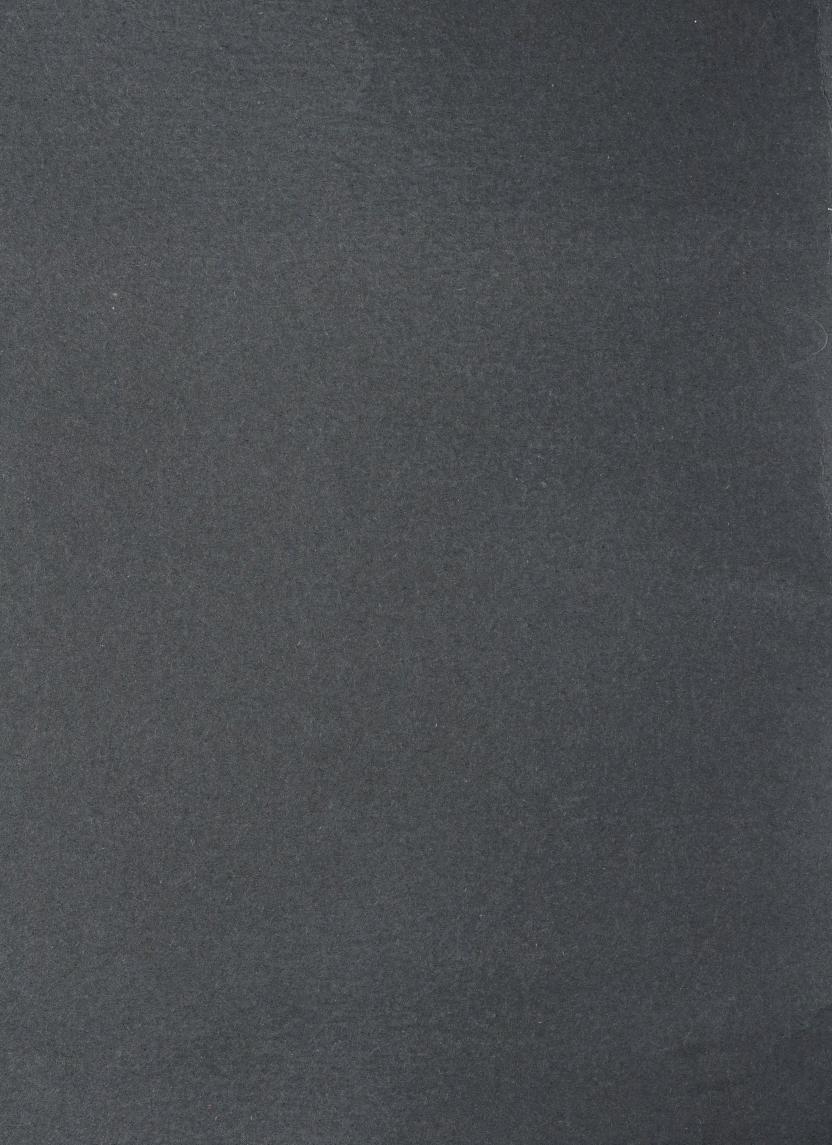
Alfred Bader fonds

Correspondence

Pinkus. 1995-97 / Prof. A.G.

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(C)		Contracts of Contracts and Annual Contracts of Contracts	2,942,9	MEN'S UNIVERSITY ARCHIVES





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

A Chemist Helping Chemists

January 13, 1997

Professor A.G. Pinkus Department of Chemistry Baylor University P.O. Box 97348 Waco, TX 76798-7348

Dear Al:

I am sorry that a long trip to England has delayed my thanking you for your delightful letter of December 10th.

Surprisingly, there wasn't a single letter to *Chemistry in Britain* about my article on Kekulé. Incidently, the only mistake that I have found so far in the article, is a typographical error which I didn't catch: the date of Woodward's Cope lecture was 1972, not 1973.

I do believe that the Beckman Center will publish the manuscript before long.

I had never heard of the Dutch actor, Hofstra, but he must be quite a guy to be able to represent three such diverse painters.

It is hard to believe that anybody in their right mind would offer a painting that might possibly be by Van Dyck, for \$25. Probably that work is sold by now, but if it isn't I would urge you to purchase it and then either send me the work itself or a pretty good photograph and I will tell you quickly what I think. Chances are that the frame is worth \$25. Needless to say that if it is a painting of any quality, I would be happy to sell it for you. But first we have to find out what it is.

With all good wishes, I remain,

Yours sincerely,





December 10, 1996

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

Dear Alfred:

Thanks for the copy of your article on the Kekulé/Loschmidt/Couper triangle. It sounds good. It will be the definitive article for this relationship. Any response from the usual critics? Do you think that the Woodward manuscript will ever be published?

Your talks on Rembrandt are being followed up by some presentations by the Dutch actor, Klaas Hofstra. (clippings enclosed). Are you familiar with his work?

The other day while looking through a new antique shop, I noticed a painting which was purported to be by Van Dyke. It is a portrait of a gentleman. It is about 10 x 10" and looked old enough and is in a wooden frame. With your expertise, I'm sure you could tell in an instance whether or not it is authentic but I could be easily fooled. The price on it was only \$25 which seems like a good buy if it is authentic. Please advise what to look for. Since listening to your talks on Rembrandt, I now look at paintings when presented the opportunity.

Sincerely,

A. G. Pinkus



3 Waco shows Dutch actor in

area today through Thursday. form three different plays in the Waco Dutch actor Klaas Hoffstra will per-

brandt, a Portrait" will be at 8 tonight at ty. Admission is free. the Jones Theatre in Hooper-Schaefer Fine Arts Building at Baylor Universi-The first performance of "Rem-

nity College. To ask questions, call ing Arts Center at McLennan Commu-Hoffstra, will be performed at 1:15 p.m. Wednesday at the Wilbur Ball Perform-752-4371. "Vincent," a solo show for children by

ask questions, call 752-4371 or 299-8283. Thursday in the Wilbur Ball Performtrec," will be performed at 7:30 p.m. ing Arts Center. Admission is free. To Hoffstra's final show, "Toulouse-Lau-

a grant from the Waco Foundation. Center. All performances are funded by day, there will be a reception at the Art Following the performance on Thurs-



The Baylor Lariat

Page 5

about unique life of famous painter Dutch actor performs one-man show

By Blake Riordan

Dutch actor Klaas Hofstra. A childhood dream of being

p.m. tonight in the Hoopershow, Rembrandt, a Portrait, at 8 Schaefer Fine Arts Center. Hofstra is performing his solo

many of the great painters in his-Hofstra, 52, has been touring the performing his solo shows about United States for the last 10 years Originally from Amsterdam,

> enrich my life mances tend to

each time." more and more self. The perfor-

hears.

his two passions, acting and wanted to find a way to pursue After high school, Hofstra

shows. It's like the perfect real-Hofstra said. "It just so haptraveling. other thing I loved, my solo pened that I was able to do the travel to the United States," "I always wanted a reason to

ization of my dreams." Hofstra said his solo shows

enjoy themselves.

allow him to actually become the painters that the performances are about.

the artists and their paintings in completely 'My shows allow me to see

understand the also learn to different light," the artist himpaintings better he said. "I can becoming 66 There is a real the audience sees and power in knowing that I am the only thing

Klaas Hofstra, Dutch actor

combination of entertainment and education. Hofstra said his shows are a mance. ground during Hofstra's perfor-

the show, they can understand it me as the character that I am in "I think if people will view Hofstra said. "I felt that I could ing life."

Hofstra plays the role of show many aspects of his amazbring Rembrandt to life again,

power

they can learn something and actor. If the audience can do that, what it's about, not me as the more clearly," he said. "I want people to look at the show and

the occurrences following his 17th century painter's life and Portrait, is a description and commentary about the famous Hofstra's show, Rembrandt, a death.

telling about his life. Slides the age of 63 Rembrandt at portrays Hofstra

self portraits will be shown Rembrandt's in the back-

"With this show, I wanted to

give the audience an insight to what the famous painter felt of slides and props he is able to about his life. Hofstra's slides are Rembrandt, and through the use

audience sees and hears."

thing

free to the public.

organic, as scenery.

mances is part tunity to do of Hofstra's solo perforpassion The oppor-

about being alone on the stage," he stage," he said. "I love acting. the freedom of have dreamed I was young "Ever since

I am the only the love of his wife do whatever Dutch actor Klaas Hofstra will perform a solo being able to I want. There show, Rembrandt, a Portrait, at knowing that telling about his life, myths surrounding him and real the Hooper-Schaefer Fine Arts formance will portray Rembrar ndt at the age of 63 Center. The per-8 p.m. tonight in

a Waco Foundation grant and is The performance is funded by solo shows 1 Community Lautrec this week at McLennan Hofstra will also perform his Vincent and Toulouse-



Courtesy photo



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

A Chemist Helping Chemists

January 22, 1997

Professor A.G. Pinkus Department of Chemistry Baylor University P.O. Box 97348 Waco, TX 76798-7348

Dear Al:

In response to your fax, I am glad that you didn't buy that lacquered photograph. Generally sellers of works of art know more than buyers, particularly when the sellers are dealers.

Your work on the cycloaddition sounds fascinating and I look forward to seeing the paper.

With all good wishes, I remain,

Yours sincerely,

AB/nik



Facsimile

Turket 1 1 1445 (17)

Date: Jan. 21, 1997

and the things of

From. A. G. Pinkus

Dept of Chemistry

Baylor University

Waco, TX 76798

(817) 755-3311

FAX: (817) 755-2403

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fo: Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee. WI 53211 Tel: (414) 277-0730 FAX: (414) 277-0709

No. of pp.: 2 including cover sheet

Dear Alfred.

On receiving your letter, I took a second more careful look at the "painting". The fact that it was still there probably indicates that it is not worth much. I made a mistake in saying that it was by Van Dyck; it is a portrait of Van Dyck. The back of the picture is wooden and the frame has cracks in it. Writing on the back (possibly in ink) is faded and hard to read. Some of the words appear to be "Pietr Smuyers...Vinchun". I don't know if these probably misspelled words (because of illegibility) have any meaning to you. However, the picture itself appears to be a lacquered-over photograph of a painting of Van Dyck rather than a painting. So that would date the item to the use of photography. So I conclude that it is probably not worth very much. At least you can see that since listening to your talks on Rembrandt, I am now looking at old paintings whereas before I paid little attention to them unless they were in museums or art galleries.

Alder reaction on which we did some research. Most texts cite the discovery by Diels and Alder as their 1928 published paper in Justus Liebigs Annalen der Chemie. We have found a paper published in 1888 which reports a [2 + 4] cycloaddition. Of course, Diels and Alder received the Nobel award for working out the generality of the reaction. The literature concerning this earlier discovery is quite involved so we are just writing up the essential parts of our research which deals with a novel mechanism for the reaction in order not to detract from the



Jen 21-1997 (1992) Exp. (1994)

report of our findings. We will defer the writing up of the more complicated historical aspects for a later historically oriented article. I will send you a copy of the latter when it is ready

With best wishes, sincerely,

A. G. Pintas





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

A Chemist Helping Chemists

May 8, 1996

Professor A.G. Pinkus Department of Chemistry Baylor University P.O. Box 97348 Waco, TX 76798-7348

Dear Al:

Enclosed is a manuscript that I have submitted to *Chemistry in Britain*. It may turn out to be too long for them, in which case I would submit it to some other journals.

I hope that you will not find serious mistakes in it.

With many thanks for your help and all good wishes, I remain,

Yours sincerely,

AB/cw

Enclosure





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

A Chemist Helping Chemists

May 23, 1996

Professor A.G. Pinkus Department of Chemistry Baylor University P.O. Box 97348 Waco, TX 76798-7348

Dear Al:

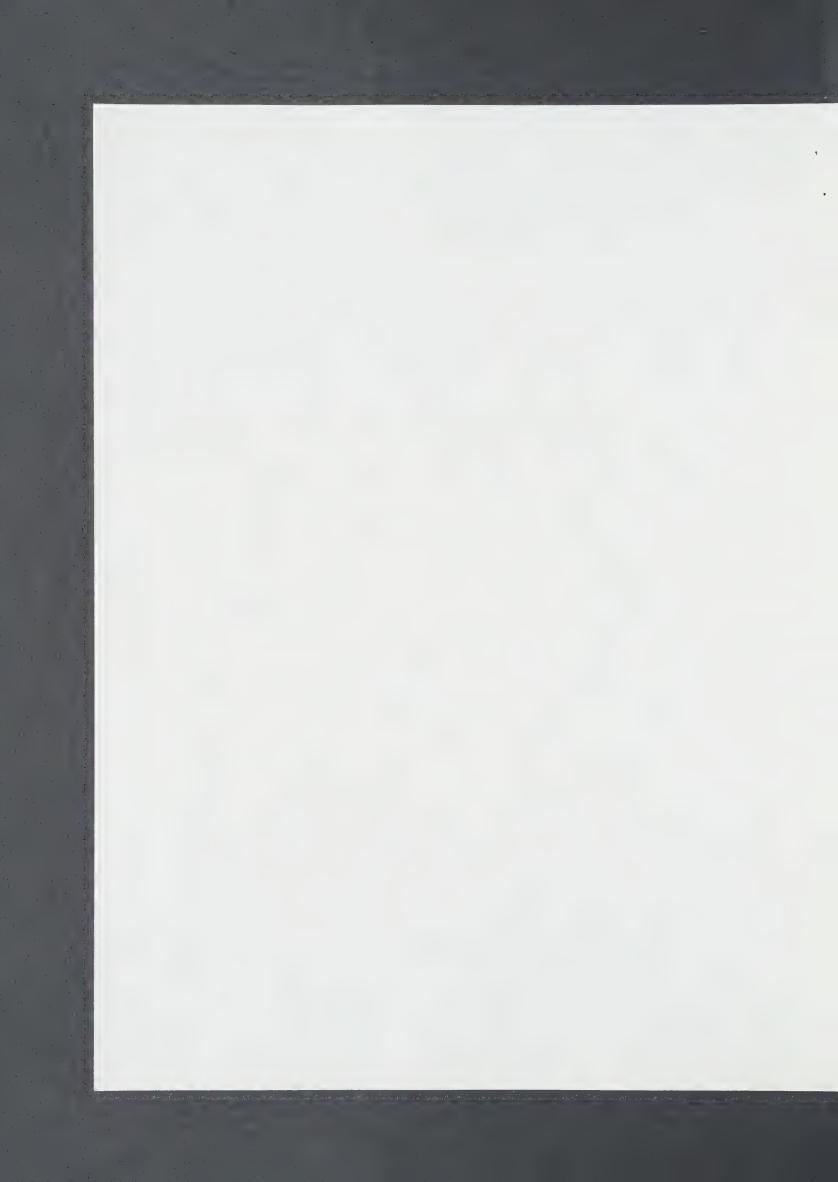
Thank you for your letter with that most interesting French article on Couper.

I am just leaving for England and will study the paper in detail during the trip.

Chemistry in Britain has told me that they like the article but want the number of references reduced. That should not be too difficult.

Best wishes, as always,

AB/cw





May 20, 1996

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

Dear Alfred:

Thanks for letting me see your manuscript on Anschütz, Couper, and Loschmidt. I thought you outlined the connections between them very well. It should not be too long for *Chemistry in Britain* and it would lose something if you had to condense it. In case it is too long for *Chem. Br.*, two other suitable journals are *Bulletin for the History of Chemistry* and *J. Chem. Educ.*.

You may be interested in an article in *Compt. Rend*. in which some pages are reproduced from the original manuscript by Couper including a mysterious 7th page which was not published. The original manuscript is in the Archives of the Academy of Science in Paris. I'm enclosing a copy of the article.

I have been busy with some research in the polymer area into which I have entered over the past few years because of the difficulty of obtaining grant funding in basic research. I have had some moderate successes with three U.S. patents issued over the past year or so and a number of publications and presentations. Now I am trying to interest some companies in commercializing the discoveries.

There was another excellent review of your autobiography in Angewandte Chemie. With so many good reviews, the book should wind up on the best-seller list. I wish you more success with it.

Sincerely,

13

A. G. Pinkus





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

A Chemist Helping Chemists

March 5, 1996

Professor A.G. Pinkus Department of Chemistry Baylor University P.O. Box 97348 Waco, TX 76798-7348

Dear Al:

Isabel and I think back to our visit to Baylor with great pleasure.

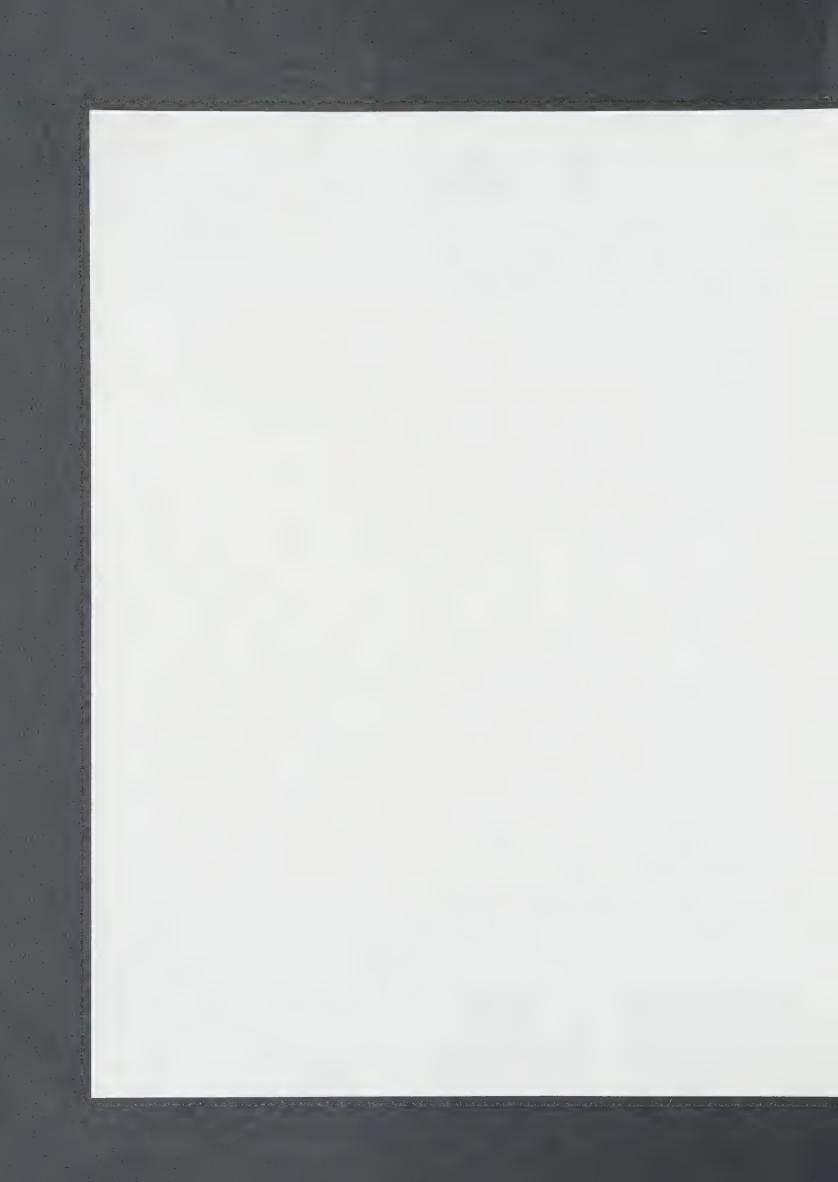
Chemistry in Britain has asked me to write a popular article on Couper.

Of course, I have your papers and the discussion of the correct structure of Couper's cyclic phosphorus compound. But the discussion what the correct structure of Couper's compound is, is lengthy and a little confusing. May I impose on you to send me what you know to be the correct structure and your leading reference, showing the correctness of that?

With many thanks for your help and best regards, I remain,

Yours sincerely,

AB/cw



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Concerning Americans who have published over 1,000 articles. II. C. Brown must have obtained accurate information on that from some reliable source since he was very thorough in his work. The conclusion of that story with reference to Gilman however, was interesting. I suspect that with the help of word processors/computer aids, that there are many authors at present with large numbers of published papers. As Prof. Stone, referring to his large list of published articles once modestly remarked 'Sometimes I wonder what it all means." And as you said "The number of papers alone does not indicate great quality." (referring to significant papers by Woodward and a book by Loschmidt). Probably only a few of a large number of papers might be really significant.

