Pd/C CATALYZED BISDECARBOXYLATION OF VICINAL DICARBOXYLIC ACIDS AND ANHYDRIDES

By

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1979

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
July, 1982

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ACKNOWLEDGMENTS

I wish to extend special thanks to my research adviser, Dr. E. J. Eisenbraun, for his patience, guidance, and friendship throughout this study.

Appreciation is expressed for the financial support of portions of this study by the Environmental Protection Agency and the United States Department of Energy.

I wish to express my gratitude to members of the research group for their friendship and help, particularly Drs. Albert Holba and Naser Pourahmady, for their time and many valuable suggestions.

I also wish to thank Ms. Charlene Fries for the typing of this thesis.

My aunt and uncle, Mr. and Mrs. Bill Johnson, deserve a very special thank you for their encouragement and moral support. Finally, I am most grateful to my wife, Suzy, and my daughter, Kristen, whose understanding, encouragement, and endless sacrifices have made this thesis possible.

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Pd/C CATALYZED BISDECARBOXYLATION OF VICINAL DICARBOXYLIC ACIDS AND ANHYDRIDES

CHAPTER I

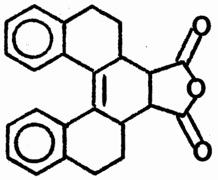
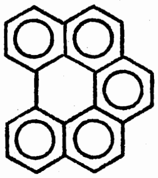
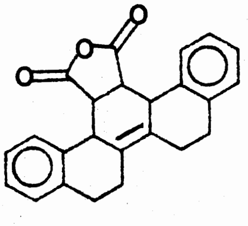
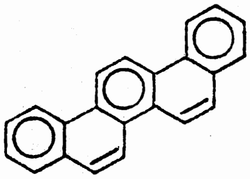
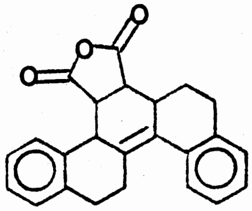
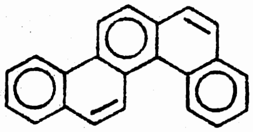
INTRODUCTION

Since the Diels-Alder reaction was introduced in 1928,[1] it has been used extensively in the synthesis of bridged hydrocarbon intermediates to polynuclear aromatic hydrocarbons. Depending on the structure, some Diels-Alder adducts can be converted to aromatic hydrocarbons by simultaneous decarboxylation and dehydrogenation using a variety of catalysts, the most notable being platinum and palladium blacks,[2] palladium on carbon (Pd/C),[3a,b,c] and palladium on charcoal with copper-chromite.[4]

This study was undertaken to determine the utility of 10% Pd/C as a decarboxylating agent for Diels-Alder adducts derived from maleic anhydride. This catalyst has been used successfully, for this purpose, with high yields by Holba[5] in the synthesis of benzo[_ghi_]perylene (_2_), picene (_4_), and benzo[_c_]chrysene (_6_) shown in Table I. This study reports the results of experiments using similar conditions of temperature, reaction time, and catalyst ratio applied to some selected vicinal dicarboxylic anhydrides.

TABLE I

Pd/C CATALYZED DECARBOXYLATION AND DEHYDROGENATION OF DIELS-ALDER ADDUCTS

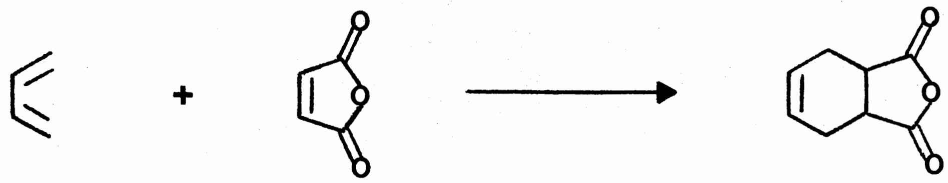
Reactant	Product	% Yield
 1	 2	**94**
 3	 4	**84**
 5	 6	**66**

CHAPTER II

HISTORICAL

The Diels-Alder reaction using maleic anhydride, followed by bisdecarboxylation with various catalysts and reagents, has been applicable in the synthesis of a wide variety of polycyclic aromatic hydrocarbons.[6] The history of the Diels-Alder reaction in the preparation of hydroaromatic anhydrides and the techniques used in decarboxylation to hydrocarbon products will be described.

Diels and Alder first published the cycloaddition of butadiene with maleic anhydride in benzene solution at 100 °C to give cis-1,2,3,6-tetrahydrophthalic anhydride (7).[1]



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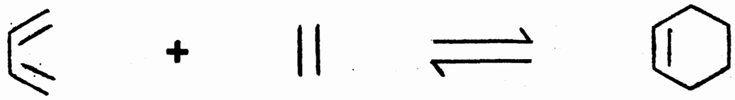
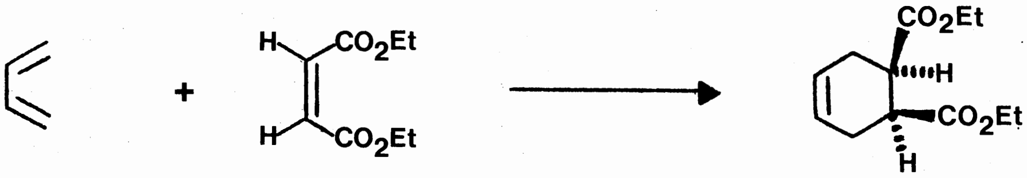
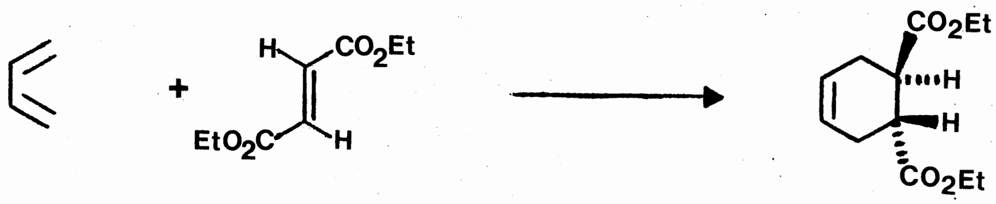
Subsequently, the combination of various diene systems and dienophiles have been used to add two or more carbons to a molecule. The Diels-Alder reaction consists of the addition of a compound containing a double or triple bond (dienophile) to the 1,4 position of a conjugated system (diene), with the formation of a six-member hydroaromatic ring as shown below.



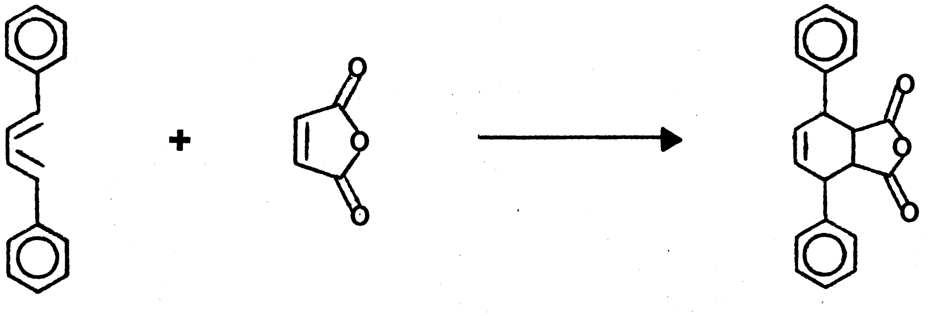
This reaction type is termed a [4+2] cycloaddition, since it involves a four-π-electron system and a two-π-electron system. All available data indicate that the reaction is a concerted process that proceeds stereospecifically by cis addition to the double bond. This specificity is demonstrated by the formation of stereospecific products from the reaction of butadiene with ethyl maleate and ethyl fumarate.[7]





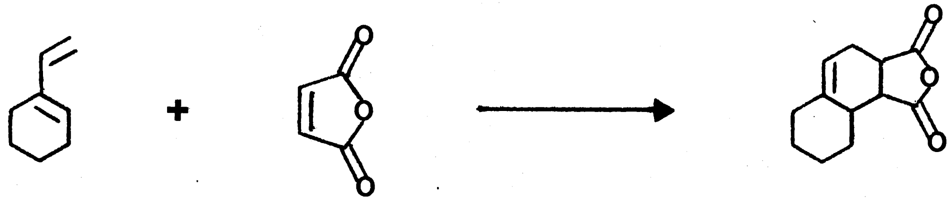
Because maleic anhydride reacts readily with a wide variety of dienes, it is the most widely used dienophile in Diels-Alder reactions. This anhydride has high activity due to its polar characteristics as well as having a planar structure. This planarity offers a minimum of steric hindrance to the formation of an addition complex, which orients the diene and dienophile prior to actual bond formation.[8]

One of the earliest reactions introduced by Diels and Alder was the addition of maleic anhydride to 1,4-diphenyl-1,3-butadiene (8) to provide a convenient route for the synthesis of the terphenyl derivative 9.[9]



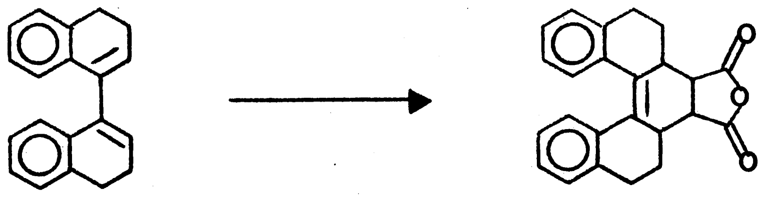
8 9

Cook and Lawrence found that 1-vinyl-1-cyclohexene (10) reacts with maleic anhydride at room temperature to give 1,2,3,5,6,7,8,8a-octahydronaphthalene-1,2-dicarboxylic anhydride (11) in 82% yield.[10]



10 11

Certain types of dienes which have the conjugated system extending over two nonfused rings are able to undergo Diels-Alder reactions. As shown below, anhydrides 1, 3, and 5 can be synthesized from hydrocarbons 12, 13, and 14 by heating each hydrocarbon in the presence of maleic anhydride. The reaction products were introduced by Weidlich[11] as intermediates for the synthesis of polycyclic aromatic hydrocarbons. Holba[5] recently synthesized anhydrides 1, 3, and 5 in 96, 87, and 84% yield, respectively, using the Weidlich procedure.



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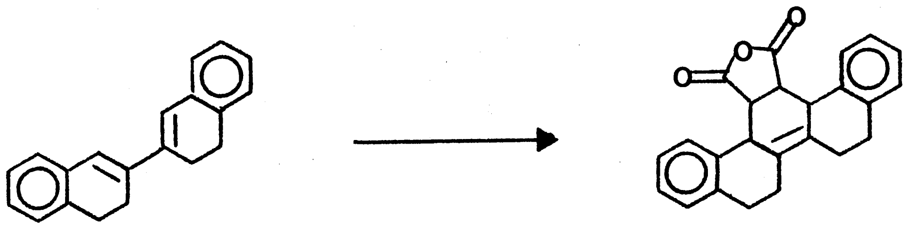

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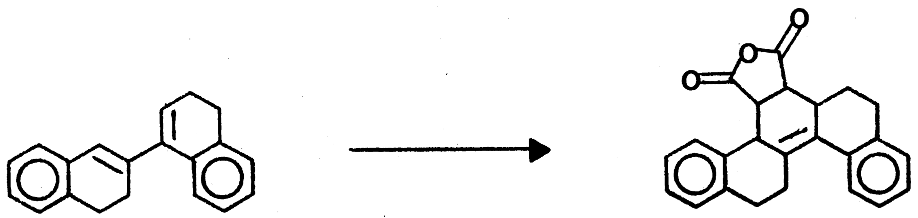

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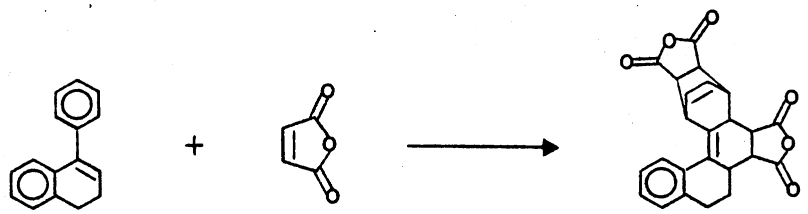
Addition of dienophiles to diene systems in which one double bond is part of an aromatic ring and the second is conjugated to this ring was used by Szmuszkovicz.[12] The bisanhydride 16 can be formed when 1-phenyl-3,4-dihydronaphthalene (15) reacts with two moles of maleic anhydride. The yield varies with the reaction temperature, from moderate at 95 °C to quantitative at 160 °C.



