Alfred Bader

Aldrich

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Aldrichimica acta

PREVIEW ISSUE

PUBLISHED BY THE ALDRICH CHEMICAL COMPANY, INC.

ALDRICHIMICA ACTA

Preview Issue
Fall 1967

Published by
ALDRICH CHEMICAL COMPANY, INC.
Milwaukee, Wisconsin

ABOUT THE COVER

A milestone was passed recently at Aldrich Chemical when our analytical laboratory recorded its 30,000th infrared spectrum on a single Beckman IR-5A spectrophotometer. The description of this event and the analytical methods used by Aldrich to safeguard product quality were published in *The Analyzer, Beckman Instruments, Inc.*, and is reprinted on page 3.

TABLE OF CONTENTS

Aldrichimica Acta replaces the previously published *Kardindex Sheets* to keep chemists informed of the latest chemical offerings by Aldrich Chemical Company, Inc. The articles also published are of general interest to users of chemicals and Aldrich customers. While the information and data included in this publication is correct and reliable to the best of our knowledge, it is not guaranteed to be so. Therefore, we cannot assume responsibility connected with the use of our chemicals or data. The information on or sale of any material is not intended as a license to operate under, or a recommendation to infringe, any patent covering any material or use.

Organic Intermediates • Biochemical Tools • Reagent Chemicals • Analytical Tools • Organo-metallics

Each chemical is carefully analyzed and stocked for your convenience.

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Telephone—(414)-374-4620

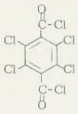
East Coast Warehouse:
78 Clinton Road, Fairfield, New Jersey 07006
Telephone—(201)-228-4750

West Coast Distributor:
Wilshire Chemical Co., Inc.,
15324 S. Broadway, Gardena, California 90247
Telephone—(213)-323-9232

No. 14,142-9

Name 2,3,5,6-Tetrachloroterephthaloyl chloride

Description and Constants



M.W. 340.81

Yellow powder

m.p. 137-144°

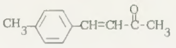
Cl content: 99.8% of theory

Price 25 g. - $3.25 100 g. - $10.50

No. 13,724-3

Name 4-(p-Tolyl)-3-buten-2-one

Description and Constants



M. W. 160.22

Moist yellow crystals

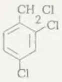
v.p.c. 98.5%

Price 5 g. - $4.00 25 g. - $12.75

No. 13,925-4

Name α, 2,4-Trichlorotoluene
(2,4-dichlorobenzyl chloride), tech.

Description and Constants



M.W. 195.48

Colorless liquid

n_D^{20} 1.5757

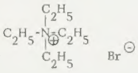
b.p. 118-119°/13 mm.

Price 250 g. - $6.50 1 Kg. - $17.50

No. 14,002-3

Name Tetraethylammonium bromide

Description and Constants



M.W. 210.17

White solid

m.p. 285-287° (dec.)

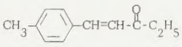
Br content: 98.2% of theory

Price 250 g. - $4.75 1 Kg. - $14.25

No. 13,725-1

Name 1-(p-Tolyl)-1-penten-3-one

Description and Constants



M.W. 174.24

Yellow crystals

m.p. 49-52°

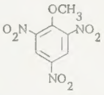
v.p.c. 99%

Price 5 g. - $4.00 25 g. - $12.75

No. 14,007-4

Name 2,4,6-Trinitroanisole

Description and Constants



M.W. 243.13

Yellow crystals

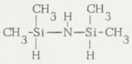
m.p. 66-68°

Price 25 g. - $5.00 100 g. - $16.50

No. 13,924-6

Name 1,1,3,3-Tetramethyldisilazane

Description and Constants



M.W. 133.34

Colorless liquid

n_D^{20} 1.4044

v.p.c. 98.5%

Reagent for converting a compound to its dimethylsilyl derivative, which as greater volatility than the corresponding trimethylsilyl derivative.

Price 10 g. - $9.50 50 g. - $34.50

No. 14,109-7

Name Transfer-ribonucleic acids
(t-RNA), dry powder

Description and Constants

Our material is prepared by Holley's modification(1, 2) of Monier's procedure(3). Excellent for use in preparation of specific amino acid acceptor fractions as reported by Makman(4) and others.

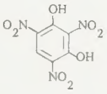
1.) J. Biol. Chem. 236, 200 (1961)
2.) Biochem. biophys. Res. Commun. 10, 186 (1963)
3.) Biochim. biophys. Acta 43, 1 (1960)
4.) Biochemistry 4, 1434 (1965)

Price 1 g. - $25.00 5 g. - $100.00 25 g. - $350.00
100 g. - $1100.00 1 Kg. - $10,400.00
5 Kg. -$8200.00/Kg.

No. 14,010-4

Name 2,4,6-Trinitroresorcinol

Description and Constants



M.W. 245.11

Light yellow powder

m.p. 176-178° (dec.)

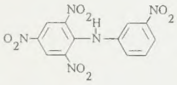
Titration 98.4%

Price 25 g. - $5.50 100 g. - $18.00

No. 13,856-8

Name 2,3',4,6-Tetranitrodiphenylamine

Description and Constants



M.W. 349.22

Yellow crystals

m.p. 210-211.5°

N content: 98% of theory

Price 10 g. - $12.00

No. 14,108-9

Name Transfer-ribonucleic acids
(t-RNA), wet paste

Description and Constants

Our material is prepared by Holley's modification(1, 2) of Monier's procedure(3). Excellent for use in preparation of specific amino acid acceptor fractions as reported by Makman(4) and others.

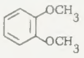
1.) J. Biol. Chem. 236, 200 (1961)
2.) Biochem. biophys. Res. Commun. 10, 186 (1963)
3.) Biochim. biophys. Acta 43, 1 (1960)
4.) Biochemistry 4, 1434 (1965)

Price 100 g. - $275.00 1 Kg. - $2600.00 5 Kg. -$2050.00/Kg.

No. 14,015-5

Name Veratrole
(o-dimethoxybenzene), puriss.

Description and Constants



M.W. 138.17

Pale yellow liquid

n_D^{20} 1.5337

b.p. 206-207°

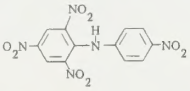
v.p.c. 99+%

Price 100 g. - $3.00 500 g. - $9.00

No. 13,854-1

Name 2,4,4',6-Tetranitrodiphenylamine

Description and Constants



M.W. 349.22

Yellow crystals

m.p. 218-221°

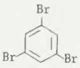
N Content: 98% of theory

Price 10 g. - $12.00

No. 14,006-6

Name 1,3,5-Tribromobenzene

Description and Constants



M.W. 314.82

Brown powder

m.p. 121-124°

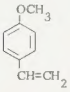
v.p.c. 99%

Price 25 g. - $6.00 100 g. - $19.75

No. 14,100-3

Name 4-Vinylanisole

Description and Constants



M.W. 134.18

Colorless liquid

n_D^{20} 1.5622

b.p. 41-42°/0.5 mm.

Price 5 g. - $9.50 25 g. - $38.00

ACHEMA
1967

Frankfurt, Germany

The World's Largest Chemical Show Held Every Three Years.

The Aldrich Chemical Company, Inc. exhibit, through its Germany sister-company (EGA-CHEMIE), attracted many visitors from throughout the world.

Achema 1967

Dr. Alfred R. Bader: Aldrich Chemical Company, Inc.

The ACHEMA, the world's greatest exhibition of chemical industry has just ended, and it is difficult to describe this without constantly resorting to superlatives. Held only every three years in Frankfurt, it is without peer either in Europe or in the United States. For a week over 2000 companies, offering mainly chemical equipment of all kinds, showed their latest to over 170,000 visitors. A tremendous amount of planning leads to the ACHEMA—many companies plan their new catalogs and many of their new products first to be shown at the ACHEMA, and most companies hope—and find—that their sales spurt substantially after the ACHEMA.

Most of the exhibitors were, of course, West German, but there was a goodly sprinkling of British, French, and American companies, and even the state-owned sales organizations from behind the Iron Curtain exhibited. Many American companies exhibited through their German representatives; Aldrich through its German sister-company, EGA-Chemie, whose stand in the Emil Fischer Strasse was in the most popular of all the exhibition buildings.

But the ACHEMA is more than just an exhibition of equipment. Many technical papers are presented and, more important, it has become the regular meeting place for many thousands of chemists from all over the world who would have to travel for many months to see the chemists they can meet here in one week. On one given morning, for instance, I discussed in four hours a curious case of isomerism of a tetrahydropyridine with Dr. Wilhelm Mathes, the great pyridine chemist of Raschig; the supply of a ton of Emery's azelaic acid for a German chemist to convert to various C_9 and C_{11} dihalides and diamines; the possible reasons why one cannot follow the *Organic Syntheses* procedure for the preparation of beta-chloropropionaldehyde acetal from now available acrolein with Dr. Alfred Griesinger of EGA; Aldrich's sales in Spain with our newly established Spanish representative, Ricorvi; and the supply and purity of pyrrole with a customer requiring this regularly in substantial quantities. Thus it went, morning, afternoon, and evening, in Europe's most crowded city, where people just smiled at you if you were looking for a room during the ACHEMA. Our friends of EGA had wisely rented rooms six months earlier in a small hotel in a town some eight miles outside of Frankfurt, and traffic was so well organized that getting in and out of Frankfurt was not too difficult. And after all the hustle and bustle of discussions all day it was pleasant to get away from it all in the evening.

I already look forward to the ACHEMA of 1970 and only wish that there were a meeting of comparable scope and organization in America.

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ALDRICH pioneered the first USABLE-CATALOG. Remember what catalogs were like before that? No structures, no empirical formulas, no classes of compounds, just accumulations of names where you might or might not have found what you were looking for.

Our USABLE CATALOG has grown like TOPSY, from one page in 1951 to 752 pages this year, and in fact, we had to decide to limit the chemicals in our main catalog to about 10,000. But there are thousands of others we could offer, many of these right on our shelves — compounds which we think are out-of-the-way, but which may help someone: be it for screening, for testing a new reaction, or for identification of an unknown.

And so we decided to offer some 5,000 of these investigational tools in a simple catalog — structures and empirical formulas only.

All of these "library" chemicals are computer-coded, so that, if you would like to have a list, say, of all our pyrroles or all our β-diketones, just write us, and we'll send you the complete list, of course at no charge.

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Division of Aldrich Chemical Company, Inc.

Available literatu

1–Adamantanamine hydroch
to be a potent antiviral a
slowing the penetration of
Product No. 11,519-3

tert.–Butoxycarbonyl azide
group in peptide synthesi
azepines and O-substituted
Product No. B8690-7

Bis-(trimethylsilyl)-acetamid
lating agent for the rapid q
melting solids to volatile liq
BSA is also used as a fast-ac
hydrogen compounds and a
cation procedure.
Product No. 12,891-0

2, 3–Diaminonaphthalene
reagent for the quantitative
metallurgical specimens, se
ples, and agricultural produ
Product No. 13,653-0

No. 14, 209-3

Name N, N-Dic
(DCU)

Description and C

M.W. 1

Yellow l

n_D^{20} 1.45

b.p. 55-

Useful i
β-chloro
addition

Price 25 g. - $

Set

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Available literature

1–Adamantanamine hydrochloride, puriss., has been found to be a potent antiviral agent, perhaps by blocking or slowing the penetration of host cells by the virus.
Product No. 11,519-3

tert.–Butoxycarbonyl azide is used as an amino blocking group in peptide synthesis and in the preparation of azepines and O-substituted hydroxylamines.
Product No. B8690-7

Bis-(trimethylsilyl)-acetamide (BSA), is an excellent silylating agent for the rapid quantitative conversion of high-melting solids to volatile liquids prior to analysis by v.p.c. BSA is also used as a fast-acting quenching agent for active hydrogen compounds and as a reactant in a novel esterification procedure.
Product No. 12,891-0

2, 3–Diaminonaphthalene (DAN), is a highly selective reagent for the quantitative determination of selenium in metallurgical specimens, semiconductors, biological samples, and agricultural products.
Product No. 13,653-0

Diazald®, N-methyl-N-nitroso-p-toluenesulfonamide is one of the most useful reagents developed for the preparation of diazomethane. For detailed procedures and technical literature references, ask for Product No. D2800-0 data sheet.

Gelarose, agarose for gel filtration, is available in ready-to-use suspensions of agarose beads, containing 2, 4, 6, 8, and 10% of agarose. For detailed data sheets with bibliography, ask for "Gelarose."

3-Hydroxypyridine. Its greatest use is in the synthesis of many types of drugs. Four important derivatives are also available and described with literature references. Recently, some derivatives of 3-hydroxypyridine have been found to function as protective agents for deoxyribonucleic acid (DNA) which has been irradiated with X-rays.
Product No. H5700-9

Polybrene® is used as an anti-heparin agent and as a diagnostic tool for selective functional studies of the anterior pituitary and zona glomerulosa of adrenal cortex.
Product No. 10, 768-9

Kardindex cards

The new chemical offerings published in the *Aldrichimica Acta* are available on permanent 4 x 6" filing cards. The cards contain important literature references and are mailed monthly, several weeks in advance of being published here, to give you a head start in your research program. Approximately 50 chemicals are listed and offered each month. Subscription is $25 per year.

No. 14, 209-3

Name N, N-Dichlorourethan (DCU)

Description and Constants

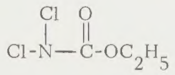
M. W. 157.99

Yellow liquid

n_D^{20} 1.4595

b.p. 55-56°/15 mm.

Useful in the synthesis of β-chlorocarbamates through addition to olefins.



$Cl-N(Cl)-C(=O)-OC_2H_5$

Price 25 g. - $5.75   100 g. - $18.00

Empirical Formula $C_3H_5Cl_2NO_2$

Handling and Shipping (#3)

Shipped in dry ice.
Store in cool, dark place.
Lachrymator! Vesicant!

Literature

J. Org. Chem. 31, 3625 (1966)
J. Org. Chem. 32, 75 (1967)

Functional Groups

Hal-5

ALDRICH CHEMICALS

Set No. 120 9/30/67   PLEASE ORDER BY BOTH NAME AND NUMBER

Please send me literature on the products checked below:

☐ 11,519-3
☐ 13,653-0
☐ H5700-9
☐ B8690-7
☐ D2800-0
☐ 10,768-9
☐ 12,891-0
☐ Gelarose

☐ Please send me additional information on your KARD-INDEX CARD service which is available at the subscription price of $25 per year.

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☐ 06 ___ Biochemical
☐ 09 ___ Organic
☐ 13 ___ Organometallic
☐ 16 ___ Pharmaceutical
☐ 35 ___ Other

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☐ 03 ___ Electronic
☐ 07 ___ General chemical
☐ 09 ___ Government
☐ 11 ___ Hospital
☐ 13 ___ Oil—Gas
☐ 15 ___ Pharmaceutical
☐ 21 ___ Other

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Title
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Division
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City
State Zip

Many of the chemicals listed in the Aldrich catalogs are available in large quantities and at substantially reduced prices. Ask for quotations.

Quantity	Chemical Name

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☐ H5700-9
☐ B8690-7
☐ D2800-0
☐ 10,768-9
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☐ 35 ___ Other

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☐ 13 ___ Oil—Gas
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☐ 10,768-9
☐ 12,891-0
☐ Gelarose

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☐ 11 ___ Hospital
☐ 13 ___ Oil—Gas
☐ 15 ___ Pharmaceutical
☐ 21 ___ Other

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Title
Company
Division
Street
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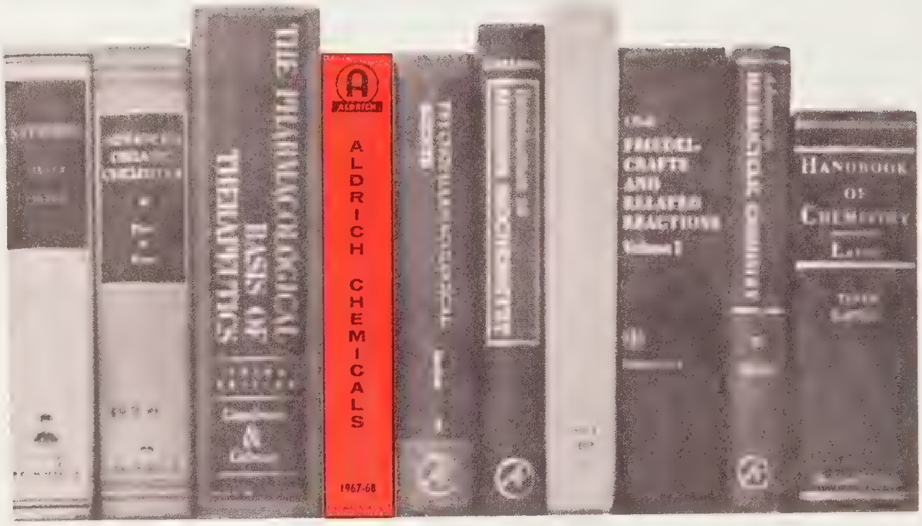

Reach for the Aldrich.

It's right on your shelf.

NEARLY 9000 ORGANIC COMPOUNDS are conveniently cross-indexed into five color-coded sections to help you locate quickly the chemicals you need. Order directly from any of three coast-to-coast stocking points for immediate processing. Organic intermediates, biochemical tools, reagent chemicals, analytical tools, organometallics . . . you'll find them all in your 752-page edition of the Aldrich Chemical catalog. And if someone "borrowed" your copy, write our main office for another.

Aldrichimica acta

VOLUME 1, NUMBER 1, 1968

PUBLISHED BY THE ALDRICH CHEMICAL COMPANY, INC.

ALDRICHIMICA ACTA

Volume 1, Number 1
1968

Published by
ALDRICH CHEMICAL COMPANY, INC.
Milwaukee, Wisconsin

Editor, Richard K. Vitek

ABOUT THE COVER

The classical alchemical painting reproduced on the front cover was done by Thomas Wyck, a Dutchman of the second half of the 17th century. This painting and other works of art are described on page 6.

TABLE OF CONTENTS

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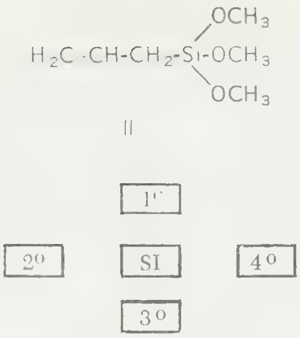


Empirical Formula

Although it would be pointless to search for an exact empirical formula, since this could be looked up rapidly in a table, it is sometimes desirable either to search for or exclude certain elements. This has been programmed into the system together with the ability to retrieve an exact number of any element or elements such as compounds containing three oxygen atoms or two sulfur atoms, etc.

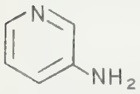
Performance and Retrieval Efficiency

The ALDRICH FIRST system was designed to retrieve pertinent information from an almost random selection of organic chemicals. It was hoped to hold noise levels (undesired retrievals) to fifty per cent or less. In practice this has varied widely.

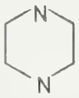
The retrieved grouping of chemicals always contains ALL of the desired chemicals exhibiting the requested information. The problem, of course, is that quite often, unexpected chemicals of *like* but not *obviously similar* characteristics are also retrieved.

Requests for CB) =N-C-C-N=

(diamines) will also retrieve

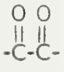


and

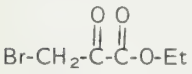


derivatives

unless rings are restricted. However, second thoughts on either of these two groupings will indicate possible new areas of interest since they do really conform to a general diamine constraint.

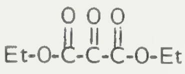
Requests for CF)  $\overset{O}{\overset{\|}{-C}}\overset{O}{\overset{\|}{-C-}}$ (α-diketones)

will also retrieve chemicals such as

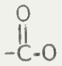
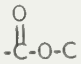


$Br\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}Et$

and



$Et\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}Et$

unless groups such as  $-\overset{O}{\overset{\|}{C}}\text{-}O$ and  $-\overset{O}{\overset{\|}{C}}\text{-}O\text{-}C$

are excluded.

In many instances, it is just these "questionable" chemicals that represent the greatest value of an information retrieval system and primarily for this reason an excessively restrictive system has been avoided.

The old fashioned way: hunting through a forest of bottles.

What's in it for Aldrich?

The more pertinent chemicals that a customer sees, the higher the probability that he will buy some of those chemicals. Therefore we consider this service primarily a marketing tool. On the other hand, computer information retrieval of this scope is seldom available to the individual who could most benefit from it. We feel that we can offer the chemist a big plus factor in pursuing his daily work. In a previous article it was also pointed out that catalogs, which represent the biggest expense in any marketing operation, rapidly become obsolete. Placing new chemicals at the fingertips of interested chemists as soon as they become available is of *value*, both to Aldrich and its customers. The ALDRICH FIRST master file is kept current and lists of chemicals retrieved therefrom are as up to date as yesterday.

Please feel free to test us. Your requests will be handled promptly and treated confidentially.

REFERENCES

1. "Indexing Spectral Absorption Data," *American Society For Testing and Materials*, 1964.
2. Feldman, A., Holland, D. B., and Jacobus, D. P., "The Automatic Encoding of Chemical Structures," *J. Chem. Doc., 3, 187* (1963).
3. Gluck, D. J., "A Chemical Structure Storage and Search System Developed at Du Pont," *J. Chem. Doc., 5, 43* (1965).
4. National Cash Register (NCR) 315, CRAM system (Card Random Access Memory).

Chemistry and art

Alfred Bader: Aldrich Chemical Company, Inc.

When I was studying Chemical Engineering in Canada, most engineering students and many of the professors believed that science and art were immiscible—only sissies (a term applied to most Arts students) concerned themselves with the fine arts. Twenty years of chemistry and collecting old paintings have convinced me that we were wrong—the Sciences and Art are not only miscible, but can greatly help each other.

Personally I get as much pleasure from the synthesis of a new product or the elucidation of a structure as I do from finding that a painting bought in some junk store or in an obscure auction turns out on cleaning to be a thing of beauty by a known master.

Naturally chemistry and physics help in the restoration, in the determination of period and country, of how much is original and what later additions.

But art also can and does help chemistry. All of us know how Fisher Scientific's reproductions of alchemical paintings add beauty to many laboratories. These paintings, mainly 17th century Dutch and Flemish works of alchemists at work, were collected between the World Wars, when it was still possible to bring together such a fine collection—today an almost impossible task. The one alchemical painting I own (front cover), by Thomas Wyck, a Dutchman of the second half of the 17th century, is a real action painting. A master alchemist surrounded by the paraphernalia of his craft—including a skeleton blowing a trumpet—guides his lab technician in the magic circle—two candles, a cross, a skull, a bible, blood, the magic staff—to say the proper incantations to turn the base metal suspended from the ceiling into gold. It would make a fine advertisement for our work of art: "Today one book suffices: the Aldrich catalog." Such paintings with alchemical and medical subjects of course often challenge you to compose ads. For instance, take the painting (Fig. 1) of the doctor examining the urine of the girl. Clearly he has told her that she is pregnant and, with no wedding ring, she is in tears. What an ad this would make for a pharmaceutical company: "If only she had known the pill!"

When we first thought about putting a painting on the cover of our catalog, both our Director of Research and I were pretty much against the idea—would not an old master painting seem out of place on a scientific catalog? But our Director of Marketing won out: If we could pioneer the usable catalog—the first catalog with structures, classes of compounds and empirical formulae, we could also be the first to add beauty to our cover. We offered a reproduction of the cover, thinking that perhaps forty or fifty chemists would request it, and thus far over two thousand have—often with hilarious comments. To quote just one, from Stanford University:

> "The Art Appreciation Group of Dr. Djerassi's lab would like to have a copy of your Squill-Pitter, Pull-Squitter, Kill-Qutter, Cull-Squirter . . . the chap who hasn't heard about ball-points on your new catalog cover."

By the time we were ready for the Library of Rare Chemicals Catalog, it was just a question of which painting to use, and surely none could express surprise at such a catalog better than our Man Surprised. The only unexpected question I have had to answer several times by telephone from chemists who do not know me: "Is that perchance a painting of me?" If only I had that much hair!

Paintings on stamps have recently become most fashionable, but Aldrich is the only company I know that uses a painting on its stock-certificate, an early Rembrandt of a man studying, a painting also used on some of our advertisements (Fig. 2). Think how appropriate some paintings

Figure 1.

Figure 2.

might be on some stock certificates: Western Union of course would use a painting by Morse who not only invented the telegraph but was also one of our ablest American painters. Helena Rubenstein could show the Mona Lisa, or perhaps one of the many Dutch portrayals of a girl dressing; and perhaps we should suggest to one of our Milwaukee beer companies that they use the Delft brewer shown in Fig. 3 . I understand that the New York Stock Exchange has some pretty strict rules about the certificates of listed companies—but that is a bridge we can cross when we come to it, and we have a long way to go.

Last year Aldrich sent our collection of Dutch and Flemish 17th century paintings to Midland and this year to the Kalamazoo Art Institute—partly in the hope of course that many of our good customers at Dow and Upjohn would become even better customers—and at least a good many chemists visited the shows (Fig. 4). Perhaps the fact that a good many descendants of the Dutch artists represented in the show live in Michigan also helped.

Figure 3.

Few realize how many chemists are also amateur artists—even though the ACS Convention shows compare favorably with most regional exhibitions. Take William Buth, our Director of Operations, for instance. Bill is not only responsible for that fine back-cover on our library catalog, but recently won first prize in the Art Exhibit by Chemists at the Chicago ACS Convention for his wood sculpture (Fig. 5).

Clearly art and chemistry are miscible in all proportions.

Today

Tomorrow

Figure 5.

Figure 4. From l. to r. Drs. Fred Bassett, Robert Levin and Douglas Shepherd of the Upjohn Company at the Kalamazoo Art Center Show of the Aldrich collection.

No. [illegible]

Name 1-Adamantanamine

Description and Constants

[illegible]

[illegible]

[illegible]

[illegible]

Price 5 g. - $3.00 25 g. - $12.00 100 g. - $40.00

No. [illegible]

Name 1-Amino-3-diethylamino-2-propanol

Description and Constants

M.W. 146.2

Colorless liquid

n_D^{20} 1.4642

v.p.c. 95[illegible]

Price 25 g. - $5.25 100 g. [illegible]

No. 14,[illegible]

Name 1-Aza-4,6-dioxabicyclo[3.3.0]octane

Description and Constants

M.W. 115.13

Colorless liquid

n_D^{20} 1.4668

b.p. 101-101.5°/28 mm

v.p.c. 9[illegible]

Price 5 g. - $7.25 25 g. - $29.75

No. 14,336-[illegible]

Name 1-Adamantyl isothiocyanate

Description and Constants

M.W. [illegible]

[illegible]

m.p. 166.5-168°

Price 10 g. - $7.50 50 g. - $31.75

No. 14,210-7

Name [illegible] dimethylthiazole hydrobromide

Description and Constants

[illegible]

[illegible]

[illegible]

[illegible]

Price [illegible]

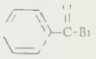
No. 13,972-6

Name Benzoyl bromide

Description and Constants

M.W. 185.03

Colorless liquid



n_D^{20} 1.5883

b.p. 218-219

Br content: 96.7% of theory

Price 50 g. - $4.25 250 g. - $19.75

No. 14,196-8

Name Agroclavine

Description and Constants

M.W. 238.33

Light tan powder

m.p. 205-207°

Price 100 mg. - $18.25

No. 14,346-4

Name 1-(2-Aminoethylamino)-2-pro[illegible]

Description and Constants

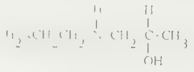
M.W. 118.18

Colorless liquid

n_D^{20} [illegible]

b.p. 177°

v.p.c. [illegible]



$H_2NCH_2CH_2\overset{H}{N}CH_2\underset{OH}{\overset{H}{C}}-CH_3$

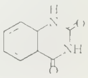
Price 500 g. - $4[illegible] 2 Kg. - $[illegible]

No. 14,202-6

Name Benzoyleneurea
[2,4(1H,3H)-quinoxalinedione]

Description and Constants

M.W. 162.15



Off-white crystals

m.p. >300°

Price 25 g. - $7.25 100 g. - $18.75

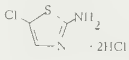
(Formerly B1300)

No. 14,345-6

Name 2-Amino-5-chlorothiazole dihydrochloride

Description and Constants

M.W. 207.51



Brown powder

m.p. 155° (dec.)

Titration 98+%

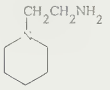
Price 5 g. - $6.00 10 g. - $10.75

No. 14,166-6

Name N-(2-Aminoethyl)-piperidine

Description and Constants

M.W. 128.22



Yellow liquid

n_D^{20} 1.4740

b.p. 186°

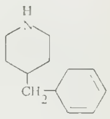
v.p.c. 99%

Price 5 g. - $11.50 10 g. - $20.50

No. 14,236-0

Name 4-Benzylpiperidine

Description and Constants



M.W. 175.28

Colorless liquid

n_D^{20} 1.5379

b.p. 279°

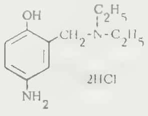
v.p.c. 97.5%

Price 25 g. - $5.50 100 g. - $18.00

No. 14,226-3

Name 4-Amino-α-diethylamino-o-cresol dihydrochloride

Description and Constants



M.W. 267.20

Off-white powder

m.p. 215-218° (dec.)

Titration 97.5%

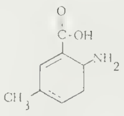
Organic intermediate; also a precursor for potential antimalarials.

Price 5 g. - $5.25 25 g. - $18.00

No. 13,790-1

Name 2-Amino-5-methylbenzoic acid
(5-methylanthranilic acid)

Description and Constants



M.W. 151.17

Tan powder

m.p. 174-177° (dec.)

Titration 96+%

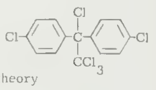
Price 100 g. - $4.50 500 g. - $19.50

No. 14,176-3

Name 1,1-Bis-(p-chlorophenyl)-1,2,2,2-tetrachloroethane

Description and Constants

M.W. 388.94



Light yellow crystals

m.p. 82-85°

Cl content: 95+% of theory

Price 250 g. - $5.75 1 Kg. - $18.75

Available literatu

1-Pyrrolidinecarbodithioic a
is widely employed for the d
of metals by atomic absor
wide variety of materials ra
such as fertilizers, plants a
such as urine, semi-conduct
electronics industry and poll
Product No. 14,269-7

Cyanomethylating Agents.
and cyanomethyl p-toluene
methylating agents for pri
amines.
Product No. 14,460-6

trans. -1, 2-Cyclobutanedica
its derivatives have recently
building blocks.
Product No. 14,531-9

1, 5-Diazabicyclo[5.4.0]und
zabicyclo[4.3.0]non-5-ene
hydrohalogenating agents

No. 14, 209-3

Name N, N-Dichl
(DCU)

Description and Con

M. W. 157

Yellow liq

n_D^{20} 1. 4595

b. p. 55-56

Useful in t
β-chloroca
addition to

Price 25 g. - $5.

Set No

FIRST CLASS
Permit No. 9040
Milwaukee, Wis.

BUSINESS REPLY MAIL
No Postage Stamp Necessary if Mailed in the United States

Aldrich CHEMICAL COMPANY, INC
2371 NORTH 30TH STREET
MILWAUKEE, WISCONSIN 53210

FIRST CLASS
Permit No. 9040
Milwaukee, Wis.

BUSINESS REPLY MAIL
No Postage Stamp Necessary if Mailed in the United States

Aldrich CHEMICAL COMPANY, INC
71 NORTH 30TH STREET
MILWAUKEE, WISCONSIN 53210

FIRST CLASS
Permit No. 9040
Milwaukee, Wis.

BUSINESS REPLY MAIL
No Postage Stamp Necessary if Mailed in the United States

Aldrich CHEMICAL COMPANY, INC
2371 NORTH 30TH STREET
MILWAUKEE, WISCONSIN

Available literature

1-Pyrrolidinecarbodithioic acid, ammonium salt (APDC) is widely employed for the determination of trace quantities of metals by atomic absorption spectrophotometry in a wide variety of materials ranging from agricultural matter such as fertilizers, plants and soils to clinical specimens such as urine, semi-conductors and related materials in the electronics industry and pollutants in water.
Product No. 14,269-7

Cyanomethylating Agents. Cyanomethyl benzenesulfonate and cyanomethyl p-toluenesulfonate are excellent cyanomethylating agents for primary, secondary and tertiary amines.
Product No. 14,460-6

trans. -1, 2-Cyclobutanedicarboxylic acid and a number of its derivatives have recently become available as new basic building blocks.
Product No. 14,531-9

1, 5-Diazabicyclo[5.4.0]undec-5-ene (DBU) and *1, 5-Diazabicyclo[4.3.0]non-5-ene* (DBN), the most versatile dehydrohalogenating agents known. Both are much more reactive than the amines traditionally used, and therefore much milder conditions can be employed.
Product No. 13,900-9

Diazoalkanes, seven precursors for the preparation of diazoalkanes (more will soon be added). Methods of preparation and literature references are available.

N,N-Dichlorourethan (DCU), a new reactive pseudohalogen, is now available in commercial quantities at substantially reduced prices.
Product No. 14,209-3

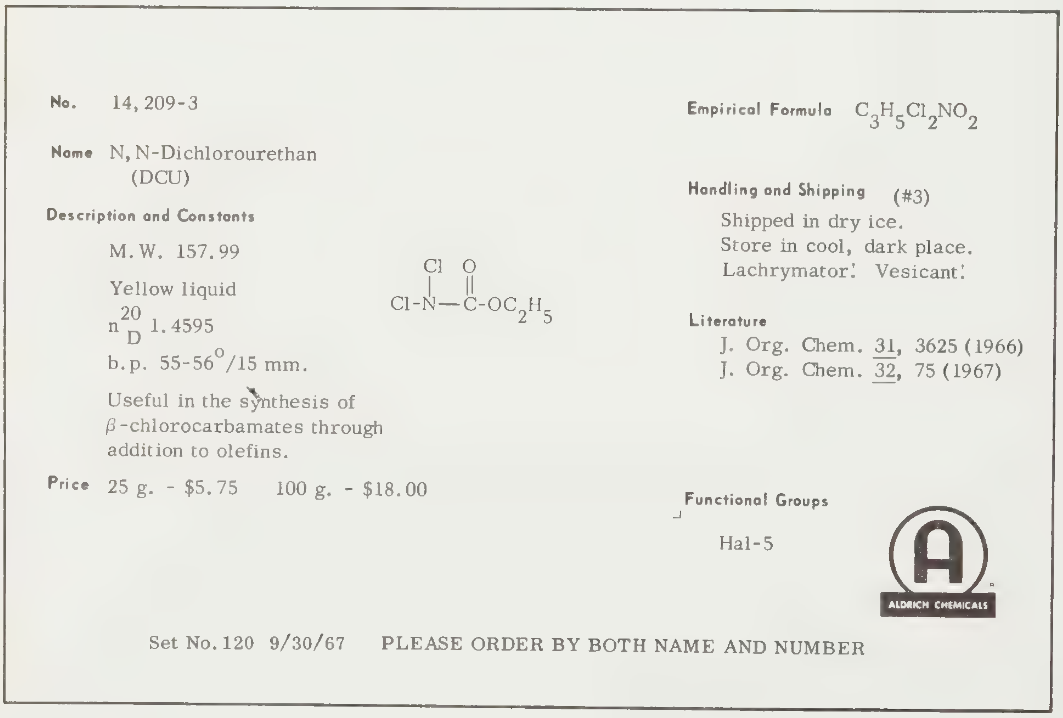
Liquid Crystals. Ask for our list of liquid crystals available from stock.

DL-α-Methyltyrosine is a specific blocking agent in the endogenous biosynthesis of catecholamines.
Product No. 12,069-3

Pyrrole, high purity (99%), is now available in commercial quantities at substantially reduced prices. Extensive literature review.
Product No. 13,170-9

Kardindex cards

The new chemical offerings published in the *Aldrichimica Acta* are available on permanent 4 x 6″ filing cards. The cards contain important literature references and are mailed monthly, several weeks in advance of being published here, to give you a head start in your research program. Approximately 50 chemicals are listed and offered each month. Subscription is $25 per year.



No. 14, 209-3

Name N, N-Dichlorourethan
(DCU)

Description and Constants

M.W. 157.99

Yellow liquid

n_D^{20} 1.4595

b.p. 55-56°/15 mm.

Useful in the synthesis of β-chlorocarbamates through addition to olefins.

$\mathrm{Cl{-}\overset{\overset{Cl}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}OC_2H_5}$

Price 25 g. - $5.75   100 g. - $18.00

Empirical Formula $C_3H_5Cl_2NO_2$

Handling and Shipping (#3)

Shipped in dry ice.
Store in cool, dark place.
Lachrymator! Vesicant!

Literature

J. Org. Chem. 31, 3625 (1966)
J. Org. Chem. 32, 75 (1967)

Functional Groups

Hal-5

Set No. 120 9/30/67 PLEASE ORDER BY BOTH NAME AND NUMBER

Please send me literature on the products checked below:

☐ 14,269-7
☐ 14,460-6
☐ 14,531-9
☐ 13,900-9
☐ 14,209-3
☐ 12,069-3
☐ 13,170-9
☐ Diazoalkanes
☐ Liquid crystals

☐ Please send me additional information on your KARD-INDEX CARD service which is available at the subscription price of $25 per year.

☐ Please send me your free 1967-68 Aldrich catalog listing 9,000 common and research organic chemicals.

☐ I would like to receive a sample copy of Modern Chemicals.

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☐ Please add my name to your mailing list.

My major areas of interest are:
☐ 02 ___ Analytical
☐ 06 ___ Biochemical
☐ 09 ___ Organic
☐ 13 ___ Organometallic
☐ 16 ___ Pharmaceutical
☐ 35 ___ Other___________

Please check one:
☐ 02 ___ Academic
☐ 03 ___ Electronic
☐ 07 ___ General chemical
☐ 09 ___ Government
☐ 11 ___ Hospital
☐ 13 ___ Oil—Gas
☐ 15 ___ Pharmaceutical
☐ 21 ___ Other___________

Name___________
Title___________
Company___________
Division___________
Street___________
City___________
State___________ Zip___________

Many of the chemicals listed in the Aldrich catalogs are available in large quantities and at substantially reduced prices. Ask for quotations.

Quantity	Chemical Name

Please send me literature on the products checked below:

☐ 14,269-7
☐ 14,460-6
☐ 14,531-9
☐ 13,900-9
☐ 14,209-3
☐ 12,069-3
☐ 13,170-9
☐ Diazoalkanes
☐ Liquid crystals

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☐ 09 ___ Organic
☐ 13 ___ Organometallic
☐ 16 ___ Pharmaceutical
☐ 35 ___ Other___________

Please check one:
☐ 02 ___ Academic
☐ 03 ___ Electronic
☐ 07 ___ General chemical
☐ 09 ___ Government
☐ 11 ___ Hospital
☐ 13 ___ Oil—Gas
☐ 15 ___ Pharmaceutical
☐ 21 ___ Other___________

Name___________
Title___________
Company___________
Division___________
Street___________
City___________
State___________ Zip___________

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Quantity	Chemical Name

Please send me literature on the products checked below:

☐ 14,269-7
☐ 14,460-6
☐ 14,531-9
☐ 13,900-9
☐ 14,209-3
☐ 12,069-3
☐ 13,170-9
☐ Diazoalkanes
☐ Liquid crystals

☐ Please send me additional information on your KARD-INDEX CARD service which is available at the subscription price of $25 per year.

☐ Please send me your free 1967-68 Aldrich catalog listing 9,000 common and research organic chemicals.

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My major areas of interest are:
☐ 02 ___ Analytical
☐ 06 ___ Biochemical
☐ 09 ___ Organic
☐ 13 ___ Organometallic
☐ 16 ___ Pharmaceutical
☐ 35 ___ Other___________

Please check one:
☐ 02 ___ Academic
☐ 03 ___ Electronic
☐ 07 ___ General chemical
☐ 09 ___ Government
☐ 11 ___ Hospital
☐ 13 ___ Oil—Gas
☐ 15 ___ Pharmaceutical
☐ 21 ___ Other___________

Name___________
Title___________
Company___________
Division___________
Street___________
City___________
State___________ Zip___________

Many of the chemicals listed in the Aldrich catalogs are available in large quantities and at substantially reduced prices. Ask for quotations.

Quantity	Chemical Name

Aldrich Chemical Company, Inc.
2371 NORTH 30th STREET
MILWAUKEE, WISCONSIN 53210

RETURN REQUESTED

BULK RATE
U.S. POSTAGE
PAID
MILWAUKEE, WISCONSIN
PERMIT NO. 552

Printed in U. S. A.

Coming your way: a library of Rare Chemicals

This valuable new catalog contains over 5000 computer-coded building blocks of research

ALDRICH pioneered the first USABLE-CATALOG. Remember what catalogs were like before that? No structures, no empirical formulas, no classes of compounds, just accumulations of names where you might or might not have found what you were looking for.

Our USABLE CATALOG has grown like TOPSY, from one page in 1951 to 752 pages this year, and in fact, we had to decide to limit the chemicals in our main catalog to about 10,000. But there are thousands of others we could offer, many of these right on our shelves — compounds which we think are out-of-the-way, but which may help someone: be it for screening, for testing a new reaction, or for identification of an unknown.

And so we decided to offer some 5,000 of these investigational tools in a simple catalog — structures and empirical formulas only.

All of these "library" chemicals are computer-coded, so that, if you would like to have a list, say, of all our pyrroles or all our B-diketones, just write us, and we'll send you the complete list, of course at no charge.

Alfred Bader Chemicals
Division of Aldrich Chemical Company, Inc.

2369 N. 30th St. • MILWAUKEE, WIS. 53210 • TEL: (414) 374-4620

Aldrichimica acta

Volume 1, Number 2, 1968

PUBLISHED BY THE ALDRICH CHEMICAL COMPANY, INC.

ALDRICHIMICA ACTA

Volume 1, Number 2
1968

Published by
ALDRICH CHEMICAL COMPANY, INC.
Milwaukee, Wisconsin

Editor, Richard K. Vitek

Assistant Editor, Kathleen D. Ryan

ABOUT THE COVER

Our chemist who collects Dutch paintings recently acquired this hitherto unpublished large (180 x 207 cms.) painting of Tobias healing his blind father, by the Dutch Rembrandt student, Paulus Lesire. The story of Tobias and Tobit was a favorite subject of baroque painters, and it is particularly charmingly depicted here with the most life-like angel Raphael, Tobias' mother, Hannah, and even Tobias' faithful companion, his dog (the only friendly dog in the Bible) getting into the act.

Lesire is known mainly for his portraits, and this is his only known biblical painting; luckily, it is fully signed. But beside the art-historical interest in this painting, we were charmed by its obvious human interest: the love and concentration of the son healing his father—a model for every doctor everywhere.

TABLE OF CONTENTS

Aldrichimica Acta replaces the previously published *Kardindex Sheets* to keep chemists informed of the latest chemical offerings by Aldrich Chemical Company, Inc. The articles also published are of general interest to users of chemicals and Aldrich customers. While the information and data included in this publication is correct and reliable to the best of our knowledge, it is not guaranteed to be so. Therefore, we cannot assume responsibility connected with the use of our chemicals or data. The information on or sale of any material is not intended as a license to operate under, or a recommendation to infringe, any patent covering any material or use.

Organic Intermediates • Biochemical Tools • Reagent Chemicals • Analytical Tools • Organo-metallics

Each chemical is carefully analyzed and stocked for your convenience.

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Telephone—(414)-374-4620

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P. O. Box AA
Cedar Knolls, New Jersey 07927
Telephone: 201-539-9494

West Coast Distributor:
Wilshire Chemical Co., Inc.,
15324 S. Broadway, Gardena, California 90247
Telephone—(213)-323-9232

Of things to come

Alfred Bader: Aldrich Chemical Company, Inc.

The most common question I am asked by friends, customers and stockholders—in fact almost invariably by anyone who discusses Aldrich with me for any length of time, is, "What will Aldrich be doing five or ten years from now?" This may seem like a simple question, and yet, could I have foreseen in 1958 or even in 1963 what we are like today? And why should our crystal ball be clearer now than then?

Nonetheless, a clear knowledge of what has happened in the fine chemical industry generally, and with Aldrich in particular, should allow us to make at least some intelligent guesses of what both will be like ten years from now.

Two fundamental changes have taken place in our industry in the last twenty years; a third is just taking place.

When I was a graduate student at Harvard in the forties, we looked into one catalog to see whether a required research chemical was available. If it was not, we made it ourselves. This catalog has remained essentially unchanged in format and size for the last twenty years. Today, however, several catalogs, American and European, offer many more chemicals, and the Aldrich catalog, listing our products not only alphabetically but also with structures and by classes of compounds and empirical formulae, makes finding a compound or class of compounds much easier.

The second fundamental change has been with purity of the compounds offered. Even only a few years ago, you could not be certain that a given chemical, particularly a liquid, in any of the standard catalogs, was pure. I venture a guess that as many as 30 or 40% of the liquids offered, while having reasonably close boiling ranges, were less than 90% pure, and a fair number would have had v.p.c.'s like Christmas trees. My old friend, Michael Carroll, the discoverer of the Carroll Reaction, said to me in 1952—"You will see, Alfred, gas-chromatography will make honest men of many of us." He was right, and gas chromatography, the greatly expanded use of spectroscopy (i.r., u.v., n.m.r.), thin layer chromatography and the scores of specific functional group methods of analysis have enabled our industry to assure high purity products.

The third change is just beginning: it is the impact of the computer on our industry. Not just the impact on inventory control and invoicing but particularly its impact on finding sources for individual products and groups of definite structural characteristics. Suppose that five years ago a medicinal chemist had found that a cyclopropylamine had a very specific pharmacologic action, and he wanted to compare the action of other cyclopropylamines and perhaps of similar cyclobutyl—and cyclopentylamines also. Where could he have gone? He would have looked into the standard catalogs under *cyclopropyl* and he would have contacted chemists who have recently published on such compounds. Then he would have gone to the literature and made analogs himself. Today Aldrich can send him, at no charge, a complete computer print-out of all our cyclopropyl, or cyclobutyl or cyclopentyl compounds among the 14,000 compounds in our two catalogs; and before long we will be able to supply him with a print-out of all the chemicals in these categories available commercially anywhere. Soon, also, all of the compounds in Chemical Abstracts will have been computer coded and our catalog will list the C.A. code numbers of all of our products, so that it will be easy to determine just what has been published on every compound offered.

Just a few years ago, we bought our first building, and the six of us, who are all still with Aldrich, felt a little lost in the cavernous 27,000 square foot building which was ten times as large as the laboratory we had rented previously. Since then, we have added 160 employees, including nine Ph.D.'s among 40 chemists in all, and we are now housed in much larger buildings and in research and production laboratories specially built for our needs. Most of our expansion in the next ten years will probably come in distribution and in production. We are just moving into a much larger warehouse in New Jersey and will probably add warehouses in Washington, D. C. and other parts of the country. We are not likely to go into the large scale production of anything, but will expand our production facilities, rapidly to be able to make up to 25 kilo lots of many more products.

Ten years ago, our Catalog No. 8 was a simple 82-page compilation of our products listed alphabetically and by classes of compounds only; Catalog No. 9 was the first catalog also to offer compounds with empirical formulae, and Catalog No. 11 with structures. Our Catalog No. 19, ten years from now will probably not look so very different from our present catalog, but our Library of Rare Chemicals catalog will probably list some 25,000 compounds rather than only the 5,000 listed in our present library catalog. Ten years ago we offered only out-of-the-way chemicals; today we also offer several thousand common organic chemicals, and long before 1978 we will undoubtedly have a complete line of every common organic chemical.

The advertisement of Fig. 1, of five years ago, states one of our most important aims: the sale of fine organic chemicals used to support fundamental research. That we have saved chemists throughout the world millions of man hours of labor by supplying chemicals not available elsewhere, is obvious. But Aldrich is today the only major supplier of organic laboratory chemicals whose major—in fact, whose only—business is in organic chemicals, and we have plowed a good share of our earnings back into fundamental research. Five years ago we had made only the modest beginning referred to in the ad. Today we have a Research Department headed by one of the country's foremost medicinal chemists, with some fourteen chemists turning out novel structural classes of chemicals of great significance to both organic and medicinal chemists.

Our dream is coming true.

PROCEEDINGS FEBRUARY 1963

. . . of things to come !

Oil on copper, 5″ × 5″ Hofstede de Groot No. 240

THE SCHOLAR BY CANDLELIGHT

One of our chemists collects Dutch paintings and managed to pick up a small, early Rembrandt in Vienna some years ago.

Discussing this painting with us, he admitted that he would prefer a late Rembrandt portrait, and yet he almost got us to share his enthusiasm for this small piece of copper. Done in Leiden when Rembrandt was in his early twenties, it clearly foreshadows the great things to come: "The Supper at Emmaus," in the Musée Jacquemart André in Paris; and the "Self-portrait Before the Easel," in Boston, painted only a year or two later.

Perhaps what struck us so forcefully about these comments was their likeness to our own dreams for Aldrich: a modest beginning—a new synthesis of indoles, our work on unsaturated phenols, on o,p'-DDD and cyclohexenones—foreshadowing the things to come: the sale of fine organic chemicals used to support fundamental research.

Figure 1

Available literatu

Aldrithiols. Two new thiol
and 4, 4′-dithiodipyridine,
They are excellent reagents
as these reagents can be use
Ellman's reagent. See san
Product No. 14,304-9

Bis-(trimethylsilyl)-acetamid
ing agent for the rapid qu
melting solids to volatile liq
BSA is also used as a fast-a
tive hydrogen compounds
esterification procedure.
Product No. 12,891-0

Diazald®, N-methyl-N-nitro
of the most useful reagents
of diazomethane. For deta
literature references, ask fo
sheet.

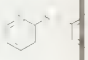
Glyoxalbis-(o-hydroxyanil) i
tative determination of Calc
references.
Product No. G1040-7

Hexamethylphosphorous tri
for the preparation of epox
Product No. 14,355-3

No. 14, 304-9

Name Aldrithiol-2
(2, 2′-dithiodipyridine)

Description and Constants



[illegible]

Price [illegible]

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Aldrich CHEMICAL COMPANY, IN

Available literature

Aldrithiols. Two new thiol reagents, 2, 2′-dithiodipyridine and 4, 4′-dithiodipyridine, are now available from stock. They are excellent reagents for estimation of thiol groups as these reagents can be used over a wider pH range than Ellman's reagent. See sample Kardindex cards below.
Product No. 14,304-9

Bis-(trimethylsilyl)-acetamide (BSA), is an excellent silylating agent for the rapid quantitative conversion of high-melting solids to volatile liquids prior to analysis by v.p.c. BSA is also used as a fast-acting quenching agent for active hydrogen compounds and as a reactant in a novel esterification procedure.
Product No. 12,891-0

Diazald®, N-methyl-N-nitroso-p-toluenesulfonamide is one of the most useful reagents developed for the preparation of diazomethane. For detailed procedures and technical literature references, ask for Product No. D2800-0 data sheet.

Glyoxalbis-(o-hydroxyanil) is a useful tool for the quantitative determination of Calcium (II). Extensive literature references.
Product No. G1040-7

Hexamethylphosphorous triamide is the reagent of choice for the preparation of epoxides from aldehydes.
Product No. 14,355-3

3-Hydroxypyridine. Its greatest use is in the synthesis of many types of drugs. Four important derivatives are also available and described with literature references. Recently, some derivatives of 3-hydroxypyridine have been found to function as protective agents of deoxyribonucleic acid (DNA) which has been irradiated with X-rays.
Product No. H5700-9

Iminostilbene is a versatile starting material for the synthesis of many new therapeutic agents.
Product No. 14,365-0

Salicylic acids. A series of new substituted salicylic acids that are of special interest to medicinal chemists. Ask for our listing of these exciting chemicals.

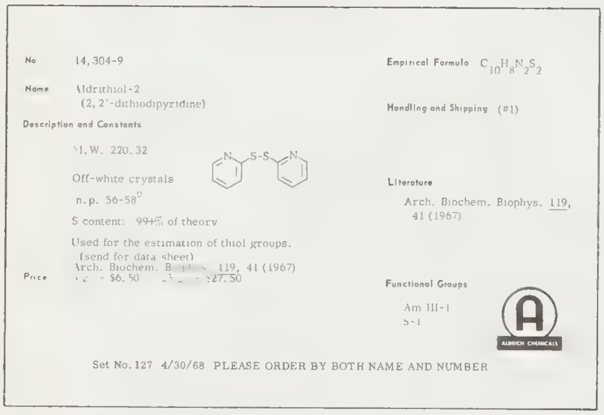
Squaric acid. Please see the feature article written by Professor Robert West that appears on page three of this issue.
Product No. 12,344-7

Tetrachlorocyclopropene is an interesting intermediate in the preparation of two new series of compounds—*triquinocyclopropanes* and *diquinoethylenes.*
Product No. 14,594-7

2, 2, 2-Trichloroethyl chloroformate is an excellent protecting agent for both aliphatic and aromatic hydroxy and amino groups.
Product No. 14,207-7

Kardindex cards

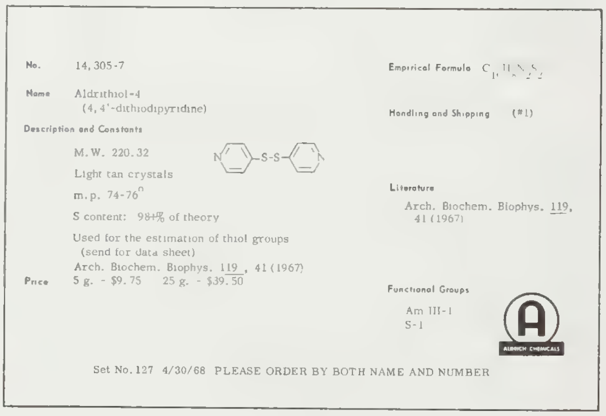
The new chemical offerings published in the *Aldrichimica Acta* are available on permanent 4 x 6″ filing cards. The cards contain important literature references and are mailed monthly, several weeks in advance of being published here, to give you a head start in your research program. Approximately 50 chemicals are listed and offered each month. Subscription is $25 per year.



No 14,304-9
Name Aldrithiol-2
(2, 2′-dithiodipyridine)
Description and Constants
M.W. 220.32
Off-white crystals
m.p. 56-58°
S content: 99+% of theory
Used for the estimation of thiol groups.
(send for data sheet)
Arch. Biochem. [illegible] 119, 41 (1967)
Price [illegible] - $6.50 [illegible] $27.50

Empirical Formula $C_{10}H_8N_2S_2$
Handling and Shipping (#1)
Literature
Arch. Biochem. Biophys. 119, 41 (1967)
Functional Groups
Am III-1
S-1

Set No. 127 4/30/68 PLEASE ORDER BY BOTH NAME AND NUMBER



No. 14,305-7
Name Aldrithiol-4
(4, 4′-dithiodipyridine)
Description and Constants
M.W. 220.32
Light tan crystals
m.p. 74-76°
S content: 98+% of theory
Used for the estimation of thiol groups
(send for data sheet)
Arch. Biochem. Biophys. 119, 41 (1967)
Price 5 g. - $9.75 25 g. - $39.50

Empirical Formula [illegible]
Handling and Shipping (#1)
Literature
Arch. Biochem. Biophys. 119, 41 (1967)
Functional Groups
Am III-1
S-1

Set No. 127 4/30/68 PLEASE ORDER BY BOTH NAME AND NUMBER

Data sheets are available
on both of these chemicals

Please send me literature on the products checked below:

☐ D2800-0 ☐ 12,344-7 ☐ 14,304-9 ☐ 14,594-7
☐ G1040-7 ☐ 12,891-0 ☐ 14,355-3 ☐ Salicylic acids
☐ H5700-9 ☐ 14,207-7 ☐ 14,365-0

☐ Please send me additional information on your KARD-INDEX CARD service which is available at the subscription price of $25 per year.