Fernanda, 1

I will write when the above proporties are worked but

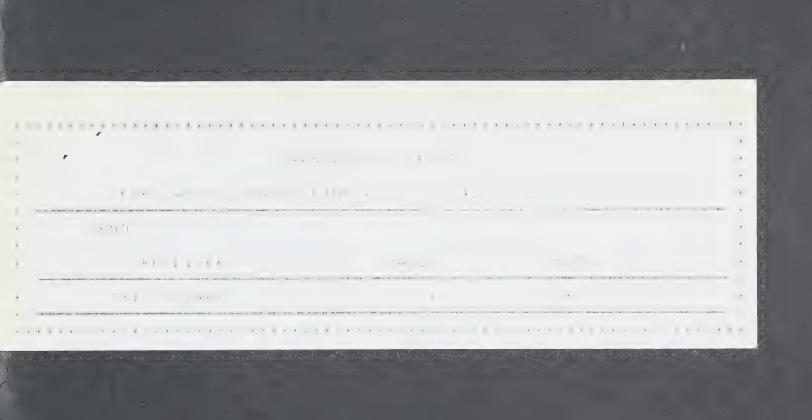
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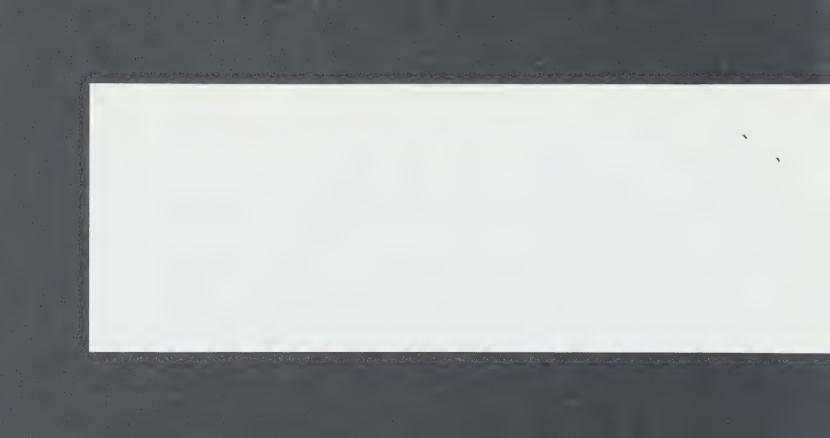
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A G Phikir







(4)

DR. ALFRED R. BADER
Suite 622
924 East Juneau Avenue
Milwaukee, Wisconsin 53202
Telephone 414-277-0730
Fax No. 414-277-0709

To: Port A. G. Darkers Myst of Chemi Any Daylo: U, New Dig Pinkus I can fax exchanges will teach me to be wire. Aprel fir ind to change my mem of tocks To 120 I am 71, and 4 halks a chang are really to much. When I wrote "the more I ke better 'I meané 6-7 m 3 days. I deal would be ACS History of Aldirch To chamistry & history structes (:)) - he schwide (1) Ansilvity, Couper & Lepinison To A. + wishing: (1) The Metercian Eye (2) Remberende RP & its collecter · (3) Bible trough Dutch Fige. Here are 6 Lalks Com al Dance





August 28, 1995

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

Dear Dr. Bader:

I was in the process of writing to you concerning the schedule of talks for your visit when I received your Faxed letter today. We have had a two-weeks break between the end of the summer session and the beginning of fall classes on the 28th (today). Now that everyone is back on campus from summer and interim vacations I will be able to finalize the complete schedule for your visit. I am taking you up on your note with respect to talks "...the more the better..." and am working out a busy schedule. To ensure audiences for the various talks I have contacted those who would have student classes or others interested in the particular topic to establish a basic group with others invited. So far I have the following lined up- the History of the Aldrich Chemical Co. to the local ACS Section with a book signing following, the two slide talks on the Detective's Eye to Art Dept. classes on Mon & Tues. mornings, the slide talk on the Rembrandt Research Project to the Art Center (offcampus) followed by book signings and looking at paintings brought in (for Sunday afternoon). By the way, one of our faculty (Dr. Busch) has a painting that he says is by Rembrandt that you might be interested in seeing. There are some faculty members who are inclined to disagree with you on "the Unimportance of a Liberal Arts Education" so I will schedule a session on that topic (probably on Monday afternoon) (and invite interested faculty and the Dean of the College of Arts & Sciences). This should make for a lively session. The Art Dept. might be interested in sponsoring another talk on art. I have not yet found a sponsor for the slide talk on "The Bible through Dutch Eyes" nor the talks on Loschmidt or Anschütz, ones that I would like to hear. In case the talk on "The Bible through Dutch Eyes" does not develop, I will try to arrange for some contact with the Waco Jewish community for you. I will also arrange for you to see the collection related to the lives and works of Robert and Elizabeth Barrett Browning which is located in the Armstrong Browning Library building. This should give you the overall schedule so far so that you can get prepared.

As I indicated earlier, I will meet you and Mrs. Bader at the DFW airport so that it will facilitate bringing copies of your autobiography from there to Waco. Thirty copies or whatever you can manage without too much trouble would seem about right. We can load them into the car for the drive to Waco so that would not be any problem.



It took me a little longer than I thought to finish reading your autobiography. I had been reading the series of autobiographies of organic chemists edited by Jeffrey Seeman with the general title of "Profiles, Pathways, and Dreams" each of which I was able to finish in a day or two as they appeared and it was on this basis that I made my estimate of how long it would take. I was impressed by your remarkable detailed memory of events that happened years ago. With such detail it is difficult to read rapidly. I only found one error in your book. Do you know that there are over 150 photographs in the book! Also I was trying to think of other American chemists who might have published over 1000 articles. The only one at the moment is F. A. Cotton (now at Texas A & M University) but he may not have had that many at that time. Also there is D. H. R. Barton (also now at Texas A & M) and Alan Katritzky (now at the University of Florida) but both were not in the U.S. at that time. Another possibility in the U. S. at present is H. F. Schaefer (now at U. Georgia; previously at Berkeley) but he did not have that many publications at that time. F. G. A. Stone (now at Baylor) at the present time has published 800-900 papers- not yet 1000. Of course, it is much easier to write now with word processors and computers than it was at that time with typewriters and carbon copies.

I will send you a more complete schedule soon but the preceding outline will give you a tentative one to follow. We will be looking forward to your visit and meeting you.

Sincerely yours,

a. 15 tentra

A. G. Pinkus



Facsimile

Date: August 8, 1995

From: A. G. Pinkus

Dept of Chemistry Baylor University Waco, TX 76798 (817) 755-3311 FAX: (817) 755-2403

(511)

To: Dr. Alfred Bader 2961 North Shepard Avenue

Milwaukee, WI 53211 Tel: (414) 277-0730 FAX: (414) 277-0709

No. of pp.: 1 including cover sheet.

Message:

* I received your note in the mail along with a copy of your air travel invoice, the cost of which will be taken care of by the ACS local section.

Just before sending off this Fax message I received your Fax. Since you will be coming on Saturday. I will try to organize a talk for that evening. In case there is a problem in getting from Dallas to Waco especially with the books, I can arrange to drive you from Dallas to Waco.

I will be finalizing the complete schedule of tasks and activities for your visit which I hope will be enjoyable for you and Mrs. Bader and will send it when completed

I will be looking forward to your visit.

Sincerely,

The wore talks

A. G. Pinkus

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Dear Prof. Pinkus

Le course I would like reimbursement

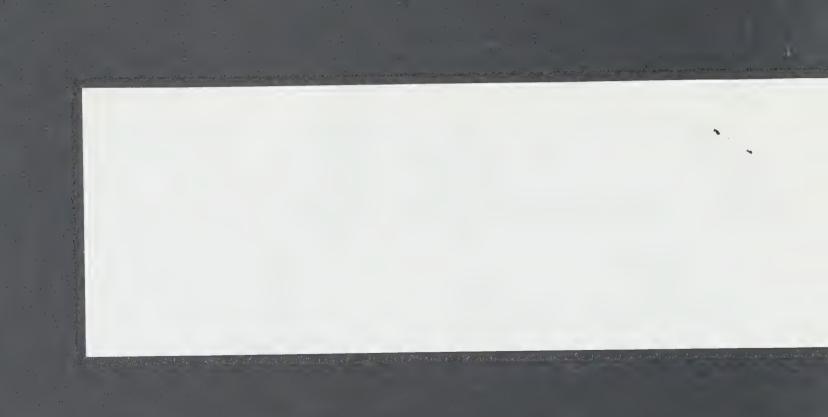
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A Chemist Helping Chemists

August 2, 1995

Via Facsimile: 817/755-2403

Professor A.G. Pinkus Department of Chemistry **Baylor University** Waco, TX 76798

Dear Professor Pinkus:

I so enjoyed finally being able to talk to you personally.

Checking with my travel agent, I find that there is a savings of several hundred dollars per person provided we fly to Dallas/Ft. Worth on Saturday, rather than Sunday.

Hence, we have booked on Midwest Express from Milwaukee to Dallas/Ft. Worth to arrive in Dallas at 3:20 p.m. on Saturday, September 9th. Please let us know what shuttle bus we can catch from the airport to Waco. Coming back, we will leave Dallas/Ft. Worth on Tuesday at 6:30 p.m.

Under separate cover today, I am sending you my autobiography, and you can let me know at your convenience whether you think I should bring some copies to Waco.

As I explained, there are two alternatives: The ACS is marketing the book at a retail price of \$25.00 and is getting a 50% discount. Also, I could bring some copies with me and, provided that you would take at least 10, would charge only \$12.50 each. Of course, I would understand if you decide that a book-signing would just be too complicated.

With all good wishes, I remain,

Yours sincerely,

AB/cw

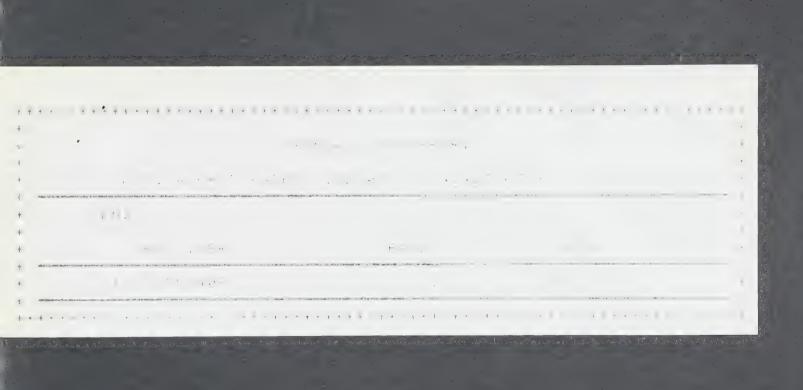
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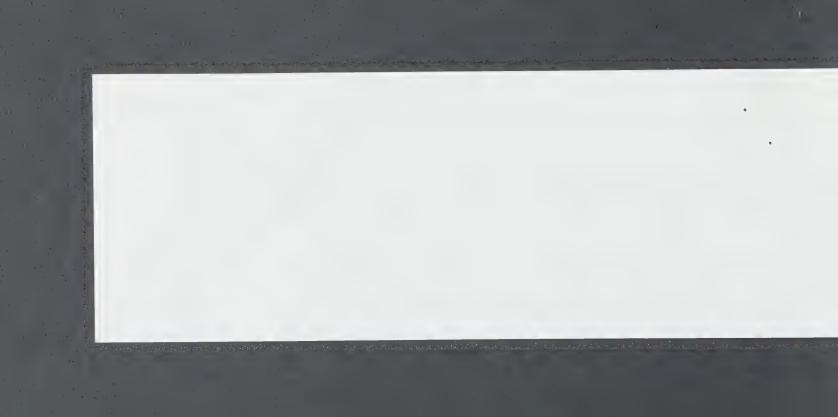
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Ofc. Ph.: 414/277-0730

Ofc. Fax: 414/277-0709







Facsimile

Date: August 2, 1995

From: A. G. Pinkut
Dept of Chemistry
Baylor University
Waco, TX 76798
(817) 755-3311
FAX: (817) 755-2403

Baukh Chemistru

10: Dr. Alfred Bader
2961 North Shepard Avenue
Milweukee, WI 53211
Tel: (414) 277-0730
FAX: (414) 277-0709
No. of pp.: 1 including cover sheet.

Message

The Dallas/Ft. Worth Airport Shuttle that I mentioned is called The Streak. The current schedule from D/FW is: 10:30 a.m.

1:30 p.m 4:00 p.m.

6:30 p.m. They go directly to the Hilton.

Return to D/FW (from the Hilton):

6:15 a.m. 9 15 a.m

11:45 a.m 2:15 p.m.

The cost is \$50 round-trip; \$30 one-way (\$5 deducted for seniors). Their phone no. is 800.460-0430.

The airline serving this trip is Delta via their Atlantic Southeast Air Airlines. The schedule from D/FW is:

7:30 a.m.

8:45 a.m

1:05 p.m.

3:25 pm.

7:15 p.m

10:40 p.m

The fare is \$108 or \$119 one-way. The fare is sometimes less when combined with a longer flight. Their phone no. is 800-282-3424. I would meet you at the airport if you decide to fly.



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

Dear Dr. Bader:

7ax 817 755

It has been a while since we corresponded. In a letter to Dr. Donald Lee of New Zealand concerning our common interest in Couper, I had mentioned that I was examining recent textbooks to see whether proper recognition to Couper's contributions to structural theory was being given. The idea of doing a complete search of textbooks on this topic occurred to me and I have collected the results of the search in the form of a paper with some interesting findings. I am enclosing a copy for any suggestions or criticisms from you. The main purpose of the paper is to call attention of textbook writers to this topic and to furnish some source references so that they can get their facts correct. I have also done an incomplete search on references in history books on this topic but the situation is more complicated so I have not included this in the present study but may do something on it in the future as I gather more data.

Since there are no references to Loschmidt's aromatic structures and other contributions in chemistry textbooks that I am aware of, a similar study cannot be done. Perhaps some of the textbook authors will begin to refer to his work in the future as a result of the

efforts you and others are making to publicize his contributions.

I expect that you are preparing for your address at the ACS Board of Directors reception at the Anaheim ACS meeting where you will receive the well-deserved Parsons Award. In addition I see from the program that there is award in Bioinorganic or Bioorganic Chemistry that you are supporting and in addition an award sponsored by the Aldrich Chemical Co., all on different days. These activities will keep you busy.

We are looking forward to your visit here Sept. 11 and 12. We have the four talks scheduled as mentioned in my previous letter and I will plan for a full schedule of activities including a tour of the Browning collection here, meetings with faculty members and other interested groups. I will arrange for accommodations for you and Mrs. Bader for Sunday and Monday nights (Sept. 10 and 11 respectively) assuming that you will arrive Sunday and leave on Tuesday as you suggested.

Best wishes on the Award ceremony.

Sincerely,

A. G. Pinkus

2 HH / Rg 854 S 6.30 pm 1250 Jos. h 70

March 20, 1995

Professor A.G. Pinkus Department of Chemistry Baylor University Waco, TX 76798

Dear Professor Pinkus:

Thank you so much for your letter of March 6th with that interesting draft of your important paper on Couper.

I can see no mistakes or omissions on first reading and wonder whether you might like to send a copy to Dr. Benfey in Philadelphia for his comments. He has worked very hard to bring Couper's name to the attention of chemists and, of course, I also hope that my efforts through Chapter 16 of my autobiography and my talk on Couper at the Loschmidt Symposium in Vienna in June will help.

Isabel and I certainly look forward to being with you in Waco from the 10th through the 12th of September.

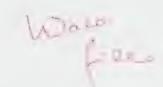
With all good wishes, I remain,

Yours sincerely,

AB/cw



BAYLOR
March 6, 1995



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

Dear Dr. Bader:

It has been a while since we corresponded. In a letter to Dr. Donald Lee of New Zealand concerning our common interest in Couper, I had mentioned that I was examining recent textbooks to see whether proper recognition to Couper's contributions to structural theory was being given. The idea of doing a complete search of textbooks on this topic occurred to me and I have collected the results of the search in the form of a paper with some interesting findings. I am enclosing a copy for any suggestions or criticisms from you. The main purpose of the paper is to call attention of textbook writers to this topic and to furnish some source references so that they can get their facts correct. I have also done an incomplete search on references in history books on this topic but the situation is more complicated so I have not included this in the present study but may do something on it in the future as I gather more data.

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Best wishes on the Award ceremony.

Sincerely,

A. G. Pinkus

a. M. Finkers



October 25, 1994

Professor A. G. Pinkus Department of Chemistry Baylor University P.O. Box 97348 Waco, Texas 76798-7348

Dear Professor Pinkus:

Thank you so much for your kind letter of October 19th in which you unfortunately do not tell me whether we will meet at the Loschmidt Symposium in Vienna in June.

I have put September 11, 1995 onto my calendar and look forward to being with you. Hopefully you will be able to arrange for me to give somewhere between 3 and 5 lectures.

Regarding the talk entitled "The Detective's Eye", I am sending you a catalog for an exhibition held at the Milwaukee Art Museum. The catalog was written by Isabel and me.

I wouldn't put anything past Professor Schiemenz. Anyone who goes around the world showing an open grave with the words "William Wiswesser" on the tombstone suggesting that Wiswesser is dead and should be left in peace, is capable of anything.

Richard Bader at McMaster is not a close relative, but if his grandparents came from a Moravian town called Kyjov, then we are distantly related.

Best wishes.

Sincerely,





October 19, 1994

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

Dear Dr. Bader:

Thank you for your good letter dated October 14th. After clearing the September 11th date with the Art Dept. as well as in our dept., I am hastening to answer your letter quickly to confirm that date before someone else does! You can make arrangements for your flight to Dallas/Ft. Worth and then to Waco on the preceding Saturday or Sunday and then leave on the 12th. The flight from DFW is on American Eagle Airlines (connected with American Airlines) or there is a limousine service, Waco Streak (a division of American Eagle) which makes round trips between DFW and the Waco Airport (in case you prefer not to fly on a smaller plane). The latter trips are coordinated with American Airline flights and reservations can be made through the travel agent. It is a little over 100 miles between DFW and Waco on Interstate 35 (about a 2 hour drive).

The chairman of the Art Dept. was interested in the talks on "The Detective's Eye". Do you have an abstract or synopsis telling what would be in those slide talks?

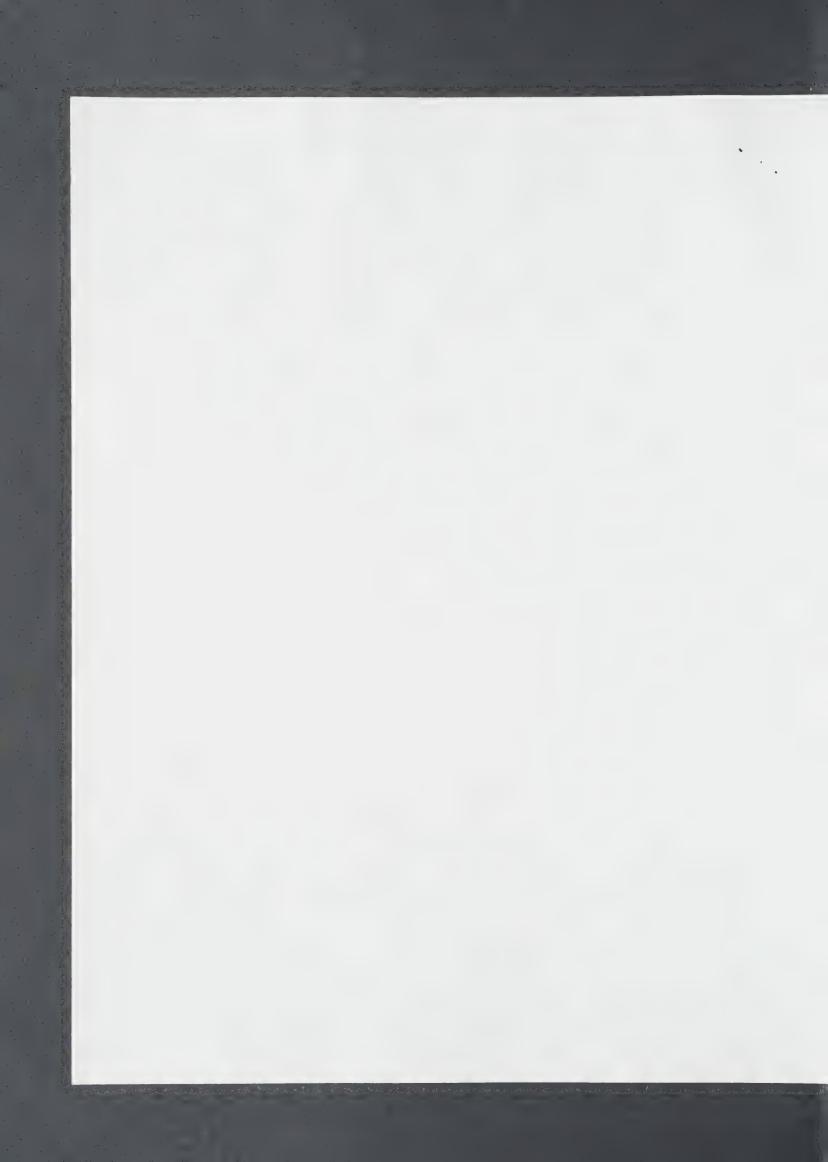
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By the way, I happened to see an interesting review paper in *Angewandte Chemie* by Prof. Richard Bader of McMaster University. I was wondering if this is your son since you mentioned in an earlier letter that you have a son who was to be married.

