I. SYNTHESIS OF 4-, 5-, AND 6-RING POLYNUCLEAR AROMATIC HYDROCARBONS

II. SODIUM-AMINE REACTIONS OF NAPHTHALENES: CYCLODIMERIZATION AND REDUCTIVE CYCLODIMERIZATION

By

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TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

PART II

LIST OF TABLES

Chapter Page

PART II

LIST OF FIGURES

PART I

SYNTHESIS OF 4-, 5-, AND 6-RING POLYNUCLEAR AROMATIC HYDROCARBONS

CHAPTER I

INTRODUCTION

Polynuclear aromatic (PNA) hydrocarbons have received increased attention in recent years because they occur naturally in petroleum[1a] and coal,[1b] are formed during petroleum refining[2a] and coal liquifaction,[2b] are synthesized by living organisms,[3] and are found as pyrolysis products[4a,b] from fossil fuel and tobacco combustion. A need has developed for pure PNA hydrocarbons[5] for use as refining, pollution, and thermodynamic standards as well as for use in studying their carcinogenic and mutagenic properties.[6a,b,c,d] Preparation of compounds in this study is part of a hydrocarbon synthesis program at Oklahoma State University, Stillwater, Oklahoma.[7]

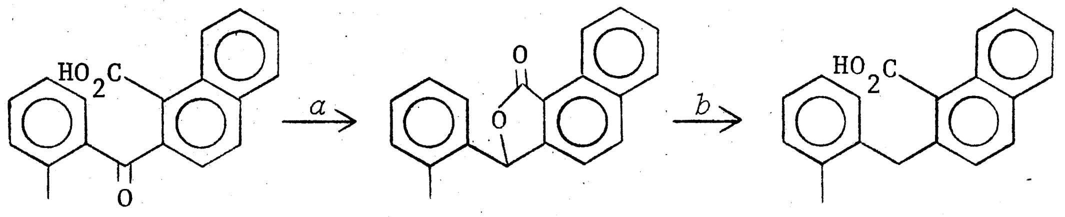
CHAPTER II

HISTORICAL

Naphthalene or naphthalene-like compounds are frequent precursors to PNA hydrocarbons.[8] The products from electrophilic substitution of naphthalene or substituted naphthalenes using either Lewis or Bronsted acid catalysis provide convenient starting materials for anthracenes, phenanthrenes, and higher fused ring systems.[9,10] Aldol condensation products of 1-tetralone and other dicyclic carbonyl compounds also provide excellent PNA source materials.[11a,b]

Friedel-Crafts or aldol reaction products often contain a carbonyl or hydroxyl at the benzylic position. High yield removal of this oxygen is usually a key step in total PNA synthesis.[12] Several methods of deoxygenation--Wolff-Kishner, Clemmensen, catalytic hydrogenolysis, etc.--are widely used[13a,b] but sometimes fail as the complexity of the reactant increases.[13c] Hydriodic acid-red phosphorus (HI-P_4)[14] in refluxing acetic acid provides an attractive alternative.

With few exceptions,[15a,b,c] HI-P_4 is most useful for deoxygenation at the benzylic position. The oxygens of di- and trinaphthyl carbinols[16] and 9-fluorenols[17a,b,c] were removed effectively with HI-P_4. 1,2'-Dinaphthylketone,[16] benzophenones,[18,19] and a substituted fluorenone[20] were also easily deoxygenated. The ketoacid <u>1</u> was reduced to the lactone <u>2</u> in 86% yield using potassium iodide and phosphoric acid. This lactone then was reduced further to acid <u>3</u> using zinc and alkali.[21]



1 2 3

[a] KI, CH_3CO_2H, P_4, H_3PO_4.
[b] Zn, NaOH.

The reduction of 3-benzoylpropionic acid gave 4-phenylbutanoic acid in 25% yield, possibly through a lactone intermediate, as well as a 15% yield of 1-tetralone.[22] Substituted 4-phenyl-3-butenoic acids can be reduced, cyclized to the tetralone, and then deoxygenated in a single, high-yield step to the substituted tetralin using syrupy phosphoric acid in conjunction with HI-P_4.[23]

The formation of a lactone product suggests alcohol intermediates for carbonyl deoxygenations. Hydroxyl displacement can be accompanied by cationic induced skeletal rearrangements.[24,25] Iodine is needed as a hydrogen carrier and is necessary in only catalytic amounts in the presence of red phosphorus and water. The red phosphorus is oxidized to phosphate when heated with the above reagents and oxygenated organic substrate.[22]

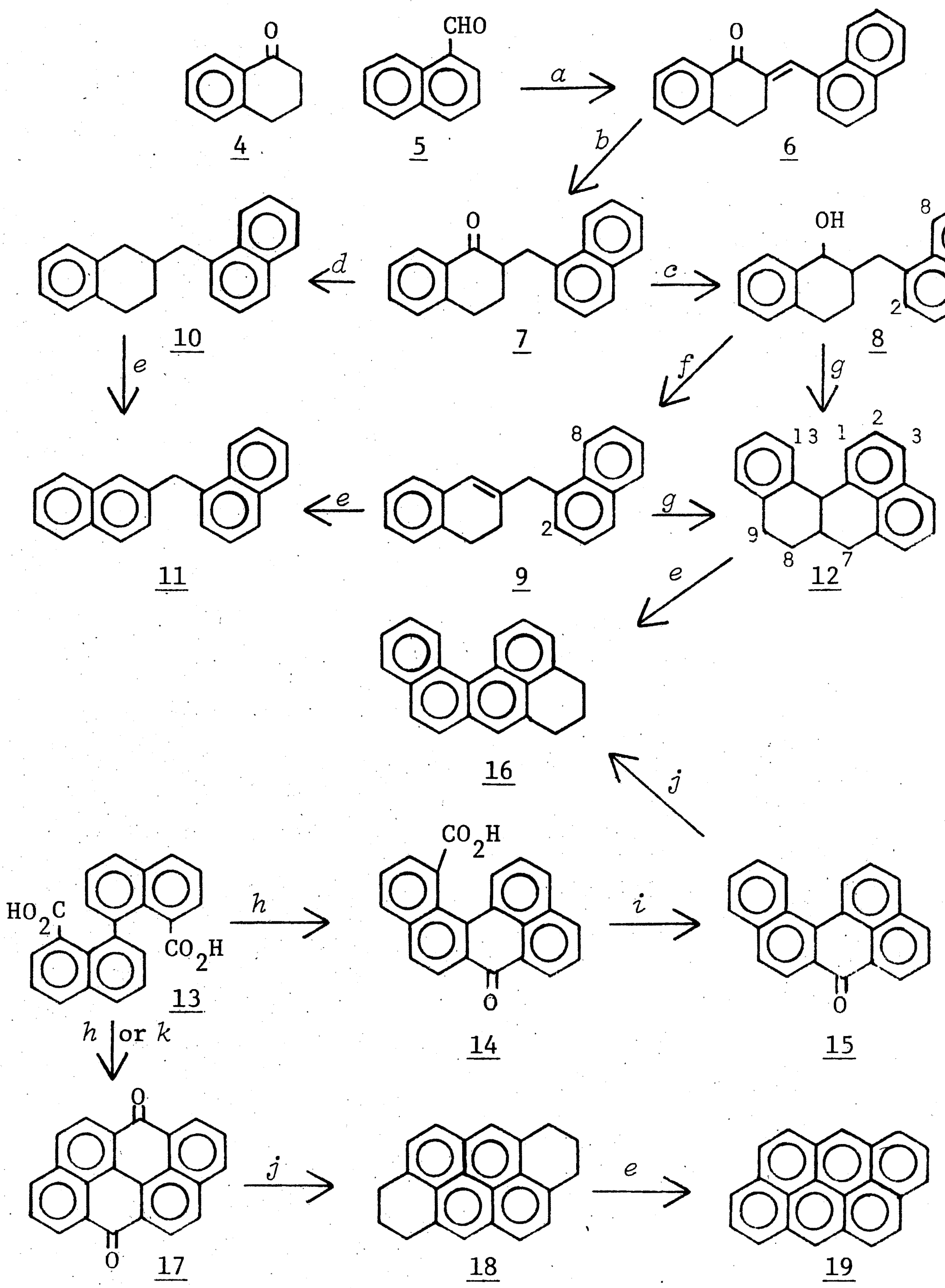
CHAPTER III

DISCUSSION AND RESULTS

5,6-Dihydro-4*H*-dibenz[*a*,*kl*]anthracene[26] (16), shown in Figure 1, is the product isolated after dehydrogenation of 7a,8,9,13b-tetrahydro-7*H*-dibenz[*a*,*kl*]anthracene (12). Hydrocarbon 16 is also the product obtained after reduction of ketone 15 using HI-P_4.[27]

The preparation of 6, a precursor to the new hydrocarbons 9, 10, and 12, is readily accomplished through aldol condensation of 4 and 5 in 73% yield. Hydrogenation of 6 to 7 occurred in 67% yield. Of the two routes shown for converting 7 to 11,[26] the preferred approach is via 10,[26] since a 62% yield is obtained in two steps. The other route involving reduction[28] of 7 to 8 occurred in 49% overall yield. However, 8 and 9[26] can be conveniently cyclized with Amberlyst-15[29] sulfonic acid resin (A-15) to the new hydrocarbon 12.[26] That cyclization occurs predominantly at C-8 of the naphthalene ring of 8 or 9, as opposed to C-2, was established by Pd/C dehydrogenation of 12 to hydrocarbon 16, as previously mentioned.

The *cis* assignment of protons at C-7a and C-13b of 12 is preferred because of the observed small coupling constant ($J_{7a,13b} = 4.2$ Hz) for the proton at C-13b and because of the lack of a significant low-field shift for the absorptions due to C-1 and C-13 protons. The models of the two conformers of 12 in the *cis* configuration show dihedral angles at 57° and 66° (calculated[30] coupling constant for intermediate angle



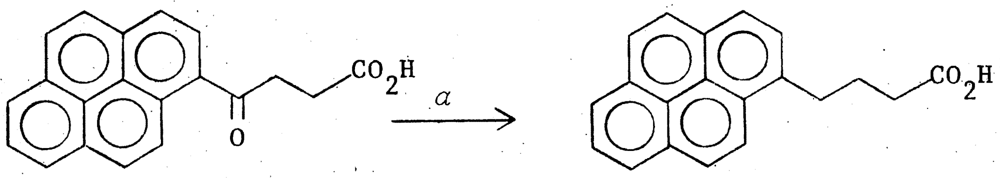
$^{a}OH^{-}$, C_2H_5OH. ^{b}Pd/C, H_2, C_2H_5OH. ^{c}DIBAH, $C_6H_5CH_3$. $^{d}NH_2NH_2$, OH^{-}, glycol, Δ. ^{e}Pd/C, Δ. $^{f}CH_3CO_2H$, Δ. ^{g}A-15, $C_6H_5CH_3$, Δ. $^{h}ZnCl_2$, CH_3CO_2H, Δ. ^{i}Cu, quinoline, Δ. ^{j}HI, P_4, CH_3CO_2H, Δ. ^{k}PPA, Δ.

Figure 1. Synthesis of Dinaphthylmethane (11), 5,6-Dihydro-4*H*-dibenz[*a*,*kl*]anthracene (16), and 1,2,3,7,8,9-Hexahydro[*def*,*mno*]chrysene (18)

of 60°, J = 2.5 Hz), whereas the model of the *trans* isomer shows a near diaxial relationship (calculated[30] coupling constant for 180°, J = 15.7 Hz) between protons at C-7a and C-13b. The model of the *trans* isomer of 12 also shows interaction for C-1 and C-13 protons, and a downfield aromatic shift similar to that noted for 16 should be observed. The absence of this shift as well as the good agreement between calculated and observed coupling constants for the C-13b proton leads us to believe that the *cis* isomer of 12 was obtained.

Monocyclization of diacid 13 with subsequent decarboxylation gives ketone 15,[27] a precursor to hydrocarbon 16. However, 115% polyphosphoric acid (PPA) effects cyclization of both carboxyl groups of 13 to give anthanthrone (17).[31] The new hydrocarbon 18, an intermediate in the synthesis of anthanthrene (19),[32] was isolated after deoxygenation of diketone 17 with HI-P_4. The structure of 18 was determined by comparison of its uv spectrum with that of pyrene. These spectra were in good agreement and the expected bathochromic shifts of absorption maxima were observed.

The deoxygenation of keto acid 20 to 21 with HI-P_4 is shown below. Attempts to prepare 21, a crucial intermediate in the synthesis of



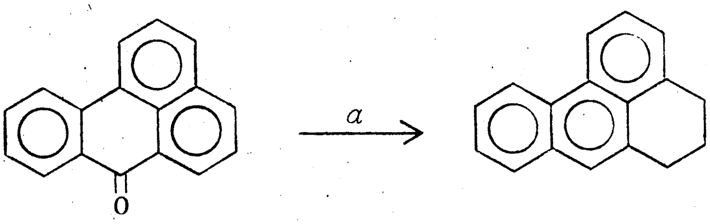
20

21

^{a}HI, P_4, CH_3CO_2H, Δ.

benzo[*a*]pyrene, by other methods of reduction (Wolff-Kishner and Pd/C hydrogenolysis) afforded little product and caused some side-chain cleavage.

Another example of the utility of HI-P_4 is the reduction of benzanthrone (<u>22</u>)[33] to <u>23</u>[34] in 74% yield. Attempts to reduce <u>22</u> using the



<u>22</u> <u>23</u>

[a] HI, P_4, CH_3CO_2H, Δ.

Wolff-Kishner method or its modifications, Raney nickel catalyzed hydrogenation, the Clemmensen procedure, or zinc dust distillation, were reported to be unsatisfactory.[35] Aluminum chloride-lithium aluminum hydride reduction[36] was also ineffective.

