I. ACID-CATALYZED DIMERIZATION OF 1,2-DIHYDRONAPHTHALENE

II. PHOTODIMERIZATION OF 1,2-DIHYDRONAPHTHALENE AND SUBSEQUENT REDUCTIVE CARBON-CARBON CLEAVAGE DURING METAL-AMMONIA REACTION

By

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PART I

ACID-CATALYZED DIMERIZATION OF 1,2-DIHYDRONAPHTHALENE

CHAPTER I

INTRODUCTION

The widespread occurrence of polynuclear aromatic (PNA) hydrocarbons, many of which have been shown to be carcinogenic, has resulted in extensive investigation of their chemical synthesis and properties.[1a,b] Recent emphasis on coal liquification procedures has intensified the study of PNA compounds.

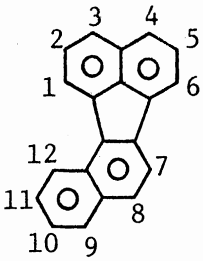
In view of this increased interest, rigorously pure samples of PNA compounds for use as standards in the study of petroleum refining and pollution control as well as obtaining thermodynamic properties has become essential.[2] The importance of purity is perhaps most significant in the study of the carcinogenic and mutagenic properties of PNA hydrocarbons.

This study is directed toward the synthesis of benzo[j]fluoranthene for use as an analytical standard by the Environmental Protection Agency. The synthesis of several partially hydrogenated derivatives of benzo[j]fluoranthene also resulted.

CHAPTER II

HISTORICAL

Benzo[j]fluoranthene (1), together with other PNA hydrocarbons, occurs naturally in the decomposition products from beech and spruce woods.[3] More significantly, this carcinogenic hydrocarbon is found as a product of incomplete combustion of fuel oils, in the operation of gas retorts and auto engines, and from the pyrolytic decomposition of tobacco leaves.[4a,b,c]



1

The pyrolysis of naphthalene on a silica surface at 700°[5] yields in addition to unreacted starting material, 0.04% benzo[j]fluoranthene and 0.04% of its isomer benzo[k]fluoranthene. Small amounts of 1,1'-binaphthyl, 1,2'-binaphthyl, 2,2'-binaphthyl were also detected.[6]

The pyrolysis of n-butylbenzene over the temperature range 300-900° yielded 0.25% benzo[j]fluoranthene. The optimum temperature was found to be 750°. Above this temperature, more complicated hydrocarbons were formed including 1,2-benzopyrene, and 1,12-benzoperylene.[7]

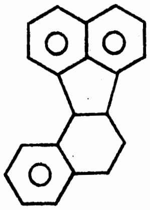
The pyrolysis of tetralin-1-^{14}C at 700° gave slightly greater amounts of benzofluoranthene derivatives: benzo[c]fluoranthene (1.8%), benzo[k]fluoranthene (1.9%), and benzo[j]fluoranthene (1.9%). Small amounts of crysene, naphthalene, and indene were also detected in the pyrolzate.[8]

Similar amounts of benzo[j]- and benzo[k]fluoranthene were obtained from pyrolysis of indene-3-^{14}C, although the yield of chrysene was increased to 2%.[9]

Benzo[j]fluoranthene (1) has been more conveniently synthesized by a variety of routes. For example, Dansi and Ferri[10] obtained a $C_{20}H_{20}$ hydrocarbon, mp 151°, by the action of $AlCl_3$ on tetralin. When this compound was treated with selenium, the dehydrogenation product was found to be a $C_{20}H_{12}$ hydrocarbon melting at 165° which gave a picrate, mp 195°. This identified the final product as benzo[j]fluoranthene (1).

Benzo[j]fluoranthene (1) was also prepared by Nenitzescu and Avram[11] through treatment of acenpahthenone with the Grignard reagent β-bromoethylbenzene. The resulting alcohol was dehydrated and cyclized simultaneously by heating with P_2O_5 at 145° to yield 6b,7,8,12b-tetrahydrobenzo[j]fluoranthene (2), mp 163°. Dehydrogenation with Pd/C gave 1.

An alternate synthesis employs the reaction of 1-tetralone with 1-naphthylmagnesium bromide. Spontaneous dehydration of the alcohol reportedly gave 3,4-dihydro-1,1'-binaphthyl (3), mp 120.5°, which



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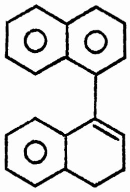
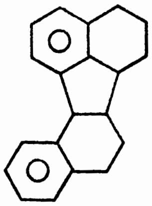


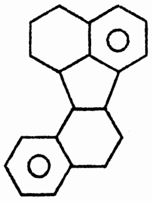
3

was cyclized with P_2O_5 at 120-140° and subsequently dehydrogenated in the presence of Pd/C to 1.

An octahydrobenzo[j]fluoranthene is obtained directly from the dimerization of 1,2-dihydronaphthalene with sulfuric acid.[12a,b] The sulfuric acid treatment yields a new dimer, mp 93°, which is not identical to the dimer, mp 151°, obtained using $AlCl_3$ or P_2O_5. Awareness of this fact lead Nenitzescu and Avram[11] to propose that the lower melting dimer possessed structure 4a and the higher melting dimer structure 34.

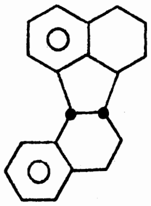


4a

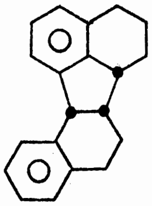


34

It was subsequently shown by Hertzler and Eisenbraun[13] that these two dimers differed in stereochemical positions of the protons in the five-membered ring and not in location of the aromatic ring. ^{1}H NMR analysis of these dimers established that the dimer, mp 93°, and the dimer, mp 153°, have structures 4b and 4c, respectively. Since 4b and 4c were dehydrogenated to benzo[j]fluoranthene, the carbon skeletons are assumed to be identical.

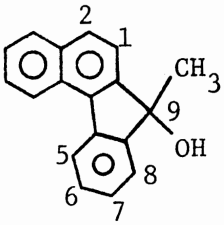


4b



4c

Decarboxylation of the anhydride (6), prepared by the reaction of maleic anhydride with 9-methylbenzo[c]fluoren-9-ol (5), with CaO produces benzo[j]fluoranthene in very low yield.[14]



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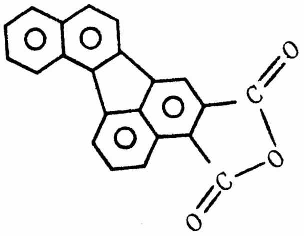
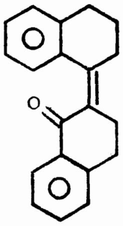


6

Evans and Smith[15] have shown that 1 may be obtained from the action of PPA on 1-tetralone when the reagents are combined and heated at 170° for 3 minutes. The octahydrobenzo[j]fluoranthene isomer 4c is also obtained in equal amounts. Presumably, 1-tetralone reacts via its enol form to produce the α,β-unsaturated ketone 7 which subsequently cyclizes to produce the diene 8. This compound is not isolated, but rather disproportionates to form 1 and 4c. It was subsequently shown by Eisenbraun et al.[16] that the olefinic bond of 7 is not in conjugation with the carbonyl moiety, but is located between carbons 1' and 2' as shown in structure 9.

Synthetic routes yielding benzo[j]fluoranthene described previously do not lend themselves to the preparation of large amounts of material. The most significant disadvantages are the low yields of product, or the formation of an inferior product which is difficult to purify. Consequently, we sought a convenient synthesis of 1 which yields an easily purified product in acceptable yield.



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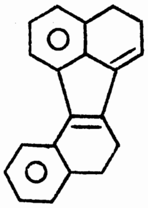

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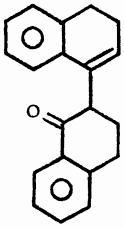
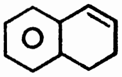


9

The acid-catalyzed dimerization of 1,2-dihydronaphthalene (10a) provides two isomeric dimers 4b and 4c, either of which may be dehydrogenated to 1 in yields in excess of 90%. When H_2SO_4 or P_2O_5 is used as the catalyst, the yield of the dimers (6-20%) is too low to be of synthetic utility. However, when Amberlyst-15,[17] a sulfonic acid resin is used, the yield of the dimers is increased to 60-80%

depending upon the conditions employed. A judicious selection of reaction conditions allows the preparation of dimers 4b or 4c as major products.



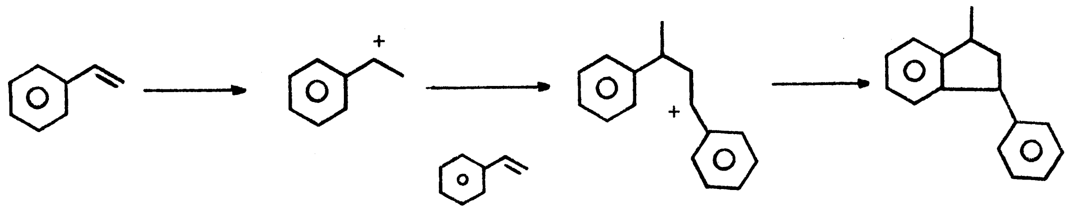
10a

CHAPTER III

DISCUSSION AND RESULTS

The dimerization of 1,2-dihydronaphthalene under the influence of H_2SO_4 or P_2O_5, may be considered to be an acid-catalyzed cyclialkylation process not unlike that of acid-catalyzed cyclialkylation of styrene. Indeed, it was the similarity of 1,2-dihydronaphthalene to styrene which encouraged von Braun and Kirschbaum[12a] to initiate a study of the polymerization properties of 1,2-dihydronaphthalene.

When an olefinic double bond is present in an aromatic side chain, alkylation may result in ring closure. Many condensed ring systems have been synthesized conveniently in this fashion.[18] In the case of styrene, treatment with protic acids has been shown to yield 1-methyl-3-phenylindane.[19] The reaction may be envisioned as a cationic process illustrated as follows:



The cyclodimerization of styrene to 1-methyl-3-phenylindan is accomplished with a variety of acids, including sulfuric, phosphoric, polyphosphoric acid, alumina-silica, perchloric acid, or chlorosulfonic acid.[20a-f]

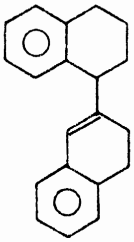
More recently, the dimerization of styrene has been investigated with the aid of a sulfonic acid resin, A-15,[17] as the catalyst using cyclohexane as solvent.[21] The yield of 1-methyl-3-phenylindan was disappointingly low. However it was shown that the ratio of cis and trans isomers of 1-methyl-3-phenylindan was 1:1. The yield was not improved by varying the conditions of the reaction.

In the case of 1-methylstyrene, the yield of the cyclized product was reported to be 80% after only four hours when A-15 in cyclohexane was used.

When 1,2-dihydronaphthalene (10a) was treated with A-15 in refluxing cyclohexane for three hours, a 51% conversion of the monomer to dimer was realized. The dimeric portion was crystallized from methanol to give a 70% yield of a white crystalline product, mp 52-53.5°. A second portion of crystals melting at 48-50° was obtained from the mother liquor. However, these could not be purified by further recrystallization.

A glc analysis at 250° of the crude reaction mixture (6' x ¼", 7% UCW-98 on Chromosorb G, 80/100 mesh) shows three components in the dimer region whose retention times were 13.7, 14.5, and 15.7 min, respectively. Injections of mixtures of known standards allowed identification of the last two hydrocarbons as the isomeric octahydrobenzo[j]fluoranthenes 4b and 4c, respectively. The major component corresponded to the new hydrocarbon, mp 52-53.5°.

An unknown compound, mp 51-52°, was previously reported by Scott and Walker[12b] when a 10% solution of 1,2-dihydronaphthalene in benzene was treated with sulfuric acid. However, the structural assignment of the compound was not given. Although the lack of experimental detail precluded repetition of their experiments, it seems reasonable to suspect that these two compounds are the same. This compound is now identified as 1,2,3,3',4,4'-hexahydro-1,2'-binaphthyl (11a).



11a

The mass spectrum of 11a shows a molecular ion at m/e 260, thus the compound must be a dimer of 10a. Of particular significance is the singlet absorption at 6.2 δ in the ^{1}H NMR which is assigned to the vinylic proton. The proposed structure is unique since it is the only structure permitting such an absorption. The ^{13}C NMR spectrum also supports the structural assignment for 11a since 5 sp^2 carbon resonances are observed in the fully decoupled spectrum which appear as singlets in the off-resonance spectrum.

The 1,2' linkage is confirmed through the facile dehydrogenation of 11a with 10% Pd/C in 1-methylnaphthalene to 1,2'-binaphthyl, mp 79-81°. The melting point was not depressed when the product was mixed with an authentic sample of 1,2'-binaphthyl.

The use of cyclohexane as a reaction solvent is particularly advantageous in the cyclization of 10a to 11a since it simultaneously affords a medium which cannot be alkylated and has a relatively low boiling point.

If 10a is allowed to react with A-15 in refluxing cyclohexane for five hours, the conversion of 1,2-dihydronaphthalene to dimeric product 11a is increased to 80%. However, the product is purified with greater difficulty because of the presence of small amounts of the cyclized dimers 4b and 4c. These impurities were removed by recrystallization from acetone. Recrystallization from the commonly used solvents (95% ethanol, isohexane, ethyl ether or benzene) did not completely remove the impurities.

If the reaction is allowed to proceed for 24 hours in refluxing cyclohexane, the ratio of dimers 11a:4b:4c was shown by glc analysis to be 22:2:1, respectively, in the order of elution from a UCW-98 glc column. These ratios were not changed appreciably after an additional 48 hours of reflux. The slow rate of cyclization may be attributed to the lower boiling point of cyclohexane, rather than polymer formation on the surface of the catalyst. Although catalyst deactivation due to polymer coating has been indicated in the case of styrene, substituted styrenes such as α-methylstyrene do not exhibit this behavior.[21]

Since the formation of the cyclized dimers 4b and 4c provide the necessary carbon skeleton for the preparation of 1, it became of interest to determine the conditions under which these dimers could be formed in good yield. A series of experiments were designed to determine the effect of temperature and catalyst on the cyclodimerization of 10a using refluxing benzene or toluene as solvents.

The sample analyses for the benzene solvent systems were carried out with a Waters M6000 HPLC instrument using a reverse phase C_{18}-μ Bondapak column, and a UV detector (254 nm). The retention times for the dimers 4b, 11a, and 4c were found to be 21.5, 23.5, and 25.5 min, respectively, using 80% acetonitrile/water with a flow rate of 2.0 mL/min. Since there are differences in the absorptivities of the dimers, the peak area is no longer proportional to the concentration of the species, and consequently the use of prepared standards was necessary. The results of the described experiment using benzene as a solvent are presented in Table I.

TABLE I

CYCLIZATION PRODUCTS OF 10a WITH A-15 IN BENZENE

		%*	
Time (h)	11a	4b	4c
24	97	-	-
48	32	68	-
72	20	79	-
96	7	93	trace
120	4	83	12
144	1	81	18

*Percentages of dimeric components only and are corrected for differences in absorbance at 254 nm.