Sincerely,

A. G. Pinkus

A.M. Perfor



October 25, 1994

Professor A. G. Pinkus Department of Chemistry Baylor University P.O. Box 97348 Waco, Texas 76798-7348

Dear Professor Pinkus:

Thank you so much for your kind letter of October 19th in which you unfortunately do not tell me whether we will meet at the Loschmidt Symposium in Vienna in June.

I have put September 11, 1995 onto my calendar and look forward to being with you. Hopefully you will be able to arrange for me to give somewhere between 3 and 5 lectures.

Regarding the talk entitled "The Detective's Eye", I am sending you a catalog for an exhibition held at the Milwaukee Art Museum. The catalog was written by Isabel and me.

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Sincerely,

A. G. Pinkus



October 14, 1994

Professor A. G. Pinkus Department of Chemistry Baylor University P.O. Box 97348 Waco, Texas 76798-7348

Dear Professor Pinkus:

Thank you for your kind letter of October 5th.

The Loschmidt Symposium is now taking shape. Schiemenz will present a paper with the innocuous title "Kugeln van Dalton bis Loschmidt, Einblicke in die Denkweise eines Genies". While the title sounds harmless, he will undoubtedly try to prove that Loschmidt did not think of benzene as six carbons in a circle.

I am supposed to give two lectures. The first will follow the Monday lectures of Djerassi, Eliel and Eschenmoser. The second will deal with Anschütz, Couper, Loschmidt and Kekulé.

Unfortunately I will not be able to be with you any time between the end of October and the 13th of November, because I am already booked to be in Canada and England.

Please don't worry about heat as we also have some 90° days in Milwaukee. Incidentally, I have been to Texas several times, and particularly enjoyed my visits to Trinity University in San Antonio. I have just never been to Baylor or Waco. Hence, if September 11th were acceptable to your Art Department, Isabel and I could fly either on the 9th or 10th and then leave on the 12th. It may well be that if we leave on the 9th, the airline tickets will be much less expensive than if we leave on the 10th, and we certainly don't want to be put up in a luxury hotel. We have often found that the cost of the extra day is very much less than the savings in airline tickets.



Professor A. G. Pinkus Baylor University October 14, 1994 Page Two

In any case, I would so enjoy meeting you personally, but perhaps we will do that first in Vienna in June.

Best regards,



Waco Conference of Christians and Jews

The Waco Conference of Christians and Jew's will hold its 14th Annual Dinner on Tuesday, October 4, 1994, at 6:30 p.m., in the Community Services Center of McLennan Community College, 4601 N. 19th st. Keynote speaker will be Rabbi Sheldon Zimmerman who heads Temple Emanu-El, a Reform synagogue located in Dallas which has almost 9000 congregants making it the largest Jewish congregation in Texas and one of the five largest Reform temples in the United States.

Rabbi Zimmerman is recognized as one of the nation's key religious leaders having given the opening prayer at the inauguration of Governor Ann Richards and traveled with Vice President Al Gore to Poland to participated in the 50th anniversary of the Warsaw Ghetto uprising. Last year he was elected as President of the

Central Conference of American Rabbis, the largest organization of rabbis in North America.

A major highlight of the event will be the recognition of Homer D. Trevino as the Humanitarian of the Year and Sam Harelik and his family as Family of the Year.

Tickets for the Annual Dinner are \$13 and can be purchased by mail through September by mailing a check to the Waco Conference of Christians and Jews, P.O. Box 21902, Waco, Texas 76702. Tickets may also be purchased at the following locations: Hillcrest Baptist Medical Center, Providence Health Center, Lake Shore Baptist Church, Temple Rodef Shalom, and Congregation Agudath Jacob.

For more information, please contact Buddy Sipe, 881-5784.

- 90-374-4 Bruceville-Eddy I.S.D. vs. Smith, Jerry Wayne MCAD# 16 260.00 38.00 4
 Being a 2.04 acre, more or less, tract of land out of the William P Henry Survey in McLennan County, Texas.
 Volume 1588, Page 24 Deed Records.
- 94-560-4 County of McLennan, et al vs. M. Talley Orand MCAD# 44 32.00 518.00 0
 Being 3.50 acres, more or less, in the O'Campo Grant #32, McLennan County, Texas.
 Volume 362, Page 163 Deed Records.
- 94-2073-4 County of McLennan, et al vs. Jesse Sallee
 MCAD# 420023000112000 and 410000184140020
 Being 4.0 acres out of the J.A. Manchaca Grant, McLennan County,
 Texas.
 Volume 457, Page 124 Deed Records.
- 93-3432-4 County of McLennan, et al vs. James R Guice
 MCAD# 20 454.00 53.00 4
 Being 5.0 Acres out of the E W Holmes Survey, McLennan County,
 Texas.
 Volume 1649, Page 141 Deed Records.
- 94-131-4 County of McLennan, et al vs. Hector G. Vela
 MCAD ≠ 20 331.00 294.00 7
 Being Lot Two (2), Block "0", out of the Meadow Lawn Subdivision of
 the Joseph Rutherford Survey, McLennan County, Texas.
 Volume 866, Page 425 Deed Records,

zoning, the Zoning Map s that territory hereinafter d wit:

Being Lots B and C it the M.A. Blocker Addition Waco, McLennan County,

Lots A12, B11, B10, D B4, A5, B5, and A in Block 29 Blocker Addition in the Cit McLennan County, Texas: 8

Lots B, 10, 11, 12, A13 and 5, in Block 30 of the N Addition in the City of Waco County, Texas;

all being located gen of La Salle between Univ Drive and South 1st Stre zoned M-3, shall be chidesignated and classified ing District and the Zoning amended accordingly.

Section 2. That a vic ordinance shall be a miso the penalty for violating t shall be as provided for in Code of Ordinances of the which shall be a max \$2,000.00, and each d exists shall be a separat

Section 3. That if a this ordinance shall be h or unconstitutional, th

BAYLOR

October 5, 1994

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

Dear Dr. Bader:

It was good to hear from you again. As I expected, you are in demand as a speaker which keeps you very busy. The schedule you sent for your visit to the University of Wisconsin-Eue Claire will be helpful in planning your visit. I appreciate that your projected visit here would be to get better acquainted personally and I hope you don't mind giving us the benefit of hearing your interesting talks. Besides in scheduling some talks we can pay travel and other costs plus an honorarium to help with expenses. I hope I can arrange to make your visit a pleasant one in view of your apprehension of Texas and that this would be your first visit to the state. We have one of the top collections housed in the Browning Library on campus of materials related to the lives and literary activities of Robert and Elizabeth Browning that might be of interest to you and Mrs. Bader. (I presume that she will also be coming?) You may not be as interested in the Texas Ranger Museum located nearby.

When I contacted the Art Dept. about the dates of Sept. 11 and 18, the Chairman said that they had a funded lecturer coming during the latter period. I am also somewhat concerned about the comfort of visitors from cooler climates in the high temperatures of September. For example, the highs last week and this were 97 degrees. Although all buildings on campus, cars, and most of buildings in Waco are air-conditioned, it is really hot outside for those not used to it. I hope you will not be upset if I suggest any of the following later dates- Oct. 30, Nov. 6 or 13 for your consideration. I thought it would take a couple of days to give two or three talks but I see that you suggest 4 or 5 over that period of time.

We would select some of your talks including the one you mentioned "The Bible through Dutch Eyes" subtitled "Rembrandt and the Jews" which can be scheduled and which should be of interest to the Waco Jewish community. There is an active Conference of Christians and Jews in Waco (see enclosed clipping of an article which coincidentally just appeared).



I received the second announcement of the Loschmidt Symposium from Prof. Fleischhacker of Vienna University along with a nice letter mentioning that you had told him of my interest in Loschmidt. Professor Gunther Schiemenz is not listed on this preliminary list of speakers but may be on a later complete program. Are you also going to present a paper? If Professor Schiemenz is going to present a negative view of Loschmidt's work, he will have to have his facts correct since most of the others there will have favorable views of Loschmidt.

Sincerely,

A. G. Pinkus

a. A. Timber





BAYLOR UNIVERSITY AMERICAN CHEMICAL SOCIETY STUDENT AFFILIATE

Department of Chemistry
Waco, Texas 76798 • 817-755-3311



31 October 1915

Dear, the Boder

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September 18, 1995

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

Dear Dr. Bader:

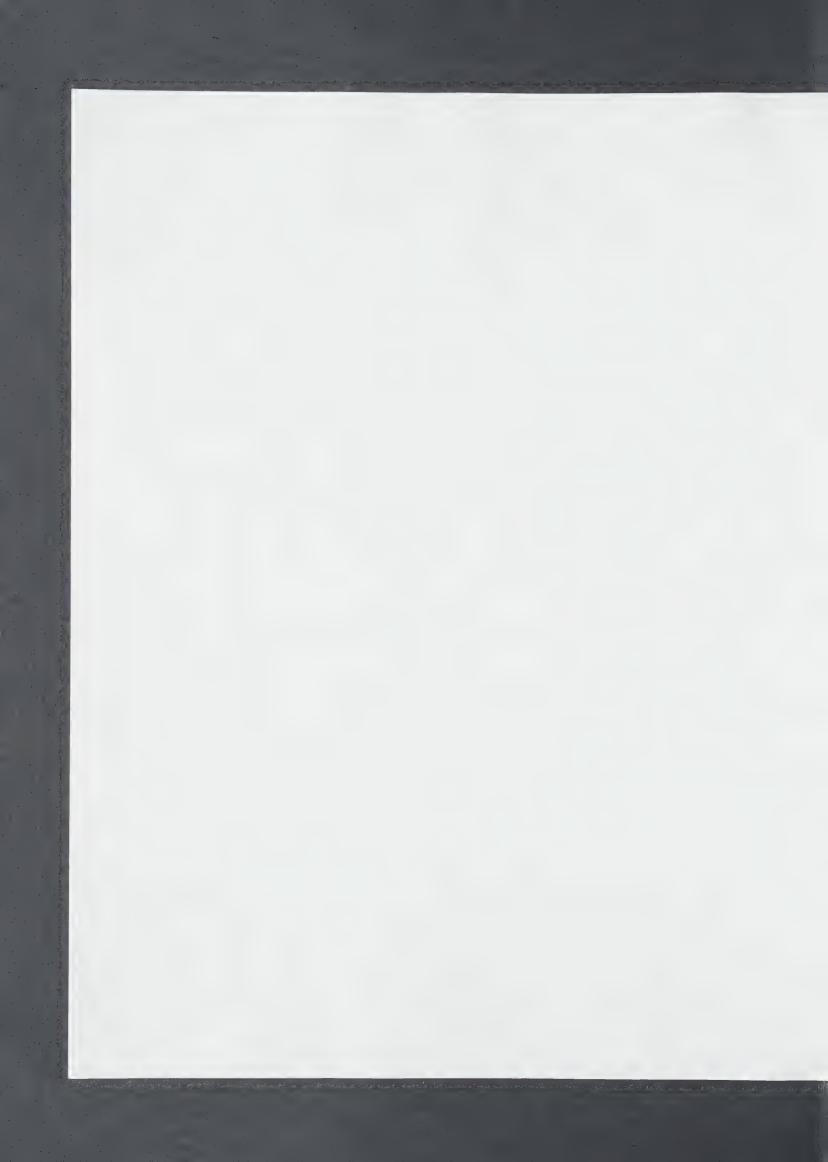
It is with much pleasure that I write expressing gratitude from the Department of Art, any my own personal thank you, for the time and effort you gave on our behalf this past week. Faculty, members of the Waco community, and particularly students have benefited immeasurably from your remarkable knowledge of art history and connoiseurship made rich by years of study. You have shared yourself and your experience. This is indeed the best gift.

We send you now to other endeavors with sincere wishes for your continued success. May good health and good fortune follow you always.

Sincerely,

John D. McClanahan Professor and Chair

JDMcC/mv





September 20, 1995

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

Dear Alfred:

Checks for reimbursement of travel expenses, etc. from the Heart o' Texas ACS Local Section (\$529.99) and the amount for 17 books (17 x \$12.50 = \$212.50) from the ACS Student Affiliate are being sent by mail. I thought I would send these now and the honorarium check later whenever I receive it from the University Lecturers Committee since the latter will probably involve some "red tape". If you have not yet received the amount for the 13 books from Joe Kagle at the Art Center, let me know and I will remind them.

I'm also sending an article on some art fraud by Hans van Meegeren involving Johannes Vermeer paintings that I found of interest. You are probably well aware of this but the article (in Chem Matters) may give a different perspective on this affair.

A cold front from Canada is coming in today so that high temperatures will be in the 60's for the next few days. I'm thankful that temperatures were at least slightly lower than the previous week during your visit.

Students and faculty are still commenting on the great talks you gave which were appreciated very much. I gave your address to the graduate student, Ms. Norfleete Day, who is writing a thesis on the Samaritans and was interested in information. She may have written by this time.

Sincerely,

A. G. Pinkus

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A Collins



Facsimile

Date: Sapi ou 1995

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2961 North Shepard Avertie Min. Blikeo, Wi 53211 Tel (414) 277-07311 FAX: (414) 277-0709 No of pp.: 2 Including cover sheet

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FAX FROM:

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

A Chemist Helping Chemists

September 14, 1995

TO:

PROFESSOR A.G. PINKUS

Department of Chemistry

Baylor University

FAX:

817/755-2403

Dear Al:

Thanks for your wonderful hospitality.

For Baylor's records, my Social Security number is

*

Attached please find the following receipts:

Airline	Ticket	stubs	for	Isabel	and	me
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2 @ \$220.20	\$ 440.40	*
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Miscellaneous	2.00	
Trans, in Milwaukee	20.00	

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\$ 529.99

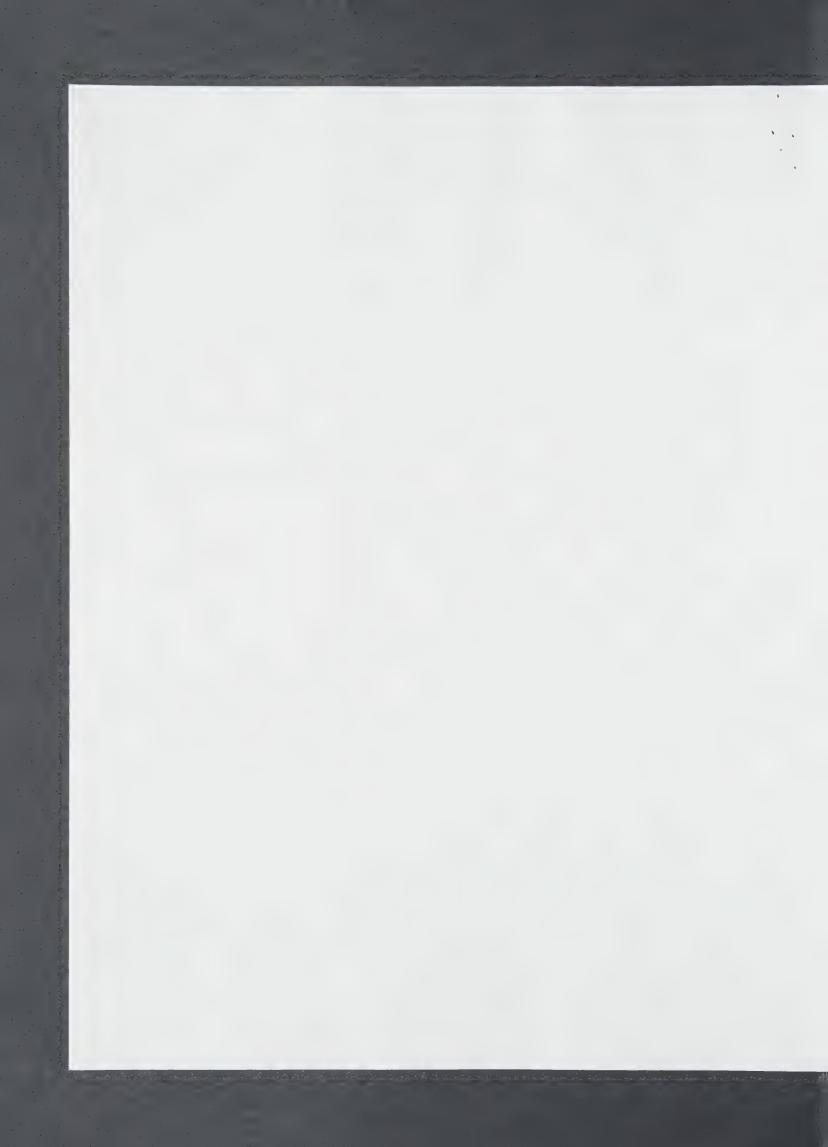
Gua Boan

With many thanks and best regards, I remain,

Yours sincerely,

AB/cw

Enclosures (Original receipts will be mailed)





ALFRED BADER FINE ARTS

DR. ALFRED BADER

ESTABLISHED 1961

September 14, 1995

Professor A.G. Pinkus Baylor University Department of Chemistry P.O. Box 97348 Waco, TX 76798-7348

BILL OF SALE

30 copies of *Adventures of a Chemist Collector* @ \$12.50 each [13 left at Art Centre] [17 left with chemists]

Hand-Delivered to Waco

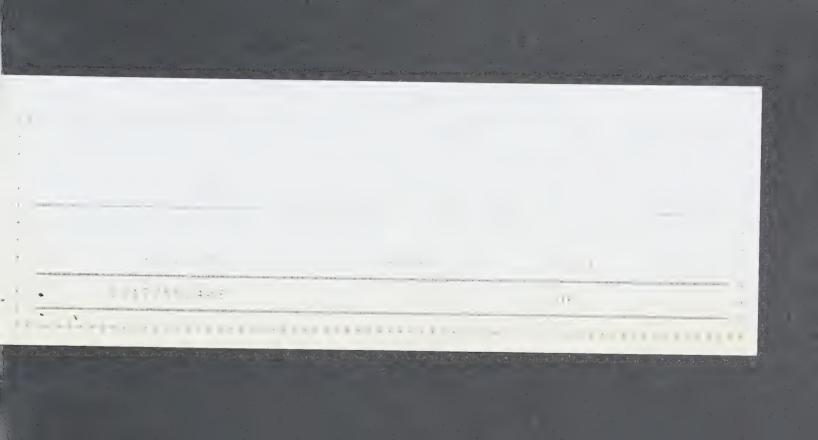
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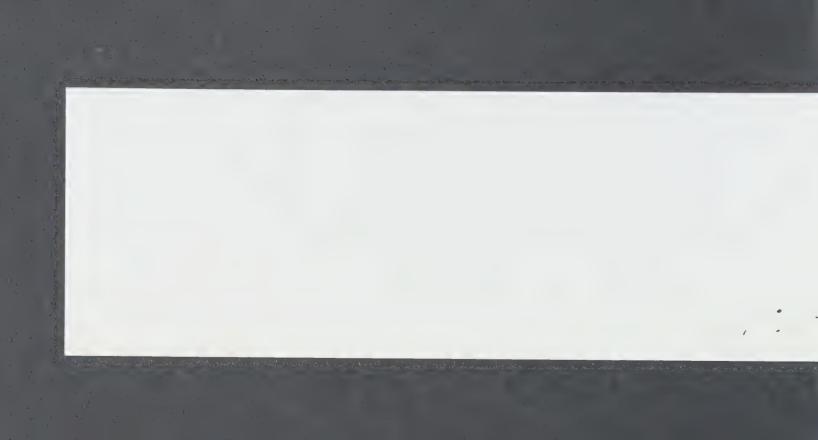
Be A regards Qua Baar

Thank you!

By Appointment Only
ASTOR HOTEL SUITE 622
924 EAST JUNEAU AVENUE
MILWAUKEE WISCONSIN USA 53202
TEL 414 277-0730 FAX 414 277-0709

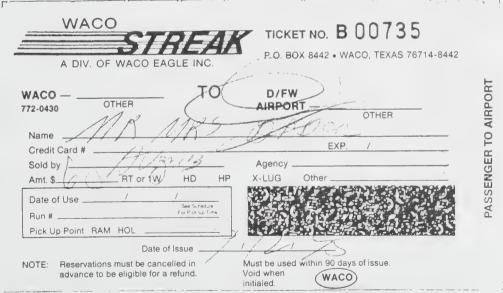






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Dr. Alfred Bader 2961 North Shepard Avenue Milwaukee, Wisconsin 53211

A Chemist Helping Chemists

September 22, 1995

Professor A.G. Pinkus Department of Chemistry Baylor University P.O. Box 97348 Waco, TX 76798-7348

Dear Al:

Thank you so much for sending me your papers dealing with the zincke and suhl reaction products.

