates, T.F. *et al. ibid.* **1988**, *110*, 5109.

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Smith, G.M. *et al. Biochemistry* **1987**, *26*, 2202. Nicholson, L.K. *et al. ibid.* **1987**, *26*, 6621.

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Bu_3SnD

Useful deuterated reducing agent.

Praly, J.P. *Tetrahedron Lett.* **1988**, *24*, 3075.

34,103-7 1g $22.50; 5g $75.00

Boron trifluoride-methanol-d_4 complex, in excess methanol-d_4

(*ca.* 12% BF_3)

$BF_3 \cdot CD_3OD$

Reagent for preparing deuterated methyl esters.

33,155-4 1g $15.00; 5g $50.00

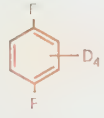
$H_2{}^{17}O$ $H_2{}^{18}O$

Low-enrichment oxygen isotopes for a variety of uses including biosynthetic and mechanistic studies.

Ackland, M.J. *et al. Chem. Commun.* **1987**, 1492. Evans, A.R.; Taylor, G.A. *J. Chem. Soc., Perkin Trans. 1* **1987**, 567.

33,208-9 Water-^{18}O, normalized, ~10 atom % ^{18}O **1g $18.50; 5g $60.25**
34,850-3 Water-^{17}O, 10 atom % ^{17}O **250mg $30.00; 1g $85.00**

1,4-Difluorobenzene-d_4, 98 atom % D



Useful molecule for spectroscopic studies; has been used in fluorescence studies at low temperatures and IR and Raman studies in the vapor phase.

Childs, A.F. *et al. J. Mol. Spectrosc.* **1983**, *102*, 56. Zimmerman, R.L.; Dunn, T.M. *ibid.* **1985**, *110*, 312.

34,746-9 250mg $27.00; 1g $90.00

Tetrakis(trimethylsilyl)-silane, 98%

$(Me_3Si)_4Si$

Solid-state NMR reference standard.

Munteau, J.V. *et al. J. Magn. Reson.* **1988**, *76*, 540.

32,992-4 1g $12.00; 10g $62.00

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Volume 22, Number 3, 1989
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About Our Cover:

Fig. 1

Our chemist-collector loves puzzles, and so he purchased this painting not only because he liked it but because he hoped to be able to identify the artist and the sitter.

A great deal has been written about the painting—for instance, by Professor David McTavish in the *Age of Rembrandt*, offered below, and we cite his description here.

This elegant portrait (oil on canvas, 96½ x 78cm) is greatly influenced by Anthony van Dyck's *Portrait of Lucas van Uffeln*, now in the Metropolitan Museum of Art, New York (Fig.1). No doubt van Dyck painted the merchant and shipowner from Antwerp in Venice in 1622, some 20 years earlier than this portrait. Van Uffeln died in Amsterdam in 1637, and his possessions were auctioned there in 1637 and 1639, and it seems likely that our artist saw the van Dyck portrait at that time.

Our portrait shows an intelligent and refined man who, having just been interrupted at his studies, turns in ¾-profile to look at the spectator. The table holds what, in the seventeenth century, was thought to be a bust of Seneca, a portrait engraving and a book of music. Together, these objects suggest the sitter's interest in the arts and learning. Although the portrait furnishes us much information about the sitter, he has not yet been identified.

Nor has the name of the painter been established unequivocally. While the portrait clearly relies on van Dyck's precedent, the components have been rearranged in a more classical way. The handling of paint is also more restrained.

In time we hope that both identities—of artist and sitter—will be determined. Don't hold your breath, however, it may take a long time.

The beauty of this work makes it a fitting cover for the elegant papers by Professor Jeremy Knowles and Dr. Keith Ingold.

Disposable polyethylene gloves only come in one size which is far from form-fitting, resulting in a loss of dexterity to the wearer. I have found a simple solution to the problem. If rubber bands, approximately 1.5cm in diameter, are placed over each gloved finger and thumb much like rings, the excessive material can be concentrated at the base of the fingers and thumb leaving the fingertips unencumbered, greatly increasing dexterity and thus reducing the risk of dropping objects or knocking them over when reaching to grasp them.

Bliss S. Phillips, Chemist
NRRC, ARS, USDA
3417 W. Capitol Dr.
Peoria, IL 61614

On reading the note on a small-scale filtration device from Messrs. Muir and Johnson [*Aldrichim. Acta* **1987,** *20*(3), 62], I was sorry to find that they had spent time perfecting something described by the late Louis F. Fieser in *Experiments in Organic Chemistry,* 2nd ed., 1941, p 322.

As a recently retired organic chemist who spent most of his working life at the bench, I have to recommend this book and the subsequent *Organic Experiments,* 1964, with a third edition in 1975, as absolutely essential reading for every organic preparative chemist. Further reading I commend includes *Morton's Laboratory Technique in Organic Chemistry,* 1938, and all the volumes of *Organic Syntheses.*

F.E. Smith
16 Broomleaf Road
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England

Any interesting shortcut or laboratory hint you'd like to share with Acta readers? Send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt.** *We reserve the right to retain all entries for consideration for future publication.*

Mechanistic Ingenuity in Enzyme Catalysis: Dehydroquinate Synthase

Jeremy R. Knowles
Department of Chemistry
Harvard University
12 Oxford Street
Cambridge, MA 02138

At first sight, enzymes are formidable catalysts. The specificity that enzymes show in substrate recognition and binding is exquisite, and the rate at which the subsequent chemical transformations are performed is extraordinary. An enzyme selects its substrate out of the thousands of metabolites in the cell, or finds its particular recognition site out of millions of more-or-less similar places on a DNA molecule, with unerring fidelity. Then, having formed the enzyme:substrate complex, a sequence of chemical steps follows at rates still unmatched by man's efforts. Yet as we learn more, and as we understand better, enzyme catalysts seem more ingenious than awesome. This shift in attitude of mechanistic enzymologists is nicely illustrated by the consideration of one enzyme, dehydroquinate synthase, which is responsible for the formation of the first six-membered carbocycle in the metabolic pathway that leads to the three aromatic amino acids.

The shikimate pathway, as illustrated in Figure 1, is the sequence of reactions that, in plants and microorganisms, produces phenylalanine, tyrosine and tryptophan, along with a host of other primary and secondary metabolites from ubiquinone to morphine.[1] The pathway begins with the condensation of phosphoenolpyruvate and erythrose 4-phosphate to give the seven-carbon keto acid, 3-deoxy-D-*arabino*-heptulosonate 7-phosphate (DAHP). This material is then converted into the carbocycle dehydroquinate (DHQ) by dehydroquinate synthase.[2,3] The pathway continues with the elaboration of the appropriate substituents and the generation of unsaturation to produce chorismate, which is the point at which the routes to the three aromatic amino acids diverge. The shikimate pathway is full of interesting and unusual enzymology, but we focus here on the second enzyme of the sequence, dehydroquinate synthase.

Dehydroquinate synthase is a monomeric protein of 362 amino acids[4] that requires, for catalytic activity, the presence of both a divalent metal cation [cobalt(II) has often been used in mechanistic studies on the enzyme, though zinc(II) is the more likely cation for the enzyme *in vivo*] and nicotinamide adenine dinucleotide (NAD^+).[2-4] The enzyme binds one metal ion and one NAD^+.[5] The need for NAD^+, a redox cofactor, is not immediately obvious since the

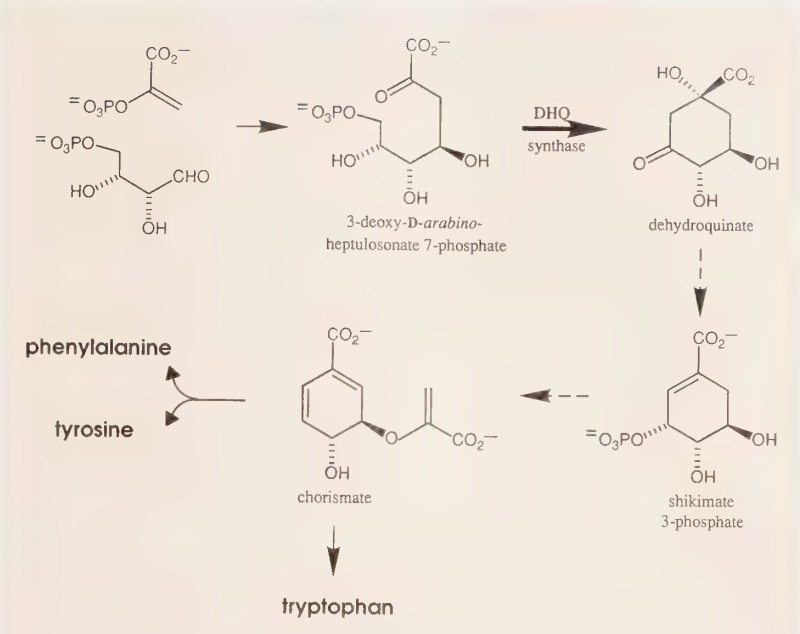


Fig. 1. ***The shikimate pathway.*** *In plants and in microorganisms, this metabolic sequence leads to the production of, among other things, the three aromatic amino acids: phenylalanine, tyrosine and tryptophan.*

Professor Jeremy Knowles (left) receiving the Alfred Bader Award in Bioorganic Chemistry from Dr. Alfred Bader.

overall conversion of DAHP to DHQ and inorganic phosphate (P_i) is redox neutral. In 1963, however, Sprinson neatly explained the NAD^+ requirement of the synthase by proposing the pathway shown in Figure 2.[2,6] In this proposal, the substrate DAHP (**1**) binds to the active site, and is oxidized at C-5 by enzyme-bound NAD^+ to produce the C-5 ketone (**I**) and NADH. The second step of the reaction then involves β-elimination of inorganic phosphate across C-6 and C-7 to yield the enone **II**. According to this pathway, the function of NAD^+ is to effect the oxidative activation of the substrate, which acidifies the C-6 proton and facilitates the phosphate elimination step. Phosphate having been lost, the enzyme-bound NADH now reduces the ketone at C-5 (regenerating the same configuration as in DAHP, **1**) to give the enol pyranose **III**. Ring opening of this species to **IV**, and then reclosure by attack of the enolate carbon (C-7) on the carbonyl group at C-2 in an intramolecular aldol reaction, produces DHQ (**2**) and completes the reaction. Chemically and logically this pathway is very attractive, and has many features that would surely have been included had an organic chemist been responsible for the design of dehydroquinate synthase.

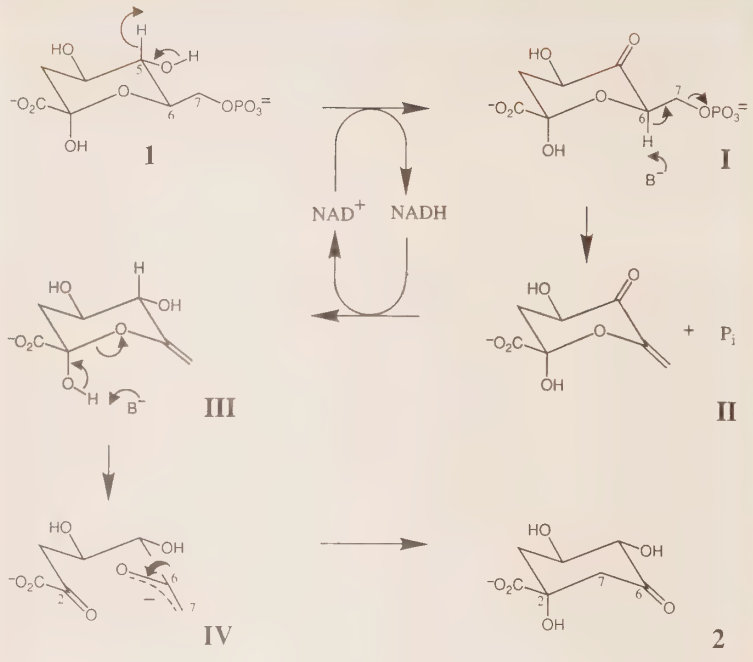
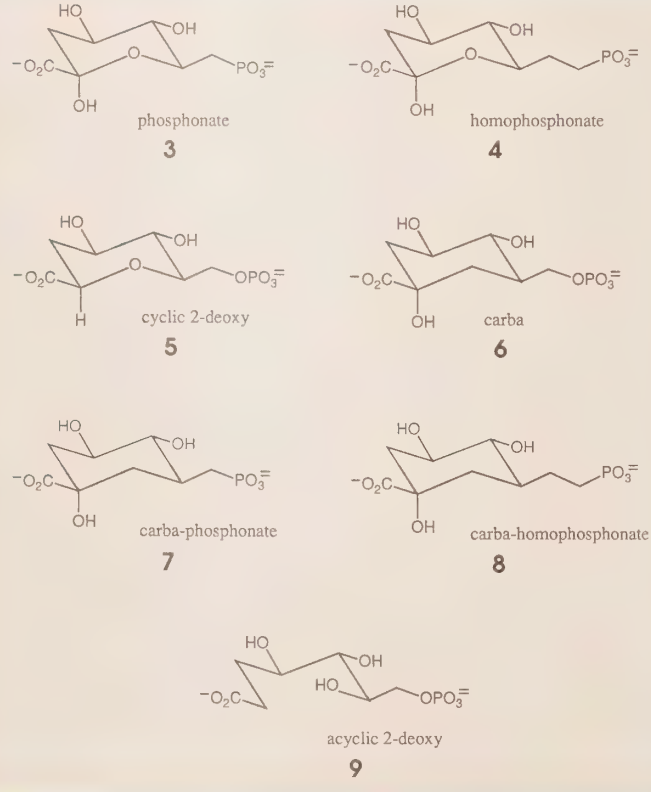


Fig. 2. The proposed mechanistic pathway followed by dehydroquinate synthase. *The substrate, 3-deoxy-D-arabino-heptulosonate 7-phosphate* ***(1)*** *is transformed in five steps to dehydroquinate* ***(2)****.*

Yet there are some troubling features for the enzymologist, not the least of which is the problem of how a monomeric enzyme, presumably having a single active site, can contain enough precisely placed catalytic groups to catalyze four different chemical processes. For the pathway of Figure 2 makes dehydroquinate synthase into a dehydrogenase, a phospho-lyase, a pyranose-opening enzyme, and an internal aldolase. Elsewhere in nature, enzymes exist whose sole function is to perform just one of these tasks, and we may reasonably ask whether dehydroquinate synthase represents what an enzyme can achieve (with the implication that most other enzymes are relatively pathetic), or whether the mechanism proposed for dehydroquinate synthase is somehow overambitious.

To attack the problems posed by the mechanism outlined in Figure 2, we have chosen to evaluate the behavior of a series of substrate analogs that, by virtue of minor structural alterations, cannot complete the reaction sequence. Thus the phosphonate analog **3** and homophosphonate analog **4** can only suffer the first catalytic step (as far as **I**, Figure 2), since the loss of P_i in the second step is (for **3** and **4**) impossible. The cyclic 2-deoxy analog **5** and the carba analog **6** can both, in principle at least, undergo the first three steps of the proposed pathway as far as **III** (Fig. 2), but can go no further because the ring-opening reaction of the fourth step is precluded.



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15,726-0

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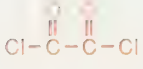

Versatile chlorinating agent.

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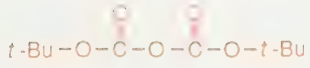
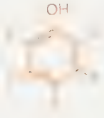


t-Boc reagent for peptide synthesis.

19,913-3

Pentafluorophenol



Preparation of PFP esters for peptide synthesis.

10,379-9

1,1′-Carbonyldiimidazole

Preparation of N-acyl amino acids.

11,553-3

1,3-Diisopropylcarbodiimide

Peptide-condensing agent.
(Send for Technical Information Bulletin No. AL-168.)

D12,540-7

Methyltriphenylphosphonium bromide

Phase-transfer reagent.

13,007-9

1-Acetylimidazole

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15,786-4

1,2,3,4,5-Pentamethylcyclopentadiene

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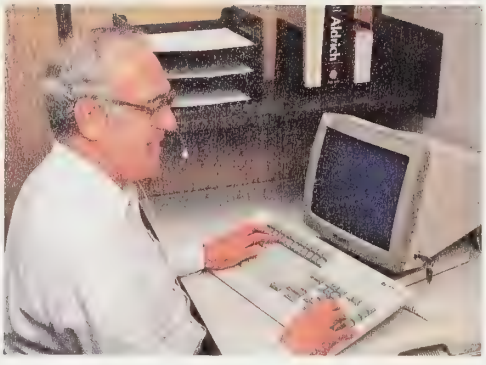

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Long-Range Electron Transfer in Proteins

Understanding and Controlling Diastereofacial Selectivity in Carbon-Carbon Bond-Forming Reactions

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Fluorine Compounds for Analysis

High volatility and electron affinity of fluorinated compounds have led to their increasing use as derivatizing agents for trace analysis. The primary areas of use are in Gas Chromatography-Electron Capture Detector (GC-ECD) and Gas Chromatography/Mass Spectrometry (GC/MS).

Gas Chromatography-Electron Capture Detector

GC-ECD is a sensitive method of detection which has found extensive use in trace quantity analysis of pesticide residues. Derivatization by fluorinated reagents allows the analysis of mixtures containing traces of amines,[1] acids [2] or amino acids,[3] at concentrations lower than 10 µg/L.

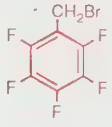
Gas Chromatography/Mass Spectrometry

GC/MS has been used recently in Selected Ion Monitoring (SIM) mode to detect heptafluorobutyric anhydride derivatives of amphetamine and methamphetamine simultaneously at concentrations down to 35 ng/ml.[4] Atropine in blood was similarly detected at concentrations down to 10 ng/ml.[5] Other reagents have been used to characterize materials such as alkyl and hydroxyalkyl nucleobase DNA adducts,[6] to identify indoles,[7] and to determine amino acids in tissues.[8]

References:

(1) Skarping, G. *et al. J. Chromatogr.* **1989**, *479*, 125. (2) Allender, W.J. *J. Anal. Toxicol.* **1990**, *14*, 45. (3) Wang, J. *Sepu* **1989**, *7*, 251. (4) Taylor, R.W.; Le, S.D.; Philip, S.; Jain, N.C. *J. Anal. Toxicol.* **1989**, *13*, 293. (5) Saady, J.J.; Poklis, A. *ibid.* **1989**, *13*, 296. (6) Saha, M.; Kresbach, G.M.; Giese, R.W.; Annan, R.S.; Vouros, P. *Biomed. Environ. Mass Spectrom.* **1989**, *18*, 958. (7) Bosin, T.R.; Faull, K.F. *ibid.* **1989**, *18*, 247. (8) Brink, C.; Carlberg, M.; Elofsson, R. *Comp. Biochem. Physiol., C: Comp. Pharmacol. Toxicol.* **1989**, *92C*, 201.

Versatile analytical reagent

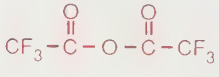


Used in the preparation of organic esters for determination by GC-ECD;[1] as well as in MS characterization of nucleobase DNA adducts,[2] quantitative GC/MS[3] and prostaglandin analysis.[4]

(1) Kawahara, F.K. *Anal. Chem.* **1968**, *40*, 2073. (2) Saha, M.; Kresbach, G.M.; Giese, R.W.; Annan, R.S.; Vouros, P. *Biomed. Environ. Mass Spectrom.* **1989**, *18*, 958. (3) Leis, H.J.; Gleispach, H.; Malle, E. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 263. (4) Rosenfeld, J.M.; Mureika-Russell, M.; Love, M. *J. Chromatogr.* **1989**, *489*, 263.

10,105-2 α-Bromo-2,3,4,5,6-pentafluorotoluene, 99 + % **1g $9.00 5g $30.40; 25g $104.85**

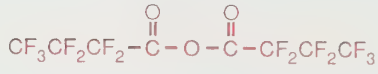
N- and O-Trifluoroacetyl derivatives precursor



For the preparation of *N*- and *O*-trifluoroacetyl derivatives of a wide range of biologically active compounds for GC analysis.

10,623-2 Trifluoroacetic anhydride, 99 + % **25g $9.05; 100g $22.25 500g $71.00**

Analytical reagent for biological amines

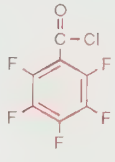


Reagent for the determination of amino acids,[1] amines in biological fluids,[2] pipecolic acid in serum or plasma,[3] and in the analysis of platelet-activating factor.[4]

(1) Wang, J. *Sepu* **1989**, *7*, 251. (2) Skarping, G. *et al. J. Chromatogr.* **1989**, *479*, 125. (3) Bocxlaer, J.F. *et al. Biomed. Environ. Mass Spectrom.* **1988**, *18*, 566. (4) Satsangi, R.K.; Ludwig, J.C.; Weintraub, S.T.; Pinckard, R.N. *J. Lipid Res.* **1989**, *30*, 929.

15,739-2 Heptafluorobutyric anhydride, 98% **5g $12.20; 25g $41.90**

Derivatizing agent for anticonvulsant standards

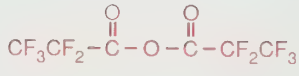


Derivatizing agent for a number of reference standards for anticonvulsion agents for analysis by GC-ECD.

Wallace, J.E.; Schwertner, H.A.; Hamilton, H.E.; Shimek, E.L. *Clin. Chem.* **1979**, *12*, 11.

10,377-2 Pentafluorobenzoyl chloride, 99% **1g $12.60; 5g $38.80; 25g $121.05**

Reagent for amines and fatty acids

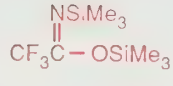


Fluorinated reagent for the determination of amines in biological fluids,[1,2] separation of amino acid enantiomers,[3] ultrasensitive analysis of microbial fatty acids,[4] and GC determination of histidine derivatives.[5]

(1) Tiljander, A.; Skarping, G.; Dalene, M. *J. Chromatogr.* **1989**, *479*, 145. (2) Sandstroem, J.F.; Skarping, G.; Dalene, M. *ibid.* **1989**, *479*, 135. (3) Abdalla, S.; Bayer, E.; Frank, H. *Chromatographia* **1987**, 83. (4) Larsson, L.; Sonesson, A.; Jimenez, J. *Eur. J. Clin. Microbiol.* **1987**, *6*, 729. (5) Rogoskin, V.A.; Krylov, A.; Khlebnikova, N.S. *J. Chromatogr.* **1987**, *423*, 33.

25,238-7 Pentafluoropropionic anhydride, 99% **5g $15.00; 25g $54.75**

Derivatizing agent for primary amines



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15,519-5 Bis(trimethylsilyl)trifluoroacetamide, 99 + % **5g $9.30 25g $40.70; 100g $135.00**

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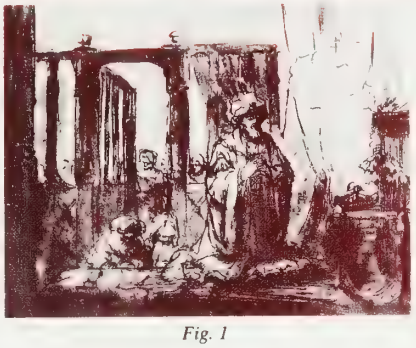

Fig. 1

Readers of our *Acta* know how much our chemist collector loves the works of one Rembrandt student, Gerbrand van den Eeckhout, who was also Rembrandt's good friend. This is our fourth cover depicting an Eeckhout.

There is a preparatory drawing (Fig. 1) for this painting (oil on canvas, 21½x 25 inches), which shows how the artist began by wanting to depict King Solomon's idol worship; note that on the very right of the drawing is the foot of an idol. However, in the painting, done in the 1660's, the King seems to be praying with great devotion. Perhaps the artist changed his mind and finally depicted Solomon praying in the Temple.

This is one of the few paintings of the Rembrandt school portraying King Solomon. It is surely significant that Rembrandt and his students concerned themselves far more with the agonies of King Saul and the vicissitudes of King David than with the successes of Solomon. In his handling of light, Eeckhout comes close to works of his teacher and friend. He contrasts the simple architectural forms of the Temple with the splendor of Solomon's clothing and jewelry, achieving that effect by the use of white dots of light, a technique used by Rembrandt in his works of the 1630's.

From Dura to Rembrandt - Studies in the History of Art

A collection of nineteen papers, seventeen in English and two in German, by Rachel Wischnitzer (1885-1989) ranging from synagogue architecture to the iconography of works by Rembrandt, together with this remarkable woman's life story, written by Prof. Bezalel Narkiss, the director of the Center for Jewish Art at the Hebrew University. A wonderful gift for any good friend.

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The Detective's Eye: Investigating the Old Masters

Twenty-three paintings that have been reproduced on our *Acta* covers and five that have been on our catalog covers were among some seventy works in an exhibit at the Milwaukee Art Museum (January 19 - March 19, 1989) for which Isabel and Alfred Bader were guest curators.

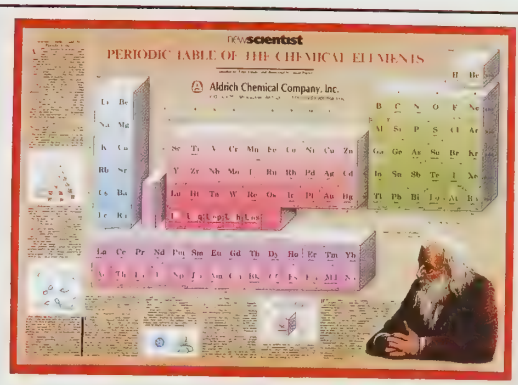
If you relish detective work and puzzles about Old Master paintings, you will find much to enjoy in this fully illustrated catalog, and you will learn something about our chemist collector's interest in art and connoisseurship as well.

Z18,350-4 **$12.00**

Lab Notes

No matter how careful laboratory technicians may be, once in a while ground glass stoppers jam in flask necks. This can be particularly annoying if it happens on a filled separatory funnel. We have solved this problem by passing a Pasteur pipette through the stopcock of the separatory funnel as shown in the figure. This allows air to come into the separatory funnel while the liquid comes out cleanly and without loss of material.

Ann Haestier
Department of Chemistry
Brandeis University
Waltham, MA 02254-9110



Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes). For submitting your idea, you will receive, *at no cost*, a laminated periodic table poster (Z15,000-2 $9.20, shown above). If we publish your *Lab Note*, you will also receive **The Detective's Eye: Investigating the Old Masters** (see previous page). We reserve the right to retain all entries for consideration for future publication.

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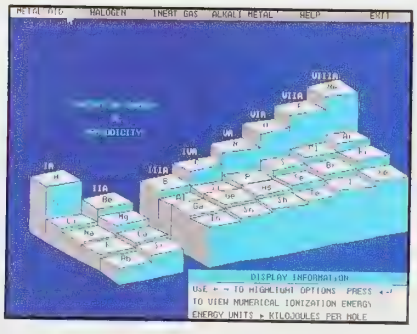

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Professor Alfred Hassner of Bar-Ilan University kindly suggested that we offer a polymeric quaternary ammonium azide reagent.[1] Alkyl, benzyl, and alpha-keto azides[2] are cleanly prepared from alkyl halides or sulfonates under mild conditions using this heterogenous reagent.

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(1) Hassner, A.; Stern, M.; Gottlich, H.E. *J. Org. Chem.* **1990**, *55*, 2304. (2) Hassner, A.; Stern, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 478.

36,834-2 Azide exchange resin, azide on Amberlite® IRA-400
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Long-Range Electron Transfer in Proteins

Harry B. Gray
Beckman Institute
California Institute of Technology
Pasadena, California 91125

Experiments in several laboratories over the last few years have established that electron transfer (ET) in modified proteins and protein-protein complexes can take place over long molecular distances (>10 Å) at biologically significant rates.[1-4] The goal of our work in this field is elucidation of the factors that control the rates of these reactions.

Ruthenated Proteins

The molecules we have employed are ones in which ruthenium ammines are attached to surface histidines of structurally characterized redox proteins.[5-7] Surface modification of a protein is expected to be nonperturbative,[8] so it can be assumed that the structure of the modified protein is the same as that of the native protein. Hence, the distance and the intervening medium involved in electron transfer between the native and synthetic protein redox sites are known. Altering the site of attachment allows both the distance and the intervening medium for electron transfer to be varied. Changing the ligands in the ruthenium modification reagent also permits driving-force effects on the rate of the reaction to be studied.

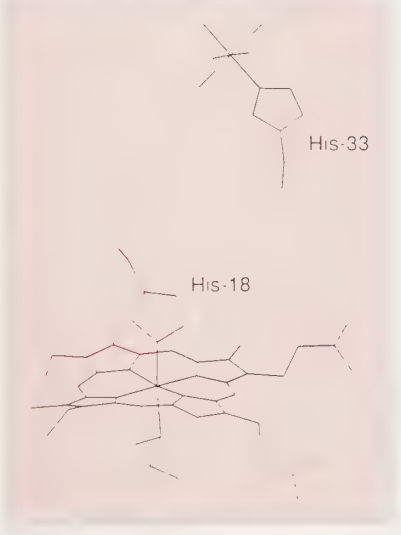

Fig. 1. Redox centers in a_5Ru(His33)cyt c. Edge-edge distances: His33 to His18, 11.7 Å; His33 to the heme, 13.2 Å.

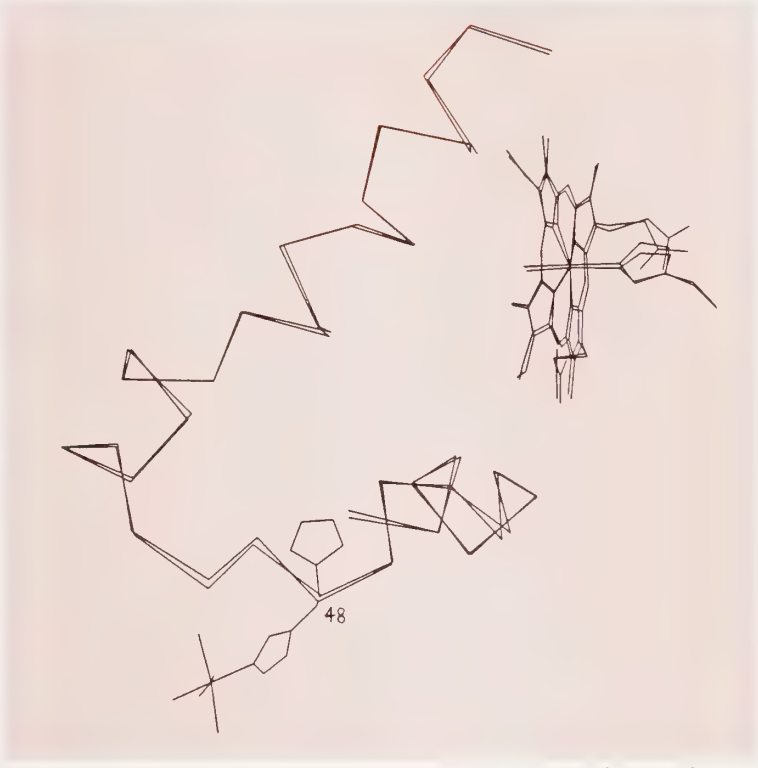

Fig. 2. Comparison of the structures of the His48 and heme regions of native and a_5Ru(His48)-modified myoglobin.

Professor Harry B. Gray (right) receiving the Alfred Bader Award in Bioinorganic or Bioorganic Chemistry from Dr. Alfred Bader.

Our modification procedure involves the reaction of aquopentaammine-ruthenium(II) (a_5Ru^{2+}) with the imidazole of a surface histidine of a protein.[6,7,9-13] Importantly, the a_5Ru(histidine)-modified proteins are relatively robust in both the Ru(II) and Ru(III) oxidation states.[14,15] Modified proteins that have been studied extensively include a_5Ru(His33)cytochrome *c* (Fig. 1)[6,9,15] and a_5Ru(His48)myoglobin (Fig. 2).[11,13]

Kinetics Methods

Flash photolysis and pulse radiolysis techniques have been employed to study electron transfer in ruthenated proteins.[3,11] The flash method used commonly to monitor $Ru^{2+} \rightarrow Fe^{3+}$ and $Ru^{2+} \rightarrow Cu^{2+}$ electron transfer is outlined in eq. 1-4 (illustrated for $Ru^{2+} \rightarrow Fe^{3+}$ electron transfer). The electron transfer reaction is initiated by photogenerated $Ru(bpy)_3^{2+*}$ (bpy = 2,2'-bipyridine), which rapidly reduces the suface ruthenium. The $Ru(bpy)_3^{3+}$ is scavenged by EDTA before it can back react with the a_5Ru^{2+}(His) group. In the case of a heme (FeP), a fast increase in absorbance due to direct reduction of Fe(III)P by $Ru(bpy)_3^{2+*}$ is followed by a slower increase in absorbance due to reduction of Fe(III)P by the Ru(II) on the protein surface.

Lieber has developed a method for the study of electron transfer from a protein metal center to a surface ruthenium.[10] In this method, $Ru(bpy)_3^{2+*}$ acts as an oxidant, selectively removing an electron from a surface a_5Ru^{2+}(His). A Ni(II) macrocycle/alkyl bromide scavenger system oxidizes the $Ru(bpy)_3^{+}$ before it can back react with a_5Ru^{3+}(His).

Electron transfer at high driving forces (values of $-\Delta G°$ in the ~1 eV range) has been investigated in zinc-porphyrin (ZnP) derivatives of ruthenated cytochrome *c* and myoglobin.[16,17] Laser excitation generates the relatively long-lived excited triplet, $^3ZnP^*$, which is a powerful reducing agent. Both excited-state electron transfer (k^*_{ET}) and thermal recombination (k^b_{ET}) reactions can be monitored in favorable cases by transient absorption spectroscopy (eq. 5-7).

The rates of electron-transfer reactions in Ru(His33)cyt *c* (M) derivatives (M = Fe,Zn) range from $3x10^1$ to $3.3x10^6$ s^{-1} (Table 1). The rates show a strong dependence on driving force ($-\Delta G°$), as predicted by Marcus.[18] Replacement of the heme in Ru(His48)Mb by several metalloporphyrins (MP: M = H_2, Pd, Pt, Cd, Mg, Zn; P = mesoporphyrin IX diacid) yields Ru(His48)Mb(MP) species in which $^3MP^* \rightarrow Ru^{3+}$ electron-transfer rates have been measured (Table 2). The electron-transfer rates again increase markedly as the driving force increases, following the same pattern as observed for Ru(His33)cyt *c* (M) derivatives. In comparing data at the same driving force, however, it is clear that electron transfer in Ru(His48)Mb(MP) is not as facile as in the cytochrome *c* system.

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*} \quad \text{(eq.1)}$$

$$Ru^{3+}(protein)Fe^{3+} + Ru(bpy)_3^{2+*} \longrightarrow Ru^{2+}(protein)Fe^{3+} + Ru(bpy)_3^{3+} \quad \text{(eq. 2)}$$

$$Ru(bpy)_3^{3+} \xrightarrow{EDTA} Ru(bpy)_3^{2+} \quad \text{(eq. 3)}$$

$$Ru^{2+}(protein)Fe^{3+} \xrightarrow{k_{ET}} Ru^{3+}(protein)Fe^{2+} \quad \text{(eq. 4)}$$

$$ZnP(protein)Ru^{3+} \xrightarrow{h\nu} {}^3ZnP^*(protein)Ru^{3+} \quad \text{(eq. 5)}$$

$$^3ZnP^*(protein)Ru^{3+} \xrightarrow{k^*_{ET}} ZnP^+(protein)Ru^{2+} \quad \text{(eq. 6)}$$

$$ZnP^+(protein)Ru^{2+} \xrightarrow{k^b_{ET}} ZnP(protein)Ru^{3+} \quad \text{(eq. 7)}$$

Table 1. ET Rates in Ru(His33)cyt *c* Derivatives[a]

Donor	Acceptor	$-\Delta G°$ (eV)	k_{ET} (s^{-1})
a_5Ru^{2+}	cyt *c* (Fe^{3+})	0.18	3.0×10^1
a_5Ru^{2+}	cyt *c* (Zn^+)	0.36	2.4×10^2
a_4(isn)Ru^{2+}	cyt *c* (Zn^+)	0.66	2.0×10^5
cyt *c* (Zn^+)	a_5Ru^{3+}	0.70	7.7×10^5
a_4(py)Ru^{2+}	cyt *c* (Zn^+)	0.74	3.5×10^5
cyt *c* (Zn^+)	a_4(py)Ru^{3+}	0.97	3.3×10^6
a_5Ru^{2+}	cyt *c* (Zn^+)	1.01	1.6×10^6
cyt *c* (Zn^+)	a_4(isn)Ru^{3+}	1.05	1.9×10^6

[a] From ref. 17: isn = isonicotinamide; py = pyridine.

Table 2. ET Rates in Ru(His48)Mb Derivatives[b]

Donor	Acceptor	$-\Delta G°$ (eV)	k_{ET} (s^{-1})
FeP	a_5Ru^{3+}	0.02	0.04
FeP	a_4(py)Ru^{3+}	0.28	2.5
$H_2P^•$	a_5Ru^{3+}	0.53	7.6×10^2
PdP•	a_5Ru^{3+}	0.70	9.1×10^3
PtP•	a_5Ru^{3+}	0.73	1.2×10^4
CdP•	a_5Ru^{3+}	0.85	6.3×10^4
MgP•	a_5Ru^{3+}	0.87	5.7×10^4
ZnP•	a_5Ru^{3+}	0.88	7.0×10^4
PdP•	a_4(py)Ru^{3+}	0.96	9.0×10^4

[b] From refs. 11 and 16.

Reorganization Energies and Electronic Couplings

In semiclassical electron-transfer theory, three parameters govern the reaction rates: the electronic coupling between the donor and acceptor (κ_E); the free-energy change for the reaction ($\Delta G°$); and a parameter (λ) related to the extent of inner-shell and solvent nuclear reorganization accompanying the electron-transfer reaction.[18] Additionally, when intrinsic electron-transfer barriers are small, the dynamics of nuclear motion can limit electron-transfer rates through the frequency factor, υ_N. These parameters describe the rate of electron transfer between a donor and acceptor held at a fixed distance and orientation (eq. 8), where R is the gas constant and T is the absolute temperature.

It is commonly assumed that for long-

Understanding and Controlling Diastereofacial Selectivity in Carbon-Carbon Bond-Forming Reactions

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Department of Chemistry
University of California
Berkeley, CA 94720

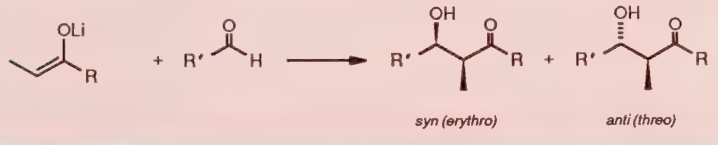
"Nature, it seems, is an organic chemist having some predilection for the aldol and related condensations..."[1]

The last two decades have witnessed a renaissance in the aldol reaction, one of the most venerable of organic reactions. This torrent of research activity was made possible by two main developments: the discovery of methods for the formation and use of preformed enolates, particularly those of lithium; and the advent of powerful analytical methods that are well suited for the analysis of diastereomeric mixtures, especially ^{13}C NMR spectrometry. The principal factor that was responsible for the rebirth of the aldol reaction as a modern method of synthesis was probably the discovery that its stereochemistry can be controlled quite effectively through the use of preformed enolates.[2] In this article, I highlight the research on stereoselective C-C bond constructions that has been carried out since 1976 by my research group at Berkeley. This research had its origin in an investigation of simple stereoselection (*syn/anti* stereoselection) in the reactions of preformed lithium enolates with aldehydes. From this topic, we moved to a study of diastereofacial selectivity in the aldol reactions of chiral enolates and chiral aldehydes. In recent years, we have extended these investigations to include reactions of electrophiles analogous to aldehydes (oxonium ions, thionium ions, immonium ions). This article provides a broad overview of these studies. Although I focus on work carried out in my research group at Berkeley, there is no intention to slight the important contributions from many other research groups, notably those of David Evans, Satoru Masamune, Teruaki Mukaiyama, Dieter Seebach, Manfred Reetz, Caesare Gennari, Manfred Braun and Ian Paterson.

The reaction between a prochiral enolate and an aldehyde can give two diastereomeric β-hydroxy ketones, sometimes referred to as *syn* (*erythro*) and *anti* (*threo*) (Scheme 1).[3] In our earliest work on the aldol reaction, we found that the relative stereochemistry of an aldol is related to that of the enolate from which it comes; *Z* enolates give *syn* aldols, and *E* enolates give *anti* aldols, provided the group attached to the oxygen-bearing carbon of the enolate is bulky.[4] This relationship was capitalized upon by the creation of several reagents that can be used to prepare *syn* or *anti* α-alkyl-β-hydroxy carboxylic acids. The useful α-trimethylsilyloxy ketone **1** (Buse's reagent)[5] and β,γ-unsaturated ketone **2** (Mori's reagent)[6] both give *Z* enolates that react with aldehydes to give only *syn* aldols (Scheme 2). The aldols derived from **1** are cleaved with periodic acid to obtain *syn* α-alkyl-β-hydroxy carboxylic acids;[7] those derived from ketone **2** are reduced and the resulting homoallylic alcohols cleaved with lead tetraacetate to acquire α-alkyl-β-hydroxy carboxaldehydes.

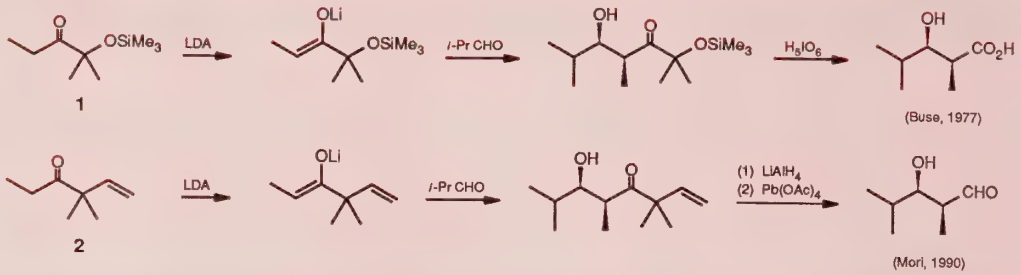
On the other hand, esters tend to give *E* enolates upon deprotonation with LDA

Scheme 1

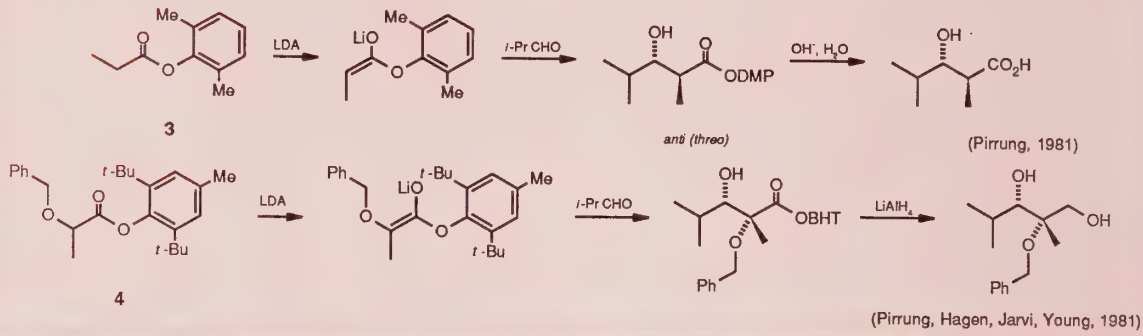


Professor Clayton H. Heathcock (right) receiving the American Chemical Society Award for Creative Work in Synthetic Organic Chemistry from Dr. Alfred Bader.

Scheme 2

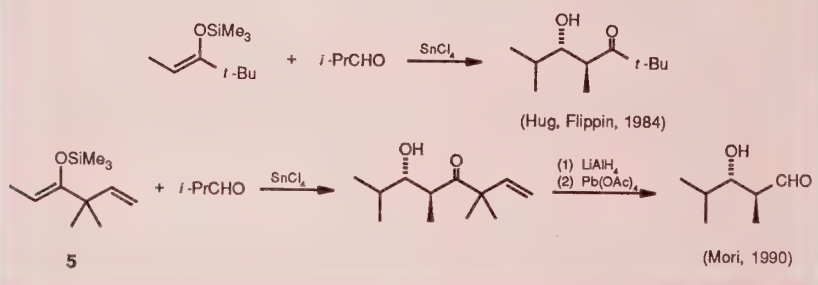


Scheme 3



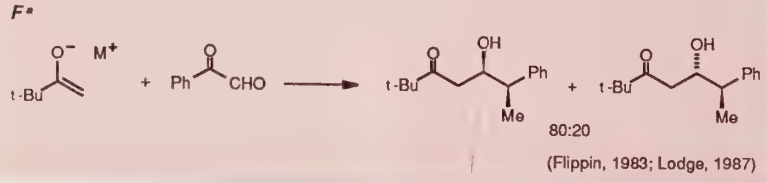
and other lithium amide bases, but the enolates of normal alkyl esters show essentially no simple stereoselection in their aldol reactions. However, the *E* enolates derived from esters of 2,6-dimethylphenol (DMP), 4-methyl-2,6-di-*tert*-butylphenol ('butylated hydroxytoluene', BHT), and 4-methoxy-2,6-di-*tert*-butylphenol ('dibutylated hydroxyanisole', DBHA) give α-alkyl-β-hydroxy esters with quite useful stereoselectivity.[8] One example is the reaction of ester **3** (Pirrung's reagent) with isobutyraldehyde (Scheme 3).[9] Remarkably, the high stereoselectivity of these hindered aryl esters carries over to the esters of α-alkoxy carboxylic acids. Thus, as shown in Scheme 3, the BHT ester of O-benzyllactic acid, **4**, gives an enolate that reacts with isobutyraldehyde to give a single aldol.[10] Reagent **4** and its analogs therefore serve as useful synthetic equivalents for the lactaldehyde enolate.

Scheme 4



Scheme 5

Facial Diastereoselectivity (One Reactant Chiral)



Parallel investigations of Lewis acid mediated aldol reactions also led to synthetically useful reagents. Although most silyl enol ethers do not show exceptional simple stereoselection in their Lewis acid mediated reactions with aldehydes,[11] those derived from *tert*-alkyl ketones do give *anti* α-alkyl-β-hydroxy ketones with good stereoselectivity (Scheme 4).[12] Compound **5**, prepared from the Mori reagent, **2**, provides a useful complement to the corresponding *syn*-selective lithium enolate.[13]

When one of the two reaction partners in an aldol reaction is chiral, there exists the possibility of a fundamentally different kind of stereoselection. In this instance, the two faces of the carbonyl acceptor or enolate donor are diastereotopic, and there exist two

New Listings

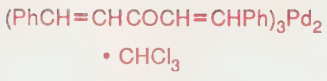
Selenophene

Building block for electrically conducting polyalkyl selenophene.

Tourillion, G. *et al. J. Electrochem. Soc.* **1990**, *137*, 1827.

36,714-1 Selenophene, 97%
1g $12.00; 5g $40.00

Cyclization Catalyst

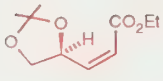


This palladium(0) complex catalyzes the regioselective cyclization of bifunctional allylic diacetates and dicarbonates with bifunctional nitrogen nucleophiles to 2-vinylpiperazines and diazacycles.[1] With enantiomerically pure carboxylic acids, cyclization of 1,6-enynes provides chiral products.[2]

(1) Tsuda, T.; Kiyoi, T.; Saegusa, T. *J. Org.Chem.* **1990**, *55*, 3388. (2) Trost, B.M.; Lee, D.C.; Rise, F. *Tetrahedron Lett.* **1989**, *30*, 651.

36,631-5 Tris(dibenzylideneacetone)dipalladium(0)chloroform adduct
250mg $13.00; 1g $36.00

Chiral Template

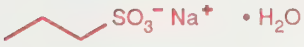


Used in a recent synthesis of AZT[1] and in the preparation of chiral cyclopropanes.[2] Treatment with DIBAL affords an allylic alcohol, derivatives of which have been used to study asymmetric induction in the Wittig rearrangement.[3]

(1) Chu, C.K.; Beach, J.W.; Ullas, G.V.; Kosugi, Y. *Tetrahedron Lett.* **1988**, *29*, 5349. (2) Krief, A.; Dumont, W.; Pasau, P. *ibid.* **1988**, *29*, 1079. Krief, A.; Dumont, W. *ibid.* **1988**, *29*, 1083. (3) Bruckner, R. *Chem. Ber.* **1989**, *122*, 193.

36,962-4 Ethyl (*S*)-(+)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-*cis*-2-propenoate, 99% **1mL $29.70**

Interesting Alkanesulfonate

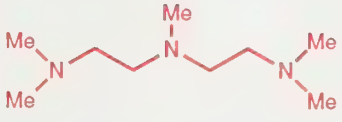


Has been utilized in surfactants,[1] polymer chemistry[2] and the preparation of etching promoters.[3]

(1) Kao Corp. Jpn. Patent 89 466, 1985; *Chem. Abstr.* **1985**, *103*, 179980q. (2) Ohtari, A.; Shimidzu, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 234. (3) Kono, T. Jpn. Patent 01 301 869, 1989; *Chem. Abstr.* **1990**, *113*, 16158v.

35,895-9 1-Propanesulfonic acid, sodium salt monohydrate, 99%
1g $10.00; 10g $60.00

Tridentate Ligand

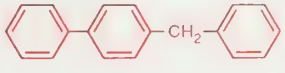


Ligand in an NMR study of complexation/aggregation of neopentyl lithium in Et_2O and THF.[1] Also used in a study of the ligand effect on selectivity of CO_2 incorporation into α,ω-diynes by low-valent nickel complexes.[2]

(1) Fraenkel, G.; Chow, A.; Winchester, W.R. *J. Am. Chem. Soc.* **1990**, *112*, 6190. (2) Derien, S.; Dunach, E.; Perichon, J. *J. Organomet. Chem.* **1990**, *385*(3), C43.

36,949-7 *N,N,N′,N′,N″*-Pentamethyldiethylenetriamine, 99%
250mL $19.00; 1L $57.50

Thermal Sensitizer



Used as a sensitizer for thermal recording paper.

Oeda, Y.; Yoshizawa, K. Jpn. Patent 01 221 277, 1989; *Chem. Abstr.* **1990**, *112*, 208029e. Jujo Paper Co., Ltd. Jpn. Patent 09 684, 1990; *Chem. Abstr.* **1990**, *113*, 88347d.

36,412-6 4-Benzylbiphenyl, 99%
5g $16.00

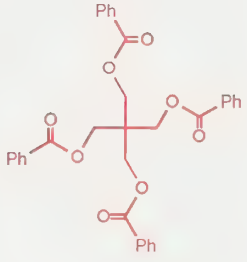
Tin(II) Acetate

Recently used in the deposition of thin films of indium-tin oxides by chemical-vapor deposition.

Maruyama, T.; Tabata, K. *Jpn. J. Appl. Phys., Part 2* **1990**, *29*, L355; *Chem. Abstr.* **1990**, *113*, 15613c.

34,516-4 Tin(II) acetate **5g $17.50**
25g $68.80

Useful Monomeric Unit

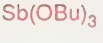


This pentaerythritol derivative has enjoyed many applications in polymer chemistry[1,2] and has been recently applied in photographic chemistry.[3]

(1) Thoese, K.; Jung, K.H. Ger. Patent 3 629 930, 1988; *Chem. Abstr.* **1989**, *109*, 39493g. (2) Espenschied, B.; Klein, P. Ger. Patent 3 532 033, 1987; *Chem. Abstr.* **1987**, *107*, 23923v. (3) Kobayashi, H.; Naruse, H. Jpn. Patent 01 101 543, 1989; *Chem. Abstr.* **1990**, *112*, 66573b.

36,937-3 Pentaerythritol tetrabenzoate, 97% **250g $12.50; 1kg $34.00**

Antimony Butoxide



Reagent in a series of studies on the formation of poly(ethylene terephthalate) with model systems.

Otton, J. *et al. J. Polym. Sci., Part A: Polym. Chem. Ed.* **1989**, *27*, 3535. Otton, J. *et al. ibid.* **1988**, *26*, 2199.

37,692-2 Antimony(III) butoxide, ~90% solution in butanol
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O	carbonyl	4
	divalent	8
	tetrahedral	2
C	6-ring planar	14
	bonded planar	2 sets
	tetrahedral	24
N	6-ring planar	4
	tetrahedral	10
P	tetrahedral	4
S	tetrahedral	2

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Volume 23, Number 1, 1990

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About Our Cover:

It won't surprise the regular readers of our *Aldrichimica Acta* that there is another painting of a *Tobias* on our cover. Our chemist-collector is so fond of this story – it is such a delightfully involved story of faith – and this is the sixth Tobias on our covers.

Here the angel is shown instructing Tobias how to hold the fish, and the faithful dog, the first friendly dog mentioned in a biblical story, is trotting along.

We don't know who painted this – French artists in Rome, like Gaspar Dughet and Francois Perrier have been suggested – but our ignorance does not diminish by one iota the beauty of this long view. To the artist, this beauty came first; he may have added the figures only because biblical paintings were considered a higher art form than mere landscapes. Little could he know in the seventeenth century that one day a chemist would buy this for both reasons: for the Tobias story and for the landscape which is almost as magical as the fish.

Telling Images – Images Révélatrices

Large, 150-page catalog of thirty-six Old Master paintings now in a travelling exhibition touring Canada. All were given by the Baders to Queen's University.

The catalog illustrates all thirty-six paintings, thirteen of them in color (none of these were in the Age of Rembrandt exhibition described below). The extensive, scholarly text, written by Professor David McTavish, is in English and French.

Z20,404-8 **$18.00**

The Detective's Eye: Investigating the Old Masters

Twenty-one paintings that have been reproduced on our *Acta* covers and five that have been on our catalog covers were among some seventy works in an exhibit at the Milwaukee Art Museum (January 19 - March 19, 1989) for which Isabel and Alfred Bader were guest curators.

If you relish detective work and puzzles about Old Master paintings, you will find much to enjoy in this fully illustrated catalog, and you will learn something about our chemist-collector's interest in art and connoisseurship as well.

Z18,350-4 **$12.00**

Pictures from the Age of Rembrandt

Twenty-eight paintings that have been reproduced on our *Acta* covers, and seven that have been on our catalog covers were among the thirty-six paintings in an exhibition of Dutch paintings at Queen's University in Kingston, Ontario. The fully illustrated catalog written by Professor David McTavish contains a wealth of art-historical information – enough for several evenings of relaxed enjoyment – probably the best value in art-history anywhere.

Z12,794-9 **$8.00**

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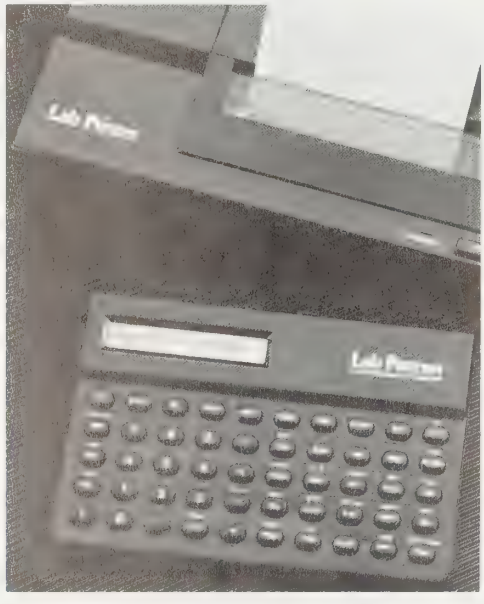

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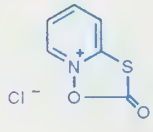
by



Dr. David Crich, University College, London, kindly suggested that we offer this thiaindolizinium salt. It was used recently in his convenient, highly selective synthesis of 2-deoxy-β-D-glycosidic linkages from the corresponding ulosonic acid O-glycosides[1] *via* Barton's thiohydroxamate-based decarboxylation methodology.[2]

Naturally, we made this compound.

(1) Crich, D.; Ritchie, T.J. *Chem. Commun.* **1988**, 1461. (2) Barton, D.H.R.; Crich, D.; Motherwell, W.B. *Tetrahedron* **1985**, *41*, 3901.

36,420-7 1-Oxa-2-oxo-3-thiaindolizinium chloride **1g $10.00; 5g $38.00**

It was no bother at all, just a pleasure to be able to help.

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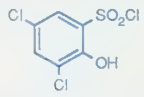
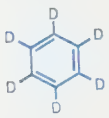


14,611-0

2-Azetidinone

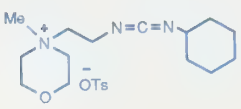
32,846-4

Benzene-d_6, 99.5 atom % D



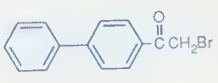
15,181-5

1-Cyclohexyl-3-(2-morpholinoethyl)carbodiimide metho-p-toluenesulfonate



C10,640-2

2-Bromo-4'-phenylacetophenone

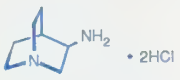


10,108-7

6,6-Dimethylfulvene

27,000-8

3-Aminoquinuclidine dihydrochloride



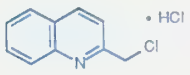
10,035-8

(Methyl sulfoxide)-d_6, 99.9 atom % D

$(CD_3)_2SO$

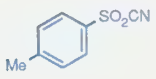
15,187-4

2-(Chloromethyl)quinoline monohydrochloride



C5,710-3

p-Toluenesulfonyl cyanide



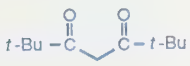
24,883-5

Tetrapropylammonium perruthenate

$RuO_4^- {}^+NPr_4$

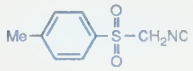
33,074-4

2,2,6,6-Tetramethyl-3,5-heptanedione



15,575-6

Tosylmethyl isocyanide

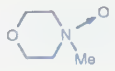


18,820-4

1,3-Cyclopentanedione

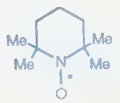
17,716-4

4-Methylmorpholine N-oxide



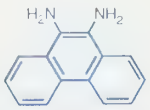
22,428-6

TEMPO, free radical



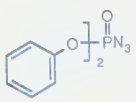
21,400-0

9,10-Diaminophenanthrene



D2,290-8

Diphenylphosphoryl azide



17,875-6

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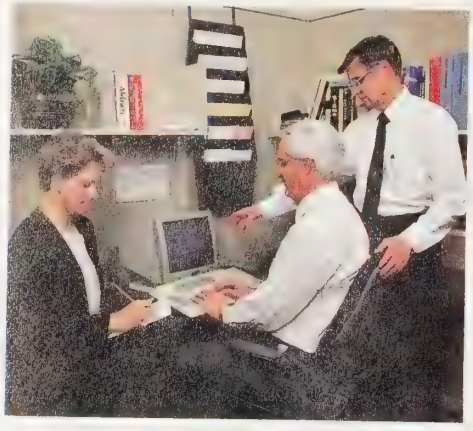

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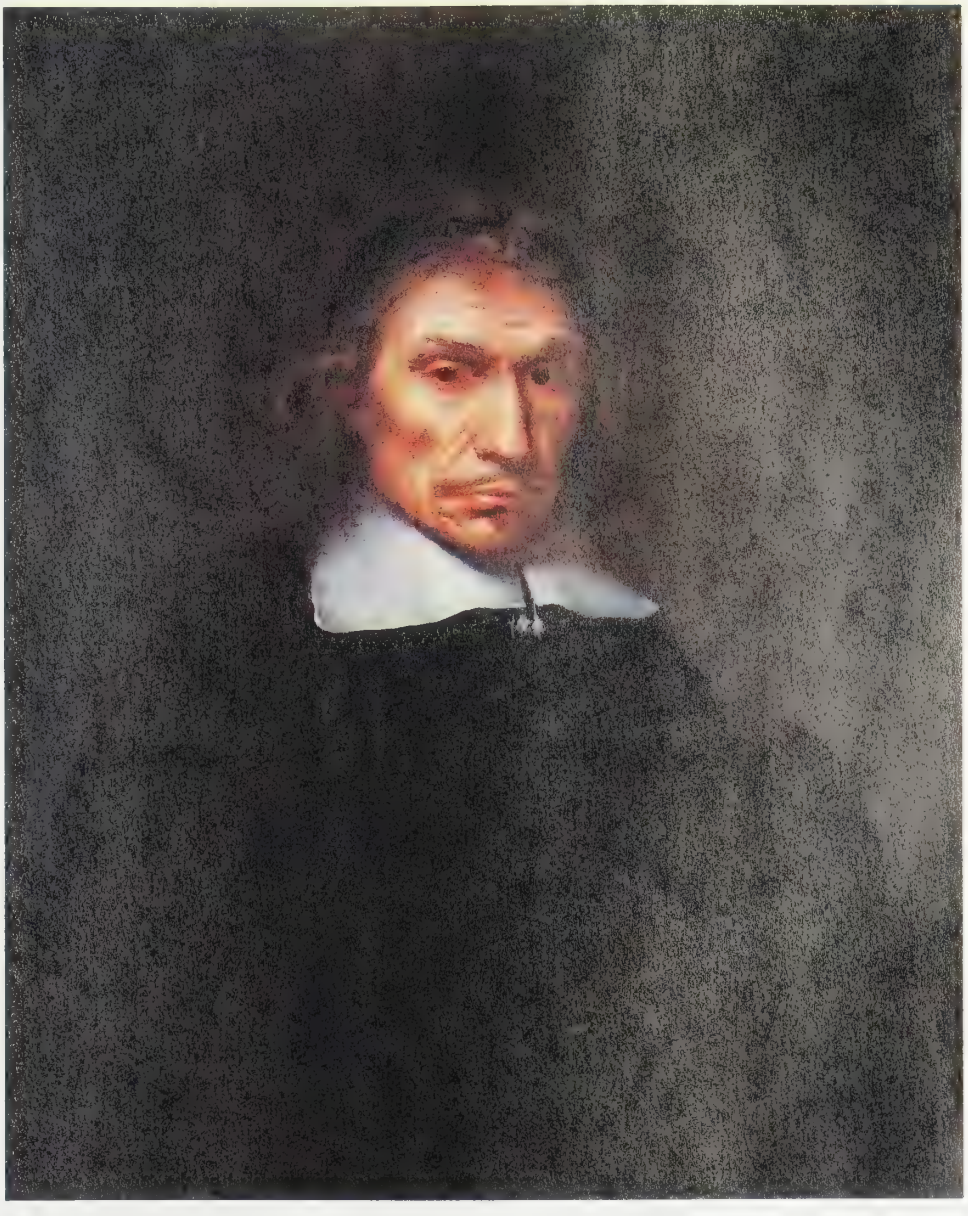

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References:

(1) Fieser, L.F. *J. Chem. Ed.* **1963**, *40*, 62.
(2) Fieser, L.F. *ibid.* **1963**, *40*, 457.
(3) Fieser, L.F. *ibid.* **1965**, *42*, 408.
(4) Fieser, L.F. *Chemistry in Three Dimensions,* 1963 (**Z10,160-5 $5.00**).

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Z18,448-9	25 sulfur atoms (yellow)	**$24.00**

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About Our Cover:

Fig. 1

Readers of the descriptions of our covers will remember how our chemist collector appreciates the works of Jan Lievens, a contemporary of Rembrandt in Leiden. Lievens' *St. Paul* graced our last catalog cover, his *Presentation in the Temple*, the cover of *Aldrichimica Acta*, Vol. 22, No. 1, 1989; both are early works. Here is a very late work, a portrait (oil on canvas, 73 x 60cm) of Jacob Junius.

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Here is a tantalizing thought: what if Lievens had not gone to England and then to Antwerp, before returning to Holland? Had he stayed in Holland, could Lievens have developed like Rembrandt? Clearly, two of Lievens' very late works not influenced by van Dyck, portraits of distinguished old men, are among the finest Dutch portraits ever.

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Jacob Junius (1608-1671) studied law in Leiden, made a fortune in Mazulipatnam in India, returned home and married late in life, in 1657. In 1667 he was elected regent of the Old and New Almshouse in Delft; perhaps this portrait was painted for that occasion. Junius was survived by his widow and three of their six children, and one wonders whether the loss of three children in infancy led to his dour appearance.

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(1) W. Sumowski, *Gemälde der Rembrandt-Schüler*, III, p 1769, describing paintings Nos. 1294 and 1295.

Lab Notes

I wish to report two laboratory techniques which I have found helpful.

(1) Are you having problems labeling NMR tubes? Try using chart edging strip. The oval sprocket holes are just right for 5-mm tubes, and you can tear off the amount you need. Two examples are shown below in Figure 1. The samples are from different printers. One sample is a perforated edging strip, readily detachable from spectra, etc. The other has to be cut from a piece of waste chart paper, but one can choose its dimensions.

(2) Recently, I had to filter a reaction product from its suspension in 50% hydrofluoric acid, and decided to use your polypropylene filter cloth (Z10,425-6) for the purpose. On inspection, this cloth appeared to be rather "wooly", and I suspected that it would be difficult to remove the solid product from it. However, a sheet of perforated polypropylene, cut to the same size and laid on top of the cloth, overcame the anticipated problem, *i.e.*, the solid material collected by filtration was easily removable. The perforated polypropylene came from a bread wrapper! That the material was in fact polypropylene was rapidly established by comparing its IR spectrum with the Aldrich reference spectrum [*FT-IR* **1**(2), 1158A]. Since then, I have also found this perforated polypropylene useful to cover samples being dried under vacuum at temperatures up to 100°C.

Fig. 1

Dr. D.J.R. Massy
School of Chemical Sciences
University of East Anglia
Norwich NR4 7TJ
England

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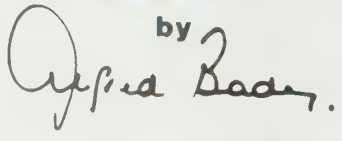
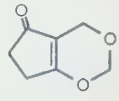


Professor Amos B. Smith, III, of the University of Pennsylvania kindly suggested that we offer this 1,3-dioxin vinylogous ester, a versatile β-ketovinyl cation equivalent.[1] The



synthetic utility of this ester was demonstrated in Professor Smith's elegant syntheses of (-)-bertyadionol,[2] jatrophone[3] and the hydroxy-jatrophones.[4]

Naturally, we made this compound.

(1) Smith, A.B. III *et al. J. Org. Chem.* **1988**, *53*, 4314. (2) *Idem J. Am. Chem. Soc.* **1986**, *108*, 3110. (3) Smith, A.B. III *Strategies and Tactics In Organic Synthesis*; Linberg, T., Ed.; Academic Press: New York, 1984; Chapter 9, pp 224-274. (4) Smith, A.B. III *et al. J. Am. Chem. Soc.* **1989**, *111*, 6648.

36,681-1 6,7-Dihydrocyclopenta-1,3-dioxin-5(4*H*)-one 500mg $35.00

It was no bother at all, just a pleasure to be able to help.

The Chiral Auxiliary $[(C_5H_5)Fe(CO)(PPh_3)]$ for Asymmetric Synthesis

Stephen G. Davies
The Dyson Perrins Laboratory
South Parks Road
Oxford, OX1 3QY
England

1. Introduction

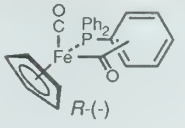
There is an increasing demand for homochiral (enantiomerically pure) compounds. This demand arises primarily from the needs of the pharmaceutical industry but applications are also emerging from the electronics and polymer sectors. There are three fundamentally different approaches to the preparation of homochiral compounds: (i) resolution, (ii) the chiral pool and (iii) asymmetric synthesis.[1-3] The latter and most general approach involves the attachment of a chiral auxiliary to a prochiral group such as an olefin, carbonyl, enolate, and methylene; the chiral auxiliary then biases the formation from the prochiral group of any new chiral center towards one configuration. During the reaction which elaborates the new chiral centers, the chiral auxiliary may be attached either temporarily or permanently, giving rise in the former case to catalytic reactions and in the latter to stoichiometric reactions.