An experiment identical to the one previously described was performed except that toluene was used as solvent. In this case, a new component appeared with retention time (glc) of 5.0 min which was not present in the experiment with benzene. Although this new product could not be obtained in a pure state, the much shorter retention time indicates that it probably is not a dimer of 10a, but may be a product resulting from the reaction of the cation 10b with toluene. A reaction of this type would be expected to lead to products whose retention times would almost certainly be much shorter than those of dimeric products. This component distills before the dimers 11a, 4b, or 4c and is not present in the dimeric fraction when the reaction products are vacuum distilled.

Because the product mixture from the reaction of 10a in toluene was complex, HPLC could not be satisfactorily used for product analysis. The reaction mixtures were therefore analyzed by glc and the results are presented in Table II.

TABLE II

CYCLIZATION PRODUCTS OF 10a WITH A-15 IN TOLUENE

		%		
Time (h)	Unknown	11a	4b	4c
24	19	1	11	69
48	15	0	9	75
72	13	0	3	82
96	13	0	3	82
110	13	0	3	82

The dimer 11a was not isolable from the reaction mixture, and 4b was rapidly equilibrated to 4c. The concentrations remain essentially constant after 72 hours.

Amberlyst XN-1011[17] is a sulfonic acid resin similar to A-15 but having greater thermal stability. The decomposition of A-15 begins at approximately 150° compared to 175-200° for XN-1011. There are also important differences in the porosity and surface areas between the two catalysts. The porosity of A-15 and XN-1011 are 32% and 24%, respectively, and surface areas are 45 meter^2/g and 28 meter^2/g, respectively.[22]

When 1,2-dihydronaphthalene is treated with XN-1011 in benzene, the ratio of dimers 11a, 4b, and 4c is significantly different from that obtained from an identical treatment of 10a with A-15. Most significantly, the dimer 4c is found in only trace amounts when XN-1011 is the catalyst whereas appreciable amounts of 11a remain in the mixture even after 96 h of reflux in benzene (Table III).

TABLE III

CYCLIZATION PRODUCTS OF 10a WITH XN-1011 IN BENZENE

		%	
Time (h)	11a	4b	4c
24	87	12	0
48	80	19	0
72	45	55	trace
96	25	74	trace

When the reaction solvent is changed from benzene to toluene, XN-1011 was shown to produce dimer 11a within 24 h. After 72 h, 11a is no longer detected in the mixture, and the ratio of 4b to 4c was found to be 6.7:1. The percentage of 4b is decreased to 52% after 96 h and 4c is increased to 25% (Table IV). The slower rate of formation of 4c is probably due to the smaller surface area and porosity of XN-1011 as compared to A-15.

TABLE IV

CYCLIZATION PRODUCTS OF 10a WITH XN-1011 IN TOLUENE

		%	
Time (h)	11a	4b	4c
24	95	4	0
48	94	4	trace
72	0	88	12
96	0	75	24

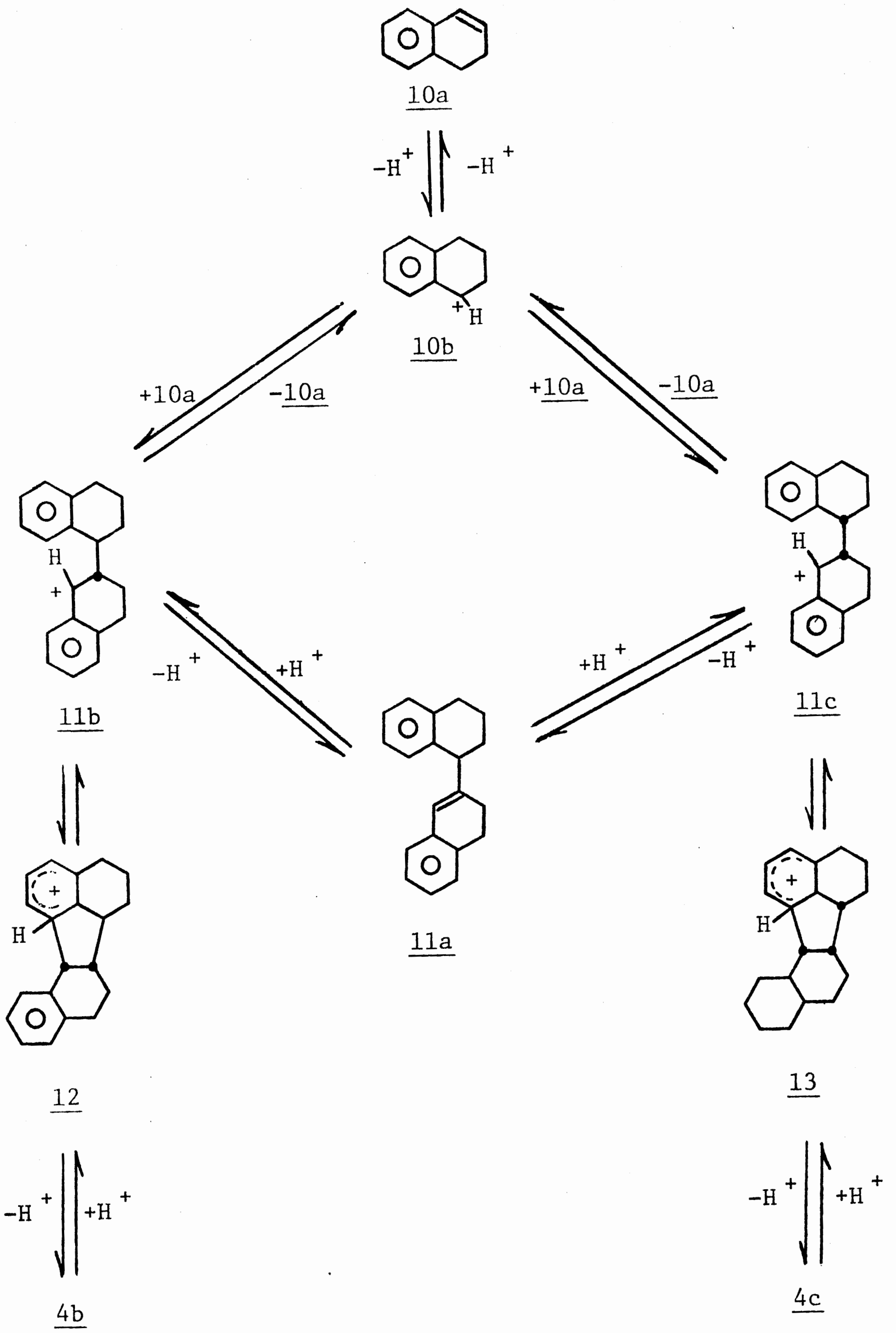
It has been noted previously[13] that the dimer 4b is obtained from catalysis by sulfuric acid whereas the higher melting dimer 4c is former from P_2O_5. A survey of the relevant literature reveals that, in general, the reactions of 1,2-dihydronaphthalene (10a) with P_2O_5 were performed at temperatures of 130-140°, but in H_2SO_4 the reaction temperatures were less than 100°. Consequently, it is not clear whether the observed specificity of these reactions is due to the difference in reaction temperatures, or whether it is due to the difference in catalysts. Since A-15 has been shown in this study to be an effective catalyst for the formation of 4b and 4c, it appears that temperature is the predominant factor. The proposed mechanism outlined in Scheme I is suggested as an explanation for these differences.

The initial step is the protonation of 10a to give carbonium ion 10b. The attack of 10b upon 10a gives rise to 11b or 11c, either of which may produce 11a through the loss of a proton. Alternatively, 11b may react to form 12, and then 4b by loss of a proton. At lower temperatures, the formation of 4b appears to be the preferred route. The dimer 4c is produced from a similar reaction of 11c.

The mechanism proposed in Scheme I suggests that the olefin dimer 11a is a common intermediate to both cyclized dimers 4b and 4c. This has been demonstrated experimentally by reacting the pure dimer 11a with A-15 in refluxing benzene for 72 h. Removal of the catalyst and solvent followed by vacuum distillation gave the dimer 4b in 81% yield. A small amount (3%) of 4c was also detected. In an analogous experiment, using toluene as the solvent, good yields (70-80%) of 4c were obtained.

It now appears that the cyclization of 1,2-dihydronaphthalene exhibits a thermodynamic-kinetic control with the dimer 4b formed initially from the cation 11b. At sufficiently high temperatures (110°), 4b may be equilibrated to 4c. The formation of 11a results from the loss of a proton from either 11b or 11c. However at the

SCHEME I


10a
$-H^+$
$-H^+$
+
H
10b
+10a
-10a
+10a
-10a
H
+
11b
H
+
11c
$-H^+$
$+H^+$
$+H^+$
$-H^+$
11a
+
H
12
+
H
13
$-H^+$
$+H^+$
4b
$-H^+$
$+H^+$
4c

higher temperatures necessary for the production of 4c, the olefin dimer 11a does not survive.

Further support of this mechanism is derived from the fact that 4c is stable in refluxing benzene containing A-15 which indicates that the reverse equilibration from 4c to 4b is not favored. However, 4c is formed from pure 4b in refluxing toluene in the presence of A-15. Dimer 4c is formed in refluxing benzene, but only after long reaction times (20% after 144 h).

To demonstrate that dimer 11a is a common intermediate in catalysis by both A-15 and P_2O_5, a sample of pure 11a was treated with P_2O_5 in tetralin at 140° for 1 h. Subsequent work-up gave a clear yellow oil. Analysis of the mixture by glc showed no detectable quantity of 11a and the ratio of 4b to 4c was 1:9. The oil was dissolved in boiling acetone which upon cooling gave white crystals of 4c in 20% yield. The melting point of this compound mixed with an authentic sample of 4c was not depressed.

In a similar experiment using pure 4b, a 27% yield of 4c was obtained. The ratio of 4b to 4c in the crude reaction mixture was 1:14 with no 11a detected.

Thus, since the dimer 4c is formed in the presence of the sulfonic acid resin, A-15, in toluene, and from P_2O_5, it seems reasonable to expect that the reported specificity of the reaction is due to thermodynamic-kinetic control rather than to differences between the acid catalysts.

The reaction of 10a in tetralin and P_2O_5 at 140° for 1 h yields the cyclized dimer 4c in 6% yield. After these crystals were removed, the mother liquor was analyzed by glc and was shown to contain

58% of 4b in addition to two other minor components. Tetralin does not appear to participate in the cyclization process except as a solvent since it was recovered unchanged with no formation of dimeric products when it was exposed to catalyst under identical conditions.

A higher yield (49%) of 4c was obtained when chlorobenzene was used as a solvent for the cyclodimerization of 10a with P_2O_5. When 10a was reacted with P_2O_5 in refluxing chlorobenzene for 1.5 h the crude reaction mixture was shown by glc to contain 4b and 4c in a ratio of 1:8. An unknown component (6%, retention time 35.0 min at 230°) was also detected together with 1% of benzo[j]fluoroanthene (1). This component may be a product of disproportionation since P_2O_5 is known to promote disproportionation of 3,3',4,4'-tetrahydro-1,1'-binaphthyl (14) to 1 and other compounds which are only partially aromatized.[23] More importantly, P_2O_5 has been shown by Nenitzescu and Avram to promote the formation of 4c and 1 from 1-tetralone.[11]

Cyclization of 10a with P_2O_5 in the absence of solvents results in lower yields of 4c (18% by glc).

The dehydrogenation of dimers 4b or 4c affords a convenient synthesis of benzo[j]fluoranthene. This synthesis is attractive since the yields of the dimer intermediates 4b or 4c has been improved from 20-40% to ≅ 80% by the use of A-15.

Dehydrogenation of either 4b or 4c in 1-methylnaphthalene with 10% Pd/C gives a high yield of 1 with no side products. If the dehydrogenation of 4b is performed as a neat melt, hydrogen is evolved rapidly at 230°. After 3 h, hydrogen evolution stopped, and subsequent work-up afforded a brown residue. Glc studies showed four peaks in addition to unreacted starting material (A, B, C, D) with retention times of 1.6, 2.0, 2.8, and 3.2 min in the ratio of 1.3:1:11.4:8.9, respectively. The last component was shown to be 1 by glc of a sample containing added authentic 1.

Trituration of the brown residue with isohexane gave yellow crystals, mp 120-130°. These crystals were shown to be a mixture of 1 and the component C with retention time of 2.8 min. A second crop of crystals, mp 70-75°, was obtained and this consisted of two components in a 1.3:1 ratio and which had retention times identical to that of the first two components.

The purity of the first crop of crystals was not improved by crystallization. They were, however, purified by chromatography on a picric acid column[24] supported over basic alumina. Isohexane was used as eluant. The first yellow fraction was collected and concentrated. Crystallization from ethanol afforded ≅ 4 g of yellow material, mp 140-145°, which were shown by glc to be enriched in component C with 15% impurity of D identified as 1.

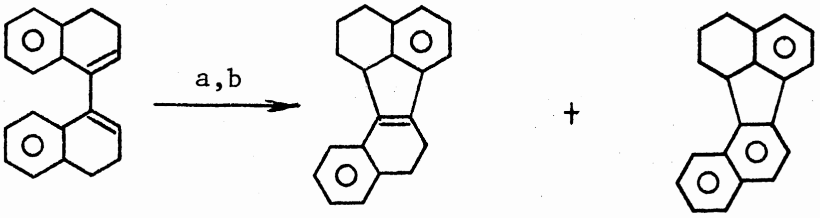
Chromatography through a freshly prepared picric acid column gave 2.3 g of pale yellow crystals, mp 140-141°, which corresponded to component C. The mass spectrum showed a molecular ion at m/e 256 indicating that dehydrogenation did not proceed to completion.

In an effort to determine the structure of this yellow intermediate from the dehydrogenation of 4b, an independent synthesis was undertaken.

A number of partially hydrogenated derivatives of benzo[j]fluoranthenes have been prepared by Crawford and Supaneker.[23] Their synthesis involves the cyclization of 3,3',4,4'-tetrahydro-1,1'-binaphthyl (14). Dehydrogenation of 14 with Pd/C in the absence of sulfur gave 1,1'-binaphthyl. When sulfur was used in conjunction with Pd/C as the catalyst, dehydrogenation was found to be accompanied by cyclization resulting in a complex mixture of partially hydrogenated benzo[j]fluoranthenes.

Cyclization of 14 in 70% H_2SO_4 reportedly[23] gave two compounds which melted at 130° and 145°. The structure of the former was assigned as 1,2,3,7,8,12c-hexahydrobenzo[j]fluoranthene (15) and the latter as 1,2,3,12c-tetrahydrobenzo[j]fluoranthene (16). Both compounds were dehydrogenated to benzo[j]fluoranthene which establishes their carbon skeleton. The synthesis is outlined in Scheme II.

SCHEME II



14 15 16

[a]70% H_2SO_4. [b]Dilution with H_2O.

Since both 15 and 15 are products which could be formed in the dehydrogenation of 4b and 4c, it became of interest to prepare them for use as standards. The method of Crawford and Supaneker,[23] which consisted of heating diene 14 with 70% H_2SO_4 on a water bath for 2 hours, was used. Dilution of the slurry followed by cooling reportedly gave crystals of 15, mp 120-129°, after recrystallization from petroleum ether. The temperature of the reaction was not specified.

