I. IMPROVED DIENE SYNTHESIS OF AROMATIC HYDROCARBONS

II. SYNTHESIS OF TETRASUBSTITUTED PHENANTHRENES

By

ALBERT GENE HOLBA

Bachelor of Science
Oklahoma State University
Stillwater, Oklahoma
1973

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree
DOCTOR OF PHILOSOPHY
July, 1980

I. IMPROVED DIENE SYNTHESIS OF
AROMATIC HYDROCARBONS
II. SYNTHESIS OF TETRASUBSTITUTED
PHENANTHRENES

Thesis Approved:

E J Eisenbraun
Thesis Adviser

Ernest M. Hodnett

Tom E. Moore

Earl D Mitchell Jr

Norman N Durham
Dean of the Graduate College

ACKNOWLEDGMENTS

I wish to thank my adviser, Dr. E. J. Eisenbraun, for his patient guidance, encouragement, and friendship when it was needed most. I am also appreciative of my committee members, Dr. E. Hodnett, Dr. T. Moore, and Dr. E. Mitchell who have each contributed to my education.

I thank the Environmental Protection Agency, the U.S. Department of Energy and Dow Chemical for their financial support of this study.

I am grateful to Mr. N. Perreira, Mr. S. Sigle, of O.S.U. and Dr. G. W. Keen and Mr. A. R. Taylor of CONOCO, Inc., for obtaining spectra necessary for this study. Thanks go to Mrs. Janet Sallee for typing the final manuscript.

I also wish to thank members of the research group for their friendship and many helpful suggestions. Particularly, I value the encouragement of Dr. P. Ruehle and the friendship of Dr. L. Pahler, Mr. T. K. Dobbs and Dr. D. L. Bymaster.

I wish to express my gratitude to my parents, Mr. and Mrs. Charlie Holba and to Mr. and Mrs. M. E. Wolff, Randy and Karen for their immeasurable encouragement and support. Finally a very special thanks goes to my wife, Marilyn, and my children, Jeff and Sara, for their patience and many sacrifices, without which, this thesis would not exist.

TABLE OF CONTENTS

PART I

PART II

LIST OF TABLES

LIST OF FIGURES

Figure Page

PART I

PART II

LIST OF SPECTRA

PART I

PART II

Spectrum Page

PART I

IMPROVED DIENE SYNTHESIS OF AROMATIC HYDROCARBONS

CHAPTER I

INTRODUCTION

The well documented occurrence of polynuclear aromatic (PNA) hydrocarbons in petroleum,[1] coal,[2] soil,[3] and the products of petroleum refining,[4a] coal liquifaction,[4b] fuel combustion,[4c] and tobacco combustion[5] has incited an interest in their physical, carcinogenic, and mutagenic properties.[6a,b,c,d] The resurgence of coal as a fuel source and its conversion to coal liquids has emphasized the importance of examining the role of PNA compounds in our present, as well as future, environment.

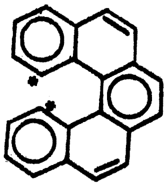
This study investigates the synthesis and purification of several PNA hydrocarbons as analytical standards for the Environmental Protection Agency.[7]

CHAPTER II

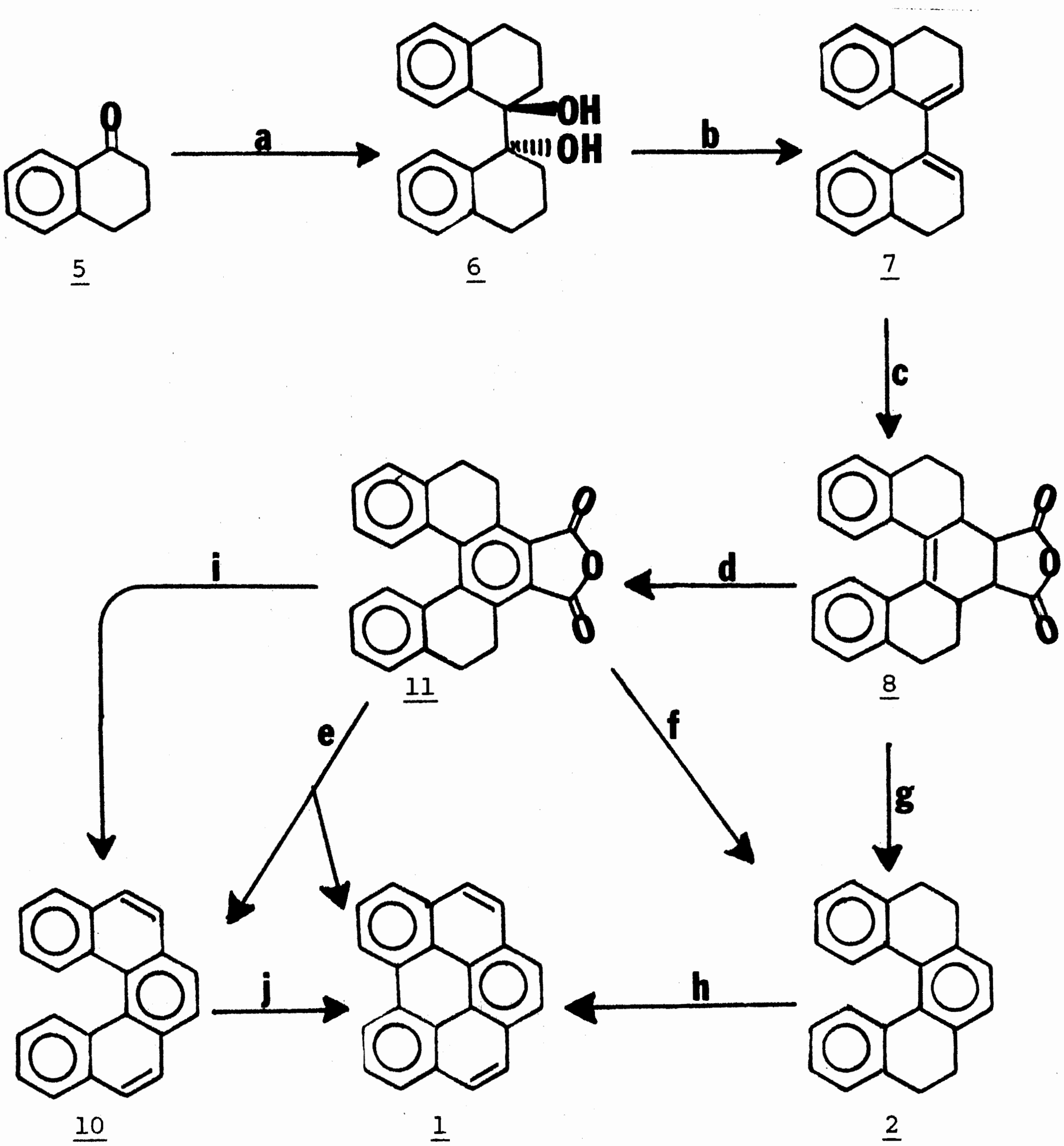
HISTORICAL

Since its emergence in 1928, the Diels-Alder reaction has proved to be a useful tool in organic synthesis[8] and particularly in the diene synthesis route to PNA hydrocarbons.[9] In the synthesis of pure benzo[ghi]perylene(1),[10] coronene(2),[10c] benzo[c]chrysene(3),[10a] and picene (4),[10a] the diene synthesis has been shown to have potential as an efficient method of ring construction. Known syntheses of 1, 2, 3 and 4 using this approach are shown respectively in Figures 1, 2, and 3. Each synthesis, however, is deficient in at least one of three critical areas: a) the production of a suitable diene, b) the reaction of the diene with maleic anhydride, or c) the decarboxylation and dehydrogenation of the Diels-Alder adduct. Our work has resulted in a distinct improvement of each of these syntheses.

Table I presents yields of the above hydrocarbons and intermediates for various steps of known synthesis routes. For benzo[ghi]perylene, pinacol coupling of 1-tetralone(5), dehydration, and reaction with maleic anhydride provided the necessary ring system in good yield. Aromatization and decarboxylation of anhydride 8 proceeds to 1 through the pentahelicene 10 system.

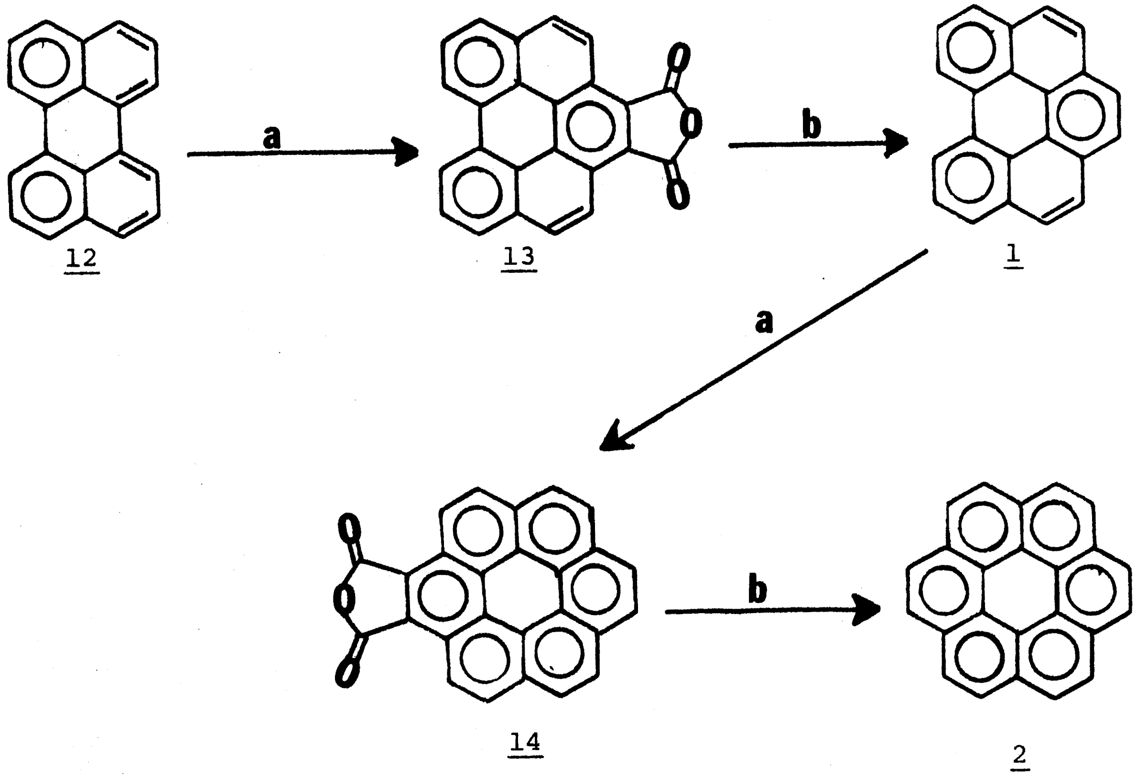


10



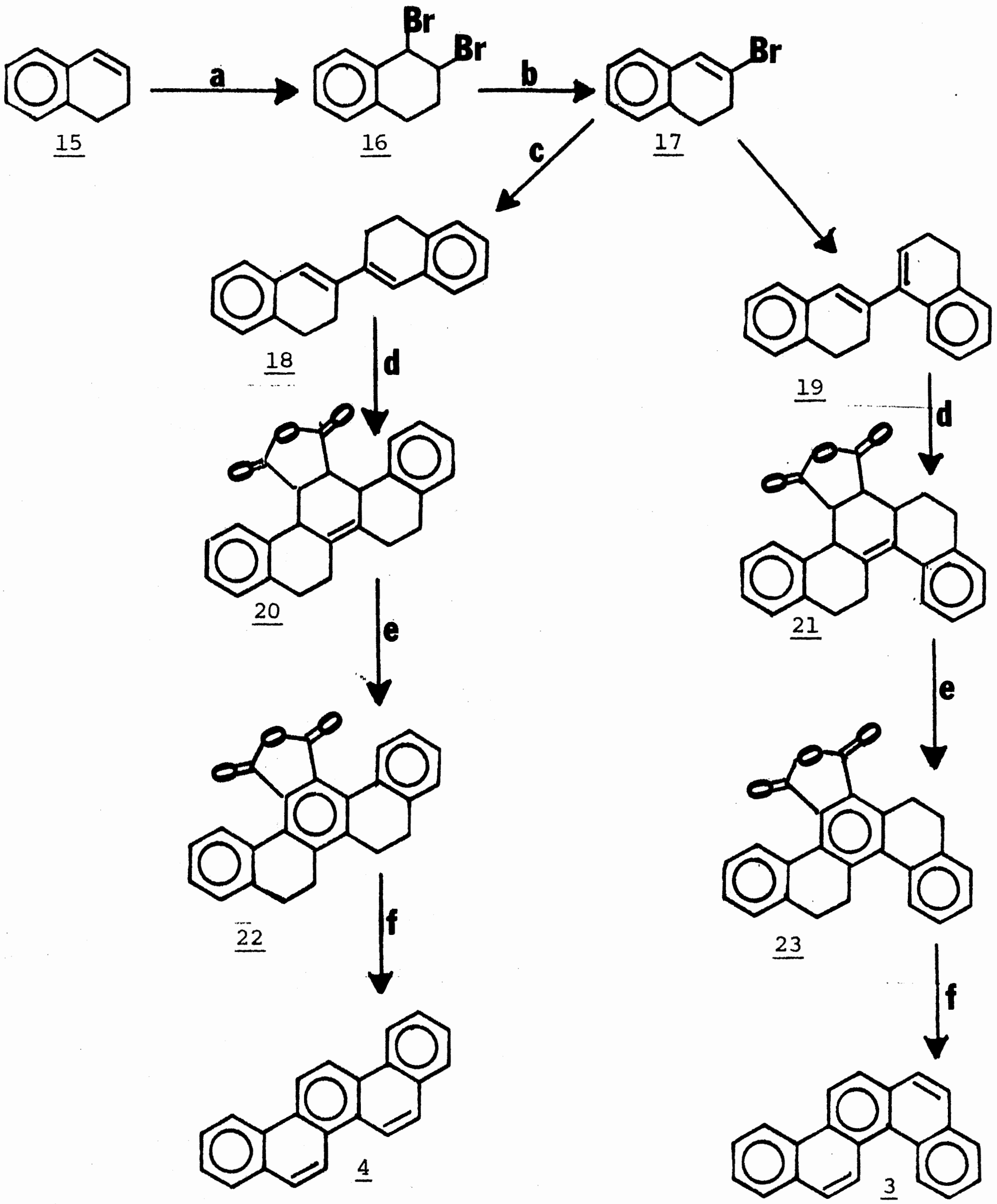
[a] Al, $HgCl_2$, C_6H_6, CH_3CH_2OH. [b] CH_3CO_2H, $(CH_3CO)_2O$, Δ. [c] Maleic anhydride.
[d] Br_2, CH_3CO_2H, $CHCl_3$. [e] Cu, $Ba(OH)_2$, N_2, Δ. [f] Cu, quinoline, Δ.
[g] PbO_2, decalin. [h] Pd/C, p-cymene, Δ. [i] Cu, $Ba(OH)_2$, $ZnCl_2$, N_2, Δ.
[j] N-Bromosuccinimide, dibenzoyl peroxide, CCl_4, then CH_3CO_2Na, CH_3CO_2H.

Figure 1. Synthesis of Benzo[*ghi*]perylene(1)



[a] Maleic anhydride, chloranil. [b] Soda Lime, Δ.

Figure 2. Synthesis of Benzo[ghi]perylene(1) and Coronene(2)



[a]Br_2. [b]Δ. [c]Mg; then CO_2. [d]Maleic anhydride, xylene. [e]Br_2, CH_3CO_2H, $CHCl_3$. [f]Cu, BaO, Δ; then Pd/C, Δ. [g]Mg; then 1-tetralone.

Figure 3. Synthesis of Benzo[c]chrysene(3) and Picene(4)

TABLE I

KNOWN SYNTHESIS ROUTES TO HYDROCARBONS 1, 2, 3 AND 4

	% Yield	Reference
Figure 1		
5 → 6 → 7	81	10b
7 → 8	75	10b
8 → 9 → 1	39	10b
8 → 11 → 1	--	10a
11 → 10	54	10a
Figure 2		
12 → 13	93	10c
13 → 1	62	10c
1 → 14	63	10c
14 → 2	66	10c
Figure 3		
17 → 19	21	11
19 → 21 → 23	81	10a
23 → 3	56	10a
Figure 3		
15 → 16 → 17	4	11
17 → 18	15	11
18 → 20 → 22	80	10a
22 → 4	64	10a

X-ray studies[12a] show that 10, unlike most aromatic systems is not planar but helical. If the system were planar the distance between the carbons marked by asterisks would be 1.4 Å. In an attempt to attain the necessary non-bonded distance of 3 Å the molecule twists as illustrated in Figure 4.[12b,12c]

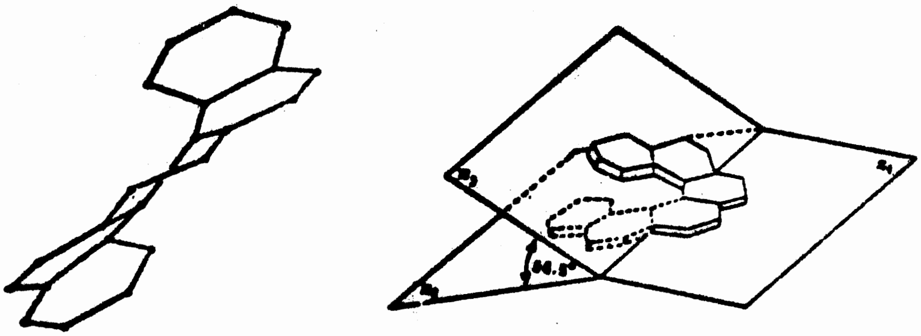


Figure 4. Conformation of Pentahelicene (10) and Hexahelicene

With the resulting decreased resonance stabilization, it is not surprising to find the system sensitive to decomposition under the harsh conditions imposed by early syntheses. Thus, Weidlich[10a] produced 10 in 54% yield from anhydride 11 while the yield of benzo[ghi]-perylene was not mentioned. Altman and Ginsburg were able to convert 8 to 10 in 37% yield, and 8 to 1 in 40% yield.

Clar[10c] has developed the only successful synthesis of coronene 2 (Figure 2). This involves two decarboxylation steps which may be effected with Soda Lime and two Diels-Alder reactions between maleic anhydride and aromatic systems. Disruption and regeneration of the aromatic system during the conversion of 1 to 14 and 12 to 13 are dependent on the presence of a dehydrogenating agent, chloranil. The crude yields are acceptable but the quality of products is disappointing. The recrystalization and sublimation necessary to give pure 14 lowered the yield to 47%.

Weidlich's route to benzo[*c*]chrysene (3) and picene (4) is dependent upon the formation of the vinylbromide 17 and its conversion to the dienes 18 and 19.[10a] Low yields of 17 made the overall yields of 3 and 4, 0.4% and 0.3% respectively. Once 17 is prepared its conversion to 3 and 4 is 10% and 8% respectively.

Low yields in the decarboxylation step has been a common weakness of each of these syntheses. A variety of decarboxylation agents are available; e.g. lead tetraacetate,[13] PbO_2-decalin,[14] PbO_2,[15] P_2O_5,[16] Cu_2O,[17] and Pd/C.[18] Examination of the literature indicates that lead tetraacetate fails for anhydrides while PbO_2-decalin often causes excess oxidation and low yields. The use of P_2O_5 is inconvenient while Cu_2O requires the use of extra steps. Pd/C also appears to be an unlikely reagent for decarboxylation because of the numerous reports[16] of low yields but isolated successes are known.[18]

Our studies with Pd/C show it is a useful reagent for oxidative decarboxylation of Diels-Alder adducts when dehydrogenation leads to an aromatic system. Improved methods of obtaining the necessary intermediates have also been developed.

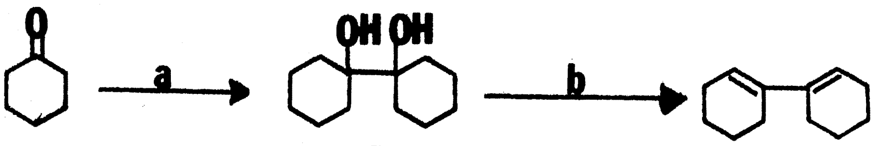
CHAPTER III

RESULTS AND DISCUSSION

Synthesis of Dienes. Polycyclic dienes may be prepared by either of two approaches. The ring system of a diene may be created and the double bonds may then be generated or a direct coupling of two olefinic species may take place affording the diene directly. An example of the former is Gruber and Adams' pinacol coupling of cyclohexanone in 35% yield to give the bicyclohexyl ring system.[19] The generation of the diene system may be accomplished through use of several dehydrating agents (10% H_2SO_4,[19] acetic acid-acetic anhydride,[10a,b] alum,[20] $POCl_3$-pyridine,[21] and DMSO[22]). DMSO proved to be the best dehydration reagent in not only yield (85%) but also purity of product and ease of workup.

An improved method for coupling cyclohexanone and other ketones is reported by Corey and co-workers using an active, low-valent titanium species.[23] Repeated attempts to duplicate the reported 90% yield of 25 failed in this laboratory, affording diol 25 in only 48% yield (Figure 5).

A similar reaction sequence was used to synthesize diene 7 from 1-tetralone (5) as illustrated in Figure 1. Use of DMSO as dehydrating agent gave a 70% yield of diene 7.



25

26

^{a}TiCl$_4$, Mg (Hg), THF. ^{b}DMSO.

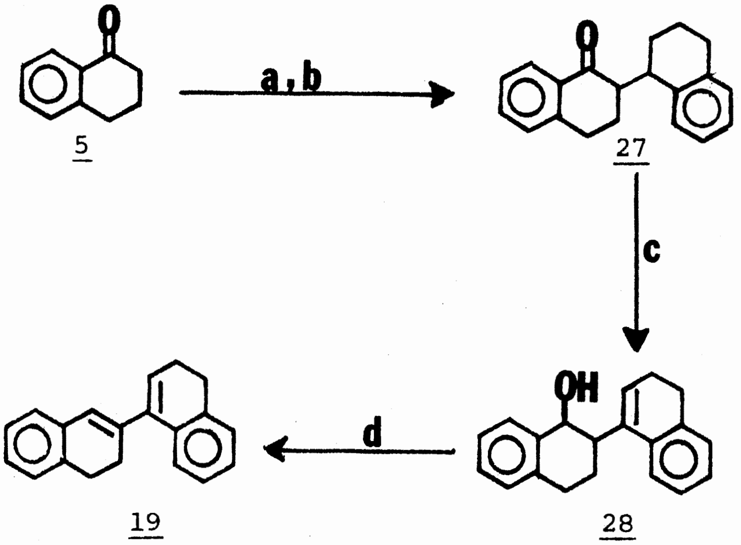
Figure 5. Synthesis of 1,1'-Bicyclohexenyl (26)

The arrangement of rings of diene 19 may be envisioned as originaging in the aldol dimer of 1-tetralone (5). Strong base provides dimers but it has been demonstrated that under extreme basic conditions the dimer is converted to naphthalene and 1-tetralone (5) in significant quantity.[24] A dimer may be isolated in 20% yield by mineral acid catalyzed condensation.[24]

The aldol dimer 27 was synthesized in 70% yield as illustrated in Figure 6 by using a Lewis acid ($TiCl_4$) and an amine to take up HCl.[25]

It is of interest that the double bond in 27 is not in conjugation with the carbonyl but rather in the ring. This structure is confirmed by ^{1}H NMR which shows a resonance at 5.77 ppm indicating one vinyl hydrogen. Reduction of 27 by diisobutylaluminum hydride and subsequent elimination afforded diene 19 in 40% yield with respect to 1-tetralone.

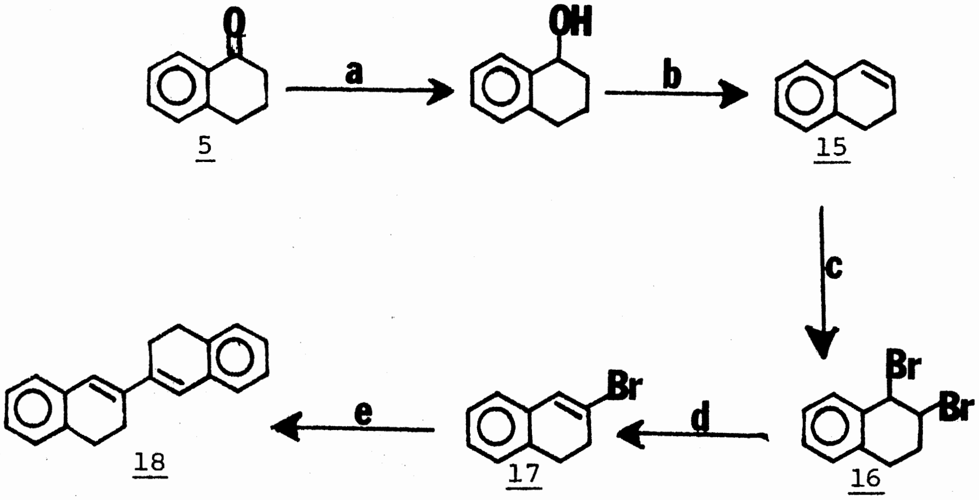
The synthesis of diene 18 provides an example in which the diene system is produced by direct union of two molecules of a vinyl halide (Figure 7). The coupling of the Grignard reagent of vinyl bromide 17 in the presence of thallium(I)bromide gives the diene directly. Diene 18 is isolated after column chromatography in 93-97% yield. This procedure, as developed by Taylor and McKillop,[26] contributes an improved



^{a}TiCl$_4$, -10°C. ^{b}1-tetralone, $(CH_3CH_2)_3N$.

^{c}DIBALH. ^{d}CH_3CO_2H, $(CH_3CO)_2O$, Δ.

Figure 6. Synthesis of 3,3',4,4'-tetrahydro-1,2'-binaphythyl (19)



^{a}DIBAH. ^{b}H^{+}, steam distillation. ^{c}Br_2,CCl_4.

^{d}DMF, Δ. ^{e}Mg, THF, then TlBr.

Figure 7. Synthesis of 3,3',4,4'-tetrahydro-2,2'-binaphthyl (18)

method for the coupling of vinyl and aryl Grignard reagents as compared to the more common cupric halide induced reaction. In this case cupric chloride induced coupling of 17 gave 18 in 45% yield.

This cannot be a viable route to 18 unless a successful synthesis of vinyl bromide 17 is developed. As shown in Figure 7, 17 may be made by first using Dobbs' pathway[28] to 1,2-dihydronaphthalene (15). This pathway consists of reduction of 1-tetralone (5) to 1-tetralol by diisobutylaluminum hydride. Subsequent dehydration in the presence of oxalic acid with concurrent steam distillation affords 15 in 70% yield. Bromination of 15 gives a 96% yield of dibromide 16.

Unfortunately the known pathways to 17 by dehydrohalogenation of dibromide 16 are unsatisfactory. In fact few examples of successful eliminations of cyclic systems of this type to vinyl bromides have been documented.[29] Adaption of Holysz's method[30] for dehydrohalogenation of α-haloketones using LiCl-Li_2CO_3-N,N-dimethylformamide produced 17. Upon distillation, the fraction collected at 95-105°C/3.5 mm was found to be isomerically pure 17 in 50-65% yield.

Variation of conditions revealed that optimum yields occur when the cyclic dibromide 16 is heated in the presence of solvent. Examination of Table II indicates that the best yields occur upon warming a solution of 16 and N,N-dimethylformamide (DMF) to 105-110°C for 5-6 h. However, good yields are obtained at reflux (152°) in 2 h.

The structure and isomeric purity of 17 was confirmed by ^1H NMR, ^{13}C NMR and mass spectral analysis (Appendix B). The ^1H NMR of vinyl bromide 17 shows a single uncoupled resonance at 6.73 ppm representing one isolated vinyl proton. The vinyl proton of 1-bromo-3,4-dihydronaphthalene would exhibit a doublet at higher field. Also the ^{13}C NMR

TABLE II

DEHYDROHALOGENATION OF 1,2-DIBROMO-1,2,3,4-TETRAHYDRONAPHTHALENE (16) IN N,N-DIMETHYLFORMAMIDE

Reactants*			Temperature °C	Time h	Yield 17, %
16	LiBr	Li_2CO_3			
0.175	0.700	0.41	152	2.5	62
0.300	-----	0.300	108-110	5.5	50
0.300	-----	-----	105	5.5	80-85
0.250	-----	-----	152	2.0	76
0.333	-----	-----	80-100	11.0	47

*The concentrations are molarity in DMF.

spectrum exhibited the expected ten resonances with no trace of isomers. The mass spectrum shows the characteristic doublet (*m/z* 210 and 208) for a monobrominated species.

Extension of this study to 1,2-dibromoindans 29a and 29b (Table III) corroborates the above work. Optimum dehydrohalogenation conditions occur upon warming in DMF thus producing vinyl bromide 30 in 60-65% yield. This compares favorably with the known syntheses of 30 (from the bromohydrin in 45-55% yield and from the dibromide in 16% yield).[29] The ^{1}H NMR of 30 has single uncoupled resonances at 6.87 and 3.55 ppm representing the vinyl hydrogen and methylene hydrogens respectively. The ^{13}C NMR exhibited the expected single resonance upfield and eight downfield resonances corresponding to the six aromatic and two vinyl carbons.

Attempts to apply this procedure to dehydrohalogenation of acyclic systems gave mixed results. Elimination of HBr from 2,3-dibromo-1-phenylethane (31) gave two of the possible bromostyrenes in only 45% yield (Figure 8).

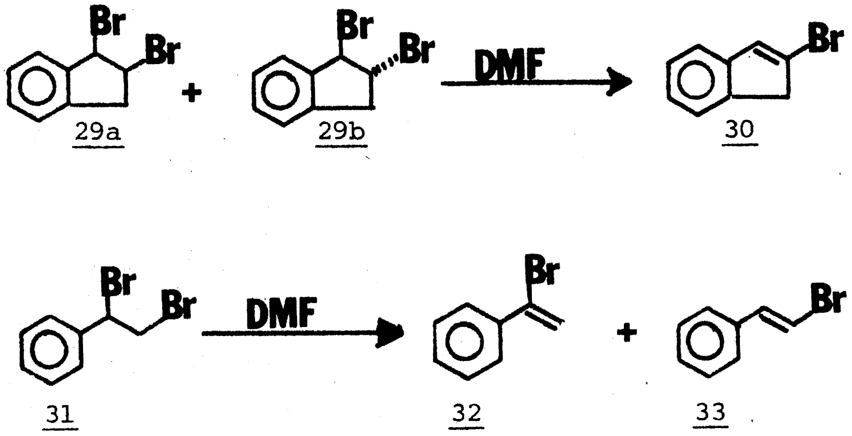


Figure 8. Dehydrobromination of cis and trans-1,2-Dibromoindan (29a and 29b) and 1,2-Dibromo-1-phenylethane (31)

TABLE III

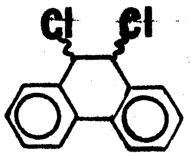
DEHYDROHALOGENATION OF 1,2-DIBROMOINDAN (29a AND 29b) IN N,N-DIMETHYLFORMAMIDE

Reactants*			Temperature	Time	Yield
29a,b	LiBr	Li_2CO_3	°C	h	30, %
0.30	0.30	0.30	105-115	6	40
0.30	0.30	----	95-114	4.5	50
0.50	----	0.55	100-113	5.5	42
0.30	----	----	110-115	6	65

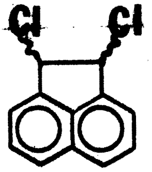
*The concentrations are molarity in DMF.