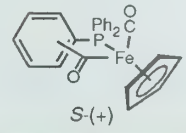
Over the past ten years at Oxford, we have been interested in developing the stoichiometric iron chiral auxiliary $[(C_5H_5)Fe(CO)(PPh_3)]$ for controlling the stereochemistry during a variety of reactions associated with the carbonyl functional group.[4-8] Described below are some of the applications we have developed for asymmetric synthesis using the iron chiral auxiliary.

2. Alkylation Reactions

In 1982 we were the first to report that enolates could be generated from transition-metal acyl complexes.[9] Deprotonation of the orange chiral iron acetyl complex $[(C_5H_5)Fe(CO)(PPh_3)COMe]$ (**1**) with butyllithium generated the blood-red enolate, which was quenched with methyl iodide to the corresponding propanoyl complex **2** in essentially quantitative yield (eq. 1).[9,10] An important feature of this and other enolates attached to the iron auxiliary is their smooth monoalkylation; no products from dialkylation are observed, which indicates that enolate exchange does not occur at a significant rate. The enolate derived from **1** is a good nucleophile reacting well with secondary iodides in good yield (*e.g.*, isopropyl iodide, 86%) without significant competition from elimination.[11] Rather surprisingly, the enolate derived from **1** undergoes C- rather than O-silylation with trimethylsilyl chloride to generate **3**.[10]

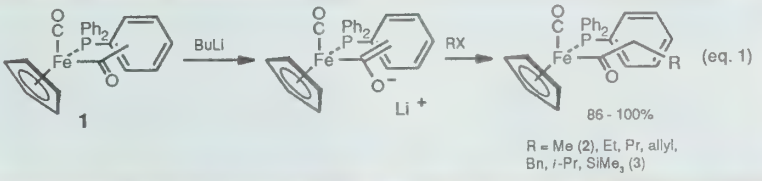
The acetyl complex **1** is octahedral in structure, with triphenylphosphine, carbon monoxide and the acetyl ligands each occupying one site, with the remaining three sites being taken by the cyclopentadienyl ligand. Complex **1** is chiral, existing as the *R*-(-) and *S*-(+) enantiomers,[12] and configurationally stable under normal conditions. The complex prefers to adopt a conformation which places the acetyl oxygen *anti* to the carbon monoxide ligand, with one of the triphenylphosphine phenyl groups approximately parallel to the plane of the acetyl ligand, thus shielding one face of the acetyl. There are no significant stereoelectronic factors influencing the conformation of the acetyl ligand; everything seems to be sterically driven.[13-15]





The acetyl carbonyl IR stretching frequency is 1601 cm^{-1}, indicating a large charge separation (Fe^+, O^-) in the ground state (Scheme 1). For this and other reasons, we draw the analogy between acetyl complex **1** and the enolate derived from ethyl acetoacetate, and between the enolate derived from **1** and the dianion from ethyl acetoacetate (Scheme 1). To emphasize the latter analogy, they both require a strong base such as butyllithium for their generation and both undergo C- not O-silylation.[10]

Deprotonation-methylation of the propanoyl complex **2** generates cleanly the elaborated



(eq. 1)

From right to left: Dr. Stephen Davies, recipient of the first Alfred Bader Award in the UK and Dr. Kay Davies; Prof. John Ward, President of the Royal Society of Chemistry; Mrs. Isabel Bader and Dr. Alfred Bader.

isobutyryl complex **4**. Further alkylations of the chiral iron acyl complexes **5** occur with essentially complete stereoselectivity (Scheme 2).[16-18] Some loss of stereocontrol is observed for small or very reactive electrophiles but, in these cases, small amounts of the minor diastereoisomer may be removed by a single crystallization. The configuration of the newly formed chiral center relative to the original iron center results from completely stereoselective generation of the *E*-enolates (Fe *trans* to R) and their reaction in the *anti* (O⁻ to CO) conformation from the unshielded face with electrophiles (Scheme 2).[16-19] Further deprotonation of the dialkylated complexes **4** or **5** does not occur since the remaining α-proton is buried in the chiral auxiliary and therefore inaccessible to base.

The absolute configuration of the new chiral center in these alkylation reactions is determined by which enantiomer of the chiral iron acetyl complex **1** is used as starting material, and by the order of addition of the alkyl groups in the sequential double-alkylation procedure. After elaboration of the α-chiral center, the chiral auxiliary may be removed by one-electron oxidants such as bromine, *N*-bromosuccinimide (NBS), ceric ion, ferric ion, etc. Bromine is generally the preferred oxidant unless there are very acid-sensitive groups present, in which case NBS is generally satisfactory. Thus, oxidation of an iron acyl complex in the presence of water, alcohol or amine gives the corresponding carboxylic acid, ester or amide, respectively. Using bromine or NBS as the oxidant, the auxiliary is recovered as $[(C_5H_5)Fe(CO)(PPh_3)Br]$.[11]

The versatility of this alkylation procedure may be illustrated by the asymmetric synthesis of captopril and *epi*-captopril (Scheme 3).[20]

3. Homochiral Succinoyl Derivatives[21,22]

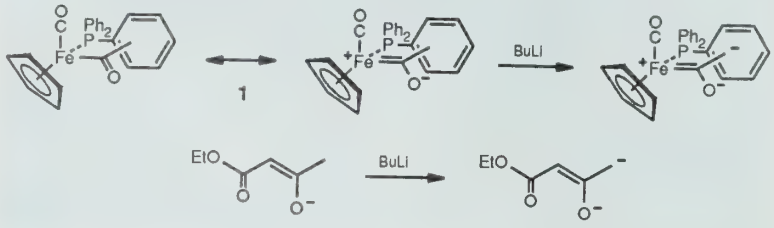
Alkylation of the enolate derived from the parent acetyl complex **1** with *tert*-butyl bromoacetate generates the succinoyl derivative **6**. As expected from the enolate chemistry described above, the succinoyl derivative **6** undergoes completely regioselective deprotonation α to the ester rather than α to the acyl carbonyl.[22] Good, although not complete, stereoselectivity is observed in the alkylation reactions of this succinoyl enolate with the major diastereoisomer being readily isolated by chromatography (eq. 2).

The chiral succinoyl derivatives have been used in the asymmetric synthesis of actinonin, (Scheme 4),[23] which has shown interesting anti-collagenase activity.

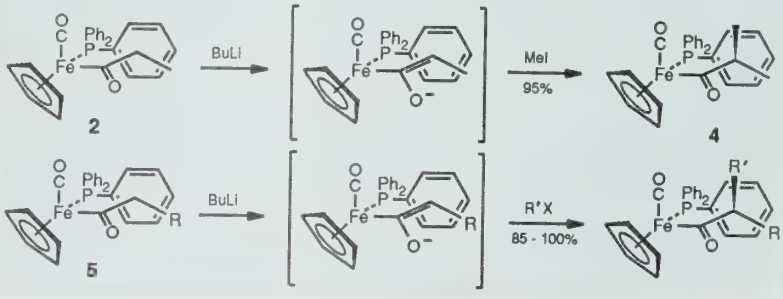
4. Asymmetric Aldol Reactions

Addition of aldehydes to the lithium enolate derived from the parent acetyl complex **1** generates the corresponding β-hydroxy acyl complexes with essentially no stereocontrol. Transmetallation of the lithium enolate to the aluminum enolate by treatment with diethylaluminum chloride prior to addition of the

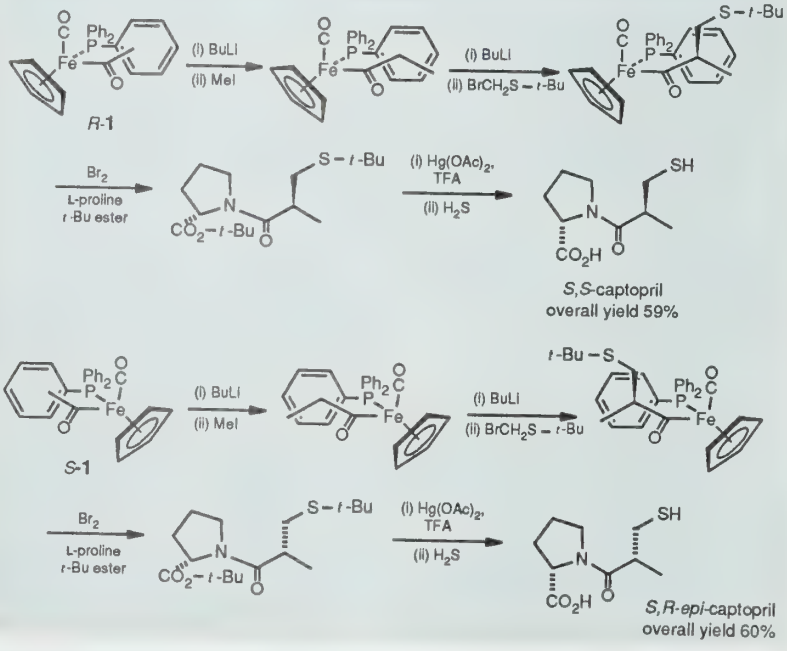
Scheme 1

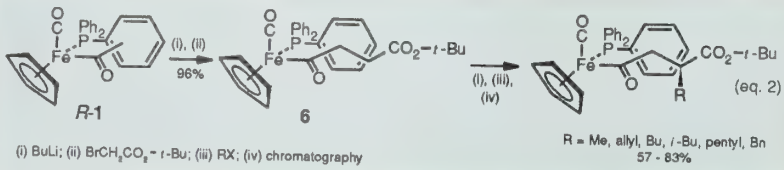


Scheme 2



Scheme 3





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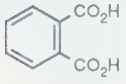
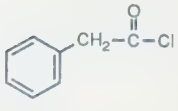


Useful synthetic tool.

P3,930-3

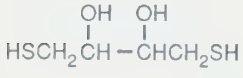
Phenylacetyl chloride



Pharmaceutical intermediate.

P1,675-3

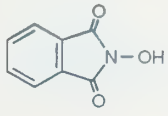
Dithiothreitol (Cleland's Reagent)



Thiol reagent.

15,046-0

N-Hydroxyphthalimide



Peptide-synthesis reagent.

H5,370-4

Tetrabutylammonium bromide

$\text{Bu}_4\text{N}^+\ \text{Br}^-$

Phase-transfer catalyst.

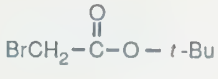
19,311-9

1H-Tetrazole

Coupling reagent for nucleotide synthesis.

24,395-7

tert-Butyl bromoacetate



Versatile pharmaceutical intermediate.

12,423-0

Trifluoromethanesulfonic anhydride

$(\text{CF}_3\text{SO}_2)_2\text{O}$

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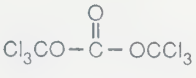
17,617-6

Triphosgene



Stable phosgene substitute.

33,075-2

2-Bromoethylamine hydrobromide

$\text{BrCH}_2\text{CH}_2\text{NH}_2 \cdot \text{HBr}$

Medicinal intermediate.

B6,570-5

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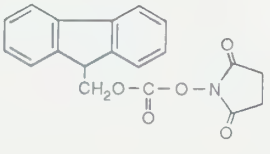

Peptide-synthesis reagent. Amine-protecting reagent.

28,950-7

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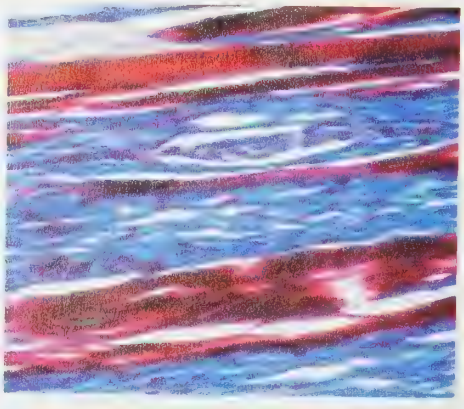

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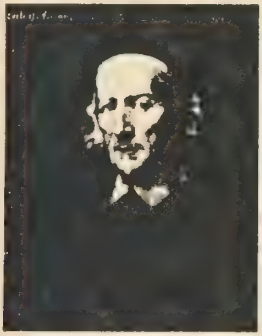

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(1) W. Sumowski, *Gemälde der Rembrandt-Schüler*, III, p 1769, describing paintings Nos. 1294 and 1295.

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Dedicated to Professor Albert Eschenmoser on his sixty-fifth birthday

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About Our Cover:

Fig. 1

Part of the story of this remarkable painting (oil on canvas, 51 x 38 inches) is told in *The Detective's Eye* (see below), the catalog of an exhibition where the painting was called *Father of the Church* (Fig. 1). However, the Maltese cross and Greek inscription disappeared during a cleaning which also revealed the turban and crown on the right. Hence this must be an oriental king, but who is this inspired figure?

Our chemist collector believes it is King David writing the Psalms, but in 17th century paintings King David as a psalmist is seldom depicted without his harp.

The painting on our cover is a masterpiece by one of Rembrandt's able students, Govaert Flinck, dating from the 1650's. It is surely fitting for the Acta dedicated to Professor Albert Eschenmoser on his 65th birthday, and containing papers by Professor Vladimir Prelog and Professor Nathan Kornblum. Professor Eschenmoser is one of Switzerland's ablest chemists, an inspiring teacher and a great man. When we asked Professor Prelog to write his paper, he said, "I cannot, but I must." Perhaps David felt like that when writing the Psalms.

The Detective's Eye: Investigating the Old Masters

Twenty-three paintings that have been reproduced on our *Acta* covers (including the one here) and five that have been on our catalog covers were among some seventy works in an exhibit at the Milwaukee Art Museum (January 19 - March 19, 1989) for which Isabel and Alfred Bader were guest curators.

If you relish detective work and puzzles about Old Master paintings, you will find much to enjoy in this fully illustrated catalog, and you will learn something about our chemist-collector's interest in art and connoisseurship as well.

Z18,350-4 **$12.00**

Telling Images – Images Révélatrices

Large, 150-page catalog of thirty-six Old Master paintings now in a travelling exhibition touring Canada. All were given by the Baders to Queen's University.

The catalog illustrates all thirty-six paintings, thirteen of them in color. The extensive, scholarly text, written by Professor David McTavish, is in English and French.

Z20,404-8 **$18.00**

Lab Notes

Workers using your tetrafluoroboric acid-diethyl ether complex, 17,641-9, might be interested in a quick NMR method to determine the titer of small volume (microliter) samples conveniently dispensed with a microliter syringe. The method is based on the fast (on NMR time scale), quantitative, reversible protonation of *N,N*-dimethylaniline, D14,575-0, to give the corresponding anilinium ion. In acetone-d_6 the proton chemical shift of the N-Me groups is 873.8 Hz (at 25.0°C, 300.1 MHz vs. TMS). The N-Me groups of the anilinium ion are shifted considerably downfield to 1064.5 Hz. Assuming rapid exchange for a system containing both species, the chemical shift is the weighted average, hence the mole fractions of *N,N*-dimethylaniline/*N,N*-dimethylanilinium tetrafluoroborate may be calculated. The advantage of the method is that the titer of very small aliquots may be determined. Equation 1 which reports mmol HBF_4-Et_2O/microliter is derived from the above chemical shifts, the density, and molar mass of *N,N*-dimethylaniline.

$$[HBF_4]=(4.141\times10^{-5})(N\text{-}Me_{ave}-873.8)R \quad \text{(eq. 1)}$$

$N\text{-}Me_{ave}$ is the observed chemical shift of the N-Me groups (Hz) in acetone-d_6 and R is the ratio of microliters *N,N*-dimethylaniline/microliters HBF_4-Et_2O. 5 microliter aliquots of *N,N*-dimethylaniline work well.

Professor C.R. Jablonski
Department of Chemistry
Memorial University of Newfoundland
St. John's, Newfoundland A1B 3X7
Canada

I have seen many people who have had a difficult time finding a Dewar flask which accommodates your cold traps Z10,310-1 and Z10,690-9. I have been using the perfect combination of the cold trap Z10,690-9 with Dewar flask Z12,078-2 since my Aldrich days over fifteen years ago.

It would be of great assistance to your customers if you would recommend the use of Dewar flask Z12,078-2 with the cold traps Z10,310-1 and Z10,690-9.

J.P. Li, Ph. D.
Sandoz Crop Protection
975 California Ave.
Palo Alto, CA 94304

Editors Note: Here is more information on the Dewar flask recommended by Dr. Li.

Z12,078-2 Dewar flask, aluminum base, plastic mesh housing, i.d. 14.3cm, depth 30cm **$162.80**

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes) and if we publish it, you will receive, at no cost, a handsome Aldrich coffee mug as well as a copy of **Pictures from the Age of Rembrandt.** *We reserve the right to retain all entries for consideration for future publication.*

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A large collection of steroids for use as reference standards is maintained at the address below. The collection includes many steroids which are not available from any other source, including samples which have been donated by numerous eminent scientists for the benefit of others. As well as the steroid hormones and their metabolites, the collection contains synthetic intermediates, rare steroids of microbiological origin, bile acids, sterols, and some steroidal alkaloids and other plant products. Milligram or microgram quantities are supplied for use in clinical, biochemical or chemical studies, such as the identification of unknown steroids, the development and standardization of micro-assay techniques, chromatography and mass spectrometry. The Curator of the Collection is glad to provide advice on matters concerning steroids whenever possible.

Enquiries, requests for detailed information and a list of available steroids, or offers of samples for the Collection, should be addressed to:

Professor D.N. Kirk
Curator of the Steroid Reference Collection
Department of Chemistry
Queen Mary and Westfield College
London, E1 4NS
U.K.

"Please Bother Us."

by

Professor Steven Ley and Dr. William Griffith at Imperial College, London, suggested we offer tetraphenylphosphonium acetatodichlorodioxoruthenate which, in the presence of *N*-methylmorpholine *N*-oxide (NMO), catalytically converts primary halides to aldehydes and secondary halides to ketones.[1] The catalyst oxidizes a variety of other functionalities and nicely complements tetrapropylammonium perruthenate, 33,074-4, another compound suggested by Professor Ley.

Naturally, we made it.

(1) Griffith, W.P.; Jolliffe, J.M.; Ley, S.V.; Williams, D.J., in preparation.

$(PPh_4)[RuO_2(OAc)Cl_2]$

37,126-2 Tetraphenylphosphonium acetatodichlorodioxoruthenate
250mg $10.50; 1g $30.00

It was no bother at all, just a pleasure to be able to help.

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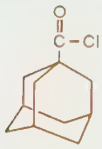
1-Adamantanecarbonyl chloride



Activating agent for DNA synthesis.

11,772-2

Borane-tetrahydrofuran complex

Hydroborating and reducing agent.

17,619-2

(-)-B-Chlorodiisopino-campheylborane

Chiral reducing agent.

31,702-0

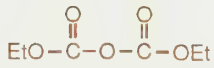
Borane-methyl sulfide complex

$BH_3 \cdot SMe_2$

Reducing agent.

17,982-5

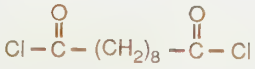
Diethyl pyrocarbonate



Reagent for histidine.

15,922-0

Sebacoyl chloride



Organic intermediate.

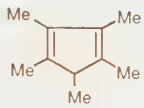
13,178-4

1H-Tetrazole

Coupling reagent for synthesis of polynucleotides.

15,569-1

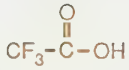
1,2,3,4,5-Pentamethylcyclo-pentadiene



Ligand for catalyst preparation.

21,402-7

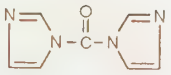
Trifluoroacetic acid



Suitable for protein sequencing.

29,953-7

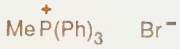
1,1'-Carbonyldiimidazole



Enzyme cross-linking agent.

11,553-3

Methyltriphenylphosphonium bromide



Wittig reagent precursor.

13,007-9

Di-tert-butyl dicarbonate

Reagent for the preparation of peptides.

19,913-3

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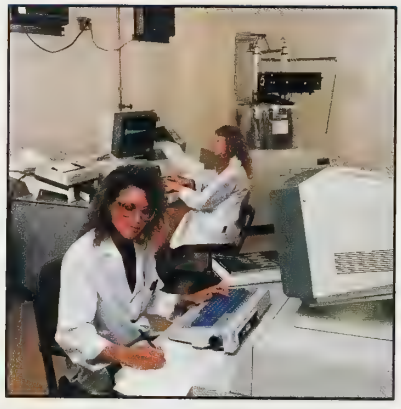

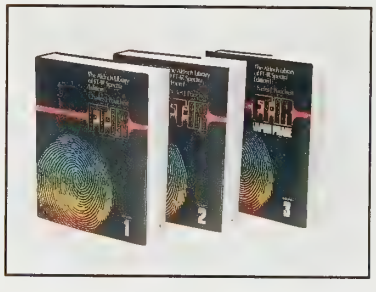

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Aldrichimica Acta

Volume 24, Number 1, 1991

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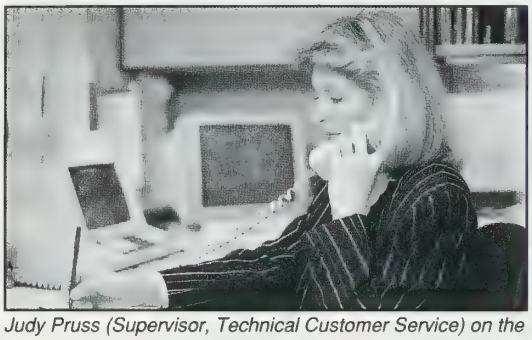
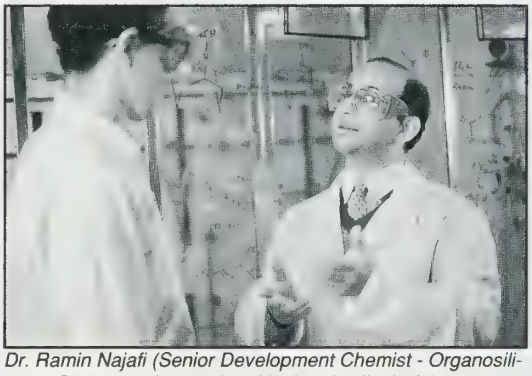
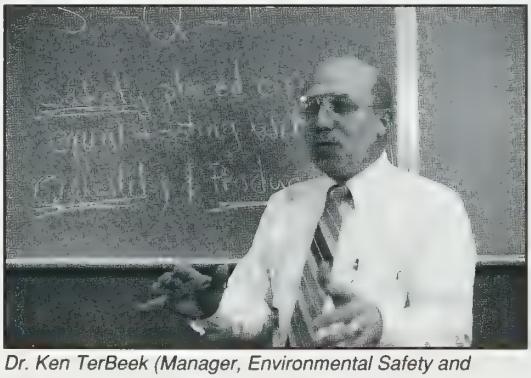


Judy Pruss (Supervisor, Technical Customer Service) on the phone with a valued customer.



Dr. Ramin Najafi (Senior Development Chemist - Organosilicons, Sheboygan) consults with chemist Jim Lefeber.



Dr. Ken TerBeek (Manager, Environmental Safety and Health Affairs) training employees on safety procedures.

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Aldrichimica Acta

Volume 24, Number 1, 1991
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About Our Cover:

Fig. 1

The Bible is the world's most diverse book: what stories of true love and unmitigated hatred, of ecstasy and depression!

When we worry about the Middle East, as we do so much right now, we can find encouragement in the story of the love of a "Jordanian" woman, Ruth, a woman who became the ancestor of David and hence of the Messiah, for her "Israeli" mother-in-law, Naomi. This is one of the most heart-warming stories.

In contrast, one of the strangest stories is illustrated on our cover, which could be called "Don't Kill the Messenger."

At first our chemist collector did not know its subject, but a good friend, Dr. Volker Manuth, explained that Willem de Poorter, a Rembrandt student, has here illustrated a story very rarely depicted in the 17th century. The first chapter of the second book of Samuel tells of the arrival of a young Amalekite before David. He has brought Saul's crown and news of the death of Jonathan and Saul on Mount Gilboa. David was stricken with grief at the news and ordered the messenger to be killed.

Why did David have him killed? Surely not only because he had brought such tragic news and had helped Saul in his suicide. It was probably also because he was an Amalekite.

During the Exodus from Egypt these wild nomads attacked the Israelites (Exodus 17:8-16), striking the hindmost, the weakest first. Moses commanded the Israelites (Deuteronomy 25:17-19), "Remember what Amalek did unto you. . .you shall blot out the remembrance of Amalek from under heaven, you shall not forget." King Saul forgot and spared the life of Agag, King of Amalek (I Samuel 15:1-35) and that led to Samuel's leaving Saul and eventually to Saul's suicide.

Dr. Manuth explained that de Poorter used a Bible illustration (Fig. 1) by Hans Holbein, the Younger, clearly showing David's deep grief and the relationship between David and the messenger.

The Amalekites have disappeared, but the spirit of terrorism has not. The kind of love that Ruth shared with Naomi must still exist, but a Ruth of today might fear her own people. How can we encourage people to think of each other as individuals, rather than as stereotypes — Amalekites or Arabs or Jews?

The Detective's Eye: Investigating the Old Masters

Twenty-three paintings that have been reproduced on our *Acta* covers and five that have been on our catalog covers were among some seventy works in an exhibit at the Milwaukee Art Museum (January 19 - March 19, 1989) for which Isabel and Alfred Bader were guest curators.

If you relish detective work and puzzles about Old Master paintings, you will find much to enjoy in this fully illustrated catalog, and you will learn something about our chemist collector's interest in art and connoisseurship as well.

Z18,350-4 **$12.00**

Lab Notes

In a recent issue of *Aldrichimica Acta* (Vol. 23, No. 2), the use of the perforated edge of a chart paper was proposed as a convenient method to label 5-mm NMR tubes. We have found that small adhesive labels (37 x 9 mm) used in the electrical industry to label electrical wires are an ideal method to label any NMR tube regardless of size. The labels have an opaque, white section suitable for writing on with ball-point pen, and they retain their adhesive power in both high- and low-temperature regimes (at least -100 to +160°C). We recommend the use of these labels for the universal labelling of NMR samples.

P.S. Farley
MRPRA
Brickendonbury
Hertford, SG13 8NL
England

Dr. H. Parkes
Department of Chemistry
Birkbeck College
Gordon House
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London, WC1H 0PP
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Editor's Note: Aldrich now carries the NMR tube labels shown here.

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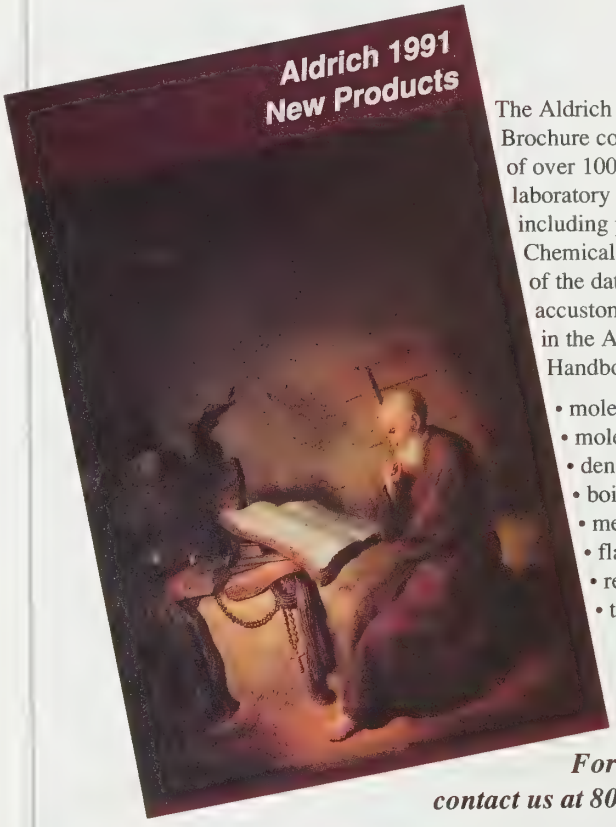
New Products Brochure



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"Please Bother Us."

by

Professor M.F. Lappert of the School of Chemistry and Molecular Sciences at the University of Sussex and Professor Philip Power of the Department of Chemistry at the University of California at Davis suggested that we offer bis(trimethylsilyl)-chloromethane. Use of the bis(trimethylsilyl)-methyl ligand has permitted the isolation of several transition-metal and main-group compounds. The most common method for the introduction of the bis(trimethylsilyl)methyl ligand is by treatment of $(Me_3Si)_2CHLi$ with an active halide. The precursor for the preparation of the lithium derivative is the chloride, $(Me_3Si)_2CHCl$.

Naturally, we made this compound.

Lappert, M.F. *Adv. Chem. Ser.* **1976,** *150,* 256. Hitchcock, P.B.; Lappert, M.F.; Leung, W.P.; Buttrus, N.H. *J. Organomet. Chem.* **1990**, *394*, 57 and references therein.

$(Me_3Si)_2CHCl$

36,174-7 Bis(trimethylsilyl)chloromethane, 97% **1g $7.00; 5g $23.00**

It was no bother at all, just a pleasure to be able to help.

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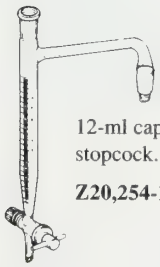

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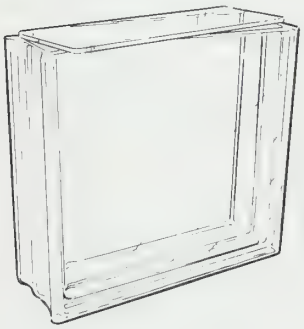
24/40	**Z16,403-8**	**$60.10**
14/20	**Z16,404-6**	**60.10**



TLC DEVELOPING TANK

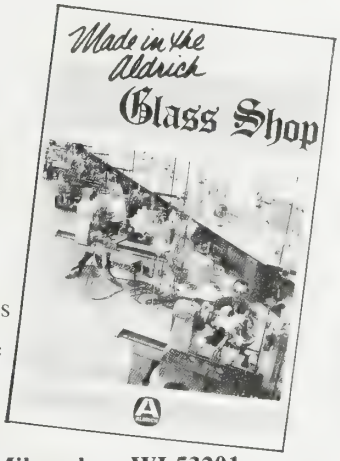
Glass, with lid.

Inner Dimensions (cm)	Catalog No.	Each
27.5 x 27.5 x 7.5	**Z12,619-5**	**$48.70**
12.1 x 10.8 x 8.3	**Z14,622-6**	**41.30**
17.5 x 16.0 x 8.2	**Z20,415-3**	**40.30**
17.5 x 16.0 x 6.2	**Z20,416-1**	**40.10**
17.5 x 11.0 x 6.2	**Z20,418-8**	**39.70**
17.5 x 6.2 x 6.8	**Z20,419-6**	**38.20**
12.5 x 11.0 x 6.5	**Z20,421-8**	**36.10**
7.5 x 15.5 x 8.0	**Z20,422-6**	**36.00**

POUR-OUT ADAPTER

For pouring from flasks or funnels without pouring over ground joint.

ⅎ Joint	Catalog No.	Each
14/20	**Z17,295-2**	**$12.50**
19/22	**Z17,296-0**	**13.50**
24/40	**Z17,297-9**	**15.00**



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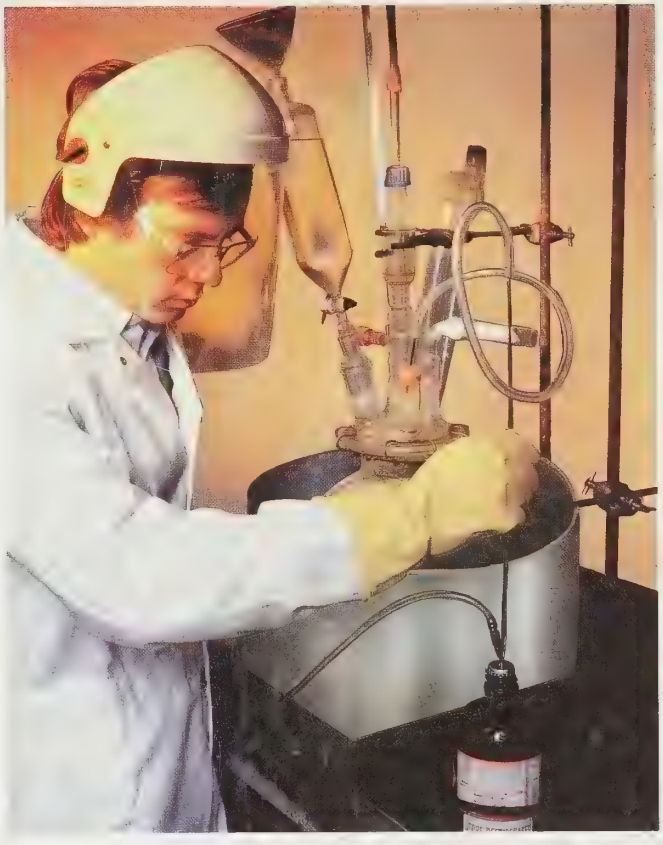

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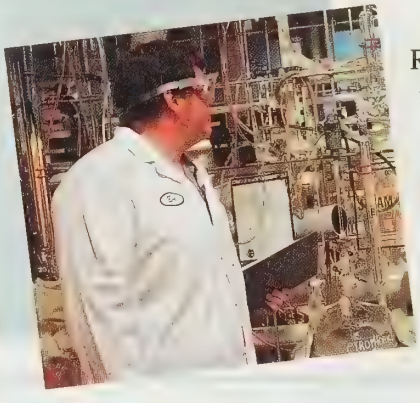

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Aldrichimica Acta

Volume 24, Number 2, 1991

Fluoroheterocyclic Compounds:
Synthesis, Reactions, and Commercial Applications

Transannular Diels-Alder Reaction on Macrocycles:
A General Strategy for the Synthesis of Polycyclic Compounds

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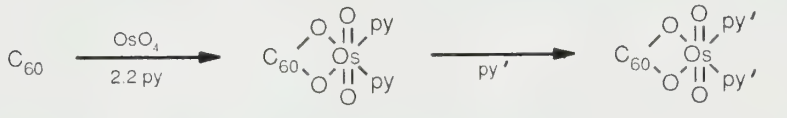
The Third Form of Carbon

The announcement of the preparation of recoverable quantities of C_{60} has created tremendous interest in this molecule. The domed, sixty-carbon cluster has been called buckminsterfullerene after the architect R. Buckminster Fuller, a champion of the geodesic dome. Buckminsterfullerene was proposed by Smalley, Kroto and co-workers in 1985 as a structure for the unusually stable, sixty-carbon fragment they observed in the gas phase.[1] In late 1990, Huffman, Kratschmer and co-workers reported the isolation of macroscopic quantities.[2] The availability of significant quantities of C_{60} has sparked a variety of research programs, ranging from studies of the fundamental properties of the molecule to applications-based work in several industries. Two of the more prominent successes in this research are described below.

Crystal Structure

Joel M. Hawkins and his group at the University of California, Berkeley have shown that the C_{60} framework is not disturbed by treatment with OsO_4 and pyridine.[3] Careful selection of reactive conditions allowed the Hawkins' group to isolate a 1:1 osmium:C_{60} species.



The derivatized C_{60} is of lower symmetry and its structure was established by X-ray crystallography. The X-ray analysis confirmed the "soccer ball" structure of C_{60}.

Electrical Properties

Robert C. Haddon and co-workers at AT&T Bell Labs have prepared conducting derivatives of C_{60}. Films of fullerenes were doped with alkali metals and the resultant materials were good electrical conductors at room temperature. The potassium derivative became superconducting at 18 K, the highest transition temperature (T_c) for a molecular superconductor.[4] These materials are not air-stable, but they highlight the tremendous potential of the fullerene molecules.

References

(1) Kroto, H.W.; Heath, J.R.; O'Brien, S.C.; Curl, R.F.; Smalley, R.E. *Nature* **1985**, *318*, 162. (2) Kratschmer, W.; Lamb, L.D.; Fostiropoulos, K.; Huffman, D.R. *ibid.* **1990**, *347*, 354. (3) Hawkins, J.M.; Meyer, A.; Lewis, T.A.; Loren, S.; Hollander, F.J. *Science* **1991**, *252*, 312. (4) Haddon, R.C. et al. *Nature* **1991**, *351*, 600.

Aldrich is pleased to offer its first product in the fullerenes line– a mixture of C_{60} and C_{70} that we call fullerite. The material is the extractable portion of the soot formed by Huffman's process and is available now from our stock. We hope to add the pure compounds and derivatives in the near future.

Please call our Technical Customer Service Department at 800-231-8327 to inquire about the status of this product line.

37,712-0 Fullerite (mixture of C_{60} and C_{70}) **25mg $60.00; 100mg $180.00**

Aldrichimica Acta

Volume 24, Number 2, 1991
A publication of the ALDRICH CHEMICAL COMPANY

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About Our Cover:

Our chemist collector loves to buy problem paintings — those with problems of attribution or with the subject in doubt. This painting (oil on canvas, 34 x 25 inches) obviously depicts Tobias catching the fish — the seventh Tobias on our *Aldrichimica Acta* covers. It is fully signed Jan van de Venne, but who was this artist? Our chemist collector knows of only one other painting with this signature, a winter landscape dated 1670, which belonged to the museum in Darmstadt but which was burnt during the last war. However, surely an artist who painted so well must have produced other works. Dealers have often erased signatures to be able to attribute works to better known and, hence, more valued painters. We don't even know whether this artist was Flemish or Dutch. Perhaps our cover will lead to other paintings, resulting in a clearer understanding of this painter's work.

The Detective's Eye: Investigating the Old Masters

Twenty-three paintings that have been reproduced on our *Acta* covers and five that have been on our catalog covers were among some seventy works in an exhibit at the Milwaukee Art Museum (January 19 - March 19, 1989) for which Isabel and Alfred Bader were guest curators.

If you relish detective work and puzzles about Old Master paintings, you will find much to enjoy in this fully illustrated catalog, and you will learn something about our chemist collector's interest in art and connoisseurship as well.

Z18,350-4 **$12.20**

Telling Images—Images Révélatrices

Large, 150-page catalog of thirty-six Old Master paintings now in a travelling exhibition touring Canada. All were given by the Baders to Queen's University.

The catalog illustrates all thirty-six paintings, thirteen of them in color. The extensive scholarly text written by Professor David McTavish is in English and French.

Z20,404-8 **$18.30**

Pictures from the Age of Rembrandt

Twenty-eight paintings that have been reproduced on our *Acta* covers, and seven that have been on our catalog covers were among the thirty-six paintings in an exhibition of Dutch paintings at Queen's University in Kingston, Ontario. The fully illustrated catalog written by Professor David McTavish contains a wealth of art-historical information — enough for several evenings of relaxed enjoyment — probably the best value in art-history anywhere.

Z12,794-9 **$8.10**

Lab Notes

I would like to contribute a useful tip to help make chromatography less tedious.

It is common to use the 'ears' on columns and pressure regulators to hold them in place with rubber bands. The pressure buildup inside the column is sometimes large enough to pop the regulator up. Due to the elasticity of the rubber bands and the release of the pressure, the regulator slams down and gets stuck. The chromatography has to be stopped because solvent addition is not possible. Recovery of the sample and cleaning of the column is also impossible. This can be avoided by using the Delrin® KECK®clips. (Figure 1) These clips usually hold if the flow rates used are near that suggested by Still and co-workers in their landmark paper (Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978,** *43,* 2923.) on flash chromatography. I have used these clips (24/40) on columns ranging from 2- to 0.2-in. width. In case of a sudden increase in pressure, the regulator is raised within the confines of the KECK clip and pressure is released.

UmaShanker Sampath
The University of Kansas
Department of Chemistry
Lawrence, KS 66045-0046

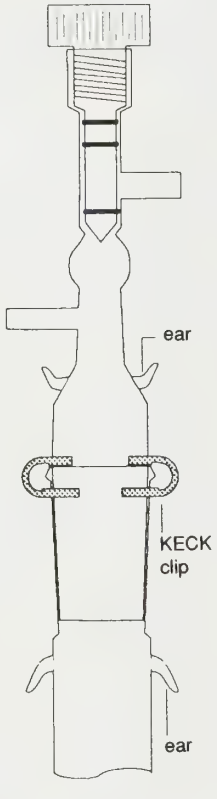

Fig. 1 - *Use of Delrin KECK clips.*

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Editor's Note: Aldrich offers a wide assortment of the Delrin KECK clips recommended by UmaShanker Sampath. Many of these are listed below. For more information contact our Technical Customer Services Department at 800-231-8327.

Delrin KECK Clips

For securing ₹ ground glass joints. Withstands temperatures to 140 °C (284 °F). Will not scratch glass.

₹ Joint	Cat. No.	Pkg of 10
10/18	**Z15,040-1**	$20.90
14/20	**Z15,042-8**	21.10
19/22	**Z15,043-6**	21.40
24/40	**Z15,044-4**	22.55
29/42	**Z15,045-2**	24.65

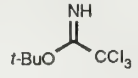
Set of five of each clip above
Z15,046-0 $50.35

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive, *at no cost*, a laminated periodic table poster. If we publish your *Lab Note*, you will also receive **The Detective's Eye: Investigating the Old Masters** (see previous page). We reserve the right to retain all entries for consideration for future publication.

"Please Bother Us."

by

Dr. R.F.W. Jackson at the University of Newcastle and Mr. D.J. Wadsworth, working with Professor S.V. Ley at Imperial College, suggested this interesting reagent for the preparation of *tert*-butyl ethers and esters.



Naturally, we made this compound.

Wessel, H.-P.; Iversen, T.; Bundle, D.R. *J. Chem. Soc., Perkin Trans. 1* **1985,** 2247. Armstrong, A.; Brackenridge, I.; Jackson, R.F.W.; Kirk, J.M. *Tetrahedron Lett.* **1988,** *29,* 2483.

36,478-9 *tert*-Butyl 2,2,2-trichloroacetimidate **5g $12.00; 25g $39.75**

It was no bother at all, just a pleasure to be able to help.

Interested in Alchemy?

In February 1931, one of the greatest chemists of this century, Professor Tadeus Reichstein, presented a lecture on the true meaning of alchemy at the ETH in Zürich.

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Z22,319-0 The Meaning of Alchemy
Z22,320-4 Der Sinn der Alchemie

Synthetic Reagents

Chiral Fumarates

These fumarates exhibit high selectivity as chiral dienophiles in Diels-Alder reactions. Recent examples include the use of **1** in the synthesis of methyl (+)-epijasmonate[1] and of **2** in the preparation of deltamethrin.[2]

(1) Helmchen, G.; Goeke, A.; Lauer, G.; Urmann, M.; Fries, J. *Angew. Chem.* **1990,** *102,* 1079. (2) Krief, A.; Lecomte, P.; Demoute, J.P.; Dumont, W. *Synthesis* **1990,** 275.

37,479-2 Bis[(*S*)-1-(ethoxycarbonyl)-ethyl] fumarate, 97% (**1**) **1g $6.00**
10g $32.00
34,891-0 (-)-Dimenthyl fumarate, 97% (**2**) **1g $12.05; 5g $40.10**

Dehydration/Decarboxylation

Has been used recently to convert arylhydroxyiminopropionic acids into arylacetonitriles in improved yields by dehydration/decarboxylation.

Kitagawa, T.; Kawaguchi, M.; Ikiuchi, M. *Chem. Pharm. Bull.* **1991,** *39,* 187.

36,643-9 1,1'-Oxalyldiimidazole
1g $14.00; 5g $47.00

Thiophile

Used to convert thionocarbonates to olefins under mild conditions.[1] Recently employed by Curran in synthetic studies directed toward the C-ring of Sesbanimide A.[2]

(1) Corey, E.J.; Hopkins, P.B. *Tetrahedron Lett.* **1982,** *23,* 1979. (2) Curran, D.P.; Chao, J.-C. *Synth. Commun.* **1990,** *20,* 3575.

37,367-2 1,3-Dimethyl-2-phenyl-1,3,2-diazaphospholidine, 97%
1g $7.00; 5g $23.70

Erythronolactone

This useful 4-carbon synthon was recently employed by Cha and Bennett in the synthesis of (-)-swansonine.

Cha, J.K.; Bennett, R.B., III Int. Patent 06 311, 1990; *Chem. Abstr.* **1990,** *113,* 212415r.

37,438-5 D-Erythronic γ-lactone
250mg $11.50; 1g $32.00

Chiral Hydroxy Ester

Key chiral starting point for a variety of biologically important target compounds including deoxyaminotetroses,[1] arylpropionic acids,[2] and some hypolipidemics.[3]

(1) Guanti, G.; Banfi, L.; Narisano, E. *Tetrahedron Lett.* **1989,** *30,* 5507. (2) Larsen, R.D.; Corley, E.G.; Davis, P.; Reider, P.J.; Grabowski, E.J.J. *J. Am. Chem. Soc.* **1989,** *111,* 7650. (3) Kathawala, F.G. Int. Patent 03 973, 1990; *Chem. Abstr.* **1990,** *113,* 172040f.

37,431-8 Dimethyl (*S*)-(-)-malate, 98%
5g $17.50; 25g $74.35

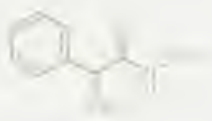
Benzeneselenol

Recently used to prepare selenium/silicon compounds as models for silicon chalcogenide glasses[1] and used as a substrate in a study of diastereoselective reactions of selenoacetals.[2]

(1) Shibao, R.K.; Keder, N.L.; Eckert, H. *Inorg. Chem.* **1990,** *29,* 4163. (2) Hoffmann, R.W.; Bewersdorf, M. *Tetrahedron Lett.* **1990,** *31,* 67.

37,515-2 Benzeneselenol, 99%
250mg $9.00; 1g $25.00

Chiral Precursor



Convenient and stable precursor to a chiral acyl nitroso dienophile. The derived Diels-Alder adducts are potential starting materials for C-nucleoside synthesis.

Miller, A.; Paterson, T.McC.; Procter, G. *Synlett* **1989,** *1,* 32. Kirby, G.W.; Nazeer, M. *Tetrahedron Lett.* **1988,** *29,* 6173. Miller, A.; Procter, G. *ibid.* **1990,** *31,* 1043.

37,373-7 (*R*)-Mandelohydroxamic acid **1g $8.00; 5g $26.50**

Melamine-Cyanurate

Employed in the preparation of flame-retardant and smoke-suppressant polyurethane compositions[1] and of dispersants for water-based solid lubricants.[2]

(1) Scarso, L. Eur. Patent 389 768, 1990; *Chem. Abstr.* **1991,** *114,* 25340w. (2) Nishizaki, K.; Mayuzumi, F. Jpn. Patent 02 145 694, 1990; *Chem. Abstr.* **1991,** *114,* 27072j.

37,242-0 Cyanuric acid, compound with melamine **100g $10.00**
500g $32.00

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Aldrichimica Acta

Volume 24, Number 3, 1991 *(Last issue in 1991)*

Organic Chemistry in Unconventional Solvents

The Molecular Basis of Biological Order

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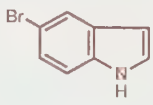
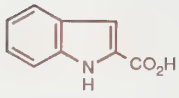
INDOLES

Since the first identification of an indole skeleton in indigo over a century ago, this nucleus has been found in various dyes, alkaloids, and plant growth hormones. It is also present in tryptophan and is a key element in various drugs such as indomethacin, the thiosemicarbazone of 1-methylisatin, and several CNS depressants. The fluorescent and phosphorescent properties of indoles have been valuable in their detection and identification, especially in biological systems.[1] Aldrich offers a number of indole derivatives, some of which are presented below. Please consult the Aldrich Catalog/Handbook for other indoles and related products.



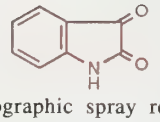
Synthesis of selective 5-hydroxytryptamine antagonists.[2]

B6,860-7 5-Bromoindole, 99%
5g $15.35; 25g $67.20



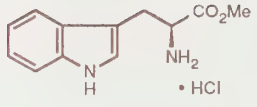
Synthesis of antitumor and antibacterial agents.[5]

I-510-9 Indole-2-carboxylic acid, 98%
5g $18.50; 10g $30.80
50g $108.00



Chromatographic spray reagent for amino acids.[8]

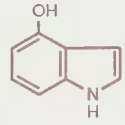
11,461-8 Isatin, 98% **5g $10.15**
100g $10.95; 500g $34.75



(-)-Indolactam-V[13] and vindorosine[14] synthesis.

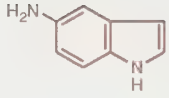
36,451-7 L-Tryptophan methyl ester hydrochloride, 98% (1) **5g $10.05**
25g $39.05

36,450-9 D-Tryptophan methyl ester hydrochloride, 98% **1g $7.20**
5g $25.40



Precursor for anticancer agents.[3]

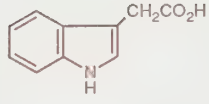
21,987-8 4-Hydroxyindole, 99%
250mg $29.15; 1g $79.50



Used in combination with hydrazones as chromogenic systems for the detection of peroxidase.[6]

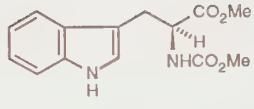
A5,965-4 5-Aminoindole, 97% (1)
1g $34.40; 5g $110.15

30,720-3 5-Aminoindole hydrochloride, 98% **250mg $13.70; 1g $38.40**



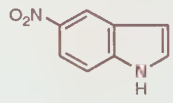
Agrochemical research.[9]

I-375-0 Indole-3-acetic acid, 98%
5g $8.30; 25g $22.30; 100g $84.35



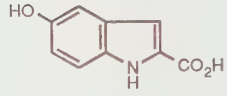
Oxyindole alkaloid synthesis.[15]

36,706-0 Nα-Methoxycarbonyl-L-tryptophan methyl ester, 98%
1g $16.50; 5g $55.00



Peptidoleukotriene antagonist synthesis.[4]

N1,760-2 5-Nitroindole, 98%
1g $17.10; 5g $57.00; 25g $154.70

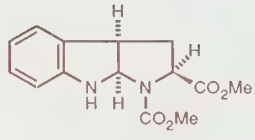


Preparation of benzodiazepines such as cholecystokinin and gastrin inhibitors.[7]

14,351-0 5-Hydroxy-2-indolecarboxylic acid, 98% **1g $40.60**
5g $137.05

Deserpidine,[10] *dl*-alloyohimbine,[11] and *dl*-deplancheine[12] synthesis.

37,652-3 3-(2-Bromoethyl)indole, 97%
1g $9.00; 5g $30.00



Synthesis of natural products.[16]

37,236-6 Dimethyl L-(+)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indole-1,2(2*H*)-dicarboxylate 1g $17.00

(1) *Heterocyclic Compounds - Indoles*; Houlihan, W.J., Ed.; Wiley Interscience: New York; 1972, Parts 1, 2, and 3. (2) Glaser, T.; Raddatz, S.; Traber, J.; Allen, G. U.S. Patent 4 870 085, 1989; *Chem. Abstr.* **1990**, *112*, 198126t. (3) Fukazawa, N.; Odate, M.; Suzuki, T.; Tsuruo, T. Jpn. Patent 2 121 966, 1990; *Chem. Abstr.* **1990**, *113*, 152477a. (4) Matassa, V.G. et al. *J. Med. Chem.* **1990**, *33*, 1781. (5) Kelley, R.C.; Warpehoski, M.A.; Wierenga, W. U.S. Patent 4 912 227, 1990; *Chem. Abstr.* **1990**, *113*, 131891r. (6) Vermeulen, N.M.J.; Petrie, C.R. Int. Patent 9 006 372, 1990; *Chem. Abstr.* **1990**, *113*, 207477h. (7) Evans, B.E.; Freidinger, R.M.; Bock, M.G. Eur. Patent 284 256, 1988; *Chem. Abstr.* **1989**, *110*, 135272a. (8) *Thin-Layer Chromatography*; Stahl, E., Ed.; Springer-Verlag: Heidelberg; 1969, p 730. (9) Sundberg, B.; Little, C.H.A. *Plant Physiol.* **1990**, *94*, 1721. (10) Baxter, E.W.; Labaree, D.; Ammon, H.L.; Mariano, P.S. *J. Am. Chem. Soc.* **1990**, *112*, 7682. (11) Lounasmaa, M.; Jokela, R. *Tetrahedron* **1990**, *46*, 615. (12) Fugii, T.; Ohba, M.; Sasaki, N. *Chem. Pharm. Bull.* **1989**, *37*, 2822. (13) Kogan, T.P.; Somers, T.C.; Venuti, M.C. *Tetrahedron* **1990**, *46*, 6623. (14) Winkler, J.D.; Scott, R.D.; Williard, P.G. *J. Am. Chem. Soc.* **1990**, *112*, 8971. (15) Irie, K.; Ishida, A.; Nakamura, T.; Oh-Ishi, T. *Chem. Pharm. Bull.* **1984**, *32*, 2126. (16) Taniguchi, M.; Angiki, T.; Nakagawa, M.; Hino, T. *ibid.* **1984**, *32*, 2544.

Aldrichimica Acta

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About Our Cover:

Readers of the *Aldrichimica Acta* have known for twenty-four years that our chemist collector prefers Dutch 17th century paintings, preferably of Biblical subjects by Rembrandt students. But occasionally he just cannot resist buying more modern paintings. So it was with this large family portrait (oil on canvas, 59 x 91 inches), which he first saw in the basement of a Paris dealer. The clothing suggests that it was painted about 1815, but where and by whom? Is the ring on the middle finger of the mother's left hand a clue to the country and denomination? The desk looks New England of the period, but there may have been desks just like this in Scandinavia. The family Bible is open at "Acts", in English.

The raw canvas was exported from England by the London firm of Jesse Middleton which supplied canvases to Rembrandt Peale and Gilbert Stuart, but probably also to European artists. The sylvestris pine of the heavy stretcher could have grown in North America or northern Europe. Prof. R. B. Hoadley and his students at the University of Massachusetts at Amherst have developed a method[1] to distinguish between them, which involves measurements of fusiform ray heights. Unfortunately, there is a range where one cannot distinguish between North American red pine and northern European Scots pine, and values obtained from this stretcher fall into that range.

What is most enchanting is the depiction of the personalities: the stern father (a minister?), the mother, concerned mainly with the welfare of the family, and each of the children, alike in some ways, yet so different. And don't overlook the dog and cat.

Our hope is that descendants of this family will recognize their ancestors and so point to where this was painted and perhaps even to the artist.

Some years ago, in *Aldrichimica Acta 11*, 3 (1978), we depicted a Dutch church, and several readers identified the church through its distinctive organ. Perhaps readers will be able to help us with this, also.

The quality of this painting makes it a fitting cover for the *Acta* with the truly exciting papers of Prof. Grieco and Dr. Williams.

1) "The Use of Fusiform Rays as a Basis for Distinguishing the Woods of *P. sylvestris* and *P. resinosa*," Zarifan, S.A. M.Sc. Thesis, University of Massachusetts at Amherst, Department of Forestry and Wildlife Management, May, 1987.

Lab Notes

I was surprised to find that one type of flask which has been made by German and Czech glassblowers for at least 50 years was not available in the U.S. Since this flask with the round bottom, the "Apollo" flask, is so useful to the organic chemist, I suggest that Aldrich might like to offer it.

It has properties similar to the Apollo space ship; when dropped on water it has two stable positions. In most cases it will stand on a bench in a stable position without a ring, and it can float on a liquid surface, even in a very unstable position, keeping the neck up. It will float in a stable position upside down in a liquid. This means that if a filled flask drops from the rotavap, most of the solution remains inside the flask. Simply close the neck with a stopper and remove it from the bath. A further advantage of the Apollo flask is that it has a larger inner volume than the round-bottom flask for the evaporation of foaming liquids, and the inner surface of the flask is easily reached with a spatula.

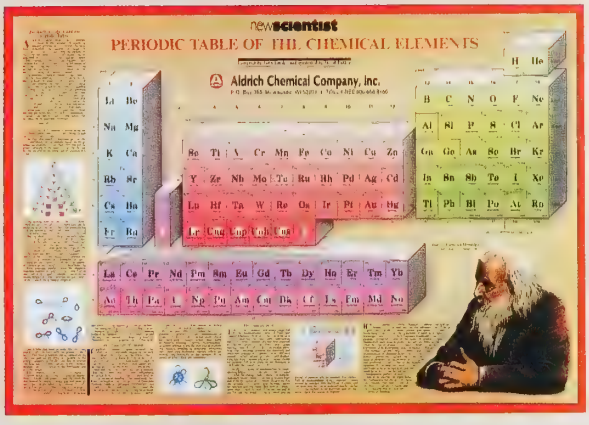
Dr. Pavel Drasar
Institute of Organic Chemistry
and Biochemistry
Czechoslovak Academy of Sciences
Flemingovo 2
CS-166 10 Praha 6
Czechoslovakia

Editor's Note: Aldrich now offers five volumes of Apollo flasks in both ₹14/20 and ₹14/23 joint sizes. These are listed below. For more information, contact our Technical Services Department at 800-231-8327.

Apollo Flasks

Low profile flasks for easy access with a spatula. Inner shape of the flask is best for the controlled evaporation of foaming solvents, such as toluene or xylene, on a rotovap.

	with ₹14/20 joint		with ₹14/23 joint	
Cap. (ml)	Cat. No.	Each	Cat. No.	Each
10	**Z22,131-7**	$10.70	**Z22,137-6**	$10.70
25	**Z22,132-5**	11.90	**Z22,138-4**	11.90
50	**Z22,133-3**	11.90	**Z22,139-2**	11.90
100	**Z22,134-1**	15.05	**Z22,140-6**	15.05
250	**Z22,136-8**	15.20	**Z22,141-4**	15.20



Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster. If we publish your *Lab Note*, you will also receive **The Detective's Eye: Investigating the Old Masters** (see previous page). We reserve the right to retain all entries for consideration for future publication.

"Please Bother Us."

by Aldrich Boaz.

Dr. Ian O'Neil of the University of Liverpool kindly suggested that we offer a reversed phase silica gel for column chromatography. Using chromatography methods, compounds such as organic stannanes,[1] amino-acids, nucleosides, carboxylic acids, and sulfonic acids may be readily separated.[2]

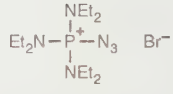
Naturally, we made this material.

(1) Farina, V. *J. Org. Chem.* **1991**, *56*, 4985. (2) O'Neil, I.A. *Synlett.* **1991**, 661.

37,763-5 Octadecyl-functionalized silica gel
25g $22.00 100g $61.00

It was no bother at all, just a pleasure to be able to help.

New Diazo Transfer Reagent



This new reagent, suggested by Prof. Ralph Raphael of Cambridge University, bears a strongly basic phosphorimine nitrogen (allowing basic autocatalysis), generates a neutral leaving group (hexaethylphosphoramidic triamide, easily removed as its hydrobromide salt), and is reportedly exceptionally stable against shock, friction, and rapid heating.

McGuiness, M.; Shechter, H. *Tetrahedron Lett.* **1990**, *31*, 4987.

38,082-2 Azidotris(diethylamino)phosphonium bromide, 98%
1g $8.50; 5g $24.00

Metal powders. . .

which have long been the basis of a whole field of metallurgy, are now becoming increasingly useful to the synthetic chemist. Their use as reducing agents is widespread in both inorganic and organic chemistry. They are also becoming important starting materials in organic syntheses. Co-condensation of metal vapors with organic ligand vapors has led to the preparation of a variety of metal complexes.[1] Recently, the Rauchfuss group prepared several transition metal-sulfur compounds by *room temperature* reaction of metal powders, sulfur, and *N*-methylimidazole.[2] Below is a listing of our metal powders from the first row of the transition metals. Of course we offer metal powders from throughout the entire periodic table. Please consult the Aldrich Catalog/Handbook for those not listed here.

Ti

36,699-4 **Titanium**, -325 mesh, 99.98%
10g $25.00; 50g $85.00

26,849-6 **Titanium**,-100 mesh, 99.9%
10g $9.75; 50g $28.40

V

26,293-5 **Vanadium**, -325 mesh, 99.5%
10g $30.95; 50g $118.35

Cr

26,626-4 **Chromium**, -100 mesh, 99.5%
50g $23.45; 250g $74.50

26,629-9 **Chromium**, -325 mesh, 99+%
100g $15.55; 500g $57.55

26,627-2 **Chromium**, -200 mesh, 99%
100g $14.40; 500g $50.55

Mn

26,614-0 **Manganese**, -50 mesh, 99.9%
100g $19.00; 500g $70.15

26,613-2 **Manganese**, -325 mesh, 99+%
250g $17.45; 1Kg $47.00

26,615-9 **Manganese**, -50 mesh, 99+%
500g $11.50; 2Kg $33.20

Fe

25,563-7 **Iron**, 99.99+%
10g $31.70; 50g $107.30

26,795-3 **Iron**, ~10µ, 99.9+%
250g $24.80; 1Kg $66.80

20,930-9 **Iron**, -325 mesh, 97%
500g $20.20; 2Kg $59.30

Co

20,307-6 **Cobalt**, 99.995%
5g $35.00; 25g $129.20

26,663-9 **Cobalt**, <2µ, 99.8%
100g $29.35; 500g $107.20

Ni

26,696-5 **Nickel**, -100 mesh, 99.999%
10g $18.90; 50g $63.95

20,390-4 **Nickel**, -100 mesh, 99.99%
100g $22.05; 500g $62.85

26,828-3 **Nickel**, submicron, 99.8%
25g $31.25; 100g $98.35

26,698-1 **Nickel**, ~3µ, 99.7%
100g $12.00; 500g $42.20

26,697-3 **Nickel**, -100 mesh, 99%
100g $10.55; 500g $38.40

Cu

20,312-2 **Copper**, 99.999%
10g $61.50; 50g $231.85

35,745-6 **Copper**, dendritic,~3µ, 99.7%
100g $10.95; 500g $38.40

26,607-8 **Copper**, -150 mesh, 99.5%
100g $11.30; 500g $39.90

26,608-6 **Copper**, -40 mesh, 99.5%
500g $19.50; 2Kg $59.20

32,646-1 **Copper**, submicron, 99+%
10g $23.65; 50g $84.95

20,778-0 **Copper**, -200 mesh, 99%
500g $18.60; 2Kg $54.90

32,645-3 **Copper**, spheres, 5-10µ, 99%
50g $9.85; 1Kg $29.95

Zn

32,493-0 **Zinc**, -100 mesh, 99.998%
10g $41.00; 50g $146.05

24,347-7 **Zinc**, -30 +100 mesh, 99%
A.C.S. reagent 500g $28.20
2.5Kg $104.75; 3Kg $135.40

26,634-5 **Zinc**, -15 +50 mesh, 99%,
A.C.S. reagent
250g $12.50; 1Kg $36.65

24,346-9 **Zinc**, 20 mesh, A.C.S.
reagent 100g $11.40
500g $28.20; 3Kg $135.40

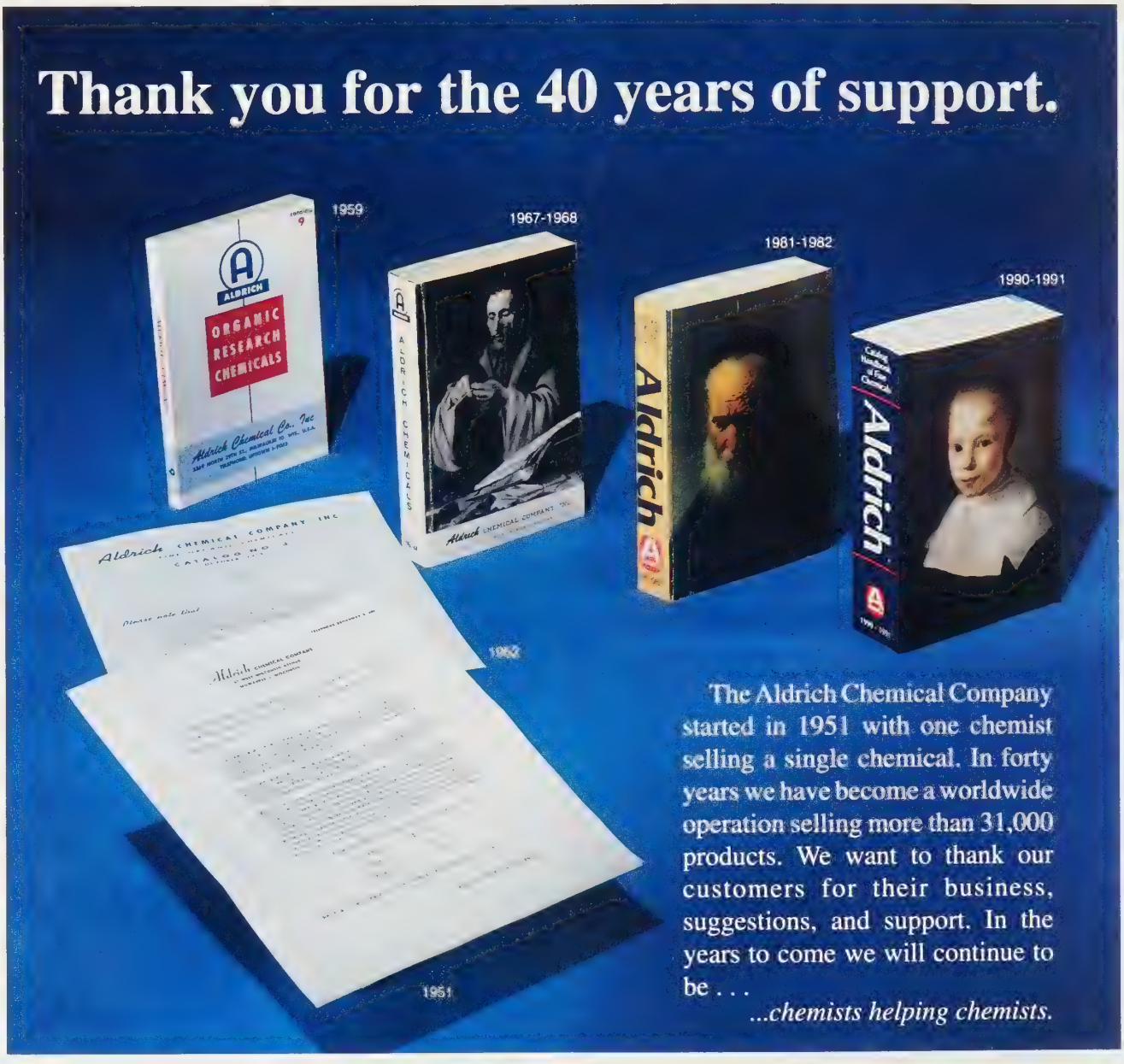
20,998-8 **Zinc**, dust, -325 mesh
100g $15.45
1Kg $27.80; 5Kg $86.50

A particle size conversion table is located in the back of the Aldrich Catalog/Handbook.

References

1. For general discussions of metal vapor synthesis see: Blackborrow, J.R.; Young, D. *Metal Vapor Synthesis in Organometallic Chemistry;* Springer-Verlag, Berlin, 1979. Timms, P.L.; Turney, T.W. *Adv. Organometal. Chem.* **1977**, *15*, 53. Green, M.L.H. *J. Organometal. Chem.* **1980**, *200*, 119. Klabunde, K. *Acc. Chem. Res.* **1975**, *8*, 393.
2. Dev, S.; Ramli, E.; Rauchfuss, T.B.; Wilson, S.R. *Inorg. Chem.* **1991**, *30*, 2514 and references contained therein.