When this reaction was attempted at 100°, sulfonation apparently resulted since no cyclized products were obtained when the solution was extracted with ethyl ether. At 50°, only unreacted starting material was recovered as indicated by a mixture melting point determination. When the reaction was performed at 65°, a small amount of white crystals, mp 115-120°, was obtained melting at 118-120° after two recrystallizations from isohexane.

Failing to reproduce the results of Crawford and Supaneker,[23] we attempted the cyclization of diene 14 with A-15 in refluxing toluene. The reaction was allowed to proceed for 110 h and glc samples were collected at 24 h intervals. Glc analysis (6' x ¼", 7% UCW on AW DMCS treated Chromosorb G at 250°) showed the presence of five components (A, B, C, D, E) whose retention times were 14.5, 15.4, 17.2, 23.2, and 27.2 min, respectively. The retention time of diene 14 under identical conditions was 14.0 min and none of the starting material was detected by injection of a prepared mixture. The percentage of these products is shown in Table V.

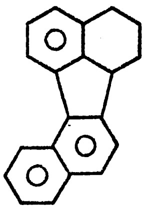
The last component (E) was isolated from the mixture by crystallization and was sublimed (120°, 0.1 mm) to give a $C_{20}H_{16}$ hydrocarbon, mp 140-141°. Crawford and Supaneker have rationalized structure 16 for this product based on the similarity of its UV spectrum with that of benzo[a]fluorene, and the presence of a quartet at 3.4 δ in the ^{1}H NMR.[23]

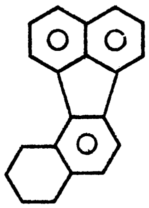
TABLE V

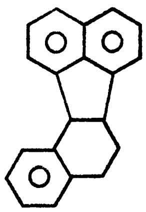
CYCLIZATION PRODUCTS OF 14 WITH A-15 IN TOLUENE

			%		
Time (h)	A	B	C	D	E
24	8.8	2.8	2.2	76.0	10.0
48	27.2	15.0	7.6	5.2	45.0
72	31.4	19.0	8.0	1.6	39.9
96	29.5	18.6	8.3	2.5	41.1

It should be considered that the UV spectrum of benzo[a]fluorene is almost indistinguishable from that of benzo[c]fluorene[25] thus 17a must also be considered a possibility. Further, the ^{1}H NMR spectrum of 17a would be expected to be similar to that of 16. The formation of 17a would require disproportionation between aromatic rings which may not be favorable under such mild conditions. ^{1}H NMR and ^{13}C NMR eliminate 17b and 2 as possible structures for the compound, mp 140-141°.


17a


17b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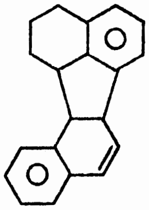
Component D was isolated by repeating the cyclization of 14 with A-15 in toluene and stopping the reaction after 12 h reflux. Removal of the solvent and catalyst gave a brown oil which was shown by glc analysis to contain five components (A, B, C, D, E) in ratios of 5.6:1.5:35:5.5, respectively. Component D, which comprised 72% of the reaction mixture, crystallized from ethanol to give a white crystalline compound, mp 128-129°. The MS and elemental analysis are consistent with $C_{20}H_{18}$. The absence of vinylic hydrogens in the ^1H NMR eliminates structures 18, 19, 20 and all other structures possessing vinylic protons. Thus the structure of this compound must be assigned either 15 or 21, which are not readily differentiated by ^1H NMR analysis.



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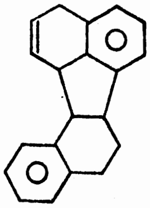

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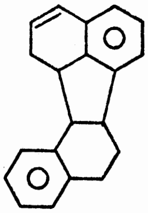

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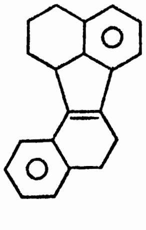
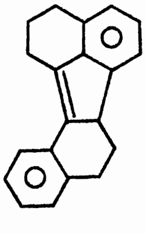
For the purpose of discussion, we shall use structure 15 for the $C_{20}H_{20}$ hydrocarbon, mp 113-114°, until there is a distinction between 15 and 21.



15



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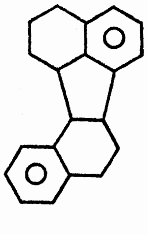
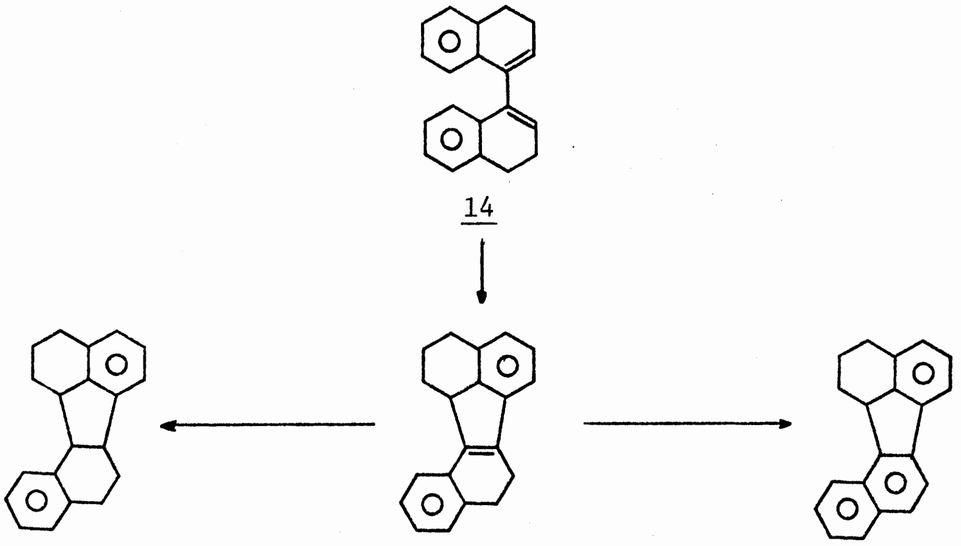


34

Components A, B, and C in the cyclization of 14 with A-14 in toluene were not isolated as pure hydrocarbons. However glc evidence suggests that they are reduced products arising from the disproportionation of 15 or 21. Component A has a retention time identical with that of the $C_{20}H_{20}$ hydrocarbon, mp 89-90°, obtained from the hydrogenation of 15 using Pd/C as the catalyst. The retention time of component B is the same as that of the $C_{20}H_{20}$ hydrocarbon, mp 113-114°, which results from the reduction of 15 with Li/NH_3. Thus, components A and B are probably isomers of 34. Further glc analysis indicates that the $C_{20}H_{20}$ dimers 4b and 4c are not present in this reaction mixture, as shown by mixed injections of authentic compounds.

The disproportionation of 15 with A-15 in toluene to 16 and 34 is a reasonable explanation for the decrease in the percentage of component D (76% at 24 h to 7.6% after 48 h). The simultaneous increase in the concentrations of components A, B, and C are consistent with such a reaction. Thus the cyclization of diene 14 with A-15 may be illustrated as follows:



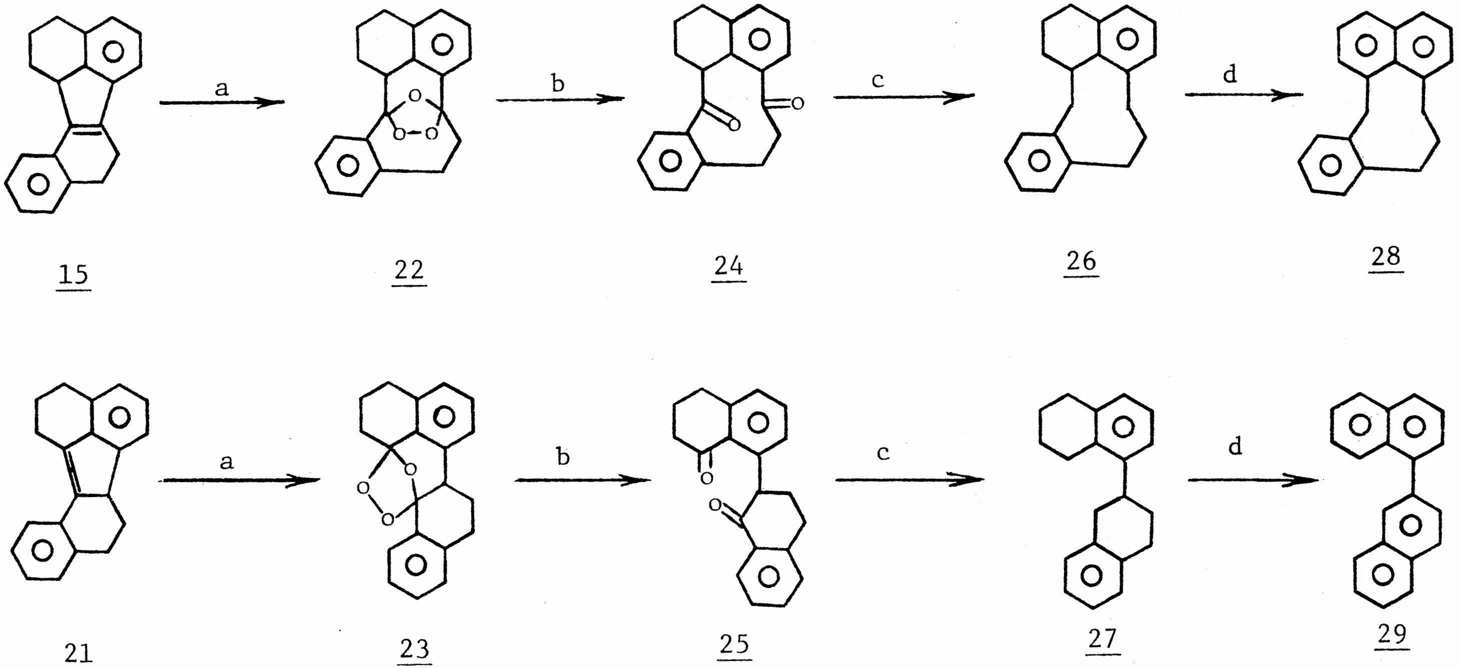
Our attempt to distinguish structures 15 and 21 via ozonolysis is outlined in Scheme III. It was anticipated that ozonolysis of the hydrocarbon, mp 128-130°, would produce the diketones 24 or 25 via reduction of the ozonides 22 or 23, respectively. Hydrogenolysis of the diketones followed by aromatization should produce hydrocarbons 28 or 29.

However, the ozonolysis does not proceed as expected. The hydrocarbon, mp 128-130°, was treated with ozone in methylene chloride until a faint blue color appeared. When this solution was treated with dimethyl sulfide according to the procedure of Pappas et al.,[26] subsequent work-up afforded a white crystalline solid which melted with decomposition at 158-160°. The IR spectrum contained no absorptions typical of hydroxyl or carbonyl functions, but did contain a weak band at 1250 cm^{-1} which may be attributed to C-O stretching. The C-O stretching in the IR may arise from epoxides 30 or 31, or alternatively from ozonides 22 or 23. Similar absorption bands have been observed in the IR spectra of epoxides and ozonides.[27]

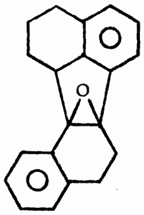
The formation of epoxides from abnormal ozonolyses has been shown to occur in sterically hindered olefins and occurs frequently in the case of 1,1-disubstituted ethylenes.[28] Criegee has noted that sterically hindered unsymmetrical olefins with two strongly electron donating groups preferentially form epoxides rather than the normal ozonides.[29] Fuson obtained an epoxide, mp 101-102°, from the ozonolysis of 1-phenyl-1-mesitylethylene (32).[30]

While the ^{1}H NMR of the product from ozonolysis of the hydrocarbon, mp 128-129°, is consistent with epoxides 30 or 31 or the ozonides 22 and 23, the ^{13}C NMR suggests that the compound, mp 158-160°

SCHEME III



$^{a}O_3/CH_2Cl_2$. $^{b}(CH_3)_2S$. $^{c}H_2$, Pd/C. ^{d}Pd/C, 1-methylnaphthalene, Δ.



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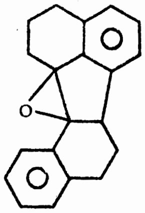

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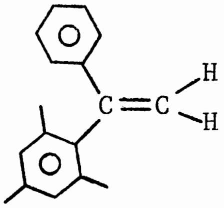
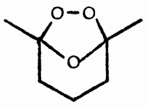


32

is not an epoxide. The singlet absorptions of the two carbons at 107 and 105 ppm are further down-field than would be expected of a normal epoxide, and appear to be more consistent with those expected of a carbon singly bonded to two oxygens.[31]

The detection of fragmentation ions at 32 and 306 amu in the mass spectrum would not be expected from either 30 or 31. In addition, the elemental analysis does not support 30 or 31 as potential structures for the compound, mp 158-160°.

Formation of stable ozonides are not uncommon and many stable ozonides have been obtained from olefins having the double bond as part of a five membered ring.[32a,b] Criegee et al. obtained the ozonide 33 in 90% yield from the ozonolysis of 1,2-dimethylpentene.[33] Analogous stable ozonides have been prepared from the ozonolysis of 1,2-diphenylindene[34] as well as from ozonolysis of 2,3-diphenylindeneone.[35]

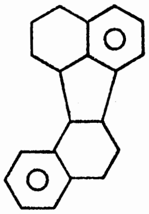


33

Dimethyl sulfide was ineffective for the reduction of the ozonide, and another ozonization of 15 was performed in which the cold methylene chloride solution containing the ozonide was poured into isopropyl alcohol containing an excess of $NaBH_4$. This solution was stirred overnight at room temperature, then refluxed for 45 min. The cooled solution was decanted, concentrated by rotary evaporation and hydrolyzed with water. Subsequent work-up afforded white crystals, mp 158-160°, which were shown to be identical through melting point of an admixture and ^1H NMR studies to those obtained from the work-up of the ozonide using dimethyl sulfide.

The product obtained from ozonolysis of 15 was hydrogenated in acetic acid using a glass apparatus equipped with hydrogen recycle.[37] The crude reaction mixture was dehydrogenated in methylnaphthalene using 10% Pd/C as catalyst. Removal of the catalyst and solvent gave a small amount of white crystals, mp 162-164°, which was not identical to the product resulting from ozonolysis of 15. Glc analysis showed a mixture of four components. However, none of these components had the same retention time as α,β-binaphthyl. Identification of this product is in progress.

Hydrogenation of the olefin 15 with Raney Nickel at 8 atmospheres pressure reportedly[23] resulted in a $C_{20}H_{20}$ compound, mp 90°, while treatment of 15 with Raney Nickel in refluxing ethanol for 16 h resulted in a $C_{20}H_{20}$ compound, mp 150°. These compounds were assigned structures 34 and 35, respectively. The evidence cited in support of structure 34 was its facile dehydrogenation to 1 and its UV spectrum which was almost identical to the UV spectrum of a $C_{20}H_{20}$ dimer, mp 91-93°, obtained by Dansi and Reggianni[36] from the dimerization of 10a.



