

REDUCTIVE AMINATION AND METAL-AMINE REDUCTION
OF POLYNUCLEAR AROMATIC HYDROCARBONS

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CHAPTER I

INTRODUCTION

The reductive amination of aromatic hydrocarbons with metals dissolved in liquid ammonia or amines is a new reaction. The term "reductive amination" has been used to describe the catalytic reduction of ketones or aldehydes in the presence of ammonia or amines. This latter reaction will not be treated extensively in this thesis because it has no connection with the current work other than a similarity in titles. Instead, the reductive amination of polynuclear aromatic hydrocarbons to tertiary or secondary amines will be reported. This reaction is an extension of the Birch reduction and a new development, in that reductive amination of polynuclear aromatic hydrocarbons takes place concurrently with, and at times in preference to, the expected Birch reduction when an aromatic hydrocarbon is treated with sodium and a primary or secondary amine. It should be pointed out that there have been no previous reports of carbon-nitrogen bond formation during Birch-type reductions.

This study was undertaken to explore the utilization of the metal-amine reduction in the synthesis of hydrocarbons for the American Petroleum Institute Standard Samples Program. Reduction of naphthalene, alkylated naphthalenes, and phenanthrenes with sodium and a broad series of primary and secondary amines was examined. Reduction with lithium, potassium, and calcium metals was also explored in

a few cases.

Additional studies were initiated involving N-deuteriohexamethylenimine and deuterium oxide as well as the use of anions from sources other than hexamethylenimine to gain an understanding of the mechanism of reductive amination.

CHAPTER II

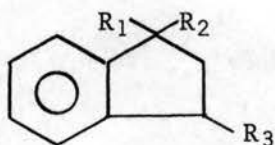
HISTORICAL

In 1937, Wooster^{1,2} reported that aromatic compounds are hydrogenated by sodium and a proton donor in liquid ammonia solution.

A. J. Birch greatly extended Wooster's observations, and as a result, the so-called Birch reduction has found considerable utility in synthetic organic chemistry. The Birch reduction of polynuclear aromatic hydrocarbons and other aromatic systems has been thoroughly explored and reviewed.^{3,4,5}

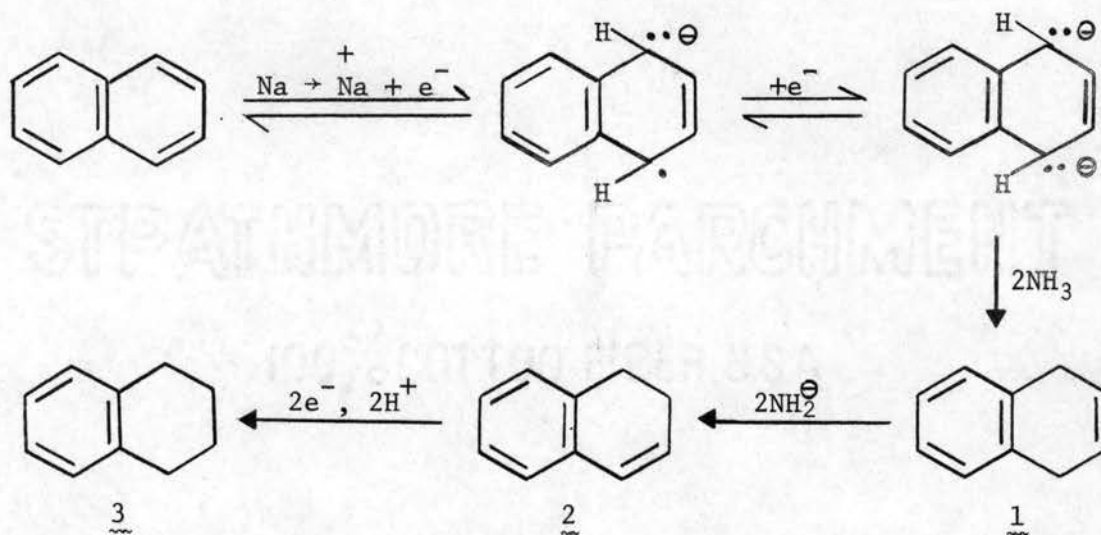
In this thesis, the historical background presented regarding Birch-type reductions will be restricted to the reduction of aromatic hydrocarbons by metals dissolved in liquid ammonia or amines. The term "reductive amination" is usually applied to the process of replacing a keto or aldehyde function with an amino group. This is accomplished by reducing the aldehyde or ketone in the presence of ammonia or amine, using hydrogen and platinum or Raney nickel catalyst.⁶ When the reducing agent is formic acid or one of its derivatives, the reductive amination reaction is known as the Leuckart reaction.⁷

The following types of amines, similar to those encountered in the current work, were prepared by reductive amination of 3-alkylindanones.^{8,9}



R₁ = hydrogen or methyl
R₂ = phenyl
R₃ = methylamino, dimethylamino, piperidino

The reduction of naphthalene by sodium in liquid ammonia was first studied by Lebeau and Picon in 1914.¹⁰ These authors observed the formation of 1,2,3,4-tetrahydronaphthalene and sodamide at room temperature. Later, Wooster and Smith confirmed the formation of 1,2,3,4-tetrahydronaphthalene and established that the reaction involved only four atoms of sodium, even when a large excess of sodium was present.¹¹ They concluded, incorrectly, that reduction proceeded by formation and protonolysis of a tetra-sodium adduct. Subsequently, the following reaction mechanism was elucidated by Hückel and Bretschneider:¹²



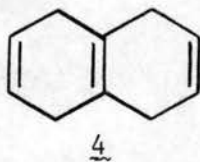
These workers observed that naphthalene reacts with two atomic proportions of sodium in liquid ammonia at -75° to -65° , to form a red complex which on decomposition with methanol gives 1,4-dihydronaphthalene (1). The complex was found to be stable at low temperatures but ammonolyzed above -50° to form 1 as well as to cause isomerization of 1 to 1,2-dihydronaphthalene (2). The latter isomer was then reduced at this temperature to 1,2,3,4-tetrahydronaphthalene (3) by sodium in ammonia. It was therefore concluded that the reduction of naphthalene

to 3 is a stepwise process, involving successive formation of a disodium adduct, protonolysis of the adduct to 1,4-dihydronaphthalene (1) and sodamide, base-induced conjugation of the double bonds in 1 to 1,2-dihydronaphthalene (2) and reduction of the latter to 3. Similar results were reported for reactions in which calcium was used.¹²

Therefore, it was inferred that the organometallic intermediates in these reactions are salts, and that the reduction is initiated by the addition of electrons to the naphthalene nucleus to form the radical anion and the dianion shown in the above mechanism. The salt-like character of the dianion is also shown by its reaction with alkyl halides to form dialkylated dihydronaphthalenes.^{13,14}

The first example of this latter reaction is recorded by Hugel and Lerer, who in 1932 prepared 1,4-dihydro-1,4-diisobutylnaphthalene from naphthalene, sodium, and isobutyl chloride in liquid ammonia solvent.¹³

With sodium and methanol, ethanol, or isopropyl alcohol in liquid ammonia at -33° , naphthalene is converted to 1,4,5,8-tetrahydronaphthalene (4). Protonolysis by an alcohol of the intermediate salts

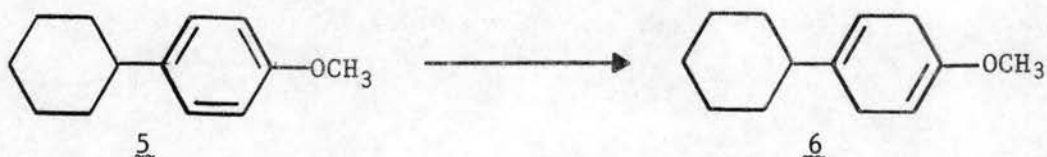


formed from the transfer of electrons from sodium to naphthalene was assumed to release alkoxide anion. However, alkoxide anion was considered to be insufficiently basic to cause shift of double bonds, and therefore, 4 was stable under these conditions. It was assumed that 1,4-dihydronaphthalene (1) is an intermediate in the formation

of 4, since 1 is similarly converted to 4.^{15,16}

Other polynuclear hydrocarbons which have been reduced in a manner similar to that employed with naphthalene include the following: anthracene to 9,10-dihydroanthracene,^{10,17} phenanthrene to 1,2,3,4-tetrahydrophenanthrene,^{18,19} and acenaphthene to tetrahydroacenaphthene.¹⁸ Both fluorene^{18,19,20} and indene^{18,19} react with sodium in liquid ammonia to form sodium salts by substitution, accompanied by some hydrogenation. Benzene and alkylated benzenes are not attacked by solutions of metals and liquid ammonia.^{21,22} Benzene, toluene, and the xylenes may be used advantageously as cosolvents during the use of solutions of metals dissolved in ammonia or amines in the reduction of many organic compounds.^{1,11,23} The first indication that metal-ammonia reagents might hydrogenate monobenzenoid substances was obtained in 1937 by Wooster and Godfrey,¹ who found that treatment of a mixture of liquid ammonia, toluene, and sodium with water gave less than the theoretical amount of hydrogen gas and a highly unsaturated hydrocarbon product. In 1942, Birch began an extended series of investigations on the reduction of monobenzenoid substances.^{5,24} These investigations soon confirmed that metal-ammonia-alcohol reagents convert monobenzenoid substances to α,δ -dihydro derivatives.

Various modifications to the Birch reduction have been reported. An important modification of the Birch reduction involves the substitution of lithium for sodium.²⁵ In the original example studied by Wilds and Nelson in 1953, ordinary Birch reduction conditions failed to reduce 4-cyclohexylanisole (5). By substituting lithium for sodium and adding the alcohol last, a yield of 88% of the crystalline dihydroanisole (6) was obtained. The higher yields of reduction products



observed when lithium was used instead of sodium were thought to be due to high concentration of metal and the higher reduction potential of lithium in ammonia (-2.99V) as compared to that of potassium or sodium (-2.59 and -2.73V). However, in 1961, Dryden and coworkers²⁶ showed that if the ammonia, which may contain colloidal iron, is distilled prior to the reaction, sodium becomes as effective as, and at times is superior to, lithium in the reduction. The explanation appears to be that iron, which is known to catalyze the formation of sodamide, does not strongly catalyze amide formation when lithium is substituted for sodium, and hence, the side reaction to formation of amide is not important as in the case of sodium.

Another modification of the Birch reduction is the use of low-molecular-weight primary amines such as methylamine, ethylamine, and propylamine. Solutions of lithium in these amines constitute powerful, but non-selective, reducing agents.^{27,28,29,30,31,32,33} These amines are generally more powerful solvents for organic molecules than ammonia is, and have higher boiling points (C₂H₅NH₂, bp 16.5°; NH₃, bp -33°). Accordingly, their use permits a higher reaction temperature and at times avoids the low solubility of the substrate in the solvent system. Benkeser and coworkers²⁷ reported the reduction of benzene to cyclohexene and cyclohexane in 51 and 17% yields respectively, and naphthalene to 1,2,3,4,5,6,7,8-octahydronaphthalene in 68% yield.

