I. THE CLEMMENSEN REDUCTION OF 2-ACETONAPHTHONE

II. STEREOCHEMICAL ASSIGNMENT OF THE ISOMERIC

2,3-DI(2-NAPHTHYL)BUTANE-2,3-DIOLS

III. REDUCTION OF ALKYLNAPHTHALENES

USING SODIUM IN DIETHYLAMINE

By

William Perry Duncan

Bachelor of Science
Kansas State College
Pittsburg, Kansas
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Master of Science
Kansas State College
Pittsburg, Kansas
1966

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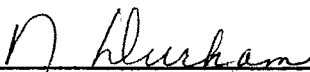III. REDUCTION OF ALKYLNAPHTHALENES

USING SODIUM IN DIETHYLAMINE

Thesis Approved:

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Thesis Adviser

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Dean of the Graduate College

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PART I

THE CLEMMENSEN REDUCTION

OF 2-ACETONAPHTHONE

CHAPTER I

INTRODUCTION AND HISTORICAL

The Clemmensen reduction of ketones to the corresponding alkanes
has been widely employed in organic synthesis and as a degradative step
in structure elucidation.[1] However, it is not generally appreciated
that the reduction of ketones may yield additional products,[1b,c]
other than the expected alkanes, depending on the structure of the
ketone and the reaction conditions employed. In this part of the dis-
sertation, an extensive investigation of the products resulting from
the Clemmensen reduction of 2-acetonaphthone (1) is reported. The
study includes the effect of reaction conditions on product distribution,
and a mechanistic interpretation is presented consistent with the
results obtained.

Clemmensen first reported the reduction of aldehydes and ketones,
using amalgamated zinc and concentrated hydrochloric acid in 1913.[2] The
reaction was reviewed by Martin[1a] in 1942, and a mechanistic survey fol-
lowed in 1959.[1b] Recently, Buchanan and Woodgate reviewed the
Clemmensen reduction of difunctional ketones.[1c] Several studies of the
reduction have been aimed at the elucidation of the mechanism of the
reaction, but as yet, none of the proposed mechanistic schemes[1b,c,3]
have been firmly established.

The Clemmensen reduction of 2-acetonaphthone (1) was first reported
in the 1930's,[4] and further reports of the same reaction have appeared

2

over the years.[5,6] In all cases the sole product cited was 2-ethyl-naphthalene (2) in yields ranging from 52%[4a] to 85%,[6] depending on reaction conditions. However, it should be noted that in 1936, Fieser and Hershberg observed considerable formation of 4-(8-methoxy-1-tetralyl)butyric acid (4) when 3-(4,8-dimethoxy-1-naphthoyl)propionic acid (3) was subjected to Clemmensen reduction conditions.[7] Reduction of the naphthalene nucleus is not usually observed under Clemmensen
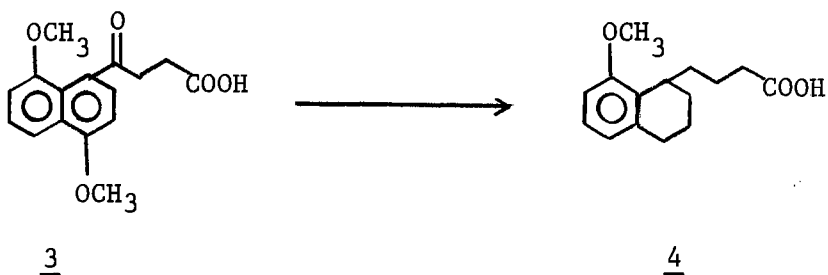
reduction conditions, and in fact, has been reported only in the case mentioned above.

CHAPTER II

DISCUSSION AND RESULTS

The author used the Clemmensen reaction to reduce the carbonyl

group of 2-acetonaphthone (1) and observed, depending upon conditions,

formation of hydrocarbon products 5, 6, and 7, which requires reduction
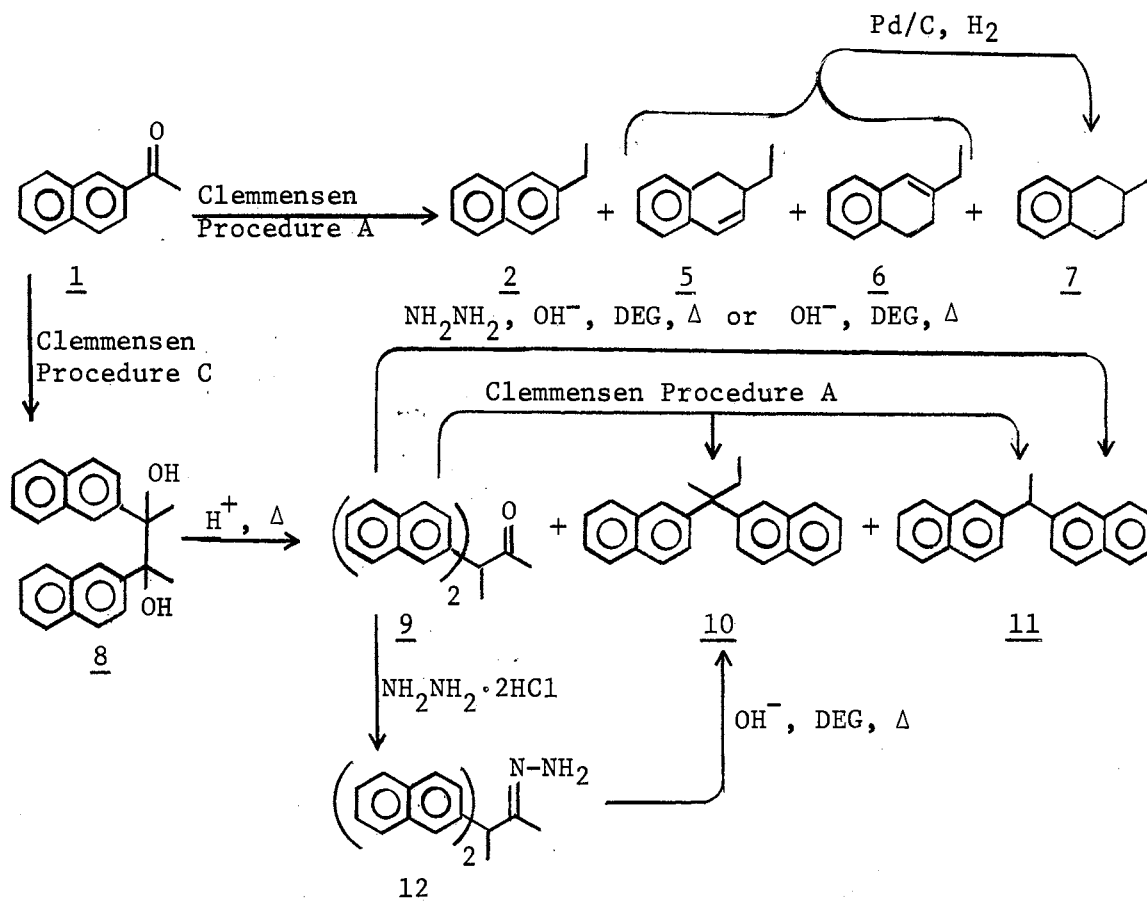
Figure 1. Reaction Scheme for the Clemmensen Reduction of
2-Acetonaphthone (1).

of the naphthalene nucleus. These hydrocarbons are significant

products (15.5% combined yield) when toluene is used as solvent.[1a] In

the absence of toluene, the conventional Clemmensen reduction[1a] of $\underline{1}$

gave relatively minor amounts of $\underline{2}$, $\underline{5}$, $\underline{6}$, and $\underline{7}$ and mainly condensation

products which included $\underline{9}$, $\underline{10}$, $\underline{11}$, and small amounts of several other

compounds having similar glc retention times. These unidentified com-

pounds may be partially reduced $\underline{9}$, $\underline{10}$ and $\underline{11}$. In addition, since dis-

tillation of the condensation products resulted in some pot residue,

polymerization products may have been present. The yields of Clemmensen

reduction products from a variety of procedures are compiled in Table I.

TABLE I

CLEMMENSEN REDUCTION OF 2-ACETONAPHTHONE

Procedure	Yield[a] of Steam-Volatile Hydrocarbon Products, %				Yield[b] of Nonvolatile Products, %		
	$\underline{2}$	$\underline{5}$	$\underline{6}$	$\underline{7}$	$\underline{9}$	$\underline{10}$	$\underline{11}$
A	61.4	13.9	1.0	0.6	1.7	2.0	0.9
B	53.7	0.2	0.2	0.1	21.1	15.2	7.3
C	42.2[c]	0.0	0.0	0.0	2.5[d]	33.6	12.0
D	40.4	0.3	0.2	trace	11.7	30.9	11.9
E	30.0	0.6	0.1	0.2	16.7	14.5	5.8

[a]Yield based on the combined weight of steam-distilled products and their glc[8a] peak ratios. [b]Yield based on the weight of distilled products and their glc[8b] peak ratios. [c]A trace of $\underline{14}$ and 0.6% of $\underline{15}$ were observed by glc.[8a] [d]In addition, 4.5% of the diol from the pinacol condensation of $\underline{1}$ was isolated from the non-steam-volatile fraction.

It is surprising that despite the numerous reports[4,5] of the Clemmensen reduction of 1, the formation of 5, 6, and 7 has gone unreported. Perhaps this is a result of the frequent use of picric acid in the purification[5,9] of 2.

The instrumental data (glc, nmr, and mass spectra) appeared to exclude those isomers of 5, 6, and 7 which could arise by reduction[10] of the aromatic ring *not adjacent* to the carbonyl group. To establish this point rigorously, the hydrocarbon mixture containing 5, 6, and 7 was hydrogenated until only 7 remained (Figure 1) and the glc of the latter was compared with that of its isomer, 6-ethyl-1,2,3,4-tetrahydro-naphthalene (13), prepared by independent Friedel-Crafts synthesis from tetralin.[11] Since the glc[8a] retention times are different, 13 must be absent, and its absence shows that it is not produced by the Clemmensen reduction of 1; hence, isomers of 5 and 6 must also be absent. The stability of 2 to Clemmensen reduction conditions is evidence against its being a precursor to 5, 6, or 7.[12]

Since alcohols and olefins have been shown to be intermediates in analogous cases,[3a,13] 1-(2-naphthyl)ethanol (14) and 2-vinylnaphthalene (15) were prepared and subjected to the Clemmensen reduction conditions of Procedure A. The alcohol 14 gave a steam-volatile hydrocarbon fraction consisting of 2:5:6:7:15 (300:13:1:2:69), whereas 15 yielded 2:5:6:7:15 (103:4.5:1:2:85).[8a] The non-steam-volatile fraction from 14 showed three glc peaks, the major one of which represented 80% of the mixture.[8b]

As shown in Table I, if toluene is used as solvent (Procedures A and B), 2, 5, 6, and 7 predominate. In the absence of toluene[1a] (Procedures D and E) or stirring (Procedures B, C, D, and E), the

formation of dimeric products is favored. At room temperature in toluene with stirring (Procedure C), it was found that the pinacol 8 could be isolated. As expected,[1a] mossy zinc (Procedures A and D) and powdered zinc (Procedures B, C, and D) gave a different array of products. Under conditions of Procedure A, the pinacol 8 was readily converted to the expected products 9 and 10 and the unexpected cleavage product 11 in the ratio 45:1:1 as determined by glc analysis.[8b] It is of interest that application of Procedure A to 8 yields a lower ratio of 10:11 (1:1) than its application to 9, which gives the 10:11 ratio as 15:1.

