





Dr. Alfred Bader 924 East Juneau, Suite 622 Milwaukee, Wisconsin 53202 Phone: 414/277-0730 Fax: 414/277-0709 E-mail: alfred@alfredbader.com

A Chemist Helping Chemists

September 12, 2003

Dr. David Harvey 1470 E. Bay Point Rd. Whitefish Bay, WI 53217

Dear David,

Last June I visited a company in Vienna, POC, which has a very interesting biocide which they call AKACID. Their descriptive bulletin is enclosed. It is marked "Confidential" but I received their specific permission to pass it by Sigma-Aldrich because it might be worthwhile listing as a product.

Note that they have EU registration but not EPA registration.

Of course you're right that many start-up companies have greatly inflated ideas of their value. So it is with POC who would like me to invest a few million dollars. This is not for me, but I do think that the product may be really interesting.

Please return the booklet at your convenience.

As you will see from the enclosed, I am giving the Glenn Ullyot Lecture at the Chemical Heritage Foundation next Thursday evening. It is entitled *The Story of Aldrich: The Rocky Road to Success* and I wish that you could listen to it.

Thank you for your letter of August 25<sup>th</sup>.

I was glad to see that Chris Hewitt is meeting with the President of Fluorous Technologies later this month. They certainly have an interesting product line and great advertisements, copy of one is enclosed.

With best wishes I remain

Yours sincerely,

MHIL

Alfred Bader AB/az Enc.



mailbox:///C|/Documents%20and%20Settings/Ann/Application%20...

Subject: FW: Coalite From: "David Hudd" <david.hudd@btinternet.com> Date: Wed, 16 Jul 2003 16:27:48 +0100

## To: <baderfa@execpc.com>

Dr Bader

I enjoyed meeting you and look forward to a visit to your castle later this year . Attached is the Coalite information

Best Regards

David

97 Gunterstone Road London W14 9BT Tel:020 7603 0589 Fax:020 7603 4515 Mob:07771 893 267

----Original Message-----From: Akfih@aol.com [mailto:Akfih@aol.com] Sent: 16 July 2003 15:41 To: david.hudd@btinternet.com Subject: Re: Coalite

David

The MD of Coalite Chemicals is George Danson and his email address is:  ${\tt gdanson@coalitechemicals.com}$ 

Regards Tony

This message scanned for viruses by CoreComm

7/17/2003 2:16 PM

Dr. Bader,

I neglected to enclose my resume in my previous letter, so here it is. Sorry about the contusion. Minorlan

> Dr. Alfred R. Bader 924 East Juneau, Suite 622 Milwaukee, WI 53292

Dr. Miroslav/Havranek Columbia University Chemistry Department, M.C.3133 3000 Broadway New York, NY 10027 E-mail: mh525@columbia.edu

November 20, 2001

### Dear Dr. Bader,

I am a Czech postdoctoral fellow at Chemistry Department, Columbia University, working in Prof. Dalibor Sames' laboratory. At the beginning of next year I plan to return home and take an academic position at the Dept. of Organic Chemistry, Institute of Chemical Technology, where I completed my Ph.D. I heard that you would support young organic chemists returning to the Czech Republic after studying in the West under a Bader fellowship. Unfortunately, I am not that case, but came to the United States immediately after finishing my Ph.D. My stay here has had a large impact on my knowledge and orientation in chemistry as a science and I wish to bring this back to my country. Therefore I am asking whether you would be willing to support my research.

In Prague, I will be working with Prof. Dalimil Dvořák, with whom I completed my Ph.D. He is interested in organometallics in organic synthesis, namely carbene complexes of iron and application of organometallic chemistry in the synthesis of new purines. I would focus on introducing a combinatorial approach to this work: First, discovery of new reactions of Fisher carbene complexes, second, discovery of new metal mediated tandem and multicomponent reactions.

My interest in chemistry started in basic school. I entered high school specialized in analytical chemistry, where I was interested in polarography and in analysis of water. At Charles University I decided to study organic chemistry, and I began working at the Academy of Science (Institute of Organic Chemistry and Biochemistry) with Dr. Dalimil Dvořák in 1989. I then worked for Dr. Ivo Starý and Dr. Jiří Závada, with whom I finished my Diploma theses. During my Ph.D. study at the Institute of Chemical Technology I developed methodology for carbon-carbon bond formation on solid phase. I also discovered and developed a coupling reaction for C-C bond formation using hydroalumination. Before my postdoctoral position I was invited to Trega bioscience in San Diego, a small company for combinatorial chemistry and biology, to apply the solid phase methodology. My current project in the laboratory of Prof. Dalibor Sames is development of C-H bond activation catalysts using combinatorial chemistry. I have experiences in organometallic chemistry, organic reaction mechanism, synthesis, analytical techniques, combinatorial and solid phase chemistry.

Your financial support would be crucial to my work. Funding is a constant problem in Czech scientific institutions—one of the reasons that American-educated Czech chemists rarely return home. Salaries are below the national average; the monthly salary for a scientist after 20 years of experience is only about 14,000 Kc (\$350). The non-regulated rent in the big cities, where research is being done, is typically 12,000 Kc for a one-bedroom apartment, so it is difficult to start living there. Despite these facts I would like to return to the Czech Republic and will do so if I have ajm / dequate funding.

I enclose my resume and list of publications. At your request I can send you a research proposal and references to my mentors. I am happy you support organic chemistry in the Czech republic giving Bader Fellowships and Bader awards and I thank you for that.

Sincerely,

Mirolar Havaluel

Miroslav Havranek



# MIROSLAV HAVRANEK

| 400 West 119 <sup>th</sup> Street, Apt. 11V | Phone: (212) 662-0237 home |
|---|----------------------------|
| New York, NY 10027                          | (212) 854-4964 work        |
|   | E-mail: mh525@columbia.edu |

## **Education and Research Experience**

| July 1998 - present | <b>Columbia University</b> , Post-Doctorate Studies in the laboratory of Dalibor Sames. Project: <i>Development of C-H bond activation catalysts using combinatorial chemistry</i> .   |
|---------------------|--|
| May - July 1998     | <b>Trega Biosciences, Inc.</b> San Diego, California<br>Project: <i>Solid phase organic and combinatorial chemistry</i>  |
| 1993 - 1998         | <b>Institute of Chemical Technology, Prague</b> , Ph.D. in Organic<br>Chemistry. Title of Ph. D. thesis: <i>Library based on the palladium</i><br><i>catalyzed C-C bond formation</i> , supervisor: Dr. Dalimil Dvorak   |
| 1988 - 1993         | <b>Charles University</b> , Faculty of Natural Science, major in Organic<br>Chemistry. Title of M. Sc. thesis: <i>Reactivity of polyfunctional</i><br><i>benzylhalogenides. Synthetic and mechanistic study</i> , supervisor:<br>Dr. Jiri Zavada (Institute of Organic Chemistry and Biochemistry,<br>Czech Academy of Sciences, Prague) |

# Publications

Havranek, M.; Dvorak, D., "3,3-Disubstituted allyl alcohols from palladium catalyzed coupling of hydroaluminated propargyl alcohols with aryl iodides" *J. Org. Chem.*, *submitted.* 

Moreira, R.; Havranek, M.; Sames, D., "New fluorogenic probes for oxygen and carbene transfer: A sensitive assay for single bead-supported catalyst," *J. Am. Chem. Soc*, **2001**, *123*, 3927.

Havranek, M.; Dvorak, D., "3-(Tributystannyl)allyl alcohols: Useful building blocks for solid-phase synthesis of skipped dienes and trienes," *Collect. Czech. Chem. Commun.* **2000**, *65*, 434.

Havranek, M.; Singh, A.; Sames, D., "Evolution and study of polymer-supported metal catalyst for oxygen atom transfer: Oxidation of alkanes and alkenes by diamide manganese complexes," *J. Am. Chem. Soc.* **1999**, *121*, 8965.

Havranek, M.; Dvorak, D., "Transmetalation from aluminum to tin: A facile preparation of 3-tributylstannyl-2-propen-1-ols," *Synthesis* **1998**, 1264.

Holy, P.; Havranek, M.; Pankova, M.; Ridvan, L.; Zavada J., "Solvent and leaving group effects on the mono vs. dialkylation of alkali salts of diethylmalonate with 1,2-bis, 1,2,4,5-tetrakis and 1,2,3,4,5,6-hexakis(halomethyl)benzenes. A new insight into selectivity control of malonester synthesis," *Tetrahedron* **1997**, *53*, 8195.

Arnold, Z.; Dvorak, D.; Havranek, M., "Covenient preparation of 1,3-Bis(dimethylamino)-trimethinium perchlorate, tetrafluoroborate and hexafluorophosphate," *Collect. Czech. Chem. Commun.* **1996**, *61*, 1637.

Havranek, M.; Husak, M.; Dvorak, D., "Synthesis of ( $\mu$ -Bis(aminocarbene))dimetal complexes of Chromium and Iron by the reaction of tertiary diamides with Cr(CO)<sub>5</sub><sup>2-</sup> or Fe(CO)<sub>4</sub><sup>2-</sup> in the presence chlorotrimethylsilane," *Organometallics* **1995**, *14*, 5024.

## References

•,

Professor Dalibor Sames Department of Chemistry Columbia University sames@chem.columbia.edu Dr. Dalimil Dvorak Institute of Chemical Technology, Prague dvorakd@vscht.cz Dr. Michal Lebl Senior Director of Automation at Illumina, Inc. San Diego michal@5z.com



22/11/01 09:35 11. 1 FAX FROM : 441316502239 2940 Deve no di la ..... DF., Lord Robert Kilpfords CBE MB ChB Mix On the (Ed. ed of Hound - vel FBA FRSE Principal and Size Upen sites BSE MISSIE MICEM Supporting Teaching, Research and Student Achievement at The University of Edinburg The University of Edinburgh Development Trust is a new to registered in works the Research



# Adventures of the Mind: the Life and Work of Josef Loschmidt

, When atoms and molecules were still quite hypothetical, Loschmidt used kinetic theory to get the first reasonable estimate of molecular size."

At first sight, this is a sentence with an impressive meaning. But who was Josef Loschmidt? His name, along with his significance as a physicist and chemist, is still unknown to people in the Czech Republic and all over the world. Loschmidt's work created the base upon which world renowned scientists built. This is the reason why the general public in the Czech Republic, as well as in English-speaking countries, should become acquainted with Josef Loschmidt. We propose the creation of a TV film and a DVD multimedia programme on his life and work.

# **Dramaturgical Concept**

We do not want to limit ourselves to a mere description of Loschmidt's work, we want to show, in particular, how Loschmidt arrived at his results.

The film will be framed in the context of search and discovery, like the paths of science: posing questions and finding answers. It will reveal step by step the man whose face is depicted on the memorial plaque in Ostrov. This perspective will enable us to present Loschmidt's basic biographical data and follow the step-by-step development of his life.

- The film will also remind us of the time in which Loschmidt lived covering not only the general political situation, but concentrating on the level of science and knowledge. How could he discover the size of molecules without being equipped with any of the instruments and computers, which are considered natural in today's world?
- 2) Contrary to the level of knowledge in the 19th century, we will try to build a picture of the process of his thinking based on his diaries and notes. How is it possible that he could describe molecular structure at the time when nobody knew for certain how substances are structered and what they consist of? We also aim to show what aids he used in his experiments, and then to reconstruct them. However, we do not just want to depict or express the dimensions of his mind, but to show that science and the pursuit of knowledge bring great adventures with them.
- 3) The film will reveal the meaning of Loschmidt's work from the perspective of today's science. We want to emphasize the general validity of his work and to show how he opened the paths of knowledge (although there are some scientists. such as August Kekulé, that did not consider it necessary to admit their acquaintance with the work of this secondary school teacher and yet were most probably inspired by it).

# Sequence of Steps

Due to the exceptional nature of the project, we suggest the following steps:

- In cooperation with Masaryk University in Brno (with Mr Jiří Damborský), collect and study available materials concerning the experiments and thoughts of Josef Loschmidt.
- 2) Prepare a written script on the life of Josef Loschmidt directing attention to detailed descriptions of his experiments and ways how he arrived at them.

- 3) Based on the script, prepare equipment that is not available now but was used by Loschmidt in his experiments. After the film is finished, the equipment can become something of a small exhibition, travelling together with his teachers' chair.
- 4) The film will be produced in two formats a TV film and a multimedia DVD programme.

# The Film and the DVD

The TV film will be designed for the general public, aiming at introducing the personality of Josef Loschmidt, his life and work as well as the way of scientific thought. The multimedia DVD programme will be more detailed and include biographical data about J. Loschmidt, links to the level of science in the 19th century, a detailed description of all experiments and preserved archival materials related to his life and work. The DVD programme could even become something like a set of instructions on how to repeat experiments with the use of simple aids.

# Use

The film will be shot for Czech Television (the expected length is two parts of approx. 28 minutes each). A foreign language version could be offered to other broadcasters, namely the Austrian TV.

The DVD programme would be a valuable addition to every library (- not only science ones) and school in the Czech Republic. Libraries and schools abroad could also be offered the English version of the multimedia DVD programme.

### **Budget**

Estimate of the budget (see Attachment) is only of orientation, it is based on the production cost of a similar project (52 minutes or 2 x 28 minutes documentary).

Budget is divided into two parts: co-producer 1 – investment of customer, co-producer 2 – our investment.

Prague, June 11th, 2004

Martin Hanzlicek Writer, Director

MgA. Jaromir Herskovic Producer. Herafilm



Dr. Alfred Bader 924 East Juneau, Suite 622 Milwaukee, Wisconsin 53202 Phone: 414/277-0730 •Fax: 414/277-0709 E-mail: baderfa@execpc.com

A Chemist Helping Chemists

May 22, 2000

Professor Dudley Herschbach Harvard University Dept. of Chemistry & Chemical Biology 12 Oxford Street Cambridge, MA 02138

Dear Dudley,

Thank you so much for your letter of May 9<sup>th</sup> with that most interesting videotape on the public television program.

May I ask a few questions and make some comments?

Who is the woman introducing the program, who appears to be quite antiscience?

It is interesting to see how the program jumps from Lavoisier to Kekulé and then really concentrates on RBW. Re Lavoisier and oxygen, have you seen or read the play entitled *Oxygen* written by Roald Hoffmann and Carl Djerassi?

RBW knew a great deal about the work of Couper, whose publication almost certainly was written before Kekulé's paper on the quadrivalence of carbon, of 1858. Unfortunately, RBW knew little or nothing of Loschmidt. I do not believe that the idea of a circular benzene came to Kekulé in front of a fire, and I enclose a summarizing paper published recently, but you probably know my thoughts anyway.

Now to turn to RBW: once he got to know Dodie Dyer, he was a different man, and absolutely shattered when she died of cancer.



Professor Dudley Herschbach May 22, 2000 Page Two

You may not have a copy of the *Aldrichimica Acta* dedicated to RBW on his 60<sup>th</sup> birthday and so I enclose a copy.

Strangely, the program discusses the fullerenes without mentioning the two chemists who received the Nobel Prizes for that work.

I was delighted to learn that the Dreyfus Foundation is indeed willing to make a substantial contribution for the preservation of the RBW papers.

I very much look forward to the two RBW biographies that are scheduled to come out soon and of course most curious to see how these accounts will mesh.

Thank you for speaking to Alan Long, who has indeed written to me about the Czech Bader Fellows. I am delighted to know of their progress.

Enclosed please find the videotape. I doubt that I would be permitted to make a copy, but if you ever see another copy elsewhere, please let me know.

Surely you know that I was not a Woodward student and yet he helped me greatly, both as a student and with Aldrich.

With all good wishes I remain

Yours sincerely,

Alfred Bader AB/az Enc.



# HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY AND CHEMICAL BIOLOGY 12 Oxford Street, Cambridge, MA 02138, USA



Dudlev R. Herschbach Baird Professor of Science

Tel: 617-495-3218 Fax: 617-495-4723 E-mail: hbach@chemistry.harvard .edu

May 9, 2000

Dr. Alfred Bader 924 East Juneau, Suite 622 Milwaukee, Wisconsin 53202

Dear Alfred:

At long last I am sending as promised a videotape of the public television program that I took part in a few years ago. I had hoped to find a copy I could simply give you, but did not succeed. Thus I would like to have this one back at some point.

As you probably have heard from Arnold Thackery, I learned that indeed the Dreyfus Foundation would be quite willing to make a substantial contribution for preservation of the Woodward papers. I haven't had any further word from Arnold since relaying that information to him six weeks or so ago. Also, right after our conversation, I talked with Alan Long, Director of the Chemical Laboratories, and requested he send you information about our Bader Fellows. He assures me he has done so.

And the same of th

Kieto

Best wishes,

Dudley Herschbach

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DH/mtp Encls.





Dr. Alfred Bader 924 East Juneau, Suite 622 Milwaukee, Wisconsin 53202 Phone: 414/277-0730 Fax: 414/277-0709 E-mail: baderfa@execpc.com

A Chemist Helping Chemists

May 25, 2000

Dr. Alan K. Long Laboratory Director Harvard University 12 Oxford Street Cambridge, MA 02138

Dear Dr. Long,

I am sorry that travels have delayed my thanking you for your informative letter of April 11<sup>th</sup> regarding the Czech Bader Fellows in Chemistry.

As you know, the understanding was that Harvard would accept one Czech Fellow each year. Now we know of course that Harvard has had difficulties getting applications from competent students. But you are now, even with the four you mentioned, several behind. Thus, I very much hope that you will be able to accept more than one during the next years, to make up for the shortfall.

My wife and I look forward to being in Cambridge in October and would very much like to discuss the details with you then.

With all good wishes I remain

Yours sincerely,

Alfred Bader AB/az <u>www.alfredbader.com</u> E: Alfred@abfa.com



# HARVARD UNIVERSITY

Office of the Director

THE CHEMICAL LABORATORIES • 12 Oxford Street • Cambridge, MA 02138 • 617 495-4283

April 11, 2000

Dr. Alfred Bader 924 East Juneau, Suite 622 Milwaukee, Wisconsin 53202

Dear Dr. Bader,

Dudley Herschbach reminded me the other day that we haven't been doing a very good job of keeping you up-to-date on the status of our Bader Fellows here in Chemistry. Here's a quick synopsis for you:

Milan Chytil you know well, of course. Milan arrived in 1994 and recently finished an excellent dissertation on the "Stereochemical Orientation of the AP-1 Heterodimer" with Greg Verdine. He has moved on to a postdoctoral fellowship working with Eric Jacobsen.

Tomas Vojkovsky arrived in 1997 and worked with E.J. Corey for two years and then six months with Eric Jacobsen. He has now left the program with a Master's degree.

We have two newer students, in the class that entered in September, 1998. Petr Vachal, from the Institute of Chemical Technology in Prague, is working with Eric Jacobsen on the development, optimization, and application of a general catalyst for the asymmetric Strecker reaction. Michal Storek, from Charles University, is working with Greg Verdine on a method for fine-mapping protein-DNA contacts on a rapid time-scale, in order to understand how regulatory proteins direct the expression of particular genes. Petr and Michael are doing very well – in fact, they both won teaching awards last fall for their work in Chem 170 and Chem 30, respectively.

This is an exciting time for the Department, not only on the student front, where we have admitted two large classes (~40 students) in a row, but also in faculty hiring, with five new faculty members last year. In addition, we've had an unprecedented run of construction projects, including a renovated lobby in Mallinckrodt, a new physical chemistry instrumentation facility, and most importantly, the Naito Laboratory building. We dedicate the Naito building tomorrow, with much fanfare, of course, and very shortly thereafter begin the demolition of Gibbs Lab to make space for a new Life Sciences building fused to Naito. Our other big impending project is the renovation of the physical chemistry office area and the addition of a new student center upstairs adjacent to the old stockroom.



I'll look forward to giving you a comprehensive tour on your next visit.

Best wishes,

Alan K. Long Laboratory Director



Your visit to Cambridge

Subject: Your visit to Cambridge Date: Fri, 24 Nov 2000 01:56:10 +0000 From: Andrew Holmes <abh1@cus.cam.ac.uk> To: baderfa@execpc.com CC: svl1000@cus.cam.ac.uk

Dear Alfred and Isabel,

It was good to see you last week. I spoke with Steve Ley and unfortunately it would seem that we cannot manage either of the days you proposed for a Christmas lecture. Thank you for the offer. We should book you up now for next year.

I appreciated your book.

Yours sincerely

Andy

Cc Prof S V Ley

Prof Andrew B Holmes (Secretary: Mrs Lilian van der Hoff)
Melville Laboratory for Polymer Synthesis (Department of Chemistry)
University of Cambridge
Pembroke Street
Cambridge CB2 3RA
U.K.
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e-mail: abhl@cus.cam.ac.uk
Korg: (NVW.chem.cam.ac.uk/CUCL/MLF.)

M





Dr. Alfred Bader 924 East Juneau, Suite 622 Milwaukee, Wisconsin 53202 Phone: 414/277-0730 Fax: 414/277-0709

A Chemist Helping Chemists

September 24, 1997

**Dr. S. Allen Heininger** 20 South Central, Suite 100 St. Louis, MO 63105

Dear Allen:

Isabel and I so enjoyed our evening with you in St. Louis and want to thank you most sincerely for your hospitality.

I was most interested to learn your views about the ACS and the Chemical Heritage Foundation and, of course, we very much hope that the problems in the latter will be straightened out.

It was fun, also, talking about some chemistry.

If you have any influence to get an exciting new monomer made at Monsanto, do consider dimerization of acrylonitrile. In the early 60s this was done under high pressure at a division of Hoechst, Griesheim, near Cologne. That dimerization yielded a mixture of cis and trans-1,2-cyclobutanedicarboxcylic acid. The cis and trans isomers were easily separated by forming the anhydride of the cis.

Needless to say that Isabel and I very much hope that you will be able to visit us in Milwaukee before long.

With all good wishes, I remain,

Yours sincerely,

AB/nik





Dr. Alfred Bader 924 East Juneau, Suite 622 Milwaukee, Wisconsin 53202 Phone: 414/277-0730 Fax: 414/277-0709

A Chemist Helping Chemists

October 7, 1997

**Professor Ned D. Heindel** Department of Chemistry Lehigh University Seeley G. Mudd Building 6 Bethlehem, PA 18015

# Dear Ned:

I am happy to know from your letter that I have your permission to use your letter to Bill Wiswesser, which made such a difference to him and to me.

We must have been among Bill's best friends and I must confess to you that I was truly staggered by how cruelly Bill was attacked by Professor Schiemenz. In several lectures Schiemenz showed an open grave and, on the tombstone, Bill's name with Schiemenz saying "Wiswesser is dead, let him rest in peace."

I enclose a rough draft of my paper which I plan to submit to The Bulletin.

Now that we have a new editor it might be accepted. The last editor, Professor Jensen, certainly would not have accepted it as he attacked one of my papers, in *Chemistry in Britain*, in an almost grotesque manner. I enclose copy of his letter. Unfortunately the editor of *Chemistry in Britain* refused to publish this.

In trying to trace how this attack came about, I have come to the conclusion that Alan Rocke, who generally is a sound scholar, was almost mesmerized by what Schiemenz wrote. And I do not think that either Rocke or Jensen really analyzed all the arguments for and against Wiswesser. This I am trying to do in the Wiswesser-Loschmidt Connection.



Professor Ned D. Heindel October 7, 1997 Page two

Of course I feel sorry what has happened to Jensen and Rocke since. As you know, they and the American Chemical Society were sued in what, I believe, was really a very unfair manner.

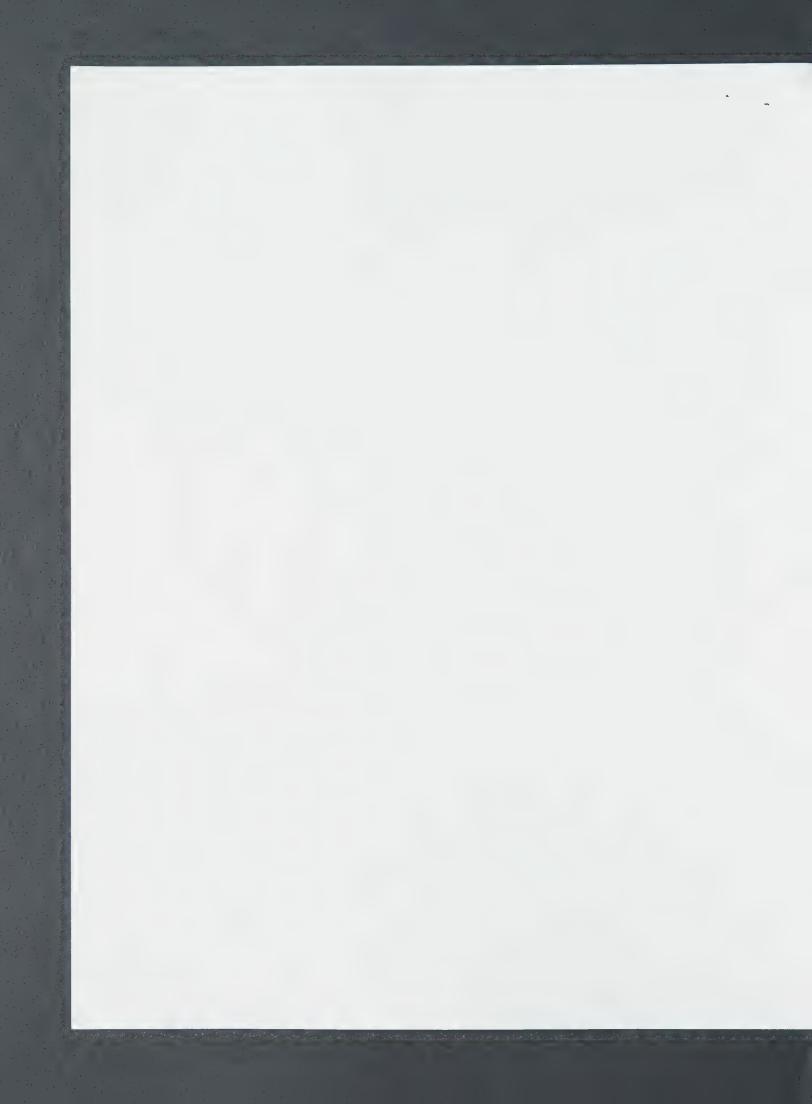
I would very much appreciate your comments about this rough draft.

With all good wishes, I remain,

Yours sincerely,

AB/nik

Enclosures



Lehigh University



Department of Chemistry telephone (215) 758-3470

Seeley G. Mudd Building 6 Bethlehem, Pennsylvania 18015

September 9, 1987

Dear Bill,

Fascinating stuff! You've got a real "find" in Loschmidt.

RE the article, I enjoyed it thoroughly but felt you'd written it for a more sophisticated readership (one interested in informational retrieval, WLN, searching, encoding, and the like)than that of the Aldrich publication.

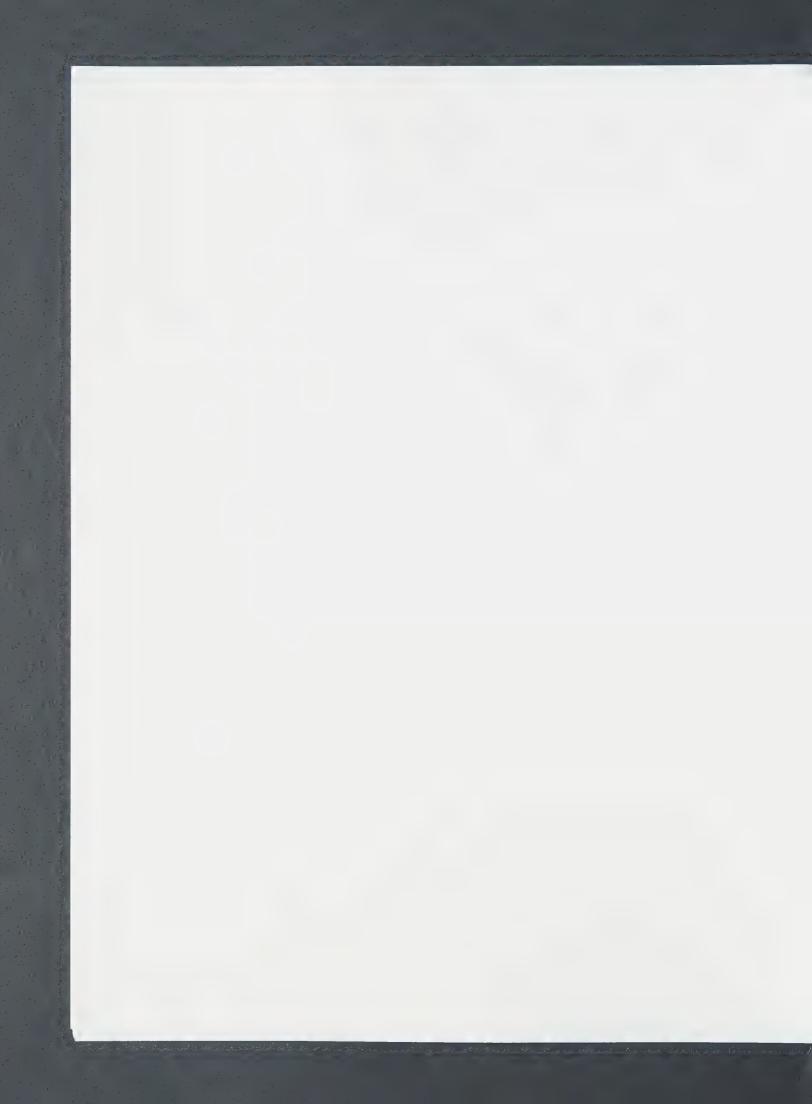
I'd bet that the chemist who reads <u>Aldrichimica Acta</u> looks for lighthearted, general history and would have little interest in follow-up material like online files of cited names, scoreboard index, structure indexes and the like. Tell us more about the man, his time, what became of his suggestions, his structural predictions. I thought your page 3 was right on target.

Aldrichimica Acta is read by at-the-bench practicing chemists because its usual content is synthetic hot-subjects and tips. This Loschmidt article will really need to aim at the uninitiated (and, alas, uninterested) in structural encodement. Several photos of parts of Loschmidt's plates illustrating these structures would add spice to the article.

Don't mean to sound negative...I'm not ... it's a great subject and you've got an exciting story to tell.

Cheers,

Ned D. Heindel





#### A Chemist Helping Chemists

August 22, 1997

Professor Ned D. Heindel Department of Chemistry Lehigh University Seeley G. Mudd Building 6 Bethlehem, PA 18015

Dear Professor Heindel:

At the San Francisco ACS meeting I gave a talk and poster session entitled "The Wiswesser-Loschmidt Connection."

I am just writing the manuscript for a paper which I hope the Bulletin for the History of Chemistry will accept. In that I would like to include an important letter from you, copy enclosed. I hope that you will approve.

Will all good wishes, I remain,

Yours sincerely,

AB/nik

Enclosure





## A Chemist Helping Chemists

July 28, 1997

Mr. Steve Hannam Chief Executive Officer BTP plc Hayes Road Cadishead, Manchester M44 5BX ENGLAND

Dear Mr. Hannam:

Many thanks for taking time last Tuesday evening to meet with me. Now I really look forward to your visit to Milwaukee in October and hope that you will be able to join Isabel and me for dinner on Monday evening October 20th.

I was interested to learn that you are looking for a managing director of Lancaster who is a chemist particularly strong in marketing. Actually Lancaster is very good in marketing - in many ways its catalogue is as good and in some even better than the Aldrich catalogue. What Lancaster really needs are many new products, both from universities and industrial companies around the world - compounds not yet listed by Aldrich.

Have a good, and surely well deserved, holiday.

With best regards, also to Ms. Potts, I remain,

Yours sincerely,

AB/nik





### **BTP plc**

Telephone: 0161 775 3945

3<sup>rd</sup> July 1997

Hayes Road, Cadishead, Manchester, M44 5BX

Telex: 669938 Facsimile: 0161 775 3970

Dr Alfred Bader White Gables 2A Holmesdale Road Bexhill-On-Sea East Sussex TN39 3QE

Dear Dr Bader

I was delighted to hear from you and thank you for the copy of your book. I have heard of you many times – particularly from Alec Ingram who is a great admirer of yours.

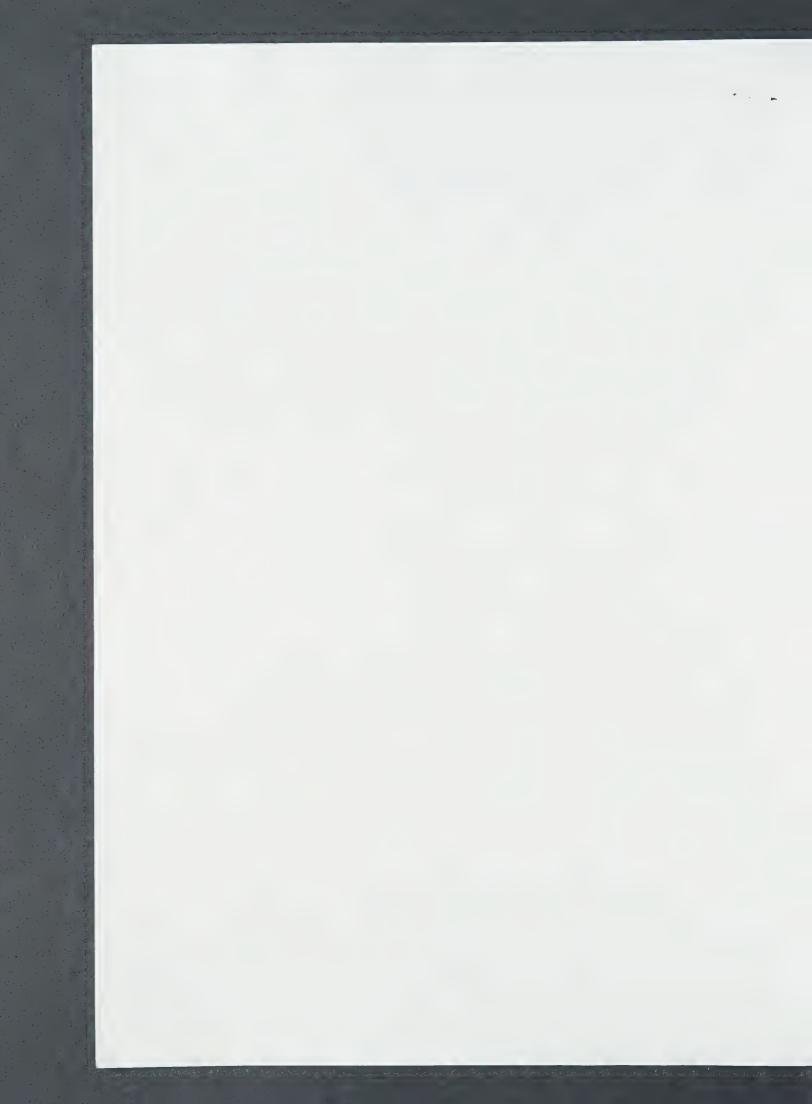
To date I have only skimmed the book but read with interest the parts on Messrs Cori and Harvey. There were obvious behaviour traits which I could recognise!

I would be delighted and honoured to meet with you but unfortunately the diary is completely full until I go on holiday at the end of July. We now own what was Henkel's leather chemical business in Oak Creek, Milwaukee and I shall be visiting this before the fall. Perhaps I could visit you at that time. I shall contact you then.

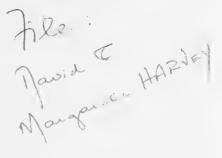
Yours in chemistry!