Reggel and co-workers have reported reduction of aromatic rings

to monoolefins by lithium in ethylenediamine.³⁴ This amine provides the most powerful and perhaps the least selective reduction of the metal-amine system. With this system, phenanthrene is reduced to a mixture of decahydro- and dodecahydrophenanthrenes in 90% yield. Recently, reduction of several polynuclear aromatic hydrocarbons with lithium in ethylenediamine has been reported.³⁵ This study also showed that aromatic hydrocarbons highly substituted by alkyl or alicyclic groups are resistant to reduction.³⁵

Another extension of the metal-amine system is the electrochemical reduction of aromatic hydrocarbons.^{36,37,38,39} The electrolysis was carried out in the presence of lithium chloride, an amine and an aromatic hydrocarbon.

CHAPTER III

RESULTS AND DISCUSSION

Secondary amines have had some use in the Birch reduction of aromatic hydrocarbons but mainly as components of a mixed solvent to moderate the reactivity of primary amines and increase the selectivity of the reduction.³² An increased selectivity in the reduction of polynuclear hydrocarbon rather than extensive reduction was sought. It was felt that this could be accomplished by proper selection of a secondary amine. Also, information on the role of secondary amines in the reduction was desired, and whether alterations in the stereochemistry of the carbon skeleton of the amine would have an effect on the Birch-type reduction. To accomplish these objectives, preliminary studies were carried out by reducing phenanthrene with sodium dissolved in a variety of amines for 6.0-6.5 hours at 25° (except for ethylamine and dimethylamine which were used at 15° and 5° respectively). These results are reported in Tables I and II. The product composition of these reactions was determined by gas chromatography and the retention times on the gas chromatograms were compared with those of authentic samples. The usual procedure was to mix the compound in question with the authentic sample and observe whether separation took place on the gas chromatograms. Individual components of a reaction mixture were easily identified by adding samples of known structure to the mixture, repeating the gas chromatography, and

TABLE I
SODIUM-AMINE REDUCTION OF PHENANTHRENE

Amine	Crude Yield, %	Distribution of Products, %				
		1	2 ^a	3 ^b	4 ^c	5 ^d
Ethylamine	76	-	24	23	8	21
Dimethylamine	70	-	56	2	6	6
Diethylamine	88	-	64	-	16	8
Diisopropylamine	89	45	34	2	1	7
Pyrrolidine	71	-	51	18	-	2
Piperidine	71	-	58	2	7	4
Hexamethylenimine	90	-	78	3	2	7
2-Methylpiperidine	84	7	64	11	-	3
2,6-Dimethylpiperidine	84	37	34	5	-	8

^aRecovered phenanthrene. ^b9,10-Dihydrophenanthrene. ^cTetrahydrophenanthrene. ^ds-Octahydrophenanthrene. ^eas-Octahydrophenanthrene.

TABLE II

METAL-HEXAMETHYLENIMINE REDUCTION OF PHENANTHRENE AT 125° FOR 9 HOURS

Metal	Crude Yield, %	Distribution of Products, %				
		2 ^a	3 ^b	4 ^c	5 ^d	6 ^e
Sodium	84	-	53	26	-	5
Lithium	76	-	3	-	30	43

^aRecovered phenanthrene. ^b9,10-Dihydrophenanthrene. ^cTetrahydrophenanthrene. ^ds-Octahydrophenanthrene. ^eas-Octahydrophenanthrene.

observing which peak was increased in height by the enrichment technique.

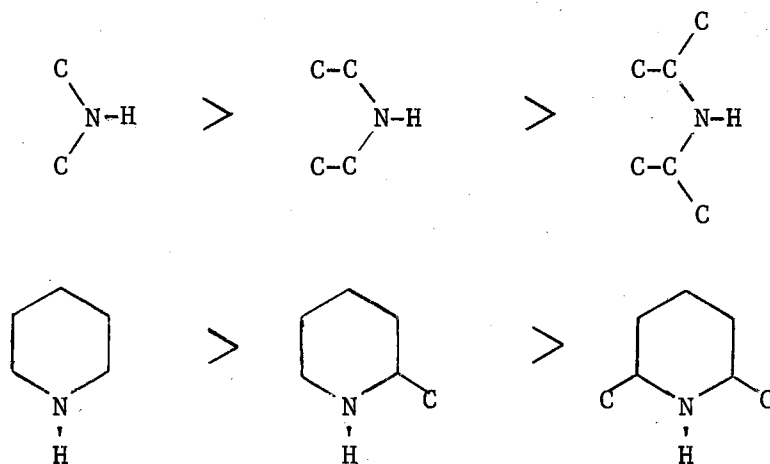
These studies showed hexamethylenimine to be the most efficient system for selective reduction of phenanthrene to 9,10-dihydrophenanthrene (78% yield) and a low combined yield of octahydrophenanthrene (12%, Table I) for the series ranging from pyrrolidine to hexamethylenimine.

The yield of tetrahydrophenanthrene and octahydrophenanthrenes is readily increased by operating at higher temperatures, or better, by substituting lithium metal for sodium (Table II). Ethylamine also gave a higher yield of octahydrophenanthrene and hence more extensive reduction (Table I). This is in keeping with the earlier observations that a lithium-primary amine combination reduces naphthalene to octahydronaphthalene. It is of interest that none of the conditions employed here were sufficiently vigorous to cause reduction of phenanthrene beyond the octahydro stage, particularly since it is well established that lithium and primary amines readily reduce benzenoid hydrocarbons.²⁷

In comparing the series pyrrolidine, piperidine, and hexamethylenimine in column 3, Table I, an increase in ring size causes increased selectivity toward accumulation of 9,10-dihydrophenanthrene. This is also reflected in the progressive decrease in yields of other reduction products as shown in Table I.

A definite difference in the effectiveness of reduction of phenanthrene was observed in the series dimethylamine>diethylamine>diisopropylamine. This trend, which may be attributed to steric hindrance about the $>N-H$ bond, becomes important either by interfering

with the removal of proton to form the anion, interfering with the approach of anion to the reaction site, or decreasing the effectiveness of the electron solvation.³ This effect was also produced by the series piperidine>2-methylpiperidine>2,6-dimethylpiperidine.

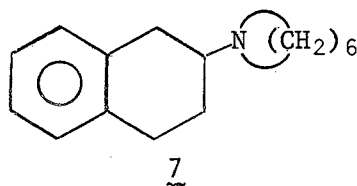


The reduction with dimethylamine was carried out at 5°, which should be considered in evaluating the trend when the comparison of yields from the dimethylamine, diethylamine, and diisopropylamine reductions is made.

A trend in selectivity of reduction of phenanthrene to 9,10-dihydrophenanthrene as well as other reduction products may be observed in Table I for pyrrolidine, piperidine, and hexamethylenimine. Hexamethylenimine is the most effective reagent of the series.

When naphthalene was stirred with sodium and hexamethylenimine, 4% of naphthalene was recovered, and only a 34% yield of hydrocarbon reduction products was obtained. The gas chromatography analysis of this material indicated that a mixture consisting of 22% of 1,2,3,4-tetrahydronaphthalene and 12% of 1,2-dihydronaphthalene had formed. The missing material was sought in the acid

washings remaining from the extraction of the reaction mixture. Upon basification of these acid washings, extraction with ether, and steam distillation of the extract to remove hexamethylenimine, there was obtained a dark-colored viscous oil which was distilled at 122-125°/0.35 mm to give a 55% yield of colorless oil. The mass spectrum of this oil showed a parent ion peak at $m/e=229$. The infrared spectrum showed absence of an N-H bond. The elemental analysis corresponded to the molecular formula $C_{16}H_{23}N$. These data and information from the nuclear magnetic resonance spectrum were used to assign structure 7 to the new reaction product. This tertiary amine was thought to result from reductive amination of naphthalene during the sodium-hexamethylenimine reduction of naphthalene.



thalene during the sodium-hexamethylenimine reduction of naphthalene.

A typical reaction illustrating both reductive amination and metal-amine reduction is shown for naphthalene in Fig. 1.

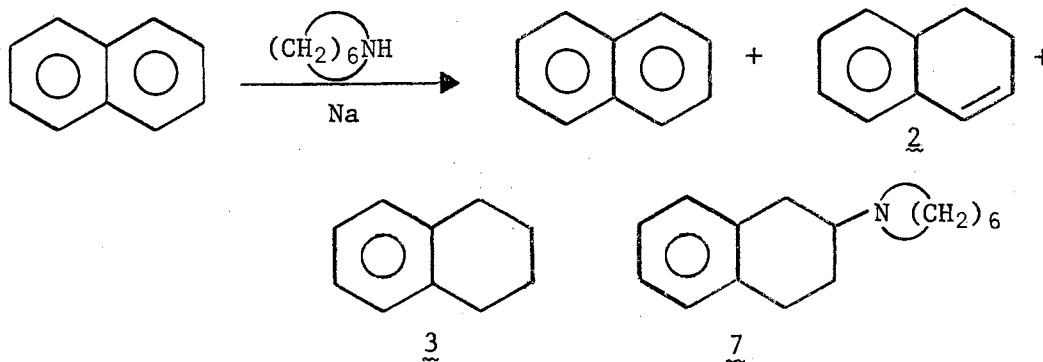


Figure 1. Products from the Reaction of Naphthalene with Sodium and Hexamethylenimine

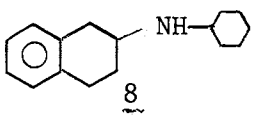
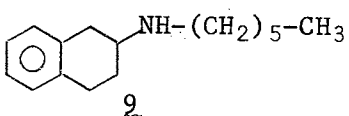
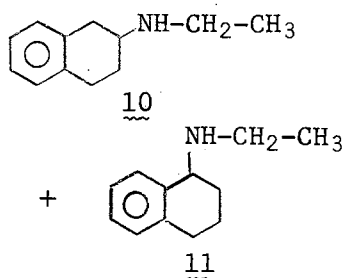
A broad series of primary and secondary amines was examined to test the generality of the reductive amination reaction, which appears to be a side reaction to the metal-amine reduction of naphthalene.⁴⁰ These results are summarized in Tables III and IV. Several alkylated naphthalenes were also caused to react with sodium and hexamethylenimine. The reductive amination products from these alkylated naphthalenes are given in Tables V, VII, and IX, while the corresponding hydrocarbon products are given in Tables VI, VIII, and X.

The products from reduction of naphthalene were analyzed by gas chromatography, and the retention times of the peaks were compared with those from authentic samples of 1,2-dihydronaphthalene and 1,2,3,4-tetrahydronaphthalene. The structures of the reductive amination products shown in Tables III, IV, V, VII, and IX were definitely established through use of NMR and mass spectroscopic data, except as noted for 20, 21, and 22 (Table V). The NMR data are summarized in Table XI. Acceptable C, H, and N analyses were obtained for each amine.

The hydrocarbon reduction products from the alkylated naphthalenes were separated by preparative gas chromatography in sufficient quantities to establish their structures through NMR and mass spectroscopic data.