These findings place some limitation on the use of the Clemmensen reduction of 1 and related compounds. Indeed, the Wolff-Kishner reduction was found to be superior for the preparation[14a] of 2. However, the conventional Wolff-Kishner conditions were unsuited to the reduction of 9 to 10 since base-promoted cleavage[14b] to 11 is a strongly competing side reaction. This side reaction may be minimized by treatment of 9 with hydrazine dihydrochloride followed by addition of alkali.[14c]

An extension of the mechanisms proposed by Brewster[3a] for the reduction of saturated and α,β-unsaturated ketones satisfactorily accounts for the products formed (Figure 2). The first step involves protonation of the carbonyl group and attachment to zinc metal at the carbonyl carbon resulting in 16a, which, through a conventional mechanistic scheme for Clemmensen reduction,[3a] gives 2 via 16b. Alternatively, as proposed by Brewster for α,β-unsaturated ketones,[3a] attachment of zinc may occur at the benzylic position β to the oxygen of the enol group resulting in the formation of 16c, a process analogous to attack of a nucleophile in the Michael condensation.[15] Loss of zinc
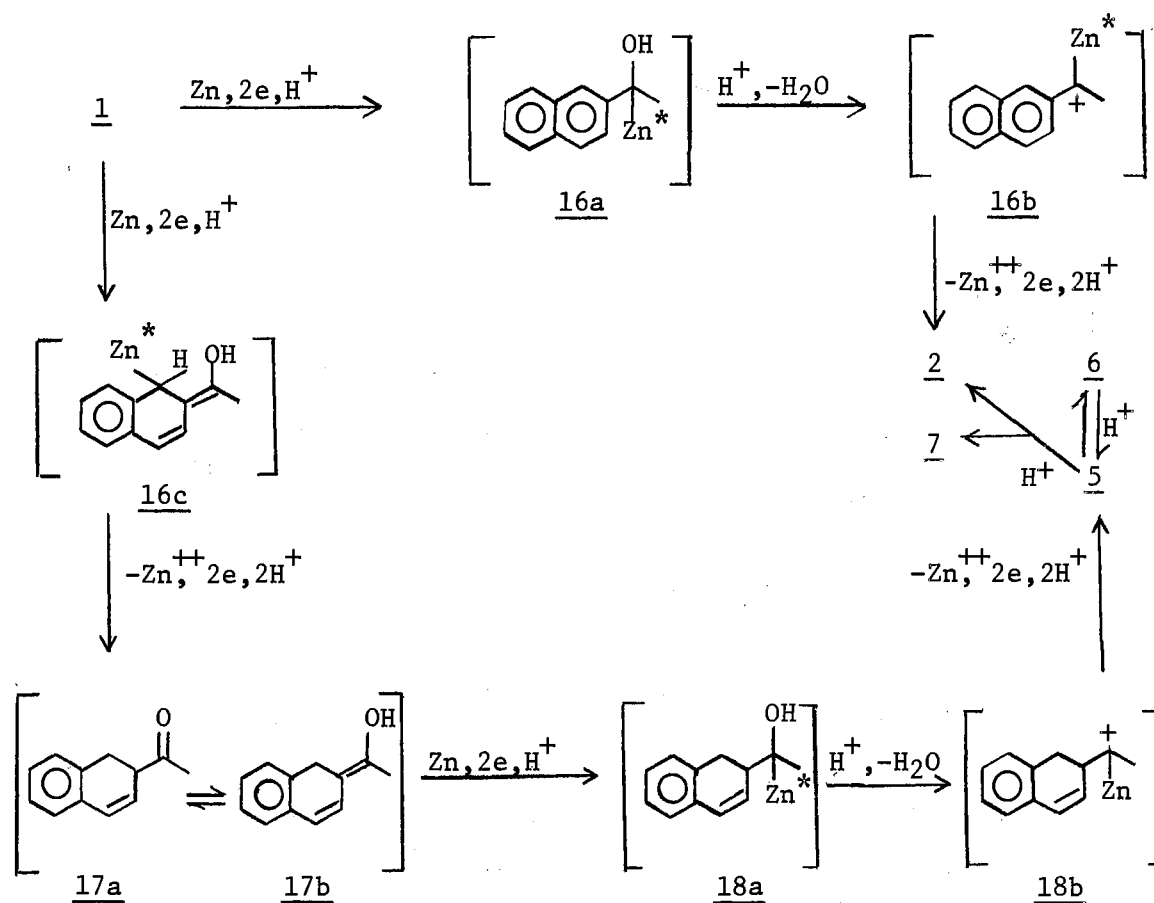
Zn* denotes the electron-rich metal surface.

Figure 2. Mechanism for the Clemmensen Reduction of 2-Acetonaphthone (1).

from 16c followed by protonation gives 17a and/or 17b, which upon further reduction and protonation gives the dihydronaphthalene 5. Acid-catalyzed isomerization and disproportionation of a mixture of 2, 5, 6, and 7 show that 5 is most affected by the conditions of Procedure A.[16]

An alternative rationalization[1c,17] involving the intermediate 20, which could be derived from either 1 or 1-acetonaphthone (22), is unlikely since there is no migration of ethyl group in either case,
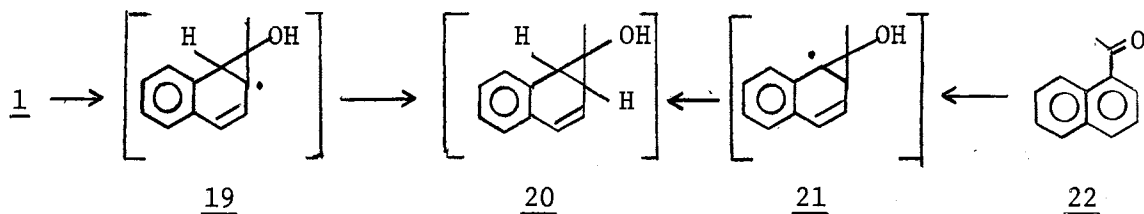
i.e. <u>1</u> does not lead to any detectable 1-ethylnaphthalene (<u>23</u>), nor

does <u>22</u> yield <u>2</u> under conditions of Procedure A as shown by glc analy-

sis.[8a] However, in addition to <u>23</u>, three partially reduced hydrocarbons

were observed in a combined yield of 5% in the reduction of <u>22</u> as com-

pared to 15.5% total yield of <u>5</u>, <u>6</u>, and <u>7</u> from <u>1</u>. The glc retention

times[8a] of these unidentified hydrocarbons were similar to those of <u>5</u>,

<u>6</u>, and <u>7</u>.

As mentioned previously when <u>14</u> was reduced under the conditions

of Procedure A, a mixture of three non-steam-volatile products resulted,

of which the major component made up 80% of the mixture. This major

component was isolated by column chromatography and shown (ir, uv, nmr,

and mass spectra) to be 2,3-dihydro-3-methyl-1-(2-naphthyl)-1<u>H</u>-benz[<u>e</u>]-

indene (<u>24</u>). Presumably this hydrocarbon can arise via the mechanistic

<u>24</u>
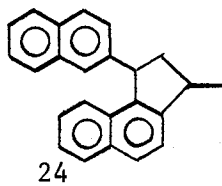
pathway shown in Figure 3. That is, <u>14</u> undergoes rapid dehydration and

protonation to the benzylic carbonium ion (<u>25</u>) which exists in
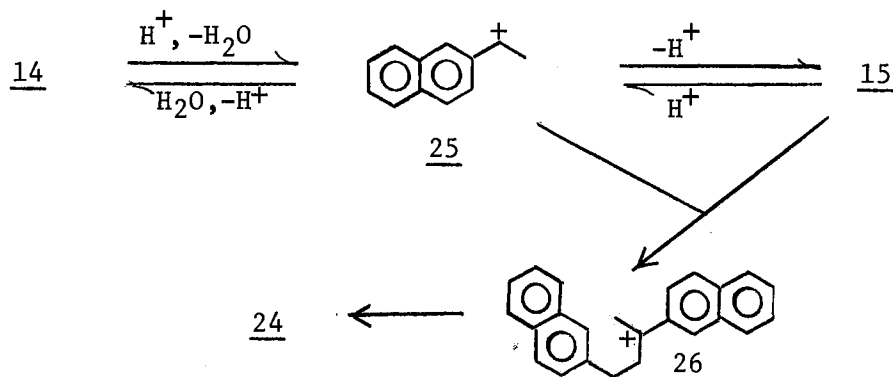
Figure 3. Mechanism for the Formation of 2,3-Dihydro-3-methyl-1-
(2-naphthyl)-1H-benz[e]indene (24).

equilibrium with the olefin 15. Thus, 25 undergoes electrophilic attack

on 15 to produce the new dimeric carbonium ion (26) which cyclizes to

24. A similar mechanism has been proposed by Paquette and Phillips in

the acid-catalyzed dehydrative expulsion of sulfur dioxide from a thi-

etane dioxide (27) to give 2,3-dihydro-1,3,3-trimethyl-1-(2-naphthyl)-

1H-benz[e]indene (28).[18]
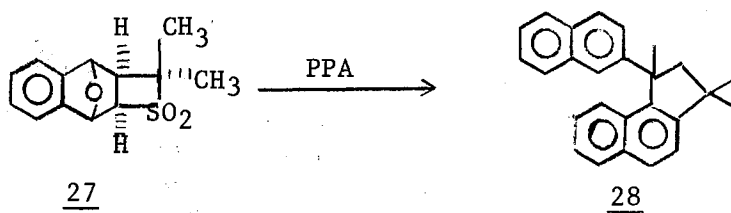
Acid-catalyzed dimerizations of vinylnaphthalenes had not been

reported until 1965 when the dimerization of 2-isopropenylnaphthalene

(29) with polyphosphoric acid (PPA) was reported to give 28.[18] However,

dimeric products derived from 1-isopropenylnaphthalene (30),[19a-e]
1-propenylnaphthalene (31),[19a] α-methylstyrene (32),[19a,20a-c] and
1,2-dihydronaphthalene[20d] are known in the literature. In addition,
the alkylation of benzene using 15 and 90% H_2SO_4 has been reported.[21]

Since corroborative evidence for the aforementioned mechanism was
needed, a more extensive investigation of the dimerization of 14 and
15 to 24 was undertaken. The results are shown in Figure 4. It is evi-
dent that 24 may be prepared quite readily from either 14 or 15 and once
formed, the product is stable to the reaction conditions. Amberlyst-15
gave a different array of products which included two major products
in a ratio of 1:2 and a trace of 24. However, treatment of this reac-
tion mixture with PPA gave 24 almost exclusively.
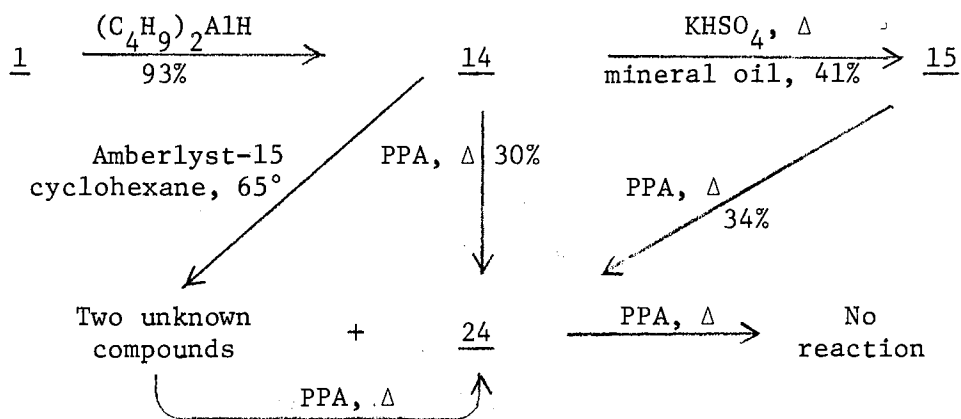
Figure 4. Preparation of 2,3-Dihydro-3-methyl-1-(2-naphthyl)-1H-benz-
[e]indene (24) From 1-(2-Naphthyl)ethanol (14) and
2-Vinylnaphthalene (15).