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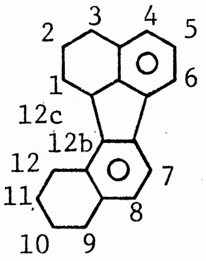

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The dimer, mp 91-93°, obtained by Dansi has been shown to have structure 4b.[13] It was of interest to determine whether the dimers obtained from hydrogenation of 15 were identical with 4b and 4c obtained from the dimerization of 1,2-dihydronaphthalene.

Hydrogenation of 15 in ethanol with Pd/C in a glass recirculating apparatus[37] gave a good yield (72%) of a white crystalline solid, mp 89-90°, whose MS is consistent with a $C_{20}H_{20}$ hydrocarbon. The melting point of this compound and an authentic sample of 4b was depressed (mp 83-88°). The ^{1}H NMR of dimer 4b is different from that of 34. Dimer 4b contains one benzhydryl proton appearing as a distinct doublet at 3.96 δ and the ^{1}H NMR of 34 shows no benzhydryl protons. In addition, the splitting due to the fjord protons of 4b are not present in the spectrum of 34. Thus dimer 34 is not identical to 4b. The structure of 34 appears to be substantiated on the basis of ^{1}H NMR although stereochemical assignment remains uncertain.

Hydrogenation of 15 with freshly prepared Raney nickel for 16 hours in refluxing ethanol gives a white crystalline compound, mp 149-150°, whose structure is assigned that of 35. The melting point of a mixture of 35 and 4c is depressed, and the ^{1}H NMR spectrum of these compounds are dissimilar. The ^{1}H NMR of 35 shows the presence of five aromatic protons (6.92-8.0 δ), and the benzhydryl proton at 12c appears as a doublet of doublets centered at 3.62 δ and 3.5 δ. These absorptions are different from those of 4c in that the benzhydryl proton of 4c appears a doublet downfield at 4.12 δ. The aliphatic proton absorptions in 4c also show a general line broadening due to increased ring strain which is not present in the spectrum of 35.

^{1}H NMR analysis is supportive of the assignment of 35. Additional support is derived from the ^{13}C NMR of 35 which shows a tertiary sp^{3} carbon absorption at 45.2 ppm, assigned to carbon 12c, which appears as a singlet in the off-resonance spectrum.

Thus, the similarity in melting points of dimer 34 to 4b and 35 to 4c is fortuitous since the compounds are not identical.

Hydrocarbon 15 was reduced with lithium in ether-ammonia and the crude reaction mixture was shown by glc to be composed of at least three components (A,B,C:2.5:1:9). The retention times of the components were 17.5, 18.6, and 21.0 min, respectively. The first component was shown to be 34 by mixed injection. The major product, C, crystallized from the crude reaction mixture and was recrystallized from 95% ethanol. These crystals were shown by glc to be greater than 97% pure and their melting point was sharp (113-114°). ^{1}H NMR spectrum showed 7 aromatic protons, 7 benzylic protons, and 6 methylene protons. Two of the methylene protons are overlapping with the benzylic protons due to their proximity to the aromatic rings. It is probable that this new compound is a stereo isomer of 34, although stereochemical assignments of 34 have not been made.

CHAPTER IV

EXPERIMENTAL

<u>Preparation of 1-Tetralol</u>. Diisobutylaluminum hydride (633 g, 4.45 mol) was added to 2.2 L of dry toluene maintained under a nitrogen atmosphere. A solution containing 585 g (4.0 mol) 1-tetralone in 1 L of toluene was added at such a rate that the temperature did not exceed 45°. The mixture was stirred for an additional 30 min before ethyl acetate (50 mL) was added. The solution was poured onto ice and acidified with conc. HCl. The toluene layer was removed and the aqueous layer was extracted twice with 300 mL portions of toluene. The combined toluene layers were washed with water and twice with a saturated Na_2CO_3 solution. This toluene solution was then filtered through solid Na_2CO_3, dried ($MgSO_4$), and concentrated under rotary evaporation. The residue was distilled (85°, 0.3 mm Hg) [lit.[38], 0.3 mm] to give 516 g (3.5 mo., 87%) of 1-tetralol.

In one case, during the distillation, approximately one half of the material solidified and did not distill at 85°, but crystallized on standing. The pot residue was recrystallized from isohexane to give white crystals, mp 83-84°, [lit.[38] mp 84-85] which were shown by ^1H NMR and mass spectral analysis to be bis(tetrahydro-1-naphthyl)-ether (<u>36</u>). Mass spectrum (70 eV) m/e (rel. intensity) 147 (73), 132 (100), 131 (67), 130 (39), 129 (25), 91 (65); ^1H NMR (CCl_4) δ

6.82-7.3 (m, 8, ArH), 4.52 (t, 2, ArCHO), 2.5-3.0 (m, 4, ArCH), 1.6-2.2 (m, 8, $-CH_2$).

Preparation of Benzo[j]fluoranthene (1). A. In a 500 mL flask equipped with a nitrogen inlet, magnetic stirrer and thermometer was placed an intimate mixture of 20.0 g (0.077 mol) of 4b and 5.0 g of 10% Pd/C. The mixture was heated slowly until liquifaction occurred and then more rapidly to 230° after which hydrogen evolved rapidly. The temperature was maintained at 240° for 3 h until evolution of hydrogen ceased. The mixture was cooled to 100° and 100 mL of toluene were added. The mixture was filtered through Dicalite and concentrated by rotary evaporation to 17.0 g of a brown residue which showed four glc peaks in addition to that of unreacted starting material. Retention times (A,B,C,D) were 1.6, 2.0, 2.8, and 3.2 min, respectively, at 250° (6' x ¼", 1% OV-17 on DMSC treated Chromosorb G). The ratios of these products were 1.3:1:11.4:8.9, respectively. The last component was shown to be 1 by mixed injection. Component C was subsequently shown to be either 16 or 17. The brown residue was recrystallized from isohexane to give 13.4 g of yellow crystals, mp 120-130°. These crystals were shown to be a mixture of 1 and component C. A second crop of crystals, mp 70-75°, was composed of the first two components.

The purity of the first crystals was not improved by recrystallization. They were purified by chromatography on a picric acid column[24] over basic alumina using isohexane as eluant. The first yellow fraction was collected and the solvent removed to give ≅ 4 g of yellow material, mp 140-145°, which was shown by glc to be enriched in component C with 15% impurity of 1 remaining.

Chromatography through a freshly prepared picric acid column gave 2.3 g of pale yellow crystals, mp 140-141°, which corresponded to component C in the glc.

B. In a 300 mL round bottomed flask equipped with a magnetic stirrer, condenser and nitrogen purge were combined 10.0 g (0.038 mol) of 4b, 1.0 g 10% Pd/C, and 150 mL of 1-methylnaphthalene. Reflux was initiated and the reaction was analyzed (glc) at intervals of 24, 48, 72, and 84 h, using a 6' x ¼" (1% OV-17 on Chromosorb G, DMCS treated) column at 250°. After 24 h, the ratio of 1:4b was 1:1.7. After 84 h, only 4% starting material remained and no other products were detected except 1. After 84 h, the solution was cooled, filtered through Dicalite and the Dicalite rinsed with warm toluene. Removal of the solvents by distillation, followed by trituration of the residue with isohexane afforded 9.0 g (0.036 mol, 94%) of 1, mp 162-164°, picrate, mp 193-195°, [lit.[9] mp 165°, picrate mp 195°]. The dimer 4c behaves similarly giving 1 in 92% yield when subjected to identical reaction conditions. Mass spectrum (8 eV) m/e (rel. intensity) 252 (100), 251 (7), 250 (20), 126 (7), 57 (8), 43 (8); ^{1}H NMR (C_6D_6) δ 8.54 (d, 2, C-1, C-12), 8.08 (d, 2, C-6, C-7), 7.12-7.88 (m, 8, ArH); ^{13}C NMR[40] ($CDCl_3$) ppm, 137.5, 137.4, 136.8, 133.7, 131.7, 130.3, 129.3, 129.3, 128.9, 128.0, 127.5, 127.0, 126.6, 126.6, 125.0, 124.9, 124.0, 123.8, 120.5, 119.5.

Preparation of cis-anti-4,5,6,6a,6b,7,8,12b-Octahydrobenzo[j]fluoranthene (4b). A. In a 2-neck fluted flask equipped with a mechanical stirrer and condenser were added 108 g (0.83 mol) of 10a, 20.0 g of A-15 and 500 mL of benzene. This mixture was heated at reflux for 96 h, cooled, filtered, and concentrated. The residue was distilled

(Kugelrohr, 110-150°, 0.1 mm Hg) to give 77.2 g (77%) of light yellow oil. Crystallization from ether/isohexane (1:1) gave 58 g (0.22 mol) white crystals of 4b, mp 92-93°. Mass spectrum (70 eV) m/e (rel. intensity) 260 (100), 259 (31), 232 (44), 217 (35), 169 (61), 78 (44); ^{1}H NMR (CCl_4) δ 6.7-7.4 (m, 6, ArH), 4.06 (J=7.4 Hz, d, 1, $CH(Ar)_2$), 2.2-2.9 (m, 6, overlapping), 1.0-2.10 (overlapping, m, 6); ^{13}C NMR ($CDCl_3$) ppm 144.4, 143.7, 137.6, 136.7, 134.1, 128.2, 128.1, 126.3, 125.8, 125.7, 125.3, 122.3, 47.4, 46.7, 42.8, 27.6, 26.7, 26.4, 23.6, 23.5.

B. In a 1 L, 2-neck fluted flask equipped with mechanical stirrer and condenser were combined 16.0 g (0.12 mol) of 11a, 10.0 g of A-14, and 600 mL of benzene. The stirred mixture was heated at reflux for 72 h, filtered to remove catalyst, and concentrated by rotary evaporation. The residue was distilled (Kugelrohr, 130-160°, 0.1 mm Hg) to give 14.8 g of clear liquid. Crystallization from isohexane yielded 13.1 g (81%) of 4b, mp 92-93°, whose melting point when combined with the product from method A was undepressed.

Preparation of cis,syn-4,5,6,6a,6b,7,8,12b-Octahydrobenzo[j]fluoranthene (4c). A. To 300 mL of toluene were added 5.0 g (0.019 mol) of 4b and 5.0 g of A-15. The suspension was heated at reflux for 48 h and filtered while warm, concentrated by rotary evaporation and distilled (Kugelrohr, 0.1 mm Hg, 110-140°). Crystallization from 95% ethanol gave 3.7 g (74%) of white crystals, mp 149-141°. A ^{1}H NMR spectrum of this product was identical to that of an authentic sample of 4c.

B. In a 3-neck, round-bottomed flask equipped with drying tube, thermometer and magnetic stirrer was placed 20.0 g of P_2O_5. A solution containing 9.9 g (0.038 mol) of 11a and 15 g of tetralin was added and the mixture was heated to 130-140° for 1 h. This mixture was poured over 500 g of ice and extracted 3 times with ethyl ether. The organic extract was washed twice with water, dried ($MgSO_4$), and concentrated by rotary evaporation. Vacuum distillation (Kugelrohr, 130-180°, 0.1 mm Hg) gave 5.1 g of yellow oil which crystallized from ethyl ether to give 2.0 g (20%) of 4c, mp 149-151°. The melting point of a mixture of this compound and that obtained from method A was undepressed, and the ^1H NMR of the product is identical with that obtained from procedure A.

C. A solution of 15 g of tetralin and 5.0 g (0.038 mol) of 10a was added to 63.0 g of PPA. This mixture was heated with stirring to 140° and maintained at this temperature for 15 min, then poured over 300 g ice. The aqueous slurry was extracted four times with 200 mL portions of ethyl ether. The organic extracts were combined, dried ($MgSO_4$), concentrated, and distilled (Kugelrohr, 0.3 mm Hg, 150-170°) to give 3.9 g of dimer. This fraction did not crystallize and was passed through a short (5 x 2 cm) column of basic aluminc (Merck activity I) using 500 mL of isohexane as eluant. Concentration of the eluate gave 2.1 g (42%) of 4c as white crystals, mp 147-149°.

D. To a solution of 150 mL of anhydrous chlorobenzene containing 20.0 g (0.154 mol) of 10a was added 80.0 g P_2O_5. The viscous mixture was further diluted with an additional 150 mL of chlorobenzene, heated at reflux for 1.5 h, then cooled and poured over 500 g ice. The aqueous slurry was extracted three times with 100 mL portions of ethyl ether. The combined extracts were washed three times with H_2O, dried ($MgSO_4$), and concentrated by rotary evaporation. The residue was distilled (Kugelrohr, 140-170°, 0.2 mm Hg) to give 13.3 g of yellow oil which did not crystallize immediately. The oil was passed through a short column of basic alumina (Merck, activity I) using isohexane as eluant. Concentration of the eluate gave 9.9 g (49%) of 4c, mp 150-153°. The mother liquor was chromatographed again through basic alumina and this procedure yielded 0.56 g of white crystals, mp 89-93°, which were shown to be 4b by ^{1}H NMR.

A rigorously pure sample of 4c was prepared by chromatographing 50.0 g of 4c, obtained by procedure A, through a picric acid column[24] using isohexane as eluant. The isohexane eluant was concentrated and the resulting residue was recrystallized twice from a 10% solution of benzene in 95% ethanol. This product was then crystallized from ethyl acetate, dried and sublimed (130°, 0.05 mm Hg). In this manner, 12.0 g of pure 4c were obtained, mp 152.5-153°. Mass spectrum (70 eV) m/e (rel. intensity) 260 (100), 233 (49), 218 (32), 170 (20), 139 (21), 129 (27), 128 (27); ^{1}H NMR (CCl_4) δ 6.7-7.40 (m, 7, ArH), 4.2 (d, 1, $CH(Ar)_2$, J=5.4 Hz), 2.85-3.28 (m, 1, ArCH in plane of aromatic ring), 2.4-2.85 (m, 5), 0.8-2.35 (overlapping m, 6); ^{13}C NMR ($CDCl_3$) ppm 144.3, 141.4, 136.7, 136.4, 134.6, 130.0, 128.8, 126.1, 125.7, 125.3, 125.2, 120.6, 47.8, 44.9, 44.4, 28.9, 26.7, 23.8, 23.7, 20.2.

1,2-Dihydronaphthalene (10a). To 516 g (3.5 mol) of 1-tetralol was added 20.0 g (0.22 mol) oxalic acid and 500 mL H_2O. The slurry was steam distilled and the distillate extracted three times with ethyl ether. The ether layers were combined, dried ($MgSO_4$), and concentrated by rotary evaporation. The residue was distilled (70°, 0.3 mm Hg) to yield 362 g (2.8 mol) of 1,2-dihydronaphthalene (10a) (80% from 1-tetralone).