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/ Steve Hannam

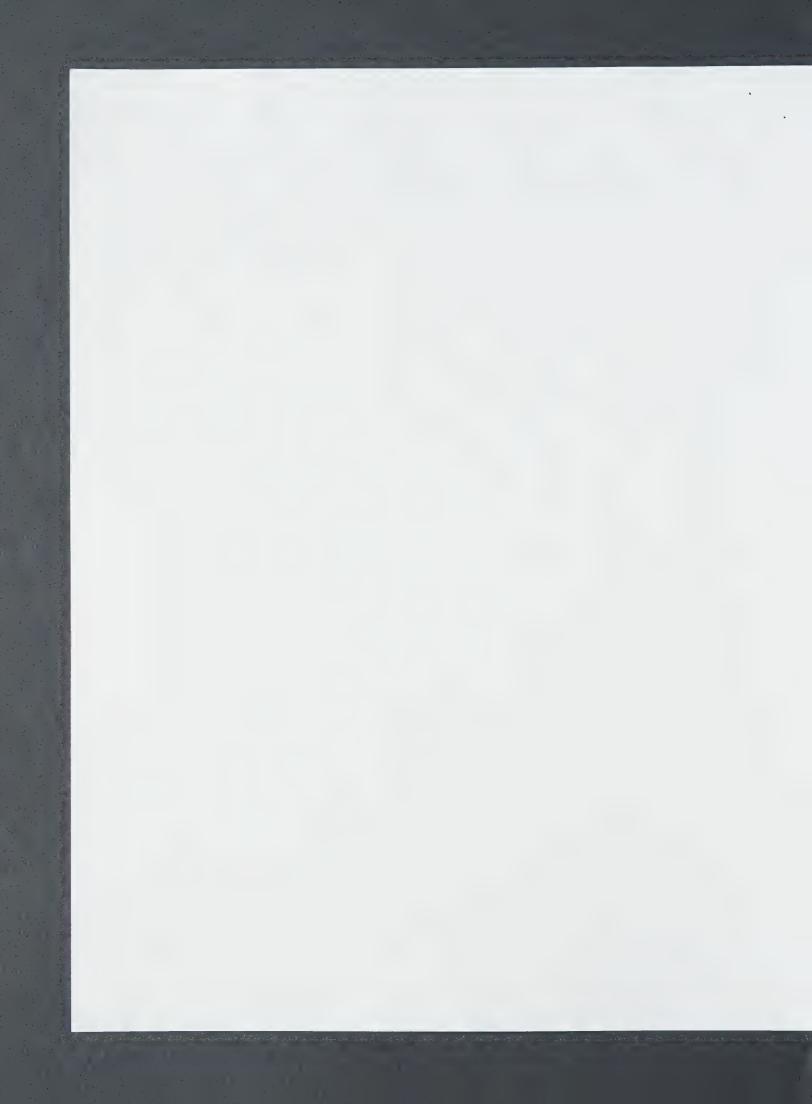


Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, Wisconsin 53211



#### A Chemist Helping Chemists

Mean Margance. Isabel El enjeged chating with you at the awards dimen. It would be fine to get toget in the new year. The encloped will intrest you; please phone Rem with your daughters Opens difference en lives - and Ke puckers of Diguna - Aldrich would be, if pavid had hitend work Lo you & less to Corr. We are just off to England, back in early January Belt wither to you and your daughters, S Xi Ple. ( und



# an AlMemo

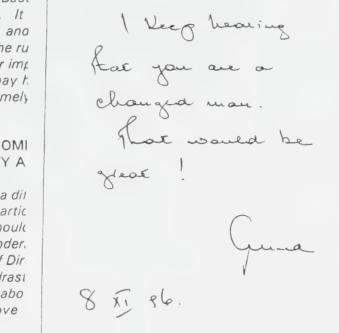
#### ALDRICH HAS BEEN PASSING ADVEI EMPLOYEES, REQUESTING ANONYMOU:

"Everyone should read Alfred Bade what you do in the Company. It Company started, flourished, and management has to observe the ru be aware of any impropriety or imp procedures. In this case, it may h consequences.' Was an extremely

#### EMPLOYEES' COMI AS THEY A

I'm glad I read the book; I really have a dit hand. I was told from someone in partic his being "kicked out" and that he should so he got what he deserves. I under, understand the action of the Board of Diror what that they would take such drast that. Otherwise, I enjoyed reading abo worldwide, his love for art and his love

Enjoyed reading Alfred's book and am r like. I can't tell you which parts of the base.



FROM DR. AL BADER

Tierre

and movement from early to later years is good. There were many things I had always been curious about that I learned.

Nice to see old names from the past; brings back some good memories; nostalgic.

The book is a well-written one, but of course, you have to keep in mind that it was written only from Alfred Bader's perspective.

Alfred Bader's life has been fascinating; I wonder still what was the most dominating factor in his young life that led him to his occupation. Someone or something obviously exerted a dominating influence upon his personality; at times being very complex and other times just an ordinary man with unique talents.

Dr. Bader has a way of romanticizing in his book. Besides being such an extraordinary business person, he emphasizes his emotions and interests vividly. He has an unusually remarkable memory, writing about incidents and situations with great detail. Yes, he must be a romantic, adventurous, mysterious and artistic person, yet practical. He is a man of many talents and traits, and it's good that he gathered everything together and wrote a worthwhile book.





A Chemist Helping Chemists

March 12, 1996

Dr. S. Allen Heininger 20 South Central, Suite 100 Clayton, MO 63015

Dear Al:

Thank you so much for your letter of March 6th.

I am sure that you will have guessed that I accepted the invitation to speak in Edwardsville because it is so close to St. Louis, and I had hoped that a number of my old friends from St. Louis would come.

Unfortunately, I have so many lecture tours planned for the next month that I will not be able to come to New Orleans, but perhaps the St. Louis ACS Section will invite me someday to give two or three talks there. A menu of my lectures is enclosed.

With all good wishes, I remain,

Yours sincerely,

AB/cw

Enclosures



S. Allen Heininger 20 South Central, Suite 100 Clayton, Missouri 63105 (314) 726-4666 (Phone and Fax)

March 6, 1996

Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, WI 53211-3435

Dear Al:

It was with great dismay that I learned thru the St. Louis Local Section Newsletter that you were scheduled to give the William J. Probst Memorial Lecture and a series of other seminars at SIU-Edwardsville on April 16th to 18th.

My problem is that I am committed to be in Hawaii that whole week to celebrate my youngest grandson's first birthday, and will miss your visit to our area completely. I would have very much enjoyed hearing all of your lectures (I must say that you have set out a very aggressive series of talks), but I guess that I'll have to wait for a later date to continue my education!

Hope to see you at the ACS meeting in New Orleans later this month, if you are planning to attend.

Best personal regards,

Sincerely,

Let Herminge

S. Allen Heininger





#### A Chemist Helping Chemists

January 17, 1996

Professor William W. Porterfield Hampden-Sydney College Hampden-Sydney, VA 23943

Dear Professor Porterfield:

I cannot tell you how happy I was to be able to study your and Dr. Walter Kruse's article, "Loschmidt and the Discovery of the Small" in the October issue of the Journal of Chemical Education.

Last June, the University of Vienna hosted a Loschmidt Symposium, and I enclose its program, as well as one of several articles I have written with Professor Christian Noe on Loschmidt's chemistry.

As Loschmidt wrote in his little book of 1861, "The main purpose of this work is to provide a deeper insight into the constitution of matter." The Loschmidt Number gave the size of the molecule. The little book gave their shapes.

Plenum will publish all of the papers presented at the Symposium in Vienna; what a pity that you and Dr. Kruse could not present your paper there.

Could you please share this letter with Dr. Kruse?

With all good wishes, I remain,

Yours sincerely,

AB/cw

Enclosures

bc: Prof. Dr. Christian Noe Dr. Robert Rosner Dr. Reinhard Schlögl





#### A Chemist Helping Chemists

January 17, 1996

Professor William W. Porterfield Department of Chemistry Hampden-Sydney College Hampden-Sydney, VA 23943

Dear Professor Porterfield:

Thank you so much for your letter of January 25th.

What a pity that you didn't present your paper in Vienna. I think that you are quite mistaken in thinking that "everybody attending the Symposium would certainly be more closely familiar with the [1865] paper" than you were. Frankly, I doubt whether more than a handful of physicists were as familiar with that key paper as you are, and you presented it so very well.

Plenum will be publishing all of the papers presented at the Symposium, probably late this year, and that will convince you how much students missed not hearing your paper.

With all good wishes, I remain,

Yours sincerely,

AB/cw

bc: Prof. Dr. Christian Noe Dr. Robert Rosner Dr. Reinhard Schlögl





# HAMPDEN-SYDNEY COLLEGE

DEPARTMENT OF CHEMISTRY

January 25, 1996

Dr. Alfred Bader 924 East Juneau, Suite 622 Milwaukee WI 53202

Dear Dr. Bader:

Walter Kruse and I very much appreciate your kindness in writing me about our annotated translation of Loschmidt's seminal article on the size of air molecules. I also appreciate the copy of your article, which I had seen in *Chemistry in Britain*, and of the program for the Loschmidt symposium last summer.

Actually, I had considered attending the symposium and even possibly presenting our paper, but frankly it seemed presumptuous inasmuch as everybody attending the symposium would certainly be more closely familiar with the paper even than we were. Our paper is really a pedagogic contribution (hence the venue) rather than any kind of true contribution to the history of science. As I know you know, Loschmidt is virtually unknown in this country and, in particular, is never mentioned in introductory courses in which other pioneers such as Dalton, Avogadro, Gibbs, and Lewis are properly credited with their conceptual discoveries. We wanted to make teaching chemists in the U.S. aware of what Loschmidt had done and how he had done it. (I admit that Walter wanted to strike a blow for Deutsche Kultur, too.)

In the end, we skipped the symposium; I'm grateful for the copy of the program, because I had wanted to see what the various contributions would be. Thanks very much for sending it along, and for your interest in our paper!

Sincerely,

W. W. Porterfield



Old Glory Jonne and Dick Hurd 7300 Halbert Drive Austin, Texas 78750 Dr. Alfred. Dader 2.761 Floth Shepard Alw HI Three Yes, Wiscensin ~ 53211~



# notice/

Charles Hurd Has commenced to roam About his new digs At the Presby Home

The move is complete ! The address below -So come by & see him ! And say "HELLO" !!!

C. D. Hurd 3200 Grant Street McGaw Care Center, #183 Evanston, Illinois 60201

Phone: (708) 570-8134



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### NORTHWESTERN UNIVERSITY

Fred Basolo Charles L and Emma H. Morrison Emeritus Professor of Chemistry Department of Chemistry

2145 Sheridan Road Evanston, Illinois 60208-3113 Telephone (708) 491-3793

Facsimile (708) 491-7 113 Internet: chemdept@ chem.nwu.edu

August 14, 1995

Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, WI 53211

Dear Al:

I am pleased to see that you and Isabel plan to visit Charles Hurd sometime this month. He is sure to be delighted to have you stop by so he can reminisce about his days as consultant with PPG. I let him know that you will telephone (708-570-8134) his room or the information desk (708-492-4800) and plan to stop and see him.

When I visited Charles recently he had been moved to the health care center, but the nurse said he was OK and he certainly seemed fine to me. At age 98 he has hearing and memory problems, otherwise he is fine. We had a good, long visit, with Charles doing much of the talking.

Enclosed is a map which should make it easy for you to find Charles. Since you know your way to our Tech building, I start you from there and all you need do is follow the yellow route. If I can be of further help just call me in the AM at 708-491-3793 or in the afternoon or evening at 708-657-9153. Except for attending some of the Chicago ACS meeting, I should be here all month.

Kind personal regards and best wishes to you and Isabel,

Sincerely,

Fred Basolo

P.S. Charles' address is : 3200 Grant St. Presbyterian Home Evanston, IL 60201

FB/jg







#### UNITED STATES PATENT SERVICES

COMMEMORATIVES AND CORPORATE INVENTOR RECOGNITION PROGRAMS FOR U.S. PATENT RECIPIENTS

Alfred Bader Alfred Bader Fine Arts Astor Hotel, Suite 622 924 East Juneau Avenue Milwaukee, Wisconsin 53202 August 15, 1995

Dear Dr. Bader,

I just wanted to write and say what a pleasure and honor it was to make your acquaintance last week. My father and I sincerely enjoyed our lunch with you. We were both grateful for the time you so graciously took to be with us. We both also enjoyed seeing your fine gallery. I confess to coveting many of the paintings that I saw, leaving me with a sense of motivation to work even harder so that one day I might be privileged to return to your gallery as a buyer.

My wife Teresa has already consumed over half your book, *The Adventures Of A Chemist Collector*. She was quite taken back by the difficult childhood you were forced to endure growing up in Austria during WWII, including separation from your family at such a young age. To have obtained the highly respected level of success that you have is truly an inspiration to anyone who thinks they have it difficult in today's world. But perhaps even more inspirational within your book are the gracious passages of remembrance and appreciation that you bestow upon those that have helped you throughout your life. To often in my generation, which is characterized by materialism and greed, my peers have taken little appreciation of those that have helped them along the way. You sir, however, have shown a true sense of understanding that we all exist and must co-exist, and those that have assisted us throughout our lives are to be honored with our appreciation.

In this regard, you have my sincerest appreciation in so graciously offering Mr. Lombardo's name at Aldrich Chemical as a possible contact for my company's line of Patent Commemoratives. As I told you in your office, so often the difficult part of business is knowing the correct contact at a company and getting that person's attention. You have kindly provided me with both and I would like to say how grateful I am to you for such.

I will sincerely look forward seeing you again in September. Best of luck to you.

Sincerely,

Ries B. Hansen Vice President

cc. F. Hansen

Administration & Manufacturing • 216 N. Green Bay Road • Suite 111 • Thiensville, Wisconsin 53092-1625 • Tel (800) 872 - 4962 • Fax (414) 238 - 1296 Research & Documentation • 3421 \*M\* Street, N.W. • Suite 1642 • Washington, DC 20007-3516



Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, Wisconsin 53211

January 6, 1995

Professor Charles Hurd 2724 Crawford Avenue Evanston, Illinois 60201

Dear Charles,

I am so sorry to note that I will once again miss coming to the Hurd Lectures at Northwestern. But a long time ago I agreed to talk to the ACS in Minneapolis on February 15th.

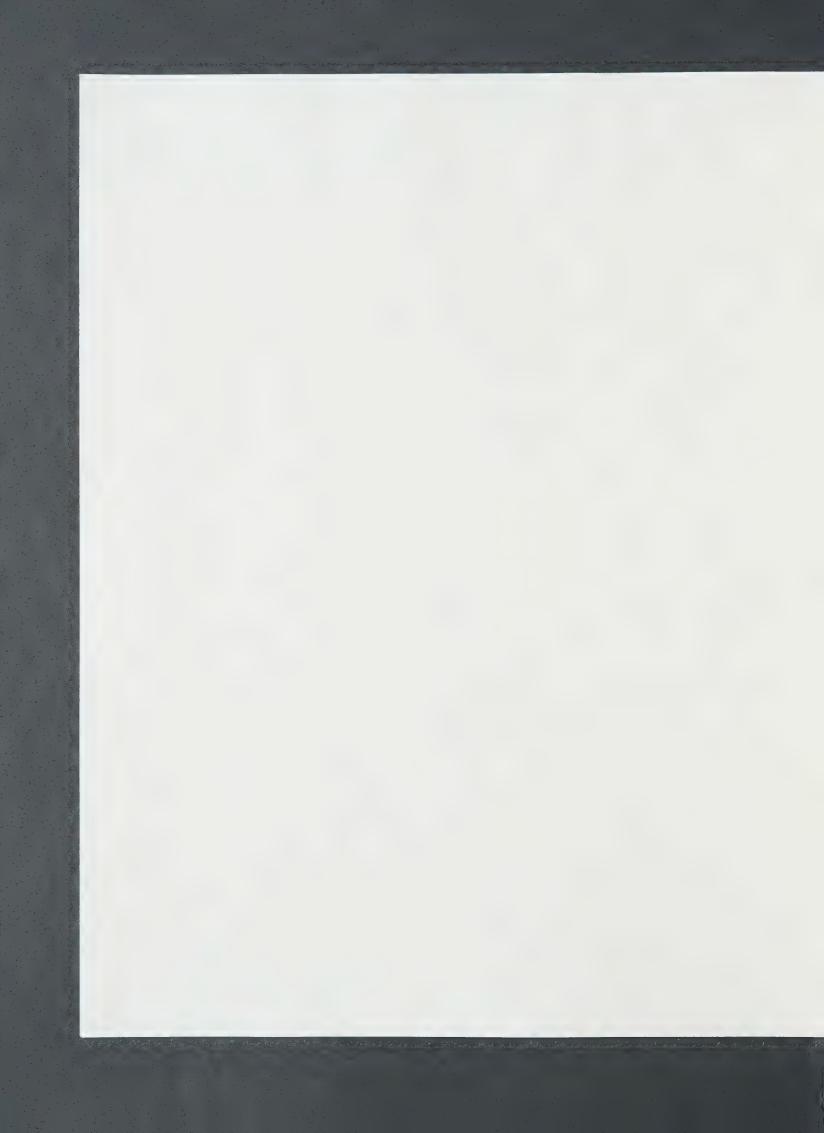
I have just finished my autobiography which will be published by Weidenfeld in April. Of course, it tells a good deal about your help and includes a good photo and your first corrections way back in May of 1953 when we were both still young and charming.

As soon as spring removes the snow, we plan to come down to visit you.

Fond regards and all good wishes for 1995.

As always,

Enclosure



Der alfred Erninden 23 Man may have contacts with addide che l'a l'aure so sure they are willing an you diketer - acitor a me Ruking that the weat like to avoid incorrect name in their building I have gone over this but to part out the surser. I you doug have the it of their no interest, simple the it all areas -Cine, evening of your to aprilia

N-methyl-N-nitroso-N'-nitroguanidine for the preparation of Diazomethane is now being distributed by the Aldrich Chemical Company.

Diazomethane is an invaluable reagent for the methylation of carboxylic acids, phenols and enols, for the preparation of heterocyclic compounds and in the Arndt-Eistert reaction. It has hitherto been prepared through intermediates which are unstable and strong skin irritants.

Diazomethane can now be prepared most simply by the action of alkali on methyl nitroso\nitroguanidine. (cf. McKay JACS <u>70</u>, 1974 (1948); McKay et al, Can. J. Res., <u>28</u>, 683 (1950); Organic Chemistry, Fieser and Fieser, 2nd. Ed. 178.)

Methyl nitroso nitroguanidine is a crystalline compound, m.p. 118°C. which has been kept in brown bottles at room temperature for over a year without decomposition. The addition of this crystalline compound to a cold 50% aqueous potassium hydroxide solution covered with ether yields diazomethane in 70-90% yield. Numerous experiments have shown that when this ethereal diazomethane solution is distilled and added to an ethereal solution of a pure carboxylic acid, then evaporation of the resulting solution leaves the analytically pure methyl ester of the acid.

N-methyl-N-nitroso-N'-nitroguanidine Prices:

| 10  | gms. | \$<br>5.00 |
|-----|------|------------|
| 25  | gms. | 10.00      |
| 100 | gms. | 25.00      |

We shall be pleased to receive your introductory order.

Aldrich CHEMICAL COMPANY, INC. 161 WEST WISCONSIN AVENUE MILWAUKEE 3, WISCONSIN

Dear alfred more in the first of the you may have contacts with aldrich Chem Co, Judge so since they are pelling out your diketene acetone adduct. Rubing that they night like to avoid incorrect names in their bulletins, I have gone will this hit to pour out the errors, + have no interest simply threw it all average of the product of the state Couch evening at your home Charles

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| 10  | gms. | \$           | 5.00  |
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| nitroso-N'- | nitı | roguanidine     | Prices:    |
|-------------|------|-----------------|------------|
| gms.        | \$   | 5.00            |            |
| gms.        |      | 10.00           |            |
| gms.        | , .  | 25.00           |            |
|             | gms. | gms. \$<br>gms. | gms. 10.00 |

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Aldrich CHEMICAL COMPANY, INC. 161 WEST WISCONSIN AVENUE

MILWAUKEE 3, WISCONSIN

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We shall be pleased to receive your introductory order.

Quarterly Reviews of Biophysics 27, 4 (1994), pp. 333-337 Printed in Great Britain



## Professor Dorothy Hodgkin

In October 1964 the *Daily Mail* carried a headline 'Grandmother wins Nobel Prize'. Dorothy Hodgkin won it 'for her determination by X-ray techniques of the structures of biologically important molecules'.

She used a physical method, X-ray crystallography, first developed by W. L. Bragg, to find the arrangements of the atoms in simple salts and minerals. She had the courage, skill, and sheer willpower to extend the method to compounds that were far more complex than anything attempted before. The most important of these were cholesterol, vitamin D, penicillin and vitamin B12. Later she was most famous for her work on insulin, but this reached its climax only five years after she had won the prize.

In the early Forties, when Howard Florey and Ernest Chain had isolated penicillin from Alexander Fleming's mould, some of the best chemists in Britain and the United States tried to find its chemical constitution. They were taken aback when a handsome young woman, using not chemistry but X-ray analysis, then still mistrusted as an upstart physical technique, had the face to tell them what it was. When Dorothy Hodgkin insisted that its core was a ring of three carbon atoms and a nitrogen which was believed to be too unstable to exist, one of the chemists, John Cornforth, exclaimed angrily: 'If that's the formula of penicillin, I'll give up chemistry and grow mushrooms'. Fortunately he swallowed his words and won the Chemistry Prize himself 30 years later. Hodgkin's formula proved right and was the starting-point for the synthesis of chemically modified penicillins that have saved many lives.

Pernicious anaemia used to be deadly until the early Thirties when it was discovered that it could be kept in check by liver extracts. In 1948 the active principle, vitamin B12, was isolated from liver in crystalline form, and chemists began to wonder what its formula was. The first X-ray diffraction pictures showed that the vitamin contained over a thousand atoms, compared to penicillin's 39; it took Hodgkin and an army of helpers eight years to solve its structure. Like penicillin, vitamin B12 showed chemical features not encountered before, such as a strange ring of nitrogens and carbon atoms surrounding its central cobalt atom and a novel kind of bond from the cobalt atom to the carbon atoms of a sugar ring that provided the clue to the vitamin's biological function. The Nobel Prize was awarded to Hodgkin not just for determining the structures of several vitally important compounds, but also for extending the bounds of chemistry itself.

In 1935 Dorothy Crowfoot, as she then was, put a crystal of insulin in front of

#### 334 Obituary

an X-ray beam and placed a photographic film behind it. That night, when she developed the film, she saw minute, regularly arranged spots forming a diffraction pattern that held out the prospect of solving insulin's structure. Later that night she wandered around the streets of Oxford, madly excited that she might be the first to determine the structure of a protein, but next morning she woke with a start: could she be sure that her crystals really were insulin rather than some trivial salt? She rushed back to the lab before breakfast. A simple spot test on a microscope showed that her crystals took up a stain characteristic for protein, which revived her hopes. She never imagined that it would take her 34 years to solve that complex structure, nor that once solved it would have practical applications. It has recently enabled genetic engineers to change the chemistry of insulin in order to improve its benefits for diabetics.

Dorothy Hodgkin's father, J. W. Crowfoot, was Education Officer in Khartoum and an archaeologist; her mother too was an archaeologist, with a particular interest in the history of weaving. When Dorothy was a child, they lived next door to the Sudan Government Chemist, Dr. A. F. Joseph. It was 'Uncle Joseph''s early encouragement that largely excited her interest in science. Later he introduced her to the Cambridge Professor of Physical Chemistry, T. Martin Lowry, who advised her to work with J. D. Bernal.

It was when Dorothy Crowfoot was 24 and working in Cambridge with Bernal on crystals of another protein, the digestive enzyme pepsin, that Bernal made his crucial discovery of their rich X-ray diffraction patterns. But, on the day that he did, her parents had taken her to London to consult a specialist about persistent pains in her hands. He diagnosed the onset of the rheumatoid arthritis that was to cripple her hands and feet, but never slowed her determined pursuit of science.

At Oxford, Dorothy Hodgkin used to labour on the structure of life in a cryptlike room tucked away in a corner of Ruskin's Cathedral of Science, the Oxford Museum. Her Gothic window was high above, as in a monk's cell, and beneath it was a gallery reachable only by a ladder. Up there she would mount her crystals for X-ray analysis, and descend precariously, clutching her treasure with one hand and balancing herself on the ladder with the other. For all its gloomy setting, Hodgkin's lab was a jolly place. As Chemistry Tutor at Somerville she always had girls doing crystal structures for their fourth year and two or three research students of either sex working for their Ph.D.s. They were a cheerful lot, not just because they were young, but because her gentle and affectionate guidance led most of them on to interesting results. Her best-known pupil, however, made her name in a career other than chemistry: Margaret Roberts, later Margaret Thatcher, worked as a fourth-year student on X-ray crystallography in Dorothy Hodgkin's laboratory. They always maintained a great affection for each other, despite their political differences.

In 1937 Dorothy had married the historian Thomas Hodgkin. They had three children and remained a devoted couple until Thomas's death in 1982. Some women intellectuals regard their children as distracting impediments to their careers, but Dorothy radiated motherly warmth even while doing scientific work. Concentration came to her so easily that she could give all her attention to a child's

chatter at one moment and switch to complex calculations the next. The Hodgkin's home was chaotic, cheerful, welcoming and hospitable to visitors, including many from the Third World.

'There are certain letters which I dread to open,' she once told me, 'and when I saw one from Buckingham Palace I left it sealed, fearing that they wanted to make me Dame Dorothy.' It would have made her feel like a *femme formidable*, which she so happily was not. She was relieved to find that the Queen offered her the Order of Merit, a much greater honour.

She pursued her crystallographic studies, not for the sake of honours, but because this was what she liked to do. There was magic about her person. She had no enemies, not even among those whose scientific theories she demolished or whose political views she opposed. Just as her X-ray cameras bared the intrinsic beauty beneath the rough surface of things, so the warmth and gentleness of her approach to people uncovered in everyone, even the most hardened scientific crook, some hidden kernel of goodness. She was once asked in a BBC radio interview whether she felt handicapped in her career by being a woman. 'As a matter of fact,' she replied gently, 'men were always particularly nice and helpful to me *because* I was a woman.' At scientific meetings she would seem lost in a dream, until she suddenly came out with some penetrating remark, usually made in a diffident tone of voice, and followed by a little laugh, as if wanting to excuse herself for having put everyone else to shame.

She shared her husband's faith in the socialist paradise, no matter whether this was in the Soviet Union, China or Vietnam, and tended to close her eyes to the evils of the Communist dictatorships. Her high standing in the Soviet scientific community was recognised in 1982 by the award of the Lomonosov Gold Medal. In 1987 she was awarded the Lenin Peace Prize, in part no doubt for her championing of the Soviet cause, but also for her efforts to ease tension between East and West as President of the 'Pugwash' conferences on Science and World Affairs.

In 1955, the first of these conferences was stimulated by the Einstein-Russell Manifesto that drew attention to the mortal danger of thermonuclear war. They have since been held annually and have brought together scientists from all countries, meeting as individuals rather than representatives of governments and seeking co-operative solutions to disarmament and the reduction of international tension. Dorothy Hodgkin was made President in 1975. In the face of diametrically opposed views often angrily expressed by scientists from East and West or North and South, a few gentle thoughtful words in her soft voice cooled tempers and forestalled crises. She cared deeply for the Arab cause in the Middle East, for the poorer African countries, for China and Vietnam, and in times of tension she helped to keep open scientific dialogue between them and the West.

In 1970 Hodgkin was elected Chancellor of Bristol University, an office to which she brought a breath of fresh air. She attended meetings regularly and often acted as the university's conscience, taking an interest in individuals, particularly if she thought they had been hard done by. She was the first chancellor of the university always to visit the Students' Union and to have lunch with its officers,



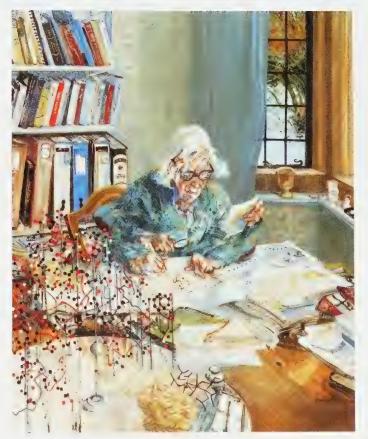
Hodgkin in 1937, the year she married Photograph: Ramsey and Muspratt By courtesy of the National Portrait Gallery, London

and she took a keen interest in the research of her crystallographic colleagues. She supported the establishment of a Hodgkin Scholarship for a student from the Third World and of Hodgkin House to accommodate overseas students, both named after her late husband, a specialist in African studies.

Dorothy Hodgkin's uncanny knack of solving difficult structures came from a combination of manual skill, mathematical ability and profound knowledge of crystallography and chemistry. It often led her and her alone to recognise what the initially blurred maps emerging from X-ray analysis were trying to tell. She will be remembered as a great chemist, a saintly, gentle and tolerant lover of people and a devoted protagonist of peace.

Max Perutz

Reproduced by permission from The Independent, Obituaries, 1 August 1994.



Magic about her person: a portrait of Hodgkin by Maggi Hambling, 1985 By courtesy of the National Portrait Gallery, London

Dorothy Mary Crowfoot, chemist: born Cairo 12 May 1910; Fellow, Somerville College, Oxford 1936–77; FRS 1947; Royal Society Wolfson Research Professor, Oxford University 1960–77 (Emeritus); Nobel Prize for Chemistry 1964; OM 1965; Chancellor, Bristol University 1970–88; Fellow, Wolfson College, Oxford 1977–82; married 1937 Thomas Hodgkin (died 1982; two sons, one daughter); died Shipston-on-Stour, Warwickshire 29 July 1994.

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Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, Wisconsin 53211

April 25, 1994

Dr. John C. Haas Rohm and Haas Building 100 Independence Mall West Philadelphia, Pennsylvania 19106 2399

Dear Dr. Haas,

Thank you for your kind invitation to join you at a breakfast meeting at the Chemist's Club on May 11th.

However, prior commitments prevent my attending.

All good wishes.

Sincerely,



JOHN C. HAAS ROHM AND HAAS BUILDING 100 INDEPENDENCE MALL WEST PHILADELPHIA, PA 19106–2399

Tel. 215-592-2626

Fax 215-592-3377

April 19th, 1994

Dr. Alfred R. Bader 2961 North Shepard Avenue Milwaukee, WI 53211

Dear Dr. Bader,

This note brings you spring greetings and an invitation to a breakfast meeting which I will be co-hosting with Paul L. Kohnstamm at The Chemists' Club (40 West 45th Street) at 9.00 a.m. on Wednesday, May 11th, ahead of the Othmer Luncheon.

As in previous years, we would like to use this breakfast gathering as an opportunity to bring our friends up-to-date on the progress of the Chemical Heritage Foundation. There is much encouraging news to report, not the least of which is being close to purchasing our own building at Independence National Historical Park. And, of course, we wish to seek your thoughts and counsel on our plans to build CHF into a cultural and educational resource of civic, national and international significance.

We very much hope that you will be able to join us for the breakfast meeting. Irene Lukoff will call you in a few days to check your availability.

Sincerely,

John C. Haas

John C. Haas Chairman Othmer Challenge Committee

cc: Mr. Paul L. Kohnstamm





#### WILLIAM F. POLIK, Ph.D CHEMISTRY DEPARTMENT

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# Hope College CHEMISTRY DEPARTMENT

Annual Report **1992-1993** 





## ANNUAL REPORT

Chemistry Department

Hope College

1992-1993

## ACKNOWLEDGMENTS

We wish to thank Mrs. Norma Plasman, Chemistry Department Assistant, for her expert help in designing and preparing this report and Tom Renner, Director of Public Relations, who assisted with the printing and photography.

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#### INTRODUCTION

The chemistry department faculty and staff send greetings to all our alumni and friends who have played a role in making chemistry at Hope College a very special enterprise. In a number of ways 1992-1993 was an unusual year. However, one factor that seems to be consistent from year to year is the high quality of the young women and men who choose to become chemistry majors. It is a pleasure and privilege to work with them.

This year's graduating class included 34 chemistry majors, the largest number in recent years. Eleven graduating majors will be attending graduate school in chemistry, biochemistry or chemical engineering in the fall. Six have been accepted into medical or dental schools at the time of this writing and two are still awaiting an acceptance. Four have jobs in chemical research in industry or academe, and one is going on into graduate work in the health sciences. We congratulate these outstanding graduates and wish them well as they move to the next phase of their lives.

June 1992 was the occasion for the Council on Undergraduate Research (CUR) Fourth National Conference on Undergraduate Research held on Hope's campus and attended by about 500 faculty and administrators from predominantly undergraduate institutions from all parts of the U.S.A. Rod Boyer, Steve Taylor, and Will Polik from chemistry spent much time and energy in organizing various aspects of the program. The Conference brought Tom Cech, the first of two Nobel Laureates in chemistry to visit campus this year, as a plenary lecturer.

The Merck Lecture Program brought three prominent chemists to campus for visits with students and faculty in addition to giving lectures. They were Professor Stephen Benkovic, Pennsyvania State University, Dr. Ruth F. Nutt, Merck & Co., and Professor Yuan T. Lee, Nobel Laureate, from the University of California, Berkeley.

Bill Mungall organized the Symposium on Synthetic Organic Chemistry which was held on Hope's campus in June, 1993. About 210 chemists and students attended. The symposium is a part of the Hope College Distinguished Scholars Program, which was initiated in 1977 and has been generously sponsored by the Parke-Davis Pharmaceutical Research Division of the Warner-Lambert Company. The 1993 Distinguished Scholar is Professor Barry M. Trost of Stanford University.

A conference for high school chemistry teachers, organized by past participants in Gene Jekel's 24 NSF sponsored summer workshops for teachers, was held during three days in July, 1992. At the closing banquet numerous tributes were made by participants to Gene, Elaine and Frank Quiring, testifying to the importance the workshops played in their professional development.

The fall of 1992 saw a 28 percent increase in enrollment in the introductory chemistry course for science majors. This in turn has led to a similar increase in enrollment in organic chemistry for the fall, 1993. This coming fall, although the freshman class will be smaller than last year's, the enrollment in the freshman chemistry course will be even larger than last year.

The summer of 1993 is a busy time for research in the department. There are 29 college students, one high school teacher, and three high school students doing research in chemistry at Hope. Three of these students are from the Netherlands and four are from other colleges and universities in the U.S.A. Two of our majors are doing research at other colleges and one is doing research in the Netherlands. The department purchased two new FT-IR spectrometers this year (Midac Model M 2000), with partial support from the DuPont College Science Grant and a Kresge Foundation grant. Bill Mungall and Will Polik did most of the legwork for this acquisition.

Will Polik and Bill Mungall also served as coauthors for a successful proposal to the National Science Foundation Instrumentation and Laboratory Improvement (NSF-ILI) program. The result was a \$45,812 grant from NSF to be matched by Hope College for a "Computational Chemistry Laboratory for Undergraduate Instruction". The funding was used to purchase a CAChe (Computer Aided Chemistry) Scientific system. An additional grant worth \$19,196 was obtained from CAChe Scientific to assist with the purchase of the system. This system promises to revolutionize the way chemistry is taught in several courses at Hope College.

A major renovation project on the chemistry floor of Peale Science Center is scheduled for summer, 1993. The far south end of the floor, formerly given over to the Kleinheksel-Van Zyl library, will be transformed into a new biochemistry-molecular biology laboratory, a Macintosh computer laboratory and a student gathering area. The library was moved into the Van Wylen library making room for the new laboratories. Funding for the project came from NSF and Keck Foundation grants and from Hope College.

Mike Silver was awarded one of eight Camille and Henry Dreyfus Foundation Scholar/Fellow grants made nationwide this year. The award, worth \$60,000, will bring a Ph.D. chemist to Hope College for a two year period to teach and do research in collaboration with Mike. Will Polik was selected to be a part of the Pew Teacher Scholar program of the Pew Midstates Science and Mathematics Consortium. This means that he will serve as a mentor for one year to a post doctoral chemist. The really big news this year is the retirement of Eugene and Elaine Jekel, Gene after 38 illustrious years on the Hope faculty. This is the first chemistry retirement since that of Dr. Gerrit Van Zyl in 1964. A separate story on this momentous event occurs later in this report. We are pleased to report that both Gene and Elaine will teach part time for us this coming year.

This is just a sampling of activities which took place this year, enough to convince you I think, that this was indeed an unusual and productive year. We thank you for your continued interest and support.

Irwin J. Brink, Chairman

## THE CHEMISTRY CLASS OF 1993

Listed below are the members of the Chemistry Class of 1993 and their plans for the immediate future.