The ^{1}H NMR spectrum of the reaction product contains doublets at 7.0 ppm and 6.63 ppm (J = 14 Hz) corresponding to *trans*-β-bromostyrene (32) and weak doublets at 6.01 and 5.69 ppm (J = 3Hz) corresponding to α-bromostyrene (33). No resonance for *cis*-β-bromostyrene (34) was observed. The signals for 32 and 34 may be distinguished by the difference in their coupling constants (J_{trans} = 14 Hz, J_{cis} = 8 Hz).[31]

It is of interest to speculate on the course of these dehydrohalogenations. Examination of the literature reveals that simple alkylhalides dehydrohalogenate in DMF in 10-80% yield during a reaction period of 1 week to 1 year at 20-30°C.[32a] Low yields are reported for dehydrohalogenation of a 2-halobutane in the presence of DMF and lithium halide at 50°C.[32b] Bimolecular (E2) dehydrohalogenation of 35a[33] and 35b[34] occurs in the presence of strong base (NaOH) in protic solvents.



35a



35b

1,2-Dibromo-1,2-diphenylethane (36) has been shown to undergo synchronous E2 debromination to stilbene 37 in the presence of I^-, Br^-, or Cl^- in DMF and to a lesser extent, nonsynchronous dehydrohalogenation.[35] An extensive mechanistic study of dehalogenation of 36 and 37 has been reported.[36] The results of an investigation of debromination versus dehydrohalogenation are illustrated in Figure 9.[36c] The authors believed a bimolecular mechanism to be operative.

DEBROMINATION

$$C_6H_5CHBrCHBrC_6H_5 \xrightarrow{X,\ DMF} C_6H_5CH{=}CHC_6H_5$$

meso-36 X=Cl^-, Br^-, I^-, DMF — trans or cis 37a

dl-36 X=Br^-, I^-

DEHYDROHALOGENATION

$$C_6H_5CHBrCHBrC_6H_5 \xrightarrow{X,\ DMF} C_6H_5CH{=}CBrC_6H_5$$

meso-36 X=F^- — 37b

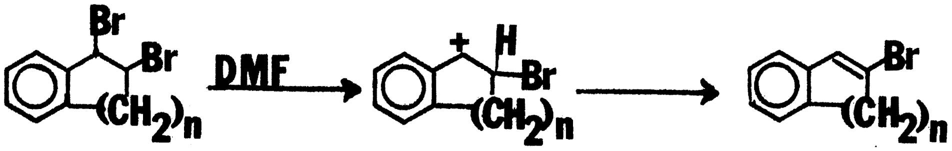
dl-36 X=F^-, Cl^-, DMF

Figure 9. Debromination Versus Dehydrohalogenation

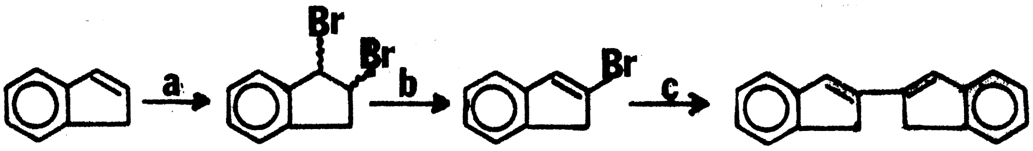
The following quotation lists some prerequisites for unimolecular elimination,[37]

> There are three main factors that favor the E1 mechanism: a substrate that gives a relatively stable carbonium ion, an ionizing solvent, and the absence of strong bases or nucleophiles.

The major products in the dehydrohalogenation of 16 and 29a-29b are consistent with the loss of a benzylic bromide ion to create a resonance stabilized carbonium ion. Polar solvents such as DMF are known to readily solvate cations.[38] In the absence of a strong nucleophile a proton is lost to solvent, thus producing the 2-bromoalkene. The presence of 32 and 33 in the elimination product of dibromide 31 implies competing mechanisms.



The thallium(I)bromide induced coupling of the Grignard reagent formed from 30 may be applied to the synthesis of 2,2'-biindenyl (35) (Figure 10). Diene 35 is produced in low yields by this method as well as by cupric chloride induced couplings.[39]



15 29a + 29b 30 35

[a]Br$_2$, CCl$_4$. [b]DMF. [c]Mg, THF; then TlBr.

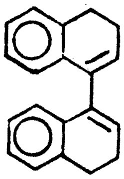
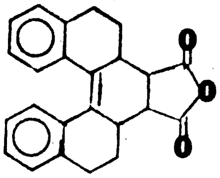
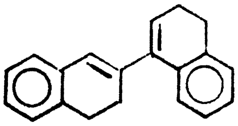
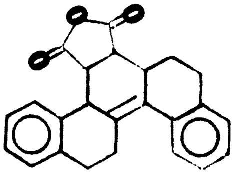
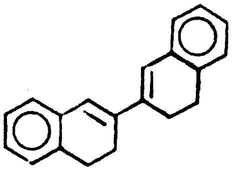
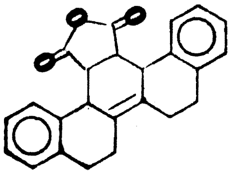
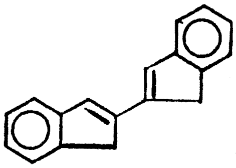
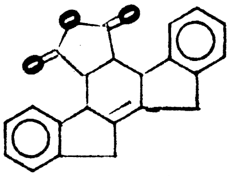
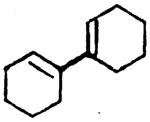
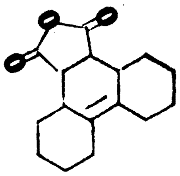
Figure 10. Synthesis of 2,2'-Biindenyl

Diels-Alder Reactions of Maleic Anhydride. The scope,[40] mechanism,[41] and theory[42] of 4+2 cycloadditions are well known. The participation of maleic anhydride as a dieneophile is also well documented.[43]

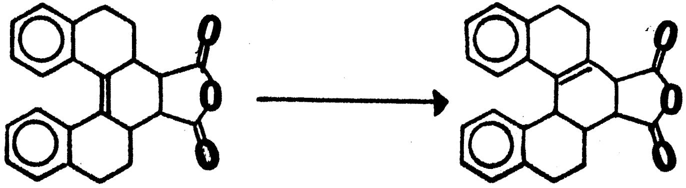
In this study, maleic anhydride is the reagent in excess and the respective dienes are the limiting reagents. Table IV presents the results of cycloadditions of maleic anhydride and various polycyclic dienes. The procedures for dienes 7, 18, 19 and 26 are taken directly from the literature with only minor variance in yields. Anhydrides 8, 20, and 21 are produced as pure products. Isomerization of the double bond in Diels-Alder adducts has been postulated[44a] and in one instance

TABLE IV

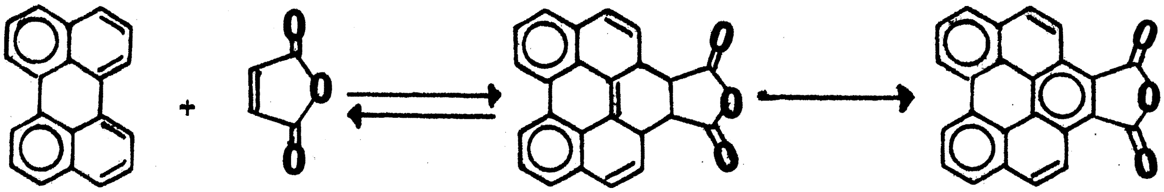
SYNTHESIS OF POLYCYCLIC ANHYDRIDES

	Diene		Product	Yield
7		8		84%
19		21		96%
18		20		87%
38		39		67%
26		40		60%

proven.[44b] Line broadening in the ^{1}H NMR and duplicate resonances in the ^{13}C NMR imply isomers of the initial Diels-Alder adducts, as illustrated below for 8, to be present. The presence of these isomers had little effect on subsequent steps, therefore their occurrence could be ignored.

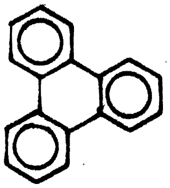


The cycloaddition reaction of an electron deficient olefin with an aromatic cisoid-butadiene-like system, as a synthetic tool, was pioneered by Clar.[45] The technique requires the initial Diels-Alder adduct react with a dehydrogenating agent before thermal cycloreversion regenerates the reactants. The dehydrogenating agent prevents the reverse Diels-Alder by: 1) rearomatization of those rings whose pi systems were disrupted during the cycloaddition and 2) creation of a new aromatic ring. A variety of hydrogen acceptors have been used, chloranil and nitrobenzene being the most popular.[10c,46,47,48]

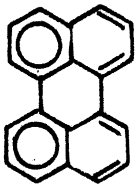


Superficially, any PNA possessing a butadiene like structure might be expected to take part in cycloaddition. Unfortunately this is not the case. Comparison of the following systems sheds light upon the reactivity of aromatic compounds.

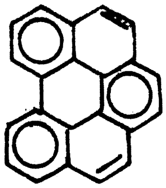
41



42



12



1

If 41 or 42 were to participate as dienes in a 4+2 cycloaddition the aromaticity of their benzene-like rings would be disrupted. MO calculations indicate 41 and 42 should be reluctant to undergo Diels-Alder reaction and experimental evidence substantiates this prediction.[47] Conversely the resonance contributors of perylene (12) show diene-like structures. MO calculations[47] as confirmed by synthetic results[10c,48] show 12 to readily undergo 4+2 cycloaddition with maleic anhydride. The resonance contributors of 1 have a triphenylene-(42)-like aromatic system. MO calculations[47] and experimentation show 1 to be a poor diene and to react sluggishly with maleic anhydride.

Chloranil has been shown to be an effective dehydrogenation agent for trapping the Diels-Alder adducts of aromatic compounds like 12 and 1 to give anhydrides such as 13 and 14 (Figure 2).[10c,46b,48] Yields are good but by-products render 13 and 14 difficult to purify. Pd/C was substituted for chloranil in an attempt to develop a cleaner procedure (Figure 11). Pd/C rapidly dehydrogenated the adduct of 12 to 13 in 76% yield. All attempts to capture the adduct of 1 failed when Pd/C was used. Addition of picric acid (a common acceptor in charge transfer complexes) did give 14 but in synthetically unacceptable yields.

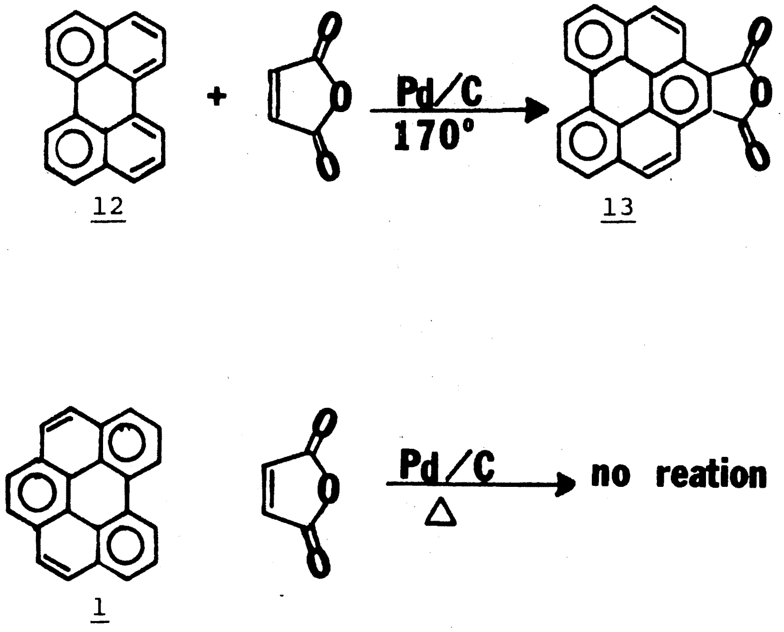
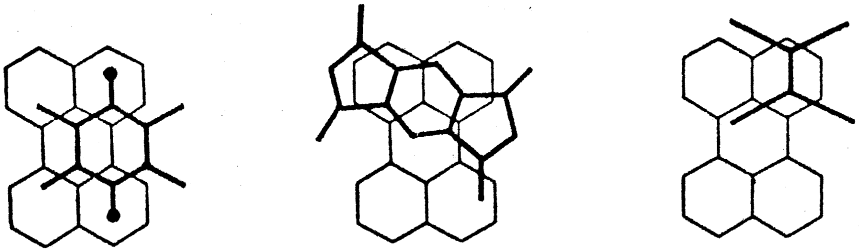


Figure 11. Pd/C Catalyzed Diels-Alder Reactions

The implication is that chloranil is more than a dehydrogenating agent. Indeed charge transfer complexes between chloranil and aromatic hydrocarbons have long been known[49] but have been unrecognized by synthetic chemists.

The full nature of chloranil's participation remains a mystery. The structures, as determined by x-ray analysis of several crystalline complexes formed by perylene are illustrated in Figure 12.[50] The proximity of the sites for fluoranil complexation and cycloadditon is intriguing but the significance of this phenomena is uncertain. The necessity of the presence of chloranil during the synthesis of 14 must be tolerated despite the purification problems which arise.



a. fluoranil-perylene complex

b. pyromellitic anhydride-perylene complex

c. tetracyanoethylene-perylene complex

Figure 12. Charge Transfer Complexes of Perylene

Anhydride 14 has a melting point in excess of 500°C and is insoluble in most organic solvents. Boiling nitrobenzene has been reported as a recrystalization solvent[10c] but is removal must also be effected. However, coronene anhydride (14) does sublime at 470-490°C/0.2 mm Hg.

High-temperature equipment was necessary to perform fractional sublimation of from 1 to 14. Figure 13 illustrates the high-temperature sand bath and the glassware which was developed to effect large scale manipulations at elevated temperatures.[51] Details of their construction may be found in Appendix C.

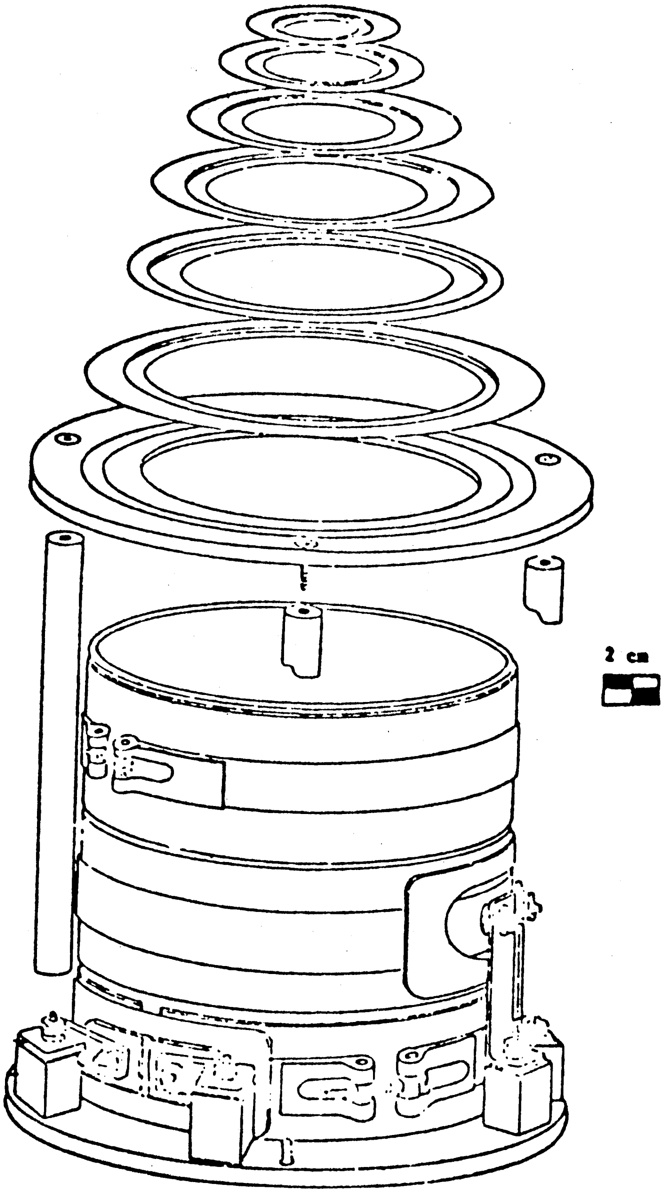


Figure 13. High-Temperature Sand-Bath Heater and Improved Sublimation Apparatus

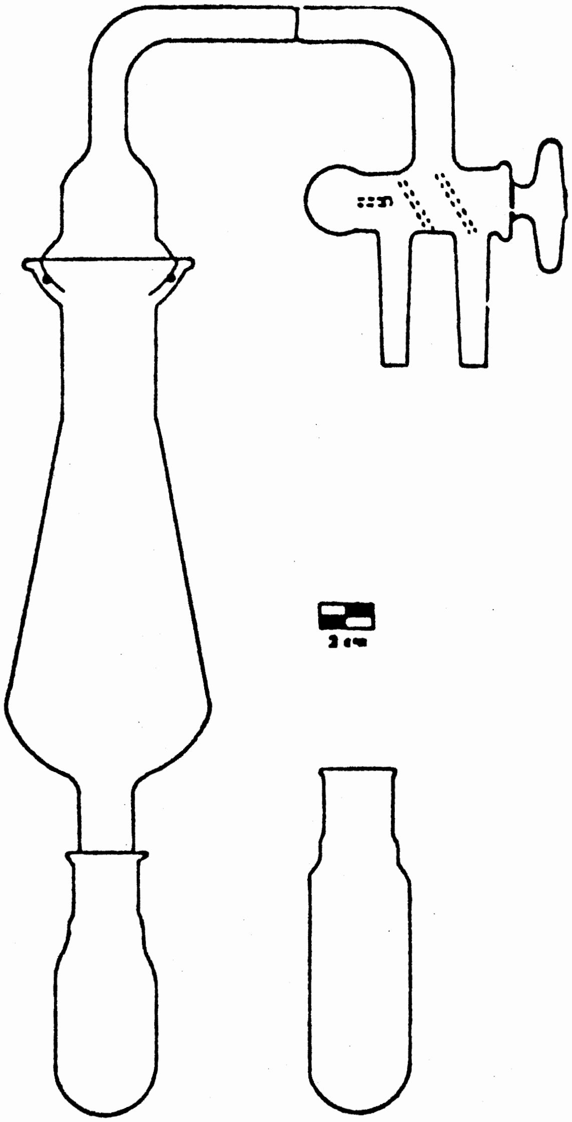


Figure 13. (Continued)

Decarboxylation and Dehydrogenation. To achieve the synthesis of hydrocarbons 1, 3 and 4, a reliable method of decarboxylating and dehydrogenating the adducts 8, 20 and 21 was needed. Pd/C was found to effect both steps.

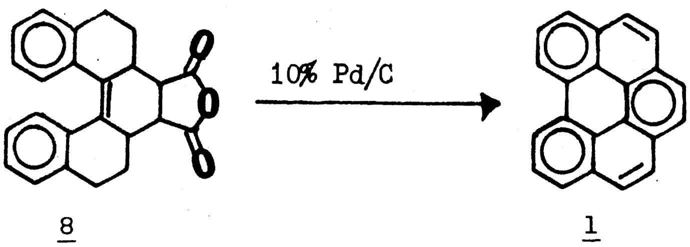
Optimization of conditions was carried out with anhydride 8 and 10% Pd/C as illustrated in Table V. Decarboxylation was monitored by reaction of the evolved CO_2 with saturated $Ba(OH)_2$ solution. Upon cessation of CO_2 evolution, the reaction product was transferred to a Soxhlet extractor[52] charged with basic alumina from which pure hydrocarbon was eluted. The major by-products are fully aromatic mono and di-acids which are retained by the alumina. Optimum yield of aromatic hydrocarbon was obtained when an intimate mixture of anhydride and Pd/C were heated above 260°C in a N_2 atmosphere.

Adaptation of this procedure to the decarboxylation and dehydrogeneration of other Diels-Alder adducts is listed in Table VI. In general this technique is efficient for the conversion of large multiring anhydrides to the corresponding hydrocarbons.

Unfortunately, the majority of known decarboxylations have been attempted with 1-, 2-, and 3-ring nonaromatic anhydrides which rarely produce hydrocarbons in yields greater than 20%.[53] Table VII shows carboxylic acids and anhydrides which are decarboxylated and aromatized in greater than 50% yield. The anhydrides in Table VII are similar to those in Table VI in that they possess an aromatic ring before treatment with catalyst. In general, synthetically useful yields of high-molecular weight hydrocarbons is achieved from partially aromatic acids and anhydrides. Pd/C with copper chromite has been shown to decarboxylate dodecahydrophenanthrene-2,3-anhydrides in good yield but this

TABLE V

REACTION CONDITIONS FOR Pd/C CATALYZED DECARBOXYLATION AND DEHYDROGENATION



Reaction Conditions	Solvent	Percent Yield of 1
235°C/18 h/N_2	methylnaphthalene	53%
230-250°/5 h	none	39%
260-265°/13 h/N_2	none	81%
264-280°/8 h/N_2 290-300°/8 h/N_2	none	94%

*Reaction time determined by cessation of CO_2 evolution. Reaction scale varied from 5-10 g of 8.

TABLE VI

Pd/C CATALYZED DECARBOXYLATION AND DEHYDROGENATION

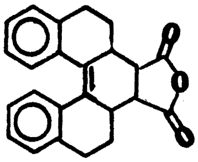
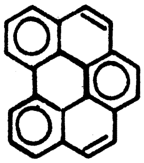
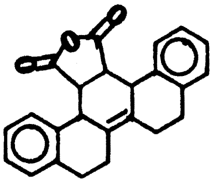
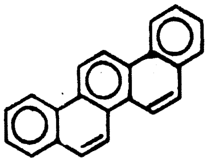
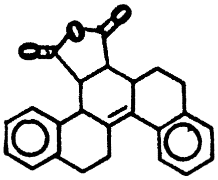
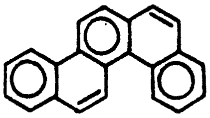
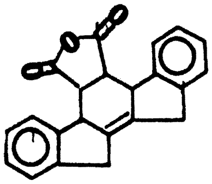
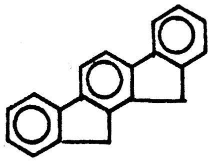
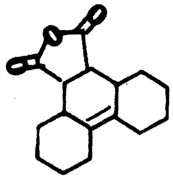
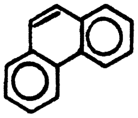
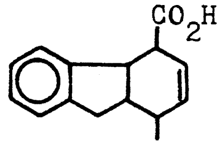
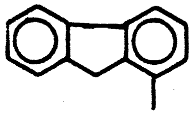
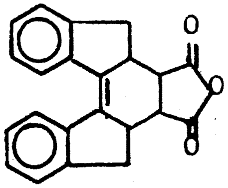
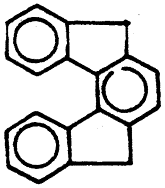
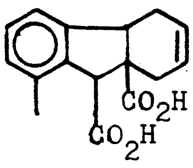
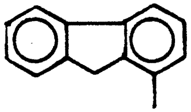
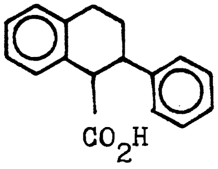
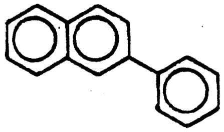
Reactant		Product		Yield
8		1		94%
20		4		84%
21		3		66%
39		43		---
40		44		0%

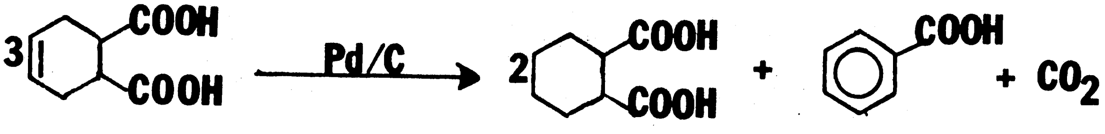
TABLE VII

OXIDATIVE DECARBOXYLATION BY Pd/C

Reactant	Conditions	Product	Yield	Reference
	15% Pd/C 280° N_2		74%	54a
	5% Pd/c 230-240° Then 360° H_2		71%	18a
	30% Pd/C 235° N_2		51%	54b
	10% Pd/C 265° N_2		103%	54c

catalyst performs poorly with other anhydrides.[55]

It has been reported that tetrahydrophthalic acid 45 undergoes transfer dehydrogenation upon treatment with palladium catalyst.[56] Re-

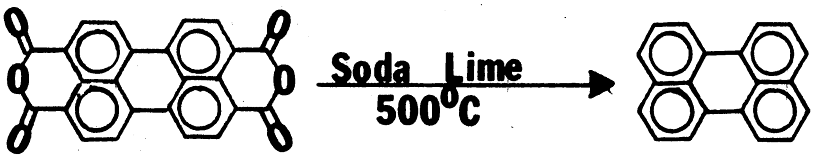


45

examination of this reaction indicated the presence of at least a dozen products among which benzaldehyde and benzoic acid were observed. The presence of benzaldehyde is interesting in that aldehydes might be intermediates in the decarboxylation of vicinal anhydrides. The decarbonylation of aromatic aldehydes by Pd/C is well described.[57]

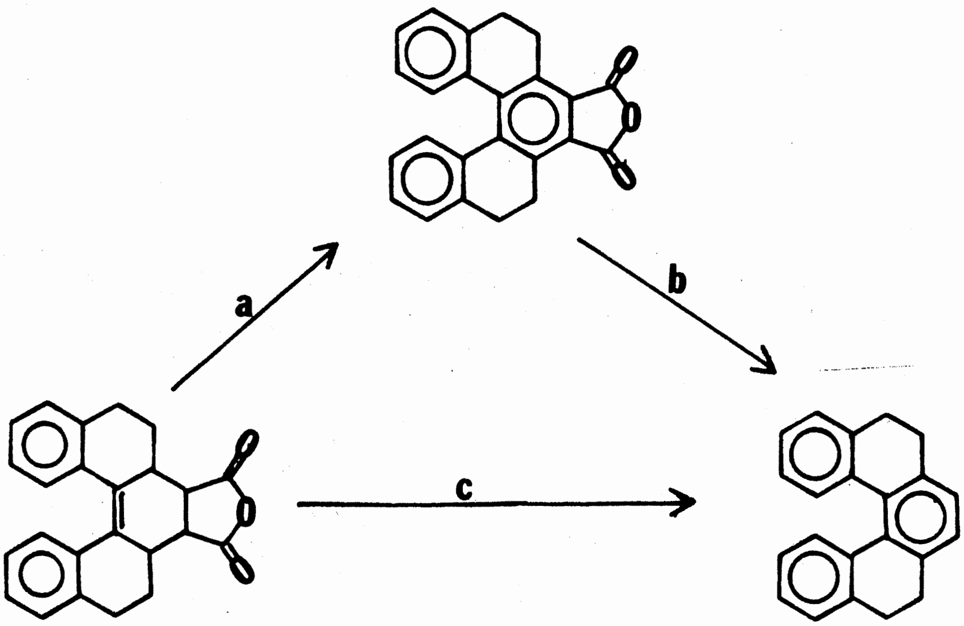
The synthesis of hydrocarbon 9 may be brought about directly by distillation of anhydride 8 over hot PbO_2 (50%) or by aromatization with bromine followed by decarboxylation with cuprous oxide and quinoline (66%) as shown in Figure 14.[58]

Coronene 2 may be produced by distillation of anhydride 14 over Soda Lime[10c] at 490-500°C (Figure 2). This reaction may be conveniently carried out using the apparatus shown in Appendix C. Use of this equipment in large-scale, high-temperature reactions permitted the synthesis of perylene 12 from the commercially available anhydride 46 in 80% yield.



46

12



$^{a}Br_2$, CH_3CO_2H. $^{b}Cu_2O$, quinoline, Δ. $^{c}PbO_2$,Δ

Figure 14. Synthesis of 1,2,7,8-Tetrahydrodibenzo[c,g]phenanthrene (9)

In summary, benzo[ghi]perylene (1) was synthesized in 54% overall yield (compared to 24%) in four steps from 1-tetralone. Improvement was made in the decarboxylation and dehydrogenation of anhydride 8(94%). The yield of picene (4) was considerably improved not only in the one-step decarboxylation and dehydrogenation of anhydride 20 (84%) but also in the formation of the key intermediate, 17, in 85% yield (versus 4%). The Grignard coupling of 17 was improved from 15% to 93%. Thus picene (4) was synthesized in 44% in six steps from 1-tetralone (5). The previous yield was 0.3%.

Benzo[c]chrysene was produced in 28% yield in three steps from 1-tetralone (5) instead of a six stage (0.4% yield) route. Also, the first efficient synthesis of a β,γ-unsaturated aldol condensation product was effected.

Equipment for high temperature manipulations improved not only reaction yields but reaction size (from milligram scale to a 25 gram scale).

CHAPTER IV

EXPERIMENTAL

dl-1,1'-Dihydroxy-1,1',2,2',3,3',4,4'-octahydro-1,1'-binaphthyl (6). Freshly distilled 1-tetralone (146 g, 1.0 mol) was placed in a 3-L, 2-neck, round-bottom flask equipped with nitrogen inlet, reflux condenser, magnetic stirring, and heating mantle. Anhydrous benzene (1400 mL), absolute ethanol (100 mL), aluminum foil (41.4 g, 2 g-atoms), and mercuric chloride were added. The system was flushed with nitrogen and brought to reflux. After 20 h, the liquid contents were decanted, washed twice with cold 10% HCl, dilute Na_2CO_3, and then with H_2O. The organic phase was dried ($MgSO_4$), filtered, and concentrated.

An analytical sample of the product was prepared by crystalization from toluene and trituration with ether to give white crystals of 6; mp 188-190°C (lit.[44a,59] 191-192°C); ^1H NMR ($CDCl_3$)[60] δ 8.15-7.30 (m, 2, ArH), 7.30-6.85 (m, 6, ArH), 3.18 (s, 2, OH), 2.85-2.40 (m, 4, ArCH), 1.75-1.00 (m, 8, $ArCH_2\underline{CH_2}\underline{CH_2}$); ^{13}C NMR[61] ($CDCl_3$) 140.2, 138.1, 128.8, 128.6, 126.9, 126.1 (Aromatic C), 58.5 (C-OH), 36.3, 31.1, 20.0 (aliphatic C); IR[62] (KBr) cm^{-1} 3530(O-H), 1440, 1280, 1070, 975, 900, 735. The remaining diol 6 was converted directly to diene without purification.