☐ Please send me your free 1967-68 Aldrich catalog listing 9,000 common and research organic chemicals.

☐ Please send me your free newly released Alfred Bader Chemicals catalog listing over 5,000 rare chemicals.

Please check one:
☐ I am already on your mailing list.
☐ Please add my name to your mailing list.

My major areas of interest are:
☐ 02 ___ Analytical
☐ 06 ___ Biochemical
☐ 09 ___ Organic
☐ 13 ___ Organometallic
☐ 16 ___ Pharmaceutical
☐ 35 ___ Other___________

Please check one:
☐ 02 ___ Academic
☐ 03 ___ Electronic
☐ 07 ___ General chemical
☐ 09 ___ Government
☐ 11 ___ Hospital
☐ 13 ___ Oil—Gas
☐ 15 ___ Pharmaceutical
☐ 21 ___ Other___________

Name ______________________________
Title ______________________________
Company ______________________________
Division ______________________________
Street ______________________________
City ______________________________
State ____________________ Zip __________

Many of the chemicals listed in the Aldrich catalogs are available in large quantities and at substantially reduced prices. Ask for quotations.

Quantity	Chemical Name

Please send me literature on the products checked below:

☐ D2800-0 ☐ 12,344-7 ☐ 14,304-9 ☐ 14,594-7
☐ G1040-7 ☐ 12,891-0 ☐ 14,355-3 ☐ Salicylic acids
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Title ______________________________
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☐ 09 ___ Government
☐ 11 ___ Hospital
☐ 13 ___ Oil—Gas
☐ 15 ___ Pharmaceutical
☐ 21 ___ Other___________

Name ______________________________
Title ______________________________
Company ______________________________
Division ______________________________
Street ______________________________
City ______________________________
State ____________________ Zip __________

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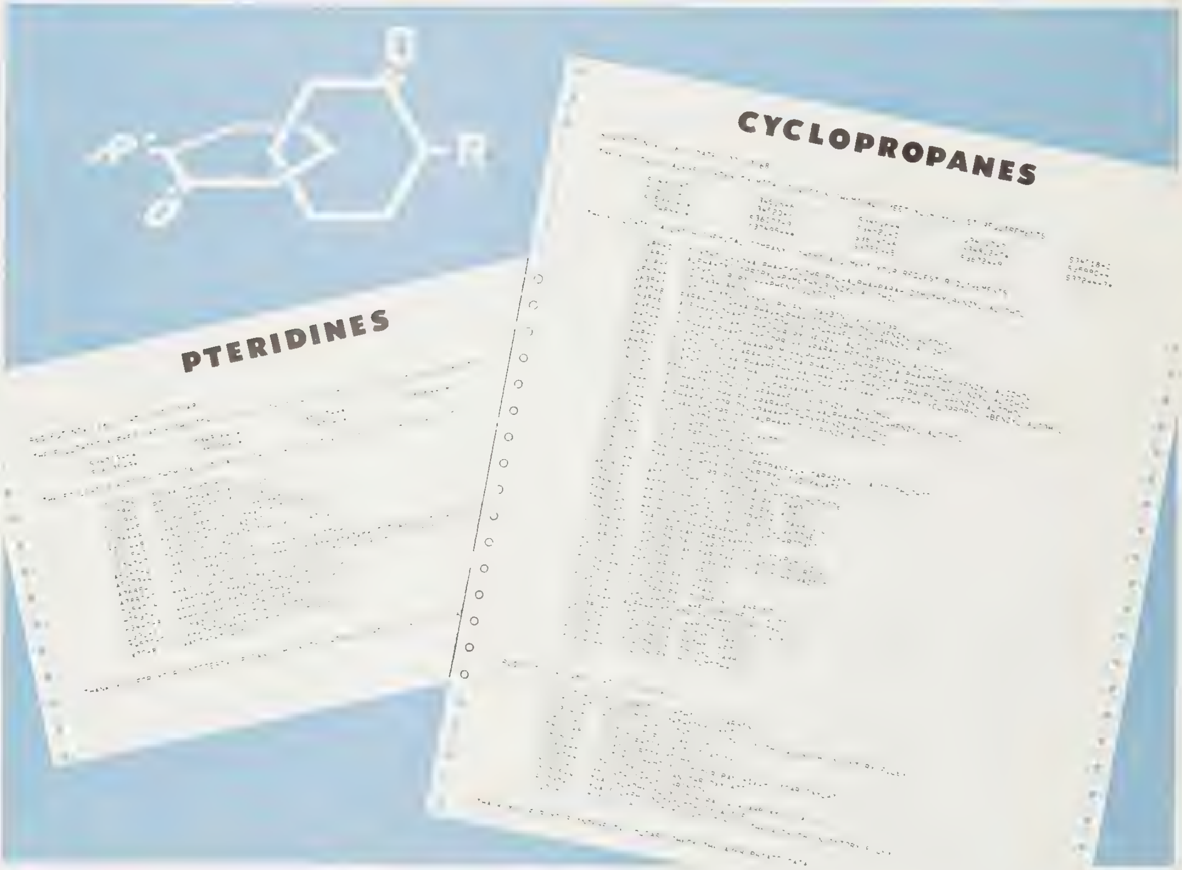
but if it does—
Aldrich will help you find it!



COMPUTER RETRIEVAL OF STRUCTURES

Write us about the types of chemicals that interest you. At no charge, we will have our computer search the 14,000 items in the combined Aldrich and Alfred Bader Chemical files and send you the print-out.

Cyclopropanes, pteridines, fluorenes, thiophenes, amino-alcohols—you name them—and we will offer them to you.

ALDRICH: The House of Chemical Vision

Aldrichimica acta

Volume 1, Number 3, 1968

PUBLISHED BY THE ALDRICH CHEMICAL COMPANY, INC.

ALDRICHIMICA ACTA

Volume 1, Number 3
1968

Published by
ALDRICH CHEMICAL COMPANY, INC.
Milwaukee, Wisconsin

Editor, Kathleen D. Ryan

ABOUT THE COVER

Our chemist who collects old master paintings is widening his interests: ten or fifteen years ago he looked only for Dutch 17th Century paintings; now he even acquires paintings of which he does not know when or where they were painted. Such is the case with the Head of a Prophet reproduced on our cover.

As our collector explains it, he was minding his own business late one afternoon in Copenhagen, after a busy day discussing chemistry with Niels Clauson-Kaas, one of Denmark's ablest chemists, when he saw this painting in a small gallery, where it had just come from the family of Gauguin, the great painter. Neither Gauguin nor the gallery-owner had any attribution. Nonetheless, our chemist bought this, and the first night could not sleep—haunted by the intensity of this painting beside his bed—Ezekiel in the Valley of Dry Bones.

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ATTENTION

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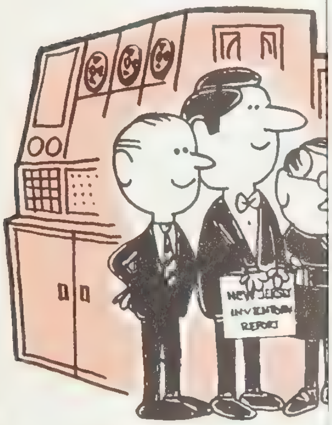
SERVICE FOR OUR E



SO WE MOVE

AND NOW IT'LL TAKE
YOU NEED FROM AL
SPEED NUMBER

ALDRICH CHE

NEW EASTERN OFFICE: 10 RIDG
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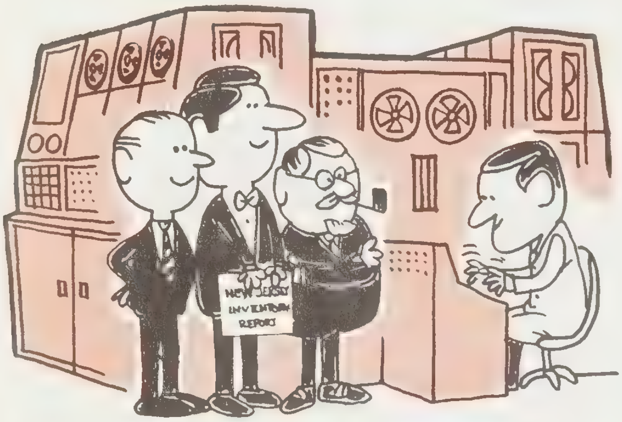

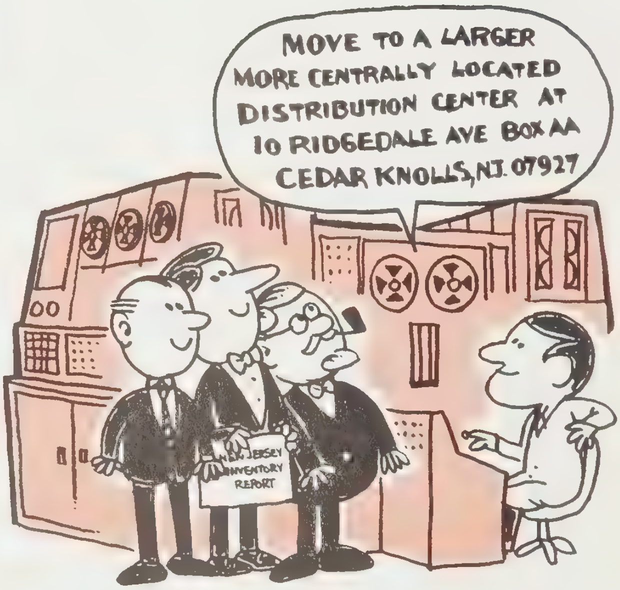

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WEST COAST DISTRIBUTOR: WILSHIRE CHEMICAL CO., INC. 15324 SOUTH BROADWAY GARDENA, CALIF. 90247 TELEPHONE 213 323 9232

AVAILABLE LITERATURE

2-Adamantanone. The first commercially available 2-substituted adamantane.
Product No. 14604-8

Diazoalkanes. A series of alkylnitronitrosoguanidines for the facile preparations of many diazoalkanes. Write for data sheet.

Fertilysin (N,N′-Octamethylenebis-(dichloroacetamide). In animals inhibits spermatogenesis without affecting production of gonadotropins.
Product No. 14750-8

Bis-Tris (2,2-Bis (hydroxymethyl)-2,2′,2″-nitrilotriethanol). A most useful buffer.
Product No. 14609-9

2′-Hydroxy-p-acetophenetidide. Of great interest in studies of the metabolism of phenacetin.
Product No. 14650-1

Metabarb (5-ethyl-5-(3-hydroxy-1-methylbutyl)-barbituric acid). Used in the study of the metabolic disposition of barbiturates.
Product No. 14610-2

Formamidoxime. Of possible interest in cancer research. Write for detailed literature review on formamidoxime and hydroxyurea.
Product No. 14019-8

3-Hydroxypyridine. Its greatest use is in the synthesis of many types of drugs. Four important derivatives are also available and described with literature references. Recently, some derivatives of 3-hydroxypyridine have been found to function as protective agents of deoxyribonucleic acid (DNA) which has been irradiated with X-rays.
Product No. H5700-9

Diazald®, N-methyl-N-nitroso-p-toluenesulfonamide is one of the most useful reagents developed for the preparation of diazomethane. For detailed procedures and technical literature references, ask for Product No. D2800-0 data sheet.

Salicylic acids. A series of new substituted salicylic acids that are of special interest to medicinal chemists. Ask for our listing of these exciting chemicals.

Please send me literature on the products checked below:

☐ 14,604-8
☐ Diazoalkanes
☐ 14,750-8
☐ 14,609-9
☐ 14,650-1
☐ 14,610-2
☐ 14,019-8
☐ H 5700-9
☐ D 2800-0
☐ Salicylic acids

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☐ Please add my name to your mailing list.

My major areas of interest are:
☐ 02 ___ Analytical
☐ 06 ___ Biochemical
☐ 09 ___ Organic
☐ 13 ___ Organometallic
☐ 07 ___ Pharmaceutical
☐ 35 ___ Other ______

Please check one:
☐ 02 ___ Academic
☐ 03 ___ Electronic
☐ 07 ___ General chemical
☐ 09 ___ Government
☐ 11 ___ Hospital
☐ 13 ___ Oil—Gas
☐ 15 ___ Pharmaceutical
☐ 21 ___ Other ______

Name ______
Title ______
Company ______
Division ______
Street ______
City ______
State ______ Zip ______

Many of the chemicals listed in the Aldrich catalogs are available in large quantities and at substantially reduced prices. Ask for quotations.

Quantity	Chemical Name

STRUCTURE OR FRAGMENT OF INTEREST

(Draw Structure or Describe)

Functional groups or classes NOT wanted ______

______

Molecular weight range if important
Min ______ Max ______

COMPUTER SEARCH REQUEST

Name ______
Title ______
Company ______
Division ______
Street ______
City ______
State ______ Zip ______

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The front cover is discussed on page 15 in Mr. Anthony M. Clark's article on Dutch art and the Aldrich Collection.

TABLE OF CONTENTS

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Dutch Art and the Aldrich Collection

Anthony M. Clark
Director, The Minneapolis Institute of Arts.

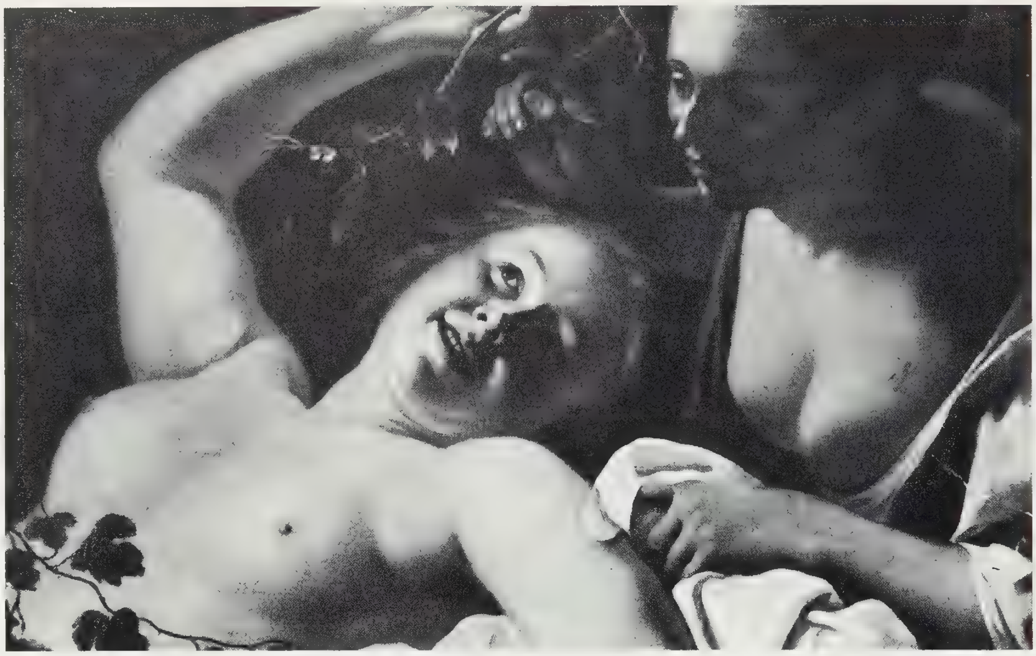
Address delivered by Mr. Anthony M. Clark at the opening of the Aldrich collection of Dutch Art at the Kalamazoo Institute of Art.

Ladies and Gentlemen:

You might ask why a scholar of 18th Century Italian paintings stands before you at this opening of your Fifth Anniversary Fund Exhibition and has the nerve to speak to you about an art so different from that which he usually studies; as if an expert on desserts and after-dinner mints was to lecture on plain roast beef. Since that is actually what I'm going to do, I hope my natural enthusiasm (and quite natural relief at the momentary change of subject) will carry us along. Also, I'm a museum man who has to look at and use public purchase funds over the wide and catholic range of man's very long and varied artistic creativity, can happily still do this with gusto, and find myself very often brought up short by paintings done in such a number and in such quality in a few decades in that small acreage of the world we call The Lowlands. It is a curious feeling for me—loving and pursuing as I do the grandly framed decorations of Italian palaces and churches, their grand frescoes, huge altars, all that great public art of a bright southern land full of artistic prodigality and emotional generosity—to turn to the private, clear, practical, modest, commonsense skies and landscapes of the Netherlands. For me it is invigorating to do so; not like a cold shower, but like coming home. How wonderful to be able to find enough pleasure in the everyday and the simply good! And that is what the Dutch were able to do. They are remembered not for their grandeur, their private and public splendor, their great buildings and town plans, magnificent gardens or fountains and piazzas, but for a simple form of art with simplest homespun subjects. Their painting, this leading art of theirs, seldom chooses to represent the great gods and heroes, the learned mythological and devotional subjects, and instead presumes to avoid the imaginative world like the plague. A table full of food, a white-washed church with a few solid, common figures, an unpretentious and frank portrait, a street scene, a wild but homespun landscape, poor peasants in a barn, a woman darning a sock, a fancy charade in a farmyard illustrating a Bible story—these were enough for faithful artists of fine technique, and enough for such giants of man's spiritual history as Franz Hals, Vermeer, and Rembrandt.

Although the exciting exhibition you open today shows Dutch *and* Flemish paintings of the 17th century, I am going to restrict my short words to the Dutch art. In this school of painting I believe that the Aldrich Collection is most interested, and the Flemish paintings that they have so well selected for you are, even including the exceptions of the Van Dyck and Cornelius de Vos portraits, those which would have felt most at home in 17th Century Holland. For remember that in the baroque century Flanders was typically a far showier place and, utterly unlike the Dutch, the Flemish began with the superb and academic—let us call it the very worldly and even vulgar (except in the imaginative opulence of a Rubens, a Van Dyck, or a Jordaens, who all had assimilated the grander inventions of Italy), and that the Flemings never approached the striking Dutch achievement unless trained in it and following its lead, as was a painter like Adriaen Brouwer (who can be seen in this exhibition).

What on earth made this Dutch achievement possible? The Republic of the United Netherlands in the 17th century is one of the happier success stories in the heritage of Western history, and one which still is, thank God, almost as familiar as it should be, what with its importance to the Anglo-Saxon tradition of liberty and commerce. Most of Europe in that grandiose century was involved in expensive and complicated wars. Great nation stood against great nation, each paralyzed, as it were, by the glory and greatness of its princely rulers. The Dutch provinces quite literally barely tolerated their ruling House of Orange; proud, free provinces were banded together freely for self-preservation, and the small nation developed a most powerful but egalitarian and unpretentious middle class, and more important, a most sound, natural prosperity. Neutral, and even negligible in the wars of the century, the Dutch became the Banker of Europe and, silently, invisibly, as the others fought, the Dutch surprisingly became the leading sea-power of the world, with most profitable colonies



(*Fig. 1*)

around the globe. The heroic Dutch navy, the bravery and industry of the Dutch Merchant Fleet, the country's geographical position all provided the most spectacular natural success of the magnificent 17th century. A traditional insistence on decentralization, the good common sense and mercantile liberalism of the ruling class, and a shrewd spirit of tolerance both towards the new and towards minorities, helped transform the prosperity towards that release and breakthrough which we see in Dutch painting, and which is—if in a modest way—really comparable to the extraordinary flowering of Athens and Greece after the Persian wars. The Dutch painting is the happiest and most natural accompaniment to this political and commercial triumph of Holland, which lasted only for a few generations. By the end of the century, power had departed and so, mainly, had the genius of art.

In 1640 a traveler wrote, "As for the art of painting and the affection of the people to pictures, I think none other go beyond them, there having been in this country many excellent men with the faculty and some at present, as Rembrandt, etc. All in general strive to adorn their houses, especially the outer and street room, with costly pieces, butchers and bakers not much inferior in their shops, which are fairly set forth; yea, many times blacksmiths, cobblers, etc., will have some picture or other by their forge or in their stall. Such is the general notion, inclination, and delight that these country natives have to painting." This is an unexaggerated account, and if you will go through a text on Dutch painting you will marvel at the vast number of so-called "minor masters," all of excellent technique and quality, who supplied the demand. The United Provinces took their religion seriously, were not fanatical but tolerated fanatics—think of the radical Protestant sects that began in Holland—but there was one morris dance, one fad, which, if it wasn't so innocent and harmless, could have been called fanaticism, and that was the Dutch love and production of paintings.

It simply can't be explained on much less frivolous grounds than that. And let us remember in passing that the size of the production has much to do with the solidarity and prosperity of the Dutch audience. It is an oversimplifictation to say that 17th Century Dutch painting is the first example of art consumption by a large middle-class audience and is also the grandparent of that ignoble descendant modern television—but there is as much truth in the first of these statements as there is cruel irony in the second of them!

As the century progressed, Amsterdam became the center of the European market, with dealers and auction houses much as there are in London or New York today, a position it held for a century longer. Local trade in the native art was hilariously intense and the single unfortunate lack of Dutch painting is a late 17th Century Daumier whose genre was the art trade as it worked throughout the fancy and low worlds of Holland. But now I'd like to speak for a moment about the collecting of Dutch art, and the beginnings of its great vogue and recognition in the world.

Remember first that since the 14th century the provinces of the Netherlands had a good native share of the fine European painters, and that craftsmanship was always of a very high order. The ancestors of the 17th Century painters were not unworthy primitives—think of Lucas van Leyden and Hieronymus Bosch—amongst the world's very greatest artists, desirable everywhere, world innovators and leaders. These older artists had, incidentally, many of the recognizable artistic virtues that are specifically and inexplicably Dutch—even the familiar Dutch artistic personality was already invented as the 17th century began (just as some of its characteristics can be found in the recent Dutch artists, such as even Van Gogh and the moderns of the Cobra group). The glorious and curious production of the Dutch 17th Century painting was, however, both very special—as brave as Dutch natural and commercial leadership—and different, and even isolated as Holland itself in the history of the 17th Century European style. Rome and Versailles *are* that style—to put the matter very simply—not Ruisdael or Brouwer, or even Hals, Vermeer, and Rembrandt.

In the first half of the century only those Dutch painters (with their Flemish cousins) who specialized in landscape and genre scenes can be said to have made their mark, by the simple expediency of having gone to Rome and literally invented their two disciplines and art forms in that city where the entire baroque age was invented. The results might be called anti-baroque and oddities of their time, but they were enormously popular and were featured in many grand and ambitious European collections—indeed, they were probably what the great princely owners liked best—more than the huge heroines, etc., of the more famous and honored painters of the day. The Dutch and Flemings became known in all European courts as the only ones who could do certain things: flower pieces, landscapes of great flavor and naturalness, scenes of low life or genre scenes—all usually pictures of informal, small format. The establishment, the leaders of the grander nations had to have these products and even one or two domesticated practitioners of them. They did not, however, buy from the best Dutch artists of the Golden Age—these were simply and obviously unknown in the Catholic nations where the great wealth and patronage lay, aside from the constant and satisfactory demand at home in Holland which consumed the supply.

There were exceptions, and among the most notable is Rembrandt. The most powerful and gifted of all the Dutch, a failed and bankrupt prophet in his own land, Rembrandt's name was known in his middle period and at the height of his comtemporary fame throughout Europe, but in quite a special way—for let us remember that Rembrandt made many etchings of great and obvious quality and that these traveled easily. Don Antonio Ruffo, a prince in Sicily, had the means to commission and buy what he wanted and was well acquainted with art. Most of his collection was painted for him by the leading Italians of his day, and he was luckily ignorant enough of Rembrandt's late career difficulties to have him paint the now famous *Aristotle Contemplating the Bust of Homer*. Apparently Prince Ruffo did not like it nearly as much as earlier and less ambitious —more "Dutch"—Rembrandts he had commissioned. Nor could he have liked it much, for such subjects were to the baroque taste, handled better otherwise than in this now terribly expensive and terribly profound picture of an old man in odd, exotic costume sadly touching the bust of another old man.

Not until the end of the century would Cosimo III, Grand Duke of Tuscany, visit Holland and fall in love with paintings by Vermeer and William van de Velde, the great marine painter. Not until the 1740's would the British begin to systematically and intelligently drain Holland of some of its best masterpieces so that Cuyp and many others simply can't be seen except *out* of Holland. Not really until the 1670's did the greatest of Amsterdam dealers even *begin* to export anything but the best Italian masters bought and collected in Holland for sale, or those numerous Italianate Dutchmen, who are not the first Dutch painters we think of today and who painted Italian scenes with limpid southern skies in clear classical orders and harmonies.

The most famous Dutch artist in 1700 was a now forgotten and neglected figure, Adrian van der Werff, called in 1721 by the learned critic, Houbraken, the greatest of all Dutch painters. Van der Werff's small and beautifully finished figures would seem by classical Dutch standards—such as those of the artists of 1640 and also those of the Aldrich Collection almost perverse, over-precious, porcellainy and rococo flies in dark amber. He was perfect for a late baroque or rococo boudoir where a Ruisdael, a Rembrandt, or even that incredible masterpiece in this exhibition by Verhout would have looked like a bull in a china shop. But as Mme. de Pompadour failed and died, the French amateurs became able to like Rembrandt and Metsu, as well as the now widely popular Italianate Dutchmen such as Dujardin and Berghem, who now deeply in-

(Fig. 2)

fluenced French 18th Century landscape painting, almost a century after their own time. Even for the British of the 18th century the Dutch artists favored and collected had to be genial and Italian, and I can only count a minority of the paintings in the present exhibition which would have then made the grade.

These would have included the bosomy Bronchorst, *(Fig. 1)* for reasons apparent in any century, most of the landscapes (which the more romantic Englishmen would have loved), the Wouverman, which is an Italianate genre scene—and the landscape by Jan Wynants, which is exactly what the young Gainsborough loved, and through the freshness and immediacy of which he was to liberate his genius and that of British art. That gem of an early Rembrandt which you have the privilege of seeing here would have been respected anywhere in Europe, even in the 17th century, right on from about 1630 when it was done. In the 18th century it would have become a valuable and celebrated work—it was engraved in a prominent French collection at that time, and one may remember that not only did Sir Joshua Reynolds claim to base his own painting style upon Michelangelo and Rembrandt, but that such surprising artists as Tiepolo and Fragonard were fully aware of Rembrandt, venerated him, and even aped his manner, if not his profundity.

If Dutch painting was collected with avidity in Britain and France in the 18th century, the beginnings of its careful study and connoisseurship only began by virtue of the impending romanticism and within the brilliant eccentricities of random collectors who, however, only opened the door a crack to some of the most exciting virtues and artists. George III was thought cheated when a rather cheap Van Mieris turned out to be only by someone called Vermeer (now probably the most thrilling of the Queen's many Dutch pictures) and the paintings by the same great Vermeer which Catherine the Great had bought in Amsterdam and which were lost in a shipwreck on their way to Russia were apparently not much regretted at the time and were probably bought as satisfactory to Italianate taste in a century still so very Italianate in taste.

The heroics of the Napoleonic age weren't a good time for Dutch virtues, but I can quickly conclude my tale of collecting by noticing that the naturalness and severe realism of the Bega, *(Fig. 2.)* the Brouwer, the several still lives in the Aldrich collection, the Jacobus Vrel, and the incredible Verhout could only have been appreciated universally with the coming of the 19th century and its scientific and social realism. How much the 19th century owes to pictures like this, how much we all owe! The Brouwer, a simple grimacing man, *(Fig. 3.)*, is a funny picture, but also a realistic physiological study that by empathy pulls our own muscles comically out of shape too, and makes us laugh. As all great comic art, it is factual and more than a caricature, it is a human and humane release. The Verhout portrait of an unpretentious brewer (see front cover) is as beautiful a piece of still life painting, and as original, daring, and elegant a work of art as anything I know. It is also, for all its intense simplicity and tiny format, as classical and potent as the finest Greek statues of the late archaic and early classical period. It is utterly clean and fresh, and as moving and great a piece of human creation, technique, and insight as possible to make. By 18th Century taste it would have seemed severe and even crude.

Anthony M. Clark—Director, The Minneapolis Institute of Arts.

(Fig. 3)

With the 19th century and our own day it became possible to see Dutch painting of the great period fully and well. That it is still possible to form, with modest means and sensible industry and shrewdness, such a collection as the Aldrich collection—in this day and age, could seem a hilarious comment on the modern art market, as well as an extraordinary evidence of a collector's talent. Indeed, it is both, but much more. As your Fifth Anniversary Fund seeks and achieves the excellent purposes of your Institute of Arts, consider and remember this collection. It does *not* take megalopolitan funds to gather and to share finest examples of man's best treasures. Works of art contain the meanings and virtues that are going to keep man alive and, if anything can, make man better. Your Fund permits you to see and to have this life-bread. Aldrich's example should show you that with energy, invention, and persistence, those natural and common qualitites of human existence, each of you can discover and achieve something important in collecting, in creating, or in simply subsisting, and all of you can achieve the purposes of the present campaign or, indeed, of any other social purpose you can think of.

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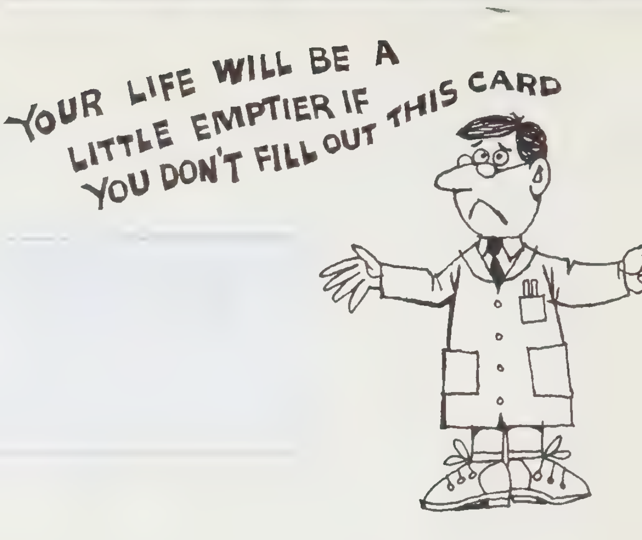

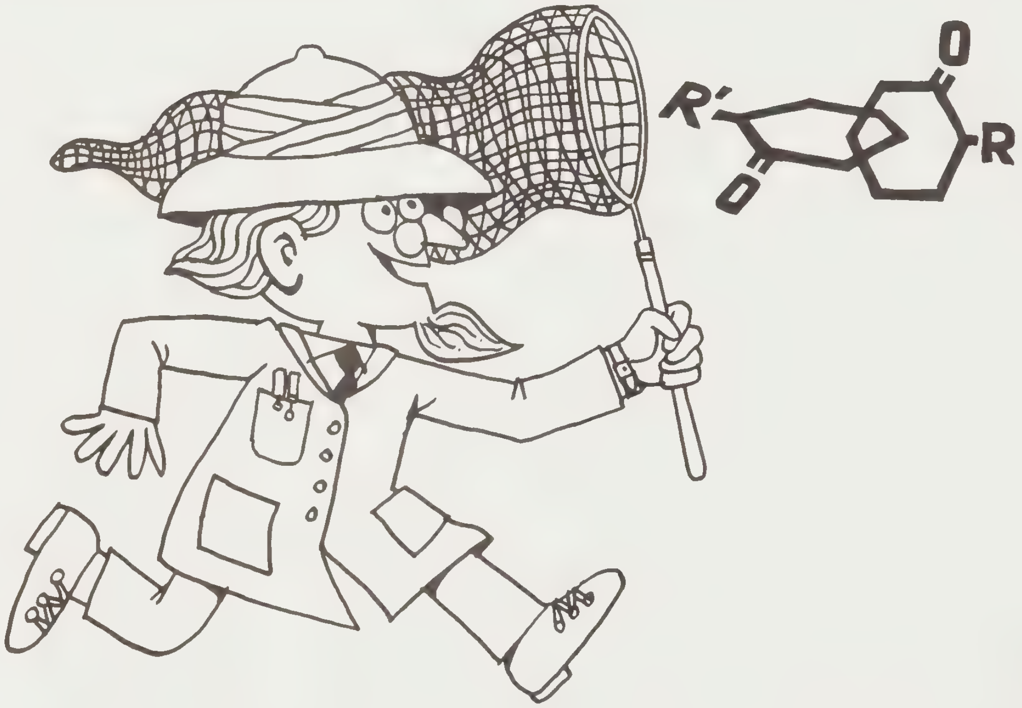

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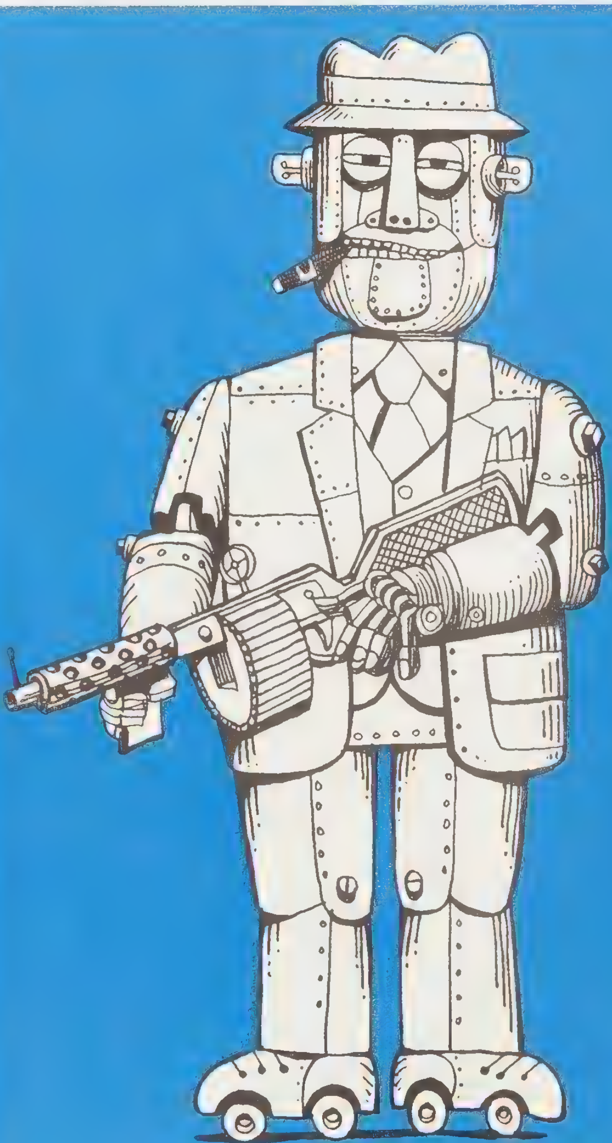

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Editor, Kathleen D. Ryan

ABOUT THE COVER

One of the least understood and most interesting artists of the 17th century was Michael Sweerts whose self-portrait you see on our cover. Flemish by birth, Dutch and Roman by artistic education, Sweerts combined in his very personal style elements of Caravaggio and the Dutch Masters. In his late thirties he joined a religious mission to the Middle East, was asked to leave the mission in Persia in 1662 and died two years later in Goa, India.

Before our chemist who collects old master paintings acquired this intense portrait, then unnamed, at a Munich gallery last summer, the skull had been overpainted by a shipping scene which was easily removed. The features of the artist and also the soft hands are similar to those of other Sweerts self-portraits, and this painting has now been accepted by art experts as one of Sweerts' self-portraits.

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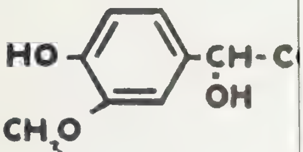

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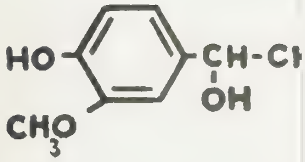

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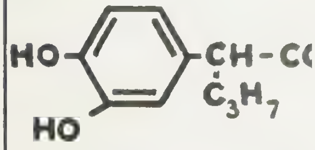

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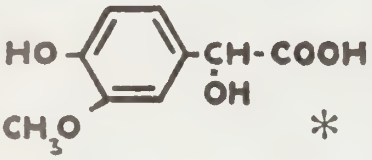

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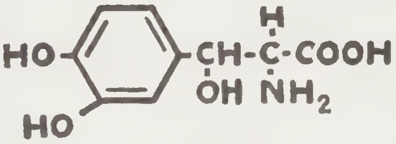

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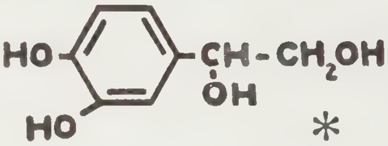

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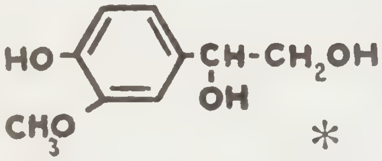

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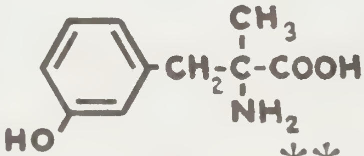

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14882-2 1g - $11.50 5g - $46.

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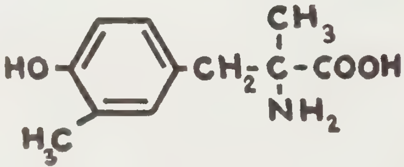

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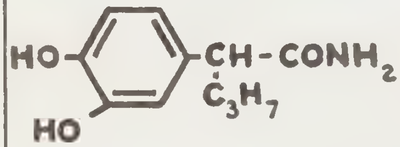

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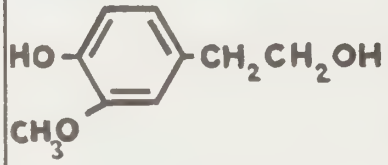

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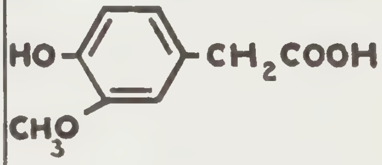

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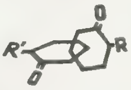

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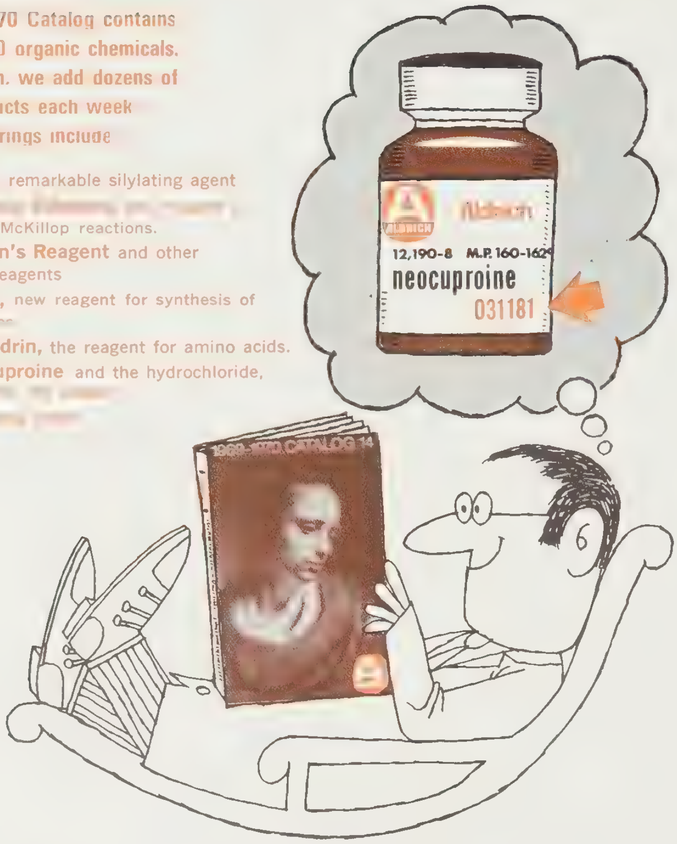

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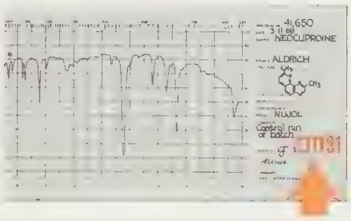

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Editor, Kathleen D. Ryan

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This beautiful view of St. Vitus' cathedral in Prague was painted by R.v. Alt in 1850. Despite the fact that it is not a Dutch 17th century painting, our chemist-collector considers it the most beautiful architectural painting in his collection. For a discussion of Prague today, see page 15.

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See page 18 for versatile new tool in amide and peptide syntheses.

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Prague Revisited

Alfred R. Bader

Ever since I was a boy, Prague has been one of my favorite cities. As a boy I had spent several summers with friends of the family living in a small town in Moravia, and the highlight of each summer had been a brief trip to Prague—das goldene Prag—my mother had called it. Between the wars, Prague was a most prosperous city; stable, busy, beautiful to look at, the most western of all Slavic cities. But what intrigued me the most was not the beautiful view of Prague with its 100 church steeples(fig. 1), or its lovely baroque architecture(fig. 2, 3), but the old town with its dozens of spooky, narrow streets and particularly the Jews' ghetto nestling into one corner, at the bend of the river Moldau. Here was the unbelievable cemetery, dating to the 15th Century, so crowded that it contained twelve layers of graves, the top—on which you walked—many feet above street level—with thousands of gravestones side by side. This had been the only bit of green in the entire ghetto, and each summer I had stood there for a little while, watching the many visitors—many of them pious Jews saying prayers at this or that grave of a famous rabbi—and I had wondered what life in the ghetto had really been like. I had also been scared by the legend of the Golem, the robot said to have been built by the most famous of all the rabbis of Prague, Rabbi Judah Löw, at the end of the 16th Century. The remains of this Golem were believed still to remain in the attic of the oldest of the synagogues, and the whole atmosphere of the ghetto tended to lend credence to the legend.

For reasons that might seem more plausible in an Alec Guinness movie, much of the ghetto survived the Nazi occupation, even though few of Prague's Jews did. There is now in the ghetto one large hall, empty but for the names of thousands of Czech Jews that were killed, but someone persuaded Hitler that history would be well served if a Jewish museum were established in the Prague ghetto, to tell the generations to come what Jews had been like—long after the last one had disappeared from the earth. And so thousands of Jewish ritual objects and truckloads of Hebrew books were sent to Prague to fill this museum, and now the Prague Jewish Museum is probably the most interesting Jewish Museum in the world—and also the emptiest of people. In the two hours my wife and I spent in the cemetery and the adjoining museum and synagogues, we saw no one but the old care-takers.

When I had first returned to Prague, after the last war in 1949, I had also been scared, but for reasons quite different from the childhood fears of the Golem. The communist coup had taken place just a year before, and it was obvious to me that the few old friends who were

Fig. 1. Beautiful church steeples of Prague

left in Prague were afraid to talk to me. There was a great deal of blatant communist propaganda, closer in type to Nazi propaganda, than the spirit of Prague I had known. Since 1949 I had been back to Prague only very occasionally, and last December was my first visit after the Russian occupation. Prague now, as on each of the previous visits since the war, seemed very drab—many lines of people shopping for food and other necessities; people uniformly colorlessly dressed, and yet the people's spirit seemed quite different. There was obviously pride in the fact that no traitors whatever could be found by the Russians to collaborate with them, something that did not occur even during the Nazi occupation when a great many Czech Quislings existed. Time and again, someone pointed out to me in one way or another that here was a historic first: Never before in recorded history has an entire people been absolutely unanimous in resisting—albeit passively—an invader. During my days in Prague, I saw only one lorry-full of Russian soldiers and a great many signs all over the city exhorting Czech leaders to be strong. Most surprising, there were also quite a few pictures of the George Washington of Czechoslovakia, Thomas G. Massaryk, who for many years had been labeled just another decadent, capitalist politician by the communists.

Fig. 2. Prague Court of Honor

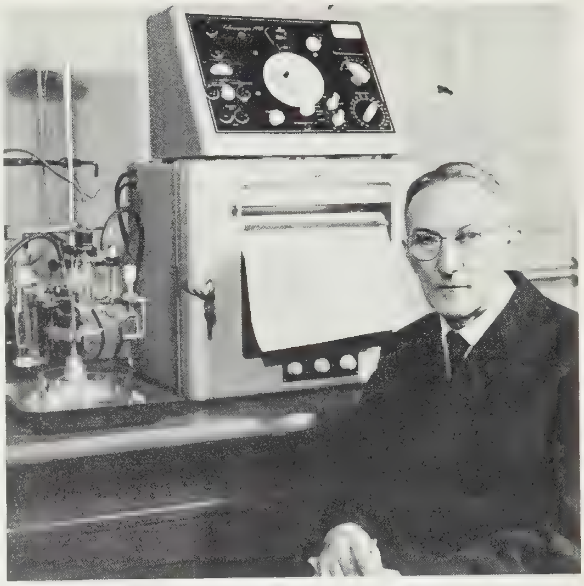

Fig. 4. Prof. J. Heyrovsky, Nobel prize winner

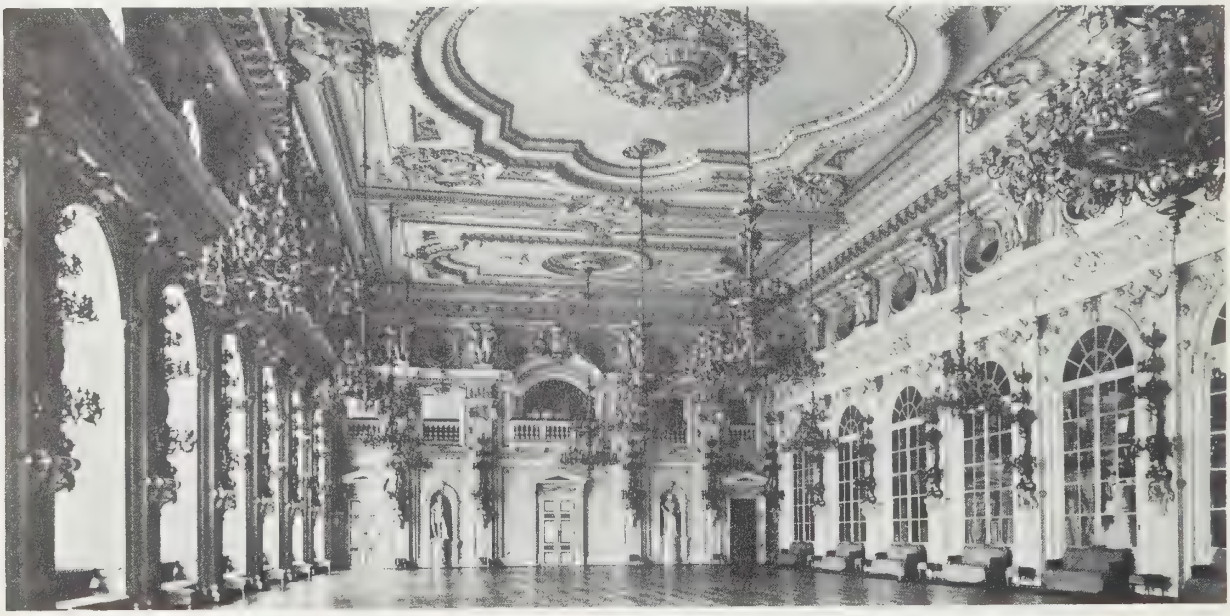

Fig. 3. Lovely baroque architecture of The Spanish Hall

Naturally, the main purpose of my trip to Prague was not to reminisce, but to discuss chemistry and chemical products with Czech chemists and with officials of the only organization in Czechoslovakia that acts both as the buying and selling agent of chemicals for all Czech industry and research, a company called "Chemapol." What strikes you most forcefully in your discussions with Czech chemists is firstly, their great and genuine desire to be in commercial and scientific contact with you, and secondly, the great difficulties which a communist society imposes on commerce, production and research.

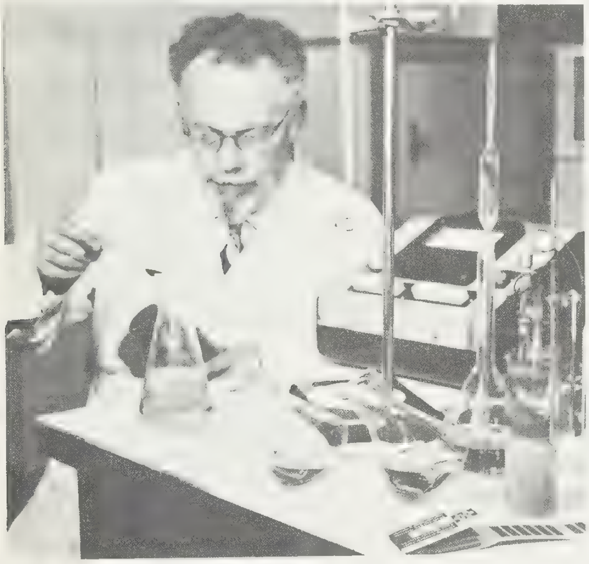

Fig. 5. Dr. Rudolf Pribil

Everything is completely organized and planned, and when talking about scheduled production and deliveries of even quite small amounts of new products, this can often be planned only for this or that quarter of the next year because the starting materials have to be obtained, and everything takes time. Communication is relatively simple; while my Czech is almost nonexistent, most chemists over 40 speak German well, and most younger men speak English, often quite fluently.

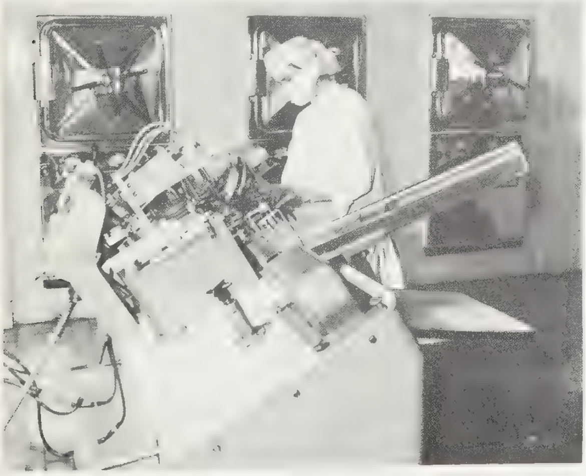

Fig. 6. Packaging of Pharmaceuticals

Fig. 7. Production of insulin

Czech chemistry has considerable tradition, and is particularly proud of its Nobel prize winner, Professor J. Heyrovsky(fig. 4), the father of polarography, and men such as Dr. R. Pribil(fig. 5) who have done a great deal of research in analytical chemistry. Naturally the Czechs have developed many new analytical reagents, and are also doing a good deal of research in inorganic chemistry, particularly in the chemistry of uranium compounds and in organometallic chemistry. Thus, for instance, chemists at The Institute for Inorganic Syntheses have developed a most interesting reducing agent, sodium dihydro-bis-(2-methoxyethoxy)-aluminate—soon to be marketed by Aldrich—which acts somewhat like lithium aluminum hydride—but has the added advantages that it is soluble in many organic solvents, is quite stable to air-oxidation, reacts calmly with water and does not ignite spontaneously. Aldehydes and ketones, acids and esters are reduced to alcohols, and oximes and nitriles to amines, in yields generally somewhat higher than with lithium aluminum hydride.

Scientists at The Academy of Sciences are doing a good deal of medicinal chemistry, particularly in cancer chemotherapy with compounds such as 6-azauridine, and the production of pharmaceutical intermediates and standard products such as insulin(fig. 6, 7) is well organized.

During my previous visits to Prague, it never happened that I was left alone with just one chemist or one Chemapol businessman—and I am sure that this was no accident. Now several talked to me alone, and much in the same vein—expressing the hope that there would return the spirit of the "Prager Frühling", the spring of Prague—a euphemism for what the spirit in Prague had been last spring, before the Russian invasion. It was a feeling I could easily share.

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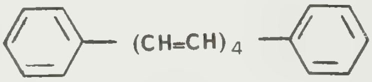
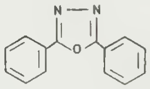
D21,000-5	R1U2U2U2U1R	
D21,021-8	T5NN DOJ CR& ER	

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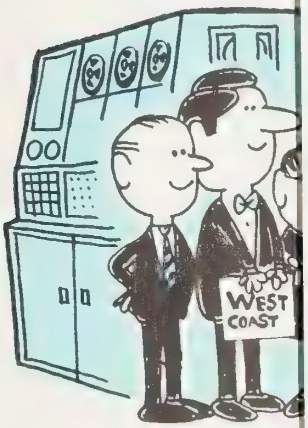

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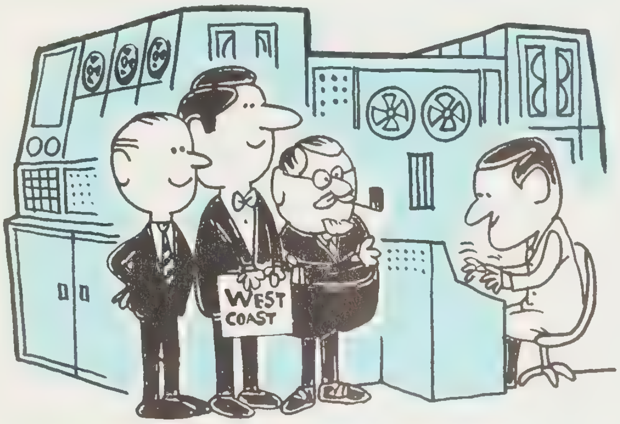
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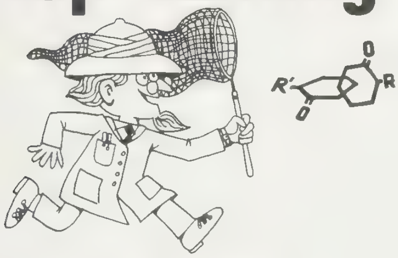

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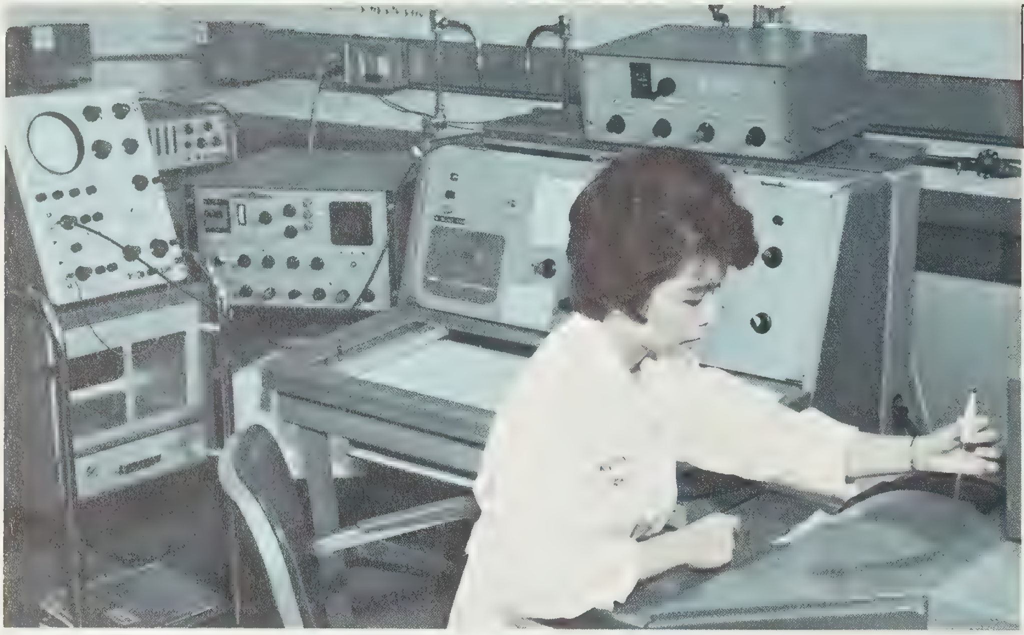

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15,181-5	**Benzene-d_6** (99.5% purity)	10 g. $17 25 g. $35 50 g. $65
15,182-3	**Chloroform-d** (99.8% purity)	50 g. $12.50 100 g. $22
15,188-2	**Deuterium oxide** (99.8% purity)	100 g. $17
15,187-4	**Dimethyl sulfoxide-d_6** (99.5% purity)	5 g. $11 10 g. $19 25 g. $40 50 g. $69.50
15,194-7	**Methyl alcohol-d_4** (99.5% purity)	5 g. $60 10 g. $100
15,232-3	**Pyridine-d_5** (99% purity)	5 g. $20 10 g. $35 25 g. $83

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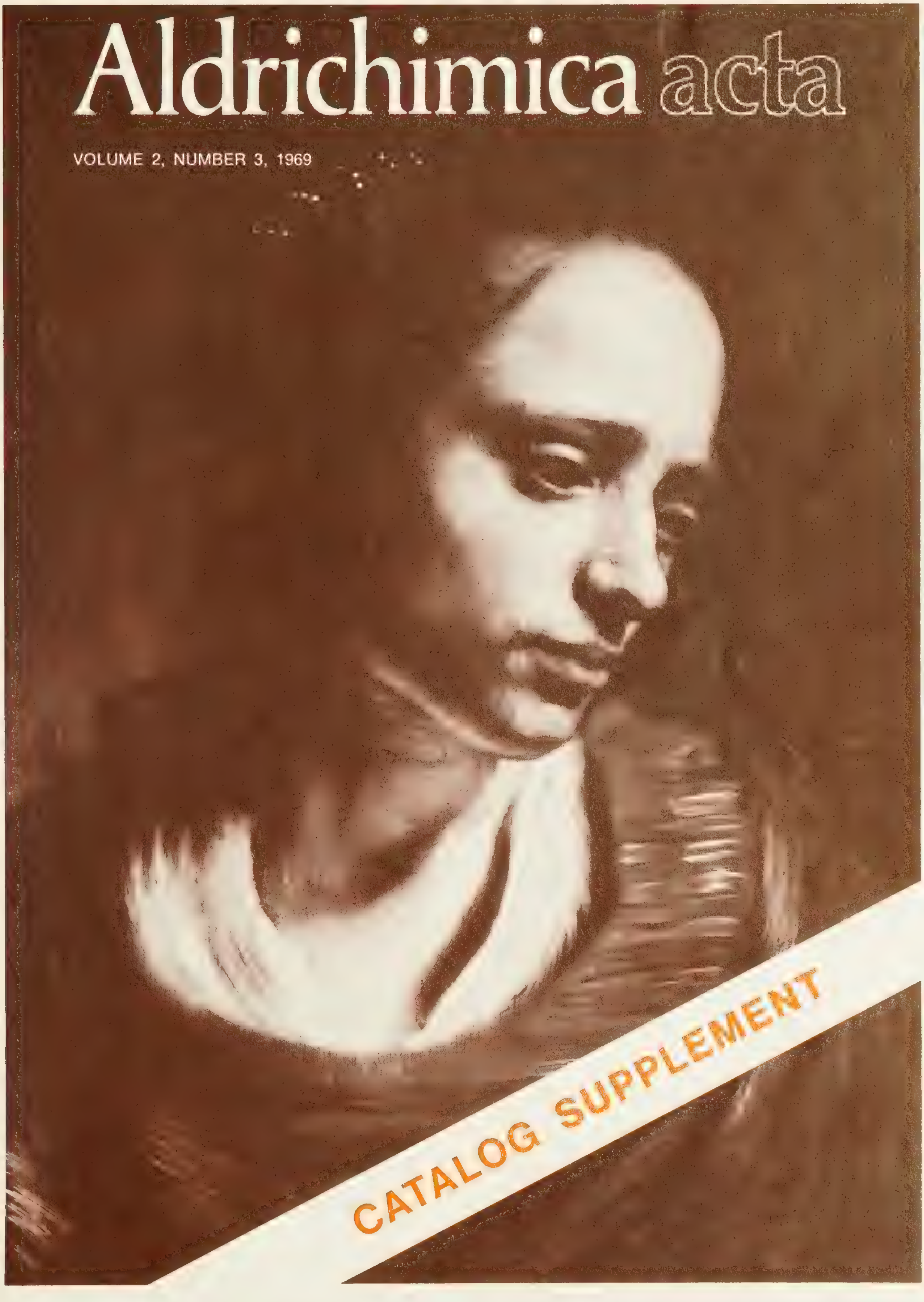
VOLUME 2, NUMBER 3, 1969



CATALOG SUPPLEMENT

PUBLISHED BY THE ALDRICH CHEMICAL COMPANY INC.