## Graduates with a Chemistry Major

Jonathan J. Bechtel, Grand Rapids, MI (B.A.), has applied to a Masters Program in Basic Health Sciences at Wayne State University. He will apply to medical school next year.

Gregory C. Bibart, Kalamazoo, MI (B.S.).

Michael Bingham, Cuttingsville, VT (B.A.).

- Nancy E. Bischer, Ruth, MI (B.S.)\*, plans to be married in July and shortly thereafter attend Michigan State University Medical School. Her career goals include opening a private practice in her home county emphasizing primary care.
- Christopher A. Briggs, Shelby, OH (B.S.), is currently working as a chemist at Parke-Davis, Holland.
- Elizabeth A. Byrn, West Lafayette, IN (B.A.), plans to attend medical school in the fall of '94 but is not sure which school she will attend.
- Scott A. Drooger, Holland, MI (B.A.), plans to attend the University of Michigan Dental School and then get into an oral and maxillofacial surgery program. He would then like to set up a practice in West Michigan as well as do medical missionary work in third world countries.
- Vicki L. Freeman, Rockford, MI (B.S.), will be working at Parke-Davis on an internship this summer. She plans to pursue a Ph.D. at the University of California-Berkeley in the department of inorganic chemistry (bioinorganic), after which she will work in either disease research or environmental chemistry.

Eric J. Freiberger, New Hartford, NY (B.A.).

- Yvonne N. Grassl, Stevensville, MI (B.S.)\*, plans to become a physician after attending Wayne State University Medical School. She then plans to get married and have a family.
- Martin F. Hentemann, Glenn, MI (B.S.), will be attending Purdue University pursuing a Ph.D. in synthetic organic chemistry. Eventually he would like to do research in drug design and synthesis with a pharmaceutical company.

- Michael S. Hermen, Beecher, IL (B.S.), will be attending the University of Michigan in the inorganic chemistry program.
- Chad A. Johnson, Monroe, MI (B.A.), will be attending the University of Indiana Medical School.
- Kristin M. Knapp, Ypsilanti, MI (B.S.), plans to work for one year before attending graduate school.
- Ericka L. Lyszak, Alpena, MI (B.S.)\*, plans to attend Harvard University. She is interested in medically-related biochemical research (academic, research institute, industry etc.).
- Andrew E. Markwart, Woodland, MI (B.A.), is looking for employment in pharmaceutical sales. In the future he would like to go to law school at Notre Dame.
- Scott A. May, Troy, MI (B.S.), will attend graduate school at Indiana University in the synthetic organic chemistry program. Eventually he would like to work for either a pharmaceutical company or in academia.
- **Paul Musherure**, Uganda, East Africa (B.S.)\*, is attending the University of Michigan Dental School.
- Kenneth S. Overway, Holland, MI (B.S.), plans to attend graduate school at Purdue University in the physical chemistry program. After receiving his Ph.D., his career goal is to become an industrial chemist.
- Amy J. Poel, Kalamazoo, MI (B.S.)\*, will be working as a research assistant with Dr. Burnatowska-Hledin of the Biology/Chemistry Departments, Hope College. She would like to work in Africa and go to graduate school. Her career goals are teaching/research at a college or university in molecular biology.

- Steven J. Ray, Kalamazoo, MI (B.S.), plans to attend Indiana University in the analytical chemistry program. He then will either go into industry or perhaps academia.
- Kenton B. Renkema, Hudsonville, MI (B.S.), plans to pursue a Ph.D. in inorganic chemistry at Indiana University.
- Shanni M. Rhoades, Fenton, MI (B.A.).
- Sandra E. Rottschafer, Holland, MI (B.A.).
- Jennifer L. Sebestl, Woodridge, IL (B.S.), plans to attend Wayne State University in pursuit of her Ph.D. in either inorganic or analytical chemistry.
- Peter H. Sheill, Trenton, MI (B.S.)\*, plans to attend Scholl College of Podiatric Medicine to become a podiatrist.
- Andrew G. Spencer, Sheridan, MI (B.S.)\*, will be attending Michigan State University in their biochemistry program.
- Brian P. Standish, Portage, MI (B.S.), is currently employed as a chemist at Zeeland Chemical Company.
- Andrew J. Toering, Plymouth, MN (B.S.), will be working as a summer intern at Exxon Research & Development Labs in New Jersey, and will be attending the Institute of Paper Science & Technology in Atlanta next fall.
- Meghan M. Tuynman, Detroit, MI (B.S.)<sup>\*</sup>, will be working at Parke-Davis Ann Arbor this summer. She will be married in August, before attending the College of Osteopathic Medicine -Kirksville. Meghan plans to practice family medicine in the future.

William C. Van Zandt, Marshall, MI (B.S.), would like to work in chemical industry as a research assistant, preferably pharmaceutical research, for at least the next few years. Beyond that, he is not sure.

Amy L. Waugh, Grand Rapids, MI (B.A.).

Mathew S. Way, Allegan, MI (B.A.).

Bernard L. Young, Brighton, MI (B.S.).

\* B.S. in Chemistry with a Biochemistry emphasis.

## Correction

William Taylor, Ypsilanti, MI (B.A.), a December, 1991 graduate, was inadvertantly omitted from the list of graduating majors in the 1991-92 Annual Report. We add his name here with apologies to Bill for this slip up.

Graduates with a Chemistry or Biochemistry Minor

Amy L. Beaver, Portage, MI (Chemistry), is seeking employment as a high school chemistry and/or biology teacher.

Mark R. Bonnell, Stow, OH (Biochemistry).

Margaret A. Chen, Battle Creek, MI (Biochemistry), plans to take additional classes and perhaps search for a research position. Within a year or two, she would like to go to medical school or graduate school in psychology or biology.

Brian E. Christofferson, Mequon, WI (Biochemistry).

- Jamie D. Crooks, Grand Rapids, MI (Biochemistry), will be attending the University of Michigan Medical School.
- Elizabeth Hain, Fairmount, IN (Chemistry), is planing to become a secondary teacher in biology and chemistry. She also hopes to coach girls basketball and later get into school administration.
- Christopher A. Lepczyk, Traverse City, MI (Chemistry).
- Corrie Listenberger, Niles, MI (Biochemistry), will enter a Master's Program in Rehabilitation Counseling at Michigan State University. She would like to work for a public or non-profit human services organization focusing on disability issues.
- Collin J. Magennis, (Chemistry), plans to enroll in Western Michigan University's Physician Assistant Program in the Fall of 1994.
- Jennifer S. Rynbrandt, Zeeland, MI (Chemistry).

Kristen L. Stoesser, Midland, MI (Biochemistry).

- Deborah C. Stone, Tullahoma, TN (Chemistry), is looking for a research position. She would like eventually to go to graduate school in a geochemistry or hydrology program, and then get a job with an environmental firm.
- Bradley S. Vander Veen, Holland, MI (Biochemistry), plans to attend Wayne State University Medical School.

Matthew D. Vizithum, Big Rapids, MI (Biochemistry).

Krista L. Widiger, Sterling Hts., MI (Chemistry), will be working at a dude ranch in Colorado for the summer before attending the University of Michigan Dental School in the Fall. Laura J. Wilson, Grosse Point Woods, MI (Biochemistry), will be attending Wright State University Medical School in Ohio.

Timothy T. Work, Portage, MI (Biochemistry).

### **1993 STUDENT AWARDS**

**Departmental Awards** 

Almon T. Godfrey Prize In Chemistry - An award to a senior chosen as the outstanding student in chemistry.

DuPont Award For Undergraduate Research in Chemistry - An award to the senior student who has done the most outstanding research in chemistry.

American Institute of Chemists Award - An award to a senior student who has exhibited diligence in study and research projects, helpfulness in the instructional laboratories, and interest in chemistry.

Junior Chemistry Journal Award An award of a subscription to Analytical Chemistry presented to an outstanding junior student in chemistry. Ericka L. Lyszak

Yvonne N. Grassl Kenneth S. Overway

Vicki L. Freeman

Rychard J. Bouwens

Organic Chemistry Book Award -An award presented to an outstanding student in organic chemistry.

Undergraduate Award for Achievement in Organic Chemistry - An award to an outstanding student in organic chemistry. Timothy Van Huis

Kathleen E. Gingras

First Year Chemistry Book Award - An award presented to an outstanding student in the first year chemistry program. Renny Abraham Ryan Wilcox

#### **Special Senior Awards**

National Science Foundation Graduate Fellowship

Ericka L. Lyszak, Honorable Mention

Gene Van Tamelen Prize for Creativity in the Sciences

Ericka L. Lyszak

Kent Medical Foundation Award

Jamie D. Crooks

The Southland Medal (Gerrit H. Albers Gold Medal)

Ericka L. Lyszak

American Association of University Women Award

Nancy E. Bischer

The Otto Vander Velde All-Campus Award

Mark R. Bonnell

## Scholarships and Fellowships

Barry M. Goldwater Scholarship

Rychard J. Bouwens Ericka L. Lyszak

The Dow Chemical Company Foundation Scholars

Ericka L. Lyszak Fredrick W. Vance Kathleen E. Gingras Rochelle L. Gauthier Jeffrey P. Ogema

The Almon T. and Harriet M. Godfrey Scholarship

Yvonne N. Grassl

The Richard Decker Scholarship

Richard E. Crumbie

### Jaecker Chemistry Scholarships for 1993-94

Peter W. Baer Rychard J. Bouwens Nickolas H. Chmiel David E. Den Haan Stephen L. De Wall Emily E. Erickson Timothy J. Ewald Nathalie Hallyn Jon A. Hammerschmidt Scott D. Hazard M. Scott Johnson Jeffrey T. Koorndyk Travis E. Long Joel C. Nemes Rebecca L. Shearer Heather L. Van Alstine Timothy Van Huis Holly J. Van Vliet Brian M. Van Zanten Wesley T. White

The Cupery Summer Research Fellowship

Timothy J. Ewald

The DeVries Summer Research Fellowship

William L. King

The Visser Summer Research Fellowship

Mark R. Whittaker

Merck Summer Research Fellowships

Stephen L. De Wall Kathleen E. Gingras Jeffrey T. Koorndyk The Dow Summer Research Fellowship

Fredrick W. Vance

Merck & Company Summer Intern

Ericka L. Lyszak

Pew Undergraduate Research Awards

Richard Blair Feler Bose

## NSF-REU Summer Research Fellowships

Rychard J. Bouwens Martha M. Grzeskowiak Timothy G. Hamilton Karl J. Kossen Elizabeth A. Pelton Eric S. Robirds Timothy Van Huis Wesley T. White

Council on Undergraduate Research (CUR) Fellowship

M. Scott Johnson

NSF-RUI Summer Research Fellowship for High School Teacher

Norman J. Hoekstra Holland Christian High School Howard Hughes High School Research Assistantships

Randy J. Kimple Rozelia O. Patino Catherine M. Rasmussen

Howard Hughes Medical Institute Summer Research Fellowships

> Brandt R. Burgess Julie M. Meyer

## All College Awards to Chemistry Students

## PHI BETA KAPPA INITIATES

Jamie D. Crooks Vicki L. Freeman Yvonne N. Grassl Ericka L. Lyszak Kenneth S. Overway Jennifer S. Rynbrandt Kirsten L. Stoesser Timothy T. Work

MORTAR BOARD (National Honor Society)

Julia A. DeGoede Nicholas B. Drzal William L. King III Heather L. Van Alstine

### SIGMA XI STUDENT RESEARCH AWARDS

Christopher A. Briggs Vicki L. Freeman Yvonne N. Grassl Michael S. Herman Kristin M. Knapp Christopher A. Lepczyk Ericka L. Lyszak Scott A. May Kenneth S. Overway Amy Poel Steven J. Ray Kenton B. Renkema Andrew G. Spencer William C. Van Zandt Laura E. Wilson Timothy T. Work

## PAPERS AND POSTERS PRESENTED BY HOPE COLLEGE STUDENTS (1992-93)

Richard G. Blair and W. F. Polik,<sup>\*</sup> "Lasers in the Undergraduate Physical Chemistry Curriculum", Fourth National Conference on Undergraduate Research (CUR), Hope College, June, 1992.

Charles D. Emery, Kenneth S. Overway, Rychard J. Bouwens, and W. F. Polik,\* "Dispersed Fluorescence Spectroscopy of Exited Rovibrational States in Formaldehyde", Fourth National Conference on Undergraduate Research, (CUR), Hope College, June, 1992.

Rychard J. Bouwens and W. F. Polik,<sup>\*</sup> "Calculation of The Rovibrational Interaction in Formaldehyde", Merck Student Research Symposium, Hope College, September, 1992 and ACS Midland Section Meeting, Delta College, Midland, MI, November, 1992.

Tineke Stegink and W. F. Polik,<sup>\*</sup> "Spectroscopy of Excited Rovibronic Levels in Formaldehyde and Acetaldehyde", Undergraduate Research Symposium, University of Groningen, The Netherlands, November, 1992.

Patrick M. Yorba and W. F. Polik,<sup>\*</sup> "Spectroscopy of Excited Rovibronic Levels in Formaldehyde and Acetaldehyde", Merck Student Research Symposium, Hope College, September, 1992.

Michael S. Hermen and M. E. Silver,<sup>\*</sup> "Isonitrile Insertion Chemistry of  $Cp_2ZrX(CH_2SiMe_3)$  and  $Cp_2ZrX(CH_2SiMe_3)$  [X = Cl,  $CH_2$ -SiMe<sub>3</sub>,  $CH_2SiMe_2OSiMe_3$ , SiMe<sub>3</sub>, Si(SiMe<sub>3</sub>)<sub>3</sub>]", ACS Midland Section Meeting, Delta College, Midland, MI, November, 1992 and Sigma Xi Student Research Symposium, Hope College, April, 1993.

Kenton B. Renkema and M. E. Silver,<sup>\*</sup> "Polymerization of Cyclic Siloxanes to Yield Linear Polymers of Narrow Molecular Weight Distribution Using Mixed K/Li Catalysts", ACS Midland Section Meeting, Delta College, Midland, MI, November, 1992 and Sigma Xi Student Research Symposium, Hope College, April, 1993.

Fredrick W. Vance and M. E. Silver,<sup>\*</sup> "Trying to Find a Way to Make  $Cp^*(allyl)Zr(CH_2PPh_2)_2$ ", Merck Student Research Symposium, Hope College, September, 1992 and ACS Midland Section Meeting, Delta College, Midland, MI, November, 1992.

Kathleen E. Gingras and M. E. Silver,<sup>\*</sup> "Requirements Necessary for a 1,2-Silyl Shift on Zirconocenes", Merck Student Research Symposium, Hope College, September, 1992 and ACS Midland Section Meeting, Delta College, Midland, MI, November, 1992.

Jason A. Fried, Yvonne N. Grassl, Mark R. Whittaker and S. K. Taylor,<sup>\*</sup> "Diastereo- and Enantioselective Reactions of Ester Enolates with Epoxides and Subsequent Lactonizations", Merck Student Research Symposium, Hope College, September, 1992.

Scott May and S. K. Taylor,\* "Competitive Cyclizations of Epoxides to Double Bond and Aromatic Positions", Merck Student Research Symposium, Hope College, September, 1992; ACS Midland Section Meeting, Delta College, Midland, MI, November, 1992; Pew Midstates Science and Mathematics Consortium Undergraduate Research Symposium in the Physical Sciences and Mathematics, Grinnell College, Grinnell, IA, November, 1992 and Sigma Xi Student Research Symposium Hope College, April, 1993.

Vicki L. Freeman and J. L. Stewart,<sup>\*</sup> "Synthesis and Characterization of Tin(II) Phenoxides", Merck Student research Symposium, Hope College, September, 1992; Seventh National Conference on Undergraduate Research (NCUR), University of Utah, Salt Lake City, UT, March, 1993 and Sigma Xi Student Research Symposium, Hope College, April, 1993.

William C. Van Zandt and J. L. Stewart,<sup>\*</sup> "Synthesis of Four Lead (II) Alkoxides and Siloxides", Merck Student Research Symposium, Hope College, September, 1992; ACS Midland Section Meeting, Delta College, Midland, MI, November, 1992; Great Lakes Chemistry Conference, Michigan State University, Lansing, MI, March, 1993 and Sigma Xi Student Research Symposium, Hope College, April, 1993.

Wesley T. White and J. L. Stewart,<sup>\*</sup> "Synthesis of Germanium(IV) Phenoxides from  $Ge(NMe_2)_4$  and 2,6-Diisopropylphenol", Merck Student Research Symposium, Hope College, September, 1992 and Third Annual Argonne Symposium for Undergraduates in Science, Engineering and Mathematics, Argonne, IL, November, 1992.

M. Scott Johnson, Jeffrey T. Koordyk, and W. S. Mungall,\* "Ladder Polymer Synthesis through Diels-Alder Chemistry", Merck Student Research Symposium, Hope College, September, 1992; Pew Midstates Science and Mathematics Consortium Undergraduate Research Symposium in the Physical Sciences and Mathematics, Grinnell College, Grinnell, IA, November, 1992; Great Lakes Chemistry Conference, Michigan State University, Lansing, MI, March, 1993 and Sigma Xi Student Research Symposium, Hope College, April, 1993.

\* Faculty Mentor

### STUDENT RESEARCH PROJECTS

Peter W. Baer Rockford, MI

Michael D. Bingham Cuttingsville, VT

Richard G. Blair Sterling Heights, MI

Feler Bose India

Rychard J. Bouwens Wayland, MI

Tammy L. Bush Holland, MI

Tammy L. Bush Holland, MI

Michael J. Camburn St. Joseph, MI "Preparation of Sterically-Demanding Thiols" (Stewart)

"Improved Advanced Chemical Demonstrations on Luminescence" (Williams)

"Laser Induced Fluorescence Spectroscopy of Diatomic Molecules" (Polik)

"Preparation of Excimer/Dye Laser System" (Polik)

"Theoretical Calculations of Rotation-Vibration Interaction in Formaldehyde" (Polik)

"Reduction of Ferritin Iron by Sulfhydryls" (Boyer)

"Expression and Staining of Vacm-1 Protein" (Burnatowska-Hledin)

"The Synthesis of Spirolactones" (Taylor) Xin Chen People's Republic of China

Stephen L. DeWall Spring Lake, MI

Christa Ellenberger Randolph-Macon, VA

Timothy J. Ewald Ann Arbor, MI

Vicki L. Freeman Rockford, MI

Jason Fried Hiram College

Kathleen E. Gingras Muskegon, MI

Yvonne N. Grassl Stevensville, MI

Timothy G. Hamilton Union Pier, MI "Rotational Energy Transfer Rates and Pathways in Formaldehyde" (Polik)

"Synthesis of Benzocyclobutanes Via Photocycloaddition Reactions" (Mungall)

"Synthesis of Tin(IV) Thiophenoxides" (Stewart)

"Development of Computer Based Experiments for the General Chemistry Lab" (Seymour)

"Characterization of Tin(II) Phenoxides" (Stewart)

"The Use of Lithium-bis(trimethylsilyl)amide in the Generation of Enolates" (Taylor)

"Synthesis of  $Cp_2ZrX(CH_2SiMe_3)$ [X=Cl, CH<sub>2</sub>SiMe<sub>3</sub>, SiMe<sub>3</sub>, Si(SiMe<sub>3</sub>)<sub>3</sub>] Compounds and their Reactivity with Isonitriles" (Silver)

"Improved Yields and Stereoselectivity in Enolate/Epoxide Reactions" (Taylor)

"Synthesis of Germanium(IV) Alkoxides" (Stewart) Jon A. Hammerschmidt Midland, MI

Michael S. Hermen Beecher, IL

M. Scott Johnson Sanford, MI

William L. King, III Holland, MI

Jeffrey T. Koorndyk Byron Center, MI

Arun Kori Atlanta, GA

Amy Lalick High School student

David J. LaPointe Milford, MI

Ericka L. Lyszak Alpena, MI "Dispersed Fluorescence Spectroscopy of Highly Excited Formaldehyde" (Polik)

"Synthesis of Methyl Isonitrile, Phenyl Isonitrile, and 9-Anthryltrimethylsilyl-chloro-methane" (Silver)

"The Polymerization of 1,2-Dihydrocyclobuta[b]naphthalene-4,7-dione" (Mungall)

"Synthesis of (bis-cyclopentadienyl)-(chloro)(9-anthryl-trimethylsilylmethyl)zirconium(IV) and its Isonitrile Insertion Chemistry" (Silver)

"The Synthesis of 1,2-Dihydrocyclobuta[b]naphthalene-4,7-dione" (Mungall)

"Synthesis of  $Cp_2ZrX(CH_2SiMe_3)$ [X=Cl,  $CH_2SiMe_3$ ,  $SiMe_3$ ,  $Si(SiMe_3)_3$ ] Compounds and their Reactivity with Isonitriles" (Silver)

"Routes to Aryl Sulfides" (Stewart)

"Kinetics of Ester Hydrolysis Reactions" (Polik)

"Sequencing of Vacm-2" (Burnatowska-Hledin) Ronald J. Matthews Muskegon, MI

Scott A. May Troy, MI

Alicia A.T. Mendenhall Port Huron, MI

Jos Nijhoff The Netherlands

Kenneth S. Overway Holland, MI

Steven J. Ray Kalamazoo, MI

Kenton B. Renkema Hudsonville, MI

Esther Rivas Holland, MI

Andrew G. Spencer Sheridan, MI

Brian P. Standish Portage, MI "Synthesis, Molecular Weight Study, and Use as a Polymerization Catalyst of  $K_4Li_4(OSiMe_3)_x(OCMe_3)_{8-x}$ " (Silver)

"Biomimetic Epoxide Cyclizations" (Taylor)

"Stable Expression of Vacm-1 Gene" (Burnatowska-Hledin)

"Synthesis of (permethylcyclopentadienyl)(tris-diphenylphosphinomethyl)zirconium(IV)" (Silver)

"Laser Induced Fluorescence Spectroscopy of Acetaldehyde" (Polik)

"Preparative-Scale Separation of Impurities in a Drug Intermediate" (Mungall)

"Synthesis of (permethylcyclopentadienyl)(tris-diphenylphosphinomethyl)zirconium(IV)" (Silver)

"Kinetics of Ester Hydrolysis Reactions" (Polik)

"The Binding of Heme and Other Ligands by Ferritin" (Boyer)

"Synthesis of (R)-2-Methoxy-1phenylethanol" (Mungall) Tineke Stegink The Netherlands

Heather Van Alstine Brooklyn, MI

Fredrick W. Vance Gaylord, MI

William C. VanZandt Marshall, MI

Brian M. VanZanten Gobles, MI

Wesley T. White Sterling Hts., MI

Mark R. Whittaker Cheboygan, MI

Matthew J. Yakes Montague, MI

Patrick M. Yorba Oxnard, CA "Dispersed Fluorescence Spectroscopy of Highly Excited Formaldehyde" (Polik)

"Synthesis of Peptide Analogs" (Mungall)

"Synthesis of (permethylcylopentadienyl)(chloro)(bis-diphenylphosphinomethyl)zirconium(IV)" (Silver)

"Synthesis of Stable, Soluble Lead(II) alkoxides and Siloxides" (Stewart)

"Synthesis of a Chiral Aluminum Hydride Reducing Agent" (Mungall)

"Synthesis of Germanium(IV) Phenoxides" (Stewart)

"Germanium Enolates Versus Aluminum Enolates" (Taylor)

"Automated Enzymatic Flow Analysis of Sugars" (Seymour)

"Dispersed Fluorescence Spectroscopy of Highly Excited Formaldehyde" (Polik)

### THE CHEMISTRY CLUB

The Chemistry Club was led this year by President Jenn Sebestl (chief organizer), Vice-President Kristi Knapp (head cheerleader), Secretaries Murphy Hentemann and Kate Gingras (publicity experts), and Treasurer Kent Renkema (soda machine slave). Dr. Will Polik served as the Club's advisor.

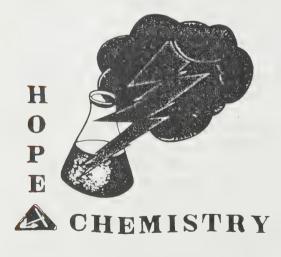
The Chem Club's year began with several picnics at Holland State Park beach during the summer for chemistry research students. Club members were well-practiced for their first activity of the academic year, a Welcome Back picnic for all returning chemistry students held at Smallenburg Park. During the fall, the Chem Club organized a trip to Argonne National Laboratories to visit the Graduate Student Fair, presented two Chemical Magic Shows to over 300 high school students visiting Hope on Science Day, participated in a Regional ACS Meeting, and hosted Dr. Douglas Swanson of the Michigan Macromolecular Institute as a seminar speaker. However, one would be in error to conclude that Chem Club activities are all work and no play. A goal of this year's officers was to involve as many students as possible in both scientific and social activities. To this end, the Club also organized a movie/pizza night, led an overnight camping trip (on which the first snowfall of the season came), organized a road rally/scavenger hunt, and held a game night at the famous Casino Polik-Stewart (Dr. Seymour was the grand winner, displaying his knowledge of the laws of probability at the blackjack table). The fall concluded with the annual Chem Club sponsored Christmas Party, complete with chemistry carols, gifts for the faculty, and a game of charades.

The spring semester opened with a Chem Club weekend ski trip at Sylvan Ski Resort in Gaylord. Service activities included sponsoring a panel discussion of women in science and math as part of the College's Women's Week, presenting hands-on chemistry experiments to over 350 elementary school children during Science Night, touring the BASF pigment plant in Holland, and visiting local elementary schools to present a hands-on approach to chemistry. Spring social functions also included a bowling night in downtown Holland and a second overnight camping trip (on which the last snowfall of the season came, and the Club declared that spring had officially arrived!). The semester concluded with an attempt to revive the Chem Club treasury through the sale of custom-designed T-shirts.

Throughout the year, the Chem Club met with the weekly seminar speakers for lunch and helped with duties around the Department. The Club took and posted photos of the Chemistry majors and kept the soda machine (their main source of income) well-stocked for thirsty chemistry students and faculty. They also published a wellreceived newsletter, informing students of upcoming activities and spreading false rumors about the faculty.

The Club looks forward to another very successful year with next year's officers: President Bryan Goodman, Vice-President Wes White, Secretary Scott Johnson, and Treasurer Jane Cook.

Dr. Bill Mungall will serve as their advisor.



# 1993 Summer Research Students





**Retiring Faculty** Eugene and Elaine Jekel

# Hope Chemistry Faculty and Staff



Front: R. Boyer, M. Burnatowska-Hledin, M. Seymour, Gene Jekel, W. Polik. Back: S. Taylor, N. Plasman, T. Gugino, Elaine Jekel, I. Brink, J. Stewart, W. Mungall, D. Williams. Missing: M. Silver.

New Chairman



Rodney F. Boyer

#### THE CHEMISTRY FACULTY

Rodney F. Boyer

B.A., Westmar College, 1964M.S., Colorado State University, 1967Ph.D., Colorado State University, 1969At Hope since 1974

The highlight of the 1992-93 academic year for Dr. Boyer was the publication of his laboratory textbook, *Modern Experimental Biochemistry*, in the second edition. The first edition which appeared in 1986 was used in at least 200 colleges and universities. The book which is published by Benjamin/Cummings is written in two parts: I. Theory and Experimental Techniques and II. Experiments. Thus, the book provides a theoretical background for students plus 25 experiments for the laboratory.

The Chemistry and Biology Departments continue to expand and enhance the Biochemistry/Molecular Biology Program. A new laboratory is being built in the former Science Library in the Peale Science Center. It will be equipped with modern instruments for biochemical research and teaching. Dr. Boyer and Dean Jim Gentile have prepared a proposal to the Howard Hughes Medical Institute to help fund the purchase of new equipment and to support student biomedical research on the Hope campus. Student interest in the fields of biomedicine and biotechnology is strong.

Dr. Boyer continues to work on a national curriculum for undergraduate biochemistry. He presented his latest ideas at a meeting of the Association of Medical and Graduate Departments of Biochemistry held in Cabo San Lucas (Baja), Mexico. This meeting was in January, 1993, during the first week of second semester classes; but, there were no complaints about leaving cold, snowy Michigan.

Student researchers in Dr. Boyer's laboratory are focusing their

efforts on the structure and function of iron storage protein, ferritin. Tammy Bush ('94) and Andy Spencer ('93) are exploring the reduction of ferritin iron and the binding of protoporphyrin and heme to the ferritin molecule. Dr. Boyer appeared on the TV Show, "Profiles in Survival," sponsored by the American Chemical Society, to discuss his work with catalytic RNA.

The Michigan Chapter of the American Heart Association has selected Dr. Boyer to serve a four-year term on the Grants Review Committee. Each December he receives about 50 grants from young biomedical researchers to review and critique. Although the workload is heavy, it is very informative and rewarding.

| Irwin J. Brink | A.B., Hope College, 1952            |
|----------------|-------------------------------------|
|                | Ph.D., University of Illinois, 1957 |
|                | At Hope since 1957                  |

Dr. Brink enjoyed a busy year as chair of a very productive department. Much of a department chair's fulfillment comes from the successes of the students, staff and faculty who make up the department. At Hope College there is much to feel fulfilled about.

One need go no further than the contents of this Annual Report for convincing evidence of this. The largest graduating class of majors in several years, a 28 percent increase in enrollment in our freshman science majors chemistry course this past fall, an unprecedented large enrollment in organic chemistry for the fall of 1993, and outstanding achievements on the part of our students are all sources of satisfaction to a department chair in spite of the scheduling and staffing headaches caused by the large enrollments. A dedicated, hard working, and cooperative faculty along with a remarkably helpful staff all contribute to a sense of "worthwhileness" in all the scrambling to meet deadlines for reports and the bearing of the weight of responsibility that somehow seems to get heavier as one passes the 60 years of age mark.

Particularly satisfying to Dr. Brink this past year were the successful promotion campaigns on behalf of Mike Seymour and Steve Taylor who are now full professors in rank and Elaine Jekel who advanced to rank of adjunct professor. The publication of the Annual Report, a time consuming task which often seems to go on for ever, continued to be rewarding. A disappointment this year was the failure to hire a person to fill a tenure track position created by the retirement of Gene Jekel. Among the most enjoyable experiences was the privilege of hosting Sylvia Ceyer ('74) and her parents on a beautiful evening in May when Sylvia was presented a Distinguished Alumnus Award at the annual Hope Alumni Banquet.

Teaching physical chemistry and introductory laboratory along with chairman's duties kept Dr. Brink busy in the fall. Teaching the freshman lecture course for science majors after an eight year hiatus and introductory laboratory was a special challenge during the spring semester. He will face a period of adjustment this year when for the first time in his 36 years on Hope's faculty he will not have Gene Jekel, his college classmate, to consult with on a daily basis. In spite of this he looks to the coming year with pleasure as a time to refocus his efforts on teaching after gratefully passing the responsibilities of department chair into the capable hands of Dr. Boyer.

Maria

A.B., McGill University, 1975 Burnatowska-Hledin Ph.D., McGill University, 1980 at Hope since 1992

Dr. Burnatowska-Hledin joined the Hope College faculty in August 1992 as Associate Professor of Chemistry and Biology. She is the first faculty member at Hope College with a joint appointment in the two departments since the turn of the century. A part of the price she pays for this unique status is attending departmental meetings of both departments and serving two department chairs.

Dr. Burnatowska-Hledin came to Hope from Michigan State University where she was an Assistant Professor in the Department of Physiology. During the fall semester she set up her laboratory at Hope, wrote research proposals and began to get students involved in her research program. During the spring semester she taught the Cell Biology course along with a section of Biochemistry Laboratory. This coming fall she will be teaching Organic Chemistry Laboratory and Physiology Laboratory.

During the spring semester, Dr. Burnatowska-Hledin had three students working on research projects and this summer is supervising four research students. She also employs a full-time laboratory technician. Her research focuses on characterizing vasopressin receptors at the molecular level and studying their function in regulating water transport and blood pressure. Her work is currently supported by the Howard Hughes Foundation, the American Heart Association of Michigan and the National Institutes of Health (NIH). She has submitted a new proposal to NIH for research support. She serves on the Grant Review Committee and the Student Research Committee, both of the American Heart Association of Michigan. She also reviews research papers for the Journal of Physiology. Elaine Z. Jekel

B.S., Greenville College, 1951M.S., Purdue University, 1953Ph.D., Purdue University, 1958At Hope 1960-61 and 1982 to date

As Adjunct Professor of Chemistry at Hope College, Dr. Elaine Jekel continued to teach the courses "Laboratory of General and Analytical Chemistry I and II." She also served as administrative assistant and secretary in organizing and operating a three-day conference for high school chemistry teachers held on campus in July, 1992.

In August, Dr. Jekel attended the American Scientific Affiliation Annual Meeting in Kona, Hawaii and the Biennial Conference on Chemical Education at the University of California, Davis; and in October, the annual meeting of the Metropolitan Detroit Science Teachers' Association at Plymouth Canton High School.

In May the faculty, administration and trustees of Hope College conferred the title "Adjunct Professor Emerita of Chemistry" upon Dr. Jekel in grateful recognition of the many years of significant contributions she has made to the Hope College community.

Together, she and her husband were honored at a number of events during the year. In October, Hope alumnus, Dick Welch, organized a recognition dinner attended by Detroit Area Chemistry Teachers. In May the Jekels were honored at a luncheon given by the Chemistry Department staff, at a dinner of the Board of Trustees, and at a Hope College recognition dinner that included present and past faculty and administrators. Eugene C. Jekel

A.B., Hope College, 1952 M.S., Purdue University, 1955 Ph.D., Purdue University, 1964 At Hope since 1955

At the beginning of the school year, Dr. Jekel announced that he would retire at the end of the 1992-93 academic year. He continued to serve as coordinator for both the freshman laboratory and lecture programs for science-track students and as chief advisor for students entering the health professions. During his tenure as Health Professions Advisor since 1977, 296 Hope College students have entered medical schools and 73 have entered dental schools. In April, he was honored at a reception arranged by the students in the Hope College Michigan Beta Chapter of Alpha Epsilon Delta, the National Pre-medical Honor Society.

This 38th year of teaching at Hope College was very eventful. He attended a number of professional meetings, often in a leadership capacity. In June, he co-presented with biology professor, Dr. Donald Cronkite, at the National Council of Undergraduate Research Conference held at Hope College. In August, he gave a paper at the Twelfth Biennial Conference on Chemical Education at University of California, Davis and in October, he co-presented with three highschool chemistry teachers at the Detroit Metropolitan Science Teachers' Association. He presented one-day Advanced Placement workshops sponsored by the College Board in Winnepeg for high-school teachers in Manitoba; in Charleston, West Virginia for teachers in that region; and in DesPlaines, Illinois for teachers in the Greater Chicago area. In April, Dr. Jekel co-presented with Dr. Lou Rice, pre-med advisor at the University of Michigan, a half-day workshop for new health professions advisors at the Central Association of Health Professions Advisors Meeting in Chicago. In June, he served as Table Leader and Reader for the AP chemistry examination and continues to serve on the test-writing committee for the 1994 Advanced Form of the ACS-NSTA Examination in Chemistry. Dr. Jekel became a member of the Task Force that produced the 1993 U.S. National Chemistry Olympiad Examination which was used by 150 local ACS sections. In October, he served as a member of the North Central Evaluation Team for the science department of New Trier High School in Winnetka, Illinois. In June, he attended the National Association of Advisors for the Health Professions meeting in Milwaukee, and in August, attended the annual American Scientific Affiliation Meeting in Kona, Hawaii. This year he again served as Faculty Marshal for formal convocations, baccalaureate and commencement.

As an appropriate follow-up activity to the 24 NSF-supported summer programs for high-school chemistry teachers, Dr. Jekel coordinated a three-day conference for past participants. John Brodemus, a 1991 participant, from H. L. Richards High School in Oaklawn, Illinois, served as program chair for the conference held in July, 1992. Sixty-five enthusiastic, professionally-active high-school teachers returned to the college at their own expense to attend this conference. Remarkably, a total of thirty-nine of the attendees volunteered as presenters.

In May the faculty, administration and trustees of Hope College conferred the title "The Hofma Professor Emeritus of Chemistry" upon Dr. Jekel in grateful recognition of the many years of significant contributions made to the Hope College Community.