Nmr analysis of a mixture of the two major components indicates
that these may be isomeric cis- and trans-dimeric olefins.[21b] The nmr

for this mixture is as follows: nmr (CCl_4) δ 7.90-7.00 (m, Ar$\underline{H}$),

6.94-6.68 (m, vinylic, benzylic), 6.73, J 17cps, (unresolved pair of

doublets, vinylic proton of <u>trans</u>-olefin), 5.21, J 10cps, (unresolved

pair of doublets, vinylic proton of <u>cis</u>-olefin), 4.63 (quartet,

Ar-C$\underline{H}$), 4.36 (quartet, Ar-C-$\underline{H}$), 1.52 (d, -CH$_3$), 1.41 (d, -CH$_3$). Based

on this evidence, tentative structures <u>33</u> and <u>34</u> are assigned.

<u>33</u>   <u>34</u>
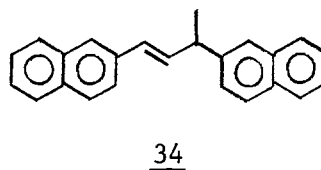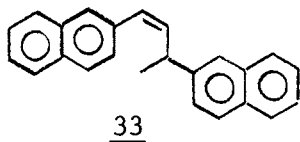
CHAPTER III

EXPERIMENTAL[22]

Zinc Amalgams.— Zinc amalgams were prepared in the following way: the desired weight of zinc [Fisher, certified reagent, mossy, or Baker and Adamson, technical (90%) dust] was placed in a flask and covered with an equal weight of distilled water. A volume of 37% hydrochloric acid equal to 5% of that of the water was added with vigorous swirling. After one minute, the calculated amount of mercuric chloride (Fisher, certified reagent) to give a 3.5% amalgam was added, and the resulting mixture was then shaken vigorously for 15 min. The amalgam was washed twice with distilled water and used at once.

General Procedures.— The Clemmensen reductions were carried out using one of the following procedures:

Procedure A.— To 220 g of mossy zinc amalgam was added 85 g (0.50 mol) of 2-acetonaphthone in 250 ml of toluene, 133 ml of distilled water, and 311 ml of concentrated hydrochloric acid. The reaction mixture was refluxed vigorously for 96 hr or until no ketone was present as determined by glc analysis.[8b] Concentrated hydrochloric acid (50 ml) was added about every 8 hr during the reaction period.

Procedure B.— To 22 g of zinc dust amalgam was added 8.5 g (0.05 mol) of 2-acetonaphthone in 25 ml of toluene, 13.3 ml of distilled water and 31.1 ml of concentrated hydrochloric acid. The refluxing reaction mixture was vigorously stirred with a mechanical stirrer

(Teflon paddle) until no ketone was present as evidenced by glc analysis.[8b] Concentrated hydrochloric acid (6 ml) was added every 2 hr during the reaction period.

Procedure C.— Same as B, excepting that a Vibro stirrer, Model No. E-1, was used to stir the reaction mixture and the reaction was carried out at 15-25°.

Procedure D.— Same as A, excepting that zinc dust was used to prepare the amalgam. Toluene was not used and the reaction mixture was stirred vigorously with a mechanical stirrer (Teflon paddle) for ca. 2.5 hr.

Procedure E.— Same as D, excepting that mossy zinc was used to prepare the amalgam.

At the end of the heating period for any of the above procedures, the reaction mixture was cooled and decanted from the zinc residue. The residue was washed thoroughly with ether and the washings were combined with the reaction mixture. The organic phase was separated and the aqueous layer was extracted with ether. The organic phase and ethereal extracts were combined, washed with water and saturated sodium bicarbonate solution, dried (Na_2SO_4), and concentrated to give a yellow, viscous residue. This residue was steam distilled to separate the volatile products from dimeric and polymeric products. The steam distillate was extracted with ether, dried (Na_2SO_4), concentrated, and analyzed by glc.[8a] The residue from the steam distillation was similarly isolated and analyzed.[8b] Separation of components was achieved by preparative glc[8c] and by column chromatography on neutral alumina. Final purification was realized by distillation and crystallization. Products were identified by spectral and elemental analysis. Data on products from

individual reactions follow:

1,2-Dihydro-2-ethylnaphthalene (5).— Bp 232-234°;[23] ir (neat)

3.30, 3.40, 3.48, 3.53, 6.72, 6.88, 7.01, 7.24, 7.77, 8.37, 8.94, 9.64,

11.05, and 11.58 μ; mass spectrum (70 eV) m/e (rel intensity) 158 (16),

130 (11), 129 (100), 128 (33), 127 (12), and 27 (7); nmr (CCl$_4$) δ 8.16-

7.77 (m, 4, Ar$\underline{H}$), 7.44-7.27 (2d, 1, vinylic adjacent to ring), 6.94-

6.75 (2d, 1, vinylic), 2.97-2.08 (m, 3, -C$\underline{H}_2$-benzylic and -CH-allylic),

1.72-1.21 (m, 2, -C$\underline{H}_2$-nonbenzylic), 0.94 (t, 3, -CH$_3$); uv max (95%

EtOH) 212 nm (log ε 4.60), 217.5 nm (log ε 4.63), 224 nm (log ε 4.47)

and 261 nm (log ε 4.23).

Anal. Calcd for C$_{12}$H$_{14}$: C, 91.08; H, 8.92. Found: C, 91.26;

H, 8.94.

3,4-Dihydro-2-ethylnaphthalene (6).— Bp 128-130° (20 mm) [lit.[24]

126-130° (20 mm)]; ir (neat), 3.32, 3.43, 3.48, 3.54, 6.74, 6.89, 6.99,

7.31, 8.32, 9.19, 11.39 and 11.76 μ; mass spectrum (70 eV) m/e (rel

intensity) 158 (41), 143 (29), 129 (100), 128 (43), 127 (13), and 115

(19); nmr (CCl$_4$) δ 6.98-6.81 (m, 4, Ar$\underline{H}$), 6.06 (broad s, 1, vinylic),

2.92-2.02 (m, 6, -C$\underline{H}_2$-benzylic and -C$\underline{H}_2$-allylic), 1.09 (t, 3, -CH$_3$);

uv max (95% EtOH) 262 nm (log ε 4.15) [lit.[24] 263 nm (log ε 4.10)].

1,2,3,4-Tetrahydro-2-ethylnaphthalene (7).— Bp 100-102° (0.2 mm)

[lit.[11] 100.9° (0.17 mm)]; ir (neat), identical with that reported in

the literature;[11] mass spectrum (70 eV) m/e (rel intensity) 160 (54),

131 (63), 115 (23), 105 (20), 104 (100), and 91 (33); nmr (CCl$_4$) δ

7.02-6.82 (m, 4, Ar$\underline{H}$), 3.03-2.13 (broad m, 4, -C$\underline{H}_2$-benzylic), 1.83-0.81

(broad m, 8, -C$\underline{H}_2$-nonbenzylic, -C$\underline{H}$- and -CH$_3$); uv max (95% EtOH) 267 nm

(log ε 2.71) and 274 nm (log ε 2.80) [lit.[11] 267 nm (log ε 2.74) and

274 nm (log ε 2.81)].

<u>3,3-Di(2-naphthyl)-2-butanone (9)</u>.— Mp 144-145°;[25a] ir (CHCl$_3$)
5.86, 6.12, 6.25, 7.37, 7.83, 8.83, 10.37, and 10.51 μ; mass spectrum
(70 eV) <u>m/e</u> (rel intensity) 324 (1), 282 (25), 281 (100), 266 (21), 265
(29), and 153 (13); nmr (CCl$_4$) δ 7.89-7.03 (m, 14, Ar<u>H</u>), 2.13 (s, 3,
-COC<u>H</u>$_3$), 2.00 (s, 3, -C-C<u>H</u>$_3$);[25b] uv max (95% EtOH) 219 nm (log ε 5.01),
222 nm (log ε 5.06), 268 nm (log ε 4.10) and 276 nm (log ε 4.10).

<u>Anal</u>. Calcd for C$_{24}$H$_{20}$O: C, 88.85; H, 6.21. Found: C, 88.66;
H, 6.37.

<u>2,2-Di(2-naphthyl)butane (10)</u>.— Mp 90-92°; ir (Nujol) 6.15, 6.27,
7.72, 7.87, 8.38, 8.87, 10.56, 11.69, and 12.22 μ; mass spectrum (70
eV) <u>m/e</u> (rel intensity) 310 (21), 282 (24), 281 (100), 266 (16), 265
(22) and 153 (15); nmr (CCl$_4$) δ 7.82-6.82 (m, 14 Ar<u>H</u>), 2.28 (quartet,
2, -CC<u>H</u>$_2$CH$_3$), 1.69 (s, 3, -C-C<u>H</u>$_3$), 0.73 (t, 3, -CH$_2$C<u>H</u>$_3$); uv max (95%
EtOH) 217 nm (log ε 4.99), 231 nm (log ε 5.05), 235 (log ε 5.08), 266.5
nm (log ε 4.11), and 275.5 nm (log ε 4.10).

<u>Anal</u>. Calcd for C$_{24}$H$_{22}$: C, 92.86; H, 7.14. Found: C, 92.73;
H, 7.24.

<u>1,1-Di(2-naphthyl)ethane (11)</u>.— Mp 95-96° [lit.[26] 95°]; ir (Nujol)
6.13, 6.24, 8.86, 10.37, 10.51, 11.13, 11.58, and 12.10 μ; mass spectrum
(70 eV) <u>m/e</u> (rel intensity) 282 (51), 268 (23), 267 (100), 266 (15), 265
(31), 252 (15); nmr (CCl$_4$) δ 7.92-7.11 (m, 14, Ar<u>H</u>), 4.35 (quartet, 1,
Ar$_2$C<u>H</u>), 1.76 (d, 3, ArCHC<u>H</u>$_3$); uv max (95% EtOH) 217 nm (log ε 5.00),
231.5 nm (log ε 5.08), 267 nm (log ε 4.08), and 276 nm (log ε 4.07).

<u>Catalytic Hydrogenation of a Mixture of 5, 6, and 7</u>.— To 100 mg
of 10% Pd/C was added a solution of 1 g of a mixture of <u>5</u>, <u>6</u>, and <u>7</u>
(28:2:1)[8a] in 150 ml of ethanol. This stirred mixture was hydrogenated
at 25° and 1 atms for 5 hr. After filtration through Dicalite, and

evaporation of the solvent, glc[8a] analysis indicated the presence of only 7.

Wolff-Kishner Reduction of 9 to a Mixture of 10 and 11.— The apparatus and procedure used has been described previously[14a] with the exception that the product was isolated by ether extraction. From 16.2 g (0.05 mol) of 9 was isolated 14.5 g of crude crystalline reaction products. These products were taken up in petroleum ether[22] and subjected to column chromatography using acidic and basic alumina with petroleum ether[22] as the eluant. Concentration of the eluant gave 12.9 g of white crystals which were shown by glc[8b] to be a mixture of 10 and 11 (3:7).