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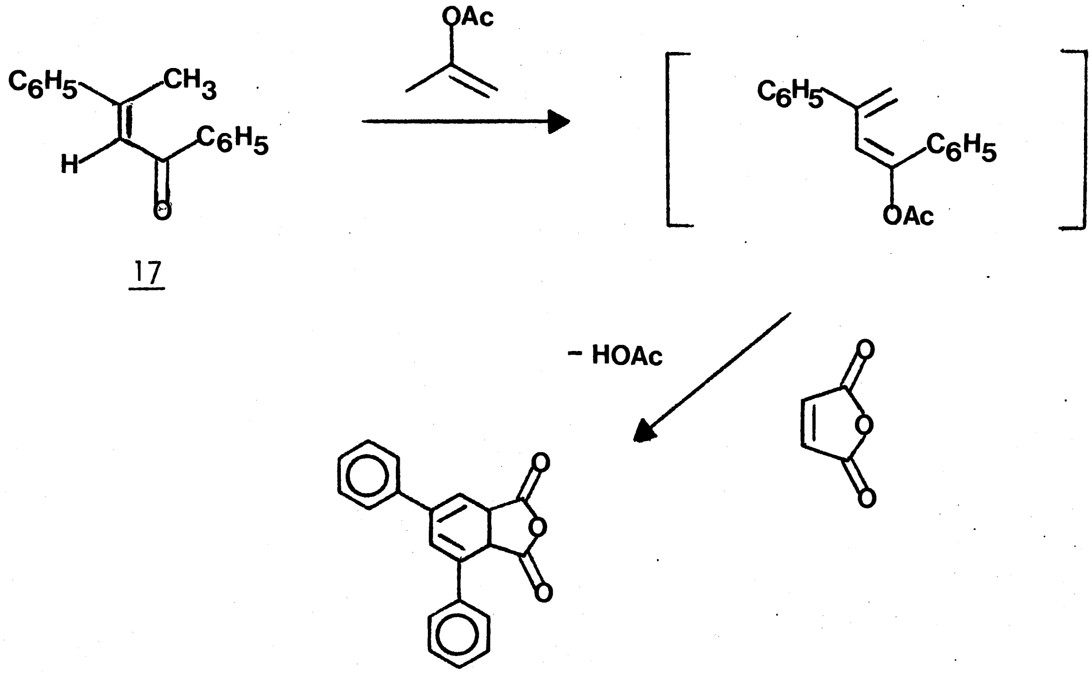
In 1970, Wolinsky published a novel synthetic route to cyclic anhydrides. Acetoxy-1,3-dienes generated in situ from α,β-unsaturated ketones can react with maleic anhydride to give Diels-Alder adducts. Heating dypnone 17 in isopropenyl acetate containing a catalytic amount of p-toluenesulfonic acid with 2.3 equivalents of maleic anhydride gives adduct 18 in 40% yield.[13]



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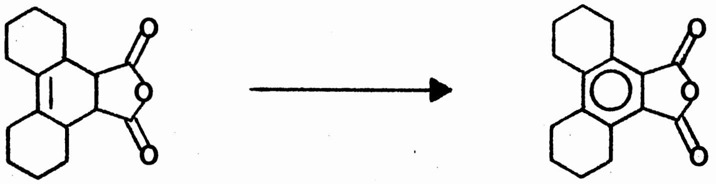
Weidlich showed that bromination of 1 and 19 in acetic acidchloroform solution resulted in aromatization through elimination of HBr to form the anhydrides 21 and 20. Aromatization occurs only in the ring bearing the anhydride moiety. Other reagents have also been used to dehydrogenate adducts from diene synthesis, the most notable being sulfur[14] and selenium.[15] These, however, lead to full aromatization in most systems.



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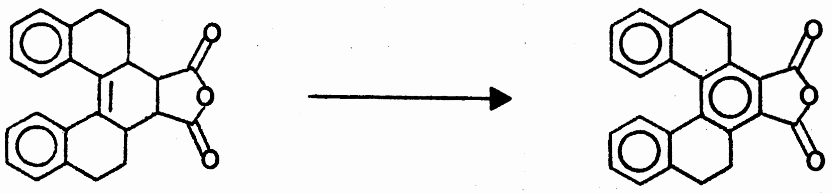
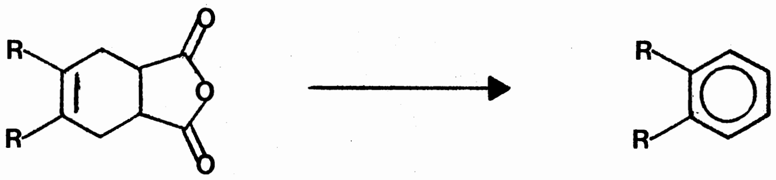


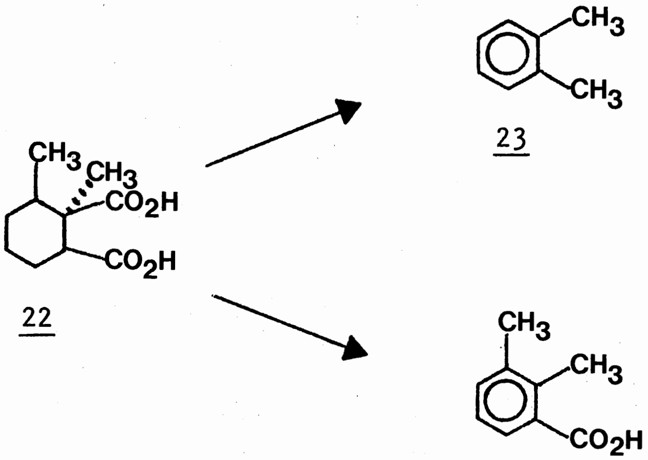
1 21

The synthesis of aromatic hydrocarbons using maleic anhydride adducts can be accomplished through reactions involving simultaneous decarboxylation and dehydrogenation as shown below.



This reaction can be effected by the use of 10% Pd/C or 5% Pd/C in the presence of copper chromite. Phosphorous pentoxide also is effective through simultaneous elimination of carbon monoxide and water.[16] This reaction sequence is synthetically useful considering that some adducts require an aromatization step prior to decarboxylation with Cu powder[17] or Cu_2O and quinoline.[18] Aromatization of diene adducts by decarboxylation followed by dehydrogenation is of only limited application since cyclization and dealkylation can accompany dehydrogenation of hydroaromatic hydrocarbons.

Dicarboxylic acids and anhydrides attached to cyclic structures have been reported to dehydrogenate and decarboxylate in a single step using Pd/C. Hexahydro-2,3-dimethylphthalic acid (22), obtained by the hydrogenation of the adduct of trans-1,3-pentadiene with methylmaleic anhydride, was converted to *O*-xylene (23) by heating with 10% Pd/C in a sealed tube at 320 °C for 24 h. Heating under the same conditions for 16 h produced only partial decarboxylation with the formation of 2,3-dimethylbenzoic acid (24).[19]



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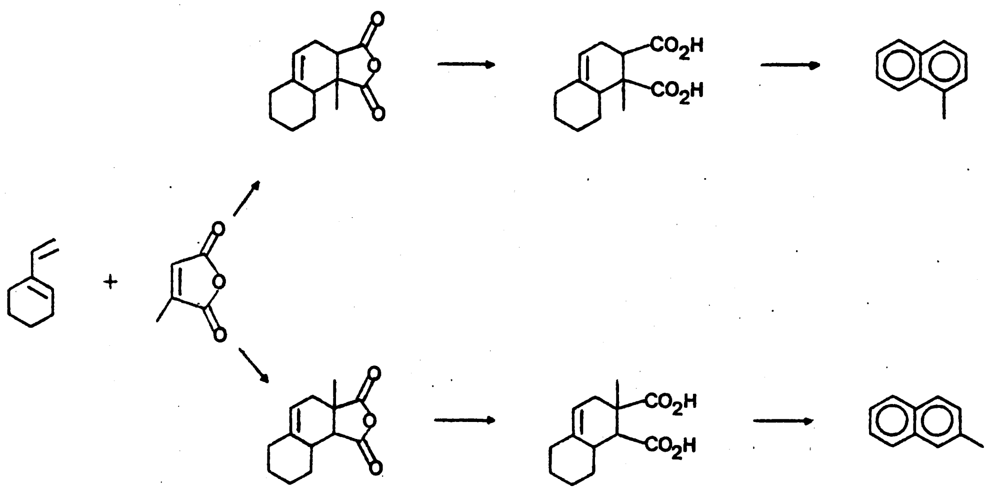
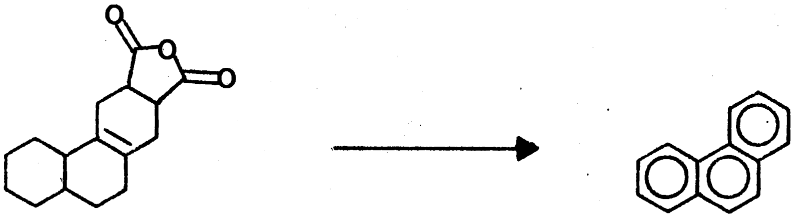
23

24

In a study of the identity of condensation products formed from 1-vinylcyclohexene and methylmaleic anhydride, Nazarov[20] converted the isomeric acids, obtained by hydrolysis of the Diels-Alder adducts, into methylnaphthalenes as shown below. Aromatization was accomplished by heating benzene solutions of the acids in the presence of 10% Pd/C in an autoclave at 360-370 °C for 18 h.



In 1959, Bailey[21] synthesized phenanthrene 26 in 67% yield by heating adduct 25 in the presence of 10% palladium on carbon and a copper chromium oxide catalyst at 275 °C for 3.5 h.



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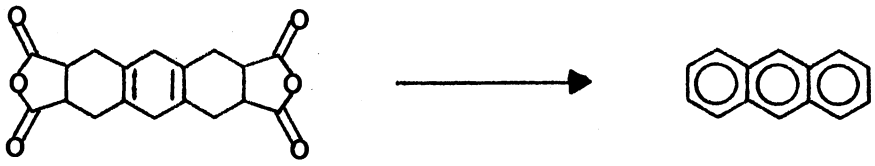
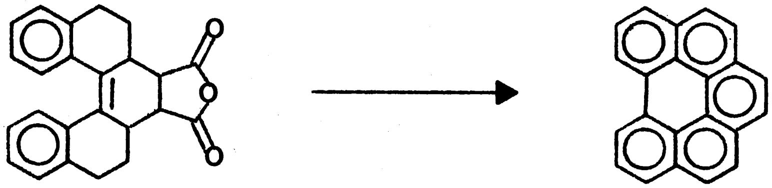
Bailey later published a synthesis of anthracene 28 which involved heating 27 at 270 °C for 3 h with a mixture of 5% palladium on carbon and copper-chromite.[22]



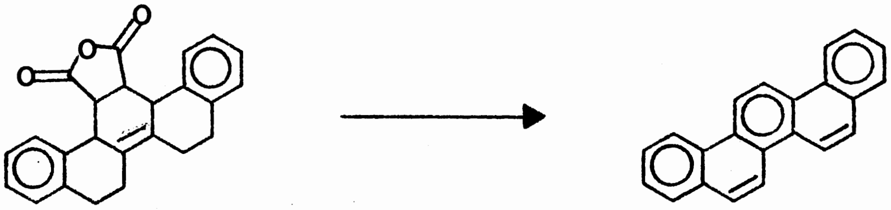
27 28

Polycyclic systems containing aromatic rings and the anhydride functional group have been shown to decarboxylate with Pd/C. A 94% yield of benzoperylene 2 was obtained by heating a mixture of anhydride 1 and 10% Pd/C at 260-280 °C for 8 h.[5] The hydrocarbon product was isolated from side products by Soxhlet extraction using basic alumina with toluene as the eluting solvent.



1 2

The synthesis of picene 4 and benzo[c]chrysene 6 was also accomplished by heating adducts 3 and 5 in the presence of 10% Pd/C for 8 h at 260-280 °C under a nitrogen atmosphere. Studies comparing the effects of the use of methylnaphthalene as a solvent and experiments using neat adduct in the decarboxylation of these systems showed best results were obtained when a solvent was omitted.[5]



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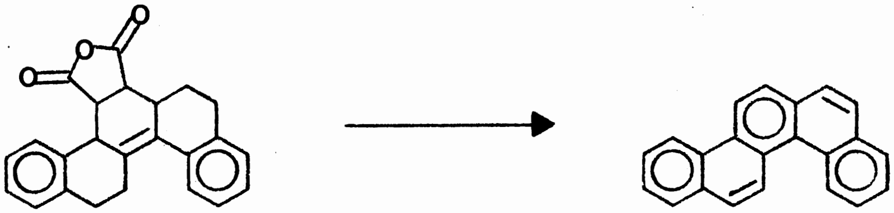

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CHAPTER III

RESULTS AND DISCUSSION

In the synthesis of Diels-Alder adducts for this study, several were made by the direct addition of maleic anhydride to a suitable diene obtained commercially or synthesized by previous researchers in this lab. Other anhydrides required three and four step synthesis before decarboxylation experiments were done.

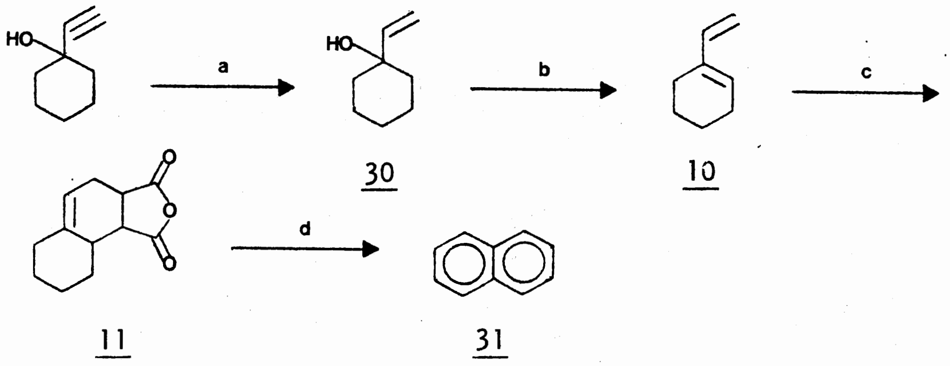
The preparation of 1,2,3,5,6,7,8,8a-octahydronaphthalene-1,2-dicarboxylic anhydride (11) using commercial ethynylcyclohexanol (29) is shown in Scheme I. Semihydrogenation of the ethynyl group was accomplished by hydrogenation with 5% Pd/$BaSO_4$ in the presence of potassium hydroxide as described by Tedeschi and Clark.[23] Using this procedure, a 78% yield of vinylcyclohexanol (30) was obtained after purification by vacuum distillation.