The cyclic phenyl boronate was prepared by mixing 1.53 g (5.2 mmol) of 6, 0.63 g (6.1 mmol) of phenylboronic acid anhydride and 100 mL of toluene. Water was removed by azeotropic distillation. The cooled yellow solution was passed through a column of neutral alumina, concentrated and dried in vacuo to give 1.7 g (86%) of white waxy solid. Trituration with cyclohexane gave 0.086 g: mp 128.5-129.5°C; ^{1}H NMR ($CDCl_3$)δ 8.02-7.90 (m, 2, ArH), 7.63.7.28 (m, 5, B-Ar-H), 7.28-7.00 (m, 6, ArH), 3.00-2.45 (m, 4, $ArCH_2$), 1.9 (t, 4, BOC-CH_2), 1.7-1.2 (m, 4, CH_2); ^{13}C NMR ($CDCl_3$) ppm, 137.7, 137.5, 135.2, 131.4, 128.7, 128.0, 127.7, 127.4, 125.4 (aromatic C), 87.8, 58.7, 35.2, 29.3, 19.0 (aliphatic C); IR (KBR) cm^{-1} 1605, 1440, 1345, 1080, 995, 920, 745, 700, 650; mass spectrum m/z (relative intensity) 380 (M^+, 14), 279 (M^+, 3), 250 (5), 147 (20), 146 (18), 130 (100), 129 (42), 128 (22), 115 (22), 91 (19).

3,3',4,4'-Tetrahydro-1,1'-binaphthyl (7). Crude diol 6 was then dissolved in a mixture of 300 mL of acetic acid and 300 mL of acetic anhydride. This solution was heated at reflux for 5 h and then concentrated under vacuum to give 88.3 g (68%) of the diene 7, mp 135-137.5°C. Elution from a Soxhlet column charged with neutral alumina by refluxing isohexane followed by filtration of the cooled eluent gave 90% recovery of white crystaline (7); mp 138-139.5°C (lit.[10b] 141°C); ^{1}H NMR ($CDCl_3$) δ 7.40-6.64 (m, 8, ArH), 6.2-5.85 (t, 2, vinyl H), 3.10-2.63 (m, 4, CH_2), 2.57-2.10 (m, 4, CH_2); ^{13}C NMR ($CDCl_3$) ppm, 138.1, 135.6, 134.5, 127.7, 127.1, 126.5, 126.1, 124.9 (sp^2 C), 28.2, 23.3 (sp^3 C); IR (KBr) cm^{-1} 1380, 1440, 1420, 1020, 940, 910, 830, 760, 730; mass spectrum m/z (relative intensity) 259 ($M+1^+$, 19), 258 (M^+, 100), 257 (22), 243 (10), 230 (17), 229 (15), 154 (8), 141 (8), 130 (8), 129 (40), 128 (40), 115 (14), 101 (11), 91 (14).

1,2,2a,3,4,4a,5,6-Octahydrodibenzo[c,g]phenanthrene-3,4-dicarboxylic acid anhydride (8). Into a 3-L, 2-neck flask fitted with thermometer and condenser was placed an intimate mixture of 141 g (0.55 mol) diene

7 and 550 g (5.6 mol) maleic anhydride. The reactants were heated to 110-140°C for 8 h. The crude product was dissolved in 6500 mL acetic acid. Upon concentration to 3500 mL and cooling, the adduct was collected by filtration and dried to give 163.3 g (84%) 8, mp 234-252°C (lit.[10b] 252-254°C); ^{1}H NMR ($CDCl_3$) δ 6.7-7.3 (m, 8, ArH), 3.5 (q, 2, methine), 1.8-3.1 (m, 10, aliphatic H); ^{13}C NMR 171.4 (C=O), 140.3, 133.5, 133.2, 129.8, 127.5, 125.2 (sp^2C) 45.6, 37.1, 29.4, 25.2 (aliphatic); IR (KBr) cm^{-1} 1840, 1770 (C=O stretch) 1440, 915, 740, 600. Mass spectrum *m/z* (relative intensity) 355 (m^+-1, 27), 354 (100), 342 (30), 293 (34), 267 (20), 257 (21), 163 (27), 155 (49), 150 (27).

Benzo[*ghi*]perylene (1) from 8. An intimate mixture of 12.1 g of 8 and 2.2 g of 10% Pd/C was placed in a 2-neck, 500 mL flask equipped with a gas inlet and condenser. After flushing with N_2, the flask was heated in a sand bath to 260-280°C for 8 h. The resulting solid was broken up with hot toluene and placed in a Soxhlet extractor[52] charged with basic alumina. The hydrocarbon was eluted with refluxing toluene to give 8.8 g (94%) of light yellow 1, mp 273-276°C (lit.[10c] mp 273°C); ^{1}H NMR ($CDCl_3$) δ8.94-9.04 (two d, 2, bay H), 8.34 (s, 2, ArH) 7.92-8.26 (m, 8, ArH).

Benzo[*ghi*]perylene (1) from 8 in methylnaphthalene. In a 2-neck, 250-mL flask equipped with magnetic stirrer, nitrogen inlet, condenser, and bubbler, were combined 5.8 g (16 mmol) of anhydride 8, 2.0 g of 10% Pd/C, and 20 g of 2-methylnaphthalene. The system was flushed with nitrogen and heated to reflux (235°C) for 18 h. After cooling, benzene was added and the black mixture was transferred to a Soxhlet extractor charged with Dicalite suspended in benzene. A forerun was collected and the hydrocarbon 1 was eluted with refluxing benzene. After evaporating, the resulting solution yielded 2.5 g (53%) light orange crystals, mp 271-273.5°C. The crude product was placed in a Soxhlet extractor above basic alumina and 1 was eluted with refluxing benzene. Pale yellow plates, mp 273.5-275°C (lit.[10c] mp 273°C), were filtered from the hot solvent.

Perylene (12). A mixture of equal volumes of 3,4,9,10-perylenetetracarboxylic dianhydride (4.0 g, 10 mmol) and Soda Lime (27 g) were placed in a reaction vessel.[63] Above this was layered 5 g Soda Lime (4-8 mesh) and a plug of glass wool. The reactor was alternately evacuated with an oil pump and flushed with argon (3 times). Upon heating, bright yellow 12 sublimed at 440-500°C/0.1 mm over a 2 h period. After cooling, the product was transferred to a Soxhlet extractor containing Merck basic alumina (40 cc) and hydrocarbon 12 was eluted with refluxing toluene in 3 h. Subsequent concentration and drying *in vacuo* gave bright yellow plates of 12 (2.1 g, 82%, mp 273-275°C, lit.[64] 269°C): ^{1}H NMR ($CDCl_3$) δ 8.20 (d, 4, H-1,6,7,12), 7.71 (d, 4, H-3,4,9,10), 7.49 (t, 4, H-2,5,8,11); mass spectrum *m/z* (relative intensity) 252 (100, M^+), 250 (19), 153 (26), 92 (46), 91 (57).

Conversion of Perylene (12) to Benzo[*ghi*]perylene-3,4-dicarboxylic anhydride (13). Perylene (1.17 g, 5 mmol) was mixed in a 300 mL, 2-neck flask with maleic anhydride (19.7 g, 0.1 mol) and 10% Pd/C (0.47 g) under a nitrogen atmosphere. The reaction mixture was heated at 170°C in a salt bath for 20 min. Gas evolved as the reaction mixture changed from an orange melt to a black glass. The product was cooled and treated with 100 mL of methanol. The resulting mixture was filtered and the filter cake was washed with methanol until no more brown material eluted. The solid was placed in a Soxhlet extractor above Dicalite and extracted with refluxing benzene for 2 h to remove 12. Extraction with refluxing toluene for 4 days gave a solution which upon concentration yielded 1.1 g (3 mmol, 71%) of red-orange 13 mp 495-510°C, (lit.[65] mp 465-470°C); IR (KBr) cm^{-1} 1820, 1750 (C=O stretch).

Coronene-1,2-dicarboxylic anhydride (14). Benzo[ghi]perylene (1) (1.85 g), chloranil (7.3 g), and maleic anhydride (22.6 g) were placed in a 300 mL flask equipped with condenser and magnetic stirrer. The mixture was refluxed for 6 h. Hydrogen chloride evolved and a dark precipitate deposited. After cooling, 30 mL of nitrobenzene were added and the suspension was gently warmed, filtered and the filter cake was washed with nitrobenzene and ether. The residue was recrystallized from 60 mL nitrobenzene to give 2.5 g reddish brown solid. The solid was placed in a Soxhlet extractor containing neutral alumina and then extracted with refluxing benzene to remove excess chloranil. The remaining brown residue and the top layer of alumina were transferred to a sublimation apparatus.[63] Sublimation yielded red-orange crystals of 14 (1.5 g, 61%) which began to sinter at 455°C and melted at 499-500°C.

Fractional Sublimation of Coronene-1,2-dicarboxylic Anhydride (14). Into a 250 mL flask (part of sublimation apparatus)[63] was placed 20.8 g (0.056 mol) of 14. The system was alternately evacuated and flushed with argon. Hydrocarbon 1 and other volatile impurities were sublimed away from the anhydride at 250-400°C (0.2 mm Hg) during 4 h. After cooling, the receiver was replaced and the system evacuated and flushed with argon (4x). The flask was again heated using the high temperature sand bath to 470-490°C (0.2 mm Hg). The bulk of the anhydride sublimed suddenly at 490°C giving 202 g (97%) of bright red-orange crystals of 14, mp 505°C, (lit.[10c] mp 490-503°C); IR (KBr) cm^{-1} 1820, 1750 (C=O stretch). TLC[66] studies showed absence of benzoperylene. However, traces of coronene were observed.

Coronene (2). A 2.0 g (0.01 mol) sample of anhydride 14 and 10 g Soda Lime were thoroughly mixed with a mortar and pestle. This mixture was placed in the bottom of the reaction flask[63] and covered with a 6 g layer of powdered Soda Lime and then 35 g of 4-8 mesh Soda Lime particles. Glass wool was then placed above the reactants. The system was alternately evacuated and flushed with argon (4x). Upon heating to 350-400°C (0.05 mm Hg), coronene sublimed above the glass wool. This sublimate was placed in a Soxhlet apparatus charged with Merck, activity I, basic alumina. The alumina was contained as a 5 cm diameter x 6 cm volume. The hydrocarbon was eluted with refluxing toluene to give a suspension of coronene 2. Cooling and filtering gave 2.4 g (80%) of 2 as bright yellow fluffy needles, mp 434-438°C.

The combined product of 8 reactions (16.2 g) was placed in a Soxhlet column charged with basic alumina and then eluted with refluxing toluene. Cooling and filtering gave 15.0 g of 2. Sublimation[63] gave 14.4 g of 2, mp 437-440°C (lit.[47] mp 440°C); mass spectrum m/z (relative intensity) 302 (M+2, 3), 301 (M+1, 26), 300 (M^+, 100), 150 (M^{+2}, 6), 100 (M^{+3}, 2) 59 (3).

1,2-Dihydronaphthalene (15). To a dry 12 L fluted flask equipped with a nitrogen inlet, stirrer, thermocouple, condenser, and addition funnel, was added, with stirring 2.2 L of dry toluene and 633.0 g (4.45 mol) of diisobutylaluminum hydride. A toluene solution (1 L) containing 585 g (4 mol) of 1-tetralone was added through a pressure equilized dropping funnel at such a rate that the temperature did not exceed 35°C. After the addition was complete, the mixture was sitrred for an additional 30 min. Ethyl acetate was then added until no further temperature rise was observed. The entire solution was then poured carefully with stirring, onto ice and allowed to warm to room temperature. Conc HCl was added slowly until pH-1 was reached. The acidified reaction product was placed in a 12 L separatory funnel and the toluene layer was separated. Filtration through Dicalite facilitated separation of layers. The aqueous layer was then extracted with toluene (3 x 300 mL). The organic layer was washed with water, then with a saturated solution of Na_2CO_3, and then again with water. The extract was filtered through solid Na_2CO_3, dried ($MgSO_4$) and concentrated by rotary evaporation to yield 516 g (87%) of crude product. Distillation at this point gives 1-tetralol bp. 85°C/10.3 mmHg (lit.[67] 93-96°/0.3 mm).

In a 2-L, 2-neck flask equipped with a steam inlet, stirrer, and condenser was placed 20.0 g oxallic acid and 516 g (3.5 mol) of crude 1-tetralol. Sufficient water (500 mL) was added to dissolve the oxallic acid and steam was introduced. The condensate was collected until it was no longer cloudy. Extraction with ether (3 x 200 mL), drying ($MgSO_4$), concentrating and distilling yielded 362 g (2.8 mol) of 1,2-dihydronaphthalene (15), bp 70°C/0.3 mm Hg. (lit.[68] 110°C/13-14 mm Hg.).

1,2-Dibromo-1,2,3,4-tetrahydronaphthalene (16). A solution of bromine (116 g, 0.715 mol) in 100 mL CCl_4 was added dropwise over a 2 h period to a solution of dihydronaphthalene (94 g, 0.723 mol) in 100 mL CCl_4 at 0°C with vigorous stirring. Solvent and excess bromine were removed by rotary evaporation to give a tan liquid which slowly solidified. Recrystalization from 500 mL of 2-propanol gave waxy white crystals 205 g (98%), bp 106-108°C/0.3 mmHg, mp 65-67°C (lit.[69] 67-68°C);

^{1}H NMR (CDCl$_3$) δ 7.36-6.98 (m, 4, ArH), 5.62 (m, 1, ArCHBr), 4.88 (m, 1, ArCHBrC$\underline{\text{H}}$Br-), 3.45-2.57 (m, 3, CH$_2$), 2.38-1.95 (m, 1, CH$_2$); ^{13}C NMR (CDCl$_3$) ppm 134.1, 132.4, 130.9, 128.9, 128.6, 126.3 (aromatic C), 51.4 (C-Br), 25.0 (CH$_2$), 24.4 (CH$_2$); IR (KBr) cm^{-1} 1440, 1420, 1210, 910, 760, 740, 700, 645.

3-Bromo-1,2-dihydronaphthalene (**17**). Into a 3-neck, 100 mL flask equipped with thermometer, nitrogen atmosphere, and condenser was placed 4.35 g (0.015 mol) dibromide **16** and 50 mL N,N-dimethylformamide. After heating at 104-105°C for 5.5 h, the cooled reaction mixture was poured into 100 mL water and 30 mL n-hexane and stirred until the emulsion dispersed. The organic layer was separated, washed twice with salt water, once with water, dried (MgSO$_4$) filtered through Dicalite. After concentration on a rotary evaporator, the product was distilled to give 2.62 g (84%) of **17** bp 93-105°C/3.6-3.7 mmHg (lit.[11] 144-146°C/17 mmHg); mass spectrum^{70} *m/z* (relative intensity) 210 (48), 208 (61), 206 (18), 129 (100), 128 (73), 127 (45); ^{1}H NMR (CDCl$_3$) δ 2.58-3.04 (m, 4, CH$_2$), 6.73 (s, 1, vinyl), 6.85-7.20 (m, 4, ArH) ^{13}C NMR (CDCl$_3$) ppm, 133.7, 132.7, 129.2, 127.3, 126.5, 125.4, 123.9, 111.9, 33.7, 29.2; IR (neat) cm^{-1} 3020, 2940, 2880, 2825, 1630, 1430, 1110, 935, 745.

3,3',4,4'-Tetrahydro-2,2'-binaphthyl (**18**). Into a 300-mL, 3-neck flask equipped with addition funnel, vented condenser, glass drain tube, and magnetic stirring, was placed 3.2 g (0.13 mol) magnesium turnings, 50 mL dry THF and a crystal of I$_2$. An argon atmosphere was maintained while a solution of vinyl bromide **17** in 40 mL dry THF was added dropwise. Upon heating to reflux, a red-black solution formed. Reflux was maintained for 2.5 h. Upon cooling, the vent was closed and the solution was transferred with positive argon pressure through the drain tube fitted with a glass wool filter into a 1-L, fluted, 3-neck flask equipped with thermometer and vented condenser and charged with 63.1 g (0.22 mol) of TlBr suspended in 210 mL of rapidly stirred, dry toluene. The residual magnesium powder was washed with five 10-mL aliquats of dry THF and these were transferred to the 1-L reaction flask. The resulting grey suspension was heated at reflux (89°C) for 6 h. All solids dissolved in the refluxing solvent. Upon cooling, the product was filtered through Dicalite to remove thallium, acidified with 500 mL 10% HCl, and again filtered through Dicalite. The organic layer was washed with two 200 mL portions of water and dried ($MgSO_4$). The filtered solution was placed directly on a column charged with basic and acidic alumina (1:1). The hydrocarbon was eluted with toluene until blue fluorescent material ceased to elute from the column. After the solvent was evaporated, fluffy pale yellow crystals of <u>18</u> were isolated (13.8 g, 97%). Trituration with 2-propanol gave 10 g, mp 156-157°C (lit.[10a] 156°C); ^{1}H NMR ($CDCl_3$) δ 7.08 (s, 8, ArH), 6.67 (s, 2, vinyl H), 3.0-2.5 (m, 8, allylic and benzylic H); ^{13}C NMR ($CDCl_3$) ppm 138.0, 135.3, 134.6, 126.8, 126.6, 126.4, 126.3, 123.1, 28.1, 24.3; mass spectrum[71] *m/z* (relative intensity) 259 (M+1, 26), 258 (M^+, 100), 256 (18), 154 (10), 141 (20), 130 (17), 129 (29), 128 (36), 115 (15); IR (KBr) cm^{-1} 1480, 1425, 940, 880, 850, 810, 740.

<u>5,6,7,8,12b,13,14,14a-Octahydropicene-13,14-dicarboxylic acid anhydride (20)</u>. To 5.0 g (19.4 mmol) of diene <u>18</u> and 7.3 g (75 mmol) freshly sublimed maleic anhydride was added 50 mL of dry toluene. The mixture slowly yellowed as it was brought to reflux. After refluxing for 4 h, toluene was removed under vacuum. After cooling, 80 mL of water was added and the mixture was warmed on the steam bath. The fluffy

colorless crystals (7.1 g) which result were removed by filtration, dissolved in 25 mL benzene and precipitated upon addition of 130 mL of isooctane. The dried colorless crystals 6.0 g (87%) of 20; mp 208-212°C (lit.[10a] mp 217-218°C); ^{1}H NMR ($CDCl_3$) δ 7.34-7.18 (q, 8, ArH), 3.92-3.66 (m, 4, aliphatic H), 3.02 (t, 1, aliphatic H) 3.0-2.6 (m, 5, aliphatic H), 2.6-1.8 (m, 2, aliphatic H); IR (KBr) cm^{-1} 1855, 1780 (C=O), 1440, 1025, 980, 920, 760, 740, 710, 620; mass spectrum m/z (relative intensity) 255 (M+1, 0.1), 354 (1), 353 (4), 259 (22), 258 (100), 181 (28), 169 (24), 131 (43), 119 (39).

Picene (4). A 200 mL flask containing a mixture of 2.109 g (5.92 mmol) of anhydride 20 and 145 mg of 10% Pd/C under a N_2 atmosphere was heated rapidly in a sand bath to a temperature of 295°C. The temperature of the sand bath stabilized at 245-250°C. Evolution of CO_2 was monitored by bubbling the gas effluent into a $Ba(OH)_2$ solution. After 8 h the reaction mixture was cooled and toluene was added. The fluffy sublimate and black residue were transferred to a Soxhlet extractor charged with 800 mL basic alumina. The hydrocarbon was eluted with refluxing toluene in 12 h. The solution was concentrated, cooled and filtered to give 1.1 g (83%) of colorless fluffy crystals of 4, mp 362-365°C (lit.[10a] mp 364°C); ^{1}H NMR (FT mode - 100 acquisitions) ($CDCl_3$) δ 9.00 (s, 2), 8.83 (d, 2), 7.46-8.22 (m, 10); mass spectrum[71] m/z (relative intensity) 279 (M+1, 26), 278 (M^+, 100), 277 (6), 276 (21), 139 (M^{+2}, 13), 138 (12), 125 (5).

3,3',4,4'-Tetrahydro-1,2'-binaphthalen-1,(2'H)-one (27). To 200 mL olefin free hexane was added 96.9 g (56.0 mL, 0.51 mol $TiCl_4$ in a N_2 atmosphere. The mixture was cooled by an ice-salt water bath to -10°C and a solution of 66 mL (72.5 g, 0.5 mol) 1-tetralone in 850 mL CH_2Cl_2, was added rapidly with vigorous stirring to give a yellow fluffy precipitate. Subsequently, a solution of 66 mL (72.5 g, 0.5 mol) 1-tetralone and 148 mL (107.4 g, 1.1 mol) of triethylamine diluted to 850 mL with CH_2Cl_2 was added. The ensuing red-black solution was stirred at -10°C for 40 min. and warmed to room temperature over 16 h. The black product was treated with 1.5 L H_2O with some gas evolution. The amber CH_2Cl_2 layer was separated, the aqueous layer was back extracted with CH_2Cl_2, and the combined organic layers were washed with H_2O (3x). After desiccation ($MgSO_4$), filtration, and concentration, the colored product was washed with 200 mL 2-propanol and again filtered to yield 96 g (70%) <u>27</u>. Recrystalization from 1 L of 2-propanol gave 79 g white crystals mp 130-133°C (lit.[24] 133-135°C); ^1H NMR ($CDCl_3$) δ 8.1 (m, 1, ArH peri to carbonyl), 7.00-7.55 (m, 7, ArH), 5.77 (m, 1, C-2' Vinyl H), 3.84 (t, 1, C-2 methine H) 3.00 (m, 2, C-4' H), 2.64-2.85 (m, 2, C-4 H), 2.1-2.45 (m, 4, C-3, 3' H); mass spectrum <u>m/z</u> (relative intensity) 275 ($M+1^+$, 21), 274 (M^+, 100), 273 (23), 256 (14), 245 (15), 155 (15), 146 (65), 141 (24), 129 (67), 128 (44), 118 (42), 115 (28), 91 (25), 90 (58).

<u>3,3',4,4'-Tetrahydro-1,2'-binaphthyl (19)</u>. A dry flask was charged with 100 mL dry toluene under a N_2 atmosphere. Diisobutylaluminum hydride (27 g-0.19 mol) was added. The vigorously stirred reaction mixture was cooled to 10°C in an ice bath before adding dropwise a solution of 10.1 g (37 mmol) of ketone <u>27</u> in 120 mL dry toluene. After 2 h had elapsed, 15 mL ethyl acetate was slowly added. Immediate evolution of H_2 took place as the temperature of the reaction mixture rose to 30°C. The resulting solution was poured onto 1 L of ice with stirring. Addition of con HCl caused the formation of a white gel but addition of

more con HCl allowed the formation of two cloudy layers. After standing overnight the layers were separated and the organic layer was washed with aqueous Na_2CO_3 and H_2O. The organic layer was dried ($MgSO_4$), filtered, and concentrated under vacuum to give 9.88 g (97%) of 28; ^1H NMR ($CDCl_3$) δ 7.5-7.0 (m, 8, ArH), 6.00 (t, 1, vinyl H), 4.66 (s, 1, OH), 3.0-2.5 (m, 5, aliphatic H), 2.5-1.5 (m, 5, aliphatic H). A solution of 9.88 g (36 mmol) of 28, 25 mL acetic acid, and 25 mL acetic anhydride was refluxed for 24 h. After cooling the solvent was evaporated and 5 mL 95% ethanol was added. Chilling followed by filtration afforded tan crystals of 19 (5.3 g - 56%). Elution with *n*-hexane through a Soxhlet extractor charged with neutral alumina afforded colorless crystals of 19, mp 90-92°C (lit.[11] 92-93°C); ^1H NMR ($CDCl_3$) δ 7.4-6.9 (m, 8, ArH), 6.53 (s, 1, C-1' vinyl H), 6.08 (t, 1, C-2 vinyl H), 3.00-2.15 (m, 8, CH_2); ^{13}C NMR ($CDCl_3$) ppm 140.7, 139.4, 136.9, 134.9, 124.6, 133.8, 127.5, 127.1, 126.8, 126.6, 126.4, 126.1, 126.0, 125.6, 125.2, 125.1, 29.3, 27.5, 23.3; mass spectrum *m/z* (relative intensity) 259 ($M+1^+$, 10), 258 (M^+, 100), 142 (18), 141 (26), 130 (22), 129 (53), 128 (53), 115 (20), 113 (35), 101 (15), 92 (25), 91 (45).

1,2,7,8,12b,13,14,14a-Octahydrobenzo[c]chrysene-13,14-dicarboxylic acid anhydride (21). Upon mixing 50 mL toluene with 2.89 g (11.2 mmol) diene 19 and 3.72 g (38 mmol) of freshly sublimed maleic anhydride, a bright yellow solution formed. The mixture was refluxed for 4 h, cooled, and concentrated. Water (80 mL) was added and the mixture was warmed on the steam bath. Filtration gave 4.30 g (mp 190-205°C) of crude product. Crystalization from 100 mL benzene:isooctane (1:10) gave 3.84 g (96%) of 21 mp 205-215°C (lit.[10a] 208°C); ^1H NMR ($CDCl_3$) δ 7.5-7.0 (m, 8, ArH), 4.03 (d, 1, methine H), 3.74-3.70 (d, 1, methine H), 3.56-

3.47 (m, 1, aliphatic H), 3.3-2.4 (m, 7, aliphatic H), 2.3-1.95 (m, 2, aliphatic H); IR (KBr) cm^{-1} 1840, 1770 (C=O), 1440, 1200, 1075, 980, 920, 745.

Benzo[c]chrysene (3). A flask containing a mixture of 1.02 g (2.86 mmol) of anhydride 21 and 147 mg (10%) Pd/C under a N_2 atmosphere was lowered into a 175°C salt bath. The temperature stabilized at 250°C. The evolution of CO_2 was monitored with saturated barium hydroxide and precipitation of $BaCO_3$ ceased after 8 h. The reaction mixture was cooled and toluene was added to break up the yellow sublimate and brittle black residue. The mixture was placed in a Soxhlet extractor charged with basic alumina and the hydrocarbon was eluted as a blue fluorescent band with refluxing toluene. The eluent was concentrated to give a light yellow oil which slowly crystalized, 0.517 g (66%). Trituration with ethanol gave fluffy yellow crystals mp 122-124°C (lit.[10a] 122°C) ^1H NMR ($CDCl_3$) δ 8.96 (d, 2, J=8.5 Hz), 8.70 (d, 2, J=8.5 Hz), 8.00-7.76 (m, 6, peri H), 7.76-7.40 (m, 4, ArH); ^{13}C NMR ($CDCl_3$) ppm 133.4, 131.3, 130.8, 130.3, 129.8, 128.2, 128.0, 127.8, 127.5, 127.2, 127.0, 126.7, 126.2, 126.1, 125.9, 125.7, 125.6, 123.1, 121.5; mass spectrum m/z (relative intensity) 279 ($M+1^+$, 15), 278 (M^+, 100), 277 (25), 276 (38), 274 (7), 254 (8), 139 (10), 138 (9), 126 (10), 125 (8), 113 (4), 101 (5), 91 (7).

Bicyclohexyl-1,1'-diol (25). In a 5-L, 3-neck, flask (equipped with an overhead-mounted motor driven paddle stirrer, N_2 inlet, and addition funnel) was combined 9.08 g (33.4 mmol) $HgCl_2$, 29.40 g (1.21 g-atom) Mg (70-80 mesh), and 300 mL dry THF. After 25 min. the cloudy solvent was siphoned away and the dark grey residue was washed (3 x 70 mL) with dry THF. A liter of THF was added and the mixture was chilled with ice-salt water. Via the addition funnel 6.8 mL (117 g - 0.61 mol) $TiCl_4$ was added dropwise to give a yellow fluffy precipitate and a black solution. To this was added rapidly with vigorous stirring 40.17 g (.41 mol) distilled cyclohexanone in 120 mL THF. The dark mixture was stirred for 40 min. at -10°C, whereupon 200 mL sat. aqueous K_2CO_3 was added as stirring was continued for 45 min. after the cooling bath was removed.

To the thick black mixture, was added 500 mL isohexane. Filtration through Dicalite removed black insoluble material and rotary evaporation removed the solvent. Partitioning between 1 L of ether and 2 L of sat. aqueous NaCl yielded an organic phase which when further extracted (H_2O), dried ($MgSO_4$), filtered, and concentrated to give 19.54 g (48%) of white fluffy crystals of <u>25</u>. Recrystalization from isohexane afforded odorless crystaline <u>25</u>, mp 122-125°C, (lit.[23] 124-125°C); ^1H NMR ($CDCl_3$) δ 2.03 (s, 1, OH), 1.18-1.0 (m, 10, CH_2); ^{13}C NMR ($CDCl_3$) ppm 75.6 (C_1-OH), 30.7 (C2+6), 25.9 (C_4), 21.8 (C3+5).

The phenyl boronate derivative was prepared for mass spectral analysis by refluxing a mixture of 1.03 g (5.2 mmol) of <u>25</u>, 0.52 g (5.0 mmol) of phenyl boronic anhydride, and 24 mL of benzene for 1 hr. Evaporation of solvent, trituration with ether, and drying under vacuum gave 1.5 g of waxy solid mp 105-110°C, ^1H NMR ($CDCl_3$) δ 7.88 (2n, 2, ortho ArH), 7.44 and 7.34 (2S, 3, meta and para ArH), 2.0-1.45 (m, 14), 1.45-1.0 (m, 6); ^{13}C NMR ($CDCL_3$) ppm 134.8, 130.8, 127.4, 84.5, 32.6, 25.9, 22.4; mass spectrum[71] <u>m/z</u> (relative intensity) 285 ($M+1^+$, 18), 284 (M^+, 97), 241 (81), 185 (24), 158 (85), 105 (67), 98 (100), 81 (74).

<u>1,1'-Bicyclohexenyl (16)</u>. A mixture of 8.46 g (43 mmol) of <u>25</u> and 35 mL (0.5 mol) DMSO was heated at 160°C for 17 h. The solution was

cooled and diluted with H_2O and isohexane. The layers were separated and the aqueous layer back extracted. The combined organic layer was washed (2x) with sat. aqueous NaCl, dried ($MgSO_4$) filtered and concentrated to give 7.0 g yellow oil with a mercaptan-like odor. The crude product was chromatographed on neutral alumina with isohexane eluent. The first 500 mL fraction was concentrated yielding 5.8 g (83%); ^{1}H NMR ($CDCl_3$) δ 5.74 (m, 2, vinyl H), 2.4-2.0 (m, 8, CH_2), 1.8-1.4 (m, 8, CH_2); ^{13}C NMR ($CDCl_3$) ppm 136.6 (C_1), 121.1 (C_2), 25.8 and 25.6 (C_3 and C_6), 23.2 and 22.6 (C_4 and C_5); IR (neat) 3050, 2925, 1620, 1450, 1440, 925, 795.