As already mentioned, the Birch-type reduction of naphthalene with secondary or primary amines was complicated by the formation of tertiary or secondary amines respectively. In the case of primary amines, a crystalline compound, m.p. 82-84°, was obtained. This was not observed when secondary amines were used. On the basis of its

TABLE III
REDUCTIVE AMINATION OF NAPHTHALENE WITH SODIUM AND PRIMARY AMINES

Amine	Temp. °C.	Structure of Reductive Amination Products	Yield of Reductive Amination Products, %	Total Yield of Reduced Hydrocarbon, %	% Yield			
					3 ^a	4 ^b	5 ^c	6 ^d
Cyclohexylamine	25	 8	45	50	13	4	14	19
<i>n</i> -Hexylamine	25	 9	43	39	-	-	25	14
Ethylamine	15	 10 + 11	17 ^e	68	-	-	24	44

^aRecovered naphthalene. ^b1,2-Dihydronaphthalene. ^c1,2,3,4-Tetrahydronaphthalene.
^d1,2,3,4,1',2',3',4'-Octahydro-2,2'-binaphthyl. ^eNMR showed ratio of 10/11 = 47/3.

TABLE IV
 REDUCTIVE AMINATION OF NAPHTHALENE WITH METAL AND SECONDARY AMINES AT 25°

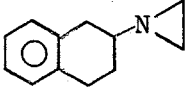
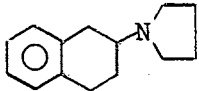
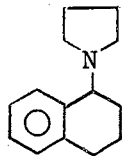
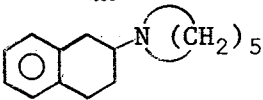
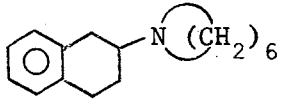
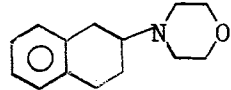
Amine	Metal	Structure of Reductive Amination Products	Yield of Reductive Amination Products, %	Total Yield of Reduced Hydrocarbons, %	% Yield		
					1	2	3 ^a
Ethylenimine	Na	 <u>12</u>	28	68	14	-	54
Pyrrolidine	Na	 <u>13</u> +  <u>14</u>	65 ^d	18	-	-	18
Piperidine	Na	 <u>15</u>	70	19	-	3	16
Hexamethylenimine	Na	 <u>7</u>	55	38	5	13	20
Morpholine	Na	 <u>16</u>	52	43	-	-	43

TABLE IV (Continued)

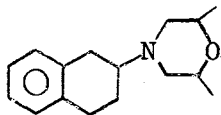
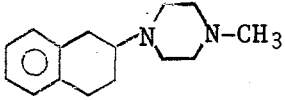
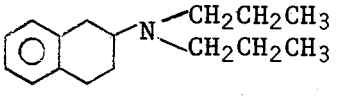
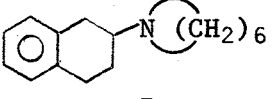
Amine	Metal	Structure of Reductive Amination Products	Yield of Reductive Amination Products, %	Total Yield of Reduced Hydrocarbons, %	% Yield		
					3 ^a	4 ^b	5 ^c
			1	2			
2,6-Dimethyl- morpholine	Na	 17	86	12	-	4	8
N-Methylpiperazine	Na	 18	73	12	1	2	9
Dipropylamine	Na	 19	7	91	4	67	20
Hexamethylenimine	K	 7	4	93 ^e	1	1	4

TABLE IV (Continued)

Amine	Metal	Structure of Reductive Amination Products	Yield of Reductive Amination Products, %	Total Yield of Reduced Hydrocarbons, %	% Yield		
					3 ^a	4 ^b	5 ^c
Hexamethylenimine	Li	--	-	93	-	-	93
Hexamethylenimine	Ca	--	-	91	81	7	3
2-Methylpyrrolidine	Na	--	-	91	11	69	11
2,5-Dimethyl- pyrrolidine	Na	--	-	83	-	76	7
2-Methylpiperidine	Na	--	-	87	9	2	76
2,6-Dimethylpiperidine	Na	--	-	97	5	10	82

^aRecovered naphthalene. ^b1,2-Dihydronaphthalene. ^c1,2,3,4-Tetrahydronaphthalene. ^dNMR showed ratio of 13/14 = 57/43. ^e87% of unidentified polymeric material resulted.

TABLE V

REDUCTIVE AMINATION OF MONOALKYLATED NAPHTHALENES WITH SODIUM AND HEXAMETHYLENIMINE AT 25°

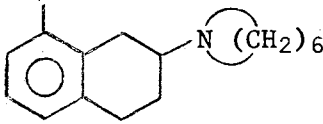
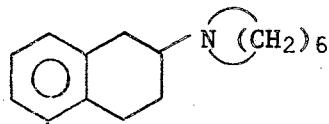
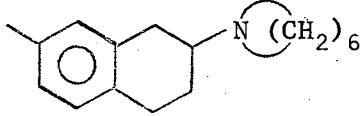
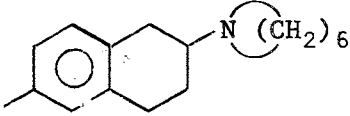
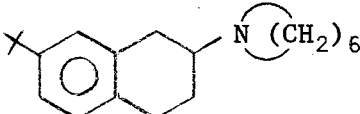
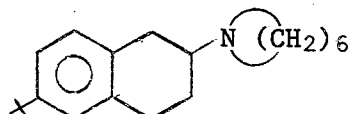
Starting Material	Yield of Reductive Amination Product, %	Structure of Reductive Amination Product	
1-Methylnaphthalene	28	 <u>20</u>	or  <u>20a</u>
2-Methylnaphthalene	45	 <u>21</u>	or  <u>21a</u>
2- <u>t</u> -Butylnaphthalene	72	 <u>22</u>	or  <u>22a</u>

TABLE VI

HYDROCARBON PRODUCTS FROM REDUCTION OF MONOALKYLATED NAPHTHALENE WITH SODIUM AND HEXAMETHYLENIMINE AT 25°

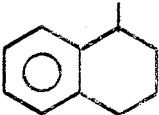
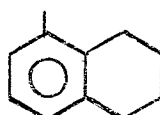
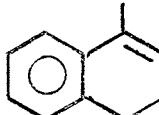
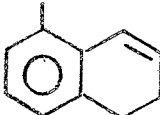
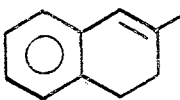

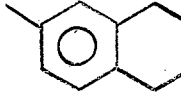
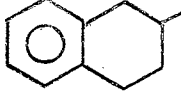
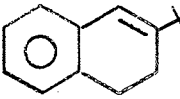
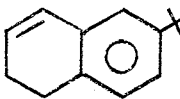
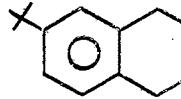
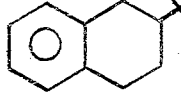
Starting Material	Total Yield of Hydrocarbon Products, %	Distribution of Hydrocarbons				
		Recovered Starting Material, %	Structure of Reduced Hydrocarbons			
1-Methyl-naphthalene	32	25	 <u>23</u> (35%)	 <u>24</u> (30%)	 <u>25</u> (5%)	 <u>26</u> (4%)
2-Methyl-naphthalene	39	<1	 <u>27</u>	 <u>28</u>	 <u>29</u> (22%)	 <u>30</u> (10%)
			$67\% \text{ of } \underline{27/28} = 80/20$			
2-t-Butyl-naphthalene	24	4	 <u>31</u>	 <u>32</u>	 <u>33</u> (10%)	 <u>34</u> (2%)
			$83\% \text{ of } \underline{31/32} = 70/30$			

TABLE VII

REDUCTIVE AMINATION OF DIALKYLATED NAPHTHALENES WITH SODIUM AND HEXAMETHYLENIMINE AT 25°

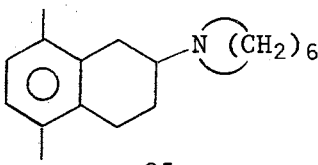
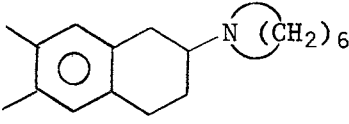
Starting Material	Reaction Time, Hours	Yield of Reductive Amination Products, %	Structure of Reduction Amination Products
1,4-Dimethylnaphthalene	32	50	 35
2,3-Dimethylnaphthalene	24	42	 36
2,6-Dimethylnaphthalene	24	-	None Formed

TABLE VIII

HYDROCARBON PRODUCTS FROM REDUCTION OF DIALKYLATED NAPHTHALENES WITH SODIUM AND HEXAMETHYLENIMINE AT 25°

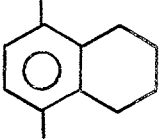
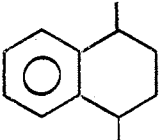
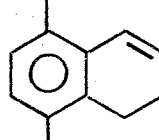
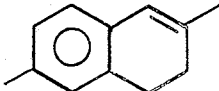
Starting Material	Total Yield of Hydrocarbon Products, %	Distribution of Hydrocarbons				
		Recovered Starting Material, %	Structure of Reduced Hydrocarbons			
1,4-Dimethyl-naphthalene	32	15				Unknown mixture (16%)
			<u>37</u> (46%)	<u>38</u> (13%)	<u>39</u> (10%)	
			2,3-Dimethyl-naphthalene	26	45	
<u>40</u> (29%)	<u>41</u> (18%)	<u>42</u> (7%)				
2,6-Dimethyl-naphthalene	74	8				
			<u>43</u> (84%)	(6%)		

TABLE IX

REDUCTIVE AMINATION OF TRIALKYLATED NAPHTHALENES WITH SODIUM AND HEXAMETHYLENIMINE AT 25°

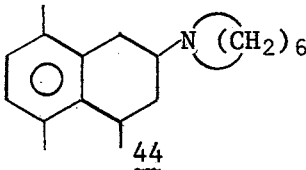
Starting Material	Reaction Time, Hours	Yield of Reductive Amination Products, %	Structure of Reduction Amination Products
1,4,5-Trimethylnaphthalene	24	48	
1,4,6-Trimethylnaphthalene	24	-	None Formed
2,3,6-Trimethylnaphthalene	32	-	None Formed

TABLE X

HYDROCARBON PRODUCTS FROM REDUCTION OF TRIALKYLATED NAPHTHALENES WITH SODIUM AND HEXAMETHYLENIMINE AT 25°

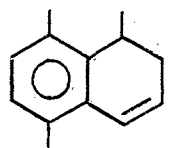
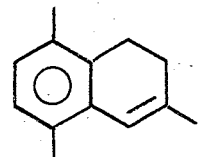
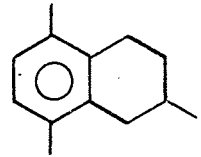
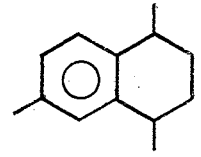
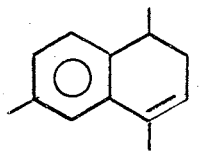
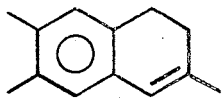
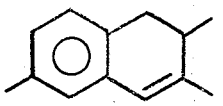
Starting Material	Total Yield of Hydrocarbon Products, %	Distribution of Hydrocarbons				
		Recovered Starting Material, %	Structure of Reduced Hydrocarbons			
1,4,5-Trimethylnaphthalene	50	16	Unknown mixture (8%)	+  + Unknown mixture (6%)		
1,4,6-Trimethylnaphthalene	91	46	 46 (23%)	 47 (13%)	 48 (13%)	 49 (5%)
2,3,6-Trimethylnaphthalene	91	4	 50 (78%)	 51 (17%)	Unknown mixture (1%)	