What a pity that the first paper wasn't published a year or two earlier. If so, I would almost certainly have studied the reaction from a commercial point of view. After all, if you can take two inexpensive materials, like *p*-cresol and carbon tetrachloride and get a dienone in fair yield, that is worth commercial investigation.

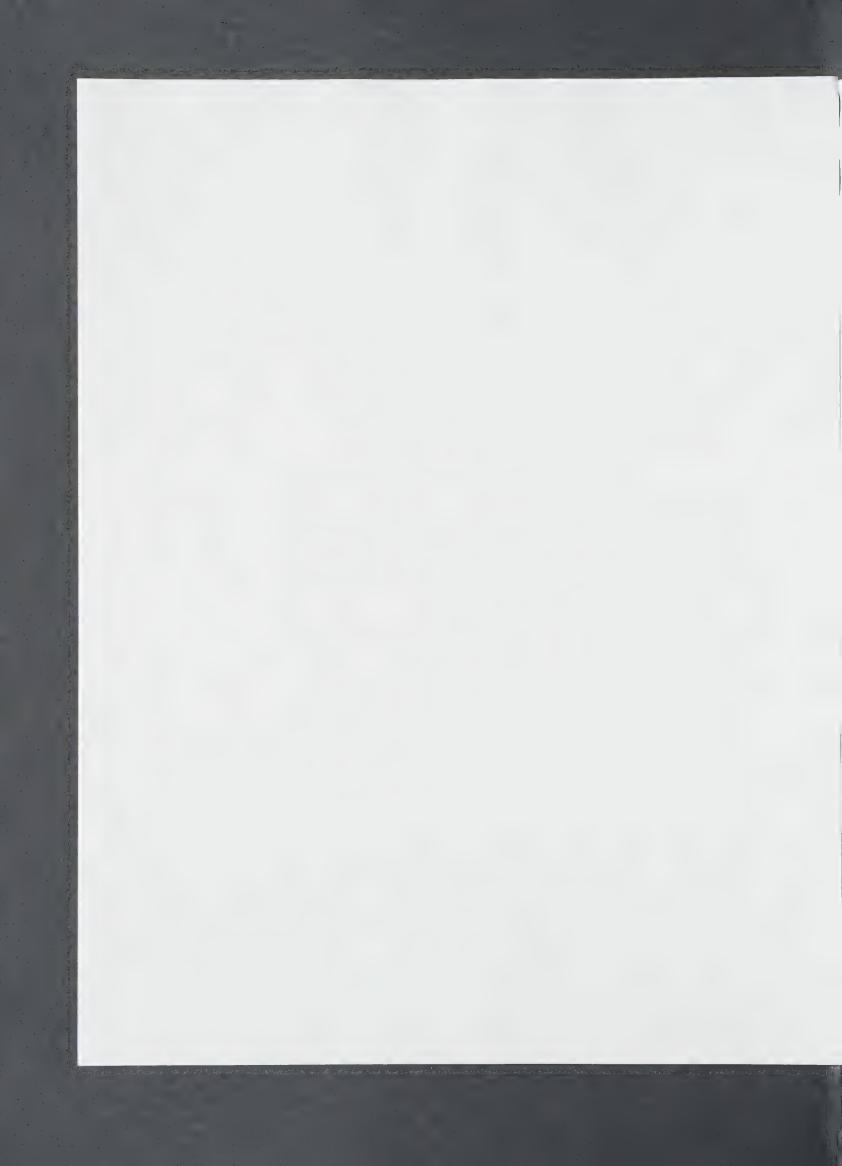
But by the time the paper appeared, I was just leaving PPG and really had my hands full trying to sell Aldrich products.

Isabel and I still talk about how much we enjoyed our days in Waco.

With all good wishes, I remain,

Yours sincerely,

AB/cw



[Contribution from the McPherson Chemical Laboratory, the Ohio State University

A STUDY OF THE ZINCKE AND SUHL REACTION

MELVIN S. NEWMAN AND A. G. PINKUS¹

Received January 18, 1954

It has been shown that *p*-alkylated phenols may react with chloroform under alkaline conditions to yield 4,4-disubstituted-2,5-cyclohexadienones (1). Less well known is the reaction discovered by Zincke and Suhl in which *p*-cresol reacts with carbon tetrachloride in the presence of aluminum chloride to yield 4-methyl-4-trichloromethyl-2,5-cyclohexadienone, I (2).

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{OH}$$
 + CCl₄ $\xrightarrow{\text{AlCl}_4}$ $\xrightarrow{\text{O}}$ $\xrightarrow{\text{O}}$

We became interested in this reaction because of the fact that its generality has never been explored in spite of the fact that it affords a possibly general method for producing compounds containing a quarternary carbon atom and also because I has been shown to undergo a number of interesting reactions (3).

In Table I are listed a number of experiments which were carried out in order to obtain a better understanding of the reaction. Although we have not completed an exhaustive study of this reaction, we feel that a number of conclusions may be drawn.

In Zincke and Suhl's procedure, aluminum chloride was added to a solution of p-cresol in carbon tetrachloride. After a period of heating, the product (I) was isolated (after hydrolysis of the reaction mixture) in about 37–42% yield. We have checked this result and also shown that it is necessary to have an excess of aluminum chloride (calculated as $AlCl_3$) over p-cresol (note experiments 1 and 2, Table I). However, a 100% excess is little better than a 25% excess (note experiments 17 and 18). Boron trifluoride and anhydrous stannic chloride were ineffectual as catalysts.

A solvent other than carbon tetrachloride was needed if the reaction of other halides was to be studied. Nitrobenzene (experiments 11, 12, 13), chlorobenzene (experiment 3), and a saturated hydrocarbon, Skellysolve B, b.p. 65–70°, (experiments 14, 15, 16) were found to be improper solvents but carbon disulfide proved excellent. In this solvent yields of 56 to 60% were obtained (experiments 17, 18, 21, 22).

The Zincke and Suhl procedure of adding aluminum chloride to a solution

¹ The material presented in this and the three accompanying papers was taken from the Ph.D. thesis of A. G. Pinkus (present address, Baylor University, Waco, Texas), Ohio State University, 1952.



TABLE I
YIELDS OBTAINED IN THE ZINCKE AND SUHL REACTION UNDER VARIOUS CONDITIONS

EXP.	p-Cresol (moles)	CCI4 (moles)	AlCl ₁ (moles)	SOLVENT (ml.)	темр., ^а °С.	TIME (min.)	METHOD ^b	CRESOL RECOV- ERED	of I, %
1	0.20	0.80	0.20	CCL	Reflux	120	1	Yes	0
2	.20	.40	.26	CCl ₄	Reflux	120	1	No	40.0
3	.20	. 25	. 23	C ₆ H ₅ Cl (30)	Reflux	120	1	No	0
4	.20	.259	.23	CS ₂ (50)	Reflux	120	1	No	51.2
5	.162	.187	.18	CS ₂ (45)	Reflux	120	2	No	25.9
6	.20	.259	.23	CS ₂ (100)	Reflux	120	1	No	53.0
7	.20	.259	. 23	CS ₂ (70)	Reflux	120	3	No	33.0
8	.20	.259	. 23	CS ₂ (50)	Reflux	25	4	Yes	2.0
9	.10	.120	.12	CS ₂ (70)	Reflux	60	4	Yes	22.1
10	.10	.10	.11	CS ₂ (40)	Reflux	90	5	Yes	46.7
11	.010	.010	.012	C ₆ H ₅ NO ₂ (4)	50	90	6	Yes	0
12	.010	.010	.012	C ₀ H ₅ NO ₂ (4)	60	150	6	Yes	0
13	.010	.010	.012	C ₆ H ₆ NO ₂ (4)	85	120	6	Yes	0
14	.010	.010	.012	Skellysolve (4)	40	120	6	Yes	0
15	.050	.050	.063	Skellysolve (30)	50	120	6	Yes	0
16	.050	.050	.063	Skellysolve (30)	75	120	6	Yes	0
17	.050	.050	.10	CS_2 (25)	50	120	6	No	58.0
18	.050	.050	.063	CS_2 (25)	50	120	6	No	56.0
19	.050	.050	.063	CS_2 (25)	18	180	6	Yes	21.3
20	.050	.050	.063	CS ₂ (25)	30	120	6	Yes	27.7
21	.10	.050	.14	CS ₂ (25)	40	120	6	Yes	59.4°
22	.050	.050	.063	CS ₂ (25)	45	120	6	No	60.3

^a Temperatures reported are those of an electrically-heated oil-bath. ^b Methods: 1. Adding aluminum chloride to the solution of p-cresol in carbon tetrachloride. 2. Reacting aluminum chloride and p-cresol in carbon disulfide, then adding carbon tetrachloride dropwise to the refluxing mixture. 3. Reverse order of addition: adding a solution of aluminum dichloride p-cresoxide in carbon disulfide dropwise to a refluxing mixture of carbon tetrachloride and aluminum chloride in carbon disulfide. 4. A solution of p-cresol in carbon disulfide added to the refluxing mixture of carbon tetrachloride, aluminum chloride, and carbon disulfide. 5. A solution of p-cresol in carbon tetrachloride added dropwise to a refluxing suspension of aluminum chloride in carbon disulfide. 6. Carbon tetrachloride added at once to the solution of aluminum dichloride p-cresoxide in carbon disulfide and then heating the mixture. ^c Yields are based on p-cresol except in experiment 21 in which it is based on carbon tetrachloride since p-cresol is in excess.

of p-cresol in carbon tetrachloride was found to be less effective than that in which a solution of p-cresol in carbon disulfide was added to a suspension of aluminum chloride in carbon disulfide. Hydrogen chloride was evolved and the chloroaluminum salt of p-cresol formed was soluble. After the completion of this step, the carbon tetrachloride was added and the mixture was heated in the range $40{\text -}50^\circ$ for two hours (experiments 17, 18, 21, 22). Examination of Table I will reveal the other variables studied.

In addition to the 56–60 % of I obtained in the best experiments there was also formed dark polymeric material. No p-cresol was recoverable. Two experiments showed that the polymer was not being formed from I. In the first I was



heated with aluminum chloride in carbon tetrachloride. An orange complex was formed but after hydrolysis and steam-distillation 97% of I was recovered. In the second I was heated with p-cresol and 2.25 moles of aluminum chloride in carbon disulfide to reflux. Both I and p-cresol were recovered in high yield. A possible explanation for the formation of polymer will be presented in the discussion of mechanism of the reaction.

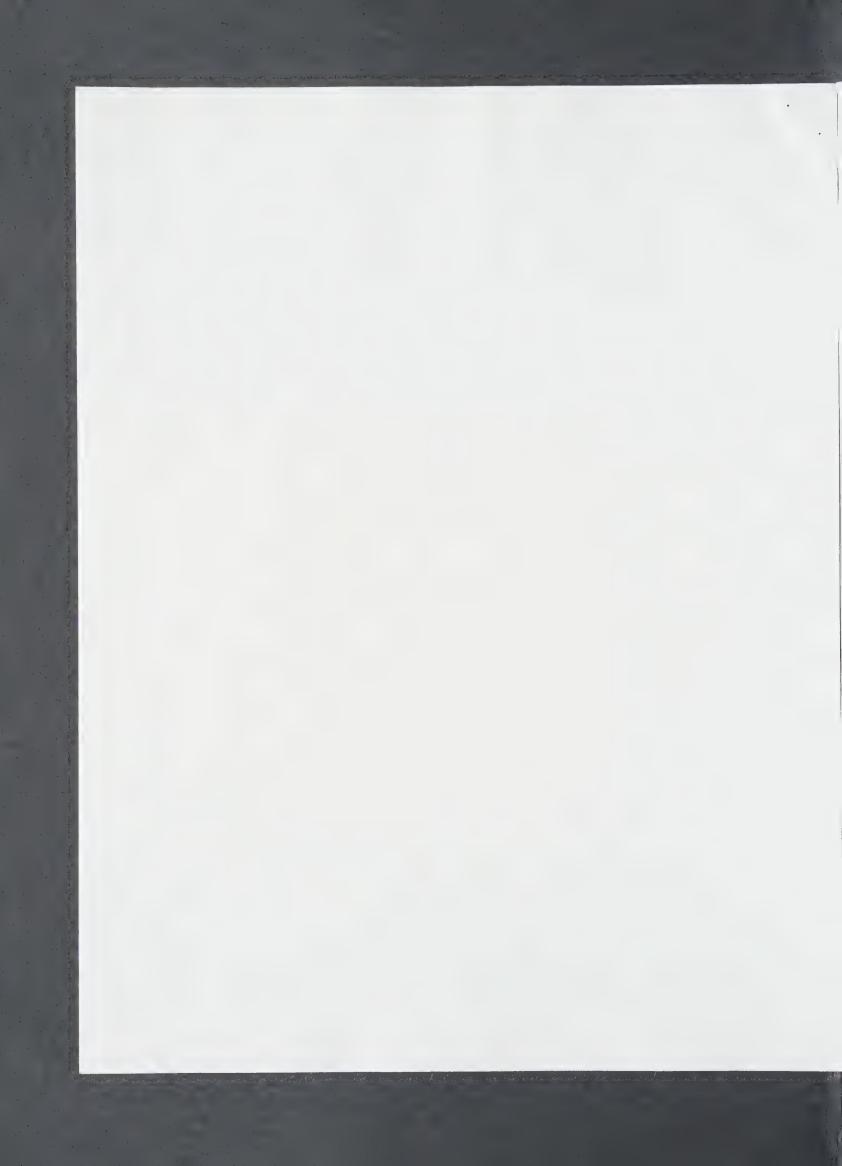
Having found a suitable solvent we were interested in exploring the generality of the reaction by using halides other than carbon tetrachloride and phenols other than p-cresol. Although exhaustive studies in each case were not performed we were unable to obtain products comparable to I with p-cresol and methyl chloride, methyl iodide, methylene chloride, chloroform, and hexachloroethane. With 1,1,1-trichloroethane, a 1.6% yield of a 2,4-dinitrophenylhydrazone having an analysis in agreement with that expected for a compound similar to I was obtained but the parent ketone was not obtained. When 2,6-dibromo-4-methylphenol and 2,6-dichloro-4-methylphenol were reacted with carbon tetrachloride 9% and 36% yields of the expected dieneones analogous to I were obtained. However, all attempts to introduce an angular trichloromethyl group into 5,6,7,8-tetrahydro-2-naphthol failed (1).

When the reaction was carried out using benzotrichloride instead of carbon tetrachloride two new reactions were discovered. The description of this work is given in the accompanying paper (4).

Our concept of the mechanism of the Zincke and Suhl reaction has aluminum chloride playing a dual role: it first reacts with p-cresol to form a chloroaluminum salt (II) with loss of hydrogen chloride; and it also activates a molecule of carbon tetrachloride by forming a loose complex, III. This complex is subject to a

nucleophilic attack on carbon by the chloroaluminum salt, as shown. The chloride ion displaced combines with the $\mathrm{AlCl_2^+}$ ion to produce aluminum chloride which remains complexed with the product (IV).

The salt II may react at three positions: on the para carbon, 1, to give the



Zincke and Suhl product (I); at the *ortho* carbon, 2, to give compounds which in the present case are probably the precursors of the polymers formed (see below) and in the case of the reactions involving benzotrichloride (4) afford ketones and dioxocins; and on the oxygen, 3, to form the carbonates which have been isolated previously (2) in the case where 2,3,5,6-tetrabromo-p-cresol was used in place of p-cresol.

In support of this mechanism, a number of facts may be cited. When p-cresol in carbon disulfide is allowed to react with aluminum chloride (mole for mole), all of the aluminum chloride goes into solution and one equivalent of hydrogen chloride is evolved. (The chloroaluminum salt (II) formed is probably not monomeric (5) but for simpler representation the monomeric form is used.) When the solvent was removed in vacuo, a colorless crystalline salt remained which, on treatment with water, yielded p-cresol. A similar type of compound has been reported for phenol (6).

The only evidence we have for a complex (III) between carbon tetrachloride and aluminum chloride is the formation of a yellow color on the aluminum chloride when heated with carbon tetrachloride. When the carbon tetrachloride was removed *in vacuo*, the color disappeared. The interaction of alkyl halides and aluminum halides has frequently been demonstrated (7).

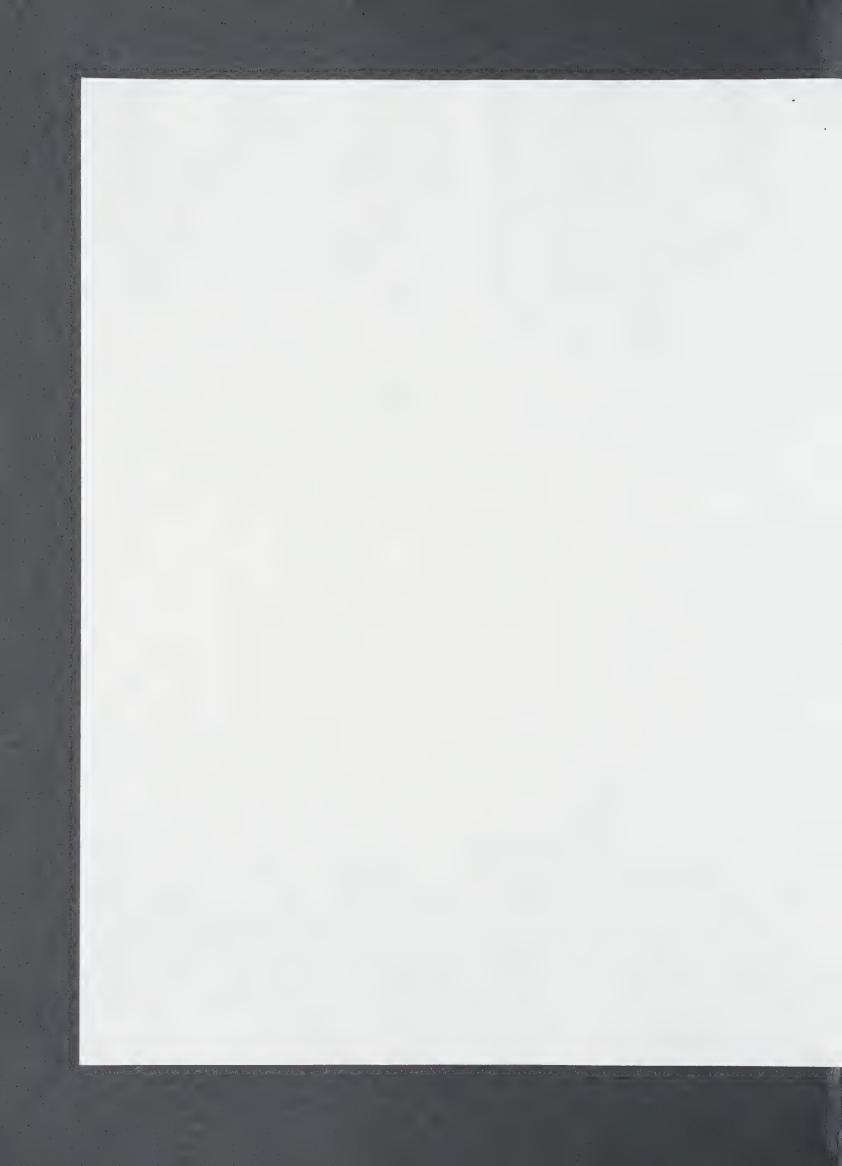
Possibly, the Zincke and Suhl reaction fails in nitrobenzene (see experiments 11, 12, 13, Table I) and in chlorobenzene (experiment 3) because the solvents inactivate the aluminum chloride toward complexing with carbon tetrachloride. When pure I is treated with aluminum chloride, an orange complex is formed. In the Zincke and Suhl reaction, the reaction mixture (both before and after hydrolysis) is dark-colored. This dark color is due to the byproducts formed. We believe these byproducts arise from reaction intermediates in which a trichloromethyl group is introduced in a position ortho to the phenolic group. In such a compound the chlorine atoms are activated by the ring and undergo further condensation leading to the polymers. The deep color is probably due to the presence of triarylmethyl type dyes (8).

EXPERIMENTAL

General. Melting points were determined in a Hershberg type (9) melting point apparatus using Anschütz total immersion thermometers. Boiling points are uncorrected. All solvents were redistilled in addition to further purification wherever noted. All analyses are by Clark Microanalytical Laboratories, Urbana, Illinois.

We wish to thank Mrs. Alfred Brooks, Robert Lieberman, and Albert C. Antoine for the infrared spectrograms which were taken on a Baird double beam recording spectrophotometer using sodium chloride optics.