<u>1,2,3,4,5,6,7,8,8a,9,10,10a-Dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride (40)</u>. A solution of 2.43 g (15 mmol) 26, 4.47 g (46 mmol) of maleic anhydride and 30 mL toluene was refluxed under Ar for 5 h. After cooling and concentration the yellow oil was heated on the steam bath with 30 mL H_2O and 20 mL hexane was added. Fluffy white crystals of 40 appeared. Filtration afforded 5.13 g white solid. Washing again with 50 mL hot water, filtration, solution in benzene and concentration gave a first crop of crystals 2.20 g (56%), mp 110-113°C, (lit.[19] 122-123°C); ^{1}H NMR ($CDCl_3$) δ 3.3 (m, 2, C-9,10 H), 2.80-2.25 (m, 4, allylic H), 2.15-1.0 (m, 14, CH_2); ^{13}C NMR ($CDCl_3$) ppm 171.5 (C=O), 129.8 (vinyl C), 43.2, 36.2, 30.1, 28.9, 26.6, 25.7 (aliphatic C).

<u>1,2-Dibromo-1-phenylethane (31)</u>. A solution of bromine (38.1 g, 0.24 mol) in 60 mL CCl_4 was added dropwise to a solution of styrene (26.2 g, 0.25 mol) in 50 mL CCl_4 at 0°C with vigorous stirring over a 1.5 h period. Near the end of the addition the flask was filled with a white precipitate. The mixture was stirred for another half hour and filtered to give white crystals of 31 (19.5 g). The mother liquor

yielded 42.9 g of 31 (total 62.4 g, 97%). Recrystalization of the first crop (19.5 g) from 100 mL of 2-propanol gave 15 g colorless crystals mp 72-72.5°C (lit.[72] mp 73°C); ^{1}H NMR ($CDCl_3$) δ 7.34 (s, 5, ArH), 5.12 (two d, 1, benzylic H, $J_{1,2}$=9 Hz, $J_{1,2}$ = 6 Hz), 3.96 and 3.99 (two d, 2, $-CH_2Br$, J=6 Hz, J=9 Hz); ^{13}C NMR ($CDCl_3$) 138.3 (C_1), 128.9 (C_4), 128.6 and 127.4 ($C_{2,6,3,5}$), 50.8 (αC), 34.9 (βC).

1,2-Dibromoindan (29a + 29b). A solution of 150 g (1.3 mol) freshly distilled indene in 1 L CH_2Cl_2 and 2 mL dimethylformamide was chilled to -67°C in dry ice-isopropyl alcohol. A solution of 183.4 g (1.15 mol) Br_2 in 450 mL CH_2Cl_2 was added at such a rate as to keep the temperature below -50°C. The solution was stirred at -30°C for 6 h. The solvent was removed under vacuum and $MgSO_4$ was added to the viscous orange oil. Filtration and Kuglerohr distillation gave 272.1 g (76%) bp 108-110°C/ 0.5% mm Hg (lit.[29] 100-105°/1 mm Hg) of 29b and 29a; IR (neat) cm^{-1} 3030, 1610, 1460, 1420, 1150, 910, 850, 735; 29a, ^{1}H NMR ($CDCl_3$) δ 7.5-7.16 (m, 4, ArH), 5.60 (s, 1, H-1), 4.82 (m, 1, H-2), 3.67 (d, 1, H-3), 3.20 (d, 1, H-3); ^{13}C NMR ($CDCl_3$) ppm 140.3 (C8+9), 129.4 (C4), 127.7 (C5), 125.4 (C6), 125.1 (C7), 57.6 (C1), 54.3 (C2), 41.3 (C3); 29b, ^{1}H NMR ($CDCl_3$) δ 7.5-7.16 (m, 4, ArH), 5.44 (d, 1, H-1), 4.42 (2t, 1, H2), 3.84 (d, 1, H-3), 3.25 (d, 1, H-3); ^{13}C NMR ($CDCl_3$) ppm 141.2 (C8+9), 129.1 (C4), 127.5 (C5), 126.6 (C6), 124.1 (C7), 58.6 (C1), 50.1 (C2), 40.4 (C3).

2-Bromoindene (30). A solution of 4.14 g (15 mmol) dibromoindan (29a and 29b) in 50 mL DMF was heated at 113-115°C for 5.75 h. The solution was cooled and 50 mL n-hexane was added. Extraction with aqueous NaCl (2x) and H_2O, followed by drying ($MgSO_4$), filtration, and concentration gave 2.7 g of liquid. The crude product was distilled and 1.86 g (64%) of 30 was collected at 76-83°C/2.5 mm Hg. The product was recrystalized from absolute ethanol and gave 30 mp 37-39°C (lit.[29] mp 39-40°C) ^1H NMR ($CDCl_3$) δ 7.60-7.0 (m, 4, ArH), 6.87 (s, 1, vinyl H), 3.55 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) ppm 143.8, 142.4, 132.8, 126.5, 124.7, 124.6, 122.9, 120.0, 45.4.

2,2'-Biindenyl (38). Freshly dried 2-bromoindene (14.95g - 77 mmol) in 50 mL dry THF was added dropwise to 1.91 g (78.6 mmol) Mg turnings in 50 mL dry THF in an Ar atmosphere. The Grignard reaction was initiated by first adding a crystal of I_2 and several drops CH_3I and then refluxing. After 15 min, the characteristic dark red solution formed. Refluxing was continued 1 h after the initial 5 h addition.

After cooling the red-black solution was forced into a glass tube containing a glass wool filter by a positive Ar pressure and into a second flask containing 43.9 g (154 mmol) TlBr in 250 mL dry toluene. In the Grignard flask, the residue was washed (3 x 10 ml) with dry THF until the washings were colorless.

The TlBr mixture refluxed for 2 h giving a grey precipitate of Tl metal and stirred at room temperature for 6 h. The precipitate was removed by filtration, the THF distilled away, and H_2O was added. More toluene was added but failed to dissolve a H_2O insoluable-acetone soluable brown slime. Filtration through dicalite enabled clean separation of phases. The red organic phase was dried ($MgSO_4$), filtered (Dicalite), and concentrated. The concentrate was placed in a Soxhlet extractor charged with neutral alumina. Elution with refluxing isohexane gave 3.2 g of uncharacterized low-melting solid and 0.62 g (7%) of pale yellow crystaline, highly insoluble 38, mp 243-246°C (lit.[39] 243°C); ^1H NMR ($CDCl_3$) δ 7.5-7.1 (m, 8, ArH), 6.92 (s, 2, vinyl H), 3.74 (s, 4, CH_2);

^{13}C NMR ($CDCl_3$) ppm 145.1, 143.2, 142.8, 127.7, 126.4, 124.8, 123.5, 120.7, 38.6; mass spectrum m/z (relative intensity) 231 ($M+1^+$, 17), 230 (M^+, 97), 229 (31), 228 (18), 226 (11), 215 (9), 202 (5), 119 (80), 115 (100), 114 (14), 101 (10), 92 (22), 91 (36).

1,2,7,8-Tetrahydrodibenzo[c,g]phenanthrene (9). An intimate mixture of 0.30 g (0.8 mmol) 8, 1.00 g (4.2 mmol) PbO_2 and 2.0 g powdered pyrex glass was placed in a 2.5 cm x 30 cm tube and the tube was evacuated to 0.4 mm Hg. The tube was heated in an aluminum block heater to 260°C over 0.5 h. After cooling the sublimate and residue were placed in a Soxhlet extractor charged with basic alumina. Elution with refluxing toluene yielded .115 g (50%) mp 141-143°C (lit.[10a] 142°,[10b] 148-149°C); ^1H NMR ($CDCl_3$) δ 6.8-7.9 (m, 10, ArH), 2.78 (d, 8, CH_2).

PART II

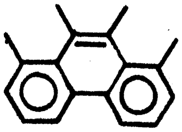
SYNTHESIS OF TETRASUBSTITUTED PHENANTHRENES

CHAPTER V

INTRODUCTION

Alkyl substituted PNA hydrocarbons are known to occur in coal liquids and as degradation products of terpenes.[75] Recently sterically hindered, high energy hydrocarbons have come under scrutiny by the Bartlesville Energy Technology Center in conjunction with the U.S. Air Force.[76] Accurate thermodynamic values (i.e. melting point, heat of combustion and heat capacity) are being tabulated.

Consequently, we undertook the synthesis of polysubstituted phenanthrenes to satisfy the Energy Technology Center's need for high purity hydrocarbons (99.95% minimum purity). Target compounds were sterically hindered hydrocarbons including 1,8,9,10-tetramethylphenanthrene (<u>47</u>) and less hindered analogues for comparison.



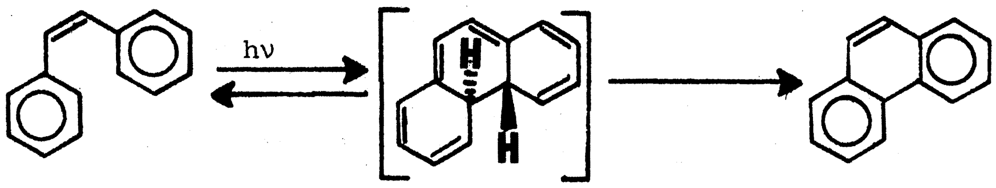
<u>47</u>

CHAPTER VI

HISTORICAL

The synthetic chemist is presented with a multitide of routes to phenanthrene and its substituted derivatives. This topic has been exhaustively reviewed.[77,78] Outstanding routes to polysubstituted phenanthrenes include the Haworth synthesis, Bogart-Cook synthesis, Pschorr synthesis and stilbene photocyclization.[77] In general, the remaining routes are either long and laborious or low yield processes. Stilbene photocyclization is the most popular method because of the simplicity of the procedure and the availability of precursors.[79]

The photocyclization entails excitation of a stilbene by radiation from a medium pressure mercury lamp, cyclization to a dihydrophenanthrene, and dehydrogenation to phenanthrene (usually by I_2 and O_2).[81]



The true nature of the excited species which undergoes cyclization remains controversial.[77,80,81] Cyclization proceeds from the cis-stilbene to give an excited trans-dihydro intermediate[82] which is believed to have the structure illustrated in Figure 15.[83]

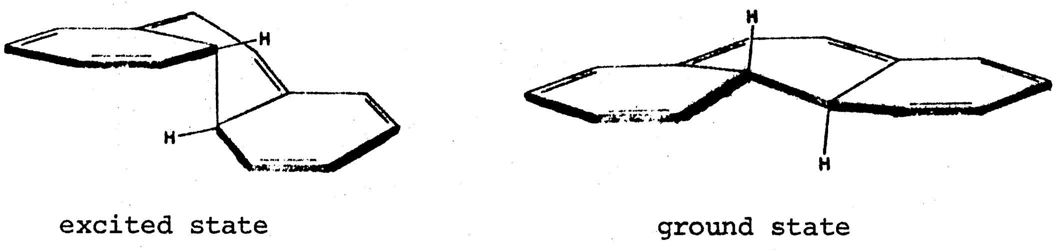
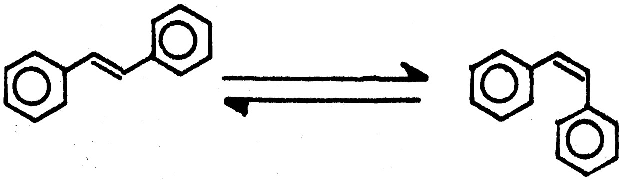


Figure 15. Approximate Representation of Photocyclization Intermediate

A variety of dehydrogenating agents have been surveyed and I_2 with air proved the most efficient.[80] Under an inert atmosphere and without a hydrogen acceptor the yield of phenanthrene is low as thermal cycloreversion to cis-stilbene becomes the dominant reaction.[80]

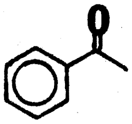
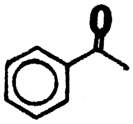
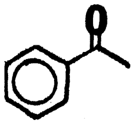
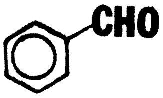
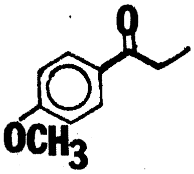
The starting stilbene may be a cis-trans mixture since cis-trans photoisomerization is facile under cyclization conditions.[84]



A host of synthetic pathways are known for substituted stilbenes.[85] Stilbene systems have been synthesized in one step in good yield from benzylic ketones and aldehydes with a new method developed by McMurry.[86] During the course of development of McMurry's reagent a surprising diversity of results have been observed. Table VIII displays stilbene

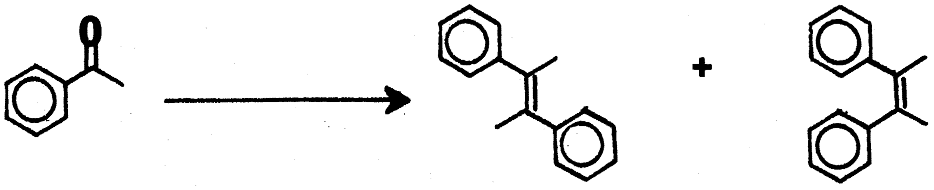
TABLE VIII

SYNTHESIS OF STILBENES BY McMURRY'S REAGENT

Carbonyl Compound	Reagent	Yield of Stilbene, %	trans/cis	Reference
	$TiCl_3 \cdot 3$ THF Mg 40°C	60	1:1	87
	$TiCl_3 \cdot 3$ THF Mg	71	4:3	87
	$TiCl_4$Zn	97	1:4	88
	$TiCl_3$ Li THF	94	9:1	86b
	$TiCl_3$ $LiAlH_3$ THF Reflux	85	1:0	86a
	$TiCl_3$ $LiAlH_4$ THF Reflux	85*	1:0	86a

*The product is a diethylstilbesterol derivative.

systems which have been synthesized with McMurry's reagent. Note that the ratio of trans and cis isomer varies with reaction conditions.



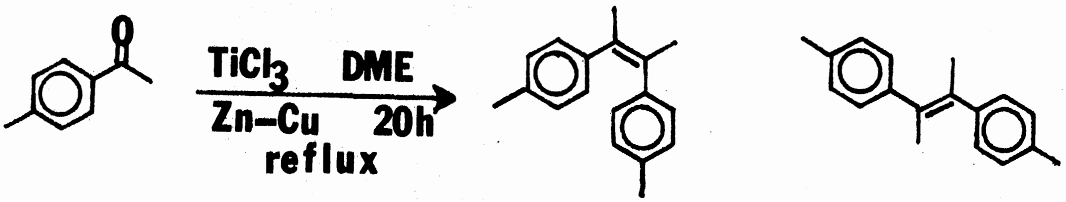
The reagent is a low valent titanium species (probably active Ti^o) which is produced when $TiCl_3$ or $TiCl_4$ reacts with a reducing agent. A mechanism has been rationalized.[86b] Recently, Zn-Cu has been shown to be an effective reducing agent. However, the use of Zn-Cu couple in the synthesis of stilbenes has not been reported.

For our purposes, it is encouraging that sterically crowded olefins may be synthesized by this method.[89]

CHAPTER VII

RESULTS AND DISCUSSION

Initially, the relatively unhindered 4,4',α,α'-tetramethylstilbenes 48 and 49 were synthesized in one step from p-methylacetophenane as shown in Figure 16. The known *cis* and *trans*-stilbenes (48) and (49) were made in 72% yield.[90] The major product was the *cis* isomer, 48, the *cis*-trans ratio was 9:1 as shown by gas chromatography.[91]



48 49

Figure 16. Synthesis of 4,4',α,α'-Tetramethylstilbenes

o-Methylacetophenone was dimerized under a variety of conditions. Analysis by gas chromatography-mass spectroscopy (GC-MS)[92] provided an efficient method of determining product ratios and identity as illustrated in Table IX. The assignment of *cis* and *trans* stereochemistry to the major tetramethylstilbene isomers (*m/z* 236) remains unresolved, but

TABLE IX

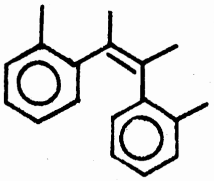
DIMERS FROM 2-METHYLACETOPHENONE

Reaction Conditions	Yield, %	Relative Percent Dimers*				
		A 236	B 236	C 236	D 238	E 238
$4TiCl_3$ 1 $LiAlH_4$ THF (67°C)	85	81	12	6	--	2
$4TiCl_3$ 1 $LiAlH_4$ DME (86°C)	57	37	35	2	13	12
$4TiCl_3$ 12 Zn-Cu DME (84°C)	84	96	4	-	--	trace

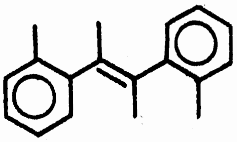
*The molecular ions are listed in order of their elution from the gas chromatograph.

structures 50 and 51 are tentatively assumed for the major isomers. Tetramethylstilbenes A and B (Table IX) have essentially identical fragmentation patterns in the mass spectrometer reinforcing their assignment as structures 50 and 51. However, the fragmentation of C is very different; its origin is unknown. This assignment is supported by ozonolysis of the major isomers back to starting 2-methylacetophenone.

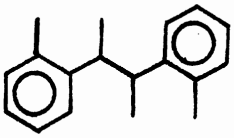
When $LiAlH_4$ serves as the reducing agent, reduction of ketone to alcohol also takes place. Once the benzylic alcohol is formed, coupling may occur to give 2,3-bis(2-methylphenyl)butane (52) with (*m/z* = 238).[92]



50

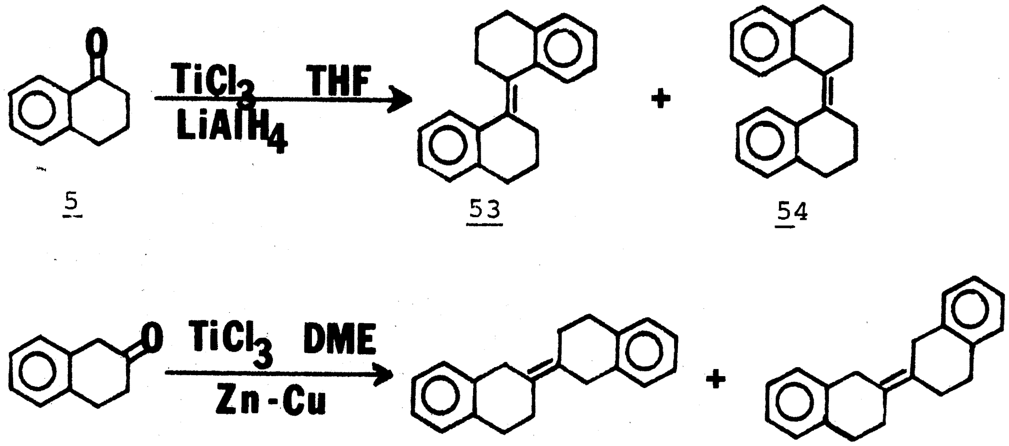


51



52

Synthesis of an analogue of 50 and 51 was carried out from 1-tetralone(5) as shown in Figure 17. The overall yield, discounting unreacted ketone was 50% with an isomer ratio of 9:1. Dimerization of the less sterically hindered 2-tetralone led to a 96% yield of dimer with only one of the possible isomers being detected.

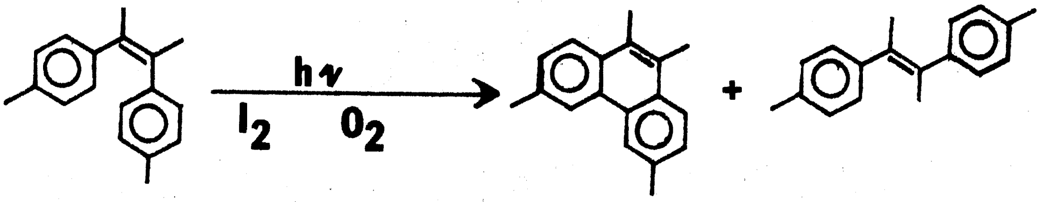


5 53 54

55 56

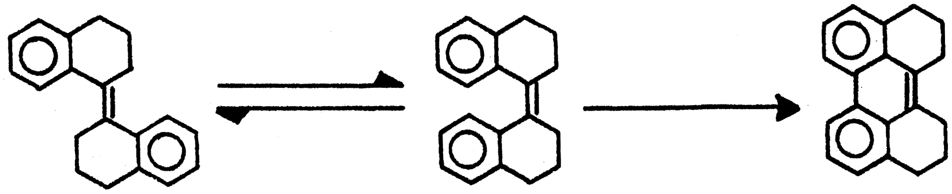
Figure 17. Dimerization of 1-tetralone and 2-tetralone

Irradiation of a cyclohexane solution of *cis*-4,4',α,α'-tetramethylstilbene 48 in the presence of I_2 and air gave the previously unknown 3,6,9,10-tetramethylphenanthrene(57) in 20% yield. Also *trans*-4,4',α,α'-tetramethylstilbene(49) was isolated in 16% yield. Separation was effected by passage through a picric acid-basic alumina column.[94]



48 57 49

Irradiation of 53 and 54 under similar conditions gave 1,2,3,10,11,12-hexahydroperylene(58) in 47% yield. This phenanthrene derivative was readily separated from starting material by passage through a picric acid column.



53 54 58

Stilbenes 50 and 51 were also photolyzed. However, only *cis*-*trans* isomerization was observed to stilbene A. GC-MS revealed no phenanthrene systems (*m/z* 234). The UV spectrum of a mixture of 50 and 51 reveals an *o*-xylene-like spectrum rather than a stilbene-like spectrum. Because of crowding by the methyl groups, the phenyl rings are forced out of planarity. This crowding prevents 50 from photocyclizing to 47.

It has been reported that 4,4'-dimethoxy-α,α'-dimethylstilbene photocyclized to the phenanthrene in the presence of $CuCl_2$, I_2 and O_2 in ethanol solution, while cyclization failed to occur in the absence of $CuCl_2$.[95] Use of these conditions had no effect on the outcome of the cyclization of 50 and 51.

Chromyl chloride is known to cyclize 1,1,2,2-tetraphenylethane to 9,10-diphenylphenanthrene.[96] Reaction of 50 and 51 with CrO_2Cl_2 was also carried out. GC-MS analysis indicates that the presence of a phenanthrene-like system as shown in Table X.

TABLE X

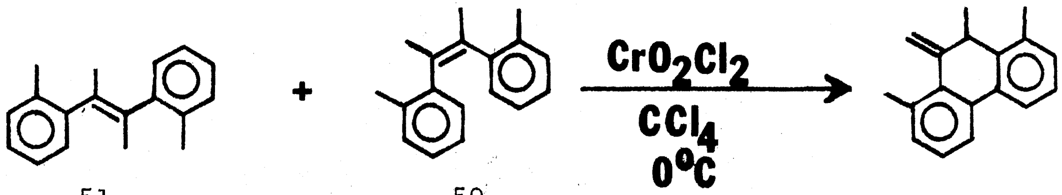
CYCLIZATION PRODUCTS WITH CrO_2Cl_2

Relative Percent of Dimers*					Phenanthrene System
A	B	C	D	E	
236	236	236	238	238	234
1.6	54.3	0.8	---	2.5	26

*The molecular ions are listed in order of their elution from the gas chromatograph.

Examination of the ^1H NMR spectrum indicates a doublet at 4.94 ppm (terminal methylene), a singlet at 2.60 ppm (aromatic methyl) and a quartet at 2.16. This spectrum would be consistent with structure 59.

In summary, four previously unknown tetrasubstituted stilbenes have been synthesized as well as a new substituted phenanthrene(57). It has been shown that sterically hindered 50 does not photocyclize to 47. Also 1,1',3,3',4,4'-hexahydro-2,2'-binaphthyl has been made for the first time.



51 50 59

CHAPTER VIII

EXPERIMENTAL

Zinc-Copper Couple.[86b] A mixture of zinc dust (230.1 g - 3.52 mole), anhydrous $CuSO_4$(18.68 g-0.12 mole) and 1 L of deoxygenated H_2O were stirred for 10 min in an argon atmosphere. The Zn-Cu couple was filtered and washed with several aliquots of H_2O(0.5 L), acetone(0.5 L), and ether (0.5 l). After drying under vacuum, 224.4 g of Zn-Cu couple was isolated and stored under argon.

General Coupling Procedure ($TiCl_3$-Zn/Cu). Into a 3-L, 3-neck flask, equipped with an addition funnel, a condenser, and a paddle stirrer and adaptor, was placed 300 mL dry dimethoxyethane (DME) and 78.2 g zinc-copper couple. Another 150 mL of DME was added before 61.95 g (0.4 mole) of $TiCl_3$ was added with vigorous stirring and a N_2 flush. More DME (50 mL) was used to wash the purple titanium salt into the flask. The mixture was refluxed for 0.5 h to complete the reduction. After cooling, a solution of 13.42 g (0.1 mole) of 2-methylacetophenone and 50 mL DME was added dropwise through the addition funnel in 0.5 h. Refluxing was resumed for 20 h. Hexane (200 mL) was added to the cooled mixture and inorganic solids were removed by filtration. Thorough washing of the filter cake followed by evaporation of the water-soluble solvent gave a mixture which was portioned with H_2O and hexane. The organic layer was washed with H_2O, dried ($MgSO_4$), filtered (dicalite), and concentrated to afford 11.4 g crude product (96%). Distillation at

104-105°C/0.5 mm yielded 10.2 g (86%) tetramethylstilbene. GC analysis[91a] shows the presence of three isomers of tetramethylstilbene as shown in Table IX: tetramethylstilbene A relative amount 96%, GC-MS[93] (retention time 15:25), m/z (rel. intensity) 237 ($M+1^+$, 20), 236 (M^+, 100), 221(33), 207(71), 206(28), 192(38), 178(12), 143(12), 129(52), 128(25), 119(26), 117(29), 115(27), 105(21), 91(32), see spectrum 15.

A tetramethylstilbene 4%, GC-MS (retention time 15:50) m/z (rel. intensity) 237 ($M+1^+$, 20), 236 (M^+, 100), 221(33), 207(70), 206(27), 192(36), 179(11), 178(11), 143(11), 129(51), 128(26), 119(24), 117(28), 115(28), 105(21), 91(31), see spectrum 16.

A tetramethylstilbene <1%, GC-MS (retention time 16:06) m/z (rel. intensity) 237 ($M+1^+$, 7), 236 (M^+, 35), 221(40), 207(14), 144(16), 129(16), 119(70), 117(100), 115(43), 91(31).

No dihydro derivative 52 was observed, GC-MS (retention time 16:39) m/z (rel. intensity) 238 (M^+, 1), 120(12), 119(100, hemicleavage), 118(28), 91(14), see spectrum 17. ^{1}H NMR and ^{13}C NMR spectra of the mixture are shown in spectra 13 and 14.

General Coupling Procedure ($TiCl_3$-$LiAlH_4$,4:1). To 100 mL of dry distilled THF was slowly added 14.02 g of McMurry's reagent ($4TiCl_3$-$LiAlH_4$ from Alfa-Ventron) to a 2-neck 500-mL flask under an Argon atmosphere. After the exothermic reaction had subsided (1 h) the solution was refluxed for 1 h. Upon cooling a solution of 6.33 g (43 mmol) of 1-tetralone (15) in 20 mL THF was added slowly with stirring. Refluxing was continued for 86 h. After cooling, 120 mL toluene and 110 mL H_2O was added to thin the viscous mixture. The black foul smelling mixture was filtered, acidified with 10% HCl and the organic layer was separated. The organic layer was washed with 10% HCl and H_2O, then dried ($MgSO_4$) and filtered. Concentration gave 5.47 g yellow oil. Kuglerohr distillation (100-150°C/0.5 mm) removed 1.4 g unreacted 1-tetralone(15). The viscous residue, 3.43 g, (90:10 ratio of isomers) (78%) was treated with 15 mL 2-propanol and yielded 1.42 g colorless crystals mp 94-100°C; ^1H NMR ($CDCl_3$) δ 7.4 (m, 8, ArH), 2.8 - 2.4 (m, 8, benzylic and allylic CH_2), 1.8 (p, 4, H-1, 12); ^{13}C NMR ($CDCl_3$) ppm 140.0, 139.4, 137.9, 137.4, 132.7, 131.4, 130.3, 129.7, 127.4, 127.1, 126.4, 125.9, 125.2, 124.4, 30.1, 29.6, 29.2, 28.2, 24.1, 23.0; IR(KBr) cm^{-1} 3050, 3000, 2915, 2880, 2830, 2825, 1590, 1480, 1445, 1110, 1050, 1030, 768, 755, 745, 500.

Photocyclization in Cyclohexane. A solution of *cis*-4,4',α,α'-tetramethylstilbene (10 mM-7.1 g), I_2(0.3 mM-0.23 g) and 3 L cyclohexane (saturated with air) was irradiated with a medium pressure, Hanovia Hg lamp, with a quartz cooling jacket for 7 h. The resulting solution was concentrated and then eluted from a column of basic alumina with hexane-toluene(9:1). Concentration of the eluate gave 6.0 g colorless crystals. Recrystalization from 95% ethanol afforded 3.6 g crystals. This was placed in a Soxhlet extractor charged with 80 cc basic alumina and 18 g lightly packed picric acid.[94] Elution with one column volume of cold hexane gave *trans*-4,4',α,α'-tetramethylstilbene(49), 1.5 g mp 102-105°C (lit.[90] mp 110°C); ^1H NMR ($CDCl_3$) δ 7.03 (m, 8, ArH), 2.30 (s, 6), 1.43 (s, 6); ^{13}C NMR ($CDCl_3$) ppm 141.4, 135.3, 132.5, 128.6, 128.0, 22.5, 21.0; IR(KBr) cm^{-1} 3065, 3035, 3010, 2965, 2900, 2840, 1500, 1435, 1350, 1110, 1085, 1015, 815, 725.

Elution of the picrate column with refluxing hexane for 0.5 h gave 0.47 g which proved to be a mixture of 49 and 57 (mp 114-120°C).

Further elution with refluxing isohexane caused decomposition of the bright orange picrate of 57 (mp 188-189°C) and eluted 3,6,9,10-tetramethylphenanthrene(57) mp 137-140°C; ^1H NMR ($CDCl_3$) δ 8.44 (s, 2, H-4,5), 7.95 (d, 2, H-1, 8), 7.40 (d, 2, H-2, 7); ^{13}C NMR ($CDCl_3$) ppm 134.1, 130.0, 128.9, 127.7, 124.1, 122.2, 21.7, 15.6.

Photocyclization With $CuCl_2$ in Ethanol. Irradiation of a solution of 2.02 g (8.6 mmol) of cis and trans-2,2',α,α'-tetramethylstilbenes 48 and 49, of 1.45 g (8.5 mmol) $CuCl_2 \cdot 2H_2O$, of 0.15 g (0.6 mmol) I_2, and 1.2 L absolute ethanol was carried out for 25 h. Air was periodically bubbled into the reaction media and 0.10 g (0.4 mmol) I_2 was added after 12 h.

The reaction product was concentrated, diluted with toluene and washed with dilute NH_4OH. The organic layer was washed with H_2O (3X), dried ($MgSO_4$), filtered, and concentrated to give 2.6 g red oil. The oil was transferred to a Soxhlet extractor charged with neutral alumina and the hydrocarbon was eluted with refluxing hexane in 2 h. Concentration gave 1.27 g of oily crystals. Recrystalization from 95% ethanol gave 0.30 g fluffy white needles, mp 91-93°C; ^1H NMR ($CDCl_3$) δ 1.63 (s, 6, CH_3), 2.32 (s, 6, $ArCH_3$), 7.14 (m, 8, ArH); ^{13}C NMR ($CDCl_3$) ppm 143.3, 134.8, 134.7, 132.7, 132.5, 129.7, 128.2, 127.9, 126.3, 125.7, 21.3, 19.6, 18.9; IR(KBr) cm^{-1} 3050, 3000, 2960, 2900, 2840, 1480, 1445, 1370, 1360, 1085, 1025, 760, 735, 725; GC-MS (retention time 14:06) m/z (rel. intensity) 237($M+1^+$, 17), 236 (M^+, 100), 221(33), 207(66), 206(28), 192(33), 178(11), 143(12), 129(52), 128(29), 119(26), 117(29), 115(29), 105(23), 91(36).