William S. Mungall B.A., State University of N.Y. at Buffalo, 1967 Ph.D., Northwestern University, 1970 At Hope since 1971

Dr. Mungall and his research students have continued their work in the area of synthetic organic chemistry. The projects are focused in three different areas: the synthesis of novel monomers that are expected to polymerize to form ladder-type structures, the synthesis and study of a new enantioselective hydride reducing agent, and the isolation of trace components in a pharmaceutical intermediate by preparative chromatography. During the past year, seven students, Steve DeWall ('95), Scott Johnson ('94), Jeff Koorndyk ('94), Steve Ray ('93), Heather Van Alstine ('94), Brian Van Zanten ('95) have worked on these projects. This summer Steve DeWall, Scott Johnson, Jeff Koorndyk, and Brian Van Zanten have each continued working on research full time for ten or twelve weeks.

Dr. Mungall taught in and coordinated the organic laboratory program during both the first and second semesters. He also taught the first-semester organic chemistry class of over eighty-six students. During the second semester, he also taught the organic chemistry section of "Super Chem". One big improvement in the organic chemistry laboratory has been the availability of two new FT-IR spectrometers for student use. These instruments were purchased as part of the Kresge Foundation Grant to the Science Division to upgrade scientific equipment.

This year, Dr. Mungall and Dr. Polik successfully obtained grants from the National Science Foundation and CAChe Scientific to set up a computational chemistry laboratory at Hope College. Part of the space in the old science library will be used for this new facility. The new computer, which is a CAChe reactivity modeling workstation, will be equipped with three high-speed CPU's, 3-D color graphics, and a color printer. Also, the workstation will act as a server for fourteen high-level Macintosh computers, so that a whole class of students can do molecular modeling or MO calculations at the same time. Students will use this equipment in several classes starting with organic chemistry. New laboratory experiments are being developed to make maximum use of this state-of-the-art technology.

This spring, Dr. Mungall organized a one-day Symposium on Synthetic Organic Chemistry at Hope College that was attended by over 200 scientists and a number of Hope students. The Symposium, which focuses on the synthesis of pharmaceutical compounds, has attracted a growing number of participants in recent years. The Symposium is supported financially by the Parke-Davis Pharmaceutical Research Division of the Warner-Lambert Company.

Dr. Mungall has continued to serve as a consultant to several local chemical companies, and three students have worked on research projects related to his consulting.

#### William F. Polik

B.A., Dartmouth College, 1982 Ph.D., University of California, Berkeley, 1988 At Hope since 1988

Dr. Polik's research group is studying highly excited molecules and reactive intermediates using laser and molecular beam techniques. This year the research group succeeded in recording a pure vibrational spectrum of formaldehyde with up to  $12,000 \text{ cm}^{-1}$  of energy, revealing details of this small but significant molecule never observed in any other laboratory. This project will reveal how regular vibrational motion of a molecule becomes increasingly chaotic as the energy of reaction is approached. In other projects, Dr. Polik's group has completed a study of rotational energy transfer in formaldehyde and has recorded high resolution laser spectra of acetaldehyde. Nine undergraduate students and one high school student worked with Dr. Polik last year. Dr. Polik's research has been funded by the National Science Foundation, Wyckoff Chemical Company, and the Exxon Education Foundation.

Dr. Polik's teaching responsibilities included Superchem I (physical organic chemistry), Physical Chemistry II (quantum mechanics and 'spectroscopy), General Chemistry Laboratory I, and Physical Chemistry Laboratories I and II. Dr. Polik worked with Dr. Seymour to introduce computers for making measurements and analyzing data in the general chemistry laboratory. Dr. Polik also introduced a new laser induced fluorescence spectroscopy experiment in the physical chemistry laboratory.

Dr. Polik served as the Chem Club advisor during the past year, participating in activities such as a late night scavenger hunt, game night (he came out a winner!), and a campout in the Allegan forest. He also has been promoting a student exchange program between Hope College and The Netherlands by hosting a dutch research student for the previous and current summers.

Dr. Polik co-wrote a successful grant proposal with Dr. Mungall to establish a computational chemistry laboratory at Hope College. A state-of-the-art CAChe system has been selected to interface with the existing Macintosh computer laboratory on the Chemistry floor of the Peale Science Center. Drs. Polik and Mungall will be incorporating the use of molecular mechanics and electronic structure calculations into their coursework next year.

Michael D. Seymour B.A., St. Johns University, 1972 Ph.D., University of Arizona, 1978 At Hope since 1978

Two major events have taken place for Dr. Seymour this past year. One is promotion to the rank of Professor and the second is approval of plans for a sabbatical leave for the 1993-94 academic year. While he is excited about the upcoming sabbatical leave with Parke-Davis in Holland, he has continued his involvement with science education activities for K-12 teachers and students. This has included presentations in Detroit, local workshops for teachers and visits to elementary schools with Hope students serving as enthusiastic assistants. Teaching assignments included the Analytical Chemistry course, Chemistry for Elementary Teachers, General Chemistry labs and second semester General Chemistry lecture. In Dr. Seymour's sections of the General lab several computer interface systems were used on a trial basis for data collection and analysis in the calorimetry, kinetics and titrimetric experiments. As an extension of his current involvement with a seven school consortium that is working to develop a library of computer based experiments for the general chemistry lab, Dr. Seymour plans to submit a proposal to equip all of the general lab stations with computer interfaced systems for data collection and analysis.

### Michael E. Silver

B.S., Fairleigh Dickinson University, 1975M.S., Cornell University, 1979Ph.D., Cornell University, 1982At Hope since 1984

Dr. Silver's research group is involved in three different research projects. The first is directed towards the synthesis of novel earlytransition metal allyl complexes to serve as precursors for reactive bimetallic compounds. The second project is directed towards functionalizing the methyl groups on polydimethylsiloxanes, industrially important surfactants and lubricants. The third project involves the ring-opening polymerization of cyclic siloxanes to obtain linear polymers with a narrow molecular weight distribution. Almost all of the compounds prepared are highly sensitive to air and moisture. Dr. Silver's students therefore become expert at working on vacuum lines and inside inert atmosphere gloveboxes, as well as performing organic and inorganic reactions and becoming proficient with such analytical techniques as GC, GC/MS, FT-IR, FT-NMR, and variable temperature NMR. This past summer, Dr. Silver's group was joined by Jos Nijhoff, an exchange student from the University of Groningen in The Netherlands. Dr. Silver's student, Ericka Lyszak, took Jos' place at Groningen. Also working in his group this summer was Ron Matthews, a chemistry teacher from Orchard View High School, Muskegon. Two high school students, Raymond Yeung and Turen Fickel, also worked in the group.

Dr. Silver teaches in the general chemistry course for majors, the general chemistry course for non-majors, the sophomore organic chemistry lab, the junior-level inorganic chemistry course, and in our senior courses, Synthesis, Structure, and Dynamics (affectionately called SU-PERCHEM), and in Chemical Instrumentation. He is currently writing a textbook in collaboration with Dr. Steven Russo of Cornell University. Dr. Silver was also awarded a Camille and Henry Dreyfus Foundation Grant of \$60,000 to support a Postdoctoral Fellow for 'two years. This will be Dr. Chris Schaller (Ph.D., Cornell University, 1993), who will arrive at Hope in August, 1993.

Dr. Silver's permanent group members continue to get older. Eight year old son Arron plasters the office door with "Star Trek Funnies" that he composes in the Mac Lab. Six year old daughter Kelsey has taken to taping hand designed cutout hearts all over Norma's office. Both of them tremendously enjoy tossing dry ice into beakers filled with soapy water. The mess it generates is truly astounding.

Joanne L. Stewart B.A., Kalamazoo College, 1982, Ph.D., University of California, Berkeley, 1988 At Hope since 1988

Dr. Stewart and her research students continue their work in the synthesis of main group metal alkoxide and thiolate compounds. With the inspiration of good music in the laboratory, summer students Bill VanZandt, Vicki Freeman, Wes White, and Christa Ellenberger (REU student from Virginia) made big strides forward in their work. The summer saw the beginning of new studies in germanium and lead chemistry, in addition to continued work on tin compounds. Two additional students, Pete Baer and Tim Hamilton, joined the group during the academic year. They and Wes White are continuing their research full-time this summer.

Dr. Stewart taught Analytical Lab in the fall with Dr. Seymour. Inorganic Chemistry in the spring, and continued her involvement in General Chemistry and Superchem. She developed several new collaborative exercises for Inorganic, involving group problem solving sessions before each exam. The students worked together enthusiastically and were very positive about how the exercises prepared them for the exams.

After helping organize a Pew workshop on cooperative learning last year, Dr. Stewart was asked to give a similar workshop as an NSF Chautauqua short course.

The workshop was held in March at the University of Puerto Rico in San Juan. There were a total of 34 participants in the workshop, 15 from the states and 19 from Puerto Rico. The diverse group of science and mathematics faculty brought lots of enthusiasm and good ideas with them. As the workshop coincided with Hope's spring break, Dr. Stewart had time to do some additional research on Puerto Rican beaches. She gives them very high marks.

Stephen K. Taylor

B.A., Pasadena College, 1969 Ph.D., University of Nevada, Reno, 1974 At Hope since 1985

This past summer, Hope College hosted the national Council on Undergraduate Research meeting, and Dr. Taylor was activities coordinator for the various events. The College received numerous compliments on many parts of the meeting and it was viewed as a highly successful program. Another responsibility that has added a lot to Dr. Taylor's workload has been his appointment to the Petroleum Research Fund Advisory Board. This entails reviewing about 65 proposals every four months and helping decide which proposals are fundable. He also serves on the Policy Committee.

Dr. Taylor enjoyed an active year professionally. One paper was published in *Tetrahedron Letters*, another in *Organic Preparations and Procedures International* (a review) and one paper was accepted in the *Journal of Organic Chemistry*. He was on sabbatical leave during the Fall semester, when he worked with John R. Stille at Michigan State University. A paper based on this and related work was presented at the National ACS Meeting in Denver, and a publication is planned at a later date. He is pursuing an entirely new direction in research, the use of enzymes in organic synthesis, and is excited about this hot new area of chemistry.

Dr. Taylor's research students for summer 1993 are Mark Whittaker ('94), Tim Van Huis ('95), and Elizabeth Pelton (an REU student from Wheaton College in Illinois). A high school student from Muskegon, Rozelia Patino, is also working in his lab.

Dr. Taylor helped coordinate the Merck Lecture series this past year. The Merck company speaker was Dr. Ruth Nutt, who spoke on peptide synthesis. Other speakers in the series were Drs. Stephen Benkovic, who is developing catalytic antibodies, and Yuan Lee, a Nobel-prize winning physical chemist. All three speakers gave outstanding lectures.

Due to Dr. Taylor's sabbatical leave, he only taught during the second semester: one organic lecture and one organic lab. A highlight of the semester was dividing the second semester lab into two onecredit hour sections. This allowed each professor more time to devote to students taking the independent synthesis part of lab. The course received some very positive comments and evaluations from students.

| Donald H. Williams | B.S., Muskingum College, 1960      |
|--------------------|------------------------------------|
|                    | Ph.D., Ohio State University, 1964 |
|                    | At Hope since 1969                 |

The Summer of 1992 ended with a flurry of activities for Dr. Williams that are typical for him. He was a teacher in two workshops on Energy Issues for the American Nuclear Society (ANS), one in Milwaukee and one in Ann Arbor. Then just before Hope classes began he presented a paper to a Symposium on "Teaching for the Allied Health Professionals" at the Washington, DC National Meeting of the American Chemical Society. Between those presentations he was one of the key speakers in a National Educational Teleconference put on by the Department of Energy promoting forthcoming outreach material from the Office of Civilian Radioactive Waste Management. The Detroit Rotary Club was the centerpiece for a day in front of Southeast Michigan radio and TV microphones. His teaching and public speaking continued into the winter.

In January, Dr. Williams taught a short course on Chemical Energy Systems for Michigan State University as a part of in-service work for teachers. This and a media tour in Albuquerque and Santa Fe was done while he taught two beginning courses at Hope, one for liberal arts students and one for pre-nursing students. During Spring Break, he spoke in Las Vegas for the U.S. Council on Energy Awareness. While there he visited three area High Schools.

For the third straight year, Dr. Williams was half-time with the Admissions Office aiding in the recruitment of outstanding science students. Maybe this is why we added a new section to the majors lab course. This role meant that he made presentations in five Michigan High Schools. The promotion of Science Day and hosting its 642 guests has increasingly fallen upon him.

Dr. Williams continues to be a consulting editor and reviewer for three publishers, works on the Environmental Health Board locally and serves as "The Answer Man" on science questions for area elementary teachers. He found time this May for his favorite activity, teaching the senior seminar, "Science and Human Values".

The Summer of 1993 has Dr. Williams working at his usual furious pace. He has just finished another workshop on Energy for in-service teachers, a week of Explorientation, two book reviews and a month of supervising the Hughes Pre-college Science Program for minority youth.

### New Faculty: Maria and Research Students



From Left: Aditi Sharangpani, Amy Poel, Alicia Elmore, Lars Warmhoudt, Dr. Maria Burnatowska-Hledin, Julie Meyer.



1992 J. and J. Neckers Lecturer A. Paul Schaap ('67)



Yuon T. Lee, Nobel Laureate, Merck Lecturer, with Will Polik



Barry M. Trost, 1993 Distinguished Scholar, with Bill Mungall

### **Retiring Faculty**

#### Eugene and Elaine Jekel

May, 1993 is a milestone in the history of the Hope College Chemistry Department in that it marks the official retirement of Eugene and Elaine Jekel, whose contributions to the Chemistry Department and the College have been extraordinary in number and quality over a period of many years.

Gene joined the chemistry faculty in 1955 fresh from graduate work at Purdue University. He married Elaine in 1960 and completed his Ph.D. in inorganic chemistry at Purdue in 1964 while on leave from Hope.

In 1964 Gene directed his first of 24 National Science Foundation supported Summer Workshops for high school chemistry teachers of Advanced Placement chemistry. More than 1,050 high school teachers from throughout the nation attended those programs at Hope College.

Gene served two three-year terms as chair of the Department of Chemistry, and since 1976 has coordinated the General Chemistry lecture and laboratory courses for science majors. In 1977 he became Hope College's chief advisor for the health professions and faculty sponsor for the Michigan Beta Chapter at Hope College of the national honorary, Alpha Epsilon Delta. From 1988 to 1992 he was national treasurer of Alpha Epsilon Delta.

In 1985 he received the National Catalyst Award of the Chemical Manufacturers Association for excellence in teaching college chemistry, and in 1987, a Distinguished Alumnus Award from Hope College. He was named in 1987 to the endowed chair, The Drs. Edward A. and Elizabeth Hofma Professor of Chemistry.

Elaine began teaching as a part time lecturer at Hope in 1960 af-

ter serving as Assistant Professor of Chemistry at Western Michigan University for four years. Beginning in 1964 she spent a number of years away from her professional career to raise their family. In 1982 she returned to teaching part time at Hope and rose to rank of Adjunct Professor of Chemistry at the time of her retirement. Her major teaching assignment at Hope has been in the General and Analytical Chemistry Laboratory course for science majors. In addition she played a leadership role in developing the course, Chemistry for Elementary Teachers. She also taught Advanced Analytical Chemistry laboratory. Elaine, in addition to her teaching responsibilities, played a key role in the administration of the Summer Workshops for high school chemistry teachers at Hope.

These few paragraphs do not begin to enumerate the countless contributions that Gene and Elaine have made to chemistry at Hope College. Everything they did was done with distinction.

We wish them well in their richly deserved retirement. Their leadership will be sorely missed. We are pleased that they will be helping out as part-time teachers in the department during the 1993-1994 academic year.

### **New Faculty**

#### Maria Burnatowska-Hledin

We welcome Dr. Maria Burnatowska-Hledin as the newest member of our faculty. She comes to us from Michigan State University where she was Assistant Professor of Physiology. She holds a joint appointment in Biology and Chemistry at Hope. She has a very active research program in molecular biology involving a number of Hope students. She and her husband, Peter have two children: Victoria age 6 and Michael age 4. Peter is a boat designer and builder and owns his own business in nearby Douglas. Maria strengthens our program at the interface of biology and chemistry where many of the most exciting developments in science are occurring. We are delighted to have her as a colleague.

### New Chairman

#### Rodney F. Boyer

Beginning July 1, 1993 Rodney Boyer takes over as chairman of the department from Irwin Brink who is completing a three-year term. The chairmanship is not new to Rod, since he previously served a three-year term from 1986-1989, a period of great advancement for the department. We look forward with enthusiasm to the next three years under Rod's skillful leadership.

### **Former Faculty Members**

F. Sheldon Wettack was a member of the chemistry faculty from 1967-1982. He served as Dean for the Natural and Social Sciences from 1975 to 1982 and left Hope to become the Dean of the Faculty of the College of Arts and Sciences at the University of Richmond. From there he went on to become President of Wabash College. He has accepted a position at Harvey Mudd College where he will be Vice President and Dean of the Faculty.

### **CHEMISTRY PUBLICATIONS (1992-93)**

\*indicates Hope Student

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B.A. Vroon<sup>\*</sup> and W.F. Polik, "Automating Motion Control with Stepper Motors", *American Laboratory*, **24**, 33-37, June 1992.

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R. Hernandez, W.H. Miller, C.B. Moore, and W.F. Polik, "A Random Matrix / Transition State Theory for the Probability Distribution of State-Specific Unimolecular Decay Rates: Generalization to Include Total Angular Momentum and Other Dynamical Symmetries", J. Chem. Phys., in press.

M.E. Silver, M.A. Serra, and B.K. Dorner,<sup>\*</sup> "Structure of an Adenine-Hydrogen Peroxide Adduct", *Acta Cryst.*, C48, 1957-1960 (1992).

M.E. Silver, E.L. Lyszak,<sup>\*</sup> J.P. O'Brien,<sup>\*</sup> D.A. Kort,<sup>\*</sup> S.K. Hendges,<sup>\*</sup> R.N. Redding,<sup>\*</sup> T.L. Bush,<sup>\*</sup> M.S. Hermen,<sup>\*</sup> K.B. Renkema,<sup>\*</sup> and J.C. Huffman "Zirconium Compounds of Hexamethyldisiloxane. Synthesis, Structure, and their Reactivity with Methyl Isocyanide", Organometallics 12, 338-342 (1993).

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L.H. Kras,<sup>\*</sup> A. Euvrard,<sup>\*</sup> Y.N. Grassl,<sup>\*</sup> S.M. Ronda,<sup>\*</sup> J.L. Stewart, "Synthesis of Sn[OCHt-Bu)<sub>2</sub>]<sub>2</sub> and Sn[OSi(t-Bu)<sub>3</sub>]<sub>2</sub>: Variable Temperature <sup>1</sup>H and <sup>119</sup>Sn NMR Studies", *Main Group Metal Chemistry*, in press.

S.K. Taylor, "Biosynthetic, Biomimetic and Related Epoxide Cyclizations. A Review", Organic Preparations and Procedures International, 24, 245 (1992).

S.K. Taylor, S.A. May<sup>\*</sup> and J.A. Hopkins,<sup>\*</sup> "Cyclizations Wherein an Epoxide Acts as the Source of Initiation and Termination Steps. Evidence for an Early Transition State in Biomimetic Epoxide Cyclizations", *Tetrahedron Lett.*, **34**, 1283 (1993).

D.H. Williams, and D.A. Sullivan, "Student Control of Content Order: Increased Student Interest", Proceeding's of The Symposium on Teaching The Allied Health Professional, in press.

# SEMINARS, WORKSHOPS, AND PAPERS PRESENTED BY CHEMISTRY FACULTY (1992-93)

R.F. Boyer, "The Undergraduate Degree in Biochemistry", Association of Medical and Graduate Departments in Biochemistry, Cabo San Lucas, Mexico, January, 1993.

R.F. Boyer, "Biochemistry Degree Recommended by ASBMB", Council on Undergraduate Research National Meeting, Hope College, June, 1992.

M. Burnatowska-Hledin, "Cloning of Vacm-1 Receptor", American Heart Association Meeting, Detroit, MI, September, 1992. E.C. Jekel, "Teacher Enhancement Programs That Promote Research-Based Learning" co-presented with D. L. Cronkite, Council of Undergraduate Research National Meeting, Hope College, June, 1992.

E.C. Jekel, "The 1992 AP Chemistry Exam: Its Content and Grading," co-presented with M. C. Johnson; "Recent Guidelines for NSF Teacher Enhancement Programs," The Three-Day Conference for High School Chemistry Teachers, Hope College, July, 1992.

E.C. Jekel, "Hope College Laboratory Experiments on Computer Disks," a part of the Symposium, "Enhancing the Role of the High School Laboratory," the Twelfth Biennial Conference on Chemical Education, University of California, Davis, CA, August, 1992.

E.C. Jekel, "Advanced Placement Program in Chemistry," Conducted day-long workshops in Winnepeg, Manitoba and in Charleston, WV, October, 1992 and in Des Plaines, IL, April, 1993.

E.C. Jekel, "Laboratory Experiments for the Advanced Placement Chemistry Course," co-presented with three high school teachers, the Fall Conference of the Metropolitan Detroit Science Teachers Association, Plymouth-Canton High School, MI, October, 1992.

E.C. Jekel, "Workshop for New Advisors," co-presented with L. Rice, Central Association of Advisors for the Health Professions Biennial Meeting, Chicago, IL, April, 1993.

W.S. Mungall, "Ladder Polymer Synthesis Through Diels-Alder Chemistry", The Dow Chemical Company, Midland, MI, March 19, 1993.

W.F. Polik, "Laser Spectroscopy of Excited Molecules", Grand Valley State University, Allendale, MI, September, 1992 University of Michigan at Dearborn, Dearborn, MI, October, 1992 and Northwestern University, Evanston, IL, March, 1993.

W.F. Polik, "Spectroscopy of Excited Rivibronic Levels in Formaldehyde and Acetaldehyde", ACS Midland Section Meeting, Delta College, Midland, MI, November 1992.

M.E. Silver, "Isonitrile Insertion Chemistry of  $Cp_2ZrX(CH_2SiMe_2 - OSiMe_3)$  and  $Cp_2ZrX(CH_2SiMe_3)[X = Cl, CH_2SiMe_3, CH_2SiMe_2 - OSiMe_3, SiMe_3, Si(SiMe_3)_3]$ , Central Michigan University, Mount Pleasant, MI, September 1992.

J.L. Stewart, "Attracting Women into Chemistry and Research", Council on Undergraduate Research National Meeting, Hope College, June, 1992.

J.L. Stewart, "Cooperative Learning in Science and Mathematics", Chautauqua Short Course, University of Puerto Rico, San Juan, PR, March, 1993.

A.E. Harms, S.K. Taylor, and J.R. Stille (Michigan State University), "Ring Formation Through Intramolecular  $S_N 2'$  Displacement of an Allylic Methoxy Substituent", 205th ACS National Meeting, Denver, CO, April, 1993.

D.H. Williams, "Student Control of Content Order: Increased Student Interest", 204th ACS National Meeting, Washington, DC, August, 1993.

### CHEMISTRY FACULTY GRANTS

R. F. Boyer, "Characterization of Apoferritin as a Ferroxidase",

American Chemical Society-Petroleum Research Fund, \$20,000, 5/91-8/92.

- R. F. Boyer, "Development of Student Projects in Biochemistry", Howard Hughes Biomedical Program, \$5,000, 1/92-12/92.
- R. F. Boyer, "Development of a Biochemistry Textbook", Brooks/ Cole Publishing Co., \$3,000, 3/91-12/94.
- R. F. Boyer, "Design of an RNA Restriction Enzyme", Howard Hughes Biomedical Program, \$5,000, 1/93-12/93.
- M. Burnatowska-Hledin, "Vasopressin Signalling in the Collecting Tubule", National Institutes of Health, \$74,194, 9/1/92 to 8/30/93.
- E. C. Jekel, "Summer Project for High School Teachers of Honors Chemistry", National Science Foundation, \$192,899, 3/1/91 to 9/30/92.
- E. C. Jekel, "Cost-sharing Support for the Hope College Summer Project for High School Chemistry Teachers", The Dow Chemical Company Foundation, \$10,000, 3/13/91 to present.
- W. S. Mungall, "Computational Chemistry Laboratory for Undergraduate Instruction", National Science Foundation, Instrumentation and Laboratory Improvement Program, \$45,812, 6/15/93 to 11/30/95 (with W.F. Polik).
- W. S. Mungall, "Computational Chemistry Laboratory for Undergraduate Instruction", CAChe Higher Education Grant, CAChe Scientific, \$19,196, 4/29/93 (with W.F. Polik).
- W. S. Mungall, "Symposium on Synthetic Organic Chemistry", Parke-Davis Pharmaceutical Research Division of the Warner-Lambert Company, \$7,000, 1/93-8/93.

- W. S. Mungall, "Synthesis of Ladder Polymers", 1993 Undergraduate Student Summer Research Fellowship in Science, Council on Undergraduate Research, \$2,500, 3/93-8/93.
- W. F. Polik, "Laser Theory, Spectroscopy, and Kinetics Equipment for Undergraduate Instruction", National Science Foundation -Instrumentation and Laboratory Improvement Program, \$44,037, 4/15/90 to 9/30/92.
- W. F. Polik, "Matching Support of Presidential Young Investigator Programs", Wyckoff Chemical Company, \$37,500, 9/1/91 to 8/30/96.
- W. F. Polik, "Presidential Young Investigator Award", National Science Foundation, \$125,000 and 1:1 matching for \$187,500, 6/1/91 5/31/96.
- W. F. Polik, "Research into Highly Excited Molecules and Reactive Intermediates using Laser and Molecular Beam Techniques", Exxon Educational Foundation, \$10,000, 10/26/92 to 7/31/93.
- W. F. Polik, "Computational Chemistry Laboratory for Undergraduate Instruction", National Science Foundation - Instrumentation and Laboratory Improvement Program, \$45,812, 6/15/93 to 11/30/93 (with W.S. Mungall).
- W. F. Polik, "Molecular Modeling Equipment Grant", CAChe Scientific, \$19,196, 4/29/93 (with W. S. Mungall).
- M. D. Seymour, "Undergraduate Research in Chemistry at Hope College", National Science Foundation REU Program. Program director for the second year of a three year \$120,000 grant to support 8 students for 10 weeks of full time research.

- M. D. Seymour, "Chemistry Workshops for Elementary Teachers", Institute for Chemical Education, \$1,750 continuation grant for 1992-93 academic year.
- M. E. Silver, "The Synthesis, Characterization, Dynamic Behavior and Reactivity of Early Transition-Metal Allyl Complexes", NSF-RUI, 5/92-4/93, \$35,000.
- M. E. Silver, Support for a High School Teacher in Summer Research, NSF-RUI, 5/92-8/92, \$5,500.
- J. L. Stewart, "Main Group Metal Alkoxide and Thiolate Compounds", American Chemical Society - Petroleum Research Fund, 8/91-8/93, \$20,000.
- J. L. Stewart, "Cooperative Learning in Science and Mathematics", National Science Foundation Short Course as part of Chautauqua Short Course Program, 3/93, \$2,500.
- J. L. Stewart, "New Synthetic Routes to Important Materials", Hope College Faculty Development Grant, Summer 1993, \$2,800.
- D. H. Williams, "Environmental Education Workshop", Joyce Foundation, Summer 1992, \$6,000.

# DEPARTMENTAL GRANTS AND GIFTS

The Chemistry Department has been the recipient of many generous gifts and donations. We are grateful to the many alumni, friends, foundations and corporations who continue to support the programs of our department. We wish to acknowledge those who have made a substantial donation to the Chemistry Department this past year. We encourage others to consider a gift for the support of our active program. A financial gift of any size can make a significant positive impact on the lives of our students.

The Jaecker Chemistry Scholarship Fund established by Mr. Harry C. Jaecker, Jr. (and the late Mildred Jaecker) of Sun City Center, FL and Southbury, CT, assists worthy students who wish to continue their studies in chemistry at Hope.

The Cupery Student Research Fellowship, established by Dr. and Mrs. Martin Cupery of Lakeland, FL and Friesland, WI, provides a stipend for a summer research student in chemistry.

The John and Ruth De Vries Chemistry Fund, established by Dr. and Mrs. John De Vries of Palo Alto, CA, provides a stipend for a summer research student in chemistry.

The J. and J. Neckers Lectureship in Chemistry established by Dr. James W. Neckers (and the late Jeanette Hoffman Neckers) of Carbondale, IL, and Holland, MI provides support to bring outstanding chemists to the Hope campus to present lectures on recent advances in chemistry. Dr. Neckers made a very generous gift to enhance the endowment of the Fund this past year. Gary Hieftje ('64) also made a substantial gift to the Fund.

The Donald W. Visser Memorial Fund, established by the California Foundation for Biochemical Research in memory of Donald W. Visser, 1937 Hope graduate and long time member of the faculty at the University of Southern California Medical School, provides a stipend and supplies for a summer research student in biochemistry/chemistry.

The James H. and Marian Klaassen Zwemer Chemistry Fund was recently established by James and Marian Zwemer of Punta Gorda Florida. The Fund will provide support for equipment and student/ faculty research.

Harold Woltman ('39) made a generous contribution to the *Chemistry Undergraduate Research Fund*. William Mungall, Michael Seymour, Michael Wedlock ('86) and Louis Padnos Iron and Metals also made substantial gifts to this fund. This endowed fund was established in 1984 to promote undergraduate research in all fields of chemistry. Income from this fund is to be used for the support of undergraduate research and student research fellowships.

The Dow Chemical Company Foundation granted \$16,000 for several scholarships. Currently, four Hope College chemistry majors receive Dow Scholarships.

The Dow Chemical Company Foundation also awarded the Department \$2500 to support the summer student research program.

The *DuPont Company* provided the Department with an unrestricted grant of \$4,000. Funds from this grant will be used to support student research and to provide partial support for the purchase of chemical instrumentation.

The Merck Company Foundation granted the department \$13,000 of which \$10,000 was used to support summer research and \$3,000 to fund the Merck Speaker Series.

The Warner-Lambert/Parke Davis Company donated \$7,000 to support the Distinguished Scholars Program in Chemistry.

Dr. Uwe Soenksen, recently retired Director of Technology Transfer at BASF Corporation Holland Pigments, made a gift to the Department of 70 volumes of "Methoden der Organischen Chemie", Houben-Weil.

# CHEMISTRY DEPARTMENT SEMINAR SERIES 1992-93

The chemistry seminar program and the Symposium on Synthetic Organic Chemistry brought in 32 visiting scientists from academic institutions and chemical industry. Also, some of our research students presented experimental results at a special symposium sponsored by Merck & Company. Our seminar program provides students, faculty and area industrial chemists with an opportunity to learn of the most recent advances in chemistry and to meet with outstanding visiting scientists. A time before each seminar is reserved so that interested Hope students can meet with the speakers to discuss graduate school, careers, research problems or other related topics. William Mungall organized the seminar program for 1992-93, and the Symposium on Synthetic Organic Chemistry in June.

| Sept. 11 | Merck Student Research Sympo-<br>sium and Poster Session   |
|----------|--|
| Sept. 18 | <b>Dr. Laura Lerner</b> , University of<br>Wisconsin-Madison - "Using High Reso-<br>lution NMR to Study Biomolecules"                              |
| Sept. 25 | <b>Dr. Douglas C. Neckers</b> , Bowling<br>Green State University - "Three Dimen-<br>sional Imaging in Medical Diagnosis and<br>Surgical Planning" |
| Oct. 2   | <b>Dr. Donald R. Dimmel</b> , The Institute<br>of Paper Science and Technology - "Pulp-<br>ing and Bleaching: The First Steps in Pa-<br>permaking" |

| Oct. 16 | Dr. A. Paul Schaap, Wayne State University - (James and Jeanette Neckers<br>Lecturer) "1,2-Dioxetanes and Chemilu-<br>minescence: From Laboratory to Medical<br>Diagnostics" |
|---------|--|
| Oct. 23 | <b>Dr. James Coward</b> , The University<br>of Michigan - "Mechanistic Bio-organic<br>Chemistry and the Design of New Drugs"   |
| Oct. 29 | <b>Dr. James L. Anderson</b> , The University of Georgia - <i>"Electrochemical Investigations of Environmental Redox Components"</i>   |
| Oct. 30 | <b>Dr. Wendell Wierenga</b> , Parke-<br>Davis/Warner Lambert Co "How Are<br>Drugs Discovered - Examples from Re-<br>search in AIDS"  |
| Nov. 6  | <b>Dr. Warren E. Piers</b> , The University of<br>Guelph, Ontario, Canada - "The Chem-<br>istry and Use of Early Transition Metal<br>Organometallic Compounds"               |
| Nov. 12 | Dr. Stephen J. Benkovic, Pennsylva-<br>nia State University (Merck Lecturer) -<br>"Catalytic Antibodies"   |
| Nov. 20 | <b>Dr. John R. Huizenga</b> , The University<br>of Rochester- "Cold Fusion: The Scien-<br>tific Fiasco of the Century"   |

| Dec. 4  | Dr. Douglas Swanson, Michigan<br>Macromolecular Institute - "Starburst/<br>Cascade and Comb-Burst Dendrimers:<br>Fundamental Building Blocks for a New<br>Nanoscopic Chemistry Set" (sponsored by<br>Hope College Chemistry Club) |
|---------|---|
| Dec. 8  | <b>Dr. David E. Cane</b> , Brown University<br>- "How Nature Makes Antibiotics"   |
| Jan. 12 | <b>Dr. Louis J. Liotta</b> , Pennsylvania State<br>University - "The Design and Develop-<br>ment of Catalytic Antibodies"   |
| Jan. 19 | <b>Dr. Mary M. Mader</b> , University of Cal-<br>ifornia, Berkeley - "Computer-Aided De-<br>sign, Synthesis, and Study of Novel Pep-<br>tide Inhibitors"  |
| Jan. 21 | Dr. Judy A. Westrick, University of<br>Colorado, Boulder - "Effects of Pregnancy<br>and Vitamin B-6 Nutriture on Alanine<br>and Aspartate Aminotransferase Activi-<br>ties in Age Fractionated Erythrocytes"                      |
| Jan. 22 | <b>Dr. Michael D. Taylor</b> , Parke-Davis<br>Warner/Lambert Company - "Ap-<br>proaches to Peptidomimetic Drug Design<br>and Delivery"  |
| Feb. 5  | Dr. William R. Roush, Indiana Uni-<br>versity - "Acyclic Diastereoselection via<br>Allyl Boron Chemistry"   |

| Feb. 10  | Chemistry Faculty, Hope College -<br>"Summer Research Informational Meet-<br>ing"  |
|----------|--|
| Feb. 19  | Dr. Robert W. Field, Massachusetts<br>Institute of Technology - "An Atom in a<br>Diatomic Molecule: Is it a Dumb Idea?"                              |
| Feb. 26  | Dr. Lloyd M. Smith, University of<br>Wisconsin-Madison - "Automated DNA<br>Sequencing: A Look into the Future"                                       |
| March 5  | Dr. Thomas V. O'Halloran, North-<br>western University - "Molecular Mecha-<br>nism of Metal Responsive Gene Expres-<br>sion"                         |
| March 9  | <b>Ms. Sheila Adamus</b> , Cornell Univer-<br>sity - "Synthesis of Molecules Designed for<br>Selective Transition State Stabilization"               |
| March 16 | <b>Dr. Ruth F. Nutt</b> , (Merck Lecturer)<br>Merck & Company - "Peptide Chemistry<br>in Drug Development"   |
| April 2  | <b>Dr. Ken Feldman</b> , Pennsylvania State<br>University - "Diasteroselective Oxidative<br>Galloyl Coupling in the Synthesis of El-<br>lagitannins" |
| April 16 | <b>Dr. George C. Su</b> , Michigan DNR Lab-<br>oratory - "Opportunities and Challenges<br>in Environmental Chemistry"                                |

April 23

June 8

July 1

**Dr. Yuan T. Lee**, (Merck Lecturer) University of California, Berkeley - "Steering Chemical Reactions Through Laser Excitation"

Dr. Barry M. Trost, Stanford University - "Catalysis - A Tool for Synthetic Efficiency"; Dr. Kevin W. Fields, The Upjohn Company - "A Practical Pilot Plant Synthesis of Cioteronel", Dr. Wilfried Hoffmann, Parke-Davis/Warner-Lambert Company - "An Experimental Approach to Thermal Process Safety". Dr. John Ng, G. D. Searle & Company - "Development of Large Scale Processes for Racemic and Enantiomerically Pure Drugs: From Prostaglandins to 5-Lipoxygenase Inhibitors", Dr. Christopher R. Schmid, Eli Lilly and Company - "Efficient and Scalable Methods for D- and L-Glyceraldehyde Surrogates", Dr. John J. Venit, - Bristol Myers Squibb Company - "Synthesis of HmG CoA Reductase Inhibitors at Pilot Plant Symposium on Synthetic Or-Scale". ganic Chemistry (Parke-Davis/Warner-Lambert Company Distinguished Scholar Program).