TABLE XI

NMR DATA FOR REDUCTIVE AMINATION PRODUCTS

Compound	Aromatic Protons Absorption, δ	Other Protons Absorption, δ
<u>7</u>	6.93 (4H, singlet)	1.60 (8H, methylene protons not adjacent to nitrogen, singlet); 1.14-2.25 (2H, methylene protons not adjacent to nitrogen or aromatic ring, broad multiplet); 2.74 (9H, methylene protons adjacent to nitrogen or aromatic ring, multiplet).
<u>8</u>	6.89 (4H, singlet)	0.61 (1H, N-H proton, singlet); 1.25-1.85 (12H, methylene protons not adjacent to nitrogen or aromatic ring, multiplet); 2.71 (6H, methylene protons adjacent to nitrogen or aromatic ring, broad multiplet).
<u>9</u>	6.94 (4H, singlet)	0.75 (1H, N-H proton, singlet); 0.88 (3H, methyl protons, singlet); 1.31 (8H, methylene protons not adjacent to nitrogen, singlet); 1.92 (2H, methylene protons not adjacent to nitrogen or aromatic ring, multiplet); 2.70 (7H, methylene protons adjacent to nitrogen or aromatic ring, multiplet).
<u>10</u> and <u>11</u>	6.96 (4H, singlet)	0.96 (1H, N-H proton, singlet); 1.08 (3H, methyl protons, triplet); 1.72 (2H, methylene protons not adjacent to nitrogen or aromatic ring, multiplet); 2.76 (7H, methylene protons adjacent to nitrogen or aromatic ring, multiplet); 3.82 (0.06H, adjacent to aromatic ring and nitrogen, indicating 6% of 1-isomer, multiplet).
<u>12</u>	6.97 (4H, singlet)	0.95 (2H, methylene protons on one side of aziridine ring, triplet); 1.20 (1H, methylene proton in tetralin ring not adjacent to nitrogen or aromatic ring, multiplet); 1.60-2.50 (2H, one methylene proton not adjacent to nitrogen or aromatic ring and one methylene proton adjacent to nitrogen in tetralin ring, multiplet); 1.56 (2H, methylene protons on other side of aziridine ring, triplet); 2.72 (4H, benzylic protons, triplet).

TABLE XI (Continued)

Compound	Aromatic Protons Absorption, δ	Other Proton Absorption, δ
<u>13</u> and <u>14</u>	6.92 (4H, singlet)	1.67 (4H, methylene protons not adjacent to nitrogen, singlet); 1.31-2.23 (2H, methylene protons not adjacent to nitrogen and aromatic ring, multiplet); 2.61 (9H, methylene protons adjacent to nitrogen or aromatic ring, multiplet); 3.68 (0.43H, adjacent to aromatic ring and nitrogen, indicating 43% of 1-isomer, multiplet).
<u>15</u>	6.91 (4H, singlet)	1.47 (6H, methylene protons not adjacent to nitrogen, singlet); 1.50-2.20 (2H, methylene protons not adjacent to nitrogen or aromatic ring, complex absorption); 2.46-2.69 (9H, methylene protons adjacent to nitrogen or aromatic ring, multiplet).
<u>16</u>	6.91 (4H, singlet)	1.66 (2H, methylene protons not adjacent to nitrogen or aromatic ring, broad multiplet); 2.55 (9H, methylene protons adjacent to nitrogen or aromatic ring, multiplet); 3.54 (4H, two equivalent methylene groups adjacent to oxygen, quartet).
<u>17</u>	6.93 (4H, singlet)	1.15 (6H, two methyl groups, 2 doublets); 1.80-2.90 (11H, methylene protons of tetralin ring and also adjacent to nitrogen, broad multiplet); 3.25-4.00 (2H, methylene protons adjacent to oxygen, broad multiplet).
<u>18</u>	6.95 (4H, singlet)	1.65 (2H, methylene protons of tetralin ring not adjacent to nitrogen or aromatic ring, broad multiplet); 2.20 (3H, methyl protons, singlet); 2.26-2.90 (15H, methylene protons adjacent to nitrogen or aromatic ring, broad multiplet).

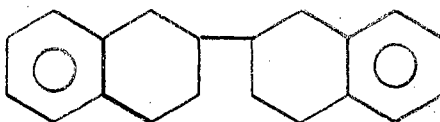
TABLE XI (Continued)

Compound	Aromatic Protons Absorption, δ	Other Proton Absorption, δ
<u>19</u>	6.94 (4H, singlet)	0.90 (6H, two equivalent methyl groups, triplet); 1.52 (4H, methylene protons not adjacent to nitrogen, multiplet); 1.90 (2H, methylene protons of tetralin ring not adjacent to nitrogen or aromatic ring, multiplet); 2.50 (4H, methylene protons adjacent to nitrogen, triplet); 2.77 (5H, methylene protons adjacent to aromatic ring and one tertiary proton adjacent to nitrogen, quartet).
<u>20</u>	6.81 (3H, singlet)	1.22-1.93 (2H, methylene protons of tetralin ring not adjacent to nitrogen or aromatic ring, multiplet); 1.59 (8H, methylene protons not adjacent to nitrogen, singlet); 2.13 (3H, methyl protons, doublet); 2.68 (9H, methylene protons adjacent to nitrogen or aromatic ring, multiplet).
<u>21</u>	6.76 (3H, singlet)	1.26-1.89 (2H, methylene protons of tetralin ring not adjacent to nitrogen or aromatic ring, broad multiplet); 1.58 (8H, four equivalent methylene groups not adjacent to nitrogen, singlet); 2.21 (3H, methyl protons, singlet); 2.69 (9H, methylene protons adjacent to nitrogen or aromatic ring, singlet).
<u>22</u>	6.95 (3H, singlet)	1.28 (9H, methyl protons, singlet); 1.59 (8H, methylene protons not adjacent to nitrogen, singlet); 1.95 (2H, methylene protons of tetralin not adjacent to nitrogen or aromatic ring, multiplet); 2.72 (9H, methylene protons adjacent to nitrogen or aromatic ring, multiplet).
<u>32</u>	6.71 (2H, singlet)	1.63 (8H, four equivalent methylene groups, singlet); 2.14 (6H, two equivalent methyl groups on aromatic ring, singlet); 2.66 (9H, protons adjacent to nitrogen or aromatic ring, broad multiplet).

TABLE XI (Continued)

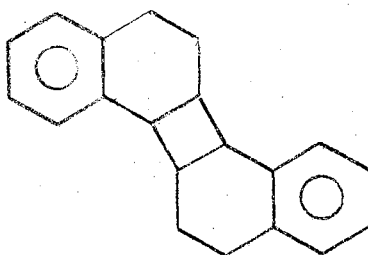
Compound	Aromatic Protons Absorption, δ	Other Proton Absorption, δ
<u>36</u>	6.69 (2H, singlet)	1.32-1.91 (2H, methylene protons not adjacent to nitrogen or aromatic ring, multiplet); 1.58 (8H, four equivalent methylene groups not adjacent to nitrogen, multiplet); 2.11 (6H, two methyl groups, singlet); 2.64 (9H, methylene protons adjacent to nitrogen or aromatic ring, multiplet).
<u>44</u>	6.72 (2H, singlet)	1.11 and 1.23 (3H, methyl group on benzylic position, doublet, $J \approx 7$ cps); 1.60 (8H, methylene protons not adjacent to nitrogen, singlet); 1.80-2.49 (2H, methylene protons not adjacent to nitrogen or aromatic ring, broad multiplet); 2.14 and 2.23 (6H, two nonequivalent methyl groups on aromatic ring); 2.68-3.30 (8H, methylene protons adjacent to nitrogen or aromatic ring, multiplet).

mass spectrum-derived molecular weight and NMR spectrum, structure 52, a stereoisomer of 1,2,3,4,1',2',3',4'-octahydro-2,2'-binaphthyl, was assigned. This compound is formed by reductive dimerization of naph-

52

thalene. The formation of this dimer^a from naphthalene was previously observed by Reggel and co-workers when sodium and ethylamine were used.⁴¹ All of the three primary amines studied, in contrast to the secondary amines, caused the formation of 52 (column 6, Table III).

When naphthalene was reduced with sodium and ethylenediamine, a 12% yield of a crystalline compound, m.p. 173-176°, resulted. The mass spectrum showed a parent ion peak at $m/e=262$ and the NMR spectrum is consistent with structure 53. A 65% yield of 1,2,3,4-tetra-

53

hydronaphthalene (3) was also obtained from the reaction which formed 53. A definite assignment of stereochemistry for 53 has not been made. Reggel and co-workers also reported the isolation of an unidentified

^aThe identity of 52 was also established by Dr. L. Reggel through infrared and mass spectroscopic comparison with his hydrocarbon.

polymeric material from the reduction of naphthalene with lithium and ethylenediamine.⁴¹

Naphthalene is reduced to dihydronaphthalene and 1,2,3,4-tetrahydronaphthalene with 2-methylpiperidine, 2,6-dimethylpiperidine, 2-methylpyrrolidine, and 2,5-dimethylpyrrolidine. However, these reactions do not produce reductive amination products. Possibly this is owing to steric hindrance of the approach of anion to a reaction site, so that the competing metal-amine reduction becomes the preferred reaction.

At room temperature, the reduction of naphthalene is sufficiently mild to permit recovery of unreacted naphthalene and isolation of some 1,2-dihydronaphthalene. When the reaction temperature is increased to 85°, however, there is complete reduction to 1,2,3,4-tetrahydronaphthalene, which is the only hydrocarbon isolated.

In general, the presence of one or more methyl groups on the naphthalene nucleus results in increased ease of reduction of the aromatic system as shown in Tables VI, VIII, and X. The exceptions are 2,3-dimethylnaphthalene, 1,4-dimethylnaphthalene, and 1,4,6-trimethylnaphthalene. More starting material survived the reaction for these three hydrocarbons than for naphthalene, and thus they were considered to be more difficult to reduce than naphthalene.

The sodium-hexamethylenimine reduction of 1,4-dimethylnaphthalene resulted in a 13% yield of 1,2,3,4-tetrahydro-1,4-dimethylnaphthalene (38). The structure of 38 was readily determined through mass and NMR spectra. The latter study showed the presence of two different methyl groups which must be adjacent to the aromatic ring to account for four aromatic protons and two benzylic protons as well as complex absorption

due to the four methylene protons. These data suggest a cis configuration for the methyl groups. The presence of trans isomer of 38 has not definitely been established. It is possible that the remaining unidentified peak (Table VIII) represents the trans isomer.

Carbon-nitrogen bond formation involving the aromatic hydrocarbon during the Birch-type reduction has not been reported previously. However, metal-catalyzed addition of amines to conjugated hydrocarbon is well-documented.^{42,43,44,45,46} This latter reaction is the final stage of reductive amination of aromatic hydrocarbons; whether amination takes place depends upon the effectiveness of competition of this reaction with the Birch-type reduction.