Anal. Calcd. for $C_{18}H_{18}$: C, 90.92; H, 8.48. Found: C, 91.27; H, 8.69.

Chromyl Chloride Cyclization. A 100 mL flask was charged with

1.14 g (4.8 mmol) tetramethylstilbenes 50 and 51 in 20 mL CCl_4. The solution was chilled to 0°C before dropwise addition of 1.07 g (6.9 mmol) CrO_2Cl_2 in 20 mL CCl_4 by an addition funnel. An argon atmosphere and vigorous stirring was maintained during the 10 min addition and 7 min reaction time. Upon addition of the bright red CrO_2Cl_2 a heavy brown precipitate formed which was removed by filtration. The filtrate was rinsed (3X) with dilute aqueous $NaHSO_4$ and CH_2Cl_2 (3X). The organic layer was separated and washed with H_2O, dried ($MgSO_4$) and concentrated to give 0.9 g of brown oil. Chromatography on basic alumina with n-hexane as eluent afforded 0.5 g oily crystals, mp 84.5-85°C; GC-MS (see Table X), peak one, retention time 13:37, mass spectrum m/z (relative intensity) 237 ($M+1^+$, 15), 236 (M^+, 100), 221(31), 207(71), 206(34), 192(33), 129(52), 128(27), 117(27), 115(26), 91(35); peak two, retention time 14:07, mass spectrum m/z (relative intensity) 237 ($M+1^+$, 17), 236 (M^+, 100), 221(31), 207(64), 206(28), 192(33), 129(50), 128(27), 117(28), 115(28), 91(34); peak three, retention time 14:27, mass spectrum m/z (relative intensity) 235 ($M+1^+$, 10), 234 (M^+, 59), 233(11), 220(17), 219(100), 218(17), 204(43), 203(24), 202(21), 129(16), 128(22), 115(40), 105(55), 91(27). ^1H NMR and ^{13}C NMR are shown in spectra 18 and 19.

BIBLIOGRAPHY AND NOTES

1. R. H. Hunt and M. J. O'Neal, "Encyclopedia of Chemical Technology", 2nd Ed., Vol. 14, R. E. Kirk and D. J. Othemer (Eds.), The Interscience Encyclopedia, Inc., New York, 1967, p. 849.

2. E. Clar, "Polycyclic Hydrocarbons", Vol. 1, Academic Press, London, 1964, p. 192.

3. M. Blumer, *Sci. Am.*, 234, 34 (1976).

4. (a) Ref. 1, Vol. 15, p. 1; (b) T. Aczel, Q. J. Foster, and J. H. Karchmer, *Am. Chem. Soc., Div. Fuel Chem.*, Prepr., *13*, 8 (1969); (c) E. E. Tompkins and R. Long, "12th Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, 1969, p. 625.

5. I. Schmeltz and D. Hoffmann, "Carcinogenesis", Vol. 1, R. I. Freudenthal and P. Jones (Eds.), Raven Press, New York, 1976, p. 225; (b) R. Stedman, *Chem. Rev.*, *68*, 153 (1968).

6. (a) G. M. Badger, "The Chemical Basis of Carcinogenic Activity", C. C. Thomas Publ., Springfield, 1962; (b) R. Schoenthal, "Carcinogenisis by Polycyclic Aromatic Hydrocarbons and by Certain Other Carcinogens", Ref. 2, p. 133; (c) L. Fishbein, W. G. Flamm, and H. L. Falk, "Chemical Mutagens", Academic Press, New York, 1970, p. 275; (d) E. C. Miller and J. A. Miller, "Chemical Mutagens", Vol. 1, A. Hollaender (Ed.), Plenum Press, New York, 1971, p. 105.

7. We wish to acknowledge support for this work from the Environmental Protection Agency (Grant R805419-010), Bartlesville Energy Technology Center under Department of Energy (Contract DE-AT19-78BS31001) and Dow Summer Fellowships.

8. (a) O. Diels and K. Alder, *Liebigs Ann. Chem.*, *460*, 98 (1928). Actually the first correct identification of the reaction was by Zincke; (b) T. Zincke and H. Gunther, *Liebigs Ann. Chem.*, 272, 243 (1893); (c) T. Zincke, *ibid*, 296, 135 (1897); (d) T. Zincke and K. H. Meyer, *ibid*, 367, 1 (1909).

9. E. Clar, "Polycyclic Hydrocarbons", Vol. 1 and 2, Academic Press, London, 1964.

10. (a) H. A. Weidlich, *Ber.*, *71*, 1203 (1938); (b) J. Altman and D. Ginsburg, *J. Chem. Soc.*, 466 (1959); (c) E. Clar and M. Zander, *J. Chem. Soc.*, 4616 (1957).

11. F. Strauss and A. Rohrbacher, Chem. Ber., 54, 40 (1921). These authors do not report a yield for 17.

12. (a) N. Campbell and H. F. Andrew, "Polycyclic Aromatic Compounds with Four or More Fused Carbocyclic Ring Systems", in Rodd's Chemistry of Carbon Compounds", second edition, Vol. IIIF, Chap. 22, S. Coffey (ed.), Elsevier Scientific Publishing Co., New York, (1974) p. 214; (b) R. H. Martin, Angew. Chem. Internat. Ed., 13, 649 (1974); (c) A. O. McIntosh, J. M. Robertson, and V. Vand, J. Chem. Soc., 1661 (1954).

13. (a) C. A. Grob, M. Ohta, and A. Weiss, Angew. Chem., 70, 343 (1958); (b) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, Helv. Chim. Acta, 41, 1191 (1958); (c) R. A. Sheldon and J. Kochi, "Oxidative Decarboxylation of Acids by Lead Tetraacetate", Organic Reactions, V-19, Robert E. Krieger Publishing Co., Huntington, N. Y., 1972, p. 279.

14. W. von Doering, M. Farber, and A. Sayigh, J. Am. Chem. Soc., 74, 4370 (1952).

15. D. V. Hertzler, J. M. Berdahl, and E. J. Eisenbraun, J. Org. Chem., 33, 2008 (1968).

16. N. R. Skvarchenko, Russian Chem. Rev., 571 (1963).

17. T. Cohen, R. W. Berninger, J. T. Wood, J. Org. Chem., 43, 837 (1978).

18. (a) von W. Deuschel, Helv. Chim. Acta, 35, 1774 (1952); (b) H. Reimlinger and A. van Overstraeten, Ber., 91, 2151 (1958).

19. E. Gruber and R. Adams, J. Am. Chem. Soc., 57, 2555 (1935).

20. E. Barnett and C. Lawrence, J. Chem. Soc., 1104 (1935).

21. D. S. Greidinger and D. Ginsburg, J. Org. Chem., 22, 1406 (1957).

22. V. Traynelis, W. Hergenrother, with H. Hanson, and J. Valicenti, J. Org. Chem., 29, 123 (1964).

23. E. J. Corey, R. L. Danheiser, and S. Chandrasekaren, J. Org. Chem., 41, 260 (1976).

24. J. M. Springer, C. W. Hinman, and E. J. Eisenbraun, with P. W. K. Flanagan and M. C. Hamming, J. Org. Chem., 35, 1260 (1970).

25. L. J. Mazza and A. Guarna, Synthesis (1980) 41.

26. A. McKillop, L. F. Elsom, and E. C. Taylor, Tetrahedron, 26, 4041 (1970).

28. Unpublished work T. K. Dobbs, L. L. Ansell, A. G. Holba, and E. J. Eisenbraun. The author wishes to thank Mr. Dobbs for sharing this technique.

29. H. D. Porter and C. M. Suter, J. Am. Chem. Soc., 57, 2022 (1935).

30. (a) R. P. Holysz, J. Am. Chem. Soc., 75, 4432, (1953); (b) R. Jolly, J. Warnant, G. Nominé, and D. Bertin, Bull. Soc. Chim. France, 366 (1958).

31. J. W. Hamersma and E. I. Snyder, J. Org. Chem. 30, 3985 (1965).

32. (a) N. Kornblum and R. K. Blackwood, J. Am. Chem. Soc., 78, 4037 (1956); (b) R. A. Bartsch, J. Org. Chem., 35, 1023 (1970).

33. P. B. D. de la Mare, N. V. Klassen, and R. Konigsberger, J. Chem. Soc., 5285 (1961).

34. S. J. Cristol and N. L. Hause, J. Am. Chem. Soc., 74, 2193 (1952).

35. E. Baciocchi and A. Schiroli, J. Chem. Soc. (B), 554 (1969).

36. (a) I. M. Mathai, K. Schug, and S. I. Miller, J. Org. Chem., 35, 1733 (1970); (b) W. K. Kwok, I. M. Mathai, and S. I. Miller, J. Org. Chem., 35, 3420 (1970); (c) W. K. Kwok and S. I. Miller, J. Org. Chem., 35, 4037 (1970).

37. W. H. Sanders and A. F. Cockerill, Mechanisms of Elimination Reactions, John Wiley and Sons, New York, 1973, p. 210.

38. A. J. Parker, Quarterly Rev., 163 (1962).

39. W. Lüttke and J. Grussdorf, Ber., 98, 140 (1965).

40. (a) J. Sauer, Angew, Chem. Internat. Edit., 5, 211 (1966); (b) T. Wagner-Jauregg, Synthesis, 165 (1980).

41. J. Sauer, ibid, 6, 16 (1967).

42. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press Inc.--Verlag Chemie Gmb H, Weinheim, Germany, 1970, p. 65.

43. M. C. Kloetzel, "The Diels-Alder Reaction With Maleic Anhydride," Org. Reactions, Vol. IV, John Wiley and Sons, Inc., New York, 1948, p. 1.

44. (a) F. Bergmann, H. E. Eschinazi, and M. Neeman, J. Org. Chem., 8, 179 (1943); (b) N. C. Deno, J. Am. Chem. Soc., 72, 4057 (1950).

45. E. Clar, Ber., 65, 846 (1932).

46. (a) E. Clar, C. T. Ironside, and M. Lander, *Tetrahedron*, *6*, 358 (1959); (b) E. Clar, M. M. Lovat, and W. Simpson, *Tetrahedron*, *30*, 3293 (1974).

47. von H. Hopff and H. R. Schweizer, *Helv. Chim. Acta*, *42*, 2315 (1959).

48. von M. Zander, *Liebigs Ann. Chem.*, *723*, 27 (1969).

49. (a) M. M. Labes, R. Sehr, and M. Bose, *J. Chem. Phys.*, *33*, 868 (1960); (b) V. P. Parini, *Russ. Chem. Rev.*, *31*, 408 (1962); (c) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," p. 96, Holden-Day Inc., San Francisco, 1964.

50. R. Foster, "Organic Charge-Transfer Complexes," p. 238, Academic Press, New York, 1969.

51. A. G. Holba, H. Hall, and E. J. Eisenbraun, *Chem. and Ind.*, in press.

52. C. E. Browne, W. L. Buchanan, E. J. Eisenbraun, *Chem. and Ind.*, (London), 35 (1977). All references to Soxhlet extractor refer to the apparatus described in this reference.

53. For reviews of decarboxylation of small ring anhydrides, see (a) Reference 16 p. 575; (b) P. N. Rylander, "Organic Synthesis With Noble Metal Catalysts", Academic Press, New York, 1973.

54. (a) N. C. Deno, *J. Am. Chem. Soc.*, 72, 4057 (1950); (b) H. O. House, F. J. Sauter, W. G. Kenyon, and J. J. Riehl, *J. Org. Chem.*, *33*, 957 (1968); (c) D. Lednicer and C. R. Hauser, *J. Am. Chem. Soc.*, *80*, 6364 (1958).

55. (a) W. J. Bailey and S. T. Quigley, *ibid.*, *81*, 5598 (1959); (b) W. J. Bailey and J. Economy, *ibid.*, *77*, 1133 (1955); (b) W. J. Bailey, E. J. Fetter, and J. Economy, *J. Org. Chem.*, *27*, 3479 (1962).

56. L. M. Jackman, *Adv. Org. Chem.*, *2*, 354 (1960).

57. J. O. Hawthorne and M. H. Wilt, *J. Org. Chem.*, *25*, 2215 (1960).

58. Unpublished work of C. E. Browne and E. J. Eisenbraun; see also reference 10a.

59. H. Goth, P. Cerutti, H. Schmid, *Helv. Chim. Acta*, *48*, 1395 (1965).

60. ^{1}H NMR spectra were obtained on a Varian XL-100A spectrometer at 100.1 MH$_z$. All spectra were run in CDCl$_3$ with a deuterium lock and shifts are in ppm from an internal standard of TMS.

61. ^{13}C NMR spectra were recorded at 25.2 MH_z in the FT mode on a Varian XL-100A interfaced with a 12K Nicolet 1080 computer. Samples were dissolved in $CDCl_3$ for a deuterium lock and shifts are reported in ppm downfield from TMS.

62. Infrared spectra were obtained on a Perkin-Elmer-197 spectrometer.

63. See Appendix C.

64. S. Iwashima and J. Aoki, Bull. Chem. Soc. Japan, 41, 2789 (1968).

65. See Reference 47, p. 2323.

66. Eastman Chromogram sheet 13181 silica gel with fluorescent indicator No. 6060 was used. Benzene was the developing solvent and UV was the developer.

67. H. Hock and S. Lang, Ber., 75B, 313 (1942).

68. F. Straus and L. Lemmel, Ber., 54, 25 (1921).

69. F. Straus and L. Lemmel, Ber., 54B, 25 (1921).

70. Low resolution mass spectra were obtained on an LKB prototype.

71. This mass spectrum obtained at high resolution on a Consolidated Electrodynamics Co. Model 21-110B interphased with a Data General Nova 3/12 data system. Spectra were scanned with a 3 min interval and heating was programmed.

72. W. Taylor, J. Chem. Soc., 343 (1937).

73. Von W. Deuschel, Helv. Chim. Acta., 34, 2403 (1951).

74. J. W. Cook, J. Chem. Soc., 1582 (1933).

75. (a) Reference 2, p. 230. (b) R. F. Brown, "Organic Chemistry", Wadsworth Publishing Co. Inc., Belmont, California, 1975, p. 846.

76. This study was supported by the Bartlesville Energy Technology Center under the Department of Energy Contract DE-AT19-78BC 31001.

77. A. J. Floyd, S. F. Dyke, and S. E. Ward, Chem. Rev., 76, 509 (1976).

78. (a) M. Sainsbury, "Aromatic Compounds with Three Fused Carbocyclic Ring Systems," in Rodd's Chemistry of Carbon Compounds," second edition, Vol. IIIH, Chapter 28, S. Coffey (ed.), Elsevier Scientific Publishing Co., New York, 1979, p. 104. (b) Reference 2, Chapter 21.

79. C. S. Wood and F. B. Mallory, J. Org. Chem., 29, 3373 (1964).

80. F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, *86*, 3094 (1964).

81. F. R. Stermitz, "Photocyclization of Stilbenes", in "Organic Photochemistry", Vol. I., O. L. Chapman (ed.), Marcel Dekker, Inc., New York, 1967, p. 247.

82. J. H. M. Cuppen and W. H. Laarhoven, *J. Am. Chem. Soc.*, 94, 5914 (1972).

83. F. B. Mallory and C. W. Mallory, *J. Am. Chem. Soc.*, *94*, 6041 (1972).

84. (a) D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum Press, New York, 1976, p. 367. (b) J. Saltiel, J. D.'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, Chap. 1, "Organic Photochemistry", Vol. III, O. L. Chapman (ed.), Marcel Dekker Inc., New York, 1973, p. 1.

85. S. H. Harper, "Diphenylalkanes, Diphenylalkenes, Diphenylalkynes, Their Derivatives and Oxidation Products", in "Rodd's Chemistry of Carbon Compounds", second edition, Vol. IIIF, Chap. 22, S. Coffey (ed.), Elsevier Scientific Publishing Co., New York, 1979, p. 19.

86. (a) J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.*, *96*, 4708 (1974); (b) J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *J. Org. Chem.*, *43*, 3255 (1978).

87. S. Tyrlik, and I. Wolochowicz, *Bull. Soc. Chim. France*, 2147 (1973).

88. T. Mukaiyama, T. Sato, and J. Harna, *Chem. Lett.* 1041 (1973).

89. (a) A. L. Baumstark, C. J. McClosky and K. E. Witt, *J. Org. Chem.*, *43*, 3609 (1978); (b) D. Lenoir, *Synthesis*, 553 (1977).

90. N. Inamoto, S. Masuda, Y. Nagai, and O. Simamura, *J. Chem. Soc.*, 1433 (1963).

91. (a) Analysis was carried out with a Hewlett-Packard 5750B Gas Chromatograph using a 6-ft x 0.25-in copper column of 1.5% OV-17 and 1.95% QF-1 on 80-100 mesh Chromosorb Q at 175^{o}C; (b) Analytical HPLC separations were performed on a Waters Associates Liquid chromatograph using microbondapak (reverse phase) columns. The eluent was $CH_3CN:H_2O$ (4:1).

92. K. B. Sharpless, R. P. Hanzlik and E. E. VanTamelen, *J. Am. Chem. Soc.*, *90*, 209 (1968).

93. Analyses were performed by Mr. A. Taylor and Dr. G. W. Keen of CONOCO Inc. with a Finnigan Model 4023 GC-MS system with a 30 m SP-2100 glass capillary column. The spectra were scanned with a 1.1 sec interval with a head pressure of 30 psig programmed from 60-260°C at 8° per minute. The probe temperature was 140°C.

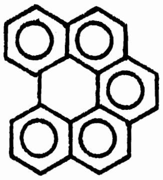
94. K. D. Cowan, Ph.D. Thesis, Oklahoma State University, 1977.

95. (a) D. J. Collins and J. J. Hobbs, *Chem. Inc.*, 1725 (1965); (b) D. J. Collins and J. J. Hobbs, *Aust. J. Chem.*, *20*, 1905 (1967).

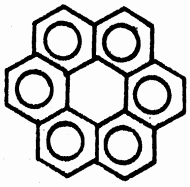
96. A. L. Gatzke, R. A. Stairs, and D. G. M. Diaper, *Can. J. Chem.*, *46*, 3695 (1968).

