REDUCTION OF ARYLNAPHTHALENES AND RELATED ARENES WITH SODIUM IN AMINES

I. PRODUCTS OF THE REACTION

II. SYNTHESIS OF ANCILLARY HYDROCARBONS

By

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PREFACE

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TABLE OF CONTENTS

Chapter Page

REDUCTION OF ARYLNAPHTHALENES AND RELATED ARENES WITH SODIUM IN AMINES
PART I. PRODUCTS OF THE REACTION

PART II. SYNTHESIS OF ANCILLARY HYDROCARBONS

Chapter Page

LIST OF TABLES

Table Page

PART I

LIST OF FIGURES

Figure Page

PART I

PART II

REDUCTION OF ARYLNAPHTHALENES AND RELATED ARENES WITH SODIUM IN AMINES

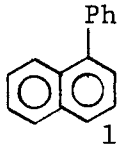
PART I

PRODUCTS OF THE REACTION

CHAPTER I

INTRODUCTION

To our knowledge, the reduction of 1-phenylnaphthalene (1), 2-phenylnaphthalene (2), and 2-benzylnaphthalene (3) with sodium in ammonia or amine solvents has not been previously reported. Initial studies in this laboratory indicate that reduction of 1- and 2-methylnaphthalenes with sodium in hexamethylenimine at 25° occurs in both the substituted and nonsubstituted naphthalene rings.[1] This research was undertaken to explore the ratios of monomeric reduced hydrocarbon products and the amounts of aminated and dimeric hydrocarbons produced when aryl- and benzyl-substituted naphthalenes are treated with sodium in amine solvents at room temperature. Since aromatic hydrocarbons 1 and 2 may be regarded as containing a benzene, a biphenyl, and a naphthalene system combined, it was of interest also to carry out sodium-amine reduction studies on benzene and biphenyl. We also studied the sodium-ammonia reduction of 1 and 2 for comparison.



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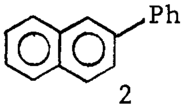

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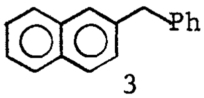


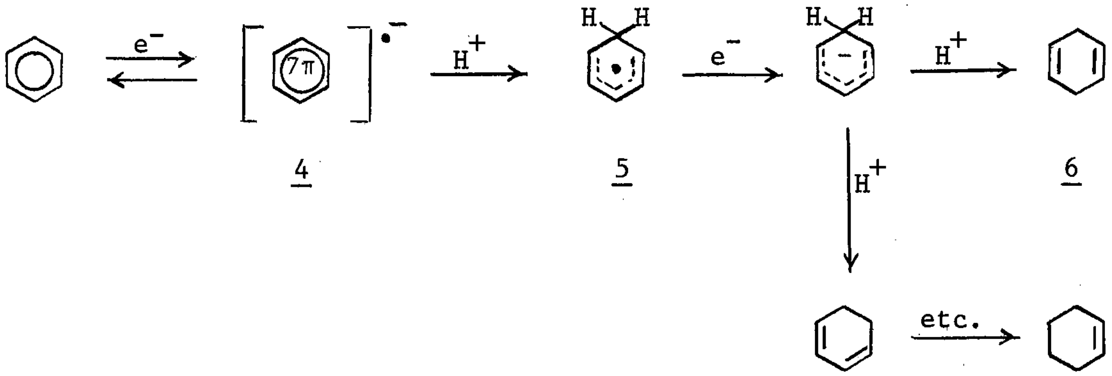
3

CHAPTER II

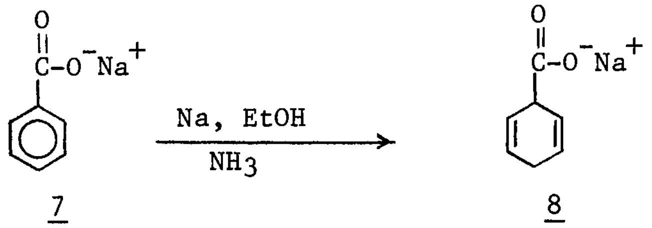
HISTORICAL

The sodium-ammonia reagent is probably the most widely used dissolving metal reductant at this time. The solution is a powerful reducing system, and has been extensively used in synthetic organic chemistry.[2] The reduction of benzenoid systems with sodium in ammonia has become strongly associated with Birch's name, who pioneered in demonstrating the practicability of the reagent.[2e,3]

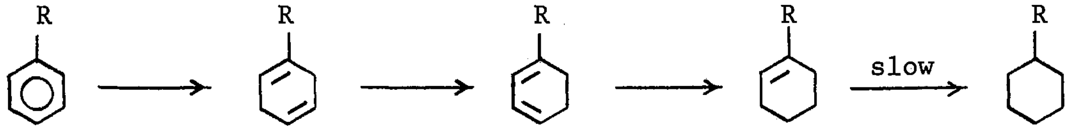
Wooster[4] reported the metal-ammonia reduction of benzene to 1,4-cyclohexadiene (6) in the presence of alcohols as proton donors. Starting in 1942, Birch[5a] made a thorough study of the reduction of benzene derivatives and proposed the following mechanism[2a] for the reduction of benzene:



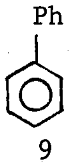
As shown, benzene is in equilibrium with a low concentration of its radical-anion (4) in sodium-ammonia solutions. Ammonia is not sufficiently acidic to supply a proton to form the radical (5) except under extreme conditions of increased temperature and pressure.[5b] Addition of a suitable acid, even one as weak as an alcohol will cause protonation of 4. Krapcho and Bothner-By[6] have studied in detail the rate differences in reductions with a lithium-ethanol-ammonia system caused by electron-withdrawing substituents and electron-donating substituents on the benzene ring, and have found that electron-withdrawing substituents facilitate the addition of electrons to the aromatic ring. They reported that preferential protonation of the radical anion occurs at positions ortho and para to electron-withdrawing groups owing to a greater electron density at these positions. Similarly, Plieninger and Ege have reported[7] that sodium benzoate (7) is reduced to the 1,4-dihydrobenzoate (8) with sodium-ethanol-ammonia reagent. Benkeser[8] has reported that metal-amine reagents usually reduce benzenoid derivatives to a mixture of substituted cyclohexenes and substituted cyclohexanes, and that the mechanism involves initial 1,4-addition of



hydrogen, isomerization to a conjugated derivative, and finally reduction to cyclohexene and cyclohexane derivatives as follow:



Hückel and Bretschneider[9a] in 1939 studied the reaction between sodium and biphenyl (9) in liquid ammonia at -70°. Methanol was used to decompose the adduct and 2-phenyl-1,3-cyclohexadiene (10) was



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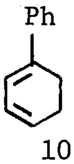

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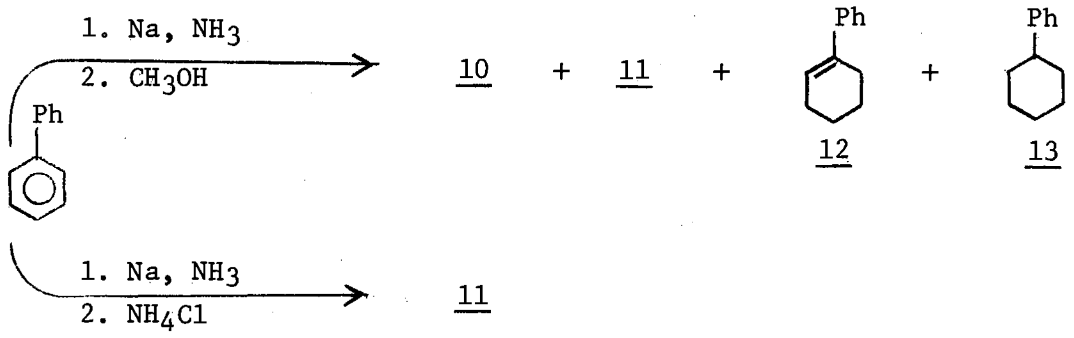
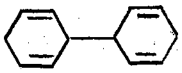
claimed as the product. In 1956 Hückel and Schwen carried out the same reaction.[9b] This time they used a shorter reaction time, decomposed the adduct with ammonium chloride, and isolated 3-phenyl-1,4-cyclohexadiene (11). These two reactions were recently repeated[10] and 10, 11, 12, and 13 were obtained from Na and NH_3 in methanol in the ratio 6:52:20:21 respectively:



With sodium-ethanol-ammonia reagent, a tetrahydrobiphenyl is produced which was considered to be 14 or 15.[11]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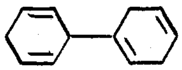
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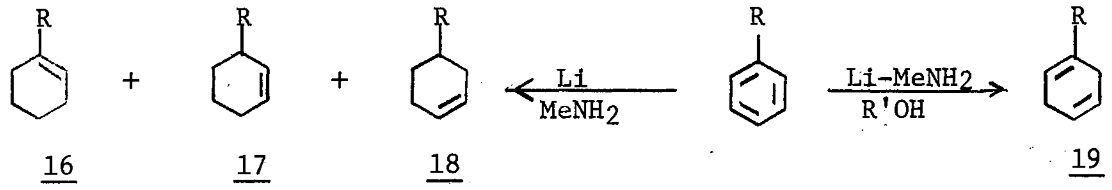
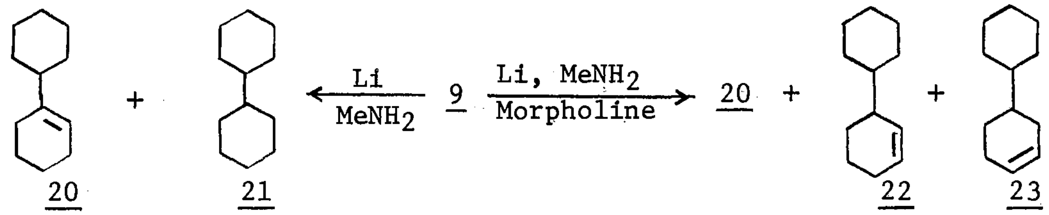
Benkeser and co-workers[12a] have shown that substituted aromatic hydrocarbons are selectively reduced to monoolefins (16), (17), and (18) by lithium-amine reagent,[12b] but that addition of alcohol[12c] to a solution of lithium in methylamine will effect reduction of substituted aromatic compounds quite selectively to a dihydro product (19).