ABOUT THE COVER AND CONTENTS

You probably recognize the painting on this issue of Acta . . . it's the same portrait we used on the cover of our 1969-70 catalog. Though the artist of the painting is unknown, the master quality of his work is obvious.

This issue of Acta serves as a supplement to our catalog, and the additional listings are further examples of the quality compounds you can expect from Aldrich. The supplement has over 400 compounds that we've added to the more than 8,000 already contained in our catalog. These are listed in alphabetical order. We have check marked the more complicated compounds to indicate that the structure is shown in the margin, also in alphabetical order.

We hope you will keep this issue near your catalog so both can serve as a ready reminder that Aldrich is always ready to provide you with the best in quality chemicals.

Volume 2, Number 3
1969

Published by
ALDRICH CHEMICAL COMPANY, INC.
Milwaukee, Wisconsin.

Editor, Kathleen D. Ryan

Organic Intermediates • Biochemical Tools • Reagent Chemicals • Analytical Tools • Organo-metallics

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Organothallium Chemistry-New Horizons in Synthesis

PUBLISHED BY THE ALDRICH CHEMICAL COMPANY, INC.

Volume 3, Number 1
1970

Published by
ALDRICH CHEMICAL COMPANY, INC.
Milwaukee, Wisconsin

Editor, Kathleen D. Ryan

ABOUT THE COVER

Our collector-chemist calls the painting of the intense little girl depicted on the cover his "Alfa-girl" because he bought it in a small Boston gallery after a day's discussion with our friends at Alfa. The gallery owner smiled at the suggestion that it looked like a sketch by John Singer Sargent, but the art-historian most knowledgeable about Sargent, Mr. David McKibbin at the Boston Athenaeum wrote: "Your head of a girl is stunning. . . . I have never been more sure of an unknown and I'd like to identify her." The canvas is on a Boston stretcher but, wrote Mr. McKibbin, "I know of no Boston subject and because the little girl is so attractive it seems unlikely had she lived here that it would not have been recorded or seen by any one who would have recorded it. Of course Sargent might have taken a prepared canvas with him to some place outside Boston such as Newport or Worcester, but I cannot think who this child might be. If you will tell me what you know of the canvas's provenance there may be a clue which I could interpret." Thereby hangs a tale of as yet uncompleted art-historical sleuthing: The gallery-owner told our chemist that he had bought the canvas from an antique store, "Recollections" in Brookline, Mass. The owner of that store well remembered the painting but the seller, a lady whose name he had forgotten, had moved to Florida; she had, he believed, once taken the sketch in payment of rent. The lady's sister still lived in Boston, and occasionally came to "Recollections"; next time she came in, he would ask her about her sister's name and address, and perhaps we shall discover our girl's identity yet.

The back of the canvas bears the name FRYE, perhaps the sitter's name, or that of a previous owner. We would appreciate hearing from any reader who knows the identity of this girl.

TABLE OF CONTENTS

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Thallium Chemistry: A Study in International Cooperation

Alfred R. Bader

Dr. Alexander McKillop and Professor Edward C. Taylor

It is not often that a chemist has the chance to witness in intimate detail the development of an important new field of chemistry. What would have been our thoughts if we could have been with Professor Grignard when he first worked with magnesium compounds? At first, perhaps, some doubt that many chemists could ever get very excited about chemistry as way-out as that of magnesium organics, then amazement, and finally the realization that he is dealing with a series of reactions so versatile that the Grignard Reaction would soon become a household word among chemists. Thus were my thoughts when I first heard about thallium chemistry.

Some two years ago, friends at the Smith Kline & French Laboratories in Philadelphia invited me to visit with them to discuss with Professor E. C. Taylor how one might market a series of thallium-organics developed with SK&F grants at Princeton and the University of East Anglia. At first I was skeptical; all I knew about thallium compounds was that they are highly toxic, and the fact that β-dicarbonyl compounds gave stable thallium salts was interesting, but hardly earth-shaking. But I knew Professor Taylor and of his brilliant work in heterocyclics, and I thought it unlikely that he would get excited over a mere curiosity. And at the meeting I was soon convinced. The work on thallium organics began with the discovery by Dr. Alexander McKillop—a puckish Scotsman and enthusiastic chemist, then a post-doctorate fellow with Professor Taylor at Princeton—that thallous ethoxide reacted cleanly with β-dicarbonyl compounds to form stable, crystalline salts. With other students of Professor Taylor, the reactions of thallous ethoxide were explored, and when Dr. McKillop returned to Britain to teach at the University of East Anglia, it was decided to continue this international cooperation in the studies of the "Taylor-McKillop Reaction." How effective this has been is witnessed eloquently by the adjoining review article and the twenty papers by Professor Taylor and Dr. McKillop there cited.

How could Aldrich help best? Offering the various thallium salts of β-dicarbonyl compounds was one, albeit minor contribution. Much more important was the availability of the key intermediates: thallous ethoxide, thallic acetate, and thallic trifluoroacetate. Thallous ethoxide presented a particular problem: the Princeton preparative procedure involved thallium metal, refluxing ethanol and gaseous oxygen, had been used only to make 500 gram quantities of thallous ethoxide and could not be used safely to make larger quantities. Dr. Walter Tschannen, the head of our "kilo lab," spent some time with Professor Taylor's group at Princeton and then came home to perfect a pilot plant method safely to make twenty to thirty kilo lots of thallous ethoxide—a method that could be scaled up to make tons if needed. Thus thallous ethoxide is now freely available and reasonably priced. Even its toxicity appears to be less of a problem: an effective and inexpensive antidote for thallium poisoning, the simple pigment Prussian Blue, has just been described [H. Heydlauf, *European J. Pharm.*, **6**, 340 (1969)].

To exploit the commercial possibilities of thallium chemistry further, it was decided to set up a small company, Thallium Limited, specifically to make the products of thallium chemistry, allowing Aldrich to be this company's marketing arm. SK&F has filed patent applications on such key intermediates as thallic trifluoroacetate, and these patents might well become valuable; a small company specializing in thallium technology would be a flexible vehicle to make these inventions commercial realities. One of Dr. McKillop's students, Dr. Lionel Elsom, heads Thallium Limited which will soon be producing a good many compounds.

Princeton, Norwich, Philadelphia, Milwaukee—far apart, and yet working together closely and with a great deal of personal satisfaction to make thallium "one of the indispensable metals in synthetic organic chemical methodology."

Organothallium Chemistry-New Horizons in Synthesis

Edward C. Taylor,

Department of Chemistry, Princeton University,

Princeton, N. J. 08540

and

Alexander McKillop,

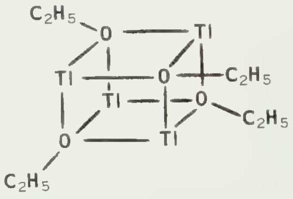
School of Chemical Sciences, University of East

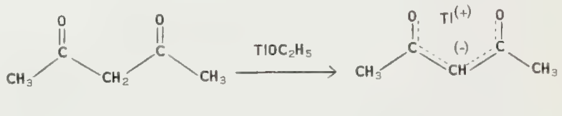
Anglia, Norwich, England

The last two decades have seen a tremendous upsurge of interest and activity in organometallic chemistry, with the result that there are now few metals the organochemistry of which has not been investigated in some detail. Prior to the initiation of our studies on organothallium chemistry in 1966, however, little was known of the organic chemistry of this group IIIB metal. This situation must be regarded as surprising, as not only is thallium abundant, inexpensive and readily available in a high state of purity, but sporadic reports during the past half century have clearly indicated that in certain reactions thallium derivatives are effective chemical intermediates. In this article we summarize the remarkable utility of thallium compounds in organic synthesis. We believe that the reactions discovered thus far presage a bright future for this versatile metal.

Our initial interest in thallium chemistry stemmed from curiosity about a statement made some years ago by Menzies and Wilkins[1] that the thallium(I) salt of ethyl acetonedicarboxylate was "readily soluble in cold ethyl or methyl iodide, thallous iodide being deposited on standing or heating". This startling statement about the apparent solubility of a β-dicarbonyl chelate in ethyl iodide (not a popular solvent for ionic compounds!) prompted the rash conclusion on our part that thallium(I) salts might be unusually covalent in character, thus raising exciting prospects of a wide spectrum of possible base-catalyzed reactions in homogeneous solution. A later report by Fear and Menzies[2] that reaction of the thallium(I) salt of ethyl acetoacetate with ethyl iodide resulted in apparent C-ethylation stimulated us to prepare some representative thallium(I) salts of β-dicarbonyl compounds and to investigate their physical and chemical properties.

We found that the most effective reagent for the formation of thallium(I) salts of β-dicarbonyl compounds was thallium(I) ethoxide. This remarkable compound is a covalent tetramer[3] which is soluble in most organic solvents (including heptane and benzene) and thus possesses considerable advantages over sodium ethoxide and other alkali metal alkoxides in that homogeneous base-catalyzed reactions can be carried out in non-polar solvents. Treatment of a benzene or petroleum ether solution of a β-dicarbonyl compound (e.g., acetylacetone, (eq. 1)) with 1 equivalent of thallium(I) ethoxide resulted in the instantaneous separation in quantitative yield of its thallium(I) salt.





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References:

1. V. Bazant, M. Capka, M. Cerny, V. Chvalovsky, K. Kochloefl, M. Kraus and J. Malek, *Tetrahedron Letters* 3303 (1968).
2. M. Capka, V. Chvalovsky, K. Kochloefl and M. Kraus, *Collection Czechoslov. Chem. Commun.*, **34**, 118 (1969).
3. M. Cerny, J. Malek, M. Capka and V. Chvalovsky, *ibid.*, **34**, 1025 (1969)
4. M. Cerny, J. Malek, M. Capka and V. Chvalovsky, *ibid.*, **34**, 1033 (1969).

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6. Acylation of heterocyclic amides.

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No. 15,386-9	Diethyl malonate, thallous salt	\$5.75/10 g.	\$21/50 g.	
No. 15,387-7	Ethyl benzoylacetate, thallous salt	\$5.75/10 g.	\$21/50 g.	
No. 15,388-5	Acetylacetone, thallous salt	\$5.75/10 g.	\$21/50 g.	
No. 15,389-3	Thallous phenoxide	\$5.75/10 g.	\$21/50 g.	
No. 15,229-3	2(1H)-Pyridone, thallium(I) salt	\$6.25/5 g.	\$21/25 g.	*\$375/1 kg.*
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VOLUME 3, NUMBER 3, 1970

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Editor, Kathleen D. Ryan

ABOUT THE COVER

Our collector-chemist is rather opinionated about many Bible characters, and the one he likes the least among the "good guys" in the Old Testament is Joseph whom he considers a brilliant organizer, a fine servant, a bad brother and a worse son. Hence we were rather surprised when he purchased recently at a London auction this large (42 x 45 inches) painting of Joseph explaining the baker's dream. From 1748 to 1951 this had been in the collection of the Dukes of Bedford at Woburn Abbey, where it had been attributed to Rembrandt. Our collector is convinced that it is not by him but by someone around 1660 strongly influenced by Rembrandt. Sometime the artist will be identified: anyone who could depict in so masterly a manner the most difficult of all subjects—communication between men—deserves to be known.

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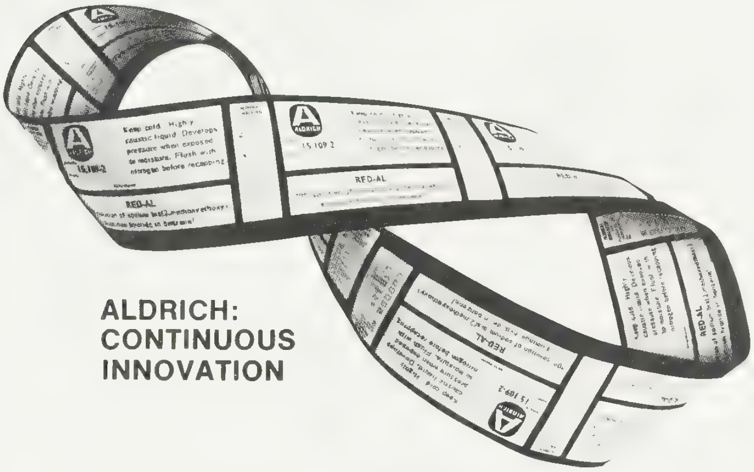
Aldrich introduces a stable, metal hydride reducing agent



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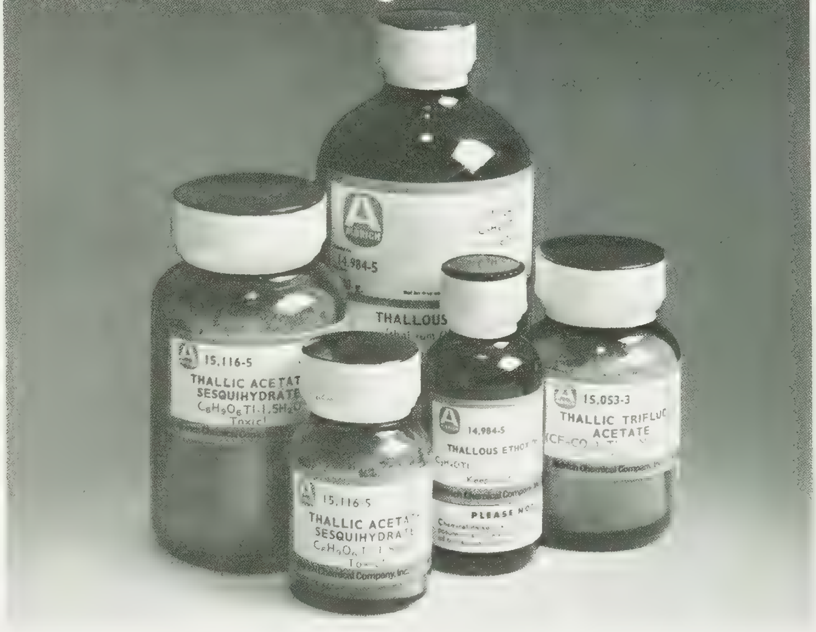

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6. Acylation of heterocyclic amides

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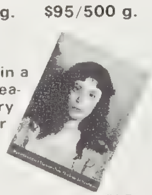
The uses of the three compounds listed above are described in a special Thallium Organics issue of *Aldrichimica Acta,* which features a thorough review article on Organothallium chemistry by Prof. Edward C. Taylor and Dr. Alexander McKillop. For your free copy, simply write the Aldrich Milwaukee office.



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ABOUT THE COVER

Our chemist who collects old paintings spent a couple of days worrying about the work reproduced on our cover. He had been visiting with our British associates, Ralph N. Emanuel Ltd. in London, at the time of last summer's biggest old master auction at Christie's, and at the preview two days before the auction had liked this work by Aert de Gelder best of all.

Aert de Gelder was one of Rembrandt's ablest and last students, who carried Rembrandt's tradition well into the 18th century. This painting hung very high at Christie's, and a heavy varnish made viewing even more difficult. Nonetheless, our collector was convinced that this was a genuine and fine Aert de Gelder, painted in the 1670's, a work quite unknown to him, and—as it turned out—unknown even to art historians.

That evening he got a rude shock when he was invited to the home of a friend, one of England's great connoisseurs of old paintings, who told him that this Aert de Gelder was the one painting in the sale that he would really like to buy. His concern was increased when next day a professor of art history at our chemist's Canadian alma mater urged him to buy just that painting for the school's collection—if three men each liked this the best, what chance had one against the scores of great dealers from all over the world? And yet the painting brought less than Christie's estimate and only a small fraction of one percent of the price of an unexciting Rembrandt in that sale. Whether this was due to the poor hanging, the dirty varnish or the fact that the painting was quite unknown and one of the first in the sale—who knows, and our chemist does not care.

To him it is much more than just a genre painting of a wineseller, the title in the auction-catalog. De Gelder liked biblical subjects, and perhaps this depicts Elisha with the widow of the prophet Obadiah (2. Kings 4) whose jars he filled with oil to allow her to repay her husband's debts.

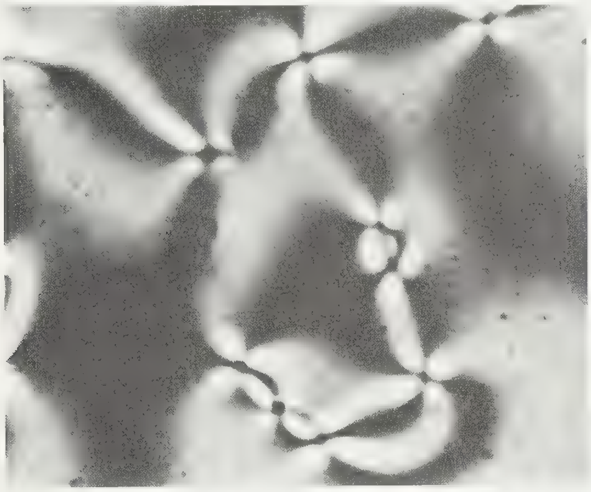
In any case, de Gelder depicted a warm human relationship—man and woman really care for each other; it is the kind of relationship that we strive for with our customers—individual service to individual human beings. If only we also could perform miracles!

TABLE OF CONTENTS

Liquid Crystals and Modern Art

Alfred R. Bader

It seems to me that the most striking difference between modern artists and the old masters lies in the effort of the modern artist to create something radically new. Abstract expressionists, pop artists, op artists—whatever they are called—vie with each other to create works which are visually distinctively new. Beauty, character, lasting impression on the viewer are less important; what counts is that the "art" be new and hence different. And so you can see in our Milwaukee Art Center a blackboard by Edward Reinhardt—the "ultimate" in art: tasteless, odorless, formless, nothing, and another blackboard with a doodle by Cy Twombly, which as a Sunday School teacher I would give no second thought before erasing from the blackboard. My grandparents would have thought us crazy, and I suspect my grandchildren will also.



1. Nematic liquid: 4,4'-dioctyloxyazoxybenzene
50x Photomicrograph

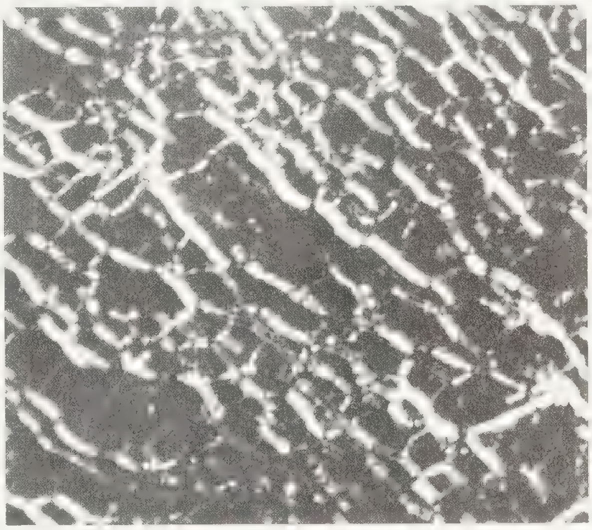
Basically this striving after the radically new is the result of the artists' traumatic experiences caused by the invention of photography. Most 19th century art was painstakingly realistic, and hence most vulnerable to the competition by the photograph. What sweet nothing could a Munich School painter depict that a photograph could not do better? Had the photograph been invented in the 17th century, the answer would have been different: no photograph can match Rembrandt's delineation of a man's character or Jakob Ruisdael's melancholy in landscapes.

What photography has done to modern artists is to separate the men from the boys. The men—artists like Andrew Wyeth and Edward Hopper—have taken up the challenge to compete with photography through mood in realism, and the ablest have been successful. The boys have taken refuge in gimmicks, and Madison Avenue has touted these as the latest in art. One of my favorite stories when I was a boy was of the artist who was introduced to a German court as one of the world's greatest portraitists. But there was one hitch: only people who had never lied would see the true beauty of these works. Naturally the prince and the princess had themselves painted and the entire court came to admire these wonderful works. Until a little boy said to his father: "Daddy—but there is nothing on the canvas." Thus it is with modern art.

Naturally artists have turned to chemistry and physics in their quest for the new. I am not thinking here of improved pigments, media or varnishes, but of the use of science to create new visual experiences. Light and sound are being used in art as they have long been used no less blatantly in advertisements on Coney Island. Optical illusions dazzle you from the walls of museums. Shapes of all kinds made from all sorts of plastics allegedly are new forms of art.

And so, naturally, liquid crystals appear in art. Liquid crystals are substances which, within definite temperature ranges, behave mechanically as liquids of varying viscosities yet exhibit many of the optical properties of crystals. It is quite a common phenomenon; it has been estimated that at least 5 of every thousand compounds are liquid crystals. Optically, liquid crystals scatter light in symmetrical patterns and reflect different colors depending on the angle from which it is viewed.

The first to observe the phenomenon of liquid crystals were the Austrian botanist, Friedrich Reinitzer, working with cholesteryl benzoate, and the German physicist, O. Lehmann, who coined the name "liquid crystal" (flüssige Kristalle), wrote the first book on the subject, and studied particularly the optical properties of liquid crystals. Around 1910, a group of students of Professor Vorländer at the University in Halle an der Saale studied the relationship between chemical structure and liquid crystallinity. Unfortunately several of these Ph.D. theses were not published, and of the most interesting of these, the thesis of M. E. Huth, 1909, is available from Aldrich. In the twenties and thirties some of the most eminent theoreticians, for instance



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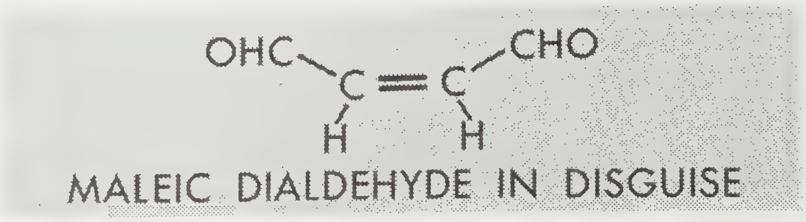
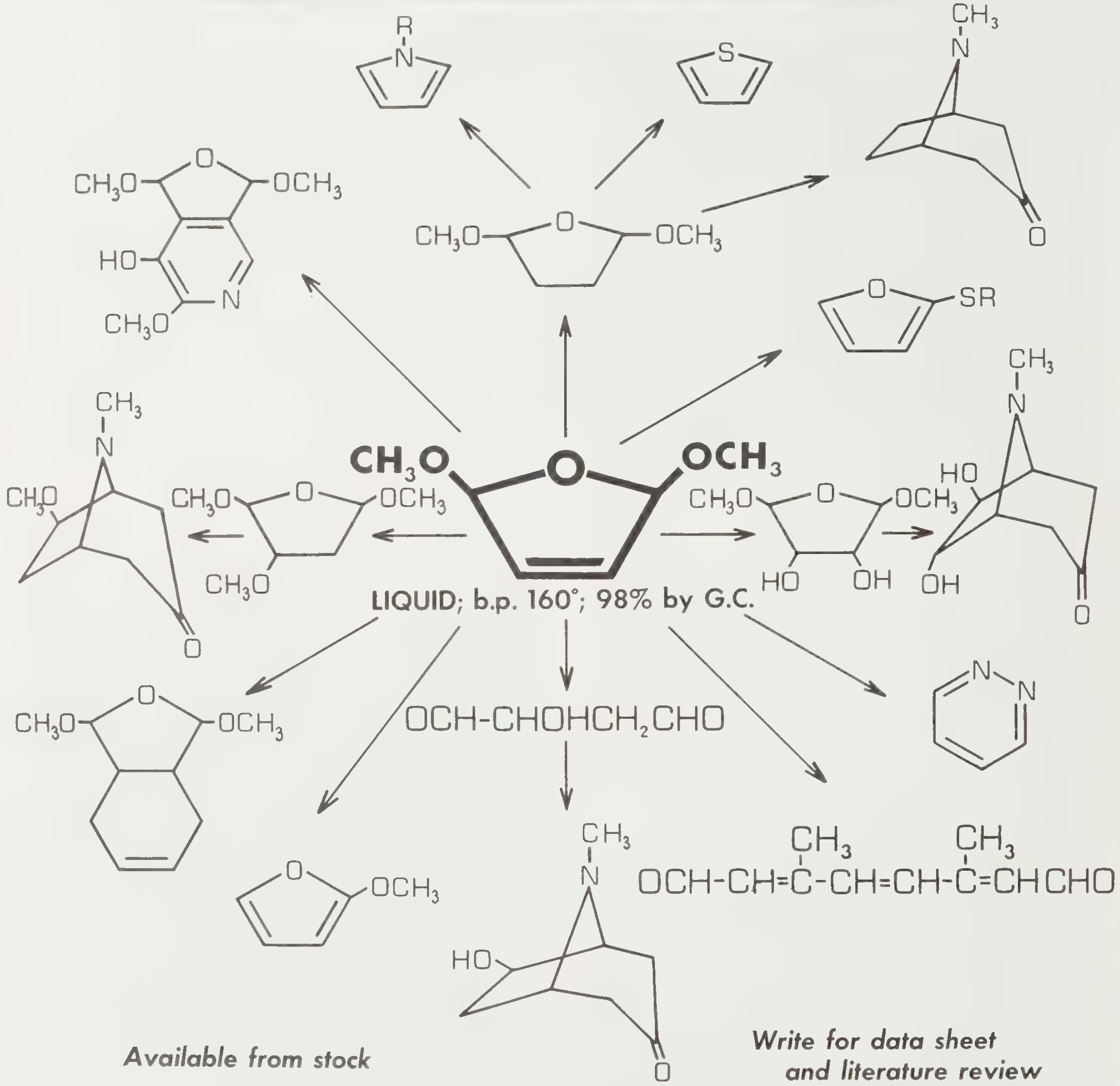


MALEIC DIALDEHYDE IN DISGUISE



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3. *Smectic liquid: many Schiff's bases of terephthaldehyde look like this.*
50x Photomicrograph
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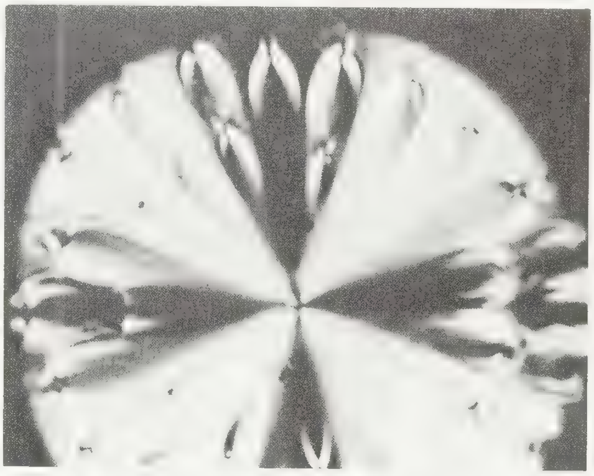
Bragg and de Broglie, studied liquid crystals, but as there then seemed to be no practical applications, the subject became one of interest only to writers of textbooks. In the late fifties however, J. L. Fergason, then at Westinghouse, G. H. Brown at Kent State University and a group of scientists in Russia under I. G. Chistyakov began intensive new studies of liquid crystals because of the hope—which has since materialized—of important practical applications. Just how much work is being done currently is evident from a compilation, available from Aldrich, of articles dealing with liquid crystals; this lists 353 papers published in 1965–69. The practical applications have ranged from optical thermometers to the detection of traces of chemical vapors and medical diagnosis, such as the detection of breast-cancer, and of course to the formation of new visual images in art. The compounds most commonly used in art have been the esters of cholesterol with which we can obtain a great many colors and, intriguingly, temperature sensitivities. A 1:1 mixture of cholesteryl pelargonate and cholesteryl oleyl carbonate, for instance gives a beautiful color play near body temperature. Add just a few percent of cholesteryl chloride, and you broaden the temperature range. Add more of the chloride and you get colors much less temperature sensitive but irridescent—with 20% chloride blue and with 30% red. Aldrich now offers some 38 cholesterol derivations with which an infinite variety of color-plays and temperature sensitivities can be obtained. For the novice, it is important to remember, that all of these cholesterol derivatives are colorless as solids and as liquids, and that they pass through the series of bright colors as they are cooled through their liquid crystal phase. Many pass in color from violet to blue to green to yellow to red to colorless; others change only from red to green; still others from red to green and back to red or from red to green to blue. In every instance, traces of impurities change the color, and this of course is the basis for the analysis of traces of solvents. An 80:20 mixture of cholesteryl pelargonate and cholesteryl chloride, for instance, is green at room temperature; a trace of chloroform changes this to red, a trace of petroleum ether to blue, and this change is reversible. The closest visual analogy that I can think of to describe the appearance of many liquid crystal mixtures is that of the black opal. Beautiful, yes—but is it really a work of art?

In this connection I can do no better than quote from letters of a very able Canadian artist, Jack Wise, whom we had sent some cholesteryl esters: "I wish I could report a great success with my experiments, but alas, body-lipid wouldn't respond to the wish for a permanent ordering. . . . As a total experience, it was invaluable to me that I again attempt to make a technological creation conform to my own aesthetic direction. I don't completely dismiss the possibilities of Liquid-Crystals in Art—but here again, man would become the servo-mechanism of a specialized substance, doing what *its* requirements dictated—function would follow form. I make no value judgment—but am, perhaps, too reactionary in my own aesthetic responses to new media. Certainly McLuhan is right about the "media" becoming the message, and I'm skeptical about a technological aesthetic replacing an iconographic one. I do see an entirely new color-television technology, walls which respond to mood—the whole gamut of environmental trips—still, of prime interest to me is the *form* of the imagery—the bones, as it were, and not the flesh. My chief difficulty was with the bleeding, mesomorphic *aliveness* of the crystals—like trying to fix a rigid pattern using a colony of ants—and I could see that an entirely new approach would have to be used in order to utilize the crystals to advantage; I just haven't the time to radically change my methodology—and the liquid crystals obviously require such a study in depth. . . . I hope you will keep in mind, though, that I have only found that liquid-crystals could not be bent to my purpose. I have long been interested in the possibilities of putting "Science" to the service of "Art," and have, alas, too often found that the artist ends up servant of the technology. Of course there is a fine point of debate as to whether the simplest of pigments isn't "technology," the most rudimentary actions in producing them "scientific." I suspect that this debate has more to do with man's psychology than his logic, that the questions will never be answered since they are 'after the fact.'



4. *Smectic droplet*
50x Photomicrograph

"And yet, after all my protestations, there remains a tantalizing quality to your liquid-crystals—far more so to me than, say, holography or the more mechanical applications of light. . . . Would it not be interesting to apply some small icon of liquid-crystals to one of the cave-walls of Altamira?"

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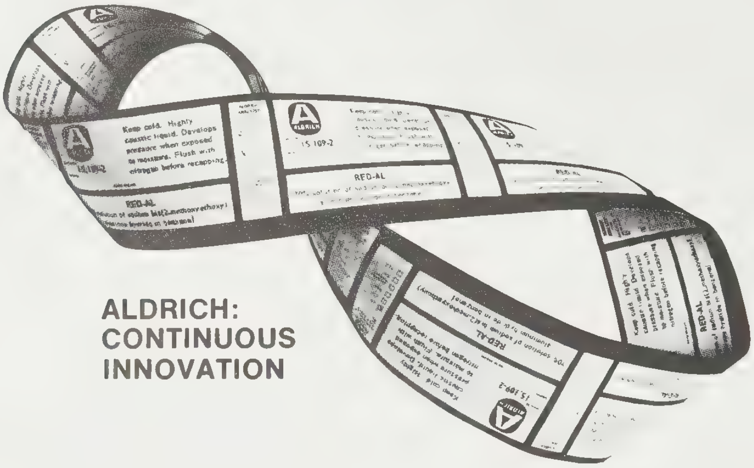

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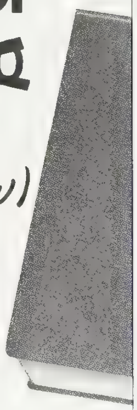

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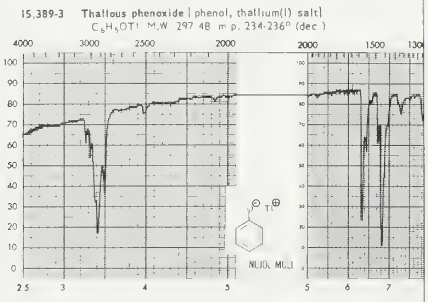

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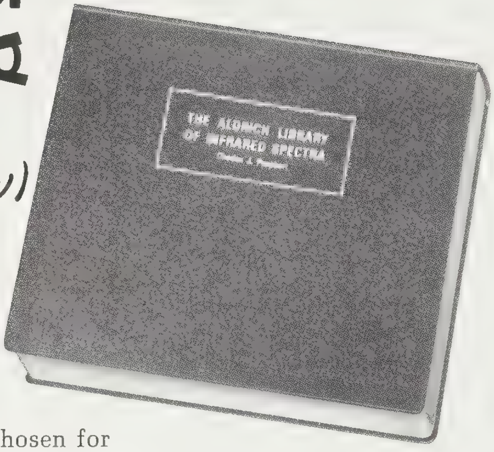
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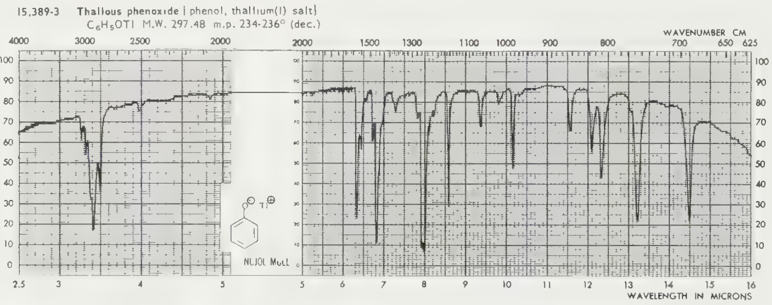
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Volume 3, Number 4, 1970

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Editor, Kathleen D. Ryan

ABOUT THE COVER

We once asked our chemist-collector what qualities he looked for first, when considering the acquisition of a painting. We had expected him to reply that the painting be by a famous artist and preferably 17th century Dutch, and we were surprised neither to be a prerequisite. Different, well-drawn and in good condition!

Whatever one might think of the painting (oil on canvas, 40 by 31 inches) here reproduced, it is certainly different. At one time it was thought to be Tuscan, though it is probably by a Haarlem artist of the middle of the 17th century—an artist who was certainly not in the mainstream of Dutch art.

Perhaps the melancholy expressions of the two boys suggest some personal tragedy in their lives, or we may see here simply an allegory on the vanities of life, on fleeting time. It has often seemed to us that of many foolish sayings "time is money" is the most mistaken. Time is life, the one commodity that money cannot buy, and this vanitas painting beautifully makes the point.

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Now MNNG has also been shown to have potent antimalarial activity *in vitro* (27). When 0.5 ml. aliquots of mouse erythrocyte suspensions, containing 4×10^8 parasites/ml., in citrate buffer $_p$H 5.0-glucose medium were mixed with 0.95 ml. medium containing no MNNG (controls), or MNNG equal to or greater than 200 μg, the mixture kept at room temperature for 25 min and then aliquots of 0.1 ml. injected intraperitoneally into 12 mice (25 g) per test (control), no parasitaemia occurred in any of the treated mice. If the amount of MNNG was reduced to 100 μg, however, parasitaemia developed on day 12. Under these conditions chloroquine, ethylmethanesulphonate and many analogues of MNNG had no effect (27). The toxicity of MNNG must make it unsuitable as an antimalaria drug, but it may well help us understand antimalarial activity of drugs better.

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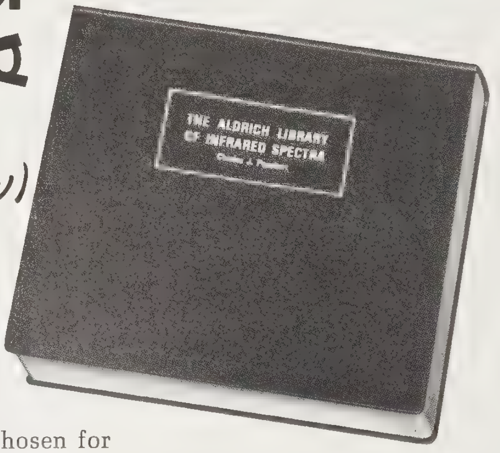

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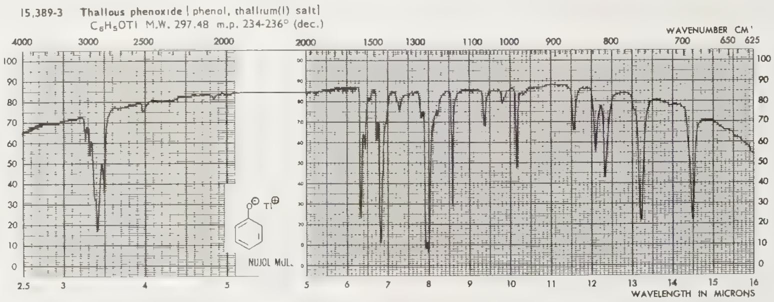

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Volume 4, Number 1, 1971

PUBLISHED BY THE ALDRICH CHEMICAL COMPANY, INC.

Volume 4, Number 1
1971

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Milwaukee, Wisconsin

Editor, Kathleen D. Ryan

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ABOUT THE COVER

Our chemist-collector seems to enjoy nothing more than to correct or determine attributions of old paintings and to figure out just what an artist had in mind.

This rather lascivious and wildly colored, large (42x59 inches) work on canvas by Aert de Gelder, signed and dated 1681, was auctioned at Christie's some years ago, and was then called Ahasuerus and Esther. De Gelder was particularly fond of the Book of Esther, and more of his works depict that story than any other. Our chemist believes, however, that this represents Tamar and Judah, rather than Esther and her uncle. Tamar had been married to Judah's two older sons, who had died, and Judah had refused to let his youngest son marry her as was required by custom later formulated in the levirate marriage law of Deuteronomy XXV, made so familiar through the story of Ruth. Tamar then pretended to be a prostitute who attracted Judah and kept his staff, signet ring and cord—clearly shown in this painting—as a pledge for payment of services rendered. When Judah heard later that Tamar was pregnant, he condemned her to death, until she sent him his own pledges saying "By the man whose these are, am I with child." No other history of a people is as honest as the Bible: David and the Messiah are the descendants of Ruth the Moabitess and Tamar the Canaanite pretending to be a whore.

If our collector is correct, one wonders why Tamar is unveiled; almost all other paintings of this subject show her heavily veiled. De Gelder is unlikely to have known of the Talmudic commentary that Tamar had been heavily veiled while in Judah's house—so that he had never seen her there—and did remove her veil after she had enticed him. Probably the artist just couldn't resist the temptation to show Tamar's eager expression—impossible to show through a veil, and, though a bachelor, de Gelder may have guessed that it is difficult to make love through a veil.

Tamar's expression is strongly reminiscent of that of a girl painted by de Gelder's master, Rembrandt, thirty six years earlier—the painting of a girl at an open door now at the Chicago Art Institute, and the painting is also related to one of Rembrandt's iconographically most puzzling works, the so-called 'Jewish Bride' in Amsterdam.

TABLE OF CONTENTS

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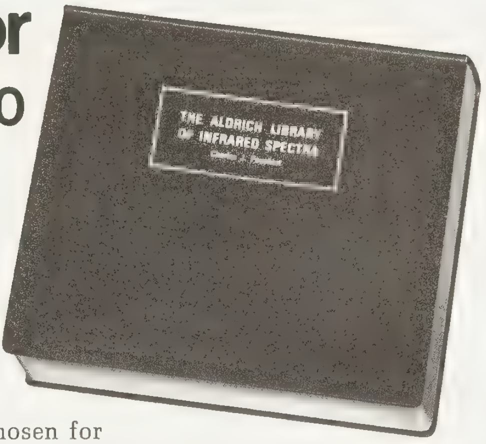

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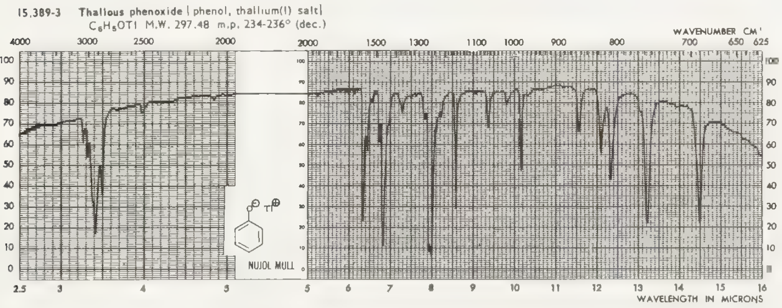

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Volume 4, Number 2, 1971

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ABOUT THE COVER

The beautiful alchemical painting depicted on our cover is discussed in the article on the opposite page.

TABLE OF CONTENTS

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Cornelis Bega's Alchemist

A Problem in Art History

Alfred Bader

One of the best known works in the collection of alchemical paintings of the Fisher Scientific Company in Pittsburgh, is a painting by Cornelis Bega called *The Chemyst* (fig. 1), familiar to most chemists through more than 9000 reproductions distributed by Fisher Scientific.[1]

Fisher describes this painting as "the gem of all alchemist paintings because of its modern rendition of highlights, the meticulous attention to all details, the flesh-tones of the alchemist, and the unusual heliotrope tint of the entire picture. In fact, the former director of fine arts of Carnegie Institute, Pittsburgh, stated that this picture would do justice to any collection in America for its artistic merit alone—without even considering its scientific interest."

Figure 1

"This particular painting was the favorite picture of the late Sir William Jackson Pope, professor of chemistry at the University of Cambridge in England, who attained just about all the honors available to a chemist, including an honorary membership in the American Chemical Society, for his contributions to the winning of World War I."

Figure 2

Certainly it is one of the two best paintings in the Fisher Collection. Unfortunately, the greatest artists—Rembrandt, Titian, Vermeer, Velasquez, for instance—did not paint alchemical subjects, and so most alchemical paintings are of greater historical than artistic interest. The Fisher Collection's other really fine alchemical painting is a study by Adriaen van der Venne (fig. 2) which unfortunately has never been reproduced.

Two years ago there appeared at Christie's a small canvas (fig. 3) which of course must be related to the Fisher painting.

The painting in London came from the collection of one of England's greatest 19th century collectors, John Sheepshanks, is signed and, except for a yellowed varnish which was easily removed, is in a fine state of preservation.

---

[1] I would like to thank Mr. John C. Pavlik, the Director of Public Relations at the Fisher Scientific Company for allowing me to reproduce the cover of *The Laboratory* and the Fisher paintings, and for his generous help in comparing the paintings.

The great English auction houses have a simple way of indicating their opinion of a painting's authenticity. If it is called "Cornelis Pietersz Bega" they believe it to be a work by the artist. If called "C. P. Bega" they believe it to be a work of the period, which *may* be the work of the artist. If just called "Bega," they don't think that it could possibly be a work by Bega, but the owner says it is. The Sheepshanks painting was called Cornelis Pietersz Bega, and because of its beauty and provenance brought an auction record for a work by Bega, and perhaps also for an alchemical painting.

Professor Pope had purchased the Fisher painting from the collection of J. C. W. Sawbridge–Earle–Drax which was auctioned also at Christie's, on May 10, 1935, was then described as a work by C. P. Bega and brought the rather unsubstantial price of 50 guineas.

Figure 3

Knowing that, it seemed possible that the Fisher painting was a copy after the Sheepshanks original. A direct comparison of the paintings side by side in Pittsburgh made it clear however that both paintings are of such fine quality, and there are so many variations of details that one cannot think of one being someone else's copy of the other, no matter how skillfully done. The Fisher painting is somewhat smaller (14½ x 13⅛ inches against 16¼ x 15 inches), on panel and signed and indistinctly dated. The Sheepshanks painting is on canvas and signed on the lower right.

Some years ago, Fisher's publication, The Laboratory (Vol. 23, Number 1; fig. 4), featured on its front cover one of the world's foremost authorities on the conservation of paintings, The Mellon Institute's Dr. Robert L. Feller, examining the Fisher painting.

When asked about the signature of the Fisher painting, he said that he had not really cleaned the painting, but only posed for the photograph; Dr. Eric C. Holmer, the restorer who really did clean the painting, is certain that the signature in the Fisher painting sits firmly on the letter in the center of the painting. Similarly, the signature on the painting on canvas was immovable by acetone during cleaning, and is certainly contemporary with the painting.

Thus the logical conclusion is that both paintings are by Cornelis Bega. It is surely conceivable that a customer had greatly admired the first work and had commissioned the artist to paint a work much like it.

But which is the first and which the second version? There certainty is much harder to attain. Comparing details, there are some in each painting better than the corresponding detail in the other. This is subjective and elusive. But I believe that there are some changes which only an artist would make when 'improving' a second version after a first. Take the pestle, for instance, at the foot of the step. In the Sheepshanks painting it is small (fig. 5) and the spatial delineation of the steps is not quite clear. In the Fisher

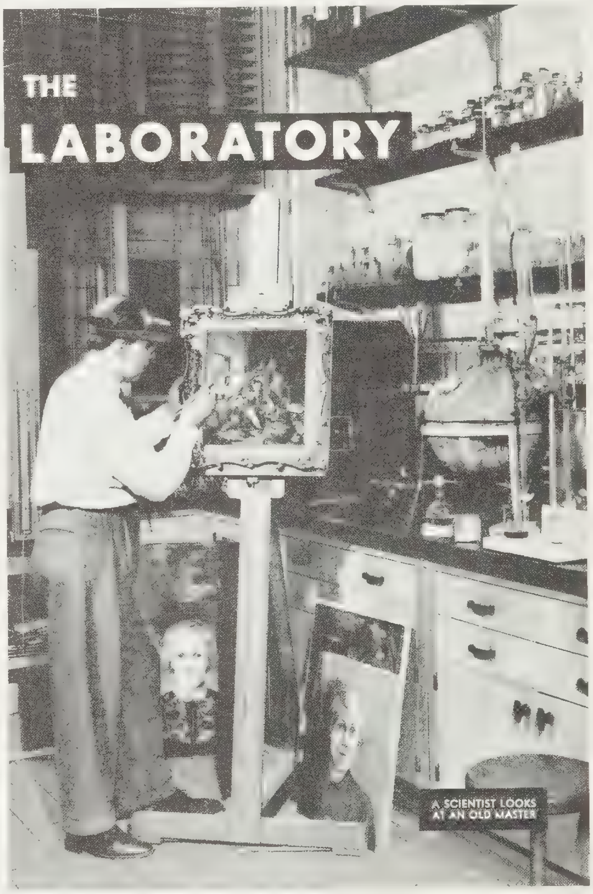
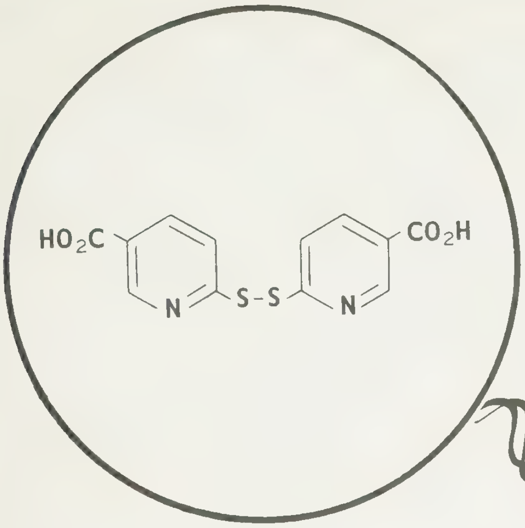


Figure 4

Featured for Biochemists



Thiol reagent and cancer research tool.

D. R. Grassetti, J. F. Murray, Jr. and H. T. Ruan, Biochem. Pharmacol., *18*, 603 (1969).
D. R. Grassetti, Nature, *228*, 282 (1970).

6, 6′-Dithiodinicotinic acid

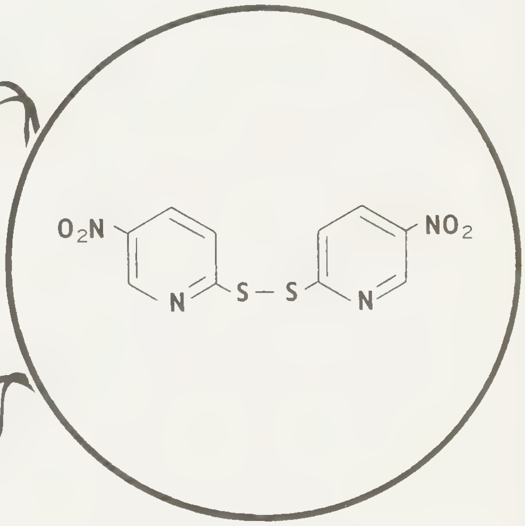
15,820-8	5 g.–$12.00	25 g.–$43.00

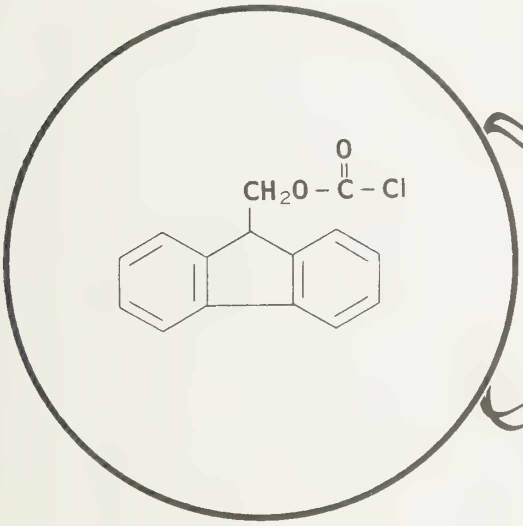
A thiol reagent giving highly colored derivatives.

D. R. Grassetti and J. F. Murray, Jr., J. Chromatogr., *41*, 121 (1969).

2, 2′-Dithiobis-(5-nitropyridine)

15, 819-4	10 g.–$10.50





Base-sensitive amino-protecting group for peptide synthesis.

L. A. Carpino and G. Y. Han, J. Amer. Chem. Soc., 92, 5748 (1970).

9-Fluorenylmethyl chloroformate

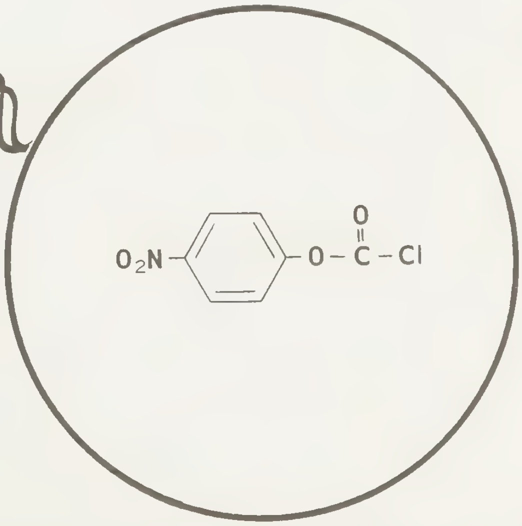
16,051-2	5 g.–$9.35	25 g.–$30.80

Hydroxyl blocker in nucleosides.

R. L. Letsinger and K. K. Ogilvie, J. Org. Chem., 32, 296 (1967).

p-Nitrophenyl chloroformate

16,021-0	25 g.–$12.00	100 g.–$39.00



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Volume 4, Number 3, 1971

Special Thiol Reagent Issue

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ABOUT THE COVER

Our collector-chemist purchased this long (50 x 88 cm, oil on panel) painting by Moses van Uyttenbrock in Holland some months ago, and was then told that it depicts Tobias and the angel. This our chemist does not believe, but thinks that it shows Jacob fighting with the angel at Peniel; the river would then be the Yabok, and the ferry dividing Jacob's property in anticipation of Esau's attack.

