

Alfred Bader Fonds

Travel Series

Chicago [1995]

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CHICAGO



ALFRED BADER FINE ARTS

DR. ALFRED BADER

ESTABLISHED 1961

September 21, 1994

Mr. Edward Minieka
1120 Lake Shore Drive
Chicago, Illinois 60611 1042

Dear Mr. Minieka:

I am sorry that a great deal of work has delayed my visiting Chicago. I am just completing a 24-chapter autobiography which has kept my wife and me busy around the clock.

Thank you for sending me the snapshot of that painting which originally came from the R. S. Johnson International Galleries, Chicago.

That gallery, I thought, has a pretty good reputation, particularly for etchings, but this work is a rather bad copy after an original by Willem van Mieris.

Naturally I plan to visit you when next in Chicago and hope you might have some better paintings for me.

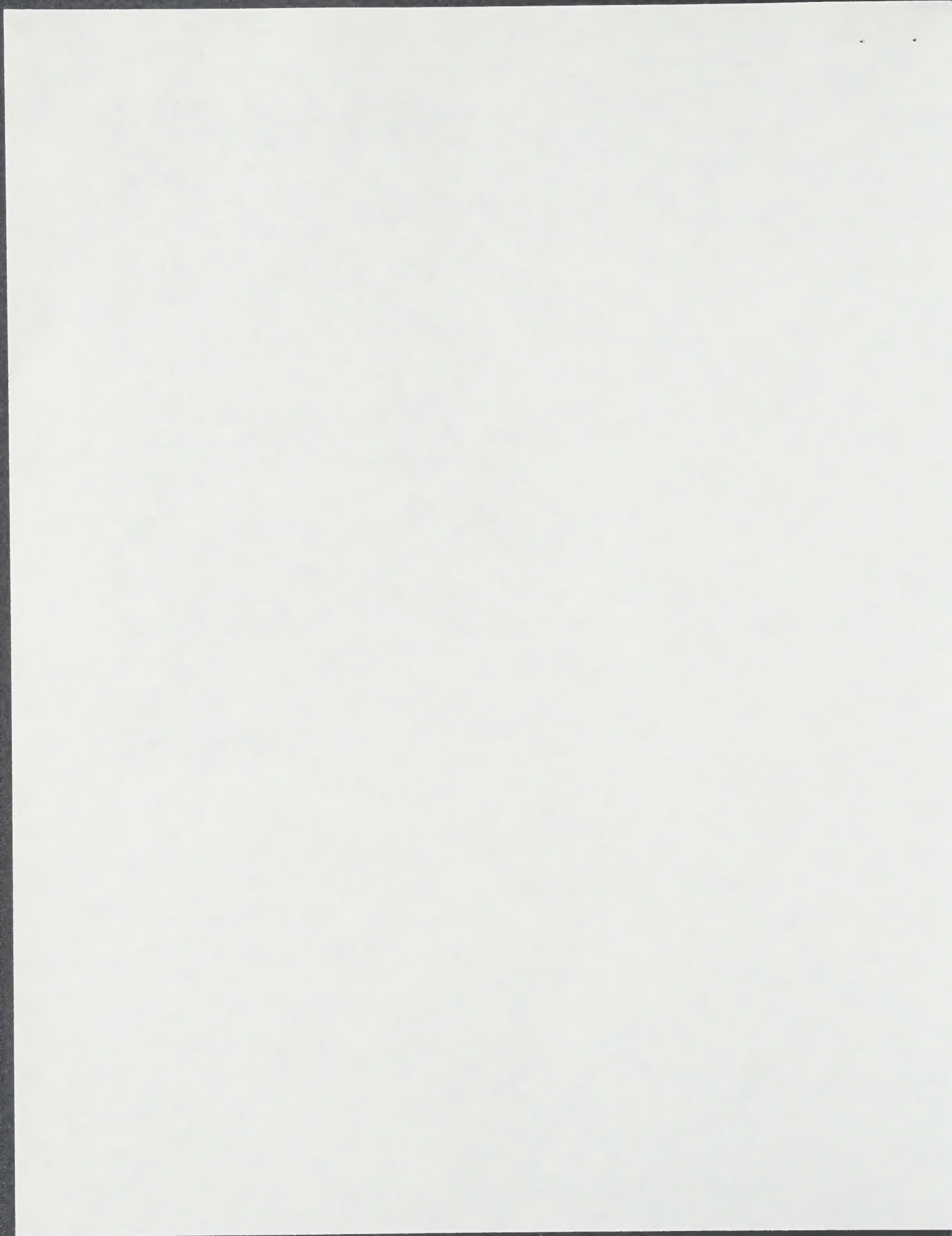
Sincerely,

Enclosure

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

Handwritten text on a small yellowed strip of paper, possibly a label or note, located at the top right corner of the page. The text is faint and illegible.





1120 LAKE SHORE DRIVE
CHICAGO, ILLINOIS 60611-1042



TELEPHONE AND FACSIMILE:
(312) 664-1573
INTERNET U09386@UIC.EDU

EDWARD MINIEKA

August 11, 1994

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

Dear Dr. Bader:

Perhaps this late 17th century Dutch gentleman holding a glass might be of interest to you or one of your clients. He is oil on panel in an ebony frame. Condition is very good. There is no signature but it looks liked the artist was someone in the circle of Franz van Mieris. The painting originally came from R.S. Johnson International Galleries, Chicago. The sight size is 6 1/2" by 5 1/2".

Happily, the consignor is not greedy so I can offer it to you for \$1300. As you know, I deal mainly in English art and antiques and don't really have a clientele for this little picture.

Please feel free to call if you have any questions.

Sincerely,

Edward Minieka
Edward Minieka

To Otto
Looks interesting
Please comment &
return photo. Thanks

Alfred Bader





ALFRED BADER FINE ARTS

DR. ALFRED BADER

ESTABLISHED 1961

April 22, 1993

Mrs. Anita Kolman
6101 North Sheridan Road, 11A
Chicago, Illinois 60660

Dear Mrs. Kolman:

It isn't every day, or even every year, that someone gives me a fine painting, and I want to thank you most sincerely for your gift, and particularly for your letter.

You have now given me a great deal of pleasure three times.

The first time was when I was able to get Professor Sumowski to write in his book that your Backer is one of the finest works by that artist which he knows.

The second time was when you made it possible for me to give the funds to Queen's University so that Queen's could buy that beautiful painting for its university art gallery.

And now the third time, with your kind letter and thoughtful gift.

I hope that when Isabel and I go to Chicago again, probably in August, you will allow us to visit with you to thank you personally.

All good wishes.

Sincerely,

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



~~██████████~~ A. KOLMAN
~~██████████~~
SUITE 1400 • ~~██████████~~ CHICAGO, ILLINOIS 60660

6101 N. Sheridan Rd^{11.}
60660 TELEPHONE
(312) ~~██████████~~
761-0444

My dearest Dr. Baider

April 12th 93

Please accept this painting as a gift to you for all your efforts in selling my Banker painting.

Why now?

And not two years ago when it was sold?

Well,

There is an expression in Arabic which I heard my mother expressing at home

"Alla ye-raa-gé ^{be} aagla" = May God return her sense her לְבָרְכָהּ to her braine."

My mother died in Israel 3 weeks ago and I have just returned from the funeral.

Perhaps this is the sort of things in life that help, or difuses wrong hurt feelings and help you see

life as it is.

Many thanks to you and may God bring you, your
wife and family good health and good life.

Sincerely

Anita Kelman

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

February 3, 1993

Professor D. F. Shriver
Morrison Professor and Chair
Department of Chemistry
Northwestern University
2145 Sheridan Road
Evanston, Illinois 60208 3113

Dear Professor Shriver:

In response to your letter of January 25th, Isabel and I would love to come and be with you some afternoon, but unfortunately, February 26th and March 11th are filled. Would any day the week of March 15th be convenient?

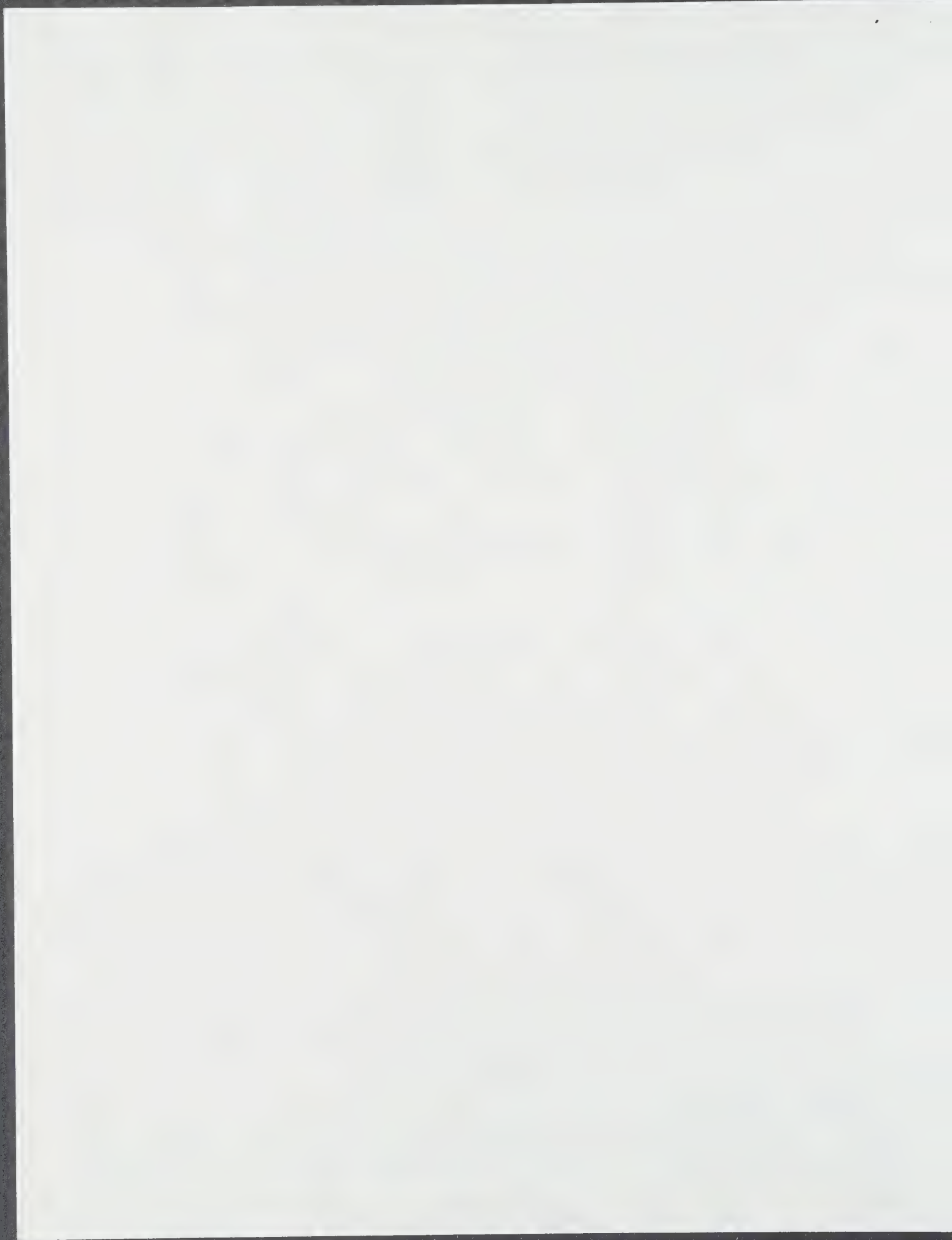
A summary of my talk on Loschmidt is enclosed.

Naturally, I hope to have a chance to visit also with Professors Hurd and Basolo.

Best regards.

Sincerely,

Enclosure



NORTHWESTERN UNIVERSITY

Department of Chemistry
2145 Sheridan Road
Evanston, Illinois 60208-3113

(708) 491-2967

January 25, 1993

Dr. Alfred Bader
2961 N Shepard Ave.
Milwaukee, WI 53211

Dear Dr. Bader:

This is a reply to your letter of October 27 in which you raised the possibility of a lecture on Josef Loschmidt. This would be an interesting addition to the department-wide colloquium series. We currently have openings on February 26 and March 11. Please give me a call if either of these fit your schedule. There should be openings later in the year if the above dates are inconvenient. You also kindly mentioned the possibility of support for the Basolo and Hurd lectures; we can discuss that when your visit.

Sincerely,



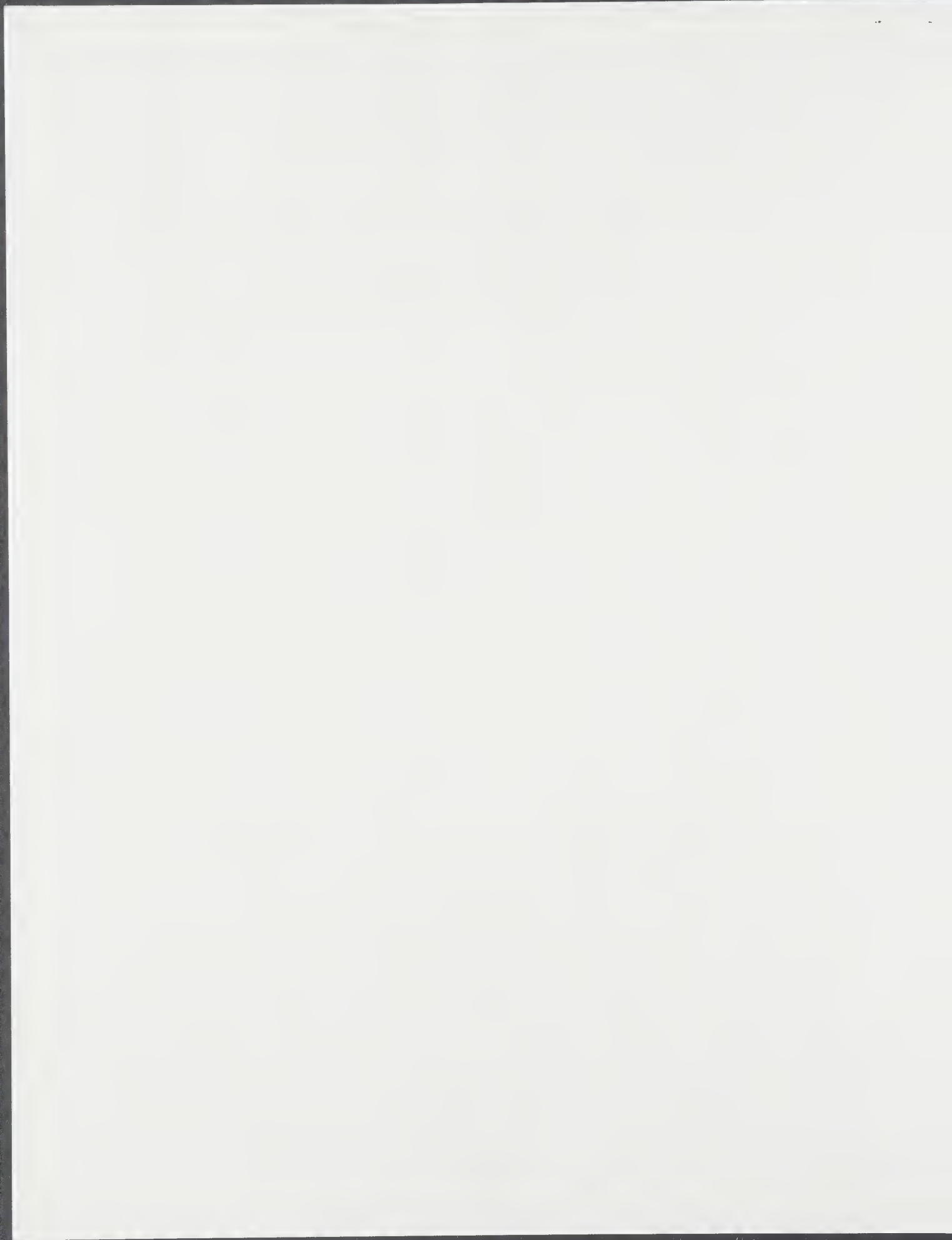
D. F. Shriver
Morrison Professor and Chair

San Antonio

C. A. S.



COLLEGE OF ARTS AND SCIENCES



Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211
September 14, 1992

Dr. Michael T. Flavin
President
MediChem Research, Inc.
Chicago Technology Park
2201 W. Campbell Park Drive
Chicago, Illinois 60612

Dear Dr. Flavin:

Thank you so much for your thoughtful letter of August 10.

I would like to meet you and look at your operation, but I visit Chicago less often than London or Ottawa. Could you, however, please send me a map showing how to get to your laboratories, and I will contact you before my next trip to Chicago.

Keep in mind that the distance from Milwaukee to Chicago is the same as that from Chicago to Milwaukee, and should business bring you to Milwaukee I will be happy to welcome you here.

Sincerely,

Trip to Chicago

MediChem Research, Inc.

Chicago Technology Park
2201 W. Campbell Park Drive
Chicago, Illinois 60612

(312) 226-7731

August 10, 1992

Dr. Alfred Bader
Chairman Emeritus
Sigma-Aldrich Corporation
940 W. Saint Paul Avenue
Milwaukee, WI 53233

Dear Dr. Bader:

Thank you for allowing me the opportunity to introduce my company to you. MediChem Research, Inc. is a contract research and development company that specializes in the synthesis of biologically active molecules.

Since our start in 1987, we have relied upon Aldrich Chemical Company as our primary supplier of chemicals. My company began as a two-person operation in a 400 square foot laboratory. Since that time we have grown to a current staff of thirteen, including three Ph.D.'s, and occupy research facilities totaling 8,200 square feet.

As president of MediChem Research, I have always admired you and your company, Dr. Bader. Your innovative approach and strong strategic planning would be an asset to a successful developing company such as our own.