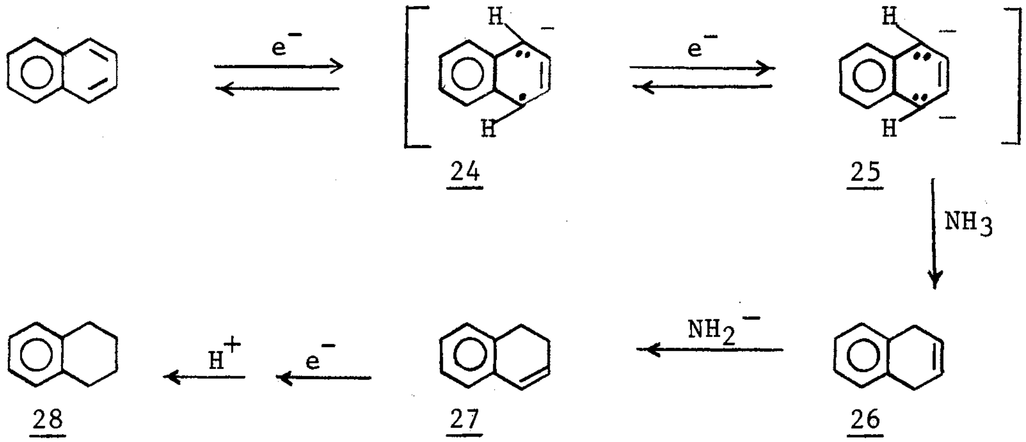


When carried out under the latter conditions, the reaction resembles the Birch reduction (sodium-ethanol-ammonia). With lithium-methylamine reagent and biphenyl, they report[12c] 49% 1-cyclohexylcyclohexene (20) and 36% bicyclohexyl (21) formed. If a secondary amine diluent such as morpholine is added, biphenyl is reduced to 92% 20 and 8% 22 and 23. Benkeser and co-workers surmise that bulky amines are slower to

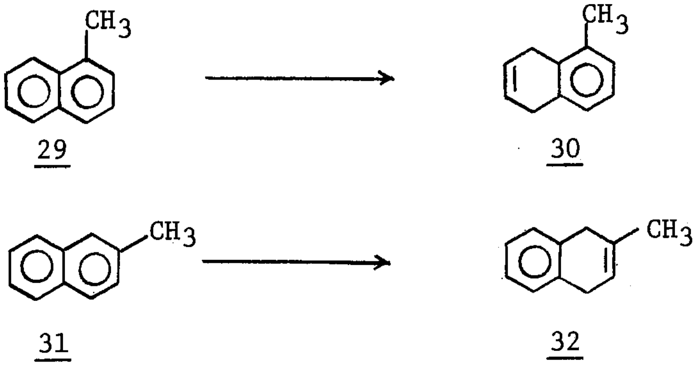


protonate anion intermediates, thus allowing more time for these reactive species to rearrange to the most thermodynamically stable form in which the cyclohexyl group is situated on the double-bonded carbon atom.[12c] Paramagnetic susceptibility[13] and electron spin resonance[14] measurements on sodium-biphenyl systems indicate that the 1:1 adduct that forms between the metal and aromatic hydrocarbon is a radical anion.

Lebeau and Picon in 1914 were the first workers to study the sodium-ammonia reduction of naphthalene.[15] In 1931 Wooster and Smith reported that 1,2,3,4-tetrahydronaphthalene (28) was the major product.[16] The reaction of naphthalene with sodium-ammonia reagent at -75° to -65° was reported by Hückel and Bretschneider in 1939 to give a red solution of dihydronaphthalene dianion (25),[9a] which was decomposed with methanol to give 1,4-dihydronaphthalene (26), subsequently converted to 1,2-dihydronaphthalene (27), and then reduced to 28. These workers proposed the following mechanism:

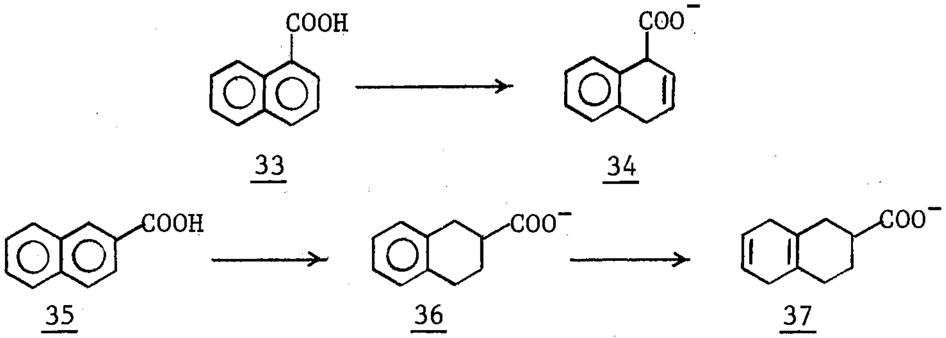


If sodium-ethanol-ammonia reagent is used, the major products are 26 and 1,4,5,8-tetrahydronaphthalene.[17] Hückel and co-workers[18] have proposed an empirical rule according to which the unsubstituted naphthalene ring is reduced more readily when substitution is at the 1-position and that the substituted ring is reduced more readily when the substituent is at the 2-position. They found that sodium-ammonia reagent reduces 1-methylnaphthalene (29) to 5-methyl-1,4-dihydronaphthalene (30), whereas sodium-methanol-ammonia reagent reduces 2-methylnaphthalene (31) to 2-methyl-1,4-dihydronaphthalene (32). Similarly, the sodium-ammonia reagent converts 1-naphthoic acid (33) to 1,4-dihydronaphthoate (34),[5a] whereas lithium-ethanol-ammonia reagent converts 2-naphthoic acid (35) to first 1,2,3,4-tetrahydronaphthalene-



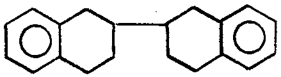
29 30 31 32

2-carboxylate (36) and then to 1,2,3,4,5,8-hexahydronaphthalene-2-carboxylate (37).[19]



33 34 35 36 37

Benkeser and co-workers were the first to substitute primary aliphatic amines such as methylamine, ethylamine, and propylamine for ammonia in these reductions.[8,20] In this new reducing system they found that naphthalene is reduced by lithium and ethylamine to a mixture of octalins and a small amount of decalin. 1,1',2,2',3,3',4,4'-Octahydro-2,2'-binaphthyl (38) was reported by Reggel and co-workers in 1961 as a major product in the sodium-ethylamine reduction of naphthalene. Also produced was a mixture of 28 and a hexahydrobinaphthyl.



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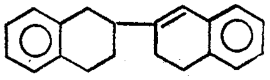
Huckel and Wartini[21] have also shown that 38 is formed when sodium is added slowly to 27 in ammonia. Recently, workers in this laboratory have reported the formation of 27, 1,2,3,3',4,4'-hexahydro-2,2'-binaphthyl (39), 5,6,6a,6b,11,12,12a,12b-octahydrodibenzo[*a,g*]biphenylene (40), and 1',2',3,3',4,4'-hexahydro-1,2'-binaphthyl (41) in the sodium-amine reduction of naphthalene.[22] A completely new type of



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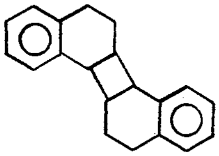

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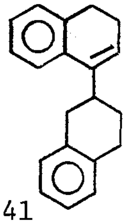