In general, the formation of the carbon-nitrogen bond during reductive amination takes place at the 3-position of the 1,2-dihydronaphthalene nucleus. The exceptions are in reactions with ethylamine (Table III) and pyrrolidine (Table IV) which cause some attack at the 4-position of 1,2-dihydronaphthalene. In both cases, the isomer with nitrogen attached at the 2-position in the final product is formed in the higher yield. The yield of reductive amination product appears to be very susceptible to steric effects in the amine moiety. For example, dipropylamine affords 7% reductive amination product whereas 2-methylpyrrolidine, 2,5-dimethylpyrrolidine, 2-methylpiperidine, and 2,6-dimethylpiperidine fail to give reductive amination products. However, as previously mentioned, all of these amines cause reduction of naphthalene to 2 and 3 in good yields as shown in Table IV.

The reductive amination reaction takes place in the less substituted ring of alkylated naphthalenes and with the examples studied, the reaction takes place at the 2-position. If the ring is substituted

by an alkyl group at either position flanking the 2- or 3-position, reductive amination does not take place. For example, 2,6-dimethylnaphthalene or 1,4,6-trimethylnaphthalene did not give any reductive amination product, as shown in Tables VII and IX respectively.

A definite assignment for the position of nitrogen attachment for the reductive amination products from 1-methylnaphthalene, 2-methylnaphthalene, and 2-t-butylnaphthalene in Table V could not be made since, for example, the NMR data did not permit distinction between 20 and 20a.

Sodium is the preferred metal for reductive amination. This was established as shown in Table IV by reducing naphthalene with hexamethylenimine and lithium, sodium, potassium, or calcium. Lithium or calcium metal in the presence of hexamethylenimine failed to give reductive amination products whereas potassium and hexamethylenimine caused the formation of 7 in 4% yield.

It is of interest to note that the use of high-molecular-weight amines caused reductive amination in preference to Birch-type reduction. For example, ethylamine gave only 17% yield of 10 and 11 while n-hexylamine and cyclohexylamine gave 43% and 45% yields of 9 and 8 respectively (Table III). A similar trend was observed in the case of cyclic secondary amines (Table IV).

The formation of reductive amination products as well as 1,2,3,4-tetrahydronaphthalenes can be explained as shown in Figure 2.

Naphthalene is first reduced to 1,4-dihydronaphthalene (1), which is isomerized to 2, which is in keeping with the currently accepted mechanism of Birch reduction. Isomerization may readily occur since the reactions were carried out, for the main part, at room

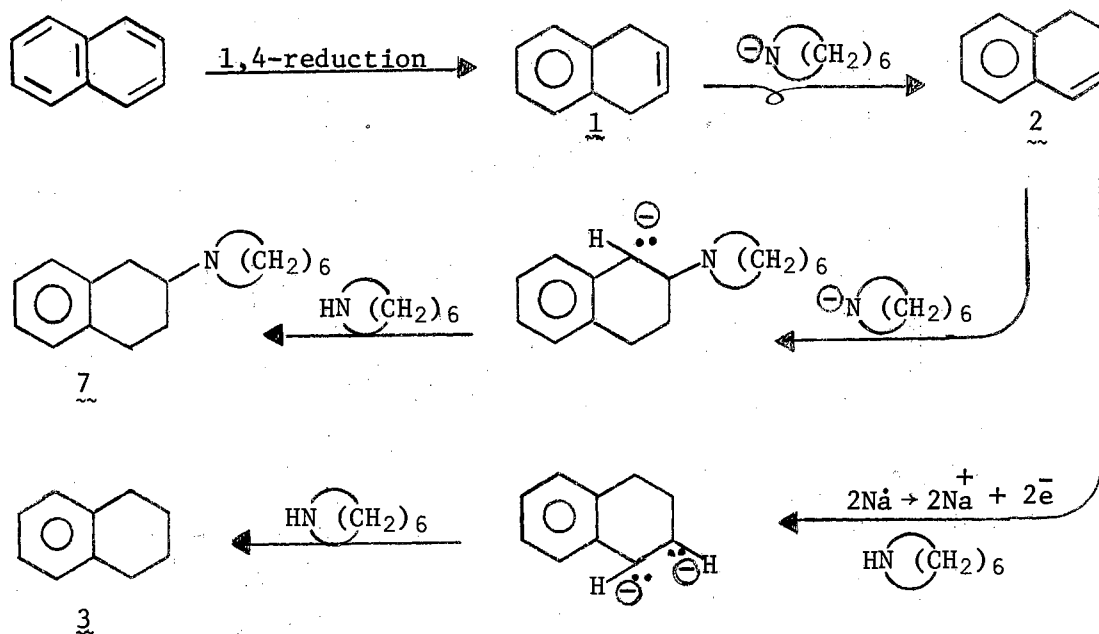


Figure 2. Route to Formation of N-(1,2,3,4-Tetrahydro-2-naphthyl)-perhydroazepine (7) and 1,2,3,4-tetrahydronaphthalene (3)

temperature, which exceeds the reaction temperature for ammonia and the low-molecular-weight amines. Nucleophilic attack of the hexamethylenimine anion to the double bond in 2 will give 7 via the indicated intermediate. To substantiate this point further, 1 and 2 were treated with sodium and hexamethylenimine under identical conditions and were found to give 7, as shown in Figure 3. Additional evidence

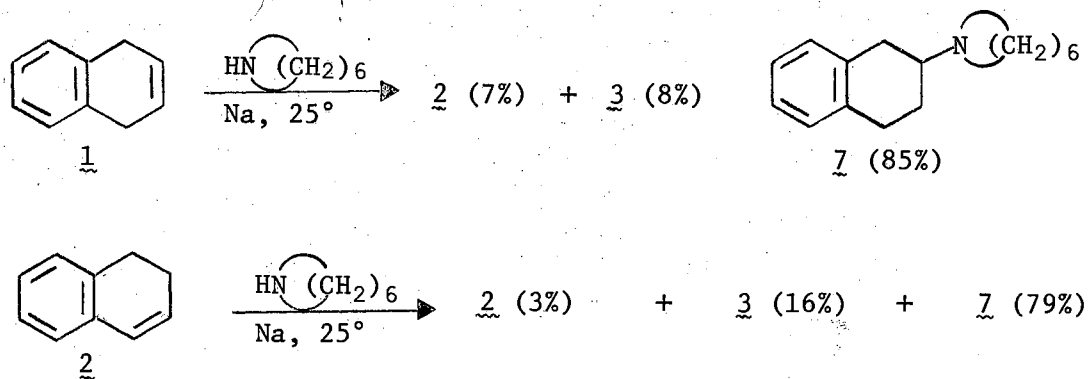
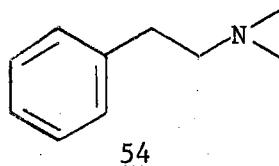


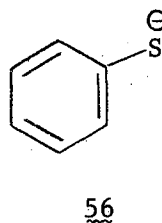
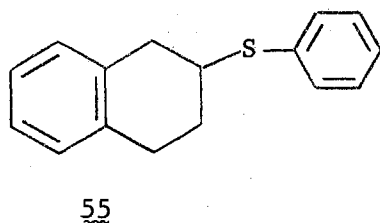
Figure 3. Reductive Amination of Dihydronaphthalene with Sodium and Hexamethylenimine.

was obtained for nucleophilic addition to 2 by treating 2 with the anion derived from the reaction of n-butyllithium and hexamethylenimine. This reaction provided 7 in 45% yield. Further, the addition of primary and secondary amines in the presence of sodium to conjugated olefins is well documented.^{44,45,46} For example, when styrene was stirred with sodium and ethylenimine at 45°, a 89% yield of 54 was obtained.⁴⁵



Attempts to add Grignard reagents to 1,2-dihydronaphthalene (2) were unsuccessful. This is in agreement with the earlier observations in which attempts to add phenylmagnesium bromide or benzylmagnesium bromide to styrene and other aryl-conjugated olefins were unsuccessful.^{47,48,49}

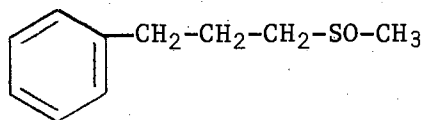
The anion derived from thiophenol through use of n-butyllithium was added to 2. This reaction gave the sulfide 55 which would be expected from nucleophilic addition of anion 56 to the conjugated double



bond of 2. The structure of 55 was confirmed through NMR and mass spectra.

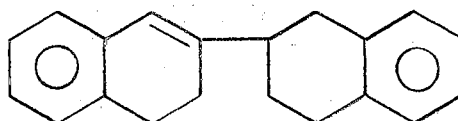
Recently, Walling and Bollyky⁵⁰ reported the addition of methyl sulfinyl carbanion, derived from dimethyl sulfoxide through the use of

sodium hydride, to aryl-conjugated olefins to give the corresponding methyl-3-arylpropyl sulfoxides in quantitative yield. For example, styrene with methyl sulfinyl carbanion gave 57 in almost quantitative yield. When 1,2-dihydronaphthalene (2) was treated with methyl



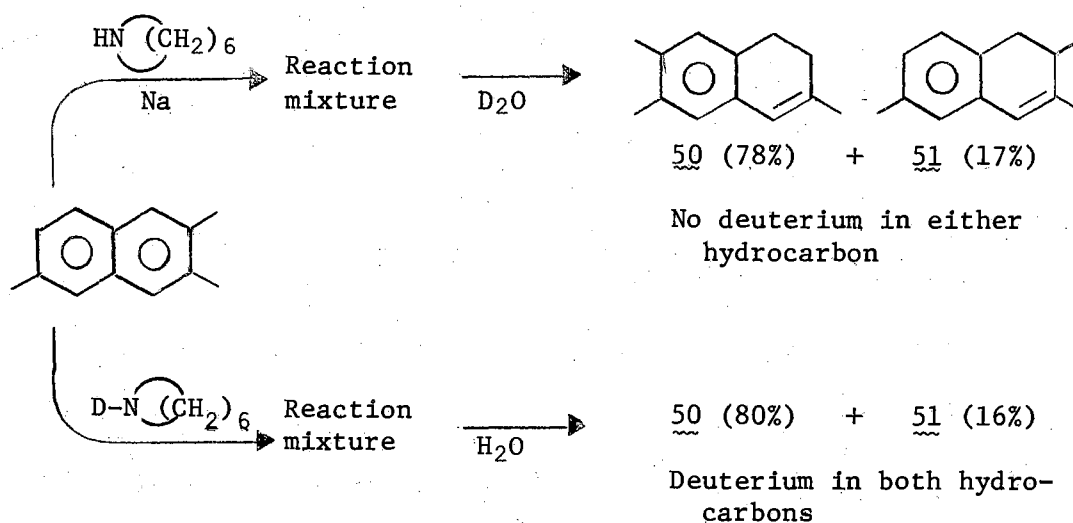
57

sulfinyl carbanion in dimethyl sulfoxide, a gum was obtained which, on distillation under reduced pressure, yielded a viscous oil. This viscous oil solidified on standing to a colorless solid. The NMR and mass spectra of this solid are consistent with the structure 58.