Thank you for the 40 years of support.



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Aldrichimica Acta

Volume 25, Number 1, 1992

A Methionine Salvage Pathway

Asymmetric Syntheses of α-Amino Acids

chemists helping chemists in research & industry

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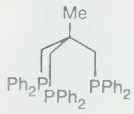
New Reagents

Tripodal Ligand



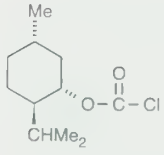
This tripodal polyphosphine forms stable complexes with most d-block metals with varying stereochemistry and oxidation states. These complexes have been used to catalyze hydrogenations, hydroformylations, acetylations, polymerizations, and oxidations.

Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics* **1990**, *9*, 226 and references cited therein.

38,074-1 1,1,1-Tris(diphenylphosphinomethyl)ethane 1g $12.00; 5g $41.00

25,910-1 Bis(2-diphenylphosphinoethyl)phenylphosphine, 97%
1g $24.05; 5g $102.70

For Asymmetric Synthesis

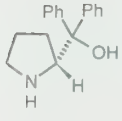


Chiral auxiliary in the asymmetric synthesis of quaternary carbon centers.

Kunisch, F.; Hobert, K.; Welzel, P. *Tetrahedron Lett.* **1985**, *26*, 5433.

37,871-2 (+)-Menthyl chloroformate 5mL $18.00; 25mL $63.00

Now Available

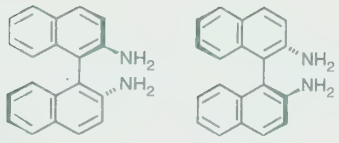


Used to prepare the corresponding oxazaborolidines which are gaining popularity as catalysts for the borane-mediated asymmetric reduction of ketones.

Corey, E.J.; Bakshi, R.K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551. Jones, T. et al. *J. Org. Chem.* **1991**, *56*, 763.

38,233-7 (*R*)-(+)-α,α-Diphenyl-2-pyrrolidinemethanol, 99%
25mg $13.25; 100mg $37.00
36,819-9 (*S*)-(-)-α,α-Diphenyl-2-pyrrolidinemethanol, 99%
250mg $12.50; 1g $34.80

Chiral Binaphthyldiamines

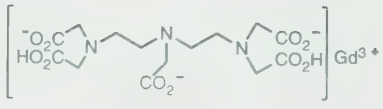


Like their diol counterparts [(*R*)- and (*S*)-binaphthols], the use of these atropisomeric diamines is rapidly increasing in asymmetric synthesis. A recent example involves their use in the synthesis of chiral lactones.

Oda, J. et al. *J. Org. Chem.* **1991**, *56*, 1112.

38,242-6 (*R*)-(+)-1,1'-Binaphthyl-2,2'-diamine, 99% **250mg $25.20; 1g $78.80**
38,243-4 (*S*)-(-)-1,1'-Binaphthyl-2,2'-diamine, 99% **250mg $25.20; 1g $78.80**

Gadopentetic acid



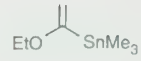
The gadolinium complex of DTPA is fast becoming a reagent of choice for MRI, Magnetic Resonance Imaging, related applications.

Karlik, S.; Florio, E.; Grant, C.W.M. *Magn. Reson. Med.* **1991**, *19*, 56; *Chem. Abstr.* **1991**, *115*, 4254b. Holz, R.C.; Horrocks, W.D., Jr. *J. Magn. Reson.* **1990**, *89*, 627; *Chem. Abstr.* **1991**, *114*, 2914x. Gennaro, M.C.; Aime, S.; Santucci, E.; Causa, M.; De Stefano, C. *Anal. Chim. Acta* **1990**, *233*, 85.

38,166-7 Diethylenetriaminepentaacetic acid gadolinium(III) dihydrogen salt hydrate, 97% **5g $7.00; 25g $23.00**

Also available from Aldrich
38,952-8 Diethylenetriaminepentaacetic acid, manganese(II) trihydrogen salt monohydrate, 98%
5g $7.00; 25g $23.00
D9390-2 Diethylenetriaminepentaacetic acid, 97% (DTPA)
100g $7.00; 500g $21.70

New Organostannane

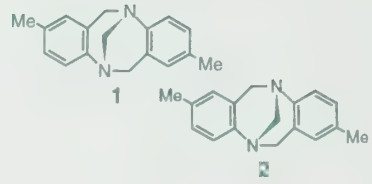


Useful reagent forming unsaturated ketones via a palladium-mediated coupling reaction with vinyl triflates.

Cheney, D.L.; Paquette, L.A. *J. Org. Chem.* **1989**, *54*, 3334.

38,183-7 1-Ethoxy-1-(trimethylstannyl)-ethylene, 99% **1g $12.25; 5g $41.00**

Chiral Amines

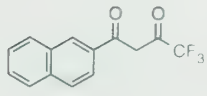


Tröger's base is a chiral heterocyclic amine that has chirality due to asymmetric nitrogen atoms prevented from configurational inversion by a methano bridge. The enantiomers (**1** and **2**) have recently been employed as chiral solvating agents.

Wilen, S.H.; Qi, J.Z.; Williard, P.G. *J. Org. Chem.* **1991**, *56*, 485.

37,464-4 (+)-Tröger's Base, 99+% (**1**) **100mg $20.10; 500mg $67.00**
37,465-2 (-)-Tröger's Base, 99+% (**2**) **100mg $20.50; 500mg $68.30**

New Ligand

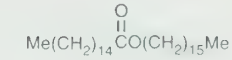


The lanthanide complexes[1] of this trifluoro substituted β-diketone are very useful in the determination of enzymes[2] and other biochemicals by time-resolved fluorescence spectroscopy.[3]

(1) Mukoyama, M.; Isayama, S.; Kato, K.; Inoki, S.; Yamada, T.; Takai, T. Jpn. Patent 2 169 539, 1990; *Chem. Abstr.* **1991**, *114*, 220198h. (2) Drevin, H. et al. Int. Patent 881 701, 1988; *Chem. Abstr.* **1990**, *113*, 55033v. (3) Morin, M. et al. *Anal. Chim. Acta* **1989**, *219*, 67.

34,363-3 4,4,4-Trifluoro-1-(2-naphthyl)-1,3-butanedione, 99%
5g $12.00; 25g $39.00

Cetyl Palmitate



Fatty acid ester with a variety of applications including cosmetic compositions and emulsifiers,[1] heat sensitive recording material,[2] and as an α-tocopherol (vitamin E) GLC reference standard.[3]

(1) Pereira, M. Eur. Patent 358 528, 1990; *Chem. Abstr.* **1990**, *113*, 237566d. (2) Koshizuka, K.; Abe, T. Eur. Patent 372 800, 1990; *Chem. Abstr.* **1991**, *114*, 45181y. (3) *United States Pharmacopeia XXII 1452.*

38,833-5 Hexadecyl hexadecanoate, 98%
10g $10.50; 50g $36.00

Aldrichimica Acta

Volume 25, Number 1, 1992
A publication of the ALDRICH CHEMICAL COMPANY

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About Our Cover:

Just ten years ago we had a painting of Rembrandt's old, and almost blind, father on the cover of our Catalog/Handbook. And so, it seems fitting now to show a study of Rembrandt's mother, done the same year, in 1629, by Rembrandt's fellow artist, Jan Lievens, who may have shared a studio with Rembrandt in Leiden.

This is one of our chemist collector's favorite works—the marvelous, delicate transparency of the headscarf with its subtle play of color provides such a foil for the face of this plain old woman—almost as if the artist wanted the scarf as a symbol of her inner goodness.

What we said about Rembrandt's father in the 1981-1982 Catalog applies equally to Rembrandt's mother: "The overpowering emotion one feels when viewing this study is that of the care of one human being for another."

If you would like to have a reproduction of this painting, please do not tear off this cover; we will be happy to send you a full color print of the painting suitable for framing (Cat. No. Z23,135-5, $2.10, postpaid).

The Detective's Eye: Investigating the Old Masters

Twenty-four paintings that have been reproduced on our *Aldrichimica Acta* covers, and five that have been on our catalog covers, were among some seventy works in an exhibit at the Milwaukee Art Museum (January 19 through March 19, 1989) for which Isabel and Alfred Bader were guest curators.

If you relish detective work and puzzles about Old Master paintings, you will find much to enjoy in this illustrated catalog, and you will learn something about our chemist collector's interest in art and connoisseurship as well.

Z18,350-4 **$12.95**

Telling Images—Images Révélatrices

Large, 150-page catalog of thirty-six Old Master paintings in an exhibition that toured Canada. All were given by the Baders to Queen's University.

The catalog illustrates all thirty-six paintings, thirteen of them in color. The extensive scholarly text written by Professor David McTavish is in English and French.

Z20,404-8 **$19.40**

From Dura to Rembrandt—Studies in the History of Art

A collection of nineteen papers, seventeen in English and two in German, by Rachel Wischnitzer (1885-1989). The content ranges from synagogue architecture to the iconography of works by Rembrandt. Includes this remarkable woman's life story (written by Professor Bezalel Narkiss, director of the Center for Jewish Art at the Hebrew University).

Z21,962-2 **$38.15**

Lab Notes

I would like to suggest some modifications to your mercury manostats (Z14,799-0/ Z15,236-6).

1. The constriction in the tube between the chambers prevents the Hg from "thumping" back and forth when the vacuum level is changed. By slowing the flow of the Hg down, it prevents the Hg from shooting down the pumping line.

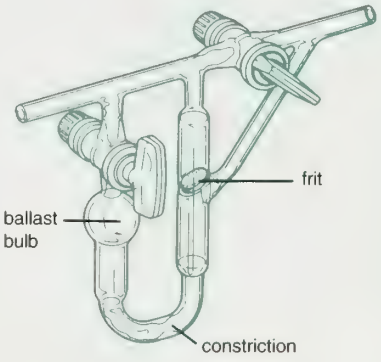
2. The smaller chamber diameters with the bulb on the trapped-air side decrease the amount of Hg needed to control the system while allowing a larger amount of ballast gas to remain in the trapped side. The Hg still can cover the frit without having to use large quantities of Hg to compensate for the larger amount of gas. This system should be able to function well with 10-12mL of Hg in the manostat.

Less Hg means less weight, less possibility of breakage, and less severe clean-up problems.

Please let me know what your glassblowers think.

Steven L. Gatton
Organic Laboratory Coordinator
Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403-0213

Editor's Note: The improved design (based on Mr. Gatton's suggestions) offers safe and accurate automatic control of vacuum pressure. It is now available to our customers, as shown below.



Aldrich mini manostats

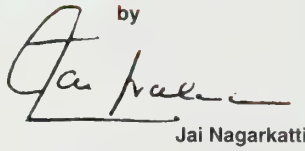
Frit porosity

(µm)	Cat. No.	Each
25-50	**Z22,557-6**	$145.00
10-20	**Z22,558-4**	147.00

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2, $9.90 value). If we publish your *Lab Note*, you will also receive **The Detective's Eye: Investigating the Old Masters** (see previous page). We reserve the right to retain all entries for consideration for future publication.

"Please Bother Us."

by



Jai Nagarkatti, President

Dr. James P. Demers of the R.W. Johnson Pharmaceutical Research Institute (Raritan, New Jersey) suggested that we offer a solution of phosphorus pentoxide in methanesulfonic acid, better known as "Eaton's Reagent".[1] This solution is an excellent alternative to polyphosphoric acid in cyclodehydration reactions leading to cyclopentenones,[2] butenolides[3] and polycyclic aromatics.[4]

Naturally, we made this reagent.

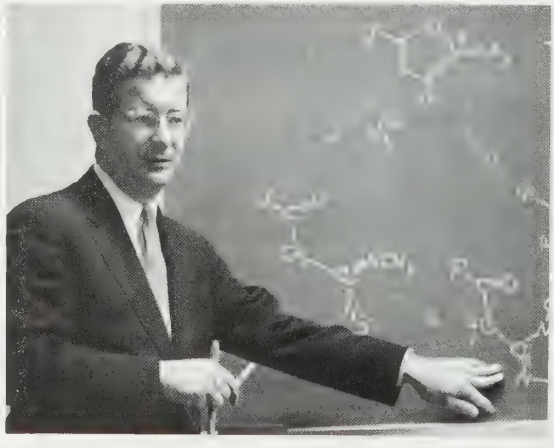
(1) Eaton, P.E.; Carlson, G.R.; Lee, J.T. *J. Org. Chem.* **1973**, *35*, 4071. (2) Eaton, P.E. et al. *J. Am. Chem. Soc.* **1977**, *99*, 2751. (3) Schultz, A.G.; Yee, Y.K. *J. Org. Chem.* **1976**, *41*, 561. (4) Axon, B.W.; Davis, B.R.; Woodgate, P.D. *J. Chem. Soc., Perkin Trans. I* **1981**, 2956.

38,081-4 Eaton's Reagent
100mL $10.50; 500mL $35.00

It was no bother at all, just a pleasure to be able to help.

Working with R. B. Woodward

Professor Robert Burns Woodward of Harvard University was one of the world's greatest organic chemists. Former students, co-workers and friends gathered at the Beckman Center for the History of Chemistry in Philadelphia April 10-11, 1992, the 75th anniversary of R.B.W.'s birth, at the opening of a scholarly exhibition detailing his life and work.



This travelling exhibition is most important because it teaches young chemists of the enormous impact one man can have.

One of the many former co-workers of R.B.W., Dr. Helmut Vorbrüggen of Schering AG, 1000 Berlin 65, Germany, has written a touching and human description of his time with R.B.W. It is available from Aldrich at no charge when requested with any order.

Z23,407-9 *Working with R. B. Woodward* by Prof. Dr. Helmut Vorbrüggen

Attention Sharpless Asymmetric Epoxidation (AE) users:

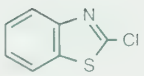
Aldrich offers two grades of anhydrous TBHP in isooctane: 3 molar and 5.5 molar. Only the 5.5 molar solution is compatible with the AE. The titanium tartrate catalyst is destroyed by hydrocarbon solvents and can tolerate only a small amount (such as that introduced with the 5.5 molar grade of TBHP) in the total solvent mixture for the reaction. Professor Sharpless has informed us that a great many chemists have inadvertently been using the 3 molar grade which introduces too much isooctane, thereby crippling the catalyst and usually leading to dramatic attrition in both enantiomeric excess and yield. Thus for the Sharpless Asymmetric Epoxidation NEVER USE the 3 molar TBHP in isooctane. The 5.5 molar grade is the only one to use, as it was specifically formulated for this reaction.

31,037-9 TBHP, Anhydrous, 3.0M in TMP
25g $10.70;100g $25.70; 500g $88.70
33,127-9 TBHP, Anhydrous, 5.5M in TMP
25g $22.60; 100g $63.70

Thiazoles and Benzothiazoles

Since their near simultaneous introduction in 1887 by Hantzsch[1] and Hoffman,[2] these compounds have been extensively used as building blocks for pharmaceutical and agricultural chemicals. They are equally important to the polymer industry as monomers, as stabilizing additives, and are important flavor constituents in foods such as apples, coffee, meats, tomatoes, etc.[3] Aldrich offers more than 100 thiazoles and benzothiazoles; a few are represented below. For additional listings, please consult the 1992-1993 Aldrich Catalog/Handbook or call our Technical Service Department at (800) 231-8327 to request a computer search. If you need a compound that is not currently available, call us at (800) 255-3756 for a custom synthesis quotation.

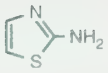
References: (1) Hantzsch, A.; Weber, H.J. *Ber* **1887**, *20*, 3118. (2) Hoffman, A. W. ibid. **1887**, *20*, 2262. (3) *The Chemistry of Heterocyclic Compounds;* Weissberger, A.; Taylor, E.C., Eds.; J. Wiley & Sons: New York, 1979; Vol. 34.



Intermediate for pesticides and anthelmintics.

Blade, R.J. Eur. Patent 346 107, 1989; *Chem. Abstr.* **1990**, *113*, 6180g.

16,757-6 2-Chlorobenzothiazole, 99%
5g $17.00; 25g $59.40



Utilized in the preparation of antiarthritic and antiinflammatory agents.

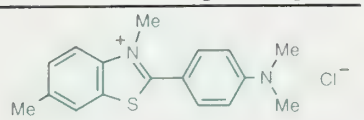
Walker, G.N. Eur. Patent 372 470, 1990; *Chem. Abstr.* **1990**, *113*, 211388x.

12,312-9 2-Aminothiazole, 97%
5g $9.55; 100g $9.85; 500g $35.80

Naturally occurring compound in sesame seed oil[1] and chicken.[2] Also used for the synthesis of platelet activating factor inhibitors.[3]

(1) Nishimura, O.; Masuda, H.; Mihara, S. *Koryo* **1990**, *165*, 91; *Chem. Abstr.* **1990**, *113*, 210350s. (2) Noleau, I.; Toulemonde, B. *Lebensm.-Wiss. Technol.* **1986**, *19*, 122; *Chem. Abstr.* **1986**, *105*, 189645q. (3) Wissner, A.; Schaub, R.E.; Sum, P.E. Eur. Patent 336, 142, 1989; *Chem. Abstr.* **1990**, *113*, 114809c.

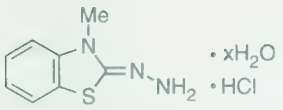
15,164-5 Thiazole, 99%
1g $21.50; 5g $85.45



Used in photosensitive films for hologram preparation.

Ishizuka, T.; Yagishita, A. Jpn. Patent 8 602 181, 1986; *Chem. Abstr.* **1986**, *104*, 216580c.

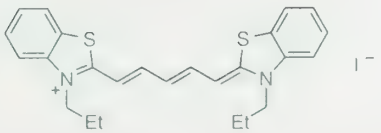
22,885-0 Thioflavin T
5g $10.00; 25g $25.80



Chromogenic substrate for peroxidase linked immunoassays.

Vermeulen, N.M.J.; Petrie, C.R. Int. Patent 90 06 372, 1990; *Chem. Abstr.* **1990**, *113*, 207477h.

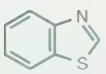
12,973-9 3-Methyl-2-benzothiazolinone hydrazone hydrochloride hydrate, 97%
5g $12.90; 25g $49.60; 100g $141.80



Fluorescent probe used in energy metabolism studies.

Bammel, B.P. et al. *Arch. Biochem. Biophys.* **1986**, *244*, 67; *Chem. Abstr.* **1986**, *104*, 84713m.

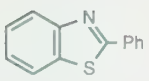
33,469-3 3,3'-Dipropylthiadicarbocyanine iodide, 97%
1g $18.40



Used in polymer synthesis[1] and as a natural flavor found in apples.[2]

(1) Odnoralova, V.N.; Vasil'eva-Sokolova, E.A. *Itogi Nauki Tekh., Ser.: Khim. Tekhnol. Vysokomol. Soedin.* **1988**, *25*, 85; *Chem. Abstr.* **1989**, *110*, 76526m. (2) Cunningham, D.G. et al. *Food Chem.* **1986**, *19*, 137; *Chem. Abstr.* **1986**, *104*, 128582z.

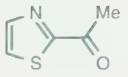
10,133-8 Benzothiazole
5g $10.95; 100g $13.80; 500g $41.20



Heat stabilizing polymer additive.

Finke, J.; Fenauer, R. Eur. Patent 384 980, 1990; *Chem. Abstr.* **1991**, *114*, 62985f.

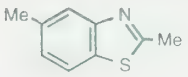
26,843-7 2-Phenylbenzothiazole, sublimed, zone refined, 99+%
1g $24.00



Masked pyruvic acid β-anion[1] and a component of the bread-like aroma in beer.[2]

(1) Dondoni, A; Fantin, G; Fogagnolo, N. *Tetrahedron Lett.* **1989**, *30*, 6063. (2) Tressl, R. et al. *Proc. Congr.-Eur. Brew. Conv.* **1981**, *18*, 391; *Chem. Abstr.* **1982**, *96*, 160714w.

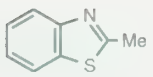
28,841-1 2-Acetylthiazole, 99%
1g $26.90; 5g $85.70



Used in the preparation of lithographic printing plates.

Laridon, U.L.; Van Brandt, R.A.; Poot, A.L. Ger. Patent 2 548 184, 1976; *Chem. Abstr.* **1977**, *86*, 131148c.

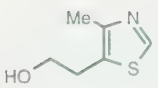
10,883-9 2,5-Dimethylbenzothiazole, 98%
5g $16.05; 25g $57.55



Precursor for 2-vinylbenzothiazoles that are used in the synthesis of plane rigidified laser dyes.

Heilig, G.; Luettke, W. *Chem. Ber.* **1986**, *119*, 3102.

11,214-3 2-Methylbenzothiazole, 99%
25g $18.00; 100g $50.35



Flavor component of roasted peanuts.[1] Also, used in antitumor agent synthesis.[2]

(1) Ho, C. et al. *J. Agric. Food Chem.* **1983**, *31*, 1384; *Chem. Abstr.* **1983**, *99*, 193396j. (2) Nomura, H.; Akimoto, H.; Inoue, K. Can. Patent 2 001 532, 1990; *Chem. Abstr.* **1991**, *114*, 82425b.

19,067-5 4-Methyl-5-thiazoleethanol, 98%
25g $10.70; 100g $35.10

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boranes
alkylaluminums
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organosilicons
Grignards

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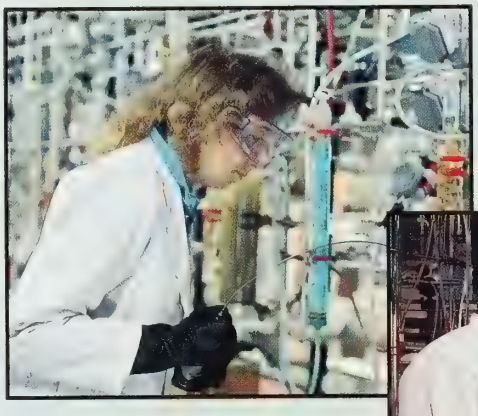

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Volume 25, Number 2, 1992

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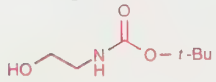
For the Medicinal Chemist

Peptide Synthon

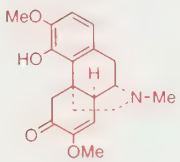


BOC-aminoethanol is useful in preparing tripeptidic β-adrenergic Ca channel blockers[1] and tetrapeptidic cortical cholecystokinin agonists.[2]

(1) Schoen, W.R. Eur. Patent 347 987, 1989; *Chem. Abstr.* **1991**, *114*, 229391y. (2) Chung, J.Y. et al. Eur. Patent 405 506, 1991; *Chem. Abstr.* **1991**, *115*, 50308v.

38,202-7 *N*-(*tert*-Butoxycarbonyl) ethanolamine, 98%
5ml $15.00; 25ml $50.00

Sinomenine

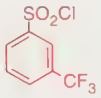


Sinomenine exhibits analgesic and anti-inflammatory activities in mice.[1] This compound was one of a number of isoquinoline alkaloids tested for mutagenicity in Salmonella typhimurium TA 100 and TA 98.[2]

(1) Huo, H.; Che, X. *Xi'an Yike Daxue Xuebao* **1989**, *10*, 346; *Chem. Abstr.* **1990**, *113*, 204591e. (2) Nozaka, T. et al. *Mutat. Res.* **1990**, *240*, 267.

36,560-2 Sinomenine **100mg $15.00**
500mg $50.00

Important Intermediate

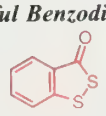


This trifluoromethylated sulfonyl chloride is an important component of compounds of medicinal[1] and agrochemical value.[2]

(1) Lang, H.J. et al. Ger. Patent 3 905 075, 1990; *Chem. Abstr.* **1991**, *114*, 163726c. (2) Oyama, H. et al. Eur. Patent 306 222, 1989; *Chem. Abstr.* **1989**, *111*, 96856t.

38,541-7 3-(Trifluoromethyl)benzene sulfonyl chloride, 95%
1g $8.00; 5g $30.00

Useful Benzodithiolone

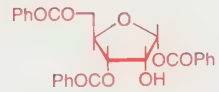


Beaucage developed the 1,1-dioxide of this reagent for high efficiency sulfurization in solid phase oligonucleotide synthesis.[1]

(1) Iyer, R. et al. *J. Am. Chem. Soc.* **1990**, *112*, 1253.

37,546-2 3*H*-1,2-Benzodithiol-3-one, 97% **1g $7.00; 5g $21.00**

Fluoroarabinose Precursor



This trisubstituted ribofuranose serves as a starting material for 2'-deoxy-2'-fluoro-arabino sugars[1] and nucleosides.[2,3]

(1) Brundidge, S.P. et al. Eur. Patent 145 978, 1985; *Chem. Abstr.* **1985**, *103*, 178579d. (2) Smee, D.F. et al. *Nucleosides* **1988**, *7*, 155. (3) Howell, H.G. et al. *J. Org. Chem.* **1988**, *53*, 85.

38,908-0 α-D-Ribofuranose 1,3,5-tribenzoate, 97% **1g $15.00; 5g $50.00**

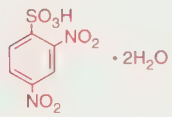
Pyrroline

This dihydropyrrole has been used in the synthesis of renin inhibitors[1] and vasodilators.[2]

(1) Rosenberg, S.H. et al. *J. Med. Chem.* **1990**, *33*, 1962. (2) Yoshino, K. et al. *ibid.* **1990**, *33*, 2192.

37,711-2 3-Pyrroline, 97%
250mg $16.00; 1g $45.00

For DNA Labelling



An extention of Forster's photobiotin-based labelling of DNA[1] is the modification of the biotin end with a simple hapten derived from this sulfonic acid.

(1) Forster, A.C. et al. *Nucleic Acid Res.* **1985**, *13*, 745. (2) Keller, G. et al. *Anal. Biochem.* **1989**, *177*, 392.

38,106-3 2,4-Dinitrobenzenesulfonic acid dihydrate, 98% **25g $11.00**
100g $32.00

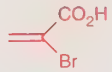
P(III) Synthon

For the preparation of difunctional phosphonoamidite coupling reagents in nucleoside chemistry.[1] Also used to prepare palladium-based carbonylation catalysts[2] and "phospha-Wittig" reagents.[3]

(1) Helinski, J. et al. *Tetrahedron Lett.* **1991**, *32*, 4981. (2) Drent, E. U.K. Patent 2 240 545, 1991; *Chem. Abstr.* **1991**, *115*, 255638z. (3) Bauer, S. et al. *Heteroat. Chem.* **1991**, *2*, 277.

33,686-6 Dichloromethylphosphine, tech., 90% **5g $15.00**

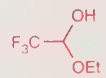
Building Blocks



Useful building block for preparing medicinally important compounds such as antineoplastic agents[1] and retroviral protease inhibitors[2].

(1) Kempf, D.J. et al. World Patent 8 910 752, 1989; *Chem. Abstr.* **1991**, *114*, 247788n. (2) Mongelli, N.; Biasoli, G.; Suarato, A.; Pezzoni, G. Ger. Patent 4 020 332, 1991; *Chem. Abstr.* **1991**, *114*, 247680w.

37,737-6 2-Bromoacrylic acid, 95%
1g $7.25; 5g $24.00



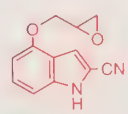
This convenient-to-handle liquid (bp: 104.5°C at 745mm Hg) serves as an excellent source for the parent aldehyde.

39,007-0 Trifluoroacetaldehyde ethyl hemiacetal, tech., 90%
1g $12.00; 5g $40.00

Useful building blocks for pharmaceuticals, agrochemicals, and fragrances. Nitrile **1** readily condenses with urea to form cytosine.

Von Itter, F.A.; Breuer, J. Ger. Patent 3 641 604, 1988; *Chem. Abstr.* **1989**, *110*, 57137u. Loqua, H.; Peeters, H.; Vogt, W. Ger. Patent 3 434 142, 1986; *Chem. Abstr.* **1986**, *105*, 60483f.

37,861-5 3,3-Diethoxypropionitrile, 95% **(1)** **25ml $18.00**
37,046-0 Diethoxyacetonitrile, 97% **1g $19.50; 5g $65.00**



The glycidyloxy side chain in this indole derivative allows easy construction of β-blocker indoles which have activity as anticancer agent enhancers,[1] binders for 5-HT1A receptors[2] and as cardiovascular agents.[3]

(1) Fukazawa, N.; Odate, M.; Suzuki, T.; Tsuruo, T. Jpn. Patent 212 924, 1990; *Chem. Abstr.* **1990**, *113*, 109311e. (2) Peroutka, S.J.; Pitha, J. Eur. Patent 338 877, 1989; *Chem. Abstr.* **1990**, *112*, 216687h. (3) Pitha, J.; Buchowiecki, W.; Milecki, J.; Kusiak, J.W. *J. Med. Chem.* **1987**, *30*, 612.

38,972-2 4-Glycidyloxy-2-indolecarbonitrile, 97% **25g $8.00**

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Volume 25, Number 2, 1992
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About Our Cover:

fig. 1

The problems posed by this painting (oil on canvas, 38½ x 32½ in.) of Hendrickje Stoffels as *Venus with Cupid* are described in detail in entry No. 34 of *The Detective's Eye* (see below). The painting was sold at an auction in New York in 1988, described as a copy after a painting (fig. 1) in the Louvre that had been attributed to Rembrandt. Cleaning revealed our painting to be of high quality—superior, our chemist collector believes, to the painting in Paris. Neither is by Rembrandt, and so a key question is whether there ever was a Rembrandt original. When this painting was sold in an auction in Berlin in 1933, it had a signature that the catalog described as "hard to read". By the time it appeared in the New York sale in 1988, the painting had been cut down and the signature lost. It looks close to the works of one of Rembrandt's ablest students, Willem Drost.

Rembrandt scholars believe that several paintings long attributed to Rembrandt, for instance, the *Polish Rider*, are really by Drost. His works will surely be studied in great detail, and in time these puzzles will be solved.

Lab Notes

Various lubricants have been used in the laboratory for years. Stopcock grease is still used by some, even for ground glass joints. Molybdenum sulfide grease or Teflon® tape is often used to prevent galling of metal threads on fittings and screw attachments. I detest the various oils and greases, as they seem to permeate the lab, and make their way into the background spectra and chromatograms of almost any system. A nice substitute, I have found, is dry Teflon® spray. Easier to use than Teflon® tape, it can be applied to threads as a very thin coat, especially useful for gas regulators or HPLC fittings. It should not be used around a GC system employing an electron capture detector, but other than that, it appears to be a nice alternative to any other lubricant.

Doug Wittmer (CT)
Millipore Corporation
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It is often critical when conducting an exploratory synthetic investigation to know something concerning the thermal stabilities of both starting materials, as well as desired products under the contemplated reaction conditions.

We have found what we believe to be a convenient, rapid and reliable solution to this problem, which could have fairly wide applicability.

The procedure consists of the following steps:

1) Filling a number of melting point capillaries with the samples to be studied, to a height of about 1.5cm.
2) The melting point bath is then heated to the desired temperature of the study.
3) When the desired temperature has been attained (and is stabilized) the sample-containing capillaries are all placed in the bath at the same time.
4) Successive samples are removed at predetermined intervals (e.g., 0.5 hr, 1.0 hr, etc.)
5) The tubes are carefully cleaned (to remove bath oil) and placed in small containers (e.g., 75mm test tubes). The lower portions of the tubes, which contain the samples, are crushed with a clean glass rod and are extracted with a small amount of a suitable solvent.
6) The extracts thus obtained are analyzed by TLC and compared with unheated standards.
7) The data obtained by this means should furnish the desired thermal-stability data.

David H. Steinberg, Ph.D.
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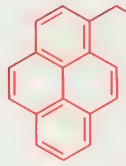
"Please Bother Us."

by Jai Nagarkatti

Jai Nagarkatti, President



Professor Tapio A. Hase of the Department of Organic Chemistry at the University of Helsinki, Finland, suggested that we offer pyrenylacetic acid, a new reagent for the titration of organolithiums and Grignard reagents.[1] An intense red dianion of this compound unmistakably identifies the titration end point.

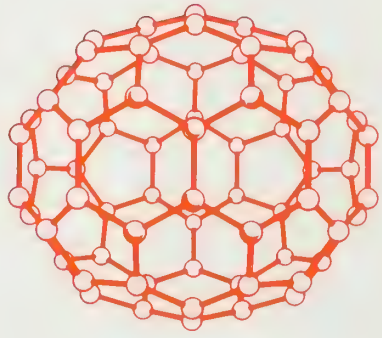
Naturally, we made it.

(1) Kiljunen, H.; Hase. T.A. *J. Org. Chem.* **1991**, *56*, 6950.

39,218-9 1-Pyreneacetic acid, 98%
1g $20.00; 5g $67.00

It was no bother at all, just a pleasure to be able to help.

Now Available: C_{70}



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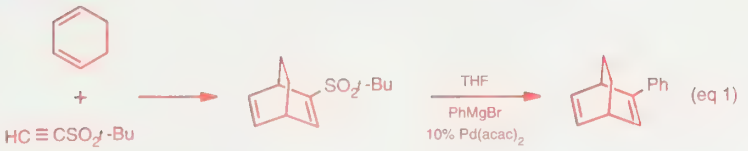
For further information on attending and contributing papers and posters contact: Professor George W. Kabalka, Chairman, IMEBORON VIII Chemistry Department, University of Tennessee, Knoxville, TN 37996-1600 USA. Fax 615-974-2997.

Grignard Reagents

Grignard reagents represent an extremely versatile class of reagents for organic synthesis. The synthetic utility and tremendous popularity of these organomagnesium halides continues to grow as exemplified below.

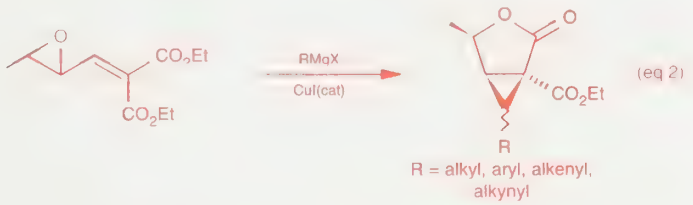
Synthesis of Monosubstituted Bicyclic Dienes

Palladium-mediated coupling of Grignard reagents with Diels-Alder adducts of sulfonyl acetylenes provide appropriately substituted bridged bicyclic products. The starting acetylenes act as reactive surrogates of alkynes which are usually poor dienophiles.[1]



Synthesis of Bicyclic Lactones

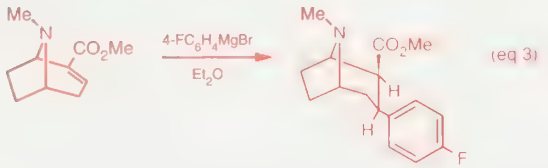
The reaction of various Grignard reagents with diethyl (2,3-epoxybutylidene)malonate provides a simple synthesis of bicyclo[3.1.0]lactones.[2]



R = alkyl, aryl, alkenyl, alkynyl

Synthesis of Tropane Congeners

The conjugate addition of 4-fluorophenylmagnesium bromide to anhydroecgnonine methyl ester yields a tropane derivative that has been used in the study of cocaine receptors.[3]



We offer a wide variety of Grignard reagents that are packaged in Sure/Seal™ bottles, Sure/Pac™ and Kilo-Lab™ metal cylinders. Nearly all of these are available in bulk quantities, custom packaged to suit your exact needs. We also offer a wide variety of accessories and equipment for handling these reactive reagents more conveniently and safely. For a complete listing of these products, see pages 1428 through 1992 of the 1992-1993 Catalog/-Handbook.

References: (1) Virgili, M.; Belloch, J.; Moyano, A.; Pericas, M.A.; Riera, A. *Tetrahedron Lett.* **1991**, *32*, 4583. (2) Kasatkin, A.N.; Biktimirou, R.K.; Tolstikov, G.A. *ibid.* **1990**, *31*, 4915. (3) Milius, R.A.; Saha, J.K.; Madras, B.K.; Neumeyer, J.L. *J. Med. Chem.* **1991**, *34*, 1728.

Partial listing of Grignards available...

Allylmagnesium bromide
22,575-4 **1.0*M* soln in diethyl ether**
100mL $13.80; 800mL $58.20
8L $290.80; 18L $545.55

Allylmagnesium chloride
22,590-8 **2.0*M* soln in tetrahydrofuran**
100mL $15.90; 800mL $78.10
8L $405.60; 18L $796.30

Butylmagnesium chloride
22,437-5 **2.0*M* soln in diethyl ether**
100mL $14.30; 800mL $45.70
29,100-5 **2.0*M* soln in tetrahydrofuran**
100mL $15.80; 800mL $48.80

sec-Butylmagnesium chloride
22,442-1 **2.0*M* soln in diethyl ether**
100mL $13.90; 800mL $40.70

tert-Butylmagnesium chloride
22,449-9 **2.0*M* soln in diethyl ether**
100mL $15.00; 800mL $65.50
36,464-9 **1.0*M* soln in tetrahydrofuran**
100mL $14.60; 800mL $64.80

Cyclohexylmagnesium chloride
22,441-3 **2.0*M* soln in diethyl ether**
100mL $13.60; 800mL $47.40

Ethylmagnesium bromide
18,987-1 **3.0*M* soln in diethyl ether**
100mL $14.00; 800mL $57.00
8L $285.95; 18L $572.00
36,467-3 **1.0*M* soln in tetrahydrofuran**
100mL $14.90; 800mL $70.40
8L $273.25; 18L $511.15

Ethylmagnesium chloride
30,033-0 **2.0*M* soln in diethyl ether**
100mL $14.20; 800mL $46.30

4-Fluorophenylmagnesium bromide
24,555-0 **2.0*M* soln in diethyl ether**
100mL $20.60; 800mL $107.10
32,882-0 **1.0*M* soln in tetrahydrofuran**
100mL $12.10; 800mL $41.60

Hexylmagnesium bromide
25,502-5 **2.0*M* soln in diethyl ether**
100mL $14.20; 800mL $46.40

Isopropylmagnesium chloride
22,438-3 **2.0*M* soln in diethyl ether**
100mL $13.60; 800mL $40.30
23,011-1 **2.0*M* soln in tetrahydrofuran**
100mL $12.60; 800mL $40.80

2-Mesitylmagnesium bromide
22,723-4 **1.0*M* soln in tetrahydrofuran**
100mL $26.00; 800mL $142.70

Methylmagnesium bromide
18,989-8 **3.0*M* soln in diethyl ether**
100mL $14.00; 800mL $54.10
8L $294.90; 18L $520.90

Methylmagnesium iodide
25,436-3 **3.0*M* soln in diethyl ether**
100mL $17.00; 800mL $89.00
8L $562.30; 18L $994.00

2-Methyl-2-phenylpropyl-magnesium chloride
37,370-2 **1.0*M* soln in diethyl ether**
100mL $9.50; 800mL $50.00

Phenylmagnesium chloride
22,444-8 **2.0*M* soln in tetrahydrofuran**
100mL $13.70; 800mL $40.90
8L $175.10; 18L $342.45

Propylmagnesium chloride
22,439-1 **2.0*M* soln in diethyl ether**
100mL $15.40; 800mL $57.00

p-Tolylmagnesium bromide
30,032-2 **1.0*M* soln in diethyl ether**
100mL $14.60; 800mL $68.50

Trimethylsilylmethylmagnesium chloride
25,602-1 **1.0*M* soln in diethyl ether**
100mL $36.30

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Chiral Products

TADDOLs

Seebach's reagents for the highly enantioselective addition of primary alkyl Grignards to ketones[1] and performing titanium-catalyzed enantioselective additions of R_2Zn to aldehydes.[2]

(1) Weber, B.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 84. (2) Schmidt, B.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1321.

39,141-7 (4*R-trans*)-2,2-Dimethyl-α,α,α',α'-tetra(1-naphthyl)-1,3-dioxolane-4,5-dimethanol, 99% **1g $20.00**
39,524-2 (4*S-trans*)-2,2-Dimethyl-α,α,α',α'-tetra(1-naphthyl)-1,3-dioxolane-4,5-dimethanol 1g $20.00
39,375-4 (4*R-trans*)-2,2-Dimethyl-α,α,α',α'-tetra-(2-naphthyl)-1,3-dioxolane-4,5-dimethanol 250mg $25.00; 1g $75.00
39,376-2 (4*S-trans*)-2,2-Dimethyl-α,α,α',α'-tetra-(2-naphthyl)-1,3-dioxolane-4,5-dimethanol 250mg $25.00; 1g $75.00

Ibuprofen Enantiomer

Enantiometric form of the anti-inflammatory agent Ibuprofen, useful in pharmacokinetic studies.

Jamali, F. et al. *J. Pharm. Sci.* **1992**, *81*, 221.

37,516-0 (*S*)-(+)-4-Isobutyl-α-methylphenylacetic acid, 99% **1g $17.05**

Solvating Agent

Used for the direct enantiomeric assay (% ee) of carboxylic acids by ^1H NMR.[1] Also has applications in agro-[2] and polydepsipeptide chemistry.[3]

(1) Fulwood, R.; Parker, D. *Tetrahedron: Asymmetry* **1992**, *3*, 25. (2) Moyne, J. Eur. Patent 352 168, 1990; *Chem. Abstr.* **1990**, *113*, 40160k. (3) In't Veld, P.J.A. et al. *Makromol. Chem.* **1990**, *191*, 1813

38,551-4 (*S*)-(-)-2-Bromopropionic acid, 99% 1g $7.00; 5g $20.50

Diels-Alder Catalyst

Optically active oxovanadium complex that is a highly efficient catalyst for the hetero Diels-Alder reaction of aldehydes with dienes providing pyrones.

Togni, A. *Organometallics* **1990**, *9*, 3106.

39,065-8 Bis[3(heptafluoropropylhydroxymethylene)-(+)-camphorato]oxovanadium, 98% **100mg $14.00; 1g $55.00**

Building Blocks

1 2

The D- and L-glutamic acid derived pyrrolidinones serve as building blocks in, for example, the synthesis of diphthamide from **1**,[1] of (R)- and (S)-4,5-diaminovaleric acids,[2] and of 5-aza-semicorrin bidendate nitrogen ligands for enantioselective catalysis.[3]

(1) Evans, D.A.; Lundy, K.M. *J. Am. Chem. Soc.* **1992**, *114*, 1495. (2) Valasinas, A.; Frydman, B.; Friedmann, H.C. *J. Org. Chem.* **1992**, *57*, 2158. (3) Leutenegger, U. et al. *Tetrahedron* **1992**, *48*, 2143.

36,635-8 (*R*)-(-)-5-(Hydroxymethyl)-2-pyrrolidinone, 99% **(1) 1g $33.40; 5g $134.90**
36,636-6 (*S*)-(+)-5-(Hydroxymethyl)-2-pyrrolidinone, 97% **(2) 1g $22.80; 5g $76.25**

This useful chiral building block has been employed in the preparation of statine,[1] the hypoglycemic englitazone,[2] and peptidic renin inhibitors.[3]

(1) Urban, F.J.; Moore, B.S. *J. Heterocycl. Chem.* **1992**, *29*, 431. (2) Kano, S. et al. *J. Org. Chem.* **1988**, *53*, 3865. (3) De, B. et al. Eur. Patent 365 992, 1990; *Chem. Abstr.* **1991**, *114*, 43580d.

37,690-6 D-3-Phenyllactic acid, 98% **1g $19.20; 5g $63.90**

We also offer:
37,909-3 (*S*)-(+)-2-Hydroxy-3-methylbutyric acid, 99% **1g $26.30; 5g $89.80**

Chiral Amines

1 2

Organometallic complexes of these amines and derived pyridines[1] provide asymmetric catalysts, for example, in conjugate additions to enones.[2] Also for the determination of structure-stereochemistry relationships in the stereospecific oxidation of NAD(P)H analogs.[3]

(1) Brunner, H.; Scheck, T. *Chem. Ber.* **1992**, *125*, 701. (2) Rossiter, B.E.; Eguchi, M. *Tetrahedron Lett.* **1990**, *31*, 965. (3) Ohno, A. et al. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 81.

39,400-9 (*R*)-(+)-*N*, α-Dimethylbenzylamine, 98% **(1) 1g $15.50; 5g $52.00**
40,135-8 (*S*)-(-)-*N*,α-Dimethylbenzylamine (2) 1g $15.50; 5g $52.00

β-*Lactam Synthon*

The chiral ketene derived from this oxazolidinone leads to chiral β-lactams via the Staudinger reaction.[1] Ojima and co-workers have extended this strategy to prepare unnatural dipeptides.[2]

(1) Evans, D.A.; Sjogren, E.B. *Tetrahedron Lett.* **1985**, *26*, 3783. (2) Ojima, I. et al. *J. Am. Chem. Soc.* **1990**, *112*, 770.

39,134-4 (*S*)-2-Oxo-4-phenyl-3-oxazolidineacetic acid, 98% **250mg $11.75; 1g $33.00**

Pharmaceutical Synthon

Z-protected imidazolidinone for sequential *N*-alkylation, e.g. in the synthesis of an angiotensin converting enzyme inhibitor.

Hayashi, K. et al. *J. Med. Chem.* **1989**, *32*, 289.

39,230-8 (*S*)-(-)-Oxo-1,5-imidazolidinedicarboxylic acid 1-benzyl ester, 98% **1g $13.50; 5g $45.00**

Aldrichimica Acta

Volume 25, Number 3, 1992 *(Last issue in 1992)*
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About Our Cover:

This painting (oil on canvas, 20 x 27in.) from the collection of The Saint Louis Art Museum (St. Louis, MO) is entitled **Capriccio: An Island in the Lagoon with a Pavilion and a Church**. The Italian artist, Antonio Canal, known as Canaletto (1697-1768), specialized in views of Venice and the Venetian countryside. The English in particular coveted images of the views and ruins they had admired on their visits to Italy. Sometimes, these scenes were inspired by but not faithful to the topographical details they purported to document. They were imaginary combinations of landscape and landmarks, known by the Italian term *capricci*. The seemingly precise line of Canaletto's architecture often denies these scenes a sense of fanciful invention; they masquerade as recorded fact.

In the St. Louis painting, the artist has combined the Venetian lagoon with some buildings from nearby Padua and a campanile from yet another source to produce a grouping of simple structure and subtle balance. The light, as always in Canaletto's work, is an important element of the painting. It bathes the buildings in radiant tones and confers upon the whole an almost unnaturalistic clarity. Human figures are secondary players in this carefully contrived arrangement. Their casual poses as they pursue various tasks belie their careful placement in the structural logic of the whole; at times they even echo the larger architectural forms. The virtuoso handling of paint, the warmth and clarity of the light, and the mastery of composition make Canaletto's paintings as appealing today as they were to his eighteenth-century clients.

This painting was one of a pair of imaginary views; its pendant included a middle ground column surmounted by a crouching figure and a domed church. The paintings were purchased by Lord Boston (1707-1775) and remained in the family until they were sold at auction in 1942.

Lab Notes

We have found a very simple method for the accurate delivery of ozone, even in submilligram amounts, into reaction mixtures.[1] Upon describing this method to many other chemists we were surprised that none had heard of this being done and are thus presenting it to your readers so that they may use it. The method consists of drawing a sample of the ozone-oxygen gas mixture from the effluent stream of an ozonizer into a 50 or 100ml syringe fitted with a small diameter Teflon® tube, measuring the ozone content, and delivering a measured amount of the gas into the reaction mixture. We measure the ozone concentration, typically 1mg/50ml when the ozonizer is set to deliver 15mg of ozone per minute, by injecting a measured portion of the sample into a solution of excess 2,3-dimethyl-2-butene in CD_3OD in an NMR tube. The ^1H NMR spectrum of the resulting reaction mixture contains three singlets due to alkene, acetone, and the CD_3OD adduct of acetone carbonyl oxide. Integration of the spectrum allows one to calculate the ozone content of the gas. The ozone content does not change upon storage of the gas in the syringe for an eight hour period.

(1) Kopecky, K.R.; Molina, J.; Rico, R. *Can. J. Chem.* **1988**, *66*, 2234.

Karl R. Kopecky
Professor of Chemistry
University of Alberta
Edmonton, Alberta
Canada T6G 2G2

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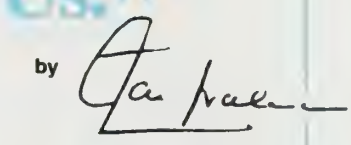
See page 69 for information on the new Aldrich Library of ^{13}C and ^1H FT-NMR Spectra.

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2, $9.90 value). If we publish your *Lab Note*, you will also receive **The Detective's Eye: Investigating the Old Masters** (see previous page). We reserve the right to retain all entries for consideration for future publication.

"Pease Bother Us."

by



Professor Robert Atkinson of the University of Leicester, Leicester, UK, suggested we offer this amino quinazolinone. Dr. Atkinson discovered that the *N*-acetoxy derivative of this amine (generated by lead tetraacetate oxidation) allows oxidative addition of nitrogen to alkenes. This method opens up a convenient pathway to aziridines![1] A stable (-20°C) solution of the derived reagent is not only useful for the aziridination of simple alkenes, but gives *syn* stereoselectivity with cyclohex-2-enols and *anti* stereoselectivity with the corresponding acetates.[2] Reaction with vinylsilanes and vinylstannanes gives silyl or stannyl substituted aziridines,[3] while enol ethers and silyl ketene acetals lead eventually to α-amino carbonyl products.[4]

Naturally, we added this product to our listings.

(1) Atkinson, R.S.; Kelly, B.J. *Tetrahedron* **1989**, *45*, 2875. (2) Idem *J. Chem. Soc., Perkin Trans. 1* **1989**, 1515. (3) Idem *J. Chem. Soc., Chem. Commun.* **1989**, 836. (4) Atkinson, R.S.; Kelly, B.J.; Williams, J. *ibid.* **1992**, 373.

38,632-4 3-Amino-2-ethyl-4(3H)-quinazolinone, 99%
1g $18.00; 5g $61.00

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34,142-8	**Ammonia**, 2.0*M* solution in methyl alcohol	5mL $10.65; 100mL $16.95; 800mL $71.70
39,269-3	**Ammonia**, 2.0*M* solution in 2-propanol	100mL $16.50; 800mL $70.00
38,824-6	**Dimethylamine**, 2.0*M* solution in methyl alcohol	25mL $9.75; 100mL $27.00
39,195-6	**Dimethylamine**, 2.0*M* solution in tetrahydrofuran	100mL $19.00; 800mL $95.00
14,587-4	**Dimethylamine**, 40 wt. % solution in water	5mL $ 8.00; 100mL $8.20; 1L $13.20; 2L $22.80
39,506-4	**Ethylamine**, 2.0*M* solution in methyl alcohol	100mL $13.00; 800mL $62.00
39,507-2	**Ethylamine**, 2.0*M* solution in tetrahydrofuran	100mL $15.00; 800mL $75.00
15,639-6	**Ethylamine**, 70 wt. % solution in water	5mL $5.35; 100mL $10.35; 500mL $11.30; 2L $29.00
39,504-8	**Methylamine**, 2.0*M* solution in methyl alcohol	100mL $34.00; 800mL $173.00
39,505-6	**Methylamine**, 2.0*M* solution in tetrahydrofuran	100mL $26.00; 800mL $131.00
M2,775-1	**Methylamine**, 40 wt. % solution in water	100mL $11.25; 1L $16.35; 2L $18.60

INORGANIC HALIDES

24,988-2	**Aluminum chloride,** 1.0*M* solution in nitrobenzene	100mL $13.50; 800mL $47.10
21,122-2	**Boron tribromide,** 1.0*M* solution in dichloromethane	100mL $34.70; 800mL $171.20
21,123-0	**Boron tribromide,** 1.0*M* solution in hexanes	100mL $29.50; 800mL $148.00
17,893-4	**Boron trichloride,** 1.0*M* solution in dichloromethane	100mL $28.40; 800mL $128.50
34,832-5	**Boron trichloride,** 1.0*M* solution in heptane	100mL $11.90; 800mL $54.20
21,124-9	**Boron trichloride,** 1.0*M* solution in hexanes	100mL $27.20; 800mL $122.90
34,545-8	**Boron trichloride,** 1.0*M* solution in *p*-xylene	100mL $13.30; 800mL $48.40
27,682-0	**Phosphorous tribromide,** 1.0*M* solution in dichloromethane	100mL $15.60; 800mL $37.80
27,681-2	**Phosphorous trichloride,** 2.0*M* solution in dichloromethane	100mL $15.60; 800mL $24.00
24,992-0	**Silicon(IV) chloride,** 1.0*M* solution in dichloromethane	100mL $16.50; 800mL $26.80
33,984-9	**Sulfur dichloride,** tech., 80%, 1.0*M* solution in dichloromethane	100mL $11.90; 800mL $16.40
29,311-3	**Sulfur monochloride,** 1.0*M* solution in dichloromethane	100mL $15.60; 800mL $26.40
27,850-5	**Sulfuryl chloride,** 1.0*M* solution in dichloromethane	100mL $14.40; 800mL $22.40
29,312-1	**Thionyl chloride,** 2.0*M* solution in dichloromethane	100mL $15.60; 800mL $28.60
25,011-2	**Tin(IV) bromide,** 1.0*M* solution in dichloromethane	100mL $24.00; 800mL $132.35
24,995-5	**Tin(IV) chloride,** 1.0*M* solution in dichloromethane	100mL $14.90; 800mL $34.20
35,749-9	**Tin(IV) chloride,** 1.0*M* solution in heptane	100mL $11.90; 800mL $29.30
30,548-0	**Titanium(III) chloride,** 1.0*M* solution in dichloromethane/THF (2:1)	100mL $23.50; 800mL $115.60
24,986-6	**Titanium(IV) chloride,** 1.0*M* solution in dichloromethane	100mL $14.80; 800mL $28.00
34,569-5	**Titanium(IV) chloride,** 1.0*M* solution in toluene	100mL $12.40; 800mL $53.60
27,683-9	**Zinc chloride,** 1.0*M* solution in diethyl ether	100mL $14.40; 800mL $32.50
36,637-4	**Zinc chloride,** 0.5*M* solution in tetrahydrofuran	100mL $33.10; 800mL $117.70

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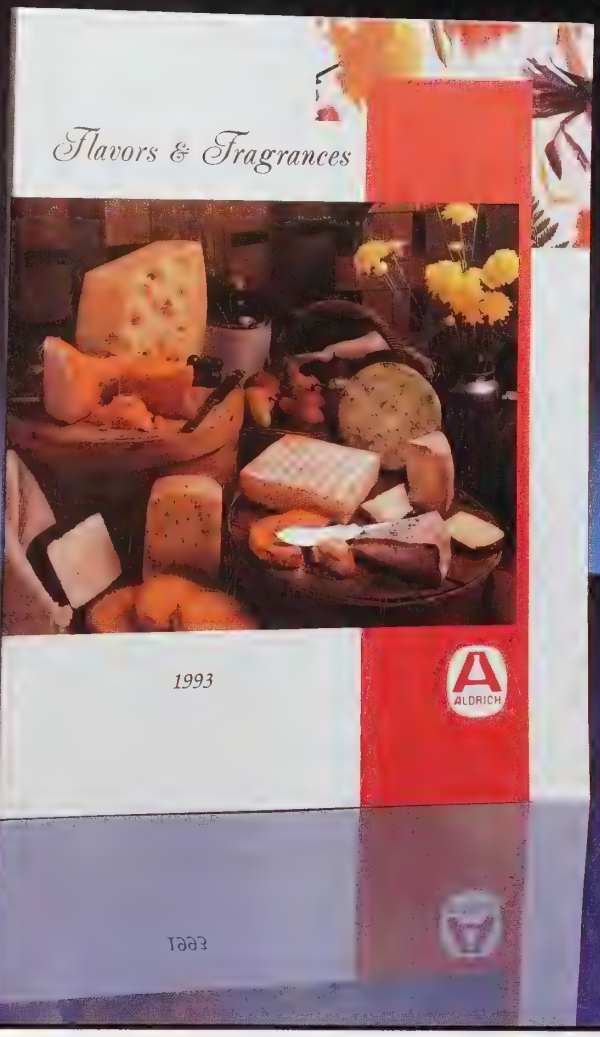

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Volume 26, Number 1, 1993

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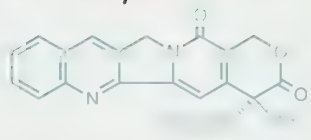
Camptothecin

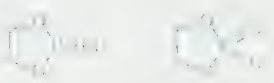


A well-known alkaloid that exhibits antileukemic/antitumor activities and has been involved in several related studies.[1,2]

(1) Andersson, H.C. et al. *Mutat. Res.* **1992**, *268*, 167. (2) Morham, S.G. et al. *J. Biol. Chem.* **1992**, *267*, 15984.

36,563-7 (*S*)-(+)-Camptothecin, 95%
100mg $19.00; 500mg $65.00

Phospholanes



Used for the phosphorylation of ascorbic acid derivatives[1] and in the synthesis of thiophosphatidylcholine,[2] phospholipids[3] and platelet activating factor (PAF) analogs.[4]

(1) Predvoditelev, D.A. et al. *Zh. Org. Khim.* **1991**, *27*, 1655. (2) Mlotkowska, B. et al. *Liebigs Ann. Chem.* **1991**, 833. (3) Golec, J.M.C.; Hedgecock, C.J.R.; Murdoch, R.; Tully, W.R. *Tetrahedron Lett.* **1992**, *33*, 551. (4) Kumar, A.; Shanker, K. *Synth. Comm.* **1991**, *21*, 1763.

39,122-0 2-Chloro-1,3,2-dioxaphospholane, 97%
5mL $20.00; 25mL $67.50

37,795-3 2-Chloro-1,3,2-dioxaphospholane-2-oxide, 95%
1g $13.05; 5g $43.70

Phosphonopropionate

A useful HEW reagent employed in the synthesis of phosphoenolpyruvate carboxylase inhibitors,[1] herbicides and pheromones.[2]

(1) McFadden, H.G. et al. *Aust. J. Chem.* **1987**, *40*, 1619. (2) Cork, A. et al. *J. Chem. Ecol.* **1991**, *17*, 789.

39,188-3 Triethyl 3-phosphonopropionate, 98%
5mL $12.00; 25mL $40.00

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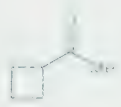
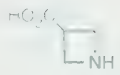


Has applications in a variety of different areas including the preparation of cyclobutylcarbinols and studies of cyclobutyl stabilized radicals[1] and carbonium ions.[2]

(1) Peters, E.N. *J. Org. Chem.* **1977**, *42*, 3015. (2) Ingold, K.U.; Maillard, B.; Walton, J.C. *J. Chem. Soc., Perkin Trans. II*, **1981**, 970.

39,448-3 Cyclobutyl methyl ketone, 98%
1g $9.00; 5g $30.00

Azetidine Derivative



Azetidine and its derivatives are valuable compounds in pharmaceutical[1] and agrochemical[2] research.

(1) Johnson, G. et al. *J. Med. Chem.* **1992**, *35*, 233. (2) Hsu, F. C.; Kleier, D.A. *Weed Sci.* **1990**, *38*, 315.

39,113-1 3-Azetidinecarboxylic acid, 98%
50mg $15.00; 250mg $49.00

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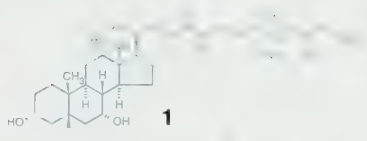

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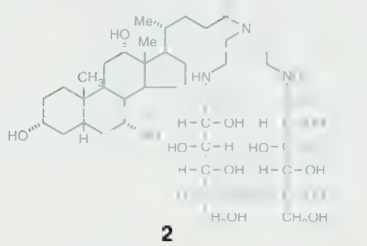


2

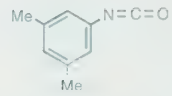
These detergents solubilize opsin and rhodopsin[1] and have value in chiral micro column liquid chromatography.[2]

(1) Gaertner, W. et al. *Photochem. Photobiol.* **1991**, *54*, 1047. (2) Hu, W. et al. *J. High Resolut. Chromatogr.* **1992**, *15*, 275.

37,423-7 3-[(3-Cholamidopropyl)dimethylammonio]-2-hydroxy-1-propanesulfonate (CHAPSO) **(1)**
500mg $18.30; 1g $30.45

34,390-0 *N,N*-Bis[3-(D-gluconamido)-propyl]cholamide (Big CHAP) **(2)**
500mg $34.05; 1g $56.55

New Isocyanates



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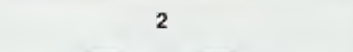


2

3

Applications include: linking with oligosaccharides and cyclodextrins for chiral chromatography stationary phases (**1**);[1] synthesis of carbodiimides from phosphinimines in preparing AZT analogs (**2**);[2] UV curable and latent catalyst-containing polymerization compositions (**3**).[3]

(1) Aburatoani, R. et al. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3606. (2) Häbich, D. *Synthesis* **1992**, 358. (3) Takahashi, Y. et al. *J. Appl. Phys.* **1991**, *70*, 6983.

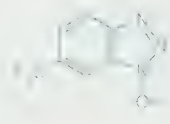
39,010-0 3,5-Dimethylphenyl isocyanate, 99% **(1)**
1g $9.50; 5g $32.00

38,906-4 Dodecyl isocyanate, 99%
(2) 1g $9.00; 5g $30.00

25,643-9 4,4'-Methylenebis(phenyl isocyanate), 98% (MDI) **(3)**
500g $14.00

38,838-6 4,4'-Methylenebis(cyclohexyl isocyanate), mixture of isomers, 90% (HMDI)
100mL $9.00; 500mL $30.00

Trifluoromethyl HOBT



This HOBT analog is quickly becoming the reagent of choice for oligonucleotide synthesis employing van Boom's HOBT-phosphotriester approach.[1] It offers advantages such as better reactivity as compared to HOBT, suppressed base phenoxylation, good stability to normal workup conditions and a non-catalytic second phosphorylation.[1,2] Other applications include the preparation of Ogura's BTBO[3] and BTBC[4] coupling agents.

(1) deVroom, E. et al. *Nucleic Acids Res.* **1986**, *14*, 5885. (2) deVroom, E. et al. *ibid.* **1987**, *15*, 9933. (3) Takeda, K. et al. *J. Org. Chem.* **1985**, *50*, 273. (4) Takeda, K. et al. *Synthesis* **1987**, 557.

39,173-5 1-Hydroxy-6-(trifluoromethyl)benzotriazole, 98%
5g $20.00; 25g $67.00

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About Our Cover:

This painting (oil on canvas, 17⅞ x 27³/₁₆ in.) from the collection of The Saint Louis Art Museum is entitled *The Dovecote* and was painted in 1758 by the French artist Francois Boucher (1703-1770). Few artists were ever so completely in sympathy with the tastes and values of their patrons as Francois Boucher. A delightful landscape painted at the height of his career, this painting is just the sort of confection that made him the favorite of Louis XIV's mistress Madame de Pompadour and her fashionable circle. The dovecote tower and other elements of the composition are based perhaps on sketches made from life, but this is no record of a particular place. Instead, Boucher has conjured up an enchanted garden as charming as it is unreal. The idealized conception of country life expressed in this painting was shared by Boucher's patrons, who, to amuse themselves, would sometimes don rustic costumes and play at milking cows or tending sheep.

Color is a key ingredient in creating the painting's delectable illusion, from the deep blue-green foliage against the frosted blue sky to the touches of pale pink and bright coral. Boucher's masterful manipulation of light and shadow and the undulating curves that animate the sky, the trees, and even the rickety bridge bespeak the plausibility of this impossible world, so fluently rendered in short strokes of thickly applied paint.

Enthusiasm for charming yet highly artificial works like this one was not universal among Boucher's contemporaries. To the philosophers of the Enlightenment, such bonbons were symptomatic of the moral and intellectual flabbiness of the French ruling class.

Lab Notes

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to: Aldrich (attn: Lab Notes, Aldrichimica Acta).

For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2, $9.90 value). If we publish your *Lab Note*, you will also receive **The Detective's Eye: Investigating the Old Masters** (see previous page). We reserve the right to retain all entries for consideration for future publication.

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Ideal for monitoring the flow of coolant water in reflux condensers. Shuts off heater power if coolant supply fails, preventing solvent boil-off and overheating of reactants as well as minimizing escape of solvent vapors. May also be used to monitor any other continuous flow process.

Monitor is supplied in three versions with different sensors to cover a range of flow rates and alarm levels. Sensors fit 8-mm i.d.. pipe and have wetted parts manufactured from PVDF, sapphire, ceramic and Viton® for good chemical resistance.

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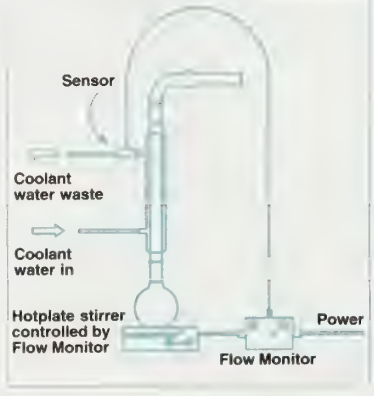

Maximum Flow Rate (L/min)	Alarm Level (L/min)	Voltage	Cat. No.	Each
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15.0	5.0	110	**Z23,991-7**	595.00
15.0	5.0	240	**Z23,992-5**	595.00
Remote Alarm		110	**Z23,993-3**	175.00
(with connectors, no cable)		240	**Z23,994-1**	175.00

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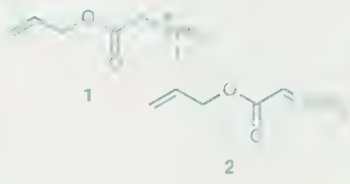
Jai Nagarkatti, President



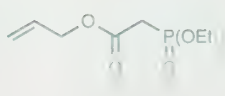
Dr. David Dean of Smith Kline Beecham Pharmaceuticals (U.K.) suggested that we offer the phosphonium salt **1** and its ylide **2**. The allyl ester group of the α,β-unsaturated esters (resulting from the Wittig reaction of aldehydes and ketones with **2**) can be readily removed using standard palladium or rhodium chemistry.

Naturally, we added these products to our listings.

Vyplel, H. et al. *J. Med. Chem.* **1991**, *34*, 2759.

39,442-4 (Allyloxycarbonylmethyl)-triphenylphosphonium iodide, 97% **(1) 10g $12.50; 50g $42.00**

39,441-6 Allyl (triphenylphosphoranylidene)acetate, 97% **(2) 5g $20.00; 25g $67.00**



The phosphonoester analogs of Wittig reagents frequently expand the scope of Wittig reactions by offering different E/Z-selectivity and modified workup conditions (i.e., easier removal of by-products). Thus, we took Dr. Dean's suggestion one step further and have added allyldiethylphosphonoacetate as a new Aldrich product as well.

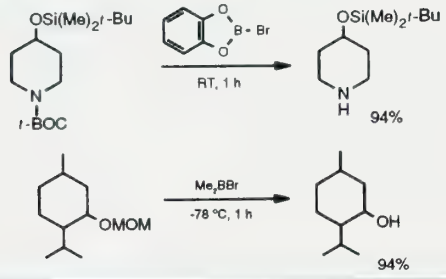
Hoffman, R.W. et al. *Liebigs Ann. Chem.* **1990**, 23.

40,570-1 Allyl diethylphosphonoacetate 5g $25.00; 25g $83.50

USEFUL BROMOBORANES AND BORON TRIFLATES

Bromoboranes and boron triflate reagents have come to prominence in recent years and their continued application makes them vital tools. Aldrich provides these reagents either neat or in solution. Some interesting applications are shown below.