Dr. Bader, I would like to take this opportunity to invite you to visit our laboratories. I know you will find the activity, innovation and entrepreneurial spirit of MediChem Research refreshing. Won't you join us for lunch and a tour of our facility?

Please feel free to contact me at (312)226-7731 to set up a convenient meeting time. I look forward to speaking with you soon.

Very truly yours,

Michael T. Flavin

Michael T. Flavin, Ph.D.
President

To

Alfred

- FOR YOUR INFORMATION
- FOR YOUR FILES
- FOR YOUR COMMENTS
- PLEASE HANDLE
- PLEASE TAKE UP WITH ME
- FOR YOUR APPROVAL
- PLEASE REPLY WITH A COPY TO THIS OFFICE
- PLEASE PREPARE AN ANSWER FOR
MY SIGNATURE
- PLEASE RETURN
- FOR YOUR SIGNATURE

Copy for you.

*Hold
for (C. Howard)*

FROM

Steve

DATE

7/68

15102



Dr. Bader: Please see Repts 24, 31, 85 and 3, 4 and 5.

W. Bader
This is the original manuscript for the journal
It includes with a long addition and correction
in the journal Chemie der Luft no 25 or 26 1992

ON THE MECHANISMS THAT GOVERN THE THERMAL BUILD-UP OF POLYCYCLIC AROMATICS AND SOOT.*

Ulbert E. Wiersum

Rizo Research Laboratories Arnhem, Corporate Research, P.O. Box 9300, 6800 SB, Arnhem The Netherlands.

Summary.

Despite the concern about environmental damage by polycyclic aromatic hydrocarbons (PAH) and their hetero analogs, in particular dioxins, present in combustion emissions, not much is known about the mechanisms and the intermediates that govern their build-up process in the high temperature gasphase¹. On the other hand PAH are very special structures in organic chemistry, as can be seen from the present excitement about the ultimate formation of the fullerenes in this process. From the early studies on, PAH have been in the center of soot, coal and carbon chemistry, and later on in cancer research. Independent from all analytical and toxicological studies and from a completely different angle, the detection of the preceding intermediates in the thermal formation of PAH, became possible with flash vacuum thermolysis techniques (FVT)^{2,3}. It is attempted in this review to rationalize empirical data from combustion studies, coal tar analysis and older pyrolysis work^{4,5}, on a molecular basis, by relating them with mechanistic concepts, available from FVT.
















POLYCYCLIC AROMATIC HYDROCARBONS (PAH).

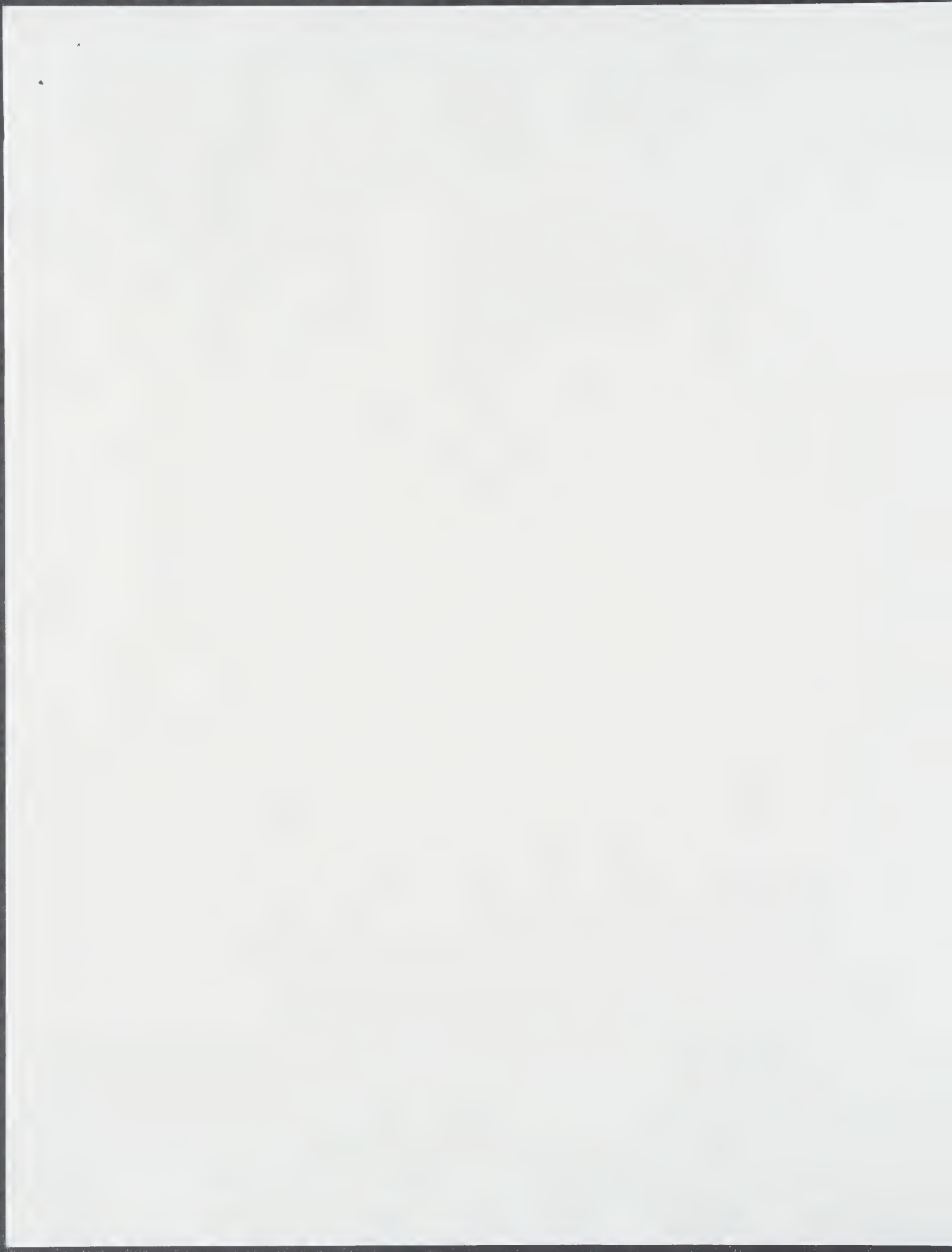
Environmental aspects:

The characterisation of PAH and their hetero analogs, like benzofurans and dioxines, occurring in soot and fly ash of combustion processes, has gained a very strong momentum, because of the environmental concern about this class. This is because of the well established toxic and mutagenic properties of some PAH⁶ and their metabolites⁷. The recent development of analytical techniques enables detection of PAH in ppm and lower concentrations. The formation of ever more PAH, mostly parent systems, but also phenols, methyl-, amino- and nitro derivatives, is detected in a large variety of

combustion processes, from waste incineration⁸, coal⁹, wood- and biomass burning¹⁰, traffic exhaust¹¹, cigarette smoking^{5,12}, to methane flames¹³ or kinetics in an ethylene feeded reactor¹⁴. Their exact identification however, in many studies of this kind¹⁵, is often restricted by the relatively few PAH that are commercially available as reference compounds. Straightforward synthetic routes for PAH are generally not available and the preparation of an individual compound is sometimes an achievement on itself. Synthetic work¹⁶, both to supply reference samples for environmental studies and model compounds to correlate structure and toxicity, is a continuous subject¹⁶. Sixteen PAH, from naphthalene to compounds with up to six fused rings (Table 1), were listed as reference compounds by the American environmental protection agency (EPA), as a representative set of PAH contaminants. These compounds are coherent because they are generally

TABLE 1: THE PAH OF THE EPA LIST

Name, Formula	Structure	Name, Formula	Structure
Naphthalene C ₁₀ H ₈		Benz[<i>a</i>]anthracene C ₁₈ H ₁₂	
Acenaphthylene C ₁₂ H ₈		Chrysene C ₁₈ H ₁₂	
Acenaphthene C ₁₂ H ₁₀		Benz[<i>b</i>]fluoranthene C ₂₀ H ₁₂	
Fluorene C ₁₃ H ₁₀		Benz[<i>k</i>]fluoranthene C ₂₀ H ₁₂	
Phenanthrene C ₁₄ H ₁₀		Benz[<i>a</i>]pyrene C ₂₀ H ₁₂	
Anthracene C ₁₄ H ₁₀		Indeno[1,2,3- <i>cd</i>]pyrene C ₂₂ H ₁₂	
Fluoranthene C ₁₆ H ₁₀		Dibenz[<i>a,h</i>]anthracene C ₂₂ H ₁₄	
Pyrene C ₁₆ H ₁₀			



found together in air, water or soil samples. On the other hand this has created the situation that characterisation of combustion emittants is sometimes focussed on the EPA series¹⁷. For example, at a glance in the Chemical Abstracts collective subject index 1982-1987, around thousand references of this kind are found for benzol[*k*]fluoranthene (12) alone.

It remains a challenge to formulate a PNH sequence, that is typical of combustion. Such a list could include some transient key compounds, that are involved in further condensations during soot formation (see below). Some characteristic combustion PNH, e.g. cyclopenta-PNH, for example aceanthrylene, (17) and acephenanthrylene, (18)¹⁹, 13,18, or pyracylene, (19)¹⁹, may degrade on exposure to sunshine or soil conditions and not be found after some time. In former days people utilized the soot from their chimneys to disinfect their garden mould. More harmful residues from the past, are left with the the PNH rich coal tar deposits, usually in unlined pits, on the grounds of coal gasification plants, that were widely operated until world war II, for household and industrial use²⁰. On the other hand PNH occur naturally in fossil fuels, both coal and petroleum^{20,21}.

The ultimate conclusion from the enormous numbers of articles spotting PNH, is that combustion, no matter what carbon and hydrogen containing fuel is burned⁵, invariably produces PNH and soot from the genotoxic variety. Since burning of fuel and organic matter occurs on an ever larger scale and many PNH are biologically rather persistent, they have become ubiquitous in the environment.

Chemical state of the art:

The advances in PNH chemistry equally inspired the formulation of the aromaticity concept in organic chemistry²², and the development of the chemical- and the petroleum industry, starting with the manufacturing of dyes from coal tar²³. Presently aromatics and their derivatives comprise about one third of the organic bulkchemicals²³.

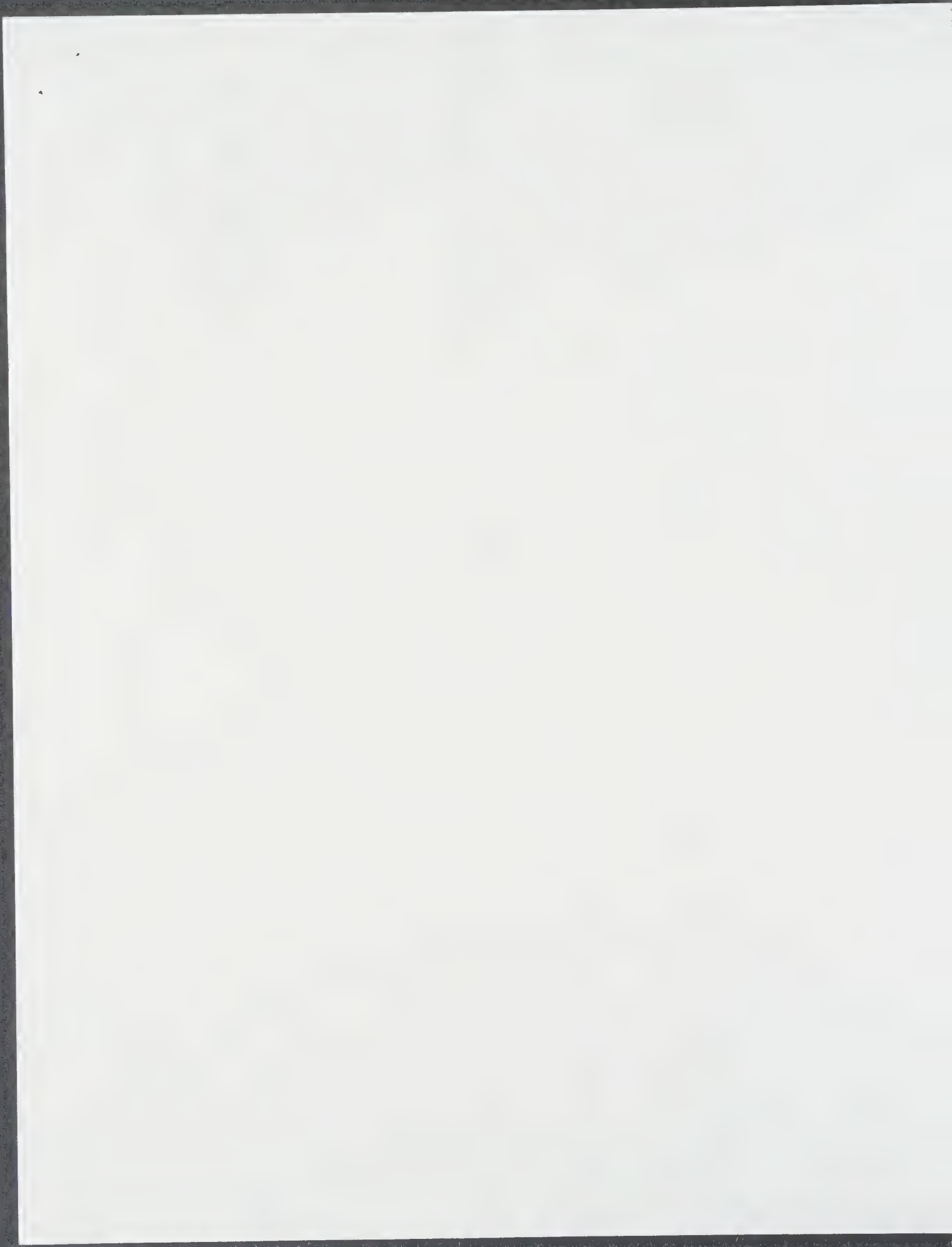
An overview of the phases, roughly marking the long and fascinating history of the chemistry of PNH, is given in Table 2.

TABLE 2: HISTORIC PERIODS MARKING PNH CHEMISTRY.

1870 - Coal tar work up and pyrolysis reactions ⁴ produced the aromatics, founding Kékulé's structure theory ²⁴ .
1900 - Based on this early work, the petroleum industry has optimised the coal tar work over the years, as the technology basis for a large range of aromatic intermediates ²³ .
1930 - PNH were implicated as the most important class of mutagens, initiating structure-activity correlation studies of toxicity ¹⁴ . Classical synthesis via Friedel-Crafts reaction followed by Elbs reaction or dehydrocyclisation ²⁵ .
1960 - Photooxygenation of stilbenes and related molecules ²⁶ . Computational studies concerning aromaticity-antiaromaticity concepts ²⁷ are ever more refined with the advances in computer technology ²⁸ .
1980 - PNH appear as the ubiquitous environmental pollutants from combustion e.g. in soot or fly ash ⁶⁻¹⁵ . Synthesis by FVT ^{2,3} .
1990 - PNH are monitored in the interstellar space ^{27,29} . The fullerene family is discovered as the third allotropic form of carbon ³⁰ .

Theoretical work:

As extended conjugated π -systems, some PNH, e.g. pyrene, (8), benzol[*k*]fluoranthene, (12), from the EPA series, feature strong fluorescence³¹, which is an analytical tool at the same time³². PNH are accessible for theoretical calculation of the coefficients and energies of the frontier orbitals of the various ringpositions³³. Calculation of the topological resonance energies, by numerical evaluation of the π -bond energies, comes to positive or negative B -values per π -electron^{27,34}, that quantitatively reveal if a PNH is



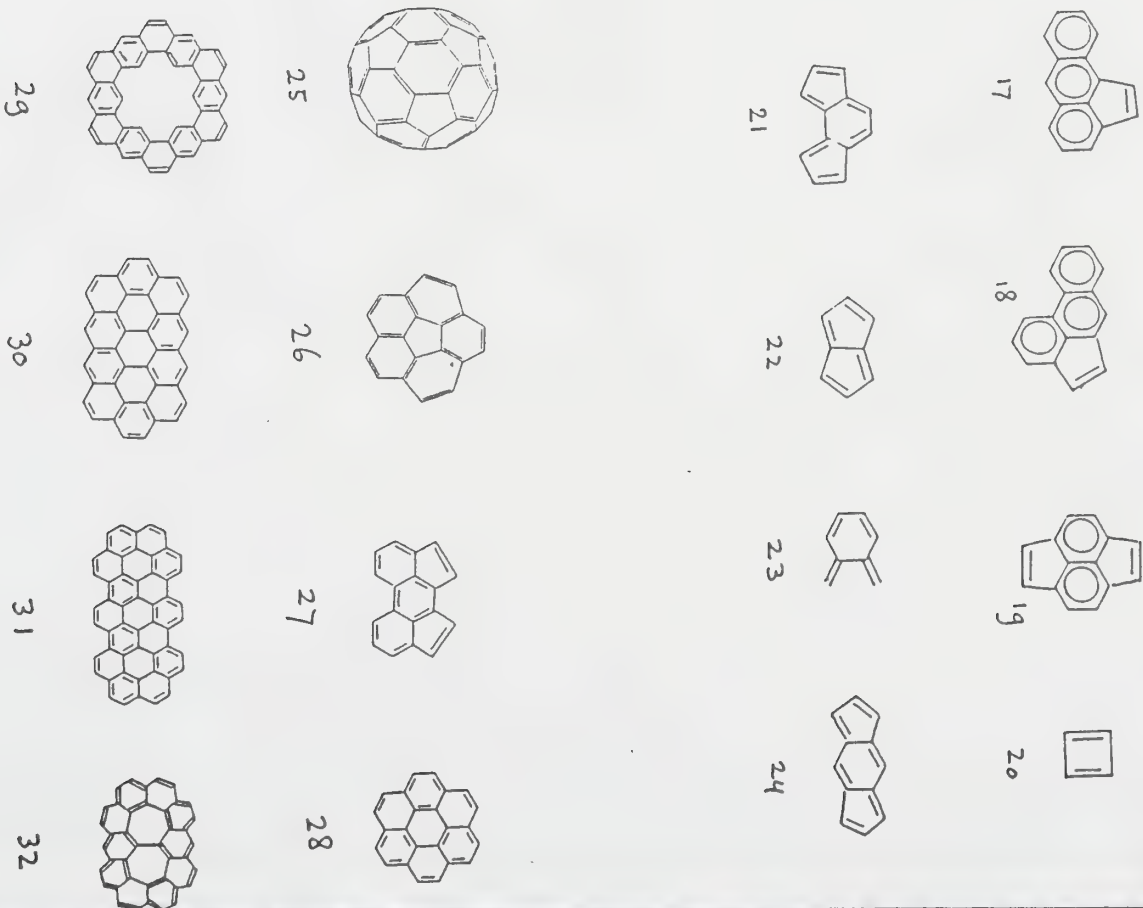
an aromatic or an antiaromatic compound respectively. In other words, they can be predicted and classified from very stable to labile to extremely reactive. In the reactive systems, although they have closed shell singlet ground states, there is only a small energy gap between the HOMO and LUMO orbitals and accordingly the triplet excited states are close in energy to the ground states. The lower the LUMO lies, the higher becomes the propensity for selfpolymerisation and attack by other molecules.³³ Usually this matches nicely with the experimental situation. Notorious examples of antiaromatics²⁷ that can not or are unlikely to be isolated, even when primarily formed, are cyclobutadiene, (20)^{28,35} and *aa*-indacene, (21)^{34,36}, (see below). Pentalene, (22)^{27,37}, *o*-xyllylene, (23)³⁴, *s*-indacene, (24)^{36,38} and pyracylene, (19)¹⁹, with β -values close to zero, can be isolated, but are highly unstable.