CHAPTER IV

EXPERIMENTAL

3,4-Dihydro-2-(1-naphthylmethylene)-1(2H)-naphthalenone (6). — A 146-g (1.0 mol) sample of 4 and a 156-g (1.0 mol) sample of 5 were dissolved in 3 ℓ of stirred 95% ethanol in a 5-ℓ flask under a nitrogen atmosphere. Sodium hydroxide (40 g, 1 mol) in 75 ml of water was then added. A blue color developed which faded in 15 min as crystals formed in the solution. Stirring was continued for 5 hr at 20-28°. The reaction mixture was filtered and the collected solid was washed with 95% ethanol (2 x 250 ml) and water (2 x 250 ml). These wet crystals were then dissolved in toluene, and the water layer was separated, the solution was dried ($MgSO_4$), and the volume was reduced by rotary evaporation until the product crystallized. The cooled suspension was then filtered to give 208 g (0.73 mol, 73%) of white, granular crystals of 6: mp 131-133° [lit.[37] 131°]; mass spectrum (70 eV) m/e (rel intensity) 284 (M^+, 63), 283 (100), 165 (18), 141 (9), 128 (11), and 90 (13); pmr ($CDCl_3$) δ 8.34 (s, 1, vinylic), 8.26-8.12 (m, 1, ArH), 8.04-7.68 (m, 3, ArH), 7.56-7.05 (m, 7, ArH), and 2.82 (s, 4, $ArCH_2CH_2$).

3,4-Dihydro-2-(1-naphthylmethyl)-1(2H)-naphthalenone (7). — The purified ketone 6 (85 g, 0.297 mol) was added to a 1-ℓ stainless steel hydrogenation vessel containing 750 ml of 95% ethanol and 2.2 g of 10% Pd/C catalyst.[38a] The vessel was evacuated, hydrogen was introduced, and the vessel was then shaken at 10 psi for five hr.[38b] Crystals that formed during the hydrogenation were dissolved in toluene and this solution was then filtered through Dicalite to remove catalyst. The filtrate was rotary evaporated to yield a dark red oil. This oil was eluted with toluene through a 5-cm (O.D.) column containing layers (top to bottom) of 2 cm of basic alumina, 3 cm of acidic alumina, and 5 cm of silica to give 57 g (0.2 mol, 67%) of colorless 7: mp 89.0-90.5° [lit.[39] 92-93°]; mass spectrum (70 eV) m/e (rel intensity) 286 (M^+, 44), 142 (16), 141 (100), 128 (14), 115 (26), and 90 (20); pmr ($CDCl_3$) δ 8.21-7.94 (m, 2, ArH), 7.84-7.52 (m, 2, ArH), 7.48-6.88 (m, 7, ArH), 4.15 (q, 1, ArCOCH), 2.96-2.42 (m, 4, $ArCH_2$) and 2.05-1.37 (m, 2, $ArCH_2\underline{CH_2}$).

1,2,3,4-Tetrahydro-2-(1-naphthylmethyl)-1-naphthol (8). — A sample (286 g, 1 mol) of 7 dissolved in toluene (1.7 ℓ) was added to a stirred solution of DIBAH[28] (288 g, 2 mol) and dry toluene (1 ℓ) at 10° over a 40-min period. The reaction was stirred for an additional 60 min before ethyl acetate (100 cc) was carefully added. The contents of the flask were poured onto ice (2 kg) and conc. HCl (700 ml) was added. The layers were separated and the toluene extract was washed with water (3 ℓ), dried ($MgSO_4$), and concentrated. Petroleum ether[40] (1.5 ℓ) was added to precipitate a solid which was collected by filtration and than dried to give 262 g (0.91 mol, 91%) of colorless 8: mp 113-115° [lit.[41] 114°]; mass spectrum (70 eV) m/e (rel intensity) 288 (M^+, 10), 270 (56), 146 (65), 142 (100), 141 (89), and 115 (59): pmr ($CDCl_3$) δ 8.22-7.97 (m, 1, ArH), 7.89-6.82 (m, 10, ArH), 4.50 (d, 1, ArC$\underline{H}$OH, J=8 cps), 3.70, 3.57 (d of d, 1, ArCHOHC$\underline{H}$, J=5 cps), 2.88-2.52 (m, 4, $ArCH_2$), 2.24-1.32 (m, 2, $ArCH_2\underline{CH_2}$), and 1.99 (s, 1, ArCHO$\underline{H}$).

2-(1-Naphthylmethyl)-3,4-dihydronaphthalene (9). — A sample (70 g, 0.24 mol) of 8 was dissolved in 225 ml of acetic acid and was then heated at reflux for 24 hr. The acetic acid volume was reduced to 50 ml by rotary evaporation and the concentrate was diluted with water (450 ml). This solution was extracted with ether (3 x 500 ml) and the ether layer was then washed twice with saturated sodium carbonate solution and once with water, dried ($MgSO_4$), and concentrated to give 43 g (0.16 mol, 66%) of 9: mp 100-102°; mass spectrum (70 eV) m/e (rel intensity) 270 (M^+, 94), 142 (100), 141 (70), 129 (90), 128 (44), and 127 (17); pmr ($CDCl_3$) δ 8.16-7.92 (m, 1, ArH), 7.90-7.61 (m, 2, ArH), 7.59-7.26 (m, 4, ArH), 7.16-6.78 (m, 4, ArH), 6.25-6.08 (m, 1, ArCH=C), 3.91 (s, 2, $\text{ArC}\underline{\text{H}}_2\text{C=CH}$), 2.76 (t, 2, ArCH_2, J=8 cps), and 2.24 (t, 2, $\text{ArCH}_2\text{C}\underline{\text{H}}_2$, J=8 cps).

Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.48; H, 6.52.

2-(1-Naphthylmethyl)-1,2,3,4-tetrahydronaphthalene (10). — A sample of 7 (60 g, 0.21 mol), hydrazine hydrate (40 ml), KOH (28 g, 0.5 mol), and diethylene glycol (800 ml) were added to a 1.2-ℓ stainless steel reaction vessel[42] and this reaction mixture was slowly heated to 250°. This temperature was maintained until 256 ml of distillate was obtained (2.5 hr). The cooled reaction mixture was added to 2 ℓ of deionized water, and this solution was then extracted with benzene (2 x 1 ℓ). The aqueous layer was acidified with conc. HCl and was again extracted with benzene (1 ℓ). The benzene extracts were combined and washed with 10% HCl (500 ml). A dark brown solid appeared which was removed by filtering. Rotary-evaporation gave a second brown solid which was eluted through a column of neutral alumina (5.0 cm x 90 cm) with petroleum ether[40] to give 39 g (0.14 mol, 68%) of colorless, crystalline 10; mp 102-104°; mass spectrum (70 eV) m/e (rel intensity) 272 (M^+, 42), 142 (100), 141 (55), 131 (82), 115 (35), and 91 (24); pmr ($CDCl_3$) δ 8.10-7.91 (m, 1, ArH), 7.88-7.61 (m, 2, ArH), 7.53-7.20 (m, 4, ArH), 7.12-6.88 (m, 4, ArH), 3.06 (d, 2, $ArCH_2$, J=7 cps), 2.93-2.36 (m, 4, $ArCH_2$), and 2.34-1.22 (m, 3, $ArCH_2\underline{CH}\underline{H}_2$).

Anal. Calcd. for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.54; H, 7.30.

1,2'-Dinaphthylmethane (11) From 2-(1-Naphthylmethyl)-1,2,3,4-tetrahydronaphthalene (10). — Catalyst (0.2 g of 10% Pd/C)[38a] and 10 (2.0 g, 0.007 mol) were heated for 2 hr under nitrogen in a 25-ml round-bottom flask equipped with a Dean-Stark trap and condenser; a Wood's metal bath at 250-300° was used. After cooling, the product and catalyst was transferred with benzene and the benzene solution was filtered. The filtrate was then diluted to 100.0 ml and the yield (90%) of 11 (mp 96-97°, lit.[16] 96°) was determined by glc.[43] Mass spectrum (70 eV) m/e (rel intensity) 268 (M^+, 100), 267 (53), 266 (16), 265 (23), 252 (17), and 141 (15); pmr ($CDCl_3$) δ 8.14-7.20 (m, 14, ArH) and 4.55 (s, 2, $ArCH_2$).

1,2'-Dinaphthylmethane (11) From 2-(1-Naphthylmethyl)-3,4-dihydronaphthalene (9). — The above dehydrogenation procedure applied to 9 gave 11 in 81% yield.[43]

7a,8,9,13b-Tetrahydro-7*H*-dibenz[*a,kl*]anthracene (12) From 1,2,3,4-Tetrahydro-2-(1-naphthylmethyl)-1-naphthol (8). — Toluene (30 ml) and 8 (2.0 g, 0.007 mol) were combined with 0.2 g of A-15[29] catalyst and this suspension was heated at reflux for 24 hr. The cooled suspension was filtered and the filtrate was rotary evaporated to dryness to give 1.9 g (0.007 mol, 100%) of 12, mp 125-135°. Two recrystallizations from isooctane[44] gave 1.4 g (0.0052 mol, 75%) of 12: mp 142-144°; mass spectrum (70 eV) m/e (rel intensity) 270 (M^+, 100), 241 (17), 179 (54), 165 (75), 129 (28), and 117 (19); pmr ($CDCl_3$) δ 7.80-7.60 (m, 2, isolated ArH), 7.49-6.90 (m, 8, ArH), 4.30 (d, 1, Ar_2CH, J=4.2 cps), 3.34-2.44 (m, 5, $Ar\underline{CH_2}CH_2\underline{CH}\underline{CH_2}Ar$), and 2.17-1.40 (m, 2, $ArCH_2\underline{CH_2}$).

Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.17; H, 6.61.

The mother liquor from the first isooctane[44] recrystallization contained 12 and an unknown compound (ratio ~1:1 by glc). The unknown compound represented a 3-4% impurity in the original reaction mixture. A field ionization mass spectral scan showed the presence of a single parent ion peak at m/e 270. Aromatization of this mother liquor with Pd/C gave two new hydrocarbons as seen by glc analysis. A low potential mass spectrum showed two parent ion peaks, one at m/e 268 (corresponding to 16) and another at m/e 266. The latter may arise from dibenzo[*a*,*g*]fluorene, the aromatized product resulting from cyclization at C-2 of 8 or 9.

7a,8,9,13b-Tetrahydro-7*H*-dibenz[*a*,*kl*]anthracene (12) From 2-(1-naphthylmethyl)-3,4-dihydronaphthalene (9). — The above cyclization procedure applied to 9 gave 12 in 80% yield.

7-Oxo-7*H*-dibenz[*a*,*kl*]anthracene-13-carboxylic acid (14). — Zinc chloride (90 g, 0.82 mol) and a sample of 13 (50.4 g, 0.147 mol) were heated in refluxing acetic acid (1350 ml) for 5 hr.[27] The cooled solution was filtered to separate a red solid which was then washed with saturated sodium carbonate solution (400 ml) and water (200 ml).

The dry, dark red solid (6.0 g, 0.019 mol, 13%) melted at 395° and 396° when mixed with a sample of 17 prepared by polyphosphoric acid cyclization.

Filtrate and washes were combined and this mixture was diluted with water to a volume of 3.5 ℓ. Filtration gave a solid which was then washed with hot water (1 ℓ). A crude, dried sample of 14 (38.3 g, 0.118 mol, 81%) was isolated. A sample of this solid (5 g) was eluted through Dicalite with benzene and then crystallized from this solvent to yield 3.7 g of 14: mp 286-288° [lit.[27] 278°]; mass spectrum (70 eV) m/e (rel intensity) 324 (M^+, 10), 306 (31), 280 (100), 278 (25), 252 (33), and 250 (31).

A pmr analysis was attempted, but a suitable solvent was not found. The keto acid 14 is very insoluble in common solvents at room temperature.

7-Oxo-7*H*-dibenz[*a*,*kl*]anthracene (15). — A suspension of crude 14 (33.3 g, 0.10 mol) and copper powder (17.0 g) in quinoline (200 ml) was heated at reflux for 10 hr.[27] Dilution (1.8 ℓ of H_2O) and filtration of the cooled reaction mixture separated a green solid. This solid was extracted with boiling benzene (3 x 600 ml). The hot benzene washes were filtered through Dicalite to remove residual copper. The benzene was reduced in volume to ca. 100 ml. A dark yellow solid separated. This solid was continuously extracted[45] through Dicalite with isohexane[40] to give 22.4 g (0.08 mol, 78%) of yellow crystals of 15, mp 185-187°. Sublimation gave yellow needles of 15: mp 186-187.5° [lit.[27] 185°]; mass spectrum (70 eV) m/e (rel intensity) 280 (M^+, 100), 252 (34), 251 (10), 250 (25), 126 (13), and 125 (6); pmr ($CDCl_3$) δ 8.87-8.43 (m, 4, ArH) and 8.36-7.55 (m, 8, ArH).

5,6-Dihydro-4*H*-dibenz[*a*,*kl*]anthracene (16) From 7a,8,9,13b-Tetrahydro-7*H*-dibenz[*a*,*kl*]anthracene (12). — Catalyst (0.2 g of 10% Pd/C)[38a] and 12 (2.0 g, 0.007 mol) were added to a 100-ml round-bottom flask, flushed with nitrogen, and then heated in a molten salt bath at 290-300° for 45 min. After cooling, the residue was dissolved in benzene (75 ml), filtered to remove catalyst, and rotary-evaporated to give 1.9 g of yellow solid. This solid was passed through a 1.4-cm x 5-cm column of neutral alumina with petroleum ether eluant[40] in a continuous-extraction, glass-fritted apparatus[45] to give 1.8 g (0.0067 mol, 91%) of 16 as colorless crystals: mp 138-140° [lit.[27] 139°]; mass spectrum (70 eV) m/e (rel intensity) 268 (M^+, 100) 267 (21), 266 (13), 265 (18), 253 (11) and 252 (18); pmr ($CDCl_3$) δ 9.18-8.79 (m, 2, ArH at C-1 and C-13), 8.01-7.10 (m, 8, ArH), 3.15 (t, 4, $ArCH_2$, J=6 cps), and 2.07 (q, 2, $ArCH_2\underline{CH_2}$, J=6 cps); uv max (95% ethanol) 200 nm (log ε 4.56), 221 (4.60), 232 (4.38), 248 (4.00), 259 (4.16), 269 (4.47), 277 (4.76), 287 (4.92), 298 (4.20), 3.08 (4.05), 3.21 (4.05), and 334 (3.83).