Numerous reagents have been used for dehydration of alcohols, the most notable being 10% H_2SO_4,[24] acetic anhydride,[11] and DMSO.[25] Anhydrous copper II sulfate has been shown to be effective as a dehydrating agent for the conversion of alcohols to olefins.[26] Vinylcyclohexanol was dehydrated by heating in the presence of anhydrous $CuSO_4$ for 1.5 h to give an 84% yield of vinyl-1-cyclohexene (10). Isolation of the product involves adding ether to the reaction mixture and then filtering the insoluble $CuSO_4$. This dehydration method has advantages over other techniques in that the workup procedure is simple, dehydration conditions are fairly mild (100-160 °C), and the reaction time is comparatively short (0.5-1.5 h). The olefin product is not contaminated with byproducts other than the evolved water. The conditions required for smooth dehydration varies with the alcohol structure, the order of reactivity being tertiary ≃ benzylic > allylic > secondary.

Attempts to react vinyl-1-cyclohexene with maleic anhydride in refluxing toluene for 3 h failed to produce any desired product. However, a 76% yield of 1,2,3,5,6,7,8,8a-octahydronaphthalene-1,2-dicarboxylic anhydride (11) was obtained by stirring 10 and maleic anhydride in toluene at room temperature for 24 h.[10]

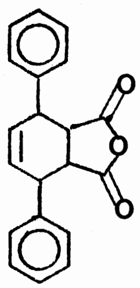
A mixture of 11 and 10% Pd/C was heated under argon at 260-280 °C for 8 h. Decarboxylation and dehydrogenation occurred, giving a 90% yield of naphthalene (31). This reaction plus others presented by Bailey[21,22] demonstrates Pd/C can be effective in decarboxylating and dehydrogenating systems which do not contain an aromatic ring.

Scheme I

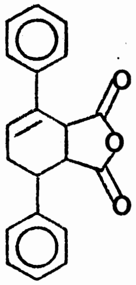


[a] H_2, 5% Pd/$BaSO_4$,KOH. [b] $CuSO_4$. [c] Maleic anhydride, room temperature. [d] 10% Pd/C, Δ.

3,6-Diphenyl-1,2,3,6-tetrahydrophthalic anhydride (9a) was synthesized by heating a mixture of 1,4-diphenylbutadiene (8) and maleic anhydride for 2 h at 130-160 °C under an argon atmosphere. An 80% yield of a mixture of anhydrides 9a and 9b was obtained after recrystallization from toluene.



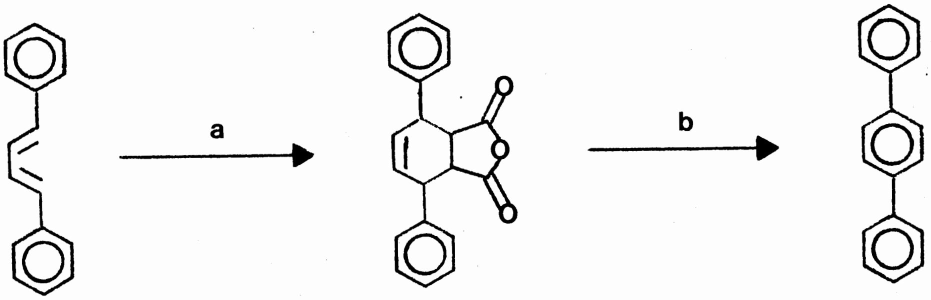
9a



9b

Anhydride 9a, heated in the presence of 10% Pd/C for 8 h at 260-280 °C, was found to decarboxylate giving terphenyl (32) in 97% yield (Scheme II). Isolation of the hydrocarbon product was done by placing

Scheme II



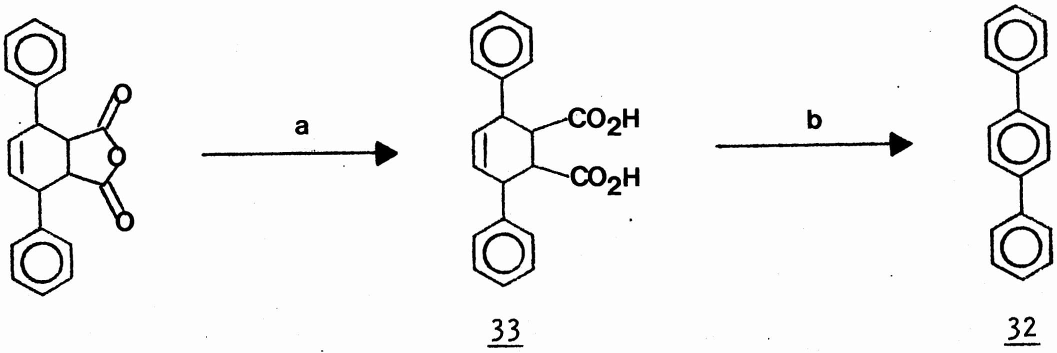
8 9a 32

a Maleic anhydride, Δ. b 10% Pd/C, Δ.

the reaction mixture, including catalyst, on a column of basic alumina contained in a Soxhlet apparatus and using toluene to elute the product.

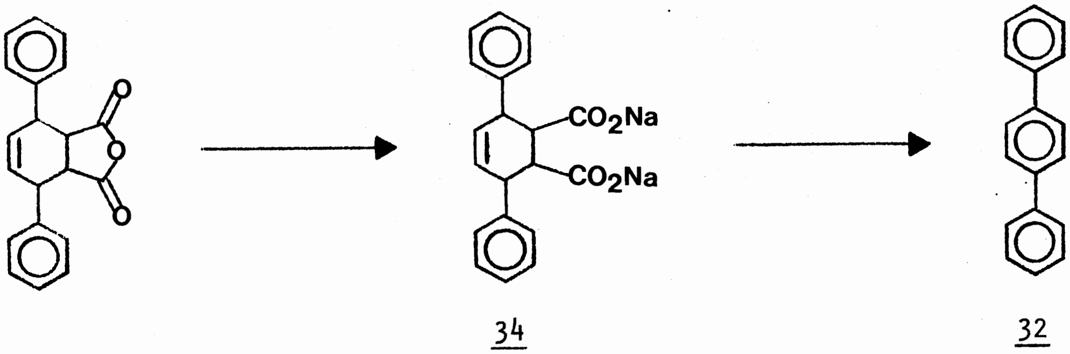
The diacid 33 was obtained by dissolving 9a in warm 10% NaOH and then acidifying with dilute HCL. Decarboxylation of 33 gave a 48% yield of 32 as shown in Scheme III.

Scheme III



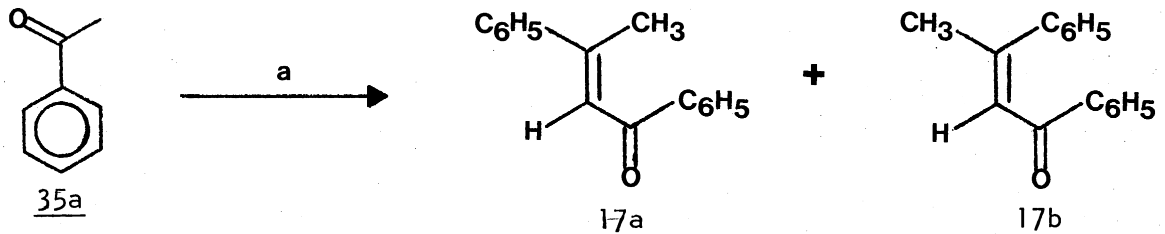
^{a} 10% NaOH, HCL. ^{b} 10% Pd/C, Δ.

Terphenyl has been synthesized by preparation of disodium-3,6-diphenyl hexahydrophthalate (34) which was subsequently distilled with zinc dust and caustic soda as shown below.[9]



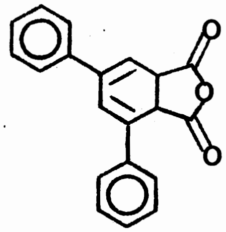
As an intermediate to the synthesis of 3,5-diphenyl-1,2-dihydrophthalic anhydride (18), 1,3-diphenyl-2-buten-1-one (17a) was prepared using a procedure introduced by Mazza and Guarna.[27] This involves the self-condensation of acetophenone (35a) in the presence of titanium (IV) chloride and triethylamine (Scheme IV). Best results are obtained by slowly adding a solution of ketone 35a and triethylamine in dichloromethane to the previously prepared titanium enolate of acetophenone 35b suspended in a cold mixture of hexane and dichloromethane. The reaction time required for optimum yield is approximately 20 h. After purification by vacuum distillation, a 69% yield of ketone 17a was isolated. E- and Z-isomers, 17a and 17b, can be separated by GLC which shows the E-isomers to be the major constituent.[28] The ^1H NMR spectrum in deuterochloroform showed two multiplets at 8.0 and 7.45 ppm corresponding to ten aromatic hydrogen atoms, a singlet at 7.12 ppm corresponding to the vinyl hydrogen, and a doublet centered at 2.58 ppm corresponding to the methyl hydrogen atoms. These data indicate the E-isomer is the predominate product, since a chemical shift value of 2.58 ppm for the methyl hydrogen was observed. Methyl hydrogens bound to the ethylenic system are more deshielded in the E-isomer by the carbonyl groups than in the Z-isomers. Differences of 0.2-0.3 ppm are observed in their ^1H NMR chemical shift.[27]

Scheme IV



$^a TiCl_4$, $(C_2H_5)_3N$.

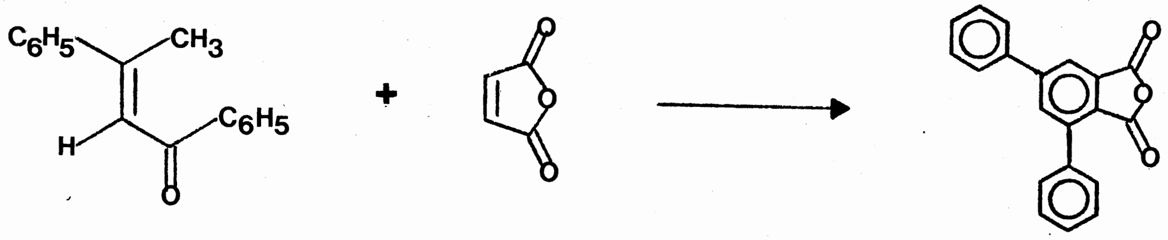
Dypnone (17a) was refluxed with maleic anhydride, isopropenyl acetate, and a catalytic amount of p-toluenesulfonic acid for 17 h under argon. The desired product from the reaction was 3,5-diphenyl-1,2-dihydrophthalic anhydride (18).[13]



18

Attempts to produce 18 by this procedure gave the aromatic anhydride 36 in 18% yield, instead of 18, as shown in Scheme V. This structure was confirmed by ^{1}H NMR which shows the two aromatic hydrogens of the center ring appearing at 8.18 and 8.22 ppm. A multiplet centered at 7.7 ppm corresponds to the other ten aromatic hydrogens. No vinyl protons were present in the spectrum. ^{13}C NMR and mass spectral data also supported this structure.

Scheme V

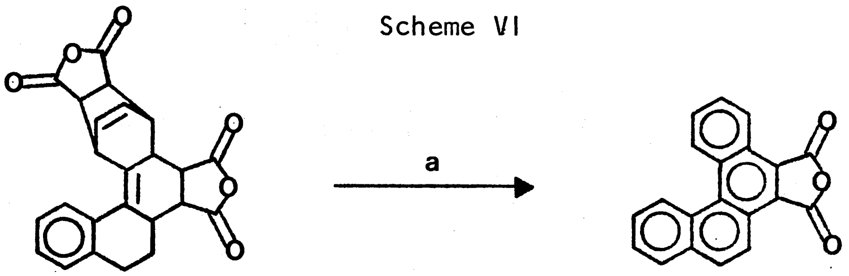


36

Decarboxylation of aromatic dicarboxylic acids, salts, and anhydrides may be accomplished by methods other than heating with Pd/C. Dry distillation with zinc dust in the presence of calcium oxide,[29] heating with copper powder in the presence of sodium carbonate and calcium oxide,[17] heating with calcium hydroxide,[30a,b] dry distillation with soda lime,[31] and boiling in quinoline with copper[18] have all proven effective in decarboxylation of various aromatic systems giving a hydrocarbon product. For Pd/C to be effective in decarboxylation, the molecule must have aliphatic hydrogens that can be readily removed from the system during the reaction. Dehydrogenation accompanies decarboxylation using this catalyst.

Studies determining the effects of heating the dianhydride 16 with 10% Pd/C showed dehydrogenation and monodecarboxylation occurred (Scheme VI). The anhydride 37 was isolated from the reaction in 81% yield. Conditions included refluxing a mixture of the dianhydride and catalyst in α-methylnaphthalene for 5 h. Szmuszkovicz reports this same conversion can be accomplished by heating the dianhydride 16 with an excess of sulfur.[12] Anhydride 37 is a useful intermediate for the synthesis of 3,4-benzophenanthrene and various substituted benzophenanthrenes since the remaining anhydride group can be removed in high yield using barium hydroxide and copper bronze.[12]

Scheme VI



16

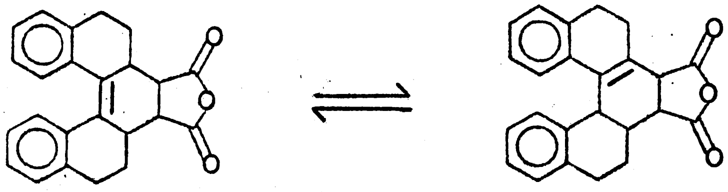
37

[a] 10% Pd/C, Δ.