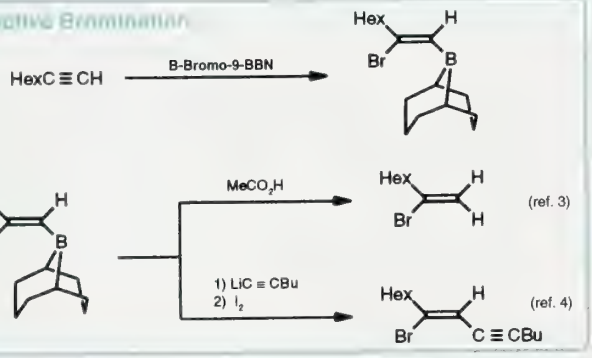
Cleavage of Protecting Groups



(ref. 1)

(ref. 2)

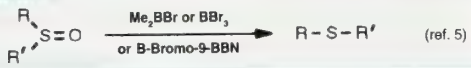
Selective Bromination



(ref. 3)

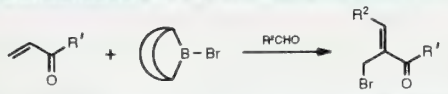
(ref. 4)

Deoxygenation



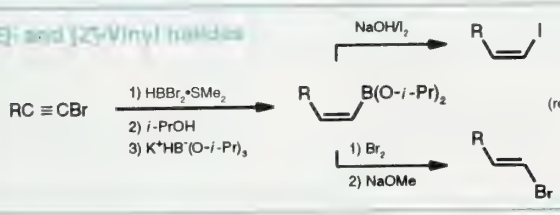
(ref. 5)

Aldol Condensation of α,β-unsaturated ketones



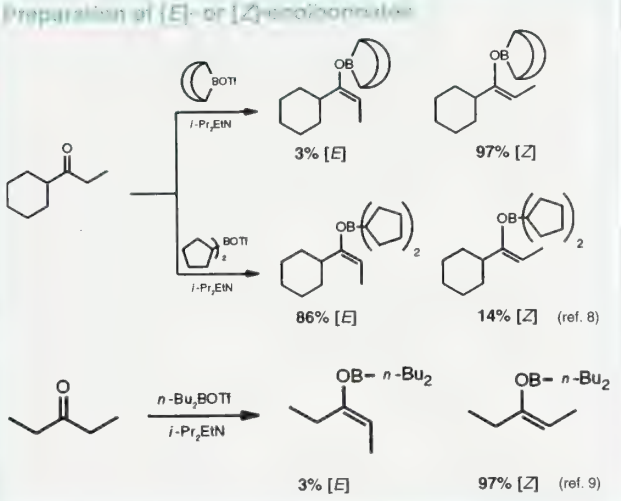
(ref. 6)

(E)- and (Z)-Vinyl halides



(ref. 7)

Preparation of (E)- or (Z)-enolborinates



(ref. 8)

(ref. 9)

References: (1) Boeckman, R.K., Jr.; Potenza, J.C. *Tetrahedron Lett.* **1985**, *26*, 1411. (2) Guindon, Y. et al. *J. Org. Chem.* **1984**, *49*, 3912. (3) Hara, S.; Dojo, H.; Takinami, S.; Suzuki, A. *Tetrahedron Lett.* **1983**, *24*, 731. (4) Hara, S.; Satoh, Y.; Ishiguro, H.; Suzuki, A. *ibid.* **1983**, *24*, 735. (5) Guindon, Y. et al. *ibid.* **1984**, *49*, 4538. (6) Shimizi, H. et al. *Synth. Commun.* **1990**, *20*, 549. (7) Brown, H.C.; Somayaji, V. *Synthesis* **1984**, 919.(8) Van Horn, D.E.; Masamune, S. *Tetrahedron Lett.* **1979**, *24*, 2229. (9) Evans, D.A. et al. *J. Am. Chem. Soc.* **1981**, *103*, 3099.

Bromoboranes	Cat. No.
B-Bromocatecholborane, 97%	**30,416-6**
10g $36.80; 50g $131.90	
Bromodimethylborane	**30,330-5**
1g $8.90; 5g $38.80; 25g $155.50	
B-Bromo-9-BBN, 1.0*M* solution in CH_2Cl_2	**25,663-3**
200mL $66.90	
Dibromoborane-methyl sulfide complex, 1.0*M* soln. in CH_2Cl_2	**25,510-6**
100g $98.70	
Monobromoborane-methyl sulfide complex	**25,509-2**
100 $98.70	
Monobromoborane-methyl sulfide complex, 1.0*M* in CH_2Cl_2	**26,206-4**
100mL $26.80; 800mL $119.25	
Boron tribromide, 99.995%	**23,036-7**
5g $12.80; 25g $42.60; 100g $127.50	
Boron tribromide, 99.99%	**20,220-7**
25g $22.70; 100g $58.90; 250g $90.20; 2kg $580.50	
Boron tribromide, 1.0*M* in CH_2Cl_2	**21,122-2**
100mL $34.70; 800mL $171.20	
Boron tribromide-methyl sulfide complex, 1.0*M* soln. in hexanes	**21,123-0**
100mL $29.50; 800mL $148.00	
Boron tribromide-methyl sulfide complex, 1.0*M* soln. in CH_2Cl_2	**24,738-3**
100mL $34.00; 800mL $168.20	

Boron triflates	Cat. No.
9-BBN triflate, 0.5*M* solution in hexanes	**25,313-8**
100mL $58.40; 800mL $263.00	
Dicyclopentylboron triflate, 0.5*M* solution in CH_2Cl_2	**24,885-1**
100mL $80.40	
Dibutylboron triflate, 1.0*M* solution in diethyl ether	**23,271-8**
100mL $57.50	
Dibutylboron triflate, 1.0*M* solution in CH_2Cl_2	**26,147-5**
100mL $57.40	

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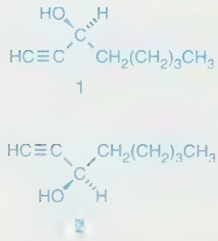


1

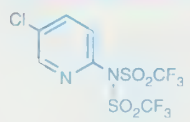
2

Key intermediates for the synthesis of prostaglandins[1] and oxygenated unsaturated fatty acid metabolites (e.g., (*S*)-coriolic acid from 1).

(1) Larock, R.C. et al. *Tetrahedron Lett.* **1989**, *30*, 5737. Stille, J.K. et al. *ibid.* ***1989***, *30*, 3645. Johnson, C.R. et al. *J. Am. Chem. Soc.* **1988**, *110*, 4726. Suzuki, M. *ibid.* **1988**, *110*, 4718. Toru, T. et al. *ibid.* **1988**, *110*, 4815. Okamoto, S. et al. *J. Org. Chem.* **1988**, *53*, 5590, Corey, E.J. et al. *Tetrahedron Lett.* **1986**, *27*, 2199.

39,396-7 (*S*)-1-Octyn-3-ol, 99% **(1) 250mg $21.00; 1g $59.00**
39,970-1 (*R*)-1-Octyn-3-ol, 99% **(2) 250mg $21.00; 1g $59.00**

Triflating Reagent



A stable, white crystalline solid which is much more reactive than *N*-phenyltriflimide providing good to excellent yields of vinyl triflates at -78° in 2 - 4 hours from the corresponding ketone enolates or dienolates.

(1) Comins, D.L.; Dehghani, A. *Tetrahedron Lett.* **1992**, *33*, 6299.

40,364-4 2-(*N,N*-Bis(trifluoromethylsulfonyl)amino)-5-chloropyridine, 97% **1g $15.00; 5g $50.00**

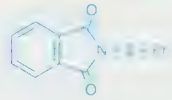
Rhodium Catalyst

A catalyst for the production of acetals under mild conditions.

Ott, J. et al. *Tetrahedron Lett.* **1989**, *30*, 6151.

38,413-5 [1,1,1-Tris(diphenylphosphinomethyl)ethane]rhodium(III) chloride, 97% **100mg $22.00; 500mg $76.00**

Phenylsulfenyl Transfer Reagent

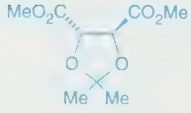


Stable alternative to phenylsulfenyl chloride for phenylsulfenylation of 1° and 2° amines,[1] thiols,[2] trialkyl phosphites[3] and at an activated carbon.[4]

(1) Harpp, D.; Back, T. *Tetrahedron Lett.* **1971**, 4953. (2) Harpp, D. et al. *ibid.* **1970**, 3551. (3) Müller, C.; Roth, H. *ibid.* **1990**, *31*, 501. (4) Grossert, J.; Dubey, P. *J. Chem. Soc., Chem. Commun.* **1982**, 1183.

39,111-5 *N*-(Phenylthio)phthalimide, 98% **5g $19.25; 25g $64.00**

Tartrate Esters

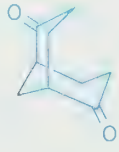


Valuable building block for TADDOL chiral auxilliaries,[1] dipyridine ligands,[2] and threitols,[3] as well as the side chain acid of isoharringtonine.[4,1a]

(1)(a) Weber, E. et al. *J. Org. Chem.* **1992**, *57*, 6825. (b)Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 99. (2) Mandai, T. et al. *Tetrahedron Lett.* **1990**, *31*, 7179. (3) Mash, E.A. et al. *Org. Synth.* **1990**, *68*, 92. (4) Zhang, G. et al. *Huaxue Xuebao* **1989**, *47*, 1087; *Chem. Abstr.* **1990**, *112*, 217321w.

35,906-8 (4*R*,5*R*)-(-)-Dimethyl 2,3-*O*-isopropylidene-L-tartrate, 97% **5ml $27.40; 25ml $114.50**
38,431-3 (4*S*,5*S*)-(+)-Dimethyl 2,3-*O*-isopropylidene-D-tartrate, 98% **1g $10.00; 5g $34.00**

Adamantane Building Block

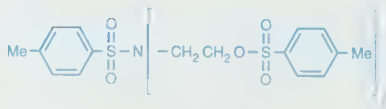


Versatile bicyclic diketone used to make a variety of interesting adamantanes (including those with a spiro-substituted cyclobutanone)[1] as well as tricyclics such as 7-hydroxyisotwistanone.[2]

(1) Lightner, D.A. et al. *J. Am. Chem. Soc.* **1985**, *107*, 7499. (2) Momose, T. et al. *Synth. Commun.* **1985**, *15*, 17.

40,472-1 (±)-Bicyclo(3.3.1)nonane-2,6-dione, 98% **250mg $10.74; 1g $30.00**

Macrocycle Building Blocks



This macrocycle building block is used to prepare selectively protected azamacrocycles,[1] carbon-bridged metallacarboranes[2] and tetrakis phosphonomethyl substituted cyclen.[3]

(1) Qian, L. et al. *J. Org. Chem.* **1991**, *56*, 4904. (2) Gomez, F.A. *Inorg. Chem.* **1992**, *31*, 3558. (3) Swinkel, D.W. et al. *Recl. Trav. Chim. Pays-Bas.* **1991**, *110*, 124.

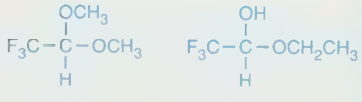
38,068-7 *N,N*-Bis[2-(*p*-tolysulfonyloxy)ethyl]-*p*-toluenesulfonamide, 97% **10g $7.45; 50g $24.50**

Useful dibromoether for the synthesis of macroheterocycles including redox-active tetrathiafulvalene linked systems[1] and polyoxaza cryptands.[2]

(1)Hansen, T.K. et al. *J. Chem. Soc., Chem. Commun.* **1992**, 1550. (2) Akiyama, M. et al. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1213.

38,220-5 2-Bromoethyl ether, tech., 90% **5mL $10.65; 25mL $35.70**

Trifluoroacetaldehyde Equivalents



1 2

These valuable liquid alternatives to gaseous unstable trifluoroacetaldehyde have been used to prepare α-trifluoromethylated alcohols for antifungals, antitumor, and chemotherapeutic agents.[1-3]

(1) Kubota, T. et al. *Tetrahedron Lett.* **1992**, *33*, 1352. (2) Kitazume, T. et al. *Tetrahedron: Asymmetry* **1991**, *2*, 235. (3) Casara, P. et al. *Tetrahedron Lett.* **1991**, *32*, 3823.

39,032-1 Trifluoroacetaldehyde dimethyl acetal, 99% **(1) 1g $19.00; 5g $65.00**
T6,200-6 Trifluoroacetaldehyde ethyl hemiacetal, 90% **(2) 5g $30.60; 25g $130.70**
39,007-0 Trifluoroacetaldehyde ethyl hemiacetal, tech., 90% **(2) 1g $12.00; 5g $40.00**

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About Our Cover:

The painting that graces our cover is a portrait of **Thaddeus Burr** (oil on canvas, 50 x 39 in., 1758-1760). With its companion painting, a portrait of Burr's wife, Eunice Dennie Burr, these paintings represent the high point of American colonial portraiture, a field that was dominated by John Singleton Copley during the period between 1753 and 1774 when Copley left for England. Copley was virtually a self-taught artist since eighteenth-century Boston offered few masters to serve as artistic models. His first works were completed when he was only fifteen, and by the late 1750's Copley had achieved a style of compelling naturalism and sumptuous surface texture.

Thaddeus Burr was a Fairfield, Connecticut landholder and a graduate of Princeton. He was a close friend of John Hancock, and was one of two Fairfield delegates to the convention in Hartford to ratify the Constitution of 1788. Burr's hip-shot pose and clean chiseled features reflect the rational ideology of the eighteenth century. His stance looks to America's political future: leaning against a classical relief, the allegorical figure of abundance makes reference both to his position as landholder as well as the Greek democratic ideals which soon would shape the ideologies of the American and French revolutions. In 1759 he married Eunice Dennie; their marriage may have been the occasion for the commission of these portraits.

Both paintings are in the collection of The Saint Louis Art Museum.

Lab Notes

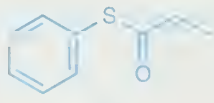
We have found a very convenient and practical way of generating free bases from salts of compounds having secondary or tertiary amines in their molecules. Generally, the free bases of such salts are liberated by dissolving them in water and then treating them with a strong base and extracting with the appropriate solvent. Recovery of the free base is frequently not quantitative. In our method the appropriate salt is placed on top of a short bed of a neutral alumina column and then eluted with a solvent containing 10% methanol in chloroform or an appropriate eluent. After removing the solvent the free base can be recovered in quantitative yield.

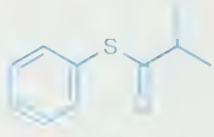
Shiv D. Kumar, Ph.D.
Specialty Chemicals Section
Radian Corporation
P.O. Box 201088
Austin, TX 78720-1088

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2, $9.90 value). If we publish your *Lab Note*, you will also receive **The Detective's Eye: Investigating the Old Masters** (see previous page). We reserve the right to retain all entries for consideration for future publication.

"Please Bother Us."

by Jai Nagarkatti, President





Professor James S. Nowick of the University of California-Irvine suggested that we make these thiol esters which are efficient acyl transfer reagents[1] and ketone synthons.[2] More recently these thiol esters have been used by Danheiser and Nowick in an efficient and general synthesis of β-lactones through condensation of their enolates with aldehydes and ketones. Since β-lactones are known to decarboxylate stereospecifically to the corresponding olefins this method also constitutes a convenient approach to the synthesis of a variety of substituted alkenes.[3]

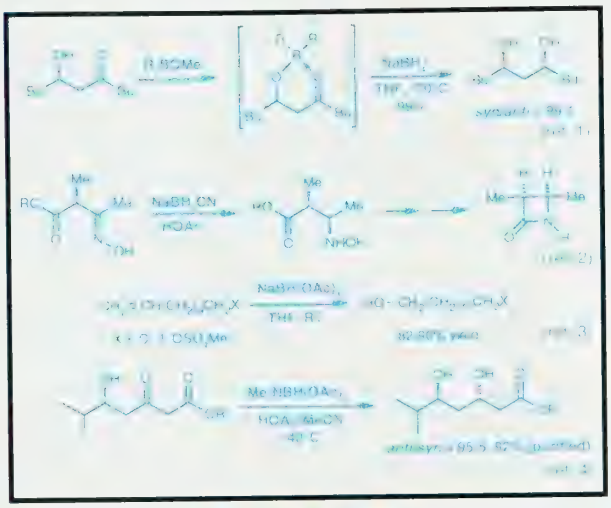
(1) Ahmad, S.; Igbal, J. *Tetrahedron Lett.* **1986**, *27*, 3791. (2) Cardellicchio, C.; Finandanese, V.; Marchene, G.; Ronzini, L. *ibid.* **1985**, *26*, 3595. Fehr, C.; Galindo, J. *J. Org. Chem.* **1988**, *53*, 1830. (3) Danheiser, R.L.; Nowick, J.S. *ibid.* **1991**, *56*, 1176.

It was no bother at all, just a pleasure to be able to help.

37,680-9 ***S*-Phenyl thiopropionate,** 98%
(1) 25g $30.35; 100g $82.00
37,663-9 ***S*-Phenyl thioisobutyrate,** 98%
(2) 25g $30.35; 100g $82.00

VERSATILE BORANES AND BOROHYDRIDES

Boranes and their corresponding metal hydride adducts are versatile reagents in organic synthesis. They have been used in the reduction of carboxylic acids, amides, nitriles, olefins, ketones, aldehydes, acid chlorides, lactones, epoxides, etc. With a proper choice of reagent, these reductions can be carried out under relatively mild conditions and with good selectivity. A few selected applications are shown in the scheme below and more listed in the notes and references.



BORANES

BH_3 Complexes

17,982-5	**Borane-methyl sulfide complex**	**100mL $69.65; 8L $1557.30; 18L $2918.95**
17,619-2	**Borane-tetrahydrofuran complex,** 1.0*M* solution in THF	**100mL $17.60; 800mL $60.30; 8L $442.60; 18L $856.90**
28,771-7	**Borane-ammonia complex,** tech., 90%	**1g $10.30; 10g $60.40**
17,897-7	**Borane-triethylamine complex,** 97%	**5g $9.50; 25g $33.90; 100g $92.70**
18,021-1	**Borane-*tert*-butylamine complex,** powder, 97%	**25g $25.80; 100g $68.20**
17,975-2	**Borane-pyridine complex**	**5g $8.15; 25g $29.10; 100g $79.60**
18,023-8	**Borane-dimethylamine complex,** 97%	**5g $9.30; 25g $33.10; 100g $102.10**

R_2BH

17,871-3	**9-BBN dimer,** crystalline, 98%	**5g $30.20; 25g $90.60; 100g $255.50**
18,891-3	**Catecholborane,** 98%	**25g $69.20; 100g $215.70; 500g $850.80**
31,034-4	**Dimesitylborane,** 90%	**250mg $21.50; 1g $60.00**
22,078-7	**Disiamylborane preparation kit**	**ea $44.00**

R_3B

29,842-5	**Tributylborane**	**50g $90.70**
29,789-5	**Tri-*sec*-butylborane,** 97%	**100g $84.05**
25,719-2	**Triethylborane,** 98%	**100g $86.30**
T8,220-1	**Triphenylboron**	**2.5g $24.10; 10g $77.40**
19,289-9	**Trisiamylborane,** 1.0*M* solution in THF	**100mL $26.00**

A FREE and complete list of Boron Reagents is available from Aldrich. Contact us for your copy!

Notes and References: (1) Chen, K.-M.; Hardtman, K.; Repie, O.; Shapiro, M.I. *Tetrahedron Lett.* **1987**, *28*, 155. (2) Chiba, T.; Ishizawa, T.; Sakaki, J.; Kaneko, C. *Chem. Pharm. Bull.* **1987**, *35*, 4672. (3) Dhillon, R.S.; Nayyar, K.; Singh, J. *Tetrahedron Lett.* **1992**, *33*, 6015. (4) Evans, D.A.; Chapman, K.T. *ibid.* **1986**, *27*, 5939. Banek, J.S. *Chemtracts- Organic Chemistry* **1992**, *5*, 188. (5) Reviews on **BH_3•SMe_2** and **BH_3•THF**, see: Lane, C.F. *Chem. Rev.* **1976**, *76*, 766. Brown, H.C.; Krishnamurthy, S. *Aldrichimica Acta* **1979**, *12*, 3. (6) **Borane-amine complexes** are used for hydroboration at elevated temperature and offer handling convenience and useful application in reduction of Schiff bases, see: Lane, C.F. *ibid.* **1973**, *6*, 51. (7) **9-BBN** used as regioselective hydroborating agent for terminal and *cis* olefins, see: Brown, H.C.; Knights, E.F.; Scouten, C.G. *J. Am. Chem. Soc.* **1974**, *96*, 7765. (8) **Catecholborane**, a monofunctional hydroborating agent used for the preparation of alkane boronic acids and esters from olefins, see: Brown, H.C.; Gupta, S.K. *ibid.* **1975**, *97*, 5249. (9) Application of **trialkylboranes**, see: Akira, S. *Acc. Chem. Res.* **1982**, *15*, 178. (10) **Sodium cyanoborohydride**: highly selective reducing agent, see: Lane, C.F. *Aldrichimica Acta* **1975**, *8*, 3. (11) **K-Selectride**: used for conjugate reduction and reductive alkylation of α,β unsaturated ketones, see: Ganem, B. *J. Org. Chem.* **1975**, *40*, 146. (12) For a review of the uses of **sodium triacetoxyborohydride**, see: Gribble, G.W.; Nutaitis, C.F. *Org. Prep. Proced. Int.* **1985**, *17*, 317.

BOROHYDRIDES

$M^+[BH_4]^-$

21,346-2	**Sodium borohydride,** 99%	**25g $19.70; 100g $69.25**
20,559-1	**Sodium borodeuteride,** 98 atom % D	**1g $27.80; 5g $86.60**
22,235-6	**Lithium borohydride,** 95%	**1g $11.30; 10g $62.40; 50g $200.75**
23,020-0	**Lithium borohydride,** 2.0*M* solution in THF	**100mL $31.60; 800mL $176.20**
20,776-4	**Potassium borohydride,** 98%	**5g $8.00; 100g $31.75; 500g $116.40**

$M^+[BH_3R]^-$

15,615-9	**Sodium cyanoborohydride,** 95%	**5g $7.60; 10g $12.60; 50g $43.80; 1kg $529.60**
19,002-0	**Sodium cyanoborodeuteride,** 98 atom % D	**1g $80.70; 5g $364.50**
38,924-2	**Potassium cyanoborodeuteride,** 98 atom % D	**250mg $32.50; 1g $90.00**
31,637-7	**Lithium thexylborohydride,** 2.0*M* solution in THF	**50mL $28.10**

$M^+[BH_2R_2]^-$

34,423-0	**Lithium 9-BBN hydride,** 1.0*M* solution in THF	**50mL $16.40; 500mL $93.70**
33,374-3	**Lithium dimethylborohydride,** 0.5*M* solution in hexanes	**50mL $30.65; 500mL $162.20**

$M^+[BHR_3]^-$

22,076-0	**K-Selectride®,** 1.0*M* solution in THF	**100mL $26.90; 800mL $183.70; 8L $819.60; 18L $1580.85**
22,077-9	**KS-Selectride®,** 1.0*M* solution in THF	**100mL $43.60**
25,704-4	**L-Selectride®,** 1.0*M* solution in THF	**200mL $52.60; 1.8L $173.60**
22,592-4	**LS-Selectride®,** 1.0*M* solution in THF	**100mL $58.40**
21,340-3	**N-Selectride®,** 1.0*M* solution in THF	**100mL $23.60; 800mL $128.60**
18,086-6	**Super-Deuteride®**(lithium triethylborodeuteride, 1.0*M* solution in THF)	**100mL $32.30; 800mL $185.70**
17,972-8	**Super-Hydride®**(lithium triethylborohydride, 1.0*M* solution in THF)	**100mL $26.70; 800mL $160.80; 8L $594.10; 18L $1167.90**
31,736-5	**Tetramethylammonium triacetoxyborohydride,** 95%	**1g $7.00; 10g $41.40; 50g $160.70**
30,213-9	**Potassium triphenylborohydride,** 0.5*M* solution in THF	**50mL $84.00**

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Aldrichimica Acta

Volume 26, Number 3, 1993

New Synthetic Methods and Strategies and Total Synthesis of Natural Products

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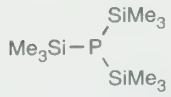
New Products

Phosphine Equivalent

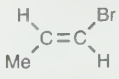


This reagent is an alternative for extremely hazardous phosphine gas (PH_3) and has been used in the preparation of indium phosphide semiconducting films.[1] Additional applications include the synthesis of tris(aminomethyl)phosphines.[2]

(1) Stuczynski, S.M. et al. *Chem. Mater.* **1991**, *3*, 379. (2) Prishchenko, A.A. et al. *Zh. Obsch. Khim.* **1991**, *61*, 1016; *Chem. Abstr.* **1992**, *116*, 6649d.

39,328-2 Tris(trimethylsilyl)phosphine, 99%
100mg $15.00; 500mg $50.00

Vinyl Halide



This important building block (e.g., for organoiron porphyrins,[1] antithrombotic cepaenes,[2] fulvenes,[3] etc.) is now available in the highly pure *trans* form.

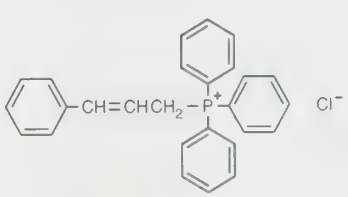
(1) Setsure, J. et al. *J. Chem. Soc., Chem. Commun.* **1992**, 328. (2) Block, E.; Zhar, S.H. *J. Org. Chem.* **1992**, *57*, 5815. (3) Silverberg, L.J. et al. *J. Organomet. Chem.* **1991**, *409*, 411.

39,110-7 *trans*-1-Bromo-1-propene, 99% **1g $13.00; 5g $43.00**

We also list the *cis* isomer.

36,867-9 *cis*-1-Bromo-1-propene, 97%
10g $19.80; 50g $65.20

Cinnamyl Wittig Reagent

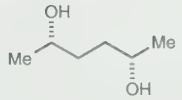


Used in a synthesis of 7α- or 7β-(4-phenylbutyl)dihydrocodeine derivatives.[1] Also featured in a survey of catalysts and substrates for the Gomberg-Bachmann synthesis of unsymmetrical biarenes[2] and in a study of internal rotation in *peri*-phenylnaphthalenes.[3]

(1) Beadle, J.R. et al. *J. Org. Chem.* **1984**, *49*, 1594. (2) Leland, D.L.; Kotick, M.P. *ibid.* **1983**, *48*, 1813. (3) Clough, R.L.; Roberts, J.D. *ibid.* **1978**, *43*, 1328.

39,267-7 Cinnamyltriphenylphosphonium chloride, 99%
5g $11.00; 25g $37.00

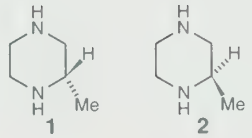
Chiral Building Blocks



Used in the synthesis of new chiral phospholanes.[1] A building block in the synthesis of *trans*-2,5-dimethylpyrrolidine.[2]

(1) Burk, M.J. et al. *Tetrahedron:Asymmetry* **1991**, *2*, 569. (2) Short, R.P. et al. *J. Org. Chem.* **1989**, *54*, 1755.

39,672-9 (2*S*,5*S*)-(+)-Hexanediol, 99%
250mg $22.50; 1g $67.00

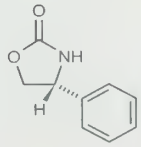


1 2

Valuable synthons for quinoline antibacterials.

Kiely, J.S.; Priebe, S.R. *Org. Prep. Proced. Int.* **1990**, *22*, 761.

39,717-2 (*S*)-(+)-2-Methylpiperazine, 99% **(1) 250mg $13.75; 1g $38.00**
39,716-4 (*R*)-(-)-2-Methylpiperazine, 99% **(2) 250mg $13.75; 1g $38.00**



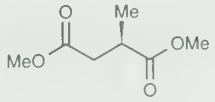
Oxazolidinone for α-amino acid synthesis[1] and the preparation of β-lactam antibiotics (e.g. in the synthesis of deoxybouvardin analogs).[2]

(1) Matsunaga, H. et al. *Chem. Pharm. Bull.* **1992**, *40*, 1077. (2) Boger, D.L.; Myers, J.B., Jr. *J. Org. Chem.* **1991**, *56*, 5385.

40,245-1 (*R*)-(-)-4-Phenyl-2-oxazolidinone, 98%
1g $30.00; 5g $102.50

We also offer the enantiomer.

37,669-8 (*S*)-(+)-4-Phenyl-2-oxazolidinone, 98%
1g $30.90; 5g $103.30

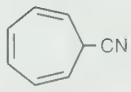


A recent synthesis of FK-SOG by Sih and co-workers employed this succinate building block.

Gu, R.L.; Sih, C.J. *Tetrahedron Lett.* **1990**, *31*, 3283.

38,209-4 Dimethyl (*R*)-(+)-methylsuccinate, 99%
1g $13.30; 5g $43.70

EPR Model

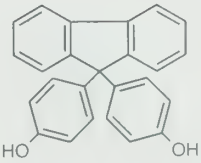


A useful model for EPR[1] and intramolecular proton transfer studies[2] of cycloheptatriene radicals and anions. The cyano substituent stabilizes the anion and can also be used to generate dihydroazocines and hydrooxocins.[3]

(1) MacCorquodale, F.; Walton, J.C. *Magn. Reson. Chem.* **1990**, *28*, 364. (2) Takahashi, K. et al. *J. Org. Chem.* **1987**, *52*, 2666. (3) Zipperer, B. et al. *Tetrahedron Lett.* **1987**, *28*, 2513.

39,332-0 2,4,6-Cycloheptatriene-1-carbonitrile, 97%
1g $18.00; 5g $60.00

Polymer Building Block

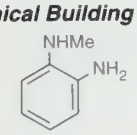


Used in the synthesis of novel poly(arylene ethers).

Wang, Z.Y.; Hay, A.S. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1045.

39,998-1 4,4'-(9-Fluorenylidene)diphenol, 97% **5g $13.00; 25g $43.00**

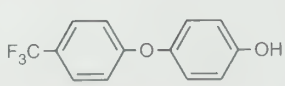
Biochemical Building Blocks



Monoalkylated *o*-phenylenediamine for the preparation of benzimidazole angiotensin antagonists and in benzimidazole/copper enzyme active site modelling.

Droege, M.W. et al. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* **1992**, *37*, 340; *Chem. Abstr.* **1992**, *117*, 19154j.

39,898-5 *N*-Methyl-1,2-phenylenediamine, 98%
5mL $22.50; 25mL $75.00



Key agrochemical intermediate, especially for pesticides and herbicides.

39,645-1 4-[4-(Trifluoromethyl)-phenoxy]phenol, 98%
5g $19.00; 25g $64.00

Aldrichimica Acta

Volume 26, Number 3, 1993
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About Our Cover:

This alluring masterpiece entitled *Portrait of a Lady* (oil on canvas, 80.7 x 65.2 cm) was painted by Jean-Marc Nattier in 1738 at the threshold of a very successful career as a portraitist of ladies of the court of Louis XV. His portraits included the King's wife, daughters, and various mistresses. In the Salon exhibition of that year Nattier exhibited three portraits: one of the Chevalier d'Orléans; one of Mlle de Canisy, wife of the Marquis d'Antin; and one of Mlle de Rohan which has not been located. Nattier was fond of painting his female sitters in mythological guises. Mlle de Rohan was represented as Hebe, the goddess of youth, usually shown with an eagle and cup. Whoever the lady in this portrait is, she is represented as Flora, goddess of flowers — a flattering device often used for the portraits of attractive women. Another Flora-figure by Nattier, still not identified, was shown in the Salon of 1746.

It was only a year before *Portrait of a Lady* was painted that Nattier had shown his first portrait in a Salon. An Academician since 1718, he had been a history painter, making drawings for engravings of Rubens' *Life of Marie de Médici* series, and admiring the work of Rubens and LeBrun. In 1717 in the Netherlands he had painted a *Battle of Poltava* for Peter the Great of Russia as well as portraits of Peter and his wife Catherine. Financial considerations probably caused him to abandon his history painting for portraiture — a genre in which he was most successful, endowing his sitters with beguiling grace and charm.

The painting is in the collection of The Saint Louis Art Museum.

Lab Notes

Hints for NMR Sample Preparation

We offer a number of deuterated NMR solvents in a variety of packages for our customers. Because of the solvents high chemical and isotopic purities as well as their hygroscopic nature, relatively small amounts of contaminants can result in unusually large impurity signals. The following suggestions should help you get the best results from deuterated solvents.

Drying all glassware at ca. 150°C for 24 hours and cooling under an inert atmosphere will ensure moisture-free surfaces. For less demanding applications, a nitrogen blanket during sample preparation may be adequate.

Use of clean, dry glassware and Teflon® accessories (e.g., NMR tube caps) will help reduce chemical impurity problems that generally arise from the leaching of chemicals from rubber or plastic surfaces (e.g., NMR tube caps). Use of a vortex mixer will eliminate the need to shake the tube contents vertically and the resultant contamination from NMR tube caps. Residual chemical vapor from equipment can also be a source of impurities, residual acetone in pipette bulbs being the most common example.

Protonated solvent residues are often effectively removed by co-evaporation with a small quantity of the desired deuterated solvent, brief (ca. 5-10 min.) high vacuum drying and then preparing the NMR sample. Some solvents such as chloroform-*d*, benzene-d_6, and toluene-d_8 will also remove residual water azeotropically.

Use of solvent from a freshly opened 0.5 or 1mL single-use ampule or from septum bottles employing a syringe-needle technique will also help.

—Aldrich Stable Isotopes Department
—NMR Laboratory Staff

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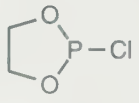
Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2, $9.90 value). If we publish your *Lab Note*, you will also receive **The Detective's Eye: Investigating the Old Masters** (see previous page). We reserve the right to retain all entries for consideration for future publication.

"Please Bother Us."

by

Jai Nagarkatti, President



Professor Dimitris S. Argyropoulos of the Pulp and Paper Research Centre at McGill University (Montreal) kindly suggested that we offer this dioxaphospholanyl chloride which is a useful derivatization reagent for ^{31}P NMR analysis of soluble lignocellulosic substances. The technique involves selective phosphitylation in the presence of pyridine of a variety of functional groups present in lignins and carbohydrates (e.g., ArOH, 1°,2°,3°-OH, RCOOH, etc.) followed by examination of the decoupled ^{31}P NMR spectrum. Signals arising from the three principal forms of phenolic hydroxyls present in lignin structures (i.e., *p*-hydroxyphenyl, guaiacyl and syringyl), the erythro and threo forms of arylglycerol-β-aryl ethers and labile protons in carbohydrates can be unambiguously assigned.

Argyropoulos, D.S.; Bolker, H.I.; Heitner, C.; Archipov, Y. *J. Wood Chem. Technol.* **1993**, *13*, 187. Archipov, Y.; Argyropoulos, D.S.; Bolker, H.I.; Heitner, C. *Carbohydrate Res.* **1991**, *220*, 49.

It was no bother at all, just a pleasure to be able to help.

39,122-0 2-Chloro-1,3,2-dioxaphospholane, 97%
5mL $20.00; 25mL $67.50

MERCURY SPILL KITS

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Products are biodegradable, non-corrosive, odorless and ADA approved. For descriptive information about the spill control products, refer to the *Replacement components* section on the right.

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Contained in a sturdy wall mountable metal case. Contents: 1 x 250mL MERCONSPRAY™, 1 x 475mL MERCONVAP™, 2 x MERCONTAINERS™ storage containers, one package Merconwipes towelettes, spill pickup tools, one pair safety goggles, two pairs nitrile gloves, two resealable plastic bags for disposal of gloves and towelettes, mercury waste labels and instruction booklet.
41,368-2 $199.00

MERCONKIT, MERCONSPRAY, MERCONVAP, and MERCONTAINER are trademarks of EPS Chemicals Inc.

MERCONKIT 2
Has all the features of MERCONKIT 1, except it is contained in a sturdy corrugated package with plastic handle.
41,369-0 $169.00

MERCONKIT 3
Contents: 1 x 250mL MERCONSPRAY, 1 x 250mL MERCONVAP, 1 x MERCONTAINER storage container, one set safety goggles, six pairs latex gloves, six resealable plastic bags in a sturdy corrugated package with plastic handle.
41,370-4 $75.00

Replacement components for spill kits

MERCONTAINER
A 16 ounce container lined with a mercury suppressing sponge. Includes plastic scoops and a foam pad to pick up small mercury spills. Provides safe containment and disposal of mercury and mercury contaminated debris.
41,373-9 $22.00 ea; 6 x 1ea $125.40

MERCONSPRAY
A pump spray designed to eliminate airborne mercury vapors over spills before cleanup.
41,371-2 250mL $20.35; 6 x 250mL $116.00

MERCONVAP
A liquid vapor suppressant and decontaminant for cleaning up floors and other areas where mercury has been spilled.
41,372-0 250mL $18.30; 6 x 250mL $104.00
475mL $28.50; 6 x 475mL $162.45

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In response to your requests we have added a line of redistilled amines which are packaged under nitrogen in Sure-Seal®bottles to maintain their integrity on storage. These conveniently dispensed amines will prove to be an asset to anyone requiring high-purity, low water, low residue nitrogen bases.

38,764-9	***N,N*-Diisopropylethylamine,** redistilled, 99.5%	**100mL $23.00; 800mL $135.00**
39,108-5	**Ethylene diamine,** redistilled, 99.5+%	**100mL $23.50; 800mL $117.00**
38,646-4	**Diisopropylamine,** redistilled, 99.5%	**100mL $19.00**
39,423-8	**Pyrrolidine,** redistilled, 99.5+%	**100mL $17.00; 800mL $82.00**
38,645-6	**Diethylamine,** redistilled, 99.5%	**100mL $16.00**
39,446-7	**Morpholine,** redistilled, 99.5+%	**100mL $21.00; 800mL $105.00**
40,727-5	***N,N*-Dimethylaniline,** redistilled, 99.5+%	**100mL $20.00; 800mL $70.00**
40,726-7	**Phenethylamine,** redistilled, 99.5+%	**100mL $40.00; 800mL $110.00**
39,143-3	***tert*-Butylamine,** redistilled, 99.5+%	**100mL $17.00; 800mL $82.00**
39,126-3	***N,N*-Dimethylethanolamine,** redistilled, 99.5+%	**100mL $14.00; 800mL $67.00**
40,771-2	**Benzylamine,** redistilled, 99.5+%	**100mL $24.00; 800mL $77.00**
40,770-4	**4-Methylmorpholine,** redistilled, 99.5+%	**100mL $20.00; 800mL $90.00**

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A variety of metal alkoxides are available as conveniently handled solutions in THF, hexanes and alcohols or as dry powders.

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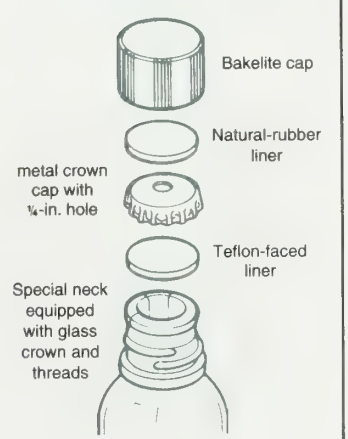
40,879-4	**Lithium methoxide,** 1.0*M* solution in methyl alcohol	**100mL $26.00; 800mL $128.00**
15,625-6*	**Sodium methoxide,** 25 wt. % solution in methanol	**25mL $12.70; 1L $16.30; 2L $25.35**
40,024-6	**Lithium ethoxide,** 1.0*M* solution in ethyl alcohol	**100mL $25.00; 800mL $135.00**
23,055-3*	**Sodium ethoxide,** 21 wt. % solution in denatured ethyl alcohol	**5mL $7.80; 100mL $8.00; 500mL $20.55**
40,025-4	**Lithium ethoxide,** 1.0*M* solution in tetrahydrofuran	**100mL $21.00; 800mL $116.00**
40,032-7	**Lithium isopropoxide,** 2.0*M* solution in tetrahydrofuran	**50mL $25.00; 250mL $90.00**
39,820-9	**Lithium *tert*-butoxide,** 1.0*M* solution in hexanes	**50mL $12.00; 250mL $40.00**
39,819-5	**Lithium *tert*-butoxide,** 1.0*M* solution in tetrahydrofuran	**50mL $12.50; 250mL $42.00**
33,134-1	**Potassium *tert*-butoxide,** 1.0*M* solution in 2-methyl-2-propanol	**100mL $13.10; 800mL $26.30**
32,865-0	**Potassium *tert*-butoxide,** 1.0*M* solution in tetrahydrofuran	**50mL $17.90; 500mL $95.20**

* Not available in Sure/Seal bottle.

Solids

34,437-0	**Lithium methoxide,** 98%	**5g $8.50; 25g $29.70; 100g $82.30**
16,499-2	**Sodium methoxide,** powder, 95%	**5g $9.50; 100g $9.70; 500g $17.75; 2kg $49.00**
29,278-8	**Potassium methoxide,** 95%	**5g $12.70; 250g $37.70**
40,020-3	**Lithium ethoxide,** 95%	**5g $16.50; 25g $55.00**
15,624-8	**Sodium ethoxide,** 96%	**5g $12.70; 100g $21.30; 500g $32.30**
33,337-9	**Potassium ethoxide,** 95%	**5g $10.65; 100g $13.65; 500g $49.95**
34,893-7	**Lithium isopropoxide,** 95%	**25g $24.00; 100g $67.40**
40,017-3	**Lithium *tert*-butoxide**	**25g $30.00; 100g $100.00**
35,927-0	**Sodium *tert*-butoxide,** 97%	**5g $10.65; 100g $20.55; 500g $76.70**
15,667-1	**Potassium *tert*-butoxide,** 95%	**5g $12.70; 100g $19.80; 500g $49.00**
28,101-8	**Sodium thiomethoxide,** 95%	**1g $10.60; 5g $32.85**

Sure/Seal™ Bottle



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A recently developed sample preparation technique, solid phase microextraction (SPME), eliminates much of the time and cost associated with preparing water samples for analysis of organic compounds. In SPME, a stationary phase-coated fused silica fiber is introduced into the water sample, and organic analytes adsorb to the phase. The analytes are desorbed from the fiber to a capillary GC column by the heated chromatograph injection port. No solvents or complicated apparatus are required. The technique has important advantages.

- *speed* — equilibrium is reached in only 2-15 minutes — ideal for quick screening
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- *versatility* — use with any gas chromatograph or GC-mass spectrometer, with split/splitless or on-column injection

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For manual sampling	**5-7302**	**$138.00**
For Varian 8100/8200 AutoSampler	**5-7303**	**138.00**
100µm stabilized polydimethylsiloxane coating		
For manual sampling	**5-7300**	**120.00**
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Phone: 800-247-6628 or 814-359-3441 ● FAX: 800-447-3044 or 814-359-3044
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Aldrichimica Acta

Volume 26, Number 4, 1993

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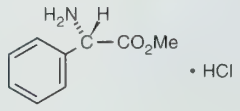
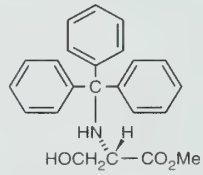


Useful chiral auxiliary which affords 6-substituted-didehydropiperidinones with high diastereoselectivity.[1] Also a recognized guest in podand-type monensin amide chiral receptors.[2]

(1) Waldmann, H.; Braun, M. *J. Org. Chem.* **1992**, *57*, 4444. (2) Maruyama, K.; Sohmiya, H.; Tsukube, H., *Tetrahedron* **1992**, *48*, 805.

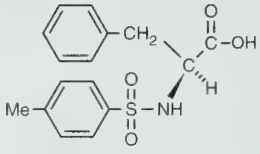
30,867-6 (*S*)-(+)-**2-Phenylglycine methyl ester hydrochloride,** 97%
10g $8.50; 50g $28.50



Chiral building block for pharmaceuticals, artificial sweeteners and PAF antagonists.

Tsuri, T. et al. *Chem. Pharm. Bull.* **1992**, *40*, 85.

41,134-5 *N*-**Trityl-L-serine methyl ester,** 99% **5g $16.00; 25g $53.50**



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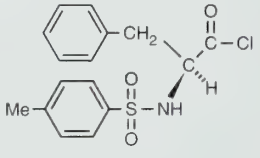


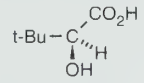
2

This acid and its acid chloride are useful resolving agents.

Hashimoto, S. et al. *Synth. Commun.* **1991**, *21*, 833.

39,384-3 *N*-*p*-**Tosyl-L-phenylalanine,** 97% **(1) 10g $16.00; 50g $53.50**
39,650-8 *N*-*p*-**Tosyl-L-phenylalaninyl chloride,** 99% **(2) 5g $20.00; 25g $67.00**

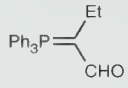
Building Blocks



Valuable starting material for chiral 2-substituted lactams[1] and α-*tert*-butyl vinyl ethers.[2]

(1) Quast, H.; Leybach, H. *Chem. Ber.* **1991**, *124*, 849. (2) Ito, M.; Kibayashi, C. *Synthesis* **1993**, 137.

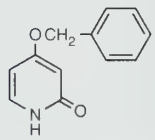
41,091-8 (*S*)-(+)-**2-Hydroxy-3,3-dimethylbutyric acid**
250mg $23.00; 1g $65.00



For the preparation of α,β-vinylogs of butyraldehyde (e.g., in the synthesis of modified retinals).

Bestmann, H.J.; Ermann, P.; Rueppel, H.; Sperling, W. *Liebigs Ann. Chem.* **1986**, 479.

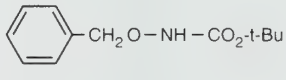
40,572-8 2-(Triphenylphosphoranylidene)butyraldehyde, 98%
1g $12.75; 5g $46.50



Important benzyl protected pyridone for the syntheses of biologically active 3-deazapyrimidine nucleosides, alkaloids, and synthetic drugs with antitumor, antiviral, and anti-hypertensive activities.[1-4]

(1) Copp, R.R.; Marquez, V.E. *J. Med. Chem.* **1991**, *34*, 208. (2) Bergmann, R.; Gericke, R. *ibid.* **1990**, *33*, 492. (3) Shone, R.L. *Tetrahedron Lett.* **1977**, *46*, 4017. (4) Katagiri, N. et al. *J. Chem. Soc., Perkin Trans. I* **1986**, *7*, 1289.

41,061-6 4-Benzyloxy-2(1*H*)-pyridone
1g $30.00; 5g $100.00

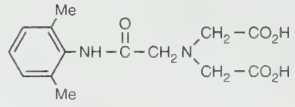


Valuable precursor to mono-alkylated *N*-hydroxylamines. It also has been used in the synthesis of the siderophores (naturally occurring ferric ion chelators) alcalignin and bisucaberin.

Bergeron, R.J.; McManis, J.S.; Perumal, P.T.; Algee, S.E. *J. Org. Chem.* **1991**, *56*, 5560.

40,769-0 *tert*-**Butyl** *N*-**(benzyloxy)-carbamate,** 99%
5g $22.50; 25g $75.00

SPECT Reagent

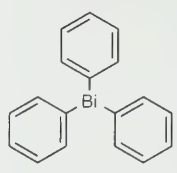


Component of a technetium-99 radiopharmaceutical.

Liu, C. *Zhongguo Yiyao Gongye Zazhi* **1991**, *22*, 153; *Chem. Abstr.* **1991**, *115*, 182767d.

41,404-2 *N*-**(2,6-Dimethylphenylcarbamoylmethyl)iminodiacetic acid,** 97%
250mg $9.25; 1g $28.20

Volatile Organometallics



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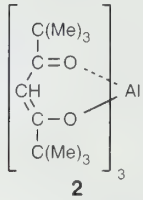


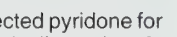
2

These bismuth and aluminum derivatives are useful in the preparation of thin films of superconducting oxides by chemical vapor deposition.[1] Triphenylbismuth also serves as a precursor to another volatile bismuth source, $Bi(fod)_3$.[2]

(1) Hashimoto, T. et al. *J. Mater. Res.* **1992**, *7*, 1336. (2) Brooks, K.C. et al. *Chem. Mater.* **1992**, *4*, 912.

39,895-0 Triphenylbismuth, 99% **(1)**
5g $13.50; 25g $45.40
39,728-8 Aluminum tris(2,2,6,6-tetramethyl-3,5-heptanedionate), 98% **(2)**
1g $24.00; 5g $93.50

Bifunctional Isothiocyanate

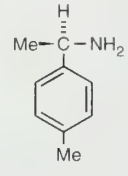


Cyclocondensation of 2-chloroethyl isothiocyanate with a variety of amines[1-3] generates fused heterocyclic products.

(1) Outcalt, R.J. *J. Heterocycl. Chem.* **1987**, *24*, 1425. (2) Fulop, F. et al. *Tetrahedron* **1991**, *47*, 7673. (3) Chern, J.W. et al. *J. Heterocycl. Chem.* **1990**, *27*, 1485.

41,059-4 2-Chloroethyl isothiocyanate, 98% **1g $14.00; 10g $53.50**

Chiral α-Methylbenzylamines



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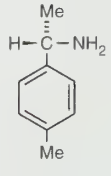

2

Compounds **1** and **2** have been used for the resolution of jasmonic acid and naproxen.

Brunner, H.; Scheck, T. *Chem. Ber.* **1992**, *125*, 701.

40,524-8 (*R*)-(+)-α,**4-Dimethylbenzylamine,** 98+% **(1)**
250mg $10.00; 1g $28.00
40,525-6 (*S*)-(-)-α,**4-Dimethylbenzylamine,** 98+% **(2)**
250mg $10.00; 1g $28.00

Aldrichimica Acta

Volume 26, Number 4, 1993
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About Our Cover:

A nostalgic glimpse of a hundred years ago entitled **New Bedford: The View Across to Fairhaven from Center Street in 1884** (oil on canvas, 18 x 24 in.) was painted by the contemporary marine artist, John Stobart. This view of Center Street, New Bedford, is almost exactly the same today as it was in this painting. If it were not for the main highway crossing the foot of the street, one would still be able to walk right into this view and down onto the wharf, which is still in commercial use. The churches across the river in Fairhaven are still there. All that is gone, and gone forever, are the whaleships that so characterized this New England harbor when it was home port to so many of the vessels between 1845 and the turn of the century.

In this painting showing Central Wharf in 1884, the brig Isabella, is at anchor in the Acushnet River. Down on the wharf to the left of the little shack that seems to be in almost all photographs ever taken of New Bedford, an older bark has been stripped down to her lower masts prior to undergoing renovation. As a form of dedication, the artist has used the names of two gentlemen on advertising signs: his good friends Richard Kugler, curator of the New Bedford Whaling Museum, and Richard Fitton, M.D., whom Stobart has immortalized as proprietor of the ship chandlery on the right.

The painting is in the collection of the artist.

Lab Notes

A common problem chemists have when chromatographing milligram quantities using a pipette column is the lack of reservoir space for the eluant. A remedy to this problem is to use a disposable 10-ml syringe as the solvent reservoir.

The pipette column is connected to a carrier gas line using silicone tubing. The needle is inserted through the tubing into the top of the pipette. This allows the constant addition of eluant to the column simply by pushing the syringe barrel when needed. No longer do you have to remove the carrier gas line, collect one fraction and repeat the process due to an empty solvent reservoir.

Dale Krolikowski
Scientist II
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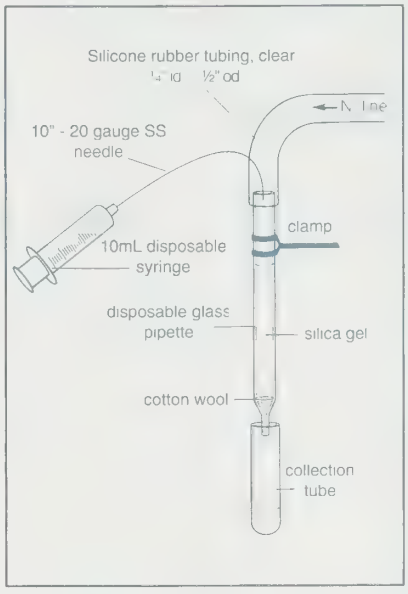
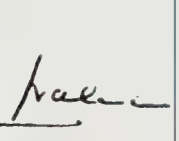


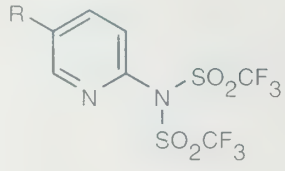
Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2). If we publish your *Lab Note*, you will also receive **The Detective's Eye: Investigating the Old Masters**. We reserve the right to retain all entries for consideration for future publication.

"Please Bother Us."

by



Jai Nagarkatti, President



1 R = H
2 R = Cl

Professor Daniel L. Comins of North Carolina State University kindly suggested that we manufacture these pyridine based triflating reagents. They are stable, white crystalline solids and are much more reactive than *N*-phenyltriflimide (Aldrich Cat. No. 29,597-3) allowing preparation of most vinyl triflates at -78°C in 2 - 4 hours.

Chromatographic purification (silica gel; EtOAc/hexane) of the product vinyl triflates is also much easier — another advantage over *N*-phenyltriflimide.

Naturally, we made these two interesting reagents.

Comins, D.L.; Dehghani, A. *Tetrahedron Lett.* **1992**, *33*, 6299.

40,363-6 2-[*N*,*N*-Bis(trifluoromethylsulfonyl)amino]pyridine, 96% **(1)**
1g $12.00; 5g $40.00

40,364-4 2-[*N*,*N*-Bis(trifluoromethylsulfonyl)amino]-5-chloropyridine, 97% **(2)**
1g $15.00; 5g $50.00

It was no bother at all, just a pleasure to be able to help.

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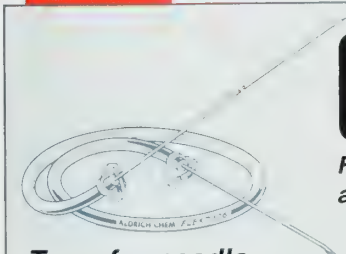
	27,099-7	Dichloromethane	16.50	25.05	38.90	83.60	162.70
	22,705-6	*N,N*-Dimethylformamide	16.50	30.70	46.80	106.30	207.60
	29,630-9	1,4-Dioxane	20.90	34.65	63.20	140.40	252.10
	27,098-9	Ethyl acetate	14.30	18.85	26.50	69.00	124.10
	29,608-2	Ether	14.30	22.80	—	126.10	208.60
	27,764-9	Ethyl alcohol	16.50	19.80	28.90	78.50	145.00
	24,665-4	Heptane	17.00	24.75	35.20	79.40	146.90
	32,241-5	Methyl alcohol	14.30	17.85	28.40	72.40	126.80
	32,863-4	1-Methyl-2-pyrrolidinone	19.80	42.25	68.90	191.10	254.60
	27,685-5	Methyl sulfoxide	18.70	39.15	67.20	—	—
	27,097-0	Pyridine	27.50	53.55	96.50	—	—
NEW!!!	40,175-7	Tetrahydrofuran, inhibitor-free	22.10	39.10	55.20	173.50	326.00
	18,656-2	Tetrahydrofuran (inhibited with 0.025% BHT)	20.90	36.65	51.10	158.80	295.60



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Aldrichimica Acta

Volume 27, Number 1, 1994

Enantioselective Synthesis of β-Amino Acids

Iodobenzene Diacetate and Related Hypervalent Iodine Reagents in the Synthesis of Heterocyclic Compounds

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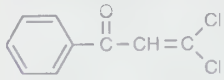
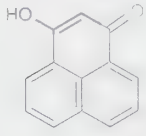


This dichlorovinyl derivative is an important building block for the synthesis of four-, five-, and six-membered heterocycles with two or three heteroatoms.[1-5]

(1) Komarova, E.N. *Zh. Org. Khim.* **1990**, *26*, 2097. (2) Schroth, W. et al. *J. Prakt. Chem.* **1990**, *332*, 148. (3) Drozd, V.N. et al. *Zh. Org. Khim.* **1989**, *25*, 2171. (4) Schroth, W. et al. *Monatsh. Chem.* **1988**, *119*, 463. (5) Spitzner, R. et al. *ibid.* **1987**, *118*, 1383.

39,882-9 3,3-Dichloro-1-phenyl-2-propen-1-one, 97% **1g $14.05**

New Phenalene

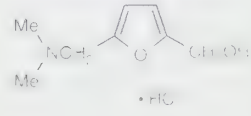


For the preparation of cyclopropylidenephenalenedione, which is a highly reactive, unstable intermediate used in a variety of cycloaddition reactions.

Vilsmaier, E. et al. *Chem. Ber.* **1989**, *122*, 1285.

40,970-7 3-Hydroxy-1*H*-phenalen-1-one, 98%
1g $21.35; 5g $71.30

Ranitioine Precursor



Employed in the synthesis of ranitioine,[1] a known anti-ulcer drug.[2,3]

(1) Cholerton, T. et al. *J. Chem. Res., Synop.* **1985**, *8*, 250. (2) Berstad, A. et al. *Scand. J. Gastroenterol.* **1980**, *15*, 637. (3) Walt, R. et al. *Gut* **1981**, *22*, 49.

41,124-8 5-(Dimethylaminomethyl)furfuryl alcohol hydrochloride, 98%
25g $22.00; 100g $63.50

Now Available

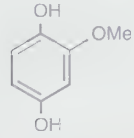
$HC{\equiv}CCH_2CH_2C{\equiv}CH$

Recently used in the improved synthesis of cyclopropa[4,5]benzocyclobutene (Rocketene).[1]

(1) McNichols, A. et al. *Synlett* **1992**, *12*, 971.

40,729-1 1,5-Hexadiyne, 50 wt.% solution in pentane
5mL $19.45; 25mL $64.80

Building Block

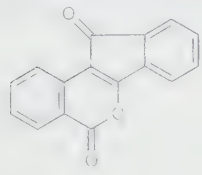


Starting material in a high-yield synthesis of 2,2-dimethyl-4-chromanones[1] and a preparation of 4-phenyl-2*H*-1-benzopyrans.[2] Used in the synthesis of 2,5-bis(tosyloxy)anisole, a substrate used in the study of the regioselective cleavage of aryl tosylates by electrochemical reduction.[3] Model compound in a study of ^{31}P-NMR spectroscopy in wood chemistry.[4]

(1) Chatarvedi, R.; Mulchandani, N.B. *Indian J. Chem., Sect. B.* **1992**, *31B*, 338. (2) Jurd, J. *J. Heterocycl. Chem.* **1991**, *28*, 983. (3) Civitello, E.R.; Rapoport, H. *J. Org. Chem.* **1992**, *57*, 834. (4) Arkhipov, Y.; Argyropoulos, D.S.; Balker, H.I.; Heitner, C. *J. Wood Chem. Technol.* **1991**, *11*, 137.

17,689-3 Methoxyhydroquinone, 98% **5g $8.10; 25g $28.10**

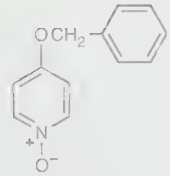
Heterocycle Precursor



Starting material in the synthesis of 6-substituted-6*H*-indeno[1,2-*c*]-isoquinoline-5,11-diones[1] and in the preparation of several 1,3-indanediones and isoquinolines.[2]

(1) Wawzonek, S. *Org. Prep. Proced. Int.* **1982**, *14*, 163. (2) Wawzonek, S.; Stowell, J.K. *J. Org. Chem.* **1968**, *33*, **896**.

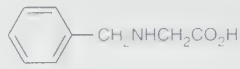
38,358-9 Benz[*d*]indeno[1,2-*b*]-pyran-5,11-dione, 98%
10g $12.45; 50g $41.05



This *N*-oxide is useful as an intermediate in oligonucleotide synthesis and as a photosensitizer in photographic and reprographic processes.

41,060-8 4-(Benzyloxy)pyridine *N*-oxide, 97%
1g $10.80; 10g $61.60

Bio-Organic Tool

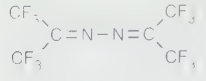


Used as a replacement for aromatic amino acid residues.[1] Starting material for the synthesis of 3,5-disubstituted-1-azanorbornanes, intermediates for novel muscarinic ligands.[2] Also utilized as a starting material in a study of the multiple alkylation and mapping of the active site of α-chymotrypsin.[3]

(1) Young, J.D.; Mitchell, A.R. *Pept.: Chem., Struct. Biol., Proc. Am. Pept. Symp.*, 11th Meeting, Los Angeles, CA, **1989**, 155. (2) Snow, R.J.; Street, L.J. *Tetrahedron Lett.* **1989**, *30*, 5795. (3) White, E.H.; Li, M.; Cousins, J.P.; Roswell, D.F. *J. Am. Chem. Soc.* **1990**, *112*, 1956.

40,426-8 *N*-Benzylglycine, 99%
5g $24.30; 25g $81.00

Fluoroheterocycle Synthon



This fluorinated azine is a useful precursor for fluoroheterocycles through [3+2] cycloaddition. Reaction occurs with many different unsaturated compounds[1] such as trienes.[2]

(1) Fokin, A.V.; Kolomiets, A.F.; Vasil'ev, N.V. *Russ. Chem. Rev. (Engl. Transl.)* **1984**, *53*, 238. (2) Abdul-Ghani, M.; Tipping, A.E. *J. Fluorine Chem.* **1993**, *63*, 5.

40,461-6 Hexafluoroacetone azine, 99%
250mg $9.20; 1g $25.95

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Brittain, J.; Gareau, Y. *Tetrahedron Lett.* **1993**, *34*, 3363.

42,215-0 Triphenylsilanethiol
1g $9.00; 5g $30.00

Aldrichimica Acta

Volume 27, Number 1, 1994
A publication of the ALDRICH CHEMICAL COMPANY

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About Our Cover:

This vibrant summer scene entitled **A Bend in the Epte River, Near Giverny** (oil on canvas, 61 x 81 cm) was painted by Claude Monet in 1888. It is an astonishingly fresh and vivid portrayal of poplar trees, in full flower, along the edge of the Epte. The effect of strong sunlight through dense foliage is brilliantly rendered by a web of sharp diagonal brushstrokes animating the upper canvas with an almost endless variety of touch and color.

Giverny, where Monet lived from 1888 until his death in 1926, is a small village at the confluence of the Seine and Epte Rivers, 60 kilometers northwest of Paris. It was at his home in this village that Monet created his famous water garden which provided him with many motifs towards the end of his career.

The painting is in the William L. Elkins Collection of the Philadelphia Museum of Art.

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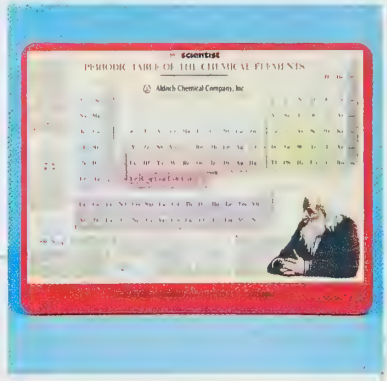
To provide researchers with up-to-date information on our new products, Sigma-Aldrich and MDL Information Systems, Inc. have entered into an agreement to include the most recent listings of chemical products available from Sigma, Fluka, Supelco, and Aldrich, including the expanded Sigma-Aldrich Rare Chemical Library, to customers of MDL's Available Chemicals Directory (ACD).

Sigma-Aldrich will provide MDL with information about their products in an electronic file to be included in the ACD. Thus, MDL customers who are ACD subscribers will have access to information about Sigma-Aldrich products critical to their research before this information appears in printed catalogs. Sigma-Aldrich currently lists over 90,000 chemical products, adding 7,500 in 1993.

The first ACD database with available chemical listings provided by Sigma-Aldrich will be released in 1994. Semi-annual updating will follow.

Lab Notes



Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. Z24,409-0) like that pictured above. It is Teflon®-coated, 8½ x 11 in., with a full-color periodic table on the front. We reserve the right to retain all entries for consideration for future publication.

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Dear Acta Reader:

The structural formula on page 101 of our previous issue (*Aldrichimica Acta* **1993**, 26(4)) representing integral generations (i.e. G = 0,1,2,...) of Starburst™ (PAMAM) dendrimers is incorrect. The formula works only for G = 0 (i.e, N = 1). A more accurate representation of the PAMAM dendrimers is indicated below.

The initiator core (I_c) is ethylenediamine, thus its multiplicity and molecular weight are N_c = 4 and M_c = 60.10, respectively. The branching multiplicity, N_b, is 2, and the repeat unit molecular weight, M_{RU}, equals 114.15.

Using these parameters and the mathematical formulas described on page 95 of the previous issue, one can calculate for a given generation, G, its molecular weight, number of repeat units, number of terminal groups and number of substituents on the periphery. Note that integral generations G = 0,1,2,... end in $-NH_2$ groups and half-integral generations G = 0.5, 1.5, 2.5,... end in $-N(CH_2CH_2CONa)_2$ groups.

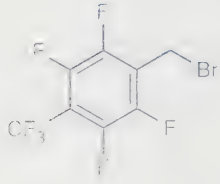
Please accept our apology for any confusion our error may have caused.

The Editorial Staff

"Please Bother Us."

by

Jai Nagarkatti, President



Professor Roger W. Giese of the Department of Pharmaceutical Sciences at Northeastern University suggested that we make TTBB, a new electrophoric derivatization reagent analogous to pentafluorobenzyl bromide (PFBB). Both TTBB and PFBB are used to enhance the detectability of substances such as DNA nucleobases, phenols, indole-amine metabolites, etc. by gas chromatography-electron-capture negative ion mass spectrometry (GC-ECNI-MS). TTBB can be used along with, or as a substitute for, PFBB to help control test interferences and confirm results.

Naturally we made this useful analytical tool.

Saha, M.; Saha, J.; Giese, R.W. *J. Chromatogr.* **1993**, *641*, 400 and references cited therein.

40,640-6 1-(Bromomethyl)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)-benzene, 98% (TTBB)
250mg $9.20; 1g $25.95

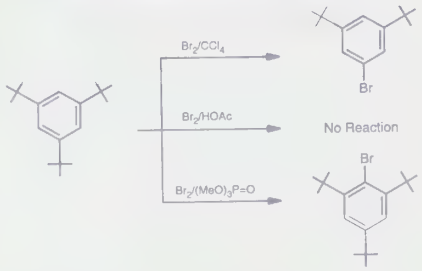
We also list:

10,105-2 α-Bromo-2,3,4,5,6-pentafluorotoluene, 99+% (PFBB)
1g $11.30; 5g $33.10; 25g $117.05

It was no bother at all, just simply a pleasure to be able to help.

NEW REAGENTS FROM OUR LABORATORIES

NEW HALOGENATION REAGENTS



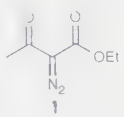
These easily handled solutions, packaged in Sure-Seal bottles, provide a complementary method for halogenation of substrates which are sensitive to the byproduct hydrogen halide.

Pearson, D.E.; Frazer, M.G.; Frazer, V.S.; Washburn, L.C. *Synthesis* **1976**, *9*, 621.

40,718-6 Bromine, 1.0*M* solution in trimethyl phosphate
100mL $25.00; 800mL $115.20

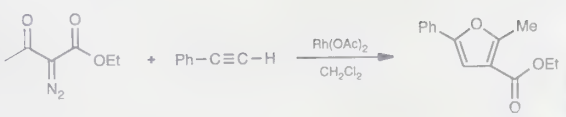
40,719-4 Chlorine, 1.0*M* solution in trimethyl phosphate
100mL $40.00; 800mL $231.50

ORGANIC DIAZO COMPOUND



1

Highly substituted furans can be synthesized via the rhodium(II) acetate catalyzed reaction of acetylenes with α-diazocarbonyl compounds such as (**1**). Yields are modest to good.