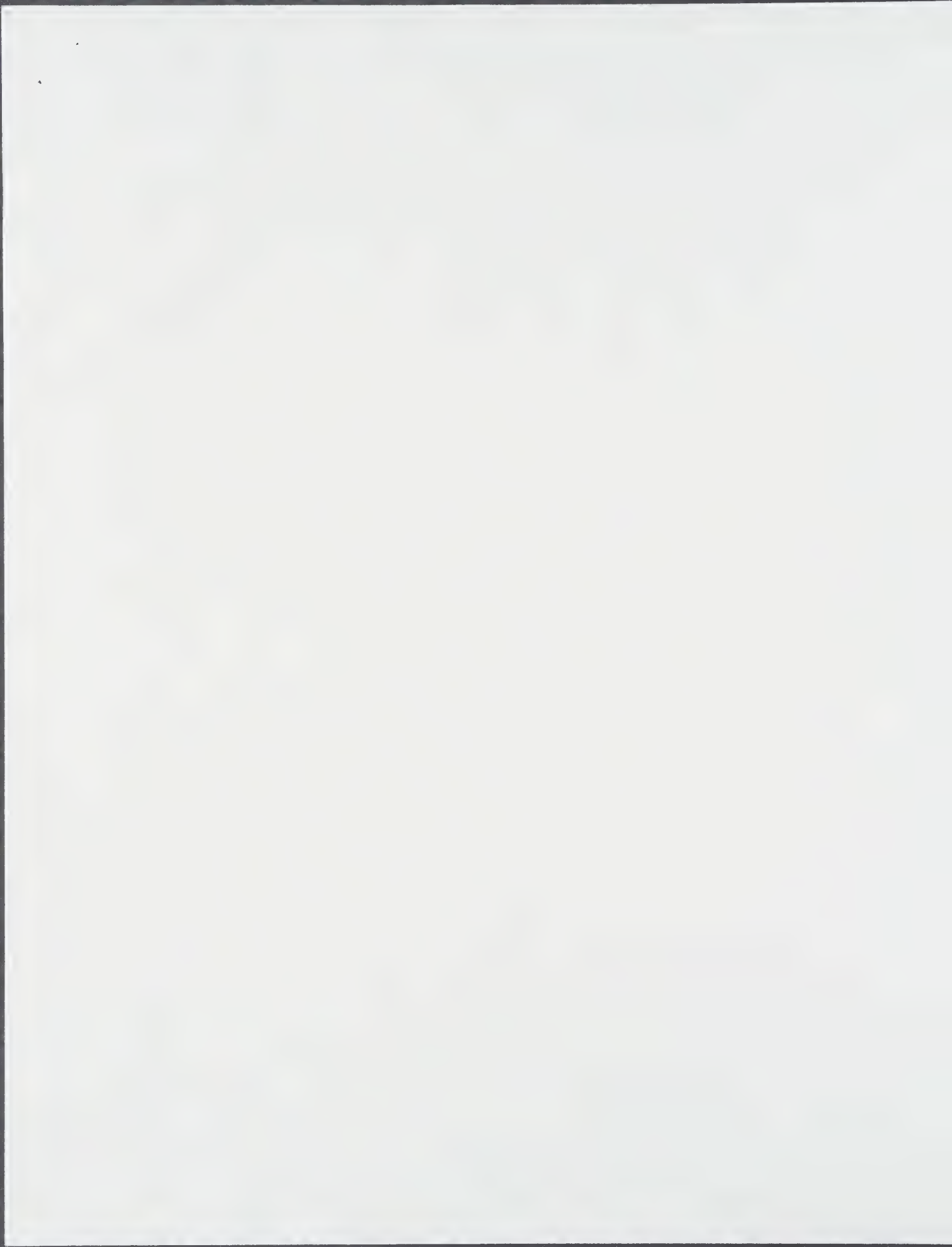
here structures 17-24

The field is recognised by the IUPAC, that sponsors the "International Symposium on Novel Aromatic Compounds", held in olympic years³⁹. The Chemical Abstracts Ring Index is a great source for tracing and naming PNH and a guideline in the almost endless amount of different possible PNH structures.

Fullerenes and substructures: superstars or curiosities?

The deduction of the fullerenes, although unconceivable without modern spectroscopy³⁰, is strictly considered based on empirical observations, much alike the 19th century examples of pyrolytic PNH formation. When a new class of PNH becomes available, the interest in its further evaluation usually develops, but the explosive output of articles concerning the fascinating fullerene family^{30,40,41}, after the discovery of buckminsterfullerene, C₆₀, buckyball, (25), is





6

unsurpassed. For most people the "molecules of the year 1991"⁴¹, emerging from the high temperature gasphase in the carbon arc, may appeal as the third allotropic form of carbon⁴², but for chemists fullerenes are in fact genuine large PAH structures, and the chemistry, in particular of 25, is well on its way^{40a}. The pronounced reactivity is due to the low lying energy of the LUMO orbitals. These orbital interactions were related to the situation in PAH substructures, that repeat themselves on the frame of 25^{40a}, like pyracylene, (19)¹⁹.

It is a challenge to synthesize smaller carbon clusters^{40b} as well as PAH that fit in the bowl shaped buckyball surface, dictated by the alternation of five and six membered rings^{40c} that are in a meta relationship^{40d} as in 2d-indacene, (21). Pyracylene, (19)¹⁹, corannulene, (26)⁴³ and cyclopent(h,i)acephenanthrylene, (27)¹⁵,⁴⁴ are among the few examples known. Very recently, NMR observations prompted the surprising conclusion that the corannulene bowl has a very low barrier to topological inversion, causing it to flip over 200,000 times per second at room temperature⁴³. Calculations of topological variations in structure show that especially the larger PAH are capable to adapt themselves to many nonplanar, chiral and nonchiral molecular geometries^{40b,45,48b}. Large PAH molecules may still have a high resonance energies in excited states so that they can survive in a hostile environment²⁷. With larger unsoluble PAH, structure determination via photoelectron spectroscopy is an analytical tool⁴⁶. Examples of flat, graphite type all six membered ring PAH are coronene, (28)²⁷,⁴⁷, kekulene, (29)⁴⁸ and the recently reported C₆₀H₆, circumanthracene, (30)^{46,49} and C₅₂H₂₀, circum(3,4)para-terphenyl (31)⁵⁰. [7,7]Circulene (32) is not flat, but has a saddlelike shape⁵¹, like some kekulene related cycloarenes

here structures 25-32

7

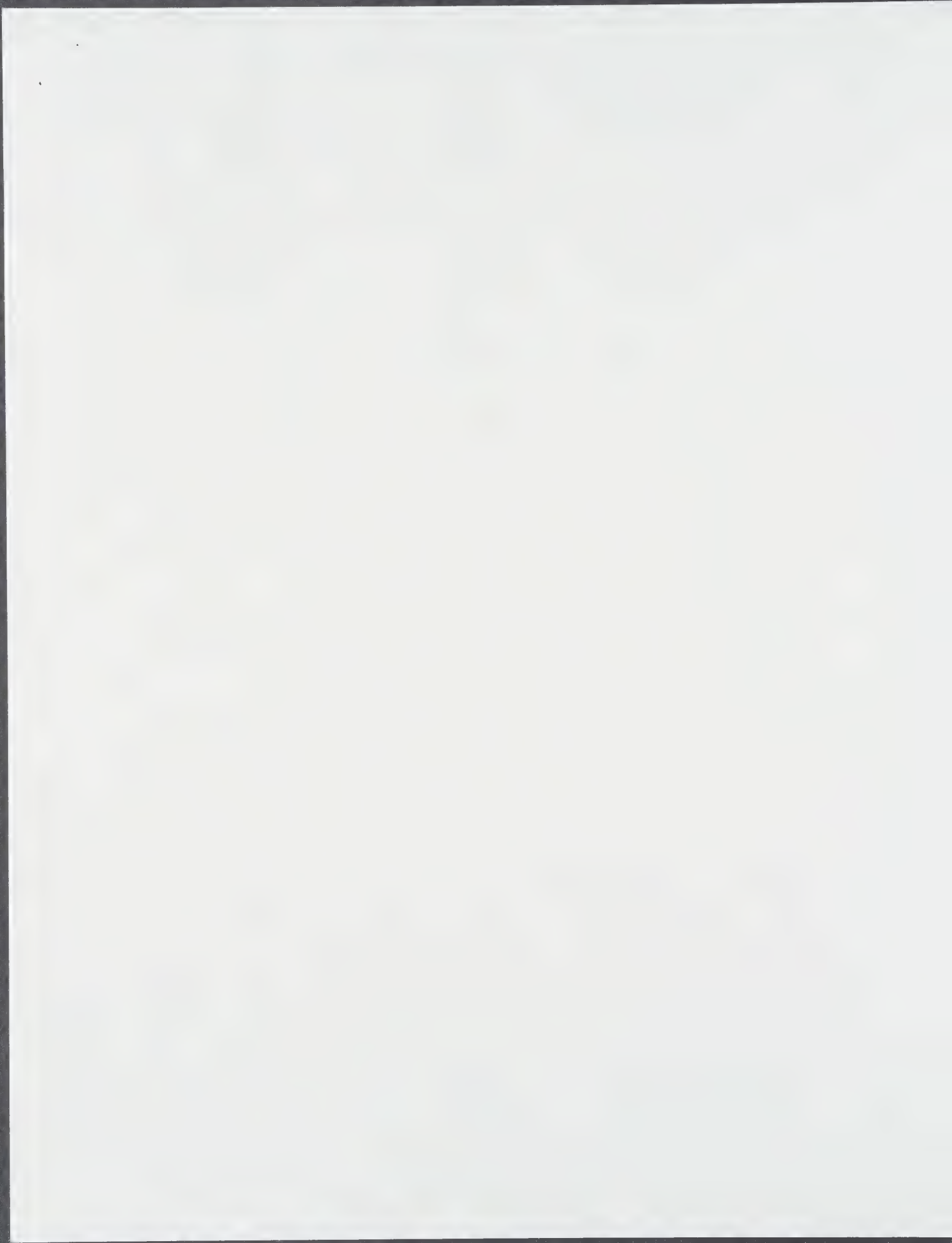
The current series of publications about the fullerenes⁴¹, allows of two striking conclusions, that may apply for in PAH chemistry in general: (i) Little is known about the mechanisms and the (sequential) reactive intermediates, foreseen by Faraday by looking in a burning candle⁵², involved in the thermal build-up of PAH and soot. (ii) New pyroaromatic systems come immediately to the forefront in computational studies, concerning aromaticity-antiaromaticity concepts^{27,34,40,45}, and in research oriented towards material science^{30c,41,53}, e.g. alignment in polymers⁵⁴, or buckyball pearl necklaces^{30c,40c}.

COAL TAR, PYROLYSIS, COMBUSTION AND SOOT.

Old summaries elaborated:

Historically, pyrolysis reactions, initially dry distillations of leaves, bones, wood, and later of coal, were applied as sources for various organic products^{3,4}. Despite the accompanying formation of tar and soot, this work gave, in the 19th century, rise to the isolation of benzene, toluene, styrene, ect. and a series of PAH. Being the only routes to aromatics at the time, one can say that pyrolysis reactions prompted the recognition of aromatic classes, in an early stage of organic chemistry^{25b,55}. Such pyrolytic processes are continued today in modern coal technology⁵⁶ and the cracking of waste plastics to fuel fractions⁵⁷. Right from the beginning of the coal tar work, individual aromatics were systematically vapourised through red hot tubes, to spot typical build up reactions of the smaller aromatics. It is interesting to read how the pioneers, in their original reports, especially in *Chemische Berichte*, describe the isolation of individual PAH and it is admirable how they assigned the correct structures. On this basis, systematic evaluations of small molecules as precursor compounds in the pyrolytic generation of PAH, were made^{5,55}.

The classic observations⁴, worthy to know when looking at PAH in



combustion mixtures, are even presently not always reasonably understood and can be reinvestigated with FVT^{2,3} (Figure). For example the formation of the EPH compounds pyrene, (8),⁵⁶ and chrysene (10),⁵⁸ by passing respectively styrene and indene through a red hot tube. Old discussions^{5,55}, concerning selective anthracene, (6), formation, where phenanthrene, (5), was expected, would have come out differently, if *o*-xyllylene, (23), had been known as a possible

here FVT figure

intermediate⁵⁹. Hydroxy-*o*-xyllylenes are thought to be intramolecularly trapped as intermediates in the Elbs synthesis². The formation of PNI with five membered rings, e.g. the cyclisations to fluorene and carbazole^{25b}, involves carbene, respectively nitrene intermediates. Benzynes and arynes are also common transients in build up reactions^{2,60} (see below).

In retrospect, some of the long known pyrolytic processes to form PMH, are intrinsically selective. This appears particularly true when they are repeated with preparative FVT (Figure). Besides, this is experimentally more convenient³.

Soot versus coal tar:

In 1955 all PNI and hetero PNI, isolated from coal tar, with certain structures, ca. 300 major constituents from over 10.000 estimated components, were listed⁶¹. Kilogram scales, sometimes