Base-Catalyzed Cleavage of 9.— The reaction vessel was a 25-ml, one-necked, flat-bottomed, stainless steel flask equipped with a Dean-Stark trap. A ball joint on the trap fitted with a Teflon O-ring provided a seal with the flask. The top of the trap directly above the reaction flask was threaded and fitted with a screw cap containing a glass tube which provided a helium inlet. The tube was sealed to the screw with silicone rubber. The glass joint above the stopcock of the trap was fitted with a straight-bore glass condenser which acted as the helium outlet. A 250-mg (0.77 mmol) sample of 9, 0.28 g of KOH pellets, 0.28 g of NaOH pellets, and 10 ml of diethylene glycol were added to the flask and the assembled system purged for several minutes with a fast stream of helium. The flow was lessened to maintain a slight positive pressure and the flask was lowered into the preheated (250°) Wood's metal bath. After 3 hr of heating, the reaction mixture was allowed to cool under a helium atmosphere. The resulting brown reaction mixture was extracted with ether. The ethereal extracts were

combined, washed with water, dried (Na_2SO_4), and concentrated. The
resulting dark brown oil was taken up in petroleum ether[22] and
subjected to column chromatography using a silica gel, neutral alumina
column, and petroleum ether as the eluant. Concentration of the eluate
gave a faint yellow oil which crystallized on trituration with petrol-
eum ether.[22] Recrystallization from 95% ethanol gave 150 mg (70%) of
11 as white crystals: mp 95-96° (lit.[26] mp 95°).

Clemmensen Reduction of 9.— Two grams (6.2 mmol) of 9 was reduced
under the conditions of Procedure A. After four days, less than 10%
of 9 had reacted to give 10:11 (15:1) as determined by glc analyses.[8b]
However, addition of powdered zinc amalgam resulted in 95% reduction in
24 additional hr to give 1.1 g (54% combined yield) of a mixture of
10:11 (15:1).[8b]

Wolff-Kishner Reduction of 9 to 10.— By use of Procedure A,[14c]
0.65 g (2 mmol) of 9 gave 0.55 g (88%) of 10.

Isolation and Reduction of 8.— Steam distillation of the products
from the reduction of 25 g (0.15 mol) of 1, using Procedure C, gave
11.5 g of nonvolatile residue. This residue was triturated with hot
petroleum ether[22] and the liquid was decanted to leave crude 8.
Recrystallization from 1:1 chloroform:ethanol gave 1.1 g (4.5%) of
white crystalline 8, mp 182-184° [lit.[25a,27] mp 184°]; ir ($CHCl_3$)
2.80, 6.25, and 8.88 μ; mass spectrum (70 eV) m/e (rel intensity)
281 (9), 172 (25), 171 (31), 155 (10), 127 (13), and 43 (100); nmr
($CDCl_3$) δ 7.96-7.13 (m, 14, ArH), 2.30 (s, 2, -OH), 1.65 (s, 6, -CH_3);
nmr (CD_3-$\overset{\overset{\text{O}}{\|}}{C}$-$CD_3$) δ 8.03-7.23 (m, 14, ArH), 2.04 (broad s, 2, -OH), 1.63
(s, 6, -CH_3); uv max (95% EtOH) 219 nm (log ε 5.42), 232 nm (log ε 5.43),
269 nm (log ε 4.09), and 277 nm (log ε 4.01).

Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47. Found: C, 83.94; H, 6.36.

The reduction of 0.24 g (0.7 mmol) of 8 using Procedure A gave 9:10:11 (4.5:1:1) as shown by glc analysis.[8b]

Reduction of 1-Acetonaphthone (22).— The reduction of 8.5 g (0.05 mol) of 22 using Procedure A gave 23 in 82% yield as shown by glc analysis.[8a] Three additional volatile hydrocarbons were also observed by glc analysis[8a] (combined yield 5%); they had retention times like those of 5, 6, and 7. The nonvolatile fraction showed three major components[8b] in a ratio of 1:1.25:1.50 which were similar in retention times to 9, 10, and 11.

6-Ethyl-1,2,3,4-tetrahydronaphthalene (13).— This compound was prepared as outlined previously[11] except that nitroethane was used as solvent. Bp 103-105° (10 mm) [lit.[11] 103.5° (9 mm)]; ir (neat), identical to that reported in the literature;[11] mass spectrum (70 eV) m/e (rel intensity) 160 (41), 145 (35), 132 (27), 131 (100), 117 (21), and 115 (20); nmr (CCl$_4$) δ 6.91-6.59 (m, 3, Ar$\underline{H}$), 2.99-2.27 (broad m, 6, ArC$\underline{H}_2$-), 2.01-1.52 (broad m, 4, -C$\underline{H}_2$- nonbenzylic), 1.17 (t, 3, -CH$_3$); uv max (95% EtOH) 265 nm (log ε 2.70), 269 nm (log ε 2.83), and 278 nm (log ε 2.86) [lit.[11] 265 nm (log ε 2.68), 270 nm (log ε 2.84) and 279 nm (log ε 2.88).

1-(2-Naphthyl)ethanol (14).— A 850-g (5.0-mol) sample of 1 dissolved in 2 1. of dry benzene was added dropwise over a 1.25-hr period to a well-stirred solution of 773 g (5.5 mol) of diisobutyl-aluminum hydride[28a] in 2 1. of dry benzene at room temperature in a nitrogen atmosphere.[28b] The reaction mixture was stirred and then cautiously poured onto ca. 5 1. of crushed ice. The resulting mixture

was acidified to pH 3 with 10% hydrochloric acid, 2 l. of ether were added, and the organic layer was separated. The resulting aqueous fraction was again extracted with ether, and the extracts were combined. After washing the organic layer twice with 500-ml portions of saturated $NaHCO_3$ solution, it was dried (Na_2SO_4) and concentrated to give 830 g (97%) of crude 14 which, when recrystallized twice from petroleum ether,[22] gave 801 g (93%) of pure 14, mp 70-72° [lit.[29] 71-72°].

2-Vinylnaphthalene (15).— A 7.5-g (0.044-mol) sample of molten 14 was added dropwise via an addition funnel to a 15-ml, round-bottom flask fitted with a Claisen condenser assembly containing 2 ml of Nujol and 1 g of $KHSO_4$ preheated to a bath temperature of 212-215° and under a pressure of 2.6 mm. Molten 14 was added at such a rate that smooth distillation occurred, ca. 30 min for complete addition. In the cooled collection flask was obtained (after drying under vacuum) 2.9 g (41%) of crude 15. Conversion of the crude product to picrate and recrystallization of the picrate from methanol gave yellow needles, mp 90-92° [lit.[30] 91-92°]. Chromatographic regeneration gave 2.5 g (35%) of 15, mp 64-66° [lit.[29,30] 65-66°]. Glc analysis indicated the purity of 15 to be 98%+.

Isolation and Identification of 2,3-Dihydro-3-methyl-1-(2-naphthyl)-1H-benz[e]indene (24).—Procedure A was used to reduce a 9.5-g (0.05-mol) sample of 14. The layers were separated and the aqueous layer was extracted twice with 50-ml portions of ether. The organic layer was washed twice with 50-ml portions of saturated $NaHCO_3$ solution and once with 50 ml of distilled water. The resulting reaction mixture was steam distilled, and both the steam-volatile and

non-steam-volatile fractions were extracted with ether. After drying

(Na_2SO_4), the ether extracts were concentrated (rotary evaporator) to

yield 0.7 g of steam-volatile products and 8.3 g of non-steam-volatile

products (three peaks via glc).[8b] A 1-g sample of the non-steam-

volatile products was dissolved in benzene and subjected to column

chromatography using silica gel and basic, acidic, and neutral alumina.

Elution with petroleum ether[22] gave twenty fractions. Fractions two

through six proved to be 90%+ pure 24. Combining these fractions and

recrystallizing from petroleum ether[22] gave white crystals, mp 124.5-

126.5°; ir (CCl_4) 3.27, 3.37, 3.48, 6.05, 6.18, 6.58, 6.87, 7.25, 7.48,

9.07, 11.22, and 11.64 μ; mass spectrum (70 eV) m/e (rel intensity)

308 (100), 293 (35), 181 (18), 180 (56), 165 (52), and 141 (24); nmr

(CCl_4) δ 6.83-6.90 (m, 13, ArH), 4.81 (t, 1, dibenzylic), 3.54-3.20

(m, 1, benzylic), 3.15-2.80 (m, 1, one proton of $-CH_2$), 1.94-1.59 (m,

1, one proton of $-CH_2$), 1.39 (d, 3, CH_3); uv max (95% EtOH) 222 nm

(log ε 5.72), 274 nm (log ε 4.56), 278 nm (log ε 4.56), 283 nm (log ε

4.54), 307 nm (log ε 3.68), 312 nm (log ε 3.62), and 320 nm (log ε 3.71).

Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.00;

H, 6.55.

Acid-Catalyzed Dimerization of 15 Using PPA.— A mixture of 4.62

g (0.03 mol) of 15 and 25 g of PPA was allowed to stand at room tem-

perature for 24 hr (deep purple color developed). The reaction was

completed by heating on a steam bath for 0.5 hr with occasional stir-

ring. The resulting reaction mixture was poured into 400 ml of cold

water with stirring. After complete decomposition was evident, the

aqueous mixture was extracted several times with 50-ml portions of

ether, washed with distilled water, dried (Na_2SO_4) and concentrated

(rotary evaporator) to give 4.4 g of crude yellow oil. This oil was dissolved in petroleum ether[22] and passed through a column of basic alumina. After elution with 2 l. of petroleum ether[22] and concentration, 4.0 g of crude clear oil was obtained. Trituration with petroleum ether[22] gave 2.5 g of white crystals. Recrystallization from petroleum ether[22] gave 1.5 g (34%) of 24, mp 124.5-126.5°.

Acid-Catalyzed Dimerization of 14 Using PPA.— A mixture of 65 g (0.38 mol) of 14 and 650 g of PPA was allowed to react (deep purple color developed) as described above for 15. Using an exactly analogous work-up procedure as above yielded 60.5 g of crude products. The resulting reaction mixture was distilled under reduced pressure yielding two fractions. Fraction one was a clear liquid, 2.8 g, bp 67-69° (0.1 mm), and was shown via glc[8b] to be a mixture of 14 and 15 in a ratio of 1:9. Fraction two, bp 197-203° (0.1 mm), was shown to be 90%+ 24 (glc)[8b] and after elution through a basic alumina column with petroleum ether gave white crystals of 24, 17.5 g (30%), mp 124-126°.

Acid-catalyzed Dimerization of 14 Using Amberlyst-15.[21c]— To a magnetically stirred reaction flask fitted with a reflux condenser was added 4.62 g (0.03 mol) of 14, 180 ml of cyclohexane and 7.5 g of Amberlyst-15. The resulting mixture was warmed on a steam bath for 0.5 hr. After cooling, the reaction mixture was decanted and concentrated (rotary evaporator). The resulting clear viscous oil was eluted through a basic alumina column with petroleum ether.[22] Removal of the petroleum ether (rotary evaporator) gave 4.5 g of a clear viscous oil which consisted of a trace of 15 and three major components (glc)[8b] in a ratio of 1:2:trace. The third peak was shown via glc[8b] mixed injection technique to be 24. The treatment of 1 g of the clear

viscous oil with 10 g of PPA at room temperature (deep purple color developed) for 24 hr and warming for 0.5 hr followed by the usual work-up procedure above gave 0.6 g of 24, mp 124-126°.