The synthesis of 1,2,2a,3,4,4a,5,6-octahydrodibenzophenanthrene-3,4-dicarboxylic acid anhydride (1) and 1,2,5,6-tetrahydrodibenzophenanthrene-3,4-dicarboxylic acid anhydride (21) are shown in Scheme VII. The coupling of α-tetralone was done on a large scale giving a 95% yield of diol 38 using a method introduced by Altman and Ginsberg.[32] This reaction involves the use of aluminum metal which donates electrons to α-tetralone forming an intermediate radical anion prior to the coupling process.

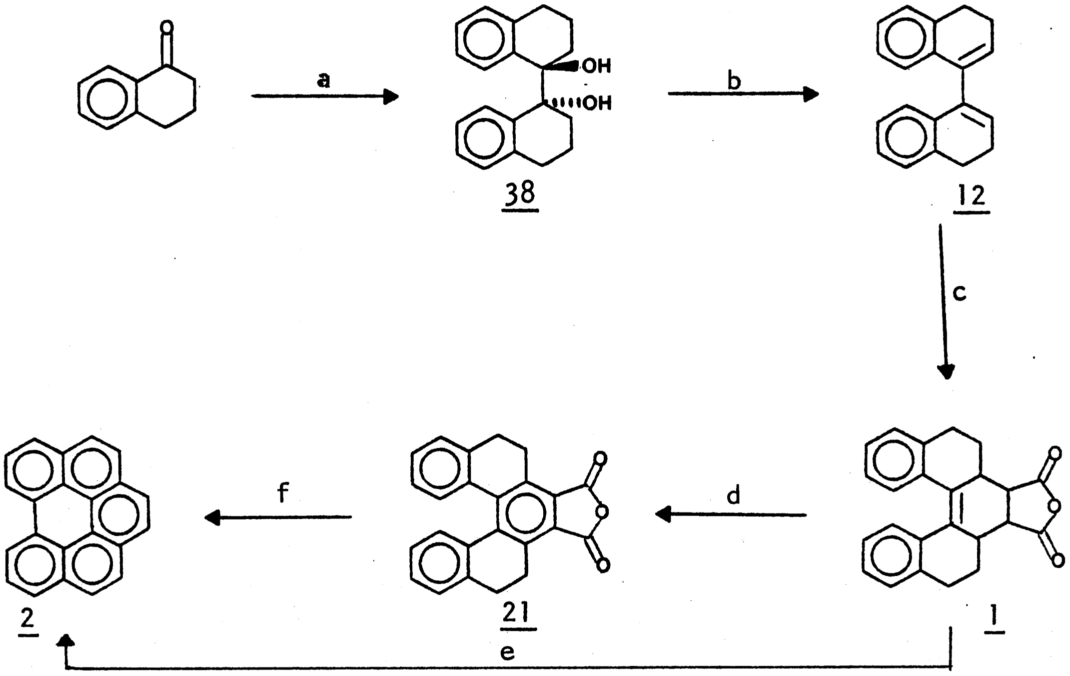
Dehydration of 38 was accomplished during 5 h using a refluxing solution of acetic acid and acetic anhydride. The diene 12 was easily isolated since it precipitates upon cooling the reaction mixture. Purification was done by eluting the crude diene through basic alumina with isooctane.

The Diels-Alder adduct 1 was produced in 81% yield by heating a mixture of diene 12 and maleic anhydride at 140 °C for 8 h. ^{1}H and ^{13}C NMR show the existence of isomers in the reaction product.[5]



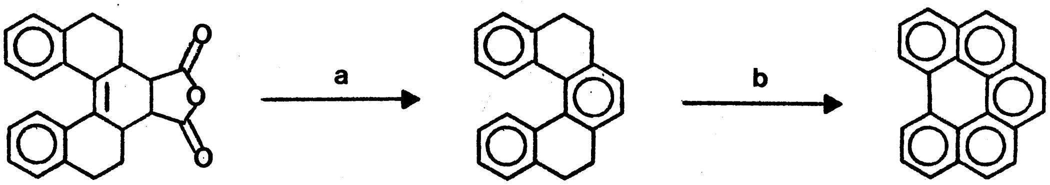
Using a procedure developed by Weidlich,[11] anhydride 1 was selectively aromatized in the ring which bears the anhydride group giving 21 in 70% yield. This reaction was done at room temperature by slowly adding a bromine-acetic acid solution to the olefin in chloroform and then stirring for 4 h.

SCHEME VII



[a]Al, $HgCl_2$, EtOH, benzene. [b]Acetic acid, acetic anhydride, Δ. [c]Maleic anhydride, Δ. [d]Br_2, CH_3CO_2H, $CHCl_3$. [e]10% Pd/C, Δ. [f]10% Pd/C, Δ.

Heating a mixture of anhydride 1 and 10% Pd/C at 260-280 °C for 8 h under an argon atmosphere gave benzoperylene (2) in 88% yield. The loss of carbon dioxide can be monitored by observing the formation of insoluble $BaCO_3$ resulting from exit gas being bubbled through barium hydroxide solution. This reaction, initially carried out by Holba,[5] provides a marked improvement over the synthesis of benzoperylene published by Altman and Ginsberg.[32] Their sequence required the formation of tetrahydrodibenzophenanthrene (39), produced in 41% yield, as an intermediate to the synthesis of benzoperylene as shown below.



39

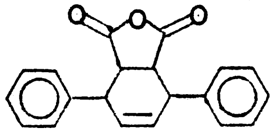
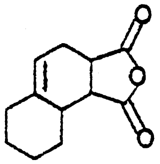
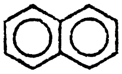
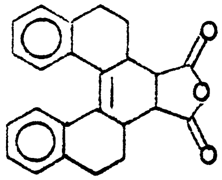
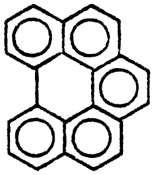
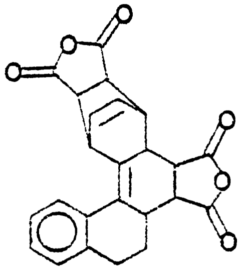
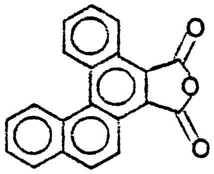
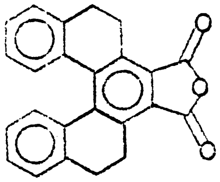
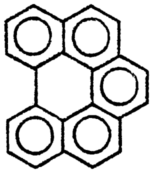
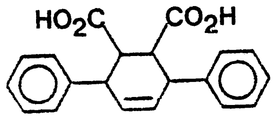
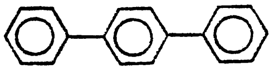
$^{a}PbO_2$, Δ. ^{b}Pd/C, Δ.

1,2,5,6-Tetrahydrodibenzophenanthrene-3,4-dicarboxylic acid anhydride mixed with 10% Pd/C and reacted under the same conditions as stated for anhydride 1 gave benzoperylene as a final product in 79% yield.

Table II summarizes the results obtained from the dehydrogenation and decarboxylation experiments using hot 10% Pd/C.

TABLE II

Pd/C CATALYZED DECARBOXYLATION AND DEHYDROGENATION

Reactant	Product	% Yield
		**97**
		**90**
		**88**
		**81**
		**79**
		**48**

CHAPTER IV

EXPERIMENTAL

1-Vinylcyclohexanol (30). A mixture of 124 g (1.0 mol) of ethynylcyclohexanol (29) and 0.30 g of powdered anhydrous KOH was warmed and stirred for 20 min. The mixture was transferred to a stainless steel hydrogenation vessel containing 150 mL of n-hexane, then 0.15 g of 5% Pd/$BaSO_4$ was added. Hydrogenation was continued for 6 h at 40 psi until approximately 71 psi of hydrogen was taken up. The temperature was kept at 20-25 °C. The hydrogenation mixture, including catalyst, was transferred to a distillation flask and concentrated to remove solvent. The pot residue was then heated at 100-110 °C for 1-2 h. Vacuum distillation (1.5 mm Hg) yielded 98.6 g (78.3%) of 30; ^{1}H NMR ($CDCl_3$) δ 6.15-5.7 (m, 1, vinyl H), 4.8-5.3 (m, 2, vinyl H), 2.55 (s, 1, OH), 2.2-0.8 (m, 10, CH_2); ^{13}C NMR ($CDCl_3$) ppm 145.6, 110.8, 71.1 (C-OH), 71.0, 37.1, 36.4, 34.2, 25.6, 25.2, 21.8, 21.6, 6.9; IR (neat) cm^{-1} 3380 (OH), 3085, 3005, 2930, 2860, 1640, 1450.

1-Vinyl-1-cyclohexene (10) from 30. To a 250-mL, 2-neck flask fitted with a condenser and thermometer, 23.8 g (0.188 mol) of vinylcyclohexanol was added along with 22.7 g (0.14 mol) of anhydrous $CuSO_4$. The mixture was stirred and heated at 110-120 °C for 1.5 h. After cooling to room temperature, ether was added and $CuSO_4$ was filtered. The ether solution was dried ($MgSO_4$) and concentrated to give 17 g (87.7%) of 10; ^{1}H NMR ($CDCl_3$) δ 6.50-6.19 (m, 1, vinyl H), 5.70 (s, 1, vinyl H), 5.20-4.81

(m, 2, vinyl H), 2.28-2.00 (m, 4, aliphatic CH), 1.84-1.40 (m, 4, aliphatic CH); ^{13}C NMR ($CDCl_3$) ppm 140.0, 135.8, 129.4, 109.2, 25.8, 23.7, 22.5, 22.4; IR (neat) cm^{-1} 3090, 3017, 3002, 2925, 2860, 1640, 1608, 1450, 1435, 990, 890, 850, 800.

1,2,3,5,6,7,8,8a-Octahydronaphthalene-1,2-dicarboxylic anhydride (11) from 10. In a 2-neck, 50-mL flask was placed 1.5 g (0.014 mol) of 10, 1.0 g (0.0102 mol) of maleic anhydride, and 9 mL dry toluene. The mixture was initially warmed until the solution became clear, then stirred under argon for 24 h at room temperature. The solvent was removed and 2.6 g of white needles crystallized at 0 °C. These were collected, washed with H_2O, and recrystallized from n-hexane to give 1.6 g (76.2%) of 11; mp 51-53 °C (lit.[10] 52-54 °C); ^{1}H NMR ($CDCl_3$) δ 5.46 (s, 1, vinyl H), 3.52-3.18 (m, 2, aliphatic CH), 2.8-2.0 (m, 11, aliphatic CH); ^{13}C NMR ($CDCl_3$) ppm 173.4, 171.3, 139.4, 115.2, 42.7, 38.1, 34.5, 29.6, 26.4, 25.5, 20.9; IR (KBr) cm^{-1} 3060, 3030, 2940, 2850, 1863, 1792, 1450, 1202, 1026, 970, 920, 898.

Naphthalene (31) from 11. Into a 25-mL, 2-neck flask fitted with thermometer and condenser was added a mixture of anhydride 11 and 0.18 g 10% Pd/C. This mixture was heated at 260-280 °C for 8 h under an argon atmosphere. After cooling, warm toluene was added and mixture was eluted through a column of basic alumina. After 24 h, 0.56 g (90%) of 31 was produced; mp 58-64 °C (lit.[33] 79-80 °C); ^{13}C NMR ($CDCl_3$) ppm 133.2, 127.6, 125.6.

3,6-Diphenyl-1,2,3,6-tetrahydrophthalic anhydride (9a). Into a 1-L, 3-neck flask fitted with thermometer and condenser, was placed 50 g (0.24 mol) of diene 8 and 34 g (0.35 mol) of maleic anhydride. The mixture was magnetically stirred and heated at 130-160 °C under argon for 2 h. The reaction mixture was allowed to cool to room temperature, 200 mL warm toluene were added and the product was filtered. Recrystallization from toluene gave 58.6 g (79.5%) of colorless crystalline 9a; mp 212-215 °C (lit.[31] 212.5-214.5 °C); ^{1}H NMR ($CDCl_3$) δ 7.44-7.22 (m, 10, ArH), 6.52 (s, 2, vinyl H), 3.88-3.62 (m, 2, aliphatic CH), 1.26 (s, 2, aliphatic CH); ^{13}C NMR ($CDCl_3$) ppm 209.3, 137.7, 131.8, 128.5, 128.4, 128.1, 127.5, 47.8, 41.5; IR (KBr) cm^{-1} 3060, 3030, 2865, 1845, 1780, 1500, 1300, 1250, 1035, 945, 750, 695.

Terphenyl (32) from 9a. A mixture of 3 g (0.01 mol) of 9a and 0.54 g of 10% Pd/C was placed in a 50-mL, 2-neck flask and then heated under an argon atmosphere at 260-280 °C for 8 h. After cooling, warm toluene was added and mixture was placed at the head of a column of basic alumina and then eluted with toluene. After 2 h of extracting, 2.2 g (97%) of 32 were isolated; mp 206-209 °C (lit.[9] 208 °C); ^{1}H NMR ($CDCl_3$) δ 7.75-7.23 (m, 14, ArH); ^{13}C NMR ($CDCl_3$) ppm 140.5, 139.9, 128.6, 127.3, 127.1, 126.8; IR (KBr) cm^{-1} 3060, 3040, 1480, 840, 745, 690.

Terphenyl (32) from 33. A mixture of 2 g (0.006 mol) of diacid 33 and 0.36 g of 10% Pd/C was processed as described for 9a to give 0.68 g (47.6%) of 32; mp 208-211 °C (lit.[9] 208 °C); ^{1}H NMR ($CDCl_3$) δ 7.75-7.23 (m, 14, ArH); ^{13}C NMR ($CDCl_3$) ppm 140.5, 139.9, 128.6, 127.3, 127.1, 126.8; IR (KBr) cm^{-1} 3060, 3040, 1480, 840, 745, 690.