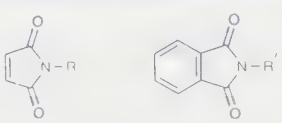


Davies, H.M.L. et al. *Org. Synth.* **1991**, *70*, 93.

50%

39,531-5 Ethyl diazoacetoacetate (1)
250mg $21.50; 1g $60.00

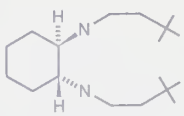
NEW MALEIMIDES AND PHTHALIMIDES



R = 	38,154-3	***N*-Cyclohexylmaleimide**, 97% **1g $16.20; 5g $54.00**
R = *t*-Butyl	38,642-1	***N*-*tert*-Butylmaleimide**, 97% **1g $15.15**
R′ = Me	40,799-2	***N*-Methylphthalimide**, 98% **5g $8.55; 25g $28.40**
R′ = Et	40,321-0	***N*-Ethylphthalimide**, 98% **1g $15.15; 5g $50.80**
R′ = Pr	41,761-0	***N*-Propylphthalimide**, 98% **1g $20.50; 5g $68.00**
R′ = Ph	41,627-4	***N*-Phenylphthalimide**, 98% **5g $11.50; 25g $46.50**

For a comprehensive listing of maleimides and phthalimides, please see the Aldrich Catalog/Handbook of Fine Chemicals.

NEW LIGANDS



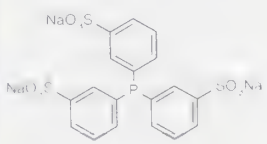
1 = 1R,2R
2 = 1S,2S

Asymmetric *cis*-dihydroxylation of olefins can be accomplished with stoichiometric quantities of osmium tetroxide in the presence of the chiral diamine ligands **1** and **2**. This methodology is reported to be complementary to conventional reagents in specific cases.

Hanessian, S. et al. *J. Org. Chem.* **1993**, *58*, 1991.

41,098-5 (1*R*,2*R*)-*N*,*N*′-Bis(3,3-dimethylbutyl)-1,2-cyclohexanediamine, 97% **(1)**
100mg $17.85; 500mg $59.40

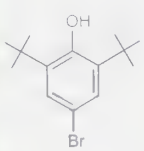
41,674-6 (1*S*,2*S*)-*N*,*N*′-Bis(3,3-dimethylbutyl)-1,2-cyclohexanediamine, 97% **(2)**
100mg $16.50; 500mg $55.00



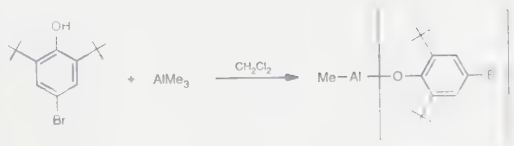
Development of biphasic catalysis has spurred interest in water-soluble organometallic complexes. Phosphinidynetris(benzenesulfonic acid) has been used to impart water solubility to an impressive number of metal complexes which in turn have demonstrated increased catalytic activity and selectivity relative to their water insoluble counterparts.

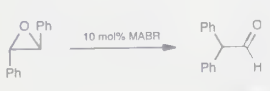
Herrmann, W.A.; Kohlpainter, C.W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524.

39,304-5 3,3′,3″-Phosphinidynetris(benzenesulfonic acid), trisodium salt, tech., 85%
500mg $33.50; 1g $56.00



Yamamoto has recently reported a general method for preparing a wide range of carbonyl compounds via the selective rearrangement of epoxides mediated by an organoaluminum complex (MABR). This complex can be conveniently prepared in situ from 4-bromo-2,6-di-*tert*-butylphenol and trimethylaluminum.





Maruoka, K. et al. *Tetrahedron Lett.* **1989**, *30*, 5607. Idem *Tetrahedron* **1991**, *47*, 6983.

39,437-8 4-Bromo-2,6-di-*tert*-butylphenol, 98% **(4)**
25g $18.00; 100g $50.00

26,856-9 Trimethylaluminum, 2.0*M* solution in hexanes
100mL $18.80; 800mL $91.40

Aldrichimica Acta

Volume 27, Number 2, 1994

Benzotriazole-Stabilized Carbanions: Generation, Reactivity, and Synthetic Utility

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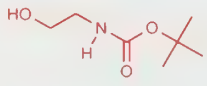
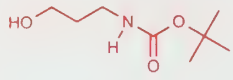


1



2

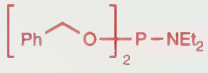
Recent applications for these amine protected, difunctional building blocks include the synthesis of phosphatidyl ethanolamines and the amino acid ornithine.[1,2]

(1) McGuigan, C. et al. *Synthesis* **1993**, 133. (2) Negro, A. et al. *Synth. Commun.* **1991**, *21*, 359.

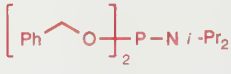
38,202-7 *N*-(*tert*-Butoxycarbonyl)-ethanolamine, 98% **(1)**

41,644-4 *tert*-Butyl *N*-(3-hydroxypropyl)carbamate, 99% **(2)**

Phosphitylation Reagents



1



2

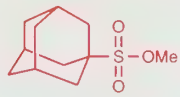
Efficient phosphitylating agents with applications in solid phase peptide synthesis,[1] oligonucleotide synthesis,[2] and the synthesis of glycosyl[3] and inositol phosphates.[4,5]

(1) De Bont, D. et al. *J. Org. Chem.* **1993**, *58*, 1309. (2) Thomson, W. et al. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1239. (3) Sim, M.M. et al. *J. Am. Chem. Soc.* **1993**, *115*, 2260. (4) Watanabe, Y. et al. *Tetrahedron Lett.* **1990**, *31*, 255. (5) Yu, K.-L. et al. *ibid.* **1988**, *29*, 797.

36,288-3 Dibenzyl diethylphosphoramidite (1)

41,643-6 Dibenzyl diisopropylphosphoramidite (2)

Adamantane Synthon



Allows facile generation of the adamantyl carbocation; serves as a useful precursor of 1-adamantyl derivatives.[1-3]

(1) Crossland, R.K. et al. *J. Org. Chem.* **1970**, *35*, 3195. (2) Bentley, T.W. et al. *ibid.* **1991**, *56*, 6238. (3) Takeuchi, K. et al. *ibid.* **1988**, *53*, 2852.

40,956-1 Methyl 1-adamantanesulfonate, 99%

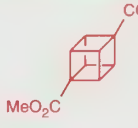
Reactive Sulfolene Precursor

The highly reactive oxirane moiety of this sulfolane makes it a useful precursor to a wide variety of sulfolene derivatives[1-4] and "dendralene-type" acyclic polyenes. The latter have increasing utility in diene-transmissive Diels-Alder reactions and in the synthesis of natural products.[5]

(1) Kursheva, L.I. et al. *Zh. Strukt. Khim.* **1992**, *33*, 145. (2) Mukhamedova, L.A. et al. *Khim. Geterotsikl. Soedin.* **1988**, *3*, 305. (3) Bezmenova, T.E. et al. *ibid.* **1983**, *12*, 1630. (4) McCormick, J.E. et al. *J. Chem. Soc., Perkin Trans 1* **1972**, 1335. (5) Cadogan, J.I.G. et al. *J. Chem. Soc., Chem. Commun.* **1991**, 114.

41,499-9 3,4-Epoxytetrahydrothiophene-1,1-dioxide, 97%

Functionalized Cubane

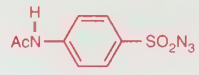


Irradiation in the presence of oxalyl chloride followed by treatment with methanol leads to tri-, tetra-, and pentacarbomethoxy cubanes.[1] Ortho-lithiation of the derived mono- and bisamides provides access to other functionalized cubanes with defined substitution patterns.[2] For example, the 1,4-bisamide affords 1,2,4,7-tetrasubstituted cubanes.[2]

(1) Bashir-Hashemi, A. *Angew. Chem., Intl. Ed. Engl.* **1993**, *32*, 612. (2) Eaton, P.E.; Xiong, Y.; Zhou, J.P. *J. Org. Chem.* **1992**, *57*, 4277.

42,124-3 Dimethyl 1,4-cubanedicarboxylate, 99%

New Diazo Transfer Agent

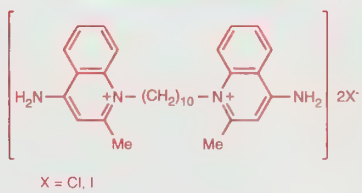


This crystalline diazo transfer agent is reported to be an effective replacement for tosyl azide. It is not impact sensitive.[1-3]

(1) Davies, H.M.L. et al. *Org. Synth.* **1992**, *70*, 93. (2) Davies, H.M.L. et al. *Synth. Commun.* **1987**, *17*, 1709. (3) Cox, G.G. et al. *Tetrahedron* **1993**, *49*, 5109.

40,476-4 4-Acetamidobenzenesulfonyl azide, 97%

Medicinal Agents



X = Cl, I

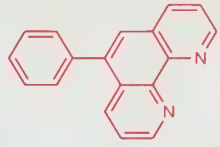
These aminoquinaldine derivatives have widespread applications in medicinal chemistry, including anticancer drugs,[1,2] antiinflammatories,[3] and antimicrobial agents.[4]

(1) Fuchtner, C. et al. *Gynecol. Oncol.* **1993**, *48*, 203. (2) Rotenberg, S.A. et al. *Cancer Res.* **1990**, *50*, 677. (3) Parkash, A.K. et al. *Int. J. Pharm.* **1993**, *92*, 151. (4) Fowler, S. et al. *ibid.* **1992**, *86*, 193.

39,992-2 Dequalinium chloride

39,993-0 Dequalinium iodide

New Phenanthroline



The above phenanthroline has been employed in the synthesis of ligands with photophysical properties[1,2] and in the structure-activity studies of heteroaromatic hydrocarbons.[3]

(1) Wallace, L. et al. *Inorg. Chem.* **1993**, *32*, 3836. (2) Alford, P.C. et al. *J. Chem. Soc., Perkin Trans. 2* **1985**, 705. (3) De Voogt, P. et al. *J. Planar Chromatogr. Mod. TLC* **1990**, *3*, 24.

41,802-1 5-Phenyl-1,10-phenanthroline, 97%

Aldrichimica Acta

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About Our Cover:

This masterpiece entitled **The Account-Keeper** (oil on canvas, 66.3 x 53.6 cm) was painted by Nicholaes Maes in 1656.

A pupil of Rembrandt, Maes' reputation stands on his genre paintings of domestic scenes with women and children. A similar interior is found in a painting in the Lichtenstein collection, although our painting features a map of the world and a sculpted bust. These lend a scholarly, even humanist, air to the subject, an old woman dozing over ledgers.

It is from Rembrandt that Maes takes the warm color scheme and soft light, which are very much different from Vermeer and his followers. If the appurtenances remind one of Vermeer (lighting from left, maps, etc.), the soft forms and broader paint handling deny it. Several other paintings have the subject matter of a dozing, elderly woman over books, notably works in the Worcester Art Museum and in the Musées Royaux des Beaux-Arts, Brussels.

The painting is in the collection of The Saint Louis Art Museum.

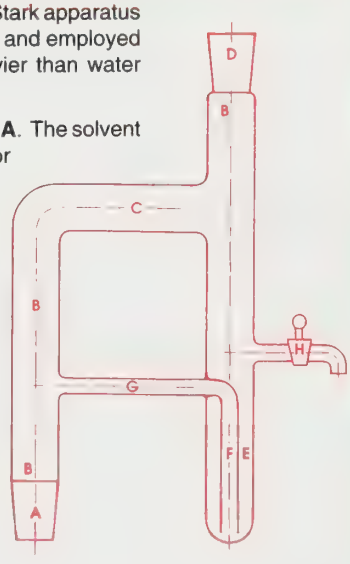
Lab Notes

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. Z24,409-0) like that pictured above. It is Teflon® coated, 8½ x 11 in., with a full-color periodic table on the front. We reserve the right to retain all entries for consideration for future publication.

Teflon is a registered trademark of E.I. du Pont de Nemours & Co., Inc.

An innovative, convenient, and compact Dean-Stark apparatus (picture enclosed) has been specially designed and employed for azeotropic distillations using solvents heavier than water (e.g., chloroform).

A distillation flask is attached to the apparatus at **A**. The solvent vapours travel via arms **B** and **C** to the condensor (fixed at the top of the apparatus at **D**), are condensed, and collect in the receiver **E**. The layers separate and the heavier liquid (chloroform), on filling the dip-tube **F**, overflows through the carrier tube **G** to the main distillation flask. The upper water layer is drained out intermittently on accumulation from the side arm **H**.

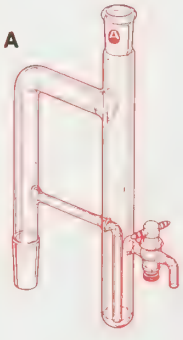


I feel this is a unique piece of equipment, simple in design, and is not available in any of the standard catalogues.

Thanking you
Yours faithfully,

Dr. A.V. Joshi
House No. 1, Sadanand Wadi
V.P. Road, Bombay - 400 004 INDIA

A

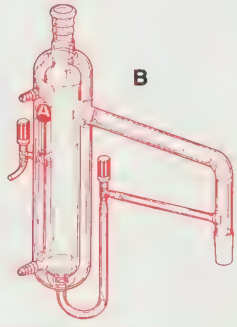


Aldrich now offers two Dean-Stark traps similar to the apparatus described by Dr. Joshi.

Dean-Stark apparatus

A. Designed specifically for azeotropic distillation using solvents heavier than water (e.g., chloroform). Solvent vapors condense and collect in the receiver, separate, and overflow through the carrier tube back to the main distillation flask. Has a 2mm-bore Teflon® stopcock and ⅎ 24/40 joints. 260mm overall height.
Z24,959-9

B

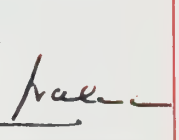


B. As above, with water cooling jacket and Teflon Rotaflo® stopcocks. 300mm overall height.
Z24,960-2

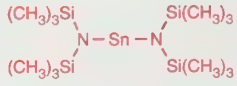
Teflon is a registered trademark of E.I. du Pont de Nemours & Co., Inc. Rotaflo is a registered trademark of Corning Glass Works.

"Please Bother Us."

by



Jai Nagarkatti, President



Dr. Eric Roskamp of Northwestern University recently suggested that we offer this interesting, thermally stable, diamagnetic[1] tin(II) amide. $Sn[N(TMS)_2]_2$ reacts with primary aldehydes to give *trans-N,N*-bis(TMS)enamines.[2] Addition of amines to $Sn[N(TMS)_2]_2$ generates in situ unsymmetrical tin(II) amides which, when treated with aldehydes/ketones,[2,3] carboxylic acids[4]/esters,[5,6] and β-amino esters,[7,8] affords *N,N*-dialkylenamines, amides, or β-lactams, respectively.

Naturally, we made this reagent.

(1) Harris, D.H.; Lappert, M.F. *J. Chem. Soc., Chem. Commun.* **1974**, 895. (2) Burnell-Curty, C.; Roskamp, E.J. *J. Org. Chem.* **1992**, *57*, 5063. (3) Idem *Synlett* **1993**, 131. (4) Idem *Tetrahedron Lett.* **1993**, *34*, 511. (5) Wang, W.-B.; Roskamp, E.J. *J. Org. Chem.* **1992**, *57*, 6101. (6) Wang, W.-B.; Restituyo, J.A.; Roskamp, E.J. *Tetrahedron Lett.* **1993**, *34*, 7217. (7) Wang, W.-B.; Roskamp, E.J. *J. Am. Chem. Soc.* **1993**, *115*, 9417. (8) Smith, L.A.; Wang, W.-B.; Burnell-Curty, C.; Roskamp, E.J. *Synlett* **1993**, 850.

40,961-8 Bis[bis(trimethylsilyl)-amino]tin(II)

It was no bother at all, just a pleasure to be able to help.

9-BBN

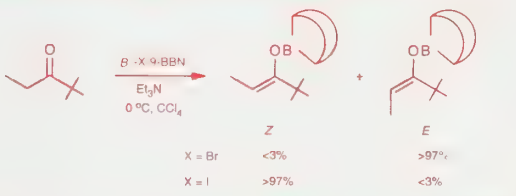
Over the last twenty years, 9-borabicyclo[3.3.1]nonane, better known as 9-BBN, has proven to be a useful regioselective hydroborating reagent for olefins.[1] Many researchers have continued to develop new transformations using this reagent as well as newer reagents derived from 9-BBN. Aldrich now lists eleven different reagents based on this structure. The following highlight some of the recent applications from this reagent family. For more information, call our Technical Service Department at 800-231-8327.

Catalysis

Organoboranes, such as 9-BBN, can participate in radical reactions. The addition of alkanethiols to alkenes is usually initiated by traditional radical sources such as peroxides. Catalytic amounts of 9-BBN will also catalyze the reaction leading to the formation of dialkyl sulfides.[2]

Enolate Formation

B-Bromo-9-BBN can be used, in the presence of triethylamine, to form enolates of ketones stereoselectively.[3] This control allows selective preparation of syn or anti products from an aldol condensation. By changing the leaving group from bromide to iodide, it is possible to completely change the stereoselectivity of the reaction.

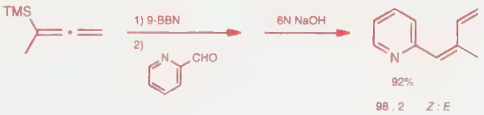


Polymer Applications

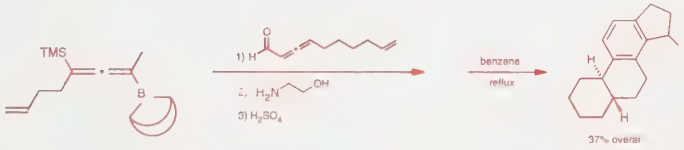
Because of the stability of borane compounds under metathesis polymerization conditions, telechelic polymers (those functionalized on both ends) can be easily prepared using 9-BBN containing monomers.[4] Once the polymer is formed, the end groups can be readily transformed into functional groups such as hydroxyl or halide.

Condensation Reactions

Nitrogen heterocycles containing a 1,3-butadiene unit are useful starting materials for a number of quinolines, indoles, and pyrroles which show biological activity.[5] These compounds are readily prepared by the condensation of substituted allylboranes with aldehydes followed by Peterson olefination.

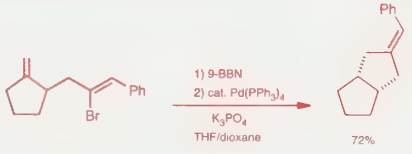


A similar condensation method has been used to produce acyclic polyolefins.[6] These in turn have been used to efficiently produce fused polycycles in a single step. The key intermediate is an allenylborane made from 9-BBN.



Intramolecular Coupling

Many important biological structures contain exocyclic olefins. The well-known Suzuki coupling reaction can be used for stereoselective intramolecular coupling to produce these useful structures.[7]



References: (1) Brown, H.C.; Knights, E.F.; Scouten, C.G. *J. Am. Chem. Soc.* **1974**, *96*, 7765. (2) Arase, A. et al. *J. Chem. Soc., Chem. Commun.* **1991**, 1444. (3) Brown, H.C. et al. *J. Org. Chem.* **1993**, *58*, 147. (4) Chung, T.C. et al. *Macromolecules* **1992**, *25*, 5137. (5) Wang, K.K.; Sattsangi, P.D. *Tetrahedron Lett.* **1992**, *33*, 5025. (6) Wang, K.K. et al. *J. Org. Chem.* **1993**, *58*, 1651. (7) Suzuki, A. et al. *Tetrahedron Lett.* **1992**, *33*, 2571.

Listings:

15,107-6 **9-BBN**, 0.5*M* solution in THF

25,663-3 *B*-**Bromo-9-BBN**, 1.0*M* solution in dichloromethane

NEW **39,664-8** *B*-*tert*-**Butyl-9-BBN**, 0.5*M* solution in THF

NEW **39,670-2** *B*-**Benzyl-9-BBN**, 0.5*M* solution in THF

17,871-3 **9-BBN dimer**, crystalline, 98%

19,385-2 **9-BBN**, 0.5*M* solution in hexanes

19,622-3 *B*-**Methoxy-9-BBN**, 1.0*M* soln in hexanes

25,313-8 **9-BBN triflate**, 0.5*M* solution in hexanes

25,883-0 **9-BBN-pyridine**, 0.5*M* soln in diethyl ether

34,423-0 **Lithium 9-BBN hydride**, 1.0*M* solution in THF

NEW **41,690-8** *B*-**Iodo-9-BBN**, 1.0*M* solution in hexanes

NEW **41,720-3** *R*-**Alpine-Borane®**, 97%, neat liquid

NEW **41,704-1** *S*-**Alpine-Borane®**, 97%, neat liquid

23,770-1 *S*-**Alpine-Borane®**, 0.5*M* solution in THF

23,273-4 *R*-**Alpine-Borane®**, 0.5*M* solution in THF

Aldrichimica Acta

Volume 27, Number 3, 1994 *(Last issue in 1994)*

The Synthetic Potential of the Intramolecular Meta-Photocycloaddition in Arene-Alkene Bichromophoric Systems Containing Oxygen in the Tether

The Trouble with Synthesis

chemists helping chemists in research & industry

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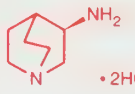
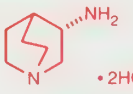
NEW PRODUCTS

CHIRAL PRODUCTS

Building Blocks



1



2

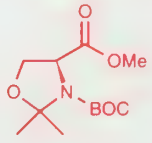
(*R*)-(+)-3-Aminoquinuclidine **1** and (*S*)-(-)-3-aminoquinuclidine **2** are important building blocks in the synthesis of several pharmaceuticals.[1-3]

(1) Langlois, M. et al. *Synth. Commun.* **1992**, *22*, 1895. (2) Peroutka, S.J. *Ann. Rev. Neurosci.* **1988**, *11*, 45. (3) Kilpatrick, G.J. et al. *Med. Res. Rev.* **1990**, *10*, 441.

41,571-5 (*R*)-(+)-3-Aminoquinuclidine dihydrochloride, 98%
250mg $10.75; 1g $30.00

41,572-3 (*S*)-(-)-3-Aminoquinuclidine dihydrochloride, 98%
250mg $10.75; 1g $30.00

Synthon

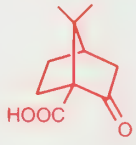


This serine derived precursor has been used to make azasugars, sphingolipids, and the amino sugar found in calicheamicin, a potent antitumor agent.[1-3]

(1) Dondoni, A. et al. *J. Chem. Soc., Chem. Commun.* **1991**, 1576. (2) Koskinen, A.M.P. et al. *Synlett* **1990**, 665. (3) Kahne, D. et al. *Tetrahedron Lett.* **1990**, *31*, 21.

41,043-8 Methyl (*S*)-3-(*tert*-butoxycarbonyl)-2,2-dimethyl-4-oxazolidinecarboxylate, 98%
1g $25.00; 5g $84.00

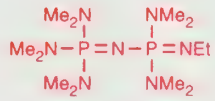
Auxiliary



Chiral auxiliary employed in the asymmetric synthesis of phosphorus analogs of amino acids and of α-substituted benzylamines.[1,2,3]

(1) Ferrari, M. et al. *Synth. Commun.* **1992**, *22*, 107. (2) Yaozhong, J. et al. *ibid.* **1990**, *20*, 15. (3) Jingen, D. et al. *Synthesis* **1991**, 963.

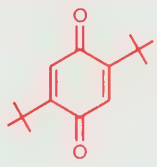
42,096-4 (1*S*)-(+)-Ketopinic acid, 99%
250mg $9.25; 1g $26.00



Extremely strong, neutral, nitrogen base—about 10^4 times more reactive than DBU in elimination reactions. For similar phosphazene bases see reference 1.

(1) Schwessinger, R. *Nachr. Chem. Tech. Lab.* **1990**, *38*, 1214.

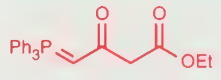
42,042-5 *N,N,N',N'*-Tetramethyl-*N''*-[tris(dimethylamino)phosphoranylidene]phosphoric triamide ethylimine, 98%
250mg $18.40; 1g $50.95



This benzoquinone is a versatile reagent, useful in medicinal chemistry,[1] mammalian and plant biochemistry,[2,3] and photochemistry.[4]

(1) Colovai, A.I. et al. *Carcinogenesis* **1993**, *14*, 1137. (2) Nakamura, H. et al. *J. Biochem.* (Tokyo) **1992**, *112*, 750. (3) Frid, E. et al. **1992**, *267*, 25908. (4) Hanaya, M. et al. *J. Organomet. Chem.* **1992**, *435*, 337.

41,964-8 2,5-Di-*tert*-butyl-1,4-benzoquinone, 99%
5g $16.50; 25g $55.00



This ylide can be coupled with glyoxals providing a one step route to 4-hydroxy cyclopentanones.[1] It has also been used to prepare 2*H*-pyran-2-ones from oxazolones.[2]

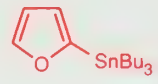
(1) Hatanaka, M. et al. *Tetrahedron Lett.* **1993**, *34*, 4837. (2) Gelmi, M.L.; Pocar, D. *Synthesis* **1992**, 453.

42,067-0 Ethyl 3-oxo-4-(triphenylphosphoranylidene)butyrate, 97%
5g $25.00; 25g $83.00

The corresponding salt is also available:

42,424-2 [3-(Ethoxycarbonyl)-2-oxopropyl]triphenylphosphonium chloride 10g $16.50; 50g $55.00

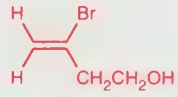
BUILDING BLOCKS



Valuable furan building block capable of Pd catalyzed coupling reactions.[1] Useful for the synthesis of 2-substituted furans[2] and heterocyclic natural products.[3] The compound has also been utilized as an umpoled carboxylate anion reagent[4] by following the coupling reaction with an oxidative cleavage of the furan ring.

(1) Bailey, T.R. *Tetrahedron Lett.* **1986**, *27*, 4407. (2) Liebeskind, L.S. et al. *J. Org. Chem.* **1993**, *58*, 3550. (3) Eicher, T. et al. *Synthesis* **1991**, 1173. Peters, D. et al. *J. Heterocycl. Chem.* **1991**, *28*, 1613. (4) Johnson, C.R. et al. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1.

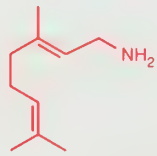
41,450-6 2-(Tributylstannyl)furan, 97% **5mL $9.00; 25mL $30.00**



The above vinyl bromide is a useful building block in the synthesis of α-methylene lactones,[1,2] tricyclic sesquiterpenes,[3] and a number of other cyclization[4] and alkylation reactions.[5]

(1) Xu, Y. et al. *Tetrahedron Lett.* **1986**, *27*, 3017. (2) Semmelhack, M.F. et al. *J. Org. Chem.* **1981**, *46*, 1723. (3) Magnus, P. et al. *ibid.* **1985**, *50*, 1621. (4) Shi, L. et al. *ibid.* **1983**, *48*, 3894. (5) Gesson, J. P. et al. *Bull. Soc. Chim. Fr.* **1992**, *129*, 227.

41,088-8 3-Bromo-3-buten-1-ol, 98%
1g $17.30; 10g $96.15



Terpene building block for a variety of biologically active and natural products.

Murahashi, S.-I. et al. *J. Org. Chem.* **1989**, *54*, 3292.

41,264-3 Geranylamine, 95%
1g $17.30; 5g $57.80

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About Our Cover:

This colorful river scene, *Jolly Flatboatmen in Port* (oil on canvas, 117.5 x 175.1cm), was painted by the American artist George Caleb Bingham in 1857 during a stay in Germany. When Bingham arrived in Europe for the first time in 1856, he brought with him the ambition of creating a history painting that would depict an important event in the development of the American West. He also brought along the memory of his well-received paintings of river life dating from the mid-1840s. These works, which had given him national visibility, suggested to him further potential.

After settling with his family in Düsseldorf, Germany, Bingham set to work on *Jolly Flatboatmen in Port*. With more than nineteen figures, it was to be his largest and most complex river painting. Moreover, unlike his earlier paintings of similar subjects, which were set in remote bends of unnamed rivers, this work was to depict a center of commerce, St. Louis. The scene shows a flatboat docked at the wharf, and boatmen amusing themselves with their own homespun entertainment, music, and dancing. The revelry is so lively that another flatboat has pulled alongside to observe it. Bingham borrowed figures from his earlier works for this painting; the tour-de-force dancing figure who holds a red handkerchief had appeared in his best-known river painting, *Jolly Flatboatmen*, 1846.

The painting is in the collection of The Saint Louis Art Museum.

Lab Notes

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. Z24,409-0) like that pictured above. It is Teflon® coated, 8½ x 11 in., with a full-color periodic table on the front. We reserve the right to retain all entries for consideration for future publication.

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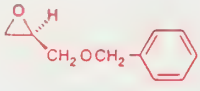
EDITOR'S NOTE

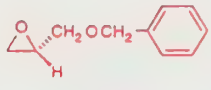
It has come to our attention that there is some confusion concerning the configuration and sign of rotation of our (*R*)-(-)- and (*S*)-(+)-benzyl glycidyl ethers (**36,352-9** and **36,353-7**, respectively).

These products were prepared according to a procedure reported by Bittman[1] and the configuration about the asymmetric center is specified in accordance with a rule change in the CIP convention for glycidol and derivatives.[2] Optical rotations for neat samples have the same sign of rotation as that reported for toluene or benzene solutions.

The correct structures for these products are indicated below. Note that the structures indicated in the 1992-1993 Aldrich Structure Index (**Z23,360-9**) are incorrect and have been revised since its publication.



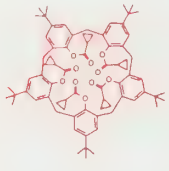
36,352-9 Benzyl (*R*)-(-)-glycidyl ether



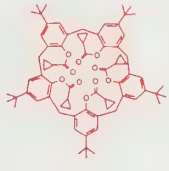
36,353-7 Benzyl (*S*)-(+)-glycidyl ether

We will be directly notifying customers of these products and apologize for any inconvenience. For more information, please contact our Technical Services Department at 800-231-9327.

(1) Byun, H.-S.; Bittman, R. *Tetrahedron Lett.* **1989**, *30*, 2751. (2) Hanson, R.M. *Chem. Rev.* **1991**, *91*, 437 and references cited therein.



Third International Conference on Calixarenes and Related Compounds



The Third International Conference on Calixarenes and Related Compounds will be held May 21-25, 1995 in Fort Worth, Texas, USA. The purpose of this preliminary annnouncement is to call your attention in the hope that you will put it on your calendar and plan to attend.

The conference site will be Texas Christian University (TCU) which has an excellent auditorium for a meeting of the anticipated size and where very reasonably-priced living and dining facilities are located on the campus within easy walking distance of the auditorium.

TCU is located in a residential neighborhood about 5 miles southwest of downtown Fort Worth. The city, with a population of about 450,000, is an interesting mixture of the old southwest of the cowboy and the new southwest of high culture.

The month of May is generally very nice, with blue skies during the day, long evenings before sunset, and pleasantly warm breezes. It should be a good time for the Conference on Calixarenes, and you might also find it an appropriate time to plan a vacation in the American Southwest.

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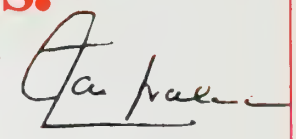
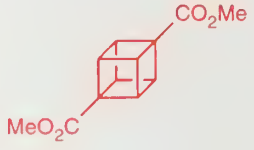


Jai Nagarkatti, President



Professor Philip E. Eaton at The University of Chicago kindly suggested that we offer cubane dimethylester which is a precursor to the parent hydrocarbon, and to a number of functionalized cubane derivatives as well.[1] For example, irradiation in the presence of oxalyl chloride followed by methanolysis leads to tri-, tetra-, and pentacarbomethoxycubanes.[2] Ortho-lithiation of the derived bisamide provides access to 1,2,4,7-tetra-substituted cubanes.[3] Curtius rearrangement leads cleanly to 1,4-diaminocubane which on oxidation with dimethyl dioxirane affords the bisnitro derivative.[4]

(1) Eaton, P.E. *Angew Chem., Int. Ed. Engl.* **1992**, *31*, 1421 and references cited therein. (2) Bashir-Hashemi, A. *ibid.* **1993**, *32*, 612. (3) Eaton, P.E.; Xiong, Y.; Zhou, J.P. *J. Org. Chem.* **1992**, *57*, 4277. (4) Eaton, P.E.; Wicks, E. *ibid.* **1988**, *53*, 5353.

42,124-3 Dimethyl 1,4-cubanedicarboxylate, 99%
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Naturally, we added this interesting cubane derivative to our listings. It was no bother at all, just a pleasure to be able to help.

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39,462-9 **REACTA-SIL (1) 10 x 1mL $40.00; 25mL $48.60**
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39,464-5 **REACTA-SIL T/P (4) 10 x 1mL $40.00; 25mL $48.60**

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39,483-1 *N,O*-**Bis(trimethylsilyl)acetamide**, derivatization grade **5mL $13.00; 10 x 1mL $45.00; 25mL $48.60**
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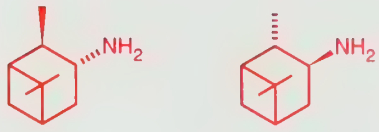
36,745-1 *N,O*-**Bis(trimethylsilyl)acetamide, with 5% TMCS 5mL $32.40; 10 x 1mL $55.00; 25mL $62.65**
39,465-3 **Bis(trimethylsilyl)trifluoroacetamide, with 10% TMCS 10 x 1mL $50.00; 25mL $64.80**
38,652-9 **Chlorotrimethylsilane**, redistilled, 99+% **100mL $23.80; 800mL $140.40**
D6,082-6 **Dichlorodimethylsilane**, 99% **5g $5.40; 100g $9.50; 500g $21.35**
39,487-4 **1-(Trimethylsilyl)imidazole**, derivatization grade **5mL $27.00; 10 x 1mL $45.00; 25mL $59.40**

References: (1) Harvey, D.J.; Horning, M.G. *J. Chromatogr.* **1973**, *76*, 51. *REACTA-SIL* (2) Sweeley, C.C. et al. *J. Amer. Chem. Soc.* **1963**, *85*, 2495. *REACTA-SIL* (3) Mamer, O.A.; Gibbs, B.F. *Clin. Chem.* **1973**, *19*, 1006. *REACTA-SIL T/P, MTBSTFA* (4) Sakauchi, N.; Horning, E.C. *Anal. Lett.* **1971**, *4*, 41. *REACTA-SIL T/P* (5) Horning, M.G. et al. *Anal. Biochem.* **1968**, 22, 248. *BSTFA* (6) Hasegawa, M.; Matsubara, I. *Anal. Biochem.* **1975**, *63*, 308. *TFAA, REACTA-SIL* (7) Brown, H.C.; Singaram, B.; Goralski, C.T. (unpublished results from the H.C. Brown and R.B. Wetherill Laboratories of Chemistry, Purdue University, West Lafayette, Indiana 47907). (8) Seyforth, D. et al. *J. Organomet. Chem.* **1972**, *44*, 279. (9) Aoyama, T.; Shiori, T. *Chem. Pharm. Bull.* **1981**, 29, 3249. (10)(a) Miwa, K. et al. *Synlett* **1994**, 107. (b) Idem *ibid.* **1994**, 109

New Chiral Derivatizing Agents

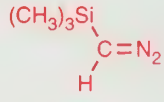


5 **6**

These chiral amines are used to determine the optical purity of carboxylic acids.[7] The method involves: activation of the carbonyl group with carbonyldiimidazole; treatment of the resulting acylimidazole with either (+)- or (-)-isopinocampheylamine to give a mixture of diastereomeric amides; and separation of the diasteromeric amides by capillary GC.

39,165-4 (1*R*,2*R*,3*R*,5*S*)-(-)-**Isopinocampheylamine**, 98% **(5) 1g $22.50; 5g $75.00**
39,166-2 (1*S*,2*S*,3*S*,5*R*)-(+)-**Isopinocampheylamine**, 98% **(6) 1g $20.80; 5g $69.15**
11,553-3 **1,1'-Carbonyldiimidazole 5g $12.15; 10g $21.75; 25g $43.90; 100g $131.75**

Safe Substitute for Diazomethane



(Trimethylsilyl)diazomethane, a thermally stable diazo compound,[8] is a safe substitute for diazomethane[9] that has been used for a variety of synthetic transformations. Aldrich offers this reagent as a convenient solution in hexanes. A recent application of this reagent includes a new synthesis of alkynes which is obtained by extension of the Colvin rearrangement of aryl alkyl ketones and aldehydes on reaction with lithium (trimethylsilyl)diazomethane.[10a] This procedure provides the corresponding homologous alkynes in high to moderate yields. A new synthesis of aldehydes from ketones, utilizing (trimethylsilyl)diazomethane in the presence of diisopropylamine, provides homologated enamines. Subsequent hydrolysis (treatment with silica gel) affords the corresponding aldehydes in good to moderate yields.[10b]

36,283-2 **(Trimethylsilyl)diazomethane**, 2.0*M* solution in hexanes **5mL $22.50; 25mL $75.10**

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Volume 28, Number 1, 1995

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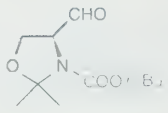
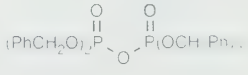


This popular serine derived building block was introduced by Professor Philip Garner of Case Western University.[1] It has been utilized extensively in natural product synthesis.[2-5]

(1) Garner, P.; Park, J.M. *J. Org. Chem.* **1987**, *52*, 2361. (2) McKillop, A. et al. *Synthesis* **1994**, 31. (3) Soai, K.; Takahashi, K. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1257. (4) Grieco, P.A.; Moher, E.D. *Tetrahedron Lett.* **1993**, *34*, 5567. (5) Guibourdenche, C. et al. *Tetrahedron: Asymmetry* **1993**, *4*, 2041

43,274-1 *tert*-**Butyl-(*S*)-4-formyl-2,2-dimethyl-3-oxazolidinecarboxylate**, 96% **250mg $30.00; 1g $83.00**

For Inositol Phosphorylation



Easily handled, relatively stable, crystalline phosphorylating agent[1] which has been employed in inositol phosphorylation.[2]

(1) Ozaki, S. et al. *J. Chem. Soc., Perkin Trans. 1* **1992**, 729. (2) Kozikowski, A.P. et al. *J. Org Chem.* **1994**, *59*, 2279.

41,863-3 **Tetrabenzyl pyrophosphate**, 98% **250mg $33.00; 1g $100.00**

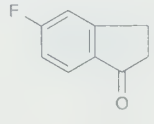
New Carbodiimide

Carbodiimide coupling agent which forms a dichloromethane soluble urea byproduct.[1] Has also been employed in the synthesis of peptides and *N*-Fmoc-amino acid anhydrides.[2]

(1) Izdebski, J. et al. *Pept. Proc., Eur. Pept. Symp., 18th* **1984**, 113. (2) Idem *Pol. J Chem.* **1994**, *68*, 403.

42,639-3 **1-*tert*-Butyl-3-ethylcarbodiimide**, 99% **1g $15.50; 5g $52.00**

For the Medicinal Chemist

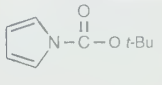


Antipsychotic and antiinflammatory agents have been prepared from this compound.[1,2]

(1) Fontenla, J.A. et al. *J. Med. Chem.* **1994**, *37*, 2564. (2) Gupta, R.C. et al. *Indian J. Chem., Sect. B* **1977**, *15B*, 641.

18,566-3 **5-Fluoro-1-indanone**, 99% **250mg $10.75; 1g $30.00**

BOC Pyrrole

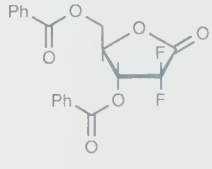


Readily undergoes cycloaddition reactions and has been used to prepare cephalosporin and cocaine analogs via Diels-Alder and 1,3-dipolar addition reactions, respectively.[1,2]

(1) Elliott, R.L. et al. *J. Org. Chem.* **1994**, *59*, 1606. (2) Davies, H.M.L. et al. *J. Med. Chem.* **1994**, *37*, 1262.

42,583-4 *tert*-**Butyl 1-pyrrolecarboxylate**, 98% **25mL $16.75; 100mL $46.75**

For Gem-citabine Synthesis

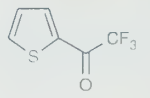


An important starting material in the preparation of 2',2'-difluoro-2'-deoxynucleosides (such as gem-citabine) which possess anticancer activity.

Chou, T.S. et al. *Synthesis* **1992**, 565.

42,256-8 **2-Deoxy-2,2-difluoro-D-*erythro*-pentonic acid γ-lactone 3,5-dibenzoate** **50mg $21.00; 250mg $70.00**

For Fungicide Synthesis

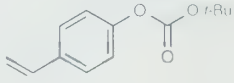


This trifluoromethyl ketone has been used to prepare fungicidal pyridine derivatives.

Sauter, F. et al. *Monatsh. Chem.* **1991**, *122*, 879

42,221-5 **2-(Trifluoroacetyl)thiophene**, 98% **1g $14.75; 5g $49.00**

New Monomer

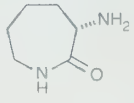


Monomer extensively utilized to prepare chemically amplified resists.[1,2]

(1) MacDonald, S.A. et al. *Chem. Mater.* **1991**, *3*, 435. (2) Idem *ibid.* **1993**, *5*, 348

39,907-8 *tert*-**Butyl 4-vinylphenyl carbonate**, 98% **5g $22.50; 25g $75.00**

Chiral Caprolactam

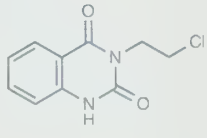


This seven membered lactam is a substructure found in a number of natural products, and is thus an important synthetic starting material. A recent example includes the preparation of capuramycin, a nucleoside antibiotic.

Knapp, S. et al. *J. Org. Chem.* **1994**, *59*, 281.

26,359-1 **L-α-Amino-ε-caprolactam**, 95% **5g $18.20; 25g $57.50**

Heterocyclic Building Block

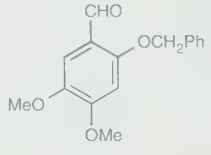


This compound has been used to prepare ketanserin analogs for serotonin receptor binding and antihypertensives.[1,2]

(1) Herndon, J.L. et al. *J. Med. Chem.* **1992**, *35*, 4903. (2) Boegesoe, K.P. et al. *ibid.* **1988**, *31*, 2247.

42,770-5 **3-(2-Chloroethyl)-2,4(1*H*,3*H*)-quinazolinedione**, 99% **1g $9.25; 5g $31.00**

Flavonoid Synthon

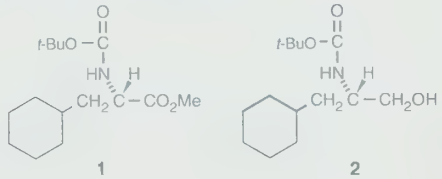


Used as a building block for the synthesis of oxygenated flavones.[1,2]

(1) Iinuma, M. et al. *Chem. Pharm. Bull.* **1986**, *34*, 2228. (2) Idem *ibid.* **1986**, *34*, 1656.

42,490-0 **2-Benzyloxy-4,5-dimethoxybenzaldehyde**, 98% **1g $23.00; 5g $77.00**

Peptide Isostere Precursors



1 2

These protected amino acid analogs are important starting materials for peptide isosteres related to the renin-angiotensin system.[1,2]

(1) Krysan, D.J. et al. *Org. Prep. Proced. Int.* **1993**, *25*, 437. (2) Iizuka, K. et al. *J. Med. Chem.* **1990**, *33*, 2707.

42,171-5 *N*-(*tert*-**Butoxycarbonyl)-3-cyclohexyl-L-alanine methyl ester**, 98% **(1)** **1g $11.50; 5g $38.00**

42,169-3 (*S*)-(-)-**2-(*tert*-Butoxycarbonylamino)-3-cyclohexyl-1-propanol**, 90% **(2)** **1g $13.50; 5g $45.30**

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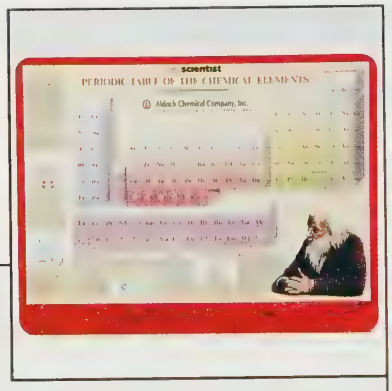

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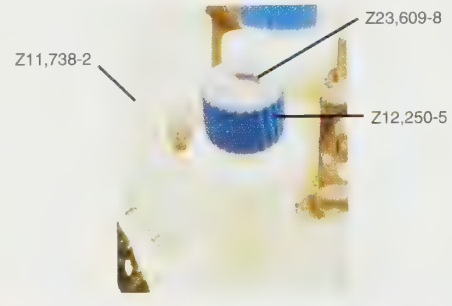

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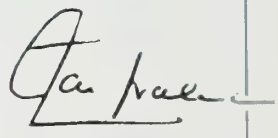


Jai Nagarkatti,
President

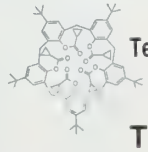
"Molecular Accordion" Synthesis

1 2

Poly-*N*-isopropylacrylamide and its derivatives have unique solution properties. For example, when this polymer is adsorbed on a liposome surface, it exhibits a reversible folding or a "molecular accordion" effect. The above two acrylamides, suggested by Dr. Francoise Winnik are the needed monomers and both are now available.

Rignsdorf, H.; Vezemer, J.; Winnik, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 315.

41,532-4 *N*-Isopropylacrylamide, 97% **(1) 10g $13.00; 50g $43.00**
42,354-8 *N*-Isopropylmethacrylamide, 97% **(2) 5g $14.25; 25g $47.50**



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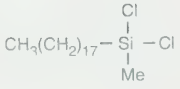
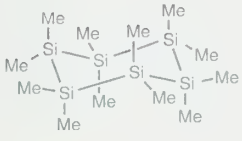


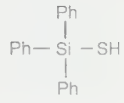
Lipophilic surface modification agent.

43,748-4 Dichloromethyloctadecylsilane, 99% **10g $25.00; 25g $53.00**



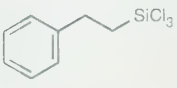
Precursor to β-SiC fibers.[1,2,3]
Generates Me_2Si: upon photolysis.[4]

43,749-2 Dodecamethylcyclohexasilane, 97% **1g $30.00; 5g $103.00**



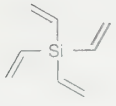
Solid H_2S equivalent.

42,215-0 Triphenylsilanethiol, 98% **1g $9.00; 5g $30.00**



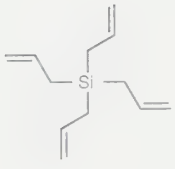
Surface modification agent.

42,003-4 Phenethyltrichlorosilane, 97% **1g $9.50; 10g $53.00**



Useful hydrosilylation substrate.[5,6,7]

31,825-6 Tetravinylsilane, 97% **5g $28.70; 25g $95.60**



Building block to dendrimers.[5,8]

42,506-0 Tetraallylsilane, 97% **1g $13.00; 5g $43.00**

References: (1) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M. *J. Mater. Sci.* **1980**, *15*, 720. (2) Yajima, S.; Hayashi, J.; Omori, M. *Chem. Lett.* **1975**, 931. (3) Yajima, S.; Okamura, K.; Hayashi, J.; Omori, M. *J. Am. Chem. Soc.* **1976**, *59*, 324. (4) Tzeng, D.; Weber, W. *J. Org. Chem.* **1981**, *46*, 693. (5) Seyferth, D.; Son, D.; Rheingold, A.; Ostrander, R. *Organometallics* **1994**, *13*, 2682. (6) Chang, P.; Hughes, T.; Zhang, Y.; Webster, G.; Poczynok, D.; Buese, M. *Polym. Chem.* **1993**, *31*, 891. (7) Zhou, L.; Roovers, J. *Macromolecules* **1993**, *26*, 963. (8) Cuadrado, I.; Morán, M.; Losada, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2575.

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*Dichloromethylphenylsilane
*Dichlorodiphenylsilane
*Chlorotrimethylsilane
*Silicon(IV) chloride
Chloropropyltrichlorosilane
Chloro(chloromethyl)dimethylsilane
Ethyltrimethoxysilane
Trichlorosilane
3-Aminopropyltriethoxysilane
N-[3-(Trimethoxysilyl)propyl]ethylenediamine
3-(trimethoxysilyl)propyl methacrylate
Glycidoxypropyltrimethoxysilane
Methyltrimethoxysilane
Chloropropyltrimethoxysilane
Hexamethyldisilazane
Phenyltrimethoxysilane
Cyclohexyldimethoxymethylsilane
Dimethoxydimethylsilane
Trimethoxypropylsilane
Isobutyltrimethoxysilane
3-(Trihydroxysilyl)propyl methylphosphonate, monosodium salt, 42% in water
[3-(Trihydroxysilyl)propyl]octadecyldimethylammonium chloride, 42 wt. % in CH_3OH
[3-(Trimethoxysilyl)propyl]octadecyldimethylammonium chloride, 72 wt. % in CH_3OH
n-Octyltriethoxysilane
Chloropropyltriethoxysilane
Isobutyltriethoxysilane
Vinyltrimethoxysilane

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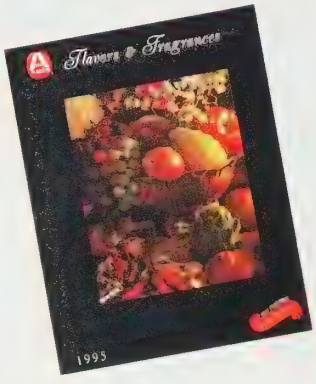

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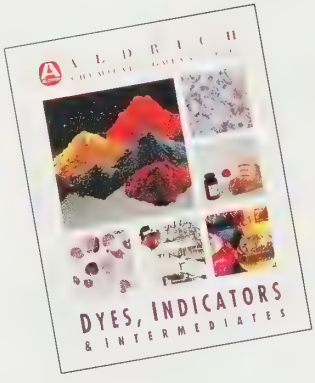

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Aldrichimica Acta

Volume 28, Number 2, 1995

Triethylamine Tris(hydrogen fluoride): Applications in Synthesis

Spontaneous Polymerizations Can Occur During Cycloaddition Reactions of Olefins and Dienes

Polyfluorinated Alkenes, Alkynes, and Allenes

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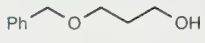
Monoprotected Diols

1



2

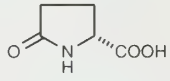
Examples of the utility of these monobenzylated diols include the syntheses of ionomycin analogs,[1] medium-membered ring ketone systems,[2] asymmetric synthesis of D- and L-2-deoxy-4-thioriboses,[3] and optically active polyols.[4]

(1) Hu, T.Q.; Weiler, L. *Can. J. Chem.* **1994**, *72*, 1500. (2) Ohtsuka, Y. et al. *Chem. Pharm. Bull.* **1992**, *40*, 617. (3) Uenishi, J. et al. *Tetrahedron: Asymmetry* **1994**, *5*, 101. (4) Bonini, C. et al. *ibid.* **1993**, *4*, 793.

42,746-2 5-Benzyloxy-1-pentanol, 97% **(1)**
5mL $35.00; 25mL $117.00

38,203-5 3-Benzyloxy-1-propanol, 97% **(2)**
5mL $23.00; 25mL $76.70

Pyroglutamic Acid

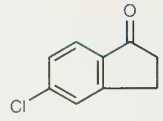


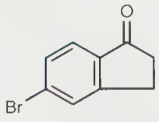
Valuable chiral material which has recently been used to prepare renin inhibitors.

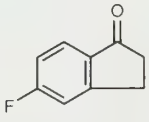
Williams, P.D. et al. *J. Med. Chem.* **1991**, *34*, 887.

42,261-4 (*R*)-(+)-2-Pyrrolidone-5-carboxylic acid, 95%
1g $8.45; 10g $46.55

Halo Indanones







The above 5-halo indanones are precursors to a variety of medicinal compounds.[1-4]

(1) Giardina, G. et al. *J. Med. Chem.* **1994**, *37*, 3482. (2) Dawson, M.I. et al. *ibid.* **1989**, *32*, 1504. (3) Fontenla, J.A. et al. *ibid.* **1994**, *37*, 2564. (4) Howbert, J.J.; Crowell, T.A. *Synth. Commun.* **1990**, *20*, 3193.

43,307-1 5-Chloro-1-indanone, 99%
1g $24.00; 5g $80.00

43,309-8 5-Bromo-1-indanone, 98% **1g $19.00**

18,566-3 5-Fluoro-1-indanone, 99%
250mg $10.75; 1g $30.00

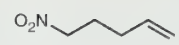
Building Block

This bromo alkyne has been used to prepare angiotensin-converting enzyme inhibitors[1] and an unusual amino acid residue found in cyclosporine.[2]

(1) Wong, P.L.; Moeller, K.D. *J. Am. Chem. Soc.* **1993**, *115*, 11434. (2) Savignac, M. et al. *Tetrahedron: Asymmetry* **1994**, *5*, 717.

42,729-2 1-Bromo-2-butyne, 99% **1g $13.50; 5g $44.00**

Agrochemical Synthesis

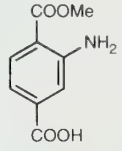


This reagent is used to synthesize allylrethrone,[1] an important intermediate for the preparation of allethrolone[2] and various pyrethrins.[3]

(1) Ballini, R. *Synthesis* **1993**, 687. (2) Le Mahieu, R.A. et al. *J. Org. Chem.* **1970**, *35*, 1687. (3) Piers, E. et al. *Can. J. Chem.* **1982**, *60*, 1256.

42,459-5 5-Nitro-1-pentene, 98%
250mg $18.75; 1g $52.00

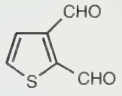
Pigment Synthesis



Trifunctional benzenoid that has been used in pigment synthesis and in other applications.

39,367-3 1-Methyl 2-aminoterephthalate, 98%
5g $12.00; 25g $40.00

Organic Metal Synthon

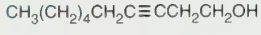


Recently used in the preparation of novel thiophene-fused TCNQ- and DCNQI-type acceptors.

De La Cruz, P. et al. *J. Org. Chem.* **1992**, *57*, 6192.

42,987-2 2,3-Thiophenedicarboxaldehyde, 97%
250mg $9.00; 1g $25.00

New Alkynol

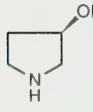


Alcohol that has been used in the synthesis of pheromones[1,2] and other natural products.[3]

(1) Preswitch, G.D. et al. *J. Chem. Ecol.* **1990**, *16*, 1761. (2) Zhang, X. et al. *ibid.* **1986**, *12*, 1263. (3) Schultz, T.W. et al. *Bull. Environ. Contam. Toxicol.* **1994**, *53*, 179.

42,275-4 3-Decyn-1-ol, 97% **1g $9.00; 5g $30.00**

Chiral Pyrrolidinols



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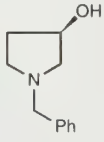

2

Parent (*R*)-3-pyrrolidinol and its *N*-benzylated derivative have been employed in the synthesis of a variety of compounds of medicinal interest.

Naylor, A. et al. *J. Med. Chem.* **1994**, *37*, 2138. Rhee, J. et al. *Korean J. Med. Chem.* **1993**, *3*, 72. Fedij, V. et al. *Tetrahedron: Asymmetry* **1994**, *5*, 1131.

43,072-2 (*R*)-(-)-3-Pyrrolidinol hydrochloride, 98%
1g $14.75; 10g $82.00

38,298-1 (*R*)-(+)-3-Pyrrolidinol, 98% **(1)**
1g $23.30; 5g $78.10

36,693-5 (*R*)-(+)-1-Benzyl-3-pyrrolidinol, 99% **(2)**
1g $26.00; 5g $87.00

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About our Cover:

The painting that graces our cover is *Flowers in a Chantilly Vase* by Louis Tessier (ca. 1760, oil on canvas, 65.1 x 54.7 cm). Tessier was a member of a family of craftsmen and artists working for the Goeblins, and his chief fame rests on the flower designs he produced for tapestries and furniture upholstery. Best known are Tessier's designs for the sixth set of enframements for Charles-Antoine Coypel's *Don Quixote* series of tapestries. He also fashioned the ornament for Boucher's *Loves of the Gods* series. In addition, he produced paintings and drawings of flowers and still lifes.

Flowers in a Chantilly Vase displays a porcelain container from the royal Chantilly porcelain factory. The vase has a delightful design, apparently influenced by Japanese prototypes, and is filled with a flower arrangement that unrealistically, but delightfully, spreads to fill the rectangular space with a riot of color and form. It bears witness to the high competence of the professional specialists in flower and still-life painting in the age of Louis XV.

The painting is in the collection of The Saint Louis Art Museum.

Manuscript Submission Information
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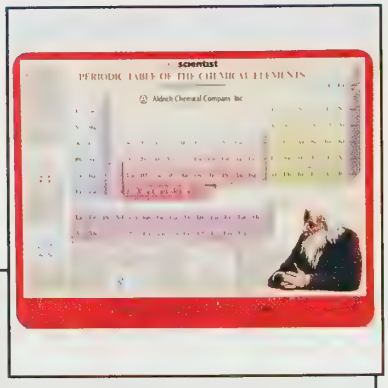
Lab Notes



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Gary L. Cramer, Water Research Analyst
Water Quality Assurance Laboratory
Department of Public Utilities Water Division
910 Dublin Road
Columbus, Ohio 43215-9052

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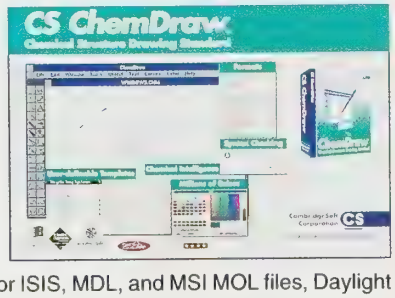

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"Please Bother Us."

by Jai Nagarkatti

Jai Nagarkatti, President

$CF_3SO_3{}^{13}CH_3$

Dr. Shafiq of the University of Rochester (currently at the University of Florida) suggested that we make methyl-^{13}C triflate, the ^{13}C-analog of methyl triflate (Cat. No. **16,428-3**). Methyl triflate is known to be one of the most powerful methylating agents, readily methylating carbon, oxygen, nitrogen, and sulfur centers.[1-4]

(1) Bates, R.B.; Taylor, S.R. *J. Org. Chem.* **1993**, *58*, 4469. (2) Stang, P.J.; White, M.R. *Aldrichimica Acta* **1983**, *16*, 15. (3) Galezowski, W.; Lewis, E.S. *J. Phys. Org. Chem.* **1994**, *7*, 90. (4) Johnson, T.J.; Arif, A.M.; Gladysz, J.A. *Organometallics* **1994**, *13*, 3182.

41,684-3 Methyl-^{13}C trifluoromethanesulfonate, 98 atom % ^{13}C
1g $70.00; 5g $233.50

$CF_3SO_3CD_3$

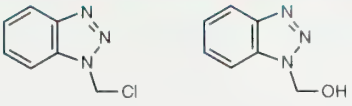
We have also added the corresponding deuterium analog.

41,685-1 Methyl-d_3 trifluoromethanesulfonate, 99 atom % D
1g $13.50; 5g $46.50

It was no bother at all, just simply a pleasure to be able to help.

Benzotriazole Chemistry

Professor Katritzky's group at the University of Florida-Gainesville has been developing important benzotriazole-based synthons with applications in a variety of chemical transformations. Many of these products are now available from Aldrich. Selected examples and applications follow. Look for more of these compounds in future *Aldrichimica Acta* issues.



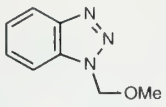
Important building blocks for a variety of benzotriazolylmethyl compounds such as fluoro-,[1] amino-,[2] and thio-[3] derivatives.

(1) Katritzky, A.R.; Szajda, M.; Lam, J.N. *Pol. J. Chem.* **1993**, *67*, 1243. (2) Katritzky, A.R.; Chang, H.-X.; Wu, J. *Synthesis* **1994**, 907. (3) Katritzky, A.R.; Ghiviriga, I.; Cundy, D.J. *Heterocycles* **1994**, *38*, 1041.

44,005-1 1-(Chloromethyl)-1*H*-benzotriazole
1g $9.00; 10g $50.00

41,023-3 1*H*-Benzotriazole-1-methanol, 98%
10g $14.60; 50g $48.60

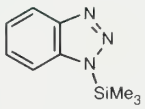
A precursor for the preparation of methyl esters and a convenient methylal anion synthon for the synthesis of α-functionalized dimethyl acetals.



(1) Katritzky, A.R.; Zhao, X.; Shcherbakova, I.V. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3295. (2) Katritzky, A.R.; Yang, Z.; Cundy, D.J. *Synth. Commun.* **1993**, *23*, 3061.

43,802-2 1-(Methoxymethyl)-1*H*-benzotriazole, 99%
250mg $9.75; 1g $27.00

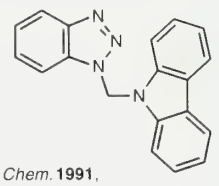
A convenient mediator in additions of Grignard reagents to imines for the preparation of secondary amines.



(1) Katritzky, A.R.; Hong, Q.; Yang, Z. *J. Org. Chem.* **1994**, *59*, 7947. (2) Idem *ibid.* **1995**, in press.

42,509-5 1-(Trimethylsilyl)-1*H*-benzotriazole, 98%
1g $12.00; 5g $40.00

A useful synthon for preparing α-functionalized aldehydes and formylsilanes. Alkylated derivatives have been used as acyl synthons for the synthesis of ketones and β-aminoketones.

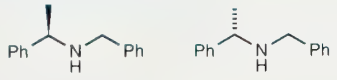


(1) Katritzky, A.R.; Yang, Z.; Lam, J.N. *J. Org. Chem.* **1991**, *56*, 2143. (2) Idem *ibid.* **1991**, *56*, 6917. (3) Idem *ibid.* **1993**, *58*, 1970. (4) Katritzky, A.R.; Yang, Z.; Hong, Q. *ibid.* **1994**, *59*, 5097.

43,803-0 9-(1*H*-Benzotriazol-1-ylmethyl)-9*H*-carbazole, 96%
250mg $8.50; 1g $24.00

More NEW Products

Chiral Ammonia Equivalents



1 **2**

Lithium and other metal amides derived from these two enantiomers serve as chiral bases in asymmetric synthesis.[1] Davies and co-workers have employed the lithium amide derived from the *R* isomer in highly diastereoselective Michael additions with α,β-unsaturated esters ultimately leading to homochiral β-amino acids.[2] These same researchers recently reported the first asymmetric Michael addition of the corresponding magnesium amide.[3]

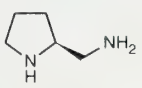
(1) Bunn, B.J. et al. *J. Chem. Soc., Perkin Trans. 1* **1993**, 3113. (2) Please see references 1-5 from reference 3 below. (3) Bunnage, M.E. et al. *Tetrahedron: Asymmetry* **1994**, *5*, 35.

42,747-0 (*S*)-(-)-*N*-Benzyl-α-methylbenzylamine, 99% **(1)** **10mL $25.50; 50mL $85.00**

43,173-7 (*R*)-(+)-*N*-Benzyl-α-methylbenzylamine, 98% **(2)** **10mL $25.50; 50mL $85.00**

Chiral Synthon

This proline derived precursor has found widespread use in the synthesis of numerous chiral compounds with antitumor activity.

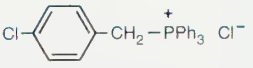


Morikawa, K. et al. *J. Pharm. Sci.* **1991**, *80*, 837.

42,288-6 (*S*)-(+)-2-(Aminomethyl)pyrrolidine, 97%
100mg $18.00; 500mg $60.00

Wittig Reagent

This reagent is used in the synthesis of chemiluminescent styrylstilbene and distyrylanthracene derivatives.[1] It is a building block in the preparation of *trans*-2-(2-*p*-chlorophenyl-*trans*-ethenyl)cyclopropane carboxylic acid, an aromatic analog of abscisic acid.[2]

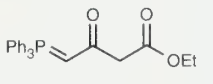


(1) Nakatsuji, S. et al. *J. Chem. Soc., Perkin Trans. 2* **1991**, 861. (2) Ladyman, J.A.R. et al. *Phytochemistry* **1988**, *27*, 3751.

42,458-7 (4-Chlorobenzyl)triphenylphosphonium chloride, 98% **5g $14.00; 25g $56.00**

New Ylide

This ylide can be coupled with glyoxals to provide a one-step route to 4-hydroxy cyclopentenones.[1] It has also been used to prepare 2*H*-pyran-2-ones from oxazolones.[2]



(1) Hatanaka, M. et al. *Tetrahedron Lett.* **1993**, *34*, 4837. (2) Gelmi, M.L.; Pocar, D. *Synthesis* **1992**, 453.

42,067-0 Ethyl 3-oxo-4-(triphenylphosphoranylidene)-butyrate **5g $25.00; 25g $83.00**

The corresponding salt is also available.

42,424-2 [3-(Ethoxycarbonyl)-2-oxopropyl]triphenylphosphonium chloride
10g $16.50; 50g $55.00

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Aldrichimica Acta

Volume 28, Number 3, 1995

Organo Iodine(III) and Thallium(III) Reagents in Organic Synthesis: Useful Methodologies Based on Oxidative Rearrangements

Rare Earth Triflates in Organic Synthesis

The Intermediacy of Transition-Metal Silicon-Bonded Complexes: Recent Developments

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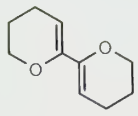
New Products

For Diol Protection

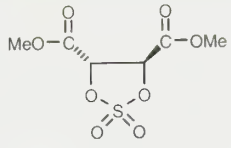


Ley and co-workers have demonstrated the utility of dispiroketal protecting groups for the protection of 1,2-diols in the preparation of a configurationally stable glyceraldehyde derivative,[1] in carbohydrate chemistry,[2] and in highly diastereoselective trapping of enolates of lactates and glycolates.[3]

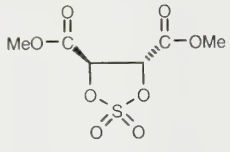
(1) Ley, S.V. et al. *Synthesis* **1992**, 52. (2) Downham, R. et al. *Tetrahedron Lett.* **1994**, *35*, 769. (3) Boons, G.-J. et al. *Tetrahedron* **1994**, *50*, 7157.

34,973-9 6,6´-Bi(3,4-dihydro-2*H*-pyran), 98%
250mg $15.50; 1g $43.00

Tartrate-Derived Cyclic Sulfates



1



2

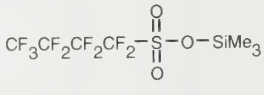
Gao and Sharpless reported that these tartrate-derived cyclic sulfates react like epoxides.[1] Ring opening with azide leads to 1,2-amino alcohols[1] and to chiral aziridines.[2]

(1) Gao, Y.; Sharpless, K.B. *J. Am. Chem. Soc.* **1988**, *110*, 7538. (2) Shustov, G.V. et al. *ibid* **1993**, *115*, 10267

44,102-3 Dimethyl (4*S*,5*S*)-1,3,2-dioxathiolane-4,5-dicarboxylate 2,2-dioxide (dimethyl D-tartrate cyclic sulfate), 97%
(1) 1g $27.25; 5g $95.40

44,101-5 Dimethyl (4*R*,5*R*)-1,3,2-dioxathiolane-4,5-dicarboxylate 2,2-dioxide (dimethyl L-tartrate cyclic sulfate), 97%
(2) 1g $27.25; 5g $95.40

TMS Nonaflate

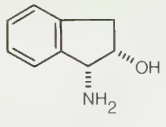


A powerful silylating agent and Lewis acid catalyst introduced by Vorbruggen with reactivity that rivals TMS triflate.