5,6-Dihydro-4*H*-dibenz[*a*,*kl*]anthracene (16) From 7-Oxo-7*H*-dibenz[*a*,*kl*]anthracene (15). — Acetic acid (200 ml), hydriodic acid (20 ml), red phosphorus (5 g), and 15 (5 g, 0.017 mol) were heated at reflux under a nitrogen atmosphere for 214 hr.[27] The cooled reaction mixture was poured into water (400 ml) and was then extracted with benzene (400 ml). The suspension was filtered to remove phosphorus. The organic layer was washed with water (400 ml), 1% sodium thiosulfate solution (300 ml), and water (400 ml). The benzene was then dried ($MgSO_4$), filtered, and rotary evaporated to isolate 5.9 g of brown oil which showed a 72% yield of 16 by glc.[46] This oil was eluted with isohexane[40] through a 2.5-cm x 17-cm column of neutral alumina to give colorless crystals of 16 (2.6 g, 0.0097 mol, 55%), mp 134-137°. For analysis, further purification was done by sublimation at 125° (0.1 mm) to give 16, mp 138-140°. The melting point of a mixture of this sample and a sample of 16 from 12 showed no depression.

Dibenzo[*def*,*mno*]chrysene-6,12-dione (17). — A commercial sample (20 g, 0.059 mol) of 1,1'-binaphthyl-8,8'-dicarboxylic acid (13) was added during a 50-min period to 115% polyphosphoric acid (100 ml) which was maintained at 85-95°. The mixture was then heated at 110° for 1.5 hr. The dark, mushy solution was then poured over 750 g of water-ice. A finely dispersed red solid was precipitated which was separated by centrifugation. The resulting solid was stirred with sodium carbonate solution (200 ml saturated sodium carbonate solution diluted with 200 ml of water) and was again separated by centrifugation. Acidification of a portion of the wash gave no unreacted acid. The red solid was stirred with water (500 ml), centrifuged, stirred with methanol (300 ml), and centrifuged again. Vacuum drying gave 16.3 g (0.053 mol, 90%) of reddish brown 17,[31] mp 393-396°, which was used in the reduction procedure. For analysis, a sample of this solid was continuously extracted[45] through neutral alumina (2.5-cm x 2.5-cm column) with benzene eluant and was then sublimed at 250° (0.05 mm) to afford bright orange crystals of 17: mp 404-406° [lit.[47] 340°]; mass spectrum (70 eV) m/e (rel intensity) 306 (M^+, 100) 278 (8), 250 (9), 248 (8), 125 (8), and 124 (5).

Insolubility of this compound in readily available solvents precluded obtaining pmr data.

1,2,3,7,8,9-Hexahydrodibenzo[*def*,*mno*]chrysene (18). — A sample of 17 (9.5 g, 0.031 mol), red phosphorus (8.6 g), 57% hydriodic acid (35 ml), and glacial acetic acid (350 ml) were heated at reflux for 235 hr. The cooled reaction mixture was poured into water (500 ml) and filtered. The collected solid was washed with water (500 ml) and a small amount of 95% ethanol (25 ml). This solid was pumped to dryness, placed over Dicalite in a continuous extractor,[45] and eluted with ether to give 6.3 g (0.024 mol, 72%) of yellow-green solid melting about 200°. Sublimation at 200° (0.07 mm) and recrystallization from methylene chloride gave yellow needles of 18: mp 231-233°; mass spectrum (70 eV) m/e (rel intensity) 282 (M^+, 100), 281 (18), 277 (11), 276 (33), 253 (7), and 126 (12); pmr ($CDCl_3$) δ 8.03-7.85 (m, 2, ArH), 7.81-7.64 (m, 4, ArH), 3.47-3.16 (m, 8, $ArCH_2$) and 2.20 (pentet, 4, $ArCH_2\underline{CH_2}$, J=6 cps); uv max (95% ethanol) 205 nm (log ε 4.60), 213 (4.27), 230 (4.21), 237 (4.58), 247 (4.86), 258 (4.13), 269 (4.43), 280 (4.74), 304 (3.60), 317 (4.00), 332 (4.43), 344 (4.42), 349 (4.61), 364 (3.77), 377 (3.12) and 384 (3.77).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.49; H, 6.46.

Dibenzo[*def*,*mno*]chrysene (19). — Catalyst (10% Pd/C,[38a] 0.1 g) and a sample of 18 (1.0 g) were heated for one hr at 290-300°. Product was separated from catalyst by continuous extraction[45] of the solid mixture with methylene chloride. The solution was evaporated to dryness and the resultant solid was extracted[45] through a 1/2" x 1/2" column of neutral alumina using toluene. Crystallization from this solvent gave amber plates of 19 (1.0 g, 100%): mp 263.5-265.5 [lit.[48] 261°]; mass spectrum (70 eV) m/e (rel intensity) 276 (M^+, 100), 277

(24), 138 (18), 274 (16), 137 (13), 275 (8), 136.5 (6), 136 (5), 138.5 (4), and 272 (3); uv max (95% ethanol) 209 nm (log ε 4.79), 213 (4.78), 232 (5.16), 242 (s, 4.79), 247 (s, 4.70), 255 (4.71), 259 (4.79), 271 (3.91), 282 (4.31), 294 (4.80), 307 (5.16), 320 (s, 4.05), 363 (3.71), 380 (4.29), 384 (4.29), 396 (s, 4.44), 401 (4.69), 406 (4.71), 421 (4.78), and 430 (5.04).

The compound was not sufficiently soluble in available solvents to obtain pmr data.

4-(3-Pyrenyl)butanoic Acid (21). — A sample of 20 (25.0 g, 0.09 mol), red phosphorus (11.0 g), and 57% hydriodic acid (20 ml) were heated under nitrogen atmosphere with refluxing acetic acid (400 ml) for 96 hr. The warm reaction mixture was filtered and was then diluted with water (1.5 ℓ), whereupon a precipitate separated. This solid was collected and was then washed with water (5 x 200 ml), dissolved in saturated sodium bicarbonate solution (200 ml), filtered, and reprecipitated by acidification with 10% hydrochloric acid. Recrystallization from toluene-isohexane[40] gave 17.0 g (0.065 mol, 72%) of colorless plates of 21: mp 187-188° [lit.[49] 187-188°]; ir (KBr) cm^{-1} 3010, 2940, 1690, 1460, 1430, 1335, 1320, 1275, 1210, 910, 820, 755, 725, and 710; mass spectrum (70 eV) m/e (rel intensity) 288 (M^+, 30), 228 (16), 227 (17), 216 (20), 215 (100), and 213 (23); pmr (DMSO-d_6) δ 8.49-7.94 (m, 9, ArH), 3.38 (t, 2, $ArCH_2$, J=7 Hz), 2.44 (t, 2, $\underline{CH_2}CO_2H$, J=7 Hz), and 2.05 (pentet, 2, $ArCH_2\underline{CH_2}$, J=7 Hz).

5,6-Dihydro-4*H*-benz[*de*]anthracene (23). — A sample (23 g, 0.10 mol) of benzanthrone (22), red phosphorus (12 g), and 57% hydriodic acid (50 ml) were mixed and were then heated for 96 hr in refluxing acetic acid (450 ml).[33] A procedure similar to that described for the separation of 16 was used to isolate a crude oil which was distilled (Kugelrohr) at 145-155° (0.1 mm) to give 20.9 g of yellow solid. A pot residue of 1.7 g remained. The distillate was eluted with isohexane[40] through a 2.5-cm x 7-cm column of basic alumina using a continuous Soxhlet extractor.[45] Crystallization from this solvent gave colorless 23 (16.2 g, 0.074 mol, 74%), mp 84-86°. A second recrystallization from isohexane[45] improved the melting point to 85.5-87° [lit.[33] 81-82°]; mass spectrum (70 eV) m/e (rel intensity) 218 (M^+, 100), 217 (34), 216 (10), 215 (24), 203 (22), and 202 (25); pmr ($CDCl_3$) δ 8.66-8.38 (m, 2, ArH), 7.83-7.21 (m, 6, ArH), 3.06 (t, 4, $ArCH_2$, J=6 cps) and 2.00 (pentet, 2, $ArCH_2\underline{CH}_2$, J=6 cps); uv max (95% ethanol) 214 nm (log ε 4.50), 225 (4.22), 2.51 (4.68), 258 (4.76), 271 (4.15), 279 (4.08), 295 (4.05) and 302 (4.12).

PART II

SODIUM-AMINE REACTIONS OF NAPHTHALENES: CYCLODIMERIZATION AND REDUCTIVE CYCLODIMERIZATION

CHAPTER V

INTRODUCTION AND HISTORICAL

The reaction of naphthalene (24) in amine solutions of alkali metals has been a subject of continuing study.[50a-d] This study is directed toward experiments that will provide basic data on this complex reaction and that will afford reaction products of synthetic value. Naphthalene has been chosen for study because it is the logical choice after benzene in the aromatic series and is the simplest of the polynuclear aromatic (PNA) hydrocarbons. Although biphenyl, a two ring system, has been studied,[51a,b,c] the data accumulated has only limited utility in application to condensed PNA hydrocarbons.

The reaction of 24 with alkali metals was first reported in 1857.[52] In this study, potassium was fused with 24 in a solvent-free, closed tube. The reduction of 24 with sodium and ammonia to 1,2,3,4-tetrahydronaphthalene (25) was reported later[53] with sodium amide also noted as a product. The stoichiometry of the reaction was confirmed as involving four atoms of sodium per molecule of naphthalene even with large sodium excess.[54]

Kinetic and mechanistic studies for the metal-amine reduction of 24 is difficult because some of the reductions occur on the surface of the dissolving metal, sometimes accompanied by hydrogen evolution. The general mechanism for the reduction of unsaturated systems is discussed in recent reviews.[55a,b] The generally accepted intermediates in the reduction of 24 to 25 are shown in Figure 2.[50b,c] The addition of an electron to form radical-anion 26 is considered to be a reversible equilibrium, and the electron can often be removed from the adduct.[56] Evidence for radical-anion intermediates in metal-amine reductions has been compiled by different groups.[57a-l]

Addition of a second electron to form dianion 27 is usually slow because of the negative charge already on 26. Solvation can be critical in formation of the dianion if electron addition is reversible. This factor is clearly illustrated by the distinction between polar ethers and ammonia in the reaction of sodium with 24.[58] In the ethers, one atom of sodium reacts reversibly to give a green salt of a radical anion, and in ammonia two atoms give the red salt of a dianion, also reversibly.

Protonation of either 26 or 27 could be reversible since the conjugate bases of most amines would be sufficiently basic to abstract protons from the benzylic position. However, with only amine protons available, it is likely that initial protonation of the anion would occur slowly.

The presence of 29, whether arrived at through 31a or 27, has been reported.[50b,59,60] Dialin 29 is readily isomerized in strong base to conjugated dialin 30.[61a,b] It has been proposed that this isomerization is a one step process.[60] This conclusion was based on high retention of deuterium when 1,4-dideuterionaphthalene was isomerized and reduced. Stepwise isomerization should require many isomerizations on the average, and consequently, a large loss of deuterium.

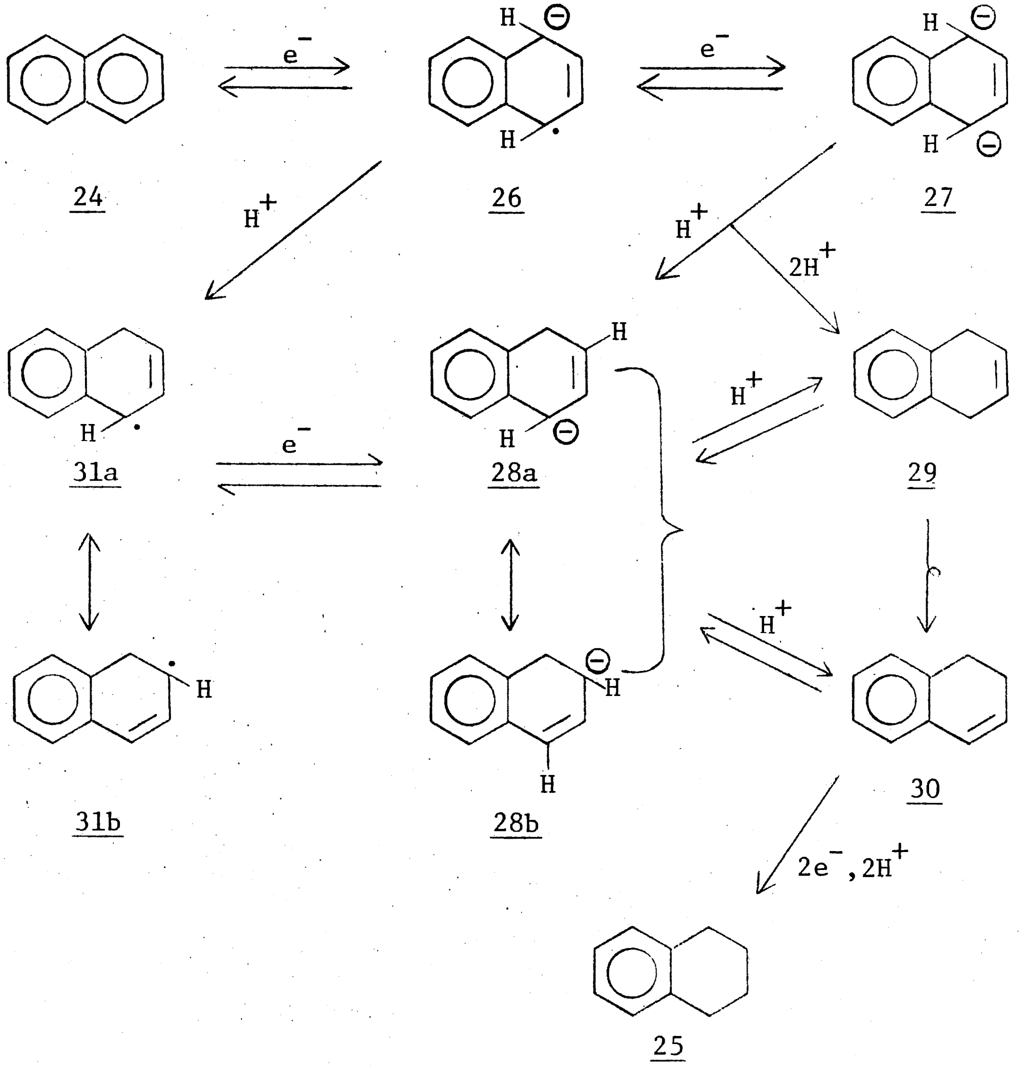
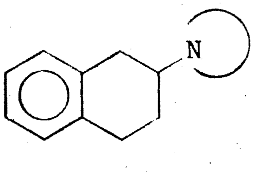


Figure 2. Mechanism for Reduction of Naphthalene With Sodium

Tetralin (25) can be reduced[62] but usually requires the presence of an alcoholic proton source and excess metal. Many factors, such as acidity of proton source, temperature, amine selection, order of reagent addition, and reaction time, influence the degree of hydrogenation and product distribution in the final reaction mixture.[55b] The effects of variations of some of these parameters are not understood completely and remain under investigation.