1,3-Diphenyl-2-buten-1-one (17a). To a 5-L, 3-neck flask under an argon atmosphere, a solution of 30 g (0.25 mol) acetophenone in anhydrous dichloromethane (500 mL) was added during 1 h by way of an addition funnel to a stirred solution of titanium (IV) chloride (47.3 g, 0.25 mol) in 100 mL n-hexane at 0-3 °C. A second portion of acetophenone (30 g, 0.25 mol) in anhydrous triethylamine (50.6 g, 0.01 mol) and anhydrous dichloromethane (500 mL) was added dropwise during 1 h with the temperature being kept at 0 °C. The mixture was allowed to reach room temperature and stirred for 18 h in the dark. Cold water (300 mL) was then added and the dichloromethane layer was separated and washed with water (3X 200 mL). The aqueous washings were extracted with 100 mL of dichloromethane and the combined organic layers were dried ($MgSO_4$) and concentrated. Vacuum distillation gave 38.26 g (68.9%) of 17a; bp 155-160 °C/ 0.5 mm Hg (lit.[27] 145-150 °C/1.5 torr); ^1H NMR ($CDCl_3$) δ 7.9-8.05 (m, 5, ArH), 7.60-7.25 (m, 5, ArH), 7.12 (s, 1, vinyl H), 2.58 (d, 3, methyl); ^{13}C NMR ($CDCl_3$) ppm 191.2, 154.6, 142.4, 139.1, 132.2, 128.9, 128.5, 128.3, 128.2, 128.0, 126.2, 121.8; IR (neat) cm^{-1} 3060, 3030, 2920, 1660, 1600, 1575, 1450, 1212, 750, 690.

3,5-Diphenylphthalic anhydride (36) from 17a. A solution of 30 g (0.135 mol) 17a and 32.26 g (0.33 mol) maleic anhydride in 26.2 mL of isopropenyl acetate containing 6.62 mg p-toluenesulfonic acid was heated at reflux for 17 h under an argon atmosphere. After cooling to room temperature, 200 mL of ethylacetate were added to dissolve material. n-Hexane was added until a precipitate began to form, then the mixture was cooled to 0 °C. A tarry material was obtained upon filtration which after further recrystallization from n-hexane-ethylacetate gave 7.36 g (18%) of 36; mp 158-167 °C (lit.[34] 176.4-177 °C); ^1H NMR (acetone-d_6) δ 8.0-7.45 (m, 10, ArH); 8.22 (s, 1, ArH), 8.18 (s, 1, ArH); ^{13}C NMR (acetone-d_6) ppm 205.9 (C = O), 136.2, 130.3, 130.1, 130.0, 129.9, 129.8, 129.7, 129.0, 128.4; IR (KBr) cm^{-1} 3060, 1850, 1780, 1620, 1445, 1360, 1230, 910, 735, 700.

Anhydride 37 from 16. Into a 50-mL, 2-neck flask, 3 g (0.008 mol) of 16 was placed with 0.3 g of 10% Pd/C and 30 mL of 1-methylnaphthalene.

The mixture was refluxed for 5 h at 235 °C. The reaction mixture was allowed to cool and toluene was added to maintain solution. Rotary evaporation was used to remove the toluene and Kogelrohr distillation removed the 1-methylnaphthalene. Trituration with n-hexane afforded 1.79 g (80.6%) of a yellow solid, 37; mp 210-222 °C (lit.[12] 249-251 °C); ^{13}C NMR ($CDCl_3$) ppm 129.3, 128.9, 128.7, 128.2, 127.7; IR (KBr) cm^{-1} 3080, 1840, 1755, 1610, 1495, 1330, 1215, 1190, 905, 790, 750.

dl-1,1'-Dihydroxy-1,1',2,2',3,3',4,4'-octahydro-1,1'-binaphthyl (38). To a 5-L, 3-neck flask equipped with nitrogen atmosphere, magnetic stirrer, and condenser, 292 g (2 mol) of α-tetralone, 2800 mL of dry benzene, 200 mL absolute ethanol, 108 g aluminum foil (cut in small squares), and 8 g of mercuric chloride were added and this mixture was heated at reflux for 24 h. The reaction mixture was cooled to room temperature and the liquid decanted away from remaining aluminum and then poured into 5 L of iced water containing 1 L of aqueous hydrochloric acid (4:1). Concentrated HCL was added until the aluminum salts dissolved. The mixture was then extracted with ether and the organic layer was washed twice with 10% HCL, dilute Na_2CO_3, and then with H_2O. The organic layer was filtered through Dicalite, dried ($MgSO_4$), and concentrated to give 280 g (95.8%) of colorless crystalline 38; mp 188-191 °C (lit.[35] 191-192 °C); ^{1}H NMR ($CDCl_3$) 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, $ArCH_2\ \underline{C}H_2\underline{C}H_2$); ^{13}C NMR ($CDCl_3$) ppm 140.2, 138.1, 128.8, 128.6, 126.9, 126.1 (Aromatic C), 58.5 ($\underline{C}$-OH), 36.3, 31.1, 20.0 (aliphatic C); IR (KBr) cm^{-1} 3530 (OH), 1440, 1280, 1070, 975, 900, 735.

3,3',4,4'-Tetrahydro-1,1'-binaphthyl (12). To a dry, 3-neck, 1-L round bottomed flask, 127 g (0.48 mol) of diol 38, 310 mL of acetic anhydride, and 340 mL acetic acid were added. The mixture was heated at reflux for 5 h, cooled to room temperature and kept overnight. A precipitate was filtered from the solvent and this was washed with methanol. The solid was then placed on a column of basic alumina contained in a Soxhlet apparatus and eluted with isooctane to give 72.6 g (64.6%) of 12; mp 138-140 °C (lit.[32] 141 °C); ^1H 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^2c), 28.2, 23.3 (Sp^2c); IR (KBr) cm^{-1} 1440, 1420, 1380, 1020, 940, 910, 830, 760, 730.

1,2,2a,3,4,4a,5,6-Octahydrodibenzo[c,g]phenanthrene-3,4-dicarboxylic acid anhydride (1). Into a 3-L, 2-neck flask, fitted with thermometer and condenser, was placed a mixture of 108.7 g (1.1 mol) of maleic anhydride and 28.47 g (0.11 mol) diene 12. The reaction was heated at 140 °C for 8 h. The crude product was then dissolved in 1300 mL acetic acid and concentrated to 900 mL, cooled, and the solid product was collected by filtration. After drying, the isolated product, 1, weighed 32 g (81.4%), mp 232-252 °C (lit.[32] 252-254 °C); ^1H NMR ($CDCl_3$) δ 6.7-7.3 (m, 8, ArH); 3.5 (q, 2, methane), 1.8-3.1 (m, 10, aliphatic H); ^{13}C NMR ($CDCl_3$) ppm 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.

1,2,5,6-Tetrahydrodibenzo[c,g]phenanthrene-3,4-dicarboxylic acid anhydride (21) from 1. A solution of 46.15 g (0.13 mol) of anhydride 1 and 1.5 L chloroform were magnetically stirred in a 3-L, 3-neck flask at room temperature under an argon atmosphere. A mixture of approximately 40.5 g of bromine and 100 mL glacial acetic acid was added dropwise to the anhydride during 20 min. The reaction mixture was then stirred at room temperature for 4 h. The reaction mixture was concentrated and 1600 mL of benzene were added to dissolve the crystals. Recrystallization using benzene-isohexane gave 31.97 g (70.1%) of a yellow solid 21; mp 277-280 °C (lit.[11] 282 °C); ^{1}H NMR ($CDCl_3$) δ 7.40-6.73 (m, 8, ArH), 3.06-2.65 (m, 8, aliphatic CH); ^{13}C NMR ($CDCl_3$) ppm 172.8 (c=o), 141.0, 139.0, 133.0, 130.8, 129.0, 128.0, 127.8, 126.4, 125.3, 28.0 (aliphatic CH_2), 24.2; IR (KBr) cm^{-1} 3065, 3020, 2950, 1835, 1760, 1595, 1400, 1355, 1225, 900, 753, 742.

Benzo[*ghi*]perylene (2) from 21. An intimate mixture of 3 g of 21 and 0.54 g 10% Pd/C were placed in a 50-mL, 2-neck flask fitted with thermometer and condenser. The reaction mixture was heated at 260-280 °C for 8 h under an argon atmosphere. After cooling, warm toluene was added to the solidified reaction product which was transferred to a Soxhlet apparatus containing basic alumina. After 48 h of extraction with toluene, 1.86 g (79%) of yellow crystals, 2, were isolated; mp 263-268 °C (lit.[32] 273 °C); ^{1}H NMR ($CDCl_3$) δ 8.94-9.04 (two d, 2, bag H), 8.34 (s, 2, ArH), 7.92-8.26 (m, 8, ArH).

Benzo[*ghi*]perylene (2) from 1. The procedure described above was applied to 1 g (0.003 mol) of 1 and 0.18 g 10% Pd/C. After 48 h of extraction, 0.68 g (88%) of 2 was produced; mp 257-267 °C (lit.[32] 273 °C); ^{1}H NMR ($CDCl_3$) δ 8.94-9.04 (two d, 2, bay H), 8.34 (s, 2, ArH), 7.92-8.26 (m, 8, ArH).

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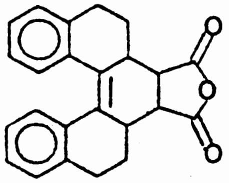
APPENDIX A

GLOSSARY OF STRUCTURES



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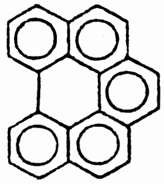

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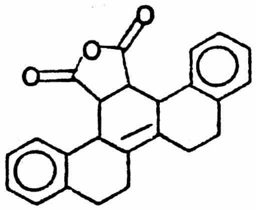

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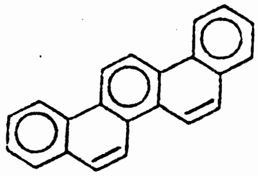

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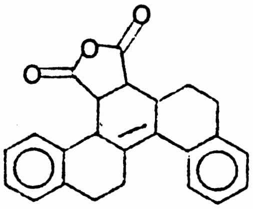

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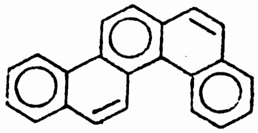

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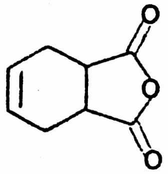

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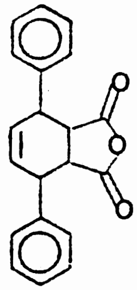

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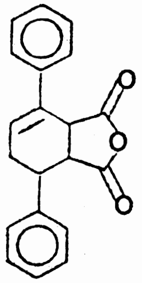

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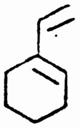

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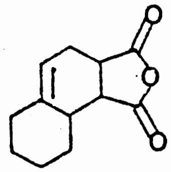

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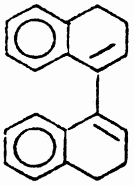

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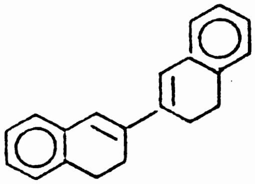

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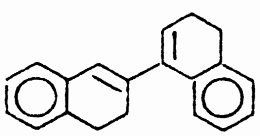

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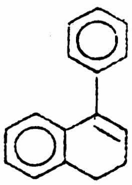

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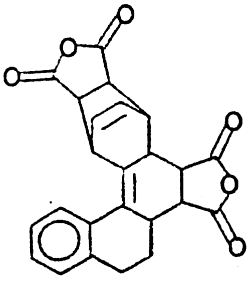

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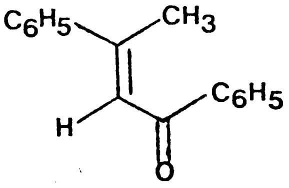

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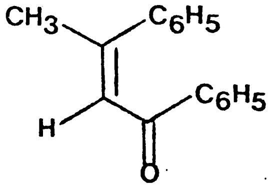

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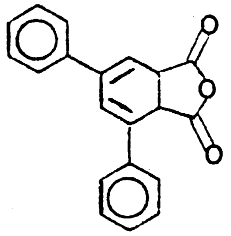

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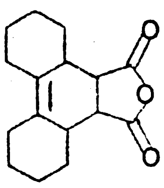

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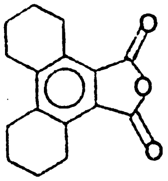

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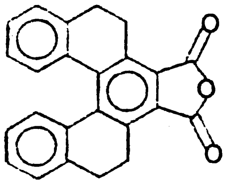

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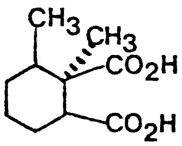

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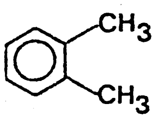

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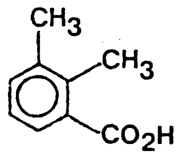

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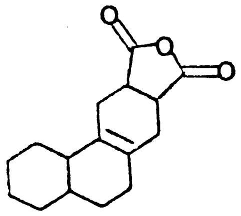

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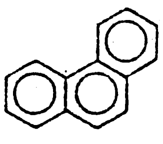

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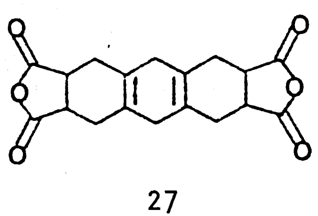

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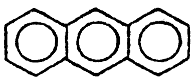

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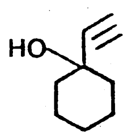

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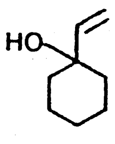

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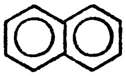

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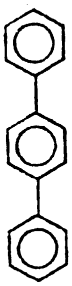