APPENDIX A

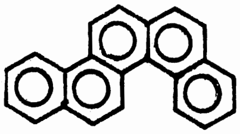
GLOSSARY OF STRUCTURES



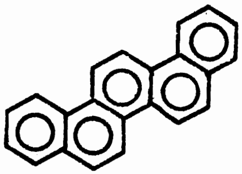
1



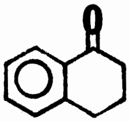
2



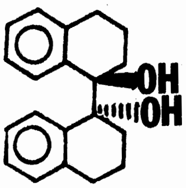
3



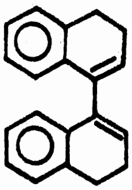
4



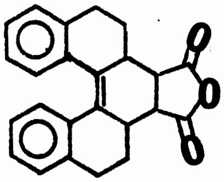
5



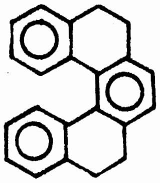
6



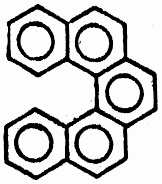
7



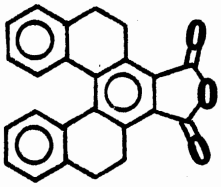
8



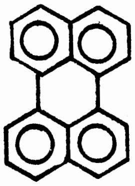
9



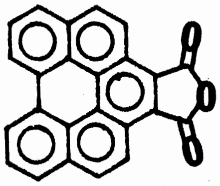
10



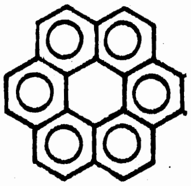
11



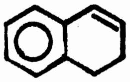
12



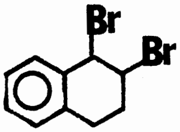
13



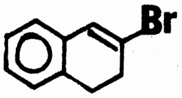
14

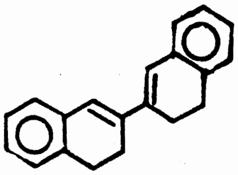


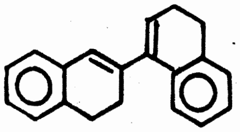
15

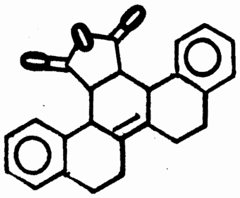


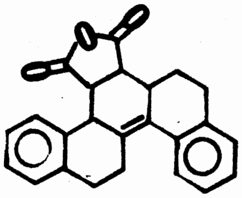
16

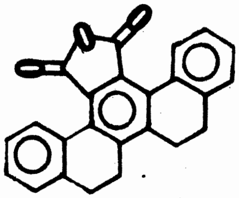

17

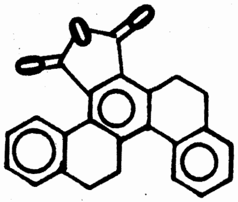

18

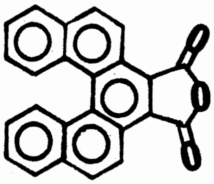

19

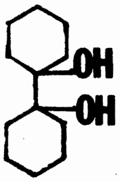

20

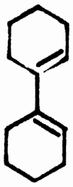

21

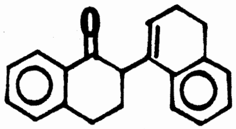

22

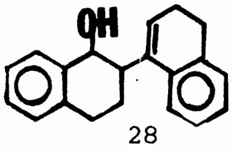

23

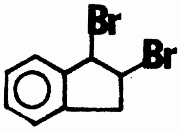

24

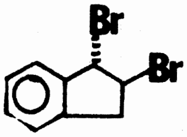

25

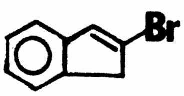

26

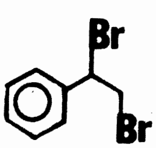

27

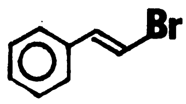

28


29a

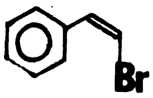

29b


30

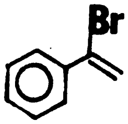

31



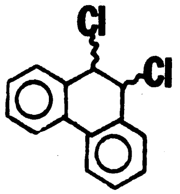
32



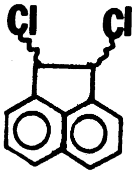
33



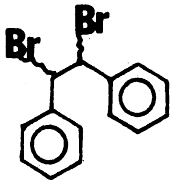
34



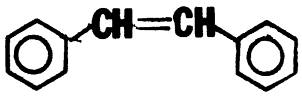
35a



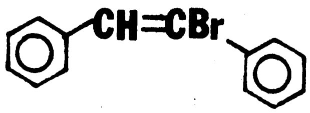
35b



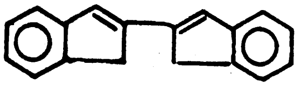
36



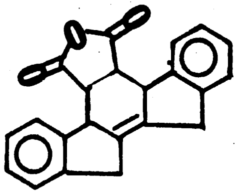
37a



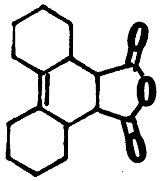
37b



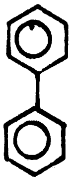
38



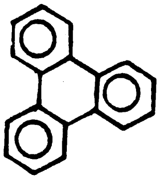
39



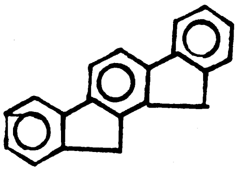
40



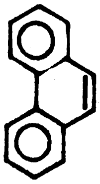
41



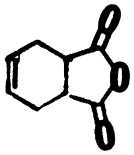
42



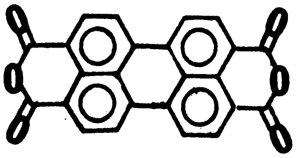
43



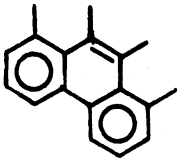
44



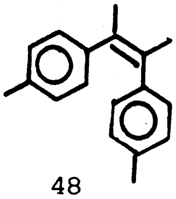
45



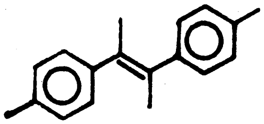
46



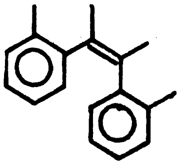
47



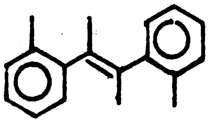
48



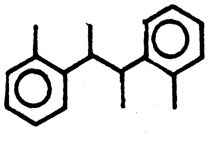
49



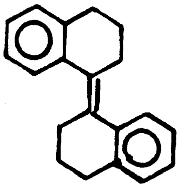
50



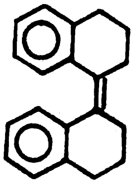
51



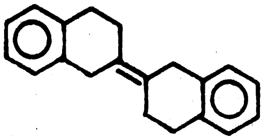
52



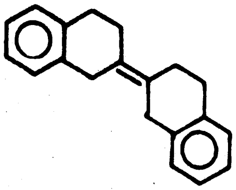
53



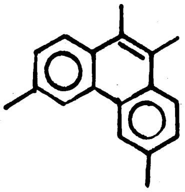
54



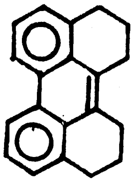
55



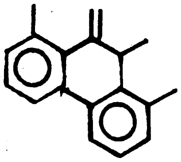
56



57



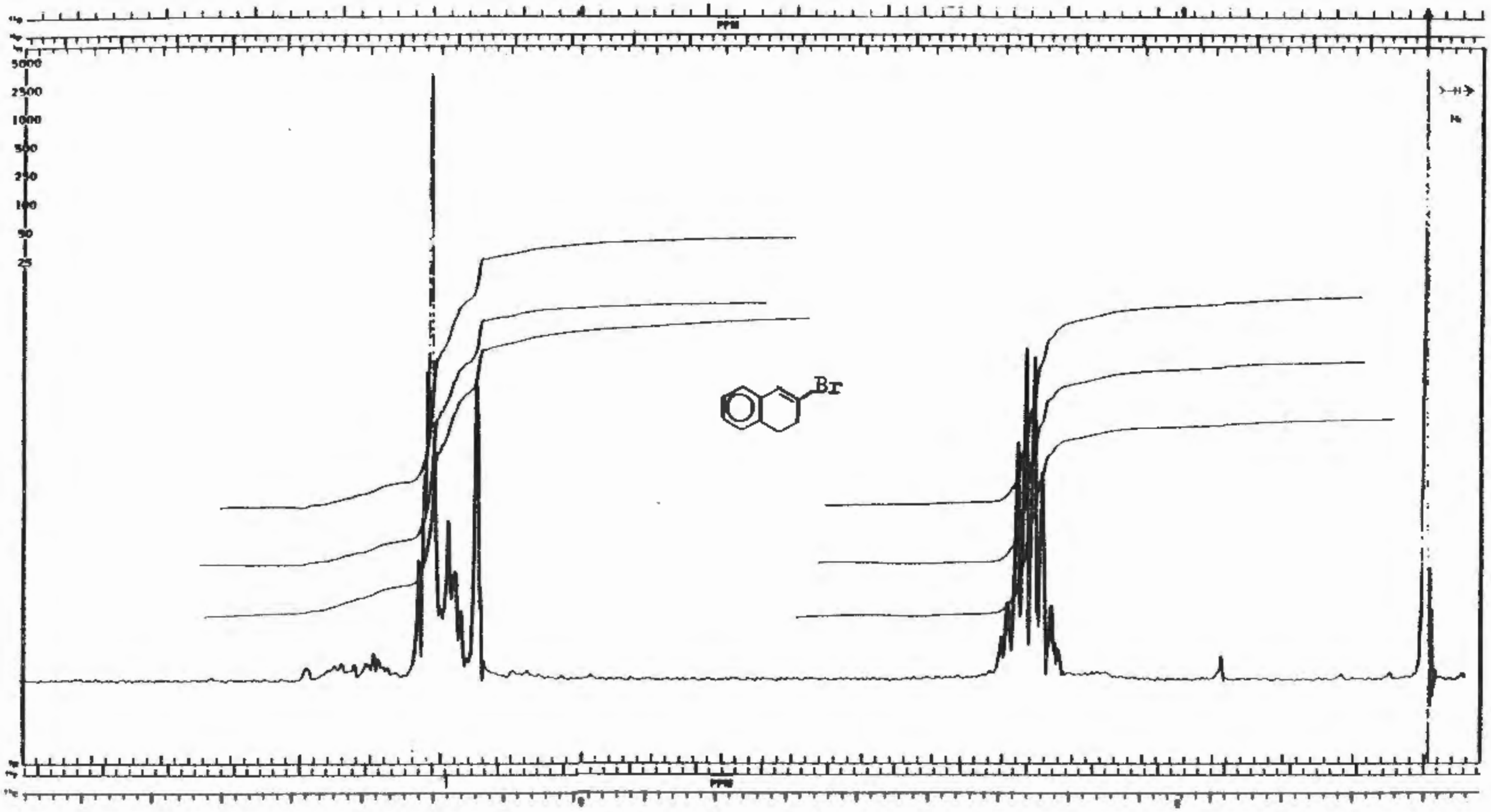
58



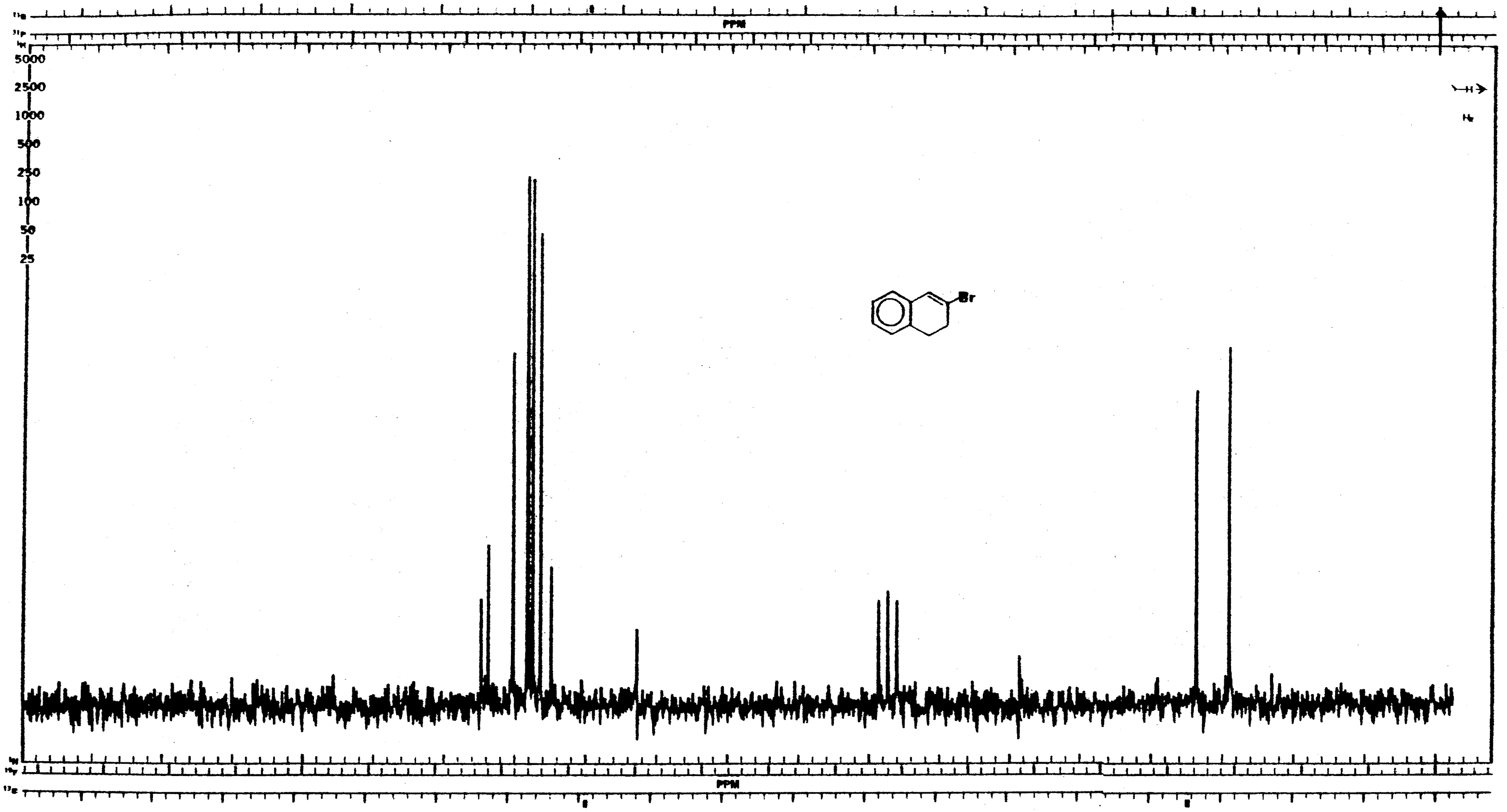
59

APPENDIX B

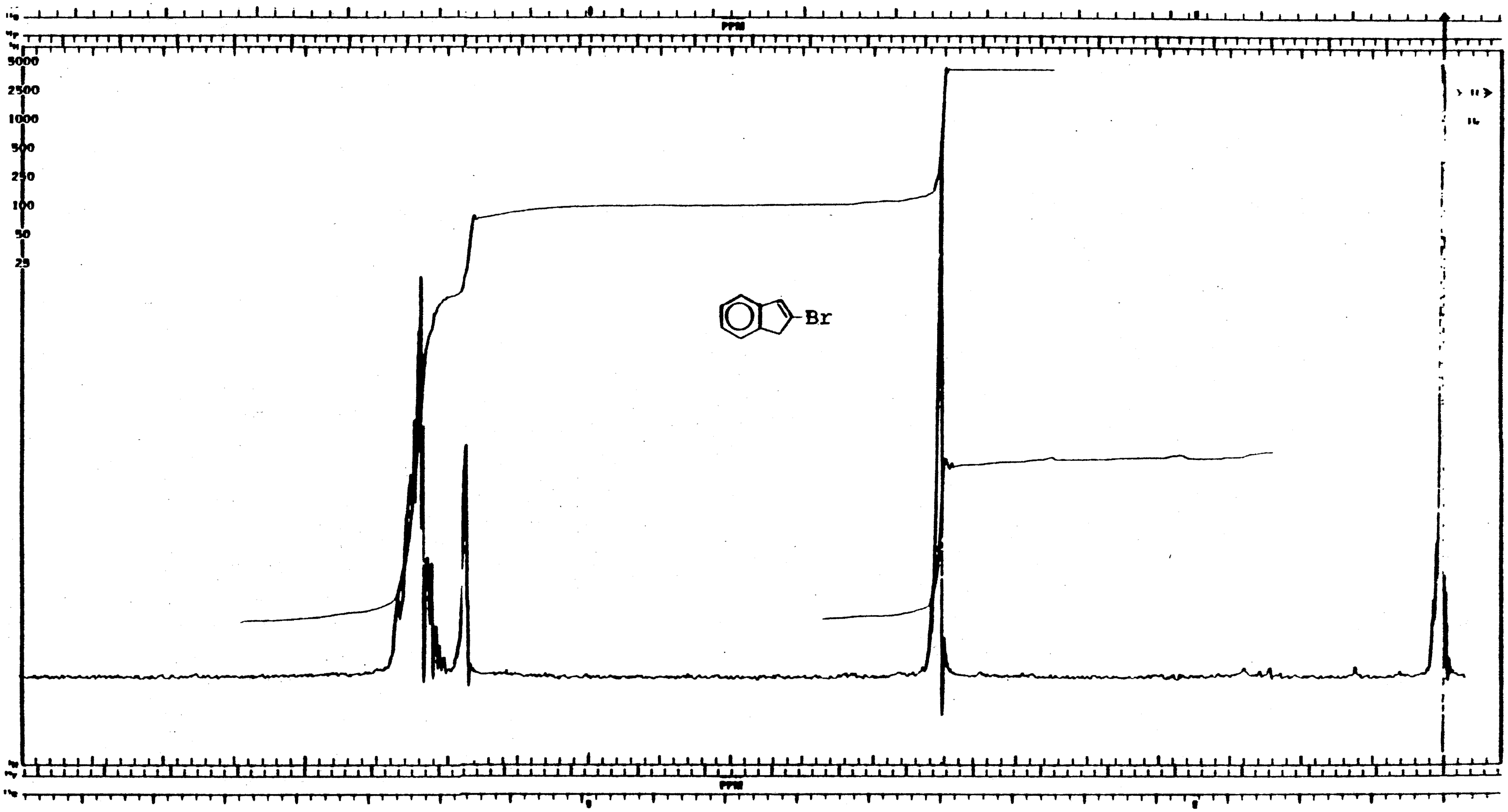
SELECTED SPECTRA



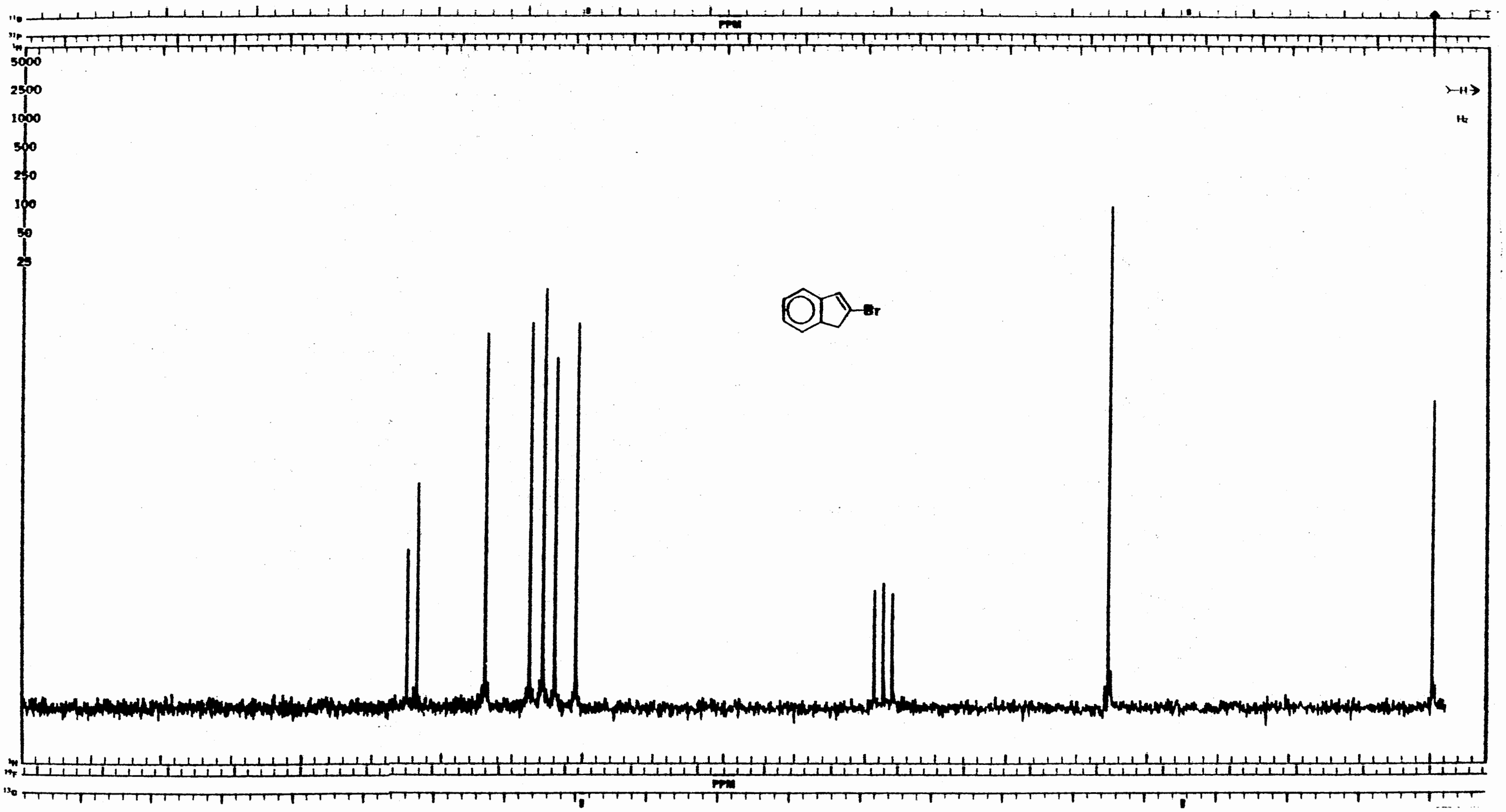
Spectrum 1. ^{1}H NMR of 3-bromo-1,2-dihydronaphthalene (<u>17</u>)



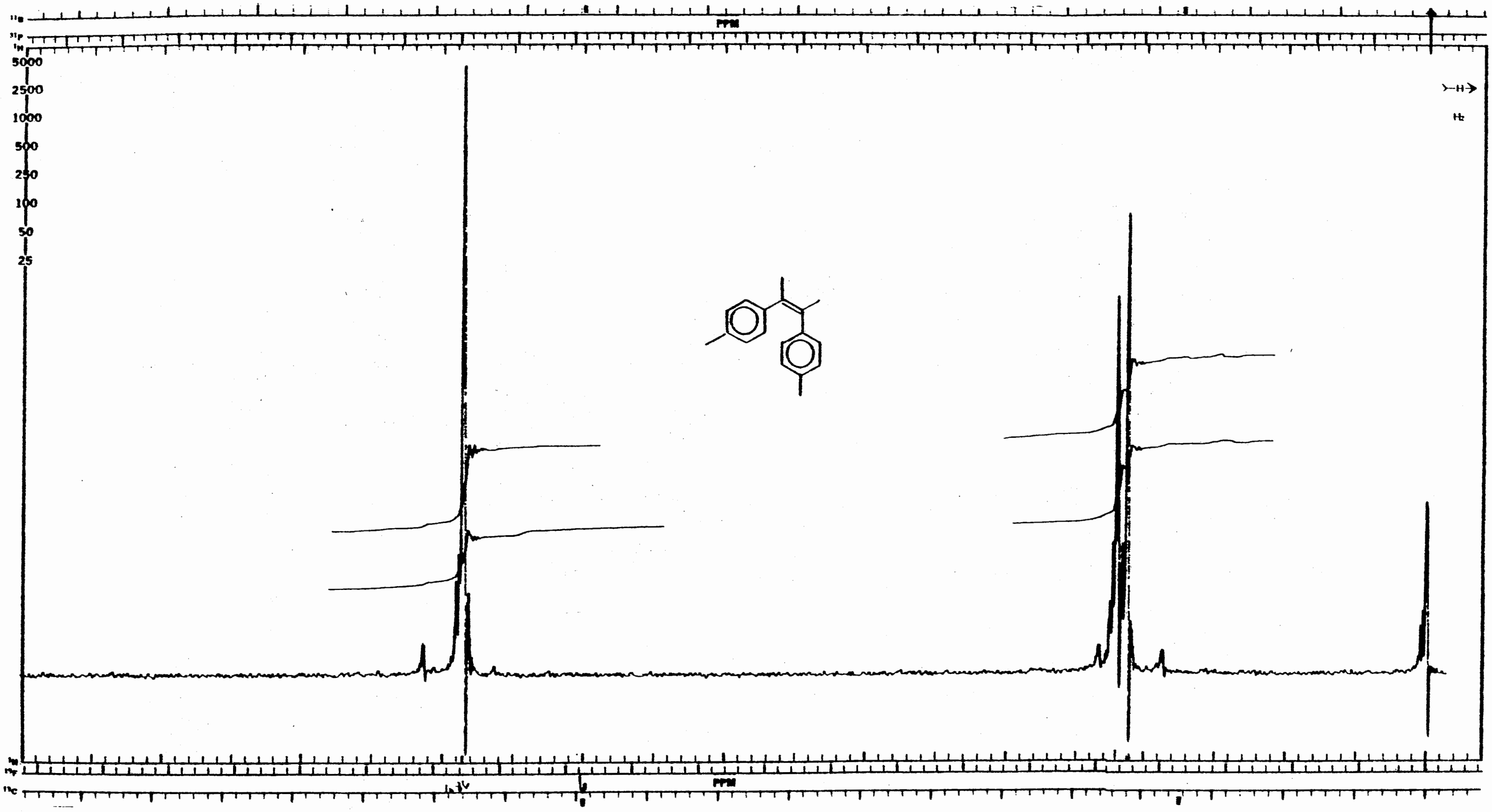
Spectrum 2. ^{13}C NMR of 3-bromo-1,2-dihydronaphthalene (<u>17</u>)



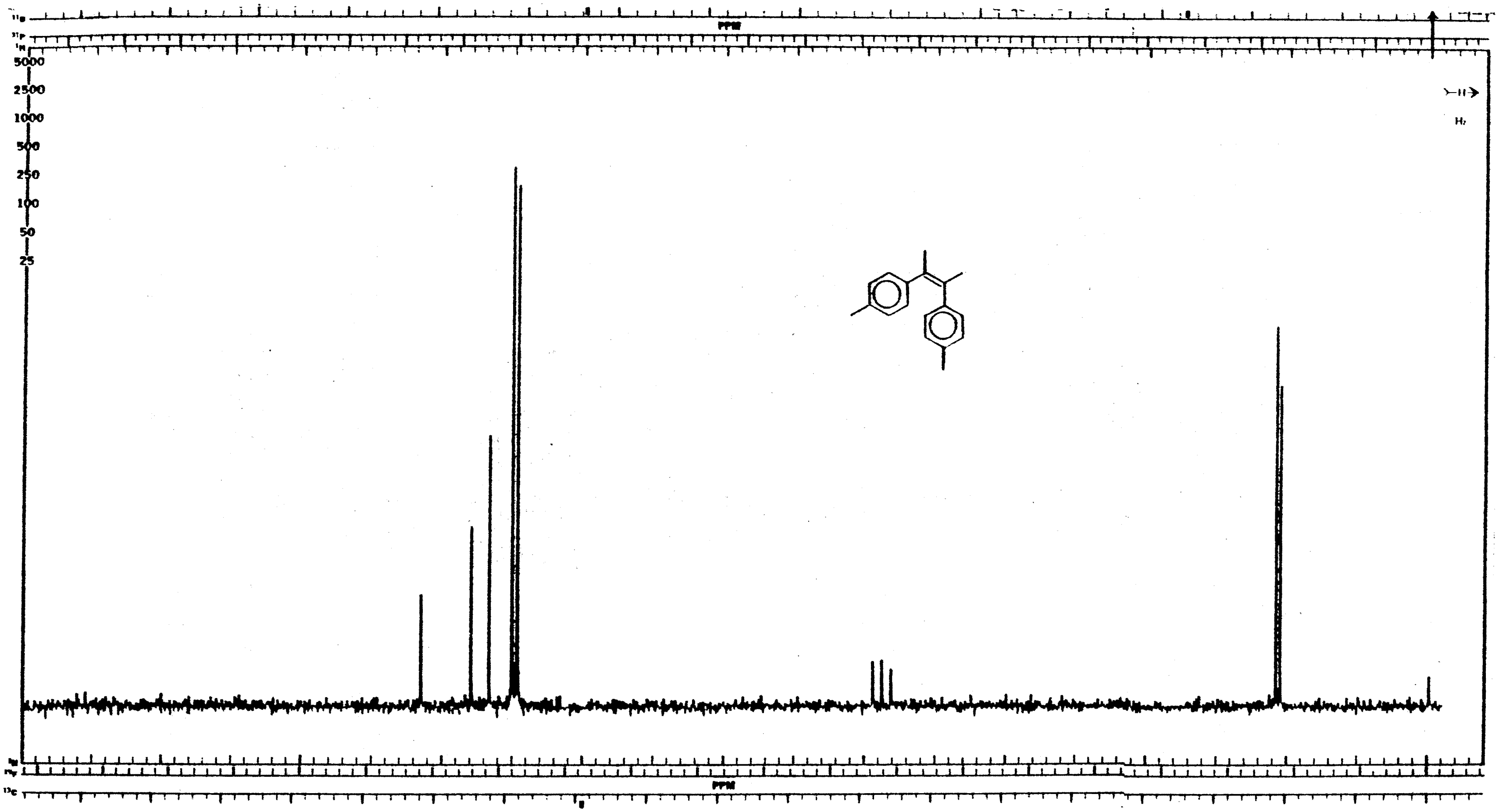
Spectrum 3. ^{1}H NMR of 2-bromoindene (<u>30</u>)



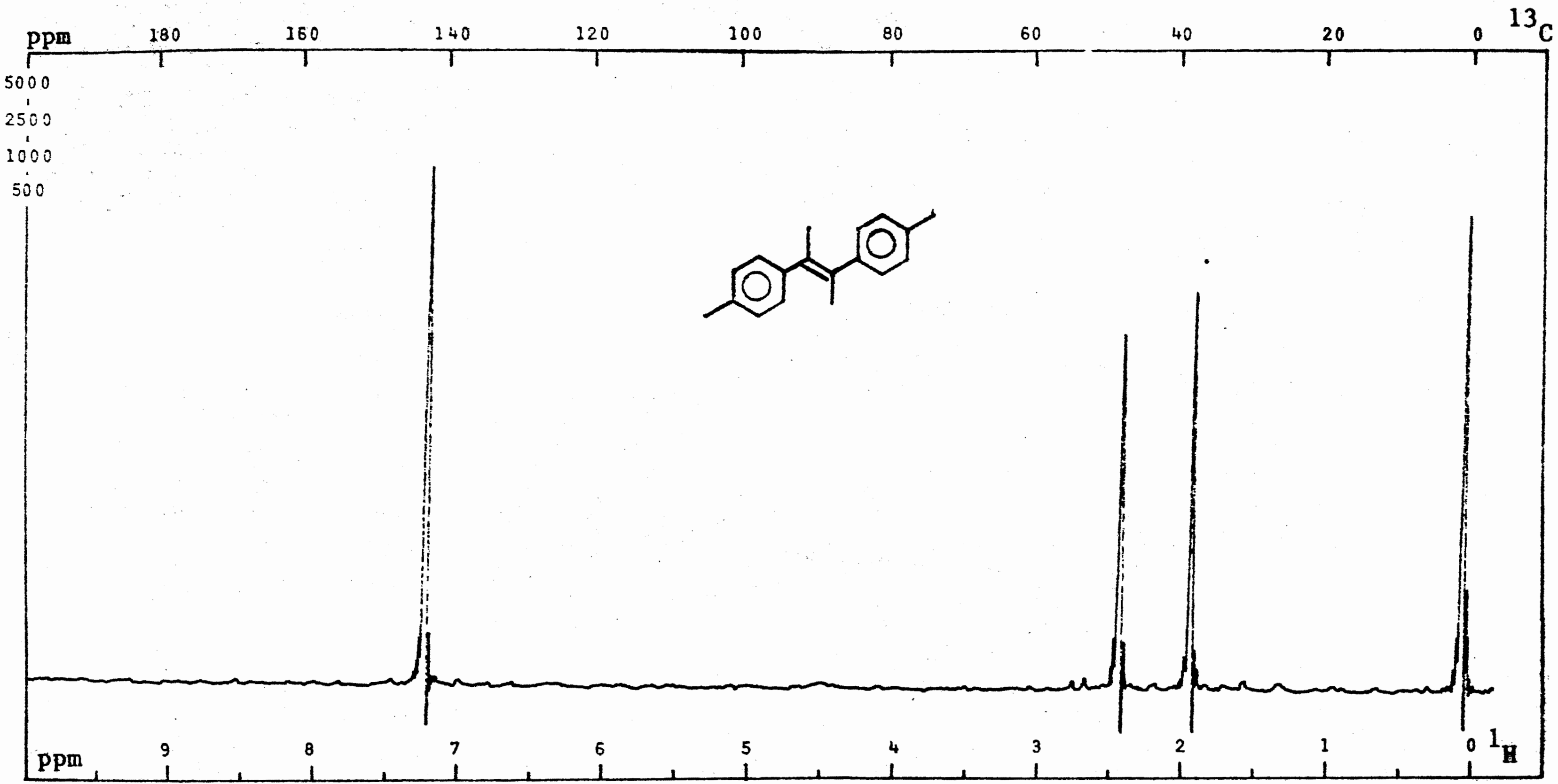
Spectrum 4. ^{13}C NMR of 2-bromoindene (30)



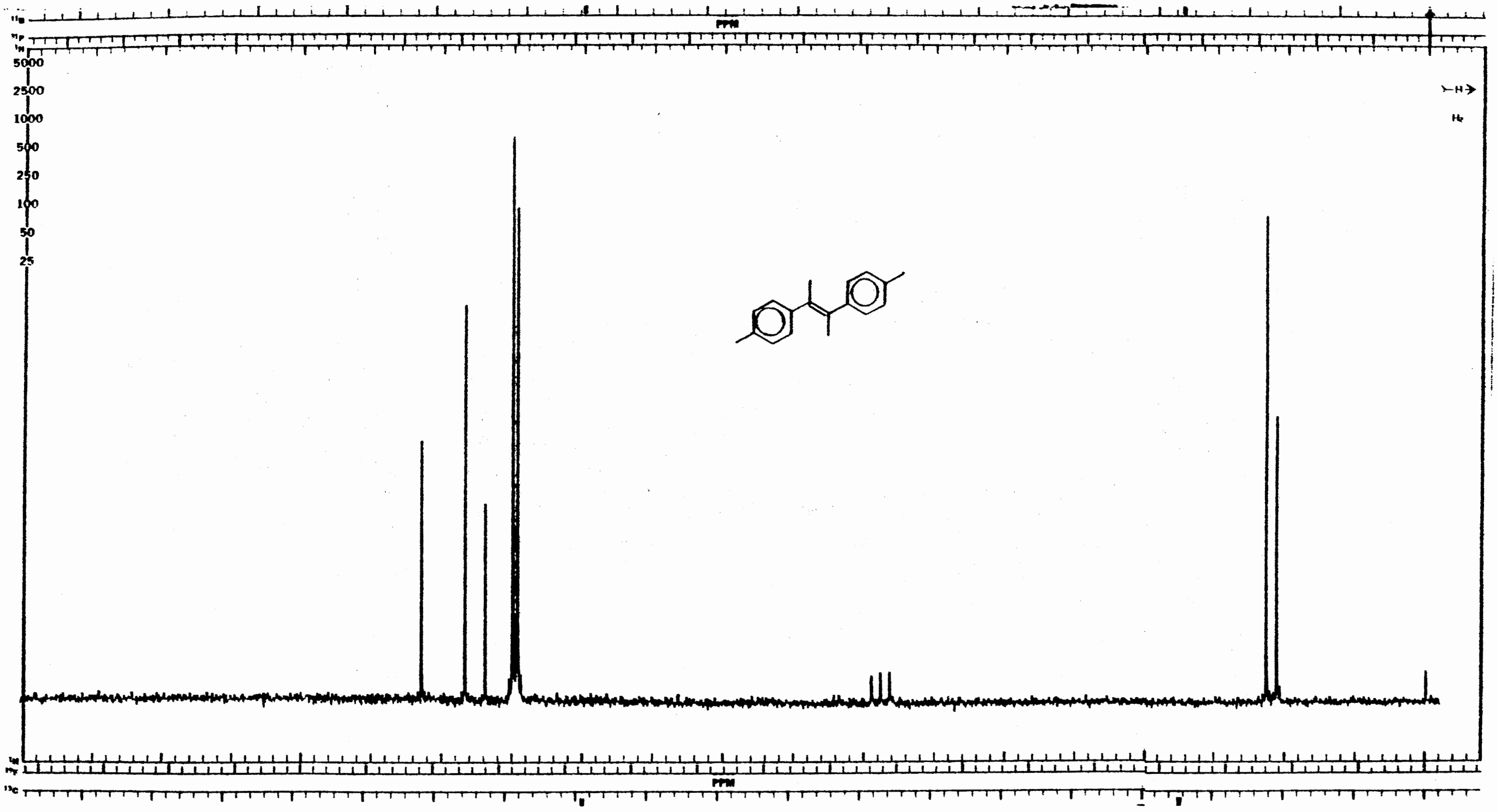
Spectrum 5. ^{1}H NMR of *cis*-4,4',α,α'-tetramethylstilbene (48)



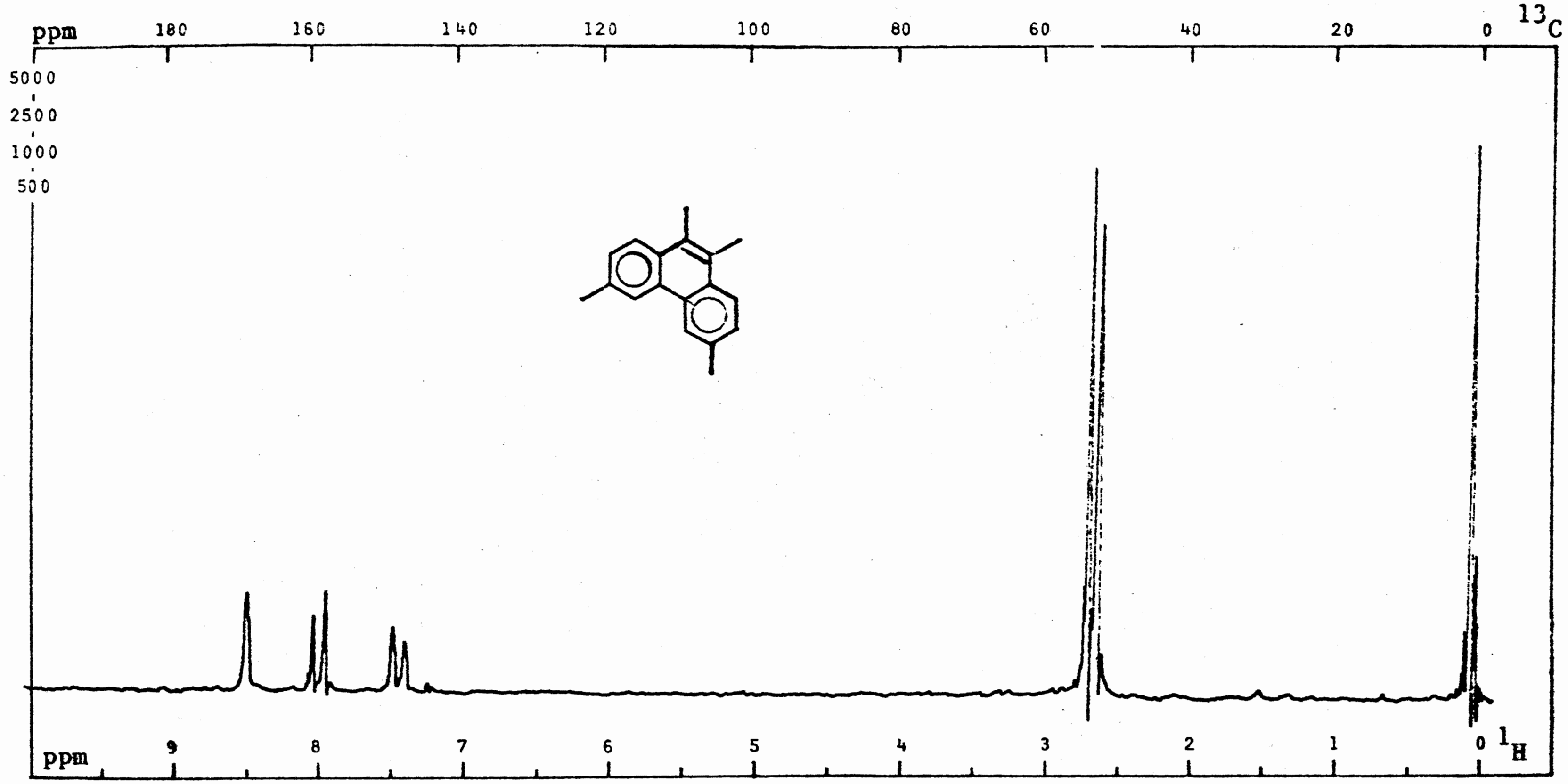
Spectrum 6. ^{13}C NMR of cis-4,4',α,α'-tetramethylstilbene (48)