This was of course *the* most important moment in Jacob's life: the fight with the evil within himself. Up to then Jacob had often acted shabbily and even dishonestly: in buying Esau's birthright, in deceiving his father, in his dealings with Laban. Now he resolved that if his life was spared the next day, he would become a truly good person, worthy of the name Israel.

This fight saved Jacob's life. Had he not been injured, and limping, Esau would surely have killed him; it is difficult even for an Esau to kill a man who can hardly walk.

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Chemicals of Special Interest

NO. 16,062-8 **FORMULA** C_7H_8O

NAME endo-Bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde, tech., 80%

DESCRIPTION

M. W. 108.14
Colorless liquid
n_D^{20} 1.4976
b. p. 45-55°/11 mm.
A prostaglandin intermediate.
Keep cold

PRICE 5 g - $9.00 25 g. - $31.00

LITERATURE

U. Axen, F. H. Lincoln and J. L. Thompson, Chem. Commun., 303 (1969).

FUNCTIONAL GROUPS

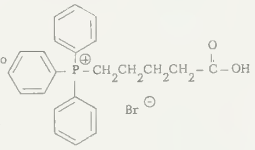
A-3

NO. 15,794-5 **FORMULA** $C_{23}H_{24}BrO_2P$

NAME (4-Carboxybutyl)triphenylphosphonium bromide, 98%

DESCRIPTION

M. W. 443.33
White powder
m. p. 205-207°
Hygroscopic.
An important prostaglandin intermediate.



PRICE 50 g. - $13.25 250 g. - $42.50

LITERATURE

E. J. Corey et al., J. Amer. Chem. Soc., 93, 1490 (1971)

FUNCTIONAL GROUPS

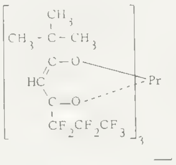
Ca-1
Phos

NO. 16,135-7 **FORMULA** $C_{30}H_{30}F_{21}O_6Pr$

NAME Resolve-Al PrFOD*, 99+%, GOLD LABEL [2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione, praseodymium(III) derivative, Rondeau's reagent]

DESCRIPTION

M. W. 1026.45
Light green crystals
A superior NMR shift reagent
Extremely hygroscopic.
Store in vacuum over P_2O_5 after opening.
*Trademark-Aldrich Chemical Co.



PRICE 1 g. - $12.00

LITERATURE

R. E. Rondeau and R. E. Sievers, J. Amer. Chem. Soc., 93, 1522 (1971).

FUNCTIONAL GROUPS

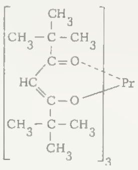
Hal-1
O. M. -5

NO. 16,088-1 **FORMULA** $C_{33}H_{57}PrO_6$

NAME Resolve-Al Pr*, 99+%, GOLD LABEL [2,2,6,6-tetramethyl-3,5-heptanedione, praseodymium(III) derivative]

DESCRIPTION

M. W. 690.73
Light green powder
m. p. 219-221°
Praseodymium analog of Resolve-Al which produces shifts of proton resonances in NMR spectra in opposite direction that Resolve-Al does.
*Trademark-Aldrich Chemical Co.



PRICE 1 g. - $12.00

LITERATURE

F. A. Hart et al., Chem. Commun., 749 (1970).

FUNCTIONAL GROUPS

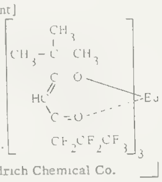
O. M. -5

NO. 16,093-8 **FORMULA** $C_{30}H_{30}EuF_{21}O_6$

NAME Resolve-Al EuFOD*, 99+%, GOLD LABEL [2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione, europium(III) derivative, Sievers' reagent]

DESCRIPTION

M. W. 1037.50
Light yellow crystals
An improved shift reagent for resolution of NMR spectra which has advantage of being more soluble than Resolve-Al.
Extremely hygroscopic. Store in vacuum over P_2O_5 after opening.



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LITERATURE

R. E. Sievers and R. E. Rondeau, J. Amer. Chem. Soc., 93, 1522 (1971).

FUNCTIONAL GROUPS

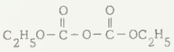
Hal-1
O. M. -5

NO. 15,922-0 **FORMULA** $C_6H_{10}O_5$

NAME Diethyl pyrocarbonate (DEP, diethyl oxydiformate)

DESCRIPTION

M. W. 162.14
Colorless liquid
n_D^{20} 1.3980
b. p. 93-94°/18 mm.
A nuclease inhibitor and a selective blocking agent for polyfunctional amines.
Keep refrigerated at all times. Decomposed by heat or water. Caution-may develop pressure.



$C_2H_5O-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-OC_2H_5$

PRICE 10 g. - $5.50 50 g. - $22.00

LITERATURE

J. Larrouquere, Bull. Soc. Chim. Fr., 35, 329 (1968)
N. J. Leonard et al., Proc. Nat. Acad. Sci. U. S., 67, 93 (1970)

FUNCTIONAL GROUPS

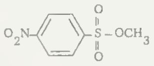
Es

NO. 16,095-4 **FORMULA** $C_7H_7NO_5S$

NAME Methyl p-nitrobenzenesulfonate, 99+%, GOLD LABEL

DESCRIPTION

M. W. 217.20
Gold crystals
m. p. 90-92°
A specific reagent for S-methylation of cysteine in peptides and proteins.



PRICE 5 g. - $9.75 25 g. - $38.00

LITERATURE

R. L. Heinrikson, Biochem. Biophys. Res. Commun., 41, 967 (1970).

FUNCTIONAL GROUPS

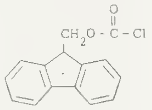
Nit
S-7

NO. 16,051-2 **FORMULA** $C_{15}H_{11}ClO_2$

NAME 9-Fluorenylmethyl chloroformate, 97%

DESCRIPTION

M. W. 258.71
Tan crystals
m. p. 62-64°
Keep cold.
An amino-protecting group for synthetic proteins which can be removed by mild base treatment.



PRICE 5 g. - $9.35 25 g. - $30.80

LITERATURE

L. A. Carpino and G. Y. Han, J. Am. Chem. Soc., 92, 5748 (1970)

FUNCTIONAL GROUPS

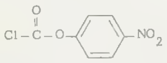
Es
Fl

NO. 16,021-0 **FORMULA** $C_7H_4ClNO_4$

NAME p-Nitrophenyl chloroformate, 97%

DESCRIPTION

M. W. 201.57
White crystals
m. p. 77-79°
Used as a blocking agent for hydroxyl groups of nucleosides.
Keep cold.



PRICE 25 g. - $12.00 100 g. - $39.00

LITERATURE

R. L. Letsinger and K. K. Ogilvie, J. Org. Chem., 32, 296 (1967)

FUNCTIONAL GROUPS

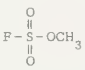
Es
Nit

NO. 16,048-2 **FORMULA** CH_3FO_3S

NAME Magic Methyl (methyl fluorosulfonate), 97%

DESCRIPTION

M. W. 114.10
Colorless liquid
n_D^{20} 1.3326
b. p. 92-94°
A powerful methylating agent.
Data sheet available.
Corrosive. Extremely toxic.



$F-\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}-OCH_3$

PRICE 100 g. - $14.00

LITERATURE

M. G. Ahmed, R. W. Alder et al., Chem. Commun., 1533 (1968)
M. G. Ahmed and R. W. Alder, ibid., 1389 (1969)

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S-7

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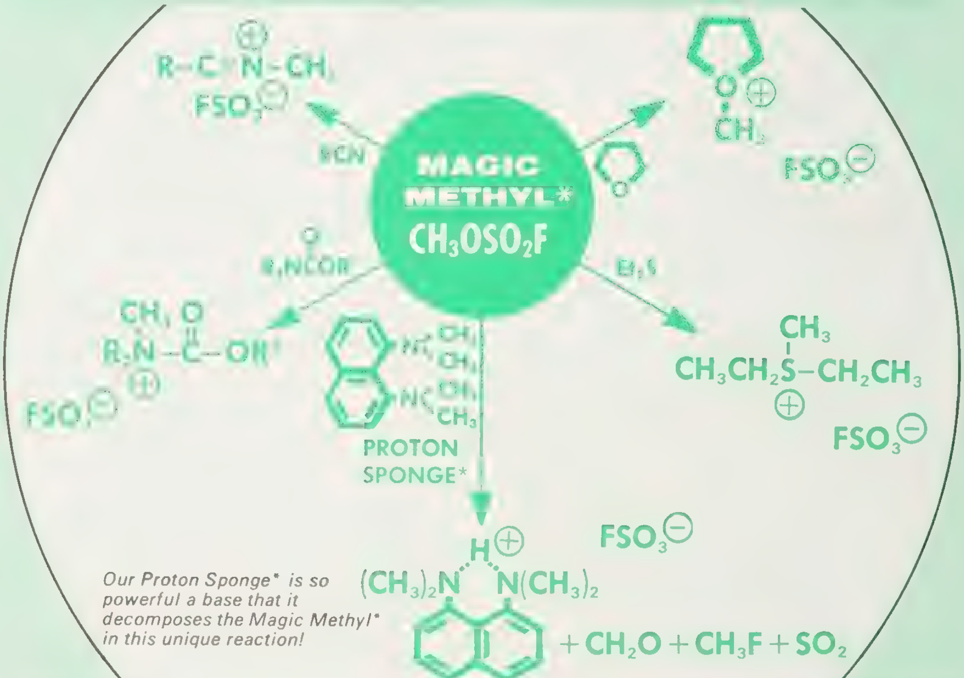

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The fact that amines[1] quaternize exothermically is not too surprising but amides[1] (eg DMF) and carbamates[2] are also readily alkylated. Some carbamates *instantly* undergo kinetically controlled O-methylation but can be equilibrated so that the N-methylated product is *highly favored*. At room temperature nitriles[1] readily yield nitrilium salts which can be reduced[3] with $NaBH_4$ to yield secondary amines. Sulfoxides[1] yield O-alkylated products and sulfides[4] give sulfonium salts which can be used synthetically[5] to form carbon-carbon bonds *via* the Stevens rearrangement. Most ethers[1] form oxonium salts but esters[1] only undergo exchange to yield methyl esters.

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Volume 4, Number 4, 1971

NMR Shift Reagents Enzyme Insolubilisation

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ABOUT OUR COVER

This large (116 x 96 cms., oil on canvas) painting, Grace before Meal, is one of our chemist-collector's favorites. Painted around 1660 by one of Rembrandt's little known followers, the Amsterdam artist Abraham van Dyck, it depicts true devotion and the love and care of the mother for her son. The enchanting still life of the simple meal of bread and milk is as beautiful as can be. Our chemist believes that the long hair of the boy and the rapport between mother and son suggest that the painting does not just represent a genre scene, but Hannah and Samuel before Samuel began his service with Eli in Shiloh.

Volume 4, Number 4
1971

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Milwaukee, Wisconsin

Editor, Kathleen D. Ryan

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APPLICATIONS—PRESENT AND FUTURE

Water-insoluble enzymes, mostly based on polysaccharide carriers, are already being applied industrially. Thus gamma-amylase derivatives are being used in experimental reactors to catalyse the hydrolysis of starch to glucose.[12] Insoluble forms of α-L-amino-acid de-N-acylase are now preferred catalysts in the large scale selective hydrolysis of L-N-acetylamino-acids in DL-N-acetylamino-acid mixtures.[13,14] This facilitates the resolution of D and L forms of the amino-acid since the L-amino-acid and D-N-acetylamino-acid are easily separated by fractional crystallisation. Water-insoluble derivatives of papain are being used to degrade soluble protein during beer production thereby preventing the development of chill-haze.

The application of proteolytic enzymes, such as papain and trypsin, is invariably accompanied by self-digestion of the enzyme. This is not possible with water-insoluble derivatives. For example, at pH 7.5 and 35°C Enzacryl CHO/trypsin is quite stable whereas the native enzyme is rapidly inactivated. Enzacryl CHO/papain is similarly stabilised and this is useful in that the enzyme is preserved during the rather slow, but necessary, pre-activation with cysteine.

Because the number of enzyme molecules which may be crowded together on a carrier surface is small compared to the number of functional groups active in enzyme binding, many of these groups do not take part in the coupling reaction. Those remaining react readily with suitable small molecules. For example, it is common practice to destroy aryl diazo groups by coupling with phenol or ß-naphthol. This sort of procedure is potentially applicable to insolubilising the enzyme within a pre-selected micro-environment. Insoluble conjugates based on Enzacryl CHO should be particularly suited to coupling a variety of small amines such as peptides, amino-acids and amino-sugars.

Because of their obvious conservation potential, water-insoluble enzymes are likely to be employed increasingly in clinical analysis. Derivatives of glucose oxidase, urease and lactate dehydrogenase have already found application. Insoluble derivatives of choline esterase and creatine phosphokinase, enzymes which are routinely estimated in body fluids, should have considerable advantages over soluble enzymes as clinico-chemical standards.

It is envisaged that Enzacryls will find application as carriers for proteins and peptides, in addition to enzymes. Enzacryl insolubilised antigens would be useful in the isolation of specific anti-bodies. Similarly, water-insoluble analogues of enzyme substrates could be employed in the single stage isolation of enzymes from crude biological fluids.

Enzymes have also been localised in solution by entrapment within collodion or nylon microcapsules.[15] Substrate and products are able to diffuse through the capsule wall. This technique has advantages for certain *in vivo* applications because immuno-evasive properties are conferred on the enzyme. However, because the enzyme is still in solution there is no possibility of enhanced stability or other improved properties. This could be overcome by micro-encapsulation of Enzacryl/enzyme conjugates.

CONCLUSION

Most enzymes, acting in their natural micro-environment, are regimented within biological membranes. Artificially insolubilised enzymes are in an analogous situation. As insolubilisation techniques improve and become more predictable it is inevitable that such derivatives will become preferred to soluble enzymes in most analytical and industrial applications. The use of Enzacryl and similar carriers will then become routine practice.

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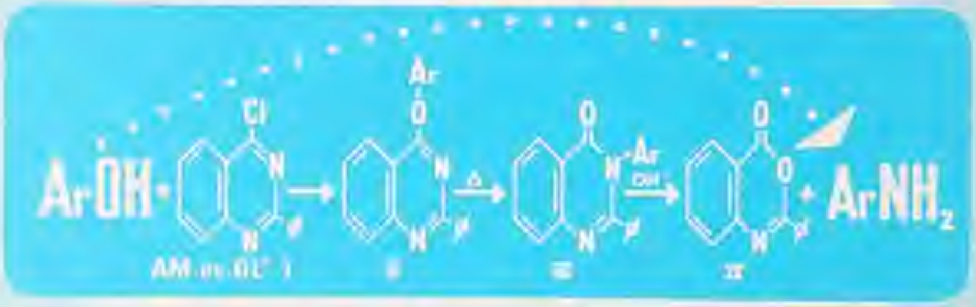
Now, however, there is a quite general procedure[1] which involves reacting AM-ex-OL* (4-chloro-2-phenylquinazoline) I with the phenol to yield the 4-aryloxy-2-phenylquinazoline II, which rearranges neat or in mineral oil at 275-325° to the 3-aryl-2-phenyl-4(3H)-quinazolinone III which is easily hydrolyzed by alkali to the aniline and 2-phenyl-4H-3,1-benzoxazin-4-one IV.



Overall yields are generally good; e.g. aniline from phenol 71%, 2,4-dichloroaniline and 2,3,6-trimethylaniline from the corresponding phenols 64 and 70% respectively. Even two steroidal phenols have been converted[2] to the amines in 67 and 58% yields.

In a typical procedure, 10 g. of phenol was added to a suspension of 5 g. of sodium hydride dispersed in mineral oil in 35 ml. of diglyme. (Sodium hydride is of course not needed if the sodium phenoxide is available. Alternatively, II can be obtained in almost quantitative yield by reacting AM-ex-OL* with the phenol and anhydrous potassium carbonate in acetone.[3]) When hydrogen evolution ceased, 24 g. of Am-ex-OL* was added. The mixture was heated to 110° for 10 minutes, cooled and poured onto ice, to yield 29.8 g. of 4-phenoxy-2-phenylquinazoline II, m.p. 112-116

Heating this quinazoline under nitrogen at 325° for 130 minutes yielded 2,3-diphenyl-4(3H)-quinazolinone III almost quantitatively. III need not be isolated. Thus, heating 16.3 g. of II in 30 ml. mineral oil under nitrogen for 4 hours at 325°, and then heating this mixture with a solution of 32 g. of KOH in 160 ml. ethylene glycol under nitrogen at 130° overnight, yielded on treatment with water, extraction with ether and treatment with HCl gas, 5.2 g. (76%) of aniline hydrochloride. The completion of the thermal rearrangement is best determined by IR or UV (II absorbs strongly at 259 mμ; III does not).

---

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Aldrichimica acta

Volume 5, Number 1, 1972

Bifunctional Catalysis

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TABLE OF CONTENTS

ABOUT THE COVER

When our chemist-collector bought this landscape (oil on panel, 20 x 29½ inches) with Elijah being fed by the ravens, he was told that it had been painted by a 16th century Flemish artist working in Italy, Lodewyk Toeput, called Pozzoserrato. Our chemist does not know the work of this artist, who died in 1604, but as this painting appears to be strongly influenced by Adam Elsheimer, the great German artist working in Italy early in the 17th century, it appears to be later, around 1615. Our collector suspects that it is by an artist whose works have been misunderstood as have almost no other artist's in the 17th century: David Teniers the Elder. Hundreds or even thousands of the early works of his son, David Teniers the Younger, and of the son's imitators, have been called works of the father, and so art-historians and collectors have connected the father's name with dim and often boring tavern interiors with peasants drinking and carousing. Actually, there is not a single documented work like this by the father, who painted beautifully balanced landscapes with biblical and mythological figures.

Perhaps we shouldn't question our chemist about paintings: whenever we do, we get an art-historical lecture, and when the painting is biblical, instruction in the Bible to boot. We asked whether he believed in the miracle of Elijah being fed by birds, and he said 'No, with all of life being a miracle, God does not resort to specific miracles,' and that the text may have been misunderstood: perhaps Elijah was fed by inhabitants of the town of Oreb, which means Raven, near the Brook of Cherith, whither he had fled—an opinion expressed in the Babylonian Talmud (Hullin 5a). All of which does not detract from the great charm of this painting: here at least Elijah is being fed by ravens, one bringing a steak, the other a twisted loaf of bread.

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(1) T. J. de Boer and H. J. Backer, Org. Syn. Coll. Vol. 4, John Wiley and Sons, New York, N. Y. 2963 p. 250.

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Acetophenones with TTN in acidic methanol undergo oxidative rearrangement2 to methyl phenylacetates, products which can be obtained only tediously by the conventional Willgerodt-Kindler reaction. In contrast, this TTN reaction can be extended3 to alkyl aryl ketones for the synthesis of **α-alkyl arylacetates.** The latter can also be prepared **in high yield** by the oxidative rearrangement4 of arylalkylacetylenes with TTN in methanol.

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ABOUT THE COVER

When we first looked at the large painting (oil on wood, 42 x 32 inches) reproduced on our cover, we couldn't help wondering: was this meant to be an advertisement for our liquid crystals which have been used on women's breasts for early signs of breast-cancer? To us, the old men looked like gynecologists in consultation, yet our chemist-collector told us that the painting depicts an apocryphal story which was a favorite of baroque artists, of Susannah being propositioned by two lecherous, old priests. Vulgarity, like beauty, must be in the eye of the beholder; to us the beautifully painted men look positively saintly, and the girl expectant rather than aghast.

Our chemist is skeptical about expertises which often accompany paintings. 'A good painting,' he says, 'does not need one, and a bad painting is not improved by a piece of paper which alleges that the painting is by the wrong artist.' This painting came with an expertise attributing it to Pieter Lastman, Rembrandt's teacher. Our chemist believes that it is Dutch, ca. 1630, but just does not know who painted it, though he hopes to find out, perhaps with the help of a reader. If you think you know, please write to us: a painter this good deserves to have his work identified.

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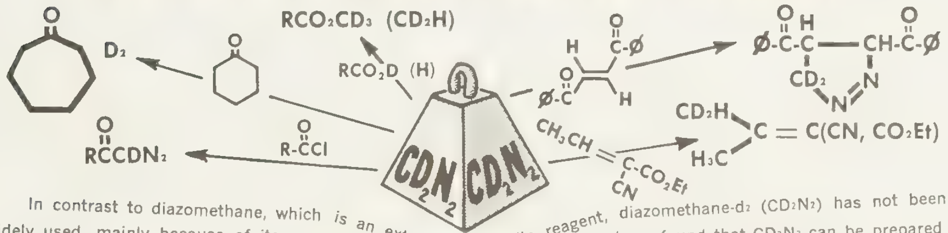
HEAVY DIAZOMETHANE



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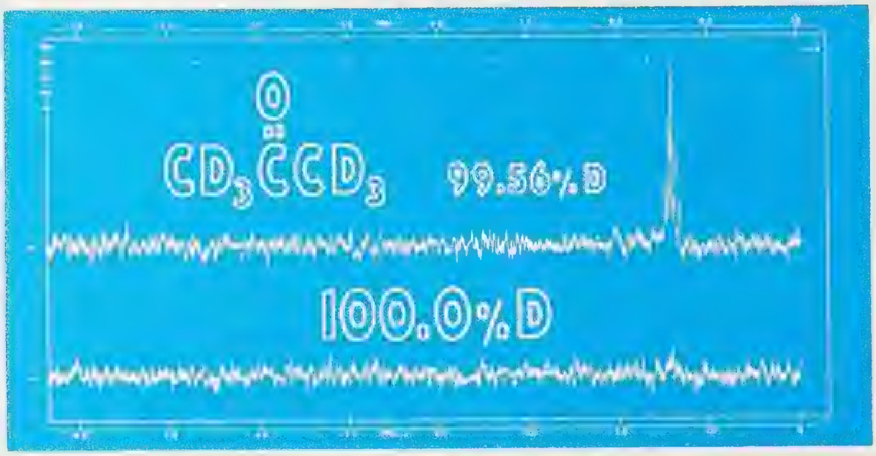

Nuclear magnetic resonance spectroscopy (nmr) is an extremely useful tool for the organic chemist; however, a prime experimental difficulty of this technique is the requirement for solvents which dissolve a wide range of compounds but which have minimal spectral absorptions. Carbon tetrachloride and carbon disulfide should be ideal choices because they have no nmr absorptions. However, they dissolve only a limited range of compounds and nmr spectra are usually obtained by using proton-containing or conventional deuterated solvents. As a result, nmr spectra often are partially masked by solvent absorptions or spinning sidebands. In addition, the availability of Fourier Transform accessories which enable nmr experiments on very dilute solutions compounds the difficulty of choosing the appropriate solvent.

We now remedy these problems by offering **100.0 atom %D** deuterated solvents. **The level of proton-containing material in these solvents cannot be detected by conventional spectrometers.** In addition to the strict requirements of 100.0 atom %D, these materials undergo the same high quality controls expected of our conventional deuterated solvents and nmr standards. We routinely examine the entire nmr spectrum for proton-containing impurities and rigorously dry hygroscopic solvents. We also carefully monitor the purity of our tetramethylsilane to exclude contamination by tetrahydrofuran or diethyl ether, excellent scavengers for fluorinated lanthanide shift reagents.

We feel that our 100.0 atom %D and our conventional deuterated solvents offer an unparalleled combination of high deuterium content and purity which now enables the observation of nmr spectra that previously were difficult or impossible to obtain.

17,586-2	Acetone-d_6 100.0 %D	5g. \$36.00; 25g. \$130.00	15,185-8	Chloroform-d 100.0 %D	10g. \$18.00; 50g. \$47.00
17,587-0	Benzene-d_6 100.0 %D	5g. \$38.00; 25g. \$135.00	15,189-0	Deuterium oxide 100.0 %D	10g. \$15.00; 50g. \$43.00
15,691-4	Dimethyl sulfoxide-d_6 100.0 %D	5g. \$35.00; 25g. \$125.00			

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17,597-8	Benzene-d_6 99.0 %D min	50g. \$45.00	17,594-3	Dimethyl sulfoxide-d_6 99.0 %D min	50g. \$37.50

Please write for a complete listing of deuterated solvents and reagents.

These products are manufactured by Diaprep, Incorporated, Division of the Aldrich Chemical Company, Milwaukee, Wisconsin

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incorporated

Aldrichimica acta

Volume 5, Number 3, 1972

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TABLE OF CONTENTS

Organic Intermediates • Biochemical Tools • Reagent Chemicals • Analytical Tools • Organo-metallics

Each chemical is carefully analyzed and stocked for your convenience.

ALDRICHIMICA ACTA

Volume 5, Number 3
1972

Published by
ALDRICH CHEMICAL COMPANY, INC.
Milwaukee, Wisconsin

Editor, Kathleen D. Ryan

ABOUT THE COVER

Our chemist-collector seldom buys paintings depicting flowers or landscapes, clearly preferring to look at people. The portrait you see here (oil on canvas, 25½ x 21 inches) came up at auction in Lucerne a few years ago, and was then called Italian, ca. 1700, which was not surprising, because it was so dirty that you could not tell what it was. Our chemist believes that it was painted by one of Rembrandt's last students, Johann Ulrich Mair, who had come to Rembrandt in the 1650's, and then returned to his native Augsburg.

Probably this is a portrait of a young Jew who lived near Rembrandt's house – almost certainly done as a study of Jesus. This student looks to us like a man with a probing mind, perhaps a mystic, certainly a man in search of God – much closer to our idea of Jesus than many sweet baroque idealizations. Man was created in God's image, Genesis tells us, and a really good portrait attests to this.

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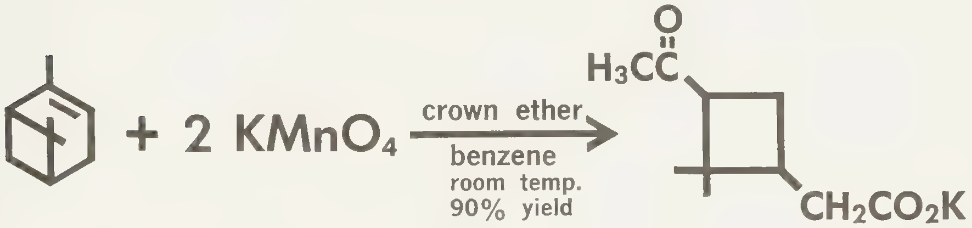
Of PURPLE BENZENE and CROWN ETHERS

Crown ethers, a class of macrocyclic polyethers, possess the spectacular ability to form with alkali metal cations, strong stoichiometric complexes soluble in non-polar solvents.[1] This unique property has important biological implications in studies of ion transport, as well as useful synthetic applications. For instance, potassium permanganate readily dissolves in benzene in the presence of dicyclohexyl-18-crown-6.[2] This purple solution oxidizes olefins, alcohols, aldehydes and aralkyl hydrocarbons in excellent yields under neutral conditions. Whereas permanganate oxidation of α-pinene proceeds only 40-60% in an aqueous medium, "purple benzene" achieves this in 90% yield.[2]



In addition, the strongly alkaline solution obtained by dissolving an equimolar mixture of potassium hydroxide and dicyclohexyl-18-crown-6 in methanol and replacing as much as possible of the methanol with benzene or toluene, readily saponifies even the highly hindered esters of 2,4,6-trimethylbenzoic acid.[3] This solution is also a powerful anionic catalyst, capable of inducing the polymerization of anhydrous formaldehyde and the trimerization of aromatic isocyanates.

Clearly the solubilizing power of crown ethers enables novel applications in catalysis, enhancement of chemical reactivity, separation and recovery of salts, electrochemistry and analytical chemistry.[1]

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15-839-9	Dibenzo-18-crown-6	2.5 g $9.75	10 g $23.00
15,840-2	Dicyclohexyl-18-crown-6, tech.	2.5 g $11.00	10 g $26.50

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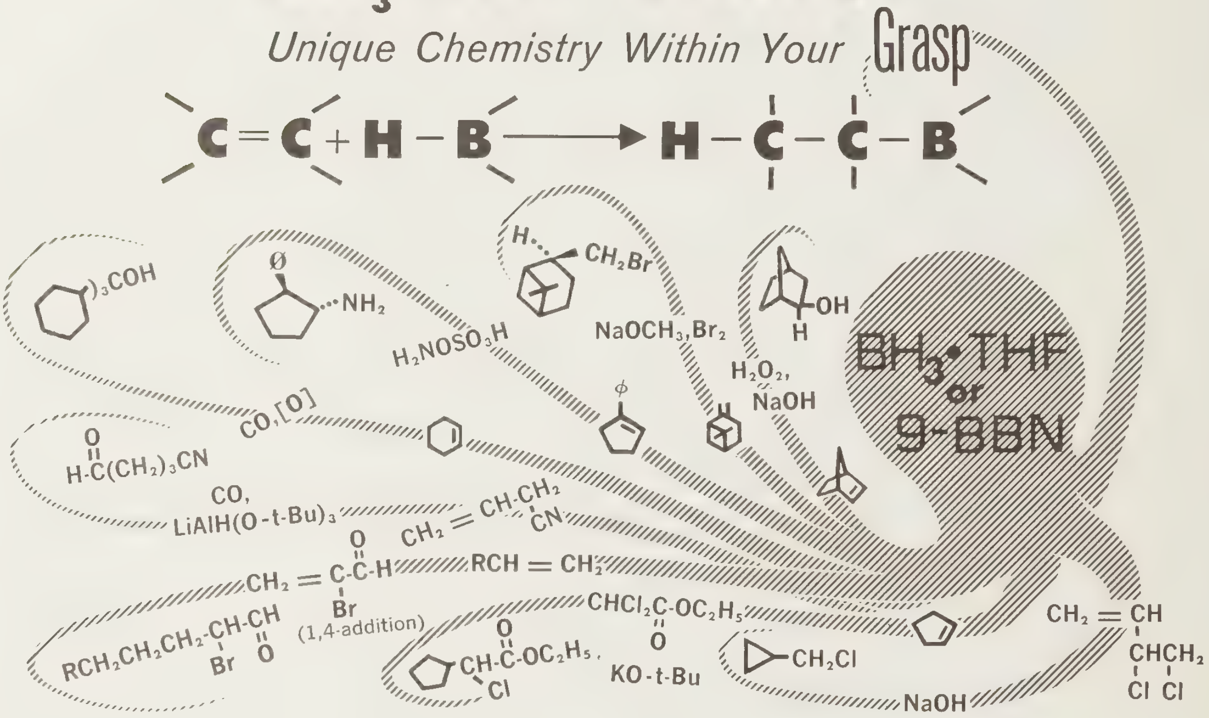
HYDROBORATION REAGENTS

now available from ALDRICH*

BH_3•THF 9-BBN

Unique Chemistry Within Your



Do these reactions look exciting? Well, they are only a small number of the many unique possibilities that are now "within your grasp" in the form of Aldrich 9-BBN and BH_3•THF.

Please write for a data sheet.

For a recent review containing pertinent literature references for these and other reactions of organoboranes see: H. C. Brown, "The Versatile Organoboranes," **Chemistry in Britain, 7,** 458 (1971).

Developed by Professor H. C. Brown and produced by Aldrich-Boranes, Inc., a division of the Aldrich Chemical Co.

15,107-6	9-BBN (9-Borabicyclo [3.3.1] nonane) (0.5M solution in tetrahydrofuran)	900g. (ca. 1 l.)	$33.75
17,619-2	Borane-tetrahydrofuran complex (1M solution in tetrahydrofuran)	900g. (ca. 1 l.)	$37.50

Aldrichimica acta

Volume 6, Number 1, 1973

Reducing Agent - Polymethylhydrosiloxane (PMHS)

Carbocation and Onium Ion Reagents

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TABLE OF CONTENTS

ALDRICHIMICA ACTA

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ABOUT THE COVER

When our chemist - collector first saw this strange depiction of Lot fleeing Sodom, at an auction in Switzerland, it was attributed to a well known Flemist artist, David Teniers the Younger, a prolific painter of many peasant scenes, most of which our chemist finds boring. The painting seemed so strongly influenced by Rembrandt, that our chemist bought the painting, hoping to have found a work by one of that master's last students. Imagine our chemist's surprise - and, we suspect, slight chagrin - when cleaning showed the work to be stunningly beautiful, albeit fully signed by David Teniers.

The story of the destruction of Sodom emphasizes the value of the individual: if only there had been ten righteous in Sodom, the city would have been spared. Abraham understood what President Kennedy put so clearly: "One man can make the difference, and every man should try." Sodom is also a turning-point in the history of man. Until then, there had been no dialogue between God and man. With Abraham trying to save the righteous, man began to talk back to God with the fierce argument "Shall not the judge of all the earth rule justly?" We have not argued fiercely enough - though Teniers tried to do his part by hinting what he thought of the morality of his day, in painting the Cathedral of Notre Dame of Antwerp right in the center of Sodom.

To us it seems particularly fitting that this wild painting grace that issue of our ACTA which describes the strongest acids and the most powerful catalysts known to man. The wild beauty of the painting challenges our imagination as do the tremendous synthetic possibilities of the work of Professor Olah, and the sheer elegance and interest of Dr. Lipowitz's review.

COLLECTORS' ITEMS

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 and biochemists near you who would be interested.

Organic Intermediates • Biochemical Tools • Reagent Chemicals • Analytical Tools • Organo-metallics

Each chemical is carefully analyzed and stocked for your convenience.

It is the **Aldrich tradition** to help the synthetic chemists by offering a wide variety of intermediates and reagents. Take peptide synthesis,[1] we generally offer one or two reagents for each peptide coupling method described in the literature to date. As each method or reagent has some disadvantages as well as advantages, a variety of reagents is necessary.

For the classic **"mixed anhydride" method,**[2] we offer **isobutyl** and **ethyl chloroformate.** Generally, isobutyl chloroformate is preferred for the preparation of peptides of moderate or high molecular weight, whereas ethyl chloroformate is preferred for the synthesis of dipeptides.[3] The **carbodiimide method**[2] is another versatile and convenient method. The most popular **DCC** is a highly reactive agent and can be used in solid-phase peptide synthesis (SPPS). Related reagents **1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide metho-p-toluenesulfonate** and **1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride** are water-soluble diimides, which permit simplified purification of the peptide product because the corresponding ureas are water-soluble. Racemization in the DCC method can be minimized or completely suppressed by using an additive,[1] such as **N-hydroxysuccinimide, N-hydroxyphthalimide, N-hydroxypiperidine** or **1-hydroxybenzotriazole.** The latter is exceptionally good at retarding racemization, prohibiting N-acylurea formation, and at improving yields of high-purity peptides.[4] These additives, of course, can be used in SPPS.[1]

The use of **DCC-pentachlorophenol** (PCP) and **DCC-pentafluorophenol** (PFP) **complexes** in the preparation of acylpeptide-PCP and -PFP active esters,[5] and other uses[6] of DCC have been described.

Another equally versatile reagent is **EEDQ** which has many more advantages: volatile and easily removable by-products, practically no racemization, usable with O-non-protected hydroxy amino acids. **EEDQ** and its more reactive analog **IIDQ,**[7] another Aldrich first, are also good for SPPS. **Woodward's reagents K and L** offer similar advantages: high yields, water soluble by-products, and usable with O-non-protected hydroxy amino acids. An **oxidation-reduction condensation method**[8] calls for **Aldrithiol-2** (2,2'-dipyridyl disulfide) and **triphenylphosphine** as coupling reagents. This system can be used in a variety of solvents at a wide range of temperature,[8] affords high yields and little racemization,[8] and can be used in SPPS.[9]

A selection of other reagents we sell are: **pivaloyl chloride,**[10] **triphenylphosphine** with **CCl_4** or **CBr_4,**[11] **triphenyl phosphite** and **imidazole,**[12] **carbonyldiimidazole,**[2] **α,α-dichloromethyl methyl ether,**[1] **chloroacetonitrile,**[*1] **p-nitrophenyl trifluoroacetate,**[*13] **2-hydroxypyridine,**[*14] **2-mercaptopyridine.**[*15]

*Active ester reagents

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Peptide Reagents Available from Aldrich

17,798-9	Isobutyl chloroformate	25g-$3.25; 100g-$7.50
E1710-0	Ethyl chloroformate	108.5g-$2.70; 500g-$4.20
D8000-2	DCC	20.6g-$3.00; 25g-$3.00; 100g-$10.00; 1kg-$45.00; 10kg-$320.00
C10,640-2	l-Cyclohexyl-3-(2-morpholinoethyl)carbodiimide metho-p-toluenesulfonate	25g-$20.00
16,146-2	1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride	10g-$10.00
15,726-0	1-Hydroxybenzotriazole monohydrate	25g-$10.50; 100g-$28.00
13,067-2	N-Hydroxysuccinimide	11.5g-$7.20; 25g-$13.85; 100g-$37.25
H5370-4	N-Hydroxyphthalimide	16.3g-$3.50; 100g-$10.10; 500g-$33.60
12,886-4	N-Hydroxypiperidine	1g-$5.30; 5g-$17.55
14,016-3	Pentachlorophenol	3kg-$8.20
10,379-9	Pentafluorophenol	10g-$18.20
15,207-2	EEDQ	25g-$6.25; 100g-$16.75; 247.3g-$39.50
17,824-1	IIDQ	25g-$6.00; 100g-$17.60
E4526-0	Woodward's reagent K	5g-$16.50; 30g-$66.00
B9695-3	Woodward's reagent L	10g-$20.00
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T8440-9	Triphenylphosphine	100g-$6.30; 262.3g-$14.25; 1kg-$41.80
T7260-5	Trimethylacetyl chloride (pivaloyl chloride)	100g-$5.65; 120.5g-$7.20
T8465-4	Triphenyl phosphite	310.3g-$2.80; 500g-$3.15; 3kg-$11.75
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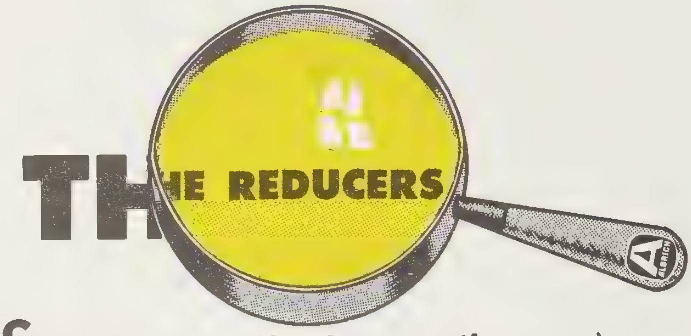

PMHS (Polymethylhydrogensiloxane)
RED-AL® [Sodium bis (2-methoxyethoxy) aluminum hydride, 70% in benzene]

PMHS, in a protic solvent with a catalyst, reduces a variety of functionalities[1] under neutral conditions and without interference from air or moisture. For example, the combination of PMHS and tetrabutyldiacetoxytin oxide dimer in ethanol is a reducing agent specific for aldehydes and ketones, ideally suited for acid or base sensitive materials. The active organotin hydride intermediate is responsible for the unique selectivity and reactivity[2] of this class of reducing agents. PMHS and stoichiometric amounts of stannoxanes also reduce[3] a variety of alkyl chlorides, bromides and iodides.

PMHS and Pd/C catalyst in ethanol provide a safe and convenient source of hydrogen for low pressure hydrogenation which may be performed in an open flask. The reduction of olefins, nitro aromatics, aralkyl bromides, and reactive alkyl chlorides[4] follows the patterns observed for catalytic hydrogenation at one atmosphere and ambient temperature.

Red-Al® **does not ignite spontaneously,** is stable to air and moisture, and yet possesses the high reactivity of $LiAlH_4$, being capable of reducing aldehydes, ketones, carboxylic acids, esters, amides, anhydrides, imides, lactones, acid chlorides, lactams, oximes and aromatic nitriles.[5] In contrast to $LiAlH_4$, Red-Al® reduces unsaturated aldehydes, ketones and acids to unsaturated alcohols. Furthermore, Red-Al® is highly soluble in aromatic hydrocarbons and ethers, and therefore is a very efficient drying agent for these solvents. The higher stability of Red-Al® permits reductions at temperatures as high as 200°. Its ease of manipulation suggests multi-kilo applications as well as micro use.

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   (b) V. Chvalovsky, et al., Collection Czechoslov. Chem. Comm., **34,** 118, 1025, 1033 (1969).

17,620-6	PMHS (polymethylhydrogensiloxane)	50g-$4.75; 250g-$15.00
17,621-4	Tetrabutyldiacetoxytin oxide dimer	25g-$6.00; 100g-$16.00
15,109-2	Red-Al® [sodium bis(2-methoxyethoxy) aluminum hydride, 70% in benzene]	250g-$9.75; 1kg-$32.00

Aldrichimica acta

Volume 6, Number 2, 1973

Special Boranes Issue

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TABLE OF CONTENTS

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Volume 6, Number 2
1973

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Organic Intermediates • Biochemical Tools • Reagent Chemicals • Analytical Tools • Organo-metallics

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ABOUT THE COVER

Our chemist-collector had often commented on his preference for paintings of people, especially biblical people, to paintings of landscapes or still life. So we were rather surprised that he had purchased the landscape (oil on canvas, 63 x 80 cm), depicted on our cover. However, when we saw the landscape, we understood: a truly great landscape - by Rembrandt, or Hercules Seghers, or Jacob Ruisdael, whose work this is - gives us a better understanding of the universe, just as a truly great portrait gives us a better understanding of man.

It seems appropriate that this painting appear on that issue of our Acta dealing with one of the most important developments in synthetic organic chemistry, hydroboration. There is great beauty in each, and both inspire the imagination.

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Two remarkable Aldrich organo-metallics never before available commercially

1

Super-Hydride*: the most powerful nucleophile known for SN2 displacements

$Li(C_2H_5)_3BH$

RX $\xrightarrow{\text{Super-Hydride*}}$ RH

Super-Hydride*
(Lithium triethylborohydride)

ArX $\xrightarrow{\text{Super-Hydride*}}$ no reaction

Recently Brown and Krishnamurthy studied the nucleophilic properties of lithium triethylborohydride.[1] It reacts 20 times faster than thiophenoxide, previously considered the most powerful, simple nucleophile in SN2 displacement of alkyl halides. **Super-Hydride*** converts *n*-octyl bromide to octane in 2 minutes at room temperature and cycloheptyl bromide to cycloheptane in 15 minutes at 65°C.

[1] H.C. Brown and S. Krishnamurthy, *J. Amer. Chem. Soc.*, **95**, 1669 (1973).

17,972-8	**Super-Hydride*** (Lithium triethylborohydride)........ 1 *M* solution in THF (900g = *ca.* 1 *l.*)	**900g**	**$34.00**
17,970-1	**Triethylborane**.. 1 *M* solution in THF (900g = *ca.* 1 *l.*)	**900g**	**$29.00**

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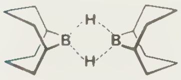
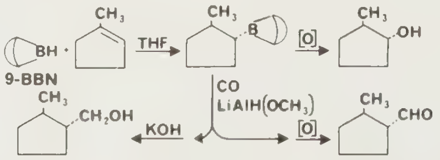
2

9-BBN powder: the most stable hydroborating agent known



Now in *SOLID* form, 9-BBN can be handled with reasonable precautions in air.[1] In addition to this important convenience factor, 9-BBN displays greater selectivity than borane, yet hydroborates even hindered olefins. The organoboranes produced may be used to produce alcohols, aldehydes or methylol analogs with retention of stereochemistry.[2]



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[2] H.C. Brown, M.M. Rogic; M.W. Rathke and G.W. Kabalka, *ibid.*, **91**, 2150 (1969).

17,871-3	**9-BBN, Powder**.................................	**25g**	**$25.00**	**100g**	**$80.00**

Aldrichimica Acta

Volume 6, Number 3
(Final Issue, 1973)

Wiswesser Line Notation

The Borane•amine Complexes

PUBLISHED BY THE ALDRICH CHEMICAL COMPANY, INC.

TABLE OF CONTENTS

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ABOUT THE COVER

When we asked our chemist-collector to suggest one of his paintings which might relate both to the Wiswesser Line Notation and to Aldrich's work on hydroboration, we did not really expect an answer because these topics covered in this issue seem so unrelated. Thus, we were surprised when he quickly pointed to a small (oil on copper, 5 x 5 in.), early Rembrandt which he had purchased in Vienna years ago. What WLN and hydroboration have in common are their fundamental importance to chemists and the tremendous possibilities for development in each. In a similar manner, 'The Scholar by Candlelight', painted by Rembrandt in Leiden in his early twenties, clearly foreshadows some of his truly great works such as 'The Supper at Emmaus' in the Musée Jacquemart André in Paris, and 'The Flight to Egypt' (recently stolen from Tours), painted only a year or two later. Thus it is with WLN and hydroboration -- both are in their early stages of development, and both are bound to affect chemistry as fundamentally as Rembrandt affected art.

COLLECTORS' ITEMS

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 and biochemists near you who would be interested.

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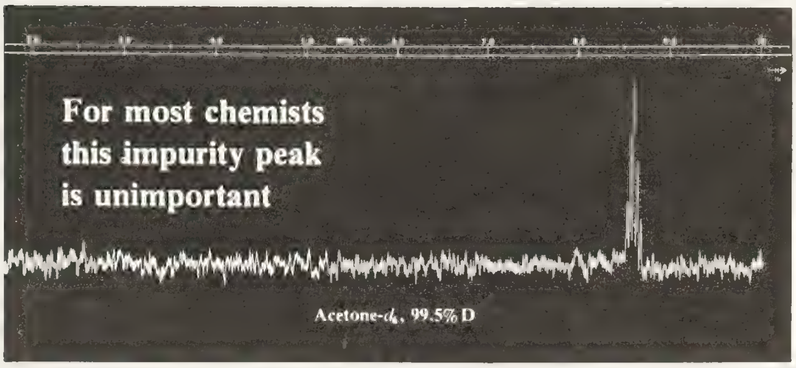

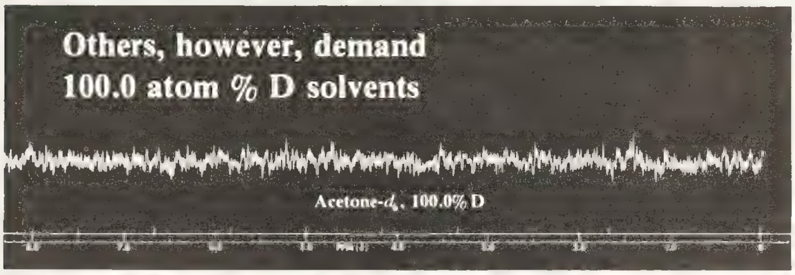

All chemists want the lowest prices on Deuterated Solvents. Aldrich satisfies everyone.

Purity specifications of deuterated solvents for nmr spectroscopy are usually given in percentage of deuterium contained in the solvents, but one rarely finds information about the chemical purity of deuterated solvents. We pay particular attention to both aspects of quality control. Our deuterium purity is always given as atom per cent deuterium as determined by nmr dilution experiments. Thus, our 99.5% benzene-d_6 contains less than 5 protons per thousand deuterons and no other detectable impurity by gas chromatography.

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15,181-5	**Benzene-d_6, 99.5%**	**10 g**	**12.25**
		25 g	**28.50**
15,182-3	**Chloroform-d, 99.8%**	**50 g**	**6.50**
		100 g	**12.50**
15,188-2	**Deuterium oxide, 99.7%**	**100 g**	**13.50**
15,187-4	**Methyl sulfoxide-d_6, 99.5%**	**10 g**	**9.50**
		25 g	**23.25**
15,232-3	**Pyridine-d_5, 99%**	**5 g**	**17.10**
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Gold Label 100.0 atom % D

17,586-2	**Acetone-d_6**	**5 g**	**$ 36.00**
		25 g	**130.00**
17,587-0	**Benzene-d_6**	**5 g**	**38.00**
		25 g	**135.00**
15,185-8	**Chloroform-d**	**10 g**	**18.00**
		50 g	**47.00**
15,189-0	**Deuterium oxide**	**10 g**	**15.00**
		50 g	**43.00**
15,691-4	**Methyl sulfoxide-d_6**	**5 g**	**35.00**
		25 g	**125.00**
17,797-0	**Pyridine-d_5**	**1 g**	**15.00**
		5 g	**68.00**

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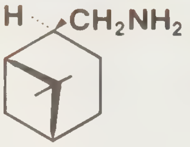
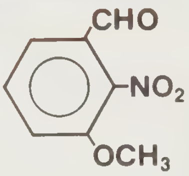
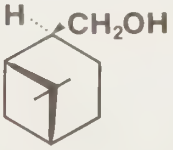


18,080-7
cis-**Myrtanylamine**
Optically active primary amine derived from a natural product.
10g $15.00

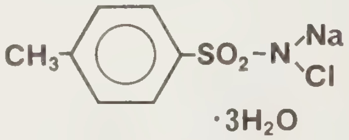


16,382-1
3-Methoxy-2-nitrobenzaldehyde
Synthetic building block
5g $9.00 25g $30.00

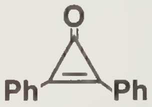
17,716-4
1,3-Cyclopentanedione
Precursor to prostaglandin intermediates
J. Org. Chem., **26**, 5206 (1961).
1g $8.00 5g $28.00



18,315-6
cis-**Myrtanol**
10g $5.50 50g $19.00

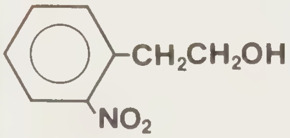


85,731-9
Chloramine-T
1kg $8.00

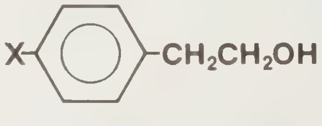


17,737-7
Diphenylcyclopropenone
1g $9.00 5g $30.00

Substituted Phenethyl Alcohols

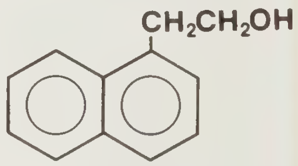


18,347-4
o-**Nitrophenethyl alcohol**
10g $9.00 50g $30.00



X = Br, Cl, NO$_2$

18,343-1 *p*-**Bromophenethyl alcohol**
10g $8.25 50g $27.00
18,342-3 *p*-**Chlorophenethyl alcohol**
10g $6.50 50g $19.00
18,346-6 *p*-**Nitrophenethyl alcohol**
10g $7.00 50g $19.80



18,345-8
1-Naphthaleneethanol
10g $6.70 50g $19.50

Aldrichimica Acta

Volume 7, Number 1, 1974

PUBLISHED BY THE ALDRICH CHEMICAL COMPANY, INC.

ALDRICHIMICA ACTA

Volume 7, Number 1
1974

Published by
ALDRICH CHEMICAL COMPANY, INC.
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Editorial Staff: Deanna R. Cruz
David W. Griffiths
Ramona H. Jules

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ABOUT THE COVER

Our chemist - collector is convinced that there are still some old masters whose ability is unappreciated, and that one of these is Leonard Bramer, the painter of this *Esther before Ahasuerus* (oil on wood, 28 ½ x 22 inches). Bramer had studied in Italy and was greatly influenced by the Venetians and Rembrandt. In fact, he provides a link between Rembrandt and the great 18th century Italian, Magnasco.

We have never greatly liked the story of Esther, and are not surprised that there was a good deal of argument by the compilers of the Bible as to whether or not this book should be included. It is not so much that we dislike stories of court intrigue as that we cringe at the all-too-kind treatment accorded King Ahasuerus, The Fool. Here is the most dangerous fool of all, the fool with power. He is not a killer himself, but a man who votes a Haman into office and then says: "Auschwitz? My Lai? Why, I never even heard of these places." Yet this fool of a king is never even criticized in the story.

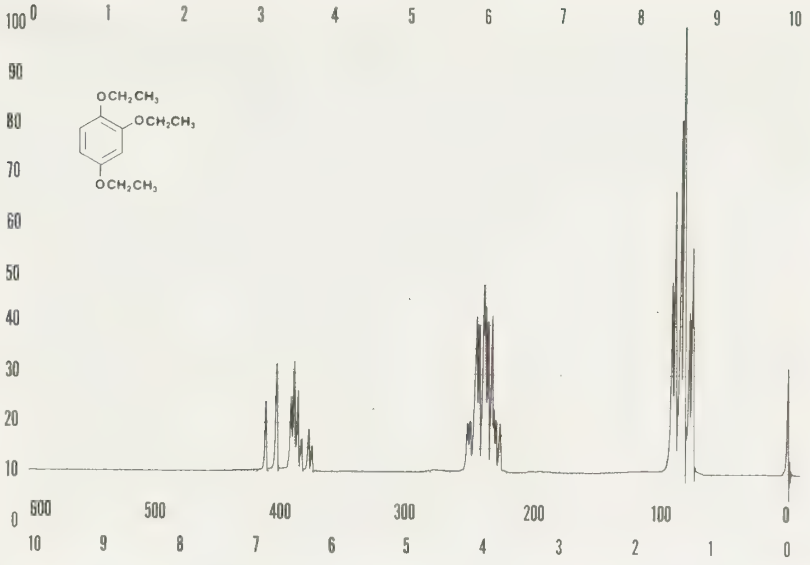
Still, when we look at this beautifully balanced study of darkness and light, our admiration for its beauty overcomes our disgust for the king.

TABLE OF CONTENTS

Organic Intermediates • Biochemical Tools • Reagent Chemicals • Analytical Tools • Organometallics

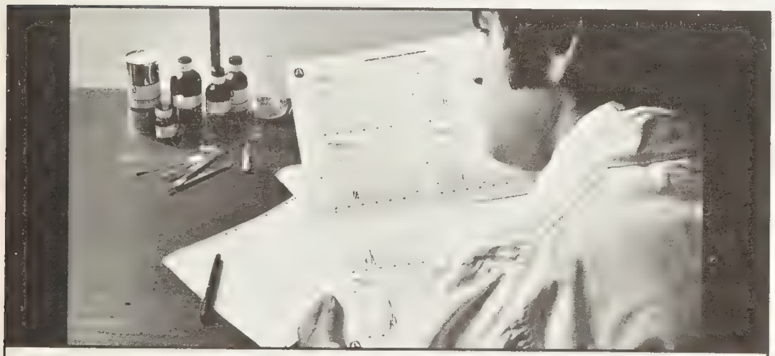
Each chemical is carefully analyzed and stocked for your convenience.

13,884-3
1,2,4-Triethoxybenzene, 99%
$C_6H_3(OC_2H_5)_3$
M.W. 210.27 m.p. 30-33° Beil. **6**,1089 **IR** 476D



Typical NMR spectrum shown actual size, as it appears in print. All spectra are recorded on a Perkin-Elmer Hitachi R-24 permanent magnet spectrometer operating at 60 MHz.

Pre-publication offer: Save $50 on the new Aldrich 10 volume NMR collection containing over 6000 spectra



Here is a list of contents in sequence of publication.

Vol. IV
(Cat. # Z10,204-0) AROMATIC hydrocarbons, halogenated hydrocarbons, ethers & phenols

Vol. V
(Cat. # Z10,205-9) AROMATIC alcohols, mercaptans, sulfides, amines, nitro & nitroso compounds

Vol. VI
(Cat. # Z10,206-7) AROMATIC ketones, aldehydes, carboxylic acids & acid salts

Vol. VII
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Vol. IX
(Cat. # Z10,209-1) AROMATIC 6-membered single & fused ring heterocycles & *N*-oxides

Vol. X
(Cat. # Z10,210-5) Sulfur-oxygen compounds, phosphorus compounds, oximes, alkynes, steroids, indole alkaloids, silanes, boranes & miscellaneous compounds

Vol. XI
(Cat. # Z10,211-3) CUMULATIVE index, listed in alphabetical and molecular formula order

All compounds illustrated are taken from the Aldrich Catalog/Handbook and are conveniently arranged by increasing molecular complexity and functionality.