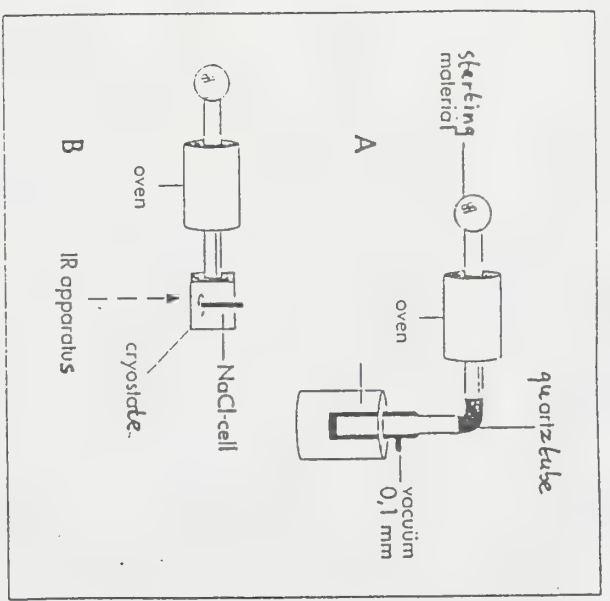
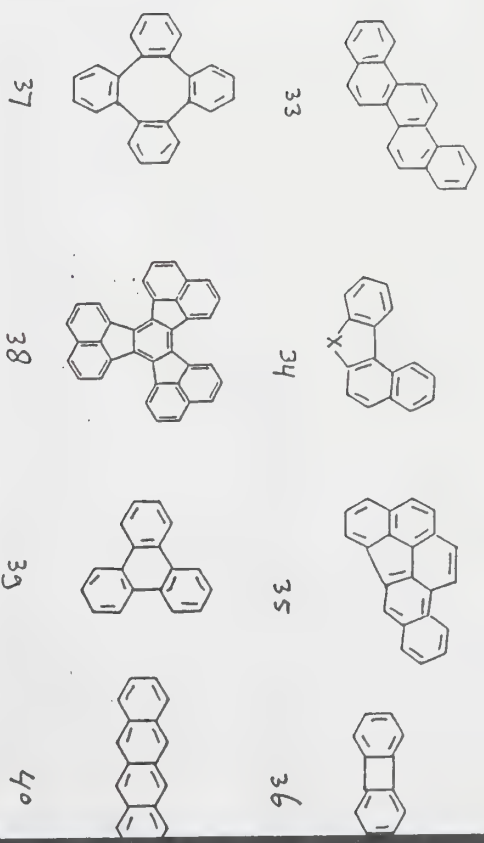
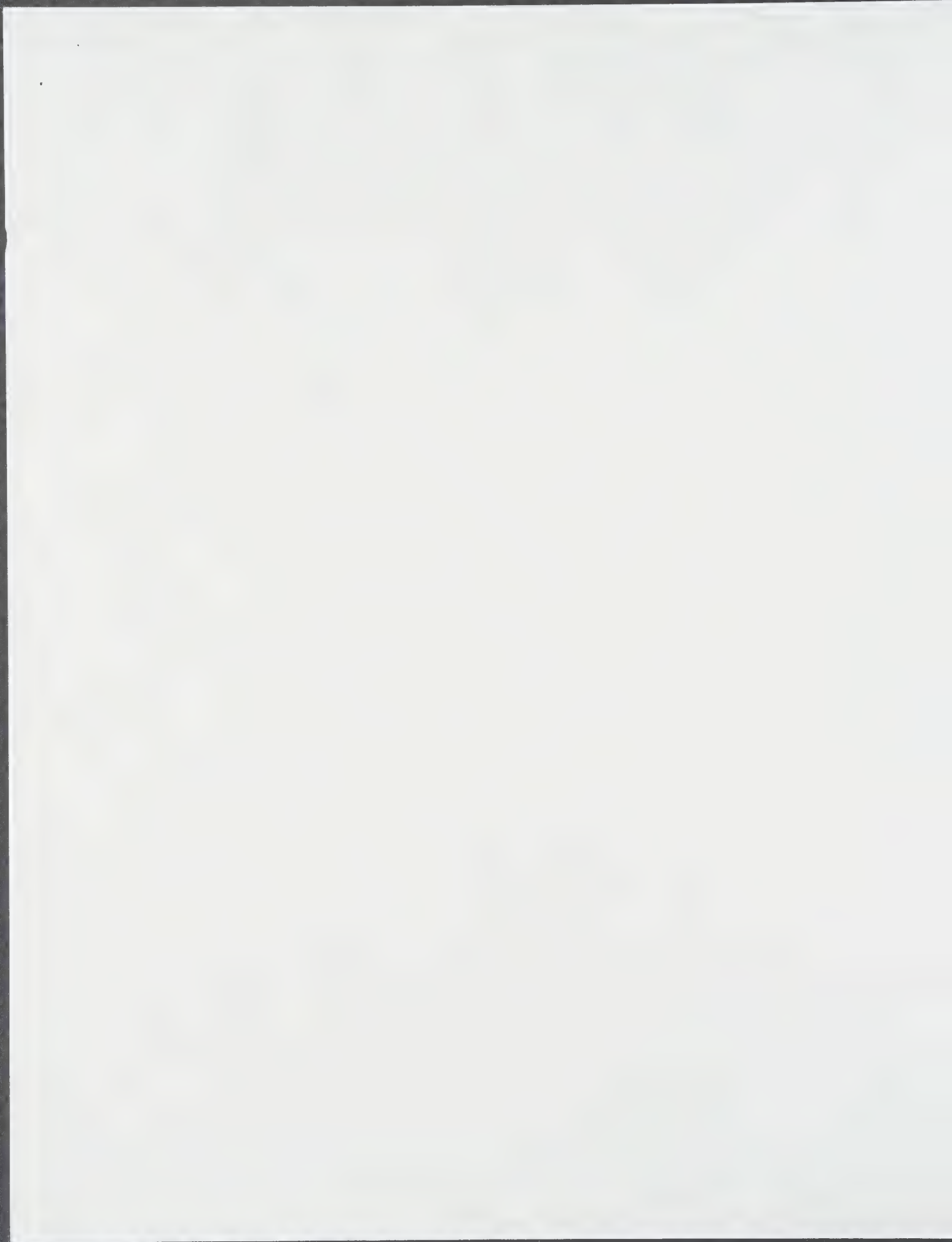


Figure: A: Preparative FVT apparatus with cold trap. A PNI or a precursor compound is sublimed into the hot quartz tube. The products are, depending on volatility, collected in the bend of the quartz tube and the cold trap. B: When the cold trap is part of a spectroscopic technique, reactives can be monitored in the cold and their sequential (condensation) reactions can be followed e.g. by warming up the IR cell.





tons⁶², were required to isolate individual PMH from various distillation fractions. The list⁶¹ is probably the shortest, but nevertheless comprehensive final documentation, of the classical coal tar period. The listed products are nicely reflected in a extensive analytical study of the soot from brown coal combustion, collected from burning it in a standard stove⁹. Nitrogen PMH, like carbazole (33) were identified from tar, collected from burning cigarettes^{5,12}. In both studies the identified PMH were categorized in types and molecular weight, including hetero (nitrogen, oxygen, sulphur) PMH. Like in the coal tar review, the reported PMH are very seldom compounds with six or more condensed rings, and even those with five rings are a minority. Here it must be emphasised that the number of possible different PMH structures does rapidly increase with more rings, without gathering much molecular weight. Among the dominant soot products of the 170 identified components, are the EPA compounds phenanthrene, (5), fluoranthene, (7), pyrene, (8), methylpyrenes, benz[*a*]anthracene, (9), chrysene, (10), and benz[e]acephenanthrylene benzol[*b*]fluoranthene, (11). Other mayor constituents are acephenanthrylene, (18), benzol[*a*]chrysene (picene), (33), benzonaphthopyroles, -furans and -thiophenes, e.g. 34, X = NH, O, S and benzol[*h*]fluoranthene (35).

here structures 33-40

A striking phenomenon in thermal behaviour of PMH is that some of them, despite their generation in the high temperature gasphase, are prone to condensation on melting, e.g. react in the molten tar phase, during work up by distillation⁶³. Soot as deposited from the gasphase on a cold surface and analysed at ambient temperatures, goes through a principally different work up condition as applied for coal tar. For example biphenylene, (36) and acenaphthylene, (2), are known to

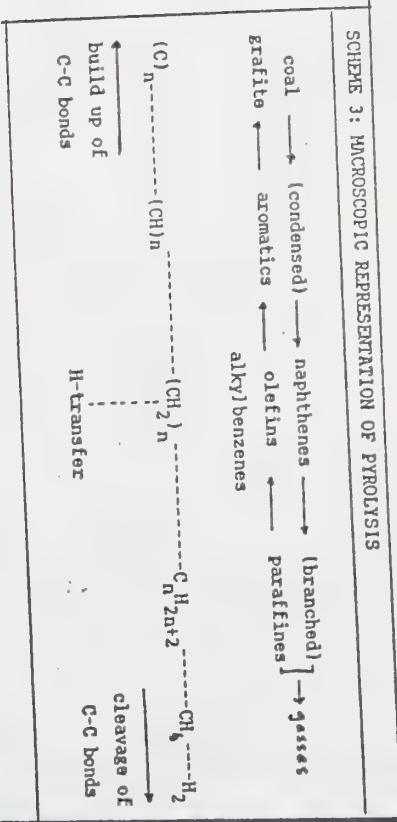
dimerise and trimerise in the melt to respectively tetraphenylene, (37)⁶⁴ and decacycene (38)⁶⁵. This phenomenon is a kinetic property, since 2 and 36 are quite stable in the hot gasphase and are found in soot of a methane flame¹³ (see below).

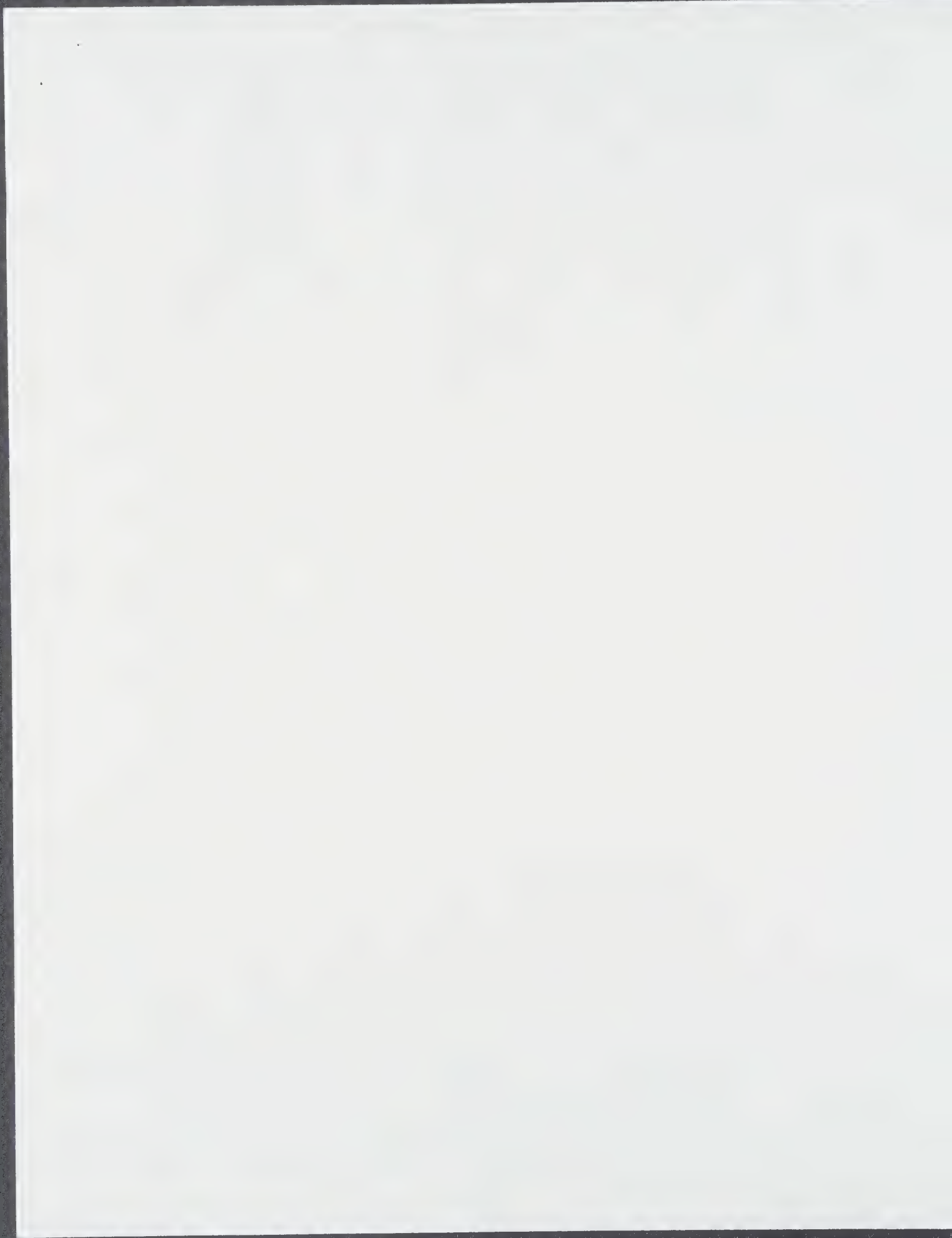
To estimate aromatic stability in the molten tar fraction, the empirical rules for alterant and nonalterant PMH, as introduced by Clar^{44,66}, apply. The more genuine benzene rings and the less quinonoid moities are required to draw alternating double bonds in the PMH skeleton, the more stable it will be. For example, alterant PMH skelton, the more stable it will be. For example, alterant triphenylene, (39), is a most stable PMH, while nonalterant pentacene (40) is not⁶⁶. Indeed, the latter compound does rapidly decompose on melting. An experimental stability ranking of the Incinerability of hazardous organic compounds, gave some EPA PMH a top position as thermally stable organics⁸.

THEMODYNAMIC AND KINETIC REPRESENTATION OF PYROLYSIS

Free carbon species:

The thermal behaviour of organic matter, in thermodynamical terms^{1a}, is summarized in scheme 3. The higher the temperature becomes, the more dissociation into the elements carbon and hydrogen occurs. At the extremes, at very high temperatures above 3000 °C, as





occurring in the carbon arc, carbon will emerge in atomic form, or can exist as the relatively stable C_2 carbene species, or $C_3 - C_{10}$ oligomers⁶⁷. For the latter types of transient cumulenyliene carbenes, although monitored in space^{29,30}, no selective ways of generation are available yet. The small carbon fragments insert immediately in organic substrate molecules⁶⁸. As free species they can only exist in very high temperature plasma's, as for example applied for depositing diamond layers⁶⁹. The controlled condensation of C_n species by cooling down the plasma emerging from the carbon arc in a helium flow around 1200 °C, brings the fullerenes in focus^{30,70}. The latter were however also reported at lower temperature in flames, e.g. of benzene⁷¹. It was suggested from work with ^{13}C enriched carbon arcs, that, on statistical grounds, the emitted C_2 fragments, if they might constitute the buckminsterfullerene, (125), frame, they do not remain connected⁷². The controlled generation of extended heterocumulenes, also significant as interstellar materials, is widely studied with FVT, directly coupled (figure) with spectroscopic techniques⁷³.

Reactive intermediates:

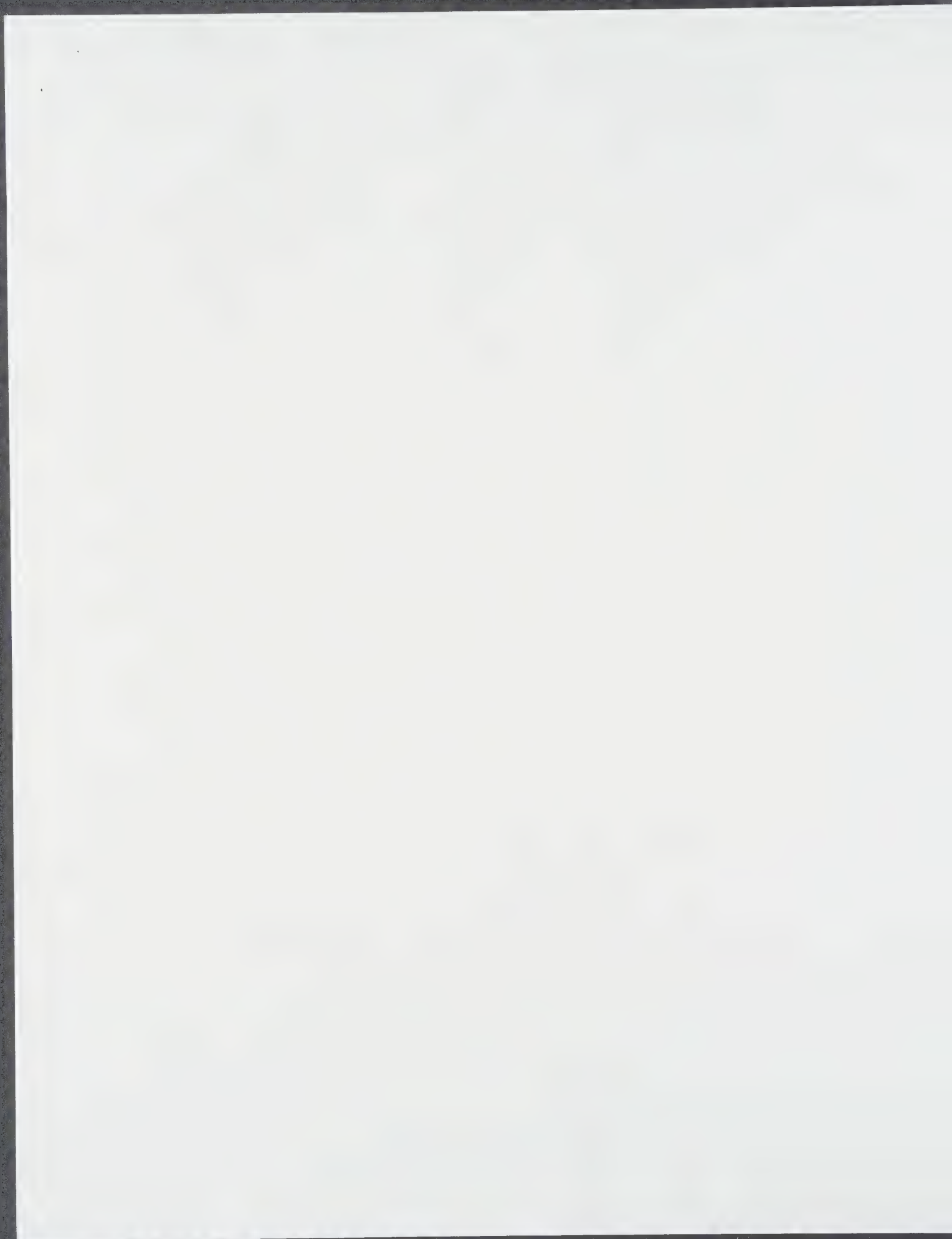
In the lower temperature regimes of combustion, between 700-1200 °C, organic C_nH_m molecules prevail. The pyrolysis of waste plastics, around 750°C, with exclusion of oxygen, produces mixtures that exactly reflect the trend in scheme 3. Methane, ethylene, butadiene, benzene, toluene, styrene, indene, naphthalene and larger PAH are major products of polyethylene pyrolysis under these conditions⁵⁷. This does however not reveal that a large number of thermodynamically rather stable, but kinetically highly reactive transient poly-unsaturated C_nH_m species must be present in the high temperature gasphase. In the hot gasphase of combustion, oxygen will give rise to formation of $C_nH_mO_p$ species and in addition, when nitrogen and sulphur are present in the feed, to $C_nH_mN_pS_qO_r$ species^{3,60}. Ideally, assuming

that condensation- and hydrogen transfer reactions do not interfere, these species dynamically equilibrate or interconvert with some of their isomers of the same molecular formula, constituting the energy surface of a particular species. The molecules that can survive best in the hot gasphase, do not possess unconjugated carbon-carbon single bonds, but are conjugated (aromatic, carbonyl) or cumulated double bond systems^{3,60}.