Preparation of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (I). In the best procedure developed, a solution of 5.41 g. (0.050 mole) of redistilled p-cresol in 5 ml. of carbon disulfide was added dropwise to a stirred suspension of 8.33 g. (0.063 mole) of powdered anhydrous aluminum chloride in 25 ml. of purified carbon disulfide. During this addition (10-15 minutes) hydrogen chloride was evolved and about one equivalent of the aluminum chloride went into solution. Redistilled carbon tetrachloride (7.70 g., 0.050 mole) was added in one portion and the mixture was then heated by an oil-bath at 45°. The color darkened and more hydrogen chloride was evolved. This additional hydrogen chloride is



undoubtedly that formed by attack at the ortho position in the side reactions leading to tar formation. As the reaction proceeded, a dark brown tarry mass collected on the sides of the flask. After two hours of heating, the solvent was removed in vacuo and the mixture was decomposed by the dropwise addition of water. The use of dilute hydrochloric acid in place of water had no noticeable effect on the yield. The dienone (I) was obtained crystalline in 6.91-g. yield by steam-distillation. A dark tar remained in the flask. Recrystallization of the product from petroleum ether (Skellysolve B, b.p. 65–70°) afforded 6.79 g. (60.3% yield) of I, m.p. 103.8–104.2°, carbonyl band at 5.95 μ (taken in mineral oil, Nujol, mull). When 7.5 g. (0.0563 mole) of aluminum chloride was added to a solution of 11.30 g. (0.050 mole) of I in 25 ml. of carbon disulfide, an orange-yellow complex formed. After two hours at reflux followed by decomposition with 10% hydrochloric acid, I was recovered in 96.6% yield (10.91 g.). It is notable that no dark tarry material was formed in this experiment.

Attempted reaction of I and p-cresol. Using a procedure similar to that in the preparation of I, a mixture of 15.0 g. (0.11 mole) of aluminum chloride, 5.41 g. of p-cresol, 11.28 g. of I, and 90 ml. of carbon disulfide was heated at reflux for two hours. There was no formation of a dark color during this time. The solvent was removed in vacuo and the mixture was decomposed by the cautious addition of water. The organic layer was taken into etherbenzene and washed with water, 10% sodium hydroxide (see below), water, and saturated sodium chloride solution, and filtered through anhydrous sodium sulfate. Removal of the solvent and recrystallization from Skellysolve B afforded 9.10 g. of I (80.8% recovery). A complete recovery of I from the mother liquors was not attempted. From the above alkaline extract was obtained 4.02 g. (74.3% recovery) of p-cresol, b.p. 88-91.5° at 10-12 mm.

2,6-Dibromo-4-methyl-4-trichloromethyl-2,5-cyclohexadienone. The reaction was run in the previously described manner using 5.0 g. (0.038 mole) of aluminum chloride, 4.0 g. (0.026 mole) of carbon tetrachloride, 40 ml. of carbon disulfide, and 6.7 g. (0.025 mole) of 2,6-dibromo-p-cresol [m.p. 47.0-48.0° prepared in 91.3% yield by bromination of p-cresol in acetic acid (10)]. The typical dark color formed a few minutes after heating at 40°. After decomposition, the mixture was taken up in benzene-ether and worked up in the usual manner. After removing some of the solvent by distillation and cooling, colorless crystals were formed. They were collected (see below for filtrate), washed with ether, and dried in vacuo. Attempted recrystallization of this product (0.6 g., m.p. 189-192°) from various mixtures of solvents gave only white amorphous material. The compound left no residue on ignition, contained halogen, did not form a phenylhydrazone by the usual procedure (11), and was not further investigated. The benzene-ether filtrate from above was extracted with 10% sodium hydroxide and the organic layer, which had taken on a bright orange-red color, was treated in the usual manner. Removal of solvent left 6.4 g. of a gummy solid which was extracted several times with ether to give a colored ether solution (see below) and 0.70 g. of a white crystalline solid, m.p. 160-165° and a second crop, 0.21 g., m.p. 159-166°, totaling 0.91 g. (9.4%) of crude 2,6-dibromo-4-methyl-4-trichloromethyl-2,5-cyclohexadienone. Sublimation at 1 mm. gave white crystals, m.p. 168.7-169.5° (carbonyl absorption at 5.95 μ, Nujol mull). Positive tests (12) for chlorine and bromine were obtained.

Anal. Calc'd for C₈H₅Br₂Cl₃O: C, 25.1; H, 1.3.

Found: C, 25.3; H, 1.2.

We were unable to prepare a phenylhydrazone confirming the previous report (3). The mixture melting point with a sample of the compound prepared by the bromination of I (3) was not depressed.

No pure compound was obtained from any other fraction of this reaction mixture. 2,6-Dichloro-4-trichloromethyl-2,5-cyclohexadienone. The reaction was run in the usual manner using 5.0 g. (0.038 mole) of aluminum chloride, 4.68 g. (0.03 mole) of carbon tetrachloride, 60 ml. of carbon disulfide, and 5.31 g. (0.030 mole) of 2,6-dichloro-p-cresol [m.p. 36.0-37.0°, prepared in 31.1% yield by chlorination of p-cresol in carbon tetrachloride (13)] On adding the carbon tetrachloride, no color change was observed after stirring for ten



minutes at room temperature. The typical dark color formed when the mixture was heated by an oil-bath at 50°. After two hours of stirring at this temperature, the solvent was removed in vacuo and the mixture was decomposed by the cautious addition of water with cooling. The mixture was taken up in benzene-ether, extracted twice with 10% sodium hydroxide, and worked up in the usual manner. Removal of solvent gave a yellow solid, which on recrystallization from cyclohexane, yielded 3.41 g. (35.5%) of 2,6-dichloro-4-methyl-4-trichloromethyl-2,5-cyclohexadienone as white prisms in two crops, m.p. 165.4-166.0° and 163.5-164.5° (carbonyl absorption at 5.93 μ , Nujol mull). This compound was previously prepared (3) by chlorination of the Zincke and Suhl ketone.

Methyl chloroform and p-cresol. The reaction was run in the usual manner at room temperature using 16.0 g. (0.1205 mole) of aluminum chloride, 10.81 g. (0.10 mole) of p-cresol, 40 ml. of carbon disulfide, and 14.0 g. (0.105 mole) of methyl chloroform [b.p. 74-74.5°, obtained through the generosity of the Dow Chemical Co., Freeport, Texas]. Extraction of the steam distillate with sodium hydroxide left a small quantity of an insoluble yellow oil which could not be crystallized. This residue was dissolved in 95% alcohol and about

of the steam distillate with sodium hydroxide left a small quantity of an insoluble yellow oil which could not be crystallized. This residue was dissolved in 95% alcohol and about 0.5 g. of 2,4-dinitrophenylhydrazine was added, the mixture being heated to effect solution. An amorphous orange precipitate which formed immediately was collected, washed with alcohol-water, and dried in vacuo, (0.02 g., m.p. 272-273°). This product did not contain halogen and was not further investigated. The filtrate was heated to boiling and one ml. of concentrated hydrochloric acid was added dropwise. On cooling, 0.60 g. of red crystals, m.p. 151-152°, separated. An analytical sample, m.p. 151.5-152.0°, was obtained by recrystallization from 95% ethanol. The compound contained chlorine inert to alcoholic silver nitrate.

Anal. Calc'd for C₁₆H₁₄Cl₂N₄O₄: C, 46.8; H, 3.7; N, 14.6.

Found: C, 47.1; H, 3.6; N, 14.7.

Accordingly this compound is probably the 2,4-dinitrophenylhydrazone of 4-(1,1-dichloroethyl)-4-methyl-2,5-cyclohexadienone. Attempts to improve the yield in this reaction showed that more polymer was formed at higher temperatures whereas no condensation occurred at temperatures around 0°.

SUMMARY

1. The yield of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone in the Zincke and Suhl reaction has been increased to $60\,\%$ (a gain of $20\,\%$) by the use of an improved method.

2. A mechanism has been presented for the Zincke and Suhl reaction.

3. The following compounds have been synthesized by means of the Zincke and Suhl reaction: 2,6-dibromo-4-methyl-4-trichloromethyl-2,5-cyclohexadienone, 2,6-dichloro-4-methyl-4-trichloromethyl-2,5-cyclohexadienone, and 4-(1,1-dichloroethyl)-4-methyl-2,5-cyclohexadienone, the latter compound being isolated as the 2,4-dinitrophenylhydrazone.

4. Attempts to use the following compounds in the Zincke and Suhl reaction with p-cresol were unsuccessful: hexachloroethane, chloroform, methylene chloride, methyl chloride, and methyl iodide.

5. Attempts to introduce an angular trichloromethyl group into 5,6,7,8-tetrahydro-2-naphthol by means of the Zincke and Suhl reaction were unsuccessful.

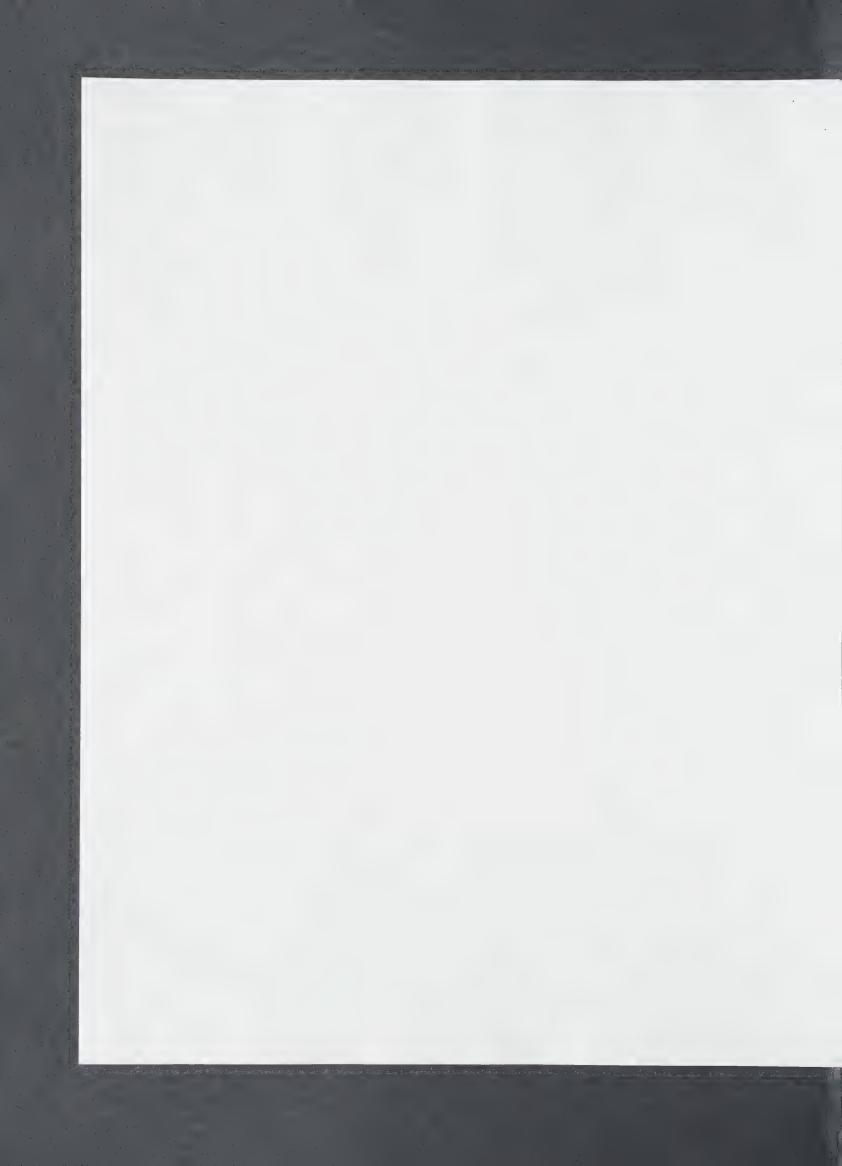
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[Contribution from the McPherson Chemical Laboratory, the Ohio State University]

THE ALUMINUM CHLORIDE-CATALYZED REACTION OF BENZOTRICHLORIDE WITH p-CRESOL

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In continuation of studies on the Zincke and Suhl reaction (1), the reaction of benzotrichloride and p-cresol was investigated. The products of this reaction consisted of 2-hydroxy-5-methylbenzophenone (I) (40.4% yield), a high-melting white compound (II) (29.4%), and a dark polymer. In spite of a careful search no trace of a substituted cyclohexadieneone similar to those formed in the Zincke and Suhl reaction (2) was found.

Analyses and molecular weight determinations indicated a formula of $C_{28}H_{22}O_3$ for II. Infrared analysis showed the absence of hydroxyl and carbonyl groups. The compound gave no color with ferric chloride solution and was inert to acetyl chloride and to potassium hydroxide in boiling ethylene glycol for 24 hours. When a solution of II in concentrated sulfuric acid was poured into water I, $C_{14}H_{12}O_2$, was obtained in almost quantitative yield. On the basis of these facts we propose that II is 6,12-diphenyl-2,8-dimethyl-6,12-epoxy-6H,12H-dibenzo[b, f][1,5] dioxocin, as indicated in the formula.

The structure of II indicated is preferred over the alternate possible structure IIa for the reason that compounds containing the heterocyclic 1,3,3-bicyclononane system in the center are fairly common. The following examples have been found in the literature (3).

On the other hand a careful review (12a) of the literature covering compounds allegedly containing a four membered ring fused to an aromatic nucleus (such as in IIa) reveals that there is insufficient evidence to establish firmly this structure in any case (12b). The structure of diphenylene (IX) however, is firmly established (13). It should also be pointed out that structures such as X and XI



are well established (3) but in these the six membered ring is non-aromatic and the carbon atoms at the points of fusion are not doubly bonded.

 \mathbf{X}

TX

XI

The structure we propose for II is similar to that proposed for "disalicylaldehyde" (XIII) and the chemical behavior (14) of the latter and II is quite comparable. A mechanism involving the stepwise formation of the bicyclic ring system through a six member ring intermediate (XII) was proposed (14). The chlorinated intermediate (XIV), which would be formed if the mechanism (see below) of condensation of benzotrichloride with p-cresol is similar to that postulated for the Zincke and Suhl reaction in the accompanying paper (2), would be expected to yield I on direct hydrolysis. On stepwise reaction of the phenolic group of one molecule of XIV with the CCl₂ group of another molecule of XIV an intermediate XIVa would be formed. Hydrolysis of the tertiary chlorine, ring closure with the remaining CCl₂ group, and cyclization of the latter tertiary chloride with the remaining OH group would yield II. The analogy with the formation of XIII is apparent.

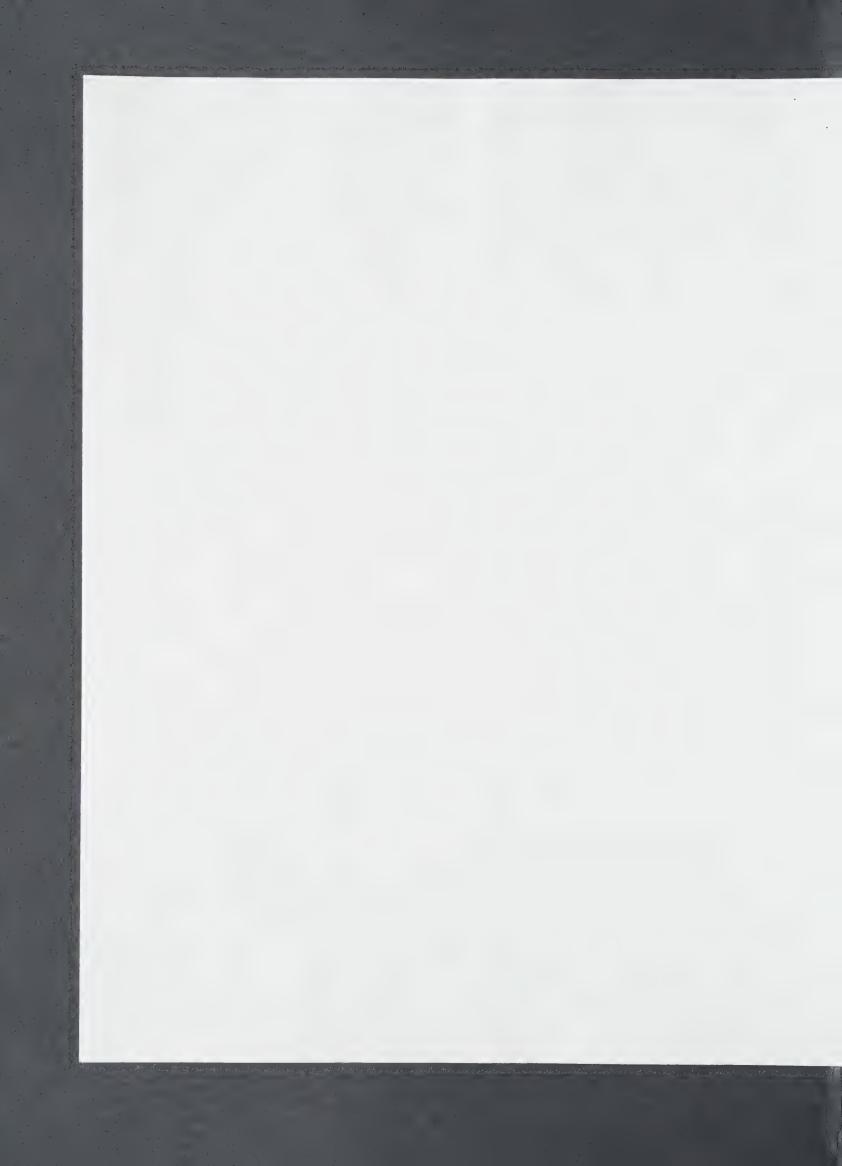


Several attempts were made to isolate the postulated intermediate (XIV), but these were unsuccessful. When the reaction mixture was treated with dry methanol, in an attempt to obtain the ketal corresponding to I, the only products obtained (in addition to the dark polymer) were I (78%) and a small amount of 2,6-dibenzoyl-p-cresol (see accompanying paper (15)). When the hydrolysis of the reaction mixture was carried out in the cold in the presence of calcium carbonate, only I (75.6% yield) was obtained, no II being detectable. Evidently acid catalysis is necessary for the formation of the dioxocin (II) from the intermediate.

However, several attempts to convert I into II with acidic reagents failed completely. Furthermore, II is quite resistant to acidic hydrolysis, the only effective method found for accomplishing this step being the dissolution of II in concentrated sulfuric acid followed by quenching of this solution in water. It is interesting to note that the solution of I in sulfuric acid is yellow whereas that of II in sulfuric acid is deep red. When the solution of II in sulfuric acid was poured into methanol only I was obtained. A dichloro compound similar to XIV has been obtained from 2-hydroxy-3,5-dibromo-4,6-dimethylbenzal-dehyde by treatment with phosphorus pentachloride (10), the corresponding dioxocin (VIII) being a by-product. Hydrolysis of this 2-hydroxy-3,5-dibromo-4,6-dimethylbenzal chloride yielded the starting aldehyde.

Several attempts were made to synthesize a compound analogous to II from disalicylide (XV) (16) by reaction with phenylmagnesium bromide and phenyllithium. Since these were unsuccessful no attempt was made with di-p-cresotide (16). It has been shown that sym-dibenzocycloöctanedione-5,11 (XVI) reacts with only one equivalent of methylmagnesium iodide (9).

When phenol replaced p-cresol in the condensation with benzotrichloride only p-hydroxybenzophenone (90%) was obtained. When chlorinated benzotrichlorides were used in place of benzotrichloride, compounds similar to I and II were



obtained, together with other compounds which are described in an accompanying paper (17).

The formation of the products, I and II, may be accounted for by a mechanism similar to that previously postulated for the formation of 4-methyl-4-trichloromethyl-2,5-cyclohexadieneone (2) from p-cresol and carbon tetrachloride. The ion pair (XVII) produced by the reaction of p-cresol with aluminum chloride, is susceptible to attack at positions 1, 2, and 3. In the case of the Zincke and Suhl reaction, condensation takes place mainly at position 1. In the case of reaction with benzotrichloride the increased steric requirements in the transition state involving benzotrichloride effectively prevent condensation from taking place at position 1. Accordingly reaction occurs at position 2 as pictured in the formula for the transition state, XVIII. The chloride ion displaced combines with the proton which is lost to yield hydrogen chloride. It is noteworthy that in this reaction the product is a chloroaluminum salt (XIX) containing an aromatic ring whereas in the Zincke and Suhl reaction the reaction product is a complex formed from aluminum chloride and a 4,4-disubstituted-2,5-cyclohexadieneone system (2).

$$\begin{bmatrix} CH_3 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} CH_3 \\ H_1 \\ CI \\ CI \\ CI \\ C_6H_5 \text{ (AlCl}_2) \end{bmatrix} \xrightarrow{+} CCl_2C_6H_5$$

$$XVII \qquad XVIII \qquad XIX$$

Acknowledgements. The authors wish to express appreciation to Dr. W. R. Stemen of Chemical Abstracts for aid in the nomenclature problem, to Dr. C. L. Wilson, Robert Lieberman, and Albert C. Antoine for the infrared spectrograms and aid in their interpretation, and to Walter Edwards for the ebullioscopic molecular weight determination.