**Dr.** Paul A. Deck, Northwestern University - "Understanding Electronic Effects in Organometallic Chemistry: Spectroscopy and Synthesis"

### Second Annual Hope Chemistry Alumni Day

Friday, October 16, 1992 marked the occasion for the Second Annual Hope Chemistry Alumni Day. Dr. A. Paul Schaap ('67), Professor of Chemistry at Wayne State University and President/Founder of Lumagen, Inc., was the featured James and Jeanette Neckers Lecturer for the day. His lecture, entitled, "1,2-Dioxetanes and Chemiluminescence: From Laboratory to Medical Diagnostics", traced the progress of dioxetane research beginning with a study of the fundamental chemical properties of these substances through their applications as ultra-sensitive detection materials used in life science research, in medical diagnostics, and in DNA fingerprinting. Dr. Schaap has established a new company, Lumagen, Inc. to produce and market his adamantyl-stabilized dioxetanes which can be chemically and enzymatically triggered to produce chemiluminescence on demand.

An open house featuring student research posters and a reception followed Dr. Schaap's lecture. The evening was topped off with a banquet attended by 59 alumni, faculty and students. A brief program featuring our own Don Williams followed the meal. A bound volume of responses from alumni, who were not able to attend but who sent greetings and information about themselves, was enjoyed by those in attendance.

The third Annual Hope Chemistry Alumni Day will be held on Friday, October 22, 1993. Dr. Sylvia T. Ceyer, ('74), W. M. Keck Foundation Professor at M.I.T. will be this year's featured speaker.

# **CHEMISTRY ALUMNI**

We sent questionnaires to alumni from the classes of 1982 and

1987. The returns from these are included below. We also learn about activities of some alumni through other channels than the questionnaire. We include this information below in a sub-section entitled **Potpourri**.

### The Chemistry Class of 1982

- Douglas J. Augustin, Destrehan, LA, received his M.S. degree (1986) from the University of Missouri - St. Louis in the field of Chemistry. He is a Process Chemist for Monsanto Company, Agricultural Group in Luling. After 11 years working for Monsanto in St. Louis, he transferred to Luling, LA. Doug will be working in the plant doing process optimization for Roundup Herbicide. He received a peer-to-peer Technical Excellence Award in 1992. For the last five years he has been working on process development and production startup for Dimension Herbicide.
- Thomas R. Bayer, Green Bay, WI, received his M.H.A. degree in Hospital Administration from Washington University (1984). He is an Assistant Administrator at St. Vincent Hospital -Green Bay. Tom and his wife Martha have three daughters; Kate (4), Alleson (2) and Elise (1 month).
- Vivek Bedi, West Bloomfield, MI, is an Account Manager with 2V Industries in Wixom, MI.
- Scott Brewer, Washington, MI, received his M.S. degree (1985) from Wayne State University in the field of Operations Research, and his M.B.A. degree (1990) from the University of Houston in Business Administration. Scott is employed as an Applications Engineer for Deneb Robotics, Auburn Hills, MI.
- Scott M. Cutshall, Carnation, WA, is employed as a Software Design Engineer at Microsoft Corporation, Systems Division in Redmond, WA.

- Thomas M. DeWeert, Bloomington, IL, received his M.D. degree from Wayne State University Medical School (1986); his Internal Medicine Residency at Mayo Clinic (1989), and received a Gastroenterology Fellowship at the University of Iowa in 1992. Tom is self-employed (Digestive Disease Consultants, Ltd.) as a Gastroenterologist.
- Andreas B. Ernst, Naperville, IL, received his Ph.D. degree (1987) from the University of Minnesota in the field of organic chemistry under Dr. W. E. Fristad. Andy is employed at the Amoco Chemical Co, New Business Research and Development Division as a Research Chemist.
- Michael J. Fischer, Muskegon, MI, received his D.D.S. degree from the University of Michigan (1986). He is a self-employed solopractitioner in general dentistry. Mike and his wife Mary Anne have two children: Jacob (7) and Peter (3). He keeps busy with his practice, family, and likes to golf and fish with what time is left.
- Barbara Funckes, Grand Rapids, MI, is employed at Amway Corporation as a Lab Technician II in the Quality Assurance Division.
- William J. Hoekstra, Bryn Mawr, PA, received his Ph.D. degree from Emory University (1986) in the field of Synthetic/Medicinal Chemistry under Dennis C. Liotta. He is employed as a Senior Scientist for R.W. Johnson Pharmaceutical Research Institute, Medicinal Chemistry Division, Spring House, PA.

His areas of study/expertise are: 1) Synthesis of Peptide Mimetics of Fibrinogen and Thrombin, 2) Synthesis of Novel Imidazoles, 3) Large Scale Peptide Synthesis.

- Paul E. Lange, Grand Blanc, MI, received his D.D.S. degree from the University of Michigan (1986). He married a fellow dentist and opened a joint family practice (1989) in Pontiac, MI. He is a member of the Michigan Dental Association and is presently serving on the Gennesee District Board of Directors.
- **Diane M. LePoire**, Portage, MI, is employed by the Upjohn Company in Kalamazoo, as a Quality Assurance Professional in the Control Division.
- Molly A. (Redmond) Lockemeyer, Sugarland, TX, received her M.S. degree from the University of Delaware (1988) in Bio-Analytical Chemistry under Steven D. Brown; her M.B.A. degree from Rice University (1992) in the field of Operations Management and Finance. Molly is a Technical Consultant for Baylor College of Medicine Technologies, Inc. (Texas Medical Center - Houston). She has a daughter Jennifer Marie. Molly has run 6 marathons and 2 triathalons.
- William F. Londo, Manchester, MI, received his M.S. degree from the University of Minnesota (1988) in Analytical/Physical Chemistry under Paul Barbara. He lived in Japan from 1985-1988, returned to the U.S. and entered the Center for Japanese Studies at the University of Michigan. In 1990-91, he was Visiting Assistant Professor of East Asian Studies at Earlham College, Richmond, IN. William returned to the History department at University of Michigan in 1991 and is working on a Ph.D. degree in medieval Japanese history under Hitami Tonomura.
- Joel C. Martinus, Wyoming, MI, received his M.B.A. degree from Grand Valley State University (1988) in Accounting. He is employed by Parke-Davis/Warner-Lambert in Holland, MI as a Cost Accountant.

- Ronald L. McKey, Stevensville, MI, received his M.D. degree from the University of Michigan Medical School (1986); he completed his Residency in Ophthalmology (Bond Certified) in 1991 from Wills Eye Hospital, Thomas Jefferson University, Philadelphia. Ron is married to Brenda Bryker ('82) and they have two sons; Kyle (4) and Colin (1 1/2).
- Molly A. (Markosky) Morrissey, Midland, MI, received an M.B.A. degree from Grand Valley State University (1990) in Marketing/Finance. Currently she is a stay-at-home mother with two children - Meghan (6) and Jillian (2).
- Susan J. Rankin, Grand Rapids, MI, received her R.N. degree in Nursing from Grand Rapids Community College (1993), and is working in the Emergency Room at Grand Rapids Metropolitan Hospital.
- Elizabeth A. Schilling, Chapel Hill, NC, received her M.S. degree from the University of Michigan (1988) in the field of Biostatistics under Michael Boehnke. She is working on her Ph.D. at the University of North Carolina - Chapel Hill in the field of Clinical Psychology under Donald Baucom.
- Thomas A. Stout, Holland, MI, received his D.D.S. degree from the University of Michigan (1985) in Dentistry and is self-employed. He and his wife (Diane) have two children; Kelsey (2 1/2 years) and Allison (2 months).
- Jody L (Foy) Tuls, Mattawan, MI, received her Ph.D. degree from the University of Arkansas in the field of Biochemistry under Frank Millett. Jody is employed by The Upjohn Company as a Research Scientist in the Control Biotechnology Development Division, Kalamazoo, MI.

- Roberta L. (Dorow) Van Alsten, Wilmington, DE, received her
  A.M. degree from Harvard University (1985) in Organic Chemistry under D.A. Evans, and her Ph.D. degree from the University of Illinois (1990) in Organic Chemistry under S.E. Denmark. She is employed in the Process Chemistry Division as a Senior Research Chemist at DuPont Merck Pharmaceutical. Bobbie and her husband, John ('81), work at the DuPont Experimental Station. They have two children, Stephanie and Craig, who are 17 months apart.
- Charles Winter, Grosse Pointe Park, MI, received his Ph.D. degree from the University of Minnesota (1986) in Organic Chemistry under Paul G. Gassman. He was a Postdoc at the University of Utah (1986-88) in the field of Organometallic Chemistry under John A. Gladysz. Chuck is employed as an Assistant Professor, Wayne State University Chemistry Department in inorganic chemistry. His wife is working on a Ph.D. degree in physical organic chemistry at Wayne State. They have two children who keep them busy when not at work.

# The Chemistry Class of 1987

- Matthew F. Brown, Mystic, CT, received his M.S. degree (1989) and his Ph.D. degree (1991) in the field of Chemistry from the University of California - San Diego under Dr. Daniel F. Harvey. He is a Research Scientist at Pfizer, Medicinal Chemistry Division, Groton, Ct.
- Timothy L. Chase, Carolina Beach, NC, received his M.D. degree from Bowman Gray School of Medicine (1991). Tim is a Resident Physician at New Hanover Regional Medical Center, Wilmington NC.

- Paul A. Deck, Evanston, IL, received his Ph.D. degree from the University of Minnesota (1993) in the field of chemistry under Paul G. Gassman. He is a Postdoctoral Fellow (Tobin Marks' Group) at Northwestern University, Chemistry Department, Inorganic Division. Paul was awarded a 1993 National Science Foundation Postdoctoral Research Fellowship. Twenty Awards were given nationally this year.
- Michael G. Dickinson, Pensacola, FL, received his M.D. degree from the University of Michigan (1991); and is completing Residency in the field of Internal Medicine from Portsmouth Naval Hospital (1992). Mike is a physician with the United States Navy Flight Surgery Division. On June 24, He will have completed six months of training in aviation medicine and will be transferred to Norfolk, VA assigned as a flight surgeon to the Naval Air Reserve Center Norfolk. He married Sarah Eberhard ('87) shortly before his graduation from medical school and in November '92, their daughter Dorothy Ann was born. In 1991 for a variety of personal reasons he had his name changed from Michael Dick to Michael Dickinson.
- Ruth A. Ettinger, Madison, WI, is working on her Ph.D. degree at the University of Wisconsin-Madison in Biochemistry under Hector F. DeLuca.
- Eric K. Gustafson, Grand Rapids, MI, received his M.D. degree from Michigan State University College of Human Medicine (1991). He is Chief Resident (3rd year and will graduate in 1994) at Saint Mary's Health Services - Family Practice Residency. Eric and Linda have three children; Anna Kristina (4 1/2), John Karl (3) and Kirsten Marie (9 months).
- David R. Heyboer, Grand Rapids, MI, received his M.D. degree from Michigan State University (1991). He is employed as a

Resident in the Internal Medicine Division at Butterworth Hospital.

- Robert R. Isacksen, Oak Park, IL, graduated from the University of Michigan in 1991 with an M.D. degree in Medicine. He is a Surgical Resident (completing 2nd year) at Loyola University Medical Center, Department of Surgery, Chicago.
- Amy L. Koorndyk, Dorr, MI, is currently at home raising two children, Rachel (4), Ryan (2), and is expecting number three in January. Currently, she is the chairperson of the Policy Council for the Allegan County Head Start Program and a board member of the Allegan County Resource Development Committee, Inc.
- John & Heidi (Baehr) Lakanen, Ann Arbor, MI. Heidi received her M.D. degree from the University of Michigan (1991) and is a Resident in Internal Medicine at St. Joseph Mercy Hospital. John received his M.S. degree from the University of Michigan (1989) in the field of Chemistry and is now working on finishing his Ph.D. degree at UM.
- Erlund J. Larson, Ann Arbor, MI, received his Ph.D. degree from The University of Michigan (1991) in the field of Inorganic Chemistry under V. L. Pecararo. He expects to receive his M.D. degree in (1996). Erlund is married to Jane (VanderPloeg) '86.
- Gary L. McBee, Ypsilanti, MI, is employed as a chemist at Flint Ink in Ann Arbor, MI. Gary is responsible for company-wide application of electron microscopy (SEM, STEM, XPS, Auger). He is also responsible for surface chemistry studies utilizing Rame-Hart Coniometer, Cann Automated Tensionmeter and Ultramicrotomy.

- Craig J. McCleary, Niles, MI, is employed by The Upjohn Company, Great Lakes Region as a sales representative. Craig was married October, 1992 in Orlando Florida to Joan Treais formerly of Cadillac, MI.
- Ellen M. (Tamminga) Meleen, L'Anse, MI, is employed as a Plant Chemist for Celotex Corporation. Her first child, Tara Rae, was born January 31, 1993.
- Kyria (Boundy) Mills, Minneapolis, MN, received her Ph.D. degree from the University of Minnesota (1992) in Biochemistry under D. Livingston. She is a Postdoctoral Fellow at the University of Minnesota, Department of Soil Science, St. Paul, MN. Kyria is doing genetic studies on the soil bacteria Rhizobium, studying the genes involved in the chemical communication between this bacteria and its symbiotic host soybean. Rhizobia invade the roots and form nodules, fixing nitrogen for the plant. She is very excited about these studies and making great progress in her projects. Her husband David will received his Ph.D. degree in microbiology in 1 1/2-2 years. Kyria would like to hear from anyone who has tried to find two scientific jobs in the same city at the same time! Any advice?
- Steven W. Mork, Midland, MI, received his M.S. degree (1989) and his Ph.D. degree (1992) from Cornell University in the field of physical chemistry under Laura A. Philips. He is employed as a Senior Research Chemist with the Dow Chemical Company in Midland.
- Steven E. Schadler, St. Joseph, MI, will receive his Ph.D. degree from the University of Notre Dame (1993) in the field of Inorganic Chemistry under A. Graham Lappin. He has just completed the defense of his dissertation which was titled "Stereose-

lectivity in Electron Transfer Reactions of Metal-Peptide Complexes".

- Timothy J. Sliede, Grand Rapids, MI, received his M.H.A. degree from Washington University School of Medicine (1992) in Hospital Administration.
- Christopher J. Whewell, Chesterland, OH, is employed by J.E. Morris & Associates, Precious Metals Specialists and loves his work. He has been issued two patents and is currently prosecuting nine more including a process for making fullerenes for \$2.20 a pound. He is trying to be the first one in his class to earn a million dollars, a portion of which will be kicked back to Hope College. Anyone out there willing to try to beat out Chris? Chris is married to Jean Morris ('87). They have two children.

No information was received from the following alumni. If you have a current address or information about any of these alumni, please let us know.

> Richard S. Blake ('82) Deborah S. Fild ('82) Michael E. Kort ('87) Ann P. LaRoche ('87) Christan J. Nyweide ('82) Edward J. Oset ('87)

Nils M. Sappok ('87) Daniel W. Smith ('87) Nancy Souders ('82) Kurt B. Thompson ('82) Sat V. Tran ('82) Raymond L. Zhang ('87)

#### Potpourri

Sylvia Ceyer ('74) is the recipient of the American Chemical Society's Nobel Laureate Signature Award For Graduate Education in Chemistry. She and her graduate student Andrew Johnson were recognized for Johnson's Ph.D. thesis research on the mechanism of the production of bulk hydrogen in metals under ultra high vacuum conditions and the mechanism of hydrogenation reactions on nickel surfaces.

John Higuchi ('89) was recently named Senior Staff Associate in charge of the American Chemical Society's Student Affiliates program. In this position he oversees the affiliation process, the faculty advisor newsletter, faculty advisor workshops, and the magazine *in Chemistry*. He will also plan and schedule undergraduate programming at national meetings.

<sup>'</sup>Robert Donia ('39) is retired from the Upjohn Company and resides in Kalamazoo with his wife Angie.

Elmer Hartgerink ('39) continues his leadership role with the Wyckoff Chemical Company as Chairman of the Board. We note with sadness the recent death of Elmer's wife, Margaret.

Judson Van Wyk ('43) is Kenan Professor of Pediatrics (Emeritus) at the University of North Carolina, Chapel Hill. He continues his research on Insolinlike Growth Factors. The University of Genoa, as a part of its celebration of the 500th Anniversary of Christopher Columbus' Encounter with North America, conferred an honorary degree upon Jud.

Jack Krum ('44) is semi-retired but is still running his own company making food ingredients. He resides in Paola Kansas.

Gradus L. Shoemaker ('44) is retired from the University of Louisville. He resides in Louisville.





Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, Wisconsin 53211

September 20, 1993

Professor William F. Polik Department of Chemistry Hope College P.O. Box 9000 Holland, Michigan 48422 9000

Dear Professor Polik:

Thank you so much for your letter of September 14th.

Isabel and I so enjoyed our two days at Hope College, and hope that five years from now you will invite us again to give some other lectures.

If you should ever be involved in starting a small chemical company, then I would be happy to help. As you perhaps know and can see from the enclosed, I was dismissed from Sigma-Aldrich two years ago, but my dismissal has had some really happy silver linings, as you can also see from the enclosed. If you should ever want to write a serious history relating to Sigma-Aldrich, then I would be happy to share with you the next chapter of my autobiography, dealing with my last years at Sigma-Aldrich.

To turn to your questions about Loschmidt: first, I don't believe that G. N. Lewis knew about Loschmidt's work. The only way he could have known would have been through Anschütz's paper in the <u>Berichte</u> in 1912 or the 1913 reprint, both written in German.

Second, I don't believe for a moment Loschmidt considered chemical structures to be two dimensional. Hardly anyone has paid attention to the six-page essay which accompanies the 1861 book. Actually, that essay is the bridge between his <u>Chemische Studien</u> of 1861 and his calculation of the Loschmidt number, and I enclose Xerox copy of page 49 stating both his main aim of both works and how he depicts molecules. His main aim was to provide a deeper insight into the constitution of matter. The Loschmidt number gave the size of the molecule. The <u>Chemische Studien</u> gave the shape of the molecule.



Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, Wisconsin 53211

Professor William F. Polik Septmeber 20, 1993 Page Two

Finally, I believe that Loschmidt thought of benzene as being a ring of six carbons, but he was not the first to depict benzene as cyclohexatriene. He simply didn't know what to do with the double bonds and stated clearly that one had to leave that "in suspenso."

Historians of chemistry were misled by structure 182, where he stated clearly that one might be tempted to think of benzene as made up of two cyclopropanes or two allyl moieties put together. But then he clearly stated that he preferred structure 185, and all of his aromatic structures are based on that ring.

In this connection, Dr. Robert Rosner's letter to <u>Chemistry in Britain</u>, copy enclosed, is particularly pertinent. Loschmidt was in the habit of writing all structures that he could think of and then choosing what he thought was the correct one. With acetic acid and benzene, he was correct; with urea, for instance, he was not.

Most of the arguments for Loschmidt are presented in Chapter 16 of Professor Wotiz's book, for which I enclose a description. Not all historians of chemistry agree with this evaluation of Loschmidt, and I enclose an article by Professor Rocke which was published in <u>Chemistry in Britain</u>, and a letter to that journal which was not published. That letter by Professor Jensen actually accused <u>Chemistry in Britain</u> of "tepid yellow journalism". As you are obviously interested in this history, I also enclose copy of my letter to Professor Jensen, who is the editor of a respected journal of the history of chemistry. Professor Jensen was at the Chicago meeting where I spoke about Loschmidt, last month, but was not able to come to the meeting.

In 1995, there will be a symposium on Loschmidt in Vienna, and I hope that much of this can be discussed constructively at that time.

All good wishes to you and your associates.

Sincerely,





September 14, 1993

Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, WI 53211

Dear Dr. Bader,

Thank you very much for visiting Hope College and presenting seminars on your three favorite topics: art, Bible, and chemistry! Chemistry students and faculty particularly enjoyed your fascinating account of Loschmidt and his wonderful book detailing the structure of organic compounds. You convinced me that Loschmidt's book was one of the most significant (and unrecognized) organic chemistry publications of the 19th century.

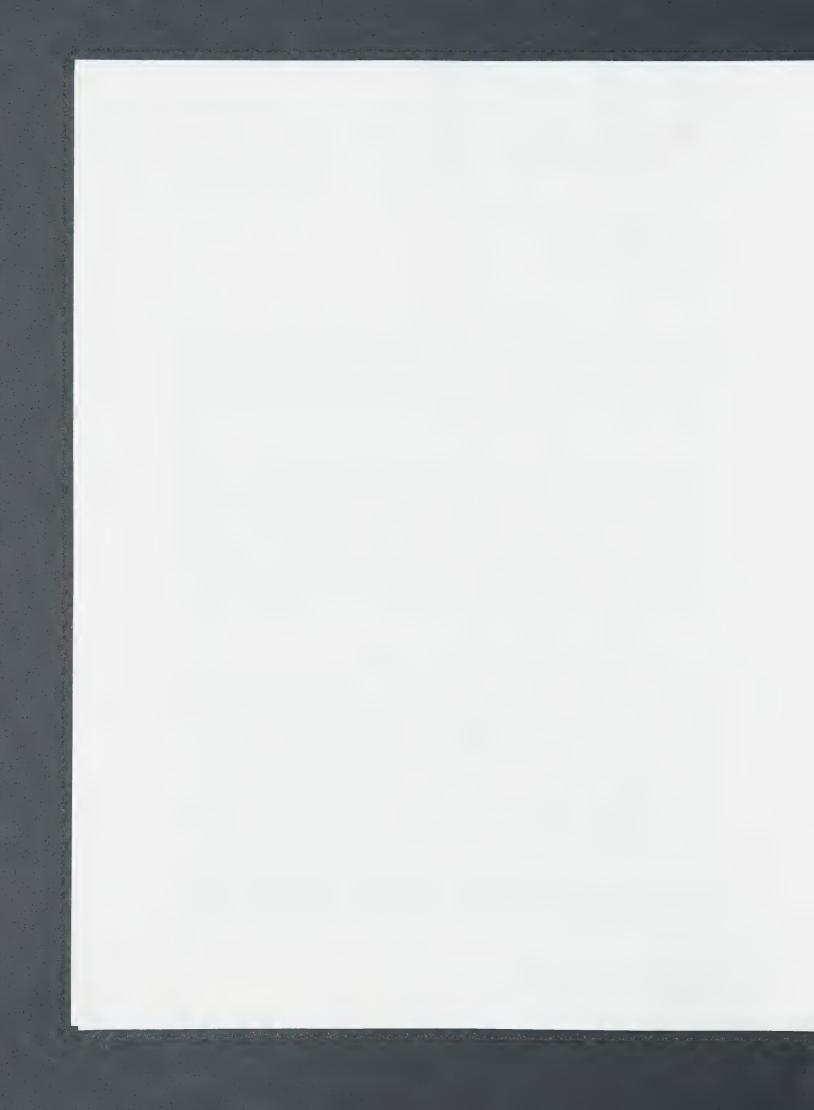
Thank you also for sending me a history of the Aldrich chemical company. I am fascinated by both intellectual and entrepreneurial accomplishments in science, and they are very often closely related. For example, there is no doubt in my mind that much of the progress in organic chemistry over the last forty years is due to the services of specialty chemical suppliers, most notably the Aldrich Chemical Company. Your company has played an invaluable role in transferring chemical technology through out the world. I am also keenly interested in how small companies develop into larger successful companies. Perhaps I will someday be involved in such a venture. At a minimum, I hope someday to write an account of some of these transformations. Your story will certainly be included!

Your seminar about Loschmidt left me with several thoughts:

First, I was overwhelmed by Loschmidt's insight into chemical connectivity and valence. Being a Berkeley graduate, I was personally struck by the parallels between Loschmidt's and G.N. Lewis' concepts of chemical bonding. I wonder if Lewis, being a physical chemist, was aware of Loschmidt's work prior to his 1916 paper "The Atom and the Molecule" in which the electron-pair bond and "the rule of eight" is described.

Second, Loschmidt seemed to have exceptional insight into chemical isomers and preferred geometries. Is there any evidence that he considered the 3-dimensionality of chemical structures? Or did he consider all chemical structures to be two dimensional, *i.e.*, flat in the plane of the page?

Finally, could Loschmidt have thought of the phenyl group as an unspecified grouping of six carbon atoms to which there were six substituents? I recognize that he drew cyclopropane as a ring of 3 carbon atoms, but there is the only way of closely packing



3 balls. Did Loschmidt provide any *direct* evidence that he conceived of phenyl as a ring of carbon atoms? Regardless, I agree with you that Kekulé was influenced by Loschmidt's work. Having seen Loschmidt's circular structures, how could he *not* be influenced?

Thank you again for your visit and for giving our students and faculty the privilege of meeting you.

Sincerely yours,

# Will Polit

William F. Polik Assistant Professor of Chemistry



Dr. Alfred Bader 2961 North Shepard Avenue Milwaukce, Wisconsin 53211

September 23, 1993

Professor William S. Mungall Department of Chemistry Hope College P.O. Box 9000 Holland, Michigan 48422 9000

Dear Bill:

Thank you so much for your gracious letter of September 13th which crossed mine of September 10th. I hope that it has not gotten lost, and I enclose copy.

As you know, I am invited to speak at a great many places, but when I think back over the last few years, Hope College and Trinity University stand out. It is interesting to realize that one led to the other.

If we are still around, I would be delighted to come back to you five years from now, but hope that you will then ask me to give more than three lectures.

All good wishes.

Sincerely,

Enclosure





DEPARTMENT OF CHEMISTRY

September 13, 1993

Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, Wisconsin 53211

Dear Alfred:

I would like to thank you and Isabel for coming to Hope College and sharing your love of art and the Bible and your enthusiasm for chemistry with us. I cannot remember when we have had a speaker who has generated as much positive conversation in the hallway among students and faculty. One idea that has emerged from these conversations is that we should have more speakers who are able to talk about the history of chemistry. This subject is often neglected in our efforts to teach science. However, your presentation has shown that students are interested in the history if it is presented in a way that illustrates the human drama that was involved and stimulates them to think about accepted concepts.

I hope that your trip back to Milwaukee went smoothly. Please send me a list of your expenses for the trip and estimated mileage so that I can arrange reimbursement. I will also arrange for the honorarium to be sent at the same time. As I mentioned in response to your question about the meaning of the title "Presidential Lecture Speaker", this title is intended to recognize outstanding speakers of broad general interest, and it carries with it funding from the President's discretionary fund. When I submitted our request to have you designated as a Presidential Lecture Speaker, I requested that you be paid a \$500 honorarium. This request was approved just a few weeks ago at the start of our semester. Only five or six speakers a year visiting Hope College receive this designation.

Again, we thank you and Isabel for an outstanding visit.

Sincerely,

ele,

William S. Mungall Professor of Chemistry



September 14, 1992

Professor William S. Mungall Department of Chemistry Hope College Holland, Michigan 49423 3698

Dear Professor Mungall:

I am sorry that a long trip to Europe has delayed my responding to your kind letter of June 24.

Of course, I know about your department, because when I was a student in the 1940s you had the finest teacher of undergraduate chemistry anywhere in the country at Hope College. My old friend, Gene van Tamelen, who later became professor at Stanford University, always talked about the quality of the department, and I spent one of my finest Christmases ever with Gene and Mary with her family, just before they were married.

In any case, I would be delighted to vist Hope College, and I enclose a choice of subjects for lectures. However, my schedule for this autumn and next spring is completely filled, but I am relatively free in September of 1993. Would one of those Fridays, say, September 10, be good for you? September 17 and 24 interfere with the Jewish holidays.

I much look forward to hearing from you.

Sincerely,

Enclosure



### HOPE COLLEGE CHEMISTRY FACULTY

- Rodney F. Boyer, Professor (B.A., Westmar College, 1964; Ph.D., Colorado State, 1969) Biochemistry; storage and utilization of biclocical iron in ferritin. catalvtic RNA.
- ological iron in ferritin, catalytic RNA. Irwin J. Brink, Professor and Chair (A.B., Hope College, 1952; Ph.D., Illinois, 1957) Physical Chemistry; thermodynamics and thermochemistry of biological molecules.
- Elaine Z. Jekel, Adjunct Associate Professor (B.S., Greenville College, 1951; Ph.D., Purdue, 1958) Analytical Chemistry; chemical
- education. Eugene C. Jekel, Professor (A.B., Hope College, 1952; Ph.D., Purdue, 1964) Inorganic Chemistry; chemical education.
- William S. Mungall, Professor (B.A., SUNY-Buffalo, 1967; Ph.D., Northwestern, 1970) Organic Chemistry; synthesis of polymers,
- William F. Polik, Assistant Professor (B.A., Dartmouth College, 1982; Ph.D., California-Berkeley, 1988) Physical Chemistry; laser spectroscopy of excited state molecules in a molecular beam.
- Michael D. Seymour, Associate Professor (B.A., St. Johns (MN), 1972; Ph.D., Arizona, 1978) Analytical Chemistry; atmospheric chemistry, chemical education.
- Michael E. Silver, Associate Professor (B.S., Fairleigh Dickinson, 1975; Ph.D., Cornell, 1982) Organometallic Chemistry; mixed early-late transition metal complexes, x-ray crystallography.
- Joanne L. Stewart, Assistant Professor (B.A., Kalamazoo College, 1982; Ph.D., California-Berkeley, 1988) Inorganic Chemistry; main group metal synthesis, heteronuclear NMR.
- Stephen K. Taylor, Associate Professor (B.A., Pasadena College, 1969; Ph.D., Nevada-Reno, 1974) Organic Chemistry; cyclization and stereoselective reactions.
- Donald H. Williams, Professor (B.S., Muskingum College, 1960; Ph.D., Ohio State, 1964) Inorganic Chemistry; environmental surveys, photochemistry, science education.

# FACTS ABOUT HOPE COLLEGE

Mission: To offer with recognized excellence, academic programs in liberal arts, in the setting of a residential, undergraduate, coeducational college, and in the context of the historic Christian faith.

**Location:** The campus is situated in a residential area two blocks from the central business district of Holland, Michigan, a community of 50,000 near the shores of Lake Michigan.

Enrollment: Approximately 2700 students; 57% women, 43% men; 40 states and 34 countries represented.

**Faculty:** 174 full-time faculty members; faculty: student ratio of 1:14.4.

Calendar: Two semesters, September-December and January-April; May term, June term, Summer term.

Majors: The curriculum offers courses in 37 major fields leading to the degree Bachelor of Arts, Bachelor of Music, Bachelor of Science or Bachelor of Science in Nursing.

**Financial Aid:** Hope College is committed to meeting 100% of a student's demonstrated financial need through scholarships, grants, loans and on-campus employment. In addition, the Chemistry Department offers several scholarships, including the Dow Foundation and Jaecker Scholarships.

**Campus Visits:** Prospective students are encouraged to visit the campus, attend classes and talk to students and professors. To arrange a visit call or write the Admissions Office:

Admissions Office Hope College Holland, MI 49423 (616) 394-7850 (800) 822-HOPE (In Michigan) (800) 845-HOPE (Out-of-State)

# HOPE COLLEGE



Department of Chemistry

Building on a Tradition

of Excellence

The Hope College Chemistry Department enjoys lege has produced an unusually large number of for the quality of its graduates. During each of the past seven years, at least one Hope College uate Fellowship. Funds for the support of the search for the period 1920-90, Hope College ranks fourth in the nation among 847 four-year private teaching and research program have come from the National Science Foundation, the National Inican Chemical Society, Dreyfus Foundation, Dow Keck Foundation, Amoco Foundation, Shell Companies Foundation and the Hewlett-Packard Coma national reputation as a center of excellence for Although the student body is of moderate size, Hope Coloutstanding scholars in chemistry. In a recent survey of Baccalaureate Sources of Chemistry PhDs conducted by the Council for Undergraduate Reundergraduate institutions with 203 PhD chemist alumni. The Department has also been recognized chemistry graduate per year has been awarded a prestigious National Science Foundation Gradstitutes of Health, Research Corporation, Amer-Chemical Foundation, Du Pont Company, Merck, Sharpe and Dohme, Warner-Lambert, the W. M undergraduate teaching and research. pany Foundation.



Degrees Offered

Hope College offers several undergraduate degrees in chemistry, including the B.A., the B.S., the B.S. with American Chemical Society certification and the B.S. with biochemistry emphasis. All chemistry degrees require one year of physics, at least

# , one year of calculus and 46 credits of liberal-arts core curriculum courses.

### Program of Study

chemistry, Analytical Chemistry, Inorganic Chem-The typical Hope College chemistry student beand Organic Chemistry (2nd year). In addition to these courses, students may also enroll in physics, math, biology, and liberal arts core curriculum and elective courses. During the junior and senior years, chemistry students enroll in a selection of the following courses: Physical Chemistry, Bioistry, and the integrated senior-level course, 'Su-Separate laboratory courses are associated with most of these classes. All classes and laboratories are taught by chemistry faculty, all of whom have a Ph.D. degree in chemistry. The program is flexible and students are encouraged to gins studies with General Chemistry (1st year) enroll in other science and liberal arts courses. perchemistry'.

### Research

dergraduate students the opportunity to develop part of the teaching program, and over thirty students are involved each academic year in chemistry or biochemistry laboratory research. During each summer, up to thirty students are paid a istry Department was recently ranked first among ber of student-coauthored publications (Journal of expertise in chemistry and biochemistry through faculty-student research. Research is an integral stipend for participation in the research program. Other chemistry students work on industrial internships during the summer. The research areas available for study are listed with the individual faculty members on the reverse side. The Chemthe very best liberal arts colleges in the total num-The Hope College Chemistry Program offers un-Chemical Education 64, 163 (1987)).

## Equipment and Facilities

The Chemistry Department is located in the Peale Science Center where laboratories are equipped with modern instruments, including an FT-nuclear magnetic resonance spectrometer, gas chromatograph/mass spectrometer, x-ray diffractometer,

UV/VIS spectrometer, laser system and others. All major instruments are equipped with computers for data acquisition and analysis. Students have access to all equipment; hence, they gain valuable hands-on experience.

## Placement of Graduates

Hope College chemistry graduates have an outstanding record of acceptance into graduate and professional schools. They are also in demand by industry for a variety of career positions. In a typical year, 25-30 chemistry majors graduate from Hope. Approximately 45% of these students attend graduate school in chemistry or biochemistry, and each of these students receives a fellowship for financial support. An average of 20% of the chemistry graduates attend medical or dental school. Approximately 35% of the chemistry graduates accept positions in industry or teaching.



Hope College Chemistry Faculty

To obtain more information about the Hope College Chemistry Department, write or call:

Chair Department of Chemistry Hope College Holland, MI 49423 (616) 394-7630 (800) 822-HOPE (In Michigan) (800) 645-HOPE (Out-of-State)



DEPARTMENT OF CHEMISTRY

June 24, 1992

Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, WI 53211

Dear Dr. Bader:

Professor Michael Doyle from Trinity University mentioned to me that you visited them in San Antonio recently and presented an excellent seminar to the undergraduates. Since I am in charge of arranging our seminar program for next year, I am writing you to extend an invitation to visit our department, meet with faculty and students, and present a seminar. A list of possible seminar dates is enclosed. We very much hope you will be able to visit us. Since you may not be familiar with Hope College, I have enclosed some information on Hope College and our department.