Not since the publication of *The Aldrich Library of Infrared Spectra* has there been such a valuable compilation of information to assist the working chemist. The volumes will be published in two- to three-month intervals. An eleventh volume will contain a complete index. Volumes may be ordered individually at $15 per copy (for a total of $165) or you may subscribe to the entire series now at the prepaid, pre-publication price of $115. Then, as each volume is completed, it will be sent out automatically. This series will be immensely useful not only to users of 60MHz instruments but also to chemists and students who wish to gain familiarity with the spectral features of different classes of compounds. Because this pre-publication offer is limited, we urge you to send your order now.

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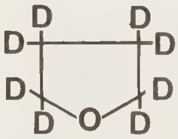

18,431-4
Tetrahydrofuran-d_8, 98 atom % D
NMR solvent.
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10g $166.00
Lowest price anywhere!

ALDRICHIMICA ACTA

Volume 7
Number 2
1974

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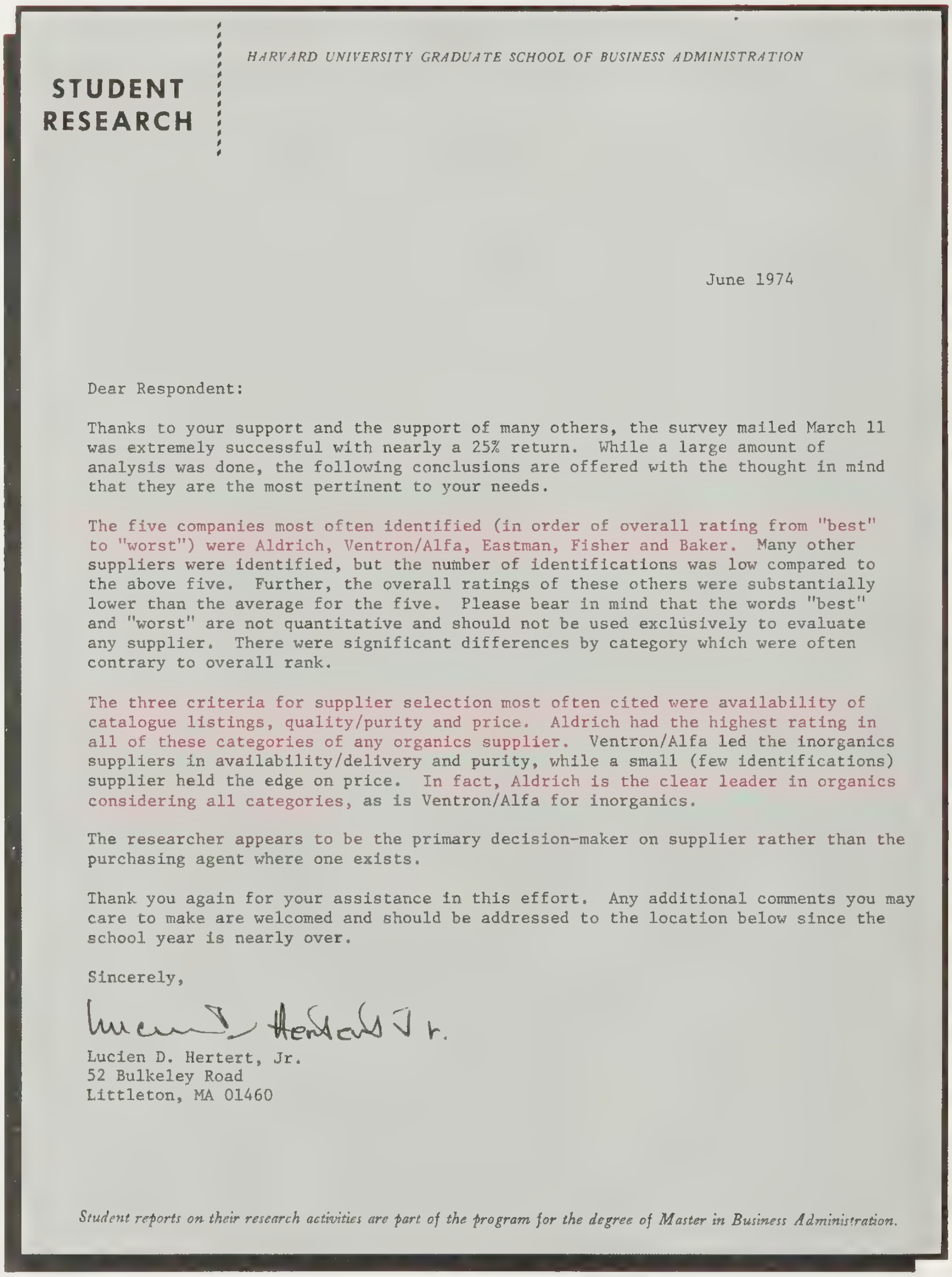
How to Make These Impossible Naphthalene Derivatives. See page 30.
Ester Reductions with Super-Hydride.™ See page 32.
Computer Retrieval of Structures. See page 35.

If you decide who supplies your organic compounds, read this important letter



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STUDENT RESEARCH

June 1974

Dear Respondent:

Thanks to your support and the support of many others, the survey mailed March 11 was extremely successful with nearly a 25% return. While a large amount of analysis was done, the following conclusions are offered with the thought in mind that they are the most pertinent to your needs.

The five companies most often identified (in order of overall rating from "best" to "worst") were Aldrich, Ventron/Alfa, Eastman, Fisher and Baker. Many other suppliers were identified, but the number of identifications was low compared to the above five. Further, the overall ratings of these others were substantially lower than the average for the five. Please bear in mind that the words "best" and "worst" are not quantitative and should not be used exclusively to evaluate any supplier. There were significant differences by category which were often contrary to overall rank.

The three criteria for supplier selection most often cited were availability of catalogue listings, quality/purity and price. Aldrich had the highest rating in all of these categories of any organics supplier. Ventron/Alfa led the inorganics suppliers in availability/delivery and purity, while a small (few identifications) supplier held the edge on price. In fact, Aldrich is the clear leader in organics considering all categories, as is Ventron/Alfa for inorganics.

The researcher appears to be the primary decision-maker on supplier rather than the purchasing agent where one exists.

Thank you again for your assistance in this effort. Any additional comments you may care to make are welcomed and should be addressed to the location below since the school year is nearly over.

Sincerely,

Lucien D. Hertert Jr.

Lucien D. Hertert, Jr.
52 Bulkeley Road
Littleton, MA 01460

Student reports on their research activities are part of the program for the degree of Master in Business Administration.

This letter was sent to all those who responded to a four-page questionnaire, part of a research project directed by Mr. Hertert. The survey was conducted without our knowledge, and contained no names of any chemical supply firms.

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Table of Contents

About the Cover

When we first saw the large *Tobias Healing his Father* (oil on panel, 92 x 122 cms), we were surprised that our chemist-collector had bought yet another depiction of this curious subject. Yet the more we looked at the painting and listened to the story of the son who healed his father's blindness, the easier it was to understand. The brilliant colors - lemon yellows and blues and reds - the flowing composition and particularly the harried face of the father that must have been modelled after the face of an Eastern Jew who wandered into Flanders in the early sixteen hundreds, must make this one of the finest works of the artist whose name has been forgotten. He painted many works, mainly of gypsies and musicians, and is known by the pseudonym Pseudo van der Venne. Many other baroque artists were also attracted to this story - not surprising when you consider the importance of eyesight to artists. Rembrandt for instance painted, drew and etched over 50 works depicting this apocryphal story, his interest probably heightened by his father's blindness.

The story of Tobias is one of the almost impossible: the story of the young man who saved his fiancee from the demon, and who cured his father's blindness. Hence it seems particularly appropriate on the cover of the issue that describes the work of Drs. Look, Hyman and coworkers - which is also of the almost impossible!

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, now is available to all chemist art-lovers.

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Volume 7, Number 3
(Final Issue, 1974)

New Reagents for Hydroboration and for Synthesis via Boranes. See page 43.

Trialkylborohydrides as New Versatile Reducing Agents in Organic Synthesis. See page 55.

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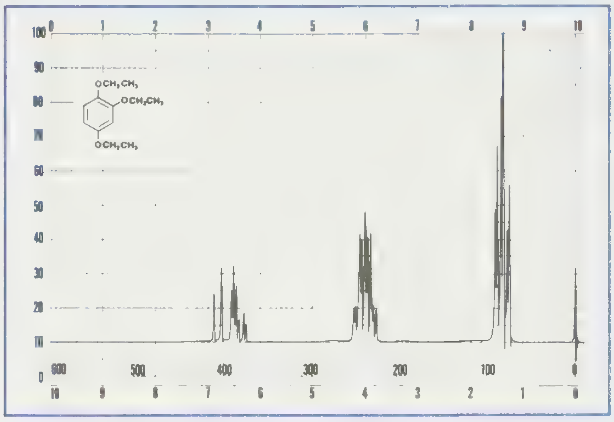
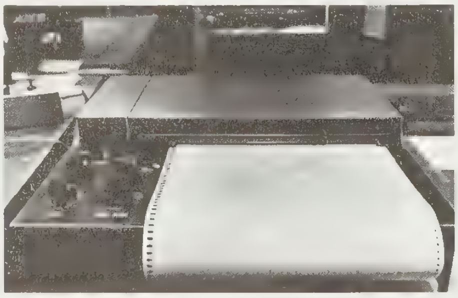
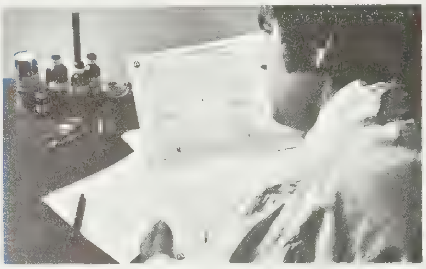


A typical NMR spectrum as it appears in the Aldrich Library of NMR Spectra (actual size 4½" x 3½").



Spectra were recorded on a Perkin-Elmer Hitachi R-24 permanent magnet spectrometer operating at 60 MHz.



Spectra are conveniently arranged by increasing molecular complexity and functionality.

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Aldrichimica Acta

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Table of Contents

About the Cover

We have often asked our chemist-collector why he buys mainly Dutch 17th century paintings preferably, it seems, of biblical subjects. Why not acquire some really first class American paintings? He has just shrugged his shoulders and replied that, with a few exceptions (*e.g.,* Edward Hopper and Charles Munch), he does not like modern American paintings, and the best 19th century masters (*e.g.,* Thomas Eakins) are too expensive. Recently, however, on a trip to Washington to visit the N.I.H., he did buy an American mid-19th century landscape by William Sonntag. Looking at this, we understand why: the haunting beauty of this scene of a bend in the Ohio River east of Cincinnati reminds us of the long views and high skies of so many of the Dutch 17th century landscapes.

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 the late Professor Wolfgang Stechow; now available to all chemist art-lovers.

Z10,118-4 $6.00

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.

We always give you more than you ask for.

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Most of our organic and biochemicals are labeled with a batch analysis number. This number corresponds to the data on file in our own Analytical Laboratories. An infrared spectrum is taken on each batch (along with the melting point or refractive index). We compare results with our own internal data and literature standards.

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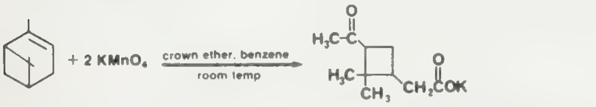
Crown Ethers

How to dissolve alkali metal salts in organic solvents

Since the discovery of their remarkable ability to solubilize alkali metal salts in non-polar solvents, crown ethers,[1a,b] a class of macrocyclic polyethers, have found novel application in synthesis. The new crown ether, **18-crown-6**, promises even greater synthetic utility by virtue of its increased complexing ability.[2] For example, in acetonitrile or benzene effective solvation of the potassium ion of potassium fluoride by **18-crown-6** results in a highly reactive fluoride ion ("naked" fluoride).[2] "Naked" fluoride is a potent base and nucleophile,[2] being capable of converting a variety of alkyl, acyl, or activated aryl halides to their respective fluorides in good yields.

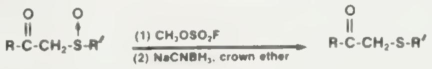
$$CH_3(CH_2)_6CH_2Br \xrightarrow[CH_3CN]{KF,\ 18\text{-crown-6}} \begin{array}{l} CH_3(CH_2)_6CH_2F\ (92\%) \\ CH_3(CH_2)_5CH{=}CH_2\ (8\%) \end{array}$$

In the presence of **dicyclohexyl-18-crown-6**, potassium permanganate readily dissolves in benzene to form a purple solution ("Purple Benzene")[3] which oxidizes alcohols, olefins, aldehydes and aralkyl hydrocarbons in excellent yield under neutral conditions.



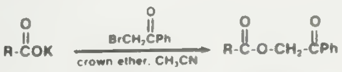
90%, *cis* (40-60% with no crown ether in an aqueous system)

Alkoxysulfonium salts, formed by alkylation of sulfoxides with Magic Methyl® (methyl fluorosulfonate), are readily reduced with sodium cyanoborohydride in the presence of crown ethers[4] to give sulfides in excellent yield. Similarly, β-ketosulfoxides are reduced to β-ketosulfides,[4] whereas extensive decomposition occurs in the absence of the crown ether.



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}R' \xrightarrow[(2)\ NaCNBH_3,\ \text{crown ether}]{(1)\ CH_3OSO_2F} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}S\text{-}R'$$

Phenacyl esters which are difficult to obtain in good yield using classical procedures are easily formed by refluxing a benzene or acetonitrile suspension of acyl salt, crown ether and α-bromoacetophenone.



$$R\text{-}\overset{\overset{O}{\|}}{C}OK \xrightarrow[\text{crown ether},\ CH_3CN]{BrCH_2\overset{\overset{O}{\|}}{C}Ph} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}Ph$$

90% yield

The alkylation of acetoacetic ester enolates gives less O-alkylated product in the presence of a crown ether,[5] especially in weakly polar solvents. **Dicyclohexyl-18-crown-6** markedly changes the rates and stereochemical course[6] of alkoxide-catalyzed carbanion-generating reactions; *e.g.*, the reaction of 5-decyl tosylate with potassium alkoxides[7] produces more *trans* olefin in the presence of **dicyclohexyl-18-crown-6**. Crown ethers also find application in the resolution of α-amino acids[8] and show promise for the preparation of organometallics[9] by catalyzing the reaction between metals and C-halogen or acidic C-H compounds. The potassium hydroxide complex of **dicyclohexyl-18-crown-6** reacts with *o*-dichlorobenzene[10] to give *o*-chloroanisole in 40-50% through a non-benzyne mechanism. Finally, crown ethers may be contrasted with our α- and β-cyclodextrins. While the cyclodextrins have a lipophilic cavity and hydrophilic shell the reverse is true of the crown ethers.[11]

References

1) (a) C.J. Pedersen, *Aldrichimica Acta*, **4**, 1 (1971); *J. Amer. Chem. Soc.*, **89**, 7017 (1967); C.J. Pedersen and H.K. Frensdorff, *Angew. Chem., Intern. Ed. Engl.*, **11**, 16 (1972). (b) J.J. Christensen, D.J. Eatough and R.M. Izatt, *Chem. Revs.*, **74**, 351 (1974).
2) C.L. Loitta and H.P. Harris, *J. Amer. Chem. Soc.*, **96**, 2250 (1974).
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7) J. Zavada, M. Svoboda and M. Pakova, *Tetrahedron Lett.*, 711 (1972).
8) R.C. Helgeson, K. Koga, J.M. Timko and D.J. Cram, *J. Amer. Chem. Soc.*, **95**, 3021 (1973); R.C. Helgeson, J.M. Timko and D.J. Cram, *ibid.*, **95**, 3023 (1973).
9) J.L. Dye, M.G. DeBacker and V.A. Nicely, *ibid.*, **92**, 5226 (1970).
10) D.J. Sam and H.E. Simmons, *ibid.*, **96**, 2252 (1974).
11) D.J. Cram and J.M. Cram, *Science*, **183**, 803 (1974).

18,665-1	**18-Crown-6**	**5g $15.00; 25g $60.00**
15,839-9	**Dibenzo-18-crown-6**	**2.5g $10.20; 10g $25.25**
15,840-2	**Dicyclohexyl-18-crown-6**	**2.5g $11.45; 10g $30.00; 100g $200.00**
85,609-6	**α-Cyclodextrin**	**1g $5.00; 5g $18.00; 25g $70.00**
85,608-8	**β-Cyclodextrin**	**5g $6.00; 25g $20.00**
16,048-2	**Magic Methyl® (methyl fluorosulfonate)**	**11.4g† $3.00; 100g $14.00**

† Designates molar unit

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15,839-9 Licensed under U.S. Patent 3,687,978

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Sodium cyanoborohydride. A highly selective reducing agent.

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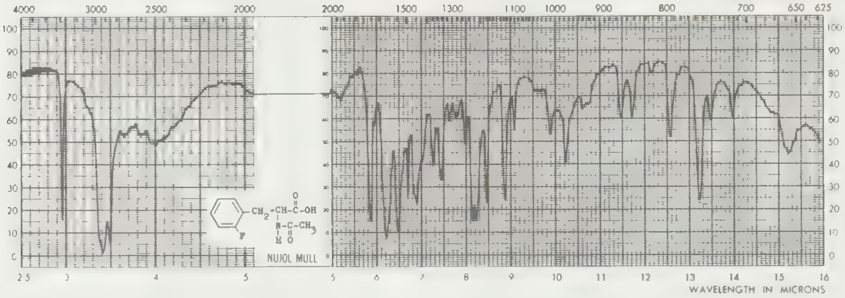
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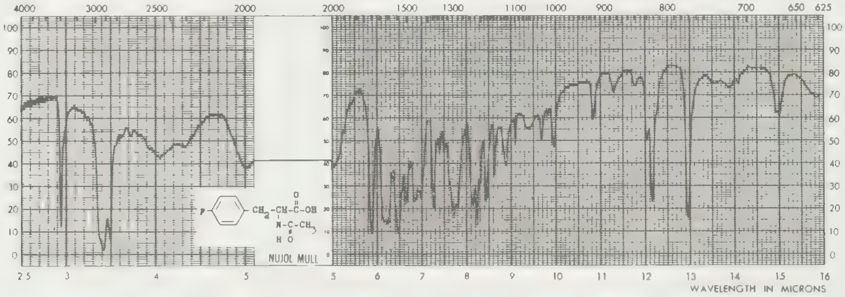
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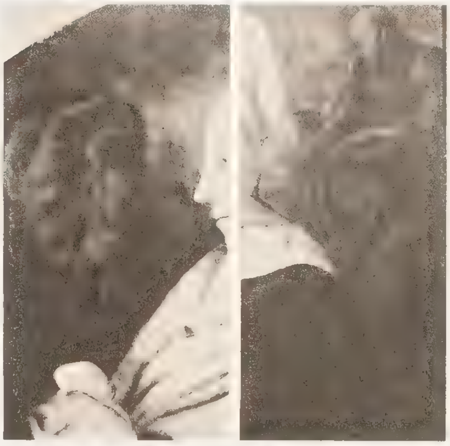
About the Cover

It is a great moment in the life of a collector when he finds himself confronted by a hitherto unknown masterpiece by a great artist - be it in a junk store, an auction or — as happened to our chemist-collector — in a farmhouse near Delft where he first saw this moving work by the greatest of Utrecht painters, Hendrick Terbrugghen. If only, he explains, it happened more often!

Our chemist believes that this painting may depict a very rare subject, *Mary Praying for the Condemned in Purgatory*. However, the iconography seems almost irrelevant. What we see here is the timeless tragedy of a woman bemoaning man's inhumanity to man - be this at Golgotha, at Auschwitz or at My Lai.

That an artist can depict anguish so that it almost hurts us physically to look at this study in grey, persuades us that art, like music, is one of God's means of communication with man.



Overexposed detail photographs of the background of our cover painting.

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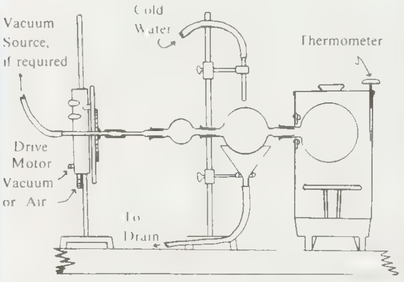
Lab Notes

How often have you encountered the problem where separation by crystallization is unsuccessful and distillation is impractical because of possible product solidification in the distillation apparatus?

In many instances, a Kugelrohr short-path distillation of the crude reaction product provides a simple method of purification, virtually eliminating any problem of plugging-up of the apparatus, while ensuring a reasonably clean separation.



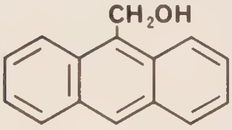
Note - 2nd bulb required only for very volatile materials

No rotating seal is present and high vacuum may be achieved, thus making the Kugelrohr especially useful for sensitive high boiling compounds. Fractionation can be easily accomplished by changing distillation tubes or receivers.

The Kugelrohr apparatus can be built according to plans published in *J. Chem. Educ.*, **41**, 279 (1964), or the complete unit may be purchased from Aldrich as stock number Z10,046-3 at $145.00.

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. All entries become the property of Aldrich Chemical Company, Inc., and cannot be returned.

9-Anthracenemethanol

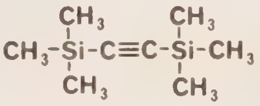


9-Anthracenemethanol is used as a protecting group for carboxylic acids. The ester is stable to hydrolysis under acidic and basic conditions but is readily cleaved under mild, selective conditions by treatment with the sodium salt of methyl mercaptan in DMF or HMPA.

N. Kornblum and A. Scott, *J. Amer. Chem. Soc.*, **96**, 590 (1974).

18,724-0 9-Anthracenemethanol
10g $9.00; 50g $38.00

Bis(trimethylsilyl)acetylene (BTMSA)



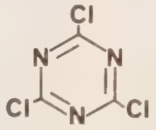
$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-C\equiv C-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

Bis(trimethylsilyl)acetylene is a useful reagent for the synthesis of acetylenic compounds, *e.g.*, terminal alkynyl ketones[1] and aryl ethynyl sulfones.[2]

1) D.R.M. Walton and F. Waugh, *J. Organometal. Chem.*, **37**, 45 (1972).
2) S.N. Bhattacharya, B.M. Josiah, and D.R.M. Walton, *Organometal. Chem. Syn.*, **1**, 145 (1970/1971).

18,743-7 Bis(trimethylsilyl)acetylene (BTMSA) **10g $18.00**

Cyanuric Chloride

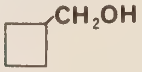


Cyanuric chloride reacts with anhydrous alcohols, without the use of free acid, to give alkyl chlorides.[1] Iodides are similarly produced with this reagent in the presence of NaI.[2] Oximes are rapidly converted to nitriles by reaction with cyanuric chloride in pyridine under mild, convenient conditions.[3]

1) S.R. Sandler, *J. Org. Chem.*, **35**, 3967 (1970).
2) S.R. Sandler, *Chem. Ind.*, 1416(1971).
3) J.K. Chakrabarti and T.M. Hotten, *Chem. Commun.*, 1226 (1972).

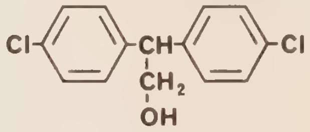
C9,550-1 Cyanuric chloride
184.4g† $3.50; 1kg $8.00

New Cyclobutane Derivative



18,791-7 Cyclobutanemethanol
5g $9.75; 25g $33.00

2,2-Bis(*p*-chlorophenyl)ethanol

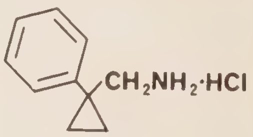


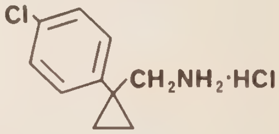
2,2-Bis(*p*-chlorophenyl)ethanol is a metabolite of DDT and a substrate for liver alcohol dehydrogenase in mammals.

J.E. Suggs, R.E. Hawk, A. Curley, and E.L. Boozer, *Science*, **168**, 582 (1970).

18,888-3 2,2-Bis(*p*-chlorophenyl)ethanol
5g $9.50

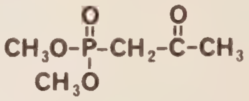
Interesting New Phenethylamines





18,769-0
1-Phenylcyclopropanemethylamine hydrochloride 5g $7.75; 25g $27.00
18,790-9
1-(*p*-Chlorophenyl)cyclopropanemethylamine hydrochloride
5g $10.00; 25g $35.00

Dimethyl (2-oxopropyl)phosphonate



$$CH_3O-\underset{CH_3O}{\overset{O}{\overset{\|}{P}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

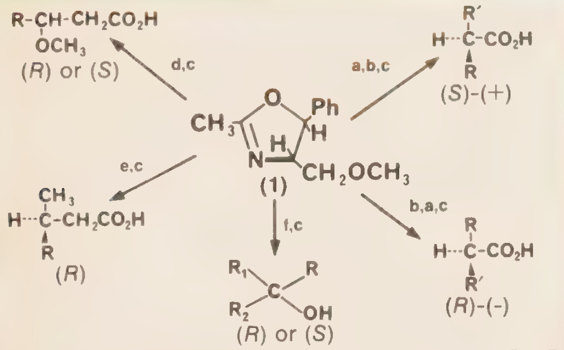
Dimethyl (2-oxopropyl)phosphonate undergoes specific alkylation at the γ-carbon *via* the dianion. It is a precursor in the general high yield synthesis of β-ketophosphonates, *e.g.*, dimethyl 2-oxoheptylphosphonate which provides a new route to a key prostaglandin reagent.

P.A. Grieco and C.S. Pogonowski, *J. Amer. Chem. Soc.*, **95**, 3071 (1973).

18,069-6
Dimethyl (2-oxopropyl)phosphonate
5g $9.00; 25g $30.00

Meyers' Reagents

For asymmetric induction and two-carbon chain elongation

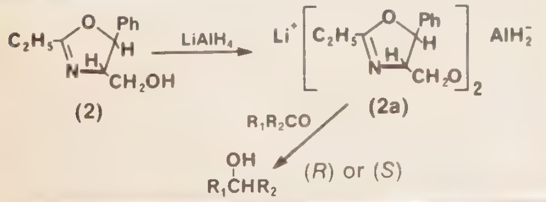


Reagents: **a)** lithium diisopropylamide (LDA), R′X **b)** LDA, RX (R precedes R′, Cahn-Ingold-Prelog sequencing) **c)** H_3O^+ **d)** BuLi, RCHO, CH_3I/HMPA **e)** LDA, CH_3CHRI **f)** RMgBr, $R_1R_2C{=}O$

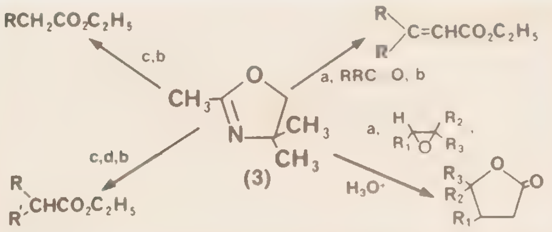
Very recently Meyers and Knaus[1] reported a versatile synthesis of *R* and *S* dialkylacetic acids from **(4*S*,5*S*)-(-)-4-methoxymethyl-2-methyl-5-phenyl-2-oxazoline (1)** *via* asymmetric induction. Thus, lithium diisopropylamide (LDA) at -78° converts the oxazoline **1** to its lithio salt. Alkylation followed by another treatment with LDA and a second alkylating agent gives, upon acid hydrolysis, the chiral acid of high optical purity (50-70%). *The order of alkyl introduction controls the stereochemistry of the final product.* When an alkyl group of lower priority (Cahn-Ingold-Prelog sequencing) is introduced, followed by a second alkyl group of higher priority, the *S* enantiomer is obtained; reversal of this order gives the *R* enantiomer.

Optically active 3-hydroxy- or 3-methoxyalkanoic acids, secondary and tertiary alcohols, and 3-methylalkanoic acids[2] also can be prepared conveniently from oxazoline **1**.

The analog, **(4*S*,5*S*)-(-)-2-ethyl-4-hydroxymethyl-5-phenyl-2-oxazoline (2)** reacts with $LiAlH_4$ to give a chiral reducing agent **(2a)** which converts ketones to chiral secondary alcohols.[3]

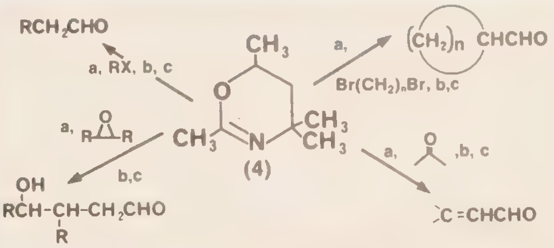


The achiral oxazoline, **2,4,4-trimethyl-2-oxazoline (3)**, provides a convenient synthesis of substituted acetic acid esters, α,β-unsaturated esters and γ-butyrolactones.[4]



Reagents: **a)** BuLi **b)** H^+, C_2H_5OH **c)** BuLi, RX **d)** BuLi, R′X

5,6-Dihydro-2,4,4,6-tetramethyl-4*H*-1,3-oxazine (4) is an excellent precursor to aldehydes.[5]



Reagents: **a)** BuLi **b)** $NaBH_4$ **c)** H_3O^+

References:
1) A.I. Meyers and G. Knaus, *J. Amer. Chem. Soc.*, 96, 6508 (1974)
2) A.I. Meyers *et al.*, *Tetrahedron Lett.*, 1333, 1341 (1974); *J. Org. Chem.*, 39, 1603 (1974).
3) A.I. Meyers and P.M. Kendall, *Tetrahedron Lett.*, 1337 (1974)
4) A.I. Meyers *et al.*, *J. Org. Chem.*, 39, 2778, 2783 (1974).
5) A.I. Meyers *et al.*, *ibid.*, 38, 36 (1973)
For a brief review of compounds (3) and (4), see E.W. Collington, *Chem Ind.*, 987 (1973).

18,765-8	**(4*S*,5*S*)-(-)-4-Methoxymethyl-2-methyl-5-phenyl-2-oxazoline**	**5g $13.50; 25g $45.00**
18,766-6	**(4*S*,5*S*)-(-)-4-Hydroxymethyl-2-methyl-5-phenyl-2-oxazoline**	**5g $7.80; 25g $26.00**
18,774-7	**(4*S*,5*S*)-(-)-2-Ethyl-4-hydroxymethyl-5-phenyl-2-oxazoline**	**5g $8.00; 25g $26.00**
17,874-8	**2,4,4-Trimethyl-2-oxazoline**	**25g $8.00 100g $21.00**
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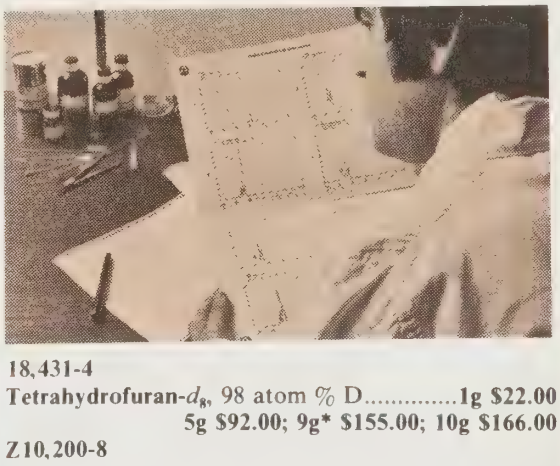

18,431-4
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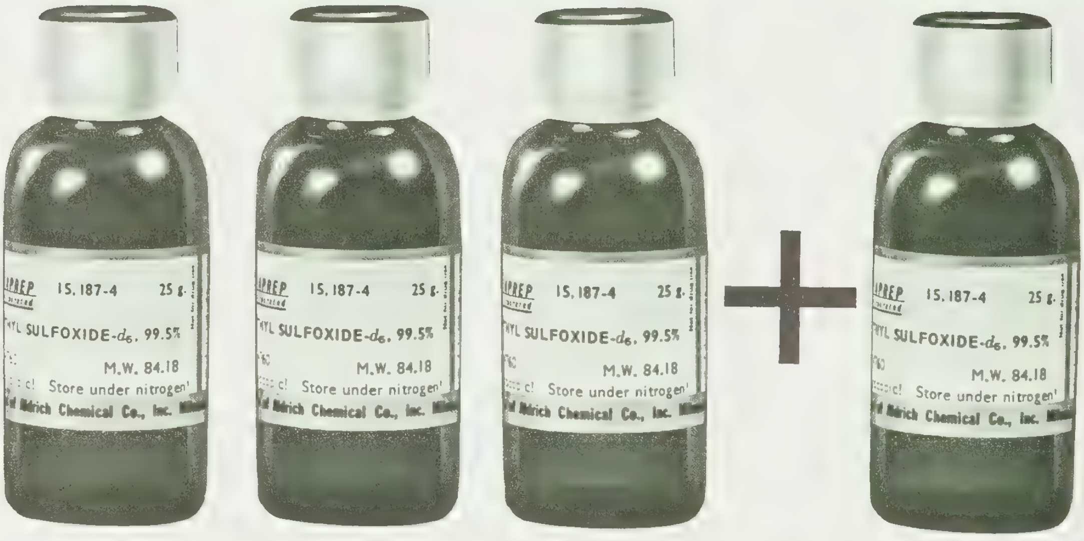

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About the Cover

Our chemist-collector has confided to us that, whenever he becomes too discouraged by events in the Middle-East, he thinks of the Book of Ruth. Hence, we were not surprised at this recent acquisition, a beautiful painting of *Boaz and Ruth* (oil on canvas, 28-1/4 x 31-1/2 inches) by one of Rembrandt's students, Gerbrand van den Eeckhout, signed and dated 1656. It shows Ruth, the Moabite, in the fields of Bethlehem meeting her future husband, Boaz.

Though the Moabites were related to the Jews through Lot, the nephew of Abraham, there was bitter enmity between them after the Exodus from Egypt. The Moabites even enlisted Balaam, one of the greatest prophets of his time, to curse the Jews, who retaliated by excluding Moabites from Israel, 'even to their tenth generation.'

Luckily, enmity on that level is often mitigated by the kindness of individuals. It is hard to find a more moving expression of such personal kindness than Ruth's words to her widowed mother-in-law, Naomi: "Thy people shall be my people, and thy God my God. Where thou diest will I die, and there will I be buried; the Lord do so to me, and more also, if aught but death part thee and me."

It is surely significant that King David, and hence the Messiah, are direct descendants of Ruth, the Moabite. Maybe there is hope for us yet.

The miracle of the Book of Ruth is not that the Messiah is a descendant of a Moabite, nor that Jews and Moabites could live together happily. Rather it lies in the true love that two people can have for one another — Naomi's and Ruth's — devoid of sex and materialism, and as beautiful as anything we know.

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Organoboranes in Organic Synthesis

George W. Kabalka
Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37916

Organoboranes are playing an increasingly important role in synthetic organic chemistry. A number of factors has contributed to the utility of the organoboranes as synthetic intermediates. Of primary importance are their reactivity and their availability. The purpose of this article is to demonstrate that the reactivity of organoboranes is readily understandable (and predictable) in terms of a few basic organic chemistry concepts.

BACKGROUND

Preparation

The myriad of new synthetic manipulations involving organoboranes would not have evolved had it not been for their ready availability. They may be prepared *via* the hydroboration reaction in essentially quantitative yields (eq 1).[1] Furthermore, the rapidity and selectivity of this reaction permit the incorporation of numerous functional substituents in the organoborane. For the first time, the synthetic chemist has available a reactive intermediate which can contain a variety of functional groups.[2,3]

$$3RCH{=}CH_2 + BH_3 \longrightarrow (RCH_2CH_2\text{-})_3B \qquad (1)$$

Reactivity

The availability of the organoboranes would be of little value if they were of limited reactivity. Fortunately, they are quite reactive in synthetic manipulations involving carbon-carbon bond formation. The boron-carbon bond does not exhibit the ionic characteristics of many organometallic reagents, however organoboranes are capable of delivering a carbanionic center under certain conditions. Due to the low polarity of the boron-carbon bonds, organoboranes do not react with electrophilic reagents at ambient temperatures.[4] Except for benzylic, allylic and allenic derivatives, organoboranes are stable to hydrolysis and do not react with carbonyl reagents.

The organoboranes are electron deficient at boron and consequently are good Lewis acids. They react readily with nucleophiles forming stable compounds known as "ate" complexes.[5] The storage of organoboranes as amine "ate" complexes has been used commercially (eq 2).

$$(CH_3)_3B + :N(CH_3)_3 \longrightarrow (CH_3)_3\overset{(-)}{B}\text{-}\overset{(+)}{N}(CH_3)_3 \qquad (2)$$

$$\Delta H = -17 \text{ Kcal/mole}$$

The fact that certain organoborane complexes can rearrange provides the key to understanding many of the new synthetic reactions involving organoboranes.

REARRANGEMENT OF ORGANOBORANE COMPLEXES

The electronic configuration, and thus the reactivity, of the boron center is significantly different in the "ate" complex than in the organoborane itself. In the uncomplexed organoborane the boron is electron deficient, whereas the opposite is true in the "ate" complex. The boron center in the "ate" complex becomes a potential carbanion donor. The donation can be intermolecular or intramolecular. The hydrolysis of tetrasubstituted borates by mineral acids is an example of an intermolecular reaction (eq 3).[6]

$$Ph_4B^{(-)} \xrightarrow{H^+} Ph_3B + PhH \qquad (3)$$

The case of intramolecular donation of an anionic center to an electron deficient center has been well documented. Such anionotropic rearrangements provide the mechanistic pathway for much of the new organoborane chemistry.[2] The rearrangements are analogous to the well known organic rearrangements such as the Beckmann, Curtius, pinacol, etc., which involve the migration of an anionic center to an electron deficient center. The electron deficiency may be due to a number of factors such as a sextet of electrons or the attachment of an electronegative substituent. A straightforward example involves the oxidation of organoboranes with amine oxides (eq 4). The reaction meets the necessary requirements for a successful rearrangement: an anion source (boron), a migrating group (alkyl), and an electron deficient center (oxygen).[7]

$$R_3B + :\overset{(-)}{\ddot{O}}\text{-}\overset{(+)}{N}R_3 \longrightarrow R_3\overset{(-)}{B}\text{-}\ddot{O}\text{-}\overset{(+)}{N}R_3 \longrightarrow R_2B\text{-}\ddot{O}R + :NR_3 \qquad (4)$$

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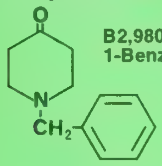
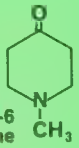
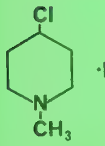


B2,980-6
1-Benzyl-4-piperidone

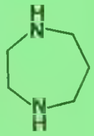


13,003-6
1-Methyl-4-piperidone

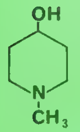


·HCl

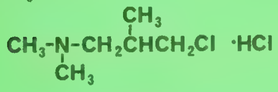
C5,630-1
4-Chloro-*N*-methylpiperidine hydrochloride



H1,660-4
Homopiperazine

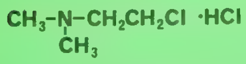


H4220-6
4-Hydroxy-*N*-methylpiperidine



$\mathrm{CH_3\text{-}N(CH_3)\text{-}CH_2CH(CH_3)CH_2Cl \cdot HCl}$

15,289-7
3-Dimethylamino-2-methylpropyl chloride hydrochloride



$\mathrm{CH_3\text{-}N(CH_3)\text{-}CH_2CH_2Cl \cdot HCl}$

D14,120-8
2-Dimethylaminoethyl chloride hydrochloride

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Substitution of one of the hydrogens of $\mathrm{NaBH_4}$ by a strong electron-withdrawing group such as a cyano group has resulted in a reducing agent that is milder than $\mathrm{NaBH_4}$. Thus, **sodium cyanoborohydride** ($\mathrm{NaBH_3CN}$) is a versatile reagent especially valuable for its ability to reduce a given functional group in the presence of various other functional groups and for its stability in aqueous systems over a broad pH range.

Sodium cyanoborohydride reduces an imminium ion much faster than a carbonyl group. This property has allowed (1) facile reduction of oximes and enamines at pH 5, (2) reductive amination of aldehydes and ketones in the presence of many sensitive functional groups, and (3) selective deoxygenation of aliphatic aldehydes and ketones *via* the *p*-tosylhydrazone. Other important selective applications of $\mathrm{NaBH_3CN}$ include the reductive alkylation of amines and hydrazines and the reductive displacement of halides and tosylates.

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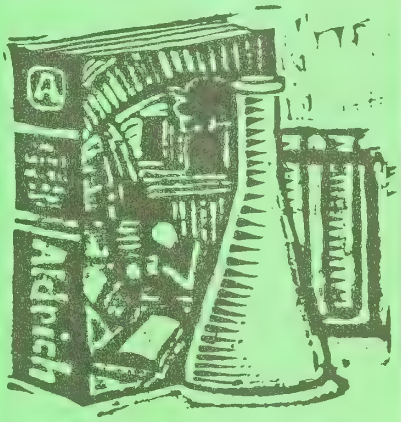

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Organolithium Reagents

• Extremely strong bases • Powerful nucleophiles

Alkyl and aryllithium reagents have assumed an extremely important place in organic synthesis mainly because of their high nucleophilicity and powerful basicity. The structures and numerous synthetic applications of organolithium compounds have been reviewed recently.[1,2] Other reviews describe their use in metallation[3] and ketone synthesis from carboxylic acid salts.[4] The preparation and use of lithium organocopper compounds have also been reviewed.[5] A few of the many applications of organolithium reagents are highlighted below.

Addition Reactions

The reactions of organolithium reagents with aldehydes and ketones have been investigated from a synthetic viewpoint.[6,7]

Alkylation of Halides

Halides can be alkylated using organocopper compounds which are readily prepared from organolithium reagents.[8]

$$2\ MeLi + CuI \longrightarrow Me_2CuLi$$

81%

The reaction of lithium dialkylcopper compounds (as in the example above) utilizes only one of the alkyl groups and frequently requires a large excess of the reagent. In the alkylation of halides and conjugate addition to α,β-unsaturated ketones, mixed organocopper compounds, such as lithium phenylthio(alkyl)cuprates, normally give higher yields.[9]

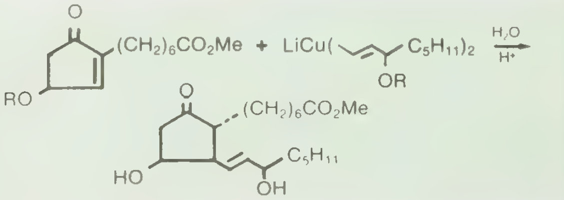
$$PhSH + n\text{-}BuLi \longrightarrow PhSLi \xrightarrow{CuI} PhSCu$$

$$t\text{-}BuLi + PhSCu \longrightarrow PhS(t\text{-}Bu)CuLi$$

$$n\text{-}C_8H_{17}I + PhS(t\text{-}Bu)CuLi \longrightarrow n\text{-}C_8H_{17}\text{-}t\text{-}Bu \quad 98\%$$

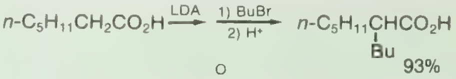
Alkylation of α,β-Unsaturated Ketones

Lithium organocopper compounds undergo conjugate addition with α,β-unsaturated ketones with high regiospecificity. This important reaction has been used successfully in the synthesis of natural products including prostaglandins.[10]



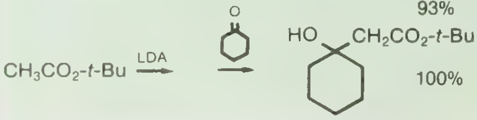
Alkylation *via* Dialkylamides

Lithium dialkylamides are powerful bases yet are weak nucleophiles. As a result, they are used in the formation of carbanions of acids[11] and esters.[12] The α-carbanions, are stable with respect to self-condensation and react with alkyl halides, acid chlorides and ketones. One widely used reagent is lithium diisopropylamide (LDA) which can be prepared from diisopropylamine and *n*-butyllithium.[11]



$$n\text{-}C_5H_{11}CH_2CO_2H \xrightarrow{LDA} \xrightarrow[2)\ H^+]{1)\ BuBr} n\text{-}C_5H_{11}\underset{Bu}{CH}CO_2H \qquad (11)$$

93%

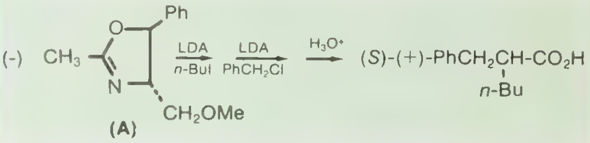


(12)

100%

Alkylation *via* Masked Carbonyl Systems

Organolithium compounds may be used in the formation of anions of masked carbonyl systems.[13] For example, LDA is used in the synthesis of chiral acids by the stepwise alkylation of (4*S*,5*S*)(-)-4-methoxymethyl-2-methyl-5-phenyl-2-oxazoline **(A)** followed by hydrolysis[14] to give the (+) acid of 70% optical purity.



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†Molar unit. Does not include weight of solvent.

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Chemical Reactions of Polymers. See page 27.

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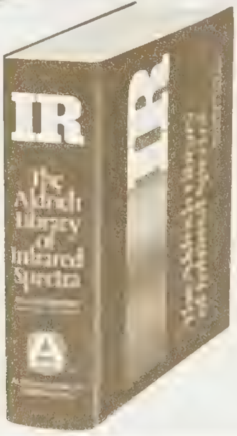

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About the Cover

When our chemist-collector first saw this noble portrait (oil on canvas $28^3/_4 \times 23^1/_4$ inches), it was called a portrait of a man, and attributed to Carel Fabritius, one of Rembrandt's ablest students. Our chemist is inclined to think that it is not by Fabritius, but by another Rembrandt student, Willem Drost, and he wonders whether it is not really a study of a woman, perhaps of Hannah praying in the Temple: surely prayer or contemplation could not be depicted more beautifully than by these clasped hands and serene face.

Rembrandt and some of his students occasionally used Italian medals as models for their paintings; and Professor Ulrich Middeldorf has pointed out that Drost used a medal of Don Inigo d'Avalos, Grand Chamberlain of Alfonso of Naples, by Pisanello as a model.

This introspective portrait invariably reminds us of Keats:
"Heard melodies are sweet, but those unheard are sweeter;----"
"She cannot fade---"
"Forever wilt thou love, and she be fair!"

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 the late Professor Wolfgang Stechow is now available to all chemist art-lovers.

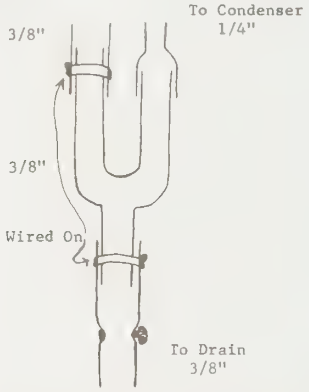
Z10,118-4 $6.00

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

PRESSURE RELIEF VALVE

During overnight or weekend refluxing, a combination of erratic water pressure and deteriorated rubber tubing results in loss of solvents and charring of reaction mixtures, or floods.



A simple solution is provided by the use of a pressure relief valve consisting of a 3/8 inch U-shaped connecting tube, two lengths of 3/8 inch soft rubber tubing and one screw clamp. The condenser outflow tube is taped or wired (or equipped with an inexpensive flow meter) so that the exiting water can be seen. The water valve is adjusted to assure a continuous flow and the screw clamp is tightened until an adequate flow of water from the condenser is obtained.

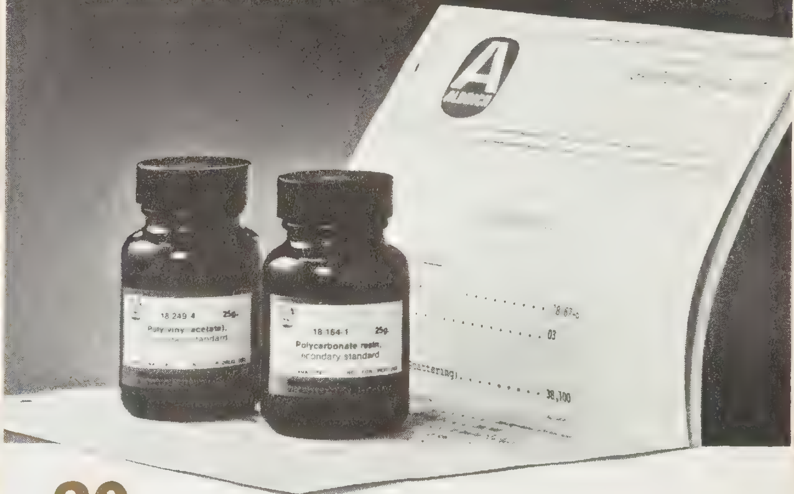
The ultimate value of this little device more than compensates for the extra water used.

Stan Davis
Davis Metals & Chemicals Co.
KB Laboratories Division
2240 Wood Street
Oakland, California 94607

PREVENT VACUUM BREAKER LEAKS

In many locations, vacuum breakers are required to prevent water supply contamination. Vacuum breakers, however, create problems in the laboratory as the slow water flow desired for condensers is insufficient for their operation, resulting in leaks and floods. One solution is to restrict the flow after the vacuum breaker. Since

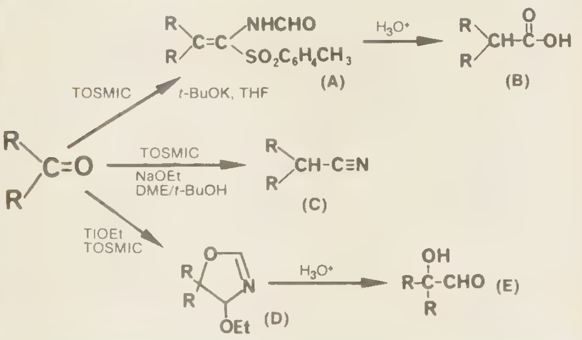
cont'd on page 34



Tosylmethyl isocyanide {TOSMIC}

★ One-carbon elongation of ketones to acids, nitriles, etc.
★ Synthesis of 5-membered heterocycles

Tosylmethyl isocyanide (*TOSMIC*), a stable crystalline solid, enables the facile and convenient conversion of a ketone into the next higher **carboxylic acid**[1] or **nitrile**.[2] Reaction of a ketone with α-metalated *TOSMIC* in THF gives **1-formylamino-1-tosylalkene** (A) which may be hydrolyzed to the corresponding **carboxylic acid** (B). In contrast, if the reaction is performed in dimethoxyethane/*t*-butanol, a high yield of **nitrile** (C) is obtained.



4-Ethoxyoxazolines (D)[3] which serve as excellent intermediates for a new and simple synthesis of **α-hydroxyaldehydes** (E)[4] are formed from the reaction of *TOSMIC* with ketones in the presence of thallous ethoxide.

TOSMIC also permits the synthesis of many difficult-to-prepare heterocycles. For example, the reaction of *TOSMIC* with an aldehyde and potassium carbonate in refluxing methanol affords the **5-substituted oxazole** (F)[5] in excellent yield *via* the intermediate **4-tosyl-Δ^2-oxazoline. 4-Tosyl-5-substituted oxazoles** (G) are obtained from acid chlorides or anhydrides.[5] *TOSMIC* and imidoyl chlorides react, in the presence of sodium hydride, to give **4-tosyl-5-substituted imidazoles** (H)[6] while **5-substituted imidazoles** (I) are formed in the analogous reaction with aldimines.[7] Whereas ethyl benzoate does not react readily with the anion of *TOSMIC*,[5] carboxymethyl dithioates give **4-tosyl-5-substituted thiazoles** (J).[8] Diazonium salts react to give **1,2,4-triazoles** (K). Reaction of *TOSMIC* anion with Michael acceptors gives **pyrroles** (L) unsubstituted in the 1 and 2 positions.[9]

References:
1. U. Schöllkopf, R. Schröder, and E. Blume, *Ann. Chem.*, **766**, 130 (1972); U. Schöllkopf and R. Schröder, *Angew. Chem., Intern. Ed. Engl.*, **11**, 311 (1972).
2. O.H. Oldenziel and A.M. van Leusen, *Syn. Comm.*, **2**, 281 (1972); *Tetrahedron Lett.*, 1357 (1973).
3. O.H. Oldenziel and A.M. van Leusen, *Tetrahedron Lett.*, 163 (1974).
4. O.H. Oldenziel and A.M. van Leusen, *ibid.*, 167 (1974).
5. A.M. van Leusen, B.E. Hoogenboom, and H. Siderius, *ibid.*, 2369 (1972).
6. A.M. van Leusen and O.H. Oldenziel, *ibid.*, 2373 (1972)
7. O.H. Oldenziel, private communication
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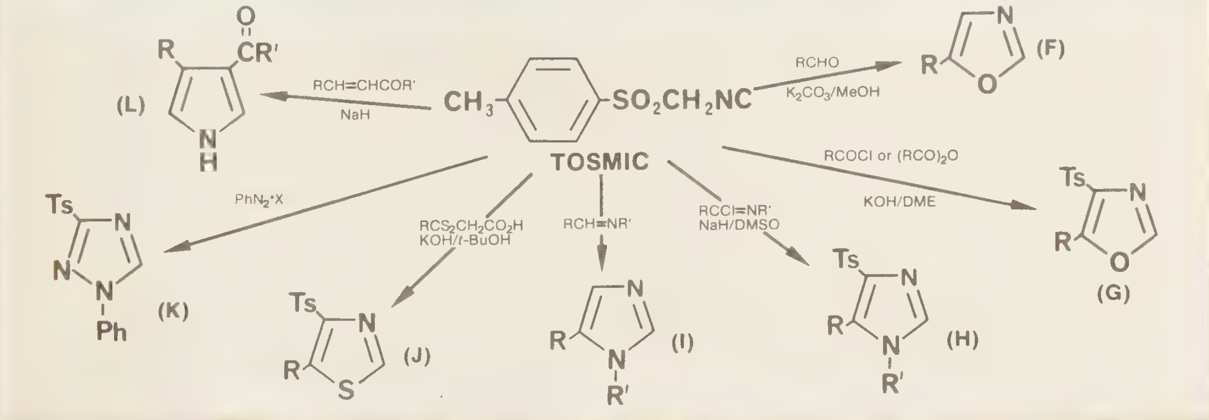
9. A.M. van Leusen, H. Siderius, B.E. Hoogenboom, and D. van Leusen, *ibid.*, 5337 (1972).

18,820-4 Tosylmethyl isocyanide..... 5g $8.00; 25g $32.00



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Dihydropyrans

For the protection of chiral and achiral alcohols

2,3-DIHYDROPYRAN

for the protection of hydroxyl functions

The formation of tetrahydropyranyl (THP) ethers by the reaction of **2,3-dihydropyran** with alcohols under mild acid catalysis[1,2] is a very useful method for protecting alcohols because THP ethers are stable to bases, Grignard reagents, metal hydrides, lithium alkyls, chromic acid oxidation, and epoxidation with alkaline hydrogen peroxide,[1] yet are easily cleaved by dilute acids.

2,3-Dihydropyran has also been used to protect carboxyl and sulfhydryl groups, the 9-nitrogen of purines, and propargylic[3] and steroidal[4] alcohols. Typical applications include the total syntheses of prostaglandins[5] and humulene.[6] Recently, it was used in the penicillin field for trapping a sulfenic acid[7] and in the syntheses of sulfur-free penicillin derivatives.[8]

References:
1) H.J.E. Loewenthal, *Tetrahedron,* **6,** 303 (1959).
2) H. Alper and L. Dinkes, *Synthesis,* 81, (1972); J.H. van Boom, J.D.M. Herschied, and C.B. Reese, *ibid.,* 169 (1973).
3) L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, John Wiley and Sons, Inc., New York, N.Y., 1967, p 256.
4) A.C. Otto, M.F. Murray, and R.L. Pederson, *J. Amer. Chem. Soc.,* **74,** 1239 (1952).
5) E.J. Corey *et al., ibid.,* **93,** 1490 (1971); P.H. Bentley, *Chem. Soc. Rev.,* **2,** 29 (1973).
6) E.J. Corey and E. Hamanaka, *J. Amer. Chem. Soc.,* **89,** 2758 (1967).
7) D.H.R. Barton *et al., J. Chem. Soc. Perkin I,* 1187 (1973).
8) S. Wolfe *et al., Can. J. Chem.,* **53,** 3996 (1974).