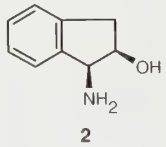
Vorbrüggen, H.; Krolikiewicz, K. *Synthesis* **1979**, 34

43,696-8 Trimethylsilyl nonafluoro-1-butanesulfonate, 98%
1g $7.75; 10g $30.00

Chiral Amino Indanols



1



2

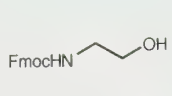
Both enantiomers of *cis*-1-amino-2-indanol have been used to synthesize HIV-1 protease inhibitors.[1] Oxazolidinones of **1** and **2** undergo selective aldol reactions with aldehydes.[2]

(1) Thompson, W.J. et al. *Tetrahedron Lett.* **1992**, *33*, 2957. Lyle, T.A. et al. *J. Med. Chem.* **1991**, *34*, 1228. (2) Ghosh, A.K. et al. *J. Chem. Soc., Chem. Commun.* **1992**, 1673.

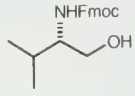
44,084-1 (1*R*,2*S*)-(+)-*cis*-1-Amino-2-indanol, 99% **(1)**
1g $18.00; 5g $60.00

44,083-3 (1*S*,2*R*)-(-)-*cis*-1-Amino-2-indanol, 99% **(2)**
1g $18.00; 5g $60.00

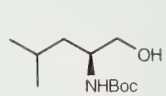
Boc/Fmoc Amino Alcohols



1



2



3

New additions to our extensive list of Cbz, Boc, and Fmoc *N*-protected amino alcohols. Call our Technical Services Department at 800-231-8327 to request a complete list of chiral, *N*-protected amino alcohols that are currently available.

Caputo, R. et al. *Tetrahedron Lett.* **1995**, *36*, 167. O'Brien, P.M. et al. *J. Med. Chem.* **1994**, *37*, 1810.

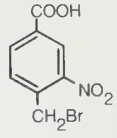
44,518-5 *N*-(9-Fluorenylmethoxycarbonyl)ethanolamine (1)
1g $18.00; 5g $60.00

44,567-3 *N*-(9-Fluorenylmethoxycarbonyl)-L-valinol (2)
1g $32.00; 5g $107.00

44,119-8 (*S*)-(-)-*N*-(*tert*-Butoxycarbonyl)-leucinol, 98% **(3)**
1g $21.00; 5g $70.00

44,632-7 (*S*)-1-(*tert*-Butoxycarbonyl)-2-pyrrolidinemethanol
1g $25.50; 5g $85.00

For Peptide Chemistry

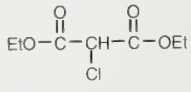


Precursor of the 4-bromomethyl-Nbb resin employed in solid-phase peptide synthesis; synthesized peptides are released from the resin via photolysis.

Nicolás, E. et al. *Tetrahedron Lett.* **1992**, *33*, 2183. Albericio, F. et al. *Tetrahedron* **1987**, *43*, 5961.

42,356-4 4-(Bromomethyl)-3-nitrobenzoic acid, 98%
1g $11.00; 5g $37.00

Diethyl Chloromalonate

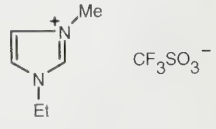


This electrophilic malonate reacts with sulfur[1] and oxygen[2] nucleophiles to produce α-thio- and α-alkoxymalonates, respectively.

(1) Atkins, E.F. et al. *Tetrahedron* **1994**, *50*, 7253. (2) Johnson, R.E.; Bacon, E.R. *Tetrahedron Lett.* **1994**, *35*, 9327.

43,778-6 Diethyl chloromalonate, 95% **5mL $19.65; 25mL $65.65**

Promising Electrolyte

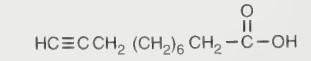


Room temperature molten salt that is a promising electrolyte.

(1) Cooper, E.I.; O'Sullivan, E.J.M. *Proc. Electrochem. Soc.* **1992**, *16*, 386. (2) Carlin, R.T. et al. *J. Electrochem. Soc.* **1994**, *141*, L73.

43,694-1 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate, 97% **1mL $43.10; 5mL $164.40**

Useful Synthon



Synthon[1-3] that has been employed in the preparation of two new phospholipid fluorescent probes.[1]

(1) Starck, J.-P. et al. *Tetrahedron* **1995**, *51*, 2629. (2) Singh, A. et al. *Biotechnol. Bioact. Polym.*; Gabelein, C.G.; Carraher, C.E., Jr., Eds.; Proc. Am. Chem. Soc. Symp., 1992; Plenum: New York, 1994; p 135. (3) Kulkarni, B.R. et al. *J. Nat. Prod.* **1994**, *57*, 537.

40,654-6 10-Undecynoic acid, 95% **1g $12.00; 5g $40.00**

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Volume 28, Number 3, 1995
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About our Cover:

Our cover displays a scenic masterpiece entitled *Landscape with Waterfall* (ca. 1665, oil on canvas, 69.4 x 56 cm) by Jacob van Ruisdael (1628/9-1682). Today, as in Goethe's time, Ruisdael is considered the undisputed master of Dutch landscape during its most heroic phase (1650-75). His subjects include scenery which he had never viewed firsthand. In the 1660s he painted a number of imaginary landscapes, all distinctly northern in character, along with waterfalls, all strongly inspired by the Scandinavian work of Allaert van Everdingen (1621-1675).

The upright format, low vantage point, expansive middleground, hills, and towering skies are very much Ruisdael's elements. However, Ruisdael's paintings have a greater power than the sum of these parts; they convey a vision that is at once romantic and grand, dark and melancholy. Like the example on our cover, many are twilight scenes, with weak and low light, transparent and grey shadow—a darkling world with transient and insignificant figures. As much as earlier Vanitas still-lifes, Ruisdael's painting bespeaks the impermanence of a passing world and the haunting grandeur of Nature.

The painting is in the collection of The Saint Louis Art Museum.

Lab Notes

In our lab we do a lot of ion chromatography. We use translucent polyethylene or propylene bottles for eluent and regenerant solutions. Determining the liquid level at a glance was always difficult. We tried many things, but a simple solution that works well is to put a handful of brightly colored Aldrich NMR tube caps in the polybottles. The caps show up really well through the bottle. They float. They are not attacked by most solutions. And they are both readily available and cheap!

J.G. Townsend, Sr. Chemist
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Research and Development
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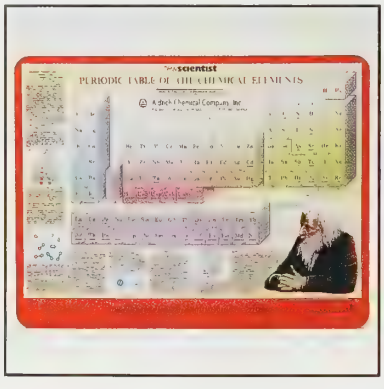
green	**Z15,331-1**	4.90/100
blue	**Z15,333-8**	4.90/100

set (100 of each color, with case) **Z15,326-5** $24.20/set

For 10-mm NMR tubes

red	**Z11,808-7**	$8.90/100

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, *Aldrichimica Acta*). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. Z24,409-0) like that pictured below. It is Teflon® coated, 8½ x 11 in., with a full-color periodic table on the front. We reserve the right to retain all entries for consideration for future publication.



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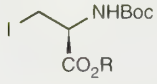
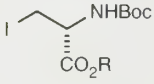
by

Jai Nagarkatti, President



1a R = CH_2Ph
1b R = CH_3



2a R = CH_2Ph
2b R = CH_3

Professor R.F.W. Jackson at the University of Newcastle, UK, suggested that we offer the enantiomeric pairs of *N*-(*tert*-butoxycarbonyl)-3-iodoalanine methyl and benzyl esters. These chiral intermediates are readily converted into organozinc reagents that are useful for the preparation of enantiomerically pure α-amino acids[1] as well as 4-oxo- and 3-aryl-α-amino acids.[2] The organozinc reagents undergo Pd(0) catalyzed coupling to give phosphonomethylphenyl alanines[3] and also form zinc/copper reagents, useful for α-amino acid synthesis.[4-6]

(1) Jackson, R.F.W. et al. *J. Chem. Soc., Chem. Commun.* **1989**, 644. (2) Jackson, R.F.W. et al. *J. Org. Chem.* **1992**, *57*, 3397. (3) Dow, R.L.; Bechle, B.M. *Synlett* **1994**, 293. (4) Bajgrowicz, J.A. et al. *Tetrahedron* **1985**, *41*, 1833. (5) Idem *Tetrahedron Lett.* **1984**, *25*, 2759. (6) Dunn, M.J. et al. *J. Org. Chem.* **1995**, *60*, 2210.

40,625-2 ***N*-(*tert*-Butoxycarbonyl)-3-iodo-L-alanine benzyl ester**, 99%
(1a)100mg $13.00; 500mg $43.20

42,602-4 ***N*-(*tert*-Butoxycarbonyl)-3-iodo-L-alanine methyl ester**, 99%
(1b) 250mg $16.25; 1g $45.00

40,626-0 ***N*-(*tert*-Butoxycarbonyl)-3-iodo-D-alanine benzyl ester**, 99%
(2a)100mg $13.00; 500mg $43.20

42,603-2 ***N*-(*tert*-Butoxycarbonyl)-3-iodo-D-alanine methyl ester**, 99%
(2b) 250mg $12.50; 1g $35.00

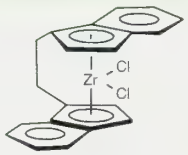
Naturally, we made these useful protected amino acid derivatives. It was no bother at all, just a pleasure to be able to help.

Metallocenes

Although metallocenes have been known since 1951,[1] the recent advent of metallocene/aluminoxane catalysts for the stereospecific polymerization of propylene[2,3] has sparked renewed interest in this class of compounds. It is well known that the behavior of the catalyst is easily tailored by modifying the substitution pattern on the cyclopentadienyl rings. One example of this is the family of stereo-rigid metallocenes where the cyclopentadienyl rings are bridged by an alkyl group. Aldrich offers a unique catalyst precursor from this family, dichloro[*rac*-ethylenebis(indenyl)]zirconium(IV), as well as the free ligand bis(indenyl)ethane. Our commitment to this growing field is reflected in our constantly expanding line of metallocenes and free ligands. Please contact our Technical Services Department at **800-231-8327** with any questions or suggestions concerning these compounds.

References: (1) Kealy, T.J.; Pauson, P.L. *Nature* **1951**, *16*, 1039. (2) Kaminsky, W.; Sinn, H. *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Springer-Verlag: Berlin, 1987. (3) Kaminsky, W.; Bark, A; Steiger, R. *J. Mol. Catal.* **1992**, *31*, 1347.

Catalysts & Catalyst Precursors



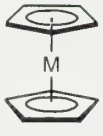
39,323-1

39,323-1 Dichloro[*rac*-ethylenebis(indenyl)]zirconium(IV) — **50mg $17.80; 250mg $59.40**

39,322-3 1,2-Bis(3-indenyl)ethane, 99% — **1g $14.00; 5g $47.00**

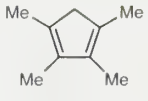
40,459-4 Methylaluminoxane, 10 wt. % solution in toluene — **100mL $48.00; 800mL $217.00**

Metallocenes



M			
Mg	37,913-1	**Bis(cyclopentadienyl)magnesium**, sublimed, 97%	**250mg $16.00; 1g $53.25**
V	37,915-8	**Bis(cyclopentadienyl)vanadium**	**250mg $23.50; 1g $70.60**
Cr	38,100-4	**Bis(cyclopentadienyl)chromium**, 95%	**250mg $19.00; 1g $65.10**
Fe	F40-8	**Ferrocene**, 98%	**5g $8.30; 100g $19.90; 500g $60.00**
Co	33,916-4	**Bis(cyclopentadienyl)cobalt**	**1g $26.50; 2g $38.40; 10g $147.80**
Ni	N752-4	**Bis(cyclopentadienyl)nickel**	**1g $13.65; 5g $45.00**
Ru	26,245-5	**Bis(cyclopentadienyl)ruthenium**, 97%	**250mg $29.70; 1g $80.20**

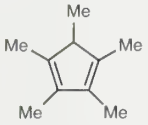
Ligands



42,447-1

NEW **42,447-1 1,2,3,4-Tetramethyl-1,3-cyclopentadiene**, *ca.* 85% — **1g $12.00; 5g $40.00**

21,402-7 1,2,3,4,5-Pentamethyl-1,3-cyclopentadiene, 95% — **1g $19.70; 5g $77.70; 25g $257.50**

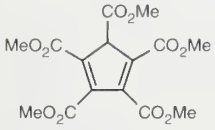


21,402-7

30,284-8 Pentamethyl cyclopentadiene-1,2,3,4,5-pentacarboxylate, 97% — **250mg $35.25; 1g $95.15**

26,393-1 Ethyltetramethylcyclopentadiene, 97%, mixture of isomers — **1g $14.30; 5g $57.50**

30,528-6 1,2,3,4,5-Pentaphenyl-1,3-cyclopentadiene, 99% — **250mg $18.50; 1g $51.40**

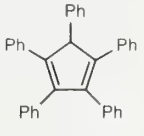


30,284-8

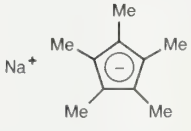
40,181-1 Sodium pentamethylcyclopentadienide, 0.5*M* solution in THF — **50mL $69.10; 100mL $115.50**

30,334-8 Lithium cyclopentadienide, 97% — **5g $26.40; 25g $88.40**

30,402-6 Sodium cyclopentadienide, 2.0*M* solution in THF — **100mL $28.50; 800mL $154.10**

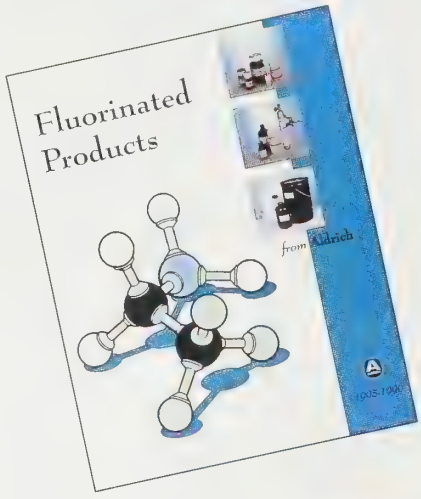


30,528-6



40,181-1

30,334-8



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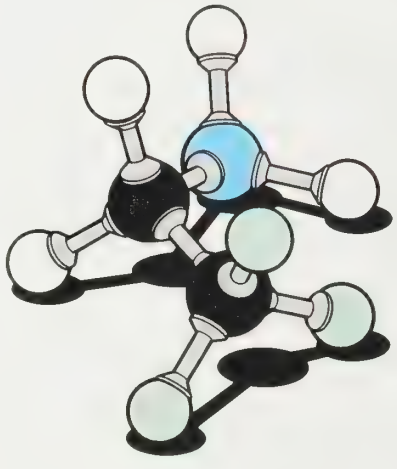

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Aldrichimica Acta

Volume 28, Number 4, 1995 *(Last issue in 1995)*

Polycyclic Cage Compounds: Reagents, Substrates, and Materials for the 21st Century

New Reactions for Forming Heterocycles and Their Use in Natural Products Synthesis

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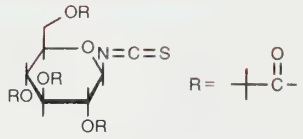
New Products

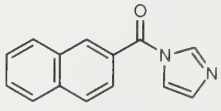
Derivatizing Reagents



An efficient derivatizing agent for the determination of enantiomeric purities of amino acids, β-blockers, and alkyloxiranes by reversed phase HPLC.

Lobell, M.; Schneider, M.P. *J. Chromatogr.* **1993**, *633*, 287.

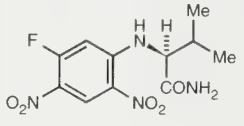
43,705-0 2,3,4,6-Tetra-*O*-pivaloyl-β-D-galactopyranosyl isothiocyanate, Fluka*brand*™ Chiraselect Reagent, 98+%, 99+% ee
100mg $44.25; 500mg $169.10



Fluorogenic reagent used to derivatize hydroxyl or amino groups of carbohydrates. Separation of the "tagged" carbohydrates by normal phase HPLC with fluorescence detection was accomplished at subpicomole sensitivity levels.

Ikemoto, N. et al. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 890.

43,894-4 1-(2-Naphthoyl)imidazole, 95% **500mg $58.30**



Valine analog of Marfey's reagent that provides improved resolution in the separation of D- and L-amino acids as well as analogs of phenylalanine and proline.[1] It has also aided in understanding the separation mechanism of these reagents.[2]

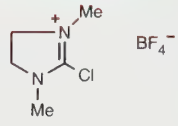
(1) Brueckner, H.; Keller-Hoehl, Ch.; Wittner, R. *Chem. Pept. Proteins* **1993**, *5/6 (Pt. A)*, 145. (2) Harada, K. et al. *Tetrahedron Lett.* **1995**, *36*, 1515.

43,706-9 Nα-(2,4-Dinitro-5-fluorophenyl)-L-valinamide, Fluka*brand*™ Chiraselect Reagent, 98+%, 99.5% ee
100mg $25.00; 500mg $96.40

Marfey's Reagent:

36,605-6 Nα-(2,4-Dinitro-5-fluorophenyl)-L-alaninamide, 98%
25mg $21.75; 100mg $60.30

Coupling Reagent

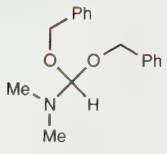


Coupling reagent for sterically hindered amino acids.

Akaji, K. et al. In *Pept. 1992, Proc. Eur. Pept. Symp., 22nd (1993)*; Scheider, C.H.; Eberle, A.N., Eds.; ESCOM: Leiden, Netherlands, 1993; pp 220-221.

43,927-4 2-Chloro-1,3-dimethyl-2-imidazolinium tetrafluoroborate, 98% **1g $24.40; 5g $92.20**

Benzylation Reagent

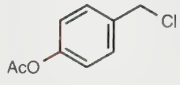


This reagent is commonly used to convert carboxylic acids to benzyl esters.[1] It has also been used to prepare 1-benzylcytosine in high yield.[2]

(1) Emmer, G. et al. *J. Med. Chem.* **1994**, *37*, 1908. (2) Helfer, D.L., II et al. *J. Org. Chem.* **1981**, *46*, 4803.

43,377-2 *N,N*-Dimethylformamide dibenzyl acetal
1g $8.90; 10g $49.65

Thiol Protection

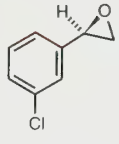


Used to protect thiols as 4-acetoxybenzyl sulfides. Regeneration of the thiol is accomplished by treatment with base.

Christensen, J.B. *Org. Prep. Proced. Int.* **1994**, *26*, 471.

43,288-1 4-(Chloromethyl)phenyl acetate, 98% **1g $11.75; 5g $39.00**

β-Blocker Synthon

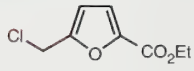


Ring opening of this chiral epoxide with amines produces amino alcohols which have been used as β-adrenergic agonists.

Bloom, J.D. et al. *J. Med. Chem.* **1992**, *35*, 3081. Badone, D.; Guzzi, U. *Bioorg. Med. Chem. Lett.* **1994**, *16*, 1921.

44,086-8 (*R*)-(+)-3-Chlorostyrene oxide, 98% **1g $27.00; 5g $90.00**

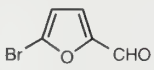
Furans



This furan derivative has been employed in the synthesis of prostaglandins,[1] heterocycles with pharmaceutical applications,[2-4] and novel fluorogenic derivatization reagents for carboxylic acids in liquid chromatography.[5]

(1) Miftakhov, M.S. et al. *Zh. Org. Khim.* **1988**, *24*, 1864. (2) Santilli, A.A. et al. *Org. Prep. Proced. Int.* **1990**, *22*, 71. (3) Sasho, S. et al. *J. Med. Chem.* **1993**, *36*, 572. (4) Usova, E.B. et al. *Khim. Geterotsikl. Soedin.* **1990**, 557. (5) Saito, M. et al. *Anal. Chim. Acta* **1995**, *300*, 243.

43,399-3 Ethyl 5-(chloromethyl)-2-furancarboxylate, 97%
1g $11.00; 5g $37.00

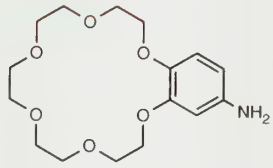


Serves as a building block in the synthesis of natural products and a variety of heterocycles.

Spirkova, K. et al. *Collect. Czech. Chem. Commun.* **1994**, *59*, 243. Mean Rejon, G.J. et al. *Afinidad* **1993**, *50*, 319. Gavrilova, S.P. et al. *Khim. Geterotsikl. Soedin.* **1993**, 322.

43,398-5 5-Bromo-2-furaldehyde, 97% **1g $8.00; 10g $45.00**

New Crown



Pendant crown ether that has been used to prepare ion-binding Langmuir-Blodgett films[1] and phospholipid bilayer membranes with ion-channel activity.[2]

(1) Anzai, J. et al. *Mater. Sci. Eng., C* **1993**, *C1(1)*, L1. (2) Otoda, K. et al. *J. Chem. Soc., Perkin Trans. 1* **1993**, 3011.

44,402-2 4´-Aminobenzo-18-crown-6, 97%
100mg $27.25; 500mg $98.10

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Available as a powder and a convenient suspension in hexanes.

29,606-6 Lithium dimethylamide, 95% **10g $33.90; 50g $111.10**
44,689-0 Lithium dimethylamide, 10 wt. % suspension in hexanes
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Aldrichimica Acta

Volume 28, Number 4, 1995 *(Last issue in 1995)*
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About our Cover:

Our cover displays *Mary Magdalene* (oil on panel, 48.6 x 40cm), painted by Jacob Cornelisz. van Oostsanen in 1519.

Oostsanen, famous for his paintings and woodcuts, was Amsterdam's first renowned artistic personality. His style was based on meticulously rendered surfaces, evocative textures, and precise detail. These characters are evident in the Magdalene's richly embroidered bodice and headdress, as well as in her jewelry and the tapestry that covers the foreground ledge.

The painting, signed and dated 1519, is one of the earliest known single representations of Mary Magdalene, who was a favored subject for devotional prayer in the sixteenth and seventeenth centuries.

The painting is in the collection of The Saint Louis Art Museum.

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Lab Notes

NMR tube cleaners (for example, Aldrich Cat. No. **Z10,724-7**, Model A) are susceptible to breaking if a standard 5-mm, 7-in. NMR tube is dropped or pulled down the length of the cleaner. This often happens when students forget to place a cap on the closed end of the NMR tube. An easy way to minimize this problem is to slide a short piece of plastic straw (ca. 1 inch) down the length of the inner tube. This prevents an NMR tube from dropping down onto the ring seal but still allows sufficient vacuum for solvent flushing.

Sincerely yours,
Alan P. Rosan, Associate Professor
Drew University
College of Liberal Arts
Madison, NJ 07940-4060

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, *Aldrichimica Acta*). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. Z15,000-2). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. Z24,409-0) like that pictured above. It is Teflon® coated, 8½ x 11 in., with a full-color periodic table on the front. We reserve the right to retain all entries for consideration for future publication.

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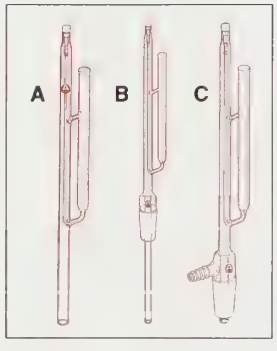
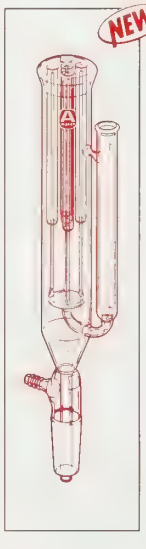
But, if you do break an NMR tube cleaner:

Integral Solvent Reservoir Models A, B, C

A tube cap placed on the closed end of an inverted NMR tube holds the tube in place and seals the system to allow efficient vacuum. Applied suction sprays solvent inside and against the closed end of the tube for thorough cleaning.

Model	For NMR ⅀Joint	tube (mm)	Cat. No.	Each
A	Tooled end	5	**Z10,724-7**	$56.00
B	24/40	5	**Z17,479-3**	71.00
C	24/40	5	**Z10,744-1**	82.20





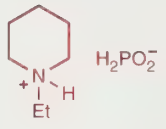
Aldrich 5-position NMR tube cleaner

Washes up to 5 NMR tubes at once and features a protective shield that virtually eliminates breakage of the internal, small diameter tubing. To use, place NMR tube cap over the closed end of the tube and insert an inverted tube into the cleaner. Solvent from the reservoir is sprayed against the interior of the tube when vacuum is applied. Tubes can be acetone rinsed and air dried while in place. Use with 5mm x 7in. NMR tubes. ⅀24/40 joint and vacuum hose connection. **Z26,698-1** $159.00

"Please Bother Us."

by Jai Nagarkatti

Jai Nagarkatti, President



Dr. Joseph Cs. Jaszberenyi of Professor D.H.R. Barton's research group at Texas A&M kindly suggested that we make this phosphorus-based hydrogen atom transfer reagent used with AIBN in radical deoxygenation, dehalogenation, and deamination.[1] The reagent is inexpensive and nontoxic as compared to the usual silicon- and tin-based reagents for deoxygenation. It also forms easily separable, water soluble by-products. The hypophosphite-AIBN method was found to be superior to traditional methods in a recently reported deoxygenation of the C-3 hydroxyl of a protected pyranose derivative.[2]

(1) Barton, D.H.R.; Jang, D.O.; Jaszberenyi, J.Cs. *Tetrahedron Lett.* **1992**, *33*, 5709. (2) Azhayev, A.; Guzaev, A.; Hovinen, J.; Mattinen, J.; Silianpää, R.; Lönnberg, H. *Synthesis* **1994**, 396.

43,617-8 1-Ethylpiperidine hypophosphite, 95%
5g $9.50; 25g $31.50

44,109-0 2,2'-Azobisisobutyronitrile, 98% (AIBN) **100g $35.00**

Aldrich Chemical Company Fellow

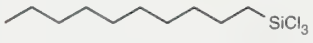
We are pleased to announce that David B. Rozema has been selected as the 1995/1996 recipient of an ACS Division of Organic Chemistry Graduate Fellowship, sponsored by Aldrich.

Mr. Rozema, a fourth year graduate student in Professor Samuel H. Gellman's research group at the University of Wisconsin-Madison, is investigating the use of small molecules—termed "artificial chaperones"—to assist protein refolding. This research has led to the development of a refolding method that relies on the sequential use of detergent and cyclodextrin to increase yields of active proteins.

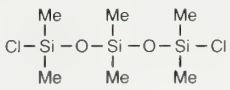
Congratulations, David! Aldrich is proud to help the research efforts of a young scientist such as yourself.

New Silanes

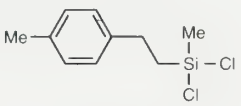
Aldrich continues to expand its line of silicon compounds to meet the needs of researchers in academia and industry. Our goal is to offer the most comprehensive listings of silicon compounds at competitive prices, and the following is a listing of our new silanes. For more information on Group 14 compounds, please consult the 1994-1995 Aldrich Catalog/Handbook or call our Technical Services Department.



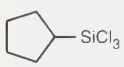
44,859-1



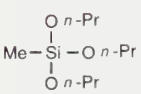
44,697-1



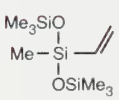
44,889-3



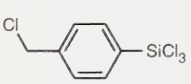
44,618-1



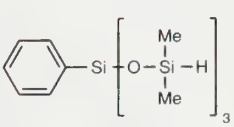
44,890-7



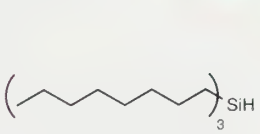
44,634-3



44,623-8



44,864-8



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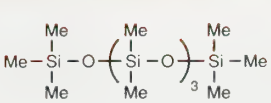
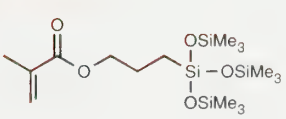
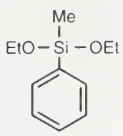


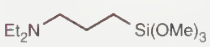
44,726-9



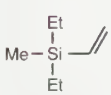
44,613-0



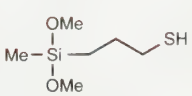
44,860-5



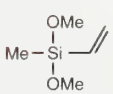
44,866-4



44,633-5



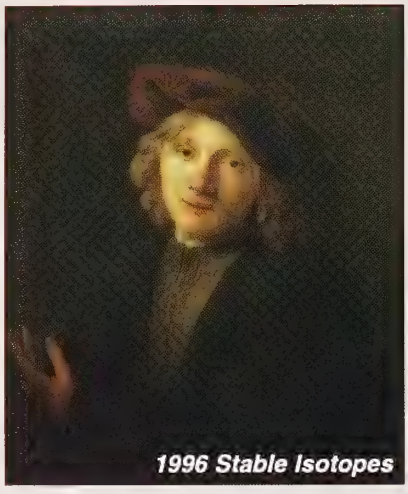
44,617-3



44,620-3

44,859-1	**Decyltrichlorosilane,** 97%	10mL $21.00; 50mL $80.00
44,697-1	**1,5-Dichloro-1,1,3,3,5,5-hexamethyltrisiloxane,** 95%	5mL $9.00; 25mL $30.00
44,889-3	**Dichloromethyl(4-methylphenethyl)silane,** 95%	25mL $20.00; 100mL $60.00
44,860-5	**Diethoxymethylphenylsilane,** 97%	10mL $17.00; 50mL $68.00
44,866-4	**[3-(Diethylamino)propyl]trimethoxysilane,** 96%	5mL $16.50; 25mL $55.00
44,633-5	**Diethylmethylvinylsilane,** 97%	5mL $25.00; 25mL $95.00
44,617-3	**3-(Dimethoxymethylsilyl)-1-propanethiol,** 95%	10mL $9.50; 50mL $31.65
44,620-3	**Dimethoxymethylvinylsilane,** 97%	25mL $28.00; 100mL $88.50
44,613-0	**3-[Tris(trimethylsilyloxy)silyl]propyl methacrylate,** 98%	5mL $10.00; 25mL $29.00
44,726-9	**Dodecamethylpentasiloxane,** 97%	10mL $9.00; 50mL $30.00
44,892-3	**Trioctylsilane,** 97%	5mL $22.00; 25mL $73.75
44,864-8	**Tris(dimethylsilyloxy)phenylsilane,** 96%	5mL $12.00; 25mL $40.00
44,623-8	**Trichloro[4-(chloromethyl)phenyl]silane,** 98%	5mL $19.50; 25mL $65.00
44,634-3	**Methylbis(trimethylsilyloxy)vinylsilane,** 98%	25mL $20.00; 100mL $66.00
44,890-7	**Methyltripropoxysilane,** 97%	5mL $13.50; 25mL $45.10
44,618-1	**Trichlorocyclopentylsilane,** 97%	5mL $14.00; 25mL $47.00

NEW for 1996



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Aldrichimica Acta

Volume 29, Number 1, 1996

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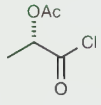
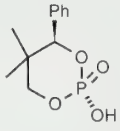


Frequently used chiral building block.[1] Also used to resolve a bicyclic α-hydroxylactone[2] and to prepare chiral phosphonates used in an enantiomeric excess assay of unprotected amino acids.[3]

(1) Zhu, J. et al. *J. Org. Chem.* **1995**, *60*, 6389. Kende, A.S. et al. *J. Am. Chem. Soc.* **1993**, *115*, 9842. (2) Burlina, F. et al. *Tetrahedron Lett.* **1994**, *35*, 8151. (3) Hulst, R. et al. *Tetrahedron* **1994**, *50*, 11721.

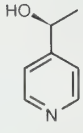
44,705-6 (*S*)-(−)-2-Acetoxypropionyl chloride, 97%
1g $13.50; 5g $45.00



New reagent employed in the determination of unprotected amino acids by ^{31}P NMR spectroscopy.

Hulst, R. et al. *Tetrahedron: Asymmetry* **1994**, *5*, 1701.

44,842-7 (2*R*,4*R*)-(−)-2-Hydroxy-5,5-dimethyl-4-phenyl-1,3,2-dioxaphosphorinane 2-oxide, 98% **1g $48.05; 5g $182.30**



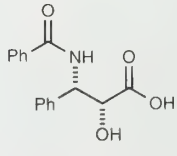
These pyridines have been used to prepare chiral ligands for asymmetric synthesis.

Orrenius, C. et al. *Tetrahedron: Asymmetry* **1994**, *5*, 1363.

44,853-2 (*R*)-(+)-α-Methyl-4-pyridinemethanol, 99%
250mg $46.50; 1g $128.55

44,854-0

44,854-0 (*S*)-(−)-α-Methyl-4-pyridinemethanol, 99%
250mg $46.50; 1g $128.55

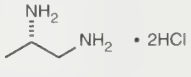


Taxol™ (Paclitaxel) C-13 side chain.

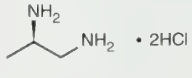
Wang, Z.-M. et al. *J. Org. Chem.* **1994**, *59*, 5104. Gou, D.-M. et al. *ibid.* **1993**, *58*, 1287.

44,437-5 *N*-Benzoyl-(2*R*,3*S*)-3-phenylisoserine, 98%
100mg $26.50; 500mg $88.00

Taxol is a trademark of Bristol-Myers Co.



41,256-2



41,255-4

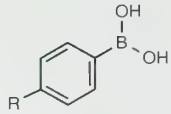
These diamines have been used for the synthesis of chiral imidazolines.

Miller, D.D. et al. *J. Med. Chem.* **1976**, *19*, 1382. Hsu, F.-L. et al. *ibid.* **1980**, *23*, 1232.

41,256-2 (*S*)-(−)-1,2-Diaminopropane dihydrochloride, 99% **250mg $10.50; 1g $29.00**

41,255-4 (*R*)-(+)-1,2-Diaminopropane dihydrochloride, 99% **250mg $7.25; 1g $20.00**

Arylboronic Acids



R = Me, Cl

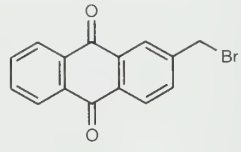
Palladium-catalyzed cross-coupling of these boronic acids with aryl- or heteroaryl halides efficiently leads to porphyrins,[1] furans,[2] and asymmetrical biaryl ketones.[3]

(1) Chan, K.S. et al. *J. Chem. Soc., Chem. Commun.* **1994**, 271. Zhou, X. et al. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2519. (2) Song, Z.Z. et al. *Liebigs Ann. Chem.* **1994**, 29. (3) Ishiyama, T. et al. *Tetrahedron Lett.* **1993**, *34*, 7595.

39,362-2 *p*-Tolylboronic acid, 97% (R = Me)
250mg $10.75; 1g $30.00

41,754-8 4-Chlorophenylboronic acid, 95% (R = Cl)
1g $8.75; 10g $48.00

Protecting Reagent

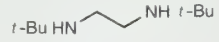


Photochemically labile protecting reagent for phosphates. Also used as a starting material for the preparation of heterosupramolecular compounds.

Furuta, T. et al. *J. Org. Chem.* **1995**, *60*, 3953. Marguerettaz, X.; Fitzmaurice, D. *J. Am. Chem. Soc.* **1994**, *116*, 5017.

44,465-0 2-(Bromomethyl)anthraquinone, 97%
1g $34.10; 5g $113.50

Hindered Amine

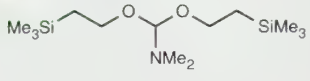


Building block for tryptamines, which are potential serotonin analogs for brain receptor studies.[1] Also used to prepare heterocyclic systems such as piperazinones,[2] germanediyls,[3] and phosphonamides.[4]

(1) Castro, J.L. et al. *J. Med. Chem.* **1994**, *37*, 3023. (2) Chassonnery, D. et al. *Bull. Soc. Chim. Fr.* **1994**, *131*, 188. (3) Herrmann, W.A. et al. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485. (4) Denmark, S.E. et al. *J. Org. Chem.* **1991**, *56*, 5063.

44,700-5 *N,N'*-Di-*tert*-butylethylenediamine, 98%
5mL $23.00; 25mL $77.00

Carboxyl Protecting Reagent

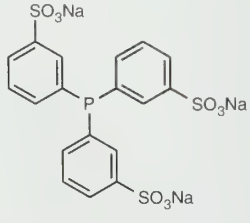


Convenient reagent for the preparation of (trimethylsilyl)ethyl esters and a frequently used reagent for carboxyl protection (e.g., in cyclopeptide synthesis). Deprotection is accomplished with HF in acetonitrile or with tetrabutylammonium fluoride.

Emmer, G. et al. *J. Med. Chem.* **1994**, *37*, 1918. Idem *ibid.* **1994**, *37*, 1908.

44,526-6 *N,N*-Dimethylformamide bis[2-(trimethylsilyl)-ethyl] acetal, 95% **1g $22.50; 5g $75.00**

New Ligand



Ligand employed in the preparation of water-soluble metal catalysts that are used in biphasic industrial processes.

Cornils, B. et al. *J. Organomet. Chem.* **1995**, *502(1-2)*, 177. Fremy, G. et al. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1474.

44,497-9 3,3',3''-Phosphinidynetris(benzenesulfonic acid), trisodium salt, 97%
1g $64.50; 5g $215.00

Aldrichimica Acta

Volume 29, Number 1, 1996
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This painting, *Fantaisie sur Tivoli* (oil on canvas, 241.1 x 193.4cm), is one of four landscapes by Hubert Robert that were commissioned by Grand Duke Serge Alexanderovitch in 1789. It displays Robert's typical combination of romantic rusticity and ancient ruins. The small round temple is based on the design of the temple of Vesta at Tivoli where Robert and Fragonard enjoyed the hospitality of the Abbé de St. Non at the Villa d'Este in the summer of 1760. The temple was well known to tourists of the Roman area and had been the subject of artists' attention since the seventeenth century.

The painting is in the collection of The Saint Louis Art Museum, Gift of Mrs. Frederic W. Allen.

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We do a lot of ion selective analysis, and our probes become coated with sample residue. It becomes very expensive to replace these probes every month, so it was important for us to clean our probes effectively but safely with no interference to our testing.

To clean and extend the life of your solid state ISE probes, try cleaning them with a mild abrasive such as a non-fluorinated toothpaste. Use your finger to apply the toothpaste and lightly rub the surface. After a sufficient amount of time, completely rinse the probe and recalibrate.

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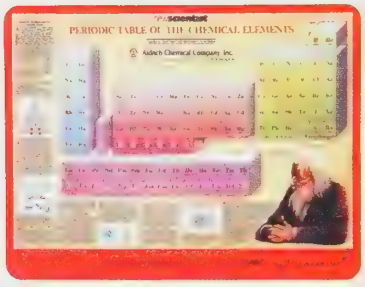

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Reference: ASTM D512-89
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Standard	**44,317-4**	38.00

References: ASTM D3868-79, EPA 340.2
Concentration range: 0.02ppm to saturation
Interferences: OH

**ISE combination electrodes have both the indicating and reference half-cells in one electrode. BNC connector
* Bottles packaged in 5 x 50mL containers. All others are 475mL bottles.

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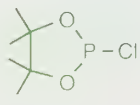
by Jai Nagarkatti, President



Professor Dimitris S. Argyropoulos (McGill University-Paprican) kindly suggested that we make this dioxaphospholane that is a phosphitylation reagent used in the quantitative analysis of hydroxyl groups in lignins by ^{31}P NMR spectroscopy. The reagent provided excellent resolution of the various phenolic hydroxyl environments including those belonging at the C5 condensed phenolic units.

Granata, A.; Argyropoulos, D.S. *J. Agric. Food Chem.* **1995**, *43*, 1538.

44,753-6 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, 95% **1g $23.75; 5g $79.00**

Naturally, we made this useful assay reagent. It was no bother at all, just a pleasure to be able to help.

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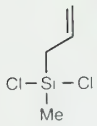

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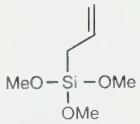

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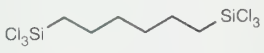

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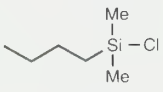

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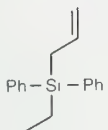
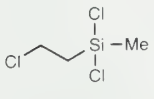


44,723-4



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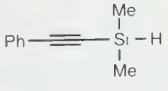
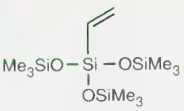


45,278-5

44,727-7	**Allyldichloromethylsilane,** 97%	**25mL $61.95; 100mL $186.90**
44,695-5	**Allyltrimethoxysilane,** 97%	**5mL $15.75; 25mL $52.50**
45,224-6	**1,6-Bis(trichlorosilyl)hexane,** 97%	**1g $7.00; 10g $25.00**
44,612-2	**Butyldimethylsilyl chloride,** 98%	**10mL $62.70; 50mL $241.10**
44,723-4	**Diallyldiphenylsilane,** 97%	**10mL $13.00; 25mL $25.00**
44,861-3	**Dichloro(2-chloroethyl)methylsilane,** 97%	**25mL $18.50; 100mL $61.00**
45,278-5	**Dimethyl(phenylethynyl)silane,** 97%	**1g $12.00; 5g $40.00**
44,862-1	**1,1,3,3,5,5-Hexamethyltrisiloxane,** 95%	**10mL $24.75; 50mL $82.25**
44,696-3	**Hexyltrichlorosilane,** 97%	**25mL $18.00; 100mL $50.00**
43,834-0	**Phenethyltrimethoxysilane,** 98%	**1g $15.75; 5g $52.75**
44,893-1	**Trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane,** 97%	**10g $30.00**
45,280-7	**Trichloro(3,3,3-trifluoropropyl)silane,** 97%	**5mL $13.50; 25mL $45.00**
45,226-2	**2-(Trichlorosilyl)ethyl acetate,** 97%	**5mL $15.00; 25mL $50.00**
45,281-5	**Trimethoxy(7-octen-1-yl)silane,** tech., 85%	**5mL $35.00; 25mL $140.00**
44,891-5	**Tris(dimethylsilyloxy)methylsilane,** 97%	**5mL $16.50; 25mL $55.00**
44,616-5	**Tris(trimethylsilyloxy)vinylsilane,** 97%	**1mL $8.95; 10mL $50.40**



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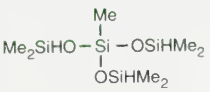

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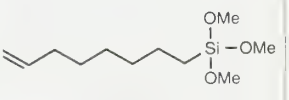

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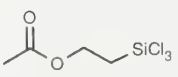

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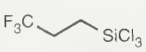

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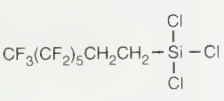

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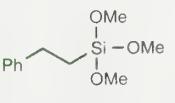
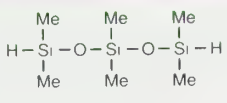


43,834-0



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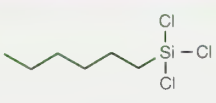

44,696-3

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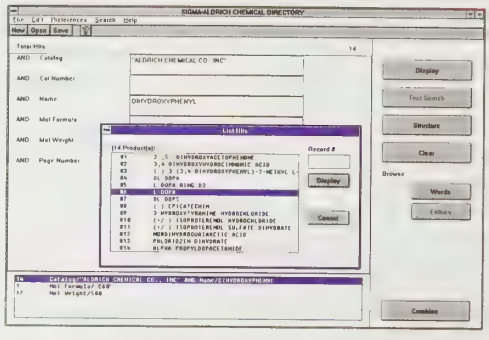

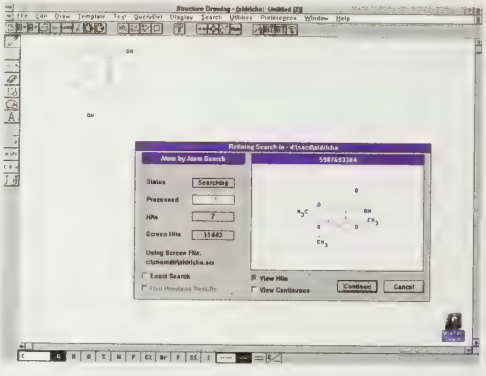

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Volume 29, Number 2, 1996

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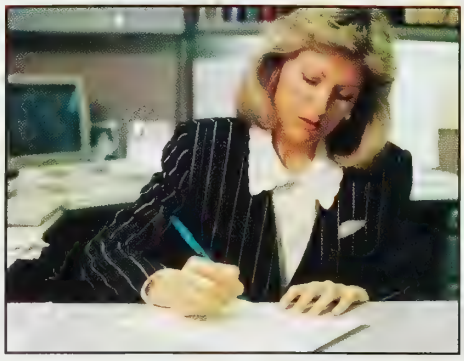

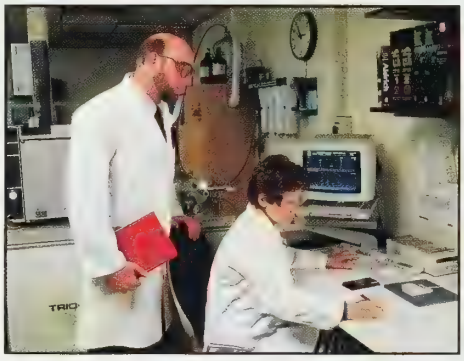

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The painting is part of the collection of French paintings at The Saint Louis Art Museum.

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Thank you,
Samuel G. Levine
Department of Chemistry
North Carolina State University
Raleigh, NC 27695

(1) Levine, S.G. *J. Chem. Educ.* **1996**, *73*, 77.

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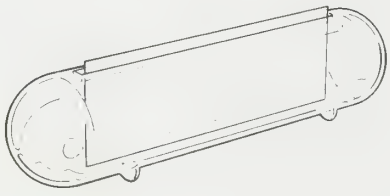

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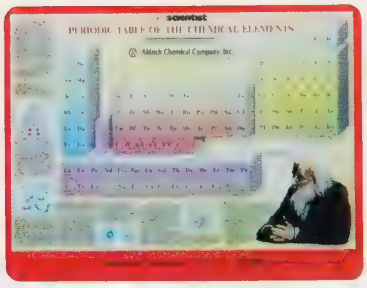

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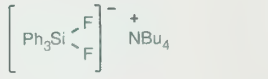

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Pilcher, A.S.; Ammon, H.L.; DeShong, P. *J. Am. Chem. Soc.* **1995**, *117*, 5166.

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29,630-9	**1,4-Dioxane,** 99.8%	19.45	39.70	59.55	182.70	178.60	277.85
27,098-9	**Ethyl acetate,** 99.8%	15.25	24.70	37.10	105.30	103.00	160.25
29,608-2	**Ether,** 99.8%	16.50	28.15	—	129.30	—	197.00
27,764-9	**Ethyl alcohol,** denatured	15.45	23.95	35.95	110.40	108.00	167.60
25,952-7	**Ethylene glycol dimethyl ether,** 99.5%	22.60	57.55	84.85	259.20	250.00	366.80
32,241-5	**Methyl alcohol,** 99.8%	14.40	19.75	29.65	90.90	89.20	138.20
32,863-4	**1-Methyl-2-pyrrolidinone,** 99.5%	22.30	51.35	77.10	236.40	231.60	359.45
27,685-5	**Methyl sulfoxide,** 99.8%	22.30	51.25	76.90	235.80	230.60	420.00[‡]
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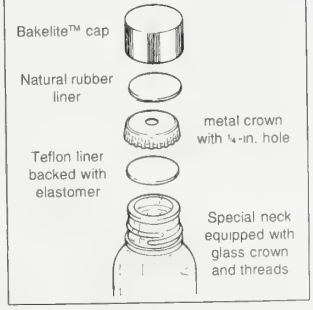

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Aldrichimica Acta

Volume 29, Number 3, 1996 *(Last issue in 1996)*

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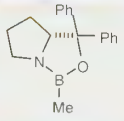
New Products

Chiral Catalysts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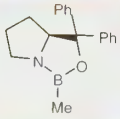
45,770-1

These oxazaborolidines are highly enantioselective catalysts for the reduction of prochiral ketones.[1,2] Examples of their use include the preparation of the natural products forskolin, lankacidin C, and salsolidine.[3-5]

(1) Corey, E.J. et al. *J. Am. Chem. Soc.* **1987**, *109*, 7925. (2) Mathre, D.J. et al. *J. Org. Chem.* **1993**, *58*, 2880. (3) Calvo, D. et al. *Tetrahedron Lett.* **1996**, *37*, 1023. (4) Kende, A.S. et al. *J. Am. Chem. Soc.* **1993**, *115*, 9842. (5) Ponzo, V.L.; Kaufman, T.S. *Tetrahedron Lett.* **1995**, *36*, 9105.

45,769-8 **(*R*)-2-Methyl-CBS-oxazaborolidine,** 1*M* solution in toluene **5mL $35.00; 25mL $117.00**
45,770-1 **(*S*)-2-Methyl-CBS-oxazaborolidine,** 1*M* solution in toluene **5mL $35.00; 25mL $117.00**

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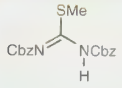
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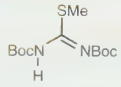
43,990-8

Amines react rapidly with these reagents providing di(Boc) or di(Cbz) protected guanidines.[1,2] Examples of their use include the synthesis of (±)-deoxyspergualin and glycoprotein IIb/IIIa inhibitors.[3,4] Unsymmetrical disubstituted guanidines are obtained by alkylation of these reagents prior to reaction with amines.[5]

(1) Chandrakumar, N.S. *Synth. Commun.* **1996**, *26*, 2613. (2) Su, W. *ibid.* **1996**, *26*, 407. (3) Verdini, A.S. et al. *Tetrahedron Lett.* **1992**, *33*, 6541. (4) Xue, C.-B.; DeGrado, W.F. *J. Org. Chem.* **1995**, *60*, 946. (5) Monache, G.D. et al. *J. Med. Chem.* **1993**, *36*, 2956.

45,878-3 **1,3-Bis(benzyloxycarbonyl)-2-methyl-2-thiopseudourea,** 98% **5g $22.00; 25g $75.00**
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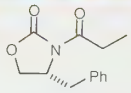
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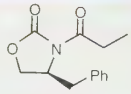
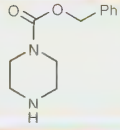

45,877-5

High diastereoselectivities are achieved when the enolates derived from these chiral auxiliaries are alkylated, acylated, or used in aldol reactions. Recent examples include synthetic studies on cyclosporine amino acids,[1] discodermolide,[2] zaragozic acid C,[3] rhizoxin,[4,5] and nargenicin.[6]

(1) Savignac, M. et al. *Tetrahedron: Asymmetry* **1994**, *5*, 717 (2) Smith, A.B., III et al. *J. Am. Chem. Soc.* **1995**, *117*, 12011. (3) Carreira, E.M.; Du Bois, J. *ibid.* **1995**, *117*, 8106. (4) Lafontaine, J.A.; Leahy, J.W. *Tetrahedron Lett.* **1995**, *36*, 6029. (5) Provencal, D.P. et al. *ibid.* **1995**, *36*, 6033. (6) Cane, D.E. et al. *J. Am. Chem. Soc.* **1993**, *115*, 527.

45,954-2 **(*R*)-(–)-4-Benzyl-3-propionyl-2-oxazolidinone,** 99% **1g $24.50; 5g $82.00**
45,877-5 **(*S*)-(+)-4-Benzyl-3-propionyl-2-oxazolidinone,** 97% **1g $24.50; 5g $82.00**

Monoprotected Diamine

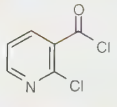


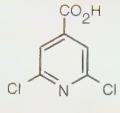
This monoprotected piperazine has been used in the synthesis of thermoplastic elastomers with oligourethane domains,[1-3] and in the preparation of piperazinylrifamycin P, which was studied as a potential antibiotic.[4]

(1) Eisenbach, C.D.; Heinemann, T. *Macromol. Chem. Phys.* **1995**, *196*, 2669. (2) Idem *Macromolecules* **1995**, *28*, 4815. (3) Eisenbach, C.D. et al. *Macromol. Chem. Phys.* **1995**, *196*, 833. (4) Cavalleri, B. et al. *J. Med. Chem.* **1990**, *33*, 1470.

45,692-6 **Benzyl 1-piperazinecarboxylate,** 98% **5mL $30.00; 25mL $100.00**

Heterocyclic Building Blocks


45,882-1


45,654-3

The antiviral agent nevirapine and analogs of the neuroleptic agent clothiapine have been prepared from this nicotinoyl chloride.

Kelly, T.A.; Patel, U.R. *J. Org. Chem.* **1995**, *60*, 1875. Liegeois, J.-F.F. et al. *J. Med. Chem.* **1994**, *37*, 519.

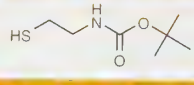
45,882-1 **2-Chloronicotinoyl chloride,** 98% **5g $48.00; 25g $160.00**

This isonicotinic acid has been extensively studied as a plant protection agent and has been utilized in the preparation of microbicides and insecticides.

Hijwegen, T.; Verhaar, M.A. *Plant Pathol.* **1995**, *44*, 756. Chamberlain, K. et al. *Pestic. Sci.* **1995**, *45*, 69.

45,654-3 **2,6-Dichloroisonicotinic acid,** 98% **1g $18.00; 5g $60.00**

Useful Synthon

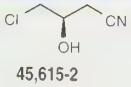


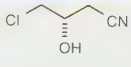
Glycopeptidomimetics and an affinity label for the glucocorticoid receptor have been prepared using this thiol.

Saha, U.K.; Roy, R. *J. Chem. Soc., Chem. Commun.* **1995**, 2571. López, S.; Simons, S.S., Jr. *J. Med. Chem.* **1991**, *34*, 1762.

45,891-0 ***tert*-Butyl *N*-(2-mercaptoethyl)carbamate,** 97% **5mL $28.50; 25mL $95.00**

Chiral Synthons

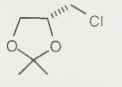

45,615-2

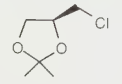

45,616-0

(–)-Carnitine and (–)-γ-amino-β-hydroxybutyric acid have been prepared using these synthons.

Kolb, H.C. et al. *Tetrahedron: Asymmetry* **1993**, *4*, 133.

45,615-2 **(*R*)-(+)-4-Chloro-3-hydroxybutyronitrile,** 97% (97% ee/GC) **1g $32.00; 5g $106.00**
45,616-0 **(*S*)-(–)-4-Chloro-3-hydroxybutyronitrile,** 97% (97% ee/GC) **1g $32.00; 5g $106.00**

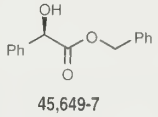

45,613-6

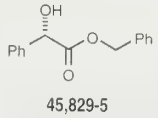

45,614-4

These synthons have been utilized in the preparation of both enantiomers of the orally active antifungal azolic agent ketoconazole.

Camps, P. et al. *Tetrahedron: Asymmetry* **1995**, *6*, 1283.

45,613-6 **(*R*)-(+)-4-(Chloromethyl)-2,2-dimethyl-1,3-dioxolane,** 98% **1g $12.25; 5g $41.00**
45,614-4 **(*S*)-(–)-4-(Chloromethyl)-2,2-dimethyl-1,3-dioxolane,** 98% **1g $12.25; 5g $41.00**


45,649-7


45,829-5

These esters have been used to prepare HMG-CoA reductase inhibitors.

Konoike, T.; Araki, Y. *J. Org. Chem.* **1994**, *59*, 7849.

45,649-7 **Benzyl (*R*)-(–)-mandelate,** 99% **5g $20.00; 25g $67.00**
45,829-5 **Benzyl (*S*)-(+)-mandelate,** 99% **5g $18.50; 25g $62.00**

Aldrichimica Acta

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This painting is part of the collection of French paintings at The Saint Louis Art Museum.

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Lab Notes

Column chromatography on silica gel is a widely used general purification method in organic chemistry, and hexane/ethyl acetate is one of the most common solvent systems. However, using this method, chemists often encounter undesirable "tailing", especially in the case of large-scale purifications. It is not unusual to have long tails during chromatographic separation, even if on a TLC plate the substance has a nice round spot. This problem not only makes purification longer and consumes large volumes of solvents, it may also affect the recovery and purity of the desired substance.

The reason for this tailing is usually a slow adsorption-desorption equilibrium on the surface of the silica gel. This problem is well known to those working with normal phase HPLC. In HPLC, the problem can be solved easily by addition of a small amount of isopropyl alcohol (~0.1%) to the mobile phase, assuming the mobile phase had not originally contained it. Such a small amount of isopropyl alcohol does not essentially increase the polarity of the mobile phase. Therefore, retention times do not change and resolution is not affected, but tailing is greatly reduced due to the increased equilibration speed.

We found that the same method works very well with regular column chromatography when hexane/ethyl acetate or a similar solvent system is used as an eluent. In this case, however, methyl alcohol is more convenient for obvious practical reasons. Depending on the substance to be purified, 0.1-0.3%, and sometimes even 0.5% (v/v) of methanol could be added to the mobile phase. This method was found to be a real timesaver during large-scale chromatographic separations.

I hope this hint proves useful to many synthetic organic chemists.

Yours sincerely,

Dr. Vladimir Khlebnikov
Shiga Research Laboratories
Roussell Morishita Co., Ltd.
1658, Ohshinohara, Yasu-gun, Yasu-cho
Shiga-ken, Japan

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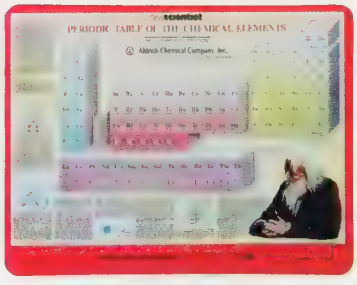

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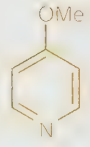
by

Jai Nagarkatti, President



Professor Daniel D. Comins of North Carolina State University kindly suggested that we make this valuable heterocyclic building block. It is readily converted to 2-substituted-2,3-dihydro-4-pyridones by acylation of the nitrogen and reaction of the resulting salt with a Grignard reagent. An asymmetric version of this reaction was used in the syntheses of a number of naturally occurring alkaloids.[1,2]

(1) Comins, D.L.; Joseph, S.P.; Goehring, R.R. *J. Am. Chem. Soc.* **1994**, *116*, 4719. (2) Comins, D.L.; Joseph, S.P. *Advances in Nitrogen Heterocycles*; JAI: Greenwich, CT, 1996; Vol. 2, p 251.

46,062-1 4-Methoxypyridine, 97%
5mL $35.00; 25mL $117.00

Naturally, we made this useful reagent. It was no bother at all, just a pleasure to be able to help.

Aldrich Chemical Company Fellow

We are pleased to announce that Janet L. Gunzner has been selected as the 1996/1997 Aldrich Chemical Company Fellow by the Organic Division of the American Chemical Society.

Ms. Gunzner is starting her fourth year of graduate study in the laboratory of Professor K.C. Nicolaou at The Scripps Research Institute, La Jolla, California. Her research is focused on new methodologies for, and synthetic routes to, the polycyclic ether maitotoxin isolated from *Gambierdiscus toxiscus* (a marine natural product of unprecedented complexity). She has previously received the Roche Award for Excellence in Organic Chemistry and the Wiener Graduate Fellowship. Additionally, as an undergraduate at Reed College, Janet was the recipient of the American Chemical Society-Portland Section Scholarship.

Congratulations, Janet! Aldrich is proud to help the research efforts of a young scientist such as yourself.

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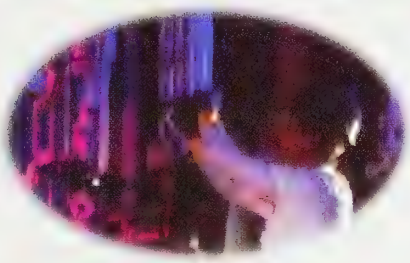

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Aldrichimica Acta

Volume 30, Number 1, 1997

Chiral Oxazolidinones in Asymmetric Synthesis

Preparation and Reactivity of Acyclic (Pentadienyl)iron(1+) Cations: Applications to Organic Synthesis

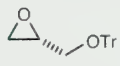
New Products

Chiral Building Blocks

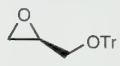
Nucleotides with activity against herpes simplex virus 1 and 2, lipid ammonium salts, and thio analogs of phospholipids have been prepared recently through ring-opening of these epoxides with cytosine derivatives,[1] amines,[2] and thiols,[3] respectively.

(1) Brodfuehrer, P.R. et al. *Tetrahedron Lett.* **1994**, *35*, 3243. (2) Bennett, M.J. et al. *ibid.* **1995**, *36*, 2207. (3) Lin, H.-K.; Gelb, M.H. *J. Am. Chem. Soc.* **1993**, *115*, 3932.

45,345-5 **(*R*)-(+)-Glycidyl trityl ether,** 98%
45,626-8 **(*S*)-(−)-Glycidyl trityl ether,** 98%



45,345-5



45,626-8

Ring opening of these epoxides with the dianion of *tert*-butyl acetoacetate[1] or with lithium acetylides[2] were important steps in the preparation of macrocyclic dilactones and pyrrolidines, respectively.

(1) Hoffman, R.V. et al. *Tetrahedron Lett.* **1996**, *37*, 2381. (2) Jones, A.D.; Knight, D.W. *Chem. Commun.* **1996**, 915.

46,151-2 **(*R*)-(+)-Propylene oxide,** 99%
23,889-9 **(*S*)-(−)-Propylene oxide,** 99%

46,151-2

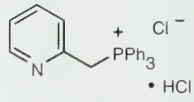
23,889-9

New Wittig Reagents

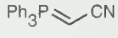
Ethenylpyridines and α,β-unsaturated nitriles are prepared from these reagents.

Buynak, J.D. et al. *J. Med. Chem.* **1995**, *38*, 1022. Hassan, A.E.A. et al. *J. Org. Chem.* **1996**, *61*, 6261. Launay, N. et al. *ibid.* **1996**, *61*, 3799.

46,213-6 **Triphenyl(2-pyridylmethyl)phosphonium chloride hydrochloride,** 98%
28,042-9 **(Triphenylphosphoranylidene)acetonitrile,** 97%



46,213-6



28,042-9

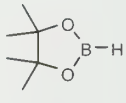
Hydroboration Reagent

Alkane or alkeneboronic esters are important organic synthons[1] which are readily prepared by reaction of this reagent with alkenes or alkynes, respectively. The reaction conditions required are milder than those necessary for catecholborane, and excellent regio- and stereoselectivity are observed. Pinacolboronates are reported to be more chromatographically stable and less moisture sensitive than catecholboronates.[2,3]

(1) Matteson, D.S. *Chem. Rev.* **1989**, *89*, 1535. (2) Pereira, S.; Srebnik, M. *Tetrahedron Lett.* **1996**, *37*, 3283. (3) Tucker, C.E. et al. *J. Org. Chem.* **1992**, *57*, 3482.

45,894-5 **4,4,5,5-Tetramethyl-1,3,2-dioxaborolane,** 1*M* solution in tetrahydrofuran

45,646-2 **4,4,5,5-Tetramethyl-1,3,2-dioxaborolane,** 97%



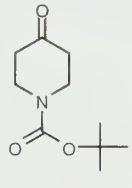
45,646-2

Heterocyclic Building Blocks

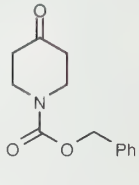
These compounds are important starting materials for 4-substituted piperidines and 4-substituted tetrahydropyridines.

Cooper, C.S. et al. *J. Med. Chem.* **1992**, *35*, 1392. Ashwood, M.S. et al. *J. Chem. Soc., Perkin Trans. 1* **1995**, 641. Lange, J.H.M. et al. *Tetrahedron* **1995**, *51*, 13447.

46,135-0 ***tert*-Butyl 4-oxo-1-piperidinecarboxylate,** 98%
46,464-3 **Benzyl 4-oxo-1-piperidinecarboxylate,** 99%



46,135-0

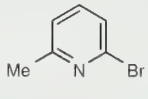


46,464-3

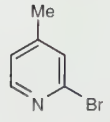
These bromopyridines have been used in aryl- and heteroaryl-coupling reactions to prepare a variety of biaryls including bipyridines[1] and thienylpyridines.[2] A wide variety of 2-substituted pyridines can also be prepared via lithium-halogen exchange.[3]

(1) Fort, Y. et al. *Tetrahedron* **1994**, *50*, 11893. (2) Li, J.J. et al. *J. Med. Chem.* **1996**, *39*, 1846. (3) Koenig, B. et al. *Chem. Ber.* **1994**, *127*, 1811.

42,911-2 **2-Bromo-6-methylpyridine,** 98%
34,998-4 **2-Bromo-4-methylpyridine,** 97%



42,911-2



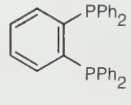
34,998-4

New Organometallic Ligand

Bis(diphenylphosphino)benzene is frequently utilized to prepare organometallic complexes.[1,2] For example, platinum catalysts for the enantioselective Baeyer-Villiger oxidation of ketones have been prepared using this ligand.[3]

(1) Crespo, O. et al. *Inorg. Chem.* **1994**, *33*, 6128. (2) Wang, P.W.; Fox, M.A. *ibid.* **1994**, *33*, 2938. (3) Gusso, A. et al. *Organometallics* **1994**, *13*, 3442.

46,027-3 **1,2-Bis(diphenylphosphino)benzene,** 97%



46,027-3

Aldrichimica Acta

Volume 30, Number 1, 1997

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About our Cover

The painting on our cover, *Attachment* (oil on canvas, 99 x 79.5cm), was painted by Sir Edwin Henry Landseer (1802-1873) in 1829. Landseer, considered in his day England's greatest painter, was known for his engaging animal images and portraits of pets, including those of Queen Victoria. Dogs are particularly prominent in his work, and none of his canine heroes so well captures the spirit of Victorian sentiment as the terrier depicted in *Attachment*. The painting is an illustration of Sir Walter Scott's short poem "Helvellyn", the story of a young man's tragic death in 1805 and his faithful terrier's long vigil beside the lifeless body. The young man suffered an accidental fall while on a climbing expedition to the Helvellyn mountain in Scotland's Lake District, and his remains lay undiscovered for three months. Scott's poem is the only account of the incident; no additional verification has ever appeared.

As depicted by Landseer, the story's setting is a dramatic backdrop of stormy sky and large imposing faces of bare rock that suggest dizzying heights. The body lies close to the edge of a high cliff, and the juxtaposition of strong light and looming shadow heightens the drama. The brightly colored areas direct the viewer's gaze to the attentive canine, who gingerly paws at her master's windswept cloak in hopes of some response.

This painting is in the collection of The Saint Louis Art Museum, gift of Mrs. Eugene A. Perry in memory of her mother, Mrs. Claude Kirkpatrick.