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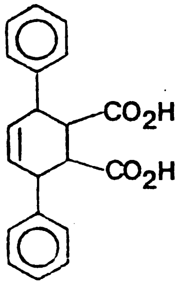

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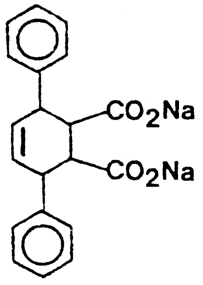

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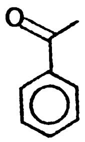

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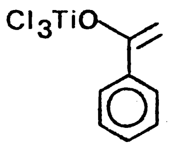

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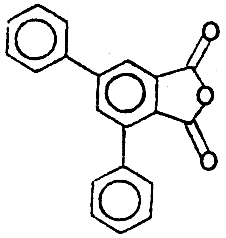

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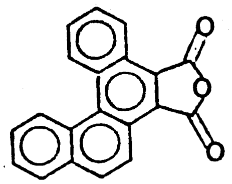

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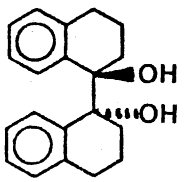

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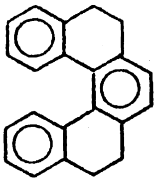

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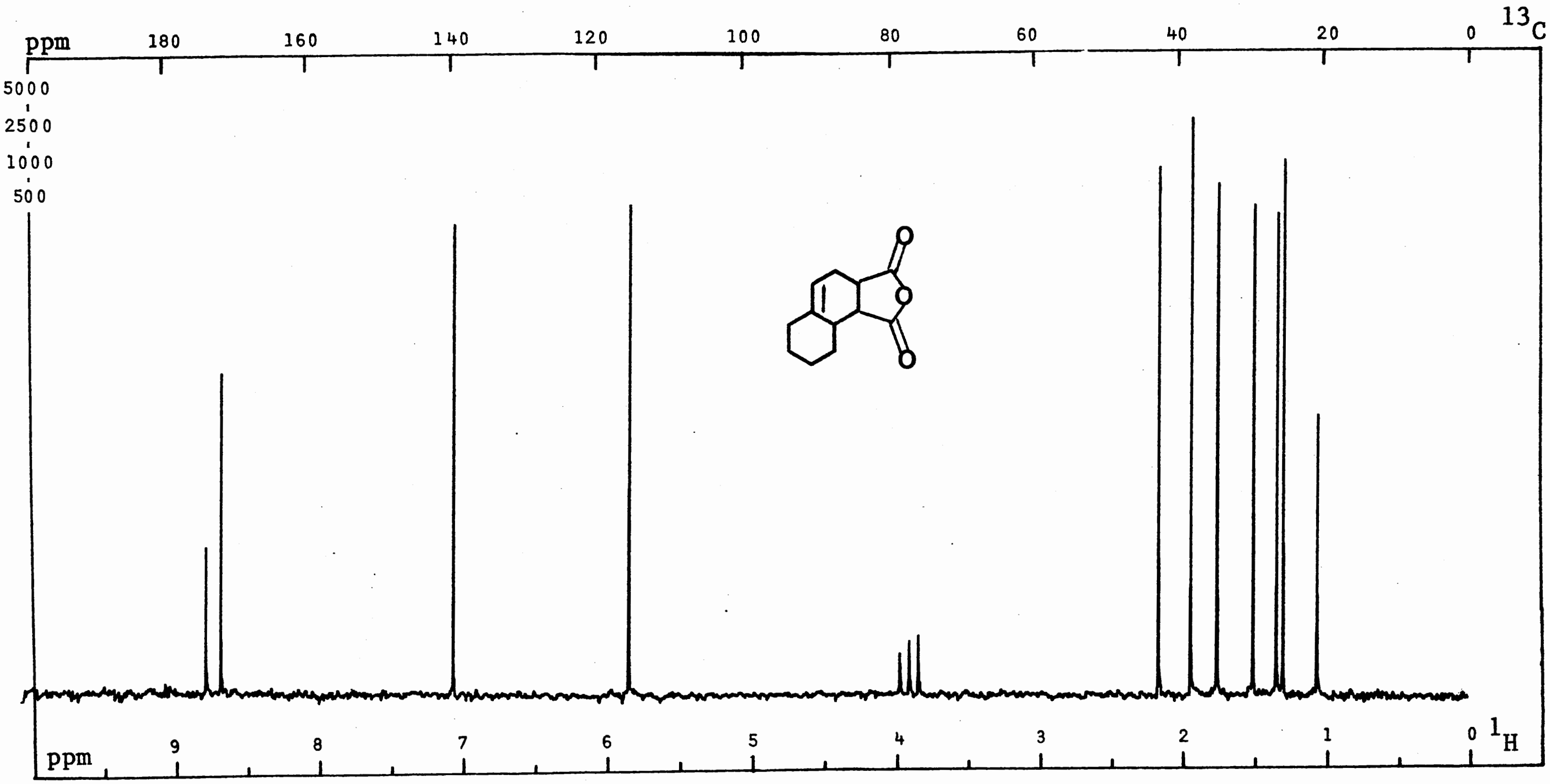
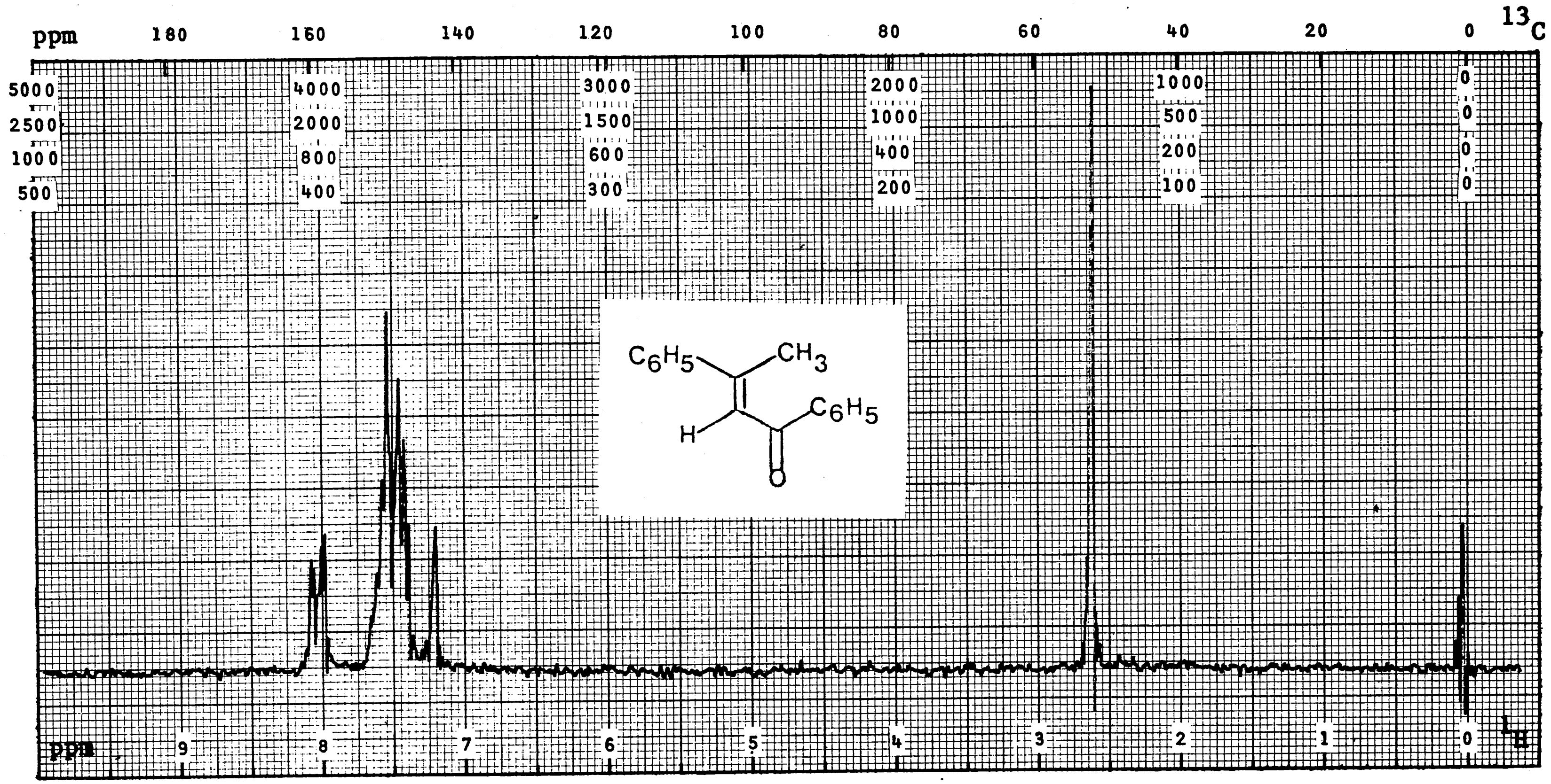
APPENDIX B