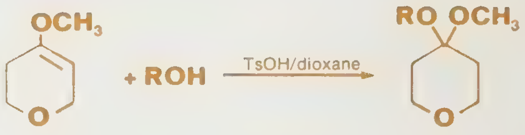
D10,620-8	**2,3-Dihydropyran....**	**100g $6.50; 500g $24.00**
		100kg $18.00/kg
		1000kg $12.00/kg

Ton quantities available from stock

5,6-DIHYDRO-4-METHOXY-2*H*-PYRAN

for the protection of chiral alcohols

The use of the tetrahydropyranyl group for protection of hydroxyls of chiral alcohols leads to the introduction of another chiral center, and undesirable mixtures of diastereoisomeric products are obtained, *e.g.,* in steroids,[1] carbohydrates,[2] and nucleosides.[3]



1 2

Reese, van Boom and coworkers[4] have demonstrated that **5,6-dihydro-4-methoxy-2*H*-pyran (1)** is an excellent reagent for the protection of optically active alcohols because the 4,4-disubstituted tetrahydropyran moiety of the products (**2**) is symmetrical, and its introduction does not therefore lead to an additional chiral center. The derivatives, which are usually crystalline, are formed in high yields by *p*-toluenesulfonic acid-catalyzed reactions in anhydrous dioxane; they are base-stable, yet are easily hydrolyzed by dilute acids.[4,5] **5,6-Dihydro-4-methoxy-2*H*-pyran** has been employed mainly in the syntheses of nucleotides and oligonucleotides;[6] it has also been used for steroidal alcohol protection.[5]

References:
1) C.W. Greenhalgh, H.B. Henbest, and E.R.H. Jones, *J. Chem. Soc.,* 1190 (1951).
2) A.N. de Belder *et al., Acta Chem. Scand.,* **16,** 623 (1962).
3) B.E. Griffin, M. Jarman, and C.B. Reese, *Tetrahedron,* **24,** 639 (1968).
4) C.B. Reese *et al., J. Amer. Chem. Soc.,* **89,** 3366 (1967); *Tetrahedron,* **26,** 1023, 1031 (1970).
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6) C.B. Reese and R. Saffhill, *Chem. Commun.,* 767 (1968); C.B. Reese and J.C.M. Stewart, *Tetrahedron Lett.,* 4273 (1968); J.H. van Boom, P.M.J. Burgers, G.R. Owen, C.B. Reese, and R. Saffhill, *Chem. Commun.,* 869 (1971); B.E. Griffin and C.B. Reese, *Tetrahedron,* **25,** 4057 (1969); J.H. van Boom, G.R. Owen, J. Preston, T. Ravindranathan, and C.B. Reese, *J.Chem. Soc. (C),* 3230 (1971); N.J. Cusack, C.B. Reese, and J.H. van Boom, *Tetrahedron Lett.,* 2209 (1973); J.H. van Boom, J.F.M. de Rooy, and C.B. Reese, *J. Chem. Soc. Perkin I,* 2513 (1973); J.H. van Boom, P.M.J. Burgers, P. van Deursen, and C.B. Reese, *Chem. Commun.,* 618 (1974).

18,917-0	**5,6-Dihydro-4-methoxy-2*H*-pyran........**	**1g $7.00**
		5g $27.00

Aldrichimica Acta

Volume 8, Number 4
(Final Issue, 1975)

Highlights. See page 39.

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Could your reactions use a little Ph-SeX?

Ph-SeX (X = Br, Cl or PhSe)

The observation that alkyl phenyl selenoxides undergo eliminations at room temperature to form olefins [1-3] is the basis for a new and convenient synthesis of allylic alcohols,[4] allylic ethers and acetates,[5] and α,β-unsaturated carbonyl compounds.[6-8] **Diphenyl diselenide** is a yellow, odorless, air-stable solid which is easily converted into the highly colored phenylselenenyl halides. The oxidations are conveniently carried out at or below room temperature using a variety of oxidants (peracetic acid, sodium periodate, hydrogen peroxide, etc.)

18,062-9 Diphenyl diselenide .... 5g $ 5.55
25g $15.00

References:
1) K.B. Sharpless and R.F. Lauer, *J. Amer. Chem. Soc.*, **94**, 7154 (1972); D.N. Jones, D. Mundy, and R.D. Whitehouse, *Chem. Commun.*, 86 (1970).
2) K.B. Sharpless and R.F. Lauer, *J. Org. Chem.*, **37**, 3973 (1972).
3) K.B. Sharpless, M.W. Young, and R.F. Lauer, *Tetrahedron Lett.*, 1979 (1973); K.B. Sharpless and M.W. Young, *J. Org. Chem.*, **40**, 947 (1975).
4) K.B. Sharpless and R.F. Lauer, *J. Amer. Chem. Soc.*, **95**, 2697 (1973); D. Seebach and A.K. Beck, *Angew. Chem., Intern. Ed Engl.*, in press.
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7) H.J. Reich, I.L. Reich, and J.M. Renga, *J. Amer. Chem. Soc*, **95**, 5813 (1973).
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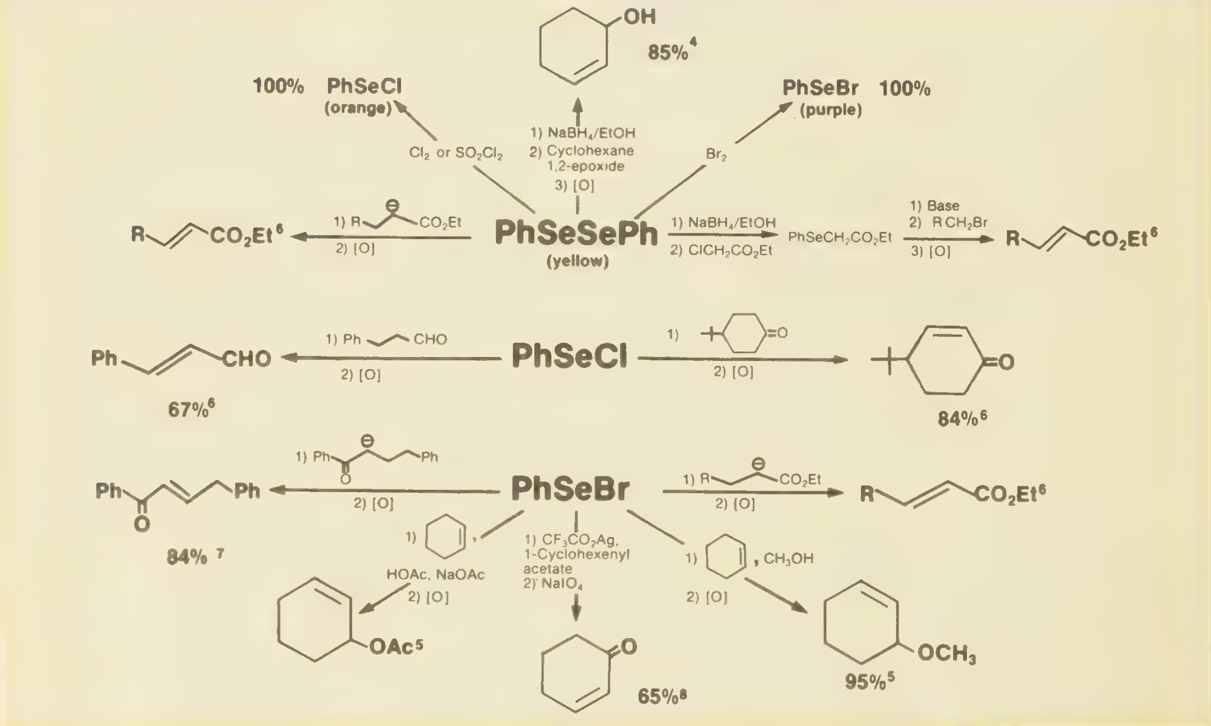
18,334-2 Phenylselenenyl chloride 10g $12.00
50g $43.10



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About the Cover

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. This fine depiction (oil on canvas, 29 1/2 x 60 inches) by a Neapolitan artist of around 1700 was purchased by our chemist collector on one of his most recent visits to Copenhagen. If only, he says, he could find a good many more such dreams of paintings.

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 the late Professor Wolfgang Stechow is now available to all chemist art-lovers.

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Lab Notes

Dear Sirs:

A survey of the experimental sections of papers in a leading chemical journal showed clearly that the advantages of dichloromethane as an extraction solvent are generally not fully appreciated.

If an organic product has been extracted from aqueous solution with CH_2Cl_2, it is rarely necessary to wash the CH_2Cl_2 solution with acid, base or water (as in an ether extraction), as the transference of most inorganic compounds (including most acids and bases) from water to CH_2Cl_2 is negligible. Exceptions include ammonium or alkylammonium salts and high-boiling water-miscible organic solvents such as DMSO or DMF; in such cases, the CH_2Cl_2 extracts must be washed several times with water.

Just as useful, and as little appreciated, is the fact that CH_2Cl_2 extracts need not be treated with a drying agent. It is sufficient to run the lower layer from the separatory funnel through a small plug of cotton wool; this will remove any droplets of water, and the last traces will come off as an azeotrope on evaporation of the CH_2Cl_2, whether this is done at atmospheric pressure or on a rotary evaporator *in vacuo*. (The cotton should have been previously washed with a little CH_2Cl_2 to remove fats.)

Errol Lewars
Department of Chemistry
Trent University, Peterborough
Ontario, Canada K9J 7B8

Gentlemen:

How many times have you done suction filtration in a Buchner funnel and flask and badly stained or contaminated your piece of dental dam? Or perhaps you have used a solvent that dissolved gum rubber, so there was no way of removing the last bit of mother liquor from the filter cake?

In such cases I have had good luck substituting thin (.002 - .005 inch) plastic film such as Teflon® FEP or polyethylene for dental dam. Any low modulus, high elongation film insoluble in your solvent should work unless it has pinholes; even

cont'd on page 45

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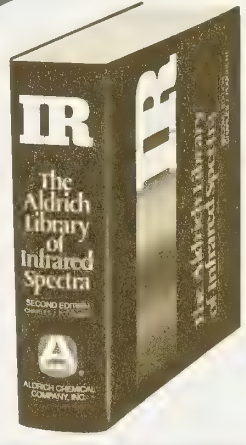

1

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2

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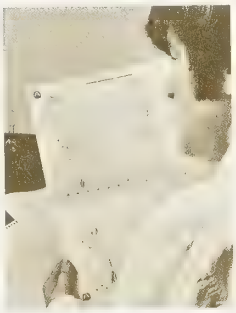

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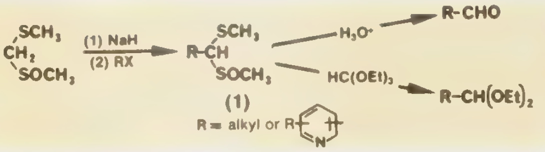
Methyl methylthiomethyl sulfoxide (MMTS, FAMSO)

A masked formaldehyde reagent

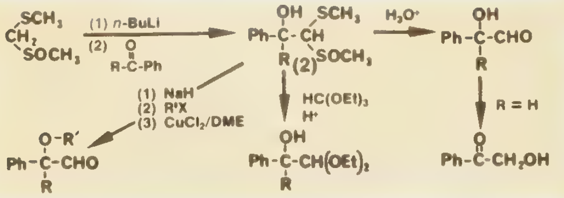
I. Aldehydes and Acetals

The carbanion derived from **methyl methylthiomethyl sulfoxide (MMTS, FAMSO)** reacts with alkyl halides to give aldehyde dimethylmercaptal *S*-oxides (**1**) which are readily hydrolyzed in acid to produce the corresponding aldehydes in excellent overall yields.[1] As an aldehyde equivalent, **1** affords directly the diethyl acetal of the corresponding aldehyde upon treatment with ethyl orthoformate.[1] This scheme has been used successfully to prepare substituted pyridinecarboxaldehydes, whereas other methods fail.[2] This synthesis is especially suitable for labile aldehydes and is superior to the 1,3-dithiane method since the carbanion is easily generated and the hydrolysis of **1** can be accomplished under mild conditions.[1] Homologation of aromatic aldehydes can be achieved using MMTS.[3]



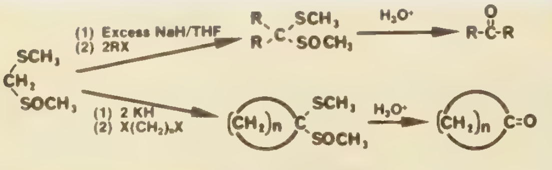
II. α-Hydroxyaldehydes and Derivatives

Treatment of the carbanion of MMTS with ketones leads to the α-hydroxyaldehyde dimethylmercaptal *S*-oxides (**2**) which can be similarly hydrolyzed to the corresponding ketones or converted to the ketals.[4] The intermediate **2** can also be formed by $NaBH_4$ reduction of a ketone compound **4** (*vide infra*).[5] Protected hydroxyaldehydes can be produced by methylation or benzylation of **2** followed by treatment with cupric chloride dihydrate in 1,2-dimethoxyethane (DME).



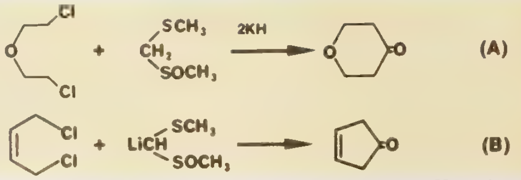
III. Dialkyl Ketones and Cyclic Ketones

In reactions analogous to the aldehyde synthesis, symmetrical dialkyl ketones,[6] substituted cyclobutanones,[7] and other cyclic ketones[8] can be prepared from MMTS.



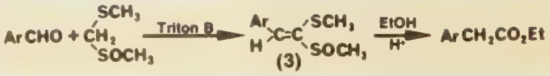
X= Br or TsO; n=2,3,4,5,6

The versatility of this method is further demonstrated by the synthesis of tetrahydro-γ-pyrone from bis(2-chloroethyl) ether (eq A) and the synthesis of 3-cyclopentenone from *cis*-1,4-dichloro-2-butene (eq B).

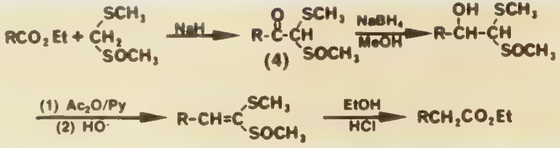


IV. Synthesis of Phenylacetic Acid Derivatives and Homologation of Esters

MMTS and aromatic aldehydes undergo Knoevenagel-type condensation to give 1-methylsulfinyl-1-methylthio-2-arylethylenes (**3**). Acid-catalyzed ethanolysis of **3** produces ethyl arylacetates in high yields.[9]

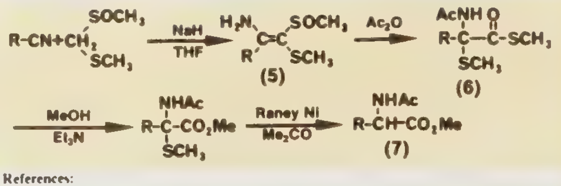


Homologation of esters can be achieved by the following sequence of reactions.[5]



V. Synthesis of α-Amino Acids from Nitriles

The carbanion of MMTS reacts with nitriles to form enaminosulfoxides (**5**) which, upon treatment with Ac_2O, afford the unusual rearranged product **6**. Ester exchange of **6** followed by desulfurization leads to the *N*-acetylamino acid ester **7**.[10] The synthesis of the methyl ester of DL-*N*-acetyl-5-hydroxytryptophan by this method is a remarkable example.[10]



References:
1) *Tetrahedron Lett.*, 3151 (1971); 2) *Chem. Commun.*, 410 (1974); 3) *Synthesis*, 385 (1975); 4) *Tetrahedron Lett.*, 2681 (1972); 5) *ibid.*, 659 (1974); 6) *Synthesis*, 117 (1974); 7) *Tetrahedron Lett.*, 3653 (1974); 8) *ibid.*, 2767 (1975); 9) *ibid.*, 1383 (1972); 10) *J. Amer. Chem. Soc.*, **96**, 1960 (1974).

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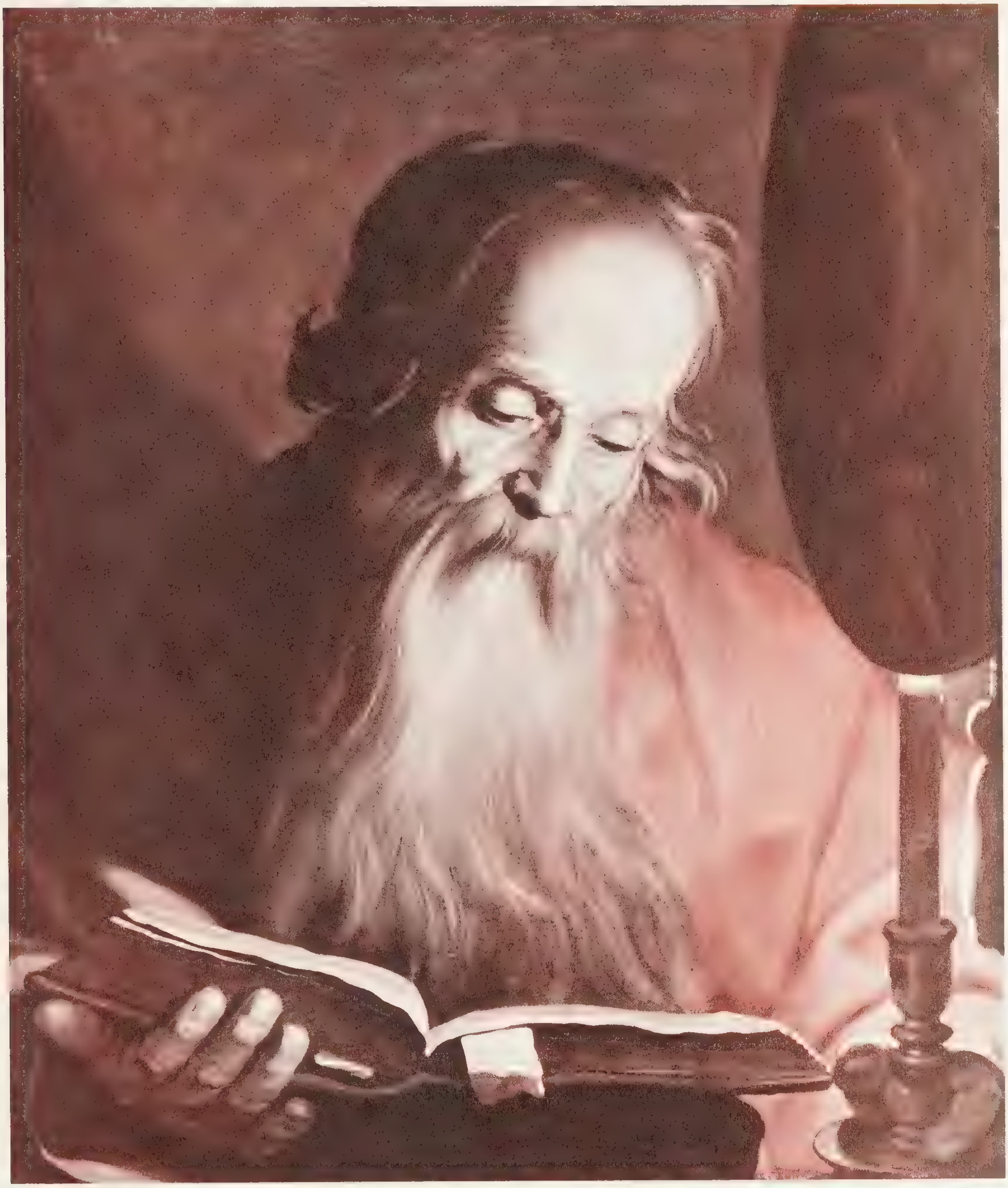

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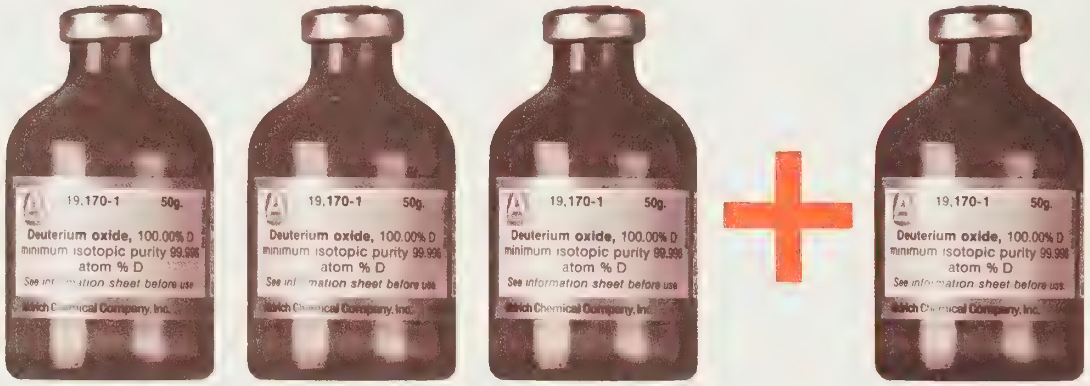

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The painting (oil on canvas 25 $^3/_8$ x 20 $^7/_8$ inches) by Abraham Bloemaert reproduced on our cover has been known to art historians for many years, but only because the artist's son, Cornelis Bloemaert, engraved it shortly after it was painted in the sixteen twenties. The whereabouts of the original had been unknown for some 350 years, so you can imagine our chemist-collector's pleasure when he discovered it in an antique store in The Hague two years ago.

Kupferstich Cornelis Bloemaerts nach Abraham Bloemaert. Hl. Hieronymus.

The inscription on the engraving answers all iconographic questions: this is *St. Jerome Studying the Old Testament* which he was the first to translate competently into Latin.

St. Jerome (*ca.* 340-420 C.E.) was one of those Church Fathers to whom the title of Saint was given not for his saintliness, but for his erudition and hard work. He was, in fact, anything but saintly: he was involved in arguments — often with more vituperation than reason — throughout his life, but is remembered far more for his scholarship than his fights with windmills.

Dr. Alfred Bader is the guest curator of an exhibition, *The Bible Through Dutch Eyes,* at the Milwaukee Art Center from April 9 to May 23. The exhibition of seventy Dutch and Flemish works includes twelve paintings which have been reproduced on *Aldrichimica Acta* covers.

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Lab Notes

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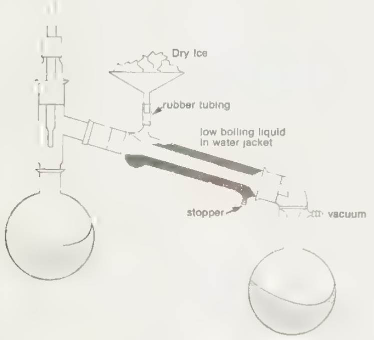
During distillation of a low-melting solid it is often difficult to prevent solidification of the distillate in the condenser. An air-cooled condenser is frequently employed to alleviate the problem, but a greater degree of temperature control can be obtained by closing the water inlet of the condenser jacket with a pipette bulb or a small cork and introducing into the water outlet a material of a boiling point close to the melting point of the distillate (*e.g.*, a solvent such as methylene chloride or methanol). Boiling of the solvent thus holds the condenser at a predetermined temperature. The solvent can be replaced as it evaporates, but it is generally more convenient to fashion a crude reflux condenser by connecting a funnel containing chunks of dry ice to the jacket outlet by means of a short length of rubber tubing.



John L. Marshall
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cont'd on page 17

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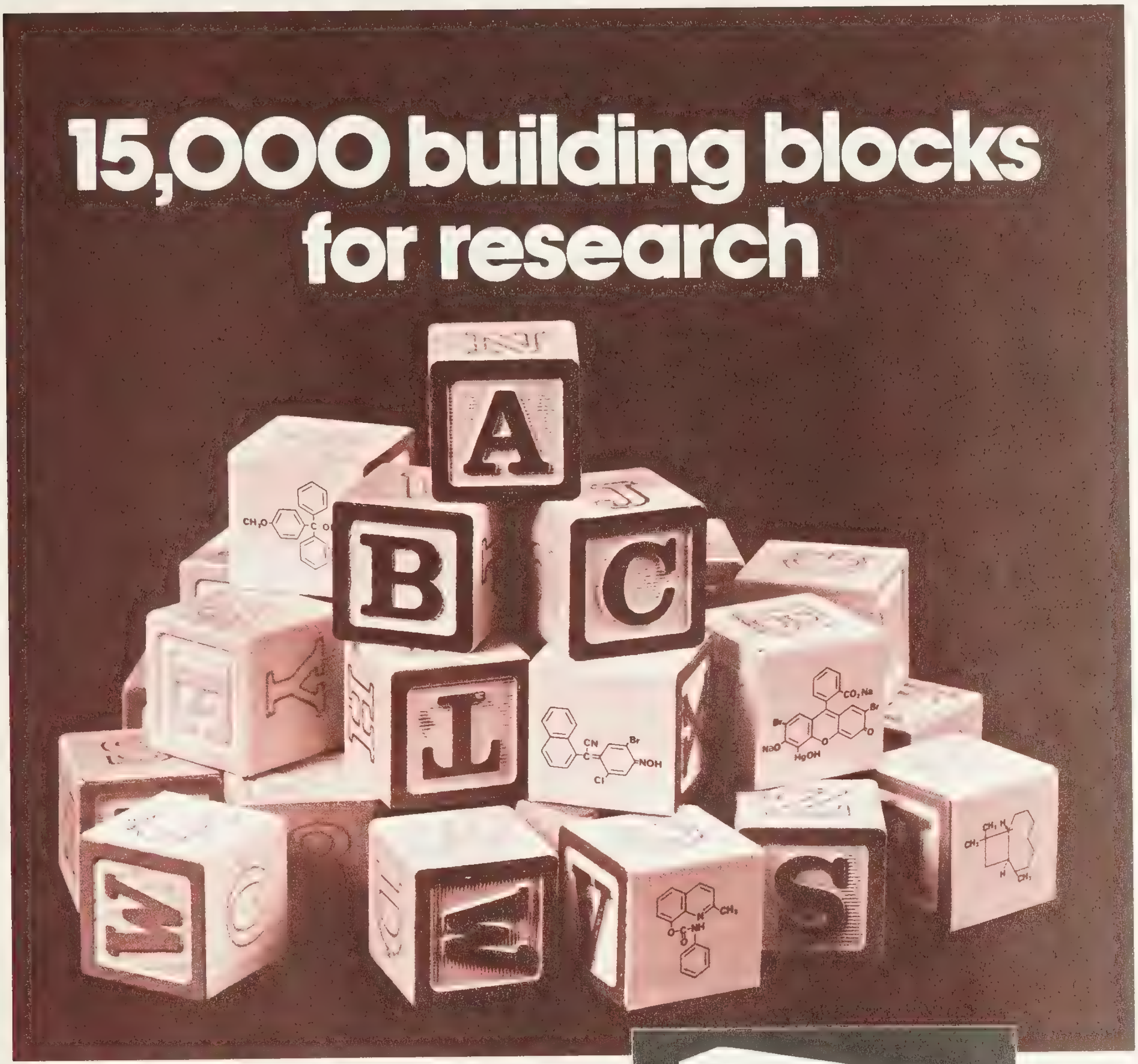

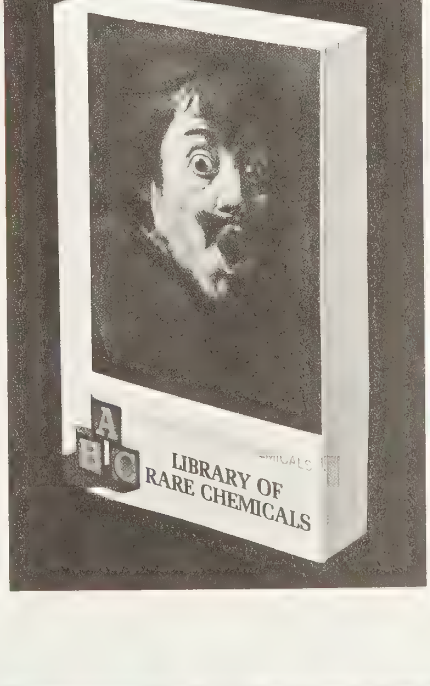

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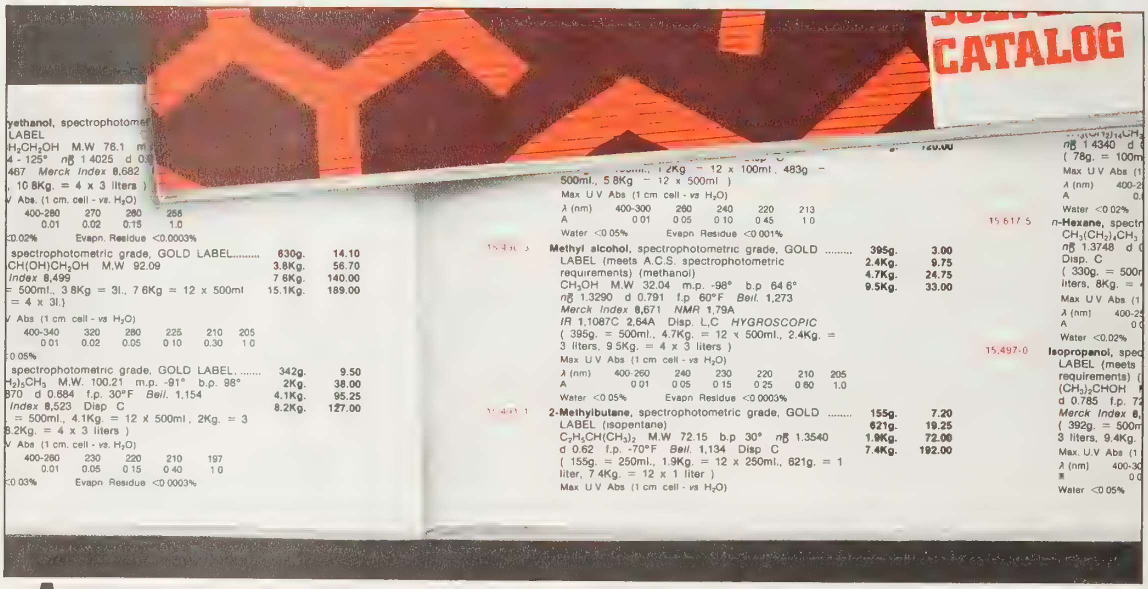

yethanol, spectrophotome
LABEL
H_2CH_2OH M.W 76.1 m
4 - 125° n_D^{20} 1 4025 d 0
467 *Merck Index* 8,682
, 10 8Kg. = 4 x 3 liters)
V Abs. (1 cm. cell - *vs.* H_2O)
400-280 270 260 255
0.01 0.02 0.15 1.0
<0.02% Evapn. Residue <0.0003%

spectrophotometric grade, GOLD LABEL......... 630g. 14.10
CH(OH)CH_2OH M.W 92.09 3.8Kg. 56.70
Index 8,499 7 6Kg. 140.00
= 500ml., 3 8Kg = 3l., 7 6Kg = 12 x 500ml 15.1Kg. 189.00
= 4 x 3l.)
V Abs (1 cm cell - *vs* H_2O)
400-340 320 260 225 210 205
0 01 0.02 0.05 0 10 0.30 1 0
0 05%

spectrophotometric grade, GOLD LABEL. 342g. 9.50
$H_2)_5CH_3$ M.W. 100.21 m.p. -91° b.p. 98° 2Kg. 38.00
870 d 0.684 f.p. 30°F *Beil.* 1,154 4.1Kg. 95.25
Index 8,523 Disp C 8.2Kg. 127.00
= 500ml., 4.1Kg. = 12 x 500ml , 2Kg. = 3
8.2Kg. = 4 x 3 liters)
V Abs (1 cm. cell - *vs.* H_2O)
400-260 230 220 210 197
0.01 0.05 0 15 0 40 1 0
<0 03% Evapn Residue <0 0003%

1 2Kg = 12 x 100ml , 483g =
500ml., 5 8Kg = 12 x 500ml)
Max U V Abs (1 cm cell - *vs* H_2O)
λ (nm) 400-300 260 240 220 213
A 0 01 0 05 0 10 0 45 1 0
Water <0 05% Evapn Residue <0 001%

Methyl alcohol, spectrophotometric grade, GOLD 395g. 3.00
LABEL (meets A.C.S. spectrophotometric 2.4Kg. 9.75
requirements) (methanol) 4.7Kg. 24.75
CH_3OH M.W 32.04 m.p. -98° b.p 64 6° 9.5Kg. 33.00
n_D^{20} 1.3290 d 0.791 f.p 60°F *Beil.* 1,273
Merck Index 8,671 *NMR* 1,79A
IR 1,1087C 2,64A Disp. L,C *HYGROSCOPIC*
(395g. = 500ml., 4.7Kg. = 12 x 500ml., 2.4Kg. =
3 liters, 9 5Kg. = 4 x 3 liters)
Max U V Abs (1 cm cell - *vs* H_2O)
λ (nm) 400-260 240 230 220 210 205
A 0 01 0 05 0 15 0 25 0 60 1.0
Water <0 05% Evapn Residue <0 0003%

2-Methylbutane, spectrophotometric grade, GOLD 155g. 7.20
LABEL (isopentane) 621g. 19.25
$C_2H_5CH(CH_3)_2$ M.W 72.15 b.p 30° n_D^{20} 1.3540 1.9Kg. 72.00
d 0.62 f.p. -70°F *Beil.* 1,134 Disp C 7.4Kg. 192.00
(155g. = 250ml., 1.9Kg. = 12 x 250ml., 621g. = 1
liter, 7 4Kg. = 12 x 1 liter)
Max U V Abs (1 cm cell - *vs* H_2O)

n_D^{20} 1 4340 d
(78g. = 100m
Max U V Abs (1
λ (nm) 400-2
A 0.
Water <0 02%

15 617 5 *n*-**Hexane,** spectr
$CH_3(CH_2)_4CH_3$
n_D^{20} 1.3748 d
Disp. C
(330g. = 500
liters, 8Kg. =
Max U V Abs (1
λ (nm) 400-2
A 0
Water <0.02%

15,497-0 **Isopropanol,** spec
LABEL (meets
requirements) (
$(CH_3)_2CHOH$
d 0.785 f.p. 7
Merck Index 8,
(392g. = 500
3 liters, 9.4Kg.
Max. U.V Abs (1
λ (nm) 400-3
0 0
Water <0 05%

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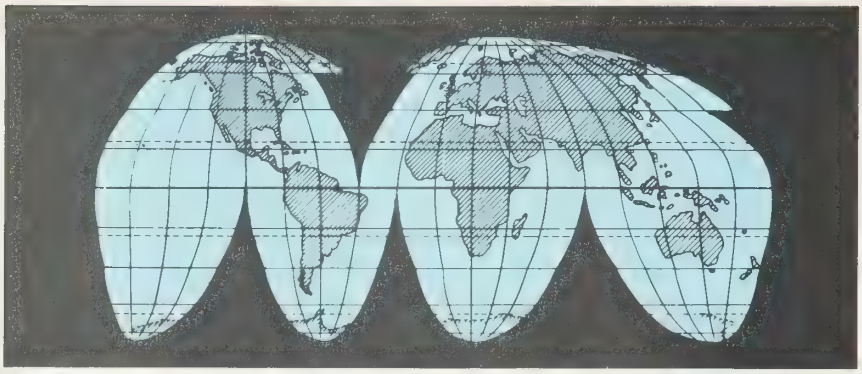

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H4,220-6	4-Hydroxy-*N*-methylpiperidine
H5,700-9	3-Hydroxypyridine
18,605-8	Butopyronoxyl (Indalone®)
N1,750-5	5-Nitroindazole
D9,140-3	Diethylcarbamyl chloride
O-880-1	Oxalyl chloride

Catalog No.	Compound
D13,555-0	2,6-Dimethoxyphenol
15,433-4	2,5-Diaminotoluene sulfate
D10,620-8	Dihydropyran
12,613-6	Diethyl methylmalonate
12,196-7	Aminoacetaldehyde dimethyl acetal
T2,740-5	Thianaphthene
M460-0	2-Mercapto-1-methylimidazole
10,889-8	4-Nitro-*o*-phenylenediamine

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Aldrich Chemical Company, Ltd.
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7924 Steinheim am Albuch
West Germany
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In Belgium/Continental Europe:
Aldrich-Europe
B-2340 Beerse
Belgium
Telephone: 014/61431

About Our Cover:

When our chemist-collector first saw this haunting painting (oil on canvas, 39 $^1/_4$ x 32 $^3/_4$ inches) it was attributed to Aert de Gelder, and the Venetian-looking column on the right had been overpainted, probably to be able to call the painting *David and Bathsheba*. However, the figure on the left is not David, but a Roman statue of a Dacian king. That statue, formerly in the Palazzo Farnese, is now in the Museum in Naples. Our chemist thinks — but is by no means certain — that the painting depicts *Esther* in the courtyard of King Ahasuerus. Our chemist-collector would welcome other suggestions.

There is a Jewish legend (*Babylonian Talmud, Megillah* 15b) that when Esther came to the court of the King (*Esther* 5,1) and reached the chamber of the idols, the Divine Presence left her and she quoted the 22nd *Psalm*, "My God, my God, why hast thou forsaken me?", the same *Psalm* quoted by Jesus in the agony of the crucifixion (*St. Matthew* 27,46). If indeed it is *Esther in the Courtyard*, then the statue represents an idol, and the winged beast on the column a symbol of the Orient.

The painting had been fully signed and dated 1666, but the signature has been altered to resemble that of Aert de Gelder, whose work it certainly is not. It is probably by another Rembrandt student, Lambert Doomer (1624-1700), who is much better known for his landscape drawings than his rare Biblical paintings.

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 the late Professor Wolfgang Stechow is now available to all chemist art-lovers.

Z10,118-4 $6.00

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

Dear Sirs:

The extraction of an organic compound from a viscous aqueous phase containing a suspended inorganic compound, such as magnesium hydroxide or chromium hydroxide, is difficult. Even if the suspended solids can be removed by filtration or centrifugation, some of the desired organic compound could be lost by being trapped within the suspended solids. Such a problem can be solved by doing the extraction in a Morton flask which also can be used as the reaction vessel. The indented sides of the flask and an overhead stirrer run at a fairly high rate effect thorough mixing of the aqueous phase and the extraction solvent. To minimize transfers, the Morton flask is equipped with a wide-bore Teflon® stopcock which is attached to the flask by a ball joint to provide a more flexible and hence less easily broken outlet. In the reaction which I ran, chromium hydroxide was very thoroughly dispersed in the thick aqueous phase so that only occasional blockage of the stopcock occurred. This extraction approach is a rather tedious batch method; however, it is worth the effort if other extraction methods have failed.

LeRoy W. Haynes
Department of Chemistry
The College of Wooster
Wooster, Ohio 44691

Gentlemen:

We have found a convenient method for handling small sublimable samples for mass spectral analysis. The crude mixture is introduced into a melting point capillary and placed in a Meltemp®. The heat is set at a convenient temperature and the material is allowed to sublime up the tube. In most cases, the solid deposits just above the point where the capillary is in contact with the Meltemp®. The tube is removed and broken at a point just under the sublimed material. The portion of the capillary containing the pure material can then be placed directly into the mass spectra sampling compartment. Using this method, we have been able to purify and obtain mass spectra on submilligram samples.

Thomas R. Nelsen
New York State Agricultural Expt. Station
Cornell University
Geneva, New York 14456

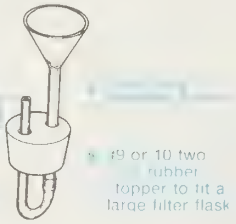
Gentlemen:

When carrying out operations involving liquids in a glove bag, one has to exercise great care to prevent moving the entire bag and spilling any liquids. This problem can be eliminated by using a lead brick sawed into quarters, each piece wrapped in a paper sack bound by tape or rubber band, and placing one in each corner of the dry bag. Before moving the dry bag, however, you must remember to "get the lead out."

Jon Howdeshell, Ph.D.
Laramie Chemical Company
P.O. Box 3611
Laramie, Wyoming 82071

Dear Sir:

An inexpensive uv/vis 1 cm cell washer can be prepared according to the following diagram:

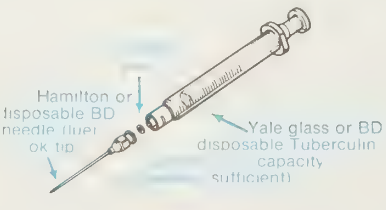


Install the completed cell washer on a one-liter or two-liter filter flask connected to a vacuum line. Set the cell over the protruding polyethylene tubing, turn on the vacuum, and pour the solvent of your choice into the funnel. After rinsing, leave the vacuum on to air-dry the cell. This design can be adapted for use with nmr tubes.

Brian Warner
Graduate Student
Department of Chemistry
Washington State University
Pullman, Washington 99163

Dear Sirs:

Frequently, it is necessary to remove solid material from small volumes of solutions to be analyzed by nmr spectroscopy or other sensitive instrumental technique. The above diagram indicates a quick, efficient no-mess procedure for such small-scale "suction-filtrations." For larger quantities of solid, or for removing decolorizing carbon, the liquid may be introduced into the plunger end of the syringe. Six or more minifilter pads may be cut from a half-inch penicillin assay pad with a small cork borer, and stored in a sample vial. No. 740-E (Schleicher & Schuell Co.) or equivalent penicillin assay pad is of adequate weight and porosity.



P.J. Macaulay
Department of Chemistry
Mount Allison University
Sackville, New Brunswick E0A 3C0
Canada

Dear Sir,

The work-up of lithium aluminum hydride reductions, particularly large-scale ones (1 to 10 moles), is not always a straightforward operation. Often gels and emulsions are obtained and these may seriously affect the yield and/or purity of the isolated product.

I wish to bring to your attention a method of work-up which affords a high recovery of the product even in the reduction of the carbomethoxy group of some complex indole alkaloids. The procedure is straightforward, relatively "foolproof" and simple.

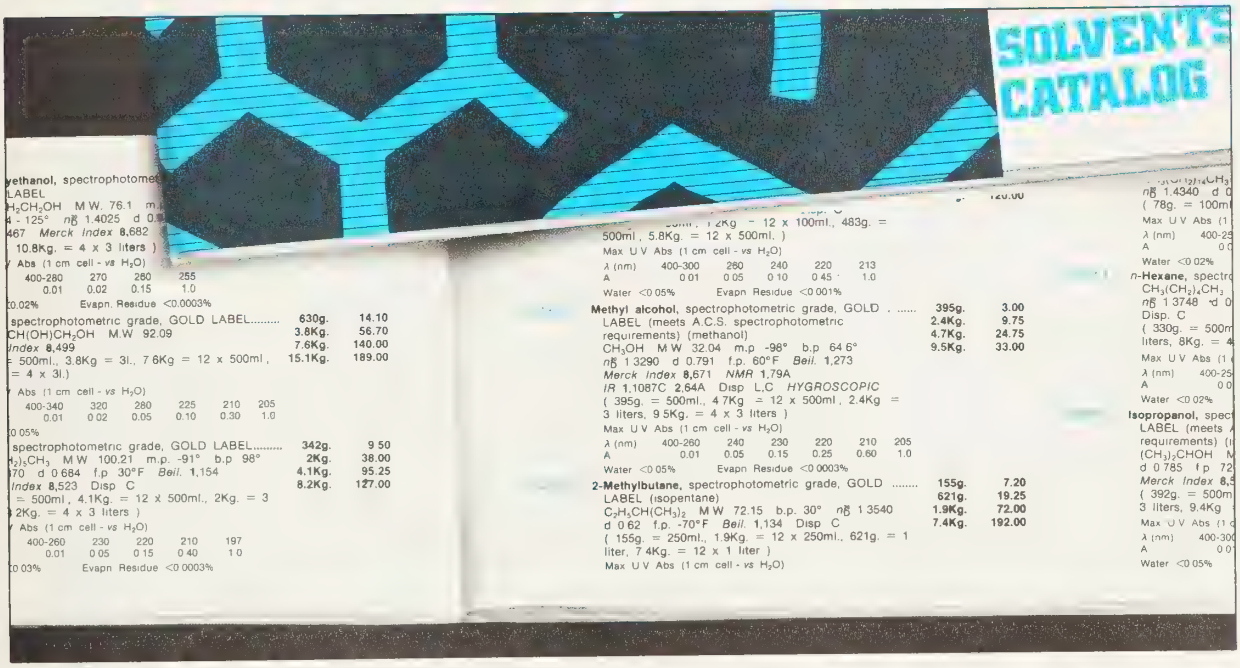
Sodium sulfate, used as a drying agent in the laboratory, is saved and recrystallized from hot water. The Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) so obtained is used in the work-up procedure described below. In this way one can obtain "double mileage" out of the sodium sulfate with an obvious saving in cost over the commonly used Rochelle salt.

Glauber's salt is added with stirring to the reaction mixture (slowly at first because the reaction is exothermic) until hydrogen evolution ceases. A slight excess is added and the reaction mixture is stirred for an additional 10 minutes. A white granular precipitate is obtained which can be filtered easily under suction. The filter cake is returned to the flask and extracted twice with hot solvent. The combined organic filtrate is evaporated to yield the reduction product mixture. Product recoveries of >90% are routine and quantitative recoveries are not uncommon in the cases so far investigated.

Adi M. Treasurywala
Departement de Chimie
Université de Sherbrooke
Sherbrooke, Quebec J1K 2R1
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 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.*

Aldrich now provides the Chemist with ultra-pure spectrophotometric solvents at substantially reduced prices.



yethanol, spectrophotome
LABEL
H_2CH_2OH M W. 76.1 m.
4 - 125° n_D^{20} 1.4025 d 0.
467 *Merck Index* 8,682
10.8Kg. = 4 x 3 liters)
Abs (1 cm cell - *vs* H_2O)
400-280 270 260 255
0.01 0.02 0.15 1.0
0.02% Evapn. Residue <0.0003%

spectrophotometric grade, GOLD LABEL......... 630g. 14.10 / 3.8Kg. 56.70 / 7.6Kg. 140.00 / 15.1Kg. 189.00
$CH(OH)CH_2OH$ M.W 92.09
Index 8,499
= 500ml., 3.8Kg = 3l., 7 6Kg = 12 x 500ml ,
= 4 x 3l.)
Abs (1 cm cell - *vs* H_2O)
400-340 320 280 225 210 205
0.01 0 02 0.05 0.10 0.30 1.0
0 05%

spectrophotometric grade, GOLD LABEL......... 342g. 9 50 / 2Kg. 38.00 / 4.1Kg. 95.25 / 8.2Kg. 127.00
$_2)_5CH_3$ M W 100.21 m.p. -91° b.p 98°
70 d 0 684 f.p 30°F *Beil.* 1,154
Index 8,523 Disp C
= 500ml , 4.1Kg. = 12 x 500ml., 2Kg. = 3
2Kg. = 4 x 3 liters)
Abs (1 cm cell - *vs* H_2O)
400-260 230 220 210 197
0.01 0 05 0 15 0 40 1 0
0 03% Evapn Residue <0 0003%

500ml , 5.8Kg. = 12 x 500ml.)
Max U V Abs (1 cm cell - *vs* H_2O)
λ (nm) 400-300 260 240 220 213
A 0 01 0 05 0 10 0 45 1.0
Water <0 05% Evapn Residue <0 001%

Methyl alcohol, spectrophotometric grade, GOLD LABEL (meets A.C.S. spectrophotometric requirements) (methanol) .... 395g. 3.00 / 2.4Kg. 9.75 / 4.7Kg. 24.75 / 9.5Kg. 33.00
CH_3OH M W 32.04 m.p -98° b.p 64 6°
n_D^{20} 1 3290 d 0.791 f.p. 60°F *Beil.* 1,273
Merck Index 8,671 *NMR* 1,79A
IR 1,1087C 2,64A Disp L,C *HYGROSCOPIC*
(395g. = 500ml., 4 7Kg = 12 x 500ml , 2.4Kg = 3 liters, 9 5Kg. = 4 x 3 liters)
Max U V Abs (1 cm cell - *vs* H_2O)
λ (nm) 400-260 240 230 220 210 205
A 0.01 0.05 0.15 0.25 0.60 1.0
Water <0 05% Evapn Residue <0 0003%

2-Methylbutane, spectrophotometric grade, GOLD LABEL (isopentane) .... 155g. 7.20 / 621g. 19.25 / 1.9Kg. 72.00 / 7.4Kg. 192.00
$C_2H_5CH(CH_3)_2$ M W 72.15 b.p. 30° n_D^{20} 1 3540
d 0 62 f.p. -70°F *Beil.* 1,134 Disp C
(155g. = 250ml., 1.9Kg. = 12 x 250ml., 621g. = 1 liter, 7 4Kg. = 12 x 1 liter)
Max U V Abs (1 cm cell - *vs* H_2O)

n_D^{20} 1.4340 d
(78g. = 100m
Max U V Abs (1
λ (nm) 400-25
A 0
Water <0 02%

n-**Hexane,** spectr
$CH_3(CH_2)_4CH_3$
n_D^{20} 1 3748 d 0
Disp. C
(330g. = 500m
liters, 8Kg. = 4
Max U V Abs (1
λ (nm) 400-25
A 0 0
Water <0 02%

Isopropanol, spec
LABEL (meets
requirements) (
$(CH_3)_2CHOH$ M
d 0 785 f p 72
Merck Index 8,5
(392g. = 500m
3 liters, 9.4Kg
Max U V Abs (1
λ (nm) 400-30
A 0 0
Water <0 05%

Aldrich has just published this special catalog supplement. It lists spectro quality solvents, each of which has been specially purified and critically analyzed both during and after production, and after packaging as well, to insure ultra high purity.

Each solvent meets or exceeds ACS specifications where established. They can be used with assurance as spectrophotometric and liquid chromatographic solvents, and in other applications where high purity, uv transparency, and low residue on evaporation are required.

For your free copy of this catalog, send your name, company name, address, and zip code to Aldrich Customer Services Dept.

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MILWAUKEE, WISCONSIN 53233

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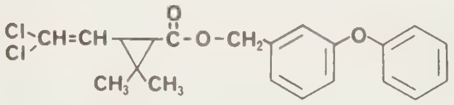
Progress in Pesticide Research

The serious ecological problems caused by the use of insecticides such as the chlorinated hydrocarbons, phosphates and carbamates have led to a reexamination of an important class of naturally occurring insecticides, the pyrethrins, and their synthetic analogs. The pioneers in this work are Dr. Michael Elliott and his co-workers at the Rothamsted Experimental Station in England who have developed many very active synthetic pyrethrins, the most promising of which are NRDC 143 (I) and NRDC 161 (II).


(I)

These synthetic pyrethrins show promise of becoming the most important insecticides known to man, more beneficial and considerably less toxic than DDT. They are the esters of *m*-phenoxybenzyl alcohol and *m*-phenoxybenzaldehyde cyanohydrin. Aldrich has produced both the alcohol and the aldehyde in commercial quantities.

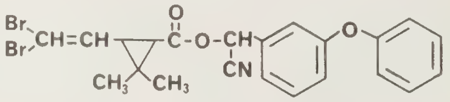
19,028-4 *m*-Phenoxybenzyl alcohol
5g $10.50 25g $35.00 1kg $600.00

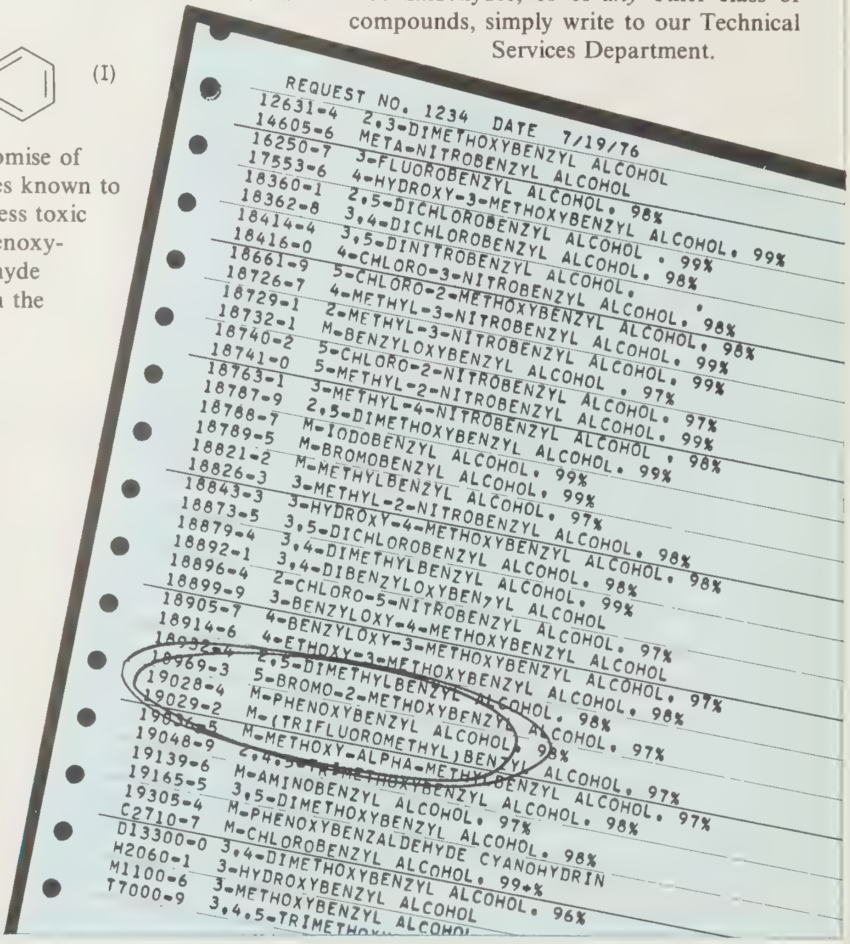
19,175-2 *m*-Phenoxybenzaldehyde
5g $7.50 25g $23.50 1kg $500.00

Aldrich

940 West Saint Paul Avenue
Milwaukee, WI 53233

On a visit with Dr. Elliott recently, we were delighted to note an Aldrich computer printout of all our benzyl alcohols on his desk — obviously of help in his choice of analogous benzyl esters. If you would like a free computer printout of all our substituted benzyl alcohols, or all our benzaldehydes, or of *any* other class of compounds, simply write to our Technical Services Department.