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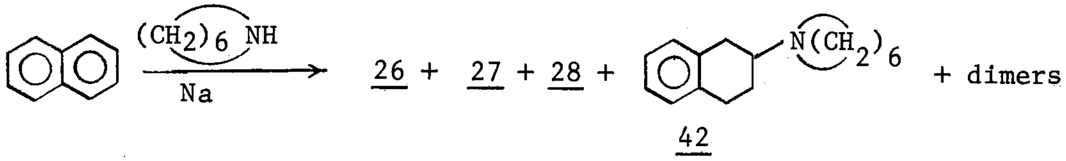
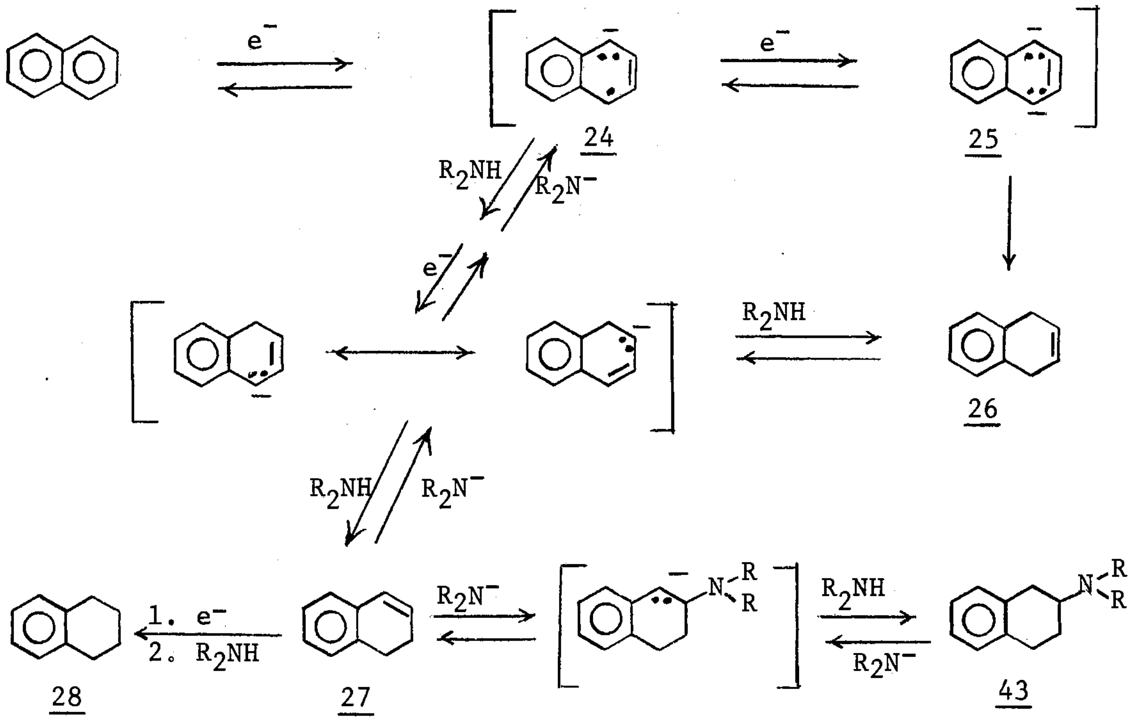
product from the sodium-amine reduction of naphthalene has been recently reported.[1,22a,23] This reaction provides a direct formation of the carbon-nitrogen bond in secondary or tertiary amines, utilizing an aromatic nucleus and a primary or secondary amine as starting materials. For example, N-(1,2,3,4-tetrahydro-2-naphthyl)hexamethylenimine (42) is formed in the sodium-hexamethylenimine reduction of



naphthalene, and the following mechanism has been proposed:

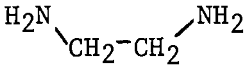


In this thesis, reductive amination products will be referred to as aminated products. The dimeric hydrocarbon products generally were found to distill below 140° (0.01 mm).

CHAPTER III

RESULTS AND DISCUSSIONS

Our studies show that only the substituted naphthalene ring is reduced in the sodium reduction of 1, 2, and 3 in ethylenediamine (44), N-methylpiperazine (45), and piperidine (46). We found similar



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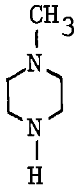

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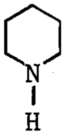
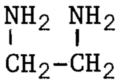
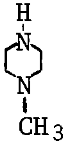
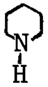
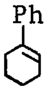


46

results for the sodium reduction of 1 and 2 in liquid ammonia at -33°. The reaction conditions and product yields of the sodium reductions that we studied in 44, 45, 46, and ammonia are summarized in Table I. The ratios of monomeric hydrocarbon products are given in Table II. In Table I, yields of dimeric products are based on the molecular weight of an octahydrobinaphthyl. Likewise, yields of aminated products are based on the molecular weight of an aminated product such as 42. Table II shows that the sodium reduction of benzene, biphenyl, 1-phenylnaphthalene, 2-phenylnaphthalene, 2-benzylnaphthalene, and 1-phenylcyclohexene in 44, 45, 46, and ammonia give hydrocarbon

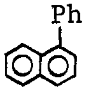
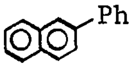
TABLE I

REACTION CONDITIONS AND PRODUCT YIELDS

Reactant Hydro-carbon	Amount of Hydrocarbon		Amount of Sodium		Nature and Volume (ml) of Amine		Reaction Mixture Color	Products				
								Monomer	Dimer		Aminated	
	g	mole	g	g-atom				g	g	% Yield	g	% Yield
 [a]	18.7	0.24	32.8	1.4	 $\overset{\overset{NH_2}{\vert}}{CH_2}-\overset{\overset{NH_2}{\vert}}{CH_2}$ 44	700	Blue green	--	--	--	--	--
 9	37.0	0.24	32.8	1.4	44	700	Blue green	20.3	0.5[b]	1	0.3	0.6
9	38.9	0.25	34.5	1.5	 45	800	Dark blue	17.4	1.6	4	2.3[c]	4
9	15.4	0.10	13.8	0.60	 46	200	Dark green	9.8	0.2	1	0.2	0.8
 12	31.6	0.20	9.2	0.40	45	200	Opaque brown	26.4	--	--	0.1	0.2
12	15.8	0.10	4.6	0.20	46	200	Red brown	5.5	--	--	0.3	1

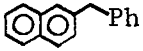
[a] 7.8 g Ethanol added. [b] Mass spectrum shows MW of 312 and 318. [c] Mass spectrum shows a MW of 258.

TABLE I (Continued)

Reactant Hydrocarbon	Amount of Hydrocarbon g	Amount of Hydrocarbon mole	Amount of Sodium g	Amount of Sodium g-atom	Nature and Volume (ml) of Amine		Reaction Mixture Color	Products Monomer g	Products Dimer g	Products Dimer % Yield	Products Aminated g	Products Aminated % Yield
 1	20.4	0.10	9.2	0.40	44	200	Blood red	17.0	0.5	2	0.1	0.4
1	20.4	0.10	9.2	0.40	45	200	Dark purple	11.8	2.1	10	2.4	8
1	20.4	0.10	9.2	0.40	46	200	Blood red	4.4	1.7	8	0.1	0.3
1[d]	20.4	0.10	4.6	0.20	NH_3	200	Blood red	19.2	0.1	1	0	--
 2	102	0.50	46.0	2.0	44	1600	Red blue	59.5	3.4	3	1.6	1
2	51	0.25	23.0	1.0	45	800	Dark purple	38.6	1.5	3	0.5	0.7

[d] Reaction temperature, -33°.

TABLE I (Continued)

Reactant Hydro-carbon	Amount of Hydrocarbon		Amount of Sodium		Nature and Volume (ml) of Amine		Reaction Mixture Color	Products				
								Monomer	Dimer		Aminated	
	g	mole	g	g-atom				g	g	% Yield	g	% Yield
2	20.4	0.10	9.2	0.40	46	200	Dark violet	17.1	1.0	5	0.5	2
2[d]	20.4	0.10	4.6	0.20	NH_3	200	Dark violet	16.4	0.1	1	0	--
 3	43.6	0.20	18.4	0.80	44	700	Blue purple	27.4	4.0	9	0.1	0.2
3	21.8	0.10	9.2	0.40	45	200	Dark purple	11.7	0.4	2	8.6	28
3	21.8	0.10	9.2	0.40	46	200	Dark purple	11.2	0.3	1	1.9	6

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[d] Reaction temperature, -33°

TABLE II

RATIO OF MONOMERIC HYDROCARBON PRODUCTS

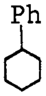
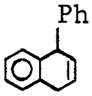
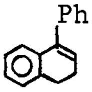
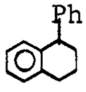
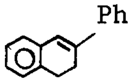
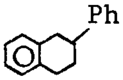
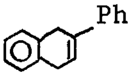
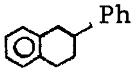
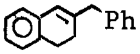
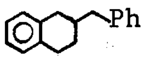
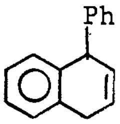
			Ratio of Monomeric Products			
Reactant Hydrocarbon	Amine Used	Reaction Time, Hr	Recovered Reactant Hydrocarbon	Reduced Hydrocarbons		
Benzene	44	9	 (99)	 (1)		
Biphenyl (9)	44	50	9 (6)	 12 (3)	 13 (10)	
9	45	48	9 (2)	12 (3)	13 (15)	
9	46	27	9 (4)	12 (5)	13 (11)	
1-Phenylcyclohexene (12)	45	19	12 (4)	13 (1)		
12	46	18	12 (1)	13 (2)		
1-Phenylnaphthalene (1)	44	6	1 (1)	 47 (4)	 48 (8)	 49 (7)
1	45	14	1 (1)	49 (10)		
1	46	11	1 (1)	49 (7)		

TABLE II (Continued)

Reactant Hydrocarbon	Amine Used	Reaction Time, Hr	Ratio of Monomeric Products: Recovered Reactant Hydrocarbon	Reduced Hydrocarbons		
1	NH_3	0.75	1 (3)	47 (1)	48 (3)	49 (3)
2-Phenylnaphthalene (2)	44	48	2 (3)	 51 (10)	 52 (7)	
2	45	11	2 (3)	51 (2)	52 (15)	
2	46	8	2 (5)	 50 (12)	 52 (2)	
2	NH_3	1	2 (9)	50 (85)	52 (1)	
2-Benzylnaphthalene (3)	44	8	2 (1)	 53 (6)		
3	45	20	3 (1)	53 (4)		
3	46	20	3 (7)	53 (14)	 54 (61)	

reduction products such as cyclohexene, phenylcyclohexane, 1,4-dihydro-1-phenylnaphthalene (47), 1,2-dihydro-4-phenylnaphthalene (48), 1,2,3,4-tetrahydro-1-phenylnaphthalene (49), 1,4-dihydro-2-phenylnaphthalene (50), 1,2-dihydro-3-phenylnaphthalene (51), 1,2,3,4-tetrahydro-2-phenylnaphthalene (52), 3-benzyl-1,2-dihydronaphthalene (53), and 2-benzyl-1,2,3,4-tetrahydronaphthalene (54). The composition of