Reaction of 24 with PPA.— A 1-g sample of 24 was added to 25 g of PPA and allowed to stand at room temperature for three days. The resulting reaction mixture was then heated on a steam bath for 2.0 hr. Following the work-up procedure described previously, 0.9 g of 24 was recovered unchanged as indicated by glc.[8b]

PART II

STEREOCHEMICAL ASSIGNMENT OF THE ISOMERIC

2,3-DI(2-NAPHTHYL)BUTANE-2,3-DIOLS

CHAPTER IV

INTRODUCTION AND HISTORICAL

In the course of the investigation of a novel Clemmensen reduction
of 2-acetonaphthone (1), described in Part I of this dissertation, a
dimeric product was isolated which was shown via ir, mass, nmr, and
uv spectra to be the corresponding pinacol 8, mp 183-184°.[25a,27] A
literature search revealed that no stereochemical assignment for meso-
2,3-di(2-naphthyl)butane-2,3-diol (35) and (±)-2,3-di(2-naphthyl)-
butane-2,3-diol (36) had been made prior to 1971.[31]

OH
OH
CH₃
CH₃
35

OH
OH
CH₃
CH₃
36
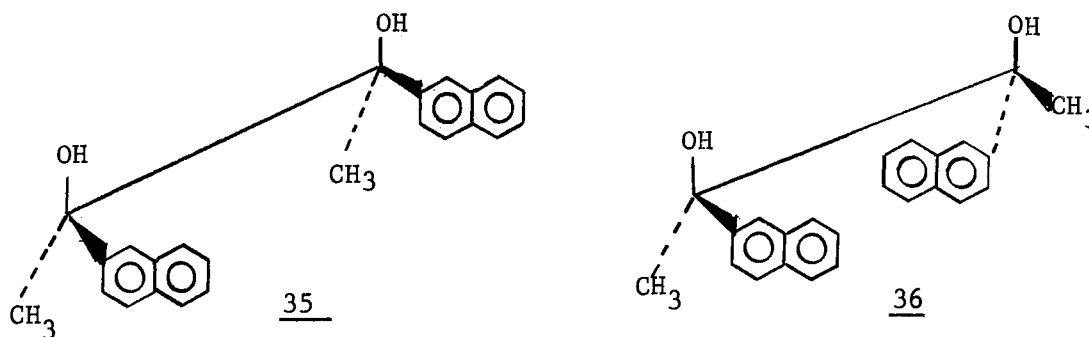
Stereochemical assignments of related meso- and (±)-pairs (pinacols
of acetophenone derivatives) had previously been made from analysis of
nmr[32] and ir[33] data. The assignment of diastereoisomeric identity using

25

ir data was based on the fact that for meso diols to have significant

intramolecular hydrogen bonding, a sterically crowded conformation is

required (38). Since this conformation is unfavorable for the meso

37   38   39
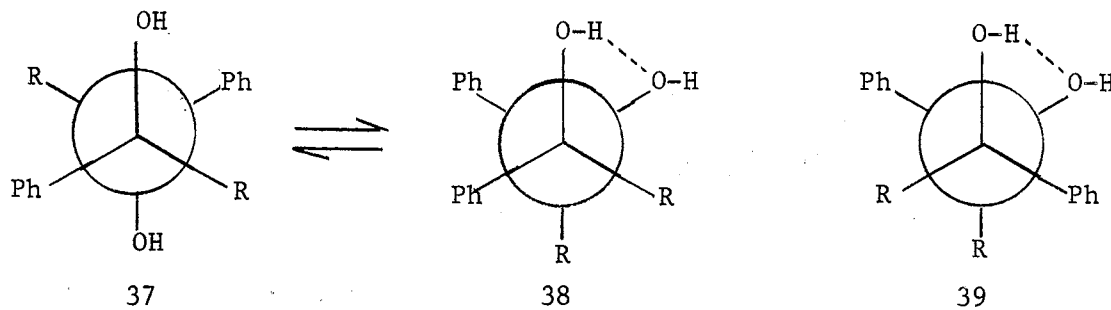
compound, only a very weak "bonded" -OH band (often only a shoulder) is

observed in the ir spectra.[33] However, this is not the case for the

(±) diastereomer (39); therefore, both the "free" and "bonded" -OH

bands are strong and distinguishable.[33]

Assignments via nmr were based on the observation that in all

pairs of pinacols examined, the hydroxylic proton chemical shift of the

(±) pair appeared at a lower field strength, presumably owing to the

more effective contribution of intramolecular hydrogen bonding in the

(±) pair 39 which *deshields* this proton.[32d] In the cases where separa-

tion between hydroxylic proton chemical shifts was insufficient, the

assignment was made based on methyl proton absorption. That is, as a

result of the relatively higher amount of intramolecular hydrogen bond-

ing in the (±) diastereomer 39, its methyl protons lie above the plane

of the phenyl groups and therefore are more effectively *shielded* than

the methyl protons of the meso form <u>37</u> and <u>38</u>. Thus, the methyl

proton absorption of <u>39</u> appears at a higher field strength.[31,32a,d]

OH

OH

$+ \quad \emptyset\text{-B(OH)}_2$

42

$\xrightarrow{\text{toluene, } \Delta}$

$\emptyset$—B—O

O

$+ \ 2\text{H}_2\text{O}$

prepared and purified by several different methods and analyzed by glc with results as shown in Table II. The considerable variation in mp of the purified pinacol is consistent with the glc analysis, that is, the higher the mp, the greater the ratio of meso:($\pm$) diol.

TABLE II

PREPARATION OF PINACOLS DERIVED FROM 2-ACETONAPHTHONE

Reaction	Yield of Purified Pinacol, %, mp	Ratio, meso:($\pm$)[a]	
		Purifi-cation	From Crude Reaction Mixture
1, Clemmensen Reduction[36]	5, 183–184°	all meso[b]	1:1.8
1, Photolysis, Et$_3$N, EtOH[27b]	40, 165–171°	1.4:1[c]	1:1.8
1, Zn (dust), NaOH, EtOH[25a]	24, 180–182°	45.3:1[d]	1:1.8

[a]Determined by glc peak ratios of the butylboronic esters using a 0.125-in. (o.d.) x 8-ft stainless steel tube containing 80–100 mesh, acid-washed, DMCS-treated Chromosorb W coated with 5% of UC W-98 silicone rubber in a Hewlett-Packard 5750 instrument operating at 280°.
[b]Recrystallized once from 1:1 chloroform:ethanol.[36] [c]Recrystallized once from 1:1 benzene:hexane.[27b] [d]Recrystallized once from 95% ethanol.[25a]

The nmr analysis depends upon the influence of the aromatic ring anisotropy on the positions of the methyl resonances,[31,32a,d] i.e. the methyl protons of the (±) pair lie above the planes of the naphthyl rings and are more effectively shielded by the π-electron system of the naphthyl groups than are the methyl protons of the meso form (see Table III). Therefore, the methyl protons of 40 appear at a lower field than the methyl protons of 41. Furthermore, as expected, a greater separation (64 Hz at 60 MHz) of the resonance signals for the methyl protons compared with the separation (6 Hz at 100 MHz) recently reported for the diols[31] was observed because in the phenylboronic esters, the groups are "locked" into position. This enhanced separation (ca. 18-fold) should allow wide application of the use of nmr spectral analysis of phenylboronic esters in the stereochemical assignments of pinacols of this type. These results substantiate the earlier report[31] that the pinacol, mp 183-184°, is indeed the meso diol.

TABLE III

ISOMERIC 2,3-DI(2-NAPHTHYL)BUTANE-2,3-DIOL ESTERS OF
PHENYLBORONIC ACID

Stereochemical Assignment	Nmr δ Values (CDCl$_3$)			
	C_6H_5	$C_{10}H_7$	CH_3	OH
35[a]	–	7.96-7.13	1.65	2.30
36	–	7.96-7.13	1.60	3.32
40	8.23-7.99	7.81-6.70	1.97	–
41	8.23-7.99	7.81-6.70	1.33	–

[a] mp 183-184°

It should be noted that the meso:($\pm$) ratio (Table II) is the same
for pinacol formation under acidic and basic conditions. The observed
ratio is in excellent agreement with the ratio obtained by electrolytic
reduction under basic conditions but does not agree with the ratio
reported for the same reduction under acidic conditions.[31] In terms
of previously employed arguments concerning the dimerization step of
the reaction,[32c,38] the above data indicate a dimerization step which
involves one molecule of the radical ion (43) and one molecule of its
conjugate acid (44). This concept allows for a significant hydrogen
bonding between the two species just prior to dimerization. Thus, the
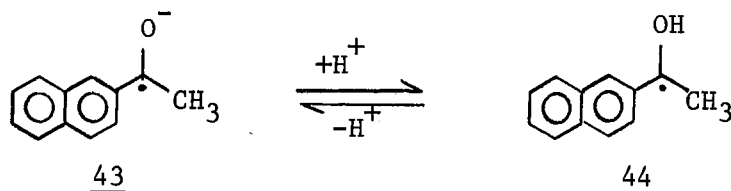
stereochemical preference in the dimerization step is controlled by
minimizing nonbonding interactions. However, in acid solution, insig-
nificant amounts of 43 would be expected to be present and dimerization
would occur by the joining of two radicals 44.[31] Since the hydrogen
bonding between two radicals would not be expected to be as strong as
hydrogen bonding between species 43 and 44, dimerization in acid solu-
tion should lead to an increased amount of meso-pinacol and thus change
the meso:($\pm$) ratio.[31] Such change is not observed under the conditions
employed (see Table II), thus creating an apparent anomaly.

PART III

REDUCTION OF ALKYLNAPHTHALENES USING

SODIUM IN DIETHYLAMINE

CHAPTER VI

INTRODUCTION

The reduction of naphthalene (45) with sodium and amines yields numerous products which include 1,2-dihydronaphthalene (46), 1,4-dihydronaphthalene (47), 1,2,3,4-tetrahydronaphthalene (48), reductive amination products, C_{20} dimers, and decreasing amounts of C_{30} and C_{40} products.[39a-c] The product distribution varies considerably, depending on the particular reaction conditions chosen and the amine selected.[39a,b] Although the reduction products are expected, the formation of the reductive amination product is less understood and a more exact knowledge of the composition of the hydrocarbon reaction products is essential to explain the various competing reactions. This becomes increasingly important for substituted naphthalenes since a steric effect may influence the course of the reaction by determining which ring is reduced and whether reductive amination occurs.[39,40] In light of these observations, the following series of alkylnaphthalenes was selected for study to help clarify these points.