Unique structures have been isolated and identified from product mixtures formed by reaction of naphthalene-reduction intermediates with solvents, other added reagents, or themselves. For example, reductive amination of naphthalene has been effected by the interaction of 24 with sodium in various primary and secondary amines.[63a,b,c] The major product is the 2-substituted tetralin, e.g. 32, with highest yields obtained using unhindered, cyclic, secondary amines as solvents. The product is proposed to arise from amide anion attack on dialin 30.



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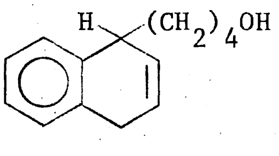

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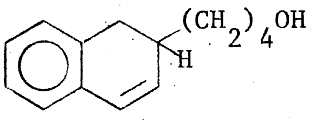

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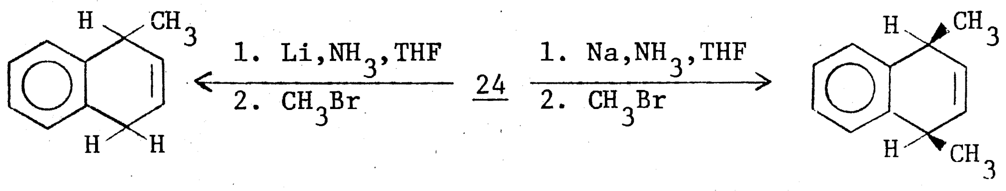
Alcohols 33 and 34 are produced in 30% and 5% yield, respectively, from photochemical reaction of lithium and naphthalene in tetrahydrofuran (THF).[64] Thermal reaction (65°) of lithium and naphthalene in

THF also affords 33 (4%) and 34 (46%)[65] but reverses the major isomer as shown. Other lithium arenides in THF are also reported to give alcoholic products using thermal reaction conditions.[65]

Reductive methylation of naphthalene to 35 and 36 has been

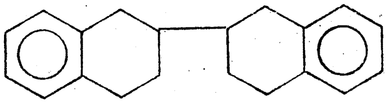


35 36

reported.[66a,b] Treatment of a solution of naphthalene in liquid ammonia-THF at -78° with lithium followed by excess methyl bromide afforded 35 in 95% yield. In contrast, analogous reaction with sodium metal furnished 36 in 93% yield. The observed metal effect is explained as a consequence of the greater tendency of lithium than sodium to form solvent-separated rather than contact ion pairs in solution[67a,b] and more facile protonation of the former by the medium.

Reductive phenylation of 24 has also been reported.[68] Reaction of 24 with potassium in liquid ammonia followed by addition of chlorobenzene or bromobenzene gives a mixture of products including 29 and 30 (33-35%), 1-phenyldihydronaphthalenes (30-32%), and 2-phenyldihydronaphthalenes (25-28%). Anion addition to a benzyne intermediate is proposed as a mechanism. Observation of phenylation at the 1- and 2-positions while noting only 1-position methylation is likely due to steric hindrance in the case of phenyl. When lithium metal was used instead of potassium metal, only reduction product and no phenylation product was isolated. In no instance was reductive diphenylation observed.

The formation of C_{20} hydrocarbons was reported as a side product from metal-ammonia reduction of 30.[59] Slow addition of sodium to 30 in ammonia gives 2,2'-octahydrobinaphthyl, mp 114°.[69] Substitution of primary alkyl amines for ammonia[70a,b] changes the reduction potential and reaction temperature range and as a result, changes the product distribution. Reductive dimerization probably occurred during the reaction of naphthalene with sodium and ethylamine although the "polymeric material" was not identified.[70a] Reggel, using similar reaction conditions, prepared and isolated 1,1',2,2',3,3',4,4'-octahydro-2,2'-binaphthyl (37), mp 85°, as well as two other dimeric products.[71] Hydrocarbon 37 was also isolated after reductive dimerization of 24 using sodium in a variety of other amines.[50b,63c] This same



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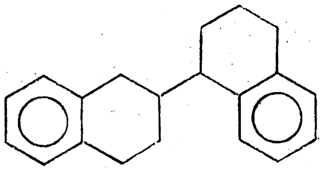

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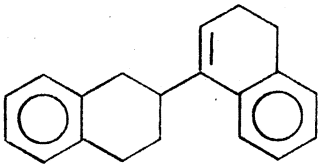

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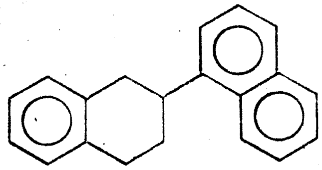

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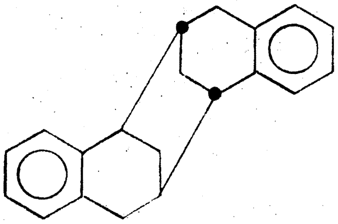
study showed that some control of specific dimer formation is possible through selection of the appropriate amine solvent. Further study showed that reductive dimerization of _24_ with sodium in dipropyl amine results in a remarkably selective formation of 1,2'-coupled dimers, _38_, _39_, and _40_.[50c,72] Ethylenediamine and lithium provides a powerful and perhaps the least selective metal-amine system.[73] This solvent, when used with limited sodium, has also been found to give dimeric material with naphthalene.[50b]

CHAPTER VI

DISCUSSION AND RESULTS

The reaction of 24 or 30 with sodium and ethylenediamine[63c,74] affords a $C_{20}H_{20}$ reductive cyclodimer mp 179-180°, which has been shown by X-ray crystallographic analysis to have structure 41,[75] rather than structure 42[63c,74] proposed earlier. Dimer 41 is also formed by reaction of dihydronaphthalene with potassium *tert*-butoxide and dimethylsulfoxide (DMSO).[50c] Wideman, using similar reaction conditions, almost certainly isolated 41 as well.[76]



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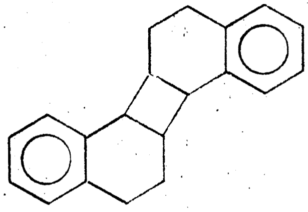

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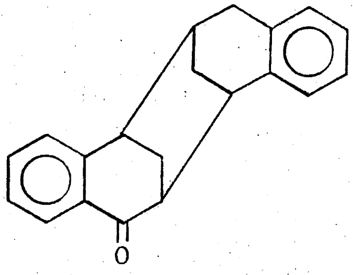
The earlier assignment of structure 42 was based on the following evidence: (1) a strong ir band at 755 cm^{-1} suggesting four adjacent aromatic protons; (2) mass spectrum showing *m/e*'s of 260 (M^{+}), 130 (hemicleavage), and 129; (3) the presence of aromatic, benzylic, and aliphatic protons in the pmr spectrum in the ratio of 8:6:6 and no vinyl-proton signal; (4) glc retention time similar to other $C_{20}H_{20}$

dimers; and (5) no obvious reaction on treatment with ozone or a dilute solution of bromine in carbon tetrachloride. This evidence also supports structure 41.

Attempts to dehydrogenate hydrocarbon 41 with Pd/C in refluxing 1-methylnaphthalene (bp 250°) or neat at 200° and 300° left the hydrocarbon unchanged. Pyrolysis of 41 gave hydrocarbons 24, 25, and 1-methylindan in the ratio of 5.5:4.7:1.[77a] Oxidation of 41 with chromium trioxide in acetic acid furnished monoketone 43, mp 178-179.5°, and diketone 44, mp 290-292°. The presence of a center of symmetry in hydrocarbon 41 is supported by formation of only one monoketone and one diketone.



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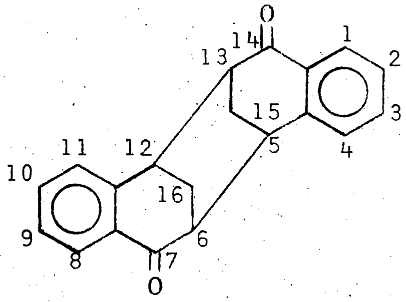

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Comparison of ir and Raman spectra[77b] of diketone 44 showed no correspondence of the major absorption bands which also suggests symmetry in 44. Base-catalyzed deuterium exchange and preparation of enol acetate and benzylidene derivatives have been attempted on 44.[77a] The diketone was unaffected by these procedures. The foregoing is most consistent with 5,6,7,12,13,14-hexahydro-5,13:6,12-dimethoanodibenzo-

[*a*,*f*]cyclodecene-7,12-dione as the structure of diketone 44. The presence of methano bridges in 44 explains its inertness to deuterium exchange and its failure to give an enol acetate or benzylidene derivative.

The cyclodimerization of dihydronaphthalene 30 or the cyclization of 39, shown in Figure 3, can produce 41 under nonreducing conditions.[50b,c,77a] For this reason, anionic rather than radical dimerization processes are favored. Initial attack of dianion 27, from either 24 or 30 (see Figure 2), on dialin 30 would result in new dianion 45. Intermediate 45 could protonate to give anion 46 which must isomerize to a more stable, conjugated specie before isolation as 39, previously noted as a metal-amine product, or before further reaction could occur, as with 47. Formation of 39 requires protonation and then deprotonation at the tertiary benzylic position of 46. Generation of anion 47 may be concerted with change of double bond position. Drieding models (anions assumed to be tetrahedral) show that intramolecular proton abstraction in going from 46 to 47 as well as intramolecular cyclization of 47 to 48 could occur readily if trans stereochemistry exists. Nucleophilic attack in 47 could proceed easily since the conjugated double bond of 47 may be situated directly above the benzylic methylene group bearing the negative charge.

Crystallographic proof of structure 41[75] allows conclusive assignment of its 100 MHz pmr absorptions. The rigidity of 41 provides a magnetically nonequivalent environment for geminal protons at C-7 and C-14 as well as C-15 and C-16 (using the numbering shown for diketone 44) as shown for structure 49. Also, the centrosymmetry of 49 requires that each of these protons has an equivalent

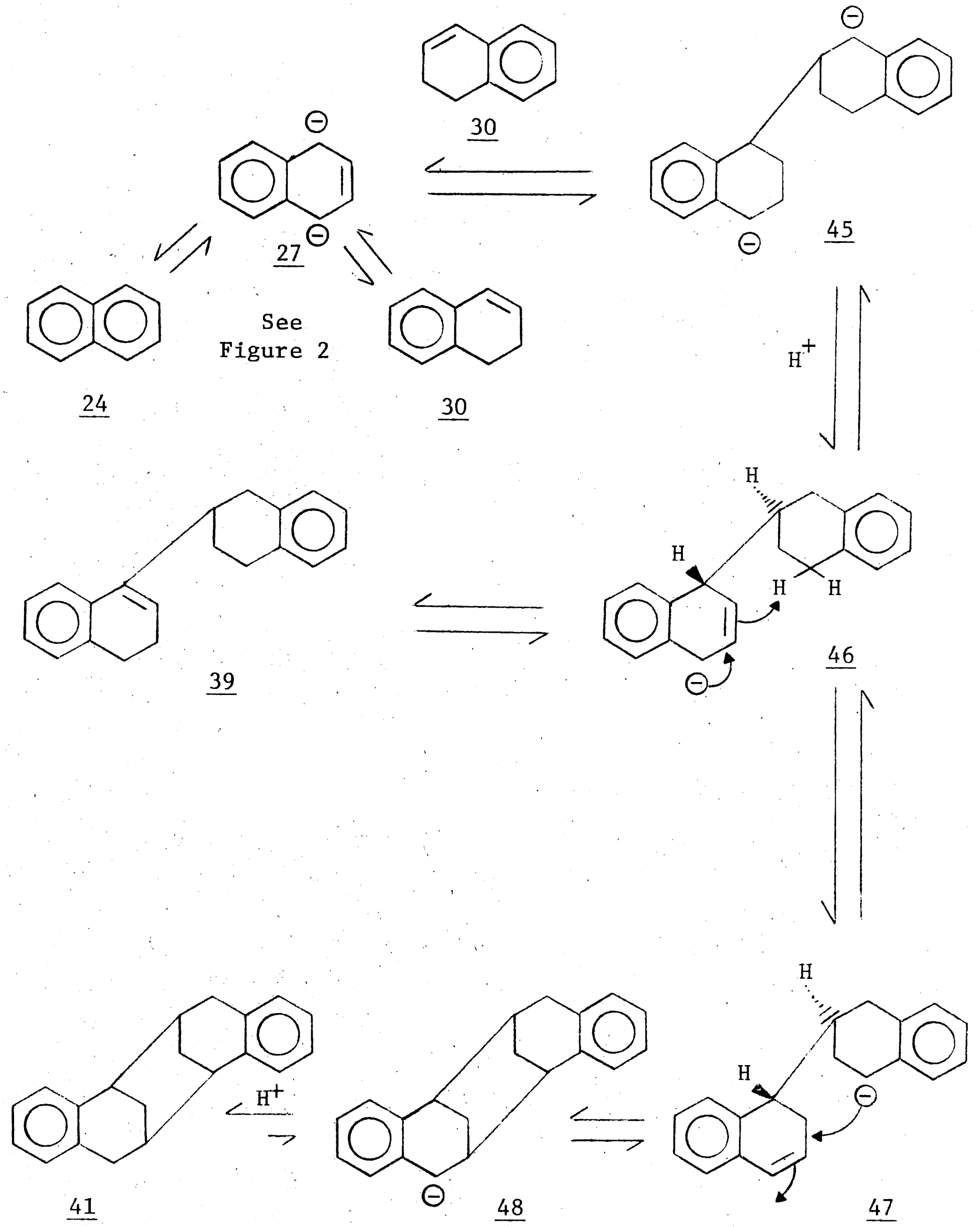
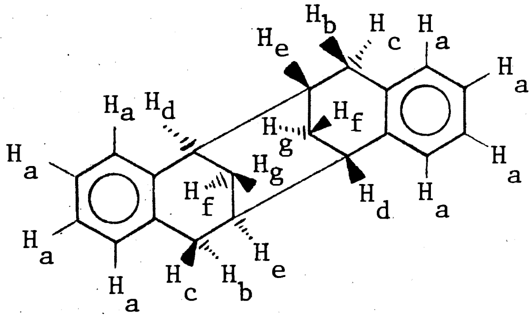