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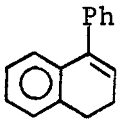

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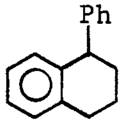

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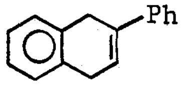

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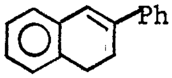

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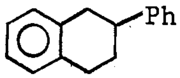

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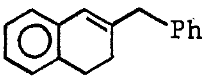

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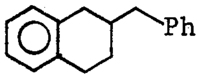

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monomeric hydrocarbon product mixtures was determined by glc, and by nmr (Table III), mass (Table IV), infrared, and uv spectral analyses. For glc analysis, the compound in question was mixed with an authentic sample and the gas chromatogram was inspected for peak separation. Specific compounds in a reaction mixture were identified by adding a sample of known structure to the mixture, repeating the gas chromatography, and noting which peak was increased in height. If a tetrahydronaphthalene was produced in a reduction reaction, it could be

TABLE III[25]

NUCLEAR MAGNETIC RESONANCE SPECTRA OF MONOMERIC HYDROCARBON PRODUCTS

Compound	Proton Absorptions (CCl_4)
2 and 47	δ 6.95-7.80 (m, 9, $Ar\underline{H}$), 5.97-6.15 (m, 1, vinylic-$C\underline{H}$), and 3.19-3.68 (m, 4, benzylic-$C\underline{H}_2$-allylic); (1.1 H extra in aromatic region indicates an impurity of 7% 2 in 47).
48	δ 6.97-7.36 (m, 9, $Ar\underline{H}$), 5.96 (t, 1, vinylic), 2.59-2.91 (m, 2, $ArC\underline{H}_2$), and 2.03-2.44 (m, 2, allylic).
49	δ 6.6-7.1 (m, 9, $Ar\underline{H}$), 3.91 (t, 1, $Ar_2C\underline{H}-CH_2-$), 2.70 (t, 2, $ArC\underline{H}_2-$) and 1.5-2.08 (m, 4, $ArCH_2C\underline{H}_2C\underline{H}_2-$).
52	δ 7.02 (s, 5, $C_6\underline{H}_5$), 6.86 (s, 4, $Ar\underline{H}$), 2.90 (m, 5, $ArC\underline{H}$), 2.05 (m, 2, $ArCH_2C\underline{H}_2-$).

TABLE IV[25]

MASS SPECTRAL DATA FOR MONOMERIC HYDROCARBON PRODUCTS

Compound	*m/e* (rel intensity)
48	206 (100), 205 (29), 202 (18), 191 (28), 128 (25), 91 (22).
49	208 (100), 180 (84), 179 (72), 178 (42), 130 (62), 91 (48).
52	208 (48), 130 (17), 104 (100), 103 (13), 91 (14), 78 (15).

removed from the mixture by distillation.[24] Mass, nmr, infrared, and uv spectrometric analyses could then be applied to the distilled tetrahydronaphthalene and to the distillation pot residue, which usually contains a mixture of unreacted aromatic hydrocarbon and dihydronaphthalenes.

A new type of stirring device was used for all sodium-amine reductions. This device (illustrated in Fig. 1 and 2) stirs the reaction mixture and shreds the sodium metal into small pieces, insuring a large metal surface area and a faster reduction. In order to prevent the reaction mixture from heating above room temperature, rubber cooling hoses were wrapped around the reaction flask. As seen in Table I, a constant ratio of 4 gram-atoms of sodium for 1 mole of substituted naphthalene was used, and 6 gram-atoms were used in the reactions applied to benzene and biphenyl. In every sodium-amine reduction, unreacted aromatic hydrocarbon and sodium were recovered at the completion of the reaction. The volume of amine and ammonia was also held at 200 ml of amine or ammonia for 0.1 mole of arene.

The sodium reduction of <u>1</u> and <u>2</u> in ammonia is much faster than in amines because sodium metal is more soluble in ammonia. The same monomeric reduced hydrocarbons were produced in both types of solvents. Aminated products and dimeric hydrocarbons were not obtained, however, in the sodium-ammonia reduction of <u>1</u> and <u>2</u>. As is seen in Table I, the colors of the reducing solutions in the amines and in ammonia were similar.

The amount of reduction appears to be dependent on the aromatic hydrocarbon starting material, the solvent, and the reaction time (temperature and pressure were nearly constant). By comparing the