Preparation of 1,2,3,3',4,4'-Hexahydro-1,2'-binaphthyl (11a). In 200 mL of cyclohexane were combined 36.0 g (0.3 mol) of 10a and 6.0 g of Amberlyst-15 resin. The suspension was stirred at reflux for three hours. The solution was then cooled, filtered, concentrated by rotary evaporation, and the remaining oil was distilled (Kugelrohr, 0.1 mm Hg). The fraction which distilled at 80-90° gave 17.0 g of colorless oil which consisted mainly of unreacted <u>10a</u>. The dimeric fraction was collected at 140-160° and gave 18.2 g (51%) of liquid material which crystallized from methanol to give 12.7 g of <u>11a</u>, mp 52-53.5°. A second crop of crystals was obtained, mp 48-50°, which could not be further purified by recrystallization. A glc analysis (6' x ¼", 7% UCW-98 on DMCS treated Chromosorb G, 80-100 mesh, isothermal 250°) of the crude reaction mixture showed the presence of at least three dimers, A:B:C (22:3:1), whose retention times were 13.7, 14.5, 15.7 min, respectively. By means of injections of mixtures with known standards, components B and C were identified as <u>4b</u> and <u>4c</u>, respectively. Structural assignment of <u>11a</u> had not previously been made. IR[41] (KBr) cm^{-1} 753, 745, 735, 1632, 1252, 1239, 1198; UV (95% ethanol) λ_{max} 265 (log ε, 4.28) and 273 (log ε, 4.26); mass spectrum (70 eV) <u>m/e</u> (rel. intensity) 260 (56), 131 (25), 130 (100), 129 (35), 128 (24), 115 (17); ^{1}H NMR (acetone-D_6) δ 1.6-2.2 (m, 6, $-CH_2$), 2.6-2.9 (m, 4, $ArCH_2$), 2.7 (t, 1, ArCH), 6.2 (s, 1, ArCH=C), 6.8-7.2 (m, 8, ArH); ^{13}C NMR ($CDCl_3$) ppm 145.3, 137.6, 137.4, 134.6, 134.5, 129.0, 128.8, 126.9, 126.2, 126.5, 162.2, 126.1, 125.8, 125.4, 124.9, 47.2, 29.8, 28.5, 25.1, 21.4.

<u>Anal</u>. Cacld for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.00; H, 7.63.

<u>Cyclization of 10a With Benzene and Amberlyst-15 Resin.</u> To 200 mL of benzene were added 5.0 g (0.04 mol) of <u>10a</u> and 5.0 g of A-15

catalyst. The suspension was heated at reflux and 2.0 mL aliquots were removed at 24 h intervals. These samples were filtered through glass wool to remove the catalyst and the glass wool was rinsed with 2.0 mL of warm acetone. The solvents were removed under N_2 atmosphere and 2.0 mL of acetonitrile were added to the residue. These samples were analyzed on a Waters HPLC using a reverse phase C_{18}-μ Bondapak column and a model 440 absorbance detector (254 nm). The retention times for dimers 11a, 4b, and 4c were 21.5, 23.5, and 25.5 min, respectively, using 80% acetonitrile/water with a flow rate of 2.0 mL/min. The percentages of 11a, 4b, and 4c were determined by comparison with weighed standards and are presented in Table I.

After 144 h the warm mixture was filtered through Dicalite to remove the catalyst and the solvent was removed by rotary evaporation. The resulting brown oil was distilled (Kugelrohr, 135-160°, 0.1 mm Hg) to give 3.2 g (64%) of light yellow oil which crystallized when triturated with ethyl ether. Recrystallization from 95% ethanol afforded 2.2 g (0.008 mol) of crystalline dimer 4b, mp 92-93°. The melting point of a mixture with an authentic sample was undepressed.

Cyclization of 10a With Amberlyst-15 in Refluxing Toluene. The procedure for the cyclization of 10a in toluene was identical to that described above except that toluene was used as the reaction solvent. The products were analyzed by glc on a 6' x ¼" column of 7% UCW-98 on DMCS treated Chromosorb G (80-100 mesh) operated isothermally at 250° and were identified by mixed injections of authentic samples. The results are presented in Table II.

After 110 h, the warm solution was filtered and concentrated by rotary evaporation. The brown oil was distilled as before and the dimeric fraction weighing 2.8 g (56%) gave a clear yellow liquid which crystallized from methanol to give 1.9 g (0.007 mol) of 4c, mp 150-152°. A melting point of a mixture of 4c and the sample was undepressed, and the ^{1}H NMR spectrum was identical to that of 4c.

Cyclization of 10a in Benzene With Amberlyst XN-1011. In 200 mL of benzene was placed 5.0 g (0.04 mol) of 10a and 5.0 g of Amberlyst XN-1011.[17] The stirred suspension was brought to reflux and samples were collected as described previously. The results of HPLC analysis are presented in Table III.

After 96 h, the catalyst was removed by filtration and the solvent removed by rotary evaporation. Vacuum distillation (Kugelrohr, 110-140°, 0.1 mm Hg) gave 3.8 g (76%) of a clear liquid which crystallized with difficulty from 95% ethanol to yield 3.2 g of white crystals, mp 85-90°. Glc analysis showed the crystals to be mainly 4b with about 15% of 11a present.

Cyclization of 10a in Toluene With Amberlyst XN-1011. To 200 mL of toluene were added 5.0 g (0.04 mol) of 10a with 5.0 g of Amberlyst XN-1011. The magnetically stirred suspension was heated at reflux for a total of 96 h and samples were collected and prepared as described previously. The samples were analyzed by glc under the same conditions as described for the cyclization of 10a with A-15 in toluene. The results are presented in Table IV. After 96 h, the catalyst and solvent were removed and the residue was distilled (Kugelrohr, 0.1 mm Hg, 110-140°) to give 3.0 g of a clear liquid which did not crystallize. A glc analysis of the distillate showed the presence of 4b and 4c in a 2:1 ratio with no 11a detectable.

Cyclization of 3,3',4,4'-Tetrahydro-1,1'-binaphthyl (14) to 1,2,-3,7,8,12c-Hexahydrobenzo[j]fluoranthene (15). A solution containing 15.0 g (0.058 mol) of diene 14 in 500 mL of toluene was added to 15.0 g of A-15. The suspension was heated at reflux for 12 h then filtered through Dicalite. The Dicalite was rinsed with an additional 200 mL of warm toluene. The filtrate was concentrated by rotary evaporation to give 13.7 g (91%) of yellowish white crystals, mp 127-130°. These crystals were dissolved in a minimum amount of hot benzene and 95% ethanol was added until the solution became turbid. Scratching gave 7.3 g white crystals, mp 128-129.5°. Cooling the solution produced an additional 4.3 g of material, mp 128-130°, which was identical to the first crop. Concentration of the mother liquor gave 1.9 g of crystals, mp 127-128°, which were only slightly less pure than the first material. UV[42] (95% ethanol) λ_{max} 305 nm, (log ε 4.37), [lit.[23] λ_{max} 314 nm, log ε 4.45]; Mass spectrum (8 eV) m/e (rel. intensity) 258 (100), 257 (17.6), 230 (19.0), 229 (19.7), 215 (21.6), 114 (25.7); ^{1}H NMR ($CDCl_3$) δ 6.9-7.6 (m, 7, ArH), 3.46 (dd, 1, C-12c), 3.2-2.4 (m, 7, overlapping), 2.2-1.18 (m, 3, overlapping); ^{13}C NMR ($CDCl_3$) ppm 144.5, 143.4, 137.3, 136.7, 133.4, 132.7, 132.3, 128.8, 126.2, 125.9, 125.7, 124.9, 124.5, 120.0, 49.5, 30.7, 28.4, 27.2, 25.4, 23.7.

Anal. Calcd for $C_{20}H_{18}$: C, 92.70; H, 7.17. Found: C, 92.98; H, 7.02.

Ozonolysis of 1,2,3,7,8,12c-Hexahydrobenzo[j]fluoranthene (15). A. An ozonolysis tube containing 50 mL of CH_2Cl_2 and 1.0 g (0.004 mol) of 15 was chilled in a Dry Ice-acetone bath and ozone was passed through the solution until a faint blue color appeared. The ozone line was disconnected and 10 mL dimethyl sulfide was added.[26] The organic solution was washed three times with 100 mL portions of water, dried ($MgSO_4$), and concentrated by rotary evaporation to give 0.7 g yellowish white crystals, mp 156-160°. The compound decomposed when a small sample was sublimed (110°, 0.05 mm Hg).

When the experiment was repeated using a 10% methanol/methylene chloride solution as the solvent, the same product was obtained in comparable yields. IR (KBr) (cm^{-1}) 1258, 1124 (C-O stretch); Mass spectrum (70 eV) <u>m/e</u> (rel. intensity) 306 (10.7), 274 (100), 273 (50.5), 272 (72.6), 271 (68.4), 256 (62.1); ^1H NMR ($CDCl_3$) δ 7.9-7.72 (m, 1, ArH), 7.42-6.94 (m, 6, ArH), 3.35 and 3.23 (dd, 1, C-12c), 3.2-2.74 (m, 4, ArCH), 2.5-1.8 (m, 6, CH_2); ^{13}C NMR ($CDCl_3$) ppm 139.6, 135.5, 135.1, 131.1, 130.6, 129.7, 128.7, 128.2, 128.1, 126.7, 126.5, 125.7, 107.3, 105.0, 44.8, 30.3, 29.4, 28.5, 28.5, 20.7.

<u>Anal</u>. Calcd for $C_{20}H_{18}O_3$: C, 78.93; H, 5.30; O, 15.77. Found: C, 77.13; H, 6.01; $C_{20}H_{18}O$ requires C, 87.56; H, 6.61; O, 5.83.

B. An ozonolysis tube containing 50 mL of CH_2Cl_2 and 2.0 g (0.008 mol) of <u>15</u> was chilled in a Dry Ice-acetone bath and ozone was passed through the solution until a faint blue color appeared. The solution was poured into a 250 mL round bottomed flask which contained 4.0 g (0.11 mol) of $NaBH_4$ and 100 mL of 2-propanol. This solution was stirred overnight, then refluxed for 1 h. The solution was then concentrated and 250 mL of H_2O was added. The aqueous solution was stirred for 6 h, then extracted (3 x 100 mL) with ethyl ether. The ether was dried ($MgSO_4$) and concentrated to give 2.3 g of a clear yellow oil. Crystallization from 95% ethanol gave 1.4 g of white crystals, mp 159-161°. The ^1H NMR spectrum of this product was identical to that of the product obtained by method A.

Reduction of 15 in Li/NH_3. In a 3-necked vertical tube equipped with a Dry Ice condenser, NH_3 inlet, and N_2 inlet previously purged with nitrogen was placed 2.0 g (0.007 mol) of 15 dissolved in 15 mL of anhydrous ethyl ether and 75 mL of NH_3. Lithium ribbon (0.1 g, 0.014 mol) was added portion wise until a permanent blue color was observed. The reaction was quenched with NH_4Cl and ammonia was allowed to evaporate. The residue was diluted with 50 mL water and extracted twice with 50 mL portions of ethyl ether. The solution was dried ($MgSO_4$) and concentrated to 1.4 g of clear oil. Trituration of the oil with ethyl ether gave 1.2 g of white crystals, mp 108-110°. Recrystallization from 95% ethanol gave 0.7 g pure white crystals, mp 113-114°. An additional 0.4 g of white crystals were obtained, mp 108-110°, from the mother liquor which were only slightly less pure than the initial crystals.

Glc analysis of the crude reaction mixture showed three peaks A:B:C (2.5:1:9) whose retention times were 17.5, 18.6, and 21.0 min, respectively. The first component was shown by injection as a mixture to be 34. The major component corresponded to the compound mp 113-114°. Mass spectrum (70 eV) *m/e* (rel. intensity) M^+ 260 (100), 217 (28), 169 (49), 145 (32), 129 (28), 128 (35); ^1H NMR ($CDCl_3$) δ 7.46-6.84 (m, 7, ArH), 3.35-2.4 (m, 9, overlapping ArCH), 2.3-1.3 (m, 4, $-CH_2-$); ^{13}C NMR ($CDCl_3$) ppm 144.3, 144.2, 140.6, 137.2, 134.2, 128.5, 126.4, 125.8, 125.5, 125.2, 124.5, 118.8, 57.3, 47.4, 43.7, 29.6, 28.8, 26.5, 24.9, 23.6.

Cyclization of 3,3',4,4'-Tetrahydro-1,1'-binaphthyl (14) to 1,2,-3,12c-Tetrahydrobenzo[j]fluoranthene (16). In a 2-neck 500 mL flask equipped with magnetic stirrer, condenser and drying tube were combined

5.0 g (0.019 mol) of diene 14, 5.0 g A-15, and 200 mL of toluene. The mixture was heated at reflux for a total of 100 h with 2.0 mL aliquots removed at 24 h intervals. The samples were filtered through glass wool and the solvent removed under N_2. The oily residues were diluted with 2.0 mL of acetonitrile and analyzed by glc (6' x ¼" UCW-98 on 80-100 mesh DMCS treated Chromosorb G) isothermally at 250°. At least five components were indicated whose retention times were 14.5, 15.4, 17.2, 23.2, 27.2, min for A, B, C, D, and E, respectively. The percentages of each of these components are given in Table V for each sample. No starting material was detected after 24 h. After 110 h, the warm solution was filtered through Dicalite and concentrated by rotary evaporation to give 1.7 g of yellow crystals of 16 or 17a, mp 135-140°. Recrystallization from 95% ethanol gave 0.7 g yellow crystals, mp 139-140°. These crystals were sublimed at 120° and 0.05 mm Hg, mp 140.5-141°. UV (95% ethanol) λ_{max} 274 nm, (log ε 4.84); Mass spectrum (9 eV) m/e (rel. intensity) 257 (22.3), 256 (100), 255 25.3), 252 (22.3), 228 (65.9); ^{1}H NMR δ 7.0-8.1 (m, 8, ArH), 3.96 (dd, 1, $CH(Ar)_2$), 2.6-3.2 (m, 3, overlapping), 2.04-2.4 (m, 2, overlapping), 1.04-1.52 (m, 1, overlapping); ^{13}C NMR ($CDCl_3$) ppm 145.9, 143.4, 139.6, 138.8, 134.8, 132.8, 131.2, 128.8, 127.7, 127.2, 125.9, 125.2, 124.7, 124.0, 119.0, 116.5, 45.2, 26.4, 25.8, 23.4.

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.62; H, 6.31.

Dehydrogenation of 11a to 1,2'-Binaphthyl (29). To an intimate mixture consisting of 1.0 g (4 m mol) of 11a and 0.5 g of 10% Pd/C was added 100 g of 1-methylnaphthalene. A nitrogen inlet tube was placed below the surface and the mixture was heated at reflux until no further evolution of hydrogen was evident (1 h). The mixture was cooled and 50 mL of toluene were added. The solution was filtered through Dicalite, concentrated and methylnaphthalene was removed by vacuum distillation. The residue crystallized from isohexane gave 0.8 g of white crystals, mp 79-81°. The melting point was undepressed when mixed with an authentic sample of 1,2'-binaphthyl (29).

Preparation of 1,2,3,9,10,11,12,12c-Octahydrobenzo[j]fluoranthene (35). Raney Nickel powder (150 g, W.R. Grace) was added portion wise to a solution of 450 mL of 50% NaOH which had been diluted to 700 mL maintaining the temperature at 75°. The slurry was digested for 30 min after addition of catalyst was complete. The base was decanted and the catalyst was washed with water to neutral pH, then washed three additional times with 95% ethanol and stored under ethanol.