Hope's chemistry seminar program is scheduled for 3:30 on Friday afternoons, but we like to have our guests spend the day visiting with faculty and students if possible. Lunchtime is set aside for the speaker to meet with students for informal discussion regarding research, careers, or other topics. Our seminar guests often visit Calvin College nearby in Grand Rapids on the preceding Thursday, the day of their seminar program. Since we work jointly in arranging our seminar schedules, I would be pleased to contact them regarding arrangements. We would be pleased to cover your travel and lodging expenses if you are able to accept our invitation.

I look forward to your reply indicating the best dates for your visit. Please contact me at your earliest convenience by telephone at (616) 394-7633.

Sincerely, Junan

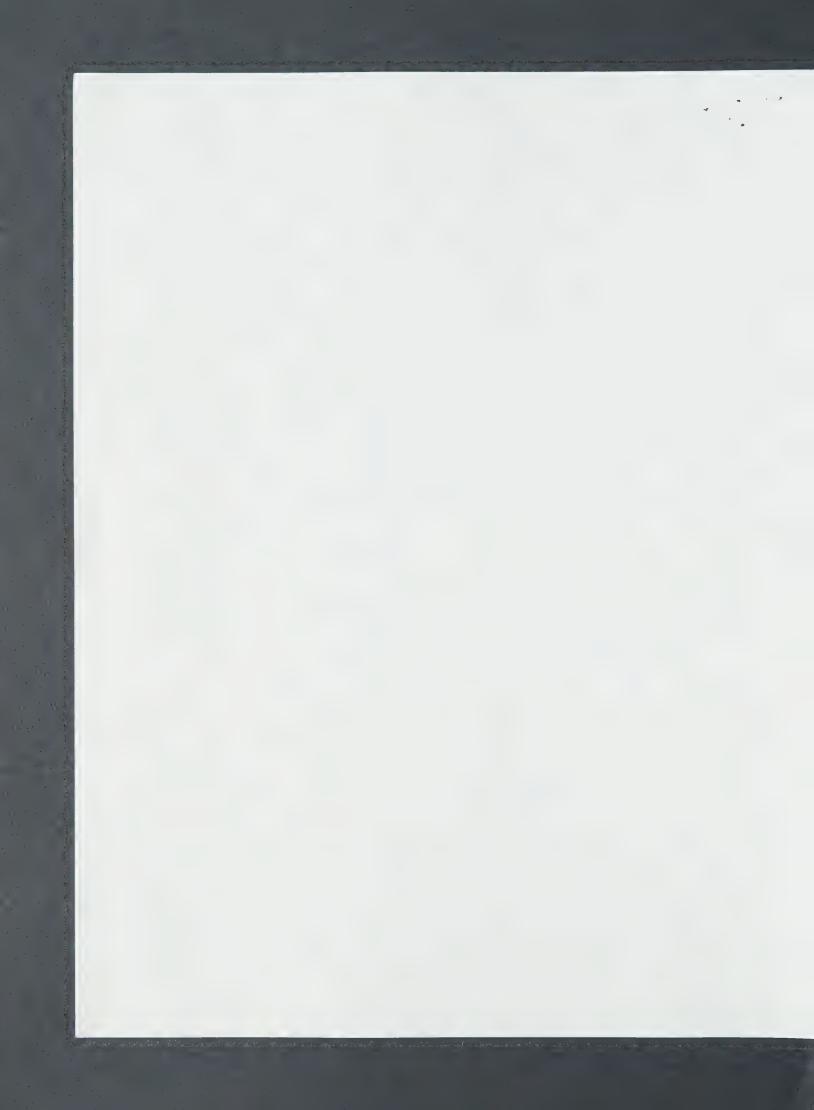
William S. Mungall Professor of Chemistry



### HOPE COLLEGE SEMINAR SCHEDULE Fall Semester 1992 3:30 PM, Peale Science Bldg.

### HOPE COLLEGE SEMINAR SCHEDULE Spring Semester 1993 3:30 PM, Peale Science Bldg.

| Date                           | Speaker   | Date               | Speaker  |
|--------------------------------|---|--------------------|--|
| Friday, Sept. 11               | Merck Student Research Symposium  | Friday, Jan. 15    |  |
| Friday, Sept. 18               |   | Friday, Jan. 22    |  |
| (Friday, Sept. 25)             | No Seminar – "The Pull"   | Friday, Jan. 29    |  |
| Friday, Oct. 2                 | Dr. Wendell Wierenga, Parke-Davis   | Friday, Feb. 5     |  |
| (Friday, Oct. 9)               | No Seminar – Fall Recess  | (Friday, Feb. 12)  | No Seminar - Winter Recess                                       |
| Friday, Oct. 16                | Homecoming Chemistry Alumni Banquet   | Friday, Feb. 19    |  |
|                                | Dr. A. Paul Schaap, Wayne State University  | Friday, Feb. 26    |  |
| Friday, Oct. 23                | Dr. James Coward, University of Michigan<br>Bioorganic                                | Friday, Mar. 5     |  |
| Friday, Oct. 30                |   | Friday, Mar. 12    |  |
| Friday, Nov. 6                 |   | (Friday, Mar. 19)  | No Seminar - Spring Recess                                       |
| Thursday, Nov. 12              | Dr. Stephen J. Benkovic, Penn. State Univ.  | (Friday, Mar. 26)  | No Seminar - Spring Recess                                       |
|                                | Biochemistry  | Friday, April 2    |  |
| Thursday, Nov. 19<br>8:00 p.m. | Dr. Paul Helquist, Univ. of Notre Dame<br>Organic (ACS Speaker - Ken Piers arranging) | (Friday, April 9)  | No Seminar – Good Friday   |
| Friday, Nov. 20                |   | Friday, April 16   |  |
| (Friday, Nov. 27)              | No Seminar – Thanksgiving Holidays  | Friday, April 23   | Dr. Yuan T. Lee, Univ. of Calif., Berkeley<br>Physical Chemistry |
| Friday, Dec. 4                 |   | (Friday, April 30) | No Seminar – Last Day of the Semester                            |
| Friday, Dec. 11                | No Seminar – Last Day of Semester   |                    |  |



September 10, 1993

Professor Joanne L. Stewart and Professor William L. Polik Department of Chemistry Hope College P.O. Box 9000 Holland, Michigan 49422 9000

Dear Joanne and Bill:

I so enjoyed meeting you yesterday.

Enclosed, as promised, is the chapter about the beginings of Aldrich, which will appear in my autobiography.

Best regards to you and your associates.

Sincerely,

Enclosure



September 10, 1993

Professor William S. Mungall Department of Chemistry Hope College P.O. Box 9000 Holland, Michigan 48422 9000

Dear Bill:

As you now, I am invited to speak at a good many places, but seldom enjoyed myself as much as I did at Hope College yesterday and today. Much of that, of course, was due to your wonderful care.

The details of my travel expenses are enclosed.

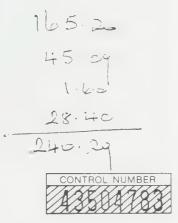
Best personal regards to you and your associates.

Sincerely,

Enclosures



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August 4, 1993

Via Fax 616 394 7923

Professor William S. Mungall Hope College Department of Chemistry Peale Science Center 35 East 12th Street Holland, Michigan 49422-9000

Dear Professor Mungall:

In response to your kind letter of July 30th, it seems to me that the lecture on "The Bible through Dutch Eyes" would be more attractive to the people in the community who might be interested if it were given on Thursday evening, rather than at 11 a.m. on Friday. Hence, I would suggest that "The Adventures of a Chemist Collector" be held at 3 p.m. on Thursday, the lecture on the Bible on Thursday evening, and then the third lecture on Josef Loschmidt on Friday. However, would it be possible to have the lecture on Loschmidt reasonably early--say, at 9 or 10 a.m. on Friday morning, rather than a 3:30 in the afternoon." If so, we could leave for home late Friday morning and be in Milwaukee on Friday evening. It is about a 6 or 7 hour drive, and I do not think that we would have the strength to leave after an afternoon talk on Friday and be home that day.

If these three talks could then be held on Thursday and Friday morning, we would plan to arrive on Thursday morning and would need a reservation at the Holiday Inn only for Thursday night.

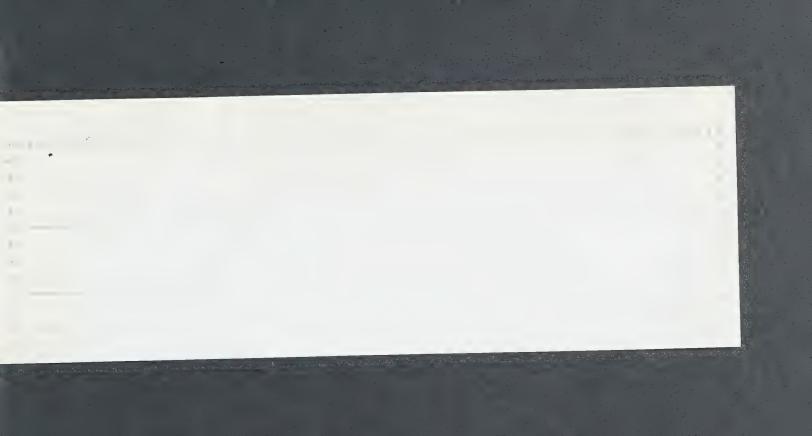
Could you please send me a map of Holland, showing both the Chemistry Department and the Holiday Inn. Many thanks for your help.

M. f. + ---

Sincerely,

() a bear









DEPARTMENT OF CHEMISTRY

July 30, 1993

Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, Wisconsin 53211

Dear Dr. Bader:

Thank you for offering to present three lectures at Hope College on September 10, 1993. I am sorry that I didn't get back to you sooner to finalize the arrangements. The three topics that you suggested sound very interesting. Since you prefer to give three lectures, would it be possible for you to give one or two of the lectures on Thursday, September 9? It would be difficult to schedule all three lectures on Friday since student generally have a full schedule of classes on Fridays and evening lectures on Friday are not very popular.

I have a suggestion for your lecture schedule. One of our art historians, Dr. Carol Mahsun, would be very interested in having you present your lecture on "The Adventures of a Chemist Collector" at 3:00 PM on Thursday, September 9, so that her art history class could attend. The second lecture, "The Bible through Dutch Eyes", could be scheduled at either 11:00 AM or in the evening on Thursday. We would probably draw interested people from the community as well as students with the evening lecture. The third lecture, "Josef Loschmidt--The Father of Molecular Modeling" would be scheduled during our usual time for chemistry seminars on Friday at 3:30 PM. If you have any misgivings about three lectures or if you are not able to come on Thursday, we can rearrange this proposed schedule.

If you could call me to let me know what arrangements would be most acceptable, I will make reservations for you and Isabel at the Holland Holiday Inn. We look forward to your visit.

Sincerely,

0.0

William S. Mungall Professor of Chemistry



March 15, 1993

Dr. Harvey Hopps Fumico, Inc. P.O. Box 8183 Amarillo, Texas 79114

Dear Harvey:

I was just going to write to you, congratulating you on the splendid article on helium which I read in my copy of <u>Chemtech</u>, when I received your copy and kind letter.

I will share that issue with my friends at Aldrich.

Heartiest congratulations.

Sincerely,

c: Dr. Stephen Branca



March 9, 1993

Dear Celtural, Some time age a month with Consedimente interestinger chamber a list on addicte of your may work I have an interst in the west helium induste, De vitien Bere faberal came l'en are an an Ac Stour pratice & mentioned there to to-He said the want. I an write ite on between me Chundell. The maple most qualified the Durian of Maines Allian full Officer cannot write without appread from HQ in wardington Teo much und take designed are la tratea low profile. So & potenticulto collect the information. See page 47 forthe result. all the cast a witte



October 13, 1994

Professor Charles Hurd 2724 Crawford Avenue Evanston, Illinois 60201

Dear Charles,

The enclosed is just a rough draft of a letter which I plan to send to C & E News. What do you think of Eastman's ad, copy enclosed? I also enclose what I think are the correct names for the ten compounds.

If only you could help Eastman as you helped Aldrich over so many years.

Fond regards.

As always,

Enclosures



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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

### 3-Bromo-2,2-dimethylcoumaran and its Reactions

BY CHARLES D. HURD AND ROSTYSLAW DOWBENKO<sup>1</sup> RECEIVED OCTOBER 31, 1959

The reaction of 2,2-dimethylcoumaran with N-bromosuccinimide yielded a highly reactive 3-bromo-2,2-dimethylcoumaran whose structure was proved by its conversion, via the acetate, the alcohol and the ketone, to a bright-red 2,4-dinitrophenyl-hydrazone, and through its reaction with methylmagnesium iodide which gave the known 2,2,3-trimethylcoumaran. While with zinc in refluxing benzene the bromide gave a polycoumaran, with magnesium or with zinc in ether solution it gave two compounds believed to be stereoisomers of 2,2,2',2'-tetramethyl-3,3'-bicoumaran. With sodium in ether solution 3-bromo-2,2-dimethylcoumaran gave a low yield of 2-isobutenylphenol. Grignard reagents and 3-bromo-2,2-dimethylcoumaran gave mainly 3-alkylated coumarans, which furnishes a convenient method of preparing 2,2,3-trialkylcoumarans from 2,2-dimethylcoumarans.

In continuation of the studies<sup>2</sup> of the cleavage of O-heterocyclic compounds, such as coumarans, chromans and benzofurans, the preparation of a model compound 3-bromo-2,2-dimethylcoumaran and its ring-opening reactions were studied because of intrinsic interest and also in connection with the possibility of application in the degradation of lignin. The results obtained, although hardly suitable to the application in the degradation of coumaran-containing materials, such as lignin, seem worth reporting on their own merit.

The reaction of N-bromosuccinimide<sup>3</sup> with cou-

(1) Weyerhaeuser Timber Foundation Fellow, 1955-1957.

C. D. Hurd and Gene L. Oliver, THIS JOURNAL, 81, 2795 (1959).
 L. Horner and E. H. Winkelmann, Angew. Chem., 71, 349 (1959).

marans has been described on several occasions,<sup>4</sup> but the isolation of the resulting bromocoumarans has not been reported. One such compound, 3-bromo-2,2-dimethylcoumaran (II), has been isolated and characterized in the present work.

An attempt to obtain a bromide from 2-methylcoumaran and N-bromosuccinimide in carbon tetrachloride failed because of the almost explosive violence of the reaction and dehydrobromination of the resulting reaction mixture. Although conditions more favorable to the desired course of the reaction and isolation might have been found, this was not

(4) E. C. Horning and D. B. Reisner, THIS JOURNAL, 72, 1514 (1950);
 T. A. Geissman, T. G. Halsall and E. Hinreiner, *ibid.*, 72, 4326 (1950);
 M. F. Grundon and N. J. McCorkindale, J. Chem. Soc., 2177 (1957).

### July 20, 1960

attempted, but attention was centered instead on 2,2-dimethylcoumaran (I) which, under usual conditions, gave in a smooth reaction a good yield of a colorless, distillable liquid which subsequently proved to be 3-bromo-2,2-dimethylcoumaran (II). The compound, on standing, rapidly became red to purple and evolved hydrogen bromide. Therefore, no satisfactory analysis could be obtained, but a crystalline phthalimido derivative<sup>5</sup> could be prepared for the purpose of characterization. High temperature and traces of metals seemed to catalyze the decomposition of the bromide.6

The reaction of 2,2-dimethylcoumaran with two and three moles of the bromosuccinimide proceeded less smoothly than with one mole. The reaction with two moles yielded, in addition to the monobromo compound, a small amount of 3,3-dibromo-2,2-dimethylcoumaran, whose presence was indicated from the fact that the product gave 2,2-dimethyl-3-coumaranone (V) on treatment with potassium acetate in acetic acid and water. The reaction of 2,2-dimethylcoumaran with three moles of N-bromosuccinimide was more complex and gave 3-bromo-2,2-dimethylcoumaran as the only isolable compound.

Structure II is the reasonable one to expect from I by the method of synthesis, and reactions of this compound also furnish supporting evidence for the structure. In the first place, reactivity of the halogen was comparable to that in benzyl bromide. Secondly, the alcohol IV obtained from it by indirect hydrolysis (via the acetate III) was oxidizable to a ketone (V); hence, substitution of bromine on the methyl group is ruled out for an alcohol derived from it would have oxidized to an acid. Again, the 2,4-dinitrophenylhydrazone of this ketone was bright red in color, which speaks for the conjugated nature of the ketone. These three items demonstrate that the bromide is of structure II, but the reactions to follow also support this conclusion.

Alcohol IV, mentioned above, seems to be the first recorded example of a simple, stable coumaranol. Ladenburg, et al.,<sup>7</sup> have reported 3-hydroxy-2-coumaranone, and Stoermer and König<sup>8</sup> have described a substance, believed to be 3-coumaranol, which was too unstable to be analyzed.

Bromide II gave 2,2-dimethyl-3-coumaranyl ether (VI), although in low yield, when it was heated with aqueous potassium carbonate solution.

Since II is a  $\beta$ -halo cyclic ether it would be expected to react with sodium, if it reacts comparably to 2-(bromomethyl)-tetrahydrofuran, 2-alkyl-3-bromotetrahydropyran and 2,4-dialkyl-3-chlorotetrahydropyran, each of which reacted with sodium to open its heterocyclic ring and form, respectively, 4-penten-1-ol,9 5-alkyl-4-penten-1-ol10 and

(5) F. Wild, "Characterisation of Organic Compounds," University Press, Cambridge, 1948.

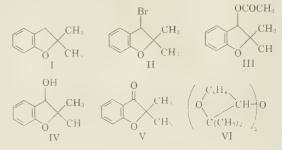
(6) Cf. E. Spath, Monatsh., 34, 1965 (1913), for dehydrohalogenation of p-methoxybenzyl halides. (7) K. Ladenburg, K. Folkers and R. Major, THIS JOURNAL, 58

(1) A. Dubling, J. Plöschl, Ber., 14, 1316 (1881).
 (2) (1936); cf. also J. Plöschl, Ber., 14, 1316 (1881).
 (8) R. Stoermer and W. König, ibid., 39, 492 (1906).
 (9) R. Paul, Bull. soc. chim., [5] 2, 745 (1935).

10) R. Brandon, J. Derfer and C. Boord, THIS JOURNAL, 72, 2120 (1950)

2,5-dialkyl-4-penten-1-ol.11 In the coumaran series Normant<sup>12</sup> obtained a mixture of 2-allylphenol

3-BROMO-2.2-DIMETHYLCOUMARAN



and 2-methylbenzofuran by reaction of sodium or magnesium with 2-(chloromethyl)-coumaran in toluene. Hence II should react analogously with sodium and open its hetero ring. Indeed, in this reaction 2-isobutenylphenol (VII) was formed together with an equal amount of neutral, halogenfree materials which were not characterized. Isobutenylphenol, which was synthesized independently from isopropylmagnesium bromide and salicylaldehyde, was identical to the VII that was prepared from II.



Treatment of II with magnesium brought about coupling to yield 2,2,2',2'-tetramethyl-3,3'-bicoumaran (VIII). Carbonation after the reaction with magnesium gave no carboxylic acid. Formation of VIII is analogous to the formation of 1,2-diphenylethane from benzyl bromide13 or to the coupling of 2-methoxybenzyl bromide14 with Grignard reagents

Actually, VIII was a separable mixture of two compounds, one melting at 171° and the other at 98°, one of which should be a meso compound and the other a racemic pair. Reasons are given later for eliminating other possible structures.

Evidence supporting structure VIII for the 171°material is: Its infrared and ultraviolet spectra were very similar to those of 2,2-dimethylcoumaran, except that in the former the intensity of the ultraviolet bands was twice that of the bands from 2,2 dimethylcoumaran. The compound was unaffected by boiling solutions of potassium permanganate or dichromate and did not react with bromine in carbon tetrachloride. Its nitration gave a yellow tetranitro derivative.

Attempts at degradation of compound 171° with hydrobromic acid failed, and only oily materials were obtained which could not be purified satisfactorily. On heating the compound with N-bromosuccinimide in carbon tetrachloride, at first bromine was formed and later hydrogen bromide was

(11) W. Parham and H. Holmquist, *ibid.*, **76**, 1173 (1954).
(12) H. Normant, *Bull. soc. chim.*, [5] **12**, 609 (1945).
(13) J. Houben and L. Kesselkaul, *Ber.*, **35**, 2523 (1902).
(14) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, Chap. V

evolved. The yellow dibromo compound which was isolated was inert to a boiling solution of potassium permanganate and remained unchanged on treatment with potassium acetate in refluxing acetic acid, from which it was concluded that nuclear bromination occurred at 5,5'. Nuclear brominations with N-bromosuccinimide were reported by Buu-Hoï<sup>15</sup> who found that anisole and other aromatic ethers are brominated in the benzene ring. Consideration of the extremely pronounced hindrance around the 3,3'-carbon-to-carbon bond in the bicoumaran, as revealed by molecular models, makes it apparent that the approach to carbon 3 by the molecule of bromosuccinimide would be very difficult if at all possible. This steric hindrance probably accounts also for the inertness of VIII toward oxidizing agents.

It is known<sup>16</sup> that ethylmagnesium bromide reacts satisfactorily with 4,4'-dimethoxybenzil. Accordingly, a synthesis of VIII was planned starting with 2,2'-dimethoxybenzil<sup>17</sup> and isopropylmagnesium bromide (to be followed by dehydration of the resulting diol and ring closure of the diene) but the 2,2'-isomer was unreactive toward isopropylmagnesium bromide even on prolonged refluxing in benzene.

The lower melting (98°) compound originally was an oil that resisted attempts at crystallization until chromatographic methods were employed. It also was unaffected by boiling potassium permanganate or chromic acid and also failed to discolor bromine in carbon tetrachloride. On nitration it vielded a tetranitro derivative which did not melt below 300°. With N-bromosuccinimide, compound 98° gave a yellow material whose melting point could not be made constant by crystallization or by chromatography.

Although VII seems to be the structure of these two substances, two other isomeric structures (IX, X) may be considered. Compound IX is olefinic and should react with cold permanganate solution, but compounds 171° or 98° failed to react even when heated. Compound X is structurally similar to compound I, and we have shown<sup>18</sup> that I is extensively oxidized by aqueous, alkaline potassium



permanganate solution at 65-70°. This strongly suggests that a compound of structure X should be similarly oxidized, certainly by boiling permanganate. Finally, the fact that compounds 98° and 171° have very similar infrared spectra strongly suggests stereoisomerism, not structural isomerism, for the two materials.

- (15) Ng. Ph. Buu-Hoi, Ann., 556, 1 (1944).
  (16) B. Dodds, L. Goldberg, W. Lawson and R. Robinson, Proc. Royal Soc. (London), B127, 140 (1939).
- (17) J. C. Irvine, J. Chem. Soc., 79, 668 (1901); N. Leonard, R. Rapala, H. Herzog and E. Blout, THIS JOURNAL, 71, 2997 (1949).
- (18) C. D. Hurd and R. Dowbenko, unpublished results.

Zinc powder behaves like magnesium toward II in giving rise to both the 98° and 171° compounds, but it resembled sodium in yielding also the phenolic compound.

Because of possible utility in the preparation of a coumaranylcoumaran (such as X) and because of additional information concerning dehydrobromination of 3-bromo-2,2-dimethylcoumaran, a reaction was studied in which it was attempted to alkylate II with itself. Analogous reactions of benzyl halides are described in the literature. It was shown, for example, by Zincke<sup>19</sup> that benzyl chloride reacts in the presence of metals, as copper, iron, zinc and silver, to form polybenzyls. Even though the condensation of II could not be controlled to produce a dimer, a polymer was obtained when its benzene solution was refluxed with zinc dust. Hydrogen bromide was evolved and an amorphous solid was obtained which did not contain any halogen, was soluble in acetone, benzene and ethyl acetate, but was precipitated by methanol from these solutions. Its molecular weight could not be determined satisfactorily by the cryoscopic approach, since the melting point depression was too small; but this did speak for a substance of a high molecular weight. Its nitration gave a yellow substance, infusible below 300°, which was not analyzed because it exploded in the combustion apparatus. Thus, it must be concluded that the evolution of hydrogen bromide in II is of the same nature as that in benzyl chloride, and is accompanied by self condensation of this compound.

Attempts at preparation of the phenyl ether from II and phenol under various conditions met with failure, hydrolysis and polymerization taking place instead. In one experiment only, when methanol and sodium methoxide<sup>20</sup> were used, was there isolated a C<sub>11</sub>H<sub>14</sub>O<sub>2</sub> compound, apparently 2,2-dimethyl-3-methoxycoumaran.

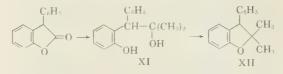
Thus, from the results presented, it may be concluded that whereas II often reacts in the manner of typical  $\beta$ -halo ethers or typical benzylic halides, there are other reactions that differ. The latter point may be illustrated by the following. Whereas substituted benzyl halides undergo with Grignard reagents the so-called coupling reaction<sup>21</sup> in which a 1,2-disubstituted ethane is formed, addition of II to an excess of methylmagnesium iodide, gave, besides a 7% yield of 2-isobutenylphenol (VII) and a 4.2% yield of compound 171°, a 53% yield of 2,2,3-trimethylcoumaran characterized by comparison with an authentic sample<sup>22</sup> and its dinitro deriva-tive.<sup>23</sup> Thus, coupling occurs here to a much lesser extent than with, *e.g.*, 2-methoxybenzyl bromide,<sup>6</sup> in which coupling is the predominant reaction. Incidentally, the formation of 2,2,3-trimethylcoumaran from II additionally supports structure II. Similarly, in the reaction with phenylmagnesium bromide II undergoes phenylation exclusively giv-ing 2.2-dimethyl-3-phenylcoumaran (XII). The ing 2,2-dimethyl-3-phenylcoumaran (XII). latter new compound was synthesized by addition of 3-phenylcoumaranone<sup>24</sup> to an excess of methylmag-

(19) T. Zincke, Ann., 159, 367 (1871), and subsequent papers.
 (20) L. Claisen, *ibid.*, 242, 210 (1925).

- (21) Reference 14.
- (22) W. M. Lauer and O. Moe, THIS JOURNAL, 65, 291 (1943). (23) C. D. Hurd and R. Dowbenko, ibid., 80, 4711 (1958).

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nesium iodide and cyclization of the resulting o-(1 - phenyl - 2 - methyl - 2 - hydroxypropyl) - phenol (XI)<sup>25</sup> with a refluxing mixture of hydrobromic and acetic acids, and proved to be indistinguishable in all properties from that obtained from II.

It should be noted that the reaction of II with Grignard reagents as illustrated in the present work represents a convenient means of arriving at 2,2,3trisubstituted coumarans, compounds difficultly accessible by other methods.

### Experimental<sup>26</sup>

The starting compounds were prepared as described in ref. 23

ref. 23. Reaction of 2,2-Dimethylcoumaran with One Mole of N-Bromosuccinimide.—A mixture of 7.4 g. (0.05 mole) of 2,2-dimethylcoumaran, 8.9 g. (0.05 mole) of N-bromosuc-cinimide, about 0.05 g. of benzoyl peroxide and 150 ml. of dry carbon tetrachloride was refluxed for 2 hr. during which time it became purple. The reaction mixture then was cooled, the solid (4.9 g.) filtered off, the red-colored filtrate washed with saturated sodium chloride solution and dried. Removal of the solvent and distillation of the residue gave, besides a small forefraction and a residue, 7.7 g. (68%) yield of a colorless liquid, b.p. 85-93° at 2 mm. A middle frac-tion b.p. 90° at 2 mm.,  $n^{28.6}$  D.15666, was analyzed. Anal. Calcd. for C<sub>10</sub>H<sub>10</sub>BrO: C, 53.10; H, 4.88. Found:

Anal. Caled. for C10H11BrO: C, 53.10; H, 4.88. Found: C, 54.41; H, 5.27

2,2-Dimethyl-3-(N-phthalimido) coumaran was obtained by refluxing for 16 hr. the bronic compound II and potassium phthalimide in tolure solution. The product appeared as white needles, m.p. 123–127°. The analytical sample, m.p. 128–128.5° (chloroform-hexane), showed a very strong band at 5.84  $\mu$  and a weak, sharp band at 5.62  $\mu$  in the infrared

Anal. Calcd. for C<sub>18</sub>H<sub>16</sub>NO<sub>8</sub>: C, 73.70; H, 5.15; N, 4.78. Found: C, 73.59; H, 5.30; N, 5.03.

Reaction of 2,2-Dimethylcoumaran with Two and Three Moles of N-Bromosuccinimide.—Under the same conditions as for one mole of N-bromosuccinimide, there was obtained from 5.20 g. (0.035 mole) of 2,2-dimethylcoumaran and 12.5 from 5.20 g. (0.035 mole) of 2,2-dimethylcoumaran and 12.5 g. (0.070 mole) of N-bromosuccinimide in 100 ml. of dry carbon tetrachloride 9.50 g. of an oil, b.p. 87.5-110° (3 mm.). The oil was heated at 100° for 2.5 hr. with 10 g. of anhydrous potassium acetate and 50 ml. of acetic acid and left overnight. The mixture was processed by pouring it into water, extracting with ether and distilling to give fractions from which a compound, m.p. 36-37°, apparently 2,2-dimethyl-3-coumaranone, could be isolated. A similar reaction of 7.4 g. (0 05 mole) of 2,2-dimethyl-coumaran and 26.7 g. (0.15 mole) of N-bromosuccinimide in 100 ml. of dry carbon tetrachloride gave rise to 6.2 g. of a colorless oil, b.p. 85-90° (2.2 mm.), apparently 3-bromo-2,2-dimethylcoumaran, and a large forefraction and tarry residue.

residue.

Conversion of 3-Bromo-2,2-dimethylcoumaran into 2,2-Dimethyl-3-coumaranyl Ether (VI).—Thirty-two grams of crude 3-bromo-2,2-dimethylcoumaran was added to a solution of 40 g. of potassium carbonate in 200 ml. of water. The resulting mixture was heated on the steam-bath for 3 hr. The mixture then was cooled, saturated with sodium chloride and extracted with ether. The extract was evapo-rated to give 24.7 g. of a yellow oil which did not give a Beilstein test for halogen. Although some crystallization

(24) A. Bistrzycki and J. Flatau, Ber., 30, 124 (1897)

(25) B. I. Arventi, Rev. Sliintifica "V. Adamachi," 29, 66 (1943);
 C. A., 38, 5217 (1944).

(26) The melting points are uncorrected. The infrared spectra of most of the compounds of interest here are listed in R. Dowbenko, Dissertation, Northwestern University, Evanston, Ill., 1958. Analyses were performed by Miss H. Beck.

could be induced by cooling its solution in a mixture of ether and pentane, this was incomplete and the oil was distilled to give, in addition to a forefraction and a residue, 4.55 g. of a material, b.p. 100–110° (2.2 mm.), which crystallized on standing to give a white solid of m.p. 85–100°. Several recrystallizations from hexane gave an analytical sample of m.p. 104-105°

Anal. Calcd. for C20H22O3: C, 77.38; H, 7.14. Found: C, 77.61; H, 6.98.

2,2-Dimethyl-3-coumaranyl Acetate (III).—The crude 3-bromo-2,2-dimethylcoumaran (from 0.1 mole of 2,2-dimethylcoumaran) was dissolved in 25 ml. of acetic acid. To the resulting red solution there was added 15 g. (0.15 mole) of freshly fused, finely divided potassium acetate, whereupon the color of the mixture changed to yellow and the temperature rose to 80°. After heating to 120° for 10 min., allowing to stand at room temperature overnight and heating again on the steam-bath for 2.5 hr., the mixture was poured into water. It then was extracted with ether. heating again on the steam-bath for 2.5 hr., the mixture was poured into water. It then was extracted with ether, the resulting extract washed with saturated solutions of sodium bicarbonate and sodium chloride and evaporated to give 20.0 g. of a yellow oil which showed a negative Beil-stein test for halogen. After two distillations there was obtained 15.6 g. (75.7% based on 2,2-dimethylcoumaran) of a colorless liquid, b.p. 90-99° (1.5 mm.). A middle fraction, b.p. 98° (1.5 mm.),  $n^{24}$ D 1.5076, was analyzed. Anal Caled, for C. H.O.: C. 69.88; H. 6.84. Found: Anal Caled. for C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>: C, 69.88; H, 6.84. Found: C, 70.12; H, 6.71.

**2,2-Dimethyl-3-coumaranol.**—A solution of 8.0 g. (0.14 mole) of potassium hydroxide in 100 ml. of methanol and 14.5 g. (0.0705 mole) of III was refluxed on the steam-bath night. The mixture then was diluted with 200 ml. of water, saturated with sodium chloride and extracted with ether. inglify the initial of the initialy

Anal. Calcd. for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>: C, 73.14; H, 7.37. Found: C, 73.37; H, 7.31.

Its benzoyl derivative was prepared from the coumaranol and benzoyl chloride in pyridine solution and had a m.p. of 57.5-58.0° (pentane-ether).

Anal. Caled. for C17H16O2: C, 76.10; H, 6.01. Found: C, 76.46; H, 6.19.

The 1-naphthylcarbamate was prepared from the coumar-anol and 1-naphthyl isocyanate in hexane solution and was obtained in the form of white rosettes, m.p. 136-137° (hexane).

Anal. Caled. for  $C_{21}H_{19}NO_3$ : C, 75.65; H, 5.74; N, 4.20. Found: C, 75.24; H, 5.67; N, 4.39.

2,2-Dimethyl-3-coumaranone (V).—To a slurry of a com-plex<sup>27</sup> of chromic oxide (4.5 g.) and dry pyridine (45 ml.) cooled to 20° there was added 2.4 g. (0.015 mole) of 2,2-dimethyl-3-coumaranol, m.p. 72–74°, in 45 ml. of pyridine. The mixture was maintained at a temperature below  $30^{\circ}$ . The mixture was maintained at a temperature betweet of the mixture was left at  $20-25^{\circ}$  for 18 hr. after which it was diluted with 200 ml. of water. The resulting mixture was extracted with a mixture of ether and benzene. The extract was washed thoroughly with dilute hydrochloric acid solution and saturated sodium chloride solution. Drying solution and saturated solution chloride solution. Drying and evaporation of the extract gave 2.3 g. of colorless plate-lets which, after several recrystallizations from ether-pentane at about  $-50^{\circ}$ , furnished the analytical sample, m.p. 39.0-39.5°, showing a carbonyl band at 5.77  $\mu$  in the infrared

(27) G. Poos, G. Arth, R. Beyler and L. Sarett, THIS JOURNAL, 75, 422 (1953).

Anal. Calcd. for C10H10O2: C, 74.05; H, 6.22. Found: C, 73.50; H, 5.92

Its 2,4-dinitrophenylhydrazone, prepared in ethanolic sulfuric acid, was obtained as bright-red needles, m.p. 212–213° (95% ethanol).

Anal. Calcd. for  $C_{16}H_{14}N_4O_5$ : C, 56.14; H, 4.12; N, 16.37. Found: C, 55.69; H, 4.37; N, 16.68.

**Reaction of 3-Bromo-2,2-dimethylcoumaran with Sodium.** —To the sodium powder (from 1.8 g., 0.078 g. atom, of sodium) suspended in 100 ml. of ether there was added dropwise a solution of 7.30 g. (0.032 mole) of 3-bromo-2,2-dimethylcoumaran in 100 ml. of ether. A white solid precipitated, but heat was not evolved. After all the bromide was added and the mixture was warmed for a short time, a reaction started as evidenced by refluxing of the solvent. After stirring and refluxing for 3 hr. the brown color changed to greenish, and the mixture was stirred and refluxed for an additional 3.5 hr. The excess of sodium was destroyed with methanol and water and then the mixture was acidified and extracted with ether. The ether extract was separated into a fraction soluble in sodium hydroxide and a neutral fraction. The latter gave on distillation at 1.7 mm. two fractions: b.p. 55–72°, 0.30 g., and b.p. 72–168°, 0.40 g. The orange-colored residue (2.90 g.) decomposed on further heating. These materials were not investigated. The alkali-soluble fraction gave on distil-lation 0.60 g. (13%) of 2-isobutenylphenol (VII), b.p. 76.5° (2.2 mm.), whose reaction with ferric chloride and whose infrared spectrum were identical with those of authen-ic 2 isobut enylphenol. Reaction of 3-Bromo-2,2-dimethylcoumaran with Sodium. whose infrared spectrum were identical with there is chloride and whose infrared spectrum were identical with those of authen-tic 2-isobutenylphenol. Its 1-naphthylcarbamate melted at 122.5-123.5° and did not show any depression in the melting point on admixture of the authentic 2-isobutenyl-phenyl 1-naphthylcarbamate.