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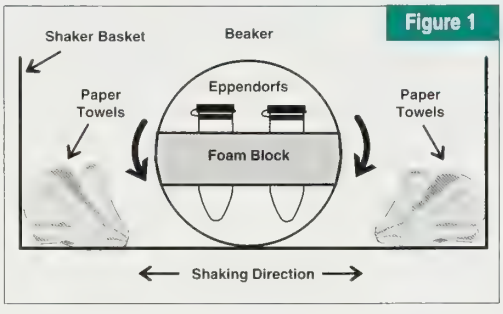
Lab Notes

Inversion Mixing on a Reciprocating Shaker

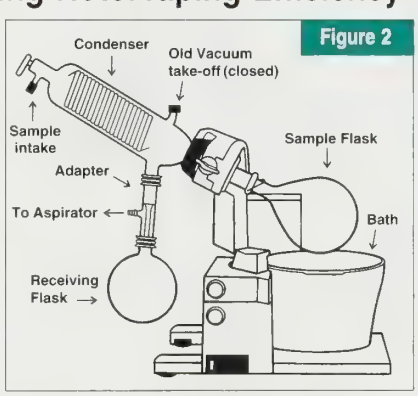
When small volumes are incubated with an affinity resin, the resin must be maintained in suspension, yet violent agitation will spread the resin on the walls of the tube. If a hematology mixer is not available, a reciprocating shaker can be used for the gentle inversion of Eppendorf tubes. A block of foam is cut to fit inside a beaker and the Eppendorf tubes are pushed into slots cut through the block (**Figure 1**). The beaker is laid on its side in the carrier basket of the shaker with its axis perpendicular to the direction of shaking. To prevent jarring impacts of the beaker with the basket walls, the sides are cushioned with crumpled-up paper towels. When the speed is set to give a rolling of the beaker, the resin continuously drops through the solution and surface tension maintains the solution at the bottom of the Eppendorf tube. This mixing device should also work with platform mixers (if a box is used to restrain the beaker!) and with the incubator baths (at a lower water level) found in biochemistry laboratories.



Vasek A. Mezl, Associate Professor
Department of Biochemistry, University of Ottawa
451 Smyth Road
Ottawa, Ontario K1H 8M5, Canada

Glass Adapter for Increasing Rotorvaping Efficiency

Submitted is an adapter that increases the efficiency of solvent evaporation under reduced pressure. Please note that this is a *general* design and may be modified to fit individual requirements dictated by the type of apparatus employed. I have used a rotary type apparatus that had the vacuum take-off exit directly opposite to the opening leading to collection of the distillate. I observed that there was competition between the two paths the distillate could take. The distillate could go to the vacuum take-off opening, as well as to the opening of the distillate-collection lead, resulting in a diminished efficiency of the distillation process. This latter is a function of the vapor pressure of the distillate at these two exits. The addition of the adapter to the apparatus altered the path of the vacuum take-off lead in such a fashion that now the distillate was collected in a flask cooled to about -35 °C. Thus, the vapor pressure of the distillate was not contributing negatively to the reduced pressure of the vacuum source, and was leading to an increased efficiency of the process. Naturally, the *old* vacuum take-off lead was closed during the distillation. **Figure 2** shows the apparatus with the adapter. It is an inexpensive addition that saves time and materials. May all your existing reduced-pressure problems evaporate with this adapter.

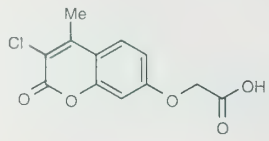


Respectfully submitted,
Harry E. Hadd, Ph.D., Associate Professor Emeritus
Indiana University Medical School
1051 B N. Jamestown Road
Decatur, GA 30033

"Please Bother Us."

by

Jai Nagarkatti, President



Dr. Lawrence Phillips of the National Cancer Institute kindly suggested that we make this coumarin derivative. The acid chloride is used as a fluorescent, precolumn derivatizing reagent for liquid chromatographic analysis of hydroxylated natural products. The postcolumn detection sensitivity is much higher for the 3-chloro-substituted compound than for the unsubstituted analog.

Phillips, L.R. et al. *Synth. Commun.* **1996**, *26*, 1805.

46,739-1 7-(Carboxymethoxy)-3-chloro-4-methylcoumarin

Naturally, we made this useful reagent. It was no bother at all, just a pleasure to be able to help.

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, *Aldrichimica Acta*). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. **Z15,000-2**). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. **Z24,409-0**). It is Teflon®-coated, 8½ x 11in., with a full-color periodic table on the front. We reserve the right to retain all entries for future consideration.

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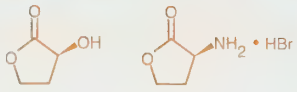
Volume 30, Number 2, 1997

Thiazole-Based Routes to Amino Hydroxy Aldehydes, and Their Use for the Synthesis of Biologically Active Compounds

Esterifications, Transesterifications, and Deesterifications Mediated by Organotin Oxides, Hydroxides, and Alkoxides

New Products

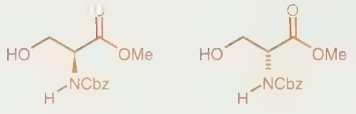


The polyether antibiotic monensin,[1] functionalized D ring side chains of vitamin D analogs,[2] and pesticides have been prepared from hydroxybutyrolactone.[3] Aminobutyrolactone has been used to prepare pseudopeptide inhibitors for Ras farnesyl-protein transferase[4] as well as selenomethionine.[5]

(1) Collum, D.B. et al. *J. Am. Chem. Soc.* **1980**, *102*, 2118. (2) Shiuey, S.-J. et al. *J. Org. Chem.* **1988**, *53*, 1040. (3) Buser, H.P. et al. *Tetrahedron* **1991**, *47*, 5709. (4) Graham, S.L. et al. *J. Med. Chem.* **1994**, *37*, 725. (5) Koch, T.; Buchardt, O. *Synthesis* **1993**, 1065.

44,423-5 **(*S*)-(–)-α-Hydroxy-γ-butyrolactone,** 97% **1g $33.50; 5g $112.00**

47,142-9 **(*S*)-(–)-α-Amino-γ-butyrolactone hydrobromide,** 99% **1g $16.00; 5g $53.50**



These protected serines have been employed as starting materials for the Cbz analog of Garner's aldehyde,[1,2] 2,3-diaminopropanol,[3] and optically active derivatives of 2-amino-1,3-propanediol.[4]

(1) Monache, G.D. et al. *Synthesis* **1995**, 1155. (2) Marshall, J.A.; Beaudoin, S. *J. Org. Chem.* **1996**, *61*, 581. (3) Demirci, F. et al. *Synthesis* **1996**, 189. (4) Kang, M. et al. *J. Org. Chem.* **1996**, *61*, 5528.

46,916-5 ***N*-Carbobenzyloxy-L-serine methyl ester** **1g $10.70; 10g $59.60**

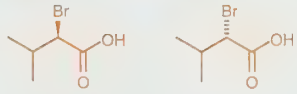
47,296-4 ***N*-Carbobenzyloxy-D-serine methyl ester,** 95% **1g $10.70; 10g $59.60**

$HN(SO_2CF_3)_2$

Transition-metal bis(trifluoromethylsulfonyl)-amides prepared using this compound are highly effective catalysts for the Friedel-Crafts reaction. For example, *p*-methoxyacetophenone is made in 99% yield in 10 minutes by reacting anisole with acetic anhydride in the presence of 20 mole percent of $Al(NTf_2)_3$.

Mikami, K. et al. *Synlett* **1996**, 171.

46,463-5 **1,1,1-Trifluoro-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide,** 97% **5g $46.55**

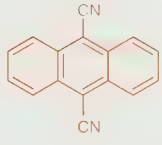


Ferroelectric liquid crystal derivatives,[1] proline-valine pseudo dipeptides which are potent inhibitors of α-chymotrypsin,[2] and β-turn peptidomimetics have been prepared using these bromoacids.[3]

(1) Sierra, T. et al. *J. Am. Chem. Soc.* **1992**, *114*, 7645. (2) Reed, P.E.; Katzenellenbogen, J.A. *J. Org. Chem.* **1991**, *56*, 2624. (3) Virgilio, A.A. et al. *Tetrahedron Lett.* **1996**, *37*, 6961.

46,210-1 **(*S*)-(–)-2-Bromo-3-methylbutyric acid,** 96% **5g $35.00; 25g $117.00**

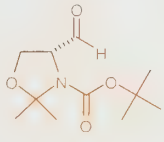
46,834-7 **(*R*)-(+)-2-Bromo-3-methylbutyric acid,** 96% **5g $35.00; 25g $117.00**



Electron acceptor recently employed in a photoinduced glycosylation reaction under neutral conditions[1] and in photosensitized radical cyclizations of α,β-unsaturated ketones containing remote double bonds.[2]

(1) Furuta, T. et al. *Chem. Commun.* **1996**, 157. (2) Pandey, G. et al. *Tetrahedron Lett.* **1994**, *35*, 7837.

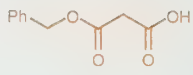
45,985-2 **9,10-Anthracenedicarbonitrile,** 97% **250mg $18.00; 1g $50.00**



Garner's aldehyde (Aldrich Cat. No. **43,274-1**) is widely utilized in the asymmetric synthesis of natural products.[1-3] The (*R*) isomer of this important synthon is now available.

(1) Hoemann, M.Z. et al. *Tetrahedron Lett.* **1996**, *37*, 953. (2) Roush, W.R.; Hunt, J.A. *J. Org. Chem.* **1995**, *60*, 798. (3) Guibourdenche, C. et al. *Tetrahedron: Asymmetry* **1993**, *4*, 2041.

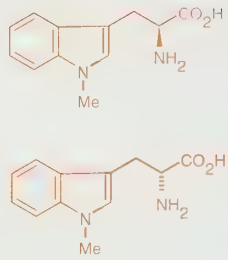
46,206-3 ***tert*-Butyl (*R*)-(+)-4-formyl-2,2-dimethyl-3-oxazolidinecarboxylate,** 96% **250mg $30.00; 1g $83.00**



This malonate mono ester has been used to synthesize potential glycoprotein IIb/IIIa antagonists[1] and isobacteriochlorins that are being used to study the biosynthesis of vitamin B_{12}.[2]

(1) Callahan, J.F. et al. *Tetrahedron* **1993**, *49*, 3479. (2) Battersby, A.R. et al. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2175.

46,065-6 ***mono*-Benzyl malonate** **1g $10.00; 10g $55.00**

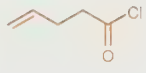


These *N*-methyltryptophans have been used to prepare a number of natural products including macroline alkaloids using the Pictet-Spengler reaction of tryptophan esters with aldehydes;[1] also used in the synthesis of 1-substituted indolactam precursors.[2]

(1) Cook, J.M. et al. *Heterocycles* **1988**, *27*, 2795. (2) Irie, K. et al. *Tetrahedron* **1995**, *51*, 6255.

45,248-3 **1-Methyl-D-tryptophan,** 95% **250mg $14.50; 1g $40.00**

44,743-9 **1-Methyl-L-tryptophan,** 95% **1g $14.00; 5g $47.00**



Chiral 2-alkylbutanedioic acids,[1] 2-alkyl-4-oxobutanoic acids,[2] and 3,5-disubstituted butyrolactones[3,4] have been prepared by diastereoselective alkylation of the acyl oxazolidinones prepared from this acid chloride followed by double bond oxidation.

(1) Azam, S. et al. *J. Chem. Soc., Perkin Trans.1* **1996**, 621. (2) Faull, A.W. et al. *J. Med. Chem.* **1995**, *38*, 686. (3) Moon, H.-S. et al. *Tetrahedron Lett.* **1994**, *35*, 8915. (4) Maligres, P.E. et al. *Tetrahedron* **1996**, *52*, 3327.

46, 847-9 **4-Pentenoyl chloride,** 98% **5mL $28.00; 25mL $93.50**

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About our Cover

The painting on our cover is *View in Suffolk* (oil on canvas, 37 x 49½ in.) by Thomas Gainsborough (1727-1788). When Gainsborough created this luminous view of the Suffolk countryside in the 1750s, landscape painting had only recently been established as an independent art form in Britain. It was still difficult for an English artist to sell enough landscapes to make a decent living, so Gainsborough, like most English painters, supported himself by doing portraits. Though landscape painting would remain for him an unprofitable sideline, Gainsborough was by far the most original and inventive English landscapist of the eighteenth century.

When he executed this early work, Gainsborough was under the spell of contemporary French painting, which he would have seen in London collections. Tied to French sensibilities is the treatment of the countryside as an elegant park, populated by carefree peasants like the handsome pair courting in the foreground. This modish artificiality, however, is tempered by Gainsborough's familiarity with the more naturalistic Dutch landscape tradition and, more importantly, by his own direct observations. Gainsborough's empathy with nature transcends conventional, imported formulas and looks ahead to the great achievements of English landscape painters of the nineteenth century.

Credit: The Saint Louis Art Museum. The John Fowler Memorial Collection, Bequest of Cora Liggett Fowler.

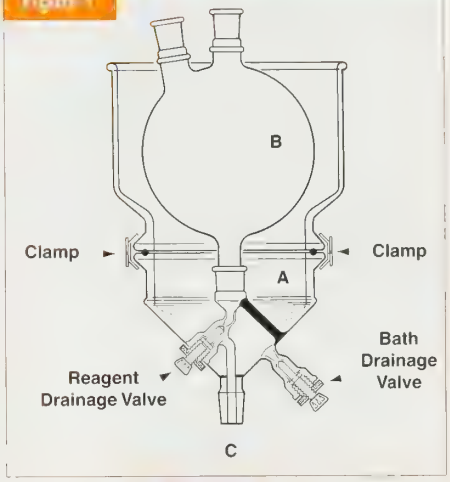
Lab Notes

A Practical Setup for the Transfer of Thermally Unstable and/or Insoluble Reagents

How often have you encountered the problem where cannulation of a reagent is impractical because of its thermal instability and/or insolubility?

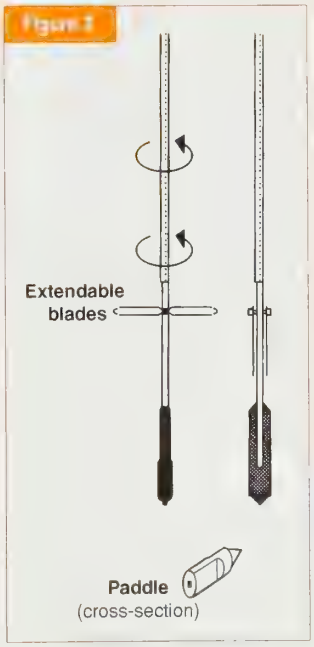
To alleviate the problem, we have found the following apparatus ideally suited for the transfer of thermally unstable and/or insoluble compounds (**Figure 1**). The design and use of this piece, to the best of our knowledge, is novel. The apparatus consists of a glass cooling bath **A** and a round bottom flask **B**. Attached to **A** is a valve, a female ground glass joint which is connected to **B**, and a male ground glass joint which can be connected to a 50–1000 mL angled two- or three-neck, round-bottom flask (**C**). The valve consists of a male joint with a threaded Teflon® nut and corresponding external glass screw threads. Flask **B** is constructed by attaching a male ground glass joint to the bottom of a 50- to 1000-mL angled two- or three-neck, round-bottom flask.

Figure 1



Cooling bath **A**, which has a slot in it to allow easy attachment, is connected to **B** containing the selected liquid. Teflon® sealing tape and a Delrin® plastic joint clip provide a tight seal. An electric motor clamped above **B** rotates a specially designed vertical rod equipped with a paddle and two extendable blades (**Figure 2**). It is essential to use a paddle that forms a good fit to the bottom of the female ground glass joint of **B**.

Figure 2



Agitation in flask **C** is achieved by placing an egg-shaped magnetic stirring bar large enough to stir the reaction mixture effectively. Flask **C** is clamped over the top of a magnetic stirrer whose flat top allows cooling or heating baths to be placed upon it. Temperatures inside **B** and **C** may be monitored by inserting a thermometer or a thermocouple probe through one of the necks. An inert atmosphere may be established through the use of rubber septa and syringe needles.

Flask **B** can be used for the preparation of lithium reagents at -78 to 25 °C; an addition funnel can be incorporated for large-scale work. Once the lithium reagent is prepared, the valve is opened and the organolithium reagent flows into flask **C** containing a solution of the appropriate electrophile.

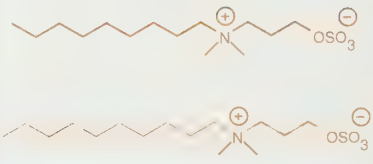
Our laboratory has employed this apparatus extensively during the preparation of 1,1,2- and 1,2,2-trisubstituted 1,2-dihydronaphthalenes via the stereospecific 1,4-addition of organolithium reagents to unprotected 1- and 2-naphthalenecarboxylic acids at low temperature.

Plunian, B.; Mortier, J.; Vaultier, M.; Toupet, L. *J. Org. Chem.* **1996**, *61*, 5206.

Jacques Mortier*, Michel Vaultier, Richard Cantegril, and Philippe Dellis
Université Rennes-1, Synthèse et électrosynthèse organiques, UMR 6510 associée au CNRS campus de Beaulieu, 35042 Rennes Cedex, France

"Please Bother Us."

by
Jai Nagarkatti, President



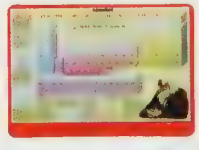
Professor Hinze at Wake Forest University kindly suggested that we offer these zwitterionic surfactants. They have been utilized for the extractive separation of hydrophilic proteins, steroids, and vitamin E. Their lack of absorbance in the ultraviolet region and their inducement of phase separation at moderate temperatures are two of the advantages that allow them to be used for heat-sensitive compounds such as vitamin E.

Saitoh, T.; Hinze, W.L. *Anal. Chem.* **1991**, *63*, 2520. Idem *Talanta* **1995**, *42*, 119. Hinze, W.L.; Pramauro, E. *Crit. Rev. Anal. Chem.* **1993**, *24*, 133.

47,260-3 ***N,N*-Dimethyl-*N*-[3-(sulfooxy)propyl]-1-nonanaminium hydroxide,** inner salt, 98% **1g $22.25; 5g $74.50**

47,258-1 ***N,N*-Dimethyl-*N*-[3-(sulfooxy)propyl]-1-decanaminium hydroxide,** inner salt, 98% **1g $22.25; 5g $74.50**

Naturally, we made these useful surfactants. It was no bother at all, just a pleasure to be able to help.



Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, *Aldrichimica Acta*). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. **Z15,000-2**). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. **Z24,409-0**). It is Teflon®-coated, 8½ x 11in., with a full-color periodic table on the front. We reserve the right to retain all entries for future consideration.

Fluka Prize

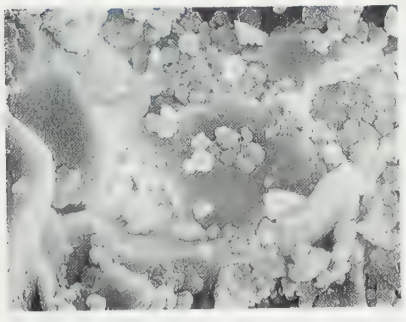
Reagent of the Year 1997

62279 Lipase, immobilized in Sol-Gel-AK from *Pseudomonas cepacia*, ~ 60 U/g, 1 g / 5 g
62281 Lipase, immobilized in Sol-Gel-AK from *Aspergillus niger*,~ 2.7 U/g, 1 g / 5 g
62277 Lipase, immobilized in Sol-Gel-AK from *Candida antarctica*,~ 1.6 U/g, 1 g / 5 g
62278 Lipase, immobilized in Sol-Gel-AK from *Candida cylindracea*,~ 16 U/g, 1 g / 5 g
62324 Lipase, immobilized in Sol-Gel-AK from hog pancreas, ~ 65 U/g, 100 mg / 500 mg
62282 Lipase, immobilized in Sol-Gel-AK from *Mucor miehei*, ~7 U/g, 1 g / 5 g
62283 Lipase, immobilized in Sol-Gel-AK from *Pseudomonas fluorescens*, ~ 55 U/g, 1g / 5 g

The Prize Winner 1997:

Manfred T. Reetz received his PhD from the University of Göttingen in 1969. After postdoctoral studies with Prof. R. W. Hoffmann he qualified as university lecturer at the University of Marburg in 1974. In 1978 he became C3-Professor at the University of Bonn and only 2 years later, in 1980, obtained a full professorship in organic chemistry at the University of Marburg. In 1993 he was appointed director of the *Max-Planck-Institut für Kohlenforschung* at Mülheim an der Ruhr, Germany. For his work in the field of organic chemistry he was awarded a *Dozentenstipendium des Fonds der Chemischen Industrie* (1976), the *Otto-Bayer-Preis* (1986), and the *Leibniz-Preis der Deutschen Forschungsgemeinschaft* (1989).

The Reagent:



Scanning electron-micrograph of a sol-gel immobilisate with *Aspergillus niger* lipase, Fluka No. **62281**

The development of immobilized lipases produced by inclusion of the enzyme in sol-gel materials has been awarded the 1997 Fluka prize. Lipases play an important role in organic synthesis. Two major problems, however, are the decreased enzyme activity in organic solvents and difficult recovery. These problems can be solved with a new immobilization procedure in which lipases are incorporated in hydrophobic organic-inorganic hybrid materials with the help of a sol-gel process.[1-3] This new class of heterogeneous biocatalysts has several advantages:

- increased enzyme activity (up to a factor of 100) for esterifications in organic solvents.[1-3]
- conservation and increase of enantioselectivity in acylation reactions.[1-5]
- remarkably high long-term stability.[1-3]
- increased temperature stability.[2]
- convenient recovery.[1-3]

The porous and lipophilic character of the lipase-containing gels[6] (see scanning electron micrograph) results in unexpectedly high activity. The new gels can be coated onto glass beads (e.g., SIRAN®) and used as heterogeneous biocatalysts in fluidized bed reactors.[7] Preliminary experiments show that catalytic reactions are also possible in water.[8] A review article will be published soon.[9]

SIRAN is a registered trademark of Schott Glaswerke, Mainz.

References:

(1) Reetz,M.T.; Zonta, A.; Simpelkamp, J. *Angew. Chem.* **1995**, *107*, 373; *Angew. Chem., Int. Ed. Engl.* **1995**,*34*, 301.
(2) Reetz,M.T.; Simpelkamp, J.; Zonta, A. Patent Appl. DE 44 08 152 A1 and EP 0 676 414 A1.
(3) Reetz,M.T.; Zonta, A.; Simpelkamp, J. *Biotechnol. Bioeng.***1996**, *49*, 527.
(4) Heidt, M.; Bornscheuer, U.; Schmidt, R.D. *Biotechnol. Tech.* **1996**, *10*, 25.
(5) Jaeger, K.-E.; Liebeton, K.; Zonta, A. Schimossek, K.; Reetz, M.T. *Appl. Microbiol. Biotechnol.* **1996**, *46*, 99.
(6) Reetz,M.T.; Zonta, A.; Simpelkamp, J.; Rufinska, A.;Tesche, B. *J. Sol- Gel Sci. Technol.* **1996**, *7*, 35.
(7) Reetz,M.T.; Zonta, A.; Simpelkamp, J.; Könen, W. *Chem. Commun. (Cambridge)* **1996**, 1397.
(8) Reetz,M.T.; Zonta, A.; Wenkel, R., unpublished results.
(9) Reetz, M.T. *Adv. Mater.*, in press.

The Fluka Prize:

The winner will be awarded the sum of sFr. 10 000.-. Nominations for the Fluka Prize "Reagent of the Year" should be submitted to the Fluka Prize Committee c/o Fluka Chemie AG, CH-9471 Buchs/ Switzerland no later than September 30th. Full details regarding the Fluka Prize are available upon request.

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Aldrichimica Acta

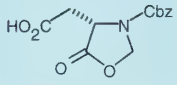
Volume 30, Number 3, 1997

Synthesis of Biologically Important Oligosaccharides and Other Glycoconjugates by the Glycal Assembly Method

Crisscross Cycloaddition Reactions

New Products

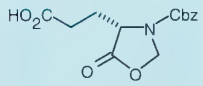
Chiral Building Blocks



Peptidomimetics, pseudopeptides, and high potency sweeteners have been prepared from these aspartic acid and glutamic acid derivatives.[1,2] A cyclic dipeptide that is an effective catalyst in the Strecker amino acid synthesis has also been prepared from the glutamic acid derivative.[3]

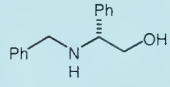
(1) Abell, A.D. et al. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1655. (2) Abell, A.D.; Oldham, M.D. *J. Org. Chem.* **1997**, *62*, 1509. (3) Iyer, M.S. et al. *J. Am. Chem. Soc.* **1996**, *118*, 4910.

46,896-7 (*S*)-(+)-3-(Benzyloxycarbonyl)-5-oxo-4-oxazolidineacetic acid, 97% **1g $27.00; 5g $90.00**



42,992-9 (*S*)-(+)-3-(Benzyloxycarbonyl)-5-oxo-4-oxazolidinepropionic acid, 97% **1g $27.00; 5g $90.00**

Starting material for α-amino phosphonic acids and 1,3-oxazolidines that can be diastereoselectively ring-opened with Grignard reagents.[1,2] Amides derived from this compound can also be alkylated diastereoselectively.[3]



(1) Maury, C. et al. *J. Org. Chem.* **1996**, *61*, 3687. (2) Higashiyama, K. et al. *J. Chem. Soc., Perkin Trans. 1* **1994**, 351. (3) Micouin, L. et al. *Tetrahedron Lett.* **1994**, *35*, 7223.

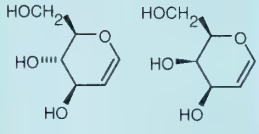
45,776-0 (*R*)-(–)-*N*-Benzyl-2-phenylglycinol, 98% **1g $21.00; 5g $70.00**

The unnatural amino acid 3'-tetrahydrofuranyl glycine has been prepared from this compound. It has been used as an asparagine surrogate in the design of HIV protease inhibitors.

Thompson, W.J. et al. *J. Am Chem. Soc.* **1993**, *115*, 801.

30,975-3 (*R*)-(–)-3-Hydroxytetrahydrofuran, 98% **250mg $21.00; 1g $58.50**

A number of oligosaccharides with biological activity have been prepared from these reagents. Examples include aureolic acid antibiotics and a human breast tumor antigen.[1,2]

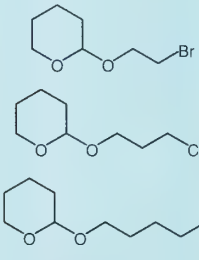


(1) Roush, W.R.; Lin, X.-F. *J. Am. Chem. Soc.* **1995**, *117*, 2236. (2) Park, T.K. et al. *ibid.* **1996**, *118*, 11488.

46,405-8 D-Glucal, 97% **1g $12.50; 10g $69.00**

46,223-3 D-Galactal, 95% **250mg $20.00; 1g $56.00**

Monoprotected Building Blocks



These compounds are widely used synthetic intermediates. Examples include the preparation of Wittig reagents, ethers, and more highly functionalized alcohols.[1-3]

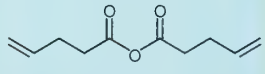
(1) Anantanarayan, A. et al. *J. Org. Chem.* **1986**, *51*, 752. (2) Marinier, A. et al. *Tetrahedron Lett.* **1988**, *29*, 6215. (3) Gibson, H.W. et al. *J. Org. Chem.* **1993**, *58*, 3748.

47,539-4 2-(2-Bromoethoxy)tetrahydro-2*H*-pyran, 96% **5mL $25.00; 25mL $83.50**

46,691-3 2-(3-Chloropropoxy)tetrahydro-2*H*-pyran, 97% **10mL $22.00; 50mL $73.50**

46,556-9 2-(4-Chlorobutoxy)tetrahydro-2*H*-pyran, 96% **1mL $13.00; 10mL $89.50**

Protecting Group for Amines

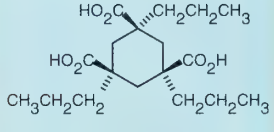


This anhydride is widely used to protect amines. For example, pent-4-enoyl protected nucleosides have been used in oligonucleotide synthesis.[1,2] Deprotection is accomplished under mild conditions.[3]

(1) Iyer, R.P. et al. *Tetrahedron* **1997**, *53*, 2731. (2) Iyer, R.P. et al. *J. Org. Chem.* **1995**, *60*, 8132. (3) Madsen, R. et al. *ibid.* **1995**, *60*, 7920.

47,180-1 4-Pentenoic anhydride, 99% **5mL $35.50; 25mL $118.00**

Kemp's Triacid Analog

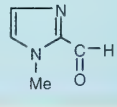


The tripropyl analog of Kemp's triacid has been used to prepare a number of compounds for molecular recognition studies.[1,2] The tripropyl groups provide enhanced solubility of the binding hosts in organic solvents.

(1) Jeong, K.-S.; Pyun, S.Y. *Tetrahedron Lett.* **1994**, *35*, 7041. (2) Wintner, E.A. et al. *J. Am. Chem. Soc.* **1994**, *116*, 8877.

43,645-3 *cis,cis*-1,3,5-Tripropyl-1,3,5-cyclohexanetricarboxylic acid, 97% **250mg $35.00; 1g $105.00**

Heterocycle Synthon



This imidazole has been used to prepare quadrupolar azolophanes and imidazolyl porphyrins.[1,2]

(1) Alcalde, E. et al. *Tetrahedron* **1996**, *52*, 15171 (2) Kobuke, Y.; Miyaji, H. *J. Am. Chem. Soc.* **1994**, *116*, 4111.

47,512-2 1-Methyl-2-imidazolecarboxaldehyde, 98% **1g $15.50; 5g $51.50**

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About our Cover

The painting on our cover is *The Country School* (oil on canvas, 54.3 x 97.5 cm) by Winslow Homer (1836-1910). In this painting, the artist depicts a rural schoolroom in an upstate New York town he had visited in 1870. The sunlight streaming through the window curtains suggests the fresh atmosphere of the country day and contrasts with the controlled geometry of the classroom.

Winslow Homer developed his interest in scenes of everyday life as a magazine illustrator in the 1850s in Boston, where he worked primarily in the medium of wood engraving. His earliest paintings feature humble scenes rendered in contrasting lights and darks. Homer's images of American life show authentic characters in their native environments, without the overly sentimental qualities that mark many contemporary genre scenes.

This painting is in the collection of The Saint Louis Art Museum.

Lab Notes

Protocol for Purifying α-Ketocarboxylic Acids

Over previous years we have had to prepare some α-ketocarboxylic acids. These compounds are key intermediates in the synthesis of many pharmaceutical products. Their purification has previously been carried out using Kugelrohr distillation or flash column chromatography. Whilst these are excellent and useful techniques in their own right, they are (1) less suited to thermally unstable compounds since recovery losses occur, and (2) it is often more difficult to elute very polar compounds in a pure state since the polar eluent, frequently needed to effect the separation, "drags down" impurities. In addition, these compounds are sometimes unstable on silica gel.

The following protocol that we have used to purify these materials is fast and reliable, and gives virtually quantitative recoveries.

The reaction solvents are removed from the reaction mixture by evaporation. The crude mixture is then treated with diethyl ether followed by potassium carbonate. The potassium ketocarboxylate salt rapidly precipitates out leaving the impurities in solution. The supernatant liquid is then decanted, and the residue is triturated with a little diethyl ether. This ether wash is also decanted. The precipitate is suspended in diethyl ether and acidified with aqueous hydrochloric acid to pH 3. After shaking, the ether layer is separated, dried, and evaporated to yield the pure α-ketocarboxylic acid almost quantitatively.

Dr. Craig J. Roxburgh
Christopher Ingold Laboratories
University College London, University of London
20 Gordon Street
London, WC1H OAJ, England

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Installing a glass capillary column in a gas chromatograph is often a frustrating process. I find that Parafilm® can help in connecting the column to the detector or inlet. A small piece (about 3 x 6 cm) is folded in half behind the ferrule and nut to hold these parts still and can be used to position the end of the column more precisely (see diagram).

The Parafilm® won't slip and is a good finger hold on the column itself. Removal is easy and leaves no adhesive residue.

Sincerely,

David Van Horn, graduate student
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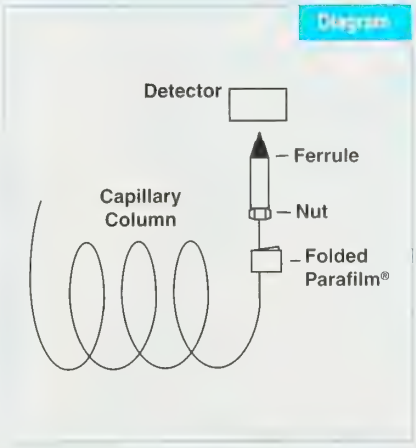
Salt Lake City, UT 84106



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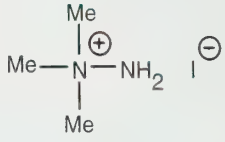


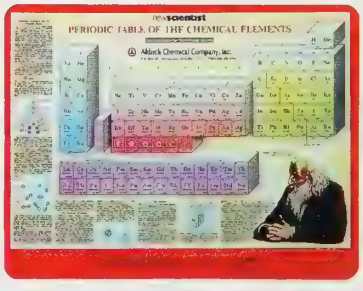
Dr. Philip Pagoria of the Lawrence Livermore National Laboratory kindly suggested we offer 1,1,1-trimethylhydrazinium iodide (TMHI). This compound acts as an aminating agent in the vicarious nucleophilic substitution of hydrogen, and is superior to other nucleophilic aromatic aminating reagents.

Chem. Eng. News **1996**, *Apr. 15*, 34.

47,162-3 1,1,1-Trimethylhydrazinium iodide, 98% 10g $19.50; 50g $65.00

Naturally, we made this useful reagent. It was no bother at all, just a pleasure to be able to help.

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, *Aldrichimica Acta*). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. **Z15,000-2**). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. **Z24,409-0**). It is Teflon®-coated, 8½ x 11in., with a full-color periodic table on the front. We reserve the right to retain all entries for future consideration.



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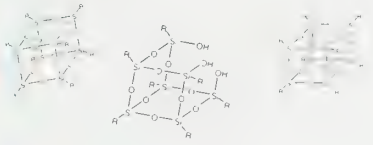
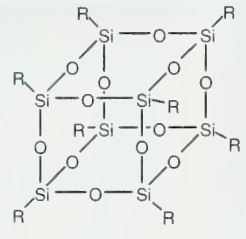
Silsesquioxanes

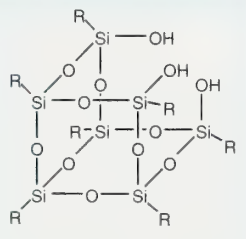


Silsesquioxanes, which possess the empirical formula $RSiO_{1.5}$, are a class of compounds that derive their name from the one and one-half, or *sesqui*, stoichiometry of oxygen bound to silicon. Substituents on silicon can include hydrogen, alkyl, alkenyl, alkoxy and aryl. The octafunctional silsesquioxanes **1** and **2** have found increased use as precursors to new inorganic/organic hybrid polymers.[1-3] The incompletely condensed trisilanol **3** can react with a variety of compounds having the formula $RMCl_3$ (M=main group), or with transition-metal complexes, to form completely condensed silsesquioxanes with one unique functional group **4-8**.[4-8]



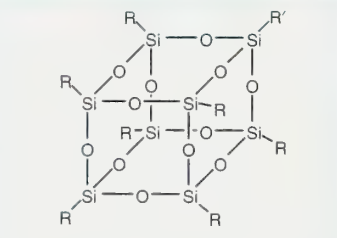
1	R=vinyl	**47,542-4**
2	R=dimethylsilyloxy	**47,654-4**

When the R group is polymerizable or graftable, the result is a novel class of compounds called **P**olyhedral **O**ligomeric **Sil**sesquioxanes, commonly called *POSS* monomers.[9,10] These monofunctional silsesquioxanes can be polymerized using standard techniques to give novel hybrid materials.[11,12]



3	R=cyclopentyl	**46,857-6**

There are numerous applications for substituted silsesquioxanes, including their use as models for silica surfaces,[13-15] Wittig reagents,[16] heterogeneous silica-supported transition-metal[17-19] and rare-earth catalysts,[20] and as preceramic coatings that can be pyrolyzed to silicon carbide (SiC),[21-23] nitrided glass (in combination with NH_3),[24] silicon oxynitride (Si_2ON_2),[25] aluminosilicates,[26,27] silica-reinforced composites,[28] and a variety of microporous materials.[29-30]



4	R′=allyl; R=cyclopentyl	**46,859-2**
5	R′=hydrogen; R=cyclopentyl	**46,858-4**
6	R′=2-(5-norbornen-2-yl)ethyl; R=cyclopentyl	**46,860-6**
7	R′=3-(methacryloyloxy)propyl; R=cyclopentyl	**46,862-2**
8	R′=4-vinylphenyl; R=cyclopentyl	**46,861-4**

Aldrich offers a growing selection of specialty silsesquioxanes with a variety of functional groups. For more information on silsesquioxanes or for organometallic compounds not listed here, please call our Technical Services Department at **800-231-8327**.

46,859-2 NEW! **1-Allyl-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane** *(Allyl-POSS)* **1g $45.00; 5g $200.00**

46,857-6 NEW! **1,3,5,7,9,11,14-Heptacyclopentyltricyclo[7.3.3.1^{5,11}]heptasiloxane-***endo***-3,7,14-triol,** 95% *(Trisilanol-POSS)* **1g $32.00; 10g $225.00**

46,862-2 NEW! **3-(3,5,7,9,11,13,15-Heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxan-1-yl)-propyl methacrylate** *(Propylmethacryl-POSS)* **1g $39.00; 10g $274.00**

46,858-4 NEW! **1-Hydrido-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane,** 95% *(Hydrido-POSS)* **1g $39.00; 10g $274.00**

46,860-6 NEW! **1-[2-(5-Norbornen-2-yl)ethyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane** *(Norbornenylethyl-POSS)* **1g $60.00; 5g $275.00**

47,654-4 NEW! **1,3,5,7,9,11,13,15-Octakis(dimethylsilyloxy)-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane** *[Octakis(dimethylsilyloxy)silsesquioxane]* **1g $20.00; 10g $150.00**

47,542-4 NEW! **1,3,5,7,9,11,13,15-Octavinylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane,** 97% *[Octavinylsilsesquioxane]* **1g $35.00; 10g $275.00**

46,861-4 NEW! **1-(4-Vinylphenyl)-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane** *(Vinylphenyl-POSS)* **1g $60.00; 5g $275.00**

References: (1) Feher, F.J. et al. *Chem. Commun.* **1997**, 1185. (2) Sellinger, A.; Laine, R.M. *Macromolecules* **1996**, *29*, 2327. (3) Sellinger, A. et al. *J. Mater. Chem.* **1996**, *8*, 1592. (4) Feher, F. J. et al. *Chem. Commun.* **1997**, 829. (5) Voigt, A. et al. *Organometallics* **1996**, *15*, 5097. (6) Feher, F.J. et al. *Polyhedron* **1995**, *14*, 3239. (7) Budzichowski, T.A. et al. *J. Am. Chem. Soc.* **1991**, *113*, 689. (8) Feher, F.J.; Weller, K.J. *Inorg. Chem.* **1991**, *30*, 880. (9) Tsuchida, A. et al. *Macromolecules* **1997**, *30*, 2818. (10) Lichtenhan, J.D et al. *Comments Inorg. Chem.* **1995**, *17*, 115. (11) Lichtenhan, J.D et al. *Macromolecules* **1995**, *28*, 8435. (12) Shokey, E. et al. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 515. (13) Feher, F.J. et al. *Organometallics* **1991**, *10*, 2526. (14) Feher, F.J.; Newman, D.A. *J. Am. Chem. Soc.* **1990**, *112*, 1931. (15) Feher, F.J. et al. *ibid.* **1989**, *111*, 1741. (16) Feher, F.J. et al. *Organometallics* **1995**, *14*, 2009. (17) Feher, F.J.; Tajima, T.L. *J. Am. Chem. Soc.* **1994**, *116*, 2145. (18) Edelmann, F.T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 586. (19) Feher, F.J. et al. *J. Am. Chem. Soc.* **1991**, *113*, 3618. (20) Herrmann, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1285. (21) Burns, G.T. et al. *Chem. Mater.* **1992**, *4*, 1313. (22) White, D. et al. *Adv. Ceram. Mater.* **1987**, *2*, 45. (23) White, D. et al. *ibid.* **1987**, *2*, 53. (24) Kamiya, K. et al. *J. Noncryst. Solids* **1986**, *83*, 208. (25) Laine, R.M. et al. *Ultrastructure Processing of Advanced Ceramics;* Mackenzie, D.J.; Ulrich, D.R., Eds.; Wiley-Interscience: New York, **1988**; p761. (26) Feher, F.J. et al. *J. Am. Chem. Soc.* **1992**, *114*, 9686. (27) Feher, F.J.; Weller, K.J. *Organometallics* **1990**, *9*, 2638. (28) Mantz, R.A. et al. *Chem. Mater.* **1996**, *8*, 1250. (29) Lee, S. et al. *J. Am. Chem. Soc.* **1994**, *116*, 11819. (30) Agaskar, P.A. *J. Chem. Soc., Chem. Commun.* **1992**, 1024.

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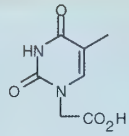
Aldrichimica Acta

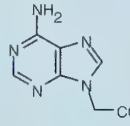
Volume 30, Number 4, 1997 *(Last issue in 1997)*

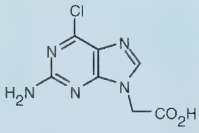
Asymmetric Synthesis Using Rhodium-Stabilized Vinylcarbenoid Intermediates

Dimethyl tricyclo[4.2.1.$0^{2,5}$]nona-3,7-diene-3,4-dicarboxylate: A Versatile Ambident Dienophile

New Products





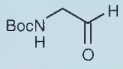


PNA Monomers

Peptide nucleic acids (PNAs) are oligonucleotide analogs capable of mimicking RNA and DNA fragments.[1] The PNA monomers shown here have been successfully coupled to alkyl *N*-(2-Boc-aminoethyl)glycinates, both in solution[1] and in the solid phase,[2] to give PNAs that are resistant to biological degradation.

(1) Farèse, A. et al. *Tetrahedron Lett.* **1996**, *37*, 1413. (2) Dueholm, K.L. et al. *J. Org. Chem.* **1994**, *59*, 5767.

44,895-8	**Thymine-1-acetic acid,** 98%	**5g $32.00; 25g $107.00**
46,176-8	**Ethyl adenine-9-acetate,** 97%	**5g $30.00; 25g $100.00**
47,856-3	**2-Amino-6-chloro-9*H*-purine-9-acetic acid,** 97%	**1g $60.00**

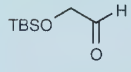


Acetaldehyde Derivatives

Boc-Protected aminoacetaldehyde has recently been used in the synthesis of peptide nucleic acids,[1] water-soluble camptothecin derivatives,[2] and *cis*-zeatin.[3]

(1) Finn, P.J. et al. *Nucleic Acids Res.* **1996**, *24*, 3357. (2) Xie, Z.-F. et al. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 2189. (3) Evidente, A. et al. *Chem. Pharm. Bull.* **1992**, *40*, 1937.

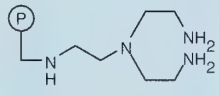
47,265-4 ***tert*-Butyl *N*-(2-oxoethyl)carbamate** **1g $21.00**

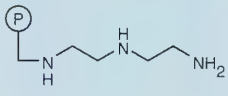


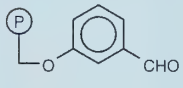
TBS-Protected hydroxyacetaldehyde was utilized in the synthesis of silyl dienol ethers,[1] and in the preparation of hydroxylated steroid side chains.[2] It also served as a building block for a 2-isocephem synthon[3] and a rhizoxin[4] structural fragment.

(1) Sodeoka, M. et al. *J. Am. Chem. Soc.* **1990**, *112*, 4906. (2) Mikami, K. et al. *J. Chem. Soc., Chem. Commun.* **1994**, 495. (3) Aszodi, J. et al. *Tetrahedron* **1990**, *46*, 1579. (4) Provencal, D.P. et al. *Tetrahedron Lett.* **1995**, *36*, 6033.

44,945-8 **(*tert*-Butyldimethylsilyloxy)acetaldehyde** **1g $28.90; 5g $95.60**







Resins for Combinatorial Synthesis

These high-loading polymeric scavengers have been used in the purification of crude reaction mixtures from solution-phase combinatorial synthesis.[1,2]

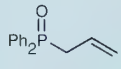
(1) Booth, R.J.; Hodges, J.C. *J. Am. Chem. Soc.* **1997**, *119*, 4882. (2) Parlow, J.J. et al. *J. Org. Chem.* **1997**, *62*, 5908.

47,210-7	**Tris(2-aminoethyl)amine, polymer-supported,** 4.0-4.5 mmol N/g resin	**5g $37.50; 25g $125.00**
47,978-0	**Diethylenetriamine, polymer-bound,** 2.5-3.0 mmol N/g resin	**5g $60.00; 25g $230.00**

This new linker has been used in solid-phase organic synthesis as an intermediate to a traceless, photolabile safety-catch linker.

Routledge, A. et al. *Tetrahedron Lett.* **1997**, *38*, 1227.

47,788-5 **3-Benzyloxybenzaldehyde, polymer-bound,** 1.0-1.5 mmol aldehyde/g resin **5g $60.00; 25g $230.00**

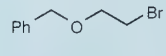


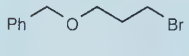
Olefination Reagent

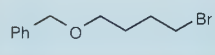
Toyota et al. have successfully employed this olefination reagent in the synthesis of many natural products, including the plant growth regulator gibberellin A_{12},[1] and the antitumor agents (+)-aphidicolin[2] and stemodin.[3] The reagent is used to prepare selectively *E*-1,3-dienes that undergo intramolecular Diels-Alder reactions to provide the proper carbocyclic framework.

(1) Toyota, M. et al. *Tetrahedron* **1995**, *51*, 6927. (2) Toyota, M. et al. *ibid.* **1996**, *52*, 10347. (3) Toyota, M. et al. *ibid.* **1994**, *50*, 1093.

47,796-6 **Allyldiphenylphosphine oxide,** 97% **10g $28.00**







Benzyl Bromoalkyl Ethers

These versatile building blocks have recently been utilized in the preparation of enantiomerically pure oxazoline *N*-oxides for asymmetric aldol condensations,[1] in the synthesis of (+)-lentiginosine,[2] and in the formation of a masked unnatural amino acid.[3]

(1) Berranger, T.; Langlois, Y. *J. Org. Chem.* **1995**, *60*, 1720. (2) Giovannini, R. et al. *ibid.* **1995**, *60*, 5706. (3) Guzi, T.J.; Macdonald, T. L. *Tetrahedron Lett.* **1996**, *37*, 2939.

47,481-9	**Benzyl 2-bromoethyl ether,** 97%	**1g $12.75; 10g $88.00**
38,204-3	**Benzyl 3-bromopropyl ether,** 98%	**1g $12.70; 10g $87.30**
45,970-4	**Benzyl 4-bromobutyl ether,** 90%	**1g $12.75; 10g $88.00**

Aldrichimica Acta

Volume 30, Number 4, 1997

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About our Cover

The Simon Vouet (1590–1649) painting on our cover, *The Muses Urania and Calliope* (oil on wood 31⅛ x 49⅜ in.), depicts two allegorical female figures reclining in front of a classical portico. On the left is the Muse of Astronomy, Urania, robed in celestial blue, wearing a diadem of six stars, and supported by an astral globe. She is accompanied by one of her eight sisters, Calliope, the Muse of Epic Poetry. Calliope holds a bound volume of Homer's *Odyssey*, one of the best known epic poems she inspired.

In all probability, this tranquil scene is part of a series executed by Vouet for a wealthy Parisian patron in the 1630s. The entire ensemble does not seem to have survived, but four other remaining works suggest that the picture's original context was a decorative scheme illustrating all nine Muses and the god of intellect, Apollo, whom they served. The picture's compositional elegance, figural equilibrium, and delicate color harmonies provided the perfect setting for *salon* life during Louis XIII's reign.

The device of incorporating the Muses in room decor appeared in late fifteenth-century Italy and continued to enjoy popularity in seventeenth-century France. By implication, the presence of the nine goddesses transformed a given architectural space into a Temple of the Muses or *Mouseion*—from which our word *museum* has evolved.

This painting is part of the Samuel H. Kress collection at the National Gallery of Art.

Lab Notes

Clean and Efficient Procedure for the Complete Removal of Reddish, Colloidal Selenium from Reaction Mixtures

The complete removal of selenium byproducts (notably H_2SeO_3)[1] from a reaction mixture is a nuisance well-known to synthetic chemists using selenium dioxide (SeO_2). Recently, we have engaged in synthesizing some formylpyridine derivatives utilizing SeO_2, and we have been troubled by the same problem. In our case, it is largely worsened by the coordination of SeO_2 and/or its secondary derivatives with the pyridine nitrogen (observed by NMR).

Though one communication was published in 1978 in your journal dealing with the removal of selenium from a reaction mixture (by briefly heating the mixture in DMF to cause the black tar formed to precipitate out of the solution),[2] the method does not work well in our experiments, even with extensive silica gel column chromatography.

We wish to report a safe, clean, and efficient procedure for the complete removal of reddish, colloidal selenium by simply stirring the reaction mixture (usually in dioxane) with anhydrous $NaHCO_3$ powder (to remove selenic acid), anhydrous $MgSO_4$ (to remove H_2O), then filtering through a thin pad of a 1:1 mixture of Florisil® and Celite® (both are available from Aldrich Chemical Co.), and rinsing the paste with a suitable solvent such as dichloromethane, ethyl acetate, or acetone. The filtrate usually gives no indication of the existence of selenium species.

(1) Fieser, L.F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, pp 992-993. (2) Milstein, S.R.; Coats, E.A. *Aldrichimica Acta* **1978**, *11*, 10.

Rex X-F. Ren, Ph.D., and
Koji Nakanishi, Ph.D.
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Many of our chemistry labs require a large amount of starch indicator on hand. Preparing starch solutions for chemistry or biology labs by suspending the starch in cold water, and then slowly bringing the suspension to a boil to dissolve the starch is a time-consuming process. A good way to speed the preparation of starch solution is first to bring water for the solution to a boil. While heating, mix the starch into a column of cold water representing about 10% of the intended starch solution. Simply dump the small volume of cold starch suspension into the boiling water. The starch will go into solution instantly. Allow to cool before use.

Leo V. Carr, Lab Manager
College Misericordia
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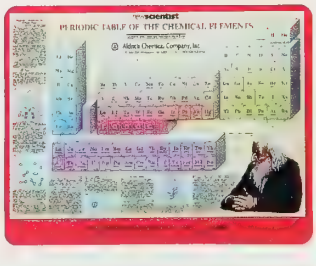
Dallas, PA 18612-1098

Editor's Note: For a discussion of the issues surrounding the dissolution of starch in water, the reader should consult, among others, the following two references: (1) Mitchell, W.A. *J. Chem. Educ.* **1977**, *54*, 132, and (2) Green, M.M.; Blankenhorn, G.; Hart, H. *ibid.* **1975**, *52*, 729.

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, *Aldrichimica Acta*). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. **Z15,000-2**). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. **Z24,409-0**). It is Teflon®-coated, 8½ x 11in., with a full-color periodic table on the front. We reserve the right to retain all entries for future consideration.



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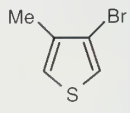

Professor Mario Leclerc at the Université de Montreal kindly suggested that we offer this thiophene. It has been used to prepare conducting and chromic regioregular polythiophenes.[1,2]

(1) Faïd, K.; Leclerc, M. *J. Chem. Soc., Chem. Commun.* **1996**, 2761. (2) Lévesque, I.; Leclerc, M. *Chem. Mater.* **1996**, *8*, 2843.

47,499-1 3-Bromo-4-methylthiophene, 95%
1g $9.50; 5g $32.00

Naturally, we made this useful compound. It was no bother at all, just a pleasure to be able to help.

It is interesting how customers see us and our commitment to service; for example, we recently received the following e-mail:

I am in receipt of Volume 30, Number 1, 1997 of your *Aldrichimica Acta* magazine.

This issue's cover, Sir Edwin Henry Landseer's "Attachment", struck me as particularly interesting. The picture depicts a "faithful terrier's long vigil beside the lifeless body." This cover generated a lot of interest in our laboratory.

My question to you is this: Does the cover have a secondary meaning?

One of the most interesting possibilities might be that the faithful terrier's vigil could be interpreted as Aldrich's long-standing commitment to its customers.

What do you think?

I look forward to more interesting choices of fine artwork on the covers of your publications.

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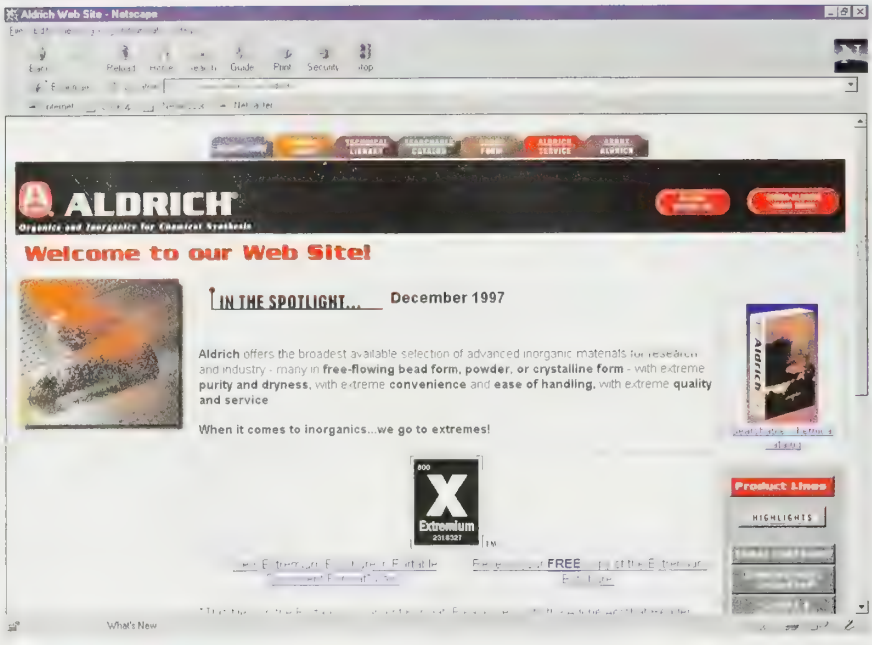

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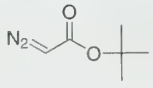
Aldrichimica Acta

Volume 31, Number 1, 1998

Applications of cis-1-Amino-2-indanol in Asymmetric Synthesis

Synthetic Applications of Zinc Borohydride

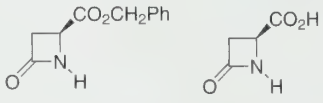
New Products



tert-Butyl diazoacetate is widely utilized for cyclopropane synthesis. High enantioselectivities have been achieved by utilizing chiral catalysts such as Co(III)-salen complexes or bisoxazolines.[1,2]

(1) Fukuda, T.; Katsuki, T. *Tetrahedron* **1997**, *53*, 7201. (2) Bedekar, A.V. et al. *J. Org. Chem.* **1997**, *62*, 2518.

48,075-4 *tert*-Butyl diazoacetate **1g $34.00**

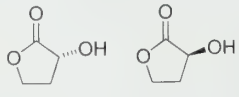


Building blocks for γ-keto-α-amino acids,[1] and lactendiynes.[2]

(1) Baldwin, J. E. et al. *Tetrahedron* **1995**, *51*, 4733. (2) Banfi, L. et al. *ibid.* **1997**, *53*, 3249.

46,897-5 Benzyl (*S*)-(–)-4-oxo-2-azetidinecarboxylate, 97% **1g $18.50; 5g $62.00**

47,327-8 (*S*)-(–)-4-Oxo-2-azetidinecarboxylic acid, 98% **500mg $28.50; 1g $48.00**

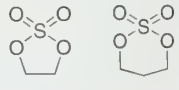


The polyether antibiotic monensin,[1] an A-ring synthon for vitamin D_3 analogs,[2] and pesticides have been prepared from these hydroxybutyrolactones.[3]

(1) Collum, D.B. et al. *J. Am. Chem. Soc.* **1980**, *102*, 2118. (2) Dauben, W.G.; Lewis, T.A. *Synlett* **1995**, 857. (3) Buser, H.P. et al. *Tetrahedron* **1991**, *47*, 5709.

44,423-5 (*S*)-(–)-α-Hydroxy-γ-butyrolactone, 97% (98% ee/GLC) **1g $33.50; 5g $112.00**

44,428-6 (*R*)-(+)-α-Hydroxy-γ-butyrolactone, 97% (98% ee/GLC) **1g $48.00**



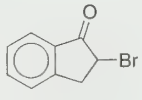
Compound **1** is often used as an ethylene oxide equivalent.[1,2] Compound **2** also undergoes ring opening through nucleophilic attack at carbon. These compounds have been utilized in the preparation of 3-(2'-hydroxyethyl)azetidin-2-ones[3] and glycol sulfonate surfactants.[4]

1 **2**

(1) Lohray, B.B. *Synthesis* **1992**, 1035. (2) Angelaud, R. et al. *Tetrahedron Lett.* **1995**, *36*, 3861. (3) Baldwin, J.E. et al. *Tetrahedron* **1995**, *51*, 5169. (4) Gautun, O.R. *Acta Chem. Scand.* **1996**, *50*, 170.

47,169-0 1,3,2-Dioxathiolane 2,2-dioxide, 98% **5g $32.50; 25g $108.50**

46,416-3 1,3-Propanediol cyclic sulfate, 98% **5g $29.75; 25g $99.00**



A number of compounds with potential pharmacological activity have been prepared from this indanone. Examples include antioxidants containing indoline chromophores,[1] and antiulcer agents derived from indeno[1,2-*d*]thiazoles.[2]

(1) Brown, D.W. et al. *Tetrahedron* **1991**, *47*, 4383. (2) Inoue, H. et al. *Yakugaku Zasshi* **1994**, *114*, 523.

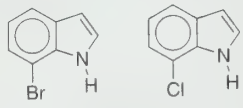
46,350-7 2-Bromo-1-indanone, 90% **5g $22.50; 25g $75.00**

$Ph_3P=NTMS$

This aza-Wittig reagent has been used to prepare *N*-Cbz-protected β-sulfinylenamines,[1] cyanine dyes,[2] and phosphorane iminato complexes of a variety of elements including sulfur, aluminum, boron, and titanium.[3-6]

(1) Arnone, A. et al. *J. Org. Chem.* **1996**, *61*, 3375. (2) Mazieres, M.R. et al. *Tetrahedron* **1995**, *51*, 1405. (3) Folkerts, H. et al. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1986. (4) Heshmatpour, F. et al. *ibid.* **1995**, *621*, 443. (5) Moehlen, M. et al. *ibid.* **1996**, *622*, 1692. (6) Ruebenstahl, T. et al. *ibid.* **1995**, *621*, 953.

47,225-5 1,1,1-Trimethyl-*N*-(triphenylphosphoranylidene)-silanamine, 97% **5g $28.50; 25g $95.00**

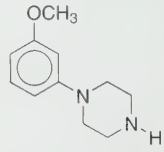


7-Substituted indoles[1,2] and indole alkaloids[2,3] are prepared from these heterocycles via palladium coupling or via the dianion.

(1) Dobson, D. R. et al. *Synlett* **1992**, 79. (2) Hutchings, R.H.; Meyers, A.I. *J. Org. Chem.* **1996**, *61*, 1004. (3) Banwell, M.G. et al. *J. Chem. Soc., Chem. Commun.* **1995**, 2551.

47,372-3 7-Bromoindole, 97% **250mg $20.00; 1g $56.00**

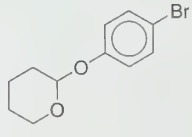
47,373-1 7-Chloroindole, 97% **250mg $20.00; 1g $56.00**



Potential high-affinity serotonin 5-HT_{1A} receptor ligands,[1] antibacterials,[2] and inhibitors of phosphodiesterases[3] have been prepared from this piperazine.

(1) Kuipers, W. et al. *J. Med. Chem.* **1995**, *38*, 1942. (2) Gadre, J. N. et al. *Indian J. Heterocycl. Chem.* **1994**, *3*, 289. (3) Monge, A. et al. *Arch. Pharm. (Weinheim, Ger.)* **1993**, *326*, 879.

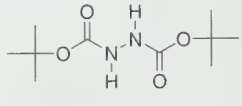
47,168-2 1-(3-Methoxyphenyl)piperazine, 95% **5g $28.00**



This protected bromophenol has been used to prepare *p*-ethynylphenol via a palladium coupling reaction.[1] A number of other *p*-substituted phenols have been synthesized using the Grignard reagent prepared from this compound.[2]

(1) Mery, S.J. et al. *Macromolecules* **1995**, *28*, 5440. (2) Ruenitz, P.C. et al. *J. Med. Chem.* **1996**, *39*, 4853.

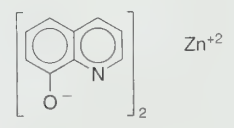
47,781-8 2-(4-Bromophenoxy)tetrahydro-2*H*-pyran, 98% **10g $18.70**



Valuable reagent for the preparation of symmetrical disubstituted hydrazines, pyrazolidines, and phthalazines.[1,2]

(1) Meissner, R. et al. *J. Am. Chem. Soc.* **1997**, *119*, 77. (2) Narukawa, Y. et al. *Tetrahedron* **1997**, *53*, 539.

14,046-5 Di-*tert*-butyl hydrazodiformate, 97% **10g $42.00**



Organic thin-film electroluminescent materials have been prepared from zinc quinolate.[1-3]

(1) Hopkins, T.A. et al. *Chem. Mater.* **1996**, *8*, 344. (2) Wang, G.M. et al. G*aodeng Xuexiao Huaxue Xuebao* **1995**, *16*, 230; *Chem. Abstr.* **1996**, *124*, 215861w. (3) Huang, Z. et al. *Gongneng Cailiao* **1995**, *26*, 362; *Chem. Abstr.* **1996**, *124*, 40857v.

47,175-5 8-Hydroxyquinoline, zinc salt, 99% **5g $25.40; 25g $84.20**

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About our Cover

The Dancing Couple (oil on canvas, 40-3/8 x 56-1/8 in.), by the Dutch artist Jan Steen (1625/26 – 1679), appears to represent a group of merrymakers. Under a vine-covered arbor outside a tavern they converse, drink, smoke, and watch a country bumpkin try to get a shy young woman to dance. Trying to play the dandy, the young peasant wears a jaunty cap adorned with cock feathers and an oversized white collar which is inappropriate for the rest of his costume. The crowds by the tents in the distance indicate that we are at a village fair or *kermis*. Steen's great empathy for the variety of characters of different ages and social classes who appear in his paintings is obvious, and extends to including himself in the picture. He is the man seated at the table stroking his companion affectionately under the chin.

More subtle meanings would have been recognized in the painting by the artist's contemporaries. The pair of figures which includes the artist himself, the old couple at the end of the table, and the loving mother holding her child in her lap all show an enduring love which contrasts with the transitory misalliance of the pair at the center of the picture. The broken eggs, the cut flowers spilled on the ground, and the boy blowing bubbles are all symbols of the transience of life and life's pleasures which would have been well understood in seventeenth century Holland.

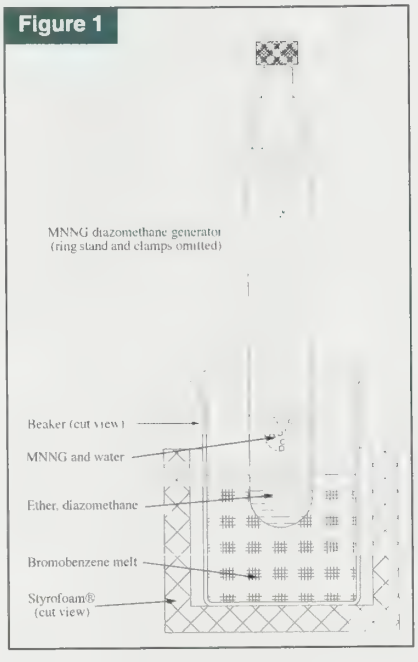
This painting is part of the Widener Collection at the National Gallery of Art.

Lab Notes

Improving the Production of Diazomethane by Generating It below Its Boiling Point

Although reactions with diazomethane are very rugged,[1] its preparation from MNNG has literally been quite volatile until we used cooling, as shown in **Figure 1**. We used the polished clear-seal-joint glass generator (Aldrich Cat. No. **Z10,159-1**) exclusively to rule out any contamination by the O-ring (Aldrich Cat. No. **Z10,100-1**). However, by using this apparatus, the chance of getting a usable diazomethane-ether solution was only slightly better than 50:50 because the gas was lost mainly through the glass joint. In contrast, a much more strongly colored ether solution is obtained when the following method is used.

Figure 1



The inner tube of the generator is charged with 1g MNNG and 1mL of water as recommended,[2] closed with two septa (the upper septum used in a previous run), placed into the outer vessel which contains about 6mL of ether (the ether should not touch the inner tube so as not to facilitate freezing of the aqueous solution in the inner tube), and the apparatus is held together with the clamp provided. The assembled generator is attached to a ring stand with an appropriate clamp and lowered into the bromobenzene melt (-31 °C), *the depth of insertion being adjusted to give an optimum between preventing the reagents from freezing (which would stop the generation of diazomethane) and having a large condensing (cold) area.* The melt is produced by pouring liquid nitrogen into bromobenzene until most (not all) of it solidifies. Here it is done in a beaker insulated with Styrofoam®; a small Dewar would probably be advantageous. After a few minutes of cooling, 1.5mL of 5 M NaOH is added over 1-2 min[2] (much faster addition than without this cooling). The buildup of pressure can be felt and monitored via the plunger of the syringe containing the NaOH solution. The reaction is allowed to continue for 30 min with occasional slight shaking of the generator, and liquid N_2 is added if needed to maintain the melt. The generator (still assembled) is then removed from the melt to allow it to warm up. Just before reaching room temperature the ether-diazomethane solution can be pipetted (positive displacement pipettes) as needed. For example, 100µL of an aqueous oxalic acid solution (can be an HPLC fraction; mobile phase: aqueous TFA; here usually below 30 mg/L oxalic), in a 5mL vial with a threaded Teflon® inlay cap, is titrated by shaking with the diazomethane solution in 100-500µL portions until the yellow color persists. After discarding the aqueous layer and evaporating the larger part of the ether layer with a micro refluxer,[3] which retains the diester, conventional MS can be used to obtain excellent mass spectra of the oxalic acid dimethyl ester. *We have used this generator hundreds of times without cooling and about twenty times with the cooling described here without ever experiencing a safety-related incident.*

References: (1) Diazomethane as a Highly Selective Fatty Acid Methylating Reagent for Use in Gas Chromatographic Analysis: Mueller, H.W. *J. Chromatogr., B* **1996**, *679*, 208. (2) The Preparation and Reactions of Diazomethane: Black, T.H. *Aldrichimica Acta* **1983**, *16*, 3. (3) Microliter Techniques in the Formation of New Derivatives for Gas Chromatographic Analysis: Dünges, W. *Anal. Chem.* **1973**, *45*, 963.

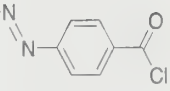
Hans W. Mueller, Ph.D.
Biotechnology Center, Justus Liebig University
Leihgestener Weg 217, D-35392 Giessen

Editor's Note: The reader should evaluate the suitability of a given experimental procedure for his/her purposes, and should exercise due caution in using any such procedure, especially for the first time. Anyone working with diazomethane must wear the proper protective attire and conduct all manipulations in a well-ventilated hood equipped with a safety shield. In addition to the references cited above, the reader is urged to consult other writeups and safety warnings about diazomethane generation and properties such as Moore, J.A.; Reed, D.E. *Org. Synth.* **1973**, *Coll. Col. V*, 351; or the *Aldrich Catalog Handbook of Fine Chemicals*, 1996-1997 ed., pp T218-220.