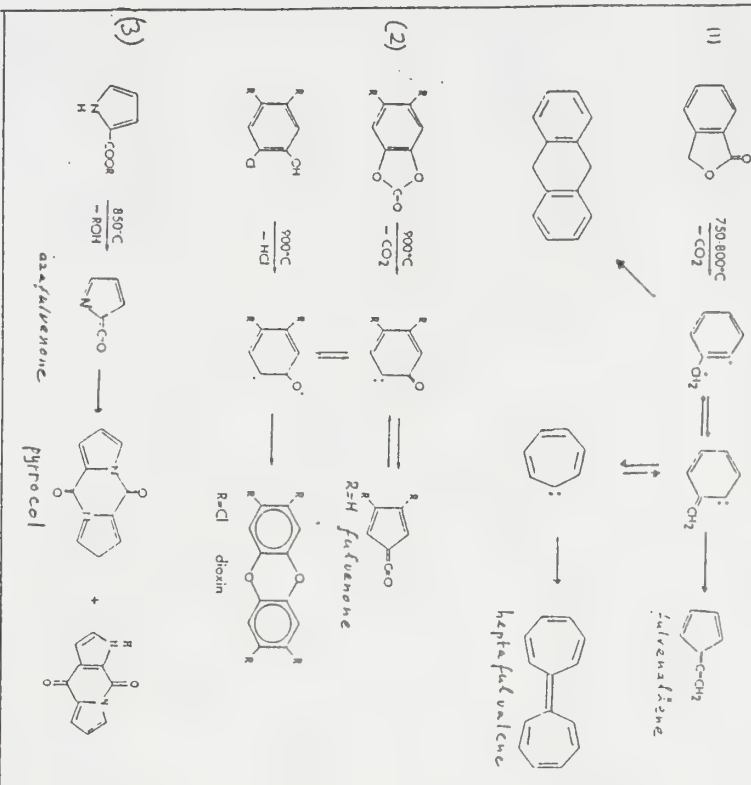
Scheme 4 shows some examples to illustrate this course. The biradical and carbene intermediates of C_7H_6 , that undergo ring contraction to fulveneallene and dimerisation to dihydroanthracene and heptafulvalene (reaction 1), are quite well studied³. Reaction 2, shows the formation of oxocyclohexadienyliene, C_6H_4O , that is isoelectronic with C_7H_6 and gives a similar ring contraction to fulvenone⁷⁴. With chlorine present under combustion conditions it will yield dichloro derivatives which than dimerises to dioxin^{1b}. Fulvenone can also decarbonylate to C_5H_4 , that in turn is a precursor for larger PAH⁷⁴. A product from isolated cigarette tar, pyrrocol and a related dimer, is formed via dimerisation of azulfulvenone^{60,75} (reaction 3). The atoms of fulveneallene and (aza)fulvenones scramble at high temperature. The reactions shown in scheme 4 can be run on milligram scale with FVT^{3,60}.

scheme 4

None of the carbon-carbon bonds in the reactive intermediates in scheme 4 will easily homolyse in a red hot pyrolysis tube or combustion chamber. Entropic factors disfavour rapid condensation of these species in the high temperature zones and there they are also less prone to further oxidative attack by hydroxyl radicals. There is ample evidence that when oxygen is present in the hot zone, it primarily abstracts hydrogen to form hydroxyl radicals, that in turn rarely add on to intermediate molecules, but rather seek other abstractable hydrogens, to end up as water⁷⁶. Besides, oxygen can be lost as carbon monoxide from various intermediates, e.g. from fulvenone.



SCHEME 4: REACTIVE INTERMEDIATES

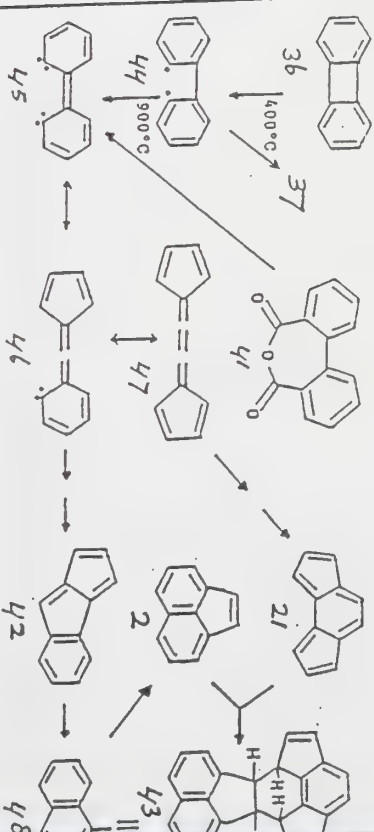


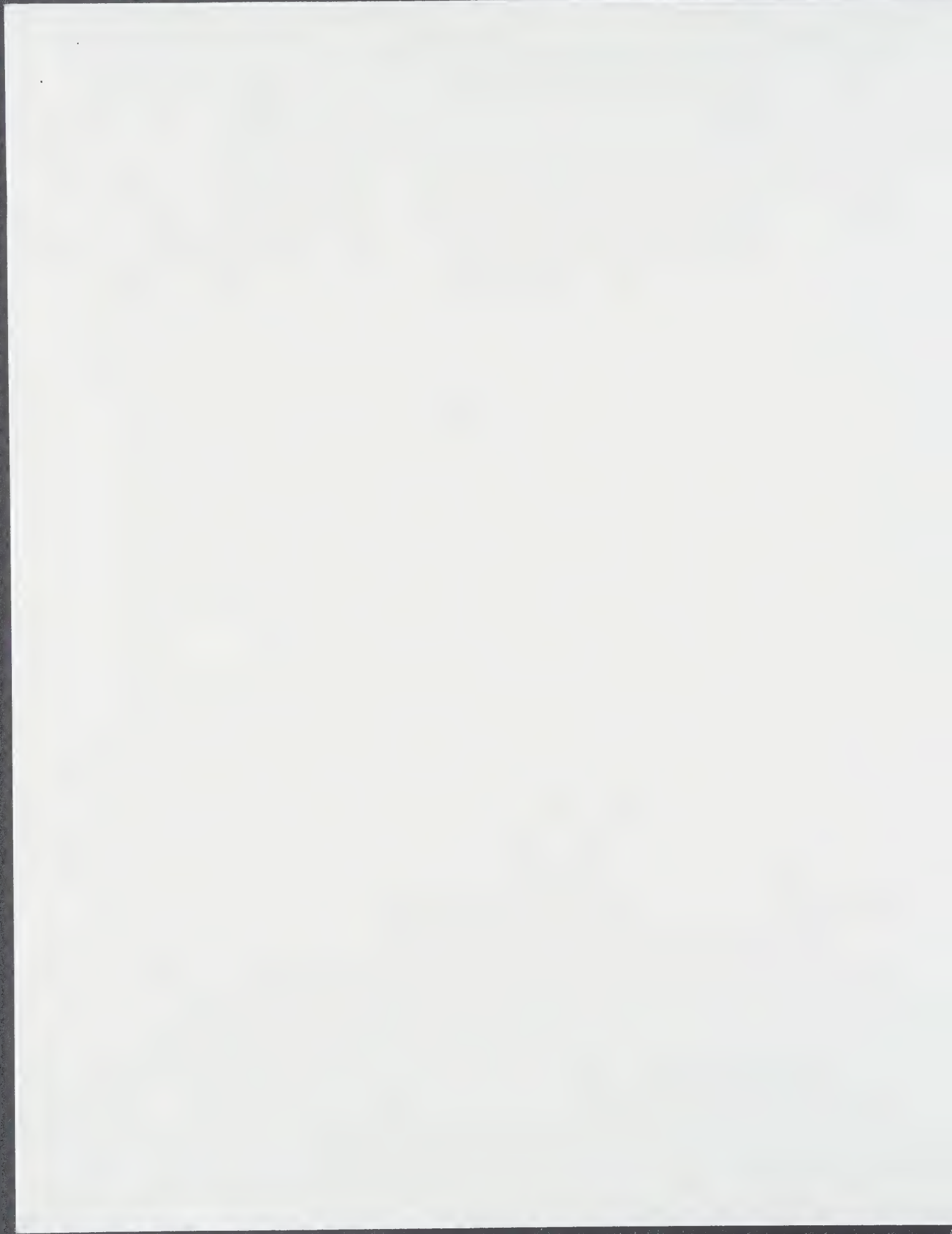
so that hydrocarbon species remain the predominant species in the hot zone. Since they are highly reactive at ambient temperature, their kinetic fate in dimerisation and condensation reactions is governed by the chance of escape to the somewhat colder area's as the outside of a flame, or outlet of a combustion instalment. Here they will undergo their typical sequential dimerisation and condensation reactions. This is what one observes while looking at a sooting flame or in a smoking fireplace. The soot particles in turn do internally homolyse at a fast rate, so that they act as a very active free radical matrix in hydrogen transfer⁷⁷. Soot contains many phenolic and benzylic sites that are notorious in radical transfer^{1a,56}. Thus, the soot must be seen as is a kinetic intermediate that dynamically interacts with the gasphase by taking up and releasing volatiles. Large PMH can be present as free species incorporated in the coal sponge⁷⁸.

The amount of (hazardous) organic PMH constituents in waste incineration and other combustion processes, is thus controlled by pressure, residence times as well as by the relative stability and kinetic behaviour of the individual reactive precursor intermediates of the particular PMH⁹.

Flash vacuum thermolysis:

As stated above, FVT (figure) brings about a unique method for closer study of the chemistry of transient reactive species. A convincing recent example is FVT of diphenylene, 36 and diphenic anhydride, 41, that provides a selective entrance into the C₁₂H₈

SCHEME 5: THE C₁₂H₈ ENERGY SURFACE.



energy surface, with transient formation of 3a-indacene (21) and cyclopent[al]indene (42) as shown in scheme 5⁷⁹. Instead of the dimer tetraphenylene, (37), another dimer 6b,7,10,10a-tetrahydro 3a-indaceno[1,8-jk][fluoranthene, (43), was obtained. Formation of 43 originates from a trapping reaction between acenaphthylene, (2) and 21. The reaction can be rationalized by assuming that the residual bond in biradical 44 is not a genuine single bond and consequently it does not rapidly cleave to form benzene, C₆H₆.⁸⁰ Instead, 44 equilibrates with the dicarbenoid species 45, that undergoes ring contraction to the pentfulvene homologs 46 and 47 from which 21 and 42 and subsequently 1-ethylnaphthalene, (48), a known precursor for 2, can arise. Although 21 is a notorious antiaromatic compound, it appears relatively stable as a transient species in the high temperature gasphase, that is immediately trapped to 43 after escape from the hot zone.

With comparable examples at hand, e.g. pyracylene, (19), pentalene, (22), and α -xylene, (23), it can be concluded from FVT work that these molecules occur as free species at high temperature, but are immediately trapped to build larger PMH on cooling. With ¹³C labeled aromatics, so called automerisation reactions indicate the occurrence of transient intermediates⁸¹.

STRATEGIC PYROLYTIC SYNTHESIS OF PMH

Methods and reviews:

Despite that modern high resolution ¹³C- and ¹H NMR, in combination with mass spectrometry, greatly facilitates structure elucidation of PMH, it remains difficult to identify unknown polyaromatics in soot and pitch mixtures without reference compounds. The isolation of individual PMH from pyrolytic tars (often with liquid crystal phases) is generally difficult. Preparative HPLC is a great help for small scale separations.

Selective routes to build up a particular skeleton are barely

needed. The most versatile methods involve pyrolytic procedures. The following reaction types deserve to be summarised:

- Elbs reaction and dehydrocyclisation²⁵.
- Thermal dehydrogenation⁸².
- Spontaneous selective build up reactions of transient intermediates^{60,75}.
- Eliminations of volatile fragments^{60,83,84}.
- Retro Diels-Alder reaction^{85,86}.
- Use of preparative FVT to generate isobenzofurans⁸⁵ and α -quinodimethanes⁸⁷ etc., as reactive building blocks.
- Selective rearrangement of PMH by FVT^{44,83}.
- Cyclisation via arylmethylene carbenes and arylketenes⁸⁴.

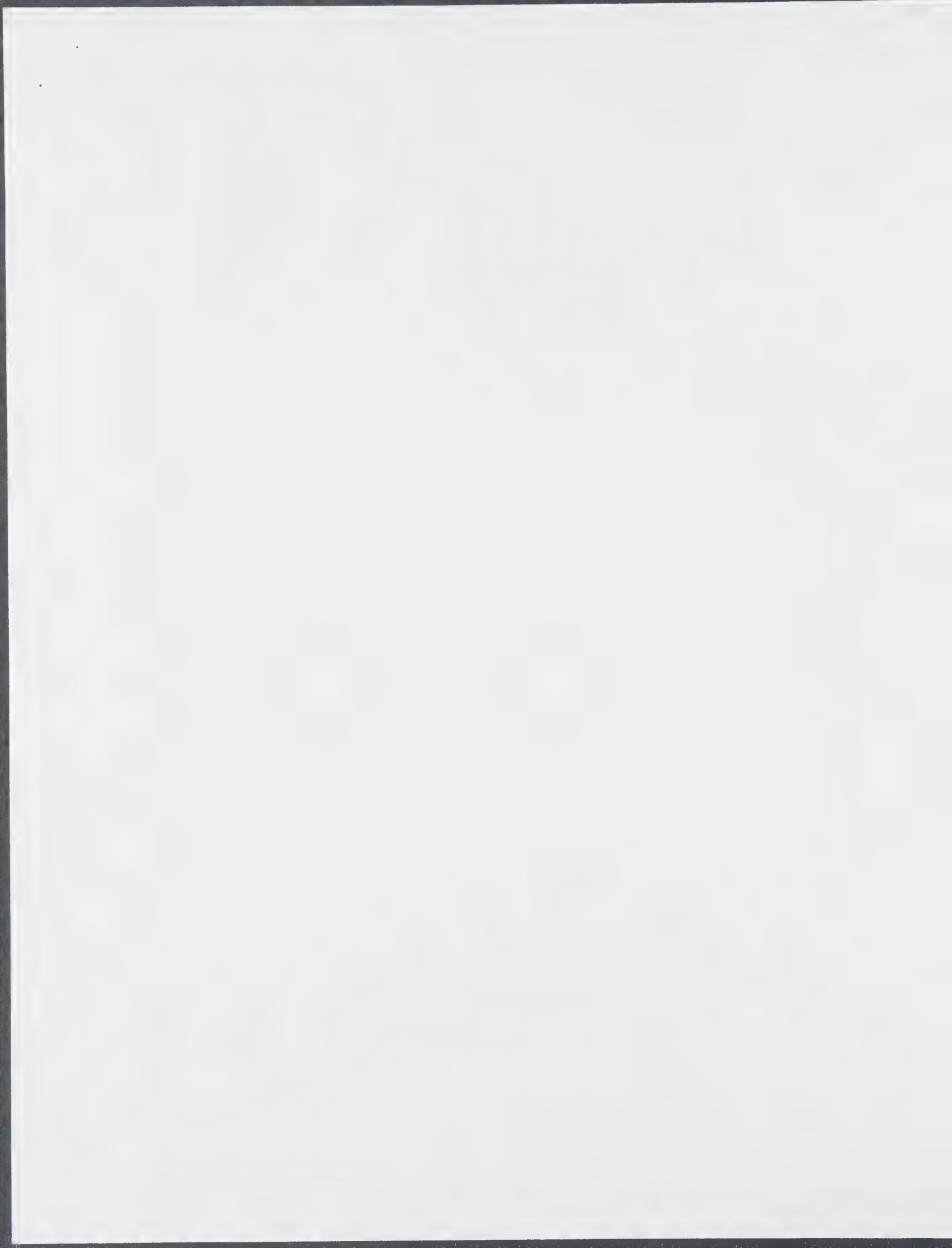
Some examples are shown in scheme 6. Elimination of CO by FVT of 6,12-chrysenquinone, yields dibenzopentalene (50)⁸³. Similarly pyrene quinones are precursors for pyracylene, (19)^{19,83}. Dibenzopyrene, (50) is generated by FVT of the tosylhydrazone of 1-acenaphthylaldehyde⁸⁸. 5,12-Naphthacenequinone, (51) and benzo[2,3]fluorene, (52), benzo[1]naphtho[2,3-d]thiophene, (53a) and

scheme 6

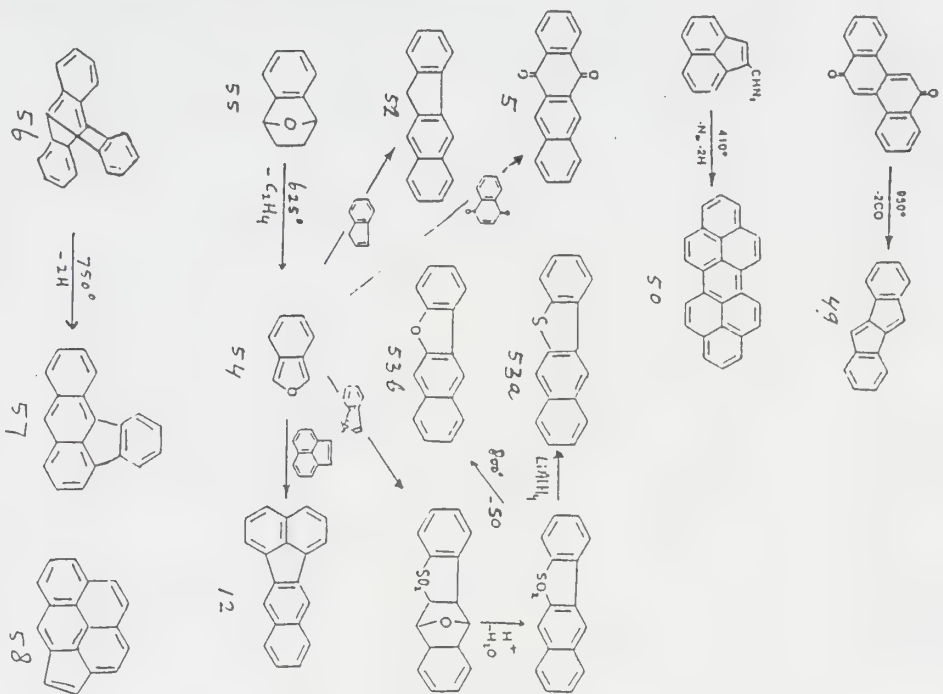
benzo[1]naphtho[2,3-d]furan, (53b) benzo[k]fluoranthene, (12), are selectively prepared via isobenzofuran, (54), generated from 1,2,3,4-tetrahydro-1,4-epoxynaphthalene, (55)⁸⁵. Triptycene (56), the benzene adduct of anthracene, rearranges to benzo[*a*]aceanthrylene (57), a constituent of bromooil soot. The acetylene-methylene carbene mechanism for cyclisation to cyclopenta PMH deserves somewhat detailed comment.