Figure 3. Mechanism for Formation of Cyclodimer 41



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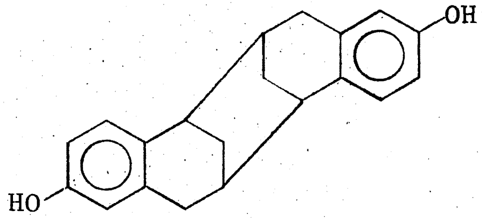
proton at the corresponding reflection position. These are labelled accordingly.

The nonequivalent geminal protons couple to give $J_{H_bH_c}$ = 18 Hz and $J_{H_fH_g}$ = 13 Hz which is readily shown by irradiating the doublet corresponding to H_f or H_g and noting coalescence. The same is true for the signals of H_b and H_c with one further complication, H_b is represented by a doublet of doublets and coalesces to a doublet ($J_{H_bH_e}$ = 6 Hz) on irradiation of H_c. The absence of a measurable coupling constant between vicinal protons H_c and H_e ($J_{H_cH_e}$ = 0 Hz) while noting one for H_b and H_e can be rationalized by calculating the dihedral angles between H_b and H_e ($\theta_1 = 36°$) and H_c and H_e ($\theta_2 = 82°$) and comparing the observed coupling constants to those predicted by the Karplus equation.[78] Dihedral angles were calculated from final X-ray coordinates and calculated coupling constants of $J_{H_bH_e}$ = 5.30 Hz and $J_{H_cH_e}$ = -0.11 Hz show good agreement with observed values.

The choice of the remaining doublet ($J_{H_dH_e}$ = 1.5 Hz) for the signal of H_d is supported by coalescence to a singlet upon irradiation of the H_e multiplet. This is further supported by the presence of a similar doublet (slightly shifted) in the spectrum of diketone 44 where H_d represents the only benzylic protons.

It is fortunate that H_b and H_c can be differentiated through their observed coupling constants with H_e. Such is not the case with H_f and H_g. Both parts of the doublets for H_f and H_g resemble broad unresolved triplets (5-8 Hz wide at peak half-height). Their shapes change to that of unresolved doublets on irradiation of H_e or H_d. It was noted that H_e and H_d nearly halve the angle between H_f and H_g (all angles calculated to be 54-65°). The equal bond angles would explain why the splitting patterns of H_f and H_g are very similar and the magnitude of the bond angles could explain why the coupling constants may be small enough (calculated to be from 1.2 to 2.7 Hz) to be effectively hidden in the broad signals previously noted.

Extension of the cyclodimerization study to methoxynaphthalenes and methoxydihydronaphthalenes was prompted by the striking similarity between 50 and diethylstilbesterol (51), a synthetic antifertility agent.[79] Application of the reaction conditions used to prepare hydrocarbon 41 to 2-methoxynaphthalene (52) did not allow isolation of a methylated derivative of 50. A glc trace of the reaction mixture



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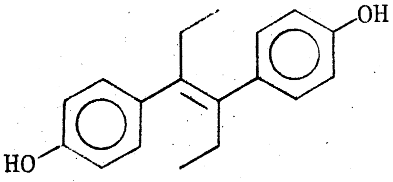
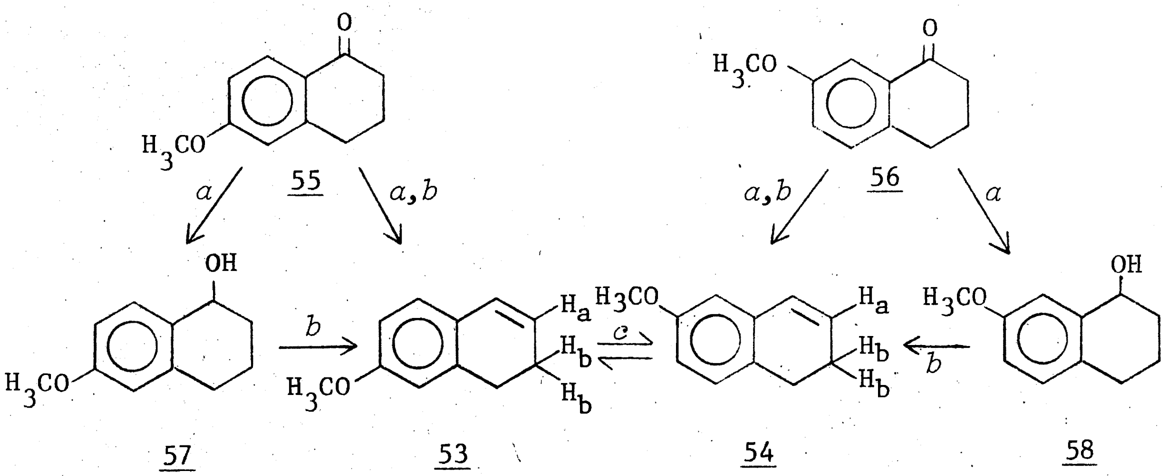


51

showed over twenty components probably formed by reduction followed by dimerization in the substituted as well as unsubstituted ring of 52.[80]

7-Methoxy-1,2-dihydronaphthalene (53) and 6-methoxy-1,2-dihydronaphthalene (54) were synthesized (shown in Figure 4) and their behavior under basic conditions were then studied. Potassium *tert*-butoxide in DMSO was found to isomerize both 53 and 54 without dimerization.



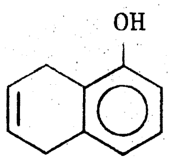
[a]DIBAH, toluene. [b]Oxalic acid, toluene, Δ. [c]KO-t-Bu, DMSO.

Figure 4. Preparation and Equilibration of 53 and 54

Synthesis routes used for producing 53 and 54 are shown in Figure 4. Diisobutylaluminum hydride[28] readily reduces 55 and 56, and this procedure is an improvement over earlier methods.[82a,b] Alcohol 57, which is obtained by reducing 55, is isolated in moderate yield by careful distillation of the reduction product. Alcohol 58 is isolated by Kugelrohr distillation of the reduction product from 56. Elimination of water from 57 or 58 to give 53 or 54, respectively, is achieved by refluxing with toluene and oxalic acid.[14] This procedure does not cause dimerization or isomerization.

Table I shows the results of equilibration studies using either 53 or 54 as starting material. These isomerizations appear to be rapid, and prolonged equilibration produces 2-methoxynaphthalene (52). Since 6-methoxy-1,2,3,4-tetrahydronaphthalene is not detected, oxidation rather than disproportionation is suggested.

Isomerization of 5,8-dihydro-1-naphthol (59) produces primarily 5,6-dihydro-1-naphthol (60) as the major product. Isomerization of the methyl ether of 59 yields the methyl ether of 60 as the major product.[81]



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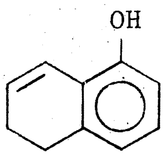

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TABLE I

EQUILIBRATION OF 7-METHOXY-1,2-DIHYDRONAPHTHALENE (53) AND 6-METHOXY-1,2-DIHYDRONAPHTHALENE[a] (54)

	Products of 53[b]			Products of 54[b]		
Reaction Time (hr)	Percent 53 + 54	Ratio 53/54	Percent 52	Percent 53 + 54	Ratio 53/54	Percent 52
0.25	98.0	1.93	2.0	97.0	1.83	3.0
0.5	97.0	1.89	3.0	96.5	1.81	3.5
1.0	94.9	1.89	5.1	95.2	1.77	4.8
2.0	91.5	1.95	8.5	90.9	1.80	9.1
3.0	89.8	1.89	10.2	88.5	1.89	11.5

[a] Equilibrations were done at ambient temperatures using 1.5 g of methoxydihydronaphthalene, 80 ml of dimethylsulfoxide, and 325-335 mg of potassium tert-butoxide.

[b] Percentages and ratios were determined by quantification of pmr spectra.

Detection of both isomers in mixtures containing 53 and 54 was possible because a vinyl-proton (H_a, Figure 4) multiplet in a pmr spectrum of 53 is centered 11 Hz upfield from a similar multiplet in a spectrum of 54.[83] High-gain expansion of the H_a signal for a sample containing 53 did not show a signal corresponding to H_a of 54. A similarly treated sample of 54 did not reveal 53. A spectrum of a mixture of 53:54 (1:1) disclosed both multiplets. For mixtures, coalescence of both vinylic multiplet signals is effected simultaneously by irradiation of the nonbenzylic-methylene-protons signal (H_b, Figure 4). The resulting doublets can be quantified. Figure 5 shows the results of pmr quantification of mixtures of 53 and 54. Points on the graph enclosed by squares represents weight percentages of standard solutions, whereas encircled points represent percentages which were calculated from pmr data.

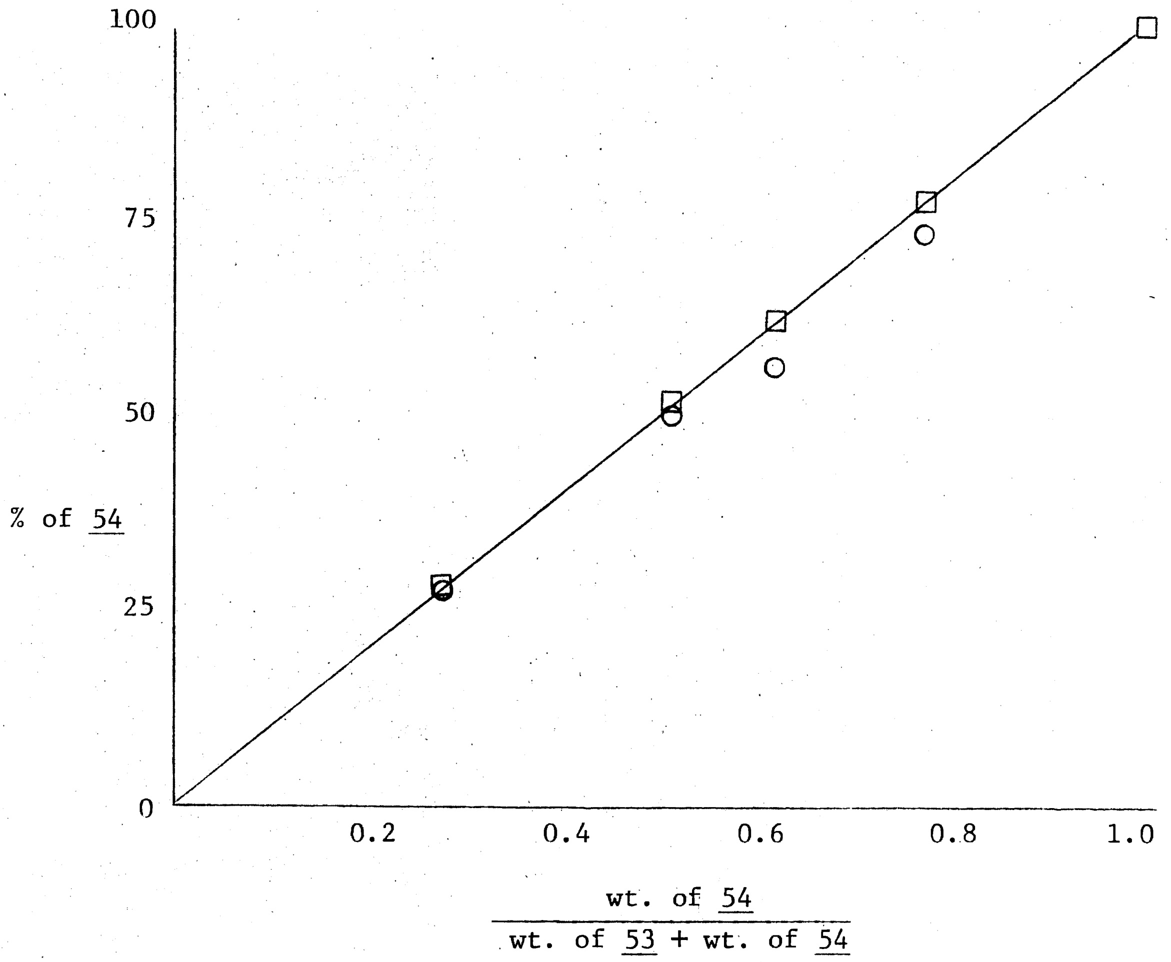


Figure 5. Quantification Plot for Standard Solutions of 53 and 54: wt. □ ; pmr analysis, ○ .