Preparation of 2-Isobutenylphenol (VII).—The prepara-tion of this compound was based on the method of Pauly and Buttlar<sup>28</sup> who treated ethylmagnesium halide with salicylaldehyde. Thus, from 111 g. (0.9 mole) of isopropyl bromide, 21.9 g. (0.9 g. atom) of magnesium and 36.6 g. (0.30 mole) of salicylaldehyde there was obtained after processing 26 g. of a liquid, b.p. 106-108° (14-20 mm.), and a large amount of yellow residue. After washing the liquid with sodium bisulfite, bicarbonate and chloride solu-tions it was dried and distilled to obtain 19.3 g. (43.5%) of 2-isobutenylphenol, b.p. 98-104.5° at 13 mm. A middle fraction, b.p. 104.5° at 13 mm., n<sup>25</sup>D 1.5539, gave with ferric chloride a greenish color which rapidly changed to brown; ultraviolet spectrum (in methanol):  $\lambda_{max} 285 m\mu$ ( $\epsilon_{max} 2980$ ),  $\lambda_{max} 242 m\mu$  ( $\epsilon_{max} 7300$ ); reported<sup>29</sup> constants for 2-isobutenylphenol: b.p. 81° at 6 mm., n<sup>20</sup>D 1.5590. Anal. Calcd. for C<sub>10</sub>H<sub>12</sub>O: C, 81.04; H, 8.16. Found: Preparation of 2-Isobutenylphenol (VII).-The prepara Anal. Calcd. for C<sub>10</sub>H<sub>12</sub>O: C, 81.04; H, 8.16. Found:

C, 80.48; H, 7.61. **2-Isobutenylphenyl 1-naphthylcarbamate** was prepared in the usual manner and melted at 122.5–123.5° (ligroin).

Anal. Calcd. for C<sub>21</sub>H<sub>19</sub>NO<sub>2</sub>: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.50; H, 5.89; N, 5.15.

2-Isobutenylphenyl 3,3-dinitrobenzoate was prepared by heating the phenol and the acid chloride in pyridine solution and was obtained as lemon-yellow crystals, m.p. 69-70°

Anal. Calcd. for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>6</sub>: C, 59.65; H, 4.12; N, 8.18. Found: C, 59.23; H, 3.98; N, 8.70.

Reaction of 3-Bromo-2,2-dimethylcoumaran with Magnesium.—To 1.74 g. (0.0715 g. atom) of magnesium turn-ings covered with 10 ml. of dry ether there was added 16.2 g. (0.0715 mole) of the bromide dissolved in 60 ml. of ether. After addition of a small portion of the bromide solution the reaction started immediately and an additional 150 ml. of dry ether was added to the reaction mixture which asof dry ether was added to the reaction mixture which as-sumed initially a blue color which then changed to deep-purple. After all the bromide solution was added the mixture was refluxed for 0.5 hr. whereupon the color changed to dark-red, but became purple again on cooling. The mix-ture then was poured onto a mixture of ether and powdered Dry Ice and was allowed to stand 1 hr. The mixture was acidified with 40 ml. of iced hydrochloric acid. The layers were separated and the aqueous layer was extracted ex-haustively with ether. The combined extract was separated into acidic, phenolic and neutral fractions. No residue was into acidic, phenolic and neutral fractions. No residue was

 (28) H. Pauly and R. V. Buttlar, Ann., 383, 230 (1911).
 (29) Q. R. Bartz, R. F. Miller and R. Adams, THIS JOURNAL, 57, 371 (1935).

obtained on evaporation of the acidic fraction, and only a negligible amount of phenolic material from the correspond-ing phenolic fraction which was not investigated further. The neutral fraction, 10.8 g., consisted of a red oil mixed with a solid. The solid was filtered off and washed with cold pentane to give 1.7 g. of slightly pink crystals, m.p. 169.5-170.5°. The analytical sample, prepared by several recrystallizations from absolute ethanol, melted at 170-171°. The compound did not react with boiling aqueous potassium permanganate or potassium dichromate solupotassium permanganate or potassium dichromate solu-tions and did not decolorize bromine in carbon tetrachloride, ultraviolet spectrum (in methanol): shoulder at 287 m $\mu$  $(\epsilon 6900), \lambda_{\max} 281 \, \mathrm{m}\mu \, (\epsilon_{\max} \, 7650).$ 

Anal. Caled. for C<sub>20</sub>H<sub>22</sub>O<sub>2</sub>: C, 81.60; H, 7.53; mol. wt., 294. Found: C, 82.05; H, 7.24; mol. wt. (in camphor), 295, 302.

Nitration<sup>23</sup> of the above compound 171° gave a **tetranitro derivative** (apparently 2,2,2',2'-tetramethyl-5,5',7,7'-tetra-nitro-3,3'-bicoumaran), yellow prisms (from acetone-methanol), m.p. 283–285° (m.p. block).

Anal. Calcd. for  $C_{20}H_{18}N_4O_{10}$ : C, 50.63; H, 3.87; N, 11.85. Found: C, 50.44; H, 3.63; N, 11.62.

The remaining filtrate from which the compound 171° was separated was freed from the solvent and a 3.65-g, sample was chromatographed on 200 g. of alumina (Merck, chromatography grade) and eluted with hexane containing chromatography grade) and eluted with hexane containing successively higher amounts of ether. The fractions eluted with 5% ether in hexane contained 1.50 g. of an oily solid of varying melting points. The fractions eluted with 10% ether in hexane contained 1.60 g. of a brown oil which failed to crystallize. The oily solid was recrystallized from methanol to give 1.35 g. (37.2%) of a compound, m.p. 86-90°. The analytical sample, prepared by several re-crystallizations from methanol, melted at 98°. Like the higher melting compound, it was inert to potassium per-mangengete potassium dichromate and brownie: ultrahigher melting compound, it was inert to potassium per-manganate, potassium dichromate and bromine; ultra-violet spectrum (in methanol):  $\lambda_{max} 292 \text{ m}\mu$  ( $\epsilon_{max} 8100$ ),  $\lambda_{max} 284 \text{ m}\mu$  ( $\epsilon_{max} 8200$ ). For comparison, the ultraviolet spectrum of 2,2-dimethylcoumaran was measured (in meth-anol): shoulder at 288 m $\mu$  ( $\epsilon$  3460),  $\lambda_{max} 281 \text{ m}\mu$  ( $\epsilon_{max}$ 4120),  $\lambda_{max} 225 \text{ m}\mu$ ( $\epsilon_{max} 7200$ ). *Anal*. Calcd. for C<sub>20</sub>H<sub>22</sub>O<sub>2</sub>: C, 81.60; H, 7.53; mol. wt., 294. Found: C, 81.55; H, 6.99; mol. wt. (in cam-phor), 304, 244. Nitration of the above compound 022

Nitration of the above compound 98° gave a tetranitro derivative as pinkish microscopic needles not melting below 300° (acetone-methanol).

Anal. Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>10</sub>: C, 50.63; 11.85. Found: C, 51.07; H, 3.79; N, 12.39. C, 50.63; H, 3.87; N,

Reaction of 3-Bromo-2,2-dimethylcoumaran with Zinc.— A small portion of a solution of 8.6 g. (0.038 mole) of 3-bromo-2,2-dimethylcoumaran in 50 ml. of ether was added to a stirred suspension of 6.5 g. (0.10 g. atom) of zinc dust in 150 ml. of ether. The mixture was warmed for a short period of time until a yellow color which developed changed to an intense green as the reaction proceeded. The rest of the solution was added dropwise with stirring, and the green mixture refluxed for 6 hr., then stirred at room temperature mixture reinvised for 6 n., then stated at form temperature overnight. After a customary separation, there was ob-tained 0.30 g. of a green-colored phenolic fraction and a neutral yellow sirup which showed a green fluorescence. On dilution with ether-hexane the latter deposited 0.80 g. (14%) of the impure compound 171°, m.p. 167–169°. The residual oil amounted to 4.5 g. A 1.5-g. sample of the oil was observation on alumina and eluted with 2%

The residual oil amounted to 4.5 g. A 1.5-g. sample of the oil was chromatographed on alumina and eluted with 2% ether-in-hexane to obtain 0.55 g. (30%) of greenish needles of impure compound 98°, m.p. 89–94°. Reaction of 3-Bromo-2,2-dimethylcoumaran with Zinc in Benzene Solution.—To a mixture of 10 g. of zinc dust and 200 ml. of dry benzene there was added 14.4 g. of 3-bromo-2.9 dimethylcours and the resulting reddish mixture 200 ml. of dry benzene there was added 14.4 g. of 3-bromo-2,2-dimethylcoumaran and the resulting reddish mixture was heated while the color changed to deep-purple, then to light-brown. The mixture was refluxed for 6 hr. during which time hydrogen bromide came off vigorously. The mixture was left overnight, then was filtered and the result-ing filtrate evaporated to give a brown oil. Dissolving the oil in acetone and adding methanol gave 10.6 g. of a slightly yellow powder melting at 213–220° and giving only a faint Beilstein test for halogen. It was soluble in acetone, ethyl acetate and benzene, but was precipitated from these solutions by methanol. It was further purified by reprecip-

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itations from acetone, then from boiling butanol, to obtain a yellowish amorphous powder melting with decomposition at 245–280° and no longer giving a positive Beilstein test. Molecular weight determination on an approximately 10% solution in camphor gave a  $1.2^\circ$  depression of the m.p. of camphor.

Anal. Calcd. for  $C_{10}H_{10}O$  (polycoumaran): C, 82.14; H, 6.91. Found: C, 80.57; H, 6.40.

Nitration of this polycoumaran gave a yellow solid, m.p.  $145-150^{\circ}$  dec., which, upon purification by reprecipitation with methanol from an acetone solution, did not melt below  $300^{\circ}$  and exploded in the combustion apparatus on attempted analysis.

Reaction of Compound 171° with Two Moles of N-Bromosuccinimide.—A mixture of 1.039 g. (3.54 mmoles) of the above compound 171°, 1.260 g. (7.08 mmoles) of N-bromosuccinimide, 50 ml. of carbon tetrachloride and about 5 mg. of benzoyl peroxide was refluxed on the steambath whereupon the mixture assumed a brown color. After 2.5 hr. the mixture became lemon-yellow and evolved hydrogen bromide. At this point heating was discontinued, the mixture was cooled and washed with water and sodium biarbonate solution. Drying and evaporating the solution gave 1.5 g. of a yellow solid, m.p. 115–160°, which was recrystallized from hexane to give 0.950 g. of yellow hard crystals of m.p. 170–174°. The compound was not attacked by boiling potassium permanganate and was recovered unchanged after refluxing for 5 hr. its solution in acetia exid with potassium acetate

Anal. Caled. for  $C_{20}H_{20}Br_2O_2$ : C, 53.12; H, 4.46. Found: C, 53.15; H, 4.42.

An analogous reaction of compound 98° with two moles of N-bromosuccinimide gave lemon-yellow crystals m.p. 168-170°. On repeated recrystallizations from hexane the melting point could not be obtained constant. Similarly, chromatography on alumina did not give good results since the melting point could not be made constant. Recrystallization from hexane of the chromatographic fractions gave a material with a melting point of 197-215°.

lization from hexane of the chromatographic fractions gave a material with a melting point of 197–215°. **Reaction of 3-Bromo-2,2-dimethylcoumaran with Phenol** in Methanol Solution: 2,2-Dimethyl-3-coumaranyl Methyl Ether.—To a solution of 5.6 g. (0.06 mole) of phenol and 3.2 g. (0.06 mole) of sodium methoxide in 50 ml. of methanol there was added 12.7 g. (0.056 mole) of 3-bromo-2,2-dimethylcoumaran dissolved in 10 ml. of methanol whereupon heat was evolved. The mixture was refluxed for 2 hr., after which most methanol distilled off and the residue was poured into water and the resulting mixture was extracted with ether. The extract was washed with sodium hydroxide solution and water, then was dried and evaporated to give 10 g. of a light-yellow oil. This was distilled to give, in addition to a forefraction and a residue, 5.60 g. of a colorless liquid, b.p. 62–62.5° (0.3 mm.). Redistillation gave an analytical sample, b.p. 71–72° (0.3 mm.),  $n^{25}$ 1.5167.

Anal. Calcd. for  $C_{11}H_{14}O_2;\ C,\ 74.13;\ H,\ 7.91.$  Found: C, 74.41; H, 7.61.

Reaction of 3-Bromo-2,2-dimethylcoumaran with Methylmagnesium Iodide.—To a stirred solution of the Grignard reagent (prepared from 6.75 g., 0.28 g. atom, of magnesium and 40 g., 0.28 mole, of methyl iodide in a total of 100 ml. of ether) there was added dropwise over a period of 1.5 hr. a solution of 16.8 g. (0.074 mole) of 3-bromo-2,2-dimethylcoumaran in 100 ml. of ether, while the reaction mixture was allowed to reflux gently. After completion of addition the mixture was refluxed for 8 hr., then was allowed to stand at room temperature for 8 hr. and finally was poured into a mixture of 100 ml. of hydrochloric acid and 200 g. of ice. Customary separation gave a phenolic and a neutral fraction. The phenolic fraction, 0.75 g. (7%), showed an infrared spectrum identical with that of 2-isobutenylphenol

except for a weak band at 5.97  $\mu$ , absent in the spectrum of authentic 2-isobutenylphenol. The neutral fraction, 11.6 g., was composed of a brown oil and white crystals. The crystals gave after purification 0.45 g. (4.2%) of compound 171°. The remaining oil was distilled to give, in addition to about 2 g. of a green-brown residue, 7.10 g. (52.7%) of a liquid, b.p. 67.5-71° at 3 mm., which was shown to be 2,2,3-trimethylcoumaran by analysis, comparison of its infrared spectrum<sup>23</sup> with that of the authentic compound, as well as by comparison of the dinitro derivatives<sup>23</sup> of the two compounds. The fraction, b.p. 70° at 3 mm.,  $n^{25}$ p 1.5165, was analyzed.

Anal. Calcd. for  $C_{11}H_{14}O$ : C, 81.44; H, 8.70. Found: C, 81.31; H, 8.49.

C, 01-01; H, 03-49. **Reaction of 3-Bromo-2,2-dimethylcoumaran with Phenylmagnesium Bromide.**—To a solution of the Grignard reagent (prepared from 5.83 g., 0.24 g. atom, of magnesium and 37.6 g., 0.24 mole, of bromobenzene in a total of 350 ml. of ether) there was added with stirring over a period of 25 min. a solution of 15.4 g. (0.0677 mole) of 3-bromo-2,2dimethylcoumaran in 150 ml. of ether. After 15 hr. of reflux the mixture was allowed to stand at room temperature for 24 hr., then was poured onto iced hydrochloric acid and worked up in the usual manner to obtain an ether extract which was washed with sodium hydroxide solution and then evaporated. Two distillations of the residue gave 9.9 g. (65%) of a colorless liquid, b.p. 123.5–128° at 1.7 mm, m.p. about 7°. Its infrared spectrum was indistinguishable from that of an authentic sample of 2,2-dimethyl-3-phenylcoumaran prepared below. An analytical sample was obtained by redistillation, b.p. 87° at 0.12 mm.,  $n^{25}$ p. 1.5735

Anal. Calcd. for  $C_{16}H_{16}O;\,\,C,\,85.68;\,\,H,\,7.19.\,$  Found: C, 85.65; H, 6.91.

Reaction of 3-Phenyl-2-coumaranone with Methylmagnesium Iodide.—To a solution of methylmagnesium iodide prepared from 0.15 mole of the reagents in 250 ml. of ether there was added with stirring over a period of 15 min. 10.5 g. (0.050 mole) of 3-phenyl-2-coumaranone,<sup>24</sup> m.p. 109–111°, in 130 ml. of benzene. The resulting solution was refluxed for 2.5 hr. and then allowed to stand at room temperature overnight. When this was poured into dilute hydrochloric acid it gave a solution whose evaporation gave 11.65 g. of a slightly colored solid, m.p. 87–114°. Recrystallization from a mixture of acetone and hexane gave 9.50 g. (78.5%) of o-(1-phenyl-2-methyl-2-hydroxypropyl)-phenol, m.p. 125– 128°. The analytical sample was obtained by recrystallization from earbon tetrachloride, m.p. 132.0–132.5°.

Anal. Calcd. for  $C_{16}H_{18}O_2$ : C, 79.31; H, 7.49. Found: C, 80.17; H, 7.39.

The monobenzoate was obtained by the Schotten–Baumann procedure, m.p.  $108-109^{\circ}$  (hexane). It showed a hydroxyl band at  $2.78 \,\mu$  and a carbonyl band at  $5.83 \,\mu$  in the infrared.

Anal. Calcd. for C<sub>23</sub>H<sub>22</sub>O<sub>3</sub>: C, 79.74; H, 6.40. Found: C. 80.02; H, 6.11.

2,2-Dimethyl-3-phenylcoumaran.—A mixture of 10.5 g. of the crude o-(1-phenyl-2-methyl-2-hydroxypropyl)-phenol, m.p. 100-110°, and 150 ml. of 1:1 acetic-48% hydrobromic acid was refluxed for 4 hr. After allowing it to stand at room temperature overnight the mixture was diluted with water and extracted with hexane-ether. The extract was washed thoroughly with a sodium hydroxide solution, water and a saturated sodium chloride solution, and then was dried and evaporated. The residue was distilled to give 4.3 g. (44%) of 2,2-dimethyl-3-phenylcoumaran, b.p. 111-120° at 0.6 mm. A middle fraction, b.p. 114-116° at 0.6 mm., n<sup>25</sup>p 1.5731, was analyzed.

Anal. Caled. for  $C_{16}H_{16}O;\ C,\ 85.68;\ H,\ 7.19.$  Found: C, 86.10; H, 7.03.

EVANSTON, ILL.





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### **Reaction of Acrylamide and Pyridinium Chloride**

ROSTYSLAW DOWBENKO

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Acrylamide and pyridinium chloride react to give N-(2-carbamylethyl)pyridinium chloride, II, whose structure was proved by hydrogenation of it to the piperidinium analog which was synthesized independently. The reaction was extended to several other heterocyclic base salts and  $\alpha,\beta$ -unsaturated amides.

Some time ago it was disclosed in a patent<sup>1</sup> that aliphatic amides, formaldehyde (or N-hydroxymethylamides) and salts of the tertiary

(1) A. W. Baldwin and E. E. Walker, U. S. Patent 2,146,392 (February 7, 1939).

heterocyclic bases react to form N-amidomethyl inium salts (I). More recently, Weaver and co-workers<sup>2</sup> investigated this reaction in more detail

(2) J. W. Weaver, H. A. Schuyten, J. G. Frick, Jr., and J. D. Reid, J. Org. Chem., 16, 1111 (1951).

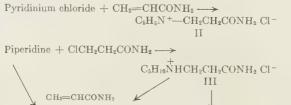
and, for stearamidomethylpyridinium chloride, demonstrated several of its transformations. In

$$RCONH_2 + CH_2O + H - N + \longrightarrow RCONHCH_2 - N + I$$

particular they studied reactions leading to *N*-alkoxymethylstearamides. In connection with other work done in these laboratories it was of interest to extend this reaction to acrylamide and other unsaturated amides in order to obtain compounds analogous to I. The reaction with acrylamide, however, took a different course and its examination forms the subject of this report.

When an equimolar mixture of acrylamide, trioxane, and pyridinium chloride was heated at 65° in pyridine solution, there was obtained a solid, m.p. 197°, which was unreactive toward methanol under Weaver's conditions<sup>2</sup> and could be recovered from the reaction mixture. Similarly, when alcohols were substituted for pyridine as solvent, or when formaldehyde was replaced by acetaldehyde, butyraldehyde, or benzaldehyde, still the same compound was obtained. In contrast, from the reaction of N-(hydroxymethyl)acrylamide and pyridinium chloride under conditions<sup>2</sup> known to give compound I, only the starting materials were recovered. Finally, omission of the aldehyde from the reaction still gave the same compound above. These results clearly indicated that aldehydes did not participate in the reaction of acrylamide and that, therefore, N-acrylamidomethylpyridinium chloride was not formed, but instead an adduct of acrylamide and pyridinium chloride was obtained. This was confirmed by analysis which revealed an empirical formula C<sub>8</sub>H<sub>11</sub>ClN<sub>2</sub>O and showed no unsaturation. The latter finding was supported also by the fact that the compound was unreactive toward cyclopentadiene and did not polymerize on heating in the presence of ammonium persulfate in aqueous or methanolic solution. This information, along with the fact that the compound was salt-like (soluble in water and methanol, insoluble in ether, acetone, and hydrocarbons), led to assignment of the structure N-(2-carbamylethyl)pyridinium chloride (II).

Structure II was proved unequivocally by catalytic hydrogenation to a crystalline piperidinium compound (III), identical with that obtained directly from 3-chloropropionamide and piperidine.



C<sub>5</sub>H<sub>10</sub>NCH<sub>2</sub>CH<sub>2</sub>CONH<sub>2</sub>

V

C<sub>5</sub>H<sub>10</sub>NHCH<sub>2</sub>CH<sub>2</sub>COOH Cl-

IV

Moreover, III could be transformed into the same free base (V) that was obtained by the addition of piperidine to acrylamide. Hydrolysis of III with hydrochloric acid yielded IV.

Addition of salts of heterocyclic bases to  $\alpha_{\beta}$ unsaturated carbonyl compounds has been reported on several occasions. Thus Barnett *et al.*<sup>3</sup> described addition of pyridine salts to benzoquinone, and Goerdeler<sup>4</sup> described addition of pyridine to maleic and acrylic acids from which the pyridinium betaines were obtained. The reaction of  $\beta$ -benzoylacrylic acid with pyridine<sup>5</sup> apparently is also of the same type and may be considered in effect a reaction of a pyridine salt.<sup>6</sup> Similarly, addition of pyridine to unsaturated compounds in the presence of halogens is also known and may be exemplified by the reaction of pyridine and 1,2-diethoxyethylene in the presence of bromine<sup>7</sup> in which compound VI is

$$C_{2}H_{5}O-CH = CH - OC_{2}H_{5} + \bigvee_{N} + Br_{2} \rightarrow$$

$$C_{2}H_{5}O-CH - \underbrace{CH}_{N \oplus} OC_{2}H_{5}$$

$$C_{2}H_{5}O-CH - \underbrace{CH}_{2}Br_{VI}$$

obtained. A recent example of interest is that reported by Heininger,<sup>8</sup> who found that cyanoethylation of pyrrolidinium chloride with acrylonitrile gives N-(2-cyanoethyl)pyrrolidinium chloride. The present case, however, apparently constitutes the first example of addition of pyridinium chloride to  $\alpha,\beta$ -unsaturated amides.

In order to test the generality of this unusually facile addition of pyridinium chloride to acrylamide, several other compounds were used in the conditions under which the former gave the adduct II. The results are summarized in Table I and are

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Chem. Soc., 74, 5491 (1952); C. D. Hurd and S. Hayao, J. Am.

(5) J. Bougault and P. Chabrier, *Compt. rend.*, 237, 1420 (1953).

(6) Cf. also N. H. Cromwell, P. L. Creger, and K. E. Cook, J. Am. Chem. Soc., 78, 4412 (1956) for a more recent discussion of this work.

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|-----------|---------|----|
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2 20 20 21

14. 14.

81 86 59 61

2 20 10 10

5.77 5.90 6.45

69 68 73 73

51.

13.

67

-

86

171.5-172.5

93

Acrylamide Acrylamide

2-Methylpyridine

15.01 96

19.00

5.946.53

48

51. 53.

 $C_{s}H_{11}CIN_{2}O$ C<sub>9</sub>H<sub>13</sub>CIN<sub>2</sub>O 000

11.

14.98 14.98

5.545.54 5.27

80

60.

 $C_{12}H_{13}CIN_2O$ 

99-200

18

Acrylamide Acrylamide

2.6-Dimethylpyridine

Quinoline

80

60.

210.5-212

ŝŝ 3 33

0

I

0

z

5

H

0

Formula

M.P., 195-197

of Product<sup>b</sup> ' . Yield

Aniide

Base

Pyridine

Calcd.

Found

recovered un-

W'AS I

methanol and acetone. <sup>e</sup> 2,6-Dimethylpyridinium chloride

general procedure (Experimental). <sup>b</sup> Before recrystallization from a mixture of

a According to the

changed

13.

67

5

53.

183-184

51

Methacrylamide Crotonamide

Acrylamide Acrylamide

Phenanthridine

Pyridine Pyridine

Isoquinoline

11 9. 9. 13. 14.

22 13.96 96

6.

37

67.01  $\mathbf{S6}$ 86

IrHicCIN<sub>2</sub>() C<sub>12</sub>H<sub>13</sub>ClN<sub>3</sub>O

> 2:34 205

3 84

225555

0000000

17.67

6.536.53

53.

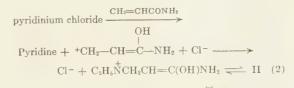
C<sub>9</sub>H<sub>16</sub>CIN<sub>2</sub>O C,H13CIN2O for the most part self-explanatory. It should be noted, however, that 2,6-dimethylpyridinium chloride was unreactive, and methacrylamide and crotonamide gave lower yields of the products. Although nonreaction of the former compound is probably due to steric hindrance in the 2,6dimethylpyridinium ion, the lower yields from the latter are probably a real reflection of decreased reactivity of these compounds, although no attempts to obtain the best yields were made. Therefore, the facile addition of salts of heteroaromatic amines to  $\alpha,\beta$ -unsaturated amides is quite general.

Several things may be said relating to the mechanism of this reaction, although no efforts were made to examine it in great detail. Two main paths appear to exist by which the reaction may proceed. The first (1) requires addition of hydrogen

CH2=CHCONH2 pyridinium chloride

 $ClCH_2CH_2CONH_2 \longrightarrow II$  (1) Pyridine

chloride to acrylamide and subsequent alkylation of pyridine with the resulting 3-chloropropionamide. That the chloroamide is not an intermediate in the reaction, however, was demonstrated when 3-chloropropionamide and pyridine under the conditions of acrylamide reaction gave a very low yield of II.9 An alternative mode of reaction is that represented by (2).<sup>10</sup> As required by this scheme, the reaction appears to be acid-catalyzed, and if this were valid the mechanism (2) is to be preferred. A still more attractive mechanism is the concerted one (3) involving the formation of a quasi six-membered ring.



$$\begin{array}{ccc} CH_2 & & \\ CH & N \\ C$$

#### EXPERIMENTAL<sup>11</sup>

Reaction of acrylamide and pyridinium chloride in the presence of trioxane. A solution of 71 g. (1.0 mole) of acrylamide, 116 g. (1.0 mole) of pyridinium chloride, 30 g. (1.0

(9) Cf. F. N. Hayes, H. K. Suzuki, and D. E. Peterson, J. Am. Chem. Soc., 72, 4524 (1950), for the failure to obtain N-(2-bromocyclohexyl)pyridinium bromide from 1,2-dibromocyclohexane on one hand, and its facile formation from cyclohexene, bromine, and pyridine on the other.

(10) For a similar formulation of the *cis-trans* interconversion of  $\alpha$ ,  $\beta$ -unsaturated ketones, *cf.* P. L. Southwick and R. J. Shozda, J. Am. Chem. Soc., 81, 8298 (1959)

(11) All melting points are uncorrected. Analyses by Dr. H. W. Galbraith, Knoxville, Tennessee.

Reaction of  $\alpha, \beta$ -Unsaturated Amides with Heterocyclic Salts<sup>a</sup>

TABLE I

mole) of trioxane, and 1 g. of hydroquinone in 500 ml. of methanol was refluxed for 3 hr. and then was allowed to stand at room temperature overnight. On concentration of the reaction mixture, dilution with acetone, and filtration there was obtained 175 g. (93%) of a hygroscopic white powder, m.p.  $181-186^{\circ}$ . Several recrystallizations from a mixture of methanol and acetone gave an analytical sample of II, m.p.  $195-197^{\circ}$ , as large needles grown in spheres.

of II, m.p. 195–197°, as large needles grown in spheres. Anal. Calcd. for C<sub>8</sub>H<sub>11</sub>ClN<sub>2</sub>O: C, 51.48; H, 5.94; Cl, 19.00; N, 15.01. Found: C, 51.69, 51.73; H, 5.77, 5.90; Cl, 18.81, 18.86; N, 14.78, 14.88.

The compound was soluble in water and methanol, but insoluble in acetone, ether, ethyl acetate, and hydrocarbon solvents. It showed no unsaturation.

Substituting pyridine or butanol for methanol as solvent, or changing the aldehyde component to acetaldehyde, butyraldehyde, or benzaldehyde gave comparable yields of compound II. Omission of trioxane from the reaction mixture still gave compound II. None of II could be obtained from N-(hydroxymethyl)acrylamide and pyridinium chloride.

Compound II was recovered unchanged on heating with cyclopentadiene in methanol solution at  $110^{\circ}$  for 10 hr. Similarly, it was unchanged on refluxing its methanolic or aqueous solution 8 hr. in the presence of potassium persulfate.

A general procedure of reaction of heterocyclic amine hydrochlorides with  $\alpha,\beta$ -unsaturated amides. To a solution of 0.20 mole of unsaturated amide and 0.20 mole of heterocyclic amine in 50 ml. of methanol is added with cooling a solution of 0.20 mole of dry hydrogen chloride in 50 ml. of methanol. The resulting solution is refluxed for 4 hr., filtered if necessary, and evaporated to about half of its original volume. It is then diluted with acetone and cooled. The product is isolated by filtration and purified by recrystallization from a mixture of methanol and acetone. Alternatively, the amine hydrochloride may be used instead of the free base and hydrochloric acid solution where more convenient.

Acrylamide and pyridinium chloride refluxing for 2 hr. gave about 85% of compound II. The yield was comparable when the reaction was run at room temperature for 1.5 hr.

Reaction of 3-chloropropionamide with pyridine. A solution of 15.8 g. (0.20 mole) of pyridine and 21.6 g. (0.20 mole) of 3-chloropropionamide<sup>12</sup> in 100 ml. of methanol was refluxed for 4 hr. and filtered. The filtrate was reduced in volume to 50 ml. and diluted with acetone. No crystallization occurred, but on standing at room temperature for over a week and further dilution with acetone the solution deposited 4.5 g. of a white solid, m.p. 185–188°, apparently compound II.

Reaction of acrylamide with pyridinium chloride with added acid and base. Three experiments were carried out using 0.20 mole of the two reactants in 50 ml. of methanol. The first was the control experiment. The second contained an additional 1 g. of pyridine and the third 5 ml. of concd. methanolic hydrogen chloride. All three runs were allowed to stand at room temperature for the same period of time; then they were diluted simultaneously with 20 ml. of acetone and allowed to stand in the cold for 1 hr. The quantities of the pyridinium compound II obtained were as follows (theoretical yield 37.4 g.): control, 6.2 g., m.p. 168– 170°; pyridine added, 5.2 g., m.p. 168–171°; hydrogen chloride added, 9.1 g., m.p. 164–168°. Hydrogenation of N-(2-carbamylethyl)pyridinium chloride

Hydrogenation of N-(2-carbanylethyl)pyridinium chloride (II). A solution of 19.9 g. (0.107 mole) of II in 200 ml. of methanol and 1.0 g. of 5% palladium on charcoal was shaken with hydrogen at an initial pressure of about 50 p.s.i. until 0.11 mole was absorbed. The catalyst was filtered off and the solvent removed almost completely. Addition of acetone

(12) H. Henecka and P. Kurtz in *Methoden d. org. Chemie (Houben-Weyl)*, E. Müller, ed., Georg Thieme Verlag, Stuttgart, 1952, Vol. VIII, p. 663. caused separation of 18.5 g. of a cream-colored solid, m.p.  $155-165^{\circ}$ . Recrystallization from a mixture of methanol and acetone raised the m.p. to  $172-175^{\circ}$ , but further purification through recrystallization caused yellowing and decomposition.

When a solution of 18.5 g. (0.10 mole) of II in 200 ml. of methanol was shaken with 0.5 g. of platinum oxide until the pressure was constant, it absorbed in 1 hr. 105% of the theoretical 0.30 mole of hydrogen to give 17.0 g. (88.5%) of the piperidinium compound III. Several recrystallizations from a mixture of methanol and acetone gave the analytical sample, m.p. 196–197°.

Anal. Caled. for  $C_8H_{17}ClN_2O$ : C, 49.86; H, 8.89; Cl, 18.40; N, 14.54. Found: C, 49.75; H, 9.14; Cl, 18.42; N, 14.60.

Hydrolysis of N-(2-carbamylethyl)piperidinium chloride (III). A mixture of 10.0 g. (0.052 mole) of III and 50 ml. of concd. hydrochloric acid was refluxed for 6 hr. Hydrochloric acid was removed by evaporating *in vacuo*, adding water and repeating the process several times. The residue was dissolved in a minimum amount of hot water, filtered, and allowed to crystallize. Filtration and recrystallization of the solid from aqueous acetone gave 7.0 g. (70%) of white shiny platelets of the acid IV, mp. 210–212°. The analytical sample, prepared by several recrystallizations from the same solvent melted at 212–213°.

Anal. Caled. for  $C_8H_{16}ClNO_2$ : C, 49.61; H, 8.33; Cl, 18.31; N, 7.23. Found: C, 50.03, 49.84; H, 8.40, 8.36; Cl, 17.05, 17.26; N, 7.04, 6.88.

Preparation of N-(2-carbamy(ethyl)piperidinium chloride (III). A solution of 17.0 g. (0.20 mole) of piperidine and 21.6 g. (0.20 mole) of 3-chloropropionamide<sup>7</sup> in 100 ml. of methanol was refluxed for 4 hr., then filtered hot and evaporated to one-half of its original volume. Acetone was added and the mixture was allowed to crystallize. Filtration gave 30.5 g. (79%) of a nearly white solid, m.p. 193-196°. The analytical sample was prepared by several recrystallizations from a mixture of methanol and acetone, m.p. 197-198°. Its melting point was not depressed by admixture of the sample prepared by the hydrogenation of N-(2carbamylethyl)pyridinium chloride. Infrared spectra of the two compounds were indistinguishable.

Anal. Calcd. for  $\rm C_8H_{17}ClN_2O$ : C, 49.86; H, 8.89; Cl, 18.40; N, 14.54. Found: C, 50.32, 50.35; H, 8.85, 8.87; Cl, 18.34, 18.37; N, 14.85, 14.65.

Reaction of N-(2-carbamylethyl)piperidinium chloride with potassium carbonate. A solution of 9.35 g. (0.0485 mole) of the piperidinium compound III and 6.9 g. (0.05 mole) of potassium carbonate in a mixture of 200 ml. of methanol and 30 ml. of water was allowed to stand overnight. The solvent was evaporated *in vacuo* and the residue was dried by azeotropic distillation with benzene. It was then dissolved in ethyl acetate, filtered from inorganic salts, and evaporated to obtain a straw-colored oil which crystallized on standing. Recrystallization from a mixture of ether and hexane gave 6.5 g. (86%) of nearly white, highly hygroscopic plates, m.p.  $63-68^{\circ}$ , dissolving in water to give a strongly alkaline solution. Several recrystallizations from the same solvent gave an analytical sample, m.p.  $80-81^{\circ}$ .

Anal. Calcd. for  $C_8H_{16}N_2O\colon C,\ 61.50;\ H,\ 10.32;\ N,\ 17.94.$  Found: C,  $61.89,\ 61.61;\ H,\ 10.15,\ 9.99;\ N,\ 17.63,\ 17.60.$ 

Preparation of 3-N-piperidylpropionamide (V). A solution of 14.2 g. (0.20 mole) of acrylamide in 50 ml. of 1,2-dimethoxyethane was added dropwise to a stirred solution of 17.0 g. (0.20 mole) of piperidine in 50 ml. of the same solvent. After stirring at room temperature for 3 hr. the solution was refluxed for the same period of time. Evaporation of the solvent *in vacuo* gave a straw-colored solid which was recrystallized from a mixture of ether and hexane to give 22.0 g. (70.5%) of a nearly white hygroscopic solid, m.p. 77–78°. The analytical sample was prepared by several recrystallizations from ether containing a small amount of methanol and hexane, m.p. 80–81°. Its melting point was undepressed on admixture of the sample prepared by treat-

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ment of III with potassium carbonate and the infrared spectra of the two compounds were identical. Anal. Calcd. for  $C_8H_{16}N_2O$ : C, 61.50; H, 10.32; N, 17.94. Found: C, 61.51, 61.34; H, 10.00, 10.19; N, 17.62, 17.59.