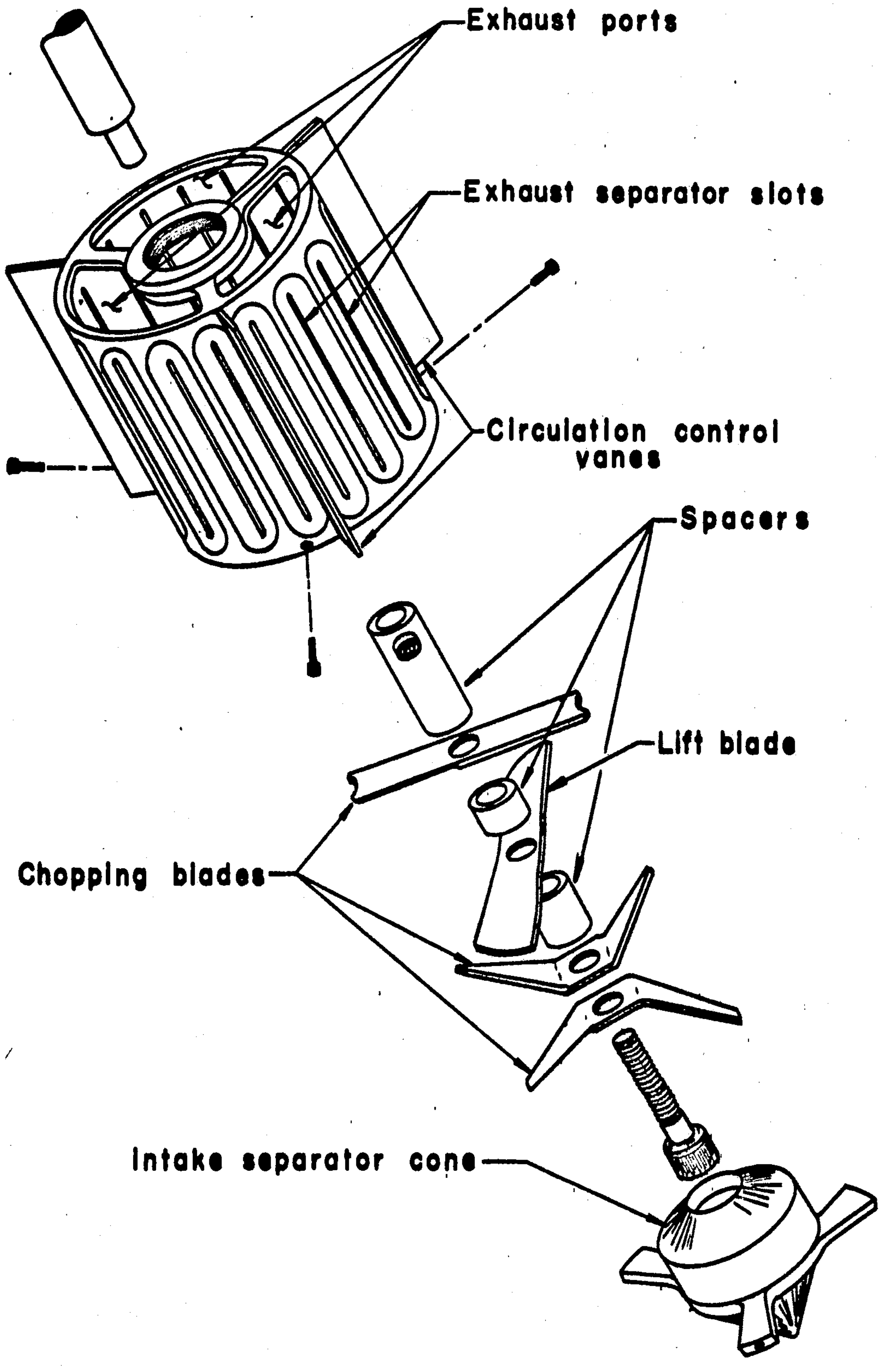


Figure 1. Stir-Shredder Assembly

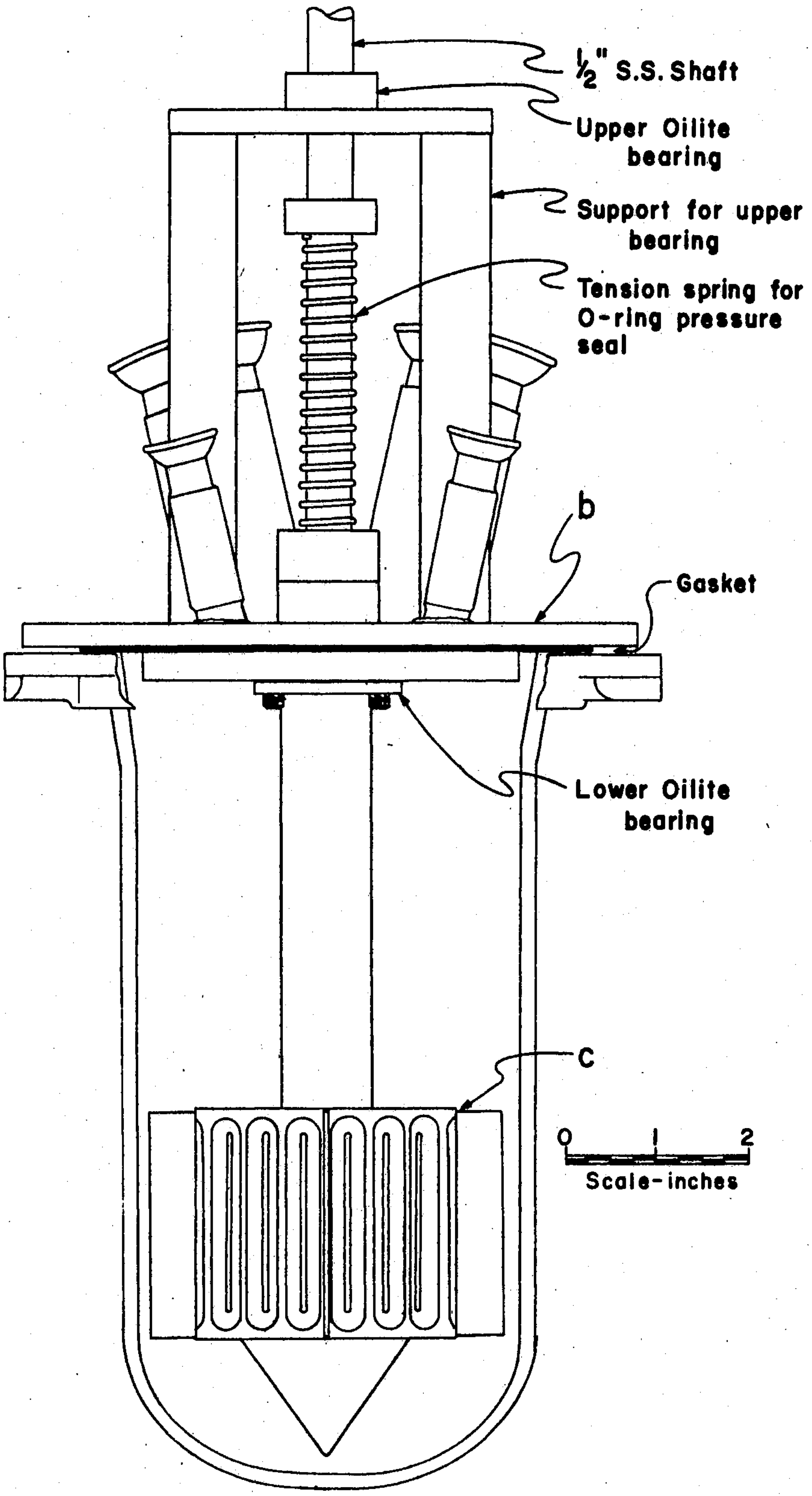


Figure 2. Sodium-Amine Reduction Apparatus

reaction times and ratios of reduced hydrocarbons in Table II, the arene starting materials can be arranged in the following decreasing order of ease of sodium-amine reduction: 1-phenylnaphthalene>2-benzylnaphthalene>2-phenylnaphthalene>biphenyl>benzene.

The gas chromatograms of the volatile products from the sodium-ethylenediamine reduction of 1 in Fig. 3 clearly show that the ratio of hydrocarbon products is dependent upon the reaction time. Samples were taken from the reaction vessel at four different reaction times and each sample was chromatographed. The four peaks on each chromatogram are due to the following compounds: peak no. 1, ethyl ether; peak no. 2, 49; peak no. 3, 48 and/or 47 (nonseparable); and peak no. 4, unreacted 1. Nuclear magnetic resonance studies on reaction samples taken at 15 minutes and 6 hours indicate that peak no. 3 represents almost exclusively 47 in the first chromatogram and a 1:2 ratio of 47:48 in the last chromatogram.

In view of the percentage yield of aminated products (Table I) for reactions carried out in 44, 45, and 46, higher yields of aminated products are produced when 45 is used as a solvent.

1,4-Dihydro-2-phenylnaphthalene (50) appears to be a new compound. Unfortunately, the purest sample of 50 that could be obtained had a 7% impurity of 2 in it. Nuclear magnetic resonance studies[25] of this sample show only the following absorptions between $\delta=0$ and $\delta=6.8$ (in CCl_4): $\delta=3.19$ to 3.68 (m, 4, benzylic-$C\underline{H}_2$-allylic) and $\delta=5.97$ to 6.15 (m, 1, vinylic-$C\underline{H}$).

As shown in Fig. 4, 48 may be formed without first forming 47. Although nmr spectra[25] taken after a short reaction time in the sodium-amine reduction of 1 and 2 indicate that the 1,4-dihydro products 47

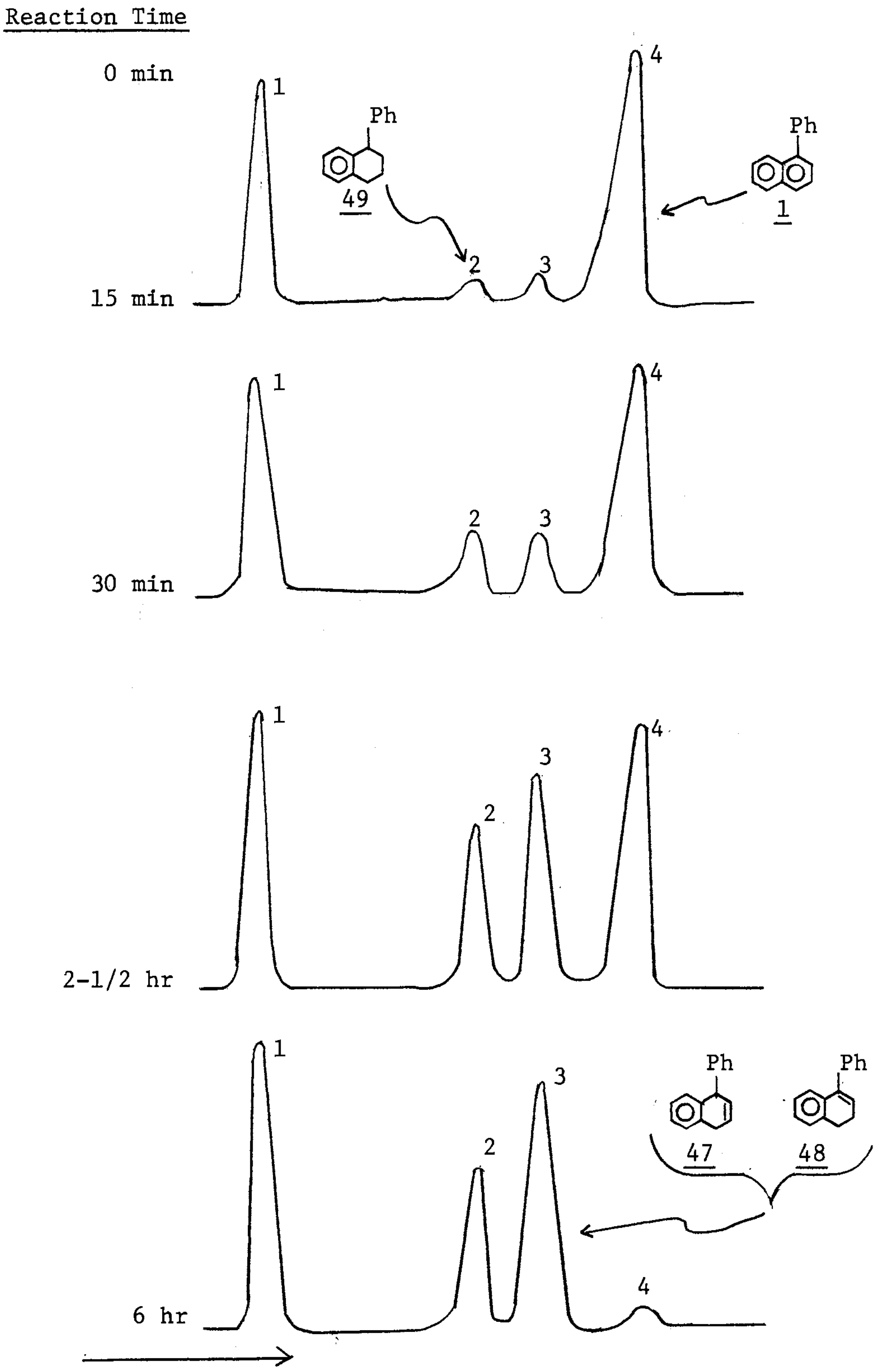


Figure 3. Gas Chromatograms^{26} of Hydrocarbon Products from the Sodium-Ethylenediamine Reduction of 1-Phenylnaphthalene (1).

and 50 are formed before the 1,2-dihydro products 48 and 51 are produced, we do not have conclusive evidence that this is always true. Although we do not know that the first electron adds to 1 at the C-4 position of the naphthalene ring, this is probably the case since the C-1 position is likely to have a higher electron density than the C-4 position.