R = CH$_3$, CH$_2$CH$_3$, C(CH$_2$)$_3$ R = CH$_3$, CH$_2$CH$_3$
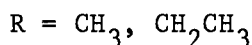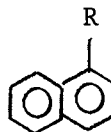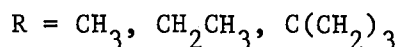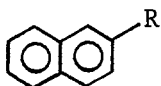
More explicitly, this study was undertaken to explore, in some detail, the ratios of monomeric reduced hydrocarbon products produced when various alkylnaphthalenes are caused to react with sodium in diethylamine (49)[41] at slightly below room temperature. Thus, steric effects of alkyl groups on the course of the reaction would be determined and significant data provided for mechanistic interpretations regarding this modification of the Birch reduction.[42]

CHAPTER VII

HISTORICAL

Although the reduction of aromatic ring systems by alkali metals

dissolved in liquid ammonia was observed by LeBeau and Picon[43] in 1914,

it was not until the extensive investigations of Birch[42a] and his col-

laborators that the method achieved acceptance as a major synthetic

tool.[42,44] The state of current knowledge, summarized in a compre-

hensive review by M. Smith,[44c] is rather surprisingly deficient regard-

ing compounds other than monobenzenoid molecules. Although some

polycyclic systems -- naphthalene,[43,45] anthracene,[46] phenan-

threne,[45a,47,50] pyrene,[48] fluorene,[49] acenaphthene[46a] and perylene[48c]

-- have been investigated using metal-ammonia reduction conditions,

very few alkyl derivatives have been studied.[44c] R. G. Harvey has

reported the lithium-ammonia reduction of a series of representative

polycyclic aromatic hydrocarbons,[50a] including some alkyl derivatives,

but no naphthalene derivatives were investigated. In addition, the

reduction of alkylanthracenes by alkali metals in a hexamethylphosphor-

amide-THF mixture has been recently reported.[50b]

An empirical rule has been proposed by Hückel and co-workers[51] for

alkyl-substituted naphthalenes. This rule states that the *unsubstituted*

ring is reduced more readily when the substituent is at the 1-position

and the *substituted* ring is reduced more readily when the substituent

is at the 2-position, e.g. 1-methylnaphthalene (50) gave

5-methyl-1,4-dihydronaphthalene (51) when reduced by sodium-ammonia

followed by NH$_4$Cl,[51a] whereas 2-methylnaphthalene (52) affords 2-methyl-

1,4-dihydronaphthalene (53) with sodium-ammonia followed by methanol.[51b]

Similar results have been obtained with the alkoxynaphthalenes (alkoxyl

cleavage may be competitive)[52,45c] and 1-naphthylamine.[53] Other exam-

ples are in the literature.[44c]
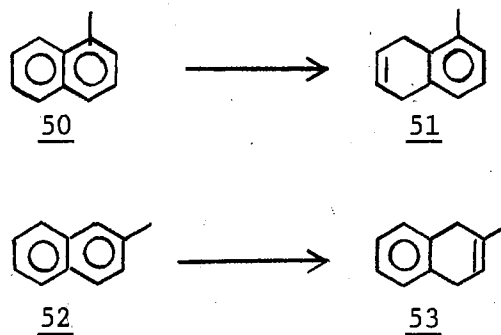
In 1937 Wooster discovered that monocyclic aromatic compounds are

reduced mainly to cyclohexadienes by alkali and alkaline earth metals

in refluxing ammonia (ca. -33°) containing a substance more acidic than

the solvent[54] (alcohols, water, etc.). Later, Birch greatly extended

the scope of this reaction[42] and proposed a mechanism.[55] More recently,

Slaugh and Raley have reported the reduction of benzene[56a] and some

alkyl-substituted benzenes[56b] under extremely high temperature and pres-

sure. As predicted by the mechanism proposed,[55] Krapcho and

Bothner-By[57] found rate differences in reductions of benzene derivatives

depending on whether they were substituted with electron-withdrawing

COO⁻Na⁺ → COO⁻Na⁺

54 55

56 57
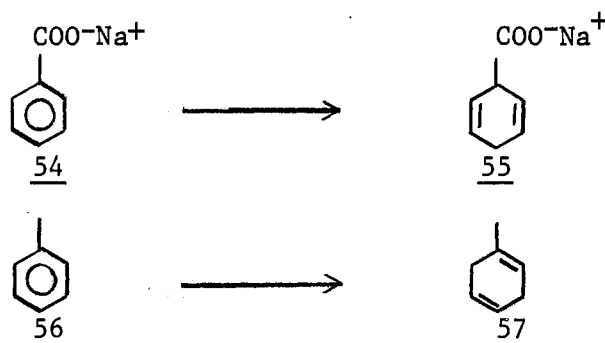
or electron-donating groups. Thus, sodium benzoate[58] (54) was reduced faster than toluene[57] (56), the position of reduction being governed by the position of greatest electron density in the intermediates.[57] A few polysubstituted benzene derivatives have been investigated and an excellent summary exists.[59] The reduction of alkyl-substituted benzoic acids with lithium in ammonia is a recent example.[60] The Birch reduction of 2,2-paracyclophane (58) has also been reported recently.[61] It has been suggested that in refluxing ammonia, lithium is better than sodium for the conversion of certain aromatic compounds to dienes.[62]

In 1939 Hückel and Bretschneider investigated the sodium-ammonia reduction of biphenyl (59) at -75° to -70°.[45a] The same reaction was studied in 1956 by Hückel and Schwen[63] using slightly different conditions; they isolated 3-phenyl-1,4-cyclohexadiene (60) instead of 1-phenylcyclohexene (61) which was claimed previously.[45a] In a more recent study,[64] 60, 61, 62, and 63 were all isolated from a reduction of 59 using sodium and ammonia in methanol. A tetrahydrobiphenyl was isolated in a comparable reaction in which ethanol was used instead of methanol.[62,65]
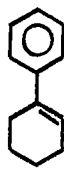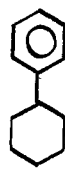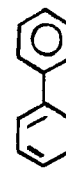
60   61   62   63

Benkeser and co-workers found low-molecular-weight amines, particularly methylamine and ethylamine, to be excellent media for reductions with lithium.[66] Aromatic compounds are reduced to mono-olefins[66a,e,g] in neat monoamines, whereas in monoamine-alcohol solutions, diolefins are obtained.[66f] The distribution of isomeric mono-olefins obtained from substituted benzenes or naphthalene was shown to be dependent upon the composition of mixed amine solvents.[66e,g,h] Lithium-amine reagents are strong enough to reduce isolated double bonds under certain conditions[66b,d] and lithium in ethylenediamine[67] is the most potent, but least selective, metal reagent thus far developed. The latter is extremely useful for completely saturating ring systems or for the reduction of very inert compounds.

The use of various higher-molecular-weight primary and secondary amines as a solvent medium for the reduction of several naphthalenes with sodium has been studied by Eisenbraun et al.[39a,b,40,68] In addition to 46, 47, and 48, the corresponding 1,2,3,4-tetrahydro-2-naphthyl-amine derivatives (64) are produced, which provides the direct formation of a carbon-nitrogen bond in secondary or tertiary amines. A mechanism has been proposed to account for these products.[39a] The C_{20} dimeric fraction is generally a complex mixture in which 65,[39a,40b-d] 66,[41] 67,[39a,c,40b-d] 68,[69] 69,[39a,40b-d,69] and 70[41] are the major components.

$$\underline{45} \xrightarrow[R_2NH]{Na} \underline{46} + \underline{47} + \underline{48} + \underline{64} + \text{dimers and trimers}$$

Mechanisms have been proposed to explain these dimeric products, but the mechanistic rationalization is still uncertain.[41,69]

<u>65</u>

<u>66</u>

<u>67</u>

<u>68</u>

<u>69</u>

<u>70</u>
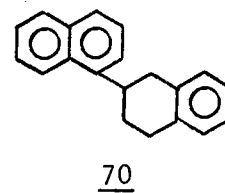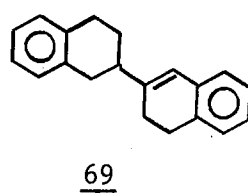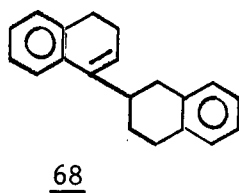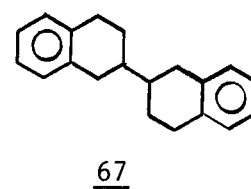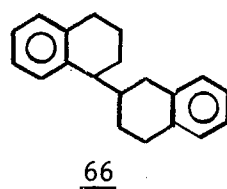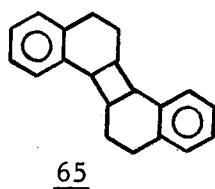
CHAPTER VIII

DISCUSSION AND RESULTS

The results of the reaction of alkylnaphthalenes using sodium in diethylamine are shown in Table IV. The dispersed sodium was generated

71

72

73

74

75
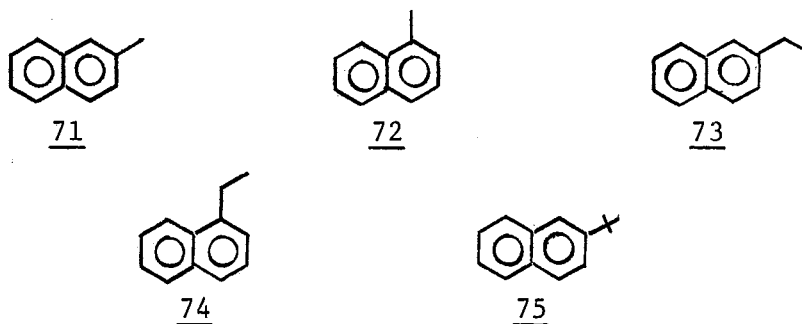
in situ using the stirring and shredding device developed in this laboratory.[70] It is evident from the data (Table IV) that reduction is the predominant reaction pathway. These data also suggest that reductive dimerization may be more important in the 1-substituted derivatives than in the 2-substituted derivatives. Although the data collected using hexamethylenimine (76) support this subtle observation,[39a] further investigation is needed for clarification.

TABLE IV

REDUCTION OF ALKYLNAPHTHALENES WITH SODIUM IN DIETHYLAMINE^a

Starting Material	Total Yield of Steam-volatile Hydrocarbon Products,^{b} %	Recovered Starting Material,^{c} %	Yield of Non-steam-volatile Hydrocarbon Products,^{e} %	Yield of Reductive Amination Products^f
2-Methylnaphthalene, 71	83.2	5.5	10.6	5.1
1-Methylnaphthalene, 72	58.7	11.8	35.2	2.6
2-Ethylnaphthalene, 73	72.8	1.9	10.7	10.5
1-Ethylnaphthalene, 74	67.8	1.9	17.4	10.5
2-t-Butylnaphthalene, 75	81.0	3.2	8.9	10.7
2-t-Butylnaphthalene, 75^d	87.2	25.1	5.0	2.6

^{a}All reaction times 2.5 hr. A red-brown color generally developed in 15 min. ^{b}Yield calculations are based on *consumed* aromatic hydrocarbon using the molecular weight of a corresponding dihydro derivative. ^{c}Based on starting aromatic hydrocarbon. ^{d}Diethylamine hydrochloride in tetramethylethylenediamine (TMEDA) used instead of diethylamine. ^{e}Based on the corresponding dimeric dihydro derivative. Glc[71] typically gave two to seven peaks. ^{f}Based on the corresponding 1,2,3,4-tetrahydro-2-naphthylamine derivative. Glc[71] indicated mixtures of two to four components.

The steam-volatile hydrocarbon fractions from reductive amination

reactions are generally rather complex mixtures of dihydro and tetra-

hydro derivatives which are extremely difficult to separate.[39a,40e]

The reactions described in Table IV are no exception, as is shown by

the gas chromatograms[8a] of the steam-volatile fractions shown in

Figures 5 and 6. The steam-volatile product mixtures were analyzed

using basic techniques of gas chromatography,[8,72] and by nmr, mass,

infrared, and uv spectroscopy.[22,73] The results of these analyses are

shown in Table V. Undoubtedly, the compositions of the reaction mix-

tures are time-dependent,[40f,41,69,74] and those reported in Table V

represent the mixture observed for a 2.5-hr reaction time.