A mechanistic rationalization for isomerization of 53 and 54 is shown in Figure 6. Double bond migration is dependent on proton removal by nucleophile followed by electron density shift and reprotonation to 63. The nonconjugated dialin 63, intermediate to 53 and 54, must be a short-lived intermediate of low concentration since it was not detected in the final reaction mixture. The equilibrium ratio of 53 and 54 may depend on the relative stabilities of 61 and 65.

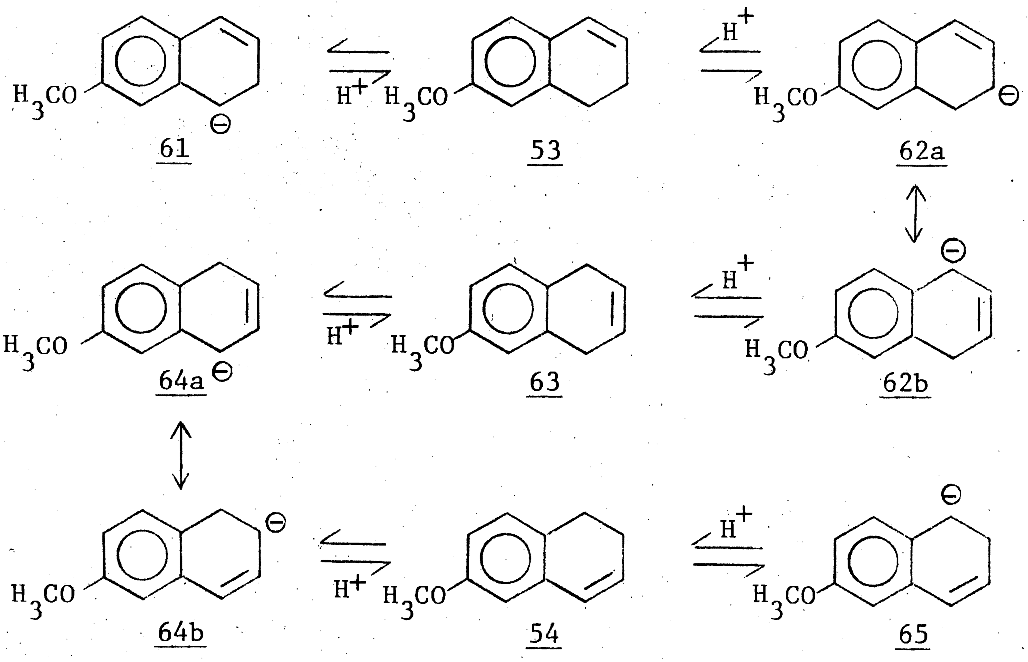


Figure 6. Mechanism for Isomerization of 53 and 54

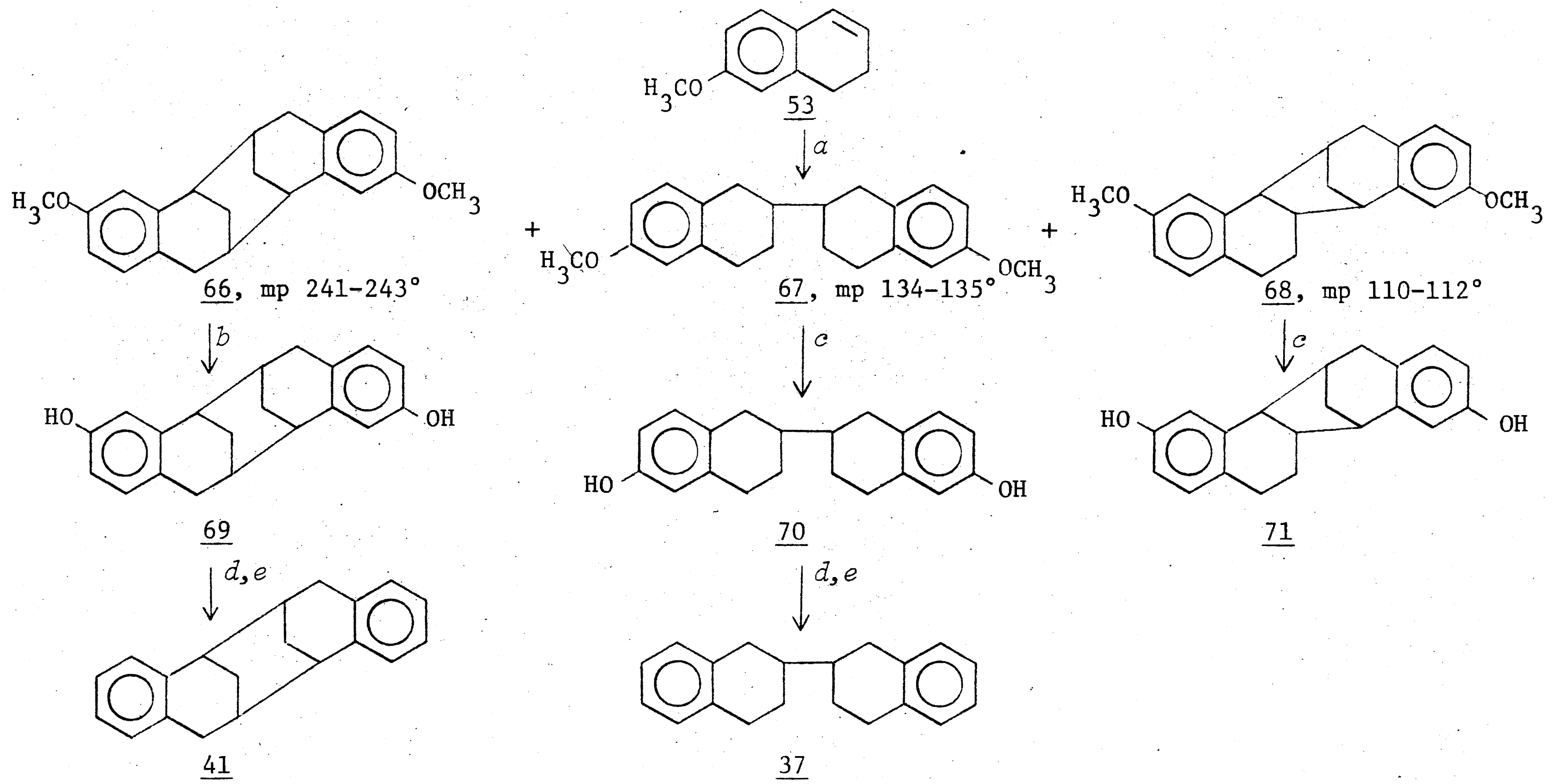
Since ketone 55 was less expensive than 56 and the equilibration experiments imply that both 53 and 54 may be present under the strongly basic, cyclodimerization conditions, dialin 53 was used for dimerization experiments. Reaction of 53 and subsequent purification gave dimers 66, 67, and 68, shown in Figure 7.

The carbon skeleton of cyclodimer 66 was related to hydrocarbon 41 by boron tribromide demethylation[84] to diphenol 69 and subsequent deoxygenation using Birch reduction of the diethylphosphate derivative.[85] The positions of methoxyl groups were determined using ^{13}C-nmr.[86]

The structure of dimer 67 was determined by an alternate synthesis.[77a] Dimer 67 was also demethylated using hot methylmagnesium iodide[87a,b] and then deoxygenated to hydrocarbon 37 using the method previously mentioned for 69. Hydrocarbon 37, mp 85°, was isolated and showed no melting point depression when mixed with a sample of 37 prepared by dimerization of naphthalene.[50b,63c]

Data taken on cyclodimer 68 did not display correlation with any hydrocarbon previously isolated from the cyclodimerization of naphthalene. X-ray crystallographic analysis was performed to elucidate this structure.[88] Cyclodimer 68 crystallizes as a racemate, mp 110-112°.

The three diphenols 69, 70, and 71 were submitted to the National Institutes of Health[89] for testing as antifertility agents. The results of this testing for diphenols 69 and 70 are shown in Table II. Diphenol 71 did not show activity; however, the actual results were not available at the time of this writing.



^{a}Na, $NH_2CH_2CH_2NH_2$. $^b CH_2Cl_2$, BBr_3. $^c CH_3MgI$, Δ. $^d (EtO)_2POCl$, NaOH. ^{e}THF, NH_3, Na.

Figure 7. Dimerization of 7-Methoxy-1,2-dihydronaphthalene (53)

TABLE II

RESULTS OF ANTIFERTILITY TESTING

Structure	Amount[a] mg/kg-day	Method of[b] Introduction	Results
	0.4	oral	9/10 rats implanted
69	0.4	subcu.	3/10 rats implanted
	0.8	subcu.	0/10 rats implanted
	1.0	oral	9/10 rats implanted
70	10.0	oral	9/10 rats implanted
	5.0	subcu.	9/10 rats implanted

[a] Dosages were given for three consecutive days following coitus.

[b] Sesame oil was used as a vehicle.

A mechanistic rationalization for 2,2'-dimerization is shown in Figure 8. Allylic anions 64a and 64b were shown previously in Figure 6 as isomerization intermediates for dialins 53 and 54. Initial orientation determines whether a 2,2'- or 1,2'-linkage is made between the monomers. Cyclization from a 2,2'-bonded intermediate has not been reported; however, 1,2'-hexahydrobinaphthyl 39 will cylize, as noted previously. Reduction of the double bond in dimer 73 gives the substituted octahydrobinaphthyl 67. Cyclodimer 66, mp 241-243°, likely is formed by an anionic process similar to that proposed for hydrocarbon 41 in Figure 3. Cyclodimer 66 was also isolated from a reaction mixture obtained from reacting dialin 53 with sodium hydride in ethylenediamine.

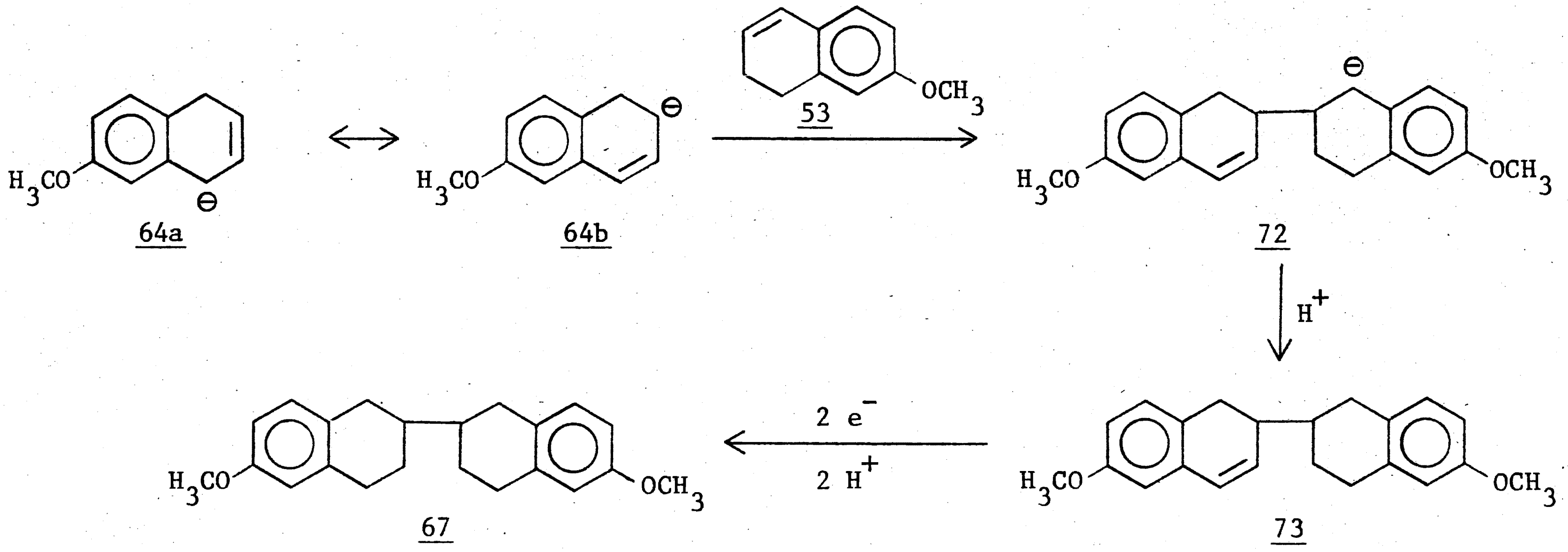


Figure 8. Mechanism for Dimerization of Methoxydihydronaphthalene

CHAPTER VII

EXPERIMENTAL

Preparation of 5,6,7,12,13,14-Hexahydro-5,13:6,12-dimethanodibenzo[*a*,*f*]cyclodecene (41). — Hydrocarbon dimer 41 was prepared by stirring 12.8 g of naphthalene, 10 g of sodium spheres, and 230 ml of anhydrous ethylenediamine at 50° for 2 hr in a previously described stir-shredding device.[72] The reaction mixture was kept under an atmosphere of nitrogen. The product mixture was allowed to cool and was then cautiously poured onto crushed ice (1-2 kg). Aqueous HCl (2200 ml of 10%) was added and the resulting mixture was extracted with 2 x 500 ml of ether. The extract was washed with 50 ml of 10% HCl, then with water and finally dried ($MgSO_4$). Concentration and distillation (Kugelrohr) at 160-170° (0.1 mm) gave 4.2 g of a dimer fraction.