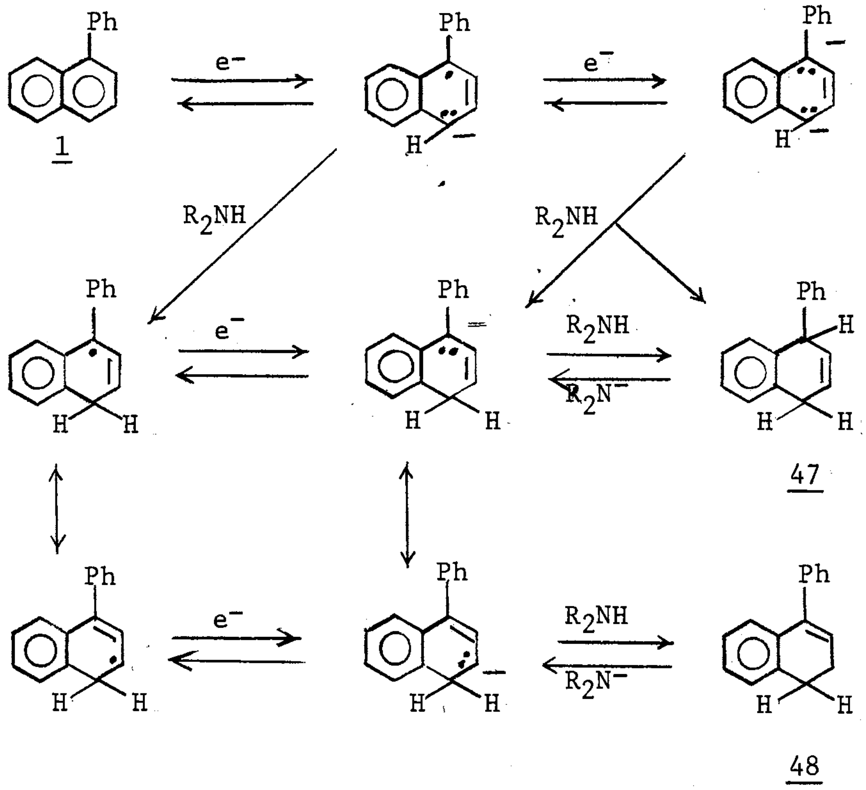


Figure 4. Mechanism for the Sodium-Amine Reduction of 1-Phenylnaphthalene (1).

CHAPTER IV

EXPERIMENTAL[25]

General Reaction Conditions.— All sodium reduction reactions on hydrocarbons using amine solvents were carried out at between 10° and room temperature under a nitrogen atmosphere in a four-necked flask equipped with a mechanical device (Fig. 1 and 2) that both stirred the reaction mixture and shredded the sodium metal into small pieces. Sodium spheres were added under a blanket of nitrogen over a period of two hours to a solution of the hydrocarbon in the amine. The reactions were stopped by pouring the reaction mixture cautiously into a beaker of crushed ice, and the organic products were extracted with ether, the ether layer was washed twice with water, and aminated products were extracted from the ether with a solution of 20% hydrochloric acid. Monomeric hydrocarbons and aminated products were separated from dimeric or polymeric products by either steam distillation or vacuum distillation. Specific reaction conditions and product yields for all sodium reductions in ammonia and amines are reported in Table I, and the ratios of monomeric hydrocarbon products are shown in Table II. The ratios of monomeric hydrocarbon products were determined by glc, nmr (Table III), and mass analysis (Table IV).

Sodium-Ethylenediamine Reduction of 1-Phenylnaphthalene (1).— To a solution of 20.4 g (0.1 mol) of 1 and 200 ml of 44 at 15° in a four-neck flask (Fig. 1 and 2) was added 9.2 g (0.4 g atom) of sodium under a blanket of nitrogen over a period of 1 hr. A blood-red color developed 15 min after the sodium was first added. The mixture was stirred at between 10° and 21° for 6 hrs, at which time any large pieces of unreacted sodium were removed. The reaction mixture was poured cautiously onto 1 l. of crushed ice and the red color disappeared. Ether was added and the mixture was washed twice with water and acidified with 20% aqueous hydrochloric acid. After the hydrocarbons had been removed by extraction with ether, the aqueous layer was made alkaline with dilute sodium hydroxide, and ether was added to extract the aminated products. The ether layer was dried ($MgSO_4$), concentrated on a film evaporator, and distilled at 0.01 mm. The fraction that distilled between 128° and 203° was a light yellow oil of aminated products (0.1 g, 0.4% based upon an expected formula of $C_{18}H_{22}N_2$). The hydrocarbon layer was neutralized with $NaHCO_3$, dried ($MgSO_4$), and concentrated on a film evaporator; vacuum distillation gave a colorless oil (17.0 g), bp 75-92° (0.01 mm), a 1:8:4:7 (<u>1</u>:<u>48</u>:<u>47</u>:<u>49</u>) mixture. This ratio was determined by glc[26] and nmr analysis. The residue of hydrocarbons from the vacuum distillation consisted of dimeric hydrocarbon products (0.5 g, 2% based upon a typical formula of $C_{32}H_{30}$). A similar procedure was used for the sodium-amine reduction of benzene, <u>1</u>, <u>2</u>, <u>3</u>, <u>9</u>, and <u>12</u>.

<u>Identification of 1,4-Dihydro-1-phenylnaphthalene (47)</u>.— Reduction product <u>47</u> was identified by comparing the nmr spectrum of the monomeric hydrocarbon product mixture from the sodium-ethylenediamine reduction of <u>1</u> with an authentic nmr spectrum of <u>47</u>. The authentic sample of <u>47</u> was obtained from the sodium-ethanol reduction of <u>1</u> according to a procedure reported by Carruthers and Hall.[27] Both

nmr spectra showed the following absorptions below δ=6.8: nmr (CCl_4) δ=5.92 (d, 2, vinylic C<u>H</u>), 4.56 (t of d, 1, double benzylic-C<u>H</u>-allylic), 3.44 (d, 2, benzylic-C$\underline{H}_2$-allylic).

<u>Identification of 1,2,3,4-Tetrahydro-1-phenylnaphthalene (49)</u>.— The monomeric hydrocarbon mixture (15.0 g) from the sodium-ethylenediamine reduction of <u>1</u> was dissolved in 55 ml of 95% ethanol, 0.7 g of 10% Pd/C catalyst was added, and the mixture was hydrogenated[25] in a 200-ml stainless steel vessel under 20 lb/in^2 pressure for 2 hrs, at which time glc studies showed only <u>1</u> and <u>49</u> remaining. The mixture was filtered, dried ($MgSO_4$), distilled at 75-95° (0.01 mm), and redistilled.[24] The distillation fraction that was collected at 75° (0.01 mm) was <u>49</u>. Mass, nmr, uv, and ir spectra of <u>49</u> and of an authentic sample were identical. A similar procedure was used to isolate and identify tetrahydronaphthalenes <u>52</u> and <u>54</u>.

<u>Sodium-Ammonia Reduction of 1-Phenylnaphthalene (1)</u>.— To a solution of 4.5 g (0.2 g-atom) of sodium in 200-ml of liquid ammonia at -33° in a 500-ml flask was added 20.4 g (0.1 mol) of <u>1</u> under an atmosphere of ammonia. After 1 min, the blue solution turned to blood-red. The reaction mixture was refluxed at -33° for 45 min and quenched with 50 ml of methanol, and the ammonia was allowed to evaporate overnight. Work-up of the mixture was similar to the procedure used in sodium-amine reductions. Monomeric hydrocarbons (19.2 g) were isolated, and glc[26] and nmr studies indicated a 3:3:1:3 ratio of <u>1</u>:<u>48</u>:<u>47</u>:<u>49</u>. No aminated products and 0.1 g (1%) of dimeric hydrocarbon products was isolated. The procedure for the sodium-ammonia reduction of <u>2</u> was similar.

REDUCTION OF ARYLNAPHTHALENES AND RELATED ARENES WITH SODIUM IN AMINES

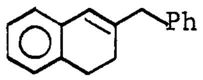
PART II

SYNTHESIS OF ANCILLARY HYDROCARBONS

CHAPTER I

INTRODUCTION

In order to study the course of sodium-amine reduction of 2-benzylnaphthalene (3), both the starting material and analytical standards of 3-benzyl-1,2-dihydronaphthalene (53), 2-benzyl-1,2,3,4-tetrahydronaphthalene (54), and 6-benzyl-1,2,3,4-tetrahydronaphthalene (55) were required.



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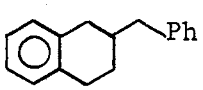

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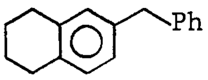

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CHAPTER II

HISTORICAL AND DISCUSSION OF RESULTS

The reactions shown in Fig. 5 were used to prepare starting material 3 and hydrocarbon analytical standards 53 and 54.[28] Of particular interest is the conversion of 2-benzylidene-3,4-dihydro-1(2H)-naphthalenone (56) to 2-benzylnaphthalene (3) in 95% yield. Hydrogenolysis of 2-benzyl-3,4-dihydro-1(2H)-naphthalenone (57) gave 2-benzyl-1,2,3,4-tetrahydronaphthalene (54) in 97% yield. The products of these reactions were free of the position isomers ordinarily produced by Friedel-Crafts alkylation reactions. However, 2,3-benzofluorene (59) was observed as a side product (ca. 3%) in the formation