EXPERIMENTAL

General. Melting points have been taken with Anschütz total immersion thermometers on the purest samples obtained. Boiling points are uncorrected. All solvents used have been redistilled in addition to further purification wherever noted. The analysis is by Clark Microanalytical Laboratories, Urbana, Illinois. Infrared absorption curves were taken on a Baird double beam recording spectrophotometer using sodium chloride prisms.

Aluminum chloride-catalyzed reaction of benzotrichloride and p-cresol. The procedure used was similar to that in the previous paper (2) using 8.33 g. (0.0625 mole) of aluminum chloride, 5.41 g. (0.050 mole) of purified p-cresol, 9.77 g. (0.050 mole) of redistilled benzotrichloride, and 20 ml. of carbon disulfide. The p-cresol and aluminum chloride were first reacted as before and then the benzotrichloride was added dropwise over 5-10 minutes to the mixture which was cooled by an ice-bath.

On addition of the benzotrichloride, the mixture turned black immediately with hydrogen chloride evolution. After two hours of stirring and cooling, the solvent was removed



in vacuo, and the mixture was decomposed by the cautious addition of water. (No difference in results was noted when dilute hydrochloric acid was used for the decomposition.) The product was taken up in benzene-ether and the layers were separated. The organic layer was washed in turn with water and a saturated sodium chloride solution and then filtered through anhydrous sodium sulfate. Most of the solvent was removed by distillation and petroleum ether, b.p. 65-70°, (Skellysolve B) was added gradually to the solution until the formation of crystals was noted. The mixture was then allowed to stand for 2-3 hours and then heated and filtered (see below for filtrate). After washing with Skellysolve B and drying 2.99 g. (29.4%) of II, m.p. 236.0-236.5°, was obtained. Recrystallization from dioxane-water gave colorless crystals, m.p. 236.5-236.7°.

Anal. Calc'd for C28H22O3: C, 82.7; H. 5.5; Mol. wt., 406.

Found: C, 82.6; H, 5.5; Mol. wt., 405 (ebullioscopic method in benzene using a differential water thermometer).

The Skellysolve filtrate from the dioxocin above was distilled to yield 4.57 g. of 2-hydroxy-5-methylbenzophenone (I) as a yellow solid, m.p. 76-83°, b.p. 119-122° at 1-2 mm. Recrystallization from Skellysolve B gave 4.30 g. (40.4%) of I as yellow leaflets, m.p. 82-83.0°. A further recrystallization raised the melting point to 83.6-84.0°, reported (18) 84°. The presence of benzotrichloride in the original mother liquor was confirmed by a color test (19). In alcohol solution, the hydroxybenzophenone gave a dark-greenish-blue color with ferric chloride. A mixture melting point with a sample of 2-hydroxy-5-methylbenzophenone prepared by a Fries rearrangement of the benzoate of p-cresol (18) was not depressed. The residue from the distillation above consisted of a dark polymer which gave a deep purple color when dissolved in acetone. This probably consists of a triphenylmethane dye of the type mentioned in the preceding paper (2).

The infrared spectrum of I in mineral oil (Nujol) and also in methylene chloride exhibited a strong carbonyl absorption band at 6.11 μ , an absorption band at 6.22 μ in the double bond region, and no absorption in the region assigned to phenolic hydroxyl band fundamentals. Compounds which have similar groupings such as o-hydroxyacetophenone and salicylaldehyde also show no hydroxyl band in this region. This phenomenon has been ascribed to hydrogen bonding (20).

An infrared curve of II in Nujol mull showed no absorption in the hydroxyl or carbonyl regions and evidenced four absorption bands in the region ascribed to unsaturation: 6.13, 6.17, 6.22, and 6.25 μ , the first and third being of corresponding intensity and the second and fourth being somewhat weaker. An infrared curve of "disalicylaldehyde" (XIII) showed two absorption bands in the same region i.e., 6.15 and 6.23 μ , which probably correspond to the two benzo groupings in this molecule.

In further experiments it was found that reactions run at room temperature and higher yielded larger amounts of dark polymer, whereas at temperatures lower than 0° reaction was incomplete after two hours. In a further search for other products, a benzene-Skelly-solve B solution of the reaction mixture was extracted with Claisen's alkali (21) but no alkali-insoluble compounds were found besides the dioxocin and the dark polymer.

Attempted reaction of the dioxocin (II) with potassium hydroxide. Following a general procedure (22) the dioxocin in diethylene glycol solution was heated with potassium hydroxide for 24 hours. Dilution with water and filtration gave back unchanged starting material.

Hydrolysis of the dioxocin (II) with sulfuric acid. A 0.037-g. sample of finely powdered dioxocin was dissolved in 2 ml. of concentrated sulfuric acid at room temperature to form a blood-red solution. Dilution with water returned I in 91% yield. When sulfuric acid solutions of II were poured into methanol or methanol solutions of excess sodium methoxide in attempts to obtain methoxylated compounds only I was found (compare 23).

Attempted syntheses of II. A solution of 0.038 g. (0.00390 mole) of disalicylide, m.p. 233-234° (16) in 60 ml. of pure tetrahydrofuran was treated with a solution of 0.0078 mole of phenylmagnesium bromide in the usual apparatus for one hour at room temperature after which time a negative test for Grignard reagent (24) was obtained. After hydrolysis



of the reaction mixture we were unable to find any trace of II. No II was formed in the reaction of phenyllithium with disalicylide.

Attempts to convert 2-hydroxy-5-methylbenzophenone (I) into the dioxocin (II). The methods tried were: heating at the melting point for two hours; heating with aluminum chloride at 85° for 11 hours; heating with phosphorus pentoxide in benzene for 3 hours and treatment with acetyl chloride and sulfuric acid under conditions used in the preparation of "disalicylaldehyde" (14). An orange-colored solid was formed with aluminum chloride and also with phosphorus pentoxide, but on decomposition with water, I was recovered in all cases except the last one in which the acetate (m.p. 63-64°) [reported (25) 64-65°] was found. When I or II were treated under the conditions used in the original reaction, they were recovered unchanged.

Attempted isolation of the dichloro intermediate (XIV). 1. Directly from the reaction mixture. At the completion of a typical reaction involving 8.33 g. of aluminum chloride, 5.41 g. of p-cresol, and 9.77 g. of benzotrichloride, the solvent was removed from the reaction solids through a sintered glass filter-stick. Evaporation of solvent under reduced pressure left no residue.

2. Decomposition with limited amounts of water. At the completion of a typical reaction, 0.90 g. (0.050 mole) of water was added dropwise and the mixture was stirred at 0° for 15 minutes. The solution was then siphoned off with the aid of a filter stick and evaporated to dryness under reduced pressure. A small quantity of a dark polymeric residue was obtained. In another experiment 3.25 g. (0.203 mole) of water was added to the reaction mixture. Removal of solvent from the filtered solution and washing the residue with dry ether left 2.9 g. (28.7%) of colorless crystals of dioxocin, m.p. 236.0-236.5°.

3. Decomposition in the presence of calcium carbonate. At the completion of a typical reaction, 6.24 g. (0.0625 mole) of finely powdered calcium carbonate was added and the mixture was decomposed by the dropwise addition of water. The product was taken up in benzene-ether and worked up in the usual manner. The residue obtained after removal of solvent was completely soluble in hot Skellysolve B, indicating the absence of II. On cooling the solution, I was obtained in two crops, 5.45 g., m.p. 82-83.5°; and 2.54 g., m.p. 80-81.5°, 75.6% yield. The mother liquors, on evaporation yielded a dark polymeric residue.

Aluminum chloride-catalyzed reaction of phenol and benzotrichloride. A procedure similar to the original one was used with 4.71 g. (0.050 mole) of phenol dissolved in 10 ml. of carbon disulfide, 9.77 g. (0.50 mole) of benzotrichloride, 8.33 g. (0.063 mole) of aluminum chloride, and 30 ml. of carbon bisulfide. The reaction was run at 0°. After working up in the usual manner a white solid was obtained by a vacuum-distillation. On recrystallization from Skellysolve B, 8.66 g. (90.2% yield) of p-hydroxybenzophenone, m.p. 132.0-133.0° was obtained as colorless crystals. Recrystallization of a small sample raised the melting point to 133.5-134.5°, reported 134-135° (26). The compound dissolved to give a colorless alkaline solution and a light pink color in aqueous alcohol with ferric chloride as observed previously (26).

SUMMARY

- 1. The aluminum chloride-catalyzed reaction of benzotrichloride and p-cresol in carbon disulfide produces a complex which on hydrolysis yields mixtures of 2-hydroxy-5-methylbenzophenone (I) and 6,12-di-phenyl-2,8-dimethyl-6,12-epoxy-6H,12H-dibenzo[b, f][1,5]dioxocin (II).
 - 2. A mechanism consistent with the facts has been proposed.
- 3. The dioxocin (II) on hydrolysis with concentrated sulfuric acid yields 2-hydroxy-5-methylbenzophenone (I).
- 4. The aluminum chloride-catalyzed reaction of benzotrichloride and phenol in carbon disulfide produces a 90% yield of p-hydroxybenzophenone.

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2,6-DIBENZOYL-p-CRESOL

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In an accompanying paper (1) the aluminum chloride-catalyzed condensation of benzotrichloride with p-cresol to yield 2-hydroxy-5-methylbenzophenone (I) and 6,12-diphenyl-2,8-dimethyl-6,12-epoxy-6H,12H-dibenzo[b,f][1,5]dioxocin, II,¹ was discussed. Several unsuccessful attempts to isolate the supposed chlorinated intermediate (III) were also described. In one case the reaction mixture, resulting from the condensation of equimolar amounts of p-cresol and benzotrichloride with a 25% excess of aluminum chloride in carbon disulfide, was carefully treated with dry methanol. A careful examination of the reaction products revealed that no dioxocin (II) was present. A 78% yield of I was obtained together with 4% of a new compound (IV), which we believe to be 2,6-dibenzoyl-p-cresol, on the basis of the evidence cited below.

Analysis and molecular weight determination establish the formula $C_{21}H_{16}O_3$. The infrared absorption curve was quite similar to that of I (1) the salient features of which were the lack of absorption in the hydroxyl region (characteristic for o-hydroxy carbonyl groups) and the peak at 6.11μ . In addition, IV showed a strong peak at 5.99μ , characteristic of the carbonyl group in conjugated ketones such as acetophenone, 5.93μ , and benzophenone, 6.04μ (2, 3). It was not possible to prepare a phenylhydrazone or a 2,4-dinitrophenylhydrazone from IV nor did it yield a color with ferric chloride.

IV is slightly soluble in aqueous sodium hydroxide and forms a sodium salt (soluble in benzene) when shaken in benzene with sodium at room temperature. On treatment of this yellow solution with acetyl chloride the colorless acetyl derivative of IV was obtained in quantitative yield. This reaction rules out structure V for our compound. Furthermore, the benzoate (V) has been described previously (4) and has different properties. It is noteworthy that the Fries rearrangement of p-cresyl benzoate is quite sluggish (5), and also the Fries rearrangement is interfered with if the phenolic moiety carries a nitro or benzoyl group (6). However, the acetate of I has been rearranged to 2-acetyl-6-benzoyl-4-methylphenol (5). The formation of tribenzoylphoroglucinol in 30% yield by

¹ The structures I and II in this paper are the same as those designated I and II in the accompanying paper, ref. (1).



heating the tribenzoate of phloroglucinol at 130–140° with aluminum chloride for 30 minutes has been reported (7) but no chemical evidence supporting the structure of the compound obtained was given. The same compound has been obtained by reaction of phenylmagnesium bromide with carbon suboxide (8).

We have synthesized 2,6-dibenzoyl-p-cresol (IV) in 59% yield by condensing 2-benzoyl-4-methylphenol (I) with benzotrichloride in nitrobenzene solution but the reaction failed in carbon disulfide, probably because of the insolubility of the dichloroaluminum (AlCl₂⁺) salt of I.

In a similar way 2,6-bis(3,4-dichlorobenzoyl)-p-cresol was synthesized in 93% yield from 2-(3,4-dichlorobenzoyl)-p-cresol and 3,4-dichlorobenzotrichloride (9). These syntheses are the first examples of what may be a general method for the direct synthesis of 2,6-diaroylphenols. It is noteworthy that the use of benzotrichlorides appears to be highly preferable to that of the corresponding benzoyl chlorides.

Under the conditions we used in condensing p-cresol with benzotrichloride (1) in carbon disulfide, 2,6-dibenzoyl-p-cresol (IV) was not formed. Only when the reaction complex was treated with methanol was it possible to isolate a small amount of IV. When the reaction complex was treated with water, no IV was formed. However, in the case of 3,4-dichlorobenzotrichloride a chlorinated analog of IV was formed directly (9). The formation of IV when the reaction complex is treated with methanol is undoubtedly due to the further condensation of unreacted benzotrichloride with some partly decomposed complex. We have always found that unreacted benzotrichloride was present after condensations involving equimolar amounts of p-cresol and benzotrichloride, but never any p-cresol. The dark resins formed in small amounts in all of these condensations undoubtedly arise from condensation of the 1:1 condensation complex with p-cresol. If some solvent, e.g. nitrobenzene, were used in which the complex formed was soluble, other results would probably be obtained. We hope to study this and other aspects of this problem.

The fact that 2,6-dibenzoyl-p-cresol (IV) is slightly soluble in aqueous sodium hydroxide but forms a sodium salt when shaken with sodium in benzene at room temperature indicates that the benzoyl group has an effect intermediate between that of secondary alkyl and tertiary alkyl groups with regard to the behavior of 2,6-disubstituted phenols towards various alkaline reagents (10).

EXPERIMENTAL

General. Melting points were taken with Anschütz total immersion thermometers. All liquids were redistilled in addition to further purification wherever noted. The molecular weight determination was by an ebullioscopic method in benzene using differential water thermometers. The authors are indebted to Walter Edwards for the ebullioscopic molecular weight determination and to Robert Lieberman for the infrared curve taken on a Baird double beam recording spectrophotometer using sodium chloride prisms.

Isolation of 2,6-dibenzoyl-p-cresol (IV). A reaction involving 5.41 g. of p-cresol, 8.33 g. of aluminum chloride, and 9.77 g. of benzotrichloride was carried out as previously described (1). At the completion of the reaction (2 hours), 40 ml. of anhydrous methanol was added dropwise to the reaction mixture at 0°. A vigorous reaction occurred with the initial formation of a yellow-orange color followed by solidification of the mixture and then subse-



quent dissolution in the excess methanol. The solution was blood-red in color. After the cautious addition of water the products were isolated in the usual manner (1). On removal of solvent, 10.9 g. of a dark solid remained. Extraction with methanol removed the dark color and left 7.54 g. of a yellow residue (see below). Evaporation of part of the methanol from the extract yielded 1.06 g. of I, m.p. 78–81° as discolored yellow crystals. On heating the yellow residue from above with petroleum ether (b.p. 65–70°, Skellysolve B), an insoluble residue remained. It was collected, washed with hot Skellysolve B, and dried in vacuo, 0.35 g., m.p. 162–164° (see below). The filtrate, on cooling, yielded I in two crops, 5.89 g. and 1.23 g.; m.p. 79–81° and 82–83° resp. The total yield of I was 78%. The high-melting residue from above was recrystallized from methanol to yield 0.33 g. (4.2% yield based on benzotrichloride) of IV, m.p. 164.8–165.0°. In the preparation of an analytical sample, the material was taken up in benzene-ether and extracted with 10% sodium hydroxide (see below for extract) to remove any traces of I which was much more soluble in alkali than IV. The solvent was removed and the residue was recrystallized from ethanol to yield yellow crystals, m.p. 166.4–166.6°.

Anal. Calc'd for C21H16O3: C, 79.7; H, 5.1; Mol. wt., 316.

Found: C, 79.7; H, 5.2; Mol. wt., 321.

The sodium hydroxide extract from above, on acidification, yielded a small amount of IV, m.p. 165.0-165.5°. This shows that very little, if any, of I was present and that IV is slightly soluble in alkali. Pure IV in alcohol solution gave no color with ferric chloride. Attempts to prepare the phenylhydrazone and the 2,4-dinitrophenylhydrazone were unsuccessful.

Synthesis of 2,6-dibenzoyl-p-cresol (IV). To a stirred suspension of 3.0 g. (0.023 mole) of aluminum chloride in nitrobenzene was added 2.12 g. (0.01 mole) of I. After stirring for 15 minutes, during which time hydrogen chloride was evolved and a homogeneous solution was formed, 1.95 g. (0.10 mole) of benzotrichloride was added. The stirred mixture was heated at 70° for two hours during which time a dark green complex separated. The mixture was treated with ice and the nitrobenzene and unreacted benzotrichloride were removed by steaming. The steam-distillation was stopped when unreacted I was observed as a yellow solid in the condenser. The residue was collected, dried, and recrystallized from alcoholbenzene. Pure IV, m.p. 166.0–166.5°, was obtained in 59% yield (1.87 g.). A mixture melting point with a sample of IV isolated as described above from the reaction of p-cresol with benzotrichloride showed no depression.

An attempt to prepare IV by condensing p-cresol with two moles of benzotrichloride in nitrobenzene failed. It is noteworthy that nitrobenzene proved to be an unsatisfactory solvent for the condensation of carbon tetrachloride with p-cresol (11). The attempted condensation of I with benzotrichloride in carbon disulfide also failed, probably because

of the insolubility of the dichloroaluminum salt of I in the solvent.

2,6-Bis(3,4-dichlorobenzoyl)-p-cresol. To a stirred suspension of 2.70 g. (0.02 mole) of aluminum chloride in 20 ml. of carbon disulfide was added a solution of 2.52 g. (0.009 mole) of 3,4-dichlorobenzoyl-p-cresol [see (9) for preparation]. Hydrogen chloride was evolved and an orange complex, partly soluble, separated. On addition of 2.38 g. (0.009 mole) of 3,4-dichlorobenzotrichloride the mixture turned very dark at room temperature but no hydrogen chloride evolution occurred until the mixture was warmed to 35°. After two hours at 35° the solvent was removed under reduced pressure and the residue was treated cautiously with cold water. The organic matter was taken into benzene-ether and after the usual washings, there was obtained by crystallization from benzene-Skellysolve V, 3.77 g. (92.8%) of 2,6-bis(3,4-dichlorobenzoyl)-p-cresol, m.p. 172.5-174.0°, in three crops The melting point was not depressed by admixture with a sample isolated from the reaction of p-cresol with 3,4-dichlorobenzotrichloride (9).

Preparation of the acetate of IV. A solution of 0.325 g. (0.0011 mole) of IV in 10 ml. of dry benzene was treated with small pieces of clean sodium at room temperature with occasional shaking over a period of two hours with gentle heating at the end to ensure complete reaction. The solution was decanted from the excess sodium and the flask and sodium



were washed with benzene until the washings were no longer colored yellow. The washings were combined with the solution. Acetyl chloride was then added dropwise to the yellow solution until decolorization was effected by one drop, six drops being used. The solution was filtered from the sodium chloride formed. On removal of solvent, 0.399 g. (99.7%) of the acetate of IV, m.p. 118-119.5° was obtained. An analytical sample was obtained by recrystallization from Skellysolve B as colorless plates, m.p. 119.4-120.0°.

Anal. Calc'd for C23H18O4: C, 77.1; H, 5.1. Found: C, 77.3; 77.3; H, 5.5, 5.4.

This acetate could not be prepared by acetylation in the usual way.

SUMMARY

1. 2,6-Dibenzoyl-p-cresol is formed on treating with methanol the complex resulting from the aluminum chloride-catalyzed reaction of p-cresol with benzotrichloride in carbon disulfide solution.

2. The synthesis of 2,6-dibenzoyl-p-cresol and 2,6-bis(3,4-dichlorobenzoyl)p-cresol has been accomplished for the first time by a new synthesis involving the condensation of a 2-aroyl-p-cresol with a benzotrichloride.

COLUMBUS 10, OHIO

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[Contribution from the McPherson Chemical Laboratory, the Ohio State University]

ALUMINUM CHLORIDE-CATALYZED REACTIONS OF CHLORINATED BENZOTRICHLORIDES WITH p-CRESOL

MELVIN S. NEWMAN AND A. G. PINKUS

Received January 18, 1954

In view of the interesting results obtained in the condensation of benzotrichloride with p-cresol in the presence of aluminum chloride (1, 2) the behavior of commercially available chlorinated benzotrichlorides (I) was examined. When 2-chloro-, 4-chloro-, 2,4-dichloro-, and 3,4-dichloro-benzotrichlorides were reacted with p-cresol, the corresponding chlorinated hydroxybenzophenones (II) and dioxocins (III) (1) were obtained. In addition, two other types of compounds were isolated in small yields, xanthones (IV) and 2,6-diaroyleresols (V) (2). The results are summarized in Table I.