The above fraction was recrystallized from toluene to give 0.5 g of colorless 41: mp 179-180°; ir (KBr) prominent bands at 755, 741, and 712 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 260 (M^+, 41), 131 (38), 130 (40), 129 (100), 128 (63), and 115 (21); pmr ($CDCl_3$) δ 7.25-6.97 (m, 8, ArH), 3.27 (d of d, $J_{H_bH_e}$ = 6 Hz and $J_{H_bH_c}$ = 18 Hz, 2, $ArCH_2$), 2.87 (d, $J_{H_bH_c}$ = 18 Hz, 2, $ArCH_2$), 2.85 (d, $J_{H_dH_e}$ = 1.5 Hz, 2, ArCH), 2.21-1.94 (m, 2, $ArCH_2C\underline{H}$), 1.78 (d, $J_{H_fH_g}$ = 13 Hz, $ArCHC\underline{H}_2$), and 1.34 (d, $J_{H_fH_g}$ = 13 Hz, 2, $ArCHC\underline{H}_2$); uv max (95% ethanol) 260 nm (log ε 2.97), 266 (3.16), and 273 (3.20).

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.85.

Attempted Catalytic Dehydrogenation of 41. — A mixture of 41 (0.4 g), mp 177-179°, and 10% Pd/C[38a] (40 mg) were heated at 200-210° in a fused salt bath for 2 hr. The reaction mixture was cooled, boiled with toluene (100 ml) and filtered to remove catalyst. The filtrate was rotary-evaporated and pumped to dryness to give recovered 41, mp 174-177°. The same sample was heated with new catalyst (40 mg) at 300° for 2 hr and treated in the same manner to give 0.4 g of 41, mp 169-175°C, and mixed with starting material, mp 174-178°. Glc studies showed a single major peak with a trace of trailing impurity. Injections of mixtures and pure starting material and sample showed identical retention times.[90a] A second sample of 41 (401 mg), catalyst (40 mg), and 1-methylnaphthalene (40 ml) were refluxed briskly for 2 hr. The warm reaction mixture was filtered and washed with 90 ml of hot toluene. This solution was rotary evaporated and distilled (Kugelrohr) to remove toluene and 1-methylnaphthalene. The resulting tan solid was recrystallized from isohexane. The first crop gave 345 mg, mp 177-179° (mixed with starting material, mp 176-179°); the second crop gave 28 mg, mp 175-177°C, with a total return of 373 mg (93%) of recovered starting material. Glc studies of this sample showed results similar to those described above.

Preparation of 5,6,7,12,13,14-Hexahydro-5,13:6,12-dimethanodibenzo[*a*,*f*]cyclodecen-7-one (43). — Hydrocarbon 41 (504 mg, 0.002 mol) and 0.28 g (0.003 mol) of a 10% aqueous chromium trioxide-acetic acid solution[91] were stirred in glacial acetic acid (450 ml) for 9 hr. The solution was poured into water (1.2 ℓ.) and extracted with chloroform

(450 ml). Gas chromatography of the concentrated extract showed a mixture of 41:43:44 (5.7:8.6:1.0).[90b] The components were separated by toluene elution through neutral alumina. Recrystallization from ether of combined fractions containing 43 gave 143 mg (0.0005 mol, 27%) of colorless needles, mp 176-178°. Further recrystallization from ether improved the mp to 178-179.5°; pmr ($CDCl_3$) δ 8.09 (d, J = 7 Hz, 1, *peri* ArH), 7.62-6.96 (m, 7, ArH), 3.31 (d of d, J = 7 Hz and J = 18 Hz, 1, ArCH), 3.14 (d, J = 4 Hz, 1, ArCH), 3.06 (d, J = 4 Hz, 1, ArCH), 2.91 (d, J = 18 Hz, 1, ArCH), 2.61 (broad s, 1, ArCOCH), 2.30-2.04 (m, 1, $ArCH_2C\underline{H}$), 1.96-1.63 (m, 3, $ArC\underline{H}C\underline{H}$) and 1.44 (d, J = 13 Hz, 1, $ArCHC\underline{H}$); ir (KBr) 1670 cm^{-1} (conjugated C=O), and 750 cm^{-1} (4 contiguous aromatic protons); uv max (95% ethanol) 253 nm (log ε 4.11), 274 (shoulder, 3.57), and 294 (broad, 3.29); mass spectrum (70 eV) m/e (rel intensity) 274 (M^+, 32), 146 (90), 131 (21), 129 (100), 128 (25), and 115 (21).

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.45; H, 6.58.

Preparation of 5,6,7,12,13,14-Hexahydro-5,13:6,12-dimethanodibenzo[*a*,*f*]cyclodecene-7,14-dione (44). — A sample (2 g, 0.008 mol) of 41 and 27.5 ml (30.3 g of solution, 0.03 mol) of a 10% aqueous chromium trioxide acetic acid solution[91] were stirred in glacial acetic acid (1 ℓ.) for 10 days. The solution was poured into water whereupon a white solid separated. This was filtered out and recrystallized from toluene to give 1.5 g of colorless crystals, mp 288-291°. Concentration of the mother liquor gave an additional 0.3 g of crystals, mp 283-288°. The total yield was 81%.

Recrystallization of the first crop of crystals from toluene:2-propanol (1:1) gave 1.2 g of colorless 44: mp 290-292°; pmr ($CDCl_3$) δ 8.11 (d, J = 7 Hz, 2, peri ArH), 7.68-7.22 (m, 6, ArH), 3.35 (broad s, 2, ArCH), 2.71 (broad s, 2, ArCOCH), and 2.26-1.76 (m, 4, $ArCH\underline{H}_2$); ir (KBr) prominent absorptions (cm^{-1}) 1599, 1477, 1466, 1454, 1347, 1296, 1258, 1233, 1190, 1153, 1124, 1115, 1089, 1016, 927, 890, 850, 823, 774, 763, and 704; Raman prominent absorptions (cm^{-1}) 1680, 1595, 1467, 1280, 1268, 1247, 1184, 1160, 1144, 1050, 1037, 1023, 935, 840, 820, 720, and 665; uv max (95% ethanol) 207 nm (log ε 4.70), 249 (4.48), and 295 (3.51); mass spectrum (70 eV) m/e (rel intensity) 288 (M^+, 71), 144 (100), 143 (43), 117 (1), 116 (1), and 115 (4).

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.46; H, 5.61.

7-Methoxy-1,2-dihydronaphthalene (53). — Diisobutylaluminum hydride[28] (266 g, 1.87 mol) was added to 1 l. of toluene kept under an atmosphere of nitrogen. Ketone 55 (300 g, 1.7 mol) was dissolved in 1 ℓ. of toluene and was then added during a 1.5-hr period. The temperature was maintained below 50°. The reaction mixture was stirred an additional 15 min before ethyl acetate (100 ml) was added. The contents of the flask were poured onto ice and the pH was reduced to 3 with conc. hydrochloric acid. The toluene layer was removed and the aqueous layer was extracted with an additional 500 ml of toluene. The combined toluene layers were washed with 10% hydrochloric acid, water, saturated Na_2CO_3 solution, and water.

Oxalic acid (2.0 g) was added to the toluene extract which was then heated at reflux to remove water by azeotropic distillation. Toluene was then removed (rotary evaporator) and the resultant oil was distilled to give 231 g (86%) of 7-methoxy-1,2-dihydronaphthalene (53): bp 90° (0.5 mm) [lit. 107-111° (2.5 mm)[82a] and 75-76° (0.3-0.4 mm)[82b]; mass spectrum (70 eV) m/e (rel intensity) 160 (M^+, 100), 159 (44), 145 (44), 117 (33), 115 (55), and 15 (38); pmr (neat) δ 6.90-6.74 (m, 1, ArH peri to vinyl H), 6.65-6.47 (m, 2, ArH), 6.34 (d, 1, ArC$\underline{H}$=CH, J = 10 Hz), 5.88-5.65 (m, 1, ArCH=C$\underline{H}$), 3.52 (s, 3, $ArOCH_3$), 2.62 (t, 2, $ArCH_2$, J = 8 Hz), and 2.26-1.97 (m, 2, $ArCH_2C\underline{H}_2$); uv max (95% ethanol) 210 nm (log ε 4.35), 268 (broad, 4.16), 298 (s, 3.13) and 309 (3.00); ir (film) cm^{-1} 3000, 2910, 2815, 1605, 1570, 1490, 1460, 1425, 1390, 1320, 1305, 1280, 1250, 1190, 1155, 1125, 1110, 1035, 1015, 870, 850, 815, 750, 710, 685, 670, and 660.

Isolation of 6-methoxy-1-tetralol (57) is also possible if toluene is carefully removed at a lower temperature under vacuum on a rotary evaporator, followed by vacuum distillation. The alcohol prepared in this manner boiled at 150° (6 mm) [lit.[82a] 175° (16 mm)]; ir (film) showed an OH stretching vibration at 3 μ, and no absorption from 3.6 to 6.1 μ.

6-Methoxy-1,2-dihydronaphthalene (54). — A procedure similar to that described above for the preparation of 53 was used to treat a sample of 56 (46.4 g, 0.26 mol). The crude reaction mixture was distilled through a short path distillation column to give 38.2 g (90%) of oil containing traces of solid oxalic acid. This oil was then redistilled to give 30.8 g of clear, colorless 54: bp 59-61° (0.03 mm) [lit.[92] bp 93-95° (1 mm)]; pmr (neat) δ 6.92-6.76 (m, 1, ArH peri to vinyl H), 6.64-6.49 (m, 2, ArH), 6.32 (d, 1, ArC$\underline{H}$=CH, J = 10 Hz), 5.99-5.76 (m, 1, ArCH=C$\underline{H}$), 3.51 (s, 3, $ArOCH_3$), 2.59 (t, 2, $ArCH_2$, J = 8 Hz), 2.26-1.98 (m, 2, $ArCH_2C\underline{H}_2$); mass spectrum (70 eV) m/e (rel intensity) 160 (M^+, 100), 159 (47), 145 (38), 144 (33), 115 (57), and 15 (39); uv max (95% ethanol) 222 nm (log ε 4.42), 252 (3.75), 261 (3.83), 270 (3.70), 302 (3.40), and 314 (3.35); ir (film) cm^{-1} 3000, 2900, 2810, 1600, 1570, 1495, 1460, 1420, 1325, 1300, 1260, 1215, 1160, 1145, 1125, 1040, 1010, 870, 855, 810, 780, 750, 715, 695, 685, and 675.

A sample (1.0 g) of crude reduction product was distilled (Kugelrohr) to give 0.9 g of clear, colorless <u>58</u>: bp 100-105° (0.03 mm); pmr ($CDCl_3$) δ 7.01-6.86 (m, 2, ArH), 6.78-6.61 (m, 1, ArH), 4.59 (t, 1, $ArC\underline{H}OH$, J = 4 Hz), 3.68 (s, 3, $ArOCH_3$), 2.86 (s, 1, $ArCHO\underline{H}$), 2.62 (t, 2, $ArCH_2$, J = 5 Hz), and 2.05-1.52 (m, 4, $ArCH_2C\underline{H}_2C\underline{H}_2$); ir (film) cm^{-1} 3290, 2900, 2810, 1600, 1570, 1495, 1440, 1310, 1270, 1250, 1225, 1155, 1110, 1060, 1035, 1000, 965, 905, 875, 855, 840, 805, 765, and 695; mass spectrum (70 eV) m/e (rel intensity) 178 (M^+, 1), 160 (100), 159 (47), 145 (33), 144 (29), and 115 (45).

<u>Anal</u>. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.92; H, 7.73.

<u>Isomerization of 7-Methoxy-1,2-dihydronaphthalene (53)</u>. — Dimethylsulfoxide (70 ml), dried over 4A mol sieves, was added to a dry flask under a nitrogen atmosphere. Potassium <u>tert</u>-butoxide[93] (325 mg) was added, and it was observed to dissolve with stirring. A sample of <u>53</u> (1.50 g) mixed with dimethylsulfoxide (10 ml) was then added. A yellow color appeared immediately which decreased in intensity as the reaction proceeded. Samples of the reaction mixture (10 ml) were taken at the time intervals noted in Table I.

The samples were poured into dilute (1:100) hydrochloric acid (4 ml) and were diluted further with water (35 ml). This solution was extracted with isohexane[40] (50 ml) which was then washed with water (3 x 50 ml), dried ($MgSO_4$), filtered, rotary-evaporated, and pumped to give a light oil. This oil was dissolved in d_6-acetone and the resulting solution was used directly for pmr analysis and subsequent glc studies.

To determine the ratio of 53 to 54 by pmr, the multiplet corresponding to the nonbenzylic, methylene protons was irradiated at ~2.25 δ which caused the non-benzylic-vinyl-proton signals of 53 and 54 (absorbing at 5.7-6.1 δ) to appear as two separate and distinct doublets (J = 9.5 Hz). The amount of 2-methoxynaphthalene present was obtained by comparing its pmr methoxy singlet with that of 53 and 54.

Glc of the reaction mixtures also showed the presence of the oxidized product. The trailing peak of a reaction mixture showed identical retention times when injected separately or co-injected with 2-methoxynaphthalene. The samples were also analyzed by glc for dimeric material; only traces (< 1%) of material were observed with retention times corresponding to dimers.

Isomerization of 6-Methoxy-1,2-dihydronaphthalene (54). — A 1.5-g sample of 54 was treated in the same manner as that described in the previous section for isomerization of compound 53. The results are listed in Table I.

Reaction of 7-Methoxy-1,2-dihydronaphthalene (53) With Sodium in Ethylenediamine. — A sample of 53 (50 g, 0.31 mol) was stirred with sodium (20 g) and ethylenediamine (700 ml) at 45° for 3 hr using a stir-shredding device similar to that described for the preparation of hydrocarbon 41. A similar isolation procedure was used to obtain a crude oil which was distilled (Kugelrohr) to give a fraction boiling at 120° (0.05 mm) containing mostly 6-methoxytetralin (2.3 g, 4.5%). Further heating to 230° (0.5 mm) gave a fraction containing dimers (24.2 g, 49%). A pot residue (16.0 g, 32%) remained.