"Please Bother Us."

by Jai Nagarkatti, President

Professor David Morris of the University of Glasgow kindly suggested that we offer 4-(phenylazo)-benzoyl chloride. This compound has been used to prepare reversible photoregulatable enzyme inhibitors[1] and photoresponsive peptides.[2]



(1) Westmark, P.R. et al. *J. Am. Chem. Soc.* **1993**, *115*, 3416. (2) Yamamoto, H. et al. *Int. J. Biol. Macromol.* **1990**, *12*, 257

17,345-2 4-(Phenylazo)benzoyl chloride, 97%
1g $16.75; 5g $56.00

Naturally, we made this useful compound. It was no bother at all, just a pleasure to be able to help.

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, *Aldrichimica Acta*). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. **Z15,000-2**). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. **Z24,409-0**). It is Teflon®-coated, 8½ x 11in., with a full-color periodic table on the front. We reserve the right to retain all entries for future consideration.

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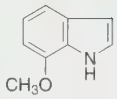
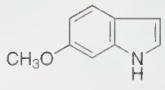
Aldrichimica Acta

Volume 31, Number 2, 1998

Benzotriazole-Based Intermediates: Reagents for Efficient Organic Synthesis

Manganese-Based Organic and Bioinorganic Transformations

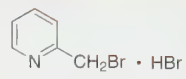
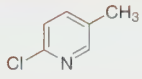
New Products

Important synthons which have been used to prepare a number of biologically active compounds. Examples include the preparation of apoyohimbines,[1] 3-(tetrahydropyridinyl)-indoles,[2] and platelet activating factor antagonists.[3]

(1) Leonard, J. et al. *Tetrahedron Lett.* **1997**, *38*, 3071. (2) Gharagozloo, P. et al. *Tetrahedron* **1996**, *52*, 10185. (3) Sheppard, G.S. et al. *J. Med. Chem.* **1994**, *37*, 2011.

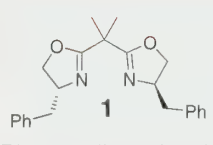
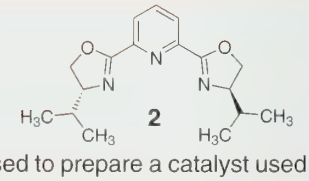
11,398-0 **7-Methoxyindole**, 97% **500mg $77.75**
13,985-8 **6-Methoxyindole**, 98% **500mg $77.75**

A number of biologically active heterocycles have been prepared from these pyridines. Examples include tachykinin NK_2 receptor antagonists and endothelin receptor antagonists.[1-3]

(1) Smith, P. W. et al. *J. Med. Chem.* **1995**, *38*, 3772. (2) Huang, L. J. et al. *Chem. Pharm. Bull.* **1992**, *40*, 2547. (3) Neidhart, W. et al. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 2223.

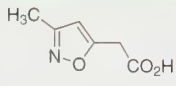
49,104-7 **2-(Bromomethyl)pyridine hydrobromide**, 98% **5g $21.00; 25g $70.00**
49,532-8 **6-Chloro-3-picoline**, 98% **5mL $21.50; 25mL $72.00**

Bisoxazoline **1** has been used to prepare a catalyst used for the hetero- and carboannulation of allenes.[1] It has also been used to prepare a catalyst for highly stereoselective iron-mediated enediene carbocyclizations.[2] A catalyst for highly enantioselective hydrosilylation of ketones and for C-H insertion reactions has been prepared from ligand **2**.[3]

(1) Larock, R.C.; Zenner, J.M. *J. Org. Chem.* **1995**, *60*, 482. (2) Takacs, J.M. et al. *J. Org. Chem.* **1995**, *60*, 3473. (3) Nishiyama, H. et al. *Organometallics* **1991**, *2*, 500.

49,530-1 **[*R*(*R**, *R**)]-(+)-2,2'-Isopropylidenebis(4-benzyl-2-oxazoline)**, 95% **250mg $32.00; 1g $89.00**
47,749-4 **2,6-Bis-[(4*R*)-(+)-isopropyl-2-oxazolin-2-yl]pyridine**, 99% **250mg $21.50; 1g $60.00**

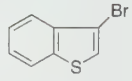


Cyclooxygenase and 5-lipoxygenase inhibitors have been prepared from this isoxazole.

Flynn, D.L. et al. *J. Med. Chem.* **1991**, *34*, 518.

48,968-9 **3-Methyl-5-isoxazoleacetic acid**, 98% **1g $15.00; 5g $50.00**

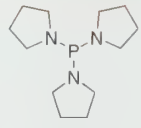
A variety of 3-substituted benzothiophenes have been prepared via lithiation of this compound. Examples include the trifluoromethyl ketone and the boronic acid.[1,2]



(1) Kerdesky, F.A.J.; Basha, A. *Tetrahedron Lett.* **1991**, *32*, 2003. (2) Thompson, W.J. et al. *J. Org. Chem.* **1988**, *53*, 2052.

49,497-6 **3-Bromothianaphthene**, 95% **5mL $26.00; 25mL $87.00**

This pyrrolidinyl phosphine has been used in the multigram synthesis of phosphorodithioate DNA.



Wiesler, W.T.; Caruthers, M.H. *J. Org. Chem.* **1996**, *61*, 4272.

49,392-9 **Tris(1-pyrrolidinyl)phosphine**, 97% **5mL $24.00; 25mL $80.00**

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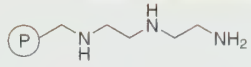
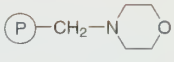


(1) Flynn, D.L. et al. *J. Am. Chem. Soc.* **1997**, *119*, 4874. (2) Parlow, J.J. et al. *J. Org. Chem.* **1997**, *62*, 5908. (3) Parlow, J.J. et al. *Tetrahedron Lett.* **1997**, *38*, 7959.

47,978-0 **Diethylenetriamine, polymer-bound**, 2.5-3.0 mmol N/g **5g $60.00; 25g $230.00**
49,438-0 **Diethylenetriamine, polymer-bound**, 4.0-5.0 mmol N/g **5g $65.00; 25g $250.00**

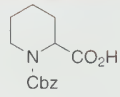
Employed as a high-capacity acid scavenger in parallel purification of reaction solutions. Often used in conjunction with other polymeric scavengers such as polymer-bound isocyanates to yield highly pure products.



Booth, R.J.; Hodges, J.C. *J. Am. Chem. Soc.* **1997**, *119*, 4882.

49,381-3 **Morpholine, polymer-bound**, 2.75-3.25 mmol N/g, 1 % cross-linked, 200-400 mesh **5g $42.00; 25g $140.00**

This protected pipecolinic acid has been used to prepare β-turn mimics and the natural product (±)-δ-coniceine.[1,2]



(1) Genin, M.J. et al. *J. Org. Chem.* **1993**, *58*, 860.
(2) Martin-Lopez, M.J.; Bermejo-Gonzalez, F. *Tetrahedron Lett.* **1994**, *35*, 4235.

49,502-6 **1-(Carbobenzyloxy)-2-piperidinecarboxylic acid**, 97% **5g $12.50; 25g $41.50**

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About Our Cover

Saint Cecilia and an Angel (oil on canvas, 34 5/8 x 42 1/2 in.) depicts Cecilia, a third-century Roman Christian. According to legend, she, her husband, Valerian, and his brother suffered martyrdom for their faith. It was said that Cecilia was so close to Heaven that she could hear the singing of the angels, and that her soul was so filled with Heavenly music that she invented the organ in order to express it. Consequently, she came to be regarded as the patron saint of music.

Although *Saint Cecilia and an Angel* traditionally has been attributed to Orazio Gentileschi (1563-1639), inconsistencies in the handling of the paint in various parts of the picture suggest that it was executed by not one, but two artists. As early as 1662 the name of Giovanni Lanfranco (1582-1647) was linked to the picture, and recent stylistic analysis and a rereading of the records documenting its provenance confirm that much of the painting was executed by Gentileschi before its completion by Lanfranco.

Study of X-radiographs, pigment analyses, and X-ray fluorescence also support this conclusion, but differences can be detected even with the naked eye. The fluid brushwork of the sleeves and boneless rubbery hands are both characteristic of Lanfranco's style, in contrast to the more literal representation of Gentileschi. The picture also shows the influence of Caravaggio, who used ordinary people rather than idealized types as models and showed them at close range emerging from a neutral space into a strong light, heightening both the realism and the expressiveness of the subject.

This painting is part of the Samuel H. Kress Collection at the National Gallery of Art.

Lab Notes

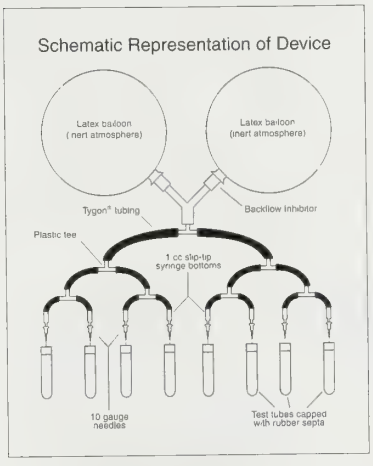
A Useful Technique for Creating and Maintaining Inert Atmospheres Simultaneously Within a Large Number of Reaction Vessels

Here is an interesting and effective method for providing respite from the cumbersome process of purging a large number of reaction vessels with an inert gas (i.e., N_2, Ar, etc.), and maintaining a positive (inert gas) pressure in all of them throughout the reaction process. In our laboratory, we carry out a large number of assays on the oxidative abilities of novel peptide ligand systems complexed with a number of different metal atoms. In order to assess each ligand's oxidative potential properly, all possible combinations of metal, ligand, oxidizing agent, and substrate must be examined in detail (as well as the necessary control environments). Needless to say, it is not unusual to be running 10-20 concurrent tests on any given day. The need to create and maintain an oxygen-free environment in each of these vessels is crucial in the determination of the effectiveness of each possible combination of components (in order to be assured that the oxygen atom was donated by the oxidizing agent). The purging process required to prepare and maintain this large number of separate inert atmospheres leads to a waste of valuable time, and can be shortened considerably through the use of the following apparatus.

The design of this apparatus is based essentially on the premise that a single source of positive pressure can be used to create and maintain inert environments in each of the reaction vessels (either from a balloon or directly from a tanked source). In prior reaction preparations and procedures, we have had to purge each reaction vessel separately, with each requiring its own source of positive pressure. Also, during the course of a reaction sequence in which separate balloons are used for individual reaction vessels, the chance that one of the balloons will pop (thereby violating the integrity of the enclosed inert atmosphere) is much greater than if only one source consisting of two balloons were used for all the vessels.

The apparatus consists of a single source of inert gas, comprised of two latex balloons equipped with backflow inhibitors. This arrangement insures the preservation of atmospheric integrity should one of the balloons pop—in which case it prevents gas loss through the hole created in the system—and maintains a positive pressure inside the reaction vessels. This gas introduction system is connected to a series of continuously branching tubes (through the use of 3-way plastic tees), each terminating in the "bottom" of a 1-mL slip-tip syringe which is fitted with a 10-gauge needle. The needle is then inserted into the septum at the top of the reaction vessel (usually a 16 x 125 mm test tube).

There are many other reasons for utilizing this apparatus besides its obvious, timesaving benefits. The use of balloons as the providers of positive inert pressure during extended-time reactions considerably reduces the amount of gas used as compared with the amount that would be needed if the "constant flow" method is employed.



Steve Flemer, Jr., Graduate Student
Department of Chemistry
University of Vermont
P.O. Box 5752
Burlington, VT 05402

Please turn to page 65 for another Lab Note selection entitled "Separating DMF from Alkylated Nucleosides by Silica Gel Column Chromatography".

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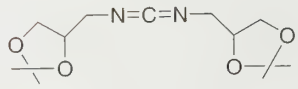


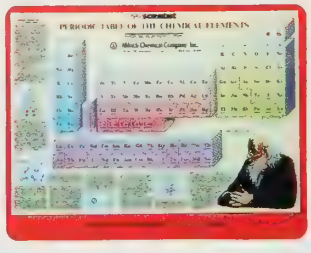
Dr. Henry Rapoport of the University of California, Berkeley kindly suggested that we make this carbodiimide (BDDC). It is an attractive alternative to dicyclohexylcarbodiimide (DCC) or diisopropylcarbodiimide (DIC) for peptide coupling reactions or O-acylations. An important advantage of BDDC versus DCC or DIC is that the urea byproduct formed during the coupling reaction is easily removed using a mild acid wash, alleviating the need for chromatographic purification of the product.

Gibson, F.S.; Park, M.S.; Rapoport, H. *J. Org. Chem.* **1994**, *59*, 7503.

48,212-9 **1,3-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethyl)carbodiimide,** 95%
1g $15.00; 10g $70.00

Naturally, we made this useful reagent. It was no bother at all, just a pleasure to be able to help.

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, *Aldrichimica Acta*). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. **Z15,000-2**). If we publish your *Lab Note*, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. **Z24,409-0**). It is Teflon®-coated, 8½ x 11in., with a full-color periodic table on the front. We reserve the right to retain all entries for future consideration.



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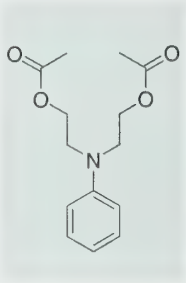
Aldrichimica Acta

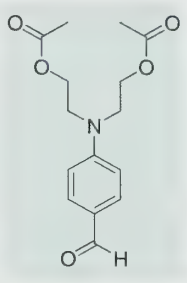
Volume 31, Number 3, 1998 (*Last issue in 1998*)

Transition-Metal-Based Lewis Acid Catalysts

New Products

Polymers with promising electro-optic features, including high second-order optical nonlinearity, good thermal and temporal stability, and low long-wavelength absorption, have been prepared from these two compounds.[1-3]



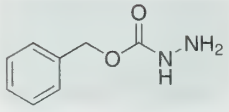


(1) Wang, P.N. et al. *Chem. Mater.* **1995**, *7*, 185. (2) Zhang, Y. et al. *Polymer* **1997**, *38*, 2893. (3) Sun, S.-S. et al. *Chem. Mater.* **1996**, *8*, 2539.

47,797-4 ***N*-Phenyldiethanolamine diacetate**, 97%
25mL $48.00

48,488-1 **4-[Bis[2-(acetyloxy)ethyl]amino]benzaldehyde**, 98%
10g $58.00

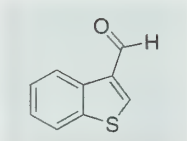
Benzyl carbazate is frequently used to prepare hydrazine-substituted compounds. Examples include azapeptides and hydrazine-substituted flavins.[1,2]



(1) Quibell, M. et al. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2843. (2) Kim, J.-M. et al. *J. Am. Chem. Soc.* **1995**, *117*, 100.

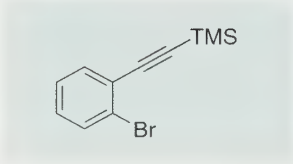
49,978-1 **Benzyl carbazate**, 98% **5g $28.00; 25g $94.00**

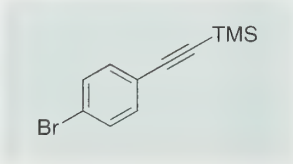
Benzo[*b*]naphtho[*d*]thiophene and [1]benzothieno[3,2-*h*]isoquinolines have been prepared from this aldehyde.[1,2]



(1) Castle, N. et al. *J. Heterocycl. Chem.* **1981**, *18*, 967. (2) Shafiee, A. et al. *ibid.* **1976**, *13*, 141.

49,496-8 **Thianaphthene-3-carboxaldehyde**, 95%
1g $20.00; 5g $67.00



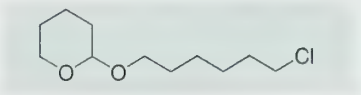


Molecular wires,[1] phenylethynyl oligomers,[2] angular phenylenes,[3] and dehydrobenzoannulenes[4] have been prepared from these arylacetylenes.

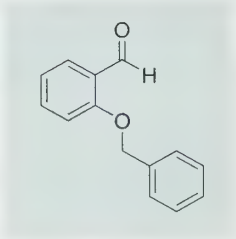
(1) Anderson, S. et al. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2383. (2) Hsung, R.P. et al. *Organometallics* **1995**, *14*, 4808. (3) Schmidt-Radde, R.H.; Vollhardt, K.P.C. *J. Am. Chem. Soc.* **1992**, *114*, 9713. (4) Haley, M.M. *Synlett* **1998**, 557.

48,469-5 **(2-Bromophenylethynyl)trimethylsilane**, 98%
5g $50.00

49,401-1 **(4-Bromophenylethynyl)trimethylsilane**, 98%
5g $35.00; 25g $117.00



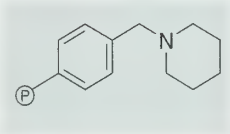
Leukotriene B_4 antagonists and blocking groups for rotaxanes have been prepared from these useful synthons.[1,2]

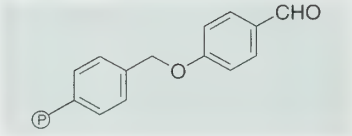


(1) Chan, W.K. et al. *J. Med. Chem.* **1996**, *39*, 3756. (2) Gibson, H.W. et al. *J. Org. Chem.* **1993**, *58*, 3748.

49,718-5 **2-(6-Chlorohexyloxy)tetrahydro-2*H*-pyran**, 95%
5mL $21.00; 25mL $70.00

49,974-9 **2-Benzyloxybenzaldehyde**, 98% **10mL $20.50; 50mL $68.50**





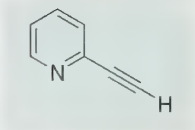
These polymer-bound reagents are used as scavengers in solid-phase organic synthesis. The polymer-bound piperidine is an acid scavenger, while the benzaldehyde is used to scavenge primary and secondary amines via formation of the imine.

Kaldor, S.W. et al. *Tetrahedron Lett.* **1996**, *37*, 7193.

49,461-5 **Piperidine, polymer-bound** **5g $40.00; 25g $140.00**

47,208-5 **4-Benzyloxybenzaldehyde, polymer-bound**
5g $50.00; 25g $167.00

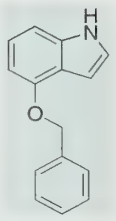
Polymers with interesting electrical properties have been prepared using ethynylpyridine.[1,2]



(1) Balogh, L. et al. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 703. (2) Gal, Y. et al. *Bull. Korean Chem. Soc.* **1998**, *19*, 22.

46,992-0 **2-Ethynylpyridine**, 98% **1g $20.00; 5g $67.00**

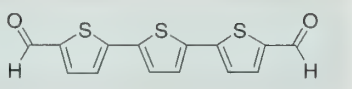
A number of heterocycles with promising pharmacological activity have been prepared from this indole.[1,2]



(1) Chan, W.K. et al. *J. Med. Chem.* **1996**, *39*, 3756. (2) Sheppard, G.S. et al. *ibid.* **1994**, *37*, 2011.

24,621-2 **4-Benzyloxyindole**, 98% **1g $102.00**

Oligothiophenes with interesting electronic and optical properties have been prepared from this terthiophene.[1,2]



(1) Novikova, T.S. et al. *Synth. Met.* **1996**, *83*, 47. (2) Wei, Y. et al. *Chem. Mater.* **1996**, *8*, 2659.

49,910-2 **2,2':5',2''-Terthiophene-5,5''-dicarboxaldehyde**, 97%
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About Our Cover

The Brown Family (oil on paper mounted on canvas, 23⅝ x 28½ in.) by the American artist Eastman Johnson (1824–1906) represents James Brown, whose father founded the international mercantile banking firm that still bears the name Brown Brothers and Company, with his wife Eliza and their grandson William in the parlor of their house on University Place in New York. It is at one time both a scene of everyday life and a group portrait, combining the two types of painting for which Johnson was best known. Signed and dated 1869, it is a record of the appearance of the home where the Browns had raised their family, commissioned from the artist in anticipation of a move further uptown to a new residence at Park Avenue and 37th Street.

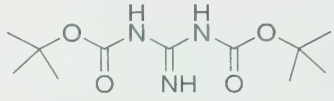
The Browns are shown seated by the fire in their comfortable parlor. Young William has interrupted his grandfather's reading of the evening paper, causing his grandmother to look up from her knitting. The room, with its paintings and other decorative objects, carved furniture, gilded frames, heavy red draperies, carved marble mantle, green wallpaper, strapwork ornament and figured carpet, reflects the affluence and social position of the Brown family. However, the appearance of this room was criticized as garish and tasteless when the painting was first exhibited. Nevertheless, when the Browns moved to their new Park Avenue home they had this room dismantled and reinstalled there, and their son John even later moved it into his own house.

This painting is a gift of David Edward Finley and Margaret Eustis Finley to the National Gallery of Art.

"Please Bother Us."

by Jai Nagarkatti

Jai Nagarkatti, President



Dr. Ganesan Vaidyanathan of the Department of Radiology at the Duke University Medical Center kindly suggested that we offer 1,3-bis(*tert*-butoxycarbonyl)guanidine. This reagent converts bromoalkanes to guanidines using sodium hydride,[1] and alcohols to guanidines using Mitsunobu's conditions.[2]

(1) Vaidyanathan, G.; Zalutsky, M.R. *J. Org. Chem.* **1997**, *62*, 4867.
(2) Dodd, D.S.; Kozikowski, A.P. *Tetrahedron Lett.* **1994**, *35*, 977.

49,687-1 1,3-Bis(*tert*-butoxycarbonyl)guanidine, 98%
5g $29.00

Naturally, we made this useful reagent. It was no bother at all, just a pleasure to be able to help.

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David R. Lide

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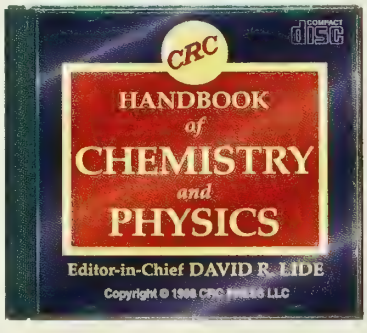

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From the Aldrich Bookshelf

Asymmetric Synthesis: Construction of Chiral Molecules Using Amino Acids

G.M. Coppola and H.F. Schuster, John Wiley & Sons, New York, NY, 1987, 393pp. Focuses on the use of amino acids and their second-generation derivatives to produce chiral reagents, intermediates, and final products.

Z16,762-2 $149.00

Stereoselective Synthesis

R.S. Atkinson, John Wiley & Sons, New York, NY, 1995, 600pp. Covers the majority of reaction types used in modern stereoselective synthesis. Introduces a simplified classification for reactions based on the number of chiral centers.

Z26,175-0 $233.10

The Logic of Chemical Synthesis

E.J. Corey and X.-M. Cheng, John Wiley & Sons, New York, NY, 1995, 436pp. Softbound. Discusses the logic underlying the analysis of complex synthetic problems.

Z27,174-8 $29.95

Molecular Spectroscopy Workbench: Advances, Applications, and Practical Advice on Modern Spectroscopic Analysis

E.W. Ciurczak, John Wiley & Sons, New York, NY, 1998, 476pp. Compiles and updates the best articles to date from the eleven-year history of *Spectroscopy* magazine's successful "Molecular Spectroscopy Workbench" column. From the fundamentals of important techniques to novel time- and money-saving ideas, it draws from a broad spectrum of recent developments in the field of molecular spectroscopy. Includes information about near- and midrange infrared techniques, optical rotation/circular dichroism, UV/Vis and fluorescence, mass spectrometry, acousto-optic tunable filters, fiber optics, and new hardware.

Z40,865-4 $79.95

Advanced Catalysts and Nanostructured Materials: Modern Synthetic Methods

W.R. Moser, Ed., Academic Press, New York, NY, 1996, 592pp. Provides a comprehensive review of the latest techniques for the preparation of advanced catalysts and solid-state materials of specific structure and morphology.

Z28,635-4 $85.00

NMR Data Processing

J.C. Hoch and A.S. Stern, Wiley-Liss, New York, NY, 1996, 196pp. Complete information about how to process, present, and perform error analysis on data obtained from modern nuclear magnetic resonance (NMR) experiments. Includes extensive examples for maximum comprehension.

Z40,858-1 $74.95

Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Two Volumes

B. Cornils and W.A. Herrmann, Eds., VCH Publishers, Weinheim, FRG, 1996, 1,246pp. Comprehensive treatment of one of the most important topics in organometallic chemistry. Explores both basic research and industrial applications through treatment of catalytic reactions and processes.

Z40,230-3 $603.75

The Encyclopedia of Reagents for Organic Synthesis

L.A. Paquette, Ed., John Wiley & Sons, New York, NY, 1995, 6234pp. Presents the facts in a "pros and cons" assessment of each reagent to give the complete picture. Where applicable, each entry includes: transformations recognized for the reagent; comparison of the specific properties of the reagent with those of other agents capable of equivalent chemistry; stereo-, regio-, and enantiocontrol qualifications.

8-volume set Z24,805-3 $3,950.00

Metal and Ligand Reactivity: An Introduction to the Organic Chemistry of Metal Complexes

E.C. Constable, VCH Publishers, New York, NY, 1996, 308pp. Introduction to the reactions and interactions between metal ions and ligands. Provides useful information for organic synthesis.

Z28,938-8 $131.25

Purification of Laboratory Chemicals

A must for any library!

4th ed., D.D. Perrin and W.L. Armarego, Eds., Butterworth, New York, NY, 1996, 450pp. Explains techniques of purification with specific methods for more than 4,000 chemicals and biochemicals.

Z28,581-1 $74.95

Asymmetric Synthetic Methodology

D.J. Ager and M.B. East, CRC Press, Boca Raton, FL, 1996, 483pp. Implements asymmetric synthesis in an industrial chemistry environment. Provides methodology to perform specific asymmetric transformations with emphasis on scope and limitations.

Z27,403-8 $113.00

Chiral Auxiliaries and Ligands in Asymmetric Synthesis

J. Seyden-Penne, John Wiley & Sons, New York, NY, 1995, 716pp. An in-depth guide for synthesis of chiral compounds in pharmaceutical and medical research. Provides an overview of the principles of physical organic chemistry governing stereoselection.

Z27,369-4 $79.95

Reductions in Organic Chemistry

2nd ed., M. Hudlicky, American Chemical Society, Washington, DC, 1996, 429pp. A compilation of the types of reductions undergone by the various classes of organic compounds. Describes the methods, reactants, and products of reductions.

Z28,591-9 $119.95

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These flasks are designed to permit complete removal of liquids using noncoring type syringe needles, gauges 12 to 20, that are used for piercing rubber septa. A small indentation or "dimple" at the bottom of the flask acts as a reservoir to collect liquids which may then be drawn off via syringe. The dimple is small enough that it does not interfere with the use of egg-shaped magnetic stirring bars.

Cap. (mL)	14/20 Joint Cat. No.	24/40 Joint Cat No.	Each
25	Z40,632-5	—	$26.00
50	Z40,633-3	—	26.00
100	Z40,634-1	Z40,636-8	36.00
250	—	Z40,637-6	39.50
500	—	Z40,638-4	42.00
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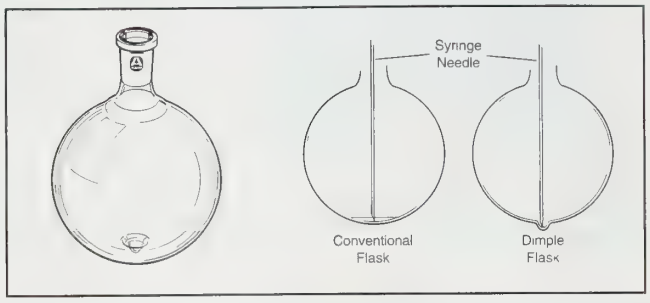

The design of these flasks was first published by Professor Brian E. Love of the East Carolina University Department of Chemistry in *Organic Preparations and Procedures International*, **1997**, *29*, 600-601.

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These unique adapters greatly simplify the transfer of solids from round-bottom flasks to vials. Precision-machined, chemically inert Teflon® PTFE adapters will not seize in the joint. A wide range of thread sizes are available to accommodate most sample vials including scintillation vials (22 mm threads).

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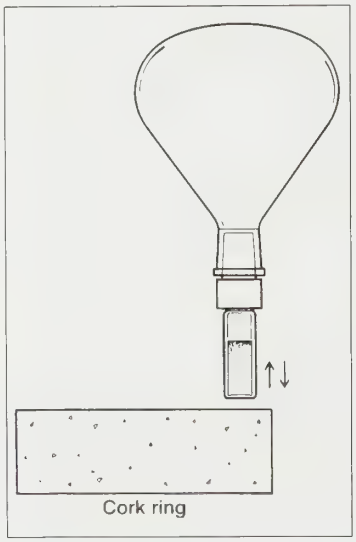

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Screw sample vial into bottle thread at top of adapter. Insert other end of adapter into flask joint. Invert assembly and gently tap* vial on a soft surface to transfer solids from flask into sample vial.

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	15-425	Z40,648-1	30.00
	20-400	Z40,650-3	30.00
	22mm	Z40,658-9	30.00
24/29	13-425	Z40,651-1	30.00
	15-425	Z40,653-8	30.00
	20-400	Z40,654-6	30.00
	22mm	Z40,659-7	30.00
29/32	13-425	Z40,655-4	30.00
	15-425	Z40,656-2	30.00
	20-400	Z40,657-0	30.00
	22mm	Z40,660-0	30.00

* Care must be used when tapping vial to prevent accidental breakage. Tapping on a cork ring or other soft surface is recommended.

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Aldrichimica Acta

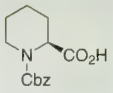
Volume 32, Number 1, 1999

Chiral Heterosubstituted 1,3-Butadienes: Synthesis and [4+2] Cycloaddition Reactions

Serine Derivatives in Organic Synthesis

New Products

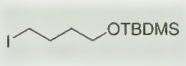
Peptides and pharmacologically active peptide mimetics have been prepared from this protected amino acid.[1,2]



(1) Benedetti, E. et al. *Protein Pept. Lett.* **1996**, *3*, 283. (2) Hauske, J. R. et al. *J. Med. Chem.* **1992**, *35*, 4284.

49,958-7 (*S*)-(–)-1-(Carbobenzyloxy)-2-piperidinecarboxylic acid, 97% **1g $18.00; 5g $60.00**

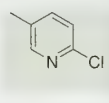
This versatile building block has been used to alkylate acetylenes, ester enolates, and allenes.[1-3]

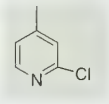


(1) Hermitage, S. A. et al. *Tetrahedron Lett.* **1998**, *39*, 3567. (2) Schostarez, H. J.; Schwartz, T. M. *J. Org. Chem.* **1996**, *61*, 8701. (3) Llerena, D. et al. *Tetrahedron* **1998**, *54*, 9373.

51,202-8 *tert*-Butyl(4-iodobutoxy)dimethylsilane, 95% **5mL $22.25; 25mL $74.00**

2-Substituted picolines have been prepared from these compounds. Examples include (2-pyridyl)indoles and endothelin receptors.[1,2]



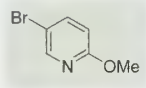


(1) Amat, M. et al. *J. Org. Chem.* **1997**, *62*, 3158. (2) Kourounakis, A. et al. *Biorg. Med. Chem. Lett.* **1997**, *7*, 2223.

49,532-8 2-Chloro-5-methylpyridine, 98% **5mL $21.50; 25mL $72.00**

11,632-7 2-Chloro-4-methylpyridine, 98% **5mL $32.50; 25mL $108.50**

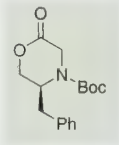
5-Substituted-2-hydroxypyridines can be prepared from this compound through lithiation in the 5-position followed by acid cleavage of the methyl ether.[1-3]



(1) Windscheif, P-M; Voegtle, F. *Synthesis* **1994**, 87. (2) Comins, D. L.; Killpack, M.O. *J. Org. Chem.* **1990**, *55*, 69. (3) Butora, G. et al. *J. Am. Chem. Soc.* **1997**, *119*, 7694.

51,029-7 5-Bromo-2-methoxypyridine, 95% **5mL $28.00; 25mL $93.00**

Chiral starting material for the preparation of enantiomerically pure α-amino acids.[1,2]



(1) Baker, W.R. et al. *Tetrahedron Lett.* **1992**, *33*, 1573. (2) Baker, W.R. et al. *ibid.* **1992**, *33*, 1577.

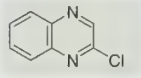
47,992-6 *tert*-Butyl (*S*)-(–)-5-benzyl-2-oxo-4-morpholinecarboxylate, 99% **1g $30.75; 5g $102.25**

Important precursor for 3-substituted or 3,4-disubstituted pyrrolines.[1,2]

(1) Francke, W. et al. *Liebigs Ann. Chem.* **1995**, 965. (2) Okada, T. et al. *Chem. Pharm. Bull.* **1993**, *41*, 132.

47,751-6 *tert*-Butyl 2,5-dihydro-1*H*-pyrrole-1-carboxylate, 97% **1g $66.60**

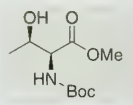
The chlorine in this compound is easily displaced by alcohols, amines, or amides.



Castle, R.N.; Masayuki, O. *J. Org. Chem.* **1961**, *26*, 954.

13,630-1 2-Chloroquinoxaline, 98% **1g $10.00; 5g $34.00**

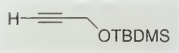
Isosteres of β-D-galactosyl-L-asparagine, 4-amino-4,6-dideoxygulopyranoside, and *N-allo*-threonine have all been prepared from this amino acid derivative.[1-3]



(1) Dondoni, A. et al. *Tetrahedron Lett.* **1998**, *39*, 6601. (2) Koskinen, A.M.P.; Otsomaa, L.A. *Tetrahedron* **1997**, *53*, 6473. (3) Williams, L. et al. *Heterocycl. Commun.* **1996**, *2*, 55.

46,565-8 *N*-(*tert*-Butoxycarbonyl)-L-threonine methyl ester, 95% **1g $10.00; 10g $55.00**

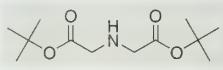
This silyl ether has been used to prepare 1-aryl-2-propyn-1-ols via palladium-catalyzed coupling of the acetylene with aryl iodides, bromides, or triflates.[1,2]



(1) Cliff, M.D.; Pyne, S.G. *Tetrahedron* **1996**, *52*, 13703. (2) Takahashi, S. et al. *Synthesis* **1980**, 627.

49,549-2 *tert*-Butyldimethyl(2-propynyloxy)silane, 97% **5mL $21.00; 25mL $70.00**

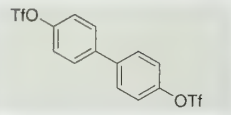
This iminodiacetate is an important precursor to europium(III) and terbium(III) chelating agents with luminescence properties.[1-3]



(1) Mukkala, V. et al. *Helv. Chim. Acta* **1992**, *75*, 1621. (2) Takalo, H. et al. *ibid.* **1996**, *79*, 789. (3) Remuinan, M.J. et al. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1099.

51,132-3 Di-*tert*-butyl iminodiacetate, 98% **1g $23.75; 5g $79.00**

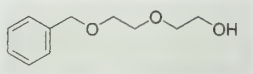
4,4'-Disubstituted biphenyls can be prepared from this ditriflate using palladium-catalyzed coupling methods.



Dolle, R.E. *J. Chem. Soc., Chem. Commun.* **1987**, 904.

51,131-5 4,4′-Biphenol bis(trifluoromethanesulfonate), 98% **25g $113.00**

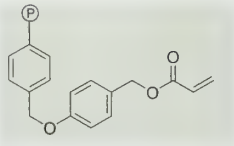
Monobenzylated di(ethylene)glycol has been used to prepare crown ethers bearing polymerizable side chains.[1-3]



(1) Collie, L. et al. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1747. (2) Peeters, E. et al. *Acta Polym.* **1996**, *47*, 485. (3) Houghton, R.P.; Southby, D.T. *Synth. Commun.* **1989**, *19*, 3199.

49,963-3 Di(ethylene glycol) benzyl ether, 97% **5mL $12.50; 25mL $41.50**

Solid-phase synthesis of β-peptoids using the Wang acrylate resin has been accomplished through Michael addition of amines. The peptoids are formed by further reaction of the resulting β-amine with acryloyl chloride followed by Michael addition of another amine. The peptoid is cleaved from the resin with trifluoroacetic acid.



Hamper, B.C. et al. *J. Org. Chem.* **1998**, *63*, 708.

51,017-3 Wang acrylate resin **1g $20.00; 10g $110.00**

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Volume 32, Number 1, 1999

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About Our Cover

A Farm in the Sunlight (oil on canvas, 32¼ in. x 26⅛ in.), painted by the Dutch artist Meindert Hobbema in 1668, is regarded as one of this artist's finest paintings. The focus of the picture is the farm buildings near the center of the composition, which are highlighted in the bright patch of sun in the middle ground. Typically, the artist draws the viewer's attention back into the space of the painting by means of pools of light which accent distantly seen objects and against which the trees closer to the foreground are silhouetted.

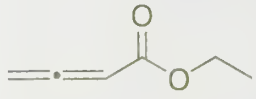
Hobbema lived and worked in Amsterdam, but his paintings almost all represent rural scenes which include farm buildings characteristic of the eastern provinces of the Netherlands, with their high-peaked roofs and half-timbered construction. Few specific sites have been identified in Hobbema's paintings, and in fact they are almost never direct observations of actual places, but usually are pure inventions of his imagination, made up of generic elements commonly found in his works. Despite this, they seem real to us and we are convinced of their fidelity to nature by the believable flow of the soft landscape, the attention to both architectural and natural details, and the careful and wonderful observation of light.

This painting is in the Andrew W. Mellon Collection at the National Gallery of Art.

"Please Bother Us."

by Jai Nagarkatti

Jai Nagarkatti, President



Dr. C. Edgar Cook (Research Triangle Institute) kindly suggested that we make ethyl 2,3-butadienoate. This acceptor-substituted allene is useful for the synthesis of β-methyleneamino acids, which constitute a class of enzyme inhibitors.[1] 1,3-Dipolar cycloadditions,[2] [3+2] cycloadditions,[3,4] and palladium-catalyzed reactions[5] have been performed with this building block.

(1) Paik, Y.H.; Dowd, P. *J. Org. Chem.* **1986**, *51*, 2910. (2) Zhao, B.-X.; Eguchi, S. *Tetrahedron* **1997**, *53*, 9575. (3) Zhu, G.; Chen, Z.; Jiang, Q.; Xiao, D.; Cao, P.; Zhang, X. *J. Am. Chem. Soc.* **1997**, *119*, 3836. (4) Zhang, C.; Lu, X. *J. Org. Chem.* **1995**, *60*, 2906. (5) Okuro, K.; Alper, H. *J. Org. Chem.* **1997**, *62*, 1566.

49,499-2 Ethyl 2,3-butadienoate, 95%
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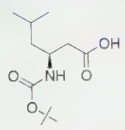

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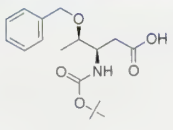

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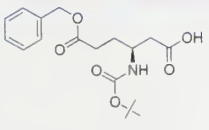

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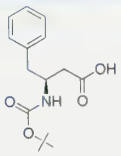

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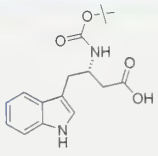

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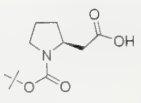

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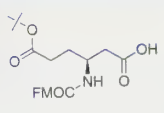
14976	**BOC-*O*-benzyl-L-β-homothreonine**	250mg $86.70; 1g $240.85
14977	**BOC-L-β-homoglutamic acid 6-benzyl ester**	250mg $86.70; 1g $240.85
14979	**BOC-L-β-homophenylalanine**	250mg $75.10; 1g $208.65
14981	**N_{β}-BOC-L-β-homotryptophan**	250mg $86.70; 1g $240.85
14982	**(*S*)-2-(1-BOC-2-pyrrolidinyl)acetic acid**	250mg $75.10; 1g $208.65

N-FMOC-protected unnatural amino acids



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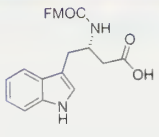

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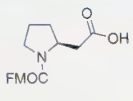

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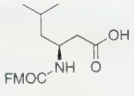

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47834	**FMOC-4-(trifluoromethyl)-D-phenylalanine**	1g $243.60; 5g $964.65
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96065	***N*-Z-D-α-cyclohexylglycine**	1g $50.40; 5g $199.60
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96077	**Z-dehydroalanine methyl ester**	250mg $40.05; 1g $111.30
96079	**Z-*N*,2-dimethylalanine**	1g $11.20; 5g $44.35
96083	**N_{α}-Z-L-2,4-diaminobutyric acid**	1g $102.90; 5g $408.75
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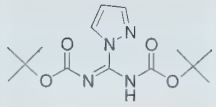
Aldrichimica Acta

Volume 32, Number 2, 1999

Enzymatic Dihydroxylation of Aromatics in Enantioselective Synthesis: Expanding Asymmetric Methodology

New Products

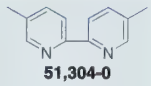
Both the solution- and solid-phase synthesis of guanidines have been accomplished with this reagent.[1-3]



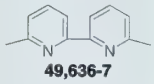
(1) Wu, Y. et al. *Synth. Commun.* **1993**, *23*, 3055. (2) An, H. et al. *Tetrahedron* **1998**, *54*, 3999. (3) Robinson, S.; Roskamp, E.J. *ibid.* **1997**, *53*, 6697.

43,416-7 ***N,N′*-Bis(*tert*-butoxycarbonyl)-1*H*-pyrazole-1-carboxamidine**, 98% 1g $25.00; 5g $83.00

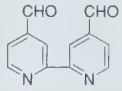
A variety of highly functional bipyridines, useful as organometallic ligands, have been prepared from these compounds. The methyl groups can be easily oxidized to the acid[1] or converted to the bromomethyl derivatives.[2,3] A number of alkenyl-substituted bipyridines have been prepared from the dicarboxaldehyde.[4,5]



51,304-0



49,636-7



47,466-5

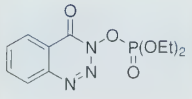
(1) Odobel, F. et al. *Tetrahedron Lett.* **1998**, *39*, 3689. (2) Schubert, U.S. et al. *ibid.* **1998**, *39*, 8643. (3) Ebmeyer, F.; Voegtle, F *Chem. Ber.* **1989**, *122*, 1725. (4) Kocian, O. et al. *Tetrahedron Lett.* **1990**, *31*, 5069. (5) Della, C. et al. *J. Heterocycl. Chem.* **1990**, *27*, 163.

51,304-0 **5,5′-Dimethyl-2,2′-dipyridyl**, 98% 5g $30.75; 25g $102.50

9,636-7 **6,6′-Dimethyl-2,2′-dipyridyl**, 98% 1g $58.00; 5g $193.50

47,466-5 **2,2′-Bipyridine-4,4′-dicarboxaldehyde**, 95% 500mg $117.00

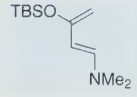
This peptide coupling agent is a stable crystalline solid, and is suitable for both solution- and solid-phase synthesis. No additives are needed to prevent racemization when using this reagent.



Fan, C-X. et al. *Synth. Commun.* **1996**, *26*, 1455.

49,596-4 **3-(Diethoxyphosphoryloxy)-1,2,3-benzotriazin-4(3*H*)-one**, 98% 5g $27.00

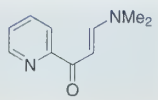
This diene has been reported to be significantly more reactive than Danishefsky's diene (1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene).



Kozmin, S.A.; Rawal, V.H. *J. Org. Chem.* **1997**, *62*, 5252.

49,595-6 ***trans*-3-(*tert*-Butyldimethylsilyloxy)-*N,N*-dimethyl-1,3-butadien-1-amine**, 90% 5g $93.50

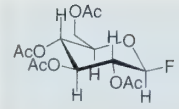
A variety of 2,2':6',2"-terpyridines can be prepared from this reagent.



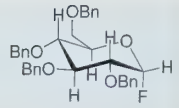
Jameson, D. L.; Guise, L. E. *Tetrahedron Lett.* **1991**, *32*, 1999.

51,167-6 **3-(Dimethylamino)-1-(2-pyridyl)-2-propen-1-one**, 95% 25g $46.50

Glycosyl fluorides are widely utilized intermediates for C-, O-, N-, or S-glycosylations.[1,2]



51,054-8



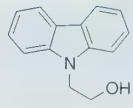
51,172-2

(1) Drew, K. N.; Gross, P. H. *J. Org. Chem.* **1991**, *56*, 509. (2) Jegou, A. et al. *Tetrahedron* **1998**, *54*, 14779.

51,054-8 **β-D-Glucopyranosyl fluoride tetraacetate**, 97% 1g $57.00

51,172-2 **2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl fluoride**, 97%, predominantly α 500mg $81.00

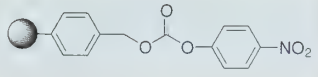
Monomers for the synthesis of azo-aromatic photoconductive polymers have been prepared from this compound.[1-3]



(1) Ho, M.S. et al. *Macromolecules* **1996**, *29*, 4613. (2) Toru, Y.; Tokuji, M. *J. Phys. Chem.* **1995**, *99*, 16047. (3) Zhao, C. et al. *Chem. Mater.* **1995**, *7*, 1237.

47,974-8 **9*H*-Carbazole-9-ethanol**, 97% 5g $24.00; 25g $80.00

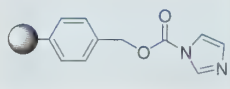
This carbonate resin is used to bind amines or amino acids as urethanes. Dipeptides and hydantoins have been prepared from these polymer-bound urethanes.[1-3]



(1) Dixit, D.M.; Leznoff, C.C. *J. Chem. Soc., Chem. Commun.* **1977**, 798. (2) Dressman, B.A. et al. *Tetrahedron Lett.* **1996**, *37*, 937. (3) Gouilleux, L. et al. *ibid.* **1996**, *37*, 7031.

49,483-6 **4-Nitrophenyl carbonate, polymer-bound** 1g $35.00; 10g $196.00

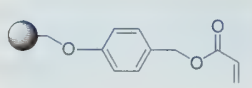
Solid-phase synthesis of peptides and peptidomimetics has been accomplished using polymer-bound carbonylimidazole. Carbamates are formed by reaction with unprotected amines. The carbamates are cleaved using trifluoroacetic acid.[1,2]



(1) Hauske, J.R.; Dorff, P. *Tetrahedron Lett.* **1995**, *36*, 1589. (2) Rotella, D.P. *J. Am. Chem. Soc.* **1996**, *118*, 12246.

49,823-8 **Carbonylimidazole, polymer-bound** 1g $21.00; 5g $70.00

Solid-phase synthesis of β-peptoids using the Wang acrylate resin has been accomplished through Michael addition of amines. The peptoids are formed by further reaction of the resulting β-amine with acryloyl chloride followed by Michael addition of another amine. The peptoid is cleaved from the resin with trifluoroacetic acid.



Hamper, B.C. et al. *J. Org. Chem.* **1998**, *63*, 708.

51,017-3 **Wang acrylate resin** 1g $35.00; 10g $192.50

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Volume 32, Number 2, 1999

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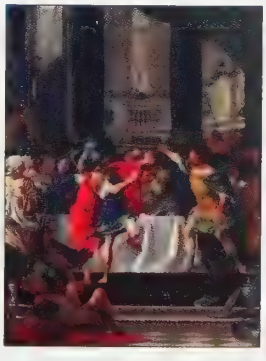


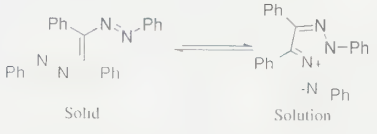
Alexander the Great Threatened by His Father (oil on canvas, 51in. x 37⅛in.) was painted by the Italian artist Donato Creti probably between 1700 and 1705. It represents a famous confrontation between Alexander and his father, King Philip of Macedon, as recorded by the ancient Greek historian Plutarch. Alexander was angered by his father's philandering and divorce from his mother, Olympia. Feelings came to a head at the banquet Philip hosted to celebrate his marriage to Cleopatra, a maiden much younger than he. Her uncle Attalus called upon the people present to pray that a legitimate heir to the Macedonian throne might be born from this union. Alexander flew into a rage, hurled his cup at Attalus, and shouted, "What about me?" Philip rose angrily and drew his sword as if to strike his son, but stumbled drunkenly and fell.

The artist chose to depict the most dramatic moment of this story, when the wedding guests are reacting to Philip's brash action. The cup Alexander has thrown lies on the step to the right. The frightened young woman wearing a diadem at the left is Cleopatra, and the astounded old man beneath the protagonists' outstreched hands is Attalus. The drama of the event is expressed not only through the emotion-charged gestures and expressions, but also by the sharply foreshortened view of the servant who has been knocked down on the left, the fluttering drapery at the upper right, the fantastic palace opening behind the banquet scene, and even the low vantage point from which we witness the action. A dynamic use of light also pervades the painting, accentuating the main actors, revealing the luxurious materials and rich colors, and illuminating distant chambers glimpsed through grand colonnades and courtyards.

This painting is part of the Samuel H. Kress Collection at the National Gallery of Art, Washington, D.C.

"Please Bother Us."

by Jai Nagarkatti, President



Professor Richard N. Butler of the National University of Ireland, Galway, kindly suggested that we make 1,2-bis(phenylazo)stilbene. This compound functions as an azolium 1,3-dipole and is useful for the preparation of triazolium salts. These salts can be easily converted to triazines, oxatriazines, or thiatriazines.

Butler, R. N.; O'Shea, D. F. *Heterocycles* **1994**, *37*, 571

51,578-7 **α,β-Bis(phenylazo)stilbene**, mixture of isomers
1g $20.75; 5g $69.00

Naturally, we made this useful reagent. It was no bother at all, just a pleasure to be able to help.

Do you have a compound that you wish Aldrich could list, and that would help you in your research by saving you time and money? If so, please send us your suggestion; we will be delighted to give it careful consideration. You can contact us in any one of the ways shown on this page or on the inside back cover

Lab Notes

Safe Transfer of Air- and Moisture-Sensitive Reagents in the Laboratory

Advances in organometallic chemistry in the last few decades have brought pyrophoric and moisture-sensitive reagents, especially those of organolithium and aluminum, into common usage in organic chemistry laboratories. The commercial availability and high selectivity of these reagents have made them indispensable in the modern chemistry laboratory, despite their highly reactive nature and the risks associated with their handling. In laboratory settings, these reagents are most conveniently transferred from commercial containers to reaction vessels by using either a syringe–needle combination or cannulation techniques,[1,2] without resorting to the use of a glove box or the Schlenk line of dedicated glassware.[3,4]

However, it is almost inevitable that small amounts of the pyrophoric liquid being transferred, e.g., *t*-BuLi solutions and Me_3Al, are exposed to the atmosphere on the tip of the needle or cannula, often causing sparks or small fires. While in most cases the fire is localized and burns out quickly, it always makes one apprehensive, considering the possibility that the sparks or fire may spread to other flammable materials abundant in organic chemistry laboratories. A simple device and a procedure to minimize such risks are described here.

A piece of glass tubing of approximately 6 mm ID and 4 cm in length is capped with rubber septa at both ends and the septa secured with copper wires. This tube is purged with inert gas and serves to protect the needle tip from being exposed to air. When withdrawing air-sensitive reagents, the needle is allowed to protrude through both septa and into the reservoir (**Figure 1**). Once the desired amount of reagent is removed, the tip of the needle or cannula is withdrawn from the reservoir and slid into the glass tubing filled with inert atmosphere, while the lower septum is kept in close contact with the cap of the reservoir to minimize exposure by the needle tip to the air during the process. The syringe or cannula is then safely transported (**Figure 2**) to the reaction flask and the sequence reversed to dispense the reagent (**Figure 3**). After the transfer is finished, the same procedure is followed to withdraw inert solvent to rinse the residual reagent from the syringe needle or cannula or to effect final quenching and cleaning. This simple device has virtually eliminated sparks associated with the transfer of pyrophoric reagents in the author's laboratory.

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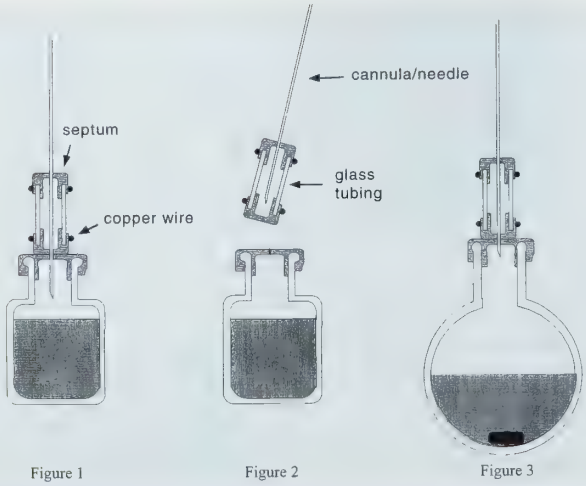

Figure 1 Figure 2 Figure 3

Maintaining a Constant Water Level in an Open, Warm-Water Bath

In our laboratories, we are required, for safety reasons, to use a steam bath to heat large-scale reactions (22-L or 50-L flask size) that contain flammable solvents (bp ≤ 80 °C, e.g., ethanol). This is accomplished by heating a water bath with steam coils that are immersed in the water. Extended periods of heating result in significant evaporation of the water, and lead to a reduction of the water level in the bath.

To maintain a constant water level in the bath during extended periods of heating, we cover the entire surface of the water with mineral oil (Aldrich cat. no. **33,077-9**). This greatly reduces the evaporation of the water, and little, if any, decomposition of the mineral oil occurs during a 72-hour period. For example, we have heated in this way a 12-L flask—in which an aldehyde deprotection step was carried out in acetone for 72 h—and observed no reduction of the water level in the bath. However, heating for more than 72 hours tends to accelerate decomposition of the oil. If longer heating times are required, the mineral oil can simply be decanted and replaced with a fresh batch.

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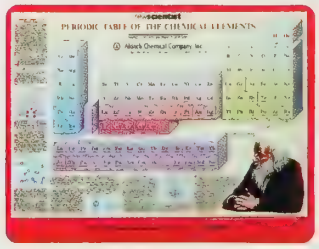

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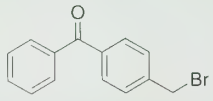
Volume 32, Number 3, 1999 (*Last issue in 1999*)

Ring-Closing Metathesis of Nitrogen-Containing Compounds: Applications to Heterocycles, Alkaloids, and Peptidomimetics

Are Two Phenyls Better than One? Synthesis and Applications of (R)-4-Diphenylmethyl-2-oxazolidinone

New Products

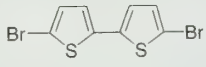
This benzophenone has been used to prepare several photoinitiators, including tetraalkylammonium salts, for acrylate polymerization.[1] It is also used to prepare photocleavable protein cross-linking agents.[2]



(1) Zhang, W. et al. *J. Org. Chem.* **1999**, *64*, 458. (2) Oatis, J.E., Jr.; Knapp, D.R. *Tetrahedron Lett.* **1998**, *39*, 1665

44,938-5 **4-(Bromomethyl)benzophenone**, 97% **5g $54.90**

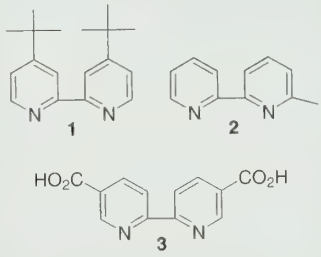
Oligothiophenes, with nonlinear optic and electrochemical applications, have been prepared from this brominated bithiophene.[1,2]



(1) Nakanishi, H. et al. *J. Org. Chem.* **1998**, *63*, 8632. (2) Roncali, J. *Chem. Rev.* **1992**, *92*, 711

51,549-3 **5,5'-Dibromo-2,2'-bithiophene**, 99% **1g $28.00; 5g $93.40**

A variety of organometallic complexes have been prepared from these bipyridines. Compounds **1** and **2** are useful for the preparation of ruthenium complexes with increased solubility in organic solvents and modified redox properties relative to those of the complexes with unsubstituted bipyridine analogs.[1,2] Compound **3** has been utilized to prepare highly functionalized bipyridines.[3]



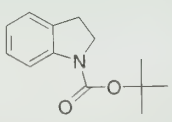
(1) Hadda, T.B.; Bozec, H.L. *Polyhedron* **1988**, 575. (2) Fabian, R.H. et al. *Inorg. Chem.* **1980**, *19*, 1977. (3) Penicaud, V. et al. *Tetrahedron Lett.* **1998**, *39*, 3689.

51,547-7 **4,4'-Di-*tert*-butyl-2,2'-dipyridyl**, 98% **(1)** **5g $31.30; 25g $104.10**

51,614-7 **6-Methyl-2,2'-dipyridyl**, 97% **(2)** **1g $74.10**

51,776-3 **2,2'-Bipyridine-5,5'-dicarboxylic acid**, 97% **(3)** **250mg $21.90; 1g $60.90**

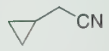
This compound is readily lithiated at C-7 using *sec*-butyllithium, and has been used to prepare a variety of 7-substituted indolines.



Meyers, A.I.; Milot, G. *J. Org. Chem.* **1993**, *58*, 6538.

51,014-9 ***tert*-Butyl indoline-1-carboxylate**, 98% **5g $27.50; 25g $91.40**

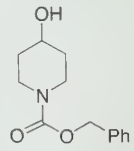
Important starting material for the preparation of cyclopropane-substituted heterocycles.[1,2]



(1) Li, Q. et al. *J. Med. Chem.* **1996**, *39*, 3070. (2) Kim, D.-K. et al. *ibid.* **1997**, *40*, 2363.

51,611-2 **Cyclopropylacetonitrile**, 97% **5g $35.60**

Useful synthon for the synthesis of biologically active quinolones[1] and fibrinogen receptor antagonists.[2]



(1) Cooper, C.S. et al. *J. Med. Chem.* **1992**, *35*, 1392. (2) Alig, L. et al. *ibid.* **1992**, *35*, 4393.

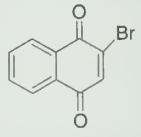
51,390-3 **Benzyl 4-hydroxy-1-piperidinecarboxylate**, 97% **10mL $49.80**

This cyclopentadiene has been used as a diene in Diels–Alder reactions,[1] and for the preparation of fulvenes[2] and metallocenes.[3]

(1) Riemshneider, R.; Nehring, R. *Monatsh. Chem.* **1959**, *90*, 568. (2) Miyake, S. et al. *Macromolecules* **1995**, *28*, 3074. (3) Drewitt, M.J. *Chem. Commun.* **1996**, 2153.

49,498-4 ***tert*-Butylcyclopentadiene**, mixture of isomers **5mL $34.80; 25mL $115.80**

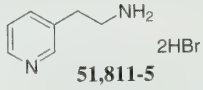
A number of anthraquinones and naphthoquinones have been prepared from this compound.[1,2]



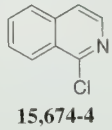
(1) Kesteleyn, B. et al. *J. Org. Chem.* **1999**, *64*, 1173. (2) Joshi, B.S. et al. *ibid.* **1994**, *59*, 8220.

51,030-0 **2-Bromo-1,4-naphthoquinone**, 98% **100g $28.50**

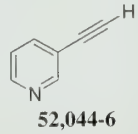
These heterocyclic synthons are widely used starting materials in medicinal chemistry.[1-4]



51,811-5



15,674-4



52,044-6

(1) Tucker, T.J. et al. *J. Med. Chem.* **1994**, *37*, 2437. (2) Moltzen, E.K. et al. *ibid.* **1994**, *37*, 4085. (3) Zhang, H. et al. *J. Org. Chem.* **1998**, *63*, 6886. (4) Hoffman, J.M. et al. *J. Med. Chem.* **1992**, *35*, 3784.

51,811-5 **3-(2-Aminoethyl)pyridine dihydrobromide**, 98% **1g $29.50; 5g $97.50**

15,674-4 **1-Chloroisoquinoline**, 95% **1g $19.30; 5g $64.50**

52,044-6 **3-Ethynylpyridine**, 98% **1g $27.70; 5g $92.40**

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About Our Cover

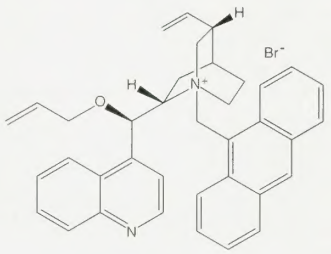
Jan Davidsz. de Heem's *Vase of Flowers* (oil on canvas, 27⅜ in. x 22¼ in.), painted about 1660, is a beautiful example of the delight that Dutch and Flemish seventeenth-century artists took in the natural world. The brilliant color, the soft texture of flower petals, the moist gleam of dew on leaves, and the detailed delineation of insects and small animals all contribute to the extraordinary illusionism of the painting. Moreover, the dynamic rhythms of the leaves, wheat stalks, peas, and flowers, and the small creatures crawling and fluttering in the air surpass mere description to make the objects represented seem almost to break through the surface of the picture. One can almost imagine the sweet scents of the flowers. The painting is far more than simply an extraordinary literal record of reality, however. It is an important expression of the imagination of the artist, who has overcome the laws of nature. Normally, this combination of flowers, fruits, and vegetables could not be in the same bouquet because they mature at different seasons of the year. Furthermore, these flowers will continue to bloom long after those in nature have withered and died. *Ars longa, vita brevis.* The painting is also filled with symbolic associations that would have been well understood in the seventeenth century. Insects and snails represent forces that are destructive of the beauties of nature. The transient loveliness of flowers is a reminder of the temporality of life. The morning glory, which opens at dawn and closes at dusk, symbolizes the light of truth.

This painting is part of the Andrew W. Mellon Collection at the National Gallery of Art, Washington, D. C.

"Please Bother Us."

by Jai Nagarkatti

Jai Nagarkatti, President



Dr. Martin J. O'Donnell (IUPUI, Indianapolis) kindly suggested that we make *O*-allyl-*N*-(9-anthracenylmethyl)-cinchonidinium bromide. This phase-transfer catalyst is useful for the enantioselective synthesis of α-amino acid derivatives.[1-3] A key step in the synthesis is the enantioselective alkylation of the enolate derived from *N*-(diphenylmethylene)glycine *tert*-butyl ester.

(1) O'Donnell, M.J. et al. *Tetrahedron* **1999**, *55*, 6347.
(2) O'Donnell, M.J. et al. *Tetrahedron Lett.* **1998**, *39*, 8775.
(3) Corey, E.J. et al. *J. Am. Chem. Soc.* **1997**, *119*, 12414.

49,961-7 ***O*-Allyl-*N*-(9-anthracenylmethyl)cinchonidinium bromide**, 95%
1g $37.90; 5g $129.20

36,448-7 ***N*-(Diphenylmethylene)-glycine *tert*-butyl ester**, 98%
250mg $11.70; 1g $32.30

Naturally, we made this useful catalyst. It was no bother at all, just a pleasure to be able to help.

Do you have a compound that you wish Aldrich could list, and that would help you in your research by saving you time and money? If so, please send us your suggestion; we will be delighted to give it careful consideration. You can contact us in any one of the ways shown on this page or on the inside back cover.

Lab Notes

A Simple, Inexpensive Apparatus for Parallel Synthesis

In recent years, combinatorial chemistry[1] has emerged as an important component in drug discovery and as a technology that can increase the productivity of pharmaceutical research tremendously. Numerous synthesizers with varying degrees of automation are available commercially, both for solution- and solid-phase synthesis. Moreover, synthesis carried out in multiwell plates requires a liquid handling system and generates only a few milligrams of products.

In an attempt to increase the number of compounds synthesized, keeping in mind the cost, we designed a simple piece of equipment that is a modification of a vacuum manifold. Initially, we used a manifold with five arms (**Figure A**). Each arm is about 7 inches in length and serves as an air condenser; a reflux condenser is attached to the top of the manifold. The apparatus can be comfortably used for higher boiling solvents, especially when a common solvent is in use, with no overflow or drying of any flask. Later on, this apparatus was modified to accommodate a larger number (10) of reaction vessels (**Figure B**). Using this apparatus in an oil bath heated on a laboratory stirrer/hotplate, we carried out a series of solution-phase ester, amide, and guanidine syntheses in both 10-mL and 15-mL flasks. Each of the reaction flasks was charged with only 5–7 mL of reaction solution, and rigorous reflux was avoided to permit the refluxing solvent (e.g., xylenes) to condense completely in the 7-in. arm and thus avoid cross-contamination. We isolated a few hundred milligrams of each product in a relatively pure form (HPLC purity of guanidine derivatives >93%) with no cross-contamination. In the absence of fancier and more costly equipment, this apparatus can be used effectively for the synthesis of analogs with a common chemistry. It does not require any additional laboratory space and may also be suitable for solid-phase synthesis.

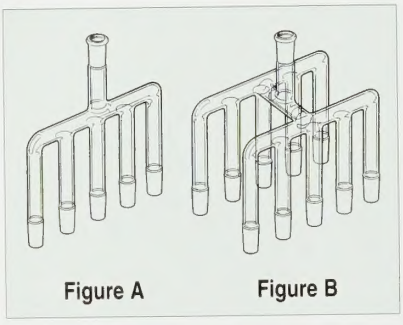


Figure A Figure B

References: (1) *Combinatorial Chemistry: Synthesis and Application*; Wilson, S.R., Czarnik, A.W., Eds.; John Wiley & Sons, Inc.: New York, NY, 1997 (**Z28,759-8**).

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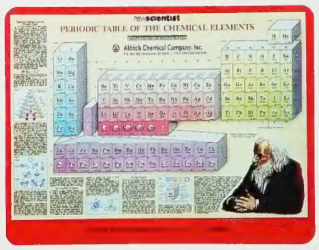
A Simple and Efficient Apparatus for Growing Crystals by Diffusion of Reacting Solutions

Growing crystals for X-ray diffraction analysis is often a challenging task. Several methods and techniques have been developed to grow good-quality crystals. Among them are the slow evaporation of saturated solutions,[1] cooling of saturated solutions, liquid diffusion, vapor diffusion, diffusion of reacting solutions,[2] and other more sophisticated methods such as crystal growing in gels.[3] In our research, we encountered difficulties growing suitable crystals of an organic host–guest complex using conventional methods. Layering one reacting solution on the other in a tube[2] gave crystals of some quality, but were too small for X-ray diffraction analysis. To overcome this problem, we designed a simple apparatus, which allows growing crystals of the complex during its formation reaction.

If compound **A** readily forms a crystalline complex with compound **B**, the size and quality of the crystals of the complex **AB** can be significantly improved by performing the reaction slowly. The apparatus shown in **Figure 1** is capable of extending the reaction time up to several weeks. The whole system is an easily made, single-piece glassware consisting of several parts:

Continued on page 90.

Do you have an innovative shortcut or unique laboratory hint you'd like to share with your fellow chemists? If so, please send it to Aldrich (attn: Lab Notes, Aldrichimica Acta). For submitting your idea, you will receive a complimentary, laminated periodic table poster (Cat. No. **Z15,000-2**). If we publish your lab note, you will also receive an Aldrich periodic table turbo mouse pad (Cat. No. **Z24,409-0**). It is Teflon®-coated, 8½ x 11 in., with a full-color periodic table on the front. We reserve the right to retain all entries for future consideration.



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