To 100 mL of 95% ethanol were added 1.0 g (4 m mol) of olefin 15 and 15.3 g of freshly prepared Raney Nickel catalyst. The mixture was heated at reflux for 16 h, cooled, and filtered. Concentration gave 0.65 g of yellow oil which crystallized from benzene/methanol (1:1) to give 0.3 g of white crystals of 35, mp 149-150°, assigned as component A.

Glc analysis (6' x ¼" 7% UCW-98 on DMCS treated Chromosorb G, 250° isothermal) of the crude reaction mixture showed the presence of four peaks A, B, C, D (27.6:4.4:1:7.2) with no starting material remaining. Injection of a mixture of the crude sample and authentic 4c showed that none of the components of the crude mixture had the same retention time as 4c. The retention times of the components were 14.8, 17.8, 20.3, 26.6 min, respectively, while the retention time of 4c was 16.6 min under identical conditions. Mass spectrum (70 eV) m/e (rel. intensity) M^+ 260 (100), 256 (51), 252 (95), 232 (52), 203 (37), 202 (40), 101 (47); ^1H NMR ($DCCl_3$) δ 6.9-7.95 (m, 5, ArH), 3.62 and 3.48 (dd, 1, H, 12c), 3.22-2.5 (m, 7, $ArCH_2$, overlapping), 2.24-1.0 (m, 7, $-CH_2$); ^{13}C NMR ($CDCl_3$) ppm 146.9, 145.6, 145.4, 139.4, 135.5, 134.8, 134.4, 128.0, 127.0, 124.8, 117.4, 116.3, 45.2, 29.8, 27.2, 25.9, 24.9, 23.5, 23.2, 23.2.

Preparation of 1,2,3,6b,7,8,12b,12c-Octahydrobenzo[j]fluoranthene (34). In a glass hydrogenation apparatus[37] fitted for hydrogen recycle were combined 1.0 g (4 m mol) of 15, 0.5 g 10% Pd/C and 200 mL of 95% ethanol. The refluxing mixture was hydrogenated until hydrogen uptake ceased (40 min). A glc analysis showed only one product in addition to a small amount (< 1%) of 15 which remained. The crude mixture was filtered through Dicalite, and the Dicalite was rinsed with small portions of ethyl ether. These solvents were concentrated by rotary evaporation to yield 0.7 g white crystals, mp 88-90°. The melting point of this product mixed with 4b was depressed (83-88°). MS (70 eV) (rel. intensity) M^+ 260 (100), 232 (17), 217 (17), 169 (26.0), 161 (24.0). ^1H NMR ($DCCl_3$) δ 6.86-7.4 (m, 7, ArH), 4.1-3.68 (m, 2, ArCH-CHAr), 3.65-3.26 (m, 1, H-12c), 2.9-2.2 (m, 5, ArCH, overlapping), 2.2-1.4 (m, 5, $-CH_2$); ^{13}C NMR ($CDCl_3$) ppm 144.0, 142.9, 138.5, 135.7, 134.5, 131.1, 128.5, 126.4, 125.3, 125.0, 124.5, 120.0, 47.7, 46.3, 42.9, 27.5, 26.4, 25.7, 24.6, 24.1.

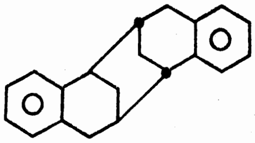
PART II

PHOTODIMERIZATION OF 1,2-DIHYDRONAPHTHALENE AND SUBSEQUENT REDUCTIVE CARBON-CARBON CLEAVAGE DURING METAL-AMMONIA REACTION

CHAPTER V

INTRODUCTION AND HISTORICAL

The dimerization of 1,2-dihydronaphthalene (10a) has been extensively investigated. Dimerization of 10a under acidic conditions results in a variety of dimers which were shown to be useful intermediates in the preparation of benzo[j]fluoranthene (1).[13] The reaction of 10a or naphthalene in sodium and ethylenediamine affords a $C_{20}H_{20}$ dimer, mp 179-180°, whose structure has been shown to be 37 by X-ray crystallographic analysis.[50] Dimer 37 is also formed by the reaction of dihydronaphthalene with potassium tert-butoxide and dimethyl sulfoxide (Me_2SO).[43-46]



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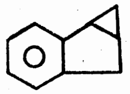
Recent interest has been directed to the photolysis of 10a. In dilute ethanol solution, benzobicyclo[3.1.0]hex-2-ene (38) is formed,[47] whereas irradiation of 10a in hexane gives polymer.[48] However, irradiation of 10a in the presence of benzophenone affords the photodimer 39, mp 71-72°.[49a,b] In addition to a single X-ray crystal analysis which confirms structure 39 as the photodimer, we report techniques leading to improved yields of 39.[50]



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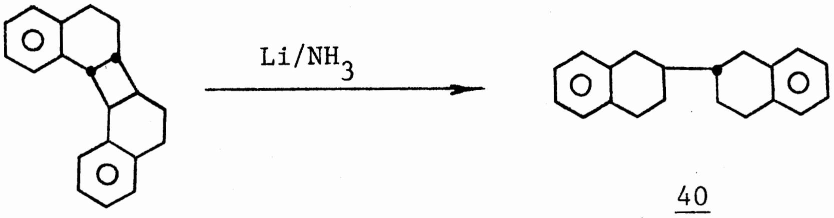
The photodimer 39 was shown to undergo a facile carbon-carbon cleavage in lithium-ammonia solution to 1,1',2,2',3,3',4,4'-octahydro-2,2'-binaphthyl (40) and similar cleavage was observed in the case of the indene photodimer 41 which converted to 2,2'-biindanyl (42).[51] The isomeric dimers 43 and 44 were inert to lithium-ammonia cleavage under comparable reaction conditions.



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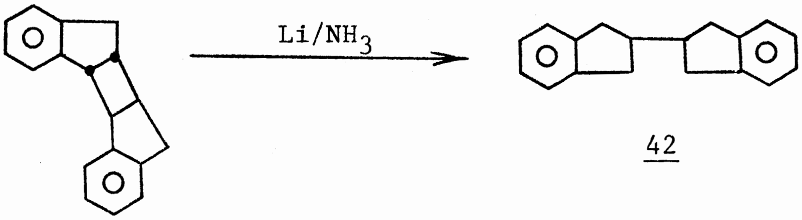

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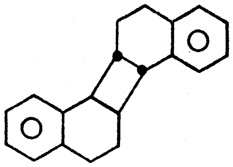

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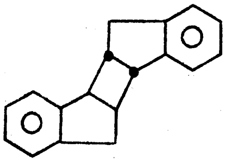

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CHAPTER VI

RESULTS AND DISCUSSION

The benzophenone sensitized irradiation of 10a in ethanol affords dimer 39 in 25% yield.[49a] The reaction suffers from the fact that a heterogeneous system is formed which complicates workup and leads to depressed yield of dimeric product. We therefore investigated the solvent effect on the photolysis of 10a using benzophenone as a sensitizer. The results are summarized in Table VI.

TABLE VI

EFFECT OF SOLVENT ON PHOTODIMERIZATION OF 10a

Moles 10a	Solvent	Moles Benzophenone	Moles 39	Dimeric Pdt. (% yield)
0.077	Neat	0.0055	0.012	32
0.038	Benzene	0.0028	0.017	86
0.038	n-Hexane	0.0028	0.012	62
0.038	Cyclohexane	0.0028	0.015	80

The sensitizer, substrate, and solvent ratio was maintained at 1:5:10. The samples were irradiated in a quartz tube for 42 h at

360 nm using a Rayonet photochemical reactor. These reactions are remarkably free of polyermization.

Salomon and Kochi have shown that perhydrobiphenylene is epimerized through photolysis in dilute acetone solution.[52] We considered that 39 might also be epimerizable, however, using the conditions of Salomon and Kochi, photolysis of 39 in acetone gave no evidence of epimerization. The photodimer 41 was also shown to be stable under the conditions.

An X-ray crystallographic analysis of 39 was performed.[53] A stereoview of the molecule is presented in Figure 1. Bond distances (Å) and bond angles (°) are given in Figures 2 and 3, respectively.

As shown in Figure 1, the molecule consists of five carbon rings fused together with a cyclobutane ring as the central ring. From Figure 1, the cis fusion of the cyclohexane rings to the central cyclobutane ring and the anti conformation of the fused rings are quite evident.

The C(12b)-C(12c) bond is significantly longer [1.579 Å] than a normal C-C single bond. The average bond distance in the cyclobutane ring in fused-ring systems is 1.551 Å.[54] In the present compound this average is 1.563 Å, indicating more strain than in previously determined organically fused cyclobutanes. Most of the strain is located in the C(12b)-C(12c) bond. The significance of this observation is supported by the facile cleavage of the elongated bond during reduction of 39 with lithium or sodium in liquid ammonia giving 1,1',2,2',3,3',4,4'-octahydro-2,2'-binaphthyl (40).[51]

Our structure agrees with that proposed by Dekker and Dekker for the product obtained from the photodimerization of

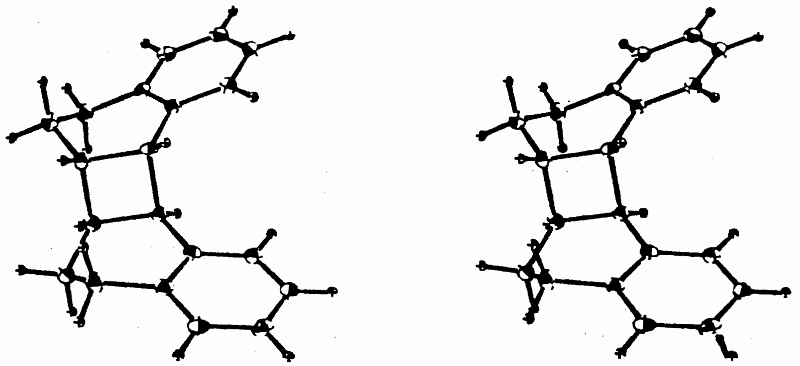


Figure 1. A Stereoview of 39

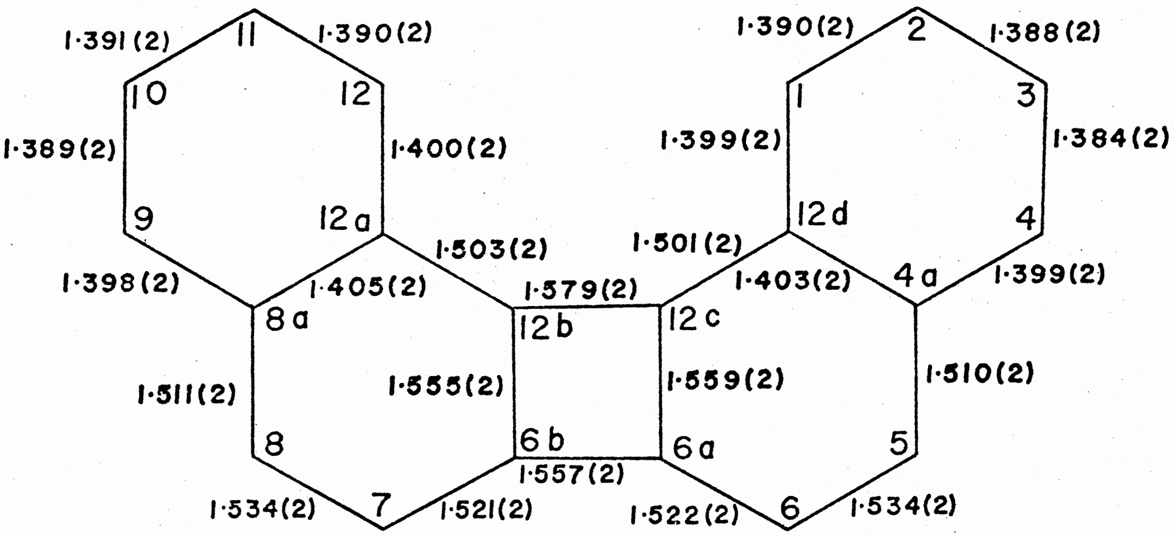


Figure 2. Bond Distances (Å)

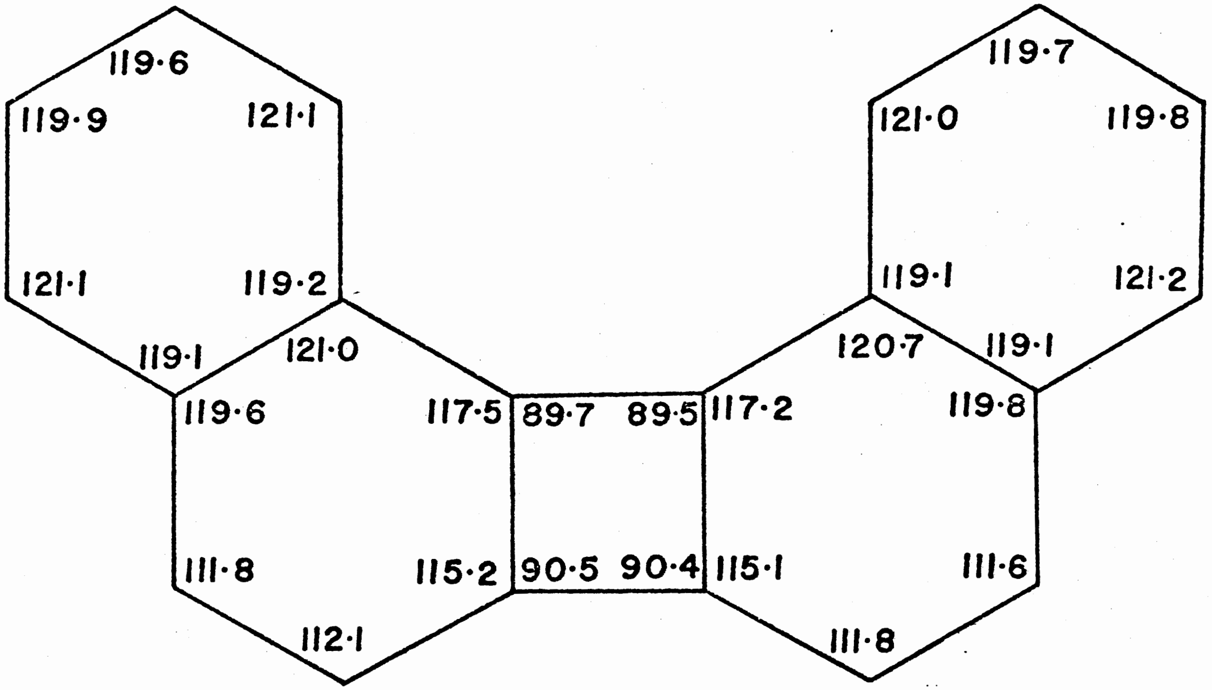
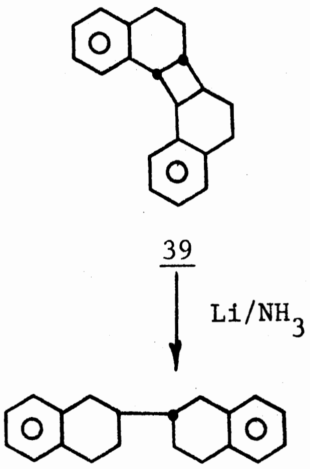


Figure 3. Bond Angles (°). Standard Deviation for all Angles is 0.1°

dihydronaphthalene.[49a,b] Their assignment resulted from analysis of the ^{1}H NMR spectrum of 39 and its oxidation products.