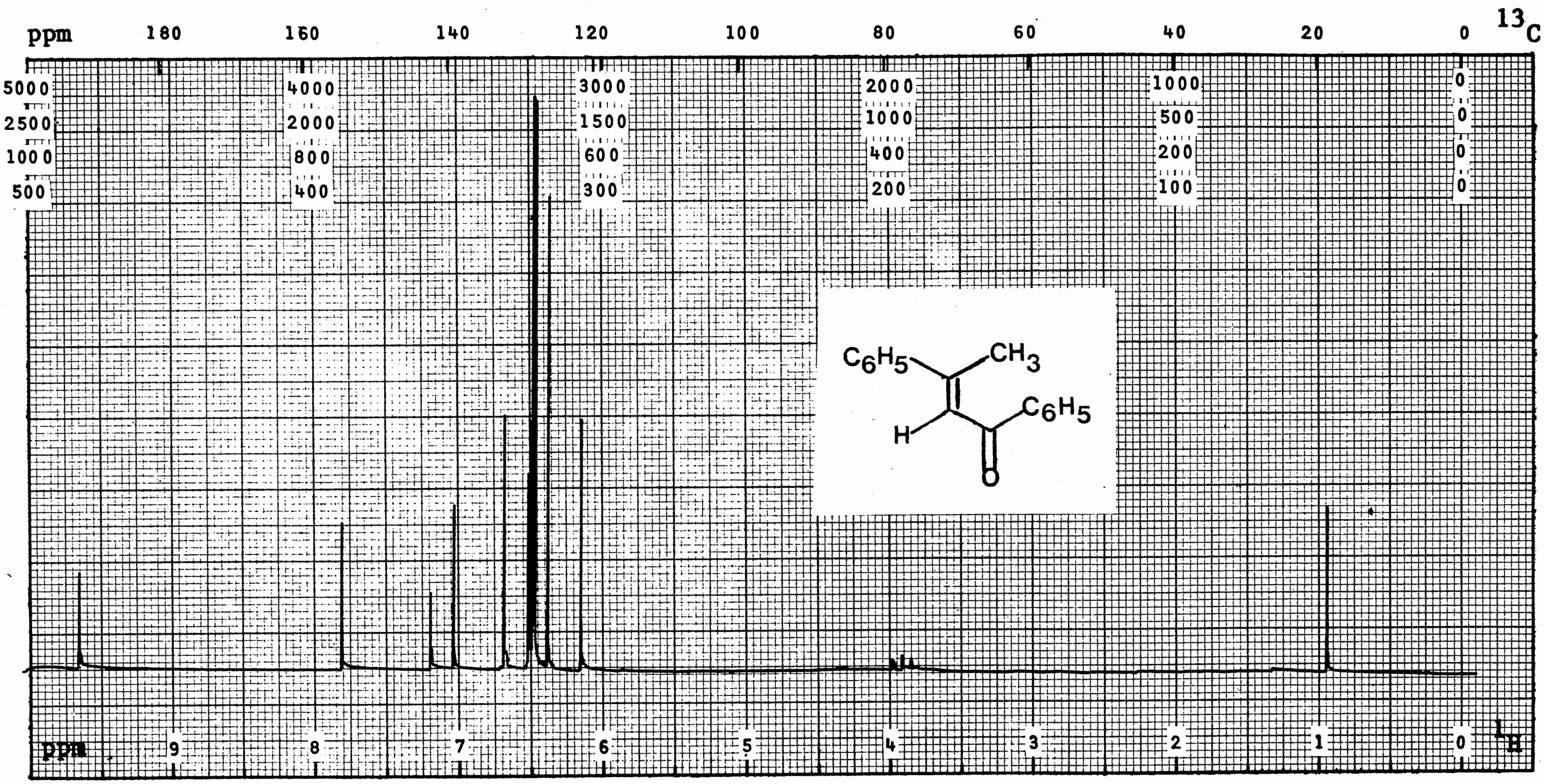
SELECTED SPECTRA



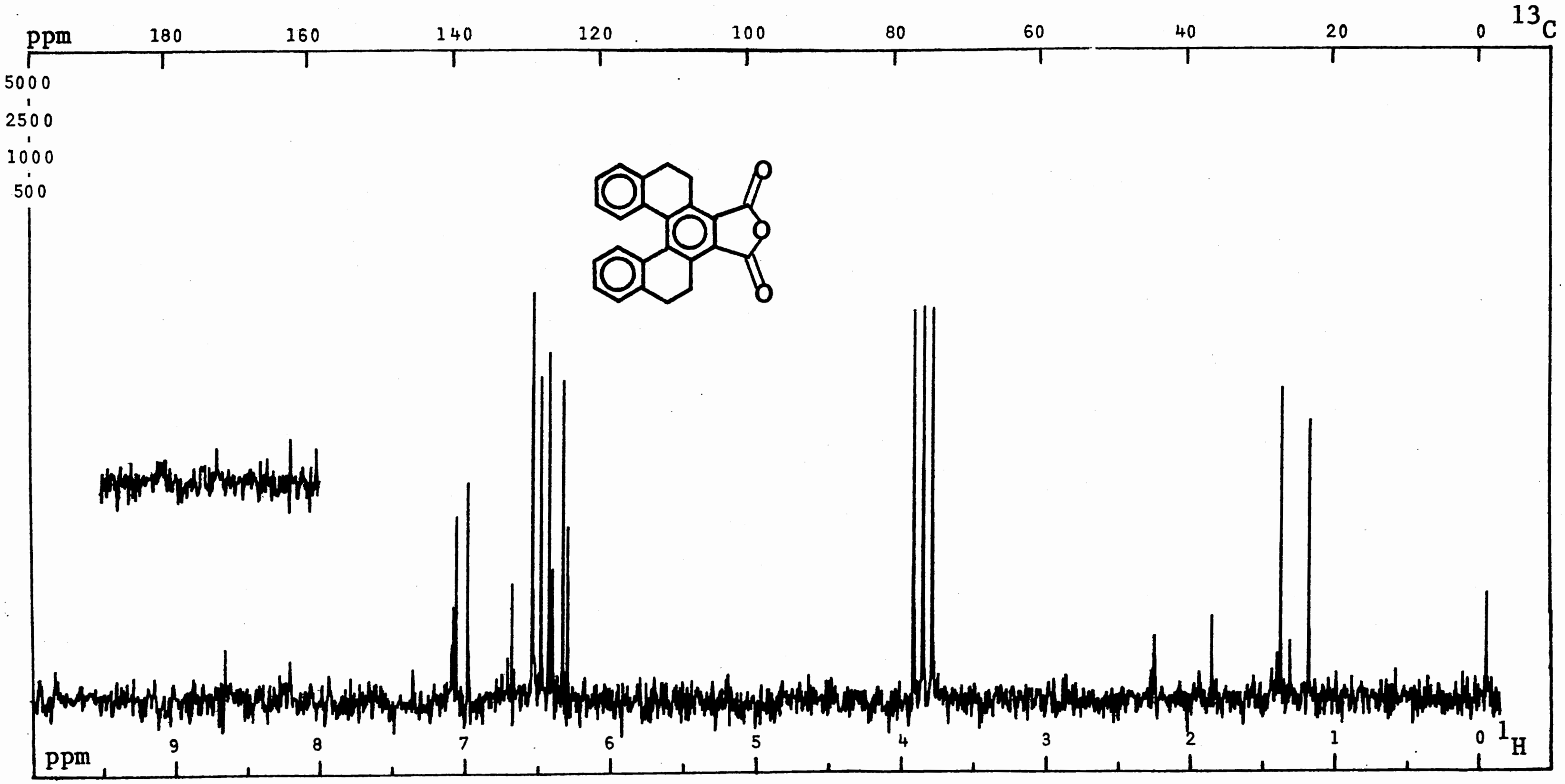
Spectrum 1. ^{13}C NMR of 1,2,3,5,6,7,8,8a-Octahydronaphthalene-1,2-dicarboxylic anhydride (11)



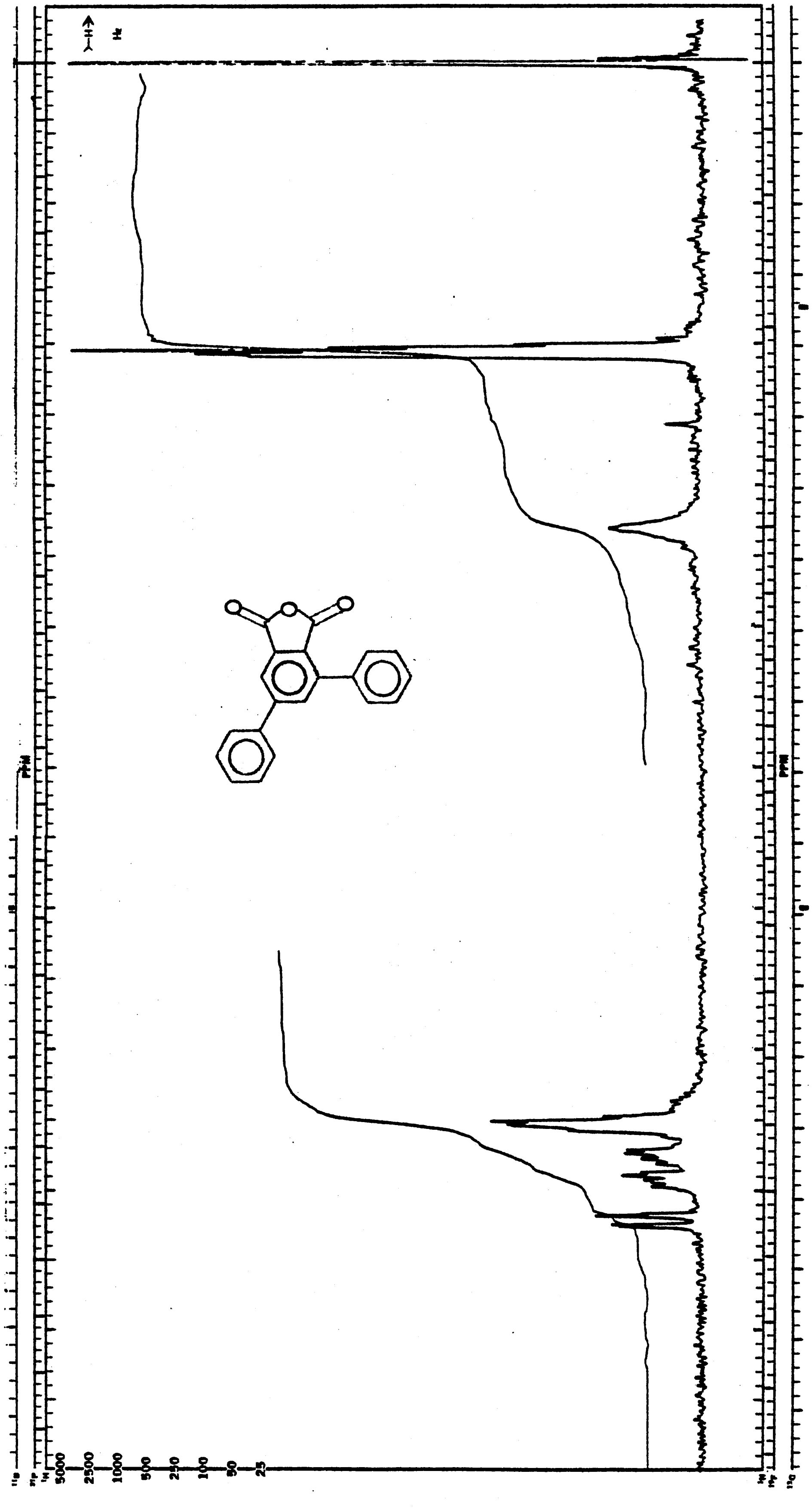
Spectrum 2. ^{1}H NMR of 1,3-Diphenyl-2-buten-1-one (17a)



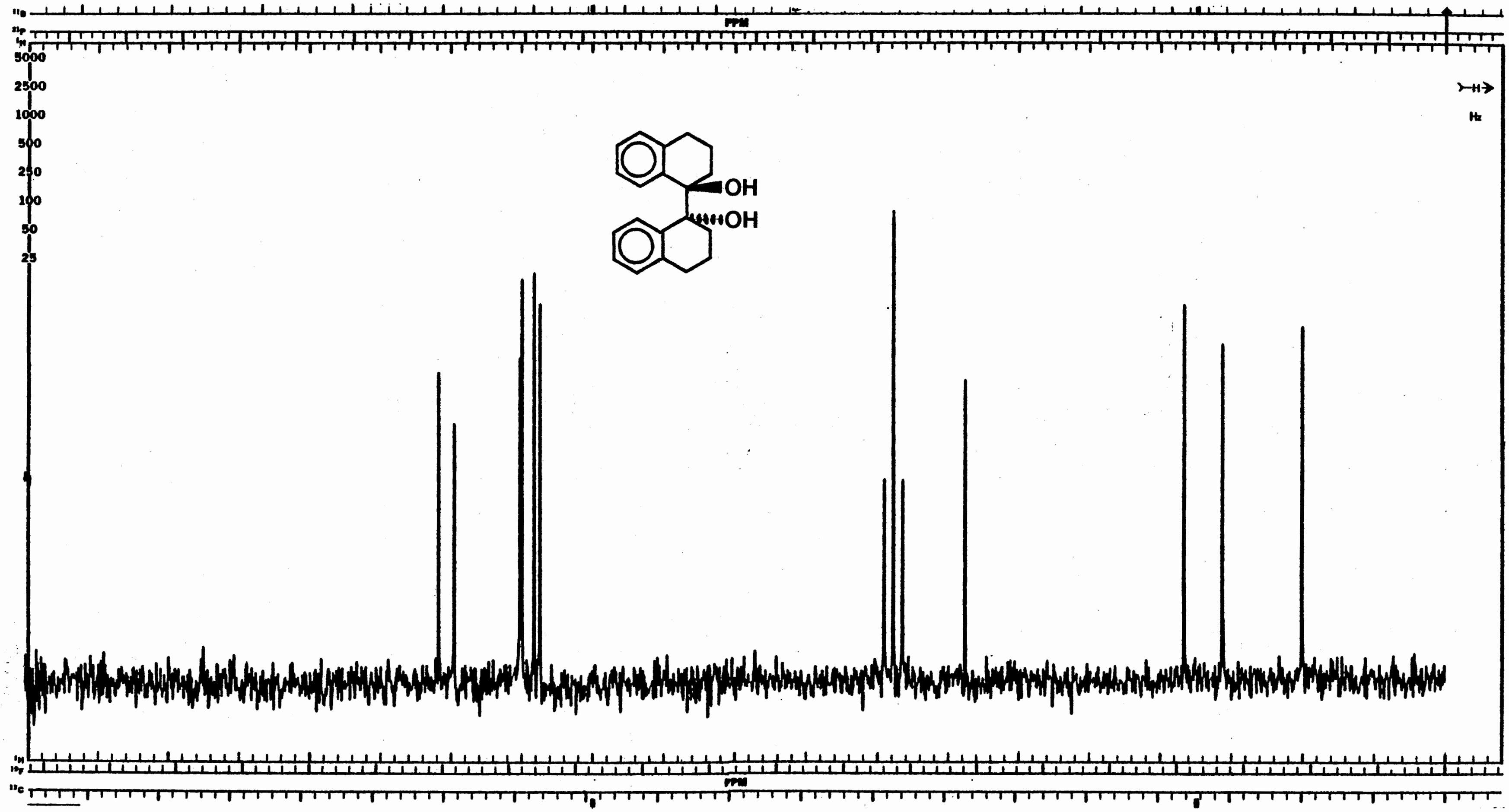
Spectrum 3. ^{13}C NMR of 1,3-Diphenyl-2-buten-1-one (17a)



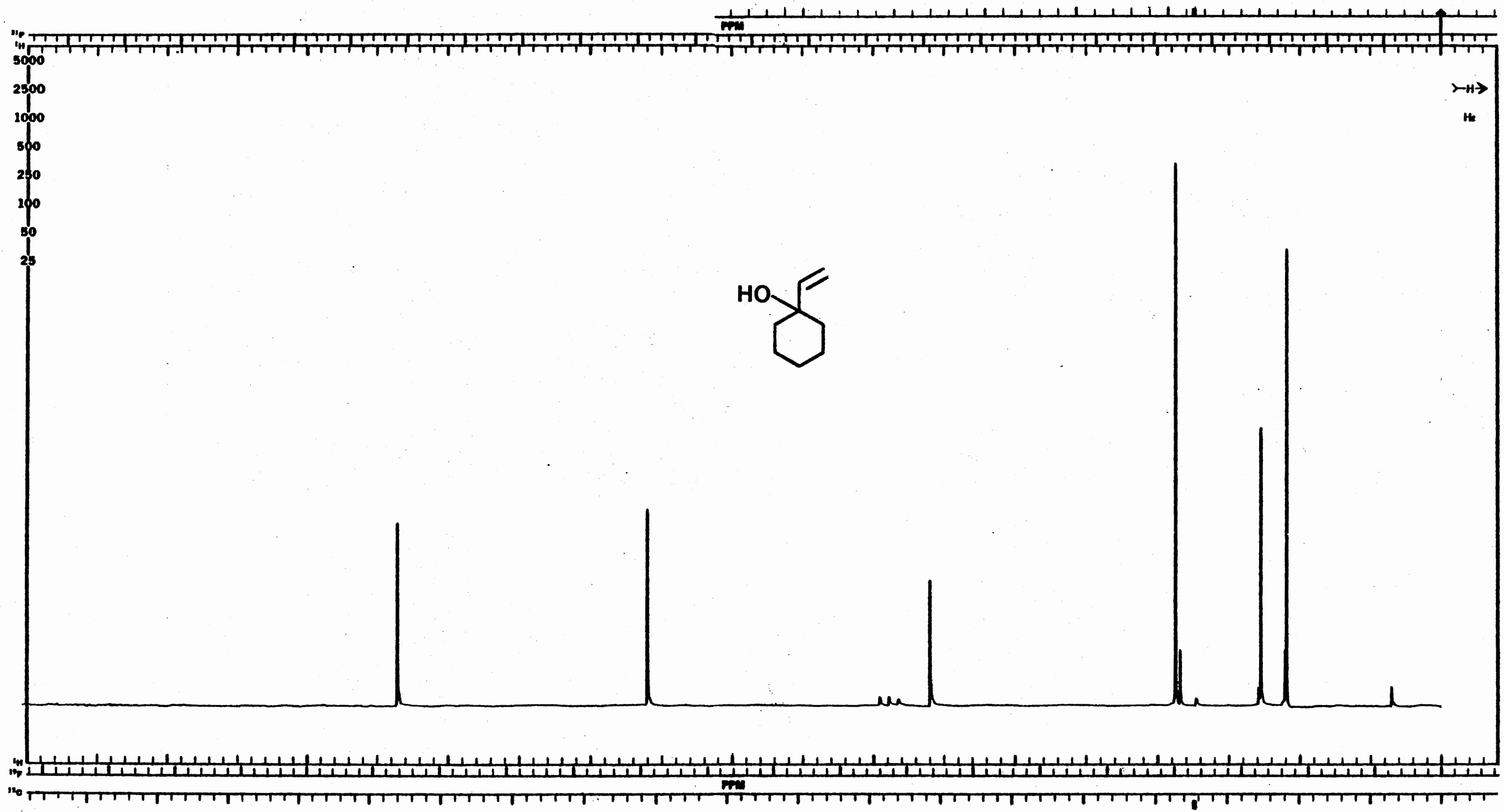
Spectrum 4. ^{13}C NMR of 1,2,5,6-Tetrahydrodibenzo[c,g]phenanthrene-3,4-dicarboxylic acid anhydride (21)