Separation of Dimers 66, 67, and 68. — The distilled dimer mixture from the previous procedure was dissolved in ether and was then cooled to -14° for 24 hr. The first crop of crystals contained only dimer 67. Subsequent crops, obtained by alternately concentrating and cooling the mother liquor, contained mixtures of 66 and 67. This procedure was repeated until crystals no longer formed. Repeated trituration of these crystalline dimer mixtures with hot ether preferentially dissolved 67 and left 66.

The mother liquor from above was pumped to remove solvent and then stored at -14°. Large crystals of 68 slowly formed during several days. These crystals were washed with isohexane[40] to remove adhering oil.

Further Purification of 66. — The solid remaining after the ether trituration described in the previous procedure was recrystallized from acetone to give white prisms of 66: mp 241-243°; mass spectrum (70 eV) m/e (rel intensity) 320 (M^+, 100), 161 (35), 160 (45), 159 (57), 43 (34), and 41 (31); ir (KBr) 9.7 μ (C-O-C stretch); pmr ($CDCl_3$) δ 7.06 (d, J = 8 Hz, 2, ArH), 6.80-6.58 (m, 4, ArH), 3.78 (s, 6, $ArOCH_3$), 3.22 (d of d, J = 7 Hz and J = 18 Hz, 2, $ArCH_2$), 2.81 (d, J = 2 Hz, 2, ArCH), 2.80 (d, J = 18 Hz, 2, $ArCH_2$), 2.22-1.96 (m, 2, $ArCH_2\underline{H}$), 1.78 (d, J = 13 Hz, 2, $ArCHC\underline{H}_2$), and 1.32 (d, J = 13 Hz, 2, $ArCHC\underline{H}_2$).

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.42; H, 7.72.

*Further Purification of **67**.* — The first crop of crystals from the distilled mixture mentioned in the separations procedure was recrystallized from isohexane-toluene[40] (9:1) to give colorless **67**: mp 134-135°; mass spectrum (70 eV) m/e (rel intensity) 322 (M^+, 100), 161 (42), 160 (32), 134 (75), 115 (14), and 91 (25); ir (KBr) 9.8 μ (C-O-C stretch); pmr ($CDCl_3$) δ 6.99 (d, J = 8 Hz, 2, ArH), 6.74-6.56 (m, 4, ArH), 3.74 (s, 6, $ArOCH_3$), 2.96-2.35 (m, 8, $ArCH_2$), 2.16-1.88 (m, 2, $ArCH_2C\underline{H}$), and 1.88-1.21 (m, 4, $ArCH_2C\underline{H}$).

Anal. Calcd. for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 82.04; H, 8.03.

*Further Purification of **68**.* — Crude **68** (4.0 g), which was isolated from the oil as described in the separations procedure, was recrystallized from ethanol (100 ml) to give 3.0 g of colorless crystals of **68**: mp 110-112°; mass spectrum (70 eV) m/e (rel intensity) 320 (M^+, 100), 161 (27), 160 (78), 159 (70), 144 (19), and 115 (32); ir (KBr) 8.0 μ (C-O-C asymmetric stretch), 9.6 μ (C-O-C symmetric stretch); pmr ($CDCl_3$) δ 7.06-6.82 (m, 3, ArH), 6.76-6.54 (m, 3, ArH), 3.76 (s, 6, $ArOCH_3$), 3.18-2.12 (envelope, 8, $ArC\underline{H}_2$ and $ArCH_2C\underline{H}$), 2.10-1.74 (m, 2, $ArCH_2C\underline{H}_2$), and 1.68-1.22 (m, 2, $ArCH_2C\underline{H}_2$); uv max (95% ethanol) 279 nm (log ε 3.71) and 287 (3.67).

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.64; H, 7.64.

*Preparation of **69**.* — A solution of 0.9 g (0.003 mol) of **66** in 200 ml of methylene chloride was treated with 2.5 g (0.02 mol) of BBr_3[84] for 12 hr. A blue oil remained after concentration using a rotary evaporator; 50 ml of water was added, causing the formation of a precipitate. The reaction mixture was extracted with ether (3 x 100 ml), and the combined ether layers were washed with 10% NaOH (2 x 100 ml). The basic extracts were neutralized with dilute hydrochloric acid, giving a precipitate. This mixture was extracted with ether (2 x 100 ml), the ether layer dried ($MgSO_4$), and the solvent removed to give 0.7 g (0.0025 mol, 85%) of the crude diphenol. This was recrystallized from ether by evaporation and then sublimed at 265° (0.2 mm) to give 0.3 g of yellow solid, mp 320°. This compound was recrystallized from methylene chloride-acetone (3:1) to give 0.15 g (0.00045 mol, 15%) of white <u>69</u>: mp 325°; uv max (95% ethanol) 282 nm (log ε 3.63); (95% ethanol, with added alkali) 300 nm (log ε 3.72); ir (KBr) 3.0 μ (-OH stretch); pmr (acetone-$\underline{d}_6$) δ 7.82 (s, 2, ArOH), 6.97 (d, J = 8 Hz, 2, ArH), 6.77-6.54 (m, 4, ArH), 3.16 (d of d, J = 7 Hz and J = 18 Hz, 2, $ArCH_2$), 2.94-2.66 (m, 4, ArCH, solvent interference), 2.20-1.95 (m, 2, $ArCH_2C\underline{H}$), 1.79 (d, J = 13 Hz, 2, $ArCHC\underline{H}_2$), and 1.27 (d, J = 13 Hz, 2, $ArCHC\underline{H}_2$); mass spectrum (70 eV) m/e (rel intensity) 292 (M^+, 100), 147 (37), 146 (48), 145 (61), 144 (14), and 115 (11).

<u>Anal</u>. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 81.96; H, 7.03.

<u>Conversion of 67 to 1,1',2,2',3,3',4,4'-Octahydro-2,2'-binaphthyl-6,6'-diol (70)</u>. — Dimer <u>67</u> (2.3 g, 0.007 mol) was placed in a 500-ml, 3-necked flask under a nitrogen atmosphere. A solution of methylmagnesium iodide (prepared from 1.2 g Mg, 20 ml ether, and 2.6 ml methyl iodide) was added, and the flask was heated in an oil bath (115°) to drive off the ether. The temperature was then raised to 175° for 15 min after which evolution of gas ceased.[87a,b] The flask was allowed to cool; the reaction mixture was treated with ice followed by dilute hydrochloric acid. The resulting precipitate was

dissolved in 100 ml of ether. The ether layer was washed with dilute HCl and filtered to remove insoluble material. The ether extract was then shaken with 10% sodium hydroxide. The basic extract was next acidified with concentrated hydrochloric acid giving a white precipitate which was redissolved in ether. The ether layer was dried ($MgSO_4$), and the ether was removed, giving 1.5 g (0.005 mol, 71%) of white solid. The solid was recrystallized from methanol containing 1% concentrated HCl to give colorless crystals, mp 214-215°. This solid was then dissolved in a minimum amount of acetone, and was further purified by high-pressure liquid chromatography.[94] The resulting chromatographic fraction was heated to remove methanol and then cooled to give white needles of diphenol <u>70</u>: mp 218-219°; uv max (95% ethanol) 282 nm (log ε 3.38); (95% ethanol, with added alkali) 290 nm (log ε 3.33); pmr (acetone-$\underline{d}_6$) δ 7.78 (s, 2, ArOH), 6.88 (d, J = 8Hz, 2, ArH), 6.66-6.50 (m, 4, ArH), 2.94-2.30 (m, 8, $ArCH_2$), 2.18-1.89 (m, 2, $ArCH_2C\underline{H}$, solvent interference), and 1.84-1.02 (m, 4, $ArCH_2C\underline{H}_2$); ir (KBr) 3.0 μ (-OH stretch); mass spectrum (70 eV) m/e (rel intensity) 294 (M^+, 12), 159 (30), 148 (21), 147 (71), 146 (100), and 145 (38).

<u>Anal</u>. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.35; H, 7.43.

<u>Preparation of Diphenol Dimer 71</u>. — A sample (1.5 g, 0.005 mol) of <u>68</u> was treated with hot methyl magnesium iodide[87a,b] as described for the preparation of <u>70</u> in the previous section. A tacky, brown semisolid (1.2 g) was obtained after workup. This material was chromatographed through acidic alumina to give 500 mg of white solid. Recrystallization from benzene gave 303 mg (22%) of white crystals, mp 166-168°. Sublimation of this sample gave 145 mg (10.6%) of

colorless <u>71</u>: mp 169-171°; ir (KBr) 3.05 μ (-OH stretch), 7.45 (-OH bend), and 8.1 (C-O stretch); pmr (acetone-$\underline{d}_6$) δ 7.88 (s, 2, ArOH), 7.00-6.76 (m, 3, ArH), 6.70-6.50 (m, 3, ArH), 3.26-2.18 (envelope, 8, $ArCH_2$ and $ArCH_2C\underline{H}$), 2.18-1.72 (m, 2, $ArCH_2C\underline{H}_2$), and 1.64-1.22 (m, 2, $ArCH_2C\underline{H}_2$); uv max (95% ethanol) 218 nm (s, log ε 4.15), 282 (3.69), and 288 (s, 3.65); (95% ethanol, with added alkali) 242 nm (log ε 4.15) and 300 (3.74); mass spectrum (70 eV) m/e (rel intensity) 292 (M^+, 75), 186 (6), 147 (38), 146 (100), 145 (92), and 144 (20).

<u>Anal</u>. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 81.89; H, 6.89.

<u>Deoxygenation of Diphenol 69 to Hydrocarbon 41</u>. — Aqueous sodium hydroxide (0.1 g in 2 ml water) was added to an ethanolic (50 ml) solution of diphenol <u>69</u> (300 mg, 0.001 mol). Diethylchlorophosphate[85] (1.0 g) was added under a nitrogen atmosphere to the cooled (0°) solution and the contents of the flask were stirred for 4 hr at room temperature. The reaction mixture was diluted with water and extracted with ether. The organic extract was washed with water and dried ($MgSO_4$), and ether was removed to give 470 mg (0.0008 mol, 82%) of oil.

Ammonia (65 ml) was condensed into a 100-ml reaction vessel containing the oily derivative in ether (15 ml) and the resulting mixture was stirred with lithium metal (40 mg) for 40 min; a blue color persisted. Ammonium chloride (150 mg) was added to the solution which was then warmed to room temperature to evaporate ammonia. The reaction mixture was diluted with ether (350 ml) and the ether extract was washed, dried ($MgSO_4$), and filtered before the ether was removed to give 118 mg of solid. This solid was continuously extracted[45] through basic alumina with isohexane-benzene (15:1) and recrystallized from isohexane[40] to give colorless crystals (21 mg, 10%) of 41, mp 175-177°. This melting point was not depressed when a sample was mixed and melted with standard 41. Glc retention times for the two pure compounds were identical and a single peak resulted from coinjection. Pmr spectra of this sample and standard 41 were indistinguishable.

Deoxygenation of Diphenol 70 to Hydrocarbon 37. — A sample of diphenol 70 (1.0 g, 0.0034 mol) was treated with diethylchlorophosphate (2.0 g) followed by reaction with lithium (0.25 g) in ammonia as described in the preceding procedure for diphenol 69. The crude reaction material (0.5 g) was chromatographed through neutral alumina with benzene eluant to give 0.3 g (0.0011 mol, 33%) of hydrocarbon 37, mp 84-85°. This melting point was not depressed when this sample was mixed with 37 prepared by dimerization of naphthalene.

Reaction of 53 With Sodium Hydride in Ethylenediamine. — Sodium hydride (25.7 g) was added to anhydrous ethylenediamine (1 ℓ) in a dry 3-ℓ, fluted flask under a nitrogen atmosphere. The mixture was stirred until gas evolution ceased (2.5 hr) before a sample of 53 (60.1 g, 0.37 mol) was added. This solution was stirred (2.5 hr) and was then poured onto ice. Conc. HCl (3 ℓ) was added and this solution was then extracted with ether (2 x 2.5 ℓ) in a 22-1 separatory funnel. The combined ehter extracts were washed with 10% HCl (1.5 ℓ), water (2 x 1 ℓ), saturated Na_2CO_3 solution (1.5 ℓ), and water (1.5 ℓ). The ether was then dried overnight ($MgSO_4$), filtered, and removed by distillation and pumping to give 50.7 g of viscous, red oil.

The oil was distilled (Kugelrohr) to 155° (0.025 mm) to give fractions containing monomeric material (5.0 g, 8.3%). Further heating to 245° (0.03 mm) gave a fraction containing dimers (38.1 g, 63%) and left a glassy pot residue (6.9 g, 11.5%).

A glc trace of the monomer fraction showed peaks with retention times corresponding to 6-methoxytetralin, 6- and/or 7-methoxy-1,2-dihydronaphthalene, and 2-methoxynaphthalene as well as three unidentified peaks. A glc of the dimeric material showed eight components.

The dimeric fraction was dissolved in ether (200 ml) and stored at -14°. After several days, crystals formed which were separated by filtration to give a white solid (1.0 g), mp 210-235°. This solid was recrystallized from toluene and then triturated with boiling ether to leave colorless crystals (0.6 g, 1%) of 66, mp 236-241°. No melting point depression was observed when this sample was mixed with cyclodimer 66 prepared from sodium and ethylenediamine dimerization of 53. The pmr spectra for the compounds from the two different sources were identical.

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90. (a) The glc studies were done on a Hewlett-Packard 5750 instrument with dual flame ionization detectors using a 1/4" x 8' copper column packed with 5% UC W-98 on 80-100 mesh AW DMCS-treated Chromosorb G operating at 260°; (c) Same conditions as 90a but at 270°.

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94. A Waters Associates 3/8" x 4' C_{18}-Bondapak column with methanol-water (7:3) eluant was used.

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Thesis: I. SYNTHESIS OF 4-, 5-, AND 6-RING POLYNUCLEAR AROMATIC HYDROCARBONS

II. SODIUM-AMINE REACTIONS OF NAPHTHALENES: CYCLODIMERIZATION AND REDUCTIVE CYCLODIMERIZATION

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