While the majority of metal-ammonia reactions (Birch reductions) do not involve carbon-carbon bond cleavage,[55] we have recently observed that the photodimers 39[50] and 41[56a,b] are selectively cleaved to hydrocarbons 40[63] and 42,[65] respectively, on treatment with lithium or sodium in ether-ammonia. Hydrocarbons 39 and 41 react rapidly and a permanent blue color is not observed until after addition of two equivalents of metal.



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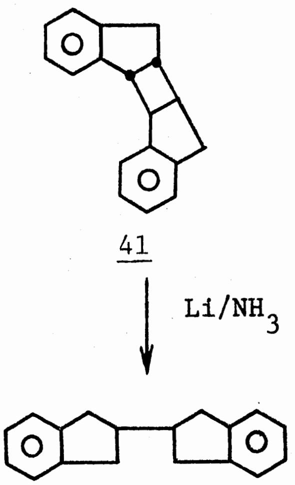
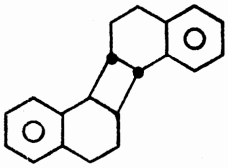


41

42

In contrast, hydrocarbons 43[50] and 44[56a,b] isomers of 39 and 41, respectively, are totally inert to the lithium-ammonia cleavage reaction under comparable conditions. We attribute this spectacular difference in reactivity to a combination of steric strain and contiguous benzylic positions in 39 and 41. The recently obtained

X-ray crystallographic analysis[50] of hydrocarbon 39 shows that the four-membered ring is planar and has an elongated bond (1.579 Å). Interestingly, it is this bond which is cleaved during the lithium-ammonia reduction. We have also determined that 45[57a] is inert to Na-NH$_3$ reductive cleavage. Comparison of structures 39, 43, and 45 suggests that relief of steric strain is involved in the reductive cleavage of 39.



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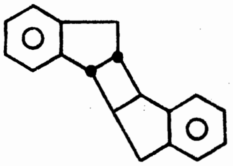

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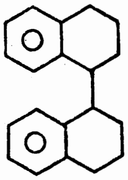

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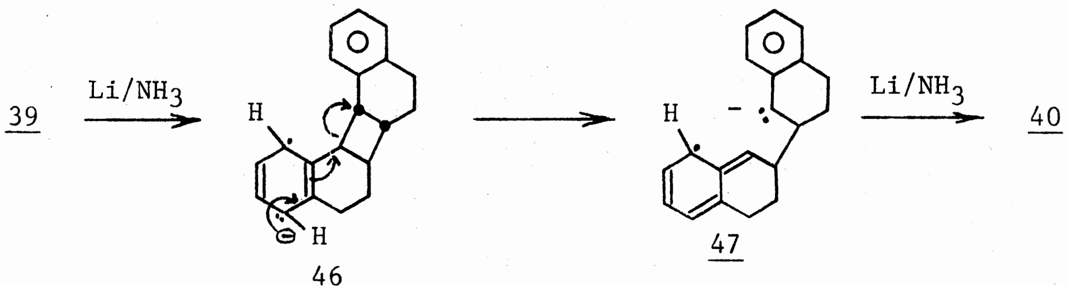
We offer the rationalization shown in Scheme IV as an explanation for the process and feel that while relief of steric strain is important, the availability of a benzylic position to stabilize the anion in structure 47 is an essential factor. Base-induced cleavage of 39 and 41 without the assistance of a reductive process is unlikely, since these hydrocarbons are stable to strong anhydrous base.[57b]

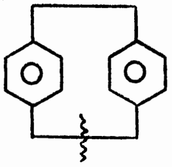
Recent reviews provide a few examples of carbon-carbon reductive cleavage.[55] The major structural features responsible for this effect are vicinal benzylic posotions and/or relief of strain, as implied above. Whereas 1,2-diarylethanes appear to be stable to

SCHEME IV



(One of several resonance contributions)

reduction,[58] tri- and tetraarylethanes are known to cleave.[59] If 48 is considered to be a diarylethane, it should be stable. However, cleavage of the carbon-carbon bond as shown indicates relief of steric strain must be essential.[60] Cleavage of the cyclobutane ring of 49 with sodium to the radical anion of acenaphthalene has been established by ESR studies.[61]



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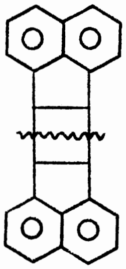

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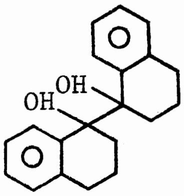
It is of interest that while hydrocarbon 45 is unaffected by the $Li-NH_3$ reaction, the diol 50[62] is cleaved to tetralin in approximately 25% yield. However, the cleavage of 50 could result from a retro-pinacol reaction,[55b] and hence this may be an unfair comparison. Nevertheless, it serves as a good reminder that predictions of reductive cleavage must be made cautiously.

While the reductive cleavage described for 39 and 41 is useful in distinguishing head-to-head and head-to-tail dimers of the type shown by 39, 41, 43, and 44, it is also useful as a stereospecific synthesis of β,β' linked hydrocarbon types illustrated by 40 and 42, which are otherwise difficult to obtain as pure hydrocarbons. Since a single product was obtained in the preparation of 40, we assume that the positions β to the aromatic rings of 39 are not involved in the reductive cleavage. This permits the stereochemical assignment shown for 40, mp 84-85°[63] and hence suggests the meso configuration for hydrocarbon 51, mp 118-199°.[64]



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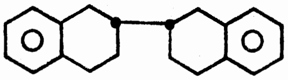

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CHAPTER VII

EXPERIMENTAL

Preparation of 5,6,6aα,6bβ,7,8,12bβ,12cα-Octahydrodibenzo[*a*,*i*]-biphenylene (39). A 70 g (0.53 mol) sample of 10a and 5 g (0.027 mol) of benzophenone were dissolved in benzene. The final volume was 250 mL. This solution was added to a quartz photochemical tube and then irradiated at 26° for 48 h with a Hanovia 450 W, medium-pressure mercury lamp enclosed in a Pyrex filter. The homogeneous solution was concentrated under reduced pressure with a rotary evaporator. The concentrate was distilled (Kugelrohr apparatus) at 145-175° (0.3 mm) to give an oil which crystallized from 95% ethanol to afford 42 g (0.16 mol) of white crystals of 39, mp 70-71°. The filtrate was concentrated, dissolved in an ether-isohexane mixture, and then eluted through a 2.5 x 10 cm column of basic alumina (Merck, activity I). Concentration of this solute gave an additional 18.6 g of 39, mp 70-72°, for an overall yield of 82%. The mass spectrum (70 eV) showed a parent ion at m/e 260. The ^1H NMR spectrum is consistent with that previously reported.[49a,b]

Effect of Solvent on Photodimerization of 10a. Samples of 10a in quartz tubes were prepared as follows: one tube contained 10 g (0.077 mol) of 10a and 1.0 g benzophenone; the other three tubes recieved a 50% (v/v) solution containing 5.0 g (0.38 mol) of 10a, an equal volume of the appropriate solvent and 0.5 g of benzophenone.

The tube contents were thoroughly mixed and then sealed under nitrogen with a Neoprene stopper. These tubes were placed in a 432 N Rayonet photochemical reactor, model RPR 100, and irradiated at room temperature for 42 h at 350 nm. The yields are summarized in Table VI.

Attempted Epimerization of 39. A solution of 0.5 g photodimer 39 in 20 mL of acetone was placed in a quartz tube capped with a Neoprene stopper. The solution was irradiated at room temperature for 72 h in a Rayonet photochemical reactor model RPR 100, at 350 nm. After photolysis, the acetone was evaporated from the mixture. The resulting residue was recrystallized and the white crystals were shown to be unchanged by mixture melting point. A GC analysis of the mother liquor showed 39 accompanied by <1% of 10a. No new peaks were observed.

Li-NH_3 Reductive Cleavage of cis,anti,cis-5,6,6aα,6bβ,7,8,12bβ,-12cα-Octahydrodibenzo[*a*,*i*]biphenylene (39) to 1,1',2,2',3,3',4,4'-Octahydro-2,2'-binaphthyl (40). To a solution of 2.0 g (7.2×10^{-3} mol) of 39, mp 71-72°, in 10 mL of dry ether and 50 mL of ammonia was added 0.11 g (1.57×10^{-2} g-atoms) of lithium in small pieces. After addition, the blue color persisted. After 1 h, the reaction was quenched with anhydrous ammonium chloride, ammonia was allowed to evaporate, and 200 mL of water was added to the residue. The reaction mixture was extracted (ether, 3 x 100 mL) and the organic layer was washed with 50 mL portions of 10% sulfuric acid, Claisen's alkali,[66] and water. The ether layer was dried ($MgSO_4$) and concentrated to give 1.95 g of a crystalline product, mp 73-78°. GC analysis[67a] of the product showed less than 2% of unreacted 39 and a major peak corresponding to 40.[63] Recrystallization of the crude product from isohexane gave 1.2 g (60% yield) of white needles, mp 84.5-85°. A second crop of 0.5 g of less pure material was obtained by concentration of the mother liquor. The total yield was 85%. The product had an identical ^1H NMR spectrum and undepressed melting point on mixing with a known sample of 40.[63]

Li-NH3 Reductive Cleavage of 4bβ,4cα,9,9aα,9bβ,10-Hexahydrocyclobuta[1,2-a:4,3-a']diindene (41) to 2,2'-Biindanyl (42). To a solution of 1.0 g (4.3×10^{-3} mol) of the photodimer 41, mp 110°, in 10 mL of ether and 50 mL of ammonia was added 0.65 g (9.3×10^{-3} g-atoms) of lithium. The reaction and product isolation was carried out as described above to give 1.0 g of a solid. GC analysis[67b] of this solid showed a major peak and no unreacted 41. Recrystallization of the product from acetone gave 0.8 g (80% yield) of white crystals of 42, mp 165-167°. [lit.[65a] mp 165-166.5°]; ^1H NMR ($CDCl_3$) δ 7.10 (m, 8, ArH), 3.20-2.90 (m, 4, $ArCH_2$), 2.83-2.30 (m, 6, $ArC\underline{H}_2C\underline{H}$); mass spectrum (70 eV) showed *m/e* 234.

Hydrogenation of 1,1',2,2',3,3',4,4'-Octahydro-1,1'-binaphthyl-1,1'-diol (50) to 1,1',2,2',3,3',4,4'-Octahydro-1,1'-binaphthyl (45). A solution of 15 g (0.051 mol) of the pinacol 50[62] in 500 mL of acetic acid and 1.5 g of 10% Pd/C was shaken in a Parr hydrogenation vessel under 50 psig hydrogen atmosphere at 60-70° for 43 h. The reaction mixture was filtered and concentrated under reduced pressure. The crude hydrogenation product was purified by chromatography on basic alumina using isohexane as eluant. The combined hydrocarbon fractions were distilled (Kugelrohr, 160-170°, 0.2 mm) to give 3.5 g (0.013 mol, 26% yield) of a clear, colorless oil;[57a,67c] ^1H NMR ($CDCl_3$) δ 7.31-6.86 (m, 8, ArH), 3.72-3.20 (m, 2, ArCH), 2.65 (t, 4,

$ArCH_2$, J=4 Hz) and 2.13-1.04 (m, 8, $ArCH_2C\underline{H}_2C\underline{H}_2$); mass spectrum (70 eV) showed *m/e* 262.

Reaction of 50 with Sodium-Ammonia. A solution of 0.8 g (0.0027 mol) of 50, mp 185-189°, [lit.[62] mp 191°] in 50 mL of THF was added to a solution of 50 mL of ammonia and 0.5 g (0.22 g-atoms) of sodium. After 1 h, the reaction was quenched by addition of solid ammonium chloride and the products isolated as previously described. The resulting oil was analyzed by GC[67c] and shown to contain 25% tetralin.

REFERENCES AND NOTES

1. (a) R. H. Hunt and M. J. O'Neal, "Encyclopedia of Chemical Technology", 2nd Ed., Vol. 14, R. E. Kirk and D. J. Othmer (Eds.), The Interscience Encyclopedia, Inc., New York, 1967, p 849; (b) E. Clar, "Polycyclic Hydrocarbons", Vol. 1, Academic Press, London, 1964, p 192.

2. E. J. Eisenbraun, *Proc. Amer. Petroleum Inst.*, **51**, 331 (1971).

3. J. Borneff and H. Kunte, *Arch. Hyg. Bakteriol.*, **147**, 401 (1963).

4. (a) T. Aczel, Q. J. Foster, and J. H. Karchmer, *Amer. Chem. Soc., Div. Fuel Chem., Prepr.*, **13**, 8 (1969); (b) L. Steubing, *Angew. Bot.*, **45**, 1, (1971); (c) M. L. Lee, M. Novotny, and K. D. Bartle, *Anal. Chem.*, **48**, 405 (1976).

5. All temperature measurements cited are recorded in degrees Celsius. Melting points obtained in this laboratory were obtained on a Hoover-Thomas melting point apparatus and are uncorrected.

6. G. M. Badger, S. D. Jolad, and T. M. Spotswood, *Aust. J. Chem.*, **17**, 771 (1964).

7. G. M. Badger, R. W. K. Kimber, and J. Novotny, *Aust. J. Chem.*, **17**(**7**), 778 (1964).

8. G. M. Badger, R. W. K. Kimber, and J. Novotny, *Aust. J. Chem.*, **15**, 616 (1962).

9. G. M. Badger, S. D. Jolad, and T. M. Spotswood, *Aust. J. Chem.*, **19**, 85 (1966).

10. A. Dansi and C. Ferri. *Gazz. Chem. Ital.*, **71**, 648 (1941).

11. C. D. Nenitzescu and M. Avram, *J. Am. Chem. Soc.*, **72**, 3486 (1950).

12. (a) J. von Braun and G. Kirschbaum, *Ber.*, **54**, 597 (1921); (b) N. D. Scott and J. F. Walker, *Industrial and Engineering Chemistry*, 312 (1940).

13. D. V. Hertzler and E. J. Eisenbraun, *Chem. and Ind.*, 877 (1969).

14. N. Campbell, N. M. Khanna, and A. Marks, *J. Chem. Soc.*, 2511 (1951).

15. R. F. Evans and J. C. Smith, *J. Chem. Soc.*, 798 (1954).

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

17. Amberlyst-15 and Amberlyst-XN1011 are macroreticular sulfonated styrene-divinylbenzene copolymer resins. These catalysts were obtained from Rohm and Haas Co., Philadelphia, PA 19105, and literature describing their use and properties may be obtained from this source.