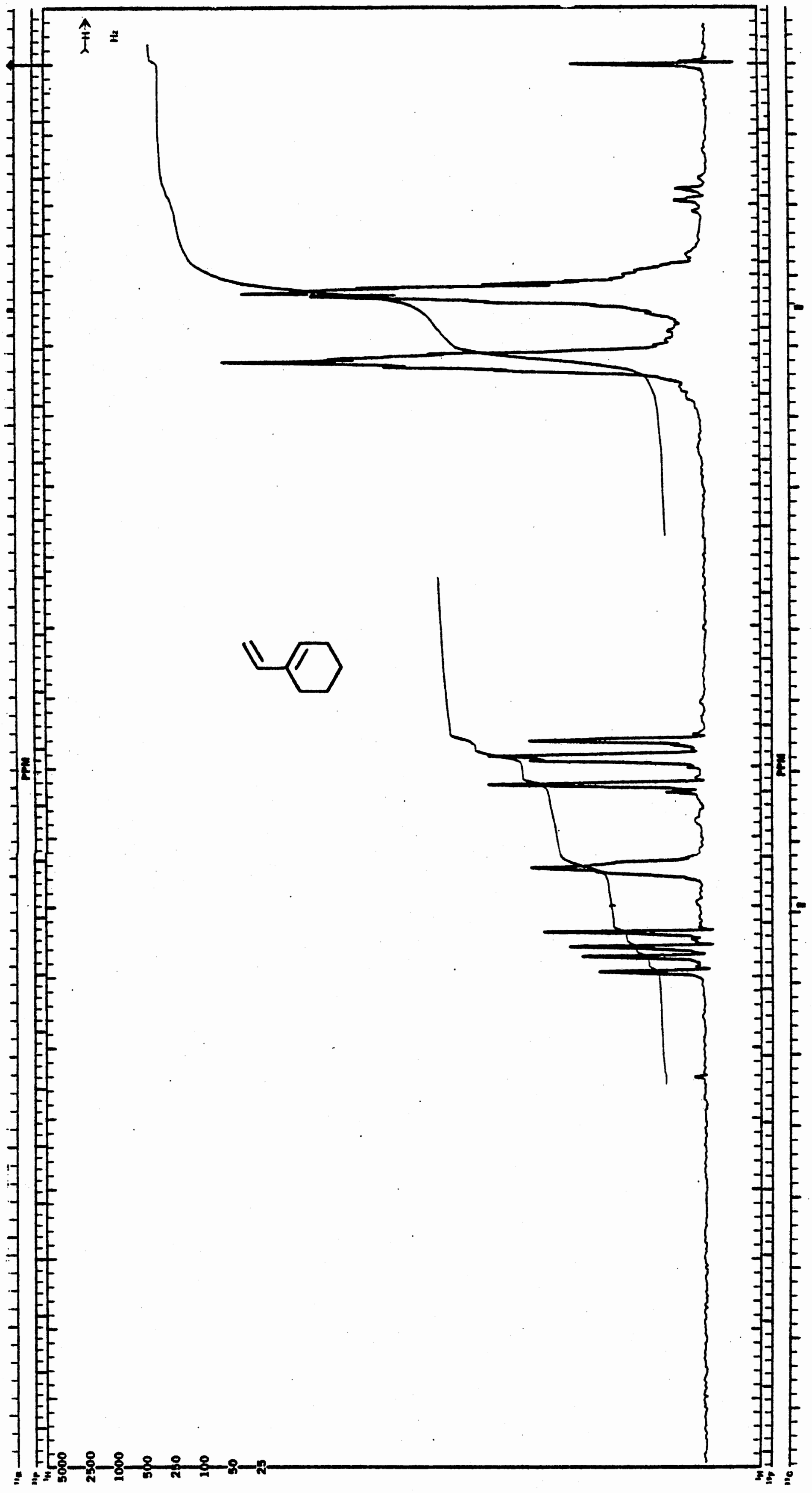
Spectrum 5. ^1H NMR of 3,5-Diphenylphthalic anhydride (<u>36</u>)



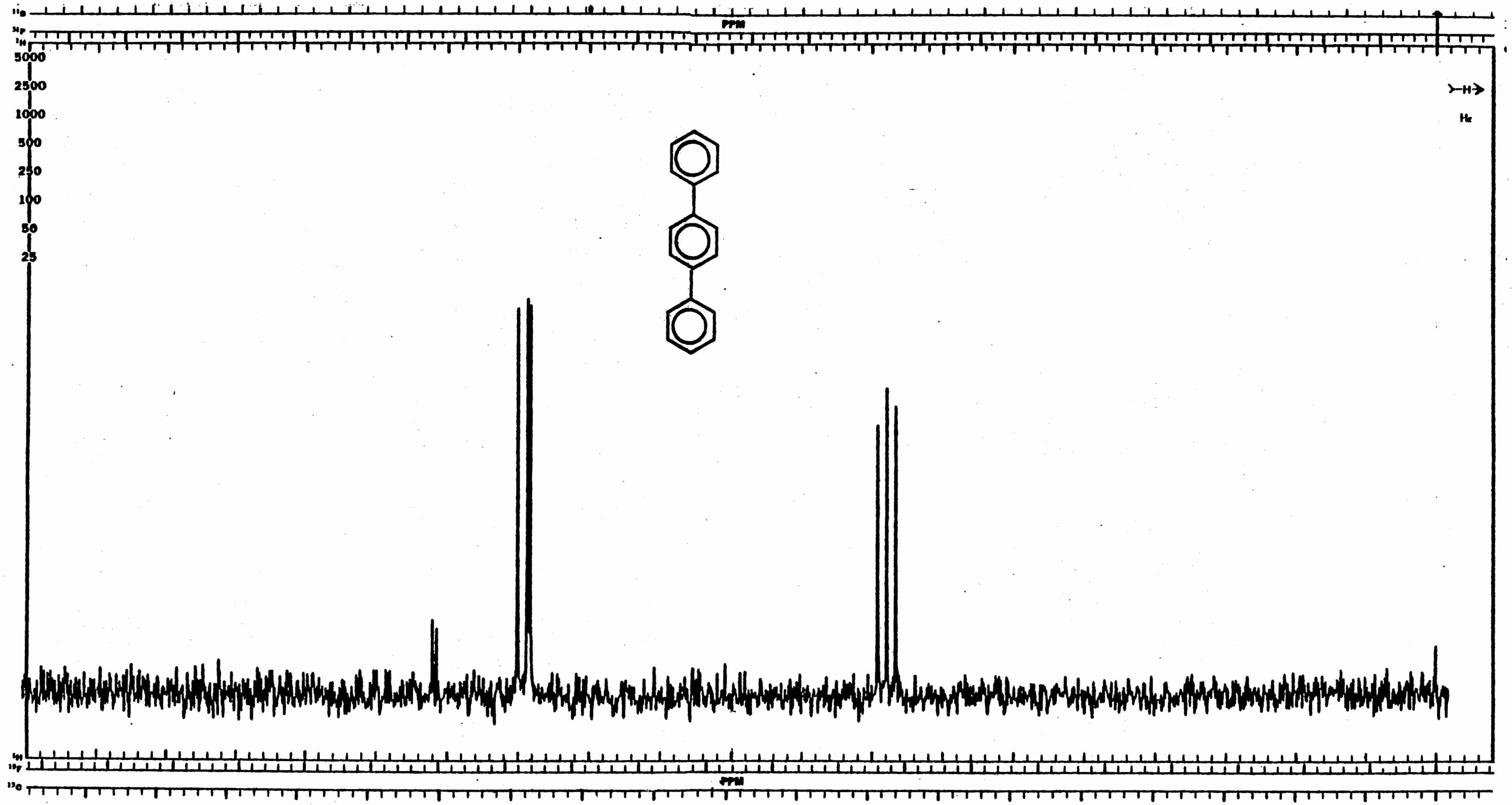
Spectrum 6. ^{13}C NMR of dl-1,1'-Dihydroxy-1,1',2,2',3,3',4,4'-octahydro-1,1',-binaphthyl (<u>38</u>)



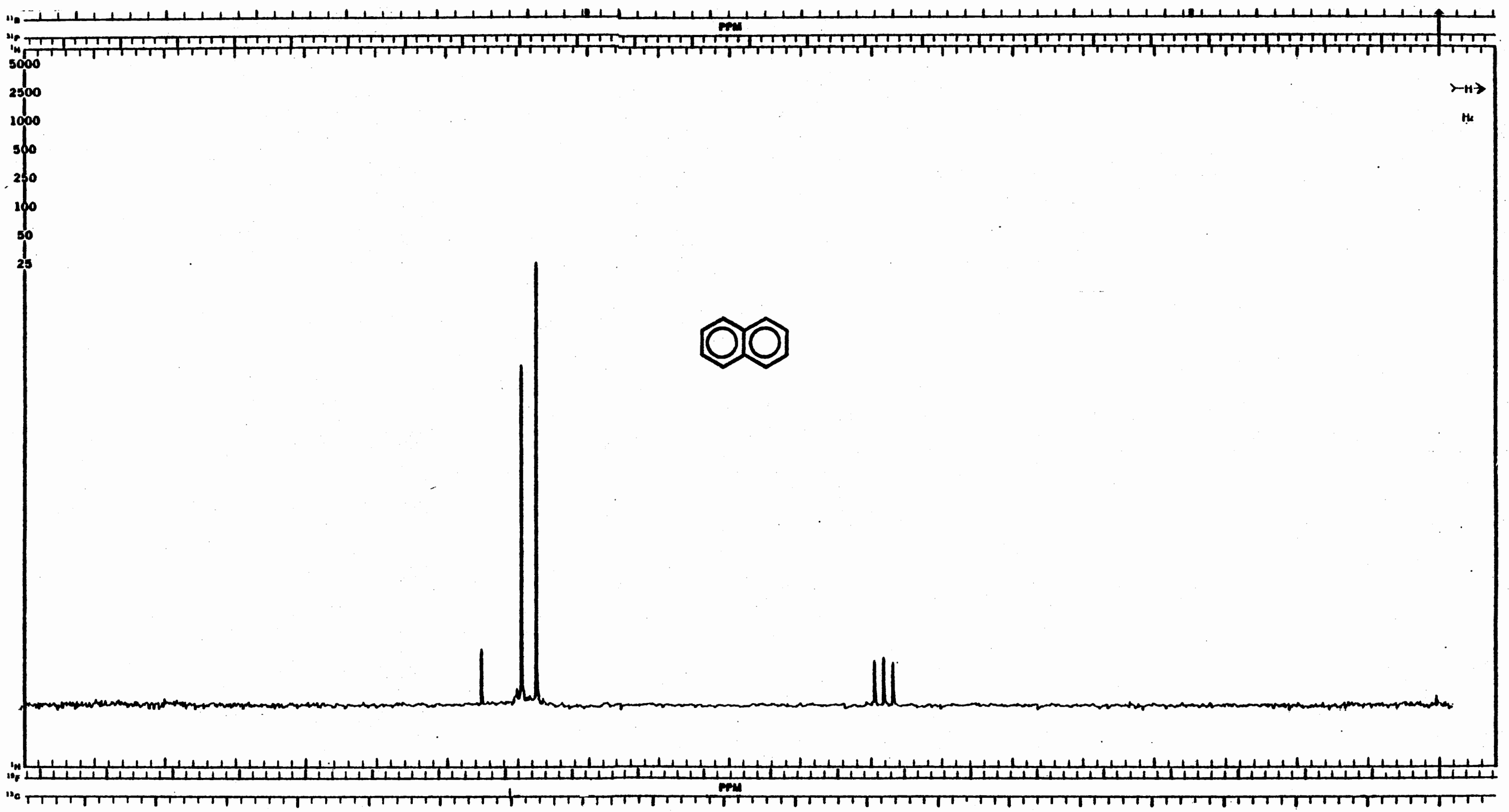
Spectrum 7. ^{13}C NMR of 1-Vinylcyclohexanol (<u>30</u>)



Spectrum 8. ^{1}H NMR of 1-Vinyl-1-cyclohexene (10)



Spectrum 9. ^{13}C NMR of Terphenyl (32)



Spectrum 10. ^{13}C NMR of Naphthalene (<u>31</u>)

VITA

Grant Richard Gamel

Candidate for the Degree of

Master of Science

Thesis: Pd/C CATALYZED BISDECARBOXYLATION OF VICINAL DICARBOXYLIC ACIDS AND ANHYDRIDES

Major Field: Chemistry

Biographical:

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