(II)



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REQUEST NO. 1234  DATE  7/19/76
12631-4  2,3-DIMETHOXYBENZYL ALCOHOL
14605-6  META-NITROBENZYL ALCOHOL
16250-7  3-FLUOROBENZYL ALCOHOL
17553-6  4-HYDROXY-3-METHOXYBENZYL ALCOHOL. 98%
18360-1  2,5-DICHLOROBENZYL ALCOHOL. 99%
18362-8  3,4-DICHLOROBENZYL ALCOHOL . 99%
18414-4  3,5-DINITROBENZYL ALCOHOL. 98%
18416-0  4-CHLORO-3-NITROBENZYL ALCOHOL.
18661-9  5-CHLORO-2-METHOXYBENZYL ALCOHOL. 98%
18726-7  4-METHYL-3-NITROBENZYL ALCOHOL. 98%
18729-1  2-METHYL-3-NITROBENZYL ALCOHOL. 99%
18732-1  M-BENZYLOXYBENZYL ALCOHOL. 99%
18740-2  5-CHLORO-2-NITROBENZYL ALCOHOL . 97%
18741-0  5-METHYL-2-NITROBENZYL ALCOHOL. 97%
18763-1  3-METHYL-4-NITROBENZYL ALCOHOL. 99%
18787-9  2,5-DIMETHOXYBENZYL ALCOHOL . 98%
18788-7  M-IODOBENZYL ALCOHOL. 99%
18789-5  M-BROMOBENZYL ALCOHOL. 99%
18821-2  M-METHYLBENZYL ALCOHOL. 99%
18826-3  3-METHYL-2-NITROBENZYL ALCOHOL. 97%
18843-3  3-HYDROXY-4-METHOXYBENZYL ALCOHOL. 98%
18873-5  3,5-DICHLOROBENZYL ALCOHOL. 98%
18879-4  3,4-DIMETHYLBENZYL ALCOHOL. 98%
18892-1  3,4-DIBENZYLOXYBEN7YL ALCOHOL. 99%
18896-4  2-CHLORO-5-NITROBENZYL ALCOHOL
18899-9  3-BENZYLOXY-4-METHOXYBENZYL ALCOHOL. 97%
18905-7  4-BENZYLOXY-3-METHOXYBENZYL ALCOHOL
18914-6  4-ETHOXY-3-METHOXYBENZYL ALCOHOL. 97%
18932-4  2,5-DIMETHYLBENZYL ALCOHOL. 98%
18969-3  5-BROMO-2-METHOXYBENZYL ALCOHOL. 98%
19028-4  M-PHENOXYBENZYL ALCOHOL. 97%
19029-2  M-(TRIFLUOROMETHYL)BENZYL ALCOHOL. 98%
19036-5  M-METHOXY-ALPHA-METHYLBENZYL ALCOHOL. 97%
19048-9  2,4,5-TRIMETHOXYBENZYL ALCOHOL. 97%
19139-6  M-AMINOBENZYL ALCOHOL. 98%
19165-5  3,5-DIMETHOXYBENZYL ALCOHOL. 97%
19305-4  M-PHENOXYBENZYL ALCOHOL. 98%
C2710-7  M-PHENOXYBENZALDEHYDE CYANOHYDRIN
D13300-0 3,4-DIMETHOXYBENZYL ALCOHOL. 99+%
H2060-1  3-HYDROXYBENZYL ALCOHOL. 96%
M1100-6  3-METHOXYBENZYL ALCOHOL
T7000-9  3,4,5-TRIMETHOX
```

Aldrichimica Acta

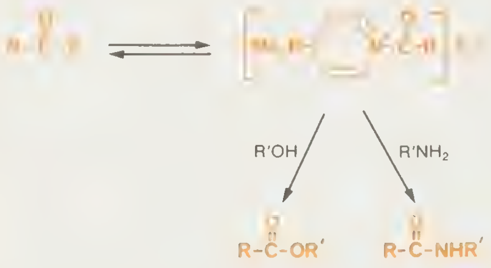
Volume 9, Number 3 (Final Issue), 1976

Phase-Transfer Catalysis in Organic Synthesis. See page 35.
Recent Advances in Synthetic Pyrethroids. See page 49.

A publication of Aldrich Chemical Company, Inc.

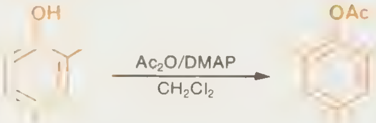
4-Dimethylaminopyridine Hypernucleophilic Acylation Catalyst

The ability of **4-dimethylaminopyridine (DMAP)** to form reactive acylpyridinium intermediates with acid anhydrides and chlorides (eq. 1) enables it to function as a nucleophilic catalyst in the acylation of even highly sterically hindered amines and phenols.

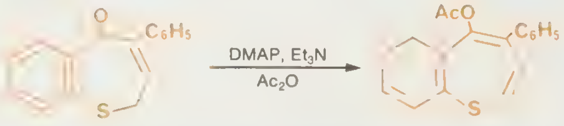


(eq. 1)

This "hypernucleophilic" catalytic activity is a consequence of the combination of the relatively high thermodynamic stability and high kinetic reactivity of the *N*-acylpyridinium intermediate. Thus, mesitol **(1)** is acetylated in nearly quantitative yield in the presence of **DMAP.** Under these conditions pyridine shows negligible catalytic activity.

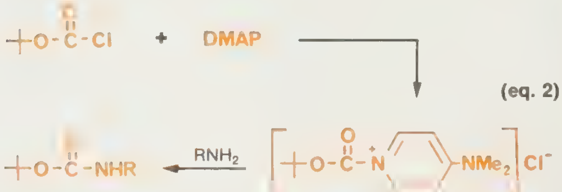


Similarly, hydrogen phthalates of hindered alcohols such as *tert*-butyl hydrogen phthalate and (-)-menthyl hydrogen phthalate can be prepared in 97% and 92% yields, respectively. Methyl cholate is acetylated at all three hydroxyl groups in quantitative yield,[1] whereas the use of pyridine as catalyst gives the 3,7-diacetate in 70% yield at room temperature.[2] The benzthiapinone **2** gives the enol acetate 3 when acetylated in the presence of **DMAP.**[3]



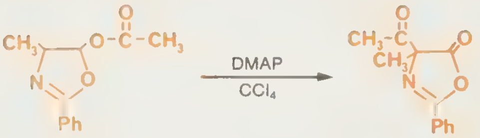
2 **3**

DMAP reacts with *tert*-butoxycarbonyl chloride to form the *tert*-butoxycarbonyl derivative which is an effective reagent for preparing *t*-BOC amino acids in aqueous solution (eq. 2).[4,5]



(eq. 2)

The "hypernucleophilic" catalytic capability of **DMAP** also enables the facile rearrangement of 2- and 4-acyloxazoles[6] (eq. 3). The same catalytic activity has led



(eq. 3)

to the extensive use of **DMAP** as a component in the preparation of polyurethanes,[7] polyamides,[8] and polyepoxides.[9]

References

1) G. Höfle and W. Steglich, *Synthesis,* 619 (1972), and references cited therein.
2) R.T. Blickenstaff and B. Orwig, *J. Org. Chem.,* **34,** 1377 (1969).
3) H. Hofmann, B. Meyer and P. Hofmann, *Angew. Chem., Int. Ed. Engl.,* **11,** 423 (1972).
4) E. Guibé-Jampel and M. Wakselman, *Chem. Commun.,* 267 (1971).
5) E. Guibé-Jampel and M. Wakselman, Fr. Patent 2,115,552; *Chem. Abstr.,* **84,** 84814q (1973).
6) W. Steglich and G. Höfle, *Tetrahedron Lett.,* 4727 (1970).
7) ICI, Brit. Pat. 990,637; *Chem. Abstr.,* **63,** 766b (1965). ICI, Brit. Pat. 996,478; *Chem. Abstr.,* **63,** 10142h (1965).
8) ICI, Brit. Pat. 1,207,673; *Chem. Abstr.,* **74,** 32529y (1971).
9) Ciba-Geigy, Brit. Pat. 1,201,756.

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Aldrichimica Acta

Volume 9, Number 3, 1976
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Table of Contents:

About Our Cover:

This being our bicentennial year, it seemed fitting to ask our chemist-collector to feature an American painting on our Acta cover. He chose this sensitive portrait (oil on canvas, $18^{1}/_{2}$ x $14^{1}/_{2}$ inches) by one of America's most prolific painters, Thomas Sully (1783-1872). The painting is monogrammed and dated 1828, and our chemist-collector believes that it may be a self-portrait which the artist painted for his sister.

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 the late Professor Wolfgang Stechow is now available to all chemist art-lovers.

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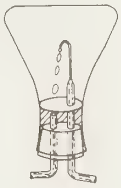
Lab Notes

Dear Sirs:

A convenient and inexpensive flow indicator can be constructed for monitoring the flow of tap water used in cooling condensers. Commonly, cooling water is run at as slow a rate as possible in order to conserve water. However, under these conditions the water flow can inadvertently stop. Thus, one must periodically check to see if the cooling water is flowing. Use of the "fountain type" flow indicator described below provides a simple means of flow detection.



As illustrated, the apparatus consists of an inverted 125-ml Erlenmeyer flask which has been fitted with a two-hole rubber stopper with inlet and outlet tubes. To prevent accidental opening of the flask during operation, the stopper is secured with an elastic band or spring-loaded tension hooks. The end of the inlet tube is constricted to about 2-3mm and adjusted to stand 2-3cm above the opening of the outlet tube. In operation the water from the tap flows through the inlet tube forming a small fountain. Since the height of this fountain is proportional to the flow rate, one can tell at a glance any changes in the rate of water flow.

Arnold Factor
General Electric Research and
Development Center
Schenectady, NY 12301

Bradford J. Factor
Glenhaven Elementary School
Scotia, NY 12302

Dear Chemists:

The electron capture detector is highly valued in gas chromatography because of its extreme sensitivity. However, this detector system has the disadvantage of becoming easily contaminated resulting in the impairment of its sensitivity. Decontamination sometimes requires several days. We assumed that E.C.D. contaminants were high-boiling materials and began trial solvent injections to "flush" the detector. We finally found that a 1:1 mixture of benzene/pyridine solvates most of these high-boiling materials. An additional benefit resulted from the benzene/pyridine injections; the sensitivity was improved by several "times".

The E.C.D. clean-up involved injecting a 1:1 solution of Nanograde benzene/pyridine 2 to 5 times in 5-25μl quantities. The column flows were left at normal values. (The inlet glass insert should be changed after the benzene/pyridine injections. Use plenty of purge N_2 while changing insert to avoid atmospheric contamination.)

Sample analyses may be performed within 2 hours of the clean-up.

Harold E. Ruark
State of Washington
Department of Social and
Health Services
P.O. Box 190
Wenatchee, WA 98801

A Sensitive Method for Detecting GLC Leaks

Detection of low flow-rate leaks is essential for maximal performance gas chromatography, but difficult and time-consuming by conventional methods based on bubble formation in a soap solution, since these techniques are dependent upon gas volume and leak speed. A simple, fast method which will unequivocally detect any leak at any flow rate has been used in our laboratories for some time. The method is based upon the equilibration of pressure across the flowmeter of the GLC: if the pressures equilibrate, the net flow indicated is zero, and thus any indication of flow, however small, is a clear sign of a leak in the system downstream of the flowmeter. Since the leak-prone parts of the GLC (column, septum, etc.) are all located after the flowmeter in the usual arrangement, the entire system can be checked in one measurement.

Conventionally, we do this test by turning off the gas and air for the detector, setting a high flow rate through the column (*e.g.*, a high pressure) and then occluding the detector outlet while watching the flowmeter (a rubber septum set in the end of a pipet, or a similar arrangement, will snugly occlude the outlet). If no flow is indicated after a minute or so, the system is tight; if there is residual flow which cannot be eliminated by making a better seal at the outlet, a leak is present. Localization (if necessary) can be accomplished by using the same method after soap application to all connectors; bubble formation is generally vigorous enough with the outlet blocked to allow immediate detection.

Susan B. Coffin
G.I. Unit - St. Marys Hospital
Mayo Clinic
Rochester, MN 55901

Dear Sirs:

An inexpensive pipet filler can be made easily by fitting a half-inch piece of $^1/_8''$ i.d. tygon tubing over the end (where the needle normally fits) of a disposable syringe and fitting a one-inch piece of $^3/_{16}''$ i.d. rubber tubing over the tygon tubing. The 12-cc size syringe is perfect for 10-ml pipets because drawing liquid up the pipet can be done rapidly as it is almost impossible to draw too much into the pipet. Larger size syringes will work with many sizes of pipets. If there is danger of contamination, the syringe can be disposed of due to the low cost.

The cost for a 12-cc syringe, such as Scientific Products No. B 2965-12, is $5.90 per 100 in the latest catalog.

The cost of pro-pipet fillers is up to $12.00 each.

Harold Lovdahl
Department of Chemistry
Lawrence University
Appleton, WI 54911

Dear Sir:

When using "Gooch" tubing to add a solid to an anhydrous system *via* a ground glass joint, one generally encounters loss of material as well as contamination of the joint involved.

We have solved this problem by using a "double Gooch" technique.

The inner "Gooch" tubing is of such a diameter that it easily fits inside the ground joint being used. Gooch tubing of a slightly larger diameter is placed on the outside of the joint. Both are attached to the flask (*e.g.*, Erlenmeyer) containing the solid to be added.

When this technique is carried out properly, no contamination of the ground joint occurs.

David H. Steinberg, Ph.D.
P and A Research
Ciba-Geigy Chemical Corp.
Ardsley, NY 10502

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.*

Recent Advances in Synthetic Pyrethroids

Alfred Bader

How is great research achieved?

Perhaps a systematic study of how research is carried out in various countries is just not possible, as it would require intimate knowledge of so many research groups. Even today, when great research is being done so openly by many academic research teams, often in the same or adjacent buildings — R.B. Woodward's or E.J. Corey's groups at Harvard, for example — there has not been a systematic study of how this differs from country to country, from industrial to academic laboratories, or even from one professor's laboratory in the same building to the next. One can come close to understanding how academic research was done fifty to a hundred years ago by reading those wonderfully informative obituaries of great chemists that appeared in the Berichte. Also, some autobiographies, such as "Aus meinem Leben" by Richard Willstätter, are most informative. Today, however, chemists write much less personally: too many heed that most foolish of sayings that time is money. Time is the one commodity that money cannot buy, and we are so busy "doing" chemistry that we seldom reflect how it could be done best.

Naturally, as a supplier of building blocks for organic chemical research, we are most interested in how research is being done, and most suggestions for our new compounds have come from great research laboratories around the world. Thus, we were very interested in meeting, and discussing research in general and his research in particular, with Dr. Michael Elliott of the Rothamsted Experimental Station in Harpenden, Hertfordshire, England, whose work is likely to change the world's agriculture as fundamentally and more lastingly than the chlorinated hydrocarbons such as DDT have done earlier.

Dr. Elliott, born in London in 1924, educated at University College at Southampton and King's College, University of London (Ph.D. and D. Sc.), is a most approachable chemist, and when I called him from London recently, he readily invited me to his laboratories in Harpenden, and he subsequently visited Aldrich for a day to discuss our interest in providing building blocks for synthetic pyrethroids. (Fig. 1 shows Dr. Elliott with Dr. Irwin Klundt and Mr. Charles Pouchert of Aldrich.)

Dr. Elliott's interest in the chemistry of pyrethrins started when he was a student with Professor Stanley Harper, with whom he moved from Southampton to London. From London, Dr. Elliott went directly to the Rothamsted Experimental Station where work on pyrethrins had been guided by Dr. Frederick Tattersfield and Dr. Charles Potter, who had realized the great importance of a stable supply of insects to the studies of structure-activity relationships, and who had built a multidisciplinary team at the Experimental Station. Today the team associated with Dr. Elliott includes organic chemists Dr. Norman F. Janes (Fig. 2) and Dr. David A. Pulman (Fig. 3), an electrophysiologist, Mr. Paul Burt, and entomologists Dr. Andrew W. Farnham and Mr. Paul H. Needham. This team works in modest, cluttered laboratories, much like university laboratories built in the thirties, and one gets no inkling

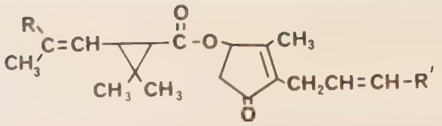
Fig. 1. From left to right, Mr. Pouchert, Dr. Elliott and Dr. Klundt.

from discussions with these modest scientists that they are doing fundamental work on which the giants of the world's chemical industry — ICI, Roussel-Uclaf, FMC, Sumitomo and others — are spending millions in efforts to commercialize these inventions.

Naturally, my first question to Dr. Elliott was how he believed his research differs in method from that in the laboratories of the industrial giants. The Rothamsted research on pyrethroids has been supported by the National Research Development Corporation which has patented the active compounds and has licensed these to the companies mentioned, and so Dr. Elliott has been able to compare their research efforts with those of his own team. In some of the laboratories of the chemical giants, one group of chemists makes the new compounds. These are then computer-coded and eventually — often months later — fed to insects by scientists who may not even know the chemists who made the chemicals, and it may be months later before the synthetic chemists get the neatly tabulated test results. All this is often impersonal and always time-consuming. At Rothamsted, a compound synthesized in the morning is sometimes tested for its insecticidal activity the same afternoon, by scientists working in proximity. They know and talk to each other, and have only one aim — to produce quickly the most active, least toxic compound of the series being studied to establish fundamental structure-activity relationships. Clearly it is easier to find active compounds in such an environment.

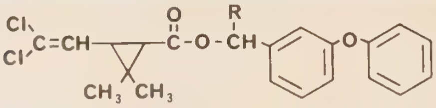
Fig. 2. Dr. Norman F. Janes

The natural pyrethrins are the active insecticidal ingredients of pyrethrum flowers. Their chemistry has been carefully reviewed;[1a–d] they are esters of cyclopropanecarboxylic acids and alkenylcyclopentenolones.

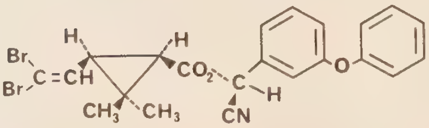


Natural Pyrethrins

R = CH_3 or CO_2CH_3
R′ = $CH=CH_2$ or CH_3 or CH_2CH_3



NRDC 143 (R=H)
NRDC 149 (R=CN)



NRDC 161

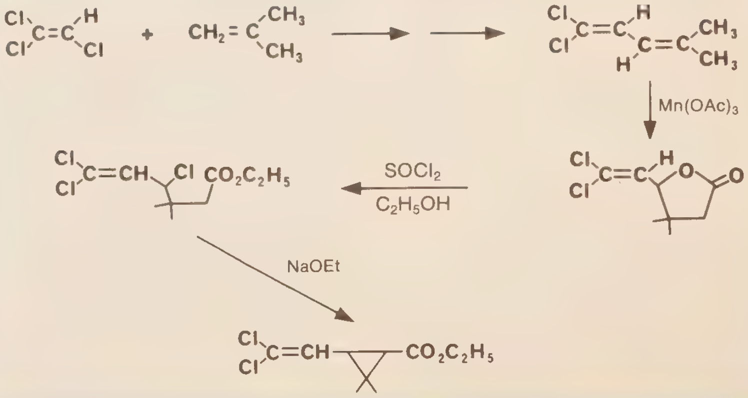
Until relatively recently, the interest in the pyrethrins as insecticides was greatly overshadowed by the interest in the chlorinated hydrocarbons, phosphates and carbamates, because these are generally much more easily made and more stable than the pyrethrins. The pyrethrins, however, have the great advantages of being biodegradable, much less volatile, and harmless to mammals, and so the environmentalists' concern about DDT, Aldrin, Dieldrin, etc., has shifted interest to the synthetic pyrethroids which have been studied by Dr. Elliott and his coworkers since the sixties. Many hundreds of analogs of the natural pyrethrins have been made, and the relationship between structure and activity has been studied in detail.[2]

To date, the three most promising compounds are NRDC 143, NRDC 149 and NRDC 161.

All three compounds appear very difficult to prepare, and their facile preparations are the result of work by some of the ablest chemists in the world's giant chemical companies.

The acid moiety was the more difficult to synthesize, and Professor Ralph A. Raphael of Cambridge University electrified this September's symposium on synthetic pyrethroids in San Francisco when he described the as yet unpublished preparation from trichloroethylene and isobutylene, developed by Dr. Peter Cleare at ICI. Trichloroethylene and isobutylene are condensed to 1,1-dichloro-4-methyl-1,3-pentadiene which is then converted to a lactone with manganic acetate. When this is treated with thionyl chloride and ethanol, it yields an ester which can be cyclized to the key cyclopropanecarboxylic ester required for NRDC 143.

FMC chemists reported a parallel synthesis of this ester at the same symposium. It proceeds *via* the same dichloromethylpentadiene, which is converted to the ester with ethyl diazoacetate. FMC reported raw materials cost by this route to be low, only about \$2.50/lb, but the cost of a plant to handle ethyl diazoacetate safely is likely to be much higher than that for the ICI process.



m-Phenoxybenzyl alcohol and *m*-phenoxybenzaldehyde are much more easily made, but how best to do this on the hundreds-of-tons scale that may be needed? We understand that an air-oxidation process from *m*-phenoxytoluene, which is readily available from phenol and *m*-cresol, has been developed. Also *m*-phenoxytoluene can be halogenated and hydrolyzed to *m*-phenoxybenzyl alcohol which can be easily oxidized to the aldehyde. Alternately, the benzal halide can be converted to the aldehyde directly. These methods, however, involve a raw material cost estimated at \$5-6 per lb of alcohol or aldehyde, which may be too high for economic feasibility.

Aldrich became interested in *m*-phenoxybenzyl alcohol when we were asked to study the reduction by hydroboration of *m*-phenoxybenzoic acid, easily made by the oxidation of *m*-phenoxytoluene. We had no problem scaling up the hydroboration and made several hundred pounds of the alcohol. However, it became clear that this process could not compete economically with the alternate routes.

Fig. 3. Dr. David A. Pulman

Shortly after completion of this work, we found a much better synthesis of *m*-phenoxybenzyl alcohol *via* the aldehyde. This uses neither *m*-phenoxytoluene nor the acid, and has an intrinsically lower raw material cost than the syntheses from *m*-phenoxytoluene. Just at that time, attention focused on NRDC 161, the ester of the cyanohydrin of the aldehyde, so the aldehyde itself became important. We believe that we have a more economical synthesis of the aldehyde than any involving the oxidation of *m*-phenoxybenzyl alcohol and, in fact, the most economical preparation of the alcohol may be *via* the reduction of the aldehyde made by our method.

We at Aldrich do not have any large-scale equipment and certainly could not make many tons ourselves. However, some time ago I discussed the industrial production of the aldehyde with one of my best friends, Bert Van Deun, at Janssen Pharmaceutica in Belgium. The Janssen engineers then scaled up the process using specific technology developed within the company, and so we have licensed Janssen to prepare the aldehyde, and hope that they will be able to fill much of the demand.

Naturally, we were most interested to learn what the contributions of the NRDC licensees have been. As we understand the situation, it is as follows: ICI may have made the greatest synthetic efforts, particularly towards NRDC 143, culminating in Dr. Cleare's work discussed. Shell appears to have concentrated on new structures, and FMC with ICI (U.S.), the licensees in the Western Hemisphere, have emphasized studies of biological activity. Roussel-Uclaf has developed elegant syntheses of chrysanthemic acid, either *via* a sulfone[3] derived from isoprene, and β,β-dimethylacrylic acid (which may explain why we have sold many tons of this recently) or *via* addition of this sulfone to an isopropylidenemalonate ester.[4] All the most active compounds are resolved, optically active isomers; for example, the (+)-*trans*-chrysanthemates and analogs are active while the (-)-*trans*-isomers are virtually inactive. Thus, resolution is very important, and the best methods appear to have been developed by chemists at Roussel-Uclaf.[5] Sumitomo's contributions have been both in synthetic innovations and of new structures. They have prepared the esters *via* the triethylamine salt of *m*-phenoxybenzyl bromide without isolation of the alcohol. Also, they have shown[6] that the cyclopropane moiety is not essential to activity: 'Sumicidin,' S5602, is the *p*-chloro-α-isopropylphenylacetate of the cyanohydrin of *m*-phenoxybenzaldehyde.

Just how active these synthetic pyrethroids are in comparison with the older insecticides can be seen from this table.[7]

	Relative toxicity to	
	house flies	mustard beetles
Parathion	37	7
DDT	4-15	11
Dieldrin	35	4-10
NRDC 161	2300	1600

This much greater insecticidal activity, coupled with their low mammalian toxicity and biodegradability, makes it appear likely that these pyrethroids will become important insecticides in the future.[8]

Because of my interest in art, I am often asked how I believe motivation between great artists and great chemists differs. The great chemists often achieve greatness because they want to be the first to reach a difficult goal: R.B. Woodward must have known that if he did not synthesize quinine or strychnine and Vitamin B_{12}, *someone else would*. A great artist paints because he knows that if he does not create this great work, no one else will. If Rembrandt had not painted that marvellous "Return of the Prodigal Son" now in the Hermitage, *no one else would have*. This rather pat answer falters when considering Dr. Elliott's work: would NRDC 161 really have been made without him and his team? Probably not, or at least not for a very long time: in the case of men like Elliott, the motivation of scientists and that of artists overlap.

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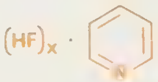
Potpourri

Hydrogen Fluoride - Pyridine
A Deblocking Agent in Peptide Synthesis



The use of **hydrogen fluoride-pyridine** (HF-pyridine) as a fluorinating agent has been reported. Thus, 2° and 3° alcohols yield alkyl fluorides,[1] cyclopropane, alkenes and alkynes are hydrofluorinated,[2] while alkenes are halofluorinated[3] and nitrofluorinated.[4]

More recently, **HF-pyridine** has been used as a reagent for cleaving a variety of protecting groups in peptide synthesis.[5] **HF-pyridine** seems to be a stable, convenient source of HF, easier and safer to use than liquid HF.

In this latter application, 100 μmol of the protected amino acid or peptide is treated with 2ml **HF-pyridine** with 0.2ml anisole as a scavenger, at room temperature for 1hr. Quantitative amino-acid analysis and tlc showed almost quantitative regeneration of the amino acid from many currently used protecting groups (see table).[5]

Protected amino acid or peptide	% Deprotected amino acid or peptide
BOC-Asp(O-Bz)-OH	98
BOC-Glu-(O-Bz)-OH	100
BOC-Thr(Bz)-OH	95
AOC-Arg(Tos)-OH	95
H-Lys-(CBZ)-OH	100
BOC-Lys-[CBZ(O-Cl)]	90
BOC-Cys-S[Bz(*p*-OMe)]-OH	93
NPS-Trp-OH	90
H-Lys(BOC)-O-*t*-Bu	97
BOC-Leu-resin	96
BOC-Pyroglu-Trp-Gly-benzhydrylamine resin	57*

*after column chromatography

HF-pyridine also proved to be an efficient deblocking reagent in solid-phase peptide synthesis (see table).

References:

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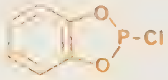
18,422-5	**Hydrogen fluoride-pyridine**	**100g $16.10**

Primary Standard for C,H,N Analyses

19,245-7	**Cyclohexanone 2,4-dinitrophenylhydrazone**	**1g $9.50**

Sulfoxide-Reducing Agent

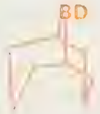


***o*-Phenylene phosphorochloridite** (2-chloro-1,3,2-benzodioxaphosphole) was recently reported to be an efficient reagent for the reduction of alkyl, aryl, and aralkyl sulfoxides to the corresponding sulfides. In contrast to the previously reported reducing agent, 2-phenoxy-1,3,2-benzodioxaphosphole, which sometimes requires a temperature of 70° for 3hr, this reagent gives good yields of sulfides after 15-60min at room temperature.

D.W. Chasar and T.M. Pratt, *Synthesis*, 262 (1976).

15,576-4	***o*-Phenylene phosphorochloridite**	**10g $5.60** **50g $18.65**

New Deuterio-borane Reagents



$BD_3 \cdot (CH_3)_2S$

19,334-8	**9-BBN-9*d***, 98+ atom % D, 0.5*M* solution in THF	**50ml $50.00**
19,353-4	**Borane-*d*$_3$-methyl sulfide complex,** 98+ atom % D, 1*M* solution in THF	**50ml $100.00**

New Enzacryl® Gels

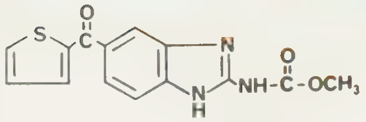
86,078-6	**Enzacryl gel K0**, extra fine (<45μ) for thin-layer permeation chromatography	**25g $37.50** **100g $100.00**
86,074-3	**Enzacryl gel K0**, fine (40-75μ)	**25g $37.50** **100g $100.00**
86,075-1	**Enzacryl gel K0**, medium (75-150μ)	**25g $37.50** **100g $100.00**
86,077-8	**Enzacryl gel K0**, coarse (150-300μ)	**25g $37.50** **100g $100.00**
86,080-8	**Enzacryl gel K4**, preswollen in water, for thin-layer permeation chromatography	**25g $32.00**
86,081-6	**Enzacryl gel K10**, preswollen in water, for thin-layer permeation chromatography	**25g $33.70**

Agarose for Gel Electrophoresis

19,115-9	**Agarose,** pure powder, standardized for use in quantitative immunoelectrophoresis. Gelling temperature (2% soln.), 42°. Relative electroendosmosis, M_r, -0.13.	**10g $15.80; 25g $26.35**
13,704-9	**Agarose,** pure powder Gelling temperature (2% soln.), 42°. Relative electroendosmosis, M_r, -0.10.	**10g $14.50; 25g $23.00**
19,415-8	**Agarose,** pure powder, for crossed immunoelectrophoresis. Gelling temperature (2% soln.), 43°. Relative electroendosmosis, M_r, -0.02.	**10g $15.80; 25g $26.35**

Nocodazole

A New Synthetic Microtubule Inhibitor



Nocodazole {methyl [5-(2-thienylcarbonyl)-1*H*-benzimidazol-2-yl]carbamate, R17934} is a new synthetic microtubule inhibitor, chemically unrelated to the microtubule-disintegrating alkaloids colchicine, the vinca alkaloids, rotenone and podophyllotoxin. Investigation into the mechanism of its activity against experimental neoplasms[1,2] revealed that the compound exhibited highly specific antimicrotubular activity, inducing the total disappearance of microtubules from neoplastic cells *in vivo*[3] and from mammalian cells in culture.[4] This activity and the ensuing cell-biological effects were identical to those produced by the antimicrotubular alkaloids. Effects include:

1) loss of directional cell movement[4]
2) alteration of cell shape[4]
3) loss of ordered subcellular organelle movements[4]
4) randomization of subcellular organelle topography[3,4,5]
5) inhibition of insulin secretion[6]
6) induction of Con-A cap formation on human polymorphonuclear leukocytes[7]
7) appearance of bundles of 10nm-filaments and annulate lamellae[3,4,8,9]
9) destruction of the mitotic spindle with ensuing mitotic block.[3,4,10]

The high degree of specificity was demonstrated by the absence of nonspecific side effects unrelated to its antimicrotubular properties.[3,4] The cell-biological effects were identical within a large dose range (0.04-100μg/ml), and concentrations that had no effect on microtubules (<0.01 μg/ml) showed no effects whatsoever on cellular structure, behavior, growth or viability.[4] The antimicrotubular activity in tissue-cultured cells was almost immediately visible and reversible.

Subsequently, it was shown that **Nocodazole** inhibited the polymerization of tubulin *in vitro* in a dose-dependent way and that it shared the same binding site on the tubulin molecule with colchicine.[11] In contrast to colchicine, however, **Nocodazole** is easily removed from its binding site.[11]

Comparison of its effects with those of colchicine should help establish the involvement of tubulin and microtubules in the studied phenomena. Colchicine-induced alterations unrelated to interaction with tubulin have indeed been reported.[12,13] The rapid penetration of **Nocodazole** and the lack of irreversible binding should facilitate short-term experiments, especially when phenomena related to the reappearance of microtubules are studied. The reversibility of its action can also be favorably exploited when cell synchronization is attempted through a reversible mitotic block.

A number of organisms that are relatively resistant to the action of colchicine could prove sensitive to **Nocodazole**. Preliminary data indicates, for instance, that **Nocodazole** shows antimicrotubular effects in fungi.[14]

The compound is stable in biological media for at least 7 days.

Thus, the availability of a synthetic compound with a simple chemical structure unrelated to the plant alkaloids and with a specific antimicrotubular activity is potentially useful in the field of microtubule research.

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19,429-8 Nocodazole 10mg \$9.00; 50mg \$30.00

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Aldrich introduced 100.0 (min. 99.96) atom % D deuterated solvents back in 1968. Gradually other manufacturers followed our lead; the most recent "introduction" was in 1975, seven years later.

Aldrich has the broadest line of 100.0 atom % D solvents. With the introduction of methyl-d_3 alcohol-*d*, 100.0 atom % D, we now offer ten 100% D solvents. And more are yet to come.

Aldrich 100.0 atom % D solvents are the best you can buy. It is the rule, rather than the exception, that the quality of these solvents exceeds specifications of 99.96 atom % D. We challenge you to compare them with any other brand.

Aldrich 100.0 Atom % D Solvents

17,586-2	**Acetone-d_6**	5g $36.00; 25g $130.00
17,587-0	**Benzene-d_6**	5g $38.00; 25g $135.00
15,185-8	**Chloroform-*d***	10g $18.00; 50g $47.00
15,189-0	**Deuterium oxide**	10g $15.00 50g $43.00
19,234-1	**Deuterium oxide,** low in paramagnetic impurities	30g $50.00
17,664-8	**Deuterium chloride,** 20% solution in D_2O	5g $42.00 25g $175.00
15,691-4	**Methyl sulfoxide-d_6**	5g $35.00 25g $125.00
17,797-0	**Pyridine-d_5**	1g $15.00; 5g $68.00 25g $245.00

The Breakthrough — 100.00 Atom % D

Aldrich recently introduced deuterium oxide, 100.00 (min. 99.996) atom % D. The specifications on this solvent are a full order of magnitude better than those of any other manufacturer.

To preserve the isotopic purity of this product, rigorous handling procedures are necessary. A data sheet outlining such procedures is packaged with every bottle of this solvent.

19,170-1	**Deuterium oxide,** 100.00 atom % D	10g $29.00 50g $75.00

Our Latest Addition — Methyl-d_3 Alcohol-*d*, 100.0 Atom % D

This grade of deuterated methanol is packaged in one-gram units, sealed under argon in serum bottles provided with a PTFE-bonded silicone cap. There is no waste: even if only 20 μl is used for a capillary tube the remainder is not contaminated.

19,416-6	**Methyl-d_3 alcohol-*d*,** 100.0 atom % D (min. isotopic purity 99.96%)	1g $19.00 5g(5 x 1g) $60.00

The Best Buy

Compare Aldrich quality, but also compare Aldrich prices. Our regular catalog prices are below "sale" prices of our competitors.

15,182-3	**Chloroform-*d*,** 99.8 % D	1kg(10 x 100g) $76.00
15,183-1	**Chloroform-*d*,** 99.8 % D, 1% TMS	1kg(10 x 100g) $76.00
15,187-4	**Methyl sulfoxide-d_6,** 99.5 % D	100g(10 x 10g) $76.00
18,596-5	**Methyl sulfoxide-d_6,** 99.5 % D, 1% TMS	100g(10 x 10g) $76.00
15,179-3	**Acetone-d_6,** 99.5 % D	100g(10 x 10g) $76.00

For smaller unit sizes and for a complete listing of our deuterated compounds, see page 946 of the 1977-1978 *Aldrich Catalog/Handbook of Organic and Biochemicals.*

Aldrichimica Acta

Volume 10, Number 1, 1977

Dedicated to Professor Robert Burns Woodward on his sixtieth birthday.

Aldrich Deuterated Solvents

Highest quality Lowest prices Personalized service

Aldrich can offer the highest quality at lowest prices because we manufacture our own deuterated solvents. We check quality at every stage of the manufacturing process, in addition to a final analysis, resulting in a superior product. For example, we enrich our own heavy water to produce our 100 atom % D solvents. As a result, these solvents have the highest isotopic purity of any on the world market — often by a very wide margin.

Aldrich's deuterated solvents are manufactured and packaged by our Diaprep Division — a small group which can offer personal service. We invite inquiries and even complaints, because we realize that we, and ultimately the entire NMR community, can gain by them. For example, our 100.00 atom % D Deuterium oxide (19,170-1) is the result of an inquiry by one customer. Its purity is ten times as high as any heavy water previously available, and it is finding worldwide use.

19,170-1	Deuterium oxide, 100.00 atom % D	10g $29.00 50g $75.00

Aldrich 100.0 Atom % D Solvents

17,586-2	Acetone-d_6	5g $36.00; 25g $130.00
17,587-0	Benzene-d_6	5g $38.00; 25g $135.00
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15,691-4	(Methyl sulfoxide)-d_6	5g $35.00 25g $125.00
17,797-0	Pyridine-d_5	1g $15.00; 5g $68.00 25g $245.00

Deuterium NMR

Just as Aldrich was the first to introduce 100 atom % deuterated solvents, we now introduce deuterium-depleted water. This new solvent (also the result of an inquiry by one customer) will make possible new work in the rapidly growing field of deuterium NMR,[1] especially work on compounds of biological interest, where the DHO resonance obliterates the resonance of the deuterons of interest.

1) Although still a new field, there is a review of Deuterium NMR containing over 300 references: H.H. Mantsch, H. Saitó, and I.C.P. Smith in "Progress in Nuclear Magnetic Resonance Spectroscopy," J.W. Emsley, J. Feeney, and L.H. Sutcliffe, Eds., London, Pergamon Press, in press.

19,529-4	Water, deuterium-depleted	25g $25.00

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Aldrichimica Acta

Volume 10, Number 1, 1977
A publication of ALDRICH CHEMICAL COMPANY, INC.

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Belgium
Telephone: 014/61431

We at Aldrich are happy to dedicate this issue of the Aldrichimica Acta to Professor Robert Burns Woodward on the occasion of his sixtieth birthday.

Professor Woodward is one of the greatest living chemists. His name conjures visions of synthetic jewels and symmetry rules, of noble prose and Nobel Prize. Before his time, the world's greatest chemists were German, English and Swiss. Through his accomplishments, example and teaching, we now have great schools of chemistry in America.

May we say what the Bible says of the greatest lawgiver: Let his eyes not be dim nor his natural strength abated — from 60 to 120.

About Our Cover:

Our chemist-collector, who has known and admired Professor Woodward since 1947, had the pleasant problem of choosing that painting in his collection most fitting for the cover of the Acta dedicated to Professor Woodward. We were not surprised that he picked this *trompe l'oeil,* once in the collection of the King of Saxony and painted by a late seventeenth century Bolognese artist, for the analogy is clear. The painting depicts the marriage of King Alexander the Great and Princess Roxana, and thus the meeting of the greatest cultures — Greek and Persian — of their time. So we find in Professor Woodward the junction of the greatest sciences of our time — chemistry and the life sciences.

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 the late Professor Wolfgang Stechow is now available to all chemist art-lovers.

Z10,118-4 $6.00

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

Few reactions in organic synthesis are as useful as the Wittig condensation. Often, however, high-purity intermediate alkyl triphenylphosphonium halides are essential for high and reproducible yields. We have developed a very general method for recrystallizing these compounds. In all cases we have experienced, the yield of the subsequent Wittig reaction has been improved by this purification.

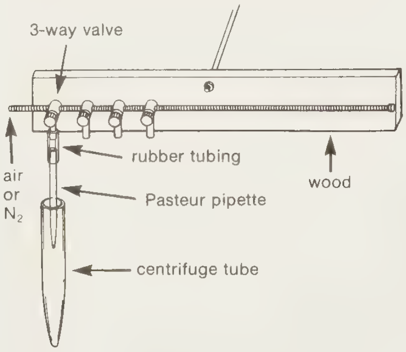
The impure phosphonium salt is dissolved in the minimum of methylene chloride (n ml). This solution is diluted with methylene chloride (n ml), then tetrahydrofuran (n ml). The resulting mixture is then concentrated to a volume of n to $2n$ ml, then cooled. The resulting crystalline material is pure phosphonium salt. Weight recovery is excellent.

This method has been applied to the purification of a wide range of both mono- and bis-phosphonium salts, and is suitable, with appropriate precautions, to the preparation of analytical samples.

Nicholas Darby, Ph.D.
Edmonton, Alberta
Canada T6C 4A9

We find the following evaporator effective and inexpensive for reducing solvent volume of sample extracts, such as urine and drug extracts, for thin layer chromatography and gas liquid chromatography.

The unit consists of one or more 3-way fish-aquarium valves connected in series and mounted on a "T" fashioned from a strip of wood and a length of threaded rod,



which can then be mounted on a ringstand. A disposable Pasteur pipette is attached to the appropriate prong of the valve to direct the flow of air or nitrogen for evaporation of solvent in a 15-ml conical bottom centrifuge tube. The rack of tubes can be placed in a water bath to promote evaporation.

Glenn Murphy, Chief Chemist
Toxicology Laboratory
Bureau for Health Services
Frankfort, Kentucky 40601

A very nice and inexpensive introduction chamber for a glove bag can be made from an empty coffee can and two pieces of copper tubing. This chamber obviates the need for evacuating and refilling the bag each time a sample is to be introduced into or removed from the bag.

The apparatus consists of a coffee can with both the metal ends cut off and replaced with the plastic caps which are provided for resealing the opened cans. Two holes are then drilled in the seam along the side of the can where it is soldered together. The two copper tubes are then soldered into these holes. To these tubes are attached a vacuum line and an inert gas line. The completed chamber can then be inserted into the opening of the glove bag, which is sealed to it by means of rubber bands.

There are two methods for flushing air from the antechamber: gas can be bled in and out simultaneously, or the can can be repeatedly pumped down and refilled. Most cans (and especially the smaller ones with low cap area) will take a respectable vacuum, and this can be improved by cementing hard plastic discs onto the outside of the plastic caps, which will help keep them from bowing inward too much.

Edward C. Greer
11 Old West, U.N.C.
Chapel Hill, N.C. 27514

When separating an organic phase from an aqueous phase, it is often difficult to distinguish one from the other on cursory examination. It often becomes necessary to consult tables of specific gravity or to carry out some other simple, but time-consuming investigation which interrupts the flow of the experiment.

I find that the following quick test produces the correct answer in most cases. A drop of each phase is placed on the edge of a piece of filter paper. Upon attempting to tear the filter paper, you will find that the aqueous spot tears without effort and the organic spot resists tearing.

Paul R. Horinka
Research Chemist
American Color and Chemical Corp.
Reading, Pa. 19603

In solution preparation in test tubes or flasks, one is faced occasionally with the problem of entrapped air, microbubbles or foam making it difficult to ascertain whether dissolution is complete. Since most labs now have ultrasonic cleaning baths, immersion of the tube or flask in the bath for one second, causes an instantaneous clearing of the solution for complete visibility.

A.C. Megalos
Senior Scientist
Technicon Instruments Corporation
Tarrytown, New York 10591

A large test tube mounted vertically with its mouth up and slightly below the surface of a stirred water bath will do an amazing job of collecting the dirt and debris that otherwise soon make such a bath murky.

R. Keith Osterheld
Professor
University of Montana
Missoula, Montana 59801

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.

By a happy coincidence, the very first telephone call I received after our advertisement "Please Bother Us" appeared in *C & E News*, was from Professor R.B. Woodward at Harvard, who was looking for an out-of-the-way quinone, 2,5-dihydroxybenzoquinone. We have over three hundred quinones in our Library of Rare Chemicals; this one was among them, so we mailed 5g to Professor Woodward that day. Also, we decided to list it in our catalog-handbook, and now have several kilos in stock for immediate shipment.

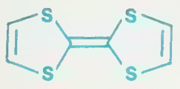
It was no bother at all, just a pleasure to be able to help.

19,546-4 2,5-Dihydroxybenzoquinone
25g $10.75; 100g $28.50

TTF and TCNQ

Components for conductivity

Tetrathiafulvalene (TTF) and several other tetrathioethylenes were originally investigated as possible electron-rich olefins.[1] It was quickly realized that the electrochemistry of **TTF** was by far the most interesting aspect of the compound. Wudl *et al.*[2,3] discovered that **TTF** formed an exceptionally stable radical cation complex with chlorine (TTF•Cl) which exhibited an unusually high electrical conductivity.



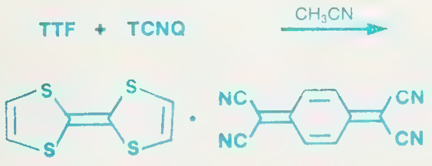
TTF

TCNQ

7,7,8,8-Tetracyanoquinodimethane (TCNQ) was first studied for its ability to form radical anions.[4,5,6] Since then, many practical applications have been discovered. For example, **TCNQ** is used in the:

1) colorimetric determination of free radical precursors[7]
2) visualization of certain nitrogen and sulfur compounds on thin-layer and paper chromatograms[7,8]
3) replacement of MnO_2 in aluminum solid electrolytic capacitors[9]
4) construction of heat-sensitive resistors[10]
5) induction of radical polymerizations (in combination with *N,N*-dimethylaniline *N*-oxide)[11]
6) construction of ion-specific electrodes.[12,13]

It was the ability of **TCNQ** to form radical anions that prompted Cowan[14] to combine it with the electron donor **TTF**. The resulting charge-transfer complex was found to contain **TTF** and **TCNQ** in a 1:1 ratio.



This complex behaves electrically and optically like a one-dimensional metal at room temperature. It has one of the highest electrical conductivities known for an organic compound, being highly anisotropic along an axis defined by the colinear stacks of **TTF** and **TCNQ**.[15] Since there was some controversy over the exact value of the conductivity, a study was performed to determine if the chemical purity of the components affected the electrical conductivity of the complex.[16] The workers concluded that crystal perfection rather than chemical purity was the factor chiefly responsible for determining the degree of conductivity. Major research efforts are currently in progress to better understand and find applications for the unusual properties of the **TTF/TCNQ** complex.[17,18,19]

Aldrich has offered **TCNQ** for many years. Now we also offer **TTF**! With the ready availability of these "components for conductivity," the **TTF/TCNQ** complex is more accessible for further studies.

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18,318-0 **Tetrathiafulvalene** (TTF).................... **1g $26.00**
15,763-5 **7,7,8,8-Tetracyanoquinodimethane** (TCNQ) **5g $17.00; 10g $31.00**

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Volume 10, Number 2, 1977

Chlorosulfonyl Isocyanate, a review. See page 23.

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About Our Cover:

Our chemist-collector purchased this sensitive portrait of a young man (oil on canvas 23 x 19 inches) at a Milwaukee gallery recently. A previous owner had bought it in an antique store in Vienna in 1926, and had then been told that it was mid-seventeenth century Dutch. Subsequently, it was exhibited at the Milwaukee Art Center as a newly discovered Frans Hals! Our chemist believes it is Italian — perhaps Bolognese — rather than Dutch, and earlier, *ca.* 1580-1590.

Latest Addition to Local Galleries Is Believed to Have Been Painted by Franz Hals and Was Purchased for $500 in an Antique Shop in Vienna

Reprinted with permission from The Milwaukee Journal, October 14, 1928, page 7.

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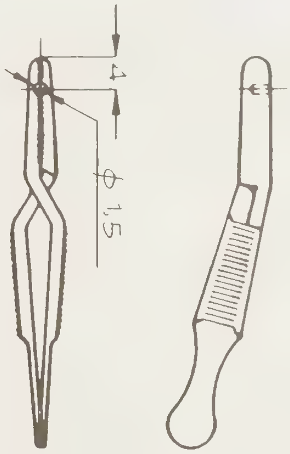
Lab Notes

Crucibles used in mass spectrometer direct-introduction probes should be handled with special tweezers that are usually pinched closed. This is important since it eliminates the need to press in order to ensure that the crucible does not drop (which is all too often the case with standard lab pincers) during manipulation, before being placed in its receptacle.

We found that surgical hemostats, which are a mass-produced item, may be converted to fit this need by drilling a small hole into them as shown in the accompanying drawing.



The diameter of the hole should be about $^1/_2$mm less then the crucible's outside diameter and have a depth of $^1/_3$ to $^1/_2$ of its length.

The crucible is held firmly by such a device and is released by squeezing.