58

The source of protons in the sodium-hexamethylenimine reduction of 2,3,6-trimethylnaphthalene was shown to be the secondary amine and not the water used to decompose the reaction mixture as follows:



Similarly, when 1,4-dihydronaphthalene (1) was treated with sodium and N-deuteriohexamethylenimine and the reaction was decomposed with water, it was found that 2, 3, and 7 obtained from this reaction contained deuterium.

Since these deuterium studies clearly demonstrate that the N-H bond is involved in the Birch-type reduction of the naphthalenes, the steric hindrance around the >N-H bond can have considerable influence on the product composition resulting from the reduction.

CHAPTER IV

EXPERIMENTAL

Melting points were taken in capillary melting point tubes using a Thomas-Hoover apparatus and are uncorrected. The centigrade scale was used for all temperature measurements. Nuclear magnetic resonance spectra were obtained with a Varian HR-60 spectrometer, using tetramethyl silane (TMS) as an internal standard ($\delta=0$). Mass spectra were obtained with a Consolidated Electrodynamics Corporation Model 21-103 C mass spectrometer. Gas chromatography analyses were obtained with an F and M Model 700 gas chromatography apparatus fitted with a thermal conductivity detector using helium as the carrier gas. Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The amines used in this work were distilled over potassium hydroxide and were commercially available except for 2-methylpyrrolidine. The dispersed sodium was prepared by heating freshly cut sodium pieces in xylene and then stirring with a high-speed stirrer while the resulting suspension was allowed to cool.

Preparation of 2-Methylpyrrolidine. One liter of dry ether and 38 g (1 mole) of lithium aluminum hydride were added to a 3-l. three-necked flask, equipped with mechanical stirrer, condenser, and an addition tube. To this stirred slurry, a solution of 99 g (1 mole) of 5-methyl-2-pyrrolidone in one-l. dry ether was added during one hour.

The reaction mixture was stirred at the reflux temperature for 2 hours, cooled, and quenched with ice water. The ether layer was separated, washed, dried over anhydrous sodium sulfate and filtered. Removal of ether and distillation of the resulting yellow oil gave 55 g (65%) of 2-methylpyrrolidine.

Preparation of N-Deuteriohexamethylenimine. Hexamethylenimine (140 ml) and deuterium oxide (30 ml) were mixed in a 300-ml flask equipped with magnetic stirrer and a distillation head. The mixture was stirred for 4 hours and was distilled at atmospheric pressure. The fraction boiling at 95°-120° was discarded and the fraction boiling at 135° was collected to give 55 ml of N-deuteriohexamethylenimine. Mass and NMR spectra showed that a 67% conversion to N-deuteriohexamethylenimine had taken place.

Preparation of 1,4-Dihydronaphthalene (1).⁵¹ Fifty grams of naphthalene in 500 ml absolute ethanol were added to a 2-l. three-necked flask, equipped with condenser, stirrer, and nitrogen inlet tube. To the stirred solution, 36 g of sodium was added over a period of one hour. The reaction mixture was heated at the reflux temperature for 3 hours. The reaction mixture was cooled, poured over a mixture of 160 ml concentrated hydrochloric acid and two liters crushed ice and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and filtered, and the ether distilled to give 52 g of yellow oil. Gas chromatography analysis of this oil on a Carbowax column showed the presence of 1,2,3,4-tetrahydronaphthalene and some unreacted naphthalene as well as the desired product. The oil was then purified by preparative gas chromatography to give 1.

Preparation of 1,2-Dihydronaphthalene (2) from 1,4-Dihydronaphthalene (1).⁵² Forty-two grams of 1 and 20 g potassium hydroxide were combined and heated in a 200-ml flask equipped with condenser. After 4 hours heating at 130°, the reaction mixture was cooled and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, filtered and distilled to give 39 g of 2.

Sodium-Amine Reduction of Phenanthrene. All reductions were carried out under a nitrogen atmosphere in a 50-ml three-necked glass tube. The reductions with dimethylamine and ethylamine were carried out under a dry ice condenser, but in all other cases, reductions were carried out at room temperature. In all cases, 2.25 g of phenanthrene and 1.5 g of dispersed sodium were placed in the reaction tube and 25 ml of amine were added. The reaction mixture showed a blue color in about 20 to 30 minutes after the addition of amine. After stirring for a desired period of time, the reaction mixture was hydrolyzed by first destroying the unreacted sodium with 95% ethanol and then adding water. The product was isolated by extraction with ether. The ether extract was washed with 10% hydrochloric acid and then with water, dried over anhydrous magnesium sulfate, and filtered, and the ether removed by distillation to give the crude hydrocarbon mixture.

Analysis of the Products from the Reduction of Phenanthrene.

The reaction products from phenanthrene were analyzed by gas chromatography at 160°, using a 4' x 1/4" column packed with Chromosorb P coated with 20% SE 30. The products were identified by comparison of retention times with those of authentic samples.

Analysis of the Sodium-Amine Reduction Products from Naphthalene and Alkylated Naphthalenes. The composition of products from the

reduction of naphthalene and alkylated naphthalenes was determined by gas chromatography at 200° on a 10' x 1/4" column packed with 80-100 mesh, acid-washed Chromosorb W coated with 25% Carbowax 20M. In the case of naphthalene, the individual components in the reaction mixture were identified by comparing their retention times with those of authentic samples.

Separation of the Individual Components in the Alkylated Naphthalene Series. The individual components from the crude reaction mixture were separated by preparative gas chromatography at 200°, using a 10' x 4" column packed with the same material as used in the analytical column. The injection size varied from 5 ml to 15 ml.

Reduction of Alkylated Naphthalenes. All reductions were carried out in a one-l. three-necked flask, equipped with a mechanical stirrer, air condenser, and a nitrogen inlet tube. The colors of the reaction mixtures in the case of alkylated naphthalenes ranged from light to dark red. A typical experiment for the reduction of 1,4-dimethylnaphthalene is described in the following procedure.

Reduction of 1,4-Dimethylnaphthalene with Sodium and Hexamethylenimine. In a typical run, 31.2 g (0.2 mole) of 1,4-dimethylnaphthalene and 18.4 g (0.8 mole) of dispersed sodium were placed in a one-l. reaction flask along with 500 ml of hexamethylenimine. The reaction mixture was stirred at room temperature for 32 hours. A red color developed in the reaction mixture after 30 minutes. After 32 hours, the unreacted sodium, which had agglomerated, was removed with forceps. The reaction mixture was then decomposed by the cautious addition of water with external cooling until the red color disappeared. The solution was diluted with water and extracted with ether. The

ether extract was washed with 10% aqueous hydrochloric acid until it was free of amine and then once more with water. The ether extract was dried over anhydrous sodium sulfate and filtered, and the ether was distilled to give 10 g (32% yield) of the crude hydrocarbon mixture. The aqueous layer and acid washings were combined and were extracted with chloroform. The chloroform extract was washed with water, dried over anhydrous sodium sulfate and filtered. Distillation of chloroform gave 14.5 g (50% yield) of colorless flakes of reductive amination product 35 as its hydrochloride, m.p. 237-242°. A part of this tertiary amine hydrochloride (5.2 g) was dissolved in 70 ml of hot, 10% sodium hydroxide solution and the free amine was extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, filtered, and the ether was distilled to give N-(1,2,3,4-tetrahydro-5,8-dimethyl-2-naphthyl)-perhydroazepine (35). The analytical data for 35 and other reductive amination products are given in Table XII.

Identification of the Products from the Reduction of 1,4-Dimethylnaphthalene. The structures 37, 38, and 39 were assigned on the basis of their mass and NMR spectra.

The mass spectrum of 37 showed a parent ion peak at $m/e = 160$ and the NMR spectrum showed absorption at $\delta = 1.73$ (4H, two equivalent methylene groups, multiplet); 2.09 (6H, two methyl groups on aromatic ring, singlet); 2.52 (4H, benzylic protons, multiplet); and 6.71 (2H, aromatic protons, singlet).

The mass spectrum of 38 showed a parent ion peak at $m/e = 160$ and the NMR spectrum showed absorption at $\delta = 1.18$ and 1.21 (3H, methyl group, doublet, $J = 3$ cps); 1.30 and 1.32 (3H, methyl group, doublet

TABLE XII
ANALYTICAL DATA OF REDUCTIVE AMINATION PRODUCTS

Reductive Amination Products	Formula	Calculated, %			Found, %		
		C	H	N	C	H	N
<u>8</u>	C ₁₆ H ₂₃ N	83.79	10.11	6.11	83.76	10.25	6.08
<u>9</u>	C ₁₆ H ₂₅ N	83.05	10.89	6.05	83.43	11.01	5.79
<u>10</u> and <u>11</u> ^a	C ₁₂ H ₁₇ N	82.23	9.78	7.99	82.22	9.64	8.07
<u>12</u>	C ₁₂ H ₁₅ N	83.19	8.73	8.09	82.98	8.79	8.02
<u>13</u> and <u>14</u> ^b	C ₁₄ H ₁₉ N	83.53	9.51	6.96	83.59	9.58	6.81
<u>15</u>	C ₁₅ H ₂₁ N	83.66	9.83	6.51	83.49	9.78	6.61
<u>7</u>	C ₁₆ H ₂₃ N	83.78	10.11	6.11	83.56	10.23	6.14
<u>16</u>	C ₁₄ H ₁₉ NO	77.38	8.81	6.45	77.11	8.89	6.43
<u>17</u>	C ₁₆ H ₂₃ NO	78.32	9.45	5.71	78.54	9.65	5.64
<u>18</u>	C ₁₅ H ₂₂ N ₂	78.21	9.63	12.16	78.28	9.75	12.01
<u>19</u>	C ₁₆ H ₂₅ N	83.05	10.89	6.05	83.12	10.98	6.02
<u>20</u>	C ₁₇ H ₂₅ N	83.89	10.35	5.76	83.67	10.46	5.62
<u>21</u>	C ₁₇ H ₂₅ N	83.89	10.35	5.76	83.90	10.36	5.73
<u>22</u>	C ₂₀ H ₃₁ N	84.14	10.95	4.91	84.04	11.13	5.15
<u>35</u>	C ₁₈ H ₂₇ N	83.99	10.57	5.44	84.18	10.83	5.52
<u>36</u>	C ₁₈ H ₂₇ N	83.99	10.57	5.44	84.03	10.23	5.68
<u>44</u>	C ₁₉ H ₂₉ N	84.07	10.77	5.16	84.24	11.34	4.52

^aA ratio of 10/11 = 47/3. ^bA ratio of 13/14 = 57/43.

J = 2 cps); 1.78 (4H, two methylene groups, broad multiplet); and 7.00 (4H, aromatic protons, singlet).

The mass spectrum of 39 gave a parent ion peak at $m/e = 158$ and the NMR spectrum showed $\delta = 2.18$ and 2.22 (6H, two different methyl groups, doublet); 2.53 and 2.65 (4H, two methylene groups, multiplet); 5.93 (1H, vinylic proton, singlet); and 6.74 (2H, aromatic proton, singlet).

Similar studies were used to establish the structures presented in Tables VI, VIII, and X.