The proportion of products isolated depended somewhat upon the method used in decomposing the reaction mixture. For example, in the reactions involving



TABLE I

YIELDS^a Obtained in the Aluminum Chloride-Catalyzed Reactions of
Benzotrichloride(s) and v-Cresol

		THEREORIDE (S) AT	p-CRESOL	
	HYDROXY- BENZOPHENONE, % (II)	DIOXOCIN, % (III)	XANTHONE, % (V)	2,6-DIBENZOYL-p- CRESOL, % (IV)
A	(1) 40.4	29.4	_	_
	78.0 75.6°	_	_	4.26
	10.0		_	
В	28.7	30.0	_	
C	34.9 ^d	16.7 ^d	19.3 ^d	
	57.3	14.0°	_	
D	22.1 ^d	32.0 ^d	10.6 ^d	
	31.8	29.8	_	-
E	56.7	8.8		14.4

^a Yields are based on the benzotrichloride. ^b Absolute methanol used in decomposition before addition of water. ^c Calcium carbonate added before decomposition with water. ^d Ether or alcohol used in working up reaction products before addition of water. ^e Benzene and hydrocarbons used in working up reaction products in conjunction with slow addition of water.

2-chloro- and 2,4-dichloro-benzotrichloride, hydroxybenzophenones (II-C and D), dioxocins (III-C and D), and xanthones (IV-C and D), were obtained if ether or alcohol were used in decomposition of the aluminum chloride complex. When benzene or petroleum ether was used, in conjunction with water, only mixtures of hydroxybenzophenones (II-C and D), and dioxocins (III-C and D), were obtained. Therefore, the xanthones were formed during the treatment of the reaction complex with ether or alcohol prior to the addition of water. The xanthones (IV-C and D), were prepared by heating the corresponding hydroxybenzophenones (II-C and D), with potassium hydroxide in ethylene glycol (3). The use of potassium hydroxide instead of sodium hydroxide (3) allows for completion of the reaction in 10 minutes at 50–60° instead of 5.5 hours at reflux (3). 2-Methylxanthone has been prepared before (3, 4) and was identical to our compound IV-C. 2-Methyl-6-chloroxanthone (IV-D) is a new compound.

According to the mechanism previously proposed (1) the reaction mixture, obtained when equimolar amounts of 2-chlorobenzotrichloride and p-cresol are condensed with the aid of aluminum chloride, contains the dichloroaluminum salt (VI) present as an insoluble complex in the carbon disulfide. When methanol or ether is used in decomposing the complex the anion formed by removing the $AlCl_2$ + as a complex ($AlCl_2$ •S+ where S is the basic solvent) evidently has a long enough life to undergo an intramolecular reaction involving the displacement of an *ortho* chlorine to yield VII which on hydrolysis yields a xanthone. When water is involved the anion picks up a proton too rapidly to undergo the cycliza-



tion and the chlorinated intermediate (VIII) is formed. On hydrolysis of VIII hydroxybenzophenones (II), or dioxocins (III), are obtained.

$$\begin{array}{c} \text{AlCl}_{2}^{1} \\ \text{CH}_{3} \\ \text{Cl}_{2} \\ \text{VI} \end{array} \rightarrow \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \text{C} \\ \text{Cl}_{2} \\ \text{VII} \end{array} \rightarrow \begin{array}{c} \text{CH}_{4} \\ \text{CCl}_{2} \\ \text{Ce}_{4} \\ \text{OH} \\ \text{VIII} \\ \end{array}$$

The absence of the dioxocin (III-A) from the reaction products when the reaction mixture of benzotrichloride and p-cresol was treated with calcium carbonate prior to decomposition with water has been discussed (1). In the cases of 2-chloro- and 2,4-dichloro-benzotrichloride, the corresponding dioxocins (III-C and D) were formed in about the same yields (see Table I) when water or more basic solvents, ether and alcohol, were used to decompose the reaction mixture. Therefore, we believe, in these cases at least, the dioxocins are formed from a complex such as IX. The elaboration of the dioxocin structure must occur during the hydrolysis as we believe it unlikely that an eight membered ring complex such as X would be formed. The internal bridging oxygen atom in the dioxocin structure (III) is the key to any mechanism involving the elaboration of the dioxocin structure by means of the stepwise formation of two six membered rings [see ref. (1) for this mechanism and note ref. (14) therein]. This oxygen can only be supplied during hydrolysis. The structures of the dioxocins are based mainly on the analogy with III-A (1) and on hydrolysis to the corresponding hydroxybenzophenones, II (see experimental).

In the condensation of 3,4-dichlorobenzotrichloride with p-cresol an appreciable amount of 2,6-di(3,4-dichlorobenzoyl)-p-cresol (V-E) was obtained. The formation of V-E did not depend upon the method used in working up the reaction products as was the case in the formation V-A (2). V-E was synthesized by treating the dichloroaluminum salt of II-E with I-E in carbon disulfide solution. The synthesis of V-A by this method was unsuccessful in carbon disulfide but successful in nitrobenzene. Hence it is apparent that the solubilities of the complex salts formed are of importance in determining the ratio of products formed.



TABLE II

ANALYSES AND PROPERTIES OF BENZOPHENONES (II) AND DIOXOGINS (III)

сомор.		M.P., °C.	ANALYSES					
	MOLECULAR FORMULA		С		Н		Cl	
			Calc'd	Found	Calc'd	Found	Calc'd	Found
IIIa	A C ₂₈ H ₂₂ O ₃ B C ₂₈ H ₂₀ Cl ₂ O ₃	236.5-236.7 254.2-255.0	82.7	82.6	5.5	5.5	14.9	14.9
	$\begin{array}{ccc} C & C_{28}H_{20}Cl_2O_3 \\ D & C_{28}H_{18}Cl_4O_3 \\ E & C_{28}H_{18}Cl_4O_8 \end{array}$	287.0-287.5 273.5-274.0 252.7-253.0	61.8	61.6*	3.3	3.5*	14.9	14.7
IIº	A B C D	83.6-84.0 66.4-67.2 76.0-77.0 92.1-92.8 90.2-90.6	59.8	59.8w	3.6	3.6**	25.2 25.2	25.3 24.7

^a All recrystallized from dioxane-water mixtures. ^b All recrystallized from Skelly-solve B except E which was recrystallized from an acetone-water mixture. All of these compounds are yellow. ^w Analyses by R. C. Warfel, Ohio State University.

Acknowledgement. We should like to take this opportunity to thank the Heyden Chemical Corporation for gifts of the benzotrichlorides used in this work.

EXPERIMENTAL

General. Melting points below 240° were taken with Anschütz total immersion thermometers. Melting points above 240° were taken on an electrically heated Fisher block with the finely powdered sample between two glass slides and are corrected to correspond with the immersion temperatures. All liquids were redistilled in addition to further purification wherever noted. Analyses by the Clark Microanalytical Laboratories, Urbana, Illinois are unmarked while those by Robert C. Warfel of The Ohio State University Chemistry Department are marked "w". We wish to thank Robert Lieberman and Albert C. Antoine for many of the infrared absorption curves which were taken on a Baird double beam recording instrument using sodium chloride prisms.

The procedure for the reactions of the chlorinated benzotrichlorides and p-cresol was the same as that used in the original reaction (1) with benzotrichloride and is not repeated. Since the methods used in the separation of the reaction products differ these are described. In Table II are listed the analytical data and properties for the dioxocins and benzophenones. In Table III are listed the significant infrared absorption bands for the dioxocins in the unsaturated region and also the carbonyl and unsaturated bands for the benzophenones.

Reaction with 4-chlorobenzotrichloride. 4-Chlorobenzotrichloride had the following properties: b.p. 99-102° at 1-2 mm., $n_{\rm p}^{25}$ 1.5704. The reaction mixture was treated in the same way as that involving benzotrichloride (1). 4'-Chloro-2-hydroxy-5-methylbenzophenone (II-B) was obtained by distillation, b.p. 143-145° at 1-2 mm. Attempted recrystallizations were unsuccessful in separating II-B from a dark-red polymeric residue.

Reaction with 2-chlorobenzotrichloride. 2-Chlorobenzotrichloride had the following properties: b.p. $102-108^{\circ}$ at 1-2 mm.; $n_{\rm b}^{25}$ 1.5788. When benzene was used in taking up the reaction products, the dioxocin and hydroxybenzophenone were obtained in a manner similar to that used with benzotrichloride (1). 2'-Chloro-2-hydroxy-5-methylbenzophenone (II-C) was obtained by distillation, b.p. $141-145^{\circ}$ at 1-2 mm. The dioxocin (III-C) was



TABLE III
INFRARED ABSORPTION DATA FOR DIOXOCINS (III) AND BENZOPHENONES (III)

DIOXOCIN ^{b, d} (III)	Unsaturated region				
A (1)	6.13	6.17	6.22	6.25	
C	6.13		6.22	6.27	
D	6.12		6.23		
E	6.13		6.22		
F (1)	6.15		6.23		
ENZOPHENONE (II)	Carbonyl		Unsaturated region		
A (1)	6.12°		6.22°		
	6.08^{b}		6.19^{b}		
Bc	6.11		6.20	6.29	
E^{b}	6.08		6.15^{f}	6.27	
	6.09			6.26	

^a Wave length in μ . ^b In Nujol suspension. ^c Approximately 10% carbon disulfide solution. ^d The absorption peaks were not well resolved for compound III B. ^e Disalicylaldehyde. ^f Shoulder.

obtained from the residue by extraction with warm ether to dissolve the dark red polymer. The remaining dioxocin was then recrystallized from dioxane-water. In other experiments when benzene-ether was used in taking up the reaction products, a mixture of the benzophenone (II-C) and 2-methylxanthone (IV-C) was obtained on vacuum-distillation. This mixture could be partly separated by fractional crystallization using Skellysolve B. The xanthone was recrystallized from methanol, m.p. 122.8–123.2°, [reported (4) 125.5°]. A sample of II-C was converted into IV-C in 66.2% yield by the reported method (3). The xanthone gave a yellowish-green fluorescence in sulfuric acid solution. When this solution was diluted with water, the xanthone was recovered unchanged. Attempts to prepare a 2,4-dinitrophenylhydrazone by the usual methods (5) were unsuccessful. A suspension of IV-C in mineral oil (Nujol) showed a carbonyl absorption band at 6.00 μ which corresponds with 6.03 μ reported (6) for xanthone in chloroform solution.

Reaction with 2,4-dichlorobenzotrichloride. 2,4-Dichlorobenzotrichloride had the following properties: b.p. 96-102° at 1-2 mm.; m.p. 47.0-48.2° [reported (7) 47-48°]. Attempts at recrystallization were unsuccessful due to the high solubility in all solvents tried. The reaction products were separated as in the case of 2-chlorobenzotrichloride except that 6-chloro-2-methylxanthone (IV-D) was recrystallized from Skellysolve B, m.p. 148.2-148.4°.

Anal. Calc'd for C₁₄H₉ClO₂: Cl, 14.5. Found: Cl, 14.8.

The xanthone gave a yellowish-green fluorescence in sulfuric acid solution. When this solution was diluted with water, IV-D was recovered unchanged. Attempts to prepare a 2,4-dinitrophenylhydrazone or a phenylhydrazone by the usual (5) methods were unsuccessful. A Nujol suspension of IV-D showed a carbonyl absorption band at 5.98 μ .

Synthesis of 6-chloro-2-methylxanthone (IV-D). In a small flask, 0.191 g. of 2,4-dichloro-2'-hydroxy-5'-methylbenzophenone was dissolved in 5 ml. of diethylene glycol with the aid of heat. About 0.1 g. of crushed potassium hydroxide was added and the mixture was heated at 50-60° with occasional shaking. A heavy precipitate formed in about ten minutes. The mixture was heated ten minutes longer, diluted with water and filtered, washing well with water. After drying, and recrystallization from Skellysolve B, 0.139 g. (83.3%) of IV-D, m.p. 148.0-148.5° was obtained. The aqueous filtrate from the reaction mixture had a bright yellow color indicating the presence of unreacted hydroxybenzophenone as the potassium salt. In the published method (3) in which sodium hydroxide is used, a reaction period of 5.5 hours at reflux temperatures is required in this type of reaction.



TABLE IV

	BULFURIC ACID HYDROLYSES OF THE DIOXOCINS (III)				
(III) DIOXOCIN	COLOR IN 100% SULFURIC	YIELD OF II OBTAINED,	MLP. of II, °C.		
A (1) B C D E	Blood-red Blood-red Orange Orange Yellow	90.7 93.3 74.4 56.7 76.4	82.0-82.5 65.5-66.0 76.0-77.0 91.5-92.5 89.5-90.5		

 $Reaction\ with\ 3,4-dichlorobenzotrichloride.\ 3,4-Dichlorobenzotrichloride\ had\ the\ follow-properties and the following and the follo$ ing properties: b.p. 80-85° at 1-2 mm.; $n_{\scriptscriptstyle D}^{25}$ 1.5868. (This compound could not be found in the literature.) The reaction products were best separated in the following manner. The dioxocin (III-E) was insoluble in hot Skellysolve B and was filtered off. Skellysolve was removed from the filtrate and the residue was taken up in acetone. Water was added to incipient crystallization. After standing for about 30 minutes the dibenzoyl-p-cresol (V-E) was collected. Further addition of water precipitated the hydroxybenzophenone (II-E). By repetition of this method of fractional precipitation V-E and II-E were more completely separated. The analytical sample of V-E was obtained by recrystallization from benzene-cyclohexane and melted at 173.6-174.0°

Anal. Calc'd for C21H12Cl4O3: C, 55.5; H. 2.7.

Foundw: C, 55.6; H, 2.6.

In alcohol solution, V-E gave no color with ferric chloride. In Nujol suspension, V-E showed a carbonyl band at $6.02~\mu$ (5.97 μ in carbon disulfide), which corresponds with that previously (2) observed for 2,6-dibenzoyl-p-cresol (V-A) at 5.99 μ . For the synthesis of

Sulfuric acid hydrolyses of the dioxocins (III). The procedure followed was essentially the same as that described (1) for the non-chlorinated dioxocin (III-A), except that in some cases, heat was needed in order to effect complete solution, a larger quantity of sulfuric acid also being used. In these cases the lower yields are probably due to increasing sulfonation. The results are in Table IV.

SUMMARY

- 1. The aluminum chloride-catalyzed reactions of four chlorinated benzotrichlorides and p-cresol were investigated and were found to yield the corresponding 2-hydroxy-5-methylbenzophenones and dioxocins. In addition, xanthones were obtained from the reactions involving benzotrichlorides bearing a chlorine in the 2-position. 2,6-Bis(3,4-dichlorobenzoyl)-p-cresol was obtained from the reaction involving 3,4-dichlorobenzotrichloride.
- 2. 6-Chloro-2-methylxanthone was prepared in $83\,\%$ yield from $2\,,4\text{-dichloro-}$ $2'\hbox{-hydroxy-}5'\hbox{-methylbenzophenone}.$
- 3. 2,6-Bis(3,4-dichlorobenzoyl)-p-cresol was prepared in 93% yield by the aluminum chloride-catalyzed reaction of 3',4'-dichloro-2-hydroxy-5-methylbenzophenone and 3,4-dichlorobenzotrichloride in carbon disulfide.
- 4. The dioxocins were each converted into the corresponding hydroxybenzophenones by sulfuric acid hydrolysis.

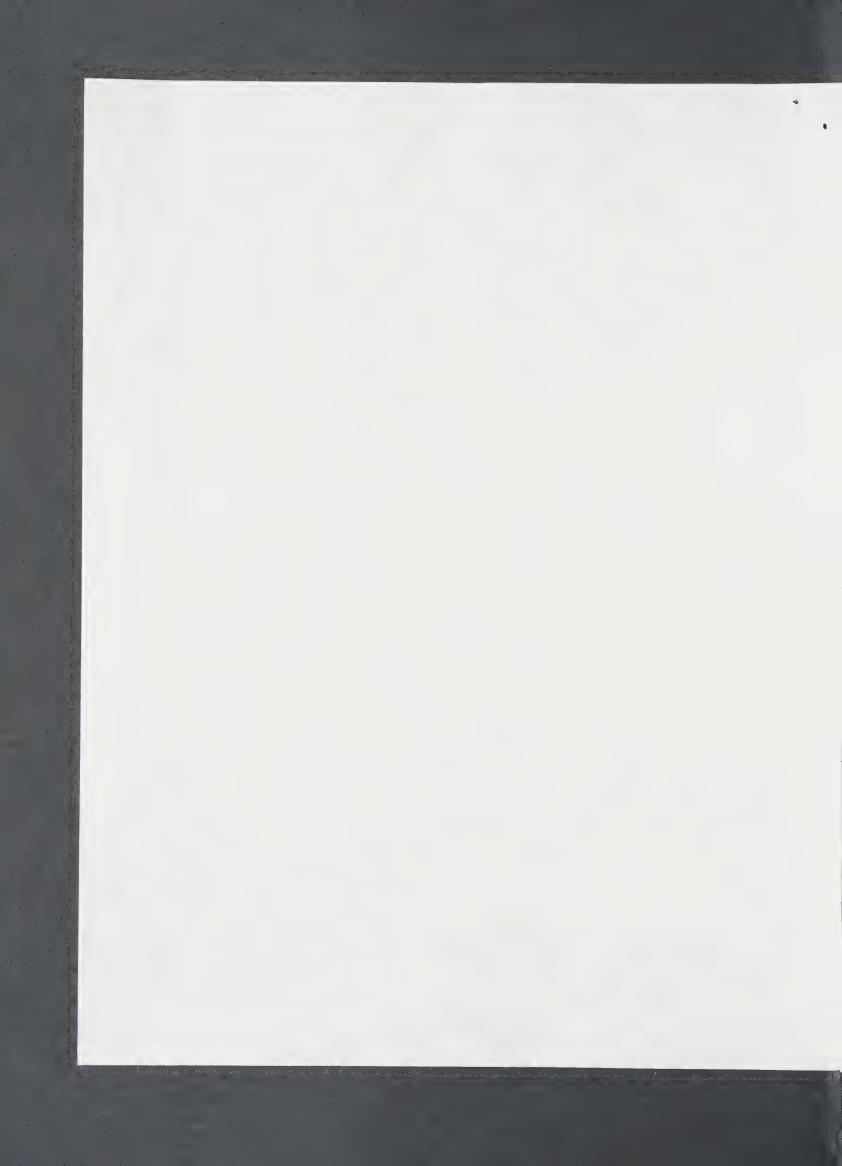
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FAX FROM:

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

A Chemist Helping Chemists

September 13, 1995

TO: PROFESSOR A.G. PINKUS

Department of Chemistry

Baylor University

FAX: 817/755-2403

Dear Al:

I am sorry that my secretary misunderstood my request about details of the restorer with whom I work on paintings.

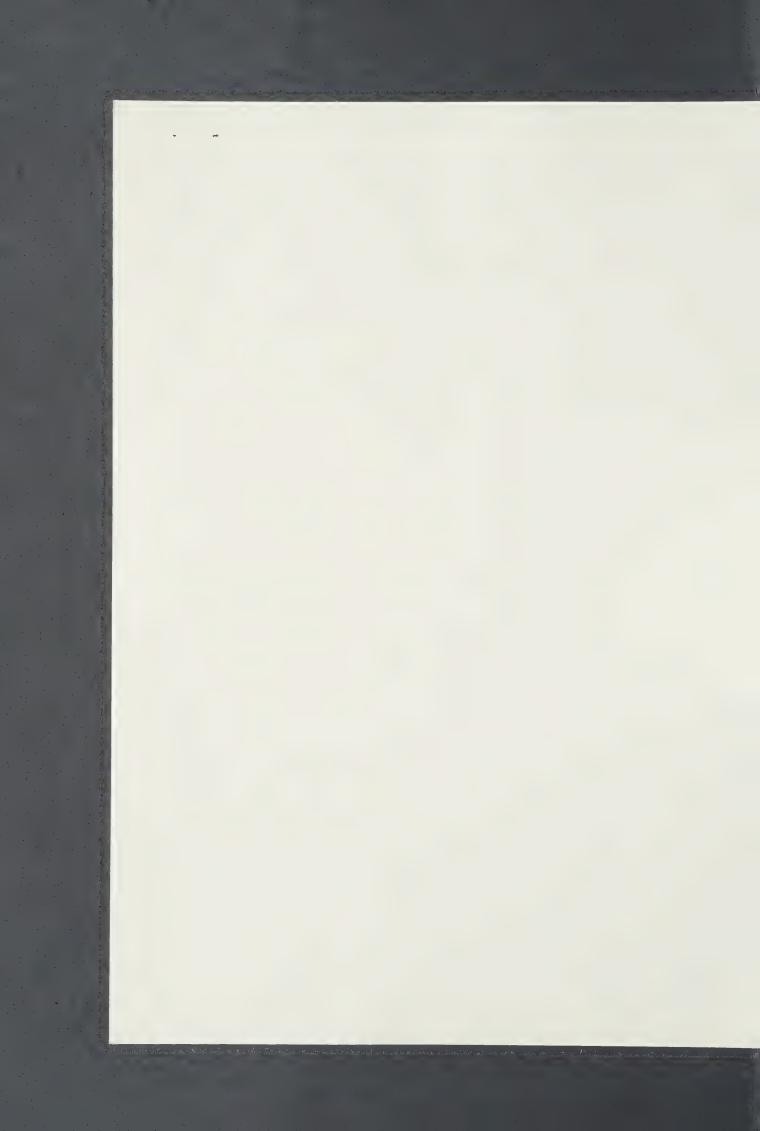
Jim deYoung works exclusively on works on paper, in the Milwaukee Art Museum.