Methylene carbenes: Precursors to cyclopenta-PMH:

The formation of cyclopenta-PMH as contaminants and potential carcinogens from combustion processes, is attracting increased interest^{15,16}. It is important to realize that combustion of gaseous



SCHEME 6: FVT PREPARATIONS OF PAH



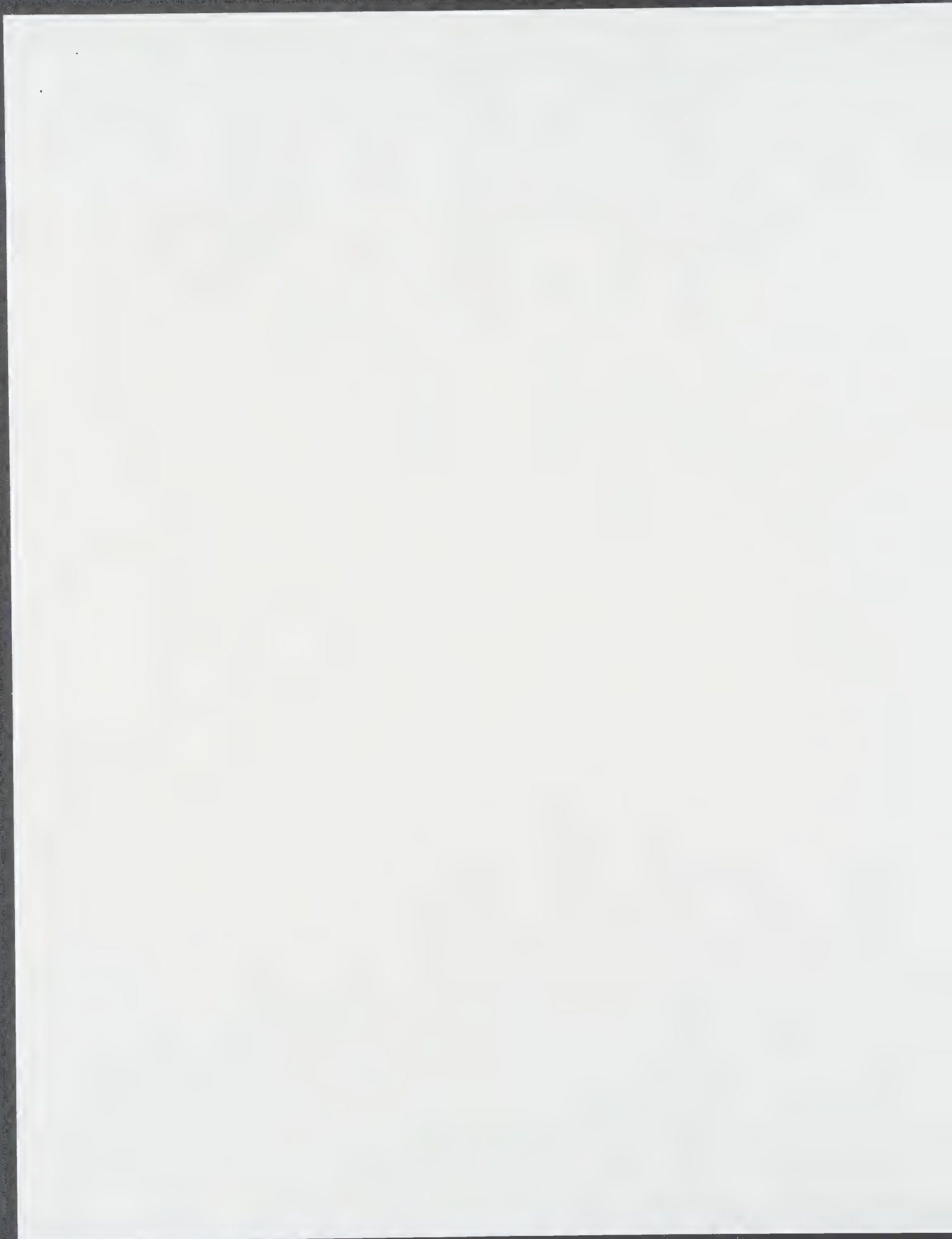
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C_1-C_6 hydrocarbons yield PAH's. With methane flames mixed with CH_2Cl_2 an intensified trend was observed towards the production of cyclopenta fused derivatives, specifically 2, 7, 18 and cyclopenta[*c*,*d*]pyrene (58)¹³. The build up of these PAH from C_1 sources very likely involves acetylenic moieties, that build up to ethynyl substituted aromatics^{1a}. These are the precursors that cyclize to produce the cyclopenta-fused PAH⁸⁴. In some instances the ethynyl group can add up as another six-membered ring to a PAH as well.

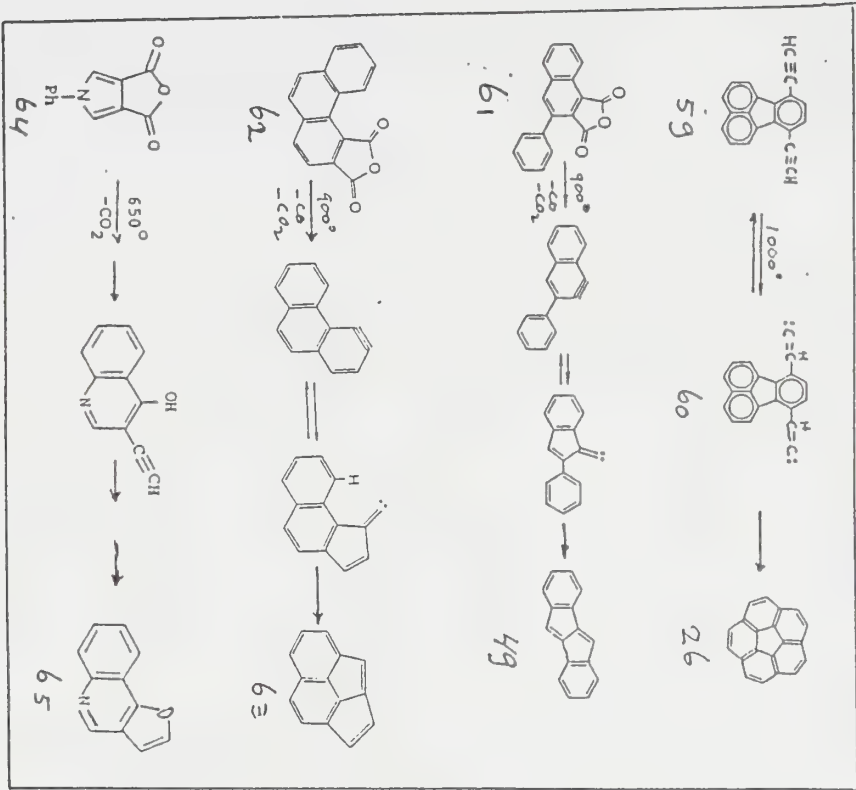
These reactions can be understood via the acetylene-methylenecarbene rearrangement⁸⁴. Methylenecarbenes result from thermal equilibration around 700 °C with acetylenes. This fundamental thermal process, discovered by Brown^{84,89}, is a key mechanism in the build up of PAH (Scheme 7). In FVT of 7,10-diethynylfluoranthene (59) to corannulene (26), the intermediate methylenecarbene, (60), can only cyclise to make six-membered rings in (26)⁴³. In the cyclisation of 1-ethynylfluoranthene (48) to acenaphthylene, (2) (see scheme 5), the ethynyl substituent is trapped in a five-membered ring⁸⁴. A related mechanism involves equilibration of primary formed aryn intermediates with cyclopentadienylidene carbenes^{80,84,89}, that undergo

scheme 7

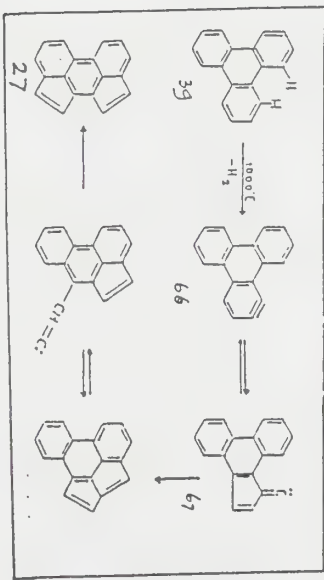
intramolecular trapping to cyclopenta derivatives as in FVT of 3-phenylnaphthalene-1,2-dicarboxylic anhydride (61) to dibenzopentalene (49) and of phenanthrene-3,4-dicarboxylic anhydride (61) to cyclopent[*b*]acenaphthylene, (63)⁸⁹. A striking FVT reaction is the formation of furo[3,4-*c*]quinoline, (65) from *N*-phenylpyrrole-3,4-dicarboxylic anhydride (64)⁹⁰. This mechanism was invoked in the selective FVT reaction of triphenylene, (39) to cyclopent[*b*]acenaphthylene (27)⁴⁴ (scheme



SCHEME 7: ACETYLENE-METHYLENE CARBENE REARRANGEMENT



SCHEME 8: ARYNYL-CYCLOPENTADIENYLIDENE CARBENE ROUTES.



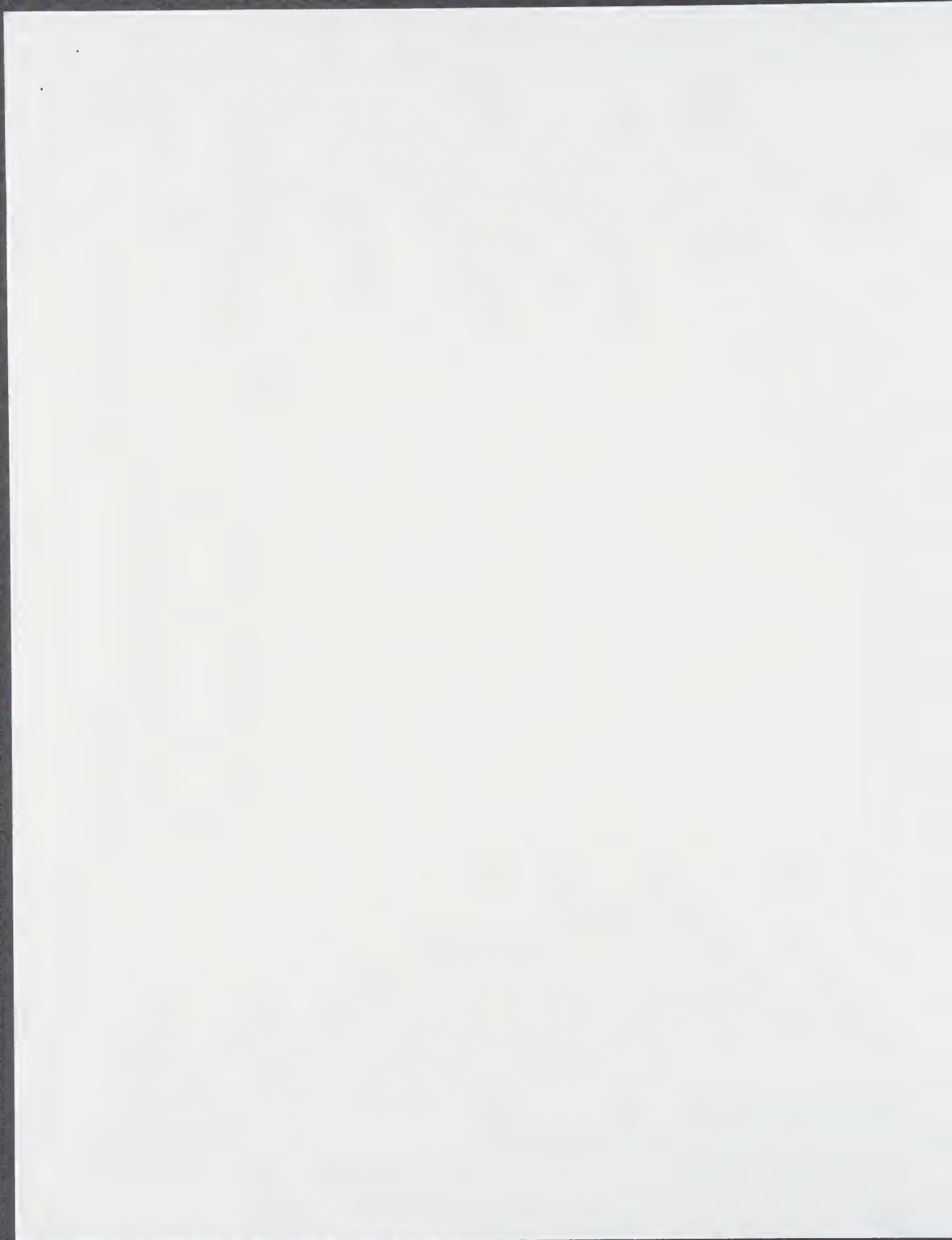
cyclopentadienylidene carbene 66, that engages in an insertion-ring-opening-insertion sequence to 27⁴⁴. Since hydrogen abstraction is to be expected a major process in combustion⁷⁶ (see above), the aryn-cyclopentadienylidene carbene routes may be quite common pathways.

CONCLUSION.

The PAH chemistry is more vividly than ever because of the environmental impact and the discovery of the fullerenes. The latter is a most important driving force for applicational and theoretical work, that certainly will radiate to other PAH systems as well. FVT can help the experimentalists both to prepare PAH and to characterise their sequential or preceding combustion products as shown for cyclopenta-PAH. In addition, a mixture obtained from FVT with a single PAH is easier to analyse, than tarry soot mixtures from combustion.

Many PAH are prepared by FVT, that sometimes has appeared to be the only available route. The recent FVT preparations of coronulene (26) and cyclopentah,ilacephenantylene, (27), compare favourably with liquid phase synthesis. Besides, some PAH can be build up in a selective way in substantial quantities, via FVT generated reactive intermediates like isobenzofuran, avoiding the tedious work up procedures needed with PAH mixtures.

8). Assuming that the peri-hydrogens are the weakest bonds in 40, it loses hydrogen to form the aryn 65, that equilibrates with the

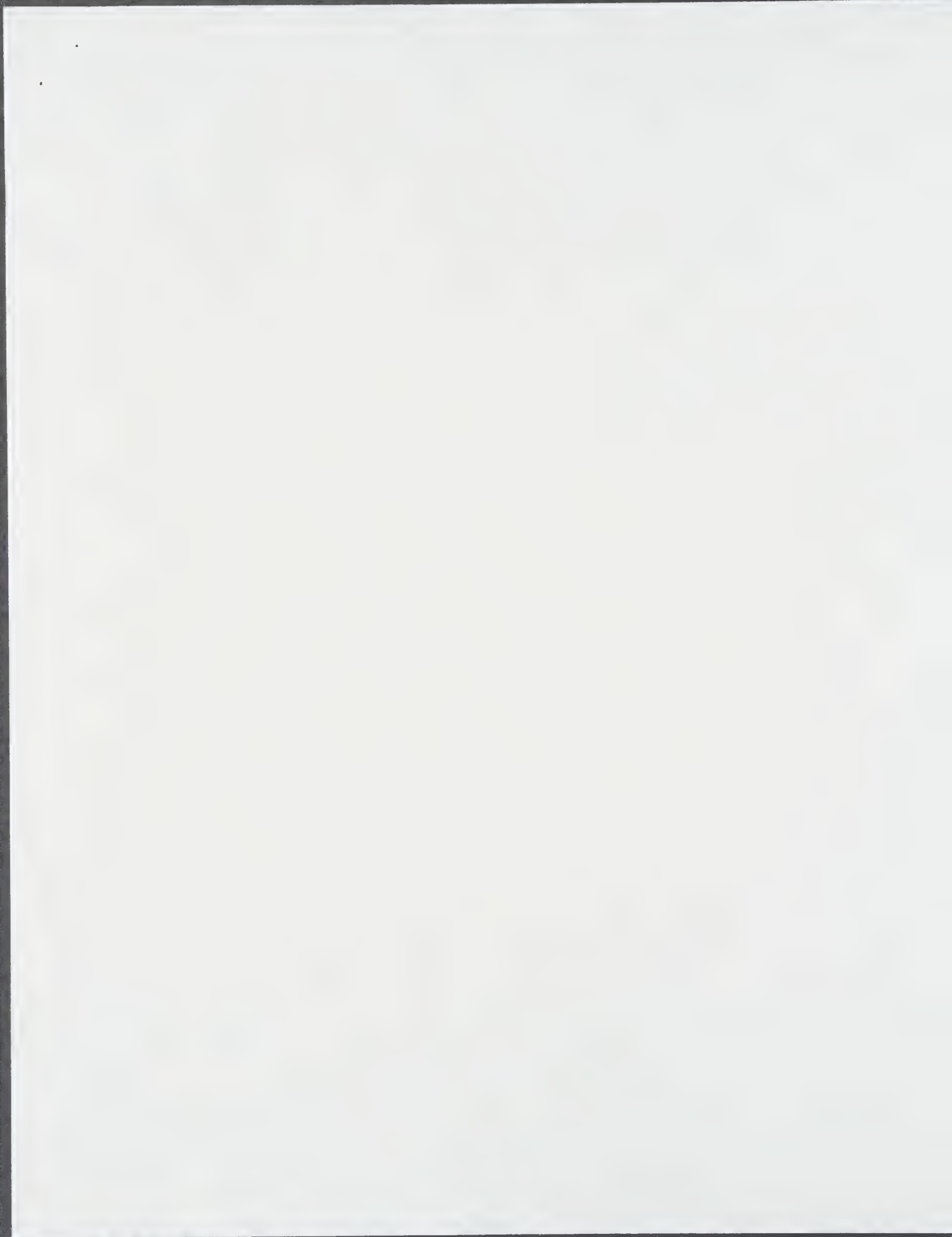


* Dedicated to professors Charles D. Hurd, emeritus, Northwestern University, Evanston, Illinois, USA, (references 4 and 5) and Roger F.C. Brown, Monash University, Clayton Victoria, Australia, (references 2, 84 and 89), who made pyrolysis a thorough subject.