Reductive Amination of Naphthalene - General Procedure. All reductive aminations of naphthalene were carried out under a nitrogen atmosphere in a 300-ml, three-necked flask, equipped with air condenser and mechanical stirrer. The reductive amination with ethylamine was carried out under a dry ice condenser, but in all other cases, the reactions were carried out at 25° . A few typical experiments are described.

Reductive Amination of Naphthalene with Sodium and Hexamethylenimine. To 6.4 g (0.05 mole) of naphthalene and 4.6 g (0.2 g atom) of dispersed sodium contained in the reaction flask was added 100 ml of hexamethylenimine. A red color usually developed within 20 minutes after the addition of hexamethylenimine. The mixture was stirred at 25° for 12 hours, and unreacted sodium, which had agglomerated, was removed. The remaining solution was cooled and treated cautiously with water until the red color disappeared, then acidified with 10% aqueous hydrochloric acid. After the hydrocarbons (2.5 g, 38%) had been removed by extraction with ether, the aqueous layer was basified with dilute sodium hydroxide, and surplus hexamethylenimine was

removed by steam distillation. The steam distillation residue was extracted with ether. Drying over anhydrous sodium sulfate and distillation yielded 6.2 g (55%) of N-(1,2,3,4-tetrahydro-2-naphthyl)-perhydroazepine (7). This crude oil was distilled at 122-125°/0.35 mm to give a colorless oil.

Reductive Amination of Naphthalene with Sodium and Ethylenimine. To 6.4 g (0.05 mole) of naphthalene and 4.6 g (0.2 g atom) of sodium contained in the reaction flask, 100 ml of ethylenimine was added. After stirring at 25° for 12 hours, unreacted sodium was removed and the surplus ethylenimine was distilled under vacuum (water aspirator). The residue in the flask was diluted with water and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate and filtered. Distillation of ether gave 7.0 g of dark oil. Gas chromatography analysis of this oil on a 10' x 3/8" column of base-washed Chromosorb W coated with Carbowax 20M (25%) showed 28% of tertiary amine 12 and 68% of hydrocarbon mixture. Since 12 is very sensitive to acid, it was isolated directly from the mixture by preparative gas chromatography using the above column. NMR data are consistent with the assigned structure.

Reductive Amination of Naphthalene (Attempted) with Calcium and Hexamethylenimine. Dispersed calcium was prepared according to a described procedure.⁵³ In a 300-ml, three-necked flask equipped with dry ice condenser, stirrer, and a gas inlet tube, 100 ml of ammonia was condensed. Calcium (4 g) was added to the ammonia and stirred until all the calcium was dissolved. Benzene (50 ml) was added to the calcium solution in ammonia and the dry ice condenser was

replaced by an air condenser. The solution was stirred and the ammonia was allowed to distill until all the ammonia disappeared and the blue color of the solution was discharged. To this calcium suspension in benzene, 6.4 g (0.05 mole) naphthalene and 100 ml of hexamethylenimine were added and the reaction mixture was stirred at 25°. After 12 hours stirring at room temperature, the pink reaction mixture was decomposed with water and worked up in the previously described manner. No reductive amination product was obtained. Analysis of the hydrocarbon (5.90 g) by gas chromatography showed it to be a mixture of 81% unreacted naphthalene, 7% 1,2-dihydronaphthalene and 3% 1,2,3,4-tetrahydronaphthalene.

Reductive Amination of Naphthalene with Sodium and Cyclohexylamine. The reaction was carried out in the same manner as already described, using 6.4 g naphthalene, 4.6 g of sodium and 100 ml cyclohexylamine. After the hydrocarbon products and reductive amination products were separated, the hydrocarbon mixture (3.4 g) was steam distilled to remove volatile components. The steam-distilled residue was extracted with ether and the ether extract was dried over anhydrous magnesium sulfate. Filtration and distillation of solvent gave 1.1 g (19% yield) of colorless crystals of 1,2,3,4,1',2',3',4'-octahydro-2,2'-binaphthyl (52), mp 83-85°. The mass spectrum of 52 showed a parent ion peak at $m/e = 262$ and the NMR spectrum showed absorption at $\delta = 1.65$, (6H, $C_{2,2'}$ and $C_{3,3'}$ protons, a broad multiplet); 2.73 (8H, benzylic protons, quartet); 6.99 (8H, aromatic protons, singlet). From the steam distillate, 2.1 g (31% yield) of oil was obtained by extracting with ether. This oil was found to be a mixture consisting of 14% 1,2,3,4-tetrahydronaphthalene, 4% 1,2-dihydronaph-

thalene, and 13% naphthalene.

Similar procedure was used for the reductive amination of naphthalene involving other primary amines.

Reduction of Naphthalene with Sodium and Ethylenediamine. To 12.8 g (0.1 mole) of naphthalene and 9.2 g (0.4 g atom) of sodium contained in the reaction flask, 200 ml of ethylenediamine was added, and the reaction mixture was stirred at room temperature. No color change was observed during the first 2 hours of stirring. The reaction mixture was then heated to 60° and was stirred at this temperature. A red color was observed after 15 minutes. After 5 hours, the reaction mixture was allowed to cool, unreacted sodium was removed, and the reaction mixture was decomposed with water and extracted with ether. The ether extract was washed with dilute hydrochloric acid, and then with water. Drying over anhydrous sodium sulfate, filtering and distilling the ether gave 9.8 g of dark oil. This oil was steam distilled and the steam distillate was extracted with ether. A 65% yield of 1,2,3,4-tetrahydronaphthalene was obtained. The steam-distillation residue was extracted with ether and the ether extract was dried over anhydrous sodium sulfate. The ether extract was filtered and distilled to give 1.5 g (12%) of 53. Sublimation of 53 afforded colorless crystals, mp 173-176°. The NMR spectrum showed a broad multiplet between 1.2-2.07 (6H, protons not adjacent to aromatic ring); a broad multiplet between 2.76-3.46 (6H, protons adjacent to aromatic ring); and a quartet at 6.99 (8H, aromatic protons).

Anal. Calcd. for C₂₀H₂₀: C, 92.26; H, 7.74

Found: C, 91.80; H, 7.79

Reaction of 1,2-Dihydronaphthalene with n-Butyllithium and Hexamethylenimine. To a 300-ml, three-necked flask equipped with condenser, stirrer, nitrogen inlet tube, and an addition funnel were added 50 ml of hexamethylenimine. A solution of 8% n-butyllithium in hexane (60 ml) was added under nitrogen over a period of 15 minutes. The temperature of the reaction flask was maintained at 25° by external cooling. A solution of 6.5 g (0.05 mole) of 1,2-dihydronaphthalene in 10 ml hexane was next added over a period of 10 minutes. The reaction mixture was stirred for 12 hours at 25°. This reaction gave 7 (2.7 g, 45% yield) and 3.2 g (50%) of unreacted 1,2-dihydronaphthalene.

Reaction of 1,2-Dihydronaphthalene with n-Butyllithium and Thiophenol. To 80 ml of thiophenol contained in a reaction flask equipped with condenser, nitrogen inlet tube, stirrer, and an addition tube, 30 ml of an 8% solution of n-butyllithium in hexane was added over a period of 15 minutes. A white precipitate formed. To the stirred suspension, 3.25 g (0.025 mole) of 1,2-dihydronaphthalene were added and the reaction mixture was stirred at 25° for 12 hours. After a 12-hour period, the reaction mixture was diluted with water and was basified with 10% sodium hydroxide solution. This basic solution was extracted with ether and the ether extract was washed with water, dried, and filtered. Distillation of ether gave 4.0 g of a dark-colored residual oil which was distilled under vacuum to give 55.

The basic aqueous layer was again extracted with ethyl acetate and the extract was washed with water, dried, and filtered. The solvent was distilled to give 1.1 g of a yellow solid which on sublimation gave colorless crystals of diphenyldisulfide. The NMR spectrum of

55 showed absorption at 1.99 (2H, methylene group not adjacent to aromatic ring and sulfur, broad multiplet); 2.72 and 2.88 (4H, benzylic protons, multiplet); 3.32 (1H, tertiary proton adjacent to sulfur, multiplet); 6.92 (4H, aromatic protons, singlet); and 7.19 (5H, aromatic protons, multiplet).

Attempted Addition of Dimethyl Sulfoxide Anion to 1,2-Dihydronaphthalene. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure. The dimethyl sulfoxide anion was prepared⁵⁴ by dissolving 0.9 g of sodium hydride in 50 ml dimethyl sulfoxide under nitrogen at 70°. After 30 minutes stirring, the reaction mixture was cooled to 25° and 3.9 g (0.03 mole) of 1,2-dihydronaphthalene in 10 ml dimethyl sulfoxide were added. After 2 hours stirring at 25°, the mixture was quenched with water, extracted with ether, and dried. Filtration and distillation of ether gave 3.8 g of a viscous oil. The oil was steam distilled to remove traces of unreacted 1,2-dihydronaphthalene and the steam-distillation residue was extracted with ether to give 3.4 g of oil. This oil was distilled at 190°/0.2 mm to give 2.0 g (49%) of 58, mp 69-72°. The mass spectrum of 58 showed a parent ion peak at $m/e = 260$ and the NMR showed absorption at 1.69-2.30 (5H, protons not adjacent to aromatic ring, broad multiplet); 2.39-3.02 (6H, benzylic protons, broad multiplet); 6.21 (1H, olefinic proton, singlet); 6.96 (8H, aromatic protons, singlet).

The structure of 58 was further confirmed by dehydrogenation in the presence of palladium-charcoal catalyst to 2,2'-binaphthyl.

Dehydrogenation of 58 to 2,2'-Binaphthyl. One gram of 58 was heated with 500 mg of 10% Pd/C catalyst under nitrogen at 280°.

After 6 hours, the crude reaction mixture was directly sublimed to give 0.7 g of colorless flakes of 2,2'-binaphthyl, mp 184-185°. A mixture of this 2,2'-binaphthyl with an authentic sample showed no depression in melting point.