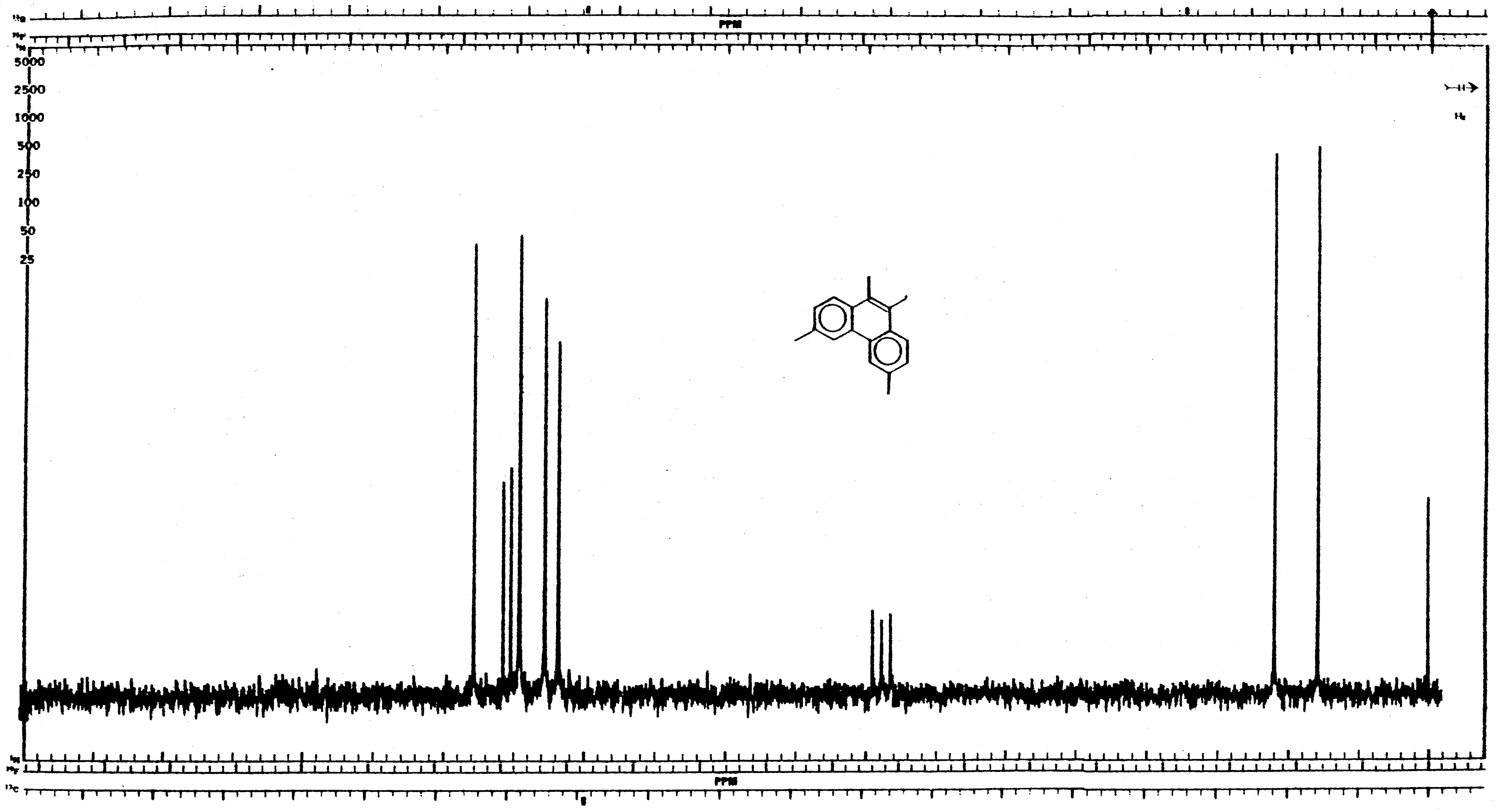
Spectrum 7. ^{1}H NMR of trans-4,4',α,α'-tetramethylstilbene (49)



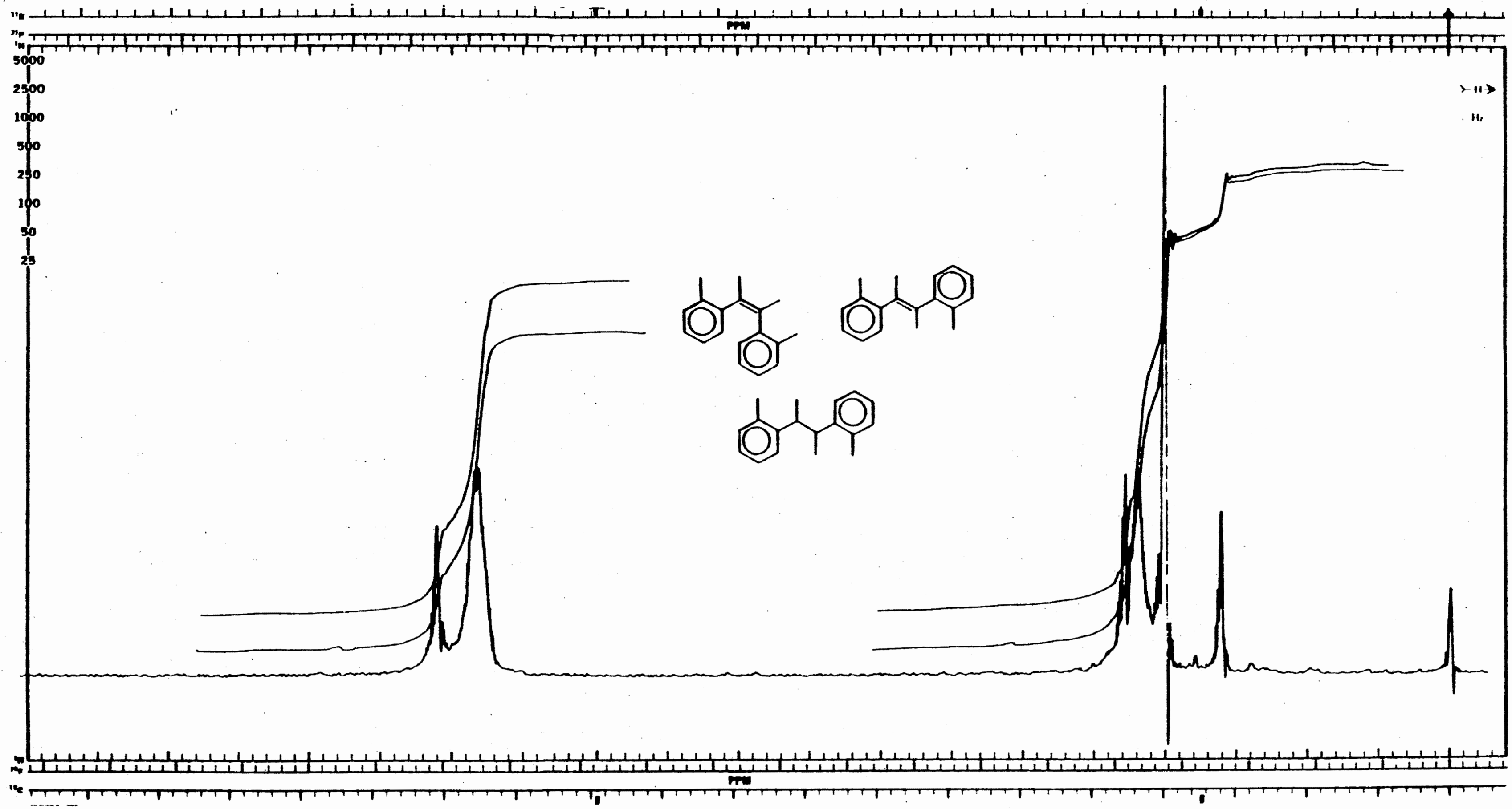
Spectrum 8. ^{13}C NMR of <u>trans</u>-4,4',α,α'-tetramethylstilbene (<u>49</u>)



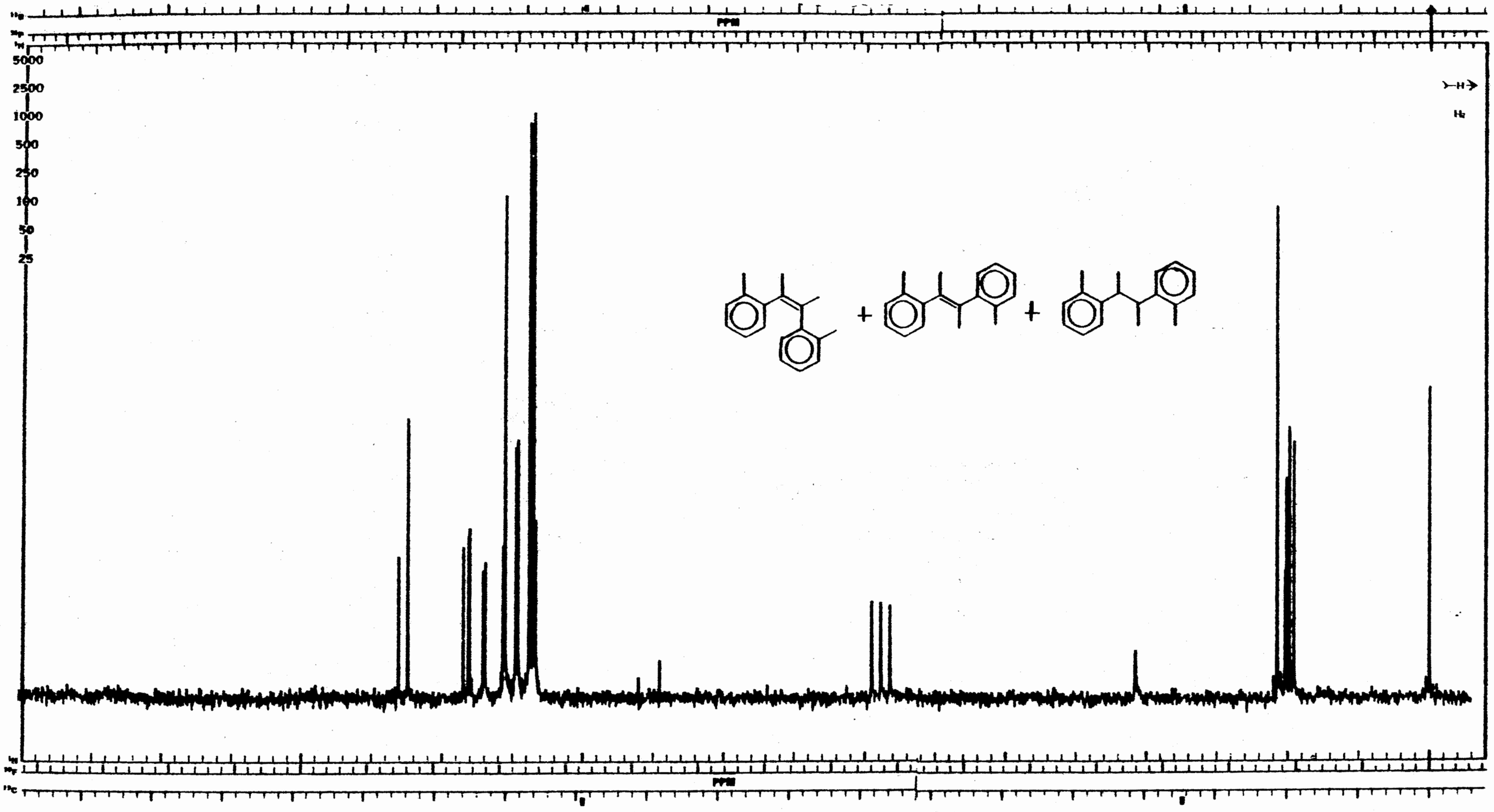
Spectrum 9. ^{1}H NMR of 3,6,9,10-tetramethylphenanthrene (<u>57</u>)



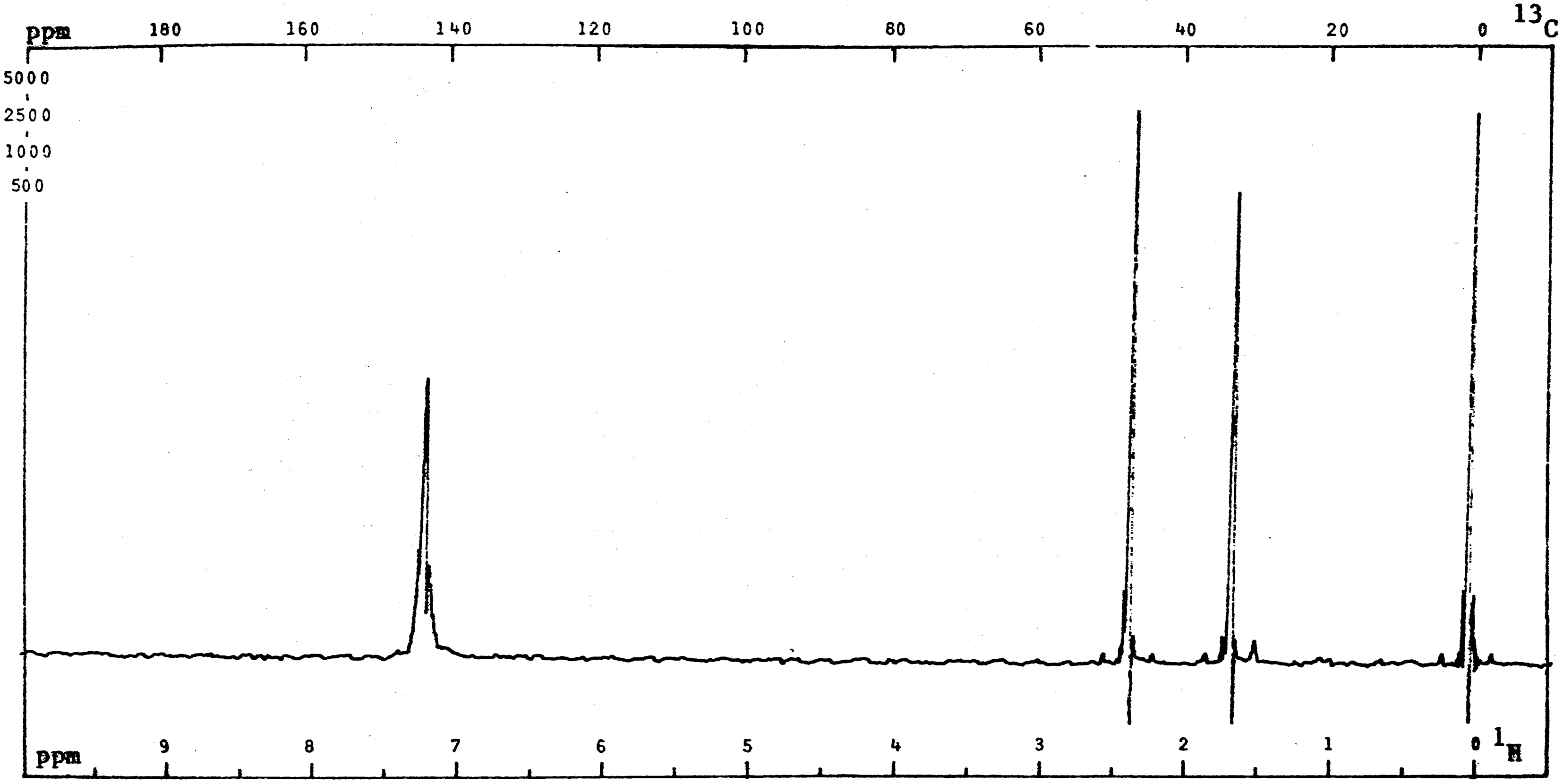
Spectrum 10. ^{13}C NMR of 3,6,9,10-tetramethylphenanthrene (<u>57</u>)



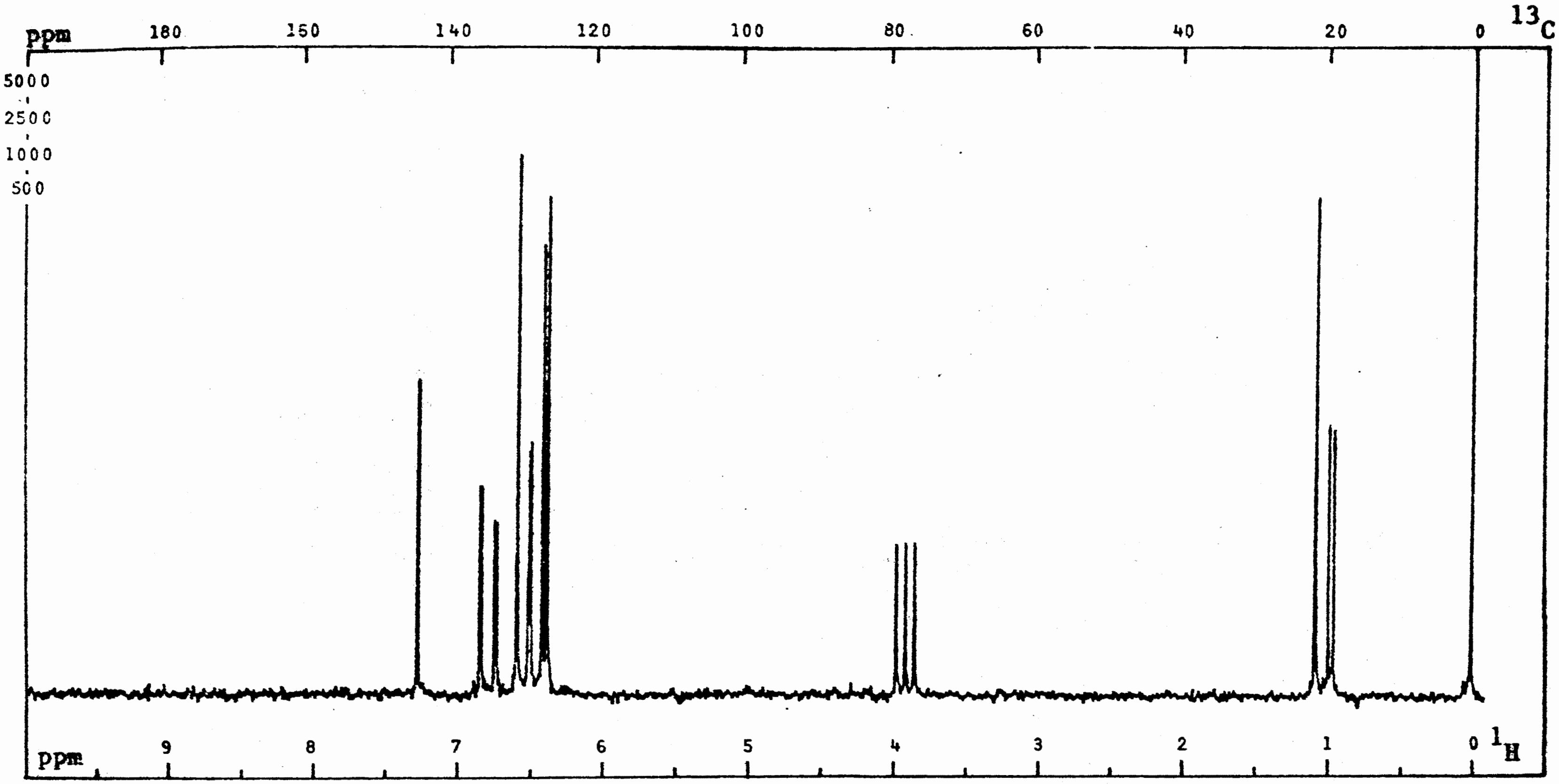
Spectrum 11. ^{1}H NMR of Product From 2-methylacetophenone With TiCl$_3$-Zn/Cu



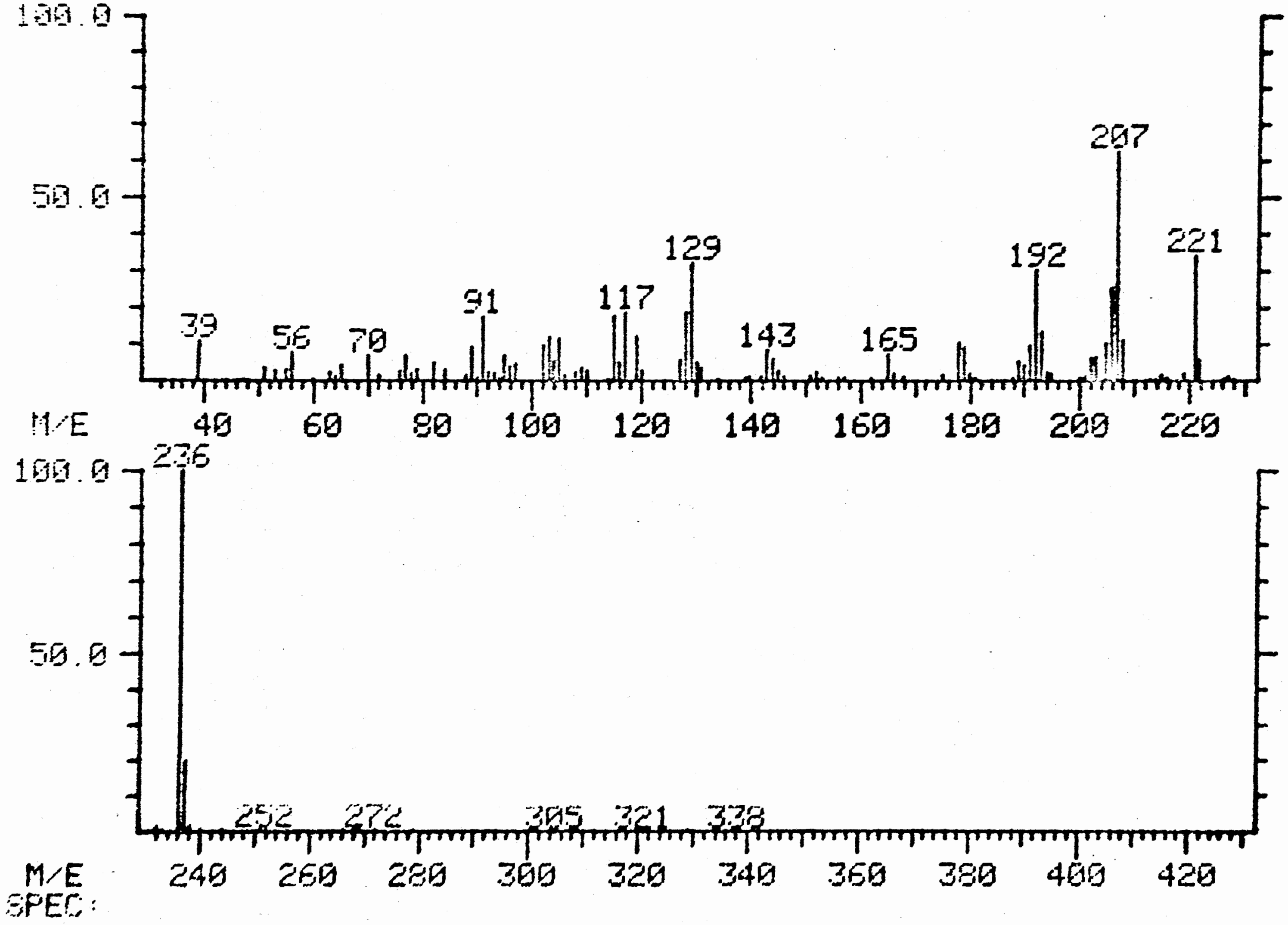
Spectrum 12. ^{13}C NMR of Product From 2-methylacetophenone With $TiCl_3$-Zn/Cu



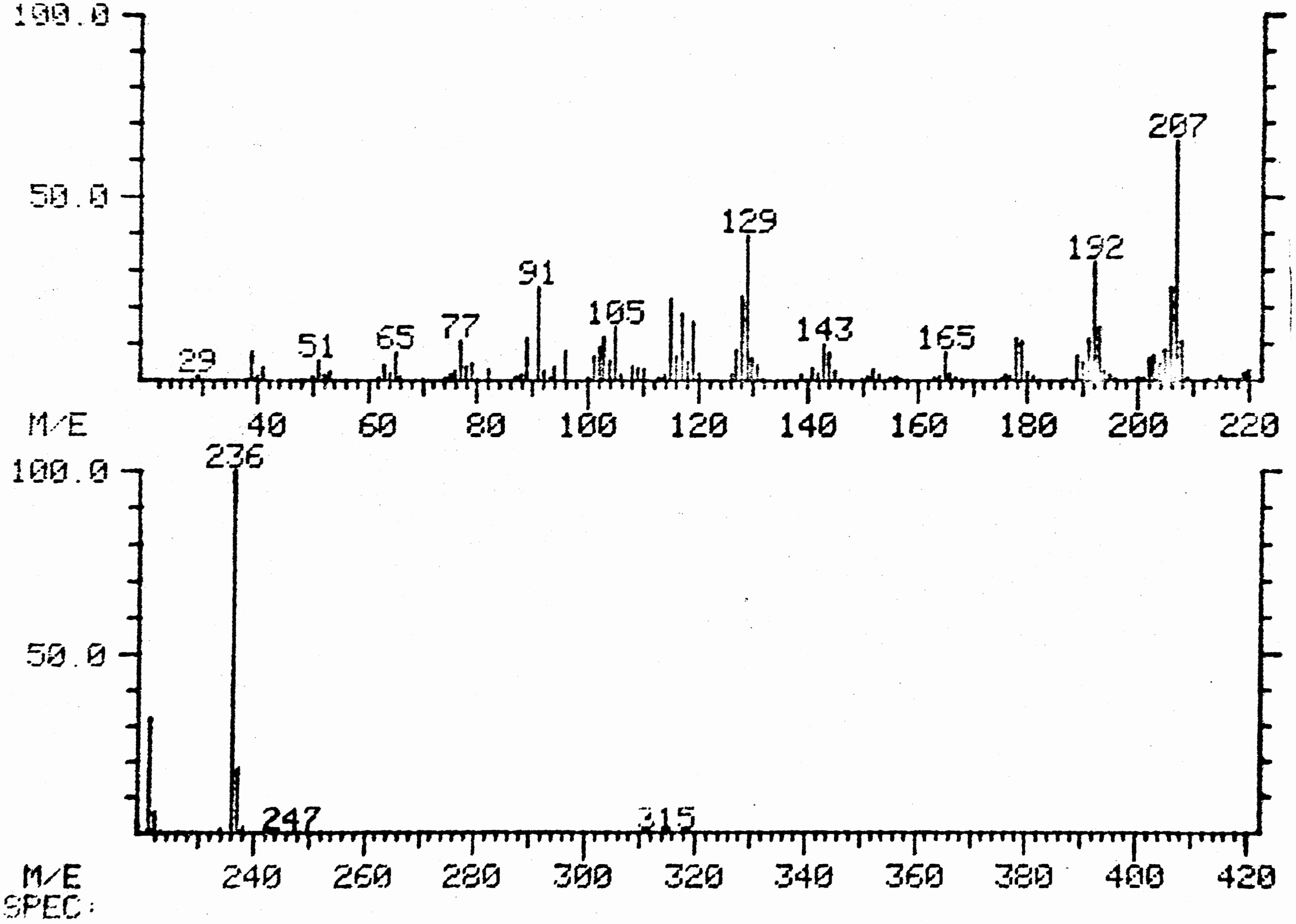
Spectrum 13. ^{1}H NMR of Photoproduct From 2,2',α,α'-tetramethylstilbene



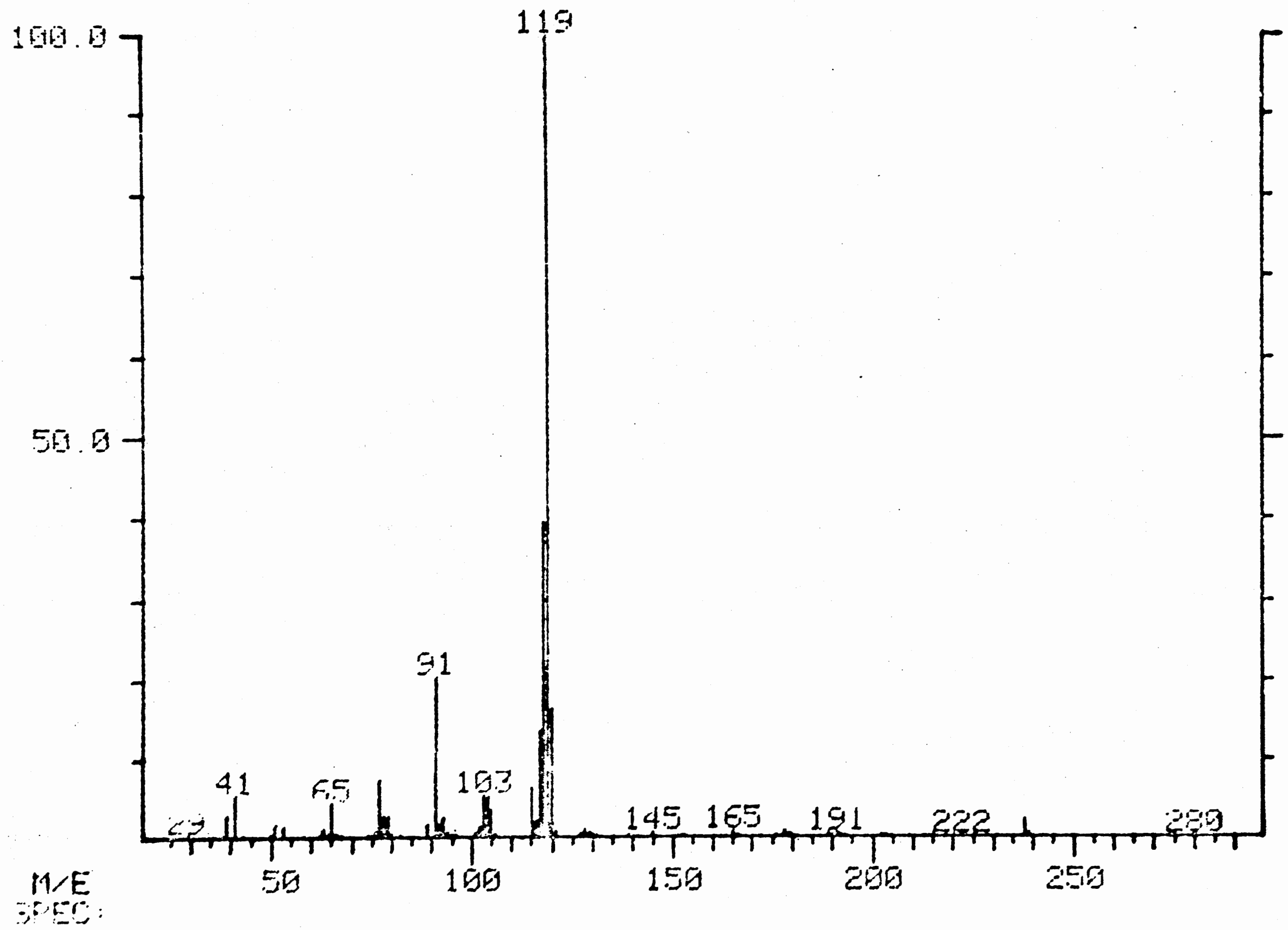
Spectrum 14. ^{13}C NMR of Photoproduct From 2,2',α,α'-tetramethylstilbene