The man who I believe can help Professor Busch is Mr. Jim Horns, whose address is 1313 - 5th Street S.E., Minneapolis, MN 55414, and whose office phone number is 612/379-3813. Please pass this on to Professor Busch.

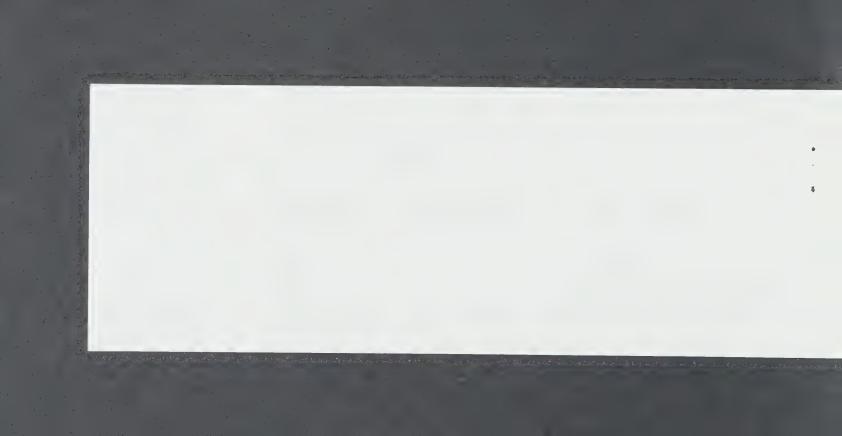
With many thanks for your help and best regards, I remain,

Yours sincerely,

AB/cw







FAX FROM:

DR. ALFRED BADER'S OFFICE

Suite 622 924 East Juneau Avenue Milwaukee, Wisconsin 53202 Telephone: 414/277-0730 Fax: 414/277-0709

September 11, 1995

TO: PROFESSOR A.G. PINKUS

Department of Chemistry

Baylor University

FAX: 817/755-2403

Dear Professor Pinkus:

Per Dr. Bader's request, here is the information for Professor Busch:

Mr. Jim deYoung The Milwaukee Art Museum 750 North Lincoln Memorial Drive

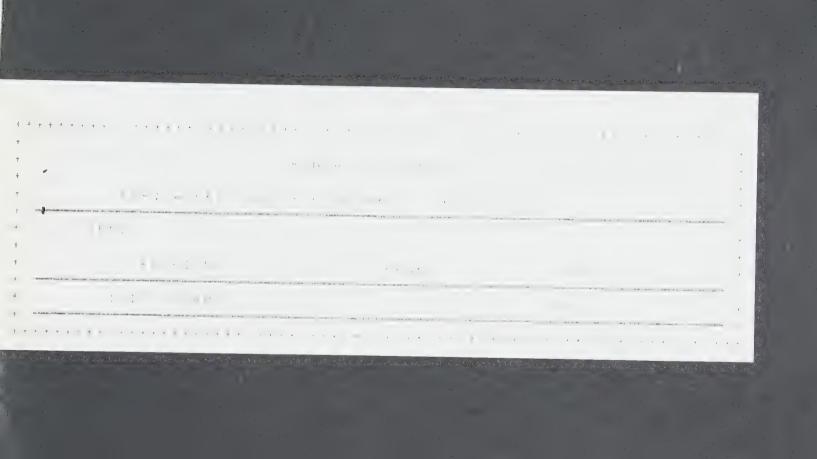
Milwaukee, WI 53202 Ph: 414/224-3275 Fax: 271-7588

Best wishes,

Cheryl Weiss Office Manager

Cheryl Weiss







FAX FROM:

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

A Chemist Helping Chemists

August 29, 1995

Page 1 of 2

TO:

PROFESSOR A.G. PINKUS

Department of Chemistry

Baylor University

FAX:

817/755-2403

Dear Professor Pinkus:

Thank you for your fast and detailed response of yesterday, but I must tell you that this scares me on several scores.

Firstly, I very much wanted to come to Waco because you are there, and you are one of the few people in the United States who know a good deal about Couper. And so, naturally, I wanted to come to speak both about Couper and Loschmidt, connected through the great personality of Richard Anschütz. And now, there may not even be a talk on either!

Secondly, as I have explained, I don't mind giving two or even three talks a day. Two is probably ideal, and four is certainly too many. But the two slide talks, each entitled "The Detective's Eye", while dealing with entirely different paintings, are so similar in content that I included them only in case some chemistry department somewhere had heard one years ago and might like to hear the second. But I think that students would be bored to hear the two talks on successive days. The talk entitled "The Bible Through Dutch Eyes" is pure art history, as, of course, is the talk, "The Rembrandt Research Project and the Collector". Hence, please do ask the Art Department to be satisfied with just one talk on "The Detective's Eye".

Thirdly, the title, "The Unimportance of a Liberal Arts Education", is a spoof, and I hadn't thought it possible that someone knowing even a little about me would take that seriously. It is a slight talk, only about 40 minutes, and if you could get a general audience for that, why not let me speak to that same audience on Couper and Loschmidt instead? I have given those talks to many audiences with many non-chemists, and I think that everyone really understood what I was talking about. It is a detective story in the history of chemistry, as you know.



PROFESSOR A.G. PINKUS Page 2 of 2

Almost all paintings that have been reasonably attributed to Rembrandt in the last 50 to 100 years were included in one of the two editions on Rembrandt's work written by Bredius and re-edited by Gerson and Bredius. Could you please ask Dr. Busch to let me know the Bredius number of his painting? If perchance it doesn't have a Bredius number, was the painting published anywhere else? Knowing that, I could prepare myself to discuss the painting with Dr. Busch.

It is very kind of you to come to the DFW Airport to pick up Isabel and me, and we will bring 30 of the books with us.

To turn now to the Americans who had published over 1,000 articles: Please remember that I was quoting H.C. Brown and not checking up on the accuracy of his statement. I do believe, though, that Herbert was correct. He certainly would not have considered Barton, Katritzky or Stone Americans, though Katritzky might by now have become an American citizen.

I used to visit Professor Stone at Bristol regularly, and he may remember that I helped him move his research chemicals to Baylor. Naturally, I hope to have the chance to see him again. When last I saw him, he had a terribly sore foot, which I hope has healed completely.

To come back to my most important concern: It appears that you have not scheduled a single lecture on chemistry to your chemistry department. Please try to schedule at least one and preferably two on Loschmidt and Couper.

With all good wishes and many thanks, I remain,

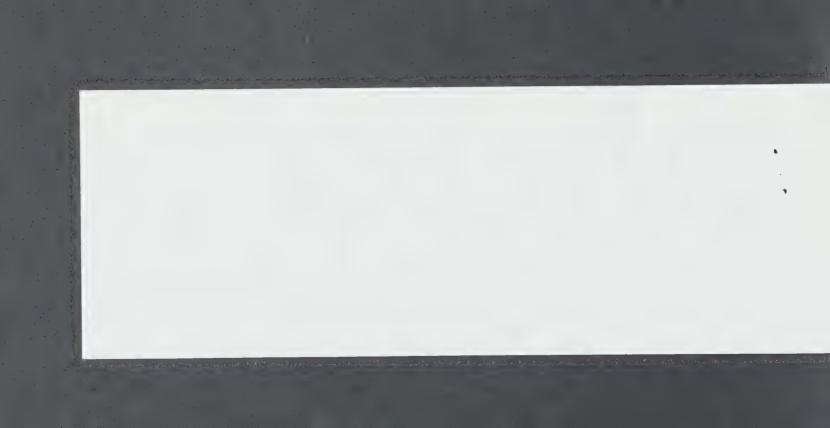
Yours sincerely,

AB/cw

Ofc. Ph.: 414/277-0730 Ofc. Fax: 414/277-0709



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BAYLOR

1 % ...

Dr. Ahred Bolle.
2961 North Snepard Avenue.
Milwankee, WI 5-211

Dear Dr Baker

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I was in the process of writing to you concerning the schedule of talks for your visit when I received your Faxed letter today. We have had a two-weeks break between the end of the summer session and the beginning of fall classes on the 28th (today). Now that everyone is back on campus from summer and interim vacations I will be able to finalize the complete schedule for your visit. I am taking you up on your note with respect to talks "...the more the better..." and am working out a busy schedule. To ensure audiences for the various talks I have contacted those who would have student classes or others interested in the particular topic to establish a basic group with others invited. So far I have the following fined ap- the History of the Aldrich Chemical Co. to the local ACS Section with a book signing following the two slide talks on the Detective's Eye to Art Dept. classes on Mon & Tuesmornings, the slide talk on the Rembrandt Research Project to the Art Center campus) followed by book signings and looking at paintings brought in (for Sunday afternoon). By the way, one of our faculty (Dr. Busch) has a painting that he says is by Rembrandt that you might be interested in seeing. There are some faculty members who are inclined to disagree with you on "the Unimportance of a Liberal Arts Education" so I will schedule a session on that topic (probably on Monday afternoon) (and invite interested facility and the Dean of the College of Arts & Sciences). This should make for a lively session. The Art Dept. might be interested in sponsoring another talk on ant. I have not yet found a sponsor for the slide talk on "The Bible through Dutch Eyes" nor the talks on Loschmidt or Anschutz, ones that I would like to hear. In case the talk on "The Bible through Dutch Eyes" does not develop, I will try to arrange for some contact with the Waco Jewish community for you. I will also arrange for you to see the collection related to the lives and works of Robert and Elizabeth Barrett Browning which is located in the Armstrong Browning Library building [1] a should give you the overall schedule so far so that you can get prepared

As I indicated earlier, I will meet you and Mrs. Bader at the DFW airport so will facilitate bringing copies of your autobiography from there to Waco. To copies or whatever you can manage without too much trouble would seem a right. We can load them into the car for the drive to Waco so that would not be any problem.



it took me a little longer than I thought to finish reading your autobiography. I had been reading the series of autobiographies of organic chemists edited by Jeffrey Seeman with the general title of "Profiles, Pathways, and Dreams" each of which I was able to finish in a day or two as they appeared and it was on this basis that I made my estimate of how long it would take. I was impressed by your remarkable detailed memory of events that happened years ago. With such detail it is difficult to read rapidly. I only found one error in your book. Do you know that there are over 150 photographs in the book! Also I was trying to think of other American chemists who might have published over 1000 articles. The only one at the moment is F. A. Cotton (now at Texas A & M University) but he may not have had that many at that time. Also there is D. H. R. Barton (also now at Texas A & M) and Alan Katritzky (now at the University of Florida) but both were not in the U.S. at that time. Another possibility in the U.S. at present is H.F. Schaefer (now at U. Georgia; previously at Berkeley) but he did not have that many publications at that time. F. G. A. Stone (now at Baylor) at the present time has published 800-900 papers- not yet 1000. Of course, it is much easier to write now with word processors and computers than it was at that time with typewriters and carbon

I will send you a more complete schedule soon 'ut the preceding outline will give you a tentative one to follow. We will be looking forward to your visit and meeting out.

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FAX FROM:

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

A Chemist Helping Chemists

September 5, 1995

TO:

PROFESSOR A.G. PINKUS

Department of Chemistry

Baylor University

FAX:

817/755-2403

Dear Professor Pinkus:

Thank you for your fax with the invitation to the gallery next Sunday. I really look forward to that and hope that the director does not object to a stranger coming in like that. (Incidentally, your fax cover sheet mentioned that you were sending five pages, including the cover, but in fact, I received only three.)

Could you please fax me the titles of my other talks - not necessarily with a timetable - so that I can get my slides and transparencies ready?

With many thanks for your help, I remain,

Yours sincerely,

AB/cw

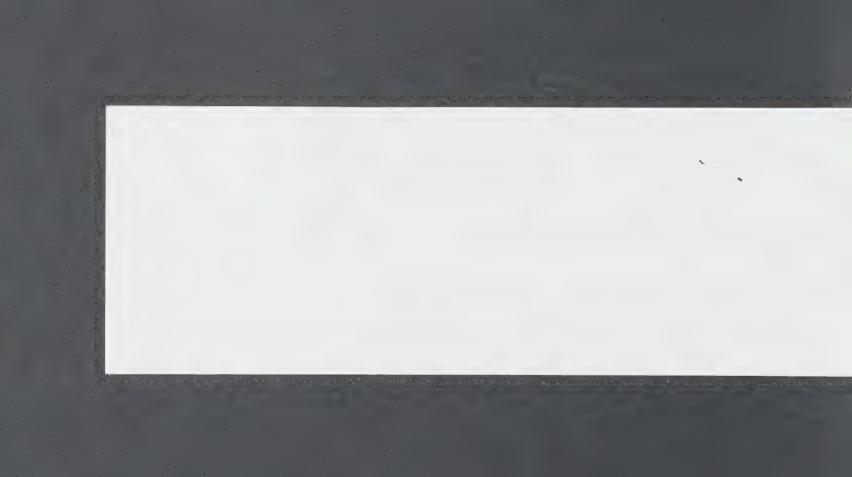
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Facsimile

Dato: Sept 5 1995

The state of the s

From: A. G. Pinkus
Dept of Chemistry
Baylor University
Waco. TX 76798
(817) 755-3311
FAX: (817) 755-2403

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, WI 53211
Tel: (414) 277-0730
FAX: (414) 277-0709
No. of pp.: 5 including cover sheet.



entrope that it is set on one of the Facsimile Date: August 9, 1995 from A G. Pinkus Dept of Chemistry Baylor University Waco, TX 76798 (817) 755-3311 FAX: (817) 755-2403 10 Dr. Aifred Bader 2961 North Shepard Avenue Milwaukee, Wi 53211 Tel: (414) 277-0730 FAX. (414) 277-0709 No. of pp.: 1 including cover street. Messaye This is to let you know that the copy of your book just arrived and to thank you for sending it. Since it will be interesting, it should not take me long to read it. I will then give you any comments. It is beautifully Illustrated and well worth the price. The book review by J. Emsley In Chemistry in Britain is about as complimentary as any I have read for a book of this type

Sincerely

A G Pirkus



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

A Chemist Helping Chemists

August 7, 1995

Professor A.G. Pinkus Department of Chemistry Baylor University P.O. Box 97348 Waco, TX 76798-7348

Dear Professor Pinkus:

Mail can be so slow, and I can thank you only now for your detailed letter of July 25th.

I wouldn't mind at all talking to your art group on late Sunday afternoon, and of the various art talks, the ones entitled "The Rembrandt Research Project and the Collector" and "The Bible Through Dutch Eyes" are, I believe, the most fitting. The second could be subtitled "Rembrandt and the Jews" and might also be of interest to a Jewish group, perhaps on that Saturday evening. In any case, I would love to look at members' paintings and tell them what I think, both about the condition and quality.

I would also love to be able to give two talks related to Loschmidt and Couper, though if only one is possible, I could talk about both together.

The only problem I foresee is how best to get from the Dallas airport to Waco. If by any chance someone in your department might be in Dallas that Saturday afternoon anyway, we love to be taken along.

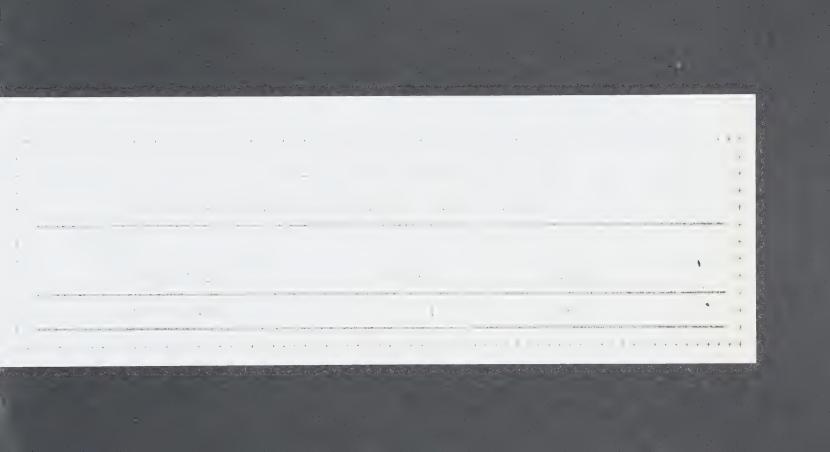
With all good wishes, I remain,

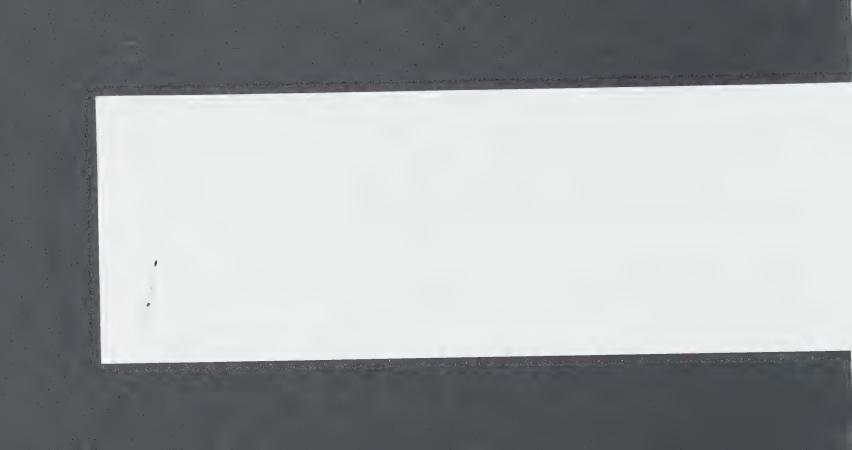
Yours sincerely,

Ofc. Ph.: 414/277-0730 Ofc. Fax: 414/277-0709

AB/cw







BAYLOR

July 25, 1995

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

Dear Dr. Bader:

You may still be vacationing in the cool climate of Europe but I thought I would write to thank you for the copies of the original correspondence relating to Couper. I have only read the letters in English (except for two in which the writing is difficult to make out); they go into more detail than the excerpts in Dobbin's paper. There is no substitute for the original. Although my reading knowledge of German is good enough to get by for reading chemical articles, it is is not good enough to get the fine points of the letters written in German even though the writing by Anschütz is very clear. It will take a bit of time for me to read those letters. It might be worthwhile to have the letters in German translated into English and published along with the letters in English. The details of the period of time when Couper left France and when he became ill are somewhat obscure and the explanation given seems unsatisfactory. The "sunstroke" explanation given by Couper's father would hardly be acceptable at the present time. I'm wondering whether there were any ancestors who had any mental problems or whether the cause might have been any of the chemicals with which Couper came in contact in his experimental work. One of the letters, however, states that "none of his relations...were ever known to be insane" according to some admission papers. Perhaps the reason is psychological and connected with his anguish over the delay in publication of his paper and the subsequent argument with Wurtz which resulted in Couper's leaving Paris for Edinburgh.

I will be interested to read your autobiography and the papers of the Loschmidt Symposium as well as your impressions of the Loschmidt Symposium.

Concerning your scheduled visit here, the arrangements are coming along well. I have reserved a room for you and Mrs. Bader at the Hilton for Sept. 10-12; it is located close to the campus. Let me know what your travel arrangements will be. Travel and housing and other costs will be taken care of or refunded to you in addition to a modest honorarium since you have been designated as a "distinguished university lecturer". The talk on "The History of the Aldrich Chemical Company" is scheduled for Monday night at 8:00 p.m. as the first meeting of the Heart o' Texas ACS Section so this talk can be directed mainly to chemists. I contacted a local art organization to see if they would be interested in sponsoring a meeting in which you would look at old paintings and give your evaluation. I got this idea from the letter you sent about one of the local ACS meeting activities scheduled. The art group were very enthusiastic about such an opportunity. However, their meetings are usually scheduled for late Sunday afternoons. I



told them that I would write and ask you about this since it would depend on your travel arrangements. They would like this to be at 6:00 p.m. or earlier. If this is not possible, I could tell them to schedule it for some other day. If it can be included, they would also be interested in hearing the slide talk on "The Rembrandt Project and the Collector" or the one on "Jan Lievens: Out of the Shadow". I will send you a complete schedule for the activities when it is all worked out.

I note that you have listed a Fax number; we have a Fax number in case you want to use it for faster communication other than the telephone. It is (817) 755-2403; however, it is not confidential since it is used by everyone in the department.

I hope you and Mrs. Bader had a good trip to Vienna and Europe.

Sincerely,

A. G. Pinkus

6. M. Frehad