Nuclear Magnetic Resonance Spectrum of 7

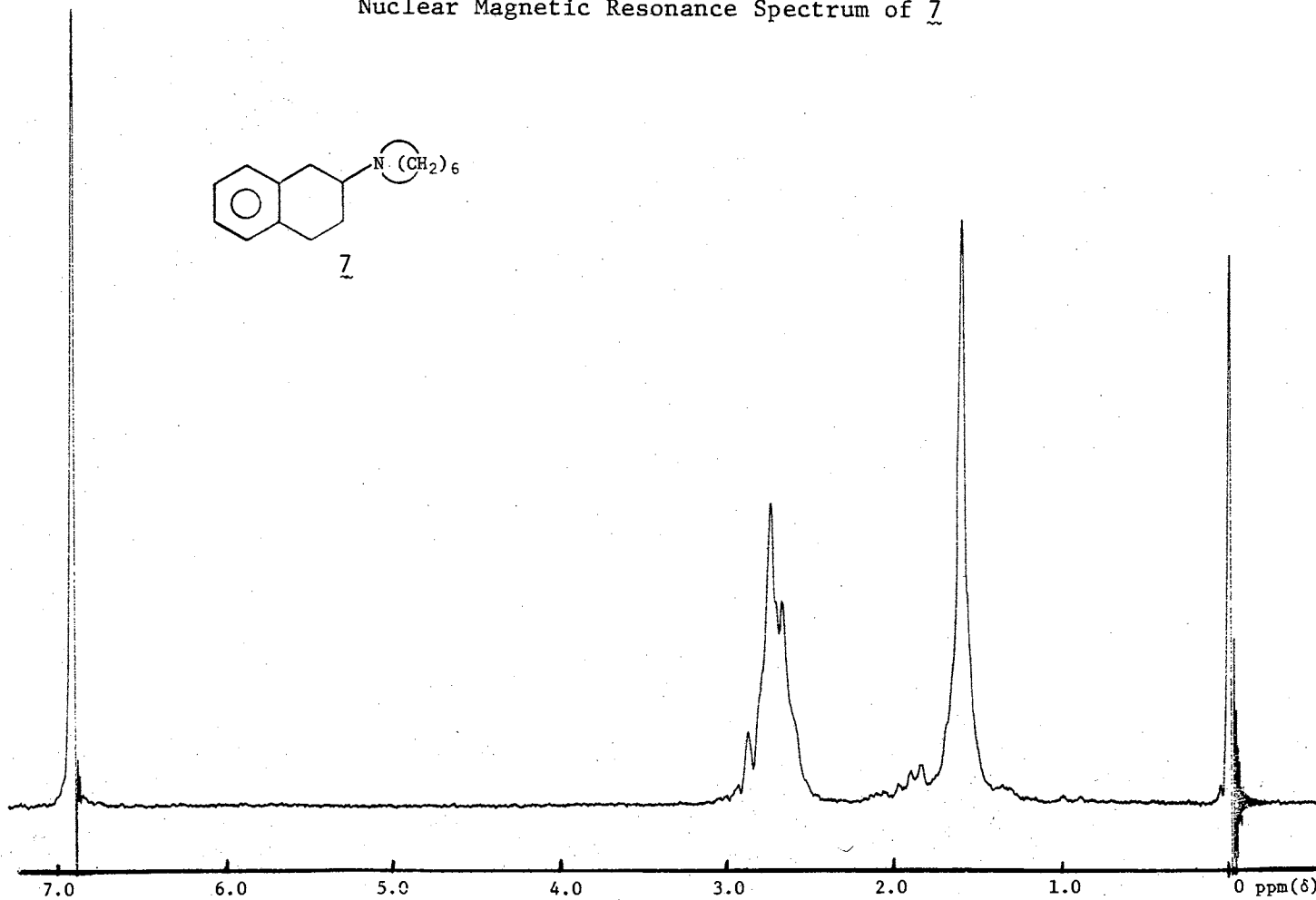
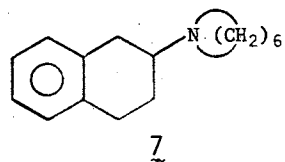
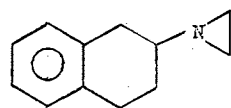


Plate I

Nuclear Magnetic Resonance Spectrum of 12



12

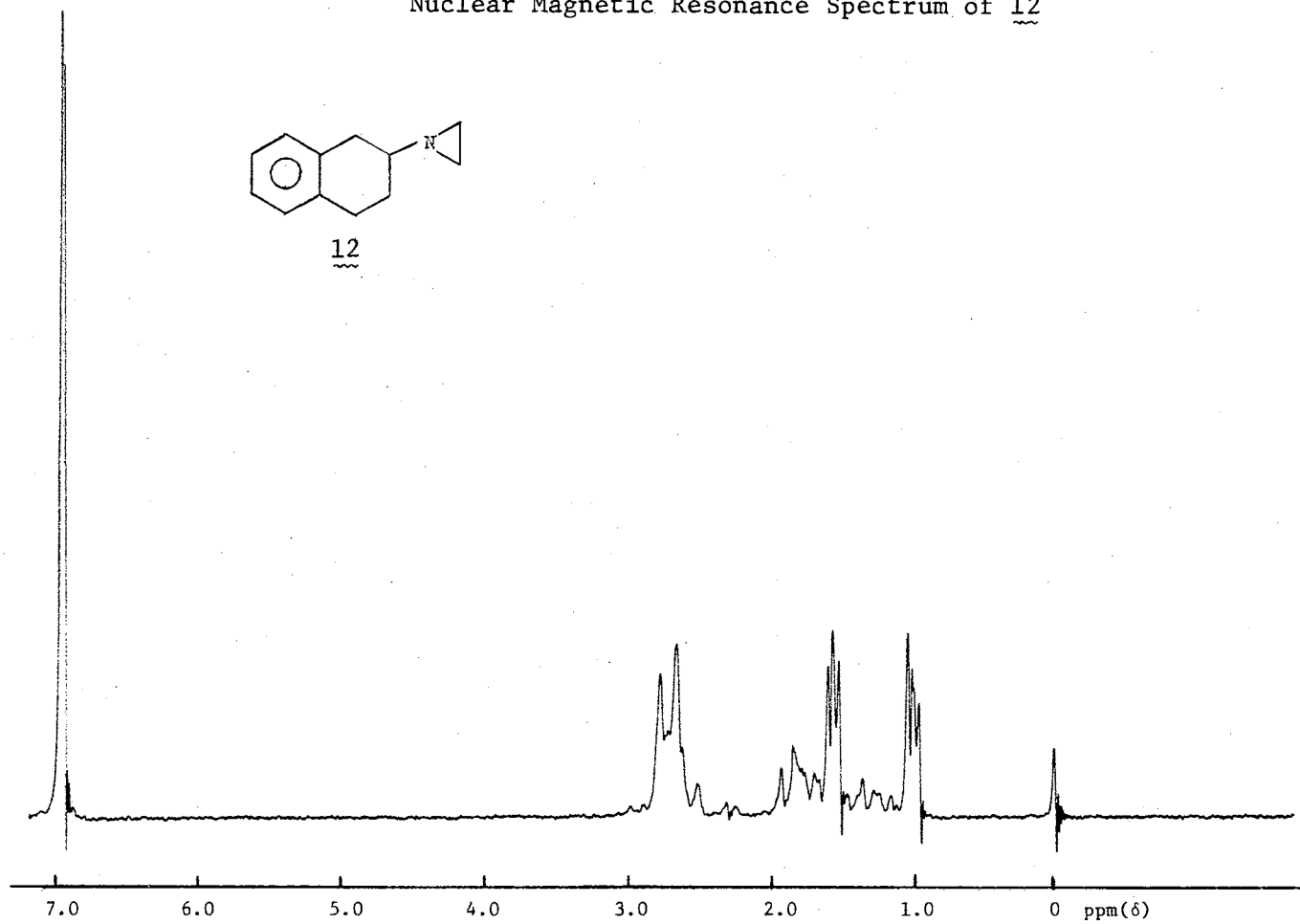


Plate II

Nuclear Magnetic Resonance Spectrum of a Mixture of 13 and 14

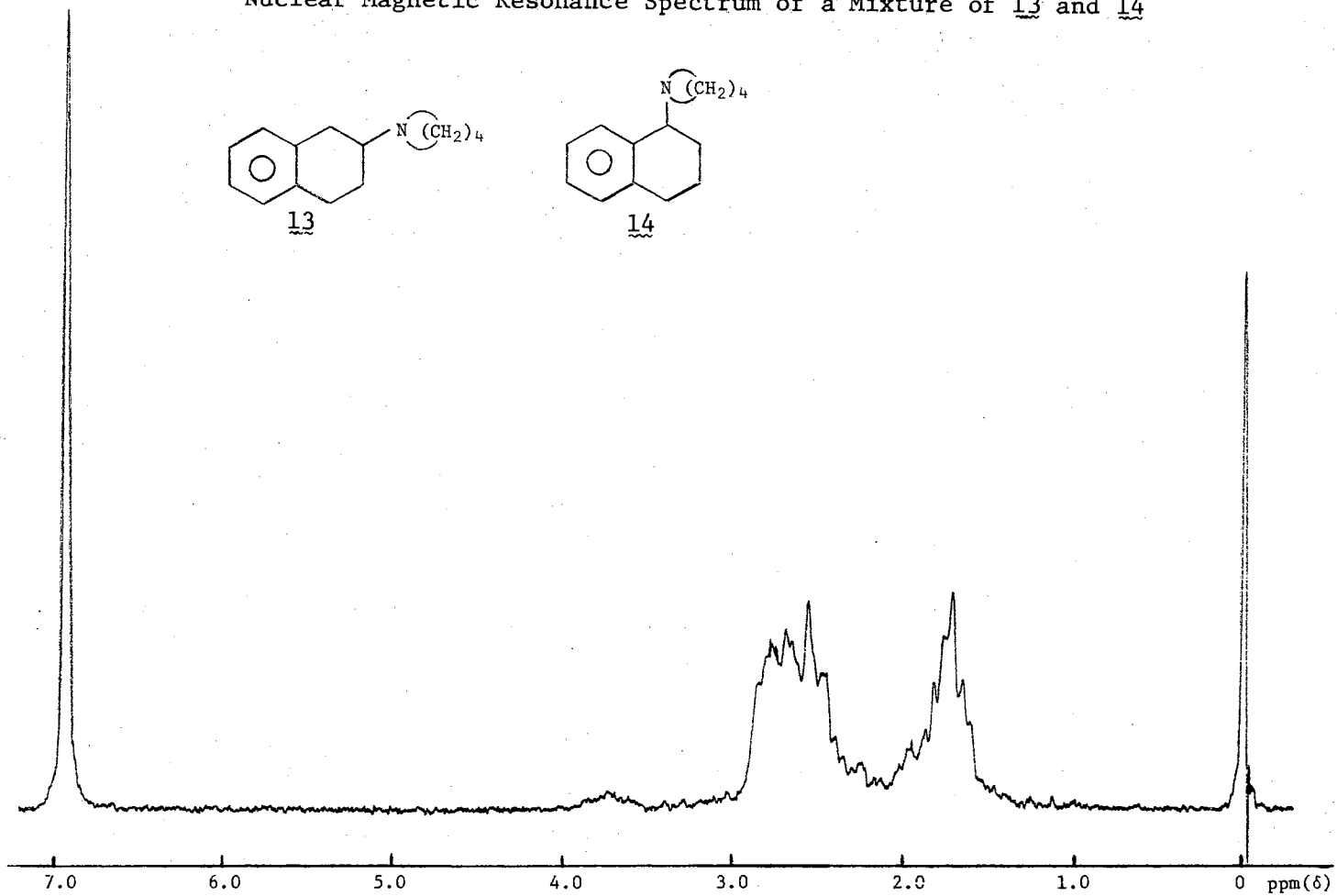
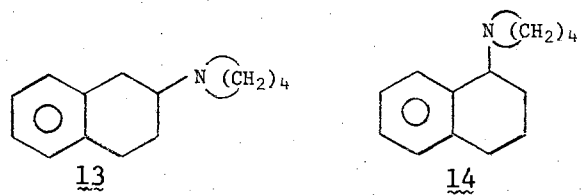


Plate III

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