18. E. D. Bertman, *Chem. Rev.*, **29**, 529 (1941).

19. A. R. Taylor, G. W. Keen, and E. J. Eisenbraun, *J. Org. Chem.*, **42**, 3477 (1977).

20. (a) R. Fittig and H. Erdmann, *Ann.*, **216**, 817 (1883); (b) H. Stobbe and G. Posnjak, *Ann.*, **371**, 287 (1909); (c) R. Stoermer and J. Kootz, *Ber.*, **61B**, 2330 (1928); (d) J. Risi and D. Gauvin, *Can. J. Research*, **B14**, 255 (1936); (e) P. E. Spoerri and M. J. Rosen, *J. Am. Chem. Soc.*, **72**, 4918 (1950); (f) M. J. Rosen, *Org. Syn.*, *Coll. Vol. 4*, 665 (1963).

21. A. R. Taylor, M.S. Thesis, Oklahoma State University, (1973).

22. "Ion Exchange Catalysis and Matrix Effects", A. R. Pitochelli, Fluid Process Chemicals, Rohm and Haas Co., Philadelphia, PA 19105.

23. M. Crawford and V. Supanaker, *J. Chem. Soc.* (*c*), 2328 (1968).

24. K. D. Cowan, L. L. Ansell, and E. J. Eisenbraun, *Chem. and Ind.*, 957 (1976).

25. R. A. Friedel, *Appl. Spectroscopy*, **11**, 13 (1957).

26. J. J. Pappas, W. P. Keavney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966).

27. L. J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley and Sons, New York, 1975, p 133.

28. P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77**, 2806 (1955).

29. Advances in Chemistry, Ozone Chemistry and Technology, Vol. 21, American Chemical Society, Washington, D.C., 1959, p 135.

30. R. C. Fuson, M. D. Armstrong, W. E. Wallace, and J. W. Kniesly, *J. Am. Chem. Soc.*, **66**, 1274 (1944).

31. J. B. Stothers, Organic Chemistry, Vol. 24, Carbon-^{13}NMR Spectroscopy, A. T. Bloomquist, H. Wasserman (Ed.), Academic Press, New York, 1972, p 271.

32. (a) R. Criegee, A. Kerchero, and H. Zinke, *Ber.*, **88**, 1878 (1955); (b) R. W. Murray and R. D. Youssefyeh, *J. Am. Chem. Soc.*, **88**, 3655 (1966).

33. R. Criegee and G. Lohaus, *Chem. Ber.*, **16**, 1 (1953).

34. P. S. Bailey, *Ber.*, **87**, 993 (1954).

35. R. Criegee, P. de Bruyn, and G. Lohaus, *Ann.*, **583**, 19 (1953).

36. A. Dansi and M. Reggiani, *Gazz. Chem. Ital.*, **78**, 801 (1948).

37. K. D. Cowan and E. J. Eisenbraun, *Chem. and Ind.*, 221 (1976).

38. H. Hoch and S. Lang, *Ber.*, **75B**, 313 (1942).

39. Mass spectra were obtained on a CEC 21-110B instrument.

40. ^{13}C NMR spectra were recorded at 25.2 MHz in the FT mode on a Varian XL-100A interfaced with a 12K Nicolet 1080 computer system. Spectra were run in $CDCl_3$ using a deuterium lock and are reported in ppm downfield from TMS (δ $CDCl_3$ = 76.9 ppm). ^{1}H NMR spectra were recorded on the same instrument and are reported in terms of δ relative to internal TMS.

41. IR spectra were obtained using a Beckman IR-5A instrument.

42. UV spectra were obtained on a Cary 14 spectrophotometer.

43. Substantial portions of the material presented in Part II of this thesis have either been published, or the manuscript is in progress. Thus, the writing style reflects the brevity found in many of the leading chemical journals.

44. See Part I of this thesis.

45. E. J. Eisenbraun, L. L. Ansell, T. K. Dobbs, L. E. Harris, D. V. Hertzler, and P. H. Ruehle, *J. Org. Chem.*, **41**, 2910 (1976).

46. L. E. Harris, Ph.D. Thesis, Oklahoma State University, Stillwater, Oklahoma, 1971.

47. H. Kleinhuis, R. L. C. Wijting, and E. Havinga, *Tetrahedron Lett.*, 255 (1971).

48. K. Salisbury, *Tetrahedron Lett.*, 737 (1971).

49. (a) J. Dekker and T. G. Dekker, *J. S. Afr. Chem. Institute*, **26**, 25 (1973); (b) *ibid.*, **28**, 122 (1975).

50. J. E. Burks, Jr., Dick van der Helm, T. K. Dobbs, L. L. Ansell, P. H. Ruehle, and E. J. Eisenbraun, *Acta Cryst.*, **34B**, 496 (1978).

51. P. H. Ruehle, T. K. Dobbs, L. L. Ansell, Dick van der Helm, and E. J. Eisenbraun, *J. Org. Chem.*, **42**, 1098 (1977).

52. R. G. Salomon and J. K. Kochi, *Tetrahedron Lett.*, 4387 (1973).

53. A complete description of the X-ray determination is published[50] and is omitted here.

54. F. A. Cotton and B. A. Frenz, *Tetrahedron*, **30**, 1587 (1974).

55. (a) R. L. Augustine, Ed., "Reduction", Marcel Dekker, Inc., New York, 1978; (b) A. J. Birch and G. Subba Rao, "Advances in Organic Chemistry", Vol. 8, E. C. Taylor, Ed., John Wiley and Sons, Inc., New York, 1972, pp 1-65.

56. (a) W. Metzner and D. Windisch, *Ann.*, **730**, 111 (1970); (b) J. Bowyer and Q. N. Porter, *Aust. J. Chem.*, **19**, 1455 (1966).

57. (a) Unpublished work this laboratory. We assume to have a mixture of *meso* and *dl* isomers; (b) Hydrocarbons *39* and *41* were separately treated with potassium *tert*-butoxide in anhydrous dimethylsulfoxide at room temperature for 2.5 h and recovered unchanged.

58. C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.*, **56**, 1133 (1934).

59. Ref. 2a, p 106.

60. J. L. Marshall and T. K. Folsom, *Tetrahedron Lett.*, 757 (1971).

61. von F. Gerson and B. Weidmann, *Helv. Chim. Acta*, **49**, 1837 (1966).

62. E. B. Barnett and C. A. Lawrence, *J. Chem. Soc.*, 1104 (1935).

63. (a) L. Reggel, H. W. Sternberg, and I. Wender, *Nature*, **190**, 81 (1961); (b) E. J. Eisenbraun, R. C. Bansal, D. V. Hertzler, and W. P. Duncan, *J. Org. Chem.*, **35**, 1265 (1970).

64. (a) W. Huckel and M. Wartini, *Ann.*, **686**, 40 (1965); (b) R. C. Bansal, Ph.D. Thesis, Oklahoma State University, 1966; (c) P. Markov, D. Lassarov, and C. Ivanov, *Ann.*, **704**, 126 (1967).

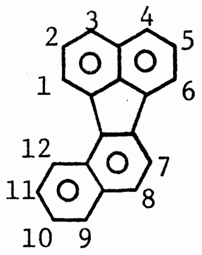
65. (a) W. Luttke and J. Grussdorf, *Ber.*, **98**, 140 (1965); (b) F. Fichter, and H. Stenzl, *Helv. Chim. Acta*, **22**, 425 (1939).

66. L. F. Fieser and Mary Fieser, "Reagents for Organic Synthesis". Vol. I, John Wiley and Sons, Inc., New York, 1967, p 153.

67. (a) An 8' x ¼" column of 80-100 mesh Chromosorb G coated with 7% UCW-98 at 230° was used; (b) Ref. 67a at 190°; (c) A 6' x ¼" column of 80-100 mesh, AW-DMCS-treated Chromosorb G coated with 3.5% N,N'-bis(*p*-methoxybenzylidine)-α,α'-b-toluidine at 220° was used.

APPENDIX

GLOSSARY OF STRUCTURES



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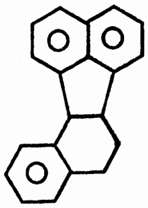

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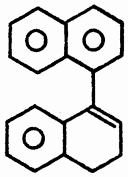

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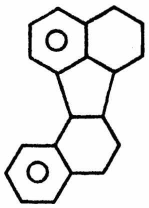

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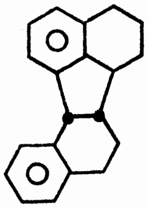

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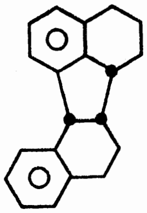

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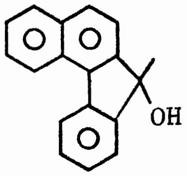

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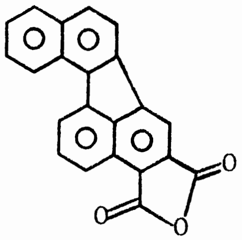

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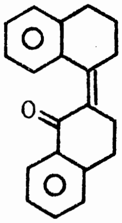

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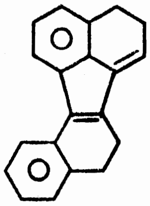

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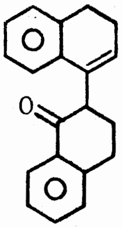

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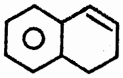

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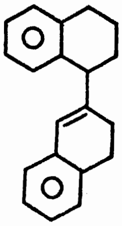

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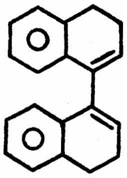

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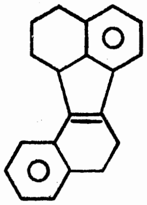

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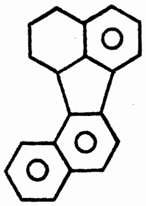

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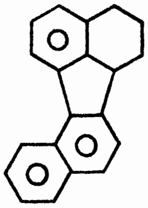

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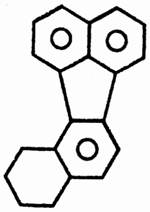

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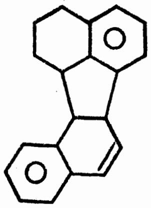

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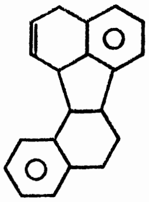

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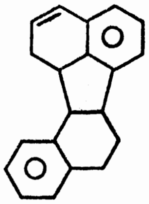

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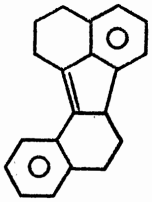

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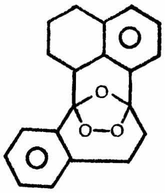

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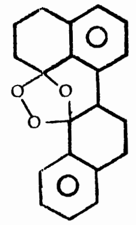

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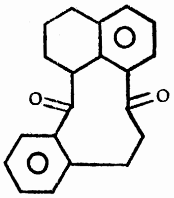

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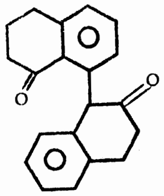

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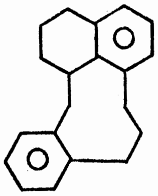

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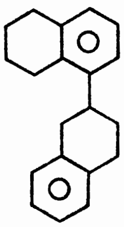

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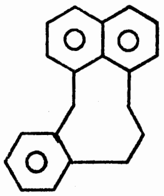

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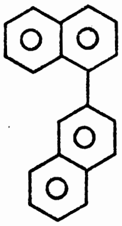

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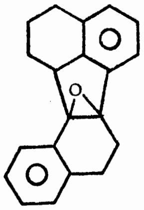

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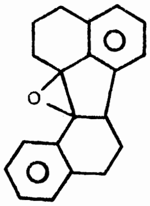

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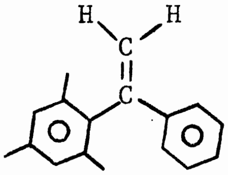

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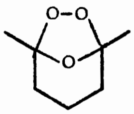

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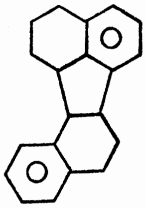

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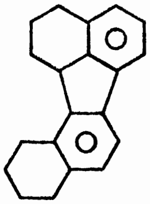

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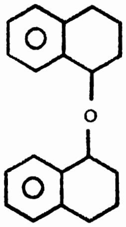

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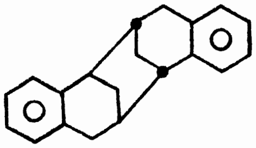

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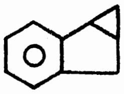

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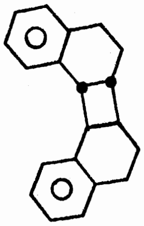

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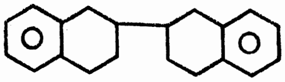

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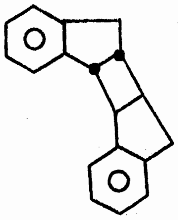

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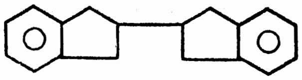

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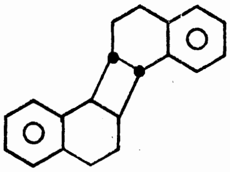

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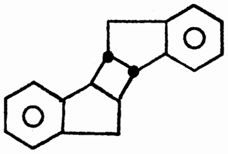

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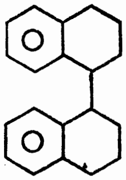

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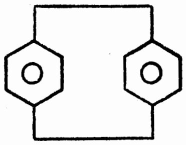

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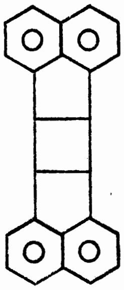

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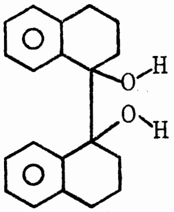

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VITA 2

Thomas Keith Dobbs

Candidate for the Degree of

Master of Science

Thesis: I. ACID-CATALYZED DIMERIZATION OF 1,2-DIHYDRONAPHTHALENE
II. PHOTODIMERIZATION OF 1,2-DIHYDRONAPHTHALENE AND SUBSEQUENT REDUCTIVE CARBON-CARBON CLEAVAGE DURING METAL-AMMONIA REACTION

Major Field: Chemistry

Biographical:

Personal Data: Born in Wellington, Texas, December 20, 1950, the son of Mr. Malcolm N. and Vivian P. Dobbs.

Education: Graduated from Borger High School, Borger, Texas, in 1969; received the Bachelor of Science degree from Southwestern Oklahoma State University, Weatherford, Oklahoma in May, 1973, with a major in chemistry and minor in mathematics; completed requirements for the Master of Science degree at Oklahoma State University in July, 1978.

Professional Experience: Analytical Chemist, Camex, Inc., Borger, Texas, 1973-1974; Graduate Teaching Assistant, Oklahoma State University, 1974; Graduate Research Assistant, Oklahoma State University, American Petroleum Institute, 1974; Graduate Research Assistant, Environmental Protection Agency, Oklahoma State University, 1975-1977; Graduate Research Assistant, Energy Research and Development Administration, Oklahoma State University, 1977-1978; Member of the American Chemical Society.