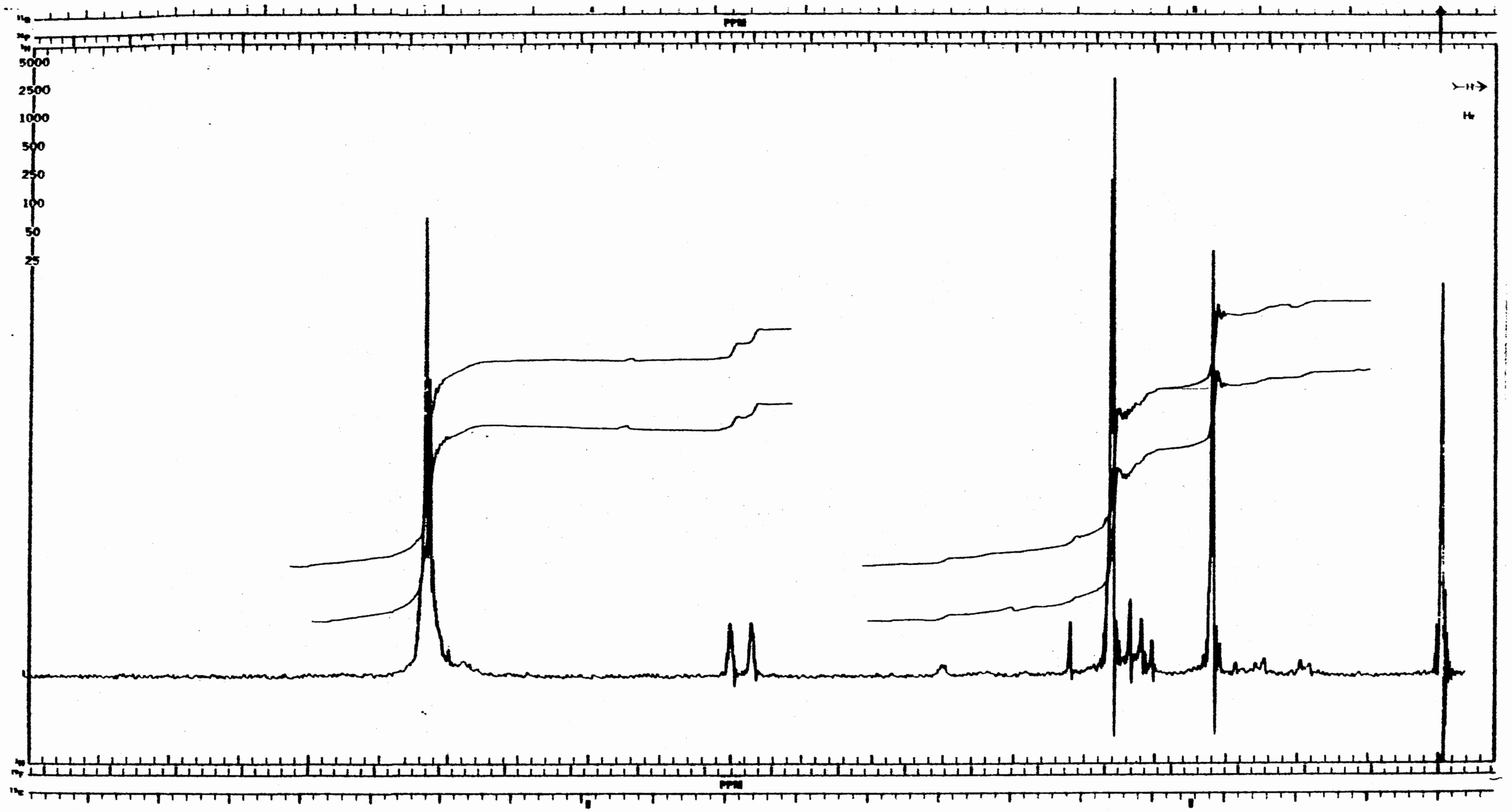
Spectrum 15. Mass Spectrum of Photoproduct and Major Isomer of 2,2',α,α'-tetramethylstilbene



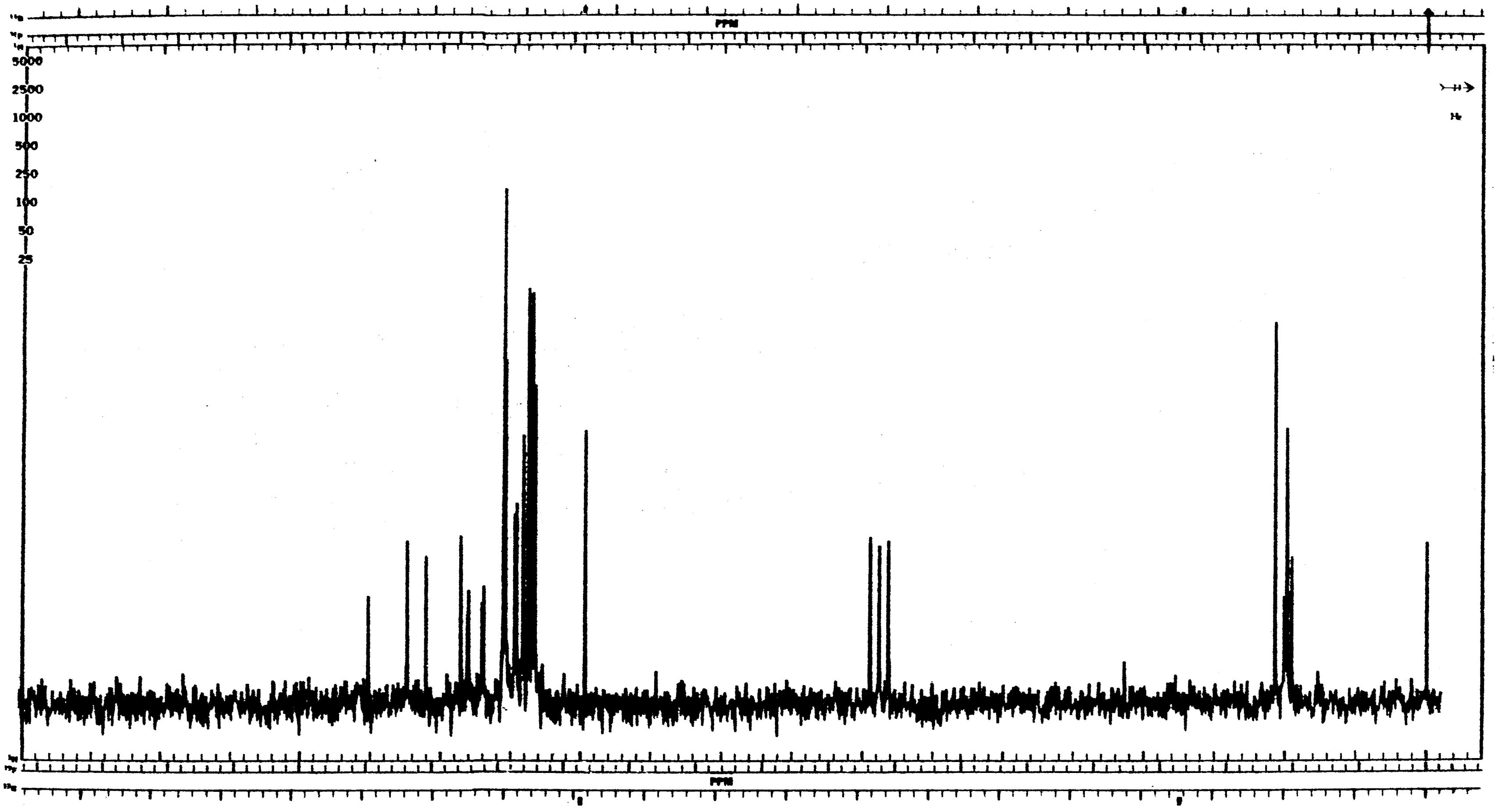
Spectrum 16. Mass Spectrum of Photoproduct and Minor Isomer of 2,2',α,α'-tetramethylphenanthrene



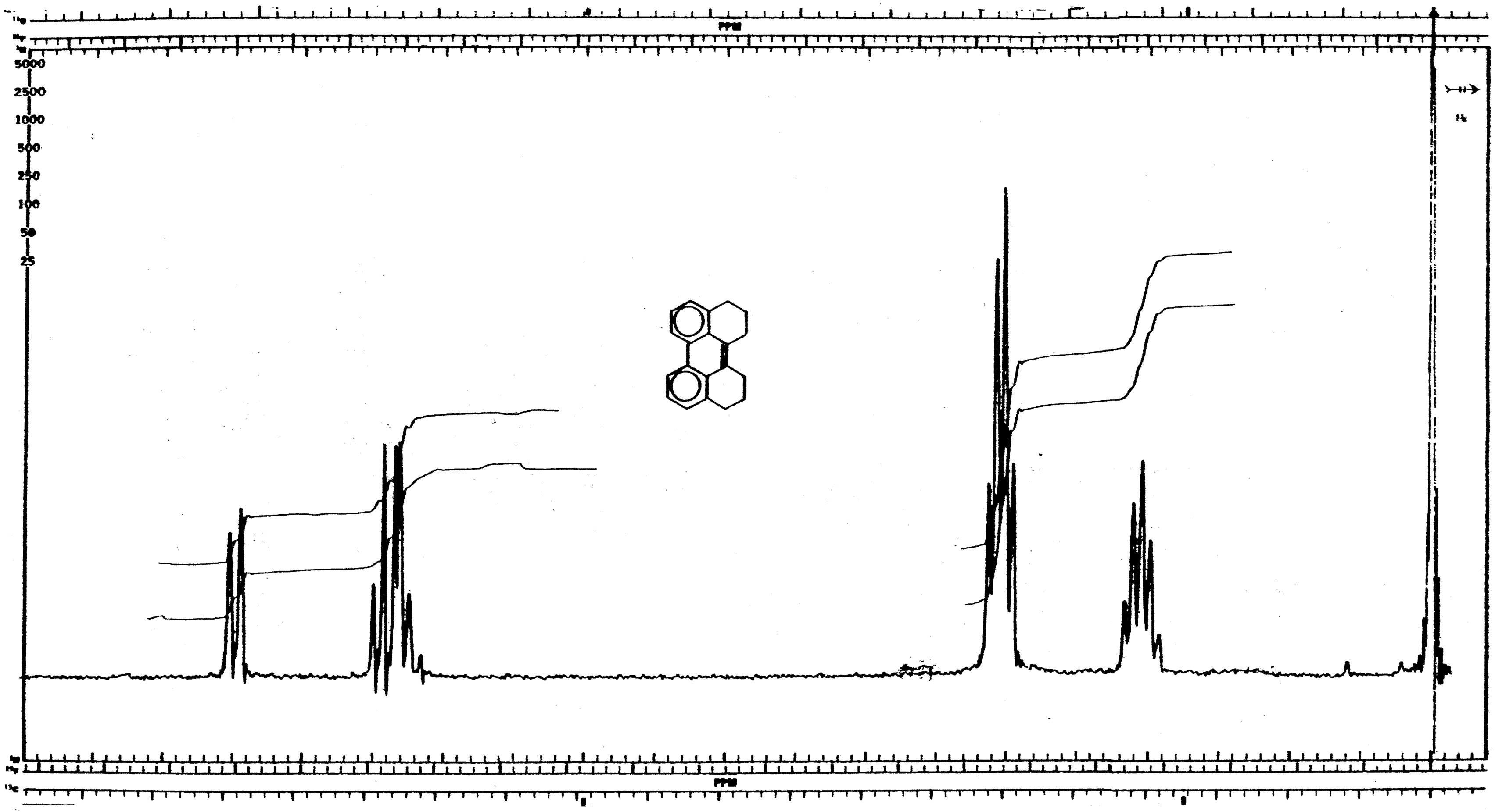
Spectrum 17. Mass Spectrum of 2,3-bis(2-methylphenyl)butane (52)



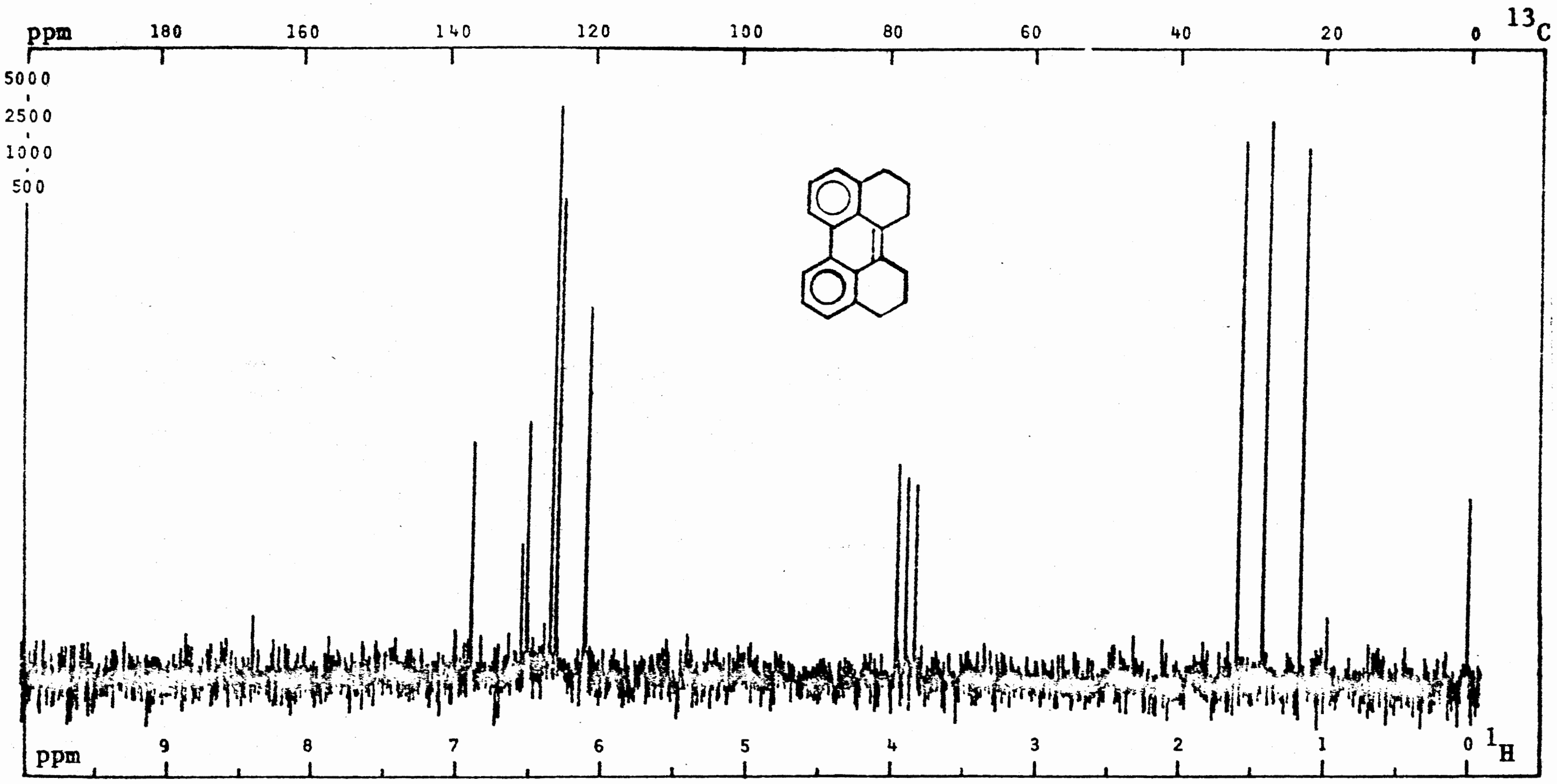
Spectrum 18. ^{1}H NMR of the Product of 2,2',α,α'-tetramethylstilbene With CrO_2Cl_2



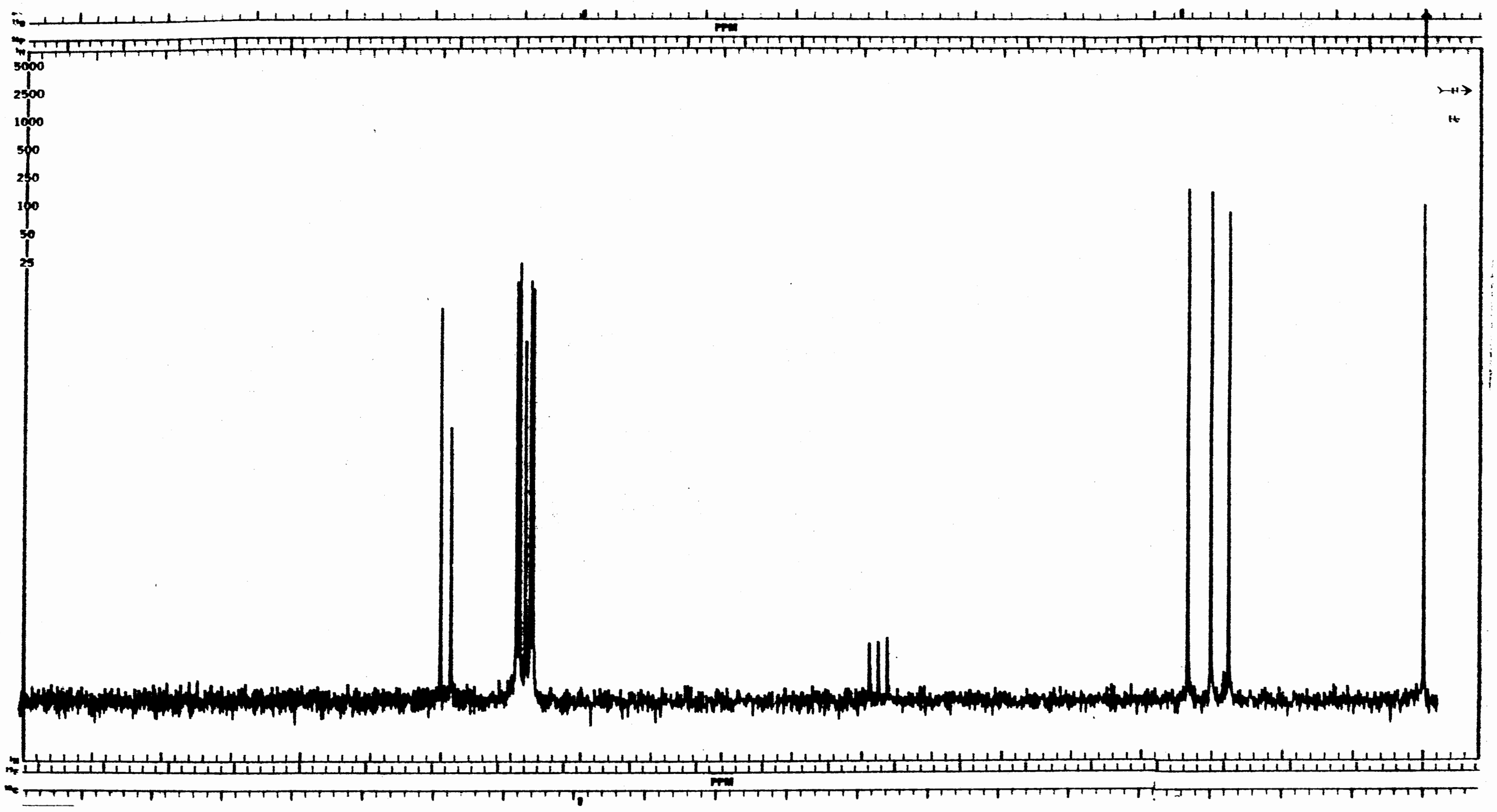
Spectrum 19. ^{13}C NMR of the Product of 2,2',α,α'-tetramethylstilbene With CrO_2Cl_2



Spectrum 20. ^{1}H NMR of 1,2,3,10,11,12-hexahydroperylene



Spectrum 21. ^{13}C NMR of 1,2,3,10,11,12-hexahydroperylene



Spectrum 22. ^{13}C NMR of the Product of 2-tetralone With $TiCl_3$-Zn/Cu

APPENDIX C

HIGH TEMPERATURE SAND-BATH HEATER AND IMPROVED SUBLIMATION APPARATUS

A HIGH-TEMPERATURE SAND-BATH HEATER AND SUBLIMATION APPARATUS

Albert G. Holba, Heinz Hall, and
Edmund J. Eisenbraun

Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, USA

We recently described a sublimation apparatus using water (0-60°C), oil (50-220°), Wood's metal (80-300°C) or a fused mixture of KNO_2:$NaNO_3$ (10:7) (145-350°) as the heating bath medium[1]. None of these is adequate for high temperature work (350-500°C). The latter is the upper working limit for glass apparatus under vacuum.

There are fluidized-bed heaters[2] for high temperature work but these are expensive and we are not aware of other designs suitable for a reaction range of 1 mL to 1 L. Our design encompases the entire size range but it may be convenient to build a smaller heater for some purposes. Because of possible flask rupture, we were unwilling to use reactive chemicals as the heater filler and settled on dry sand[3] as the most suitable medium.

The heater in Figure 1 is constructed by encircling the stainless steel cylinder <u>b</u> with 3 high temperature band heaters <u>a</u>.[4] The post terminals provided with the heaters were found to be easily damaged and consequently we developed the sturdy copper conductor <u>d</u> and its ceramic support e as an improved electrical connection. Parts d and e are anchored securely to the aluminum frame c. To withstand the high temperature, 2-mm, single strand copper wire leads were used. A ground to the aluminum frame was also installed. The multiple size lid f provides an adequate cover for reaction flasks.

Thermal insulation is provided by a layer of Pyrex wool fiber covered with several layers of glass tape. The thermal insulation provides some electrical insulation. However, if electrical insulation is critical it may be achieved by surrounding the heater with a ceramic cylinder.

At 110 volts the three heaters will require about 2 h to provide approximately 500°C at the center of the bath filled with sand. If equal potential is applied to the three heaters, the upper portion of the sand bath will become hotter by 10-20°C but since the heaters are independently wired, the vertical temperature gradient can be controlled.

The glass apparatus of Figure 2 is an adaptation of a previously described sublimation apparatus.[1] Use of Clear-Seal joint[5] b is advantageous since this allows the receiver c to be changed and thus makes fractional sublimation possible. Another advantage to using a Clear-Seal joint is that lubrication is not needed to retain a vacuum (0.1 mm). The course frit at e of Figure 2 was added to prevent passage of sublimate and is useful in preventing return of particulate matter and stopcock grease to flask c when the vacuum is released through the 3-way stopcock f. Using the 3-way stopcock f permits introduction of an inert atmosphere before and after sublimation or evacuation. Surprisingly, the frit e did not clog with sublimate during any of our uses although sublimate was carried to that point. Perylene, *peri*-xanthenoxanthene, coronene, and 1,2-benzoperylene anhydride were sublimed at 190°, 260°, 300°, and 490°C (0.02, 0.15, 0.03, and 0.2 mm) respectively.

Acknowledgement. We thank the Environmental Protection Agency under grant R805419-010 and the Bartlesville Energy Technology Center under Department of Energy Contract DE-AT19-78BC31001 for support.

REFERENCES

(1) Eisenbraun, E. J., Moyer, C. J., and Vuppalapaty, P. *Chem. Ind.*, 229 (1978).

(2) Techne Inc., 3700 Brunswick Pike, Princeton, N.J. 08540, USA.

(3) Alumina is used in commercial fluidized-bed baths[2].

(4) High temperature band heater, 5 cm wide x 15 cm diameter, Watlow Code No. 30845A, 110 Volt, 425 Watt, Watlow 12001 Lackland Rd., St. Louis, MO. 63141, USA.

(5) Joint, $ 24/25, Clear Seal, Wheaton Scientific, 1000 N. Tenth St., Millville, N.J. 08332, USA.

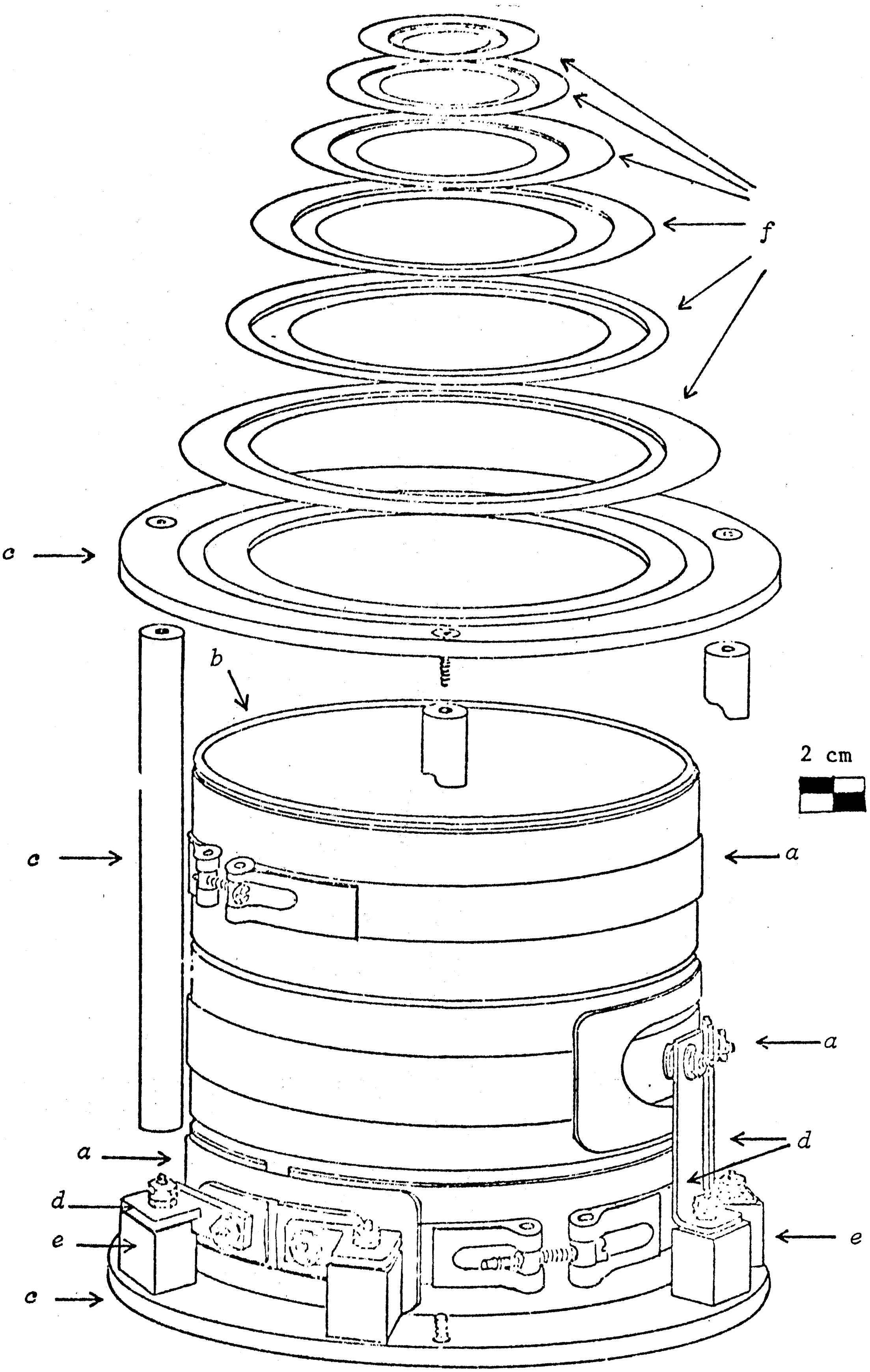


Figure 1. Flask Heater

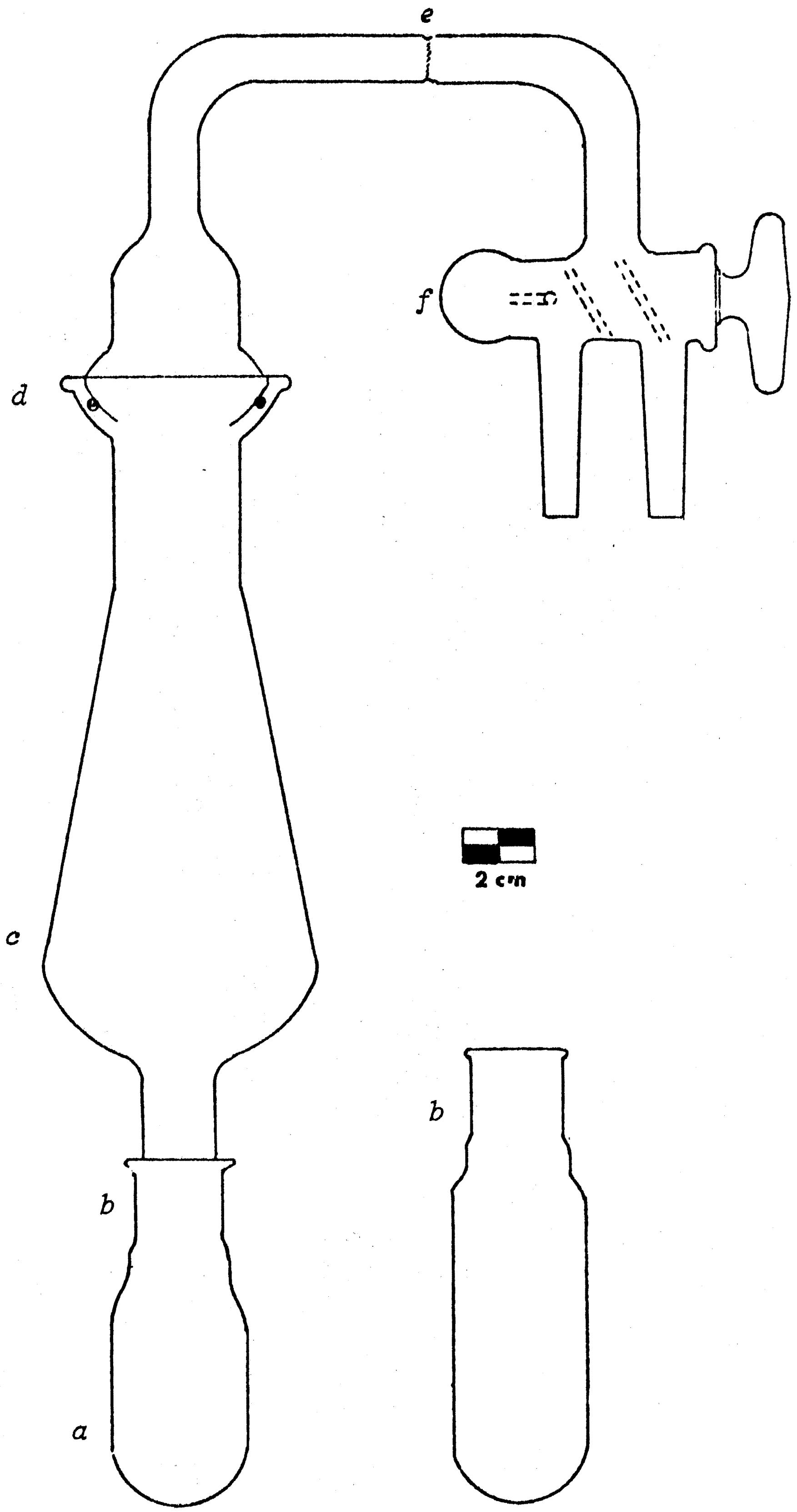


Figure 2. Glass Reactor Assembly

VITA

Albert Gene Holba

Candidate for the Degree of

Doctor of Philosophy

Thesis: I. AN IMPROVED DIENE SYNTHESIS OF POLYNUCLEAR AROMATIC HYDROCARBONS

II. SYNTHESIS OF TETRASUBSTITUTED PHENANTHRENES

Major Field: Chemistry

Biographical:

Personal Data: Born in Stillwater, Oklahoma, March 20, 1951, the son of Charlie and Lillie Holba.

Education: Graduated from Morrison High School, Morrison, Oklahoma, 1969; received the Bachelor of Science degree in Chemistry in 1973 from Oklahoma State University; completed requirements for the Doctor of Philosophy degree at Oklahoma State University in July, 1980.

Professional Experience: Technician, Biochemistry Department, Oklahoma State University, 1973-1974; graduate teaching assistant, Oklahoma State University, 1974-1979; graduate research assistant, Environmental Protection Agency 1975-1980; teaching assistant, Oklahoma State University, 1979; Dow Fellowship, Oklahoma State University, 1978-1979; member of Phi Lambda Upsilon.