The hydrocarbons 78, 80, and 90 were independently synthesized by

dehydration of the corresponding benzylic alcohol using A-15.[21b,75]

78   80   90
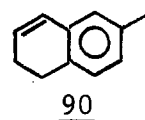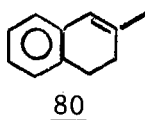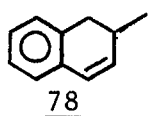
Compound 90 was subsequently shown not to be present among the steam-

volatile hydrocarbons obtained from sodium-diethylamine reduction of

71.[72] Compound 90 was prepared by a conventional Friedel-Crafts synthe-

sis.[76] The other two compounds 78 and 80 were prepared from benzylic

alcohols available from previous studies in this laboratory.[77a]

To facilitate the separation of the aforementioned complex mixtures

by identification of the tetrahydronaphthalenes, a partial Pd/C
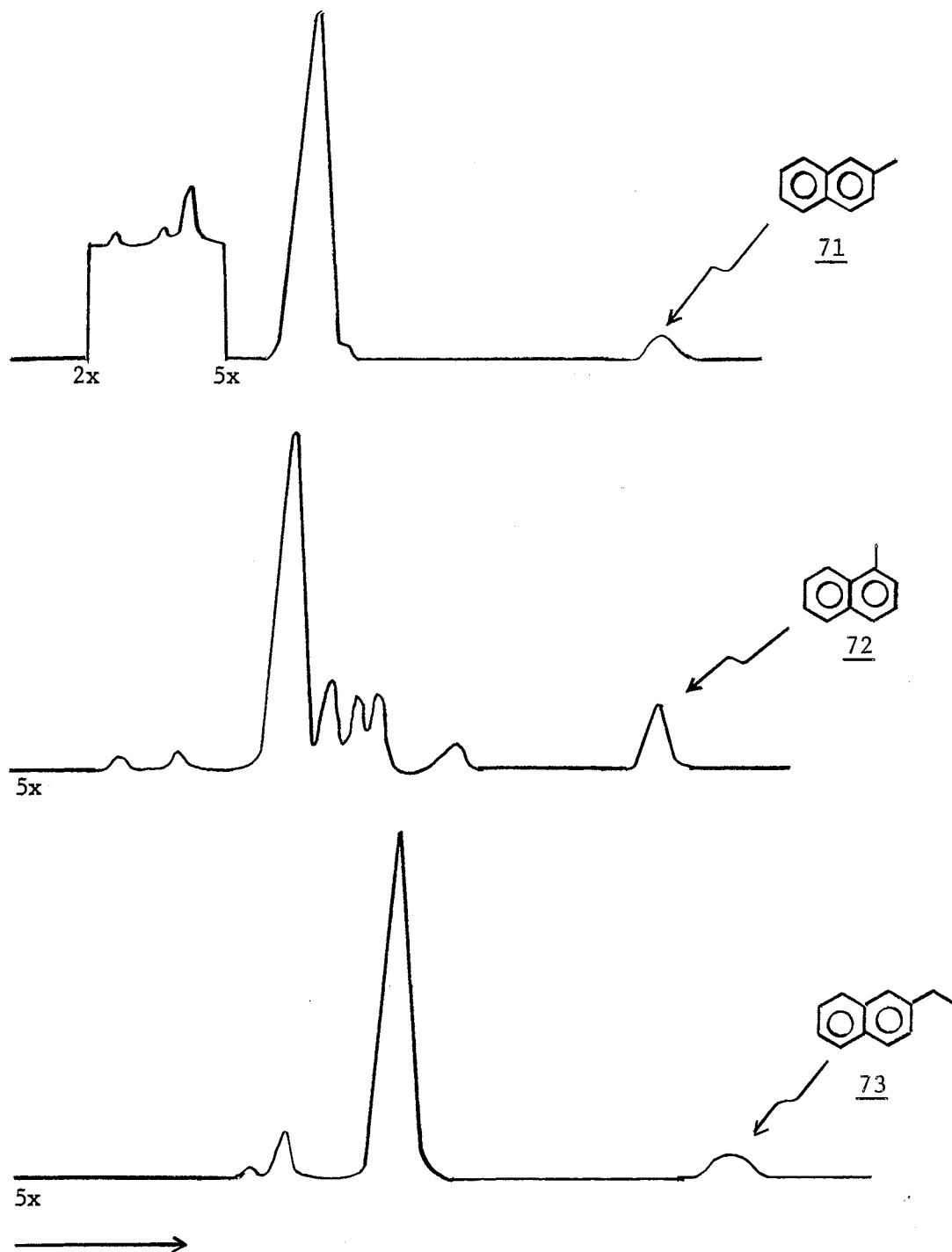
Figure 5. Gas Chromatograms[8a] of the Steam-volatile Products From the Sodium-diethylamine Reduction of 71, 72, and 73.
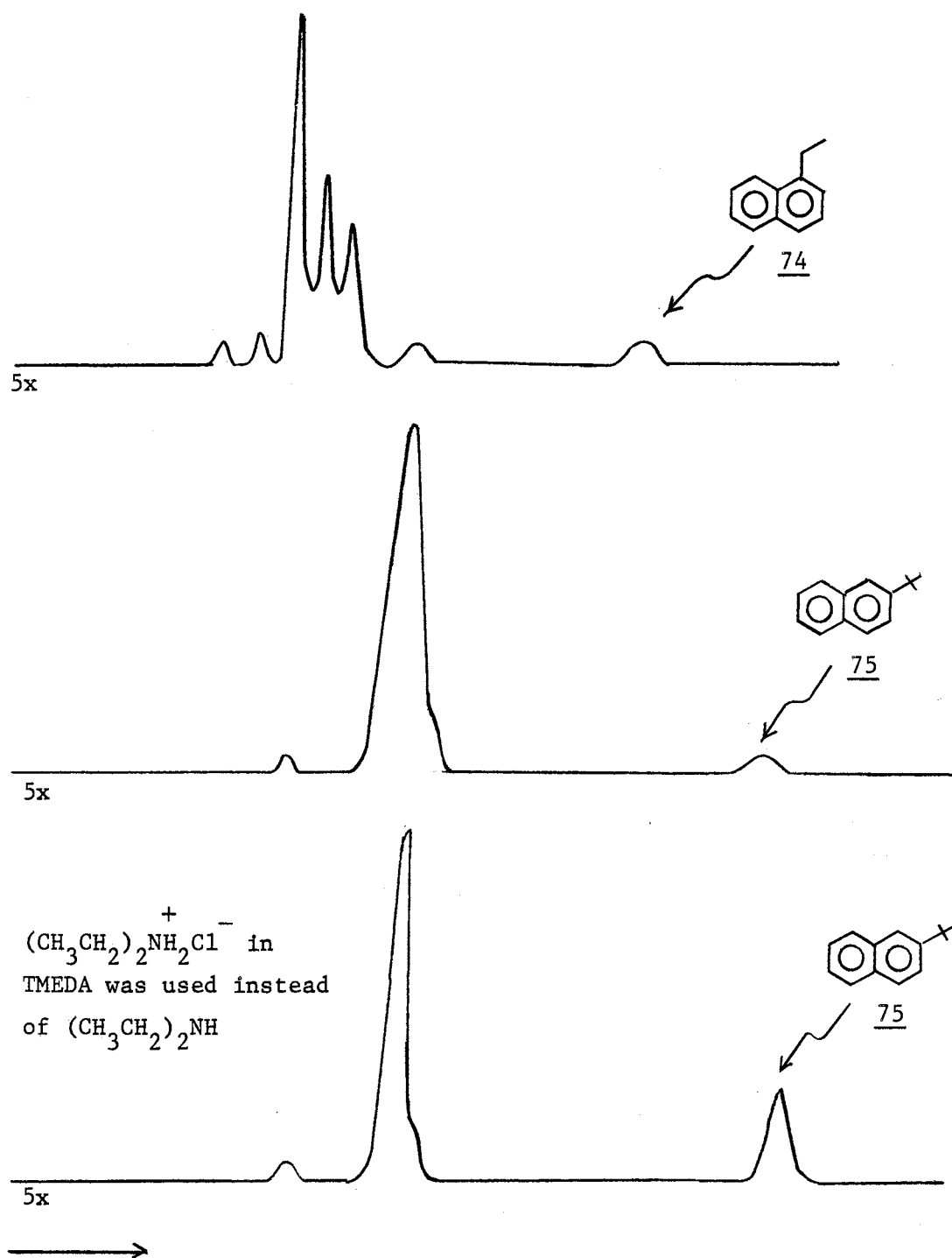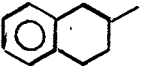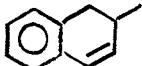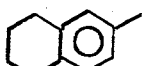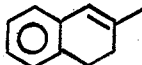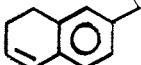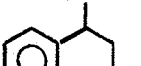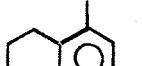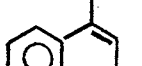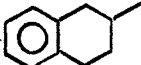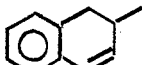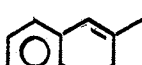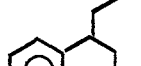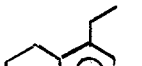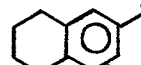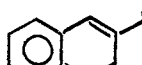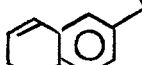
Figure 6. Gas Chromatograms[8a] of the Steam-volatile Products From the Sodium-diethylamine Reduction of 74 and 75.

TABLE V

RATIO OF STEAM-VOLATILE HYDROCARBON PRODUCTS FROM SODIUM-DIETHYLAMINE REDUCTION

Starting Material	Recovered Starting Material	Ratio of Steam-volatile Hydrocarbon Products[8a] Reduced Steam-volatile Hydrocarbon Products [a]			
2-Methylnaphthalene, 71	71 (12)	77 (1)	78 (2)	79 (5)	80 ⎤ (159) 80/20 81
1-Methylnaphthalene, 72	72 (27)	82 (1) U[c] (1)	83 (67)	84 (17)	U (16) U (16) U (16)
2-Ethylnaphthalene, 73	73 (3)	7 (1)	5 (7)	6 ⎤ + (109) U	
1-Ethylnaphthalene, 74	74 (3)	85 (1) U (2)	86 (19)	U (11) U (8) U (1)	
2-t-Butylnaphthalene, 75	75 (2)	87 (1)	88 ⎤ + 89 (39) 70/30		
75[b]	75 (41)	87 (1) 88 ⎤ + 89 (105) 70/30			

[a]Listed in the order of retention times from glc column.[8a] [b]Diethylamine hydrochloride in TMEDA used instead of diethylamine. [c]U = unknown compound.

dehydrogenation technique was developed in which 56 was used as the solvent (benzene, xylenes, p-cymene and 3,5-dimethyl-t-butylbenzene were also evaluated).[78] As anticipated,[79] the dihydronaphthalenes were aromatized much more easily than the corresponding tetrahydronaphthalenes, and, depending on the system, conditions could be chosen such that the dihydronaphthalenes completely disappeared, whereas the tetrahydronaphthalenes survived. The results of the application of this technique to the steam-volatile hydrocarbon mixtures is shown in Table VI. These data, if taken as a *real ratio* of the amount of reduction in each ring, is very misleading, i.e. a large steric effect is indicated in the 2-alkylnaphthalene series, whereas no effect is manifest for the 1-alkylnaphthalenes. Thus, contrary to the empirical rule stated by Hückel[51] for metal-ammonia reductions, the sodium-diethylamine reduction of 2-alkylnaphthalenes gives reduction in both rings with predominant *unsubstituted ring* reduction for 75. In addition, the 1-alkylnaphthalenes give reduction in both rings with predominant reduction in the unsubstituted ring as Hückel's empirical rule[51] predicts. However, since the starting materials were complex mixtures of dihydro-, tetrahydro- and aromatic hydrocarbons, there is no reason to expect a simple disproportionation process to operate,[79] i.e. whereas 78 or 90 gave a 1:1 disproportionation to 77 and 71, a known mixture of 77, 78, 79, 90, and 71 gave results impossible to interpret as a 1:1 disproportionation of the olefins (internal standard was 75)[79c] and indicating a very complex disproportion process.