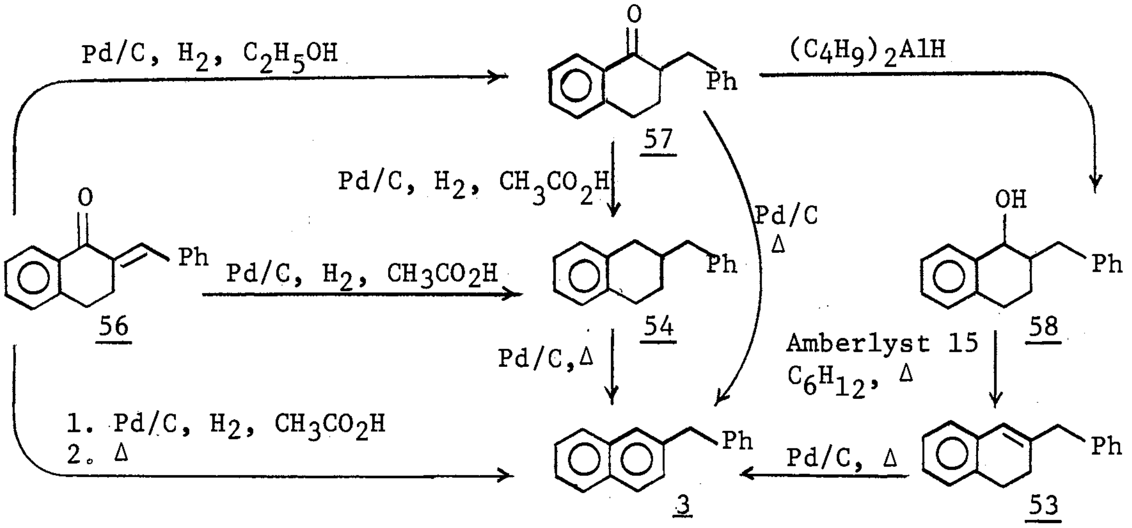
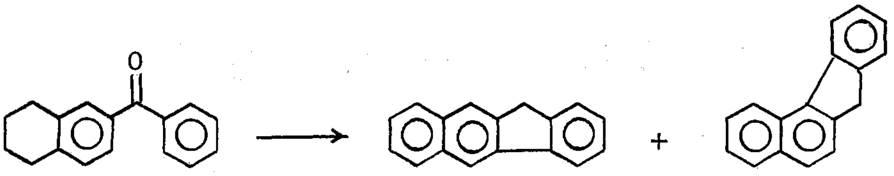


Figure 5. Reaction Scheme for Preparation of 2-Benzylnaphthalene (3), 3-Benzyl-1,2-dihydronaphthalene (53), and 2-Benzyl-1,2,3,4-tetrahydronaphthalene (54).

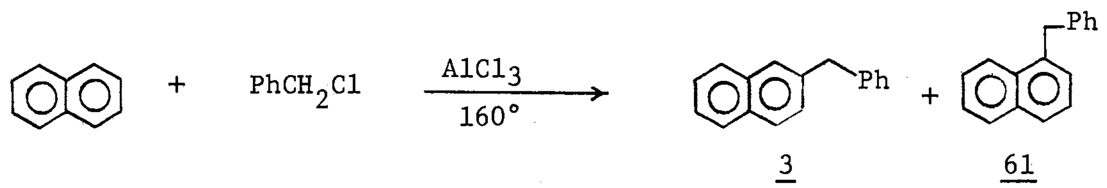
of 3 but not of 53 or 54. Orchin, Woolfolk, and Reggel[29b] have reported that 2,3-benzofluorene (59) and 3,4-benzofluorene (60) formed in small quantities in the aromatic cyclodehydrogenation of phenyl 5,6,7,8-tetrahydro-2-naphthyl ketone over a chromia-on-alumina catalyst at 450-470°. They have surmised that both 59 and 60 were formed via 2-benzylnaphthalene. In our studies the identity of 59 was established by comparison of its nmr and mass spectra with those of 1,2-, 2,3-, and 3,4-benzofluorene.



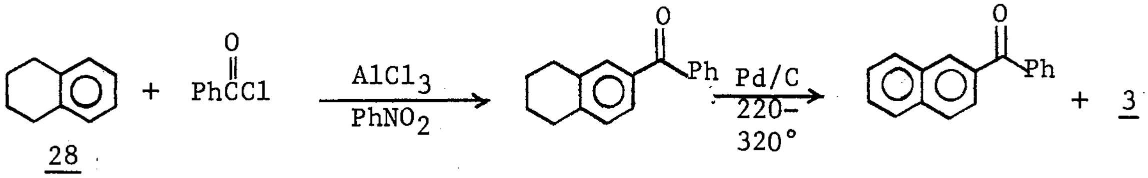
59 60

The dehydrogenation of naphthalenones and other unsaturated ketones[30] and particularly 56[31,32] frequently leads to phenols.[33] However, in some cases,[34] naphthalenes may be obtained in high yields, and hydrogenation, hydrogenolysis and dehydrogenation (Fig. 5) provide attractive routes to arenes.

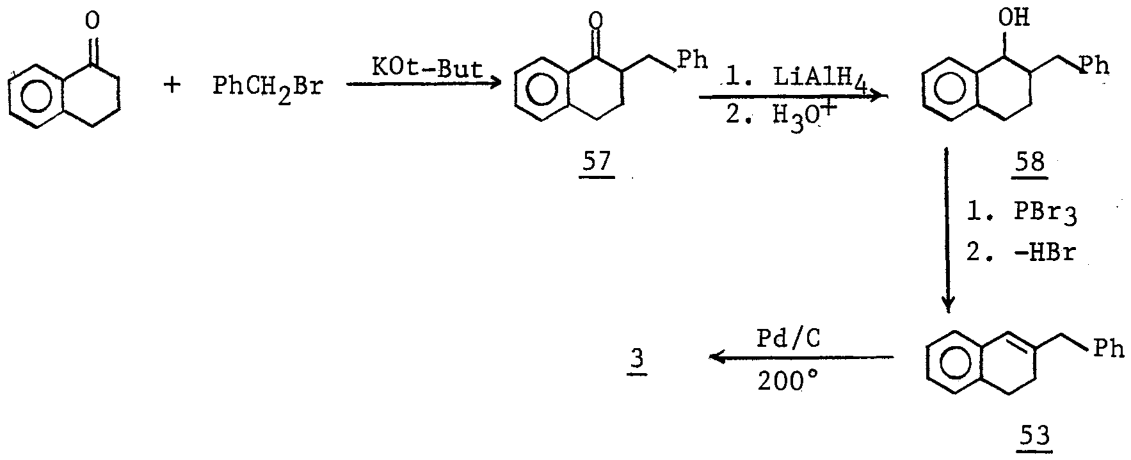
Previously 3 has been reported synthesized by several routes. Roux in 1887 reported the formation of 3 and 1-benzylnaphthalene (61) from the Friedel-Crafts alkylation of naphthalene with benzyl chloride in the presence of $AlCl_3$.[35] Orchin, Woolfolk, and Reggel[29b] prepared 3 in a two-step synthesis starting with the Friedel-Crafts benzoylation



of tetralin (28). Finally, in 1957 Evans[36] reported the preparation of 3 in a four-step reaction scheme starting with the condensation



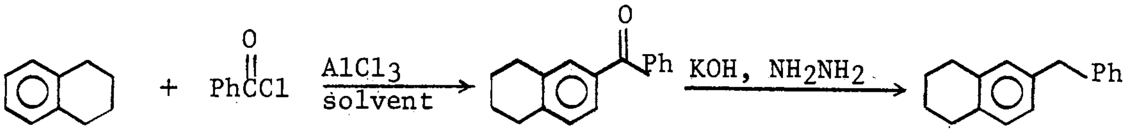
of 3,4-dihydro-1(2H)-naphthalenone and benzyl bromide.



The formation of 3 from 56 probably proceeds through 57 and 54 by successive hydrogenation and dehydrogenation. At this time, there is no evidence that 2-benzyl-1,2,3,4-tetrahydro-1-naphthol (58) or 3-benzyl-1,2-dihydronaphthalene (53) is involved. However, it should be noted that catalytic dehydrogenation of 57 and 58 leads to mixtures of products whereas dehydrogenation of 53 and 54 gives 3 in high yield. The intermediates 53, 54, 57, and 58 were prepared separately and the indicated conversions[37] to 3 were carried out.

The preparations of 58 by reduction of 57 with diisobutylaluminum hydride is probably superior to reduction with lithium aluminum hydride and is recommended.[36] The dehydration[38] of 58 to 53 with Amberlyst 15 is convenient and provides an attractive alternate route to 3.

6-Benzyl-1,2,3,4-tetrahydronaphthalene (55) was also required as an analytical standard and was synthesized in the following manner:



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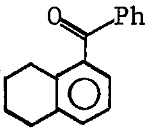
Previous reports of the Friedel-Crafts benzoylation of tetralin (28) claim the exclusive formation of phenyl 5,6,7,8-tetrahydro-2-naphthyl ketone (62).[39] However, we found that phenyl 5,6,7,8-tetrahydro-1-naphthyl ketone (63) was also produced in the reaction. In a similar



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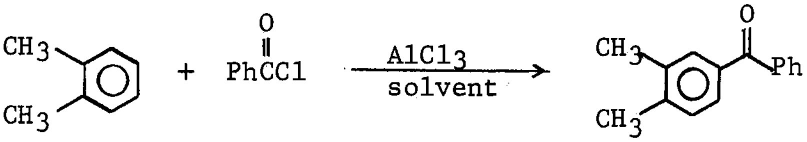
Friedel-Crafts benzoylation of ortho-xylene (64), only one product (65) was reported.[39] We undertook a study of the Friedel-Crafts benzoylation



64

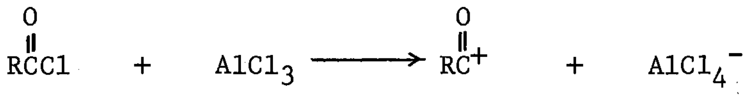
65

of 28 in order to increase the yield of 62, which is an intermediate in producing 55, and to determine whether 63 is formed. In this study we have attempted to understand the influence of the type of solvent on the product ratio in the benzoylation of 28.