Acknowledgment. The author expresses his appreciation to Mr. R. F. Cornuet for a very able technical assistance, to Drs. C. L. Parris and W.- H. Chang for stimulating discussions and suggestions, to Drs. H. L. Gerhart, S. W. Gloyer, and R. M. Christenson for continued interest and en-couragement, and to Professor C. D. Hurd for reading the manuscript.

Springdale, Pa.



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#### Reaction of Acrylamide and Pyridinium Chloride

#### ROSTYSLAW DOWBENKO

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Acrylamide and pyridinium chloride react to give N-(2-carbamylethyl)pyridinium chloride, II, whose structure was proved by hydrogenation of it to the piperidinium analog which was synthesized independently. The reaction was extended to several other heterocyclic base salts and  $\alpha$ , $\beta$ -unsaturated amides.

Some time ago it was disclosed in a patent<sup>1</sup> that aliphatic amides, formaldehyde (or N-hydroxymethylamides) and salts of the tertiary

heterocyclic bases react to form N-amidomethyl inium salts (I). More recently, Weaver and co-workers<sup>2</sup> investigated this reaction in more detail

(1) A. W. Baldwin and E. E. Walker, U. S. Patent 2,146,392 (February 7, 1939).

(2) J. W. Weaver, H. A. Schuyten, J. G. Frick, Jr., and J. D. Reid, J. Org. Chem., 16, 1111 (1951).

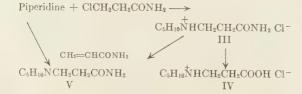
and, for stearamidomethylpyridinium chloride, demonstrated several of its transformations. In

$$RCONH_2 + CH_2O + H - N + \longrightarrow RCONHCH_2 - N + I$$

particular they studied reactions leading to *N*-alkoxymethylstearamides. In connection with other work done in these laboratories it was of interest to extend this reaction to acrylamide and other unsaturated amides in order to obtain compounds analogous to I. The reaction with acrylamide, however, took a different course and its examination forms the subject of this report.

When an equimolar mixture of acrylamide, trioxane, and pyridinium chloride was heated at 65° in pyridine solution, there was obtained a solid. m.p. 197°, which was unreactive toward methanol under Weaver's conditions<sup>2</sup> and could be recovered from the reaction mixture. Similarly, when alcohols were substituted for pyridine as solvent, or when formaldehyde was replaced by acetaldehyde, butyraldehyde, or benzaldehyde, still the same compound was obtained. In contrast, from the reaction of N-(hydroxymethyl)acrylamide and pyridinium chloride under conditions<sup>2</sup> known to give compound I, only the starting materials were recovered. Finally, omission of the aldehyde from the reaction still gave the same compound above. These results clearly indicated that aldehydes did not participate in the reaction of acrylamide and that, therefore, N-acrylamidomethylpyridinium chloride was not formed, but instead an adduct of acrylamide and pyridinium chloride was obtained. This was confirmed by analysis which revealed an empirical formula C<sub>8</sub>H<sub>11</sub>ClN<sub>2</sub>O and showed no unsaturation. The latter finding was supported also by the fact that the compound was unreactive toward cyclopentadiene and did not polymerize on heating in the presence of ammonium persulfate in aqueous or methanolic solution. This information, along with the fact that the compound was salt-like (soluble in water and methanol, insoluble in ether, acetone, and hydrocarbons), led to assignment of the structure N-(2-carbamylethyl)pyridinium chloride (II).

Structure II was proved unequivocally by catalytic hydrogenation to a crystalline piperidinium compound (III), identical with that obtained directly from 3-chloropropionamide and piperidine.



Moreover, III could be transformed into the same free base (V) that was obtained by the addition of piperidine to acrylamide. Hydrolysis of III with hydrochloric acid yielded IV.

Addition of salts of heterocyclic bases to  $\alpha,\beta$ unsaturated carbonyl compounds has been reported on several occasions. Thus Barnett *et al.*<sup>3</sup> described addition of pyridine salts to benzoquinone, and Goerdeler<sup>4</sup> described addition of pyridine to maleic and acrylic acids from which the pyridinium betaines were obtained. The reaction of  $\beta$ -benzoylacrylic acid with pyridine<sup>5</sup> apparently is also of the same type and may be considered in effect a reaction of a pyridine salt.<sup>6</sup> Similarly, addition of pyridine to unsaturated compounds in the presence of halogens is also known and may be exemplified by the reaction of pyridine and 1,2-diethoxyethylene in the presence of bromine<sup>7</sup> in which compound VI is

$$C_{2}H_{5}O-CH=CH-OC_{2}H_{5} + \bigvee_{N} + Br_{2} \rightarrow$$

$$C_{2}H_{5}O-CH-CH-OC_{2}H_{5}$$

$$C_{3}H_{5}O-CH-CH-OC_{2}H_{5}$$

$$2 Br^{-}$$
VI

obtained. A recent example of interest is that reported by Heininger,<sup>8</sup> who found that cyanoethylation of pyrrolidinium chloride with acrylonitrile gives N-(2-cyanoethyl)pyrrolidinium chloride. The present case, however, apparently constitutes the first example of addition of pyridinium chloride to  $\alpha,\beta$ -unsaturated amides.

In order to test the generality of this unusually facile addition of pyridinium chloride to acrylamide, several other compounds were used in the conditions under which the former gave the adduct II. The results are summarized in Table I and are

J. Chem. Soc., 125, 1035 (1924).
(4) J. Goerdeler, Methoden d. org. Chemie (Houben-Weyl),
E. Müller, ed., Georg Thieme Verlag, Stuttgart, 1958, Vol.
XI/2, p. 612. For similar reactions cf. also O. Lutz, Ber.,
43, 2636 (1910); O. Lutz, J. Russ. Phys. Chem. Soc., 47,
1549 (1915); P. Pfeiffer and A. Langenberg, Ber., 43,
2926 (1910); P. Pfeiffer, Ber., 47, 1580 (1914); O. Lutz, R.
Klein, and A. Jirgenson, Ann., 505, 307 (1933); O. Lutz
and A. Krauklis, Ber., 69, 419 (1936); G. LaParola, Gazz.
Chim. Ital., 67, 645 (1937); F. Bergmann, J. Am. Chem.
Soc., 60, 2811 (1938); Y. Ogata, K. Tsunemitsu, and R.
Oda, Bull. Inst. Phys. Chem. Research (Tokyo) Chem. Ed.,
23, 281 (1944); R. Adams and I. J. Pachter, J. Am. Chem.
Soc., 77, 117 (1955).

(5) J. Bougault and P. Chabrier, Compt. rend., 237, 1420 (1953).

(6) Cf. also N. H. Cromwell, P. L. Creger, and K. E. Cook, J. Am. Chem. Soc., 78, 4412 (1956) for a more recent discussion of this work.

(7) H. Baganz, Chem. Ber., 87, 1373 (1954); cf. also ref. 3.
(8) S. A. Heininger, J. Org. Chem., 22, 704 (1957).

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<sup>(3)</sup> E. de B. Barnett, J. W. Cook, and W. C. Peck, J. Chem. Soc., 125, 1035 (1924).

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|------|---|----|----|---|
|------|---|----|----|---|

TABLE I

16 88 23 2 11110002064 14. 14. 81 86 59 61 5 W'AS 191911111111 8 8 1-1-Found chloride 77 90 69 II 0000 general procedure (Experimental). <sup>b</sup> Before recrystallization from a mixture of methanol and acetone. <sup>c</sup> 2, 6-Dimethylpyridinium 69 68 68 77 51. 60 61 6113.96 17 969615.01 84 84 Z 11. 9. 13. 13. Ξ 98 .37 67 67 19.006798 Reaction of  $\alpha, \beta$ -Unsaturated Amides with Heterocyclic Salts<sup>a</sup> 5 17. 14. Ŧ 2 5 1-Calcd. 5.945.545.545.27.53 53 53 Ξ 9 9 67.01 86 86 51.48 80 86 80 0 60. 60. 23 53 C12H1ACIN2O ChHICUN20  $\mathrm{C}_{12}\mathrm{H}_{13}\mathrm{Cl}\,\mathrm{N}_2\mathrm{O}$ C<sub>9</sub>H<sub>18</sub>CIN<sub>2</sub>O C"H<sub>13</sub>CIN<sub>2</sub>O C<sub>9</sub>H<sub>13</sub>ClN<sub>2</sub>O C<sub>8</sub>H<sub>11</sub>CIN<sub>2</sub>O Formula 5 [71.5-172. 210.5-212 0 M.P., 195 - 19783-184 99-200234 205 of Product<sup>b</sup> ', Yield 12 \* 33 66 93 1 53 Methacrylamide Crotonamide Acrylamide Acrylamide Acrylamide Acrylamide Acrylamide Amide Acrylamide 2,6-Dimethylpyridine a According to the 2-Methylpyridine Phenanthridine Base Isoquinoline Quinoline Pyridine Pvridine Pyridine

REACTION OF ACRYLAMIDE AND PYRIDINIUM CHLORIDE

for the most part self-explanatory. It should be noted, however, that 2,6-dimethylpyridinium chloride was unreactive, and methacrylamide and crotonamide gave lower yields of the products. Although nonreaction of the former compound is probably due to steric hindrance in the 2,6dimethylpyridinium ion, the lower yields from the latter are probably a real reflection of decreased reactivity of these compounds, although no attempts to obtain the best yields were made. Therefore, the facile addition of salts of heteroaromatic amines to  $\alpha,\beta$ -unsaturated amides is quite general.

Several things may be said relating to the mechanism of this reaction, although no efforts were made to examine it in great detail. Two main paths appear to exist by which the reaction may proceed. The first (1) requires addition of hydrogen

pyridinium chloride 
$$\xrightarrow{\text{CH}_2 = \text{CH} \text{ONH}_2}$$
  
 $\xrightarrow{\text{ClCH}_2\text{CH}_2\text{CONH}_2}$   $\xrightarrow{\text{Pyridine}}$  II (1)

chloride to acrylamide and subsequent alkylation of pyridine with the resulting 3-chloropropionamide. That the chloroamide is not an intermediate in the reaction, however, was demonstrated when 3-chloropropionamide and pyridine under the conditions of acrylamide reaction gave a very low yield of II.9 An alternative mode of reaction is that represented by (2).<sup>10</sup> As required by this scheme, the reaction appears to be acid-catalyzed, and if this were valid the mechanism (2) is to be preferred. A still more attractive mechanism is the concerted one (3) involving the formation of a quasi six-membered ring.

CH2=CHCONH2 pyridinium chloride -

Pyridine + +CH<sub>2</sub>-CH=C-NH<sub>2</sub> + Cl<sup>-</sup> 
$$\longrightarrow$$
  
Cl<sup>-</sup> + C<sub>8</sub>H<sub>6</sub><sup>+</sup>NCH<sub>2</sub>CH=C(OH)NH<sub>2</sub>  $\rightleftharpoons$  II (2)

ОЦ

$$\begin{array}{c} CH_{2} \\ CH \\ CH \\ H_{2}N \end{array} \xrightarrow{(N+)} H CI^{\ominus} \xrightarrow{(CH)} H_{2}N \xrightarrow{(CH)} H \xrightarrow{(CH)} H$$

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Anal. Calcd. for  $C_8H_{17}ClN_2O$ : C, 49.86; H, 8.89; Cl, 18.40; N, 14.54. Found: C, 49.75; H, 9.14; Cl, 18.42; N, 14.60.

Hydrolysis of N-(2-carbamylethyl)piperidinium chloride (III). A mixture of 10.0 g. (0.052 mole) of III and 50 ml. of concd. hydrochloric acid was refluxed for 6 hr. Hydrochloric acid was removed by evaporating *in vacuo*, adding water and repeating the process several times. The residue was dissolved in a minimum amount of hot water, filtered, and allowed to crystallize. Filtration and recrystallization of the solid from aqueous acetone gave 7.0 g. (70%) of white shiny platelets of the acid IV, mp. 210–212°. The analytical sample, prepared by several recrystallizations from the same solvent melted at 212–213°.

Anal. Caled. for  $C_8H_{16}ClNO_2$ : C, 49.61; H, 8.33; Cl, 18.31; N, 7.23. Found: C, 50.03, 49.84; H, 8.40, 8.36; Cl, 17.05, 17.26; N, 7.04, 6.88.

Preparation of N-(2-carbamylethyl)piperidinium chloride (III). A solution of 17.0 g. (0.20 mole) of piperidine and 21.6 g. (0.20 mole) of 3-chloropropionamide<sup>7</sup> in 100 ml, of methanol was refluxed for 4 hr., then filtered hot and evaporated to one-half of its original volume. Acetone was added and the mixture was allowed to crystallize. Filtration gave 30.5 g. (79%) of a nearly white solid, m.p. 193-196°. The analytical sample was prepared by several recrystallizations from a mixture of methanol and acetone, m.p. 197-198°. Its melting point was not depressed by admixture of the sample prepared by the hydrogenation of N-(2carbamylethyl)pyridinium chloride. Infrared spectra of the two compounds were indistinguishable.

Anal. Calcd. for  $\rm C_{3}H_{17}ClN_{2}O$ : C, 49.86; H, 8.89; Cl, 18.40; N, 14.54. Found: C, 50.32, 50.35; H, 8.85, 8.87; Cl, 18.34, 18.37; N, 14.85, 14.65.

Reaction of N-(2-carbamylethyl)piperidinium chloride with potassium carbonate. A solution of 9.35 g. (0.0485 mole) of the piperidinium compound III and 6.9 g. (0.05 mole) of potassium carbonate in a mixture of 200 ml. of methanol and 30 ml. of water was allowed to stand overnight. The solvent was evaporated *in vacuo* and the residue was dried by azeotropic distillation with benzene. It was then dissolved in ethyl acetate, filtered from inorganic salts, and evaporated to obtain a straw-colored oil which crystallized on standing. Recrystallization from a mixture of ether and hexane gave 6.5 g. (86%) of nearly white, highly hygroscopic plates, m.p. 63–68°, dissolving in water to give a strongly alkaline solution. Several recrystallizations from the same solvent gave an analytical sample, m.p. 80–81°.

Anal. Calcd. for  $C_8H_{16}N_2O$ : C, 61.50; H, 10.32; N, 17.94. Found: C, 61.89, 61.61; H, 10.15, 9.99; N, 17.63, 17.60.

Preparation of 3-N-piperidylpropionamide (V). A solution of 14.2 g. (0.20 mole) of acrylamide in 50 ml. of 1,2-dimethoxyethane was added dropwise to a stirred solution of 17.0 g. (0.20 mole) of piperidine in 50 ml. of the same solvent. After stirring at room temperature for 3 hr. the solution was refluxed for the same period of time. Evaporation of the solvent *in vacuo* gave a straw-colored solid which was recrystallized from a mixture of ether and hexane to give 22.0 g. (70.5%) of a nearly white hygroscopic solid, m.p. 77-78°. The analytical sample was prepared by several recrystallizations from ether containing a small amount of methanol and hexane, m.p.  $80\text{--}81^\circ$ . Its melting point was undepressed on admixture of the sample prepared by treat-

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**JULY 1960** 

ment of III with potassium carbonate and the infrared

spectra of the two compounds were identical. Anal. Caled. for  $C_8H_{16}N_2O$ : C, 61.50; H, 10.32; N, 17.94. Found: C, 61.51, 61.34; H, 10.00, 10.19; N, 17.62, 17.59.

Acknowledgment. The author expresses his appreciation to Mr. R. F. Cornuet for a very able technical assistance, to Drs. C. L. Parris and W.-

H. Chang for stimulating discussions and suggestions, to Drs. H. L. Gerhart, S. W. Gloyer, and R. M. Christenson for continued interest and encouragement, and to Professor C. D. Hurd for reading the manuscript.

Springdale, Pa.



Dr. Alfred R. Bader 2961 North Shepard Avenue Milwaukee, Wisconsin 53211

September 9, 1992

Dr. Zoltan Hajos Pauler u 2, Apt. 21 1013 Budapest I. Hungary

Dear Dr. Hajos:

Thank you so much for your detailed and interesting letter of May 26.

I left Milwaukee for Europe on May 8 and returned only quite recently. Hence, please do not mind my delay in thanking you only now.

Of course I know Dr. Al Runquist, who was Manager of Technical Services in 1987 and is now Manager of Purchasing, well, indeed. He is an able chemist, Ph.D. from Northwestern University and also a really kind and caring person. When he wrote to you in 1987 that Aldrich cannot include all references and tries to concentrate on papers dealing with uses, rather than with preparations, he meant that sincerely, and I am certain he was not trying to be hurtful.

Your late aunt, Mrs. Barbara Groth, we very well known in Milwaukee musical circles, and I sorry that I did not know that she was your aunt as we could have had fun talking about you and Hungary.

Life goes on, and I m exceedingly busy, with lots of lecture tours and working botyh with chemistry and paintings.

Best personal regards,



Soltan G. Majos Pauler u 2, Apt. 21 1013-Eudarest I. Hungary

May 26, 1992

Alfred Bader, Ph.D. 940 West Saint Paul Avenue Milwaukee, WI 53233 USA

Dear Doctor Bader:

As a long-time admirer of your achievements I was saddened to read on p.39 of C&EN April 6, 1992 that " Alfred Bader Says Sigma-Aldrich Is Forcing Him OUT After 41 Years ".

The article quotes you as saying " I felt I needed to clear my name, to let my friends and colleagues know that I have done nothing wrong."

A similar feeling urges me to write to you, and to share with you some thoughts.

On June 3, 1987 I wrote you a letter, which was answered by Alfonse W. Runquist, Ph.D. in your absence.

He refused to quote our work describing the discovery of the optically active bicyclic ketol, Aldrich 29,793-3. Thus, I received similar treatment from the same people five years ago, which you have been experiencing more recently.

In sharp contrast, a paper from Hoffman-La Roche, Inc., Nutley, NJ described " Compactin From Hajos (-)-enedione " in Tetrahedron Letters 1990, 31, 5599. The Roche paper appeared exactly at the time of my resignation and early retirement, forty years after the receipt of my doctorate.

We have yet another thing in common: while you were instrumental in the scientific/industrial development of Milwaukee, Wisconsin, my relatives contributed to the cultural welfare of the same city.

My late aunt Mrs. Barbara Gabor Groth ( nee Barbara Hajos ) and her daughter the late <sup>M</sup>rs. Robert L. Christiansen were both responsible over decades for arranging and/or participating in a great many musical events in your city.

With the hope that this letter shall find its destination, I hope that it will find you in good health and in a happier mood.

Sincerely,

Jottan Hayo



#### HARVARD UNIVERSITY

PROFESSOR DAVID A. EVANS

DEPARTMENT OF CHEMISTRY • 12 Oxford Street • Cambridge • MA 02138 • (617) 495-2948

November 21, 1988

Dr. Alfred Bader, President Aldrich Chemical Company P.O. Box 355 Milwaukee, WI 53201

in the set of the

#### Dear Alfred:

After having reflected at some length on your recent visit with me, I have decided to write to you to express my reaction to some of your comments.

I should preface this commentary with the reminder that you and I, and my students, have worked together in what I felt was a cordial relationship for quite a number of years. I have given you a number of suggestions for potential products and have provided you with unpublished experimental procedures for chemicals which you have marketed. I have also provided an article to you for your journal, Aldrichimica Acta. I also do a substantial annual business with your company.

Having said this, I was not prepared for your diatribe in my office on November 11th on the poor judgement exercised by this department in not promoting Gilbert Stork which was thrown in with the flaunting of other perceived departmental indiscretions. I should point out to you that I was nine years old at the time of the Stork tenure decision, and not having yet been appointed to the Harvard professorial staff, refuse to take responsibility for this departmental action. Don't you think that it is time to bury this issue?

With regard to the broader issue of promotion and tenure, I have always been and will continue to be an strong advocate of "growing your own" faculty if at all possible. At the present time my junior faculty colleagues are being heavily supported in their research efforts by the department, and we, the senior faculty, have worked very hard to successfully promote them for unrestricted research support. At the same time, I am also an advocate of a course of action which results in the accumulation of the best possible faculty colleagues. Surely you must also embrace similar objectives for the personnel in your own organization.

I suspect that our Chemistry Department is probably one of your largest university accounts as a consequence of the research activities of the Organic Group. It seems to me that you are really shooting yourself in the foot when you come around here and complain to me, George Whitesides, and Stuart Schreiber, about events long past. All three of us are recent arrivals, we share very similar views on the "care and feeding of the young", and we are all working very hard on behalf of the department.

I would hope that we might continue to work together as friends.

Sincerely,

) and Fran

David A. Evans Professor of Chemistry



December 29, 1988

Frofessor David A. Evans Harvard University

Dear David,

"y secretary has forwarded your singular letter of November 21 to England where Isabel and I are spending Christmas after interesting visits to many British universities.

When I read your letter I was't sure whether to be hop y or sadhappy because it shows that our hopes and wisnes for the de arthent are the same; sad because your writing about by "distribe" makes it clear that I really hurt your feelings. A man of your stature wouldn't use such landwage unless deeply hurt. The dictionary defines distribe as "denunciptory hermague". Clearly you and I have this in common: we are purt by accusations renceived to be unjust. Of course I don't blame you for Cilbert Stork not getting tenure.some

38 years ago, nor for the fact that not a single junior ffculty member in organic chemistry since then has gotten tenure. You know better than I how appy brilliant chemists have left Harvard to succeed elsewhere. I am just delighted to know that you and Stuart Schreiber and George whitesides are wor ing together to change that. George Whitesides may have told you that we have a bet that this will be changed within five years, and I hope that I will lose. I wasn't really complaining "about events long past": no one has been promoted yet.

For many years I was on the board of Overseers Committee on chemistry and year after year the Committee recommended that this policy be changed-all to no avail. Finally I resigned in disgust.

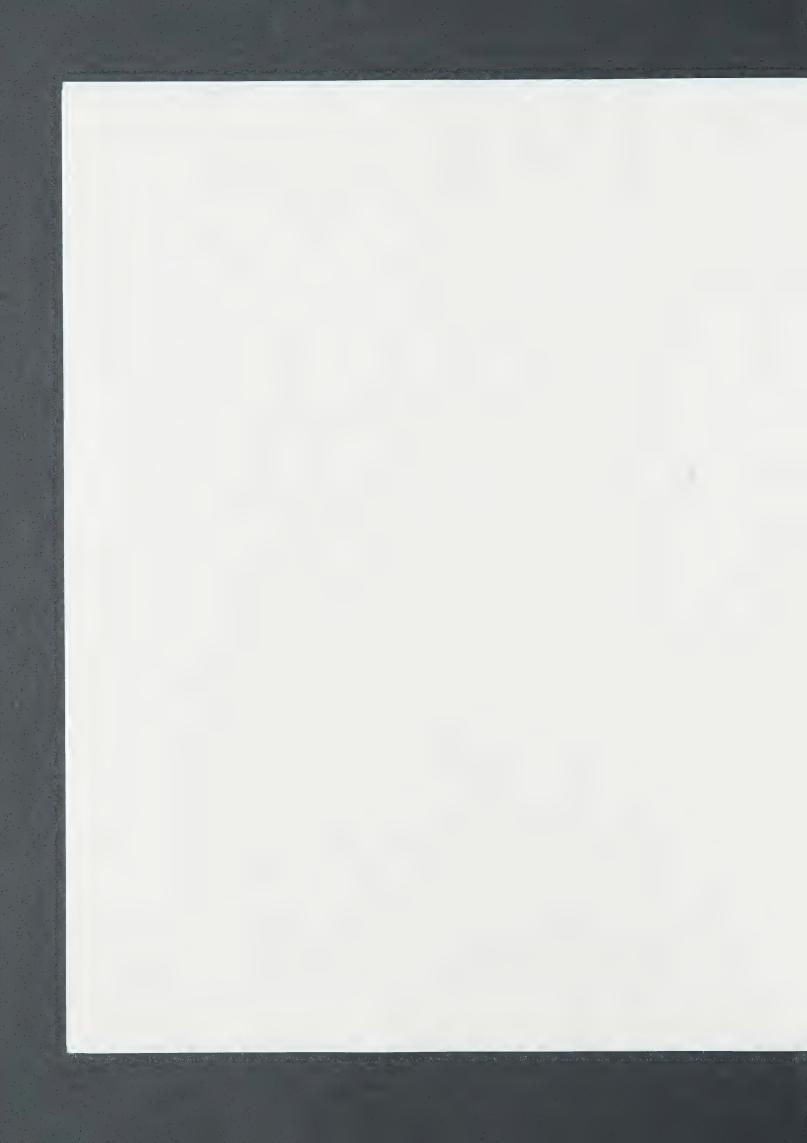
were I an outsider, you might be more justified in your displeasure. But I am a graduate of Harvard and for the last 40 years-since you were seven-I have tried in all sorts of different ways to help the department. In the 1940's, ours was the best chemistry department in the country; since the fifties until recently it was not, and of course I am happy to know that you and many of your colleagues are trying to change this.

Igain, you must know better than I why it was not. But surely the nonpromotion of junior faculty was one important reason. You coming from Onl Tech and Stuart from Yale know what it means to have a great team, each faculty marbes beloing the others. Harvard and (and still has) some of the worl?" most brilling.

. . . .

- - it with the

- your are



chemists, but who was helping others in the sixties and seventies the way Gilbert Stork or Jack Roberts or Sam Danishefsky are? Clearly you are changing this and I am glad.

You are running into an open door when you remind se of the many ways you and others in the department have helped Aldrich; I could add many other examples, set I don't think that it has been a one-way street. We really have tried to help chesists, and other companies have followed our lead. Here would research be, if chesists still had to rely on Kodak chesicals? I enclose a chapter from my biography which hight amuse you: note what in important part warvard ploted in the founding of Aldrich and since them you had Raw and Sj and many others at Harving nave suggested **Several** new compounds. I don't think It's my nature to forget my friends.

Please do share this letter with Stuart Schreiber and George chitesides. There have been intermittent mail strikes in Britain and I don't know how long this letter will take to reach you. Hopefully it will arrive in time for Isabel's and my best ishes for a happy new year.

Sincerely,

Jup. a Baar



#### HARVARD UNIVERSITY

PROFESSOR DAVID A. EVANS

DEPARTMENT OF CHEMISTRY • 12 Oxford Street • Cambridge • MA 02138 • (617) 495-2948

March 23, 1988

Dr. Alfred Bader, President Aldrich Chemical Company P.O. Box 355 Milwaukee, WI 53201

Dear Alfred:

I recently attended the Roberts Symposium at Caltech honoring Jack's 70th birthday. While there, Jack mentioned that you had talked with him, with some concern, about the exchange of letters which recently took place between the two of us.

The purpose of this letter is to formally acknowledge your response and to congratulate you for showing concern for the welfare of the department. I look forward to working together with you in actually helping in a constructive manner with some of the serious problems which face all of us in academia in general and at Harvard in particular in the upcoming years.

In our exchange of views, both of us have spoken directly and from the heart. I have heard your position on several occasions and now you know where I stand as well. As far as I am concerned the issue is closed. As I said in my last letter to you:

I would hope that we might continue to work together as friends.

Sincerely,

chile -

David A. Evans Professor of Chemistry



#### **Hood College**

Frederick, Maryland 21701-9988 (301) 663-3131 FAX (301) 694-7653

May 20, 1992

Dr. Alfred Bader Aldrich Chemical Company 1001 West Saint Paul Avenue Milwaukee, Wisconsin 53233

Dear Dr. Bader,

Several of us science faculty here at Hood share your love of chemistry as well as art, and we have enjoyed your "Aldrichimica Acta" covers over the years. By sharing these covers with our colleagues in the art department, they too have become enthusiastic about the possibility of having you visit our campus. If you have business in the Washington area in the next year or so, perhaps you might be able to arrange a side trip to Hood. Frederick is less than an hour away from Washington.

A presentation by you would fit in beautifully with our goal of getting students to see the importance and relevance of chemistry to essentially all aspects of life. As a liberal arts college, we try to use an interdisciplinary approach as much as possible in our courses. Consequently, we often have students who combine their academic interests with double majors such as in chemistry and art. We hope that your schedule might allow you to accept our invitation. Please call or write if I can answer any questions. I look forward to hearing from you.

Sincerely yours, Sharrow H Brith

Sharron W. Smith, Professor of Chemistry



degree in biochemistry from California State University Laura Olsen, B.S., department assistant and chemical safety officer for the College, earned her bachelor's cluster compounds. in the area of laser photoionization of molecular and ion University. A physical chemist, her research interests are earned her doctorate from The Pennsylvania State Susan Morgan, Ph.D., assistant professor of chemistry, chemistry courses. summer developing new experiments for his organic continues to be his special interest, and his research has Chemistry. He earned his doctorate in organic chemistry George Kleinspehn, Ph.D., is the Whitaker Professor of area of interest is using computers to numerically solve Allen Flora, Ph.D., assistant professor of physics, earned compounds. atom-like particles react with various organic chemical measure magnetic and decay properties and study how Columbia to work with colleagues. Using a proton beam and physics faculty teach both the classes and the labs. students reach their academic goals." Hood's chemistry Hayward. Environmental chemistry and hazardous waste nitrogen compounds. He spends a portion of each ranged from pyrroles and porphyrins to acyclic organic from The Johns Hopkins University. Organic chemistry physics problems, involving modeling equations to his doctorate from the University of Virginia. One current accelerator to produce sub-atomic particles, they travels each summer to the University of British chemical kinetics (sub-atomic particle chemistry). He John Stadlbauer, Ph.D., assistant professor of chemistry Hood's Mortar Board Excellence in Teaching Award. engaged in research, our primary effort is to help explains Dr. Stadlbauer. "Although some of us are provide solutions for simple quantum mechanics involved in a research project studying muonium and chair of the department, earned his doctorate from member has been selected by students to receive problems. New Mexico State University. An analytical chemist, he is "The focus of this department is on teaching, University of Vermont Medical School Twice in recent years, a chemistry faculty Old Dominion University The American University, chemistry program Faculty

> she did postdoctoral research at the National Institutes of Sharron Smith, Ph.D., professor of chemistry, holds a a Beneficial-Hodson Faculty Fellow doing molecular doctorate from the University of Kentucky. A biochemist, Facility. biology research at the Frederick Cancer Research Health, and recently completed a semester sabbatical as

Hood actively subscribes to a policy of equal educational and employment opportunity.

### Hood I College

# Bioche

Pre-veterinary studies **Pre-medical studies Pre-dental studies** 

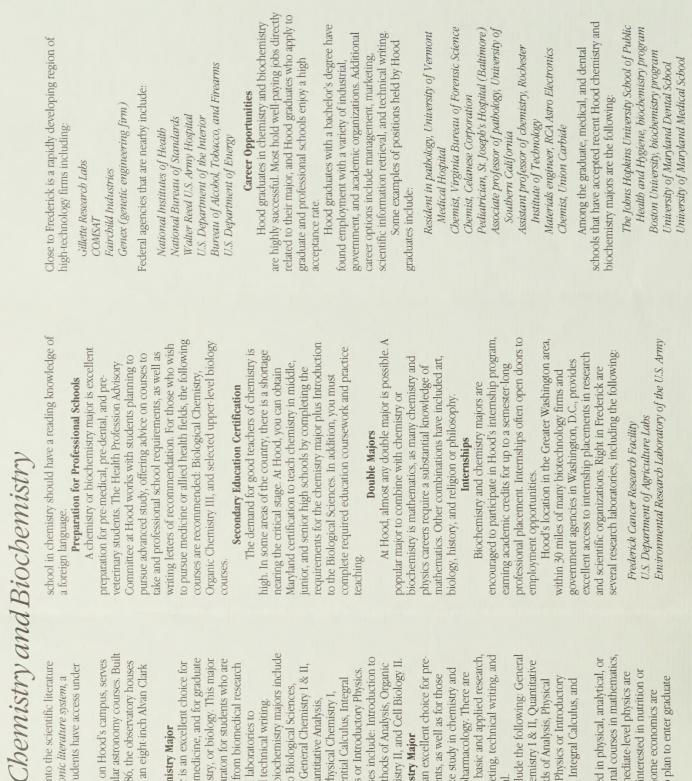


management are topics of current research.

Albert Einstein, 1879-1955

nothing more than a refinement of everyday thinking."

"The whole of science is



Hood College

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Up-to-date research into the scientific literature

The Williams Observatory, on Hood's campus, serves several telescopes, including an eight-inch Alvan Clark

scientific fields, consider a major in chemistry

challenging academic program that will

in a rigorous and

vou are interested

prepare you for medical school, dental school. or graduate study in a range of 'Historically there has been a social barrier that

or biochemistry.

says Dr. John Stadlbauer, chair of the Department of

says women don't belong in the physical sciences, Chemistry, Physics, and Astronomy. "At Hood, we

Courses required of biochemistry majors include students planning careers in medicine, and for graduate study in chemistry, biochemistry, or biology. This major also provides excellent preparaton for students who are A biochemistry major is an excellent choice for interested in careers ranging from biomedical research management, marketing, and technical writing. in government and industrial laboratories to

Microbiology, Cell Biology I, General Chemistry I & II, Calculus, and General Physics or Introductory Physics. Seminar in Chemistry, Differential Calculus, Integral the following: Introduction to Biological Sciences, Biological Chemistry I & II, Physical Chemistry I, Organic Chemistry I & II, Quantitative Analysis,

biochemistry consists of

some work in physics

a combination of chemistry and biology courses, again

and mathematics. The major in core of chemistry courses with

and biochemistry available in Frederick and the rest of

the Greater Washington metropolitan area.

Also, you can earn certi

numerous internship opportunities in both chemistry

with some physics and mathematics. There are

biochemistry with other academic disciplines, provide

educaton. Double majors, combining chemistry or

ticaton in secondary

additional options for individualizing your academic

program. The department also offers courses in astronomy and physics, although majors are not

and biochemistry. The major in chemistry consists of a

The department offers two majors; chemistry

any discipline. We are pleased with the success of our

chemistry and biochemistry majors."

develop the self confidence they need to succeed in

necessary to encourage our students to learn and

provide the academic leadership and direction

Chemistry III, Physical Chemistry II, and Cell Biology II. Computing, Instrumental Methods of Analysis, Organic The Chemistry Major

who are interested in graduate study in chemistry and such fields as toxicology or pharmacology. There are medical and pre-dental students, as well as for those scientific information retrieval.

laboratory instruments and equipment, including the

following:

nuclear magnetic resonance spectrometer

infrared visible and ultraviolet

College labs are equipped with specialized

Special Equipment and Resources

available in these areas.

Chemistry I & II, Organic Chemistry I & II, Quantitative Analysis, Instrumental Methods of Analysis, Physical Physics, Differential Calculus, Integral Calculus, and Computer Survival Skills.

theoretical chemistry, additional courses in mathematics, For students interested in physical, analytical, or computer science, and intermediate-level physics are recommended. For students interested in nutrition or recommended. Students who plan to enter graduate textiles, selected courses in home economics are

applications, computers offer simulations of chemistry

Used as a tool in scientific research

high-performance liquid chromatograph

refrigerated ultracentrifuge

bomb calorimeter

gas-liquid cbromatograph

spectrophotometers

laboratory experiments and computer "games" that

teach theoretical chemistry

national database to which students have access under is possible through an *electronic literature system*, a faculty supervision.

as the center of Hood's popular astronomy courses. Built in 1924, and renovated in 1986, the observatory houses telescope.

## The Biochemistry Major

Recommended courses include: Introduction to

opportunities for chemists in basic and applied research teaching, management, marketing, technical writing, and A chemistry major is an excellent choice for pre-

Required courses include the following: General Chemistry, Seminar, General Physics or Introductory