** In this respect PAH, can be seen as natural products; this may encourage natural product chemists to define target PAH molecules.

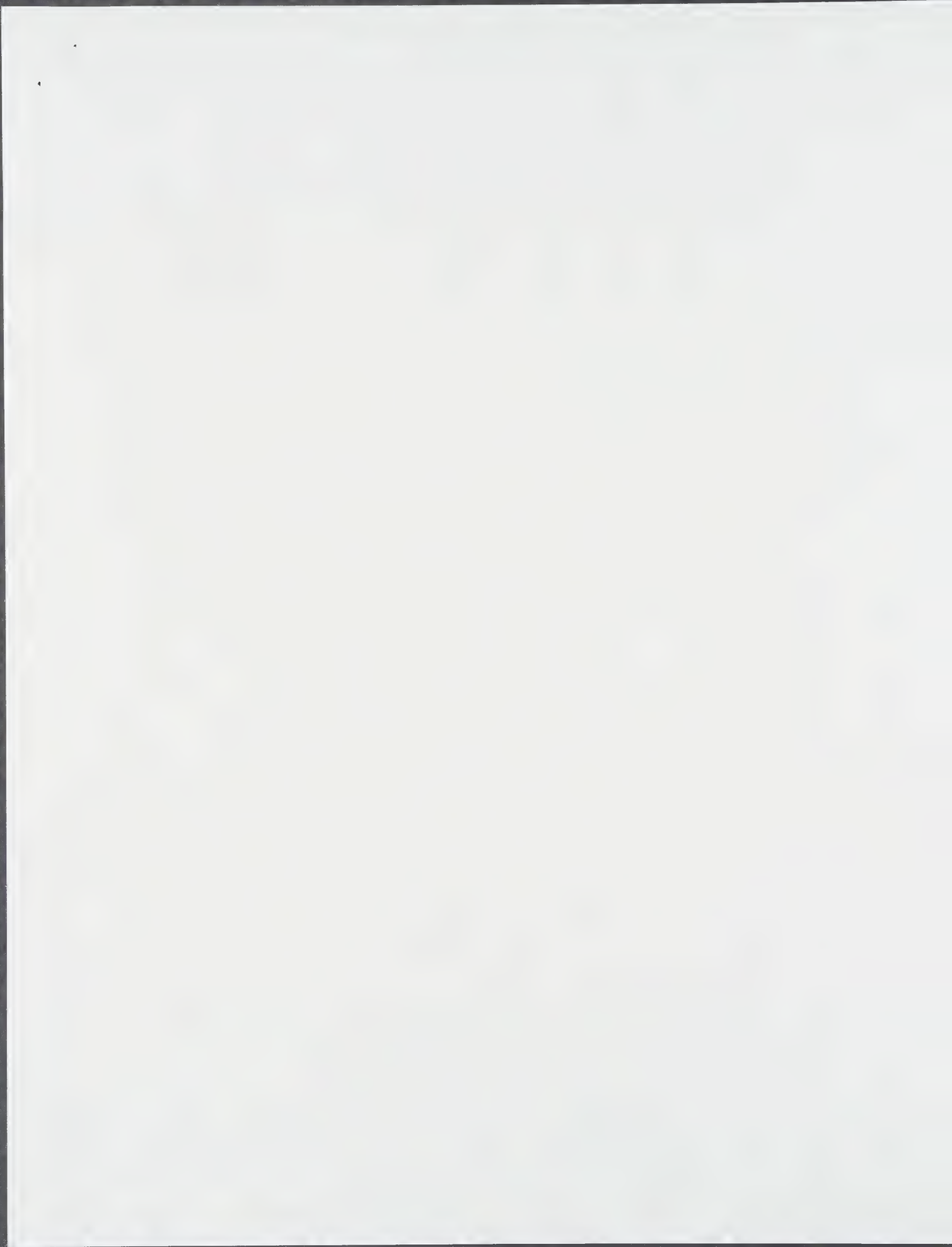
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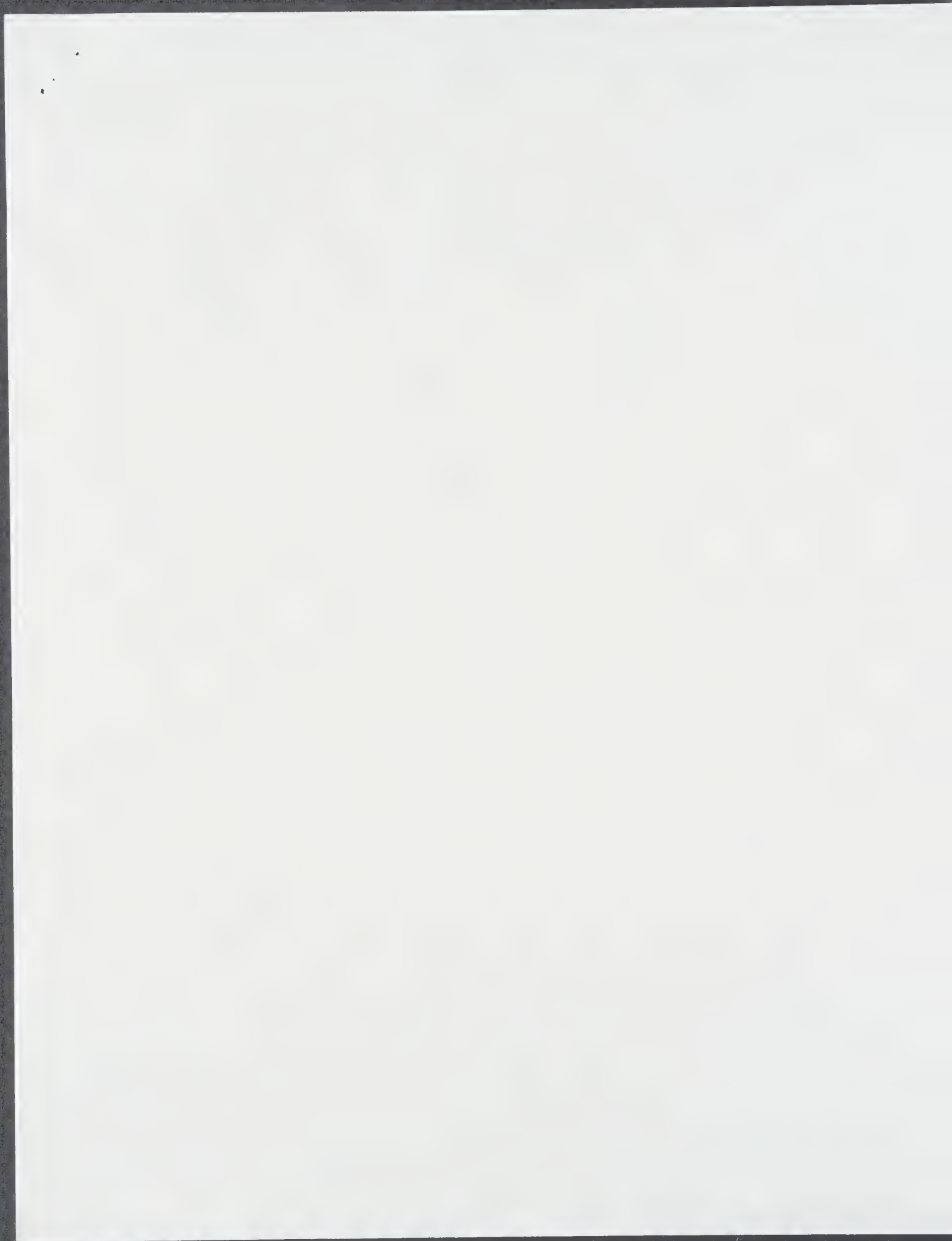


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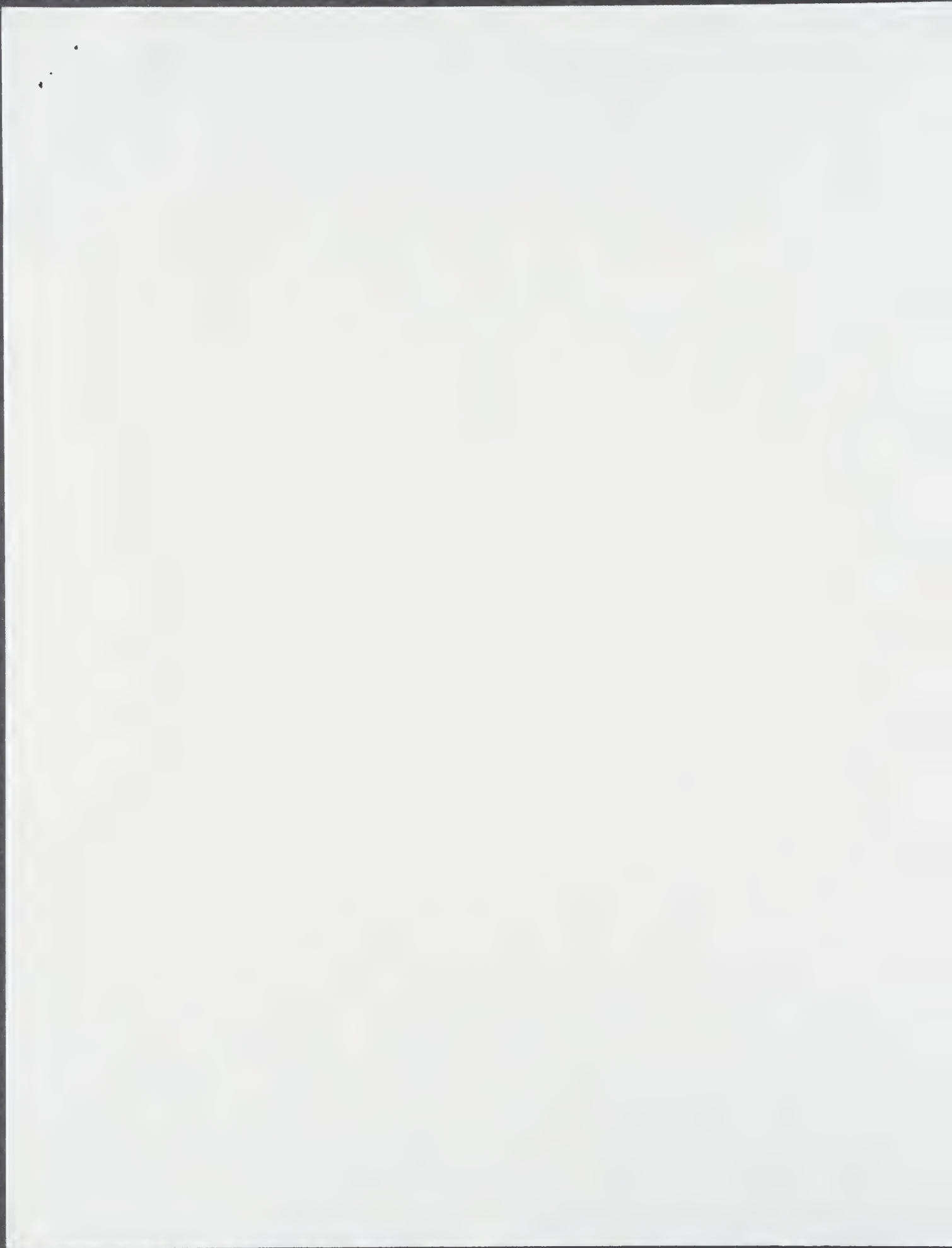
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Dr. Alfred Bader
Chairman Emeritus

M



February 27, 1992

Prof. Charles D. Hurd
2724 Crawford Avenue
Evanston, Illinois 60201

Dear Charles:

It has now been almost 40 years that you have been helping us by correcting the nomenclature in our catalog. In your first efforts, in the fifties, the catalog was just a few pages, and I hope that you have seen our latest catalog and like it.

The problem which you raise with our TCNQ-F₄, is a very difficult one. You see, we named this compound in analogy to our TCNQ, 15763-5, which we have called tetracyanoquinodimethane for over 20 years. The name TCNQ, tetracyanoquinodimethane, has just been so widely accepted.

As soon as we can be certain of stable weather, we want to come down for a visit to discuss this and many other matters.

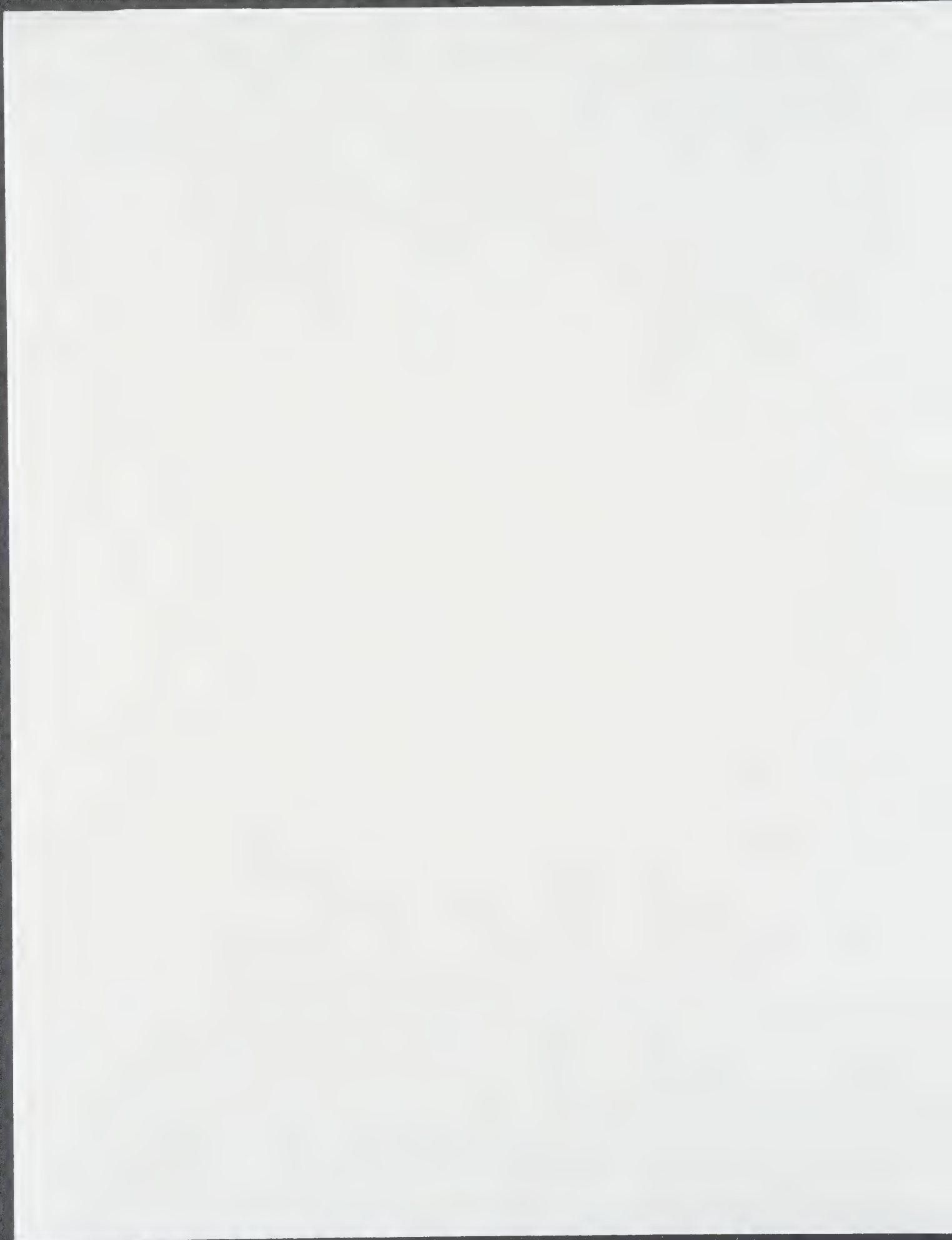
Fond regards.

As always,

Alfred Bader
AB:mmh
c: Mr. David Griffiths

SIGMA-ALDRICH

P.O. Box 355 Milwaukee Wisconsin 53201 USA Telephone (414) 273-3850 Cable Aldrichem TWX 910-262-3052 Telex 26-843



Dr. Alfred Bader
Chairman Emeritus

October 29, 1991

Sept '92



Prof. John Wotiz
Department of Chemistry & Biochemistry
Southern Illinois University
Carbondale, Illinois 62901 4409

Dear John:

Thank you for your kind letter of October 24.

You must have realized how very much Isabel and I enjoyed being able to spend an evening with you.

However, my calendar for January and February is completely filled, and anyway, the winter months are not good months to travel in Illinois and Wisconsin.

Please consider whether a date in September would be suitable, and if so, could I impose upon you to ask the chemists in Urbana whether they might also enjoy a visit from us. We would drive, which is much less expensive than flying.