Therefore, we turned our attention to hydrogenation as a possible indicator of which ring undergoes preferential reduction. This procedure[73] proved to be quite effective since very little disproportionation

TABLE VI

DISPROPORTIONATION OF STEAM-VOLATILE PRODUCTS FROM
SODIUM-DIETHYLAMINE REDUCTION[a]

Starting Material[c]	Ratio of Disproportionation Products[b]		
71	77 (1.1)	79 (1.0)	71 (2.2)
72	82 (1.0)	83 (6.0)	72 (6.3)
73	7 (1.0)	13 (1.4)	73 (2.5)
74	85 (1.0)	86 (5.9)	74 (4.8)
75	87 (19.1)	91 (1.7)	75 (23.8)

[a]All reactions were carried out according to the procedure described previously[73,78] with reaction times of 1 hr. [b]Listed in the order of retention times from glc[8a] column. [c]Starting materials are the steam-volatile hydrocarbon fractions from the aromatic hydrocarbons listed.

occurs and the aromatic hydrocarbons are essentially inert to the hydrogenation conditions.[80] The results are shown in Table VII. Again, the data indicate reduction in either ring for both the 1-alkyl- and 2-alkyl-naphthalenes. Although a *definite* steric effect is noted for the 2-alkylnaphthalenes, it is not as pronounced as indicated by the disproportionation data. As predicted by Hückel's empirical rule,[51] these data show predominant reduction in the unsubstituted ring for the 1-alkylnaphthalenes.

Mechanistically, the data can be rationalized in terms of the suggested equilibria involved in the currently accepted mechanism for

TABLE VII

HYDROGENATION OF STEAM-VOLATILE PRODUCTS FROM
SODIUM-DIETHYLAMINE REDUCTION

Starting Material[b]	Ratio of Hydrogenation Products[a]		
71	77 (6.3)	79 (3.0)	71 (1)
72	82 (1.1)	83 (4.1)	72 (1)
73	7 (15.5)	91 (10.3)	73 (1)
74	85 (2)	86 (7.8)	74 (1)
75	87 (7.7)	91 (1.7)	75 (1)

[a]Listed in the order of retention times from glc[8a] column. [b]Starting
materials are the steam-volatile hydrocarbon fractions from the aromatic
hydrocarbons listed.

metal-amine reductions,[39a] i.e. the same equilibria are involved with

the position of reduction being altered by the alkyl groups. Undoubted-

ly, an initial 1,4-addition occurs (in either ring), followed by isom-

erization and/or further reduction. Thus, the composition of the final

product mixture represents a thermodynamic equilibrium mixture for the

particular reaction conditions employed. Although Hückel's empirical

rule[51] holds well for methylnaphthalenes and other substituted naphtha-

lenes[44c] in metal-ammonia reactions, it obviously must be applied with

caution in metal-amine reactions, at least in the case of alkyl-

naphthalenes.

CHAPTER IX

EXPERIMENTAL[22,81]

General Reaction Conditions for Sodium-diethylamine Reductions.—
All reductions were carried out in a similar manner utilizing the
stir-shredding device.[70] The equipment was dried before and after
assembly (heat gun) and flushed with dry nitrogen for ca. 10 min.
before addition of any reactants. The temperature of the solution was
monitored via a thermocouple (inserted through one of the large open-
ings). The temperature was maintained at room temperature by wrapping
the reaction flask with a rubber cooling tube.

The amine and hydrocarbon were introduced through a large opening
in the top and stirred briefly to complete solution. Sodium was then
added rather slowly under a blanket of nitrogen over a 1-hr. period
from a flask attached to one of the large openings by Gooch tubing. A
light yellow color developed in ca. 15 min. and rapidly changed to an
opaque red-brown color. The solution remained a dark red-brown for the
remainder of the 2.5-hr reaction time.

The reactions were stopped by pouring the reaction mixture (slowly
and cautiously) into a beaker of crushed ice. The resulting reaction
mixture was extracted with ether to remove the organic products and
aminated products removed from the ether layer by acidifying with 10%
hydrochloric acid. Monomeric hydrocarbons were separated from dimeric
products by steam distillation.

Sodium-diethylamine Reduction of 2-Methylnaphthalene (71).— To

56.8 g (0.4 mol) of 71 and 800 ml of 49 contained in the reaction flask

was added 36.8 g (1.6 g-atom) of sodium over a period of 1 hr. A light

yellow color developed in 10 min. and the solution turned dark red-brown

in an additional 2 min. This color remained until quenched (2.5 hr)

with ca. 1 1. of crushed ice. The temperature range during the reac-

tion was 15-21°. The resulting reaction mixture was extracted with 2 1.

of ether and aminated products removed from the ether layer by acidify-

ing with 10% hydrochloric acid. The ether layer, containing the hydro-

carbons, was washed with water, 10% HCl, and again with water until

neutral. The acidic aqueous solution was then made basic with 20% NaOH

and extracted with ether. This amine containing ether layer was washed

with water, dried (Na_2SO_4), and concentrated (rotary evaporator) to

give 4.2 g (5.1%) of amines. The hydrocarbon containing ether layer

was concentrated (rotary evaporator) and steam distilled. Both the pot

residue and distillate were extracted with ether and dried (Na_2SO_4).

The ether extract of the distillate was concentrated (rotary evaporator)

yielding 48.7 g (83.2%) of steam-volatile hydrocarbons. Glc[8a] analysis

showed this to be a mixture of 71:77:78:79:80 plus 81 (12:1:2:5:159).

The ether extract of the pot residue was concentrated (rotary evapor-

ator) to yield 5.8 g (10.6%) of dimers. A similar procedure was used

for the other reductions shown in Table IV.

Compounds 5,[36] 6,[36] 7,[36,11] 13,[36,11] 77,[83] 79,[83] 80,[40e,84] 81,[40e]

82,[85] 83,[85b,86] 84,[87] 85,[11] 86,[11,85b] 87,[88] 88,[40e] 89,[40e] 90,[89] and

91[90] are all known compounds. These compounds were synthesized using a

variety of methods.[91] All data collected on these compounds complement

the data reported in the literature. A literature search revealed that

78 has not been previously described (see below).

1,2-Dihydro-2-methylnaphthalene (78).— Bp 35-37° (0.05 mm); ir
(neat) 3.30, 3.38, 3.48, 6.73, 6.88, 7.01, 12.78, 13.18, 13.51, and
14.43 µ; mass spectrum (70 eV) m/e (rel intensity) 144 (35), 142 (13),
129 (100), 128 (35), 127 (14), and 115 (19); nmr (CCl$_4$) δ 7.73-6.76
(m, 4, ArH), 6.40-6.24 (pair of doublets, 1, benzylic, vinylic), 5.87-
5.64 (pair of doublets, 1, vinylic), 3.00-2.32 (m, 3, benzylic -CH$_2$ and
CH$_3$-CH), 1.05 (d, 3, -CH$_3$); uv max (95% EtOH) 212 nm (log ε 4.58), 218
nm (log ε 4.61), 223 nm (log ε 4.45) and 260 nm (log ε 4.20).

Anal. Calcd for C$_{11}$H$_{12}$: C, 91.61; H, 8.39. Found: C, 91.72;
H, 8.27.

General Procedure for Disproportionation of Mixtures Containing
Steam-volatile Dihydronaphthalenes.— To a 200-ml one-neck flask
equipped with a reflux condenser and stirred magnetically (Teflon-
covered magnet) was added 1 g of the hydrocarbon mixture, 100 ml of
toluene 56, and 100 mg of 10% Pd/C.[82]   The reaction mixture was
refluxed vigorously (heating mantle, 70 V) for 1 hr, allowed to cool,
filtered through Dicalite filter aid, and analyzed by glc.[8a]

General Procedure for Catalytic Hydrogenation of Mixtures
Containing Steam-volatile Dihydronaphthalenes.— To 100 mg of 10% Pd/C
contained in a 200-ml fluted flask was added a solution of 1 g of the
hydrocarbon mixture in 100 ml of 95% ethanol. This stirred (Teflon-
covered magnet) mixture was hydrogenated at 25° and 1 atm. for 1 hr.
After filtration (Dicalite filter aid), the mixture was analyzed by
glc.[8a]

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8. (a) A 0.25-in. (o.d.) x 12-ft copper column containing 80-100 mesh,
   acid-washed Chromosorb W coated with 25% Carbowax 20M was used
   in a Beckmann GC-2A instrument operating at 220°; (b) A
   0.125-in. (o.d.) x 8-ft stainless steel column containing 80-
   100 mesh, acid-washed, DMCS-treated Chromosorb W coated with
   5% of UCW-98 silicone rubber was used in Hewlett-Packard 5750
   instrument operating at 280°; (c) Glc preparative separations
   were made with an F and M Model 700 chromatograph using a
   0.375-in. (o.d.) x 10-ft column containing 80-100 mesh, acid-
   washed Chromosorb W coated with 25% Carbowax 20M and heated at
   150°.

9. For a convenient procedure for the separation, purification, and cleavage of the picrates of 1 and 22, see A. I. Vogel, "Practical Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., 1966, p. 767.

10. Our data do not exclude exchange of protons in the aromatic ring of 5, 6, or 7.

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12. Ethylnaphthalene was recovered unchanged after exposure to the reduction conditions of Procedure A for four days.

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16. Exposure of a mixture of 2, 5, 6, and 7 (6.0:4.6:1.7:1) under the conditions of Procedure A for three days resulted in the new ratio 5.8:3.4:1.7:1.

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72. If possible, the unknown sample was mix-injected with a known authentic sample and the gas chromatogram examined for peak separation. Analysis for a specific compound in a reaction mixture was accomplished by mix-injecting the known sample and mixture, and noting which peak increased in height. The known samples were obtained by preparative glc[8c] or independent synthesis.[73]

73. See EXPERIMENTAL of Part III.

74. This has been shown with 71 by taking samples from the reaction vessel at various reaction times and analyzing them via glc.[8a]

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80. This was determined by experiments using known samples of olefins 78 and 90 with an internal standard of _t_-butylbenzene or known samples of the arene starting materials with the same internal standard, subjecting these mixtures to the hydrogenation conditions, followed by glc[8a] analysis.

81. The diethylamine (Union Carbide Co.) used in this study was stirred for _ca._ 24 hr with KOH and then distilled from fresh KOH. The sodium was reagent grade (Matheson, Coleman and Bell Co.), 2-6 mm spheres and was washed with acid-treated, redistilled petroleum ether, bp 60-68°, before use.

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91. See reference 5a under the appropriate name of the compound.

VITA

William Perry Duncan

Candidate for the Degree of

Doctor of Philosophy

Thesis: I.   THE CLEMMENSEN REDUCTION OF 2-ACETONAPHTHONE
        II. STEREOCHEMICAL ASSIGNMENT OF THE ISOMERIC
             2,3-DI-(2-NAPHTHYL)BUTANE-2,3-DIOLS
        III. REDUCTION OF ALKYLNAPHTHALENES USING SODIUM
             IN DIETHYLAMINE

Major Field: Chemistry

Biographical:

   Personal Data: Born in Chetopa, Kansas, March 31, 1943, the son
       of Perry L. and Agnes M. Duncan.

   Education: Graduated from Chetopa Public High School, Chetopa,
       Kansas in 1961; received the Bachelor of Science degree from
       Kansas State College, Pittsburg, Kansas, in June, 1965, with
       a major in Chemistry and minor in Mathematics; received the
       Master of Science degree from Kansas State College in August,
       1966, with a major in Organic Chemistry; completed require-
       ments for the Doctor of Philosophy degree at Oklahoma
       State University in July, 1972.

   Professional Experience: Graduate Teaching Assistant, Kansas
       State College, 1965-66; Instructor in Chemistry, 1966-70,
       Panhandle State College, Goodwell, Oklahoma; N.S.F. Research
       Participation Program for College Teachers participant,
       Oklahoma State University, summer of 1967, and University of
       Wyoming, Laramie, Wyoming, summer of 1969; N.S.F. Science
       Faculty Fellow, Oklahoma State University, 1970-71; Graduate
       Research Assistant, American Petroleum Institute, Oklahoma
       State University, 1971-72; Member of American Chemical
       Society, Phi Lambda Upsilon, and Omicron Delta Kappa.