We believe that the community of mass-spectrometrists would benefit from this idea.

Meir Peled and Adam Vincze
Israel Institute for
Biological Research
Ness-Ziona, P.O.B. 19, Israel

We have found the following apparatus ideally suited for the preparation of totally dry samples for Fourier transform nmr experiments where the slightest trace of water can obscure important peaks or cause unwanted line broadening.

The unit is constructed from the barrel of a 0.5-ml Luer lock syringe (preferably one whose plunger has been broken) and a 15-ml volumetric pipette. The end of the syringe barrel is cut off as is all but 1in. of the narrow tubing of the volumetric pipette. The two pieces are then joined. One end is filled with glass wool, and then fine (5Å) molecular sieves are poured into the "column" until they just start to fill the narrow tubing. A 6-in. stainless steel syringe needle is attached to the Luer lock and the entire apparatus is baked at 300°C for at least 12 hours to activate the sieves. The apparatus is then cooled in a dessicator or, preferably, by passing a slow, steady stream of purified dry nitrogen through the column.

After the column has cooled to slightly above room temperature, the solvent to be dried is injected through the glass wool into the sieves. The solvent is then dispensed through the needle into a septum-equipped nmr tube which has been attached to a vacuum pump for at least 4 hours. A small-gauge needle is used as a vent on the nmr tube. The solvent-transfer is accomplished by attaching a nitrogen line to the column, and to increase the flow rate, the column can be warmed with a heat gun.

The column can be reused immediately after transfer. We have obtained four dry samples before having to reactivate the column.

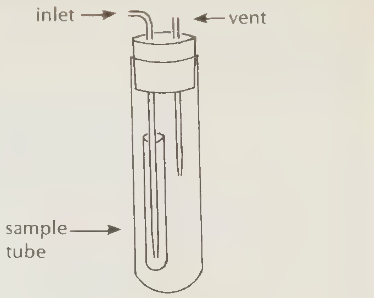
Joseph Alper
University of Wisconsin
Department of Biochemistry
420 Henry Mall
Madison, WI 53705

A common problem encountered in the use of silver chloride infrared cells is their darkening upon exposure to light. A simple and effective method of clearing up these darkened cells consists of simply soaking them in pyridine, wiping with a soft towel, and then rinsing with carbon tetrachloride. Clarity very close to that of brand new cells is achieved.

Thomas E. Nemo
Chemistry Department
University of Michigan
Ann Arbor, Michigan 48109

I have found the following trap very convenient for manually collecting nmr samples quickly and efficiently from a gas chromatograph. The trap consists of a 200 x 25mm test tube with a #4 2-hole stopper which is fitted with an inlet and a vent, both of which are easily fashioned from disposable pipets or 7-mm glass tubing. An nmr tube is simply placed in the test tube and the inlet tube inserted into it for collection.

After collection of a sample, the nmr solvent of choice can be measured out by syringe and flushed through the inlet tube.



Lee Flippin
Graduate Student
Department of Chemistry
University of Colorado
Boulder, Colorado 80309

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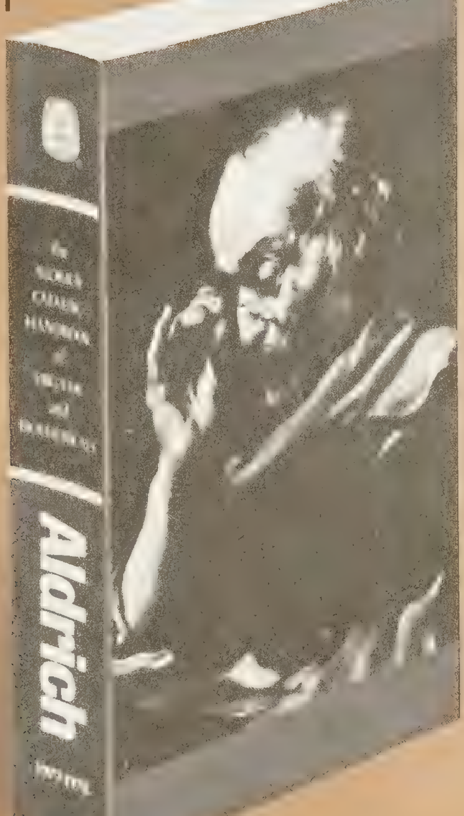
"Please Bother Us."

by Alfred Bader.

During a recent visit to the University of Michigan, Professor Richard G. Lawton told me of a very interesting new biochemical reagent, Cyssor I (an acronym for cysteine-specific scission by an organic reagent), which he thought would be of great interest as a reagent for cysteine modification and cleavage of proteins [T.J. Holmes and R.G. Lawton, *J. Am. Chem. Soc.*, **99**, 1984 (1977)]. Professor Lawton thought that the availability of this reagent would help many biochemists, and he asked whether we would try to make it. Naturally, we tried and are happy to offer it.

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

19,584-7 Cyssor I [2-methyl-N^1-benzenesulfonyl-N^4-(bromoacetyl)quinonediimide]
1g $12.00; 5g $48.00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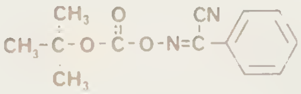
Aldrich's nonexplosive replacement for *t*-BOC azide

t-Butoxycarbonyl azide (*t*-BOC azide) has long been offered by Aldrich as an amino-blocking reagent especially useful in the synthesis of *t*-BOC-amino acids for peptide synthesis. A recent study performed on behalf of Aldrich revealed that *t*-BOC azide is thermally unstable and shock-sensitive. This has prompted us to withdraw the product from our listing and offer **BOC-ON** in its place.

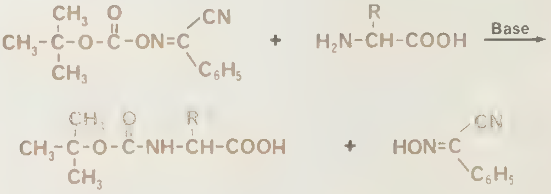


BOC-ON [2-(*t*-butoxycarbonyloxyimino)-2-phenylacetonitrile] shows promise of becoming the reagent of choice for *t*-butoxycarbonylation of amino groups, affording contaminant-free *t*-BOC-amino acids in high yield (see Table 1). **BOC-ON** is highly reactive, the carbonylation reaction being complete in 4-5 hours at room temperature. In contrast, 2-*t*-butoxycarbonylthio-4,6-dimethylpyrimidine, another *t*-butoxycarbonylating reagent, generally requires 20 hours for reaction completion while *t*-BOC azide sometimes requires a temperature of 50-60°. The latter is particularly disadvantageous considering that *t*-BOC azide may decompose with detonation above 80°. Moreover, *t*-BOC azide is a liquid whose vapors cause severe headaches and heart palpitations, whereas **BOC-ON** is crystalline.

Table 1

t-BOC-amino acid	Reaction time, hr	Yield, %
-Gly-OH	2	86.9
-Leu-OH	3	72.0
-Met-OH·DCHA	3	82.1
-Ph-OH·DCHA	5	98.2
-Thr-OH·DCHA	3	99.7
-Tyr-OH·DCHA	4	81.8

t-Butoxycarbonylation with **BOC-ON** simply requires stirring a dioxane solution of the amino acid with a 10% excess of the reagent and a 50% excess of triethylamine at room temperature for several hours. The by-product, 2-hydroxyimino-2-phenylacetonitrile, is removed by extraction into ether, benzene, or ethyl acetate, and the *t*-BOC-amino acid is extracted from the aqueous layer with ethyl acetate after acidification with 5% citric acid.



BOC-ON is very soluble in ethyl acetate, ether, benzene, chloroform, dioxane, and acetone. It is soluble in methanol, isopropanol, and *t*-butanol, and insoluble in petroleum ether and water. It should be stored in a brown bottle at -20° C to prolong its shelf-life. It undergoes gradual decomposition with evolution of carbon dioxide after several weeks at room temperature.

A detailed data sheet on **BOC-ON** is available on request.

References:

M. Itoh, D. Hagiwara, and T. Kamiya, *Tetrahedron Lett.*, 4393 (1975); *Bull. Chem. Soc. Jpn.*, **50**, 718 (1977).

19,337-2 BOC-ON **5g \$8.00; 25g \$30.00**
100g \$80.00

Aldrichimica Acta

Volume 10, Number 3, 1977

Deuterium NMR. See page 35.
Selective Reductions Using Borane Complexes. See page 41.

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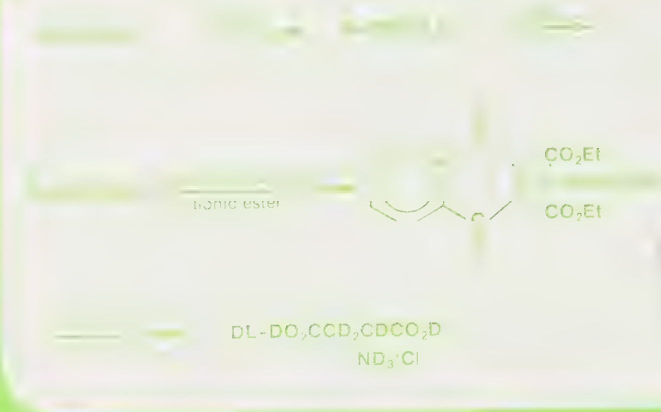
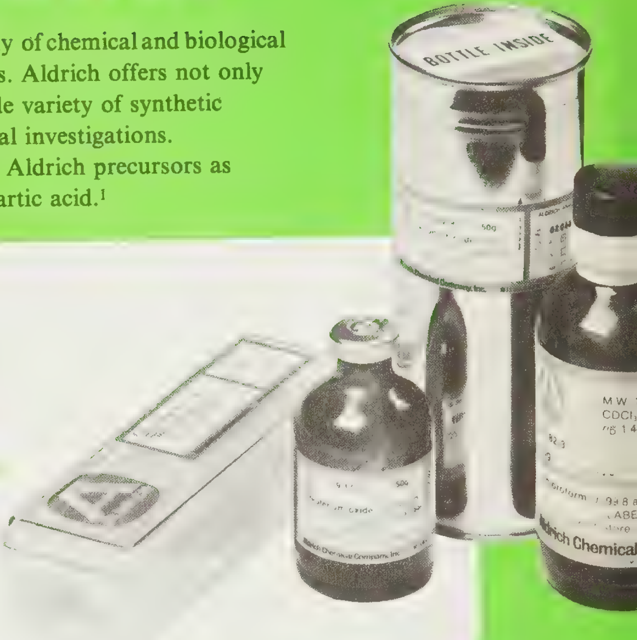
Deuterated compounds from Aldrich

Deuterated compounds have wide potential for the study of chemical and biological systems and in the elucidation of reaction mechanisms. Aldrich offers not only highest quality deuterated solvents, but also a wide variety of synthetic intermediates for both chemical and biological investigations. Deuterated amino acids are readily prepared from Aldrich precursors as in this synthesis of deuterated DL-aspartic acid.[1]





1) A.T. Blomquist, B.F. Hiscock, and D.H. Harpp, *J. Org. Chem.*, **31**, 4121 (1966).

15,178-5	Acetic-d_3 acid-d, 99.5 atom %	5g \$6.00; 25g \$26.00
17,607-9	Acetic-d_3 acid, sodium salt, 99+ atom %	5g \$20.00
15,190-4	Ethyl alcohol-d, 99.5 atom %	25g \$10.00
17,672-9	Deuterium chloride, 20% in D_2O, 99+ atom %	50g \$26.00
17,581-1	L-Glutamic-$N,N,2$-d_3 acid-d_2, 98+ atom %	100mg \$30.00
17,583-8	Glycine-d_5, 98+ atom %	1g \$30.00
17,585-4	Malonic-d_2 acid-d_2, 99+ atom %	10g \$ 8.50

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19,353-4	Borane-d_3-methyl sulfide complex, 98+ atom %, 1M in THF	50ml \$100.00
19,310-0	Lithium aluminum deuteride, 98 atom %	1g \$12.50
18,086-6	Super-Deuteride®, 1M in THF	500ml \$52.00
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About Our Cover:

One of the great differences between the Bible and the histories of most peoples is the forthrightness with which the Bible describes its heroes. The Biblical heroes are described as very human, with frailties and sins often surpassing those of ordinary people. King David, the great psalmist, is considered one of the greatest of Biblical kings. His greatest weakness involved sex, and it is interesting to compare the two best known of his eighteen wives, Bathsheba and Abigail. Each was married when she met David. Bathsheba, David's most famous wife, was willing to commit adultery (and may have enticed David to do so) and stood by idly in her husband's murder. Abigail, by contrast, saved her churlish husband Nabal, though she could not save him from his own greed: he suffered a stroke when he heard of all the provisions Abigail had given to David and his band of outlaws. Jewish tradition says that the four women of surpassing beauty were Sarah, Rahab, Abigail and Esther, and one cannot but wonder what David's life would have been like if he had loved only that beautiful, sensitive and intelligent woman.

This painting (oil on copper, 19-3/4 x 31-1/4 inches) by Frans Francken the Younger, signed and dated 1630, depicts the first encounter of Abigail with David, when she and her maidens bring provisions to appease him. Particularly amusing is David depicted as a medieval knight complete with a banner bearing a harp.

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 the late Professor Wolfgang Stechow is now available to all chemist art-lovers.

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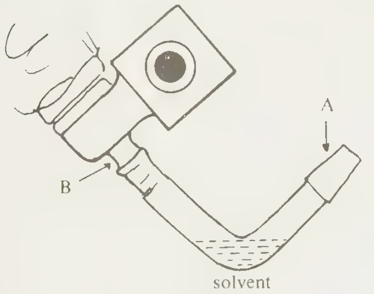
Many of the early issues of the *Aldrichimica Acta* have become very rare. Please do not throw your issues away. In time, we believe that complete sets will become valuable, and — if you do not want to keep them — there probably are chemists near you who would be interested.

Lab Notes

We wish to report a quick and easy method for cleaning a rotary evaporator. A bent connecting tube (distilling apparatus adapter A) is attached to the spindle B. Vacuum is applied on the rotary evaporator. Solvent is introduced through A with a wash bottle. The opening at A is blocked with the thumb until vacuum develops. Controlled release of thumb pressure causes the wash liquid to be aspirated into the condenser. This method consumes little solvent and cleans even the upper parts of the condenser.



Thierry M. de Theux and
Jacques H. Poupaert
Department of Medicinal Chemistry
School of Pharmacy
University of Louvain
B - 1200 Brussels, Belgium

A disturbing problem in overnight chromatographic column operation is the difficulty in adjustment of the stopcock to give a consistent flow rate over long periods of time. A dependable and inexpensive solution to this problem involves the attachment of a length of small-diameter tubing such as polyethylene catheter tubing (.07″ i.d.) to the bottom of the column.

The tubing should be at least as long as the column and the free end of the tubing raised to a level slightly below the solvent level on the column. The tubing can be attached to the bottom of the column with a short length of rubber tubing or a suitable plastic adapter. By opening the stopcock completely and raising or lowering the end of the small-diameter tubing, the flow rate can be accurately adjusted from no flow to the maximum flow rate of the column. Since there is no constriction in the tubing, small particles in the effluent cannot stop the flow as frequently occurs in a partially closed stopcock. A uv monitor can be easily spliced in series with the tubing leading from the column to the fraction collector. A constant-level, "chicken feeder" type solvent supply system such as an inverted volumetric flask should be used to add solvent to the column.

Robert D. Elliott
Southern Research Institute
Birmingham, Alabama 35205

The difficulty and inconvenience associated with accurate control of slow addition using standard addition funnels lead many to use the more expensive Hershberg funnel or a syringe pump. A simpler solution providing excellent results is the following: the plug of an ordinary addition funnel is scored with a file to about 90° around from one hole; this procedure is repeated on the other side. The flow rate is now much more finely metered. A uniform scratch gives a flow proportional to plug rotation; a tapered one provides a larger range of flow rates. In either case, the exact dimensions and alignment are not critical. The same technique works equally well for Teflon® plugs; here a razor blade may prove more effective than a file.

Alaric Naiman
Department of Chemistry
University of California
Berkeley, CA 94720

Many laboratory-scale reactions are carried out at Dry-Ice/acetone temperatures over periods of several hours. The scale of these reactions is frequently such that the reaction flask will not fit into normal-size Dewar vessels, and large Dewar vessels are expensive. We have found that a large crystallizing dish placed in a cardboard, or preferably wooden, box and surrounded by vermiculite (often obtainable as the packing around chemicals) is ideal for such cold baths. A cardboard top taped or nailed to the box and with a hole cut for the crystallizing dish ensures that the vermiculite remains in place. Vermiculite has the advantage over polystyrene in that it does not "dissolve" during solvent spill-over. This apparatus can also be used with a magnetic stirrer whereas, with Dewar vessels, this is often difficult.

P. Horsewood
Department of Chemistry
McMaster University
Hamilton, Ontario L8S 4M1

When extracting with chloroform from an aqueous phase of a very darkly colored reaction mixture, the problem of determining the point of division between the two phases in the separatory funnel often arises.

Given that a reasonably good phase separation has taken place, a small quantity of Celite filter-aid added through the top of the separatory funnel will settle down between the two phases, thus clearly delineating the point of separation. The Celite can later be filtered off.

James P. Hasak
270 Baldwin Road
Parsippany, NJ 07054

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.

A number of biochemists had talked to me about the great usefulness of methotrexate (MTX, amethopterin) in the isolation of enzymes by affinity chromatography [B.T. Kaufman and J.V. Pierce, *Biochem. Biophys. Res. Commun.*, **44**, 608 (1971); B.T. Kaufman and V.K. Kemerer, *Arch. Biochem. Biophys.*, **172**, 289 (1976); B.T. Kaufman, *Methods Enzymol.*, **34**, 272 (1974)].

The only difficulty was that methotrexate was selling at hundreds of dollars per gram! The synthesis is quite involved and of many steps, but we are happy to be able to help. We now offer methotrexate at $62/g and we'll be able to reduce the price substantially for larger quantities.

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

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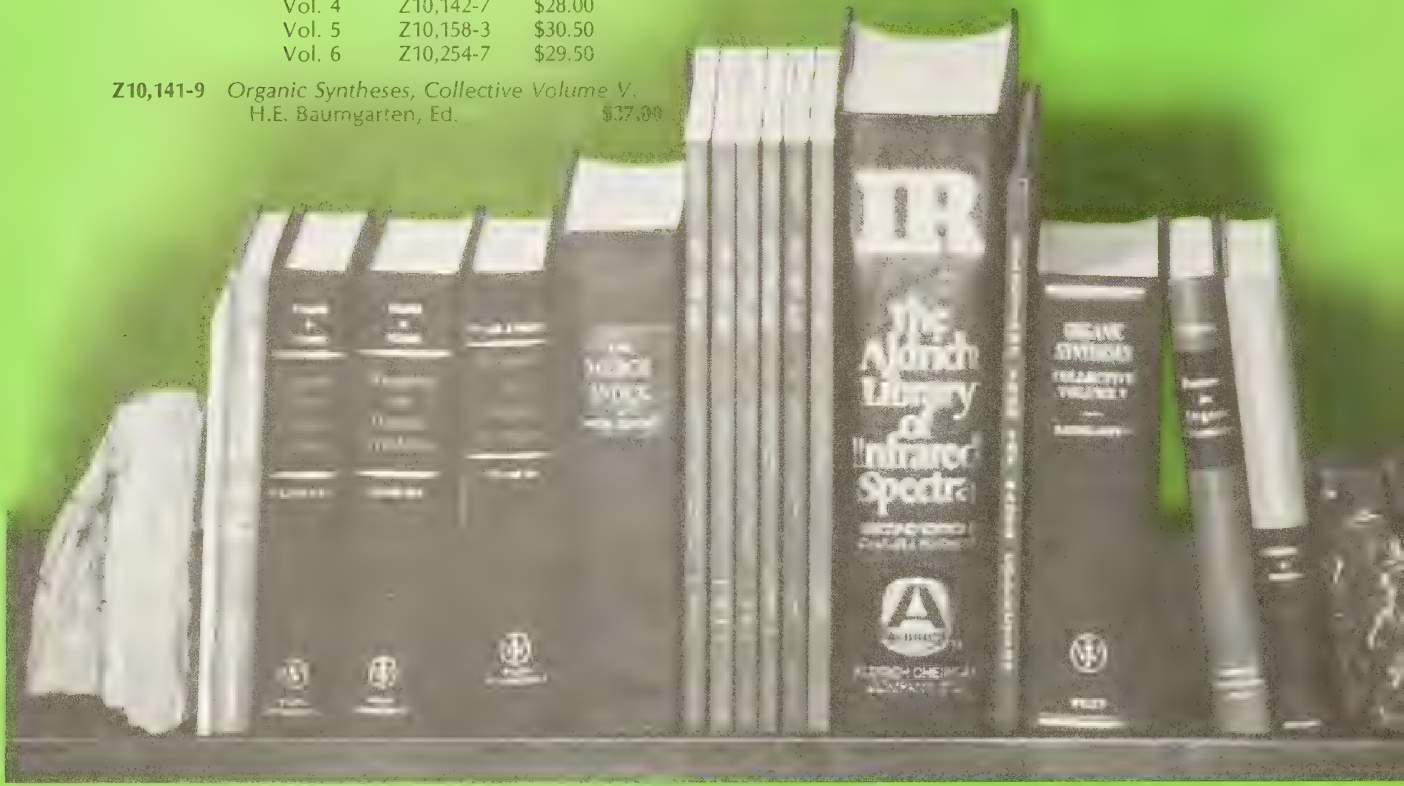

Aldrichimica Acta
Volume 10, Number 4, 1977

Lanthanide NMR Shift Reagents. See page 54.
Synthesis of Conjugated Lactones. See page 64.

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15,189-0	Deuterium oxide	10g $15.00 50g $43.00
19,234-1	Deuterium oxide, low in paramagnetic impurities	30g $50.00
17,664-8	Deuterium chloride, 20% solution in D_2O	5g $42.00 25g $175.00
19,416-6	Methyl-d_3 alcohol-d	1g $19.00 5g(5 x 1g) $60.00
15,691-4	(Methyl sulfoxide)-d_6	5g $35.00 25g $125.00
17,797-0	Pyridine-d_5	1g $15.00; 5g $68.00 25g $245.00

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About Our Cover:

One of our chemist-collector's most interesting paintings is this curious depiction of King Saul and the witch of Endor, by Ferdinand Bol, one of Rembrandt's students, painted around 1650.

Here Saul is shown on his knees in a 'magic circle' complete with skull and crossbones, used in necromancy in the seventeenth century. The despondent figure of Saul is reminiscent of the figure of Judas in Rembrandt's painting of 1629 shown below. Judas and Saul both died the next day, and Bol showed deep insight by depicting Saul in his despair as Rembrandt had painted Judas.

There has been a great deal of discussion among Jewish scholars whether the apparition of Samuel was genuine, hallucination, or an imposture. The Rabbis of the Talmud, while condemning necromancy, also believed in it. Most later scholars either believed that the witch had no powers, but that God wanted the ghost of Samuel to appear to Saul (so Saadya and Nachmanides) or considered it a total fraud (so Maimonides and Ibn Ezra).

Believers in ghosts know that ghosts throw no shadows and one wonders why Ferdinand Bol made the shadow of the ghost of Samuel so prominent.

Rembrandt, *Judas Returning the Thirty Pieces of Silver*

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A Practical Guide To Uses of Lanthanide NMR Shift Reagents

Katherine A. Kime
and
Robert E. Sievers
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Boulder, Colorado 80309

Lanthanide nmr shift reagents have become extremely valuable tools in a relatively short period of time. The potential user of nmr shift reagents needs to know what types of information can be obtained from their use, and how this information can be used in solving problems of chemical importance. This article is concerned with these questions, and topics such as stereochemical studies, polymer studies, chiral shift reagents, and the factors important in choosing a shift reagent for a particular application will also be discussed. Several general works on shift reagents have been published.[1-6] The present paper is intended primarily as a practical user's guide, in contrast with several previous reviews which were directed principally at people doing research on shift reagents.

In 1969, Hinckley[7] found that the dipyridine adduct of $Eu(thd)_3$ [$Eu(thd)_3$ = tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III), also called $Eu(dpm)_3$, where $Eu(dpm)_3$ = tris(dipivaloylmethanato)europium(III)] induced shifts in the nmr spectrum of cholesterol monohydrate. Sanders and Williams[8] then found that unsolvated $Eu(thd)_3$ was even more effective as a shift reagent than the dipyridine adduct, inducing shifts up to four times as great in magnitude. Since this early work, over 600 publications concerning shift reagents have appeared. Approximately 400 of the earlier articles are referenced in the bibliography of the book, "Nuclear Magnetic Resonance Shift Reagents,"[2] so they are not repeated here.

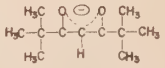
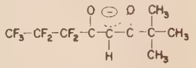
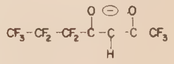
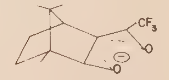
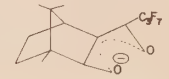
The most commonly used shift reagents are lanthanide β-diketonates. They function by acting as Lewis acids, forming a complex with the substance under analysis, which acts as a nucleophile. Induced shifts are attributed to a pseudo-contact, or dipolar, interaction between the shift reagent and the nucleophile.[2] What one normally sees in the "shifted spectrum" are averaged environments of the nuclei in the complexed and uncomplexed nucleophiles. The position of a given peak is consequently related to the stability of the complex formed, the amount of shift reagent added, and the McConnell-Robertson equation, which will be discussed later.

A reasonably large number of different combinations of β-diketonates and lanthanide metals can serve as shift reagents. The most commonly used metal chelates are those of Eu(III) and Yb(III), which normally induce downfield shifts, and Pr(III), which induces upfield shifts. In the earliest studies, complexes of the thd ligands were usually employed. In 1971, Rondeau and Sievers[9] reported that shift reagents which contained the fluorinated ligand, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, $Eu(fod)_3$ and $Pr(fod)_3$, were superior to $Eu(thd)_3$ in clarifying spectra. Figure 1 shows the effectiveness of the fod chelate in altering the spectra of di-*n*-butyl ether. The success of the fluorinated shift reagents was attributed to their improved solubility and increased Lewis acidity due to the electron-withdrawing effect of the fluorine atoms. Table I lists β-diketonates which are commonly employed as ligands.

APPLICATIONS

The simplification and clarification of spectra often yield a great deal of useful information. An elegant example of the use of shift reagents is shown in Figure 2.[10] The completely unintelligible spectrum of friedelan-3β-ol is greatly spread out and simplified, leading to assignment of almost all proton resonances. Demarco *et al.*[11] obtained a first order spectrum of *cis*-4-*tert*-butylcyclohexanol in $CDCl_3$ with addition of increasing amounts of $Eu(thd)_3$. They were then able to determine approximate

Table I. β-Diketonates Commonly Employed as Shift Reagent Ligands[a]

Ligand	Abbreviation	Structure of Anion
2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane)	thd (tmhd) (dpm)	
6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)	fod	
1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedione (1,1,1,2,2,3.3,7,7,7-decafluoro-4,6-heptanedione)	dfhd	
3-trifluoroacetyl-*d*-camphor [3-(trifluoromethylhydroxymethylene)-*d*-camphor]	facam	
3-heptafluorobutyryl-*d*-camphor [3-(heptafluoropropylhydroxymethylene)-*d*-camphor]	hfbc	

[a] Less preferred names and abbreviations are given in parentheses.

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Aldrichimica Acta

Volume 11, Number 1, 1978

A Status Report on Biological Stains. See page 3.
Chemical Reactions of 2,3-Cycloalkenopyridines. See page 13.

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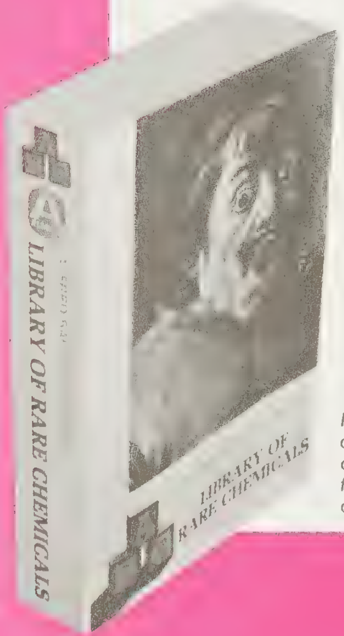
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About Our Cover:

Our chemist-collector loves puzzles — puzzles of authorship and iconography. So he purchased the painting (oil on panel, 18 $^{1}/_{2}$ x 24 $^{3}/_{4}$ inches) shown on our cover, knowing it involved two puzzles.

It is signed 'de Gelder f.' Aert de Gelder was one of Rembrandt's last students, and is one of our collector's favorite artists. Yet this painting does not look like any work of de Gelder that our collector has ever seen, and so he wonders whether he misreads the signature, or whether it is an early work of de Gelder before the artist came under Rembrandt's influence.

The other puzzle involves the scene depicted. It has been called *Esther before Ahasuerus*, specifically when Esther comes before the King knowing her life depends on his stretching out his scepter. In many Dutch depictions of this subject, Esther faints, a detail taken from the apocryphal rather than the Biblical Book of Esther. Here, the beautiful, young Esther is as self-assured as could be, in delightful contrast to the King. But is it really Esther? Or could it be the King's first wife, Vashti, refusing to dance before the King? Or perhaps even a non-Biblical subject?

Our chemist dislikes the Book of Esther more than any other book of the Bible, because one of the two villains of the story, Ahasuerus, that gluttonous King, without whose acquiescence Haman would never have succeeded in the first place, not only goes scot-free but is rewarded by marriage to Esther. Why then, we asked our chemist, did he buy another painting of Esther? Well, he replied, beauty, in this case particularly of color, comes first, and perhaps what has happened with the first painting of 'Esther' illustrated on the *Aldrichimica Acta,* Vol. 7, No. 1 (1974) will happen again: that work by Leonard Bramer was shown later to be of the *Queen of Sheba before King Solomon* rather than Esther before Ahasuerus. The Lions of Judah in the throne, the gifts in the left foreground and the absence of the King's scepter are proof that it depicts the Ethiopian Queen rather than Esther.

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 the late Professor Wolfgang Stechow is now available to all chemist art-lovers.

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At last! a responsible, expert source for biological stains and dyes

Meet Dr. Floyd Green, member of and consultant to the Board of Trustees of the Biological Stains Commission and a fourteen-year member of the ACS Analytical Reagents Committee.

Dr. Green is the quiet, capable man heading the Aldrich Chemical Company's growing new Stain and Dye Division that, with good reason, bears his name. When he joined Aldrich in the fall of '77, it was expressly for the purpose of establishing and directing the new division which was being created to fill the void caused by legislation and economic conditions that had strangled many commercial dye sources. To take on this task, Dr. Green gave up his own business — Aristo Custom Chemicals, Inc., Cincinnati, Ohio.

Today, he deserves world-wide respect for his record as a manufacturing chemist and for his comprehensive knowledge in the area of stains and dyes.

In college, Green had been leaning originally toward a career in medicine. He received his baccalaureate in biology from Maryville College in Maryville, Tennessee, but then World War II came. He joined the Navy which sent him to the Naval Medical School in Bethesda, Maryland. His training there centered on malaria and epidemiology. Subsequently, he was sent to the Pacific theater where he spent the next 26 months obtaining epidemiological profiles on the native population. It was there that he had his first exposure to stains, having had to prepare and analyze thousands of blood smears daily.

When the war ended, Green went to work as an assistant to one of the U.S. pioneers in biological stains, Arthur Coleman, who was one of the entrepreneurs in the field (Coleman and Bell). Green worked directly with Coleman for five years. The work was difficult. It was then that he became aware of the lack of reliable published information on stains and dyes.

All in all, Green invested 27 years with MCB, though he found time to attain the M.S. in chemistry from the University of Cincinnati in 1950. He also received an M.S. in biochemistry and chemistry in 1967 and a Ph.D. in 1969 from St. Thomas Institute of Advanced Studies. His thesis for the latter was based on work he had done with a University of Illinois pathologist. Their months of work together — alternate weekends in Illinois and Ohio — were directed toward cross-linking agents relative to stabilizing and preserving badly decayed teeth. Their initial work sought to use Procion dyes to stabilize collagen in teeth pulp, and it evolved into the development of colorless cross-linking agents to replace the Procions. Consequently, papers were presented to the Dental Research Institute and 13 patents were issued.

During his years with MCB and after, Green did additional graduate work at St. Xavier and M.I.T.

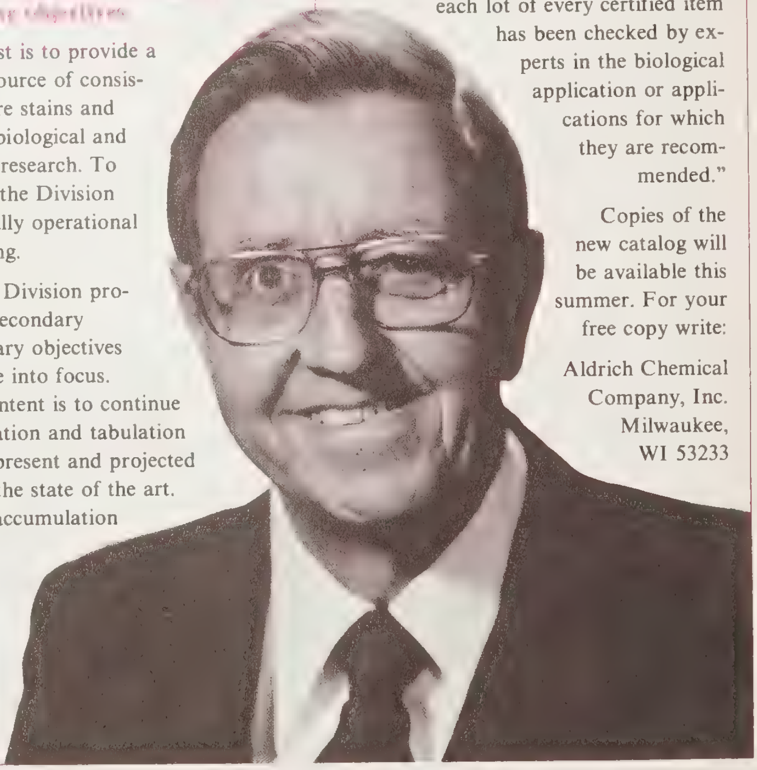
Dr. Green and the Floyd Green Stain and Dye Division of the Aldrich Chemical Company, Inc. have three objectives.

The first is to provide a reliable source of consistently pure stains and dyes for biological and scientific research. To this end, the Division will be fully operational this Spring.

As the Division progresses, secondary and tertiary objectives will come into focus. Green's intent is to continue accumulation and tabulation of past, present and projected data on the state of the art. It's this accumulation that will form the basis for what, in fact, might be this country's, if not the world's, first library of stains and dyes; and following this development, the Division could well become a center for consultation within the industry.

As Green puts it in the foreword to the Division's first catalog: "This manufacturing division is dedicated to providing quality products whether well known or only recently described in the literature. The scope of the manufacturing capability of this division sets it apart from most other domestic sources of biological stains and chemical indicators, and the uniqueness does not stop there. Indeed, traditional quality-control methods have been supplemented with cross checks wherever appropriate. For example, uv-visible and wet-method dye-concentration determinations are routinely correlated to C, H and N determinations.

"Items that are on the Biological Stain Commission list of certified stains are submitted to the Commission for certification. Thus, you can be assured that each lot of every certified item has been checked by experts in the biological application or applications for which they are recommended."



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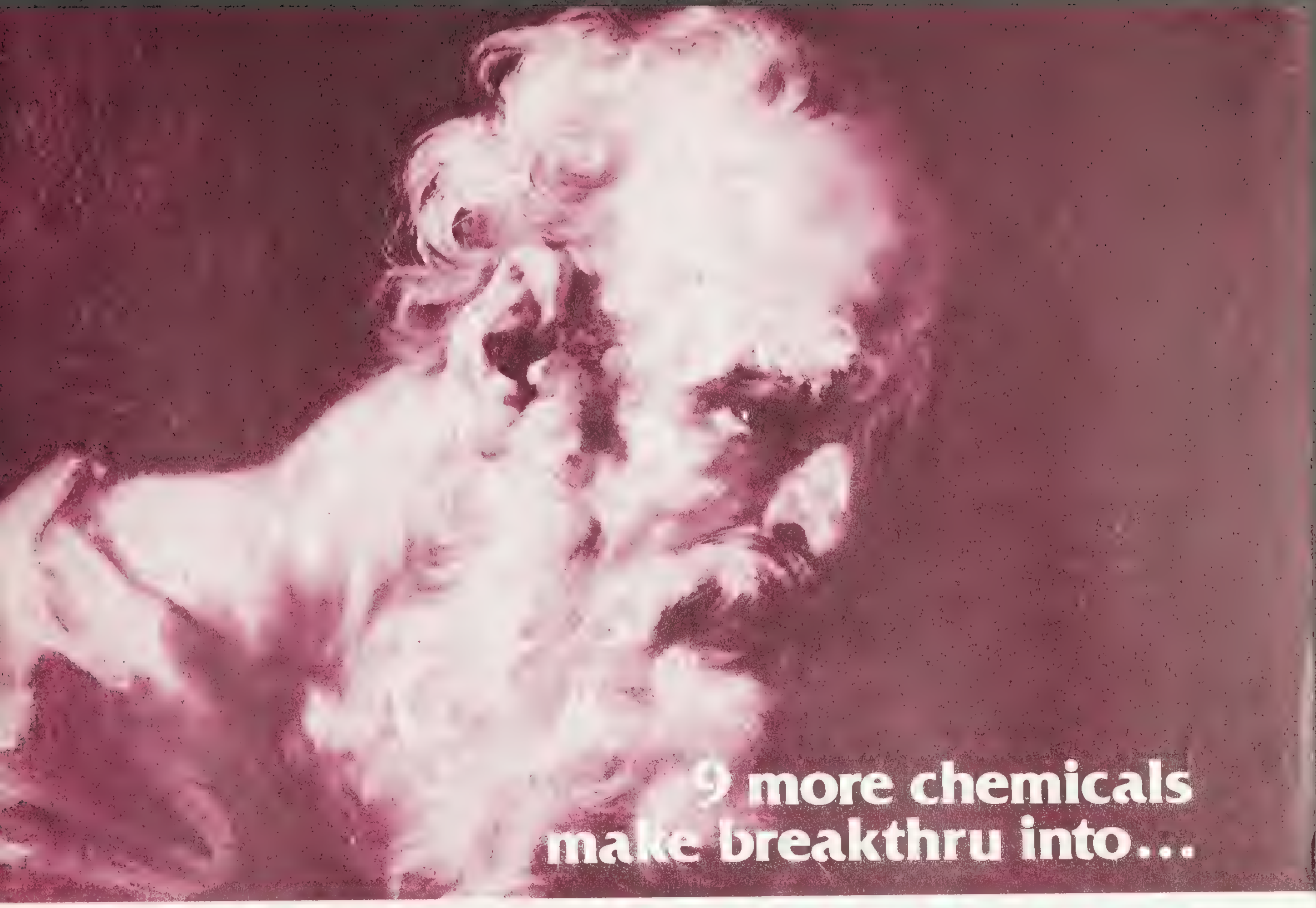
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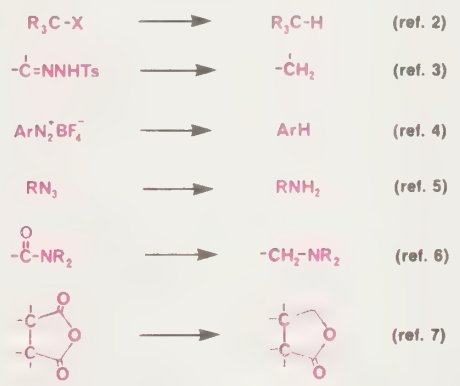
$NaBH_4$ readily reduces aldehydes and ketones in aqueous or alcoholic solvents. In an aprotic solvent such as diglyme, acid chlorides are rapidly reduced to alcohols. In the above solvents at 25°C, many other functional groups, including lactones, epoxides, esters, carboxylic acids and salts, nitriles, and nitro groups are essentially inert to $NaBH_4$.[1]

The reduction of aldehydes, ketones, and acid chlorides with **$NaBH_4$** is well known. However, numerous other interesting reductions have been reported using this reagent. The following are a few examples:



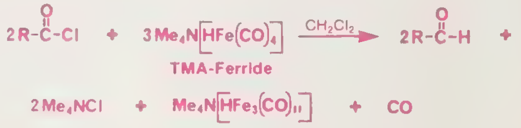
References:
1) H.C. Brown, "Hydroboration," W.A. Benjamin, Inc., New York, N.Y., 1962 (Aldrich Catalog No. Z10, 078-1, $20.00).
2) H.M. Bell and H.C. Brown, *J. Am. Chem. Soc.*, **88**, 1473 (1966); R.O. Hutchins, *et al.*, *J. Org. Chem.*, **36**, 1568 (1971).
3) L. Caglioti, *Tetrahedron*, **22**, 487 (1966).
4) J.B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 1251 (1961).
5) P.A.S. Smith, *et al.*, *ibid.*, **84**, 485 (1962).
6) Y. Kikugawa, *et al.*, *Chem. Pharm. Bull.*, **17**, 98 (1969).
7) D.M. Bailey and R.E. Johnson, *J. Org. Chem.*, **35**, 3574 (1970); S. Takano and K. Ogasawara, *Synthesis*, 42 (1974).

19,807-2 Sodium borohydride 100g $13.10
500g $38.50; 2kg $121.00

TMA-Ferride™

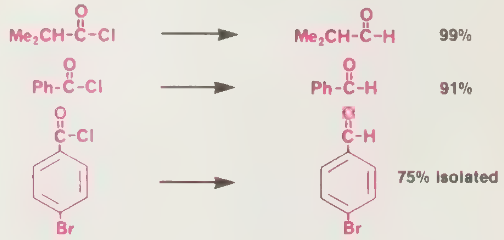
Recently, Cole and Pettit described the preparation and utility of a new reducing agent, **tetramethylammonium hydridoirontetracarbonyl.**[1] Aldrich now offers this reagent under the trade name **TMA-Ferride.™**

TMA-Ferride provides a mild and facile method for the reduction of acid chlorides to aldehydes in excellent yields.



$$2R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + \underset{\text{TMA-Ferride}}{3Me_4N[HFe(CO)_4]} \xrightarrow{CH_2Cl_2} 2R\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + 2Me_4NCl + Me_4N[HFe_3(CO)_{11}] + CO$$

This procedure was applied to several acid chlorides, including the following:



The ease and simplicity of this conversion of acid chlorides to aldehydes provides an improvement over existing methods.

Sodium and potassium hydridoirontetracarbonyl are useful for reductive alkylations,[2] hydroacylations,[3] dehydrogenations,[4] desulfurizations,[5] and hydrogenations.[6] However, the alkali metal hydridoirontetracarbonyl reagents can only be prepared and utilized in concentrated alkaline solutions. **TMA-Ferride** now provides a neutral source of the interesting hydridoirontetracarbonyl anion.

References:
1) T.E. Cole and R. Pettit, *Tetrahedron Lett.*, 781 (1977).
2) G.P. Boldrini, *et al.*, *Chem. Commun.*, 359 (1974), and *Synthesis*, 733 (1974); Y. Watanabe, *et al.*, *Tetrahedron Lett.*, 1879 (1974), and *Chem. Lett.*, 1265 (1974).
3) T. Mitsudo, *et al.*, *ibid.*, 1385 (1974).
4) H. Alper, *Tetrahedron Lett.*, 2257 (1975).
5) H. Alper, *J. Org. Chem.*, **40**, 2694 (1975); H. Alper and H.-N. Paik, *ibid.*, **42**, 3522 (1977).
6) R. Noyori, *et al.*, *ibid.*, **37**, 1542 (1972).

19,943-5 TMA-Ferride™ 50g $38.00

Aldrichimica Acta

Volume 11, Number 2, 1978

Recent Progress in Macrolide Synthesis. See Page 23.

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About Our Cover:

As we have mentioned before, our chemist-collector likes nothing better than to determine the meaning and authorship of old paintings. Some years ago he bought the wild and colorful painting (oil on canvas, 29 x 46 inches) reproduced here, at an auction in Lucerne. It was attributed then to Aert de Gelder and was called *The Counting of the Children in Bethlehem*. De Gelder is one of our chemist's favorite artists, and he is convinced that that attribution was as wrong as the title — in fact, no counting of the children in Bethlehem is recorded in the Bible. At first our chemist thought that it might depict the judgment of Solomon or, perhaps, Elisha with the widow of Obadiah (II Kings *4*), but now he is convinced that it is really *Joseph Selling Food to the Egyptians*. Pharaoh had "arrayed Joseph in vestures of fine linen, and put a gold chain about his neck" (Genesis *41*, 42). The scene is based on the 47th chapter of Genesis, when the Egyptians had become desperate and were selling themselves and their families to Pharaoh.

Our chemist believes that this painting is by a greatly underrated Amsterdam mid-seventeenth century painter, Jan van Noordt, who, from this painting, appears as a link between Rembrandt and the Venetian masters of the 18th century. The girl on the left looking at us seems to have walked right out of Rembrandt's *Nightwatch*; yet the whole atmosphere and, particularly, the bright colors, blue, gold and pink, remind us more of Tiepolo and his followers, or — in the draftsmanship of the social realism on the left — even of Daumier!

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1-Bromo-2,2-dimethoxypropane is a precursor to 3-bromo-2-methoxy-1-propene, a monoalkylating agent that introduces the acetonyl side chain into acids, nitriles, esters, ketones, dialkylamides, enamines and imines in good to excellent yields. Alkylation of the lithium salt of imines, followed by hydrolysis, leads to α-acetonyl ketones which undergo cyclization to yield 3,4-disubstituted cyclopentenones.

R.M. Jacobson, R.A. Raths, and J.H. McDonald III, *J. Org. Chem.*, **42**, 2545 (1977).

20,880-9 1-Bromo-2,2-dimethoxypropane 10g $7.50
50g $25.00

1,3-Propanediol

1,3-Propanediol has been used recently by Professor John C. Stowell for the synthesis of γ-keto aldehydes and ketones. The synthetic sequence is, in effect, a versatile, three-carbon homologation.

J.C. Stowell, *J. Org. Chem.*, **41**, 560 (1976).

P5040-4 1,3-Propanediol (trimethylene glycol) **100g $7.50**
500g $31.35

Ethyl α-Bromocyclobutanecarboxylate

This bifunctional ester is a convenient precursor to ethyl cyclobutenecarboxylate, a useful 4-carbon component in the photochemically mediated synthesis of functionalized cyclohexane derivatives.

Wender and Lechleiter have recently applied their annulation methodology to the synthesis of (±)-10-epijuneol.

P.A. Wender and J.C. Lechleiter, *J. Am. Chem. Soc.*, **100**, 4321 (1978).

19,729-7 Ethyl α-bromocyclobutanecarboxylate 5g $16.35
25g $58.50

New Oxidizing Agent

Barium manganate was recently reported as an efficient reagent for the oxidation of primary and secondary alcohols to carbonyl compounds. Yields of 80-95% were obtained when the alcohols were stirred with an excess of $BaMnO_4$ at room temperature for 4-16 hours.

H. Firouzabadi and E. Ghaderi, *Tetrahedron Lett.*, 839 (1978).

21,019-6 Barium manganate 25g $18.00
100g $48.00

Reactive Diene

5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene, a highly reactive diene, was used by Jung and Hudspeth to achieve three-carbon annulation, the formation of five-membered rings from olefins.

M.E. Jung and J.P. Hudspeth, *J. Am. Chem. Soc.*, **99**, 5508 (1977).

20,098-0 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene
25g $20.00

A Novel Wittig-Horner Reagent

Only a few examples are known for the condensation of α-substituted triethyl phosphonoacetates with ketones. The Wittig-Horner reaction of **triethyl 2-phosphonopropionate** with a wide variety of ketones forms tetrasubstituted acrylates in high yield (40-85%).

1) G. Gallagher, Jr. and R.L. Webb, *Synthesis*, 122 (1974).
2) O.P. Vig, R.C. Anand, S.D. Sharma, and M.L. Sharma, *J. Indian Chem. Soc.*, 52, 859 (1975).

17,465-3 Triethyl 2-phosphonopropionate 10g $8.40
50g $28.00

Benzothiazoles: Carbonyl Equivalents

Recently, Corey and Boger used vinylbenzothiazoles, equivalents of formyl-stabilized anions or formyl-substituted Michael acceptors, as intermediates for the conversion of cyclic ketones into spiro and fused annulation products. The vinylbenzothiazoles were easily prepared from the lithiobenzothiazoles. The extension of this work and its application to interesting synthetic problems will surely be the subject of future research.

E.J. Corey and D.L. Boger, *Tetrahedron Lett.*, 5, 9, 13 (1978).

10,133-8 Benzothiazole 100g $8.00
500g $14.50
11,214-3 2-Methylbenzothiazole
100g $9.35; 500g $31.70

N-Chlorocarbonyl Isocyanate

N-Chlorocarbonyl isocyanate reacts with alcohols, phenols, mercaptans, secondary amines, sulfonamides, imines, and certain olefins and carbonyl compounds to produce a variety of interesting derivatives, including novel heterocyclic systems.

The chemistry of this versatile building block is the subject of a recent review.[1]

1) H. Hagemann, *Angew. Chem., Int. Ed. Engl.*, **16**, 743 (1977).

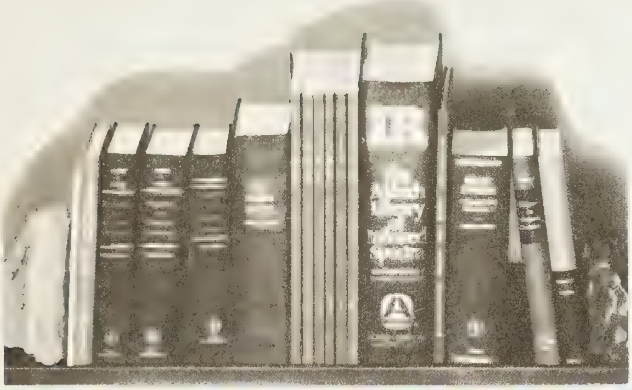
20,100-6 *N*-Chlorocarbonyl isocyanate
5g $10.00; 25g $33.75

New Reagent for α-Methylenation of Ketones

***N*-Methylanilinium trifluoroacetate** has been found to be an efficient reagent for the direct α-methylenation of ketones in a mild and simple reaction giving good yields of α-methylene ketones.

J.-L. Gras, *Tetrahedron Lett.*, 2111 (1978).

21,008-0 *N*-Methylanilinium trifluoroacetate 25g $6.50
100g $22.00



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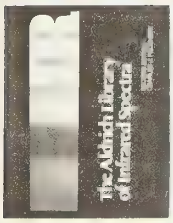

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STAINS & DYES

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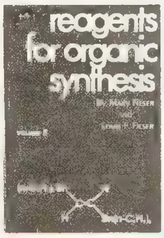
Z10,341-1	N. I. Sax, "Dangerous Properties of Industrial Materials," Van Nostrand Reinhold Co., New York, NY, 1975.	$44.50
Z10,274-1	K. Verschueren, "Handbook of Environmental Data on Organic Chemicals," Van Nostrand Reinhold Co., New York, NY, 1977.	$37.50



REAGENTS FOR ORGANIC SYNTHESIS, by Mary Fieser and Louis F. Fieser.
This is Volume 5 and it covers literature on reagents published from 1972 to August 1974. The book includes references to approximately 350 reagents reviewed by the Fiesers for the first time as well as references to over 400 previously discussed reagents. Order Z10,158-3; Price, $32.75.

ORGANIC SYNTHESIS

Z10,313-6	W. P. Weber and G. W. Gokel, "Phase Transfer Catalysis in Organic Synthesis," Springer-Verlag, New York, NY, 1977.	$29.80
Z10,255-5	M. Fieser and L. F. Fieser, "Reagents for Organic Synthesis," 6-volume set, Wiley-Interscience, New York, NY.	$160.00

Vol.	Cat. No.	Price	Year
Vol. I	Z10,250-4	$47.00	1967
Vol. II	Z10,251-2	$29.25	1969
Vol. III	Z10,252-0	$28.50	1972
Vol. IV	Z10,142-7	$30.00	1974
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"Organic Syntheses," Collective Volume Series, John Wiley & Sons, Inc., New York, NY.

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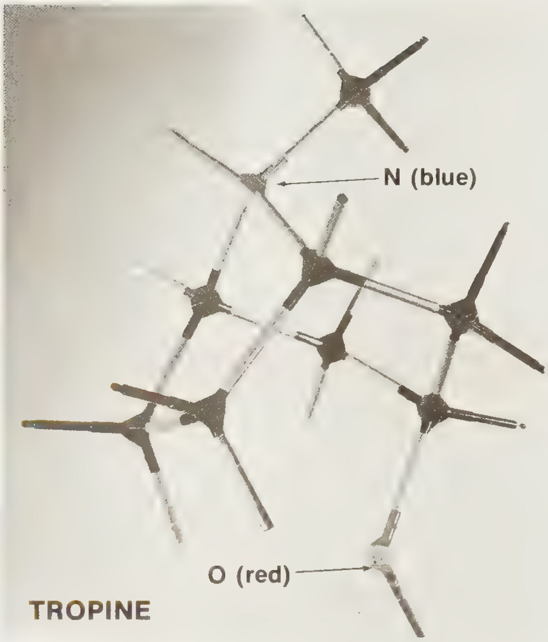
References:
(1) L.F. Fieser, *J. Chem. Ed.*, **40,** 62 (1963).
(2) L.F. Fieser, *ibid.*, **40,** 457 (1963).
(3) L.F. Fieser, *ibid.*, **42,** 408 (1965).
(4) L.F. Fieser, "Chemistry in Three Dimensions," Aldrich Catalog Number Z10,160-5.



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Aldrichimica Acta

Volume 11, Number 3, 1978
(Last issue in 1978)

Selenium Reagents. See Page 43.
Organic Sulfur Compounds in Organic Synthesis. See Page 51.

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About Our Cover:

Some time ago, our chemist-collector was invited to speak to the New Orleans section of the ACS, and there he saw, in an elegant furniture store, this beautiful painting of a church interior (oil on canvas, 36 x $42^{1}/_{2}$ inches). The painting was nameless, rather dirty and hung so high that it was difficult to see; yet our chemist was so struck by its beauty and particularly by the subtle handling of light, that he bought it.

He now believes that it was painted by one of the able mid-seventeenth century Dutch painters, Job Berckheyde, and that it depicts a Protestant church — perhaps real, perhaps imaginary. If any of our Dutch readers knows the specific church, please let our collector know.

Our chemist is a Jew, and we asked him whether he had any qualms about buying a painting of a church. He replied, "Of course not. Whenever I am in a beautiful church or see a fine painting of one, I realize with what devotion it was built or painted, and I think of Jacob's exclamation at Bethel — 'This is none other but the house of God, and this is the gate to heaven.' "

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

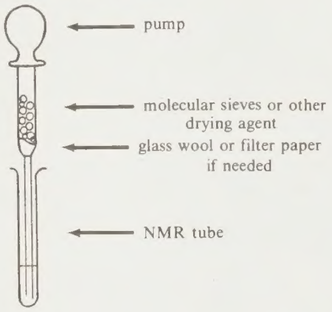
Also, many paintings reproduced on our Acta covers were shown at the Milwaukee Art Center in an exhibition, "The Bible Through Dutch Eyes," arranged by Dr. Bader in 1976. The fully illustrated catalog with 66 black-and-white and 4 full-color reproductions contains many art historical and Biblical comments.

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

I would like to report a convenient method of drying a small amount of sample inside an NMR tube.



Often, after obtaining a spectrum, we found that the sample contained moisture. Here is a good way to dry a sample. Fill a disposable pipet (which can be made from glass tubing to desired length) with molecular sieves and any other drying agent, then pump the sample solution through a few times. The solution will be thoroughly dry, and the drying agent can be washed with a small amount of solvent.

Jordan C. Fan
Department of Chemistry
Cleveland State University
Cleveland, Ohio 44115

Sintered glass filter funnels are often difficult to clean. The following procedure works quite well. Place the funnel in a beaker or other suitable container. Add concentrated H_2SO_4 to completely cover the bottom of the funnel. *Carefully* add 5-6 drops of 30% H_2O_2 down the side of the funnel. Mixture will effervesce and froth while cleaning the glass frit. After emptying the acid, run water through the filter to rinse out the acid.

S.G. Zipp
Research Associate
State University of New York
College at Cortland
Cortland, New York 13045

Rapid elimination of water and ethanol from chloroform

Chloroform always contains water and ethanol (*ca.* 0.5% w/w, added as stabilizer); however, for some syntheses (*e.g.*, Schotten-Baumann reactions) it is preferable to use a solvent free of hydroxyl-containing impurities.

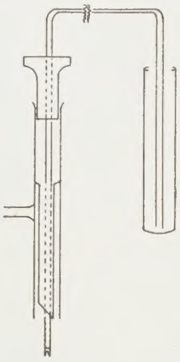
For an expedient purification of a desired quantity, phosphorus pentoxide is poured into chloroform; anhydrous solvent is recovered by vacuum distillation on a rotating evaporator. (Note: an efficient dessicant guard tube should be placed between the evaporator and the water aspirator!)

The solvent is stable for some days in dark bottles, as checked by the absence of the 1809 cm^{-1} absorption (C = O vibration of phosgene) in its IR spectrum.

Jean-Claude Bollinger
Laboratoire de Chimie Générale
et Analytique
Faculté des Sciences
123 rue Albert Thomas
87060 Limoges, Cedex, France

For those who routinely use fraction collectors, the transfer of fractions from test tubes to some larger vessel is very tedious, not to mention the possibility of spilled fractions and broken test tubes.

In our laboratories, we have solved these problems in a very simple manner. Shown below is a diagram of a vacuum-transfer apparatus. It consists of a vacuum adapter with 14/20 ground-glass joints, a 14 x 18-mm rubber septum and 1-m length of 1.55-mm i.d. Teflon tubing. The septum is placed on the top joint and the Teflon-tubing inserted to 1-2cm beyond the drip spout.



When vacuum is applied, the free end of the tubing is immersed into the fraction tube. All the solvent is then drawn into the collection flask. After rinsing twice, the test tube is ready for reuse without having been removed from the fraction collector. Of course, this process does not eliminate periodic cleaning of all the test tubes.

John N. Dynak
Postdoctoral Fellow
Department of Chemistry
University of California
Los Angeles, California 90024

"Please Bother Us."

by Alfred Bader.

For many years the Fieser molecular models were the best models and by far the least expensive on the market. Then their production stopped and they became collector items. As a Fieser student, I really missed them and was just so happy when I was able to arrange for their production recently. We decided to offer them in research kits containing 30 carbon atoms, enough that one could build a steroid model.

Many professors then called and wrote, suggesting that there was real need for these models for undergraduates also, but that students would not want to spend $18.00 for a research kit. We had several choices, *e.g.*, offer a smaller kit at $8.00 to $10.00, or offer the models so inexpensively to chemistry department storerooms, that the models could be resold individually to students at very low prices. We chose the latter, and offer the models in lots of 100. Thus, storerooms can now offer, say, six carbon atoms, one oxygen and one nitrogen model for under $4.00.

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

Z10,400-0	**Fieser Molecular Model Research Kit**	**$18.00**
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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 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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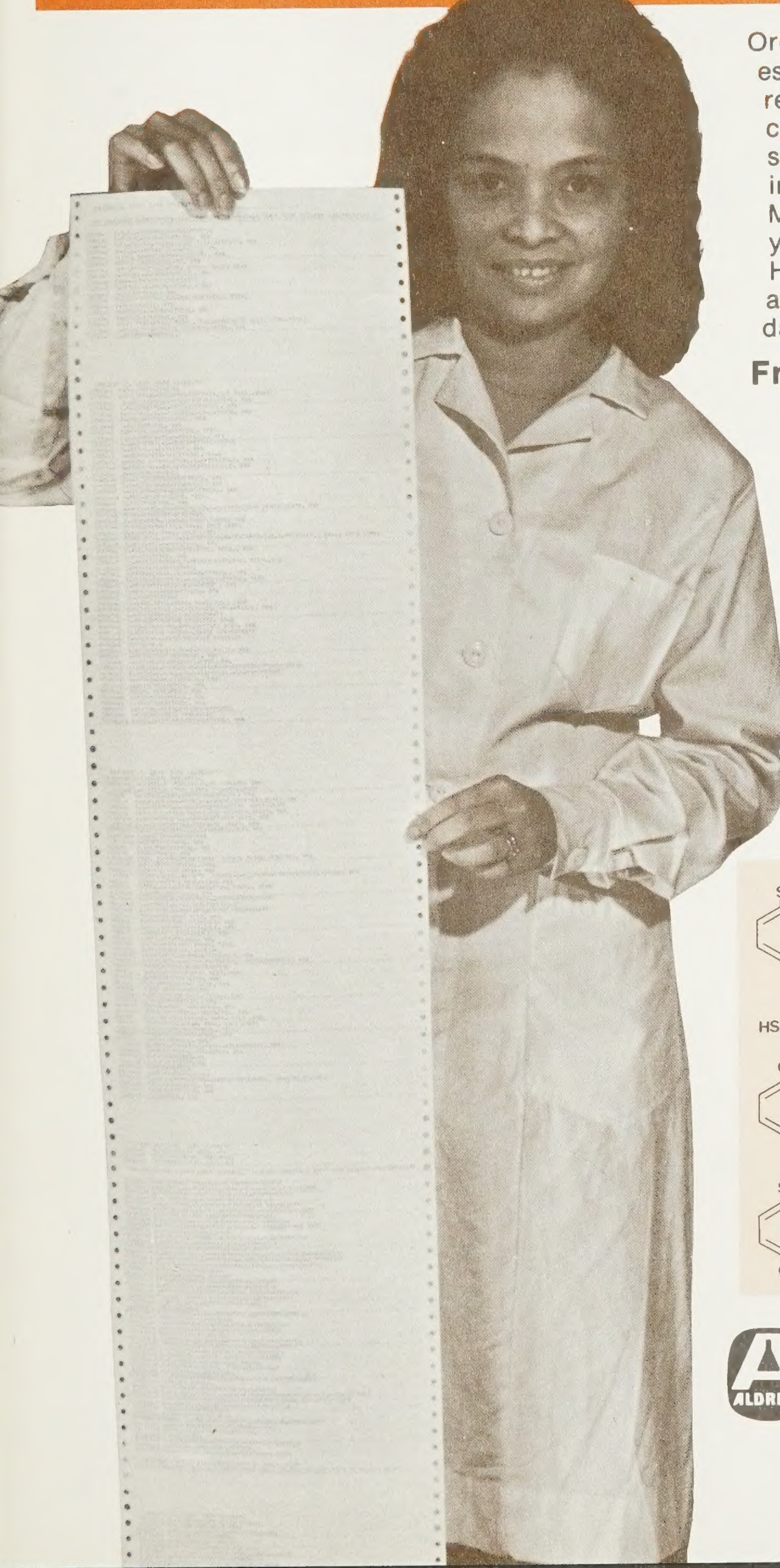

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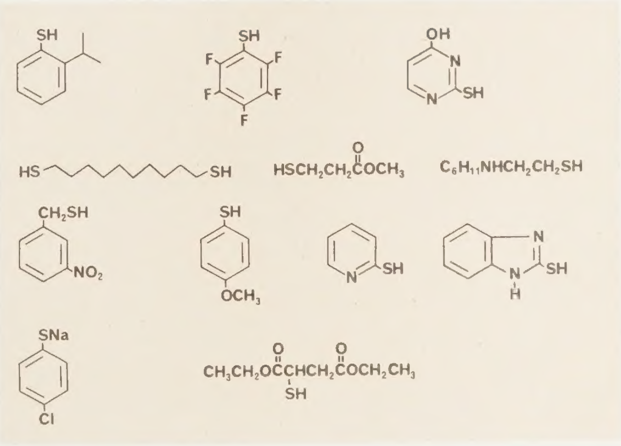
*See for example, the following reviews: B.-T. Gröbel and D. Seebach, *Synthesis*, 357 (1977); L. Field, *ibid.*, 101 (1972); E. Block, *J. Chem. Ed.*, **48,** 814 (1971).



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Check our 1979/80 Catalog/Handbook. If you don't find what you need, give us a call. We probably will want to add it to our inventory if we haven't done so already. We want to be *the* chemical source you can rely on, so your input counts. Our expectations are great and yours can be too.

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