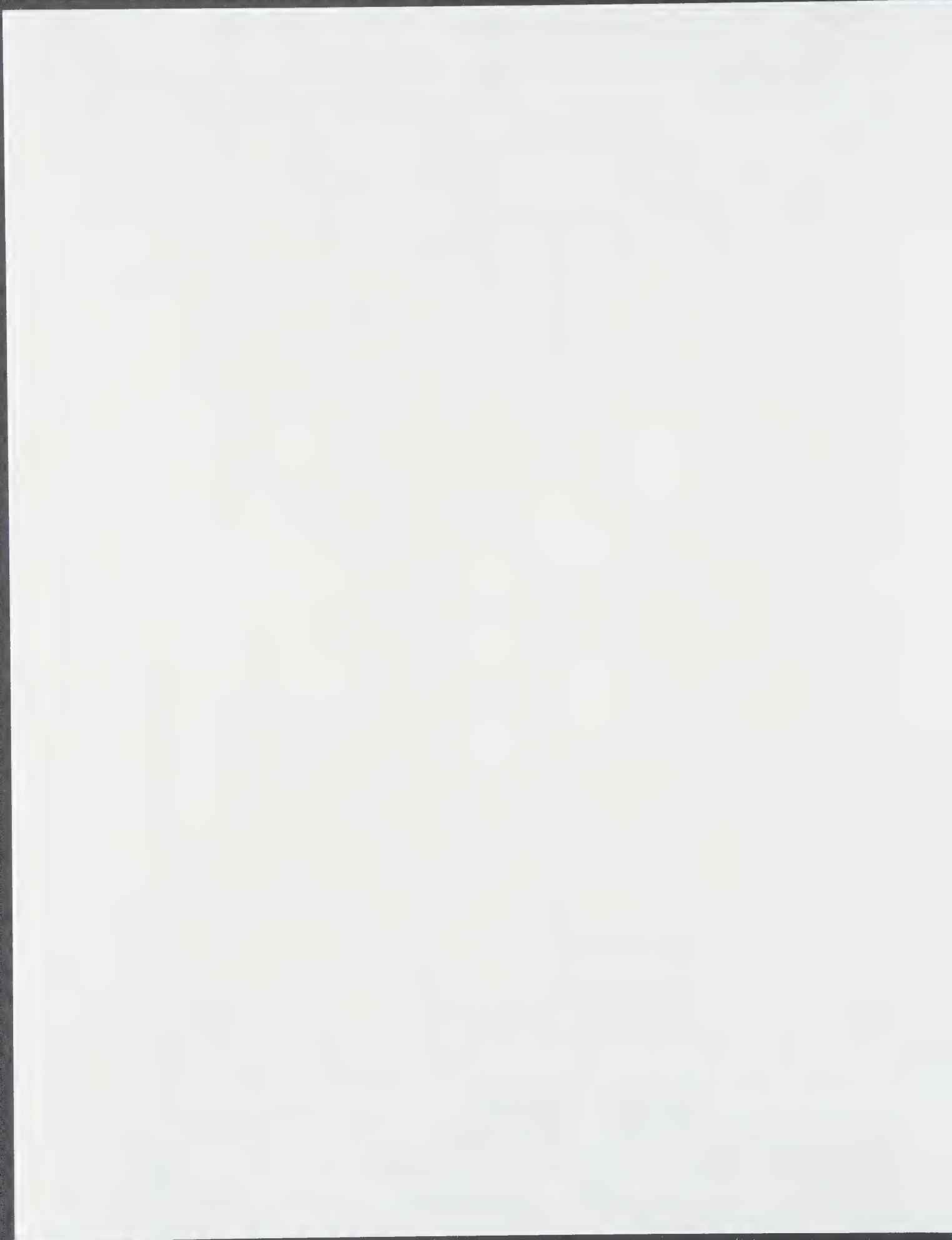
All good wishes.

Sincerely,

Alfred Bader

SIGMA-ALDRICH

P.O. Box 355 Milwaukee Wisconsin 53201 USA Telephone (414) 273-3850 Cable Aldrichem TWX 910-262-3052 Telex 26-843



Dr. Alfred Bader
Chairman



November 7, 1990

Handwritten mark, possibly initials 'H'.

Mrs. Anita Kolman
6101 North Sheridan Road 11A
Chicago, Illinois 60660

Dear Mrs. Kolman:

I am sorry to read about the difficulties with your beautiful Backer, although I must tell you that I am not surprised.

Once a painting has gone through auction and has been unsold, most collectors shy away from it and so does my friend who initially was most interested. He told me that it has been offered to museums for considerably less, and that when he saw it at auction in New York, he was unhappy about the manner in which it was restored.

I wasn't at the New York auctions in May, but when next I come to Chicago, probably in January, I will try to visit with you and look at the bottom painting.

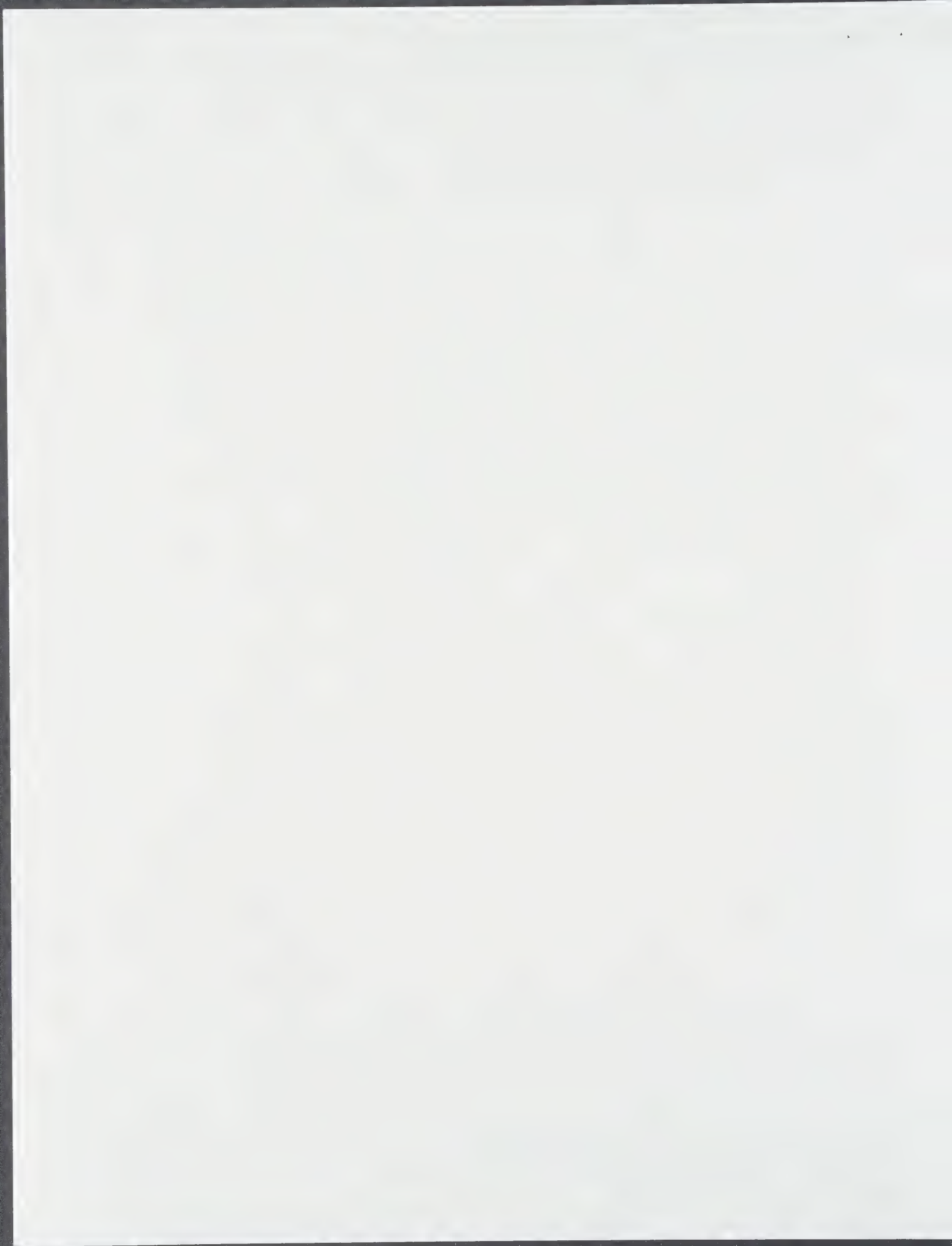
Best regards.

Sincerely,

Alfred Bader
AB:mmh

SIGMA-ALDRICH

P.O. Box 355, Milwaukee, Wisconsin 53201 USA, Telephone (414) 273-3850, Cable Aldrichem TWX 910-262-3052, Telex 26-843, FAX 414-273-4979



6101 N. Sheridan Rd 11F
Chicago 6061

Oct 24th 1990

312-761-0441

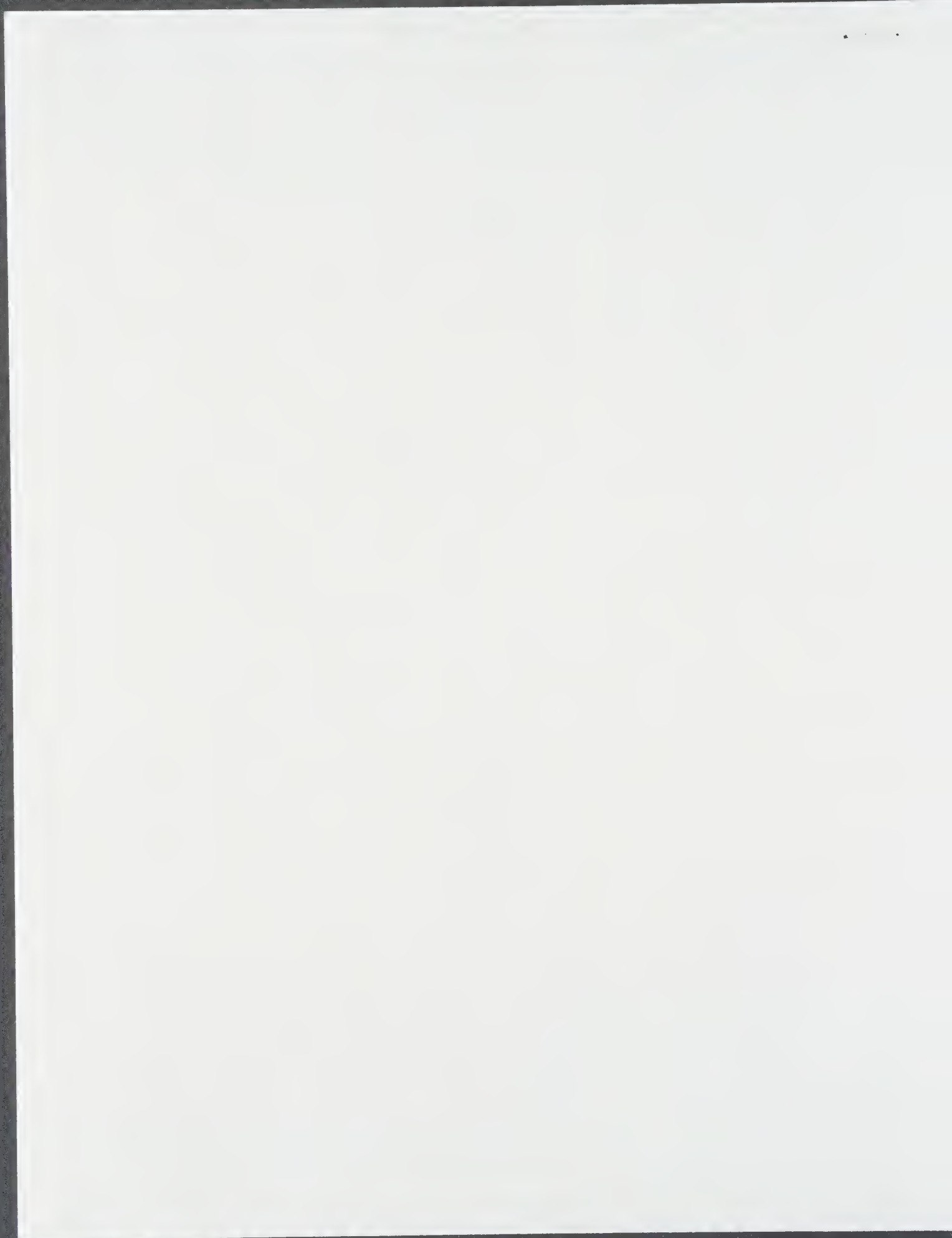
Dear Dr. Bader

I wish I had taken your advice, years ago, to sell the painting of Baaker to your friend who offered 32^k for it.

Of course, my lack of experience and ignorance of this field, plus the fact that I was so poor (and no one knows how poor I was ~~than~~^{as} you do, for I had never allowed anyone to see me in that hole; that was the year after my financial reverses) and having lost all my real-estate properties in fraud, - I was afraid to part with the last dollar I had, so to speak.

However, if your friend is still interested, I will sell it to him for that price, with my apologies ^{to him} of being so naive as to expect miracles.

I hope you and your family are all well. I was in N.Y. for the Christie Auction May 89, I hoped to see you but I did not; Or perhaps I was not sure it was you; I don't have a good memory of faces and often get in deep trouble because





Chemists Helping Chemists in Research and Industry

aldrich chemical company, inc.

Dr. Alfred Bader
Chairman

March 9, 1990

Prof. Herbert C. Friedmann
Department of Biochemistry and
Molecular Biology
University of Chicago
920 East 58th Street
Chicago, Illinois 60637

Dear Prof. Friedmann:

Thank you for your thoughtfulness in sending me The New Yorker with the article on the Rembrandt Research Project. I had indeed read it, and in fact, made some copies to send to art historians in Germany. It is good to have another copy for another friend.

As a small token of my appreciation, please find enclosed some reproductions of paintings by Rembrandt and his students.

If you ever come to Milwaukee, I would be happy to meet you personally and show you my collection.

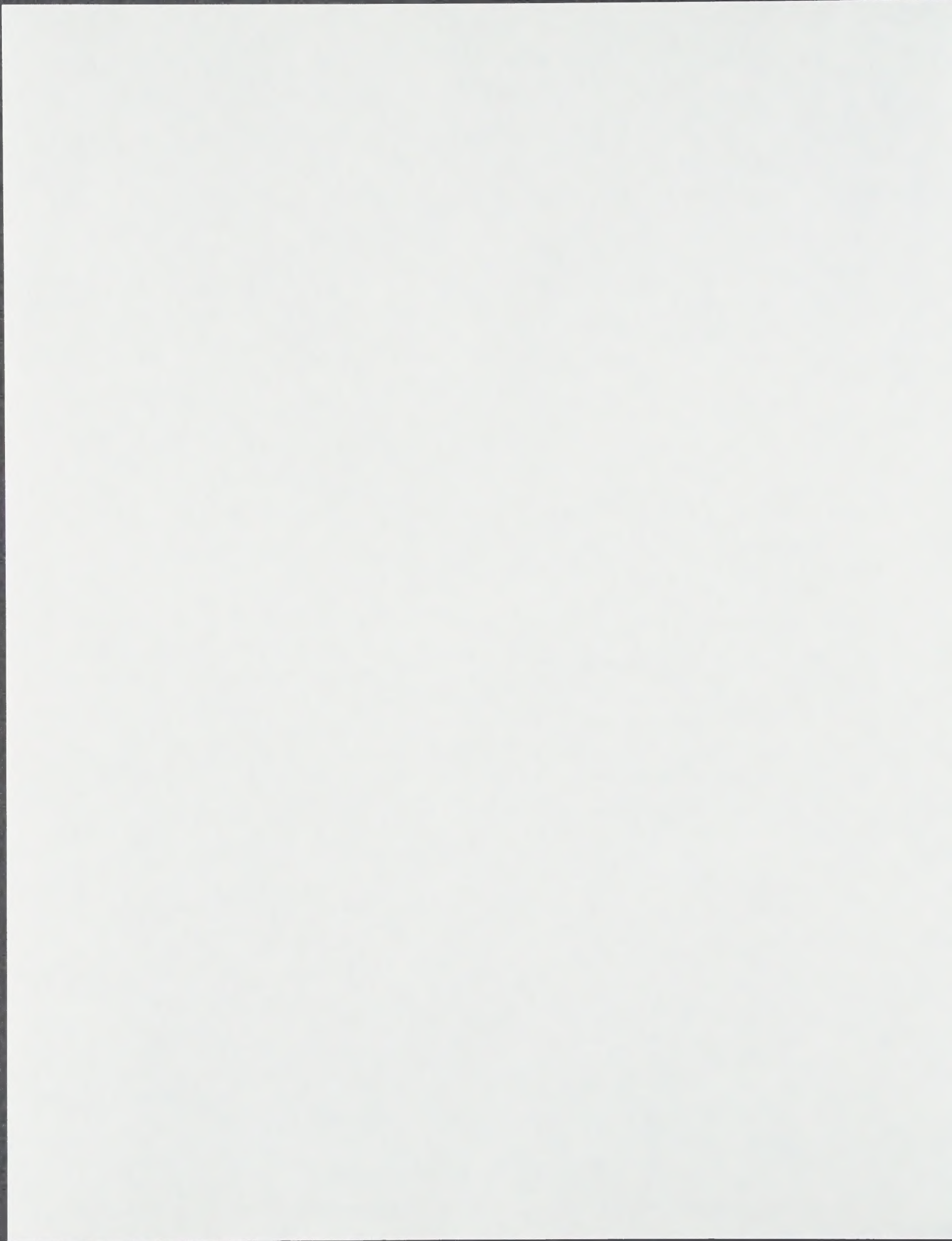
Best regards.

Sincerely,

Alfred Bader

AB:mmh

Enclosures





Chemists Helping Chemists in Research and Industry

aldrich chemical company, inc.

Chicago

Dr. Alfred Bader
Chairman

January 2, 1990

Dr. Robert M. Moriarty
President
Steroids Ltd.
Chicago Technology Park
2201 West Campbell Park Drive
P.O. Box 6836
Chicago, Illinois 60612

Dear Dr. Moriarty:

I am sorry that a trip to Europe has delayed my thanking you for your thoughtful letter of December 1st.

I had not realized that you are actively involved in steroid synthesis, and, under the circumstances, it seems to me that Dr. Julilan's collection really must have more value with you than in our Library.

We do get inquiries for steroid syntheses from time to time, syntheses which usually we decline. From now on, I would like to suggest to prospective customers that they contact you.

As we are physically so close, I do hope that we will be able to meet personally before long.

Best Wishes of the Season.

Sincerely,

Alfred Bader

AB:mmh