Ever since its first description in 1877, the Friedel-Crafts reaction has been important in organic synthesis. At present, the most detailed review of the area is a four-volume treatise edited by G. A. Olah.[39] A Friedel-Crafts acylation to prepare ketones usually involves the reaction of an arene and an acylating agent, in the presence of a Lewis acid catalyst. When aromatic rings bearing ortho-para-directing groups are acylated, para-ketones are produced to almost complete exclusion of the corresponding ortho-ketones. Exceptions to this are known and have been reported.[40] Acylation reactions are complete when little more than a molecular proportion of catalyst is used.[41] Too little catalyst lowers the overall yield because of incomplete utilization of the acylating agent and, in some cases, it may cause self-condensation of the only partially complexed ketone. An excess of catalyst often gives appreciable amounts of tar.

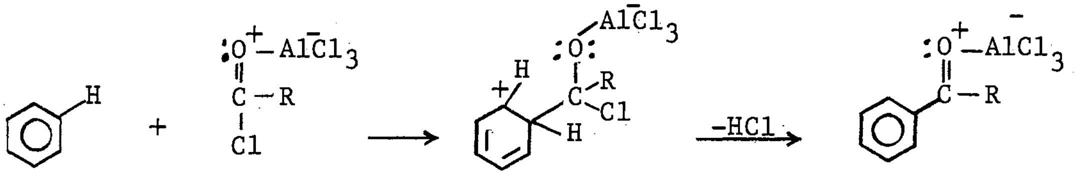
The choice of solvent may have an important effect on the Friedel-Crafts reaction. Numerous reaction media have been used. They may be divided into two groups; one produces a solution and the other gives a suspension of catalyst and/or complex as a heterogeneous system. Polar solvents such as nitrobenzene and nitroethane solvate and dissolve both the aluminum chloride and the acyl chloride-aluminum chloride complex, and usually also the aluminum chloride complex of the resulting ketone.[42] Nonpolar liquids having the properties of carbon disulfide do not dissolve the aluminum chloride or aluminum chloride complexes to any appreciable extent. Chloroform and methylene chloride are intermediate in solvent power.

The mechanism of Friedel-Crafts acylation is probably dual depending on conditions.[43] The attacking species is usually the acyl cation, either as an ion pair or as a free ion. Under some conditions,



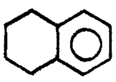
$$\mathrm{R\overset{\overset{O}{\|}}{C}Cl} + \mathrm{AlCl_3} \longrightarrow \mathrm{R\overset{\overset{O}{\|}}{C}{}^{+}} + \mathrm{AlCl_4^{-}}$$

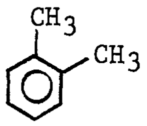
it is a 1:1 complex of acyl chloride and aluminum chloride that attacks the aromatic ring. If the R group is sterically hindered, then the



mechanism probably involves the attack of a free acyl cation on the aromatic ring.[44] In nitrobenzene, a polar solvent, the ion CH_3CO^+ has been detected.[45] However, in the nonpolar chloroform, only the catalyst complex, and not the free ion, is present.

The similary of 28 and 64 invites comparison studies. Brown and co-workers[46] have reported that the C-4 position is the sole point of


28

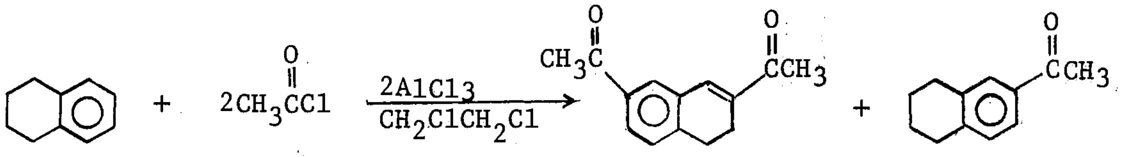


64

substitution in the benzoylation of 64 in the presence of aluminum chloride at 25°, and that the relative rates of reaction in the solvents methylene chloride, benzoyl chloride, and nitrobenzene are

1393, 1120, and 1360.

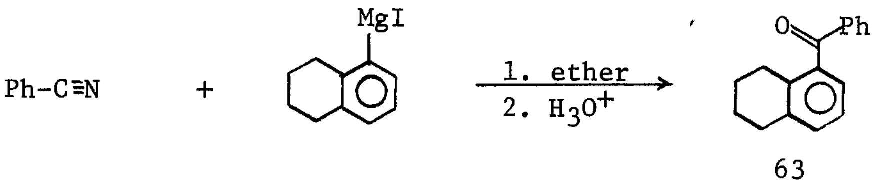
Scharwin[47] and Barbot[48] studied the acetylation and benzoylation of tetralin in 1902 and 1930. Scharwin used carbon disulfide as a solvent and did not report formation of the alpha substituted ketone. Barbot, using excess tetralin as a solvent, reported exclusive formation of the beta substituted ketone. Using excess acetyl chloride and aluminum chloride, Baddeley, Wrench, and Williamson[49] obtained 3,6-diacetyl-1,2-dihydronaphthalene (66) (minor product) and methyl 5,6,7,8-tetrahydro-2-naphthyl ketone (67). Other investigators have



28 66 67

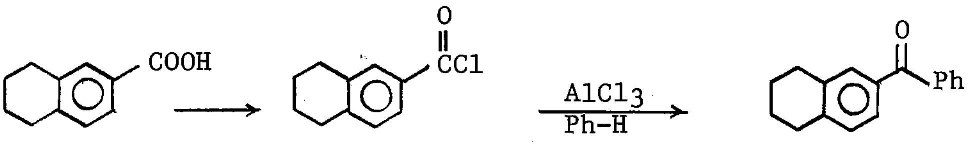
reported yields of 67 up to 93%.[50]

Although 63 has been made by Bachmann and Brockway[29a] by the reaction of benzonitrile and the Grignard reagent of 5-iodo-1,2,3,4-tetrahydronaphthalene, it does not appear to have been reported as a



63

product of the benzoylation of 28. Pure 62 was sought as a precursor to 6-benzyl-1,2,3,4-tetrahydronaphthalene (55) since 55 is not readily prepared by hydrogenation of 2-benzylnaphthalene. It has been prepared by reaction of 5,6,7,8-tetrahydro-2-naphthonitrile with phenylmagnesium bromide,[29a] or by acylation of benzene with 5,6,7,8-tetrahydro-2-naphthoyl chloride in the presence of aluminum chloride.[51]



62

We attempted to increase the yield of 62 by varying the solvent in the Friedel-Crafts reaction. The most effective solvent was nitroethane which, according to glc analysis[26] at 300° gave 1:15 as the value of the ratio 63:62. Other solvents tried and the 63:62 ratios they produced were nitrobenzene,[29b] 1:10; chloroform, 1:9; and carbon disulfide,[29a,47] 1:7. With nitroethane as solvent, the preparation of 62 readily purified by recrystallization from aqueous methanol is readily accomplished. The Wolff-Kishner reduction[52] of 62 was found to be superior to catalytic hydrogenolysis[51] using Pd/C catalyst[28b,34c] and gave 55 in 79% yield.

CHAPTER III

EXPERIMENTAL[25]

2-Benzylidene-3,4-dihydro-1(2H)-naphthalenone (56).— The ketone was prepared by condensation of 1460 g (10 mol) of 3,4-dihydro-1(2H)-naphthalenone and 1265 g (11 mol) benzaldehyde in a vigorously agitated[53] mixture of 8 l. of 95% ethanol and 1 l. of H_2O containing 545 g (13 mol) of sodium hydroxide. The reaction mixture was stirred for 5 hrs at 20-30°, after which gas chromatography[26] showed that less than 1% of starting ketone remained. The reaction mixture was centrifuged and water was added to the centrifuged liquid to cause additional crystallization. The product was crystallized from hot isopropyl alcohol to give 2140 g (97%) of *56*: mp 107° [lit.[54a] mp 107°]; nmr (CCl_4) δ 8.07 (m, 1, Ar*H* peri to carbonyl), 7.77 (t, 1, vinylic), 7.33 (m, 8, Ar*H*), 2.97 (m, 4, $-CH_2C\underline{H}_2-$);[54b] mass spectrum *m/e* (rel intensity) 234 (100), 115 (13), 91 (13), 90 (13), 89 (9), and 77 (5).

2-Benzylnaphthalene (3).

A. From 56.— A 400-g sample of *56* was hydrogenated at 65° and 50-60 psi in 750 ml acetic acid in the presence of 40 g of 10% Pd/C catalyst for 25 hr.[54a] The excess hydrogen was vented, and the entire hydrogenation flask contents were transferred to a 2-l. round-bottomed flask equipped with heating mantle, magnetic stirring bar, short Vigreux column, and distillation receiver. The acetic acid was distilled rapidly and heating was continued until the flask temperature rose to 300° and dehydrogenation took place. Gas chromatography of the crude product showed the ratio naphthalene:3:2,3-benzofluorene to be 2:197:1.[55] Distillation through a 16-in. vacuum-jacketed Vigreux column gave 339 g (91%) of crystalline 3. A portion of the distillate was dissolved in petroleum ether (bp 60-68°) and the solution was passed through a short column of acid-washed alumina to removed colored impurities. The product 3 was obtained as colorless crystals: bp 154° (0.05 mm) [lit.[56] bp 350° (760 mm)]; mp 54-55° [lit.[36] 54-55°]; nmr (CCl_4) δ 7.0-7.7 (m, 7, $C_{10}\underline{H}_7$), 7.08 (s, 5, $C_6\underline{H}_5$), 3.92 (s, 2, $C\underline{H}_2$); mass spectrum (70 eV) m/e (rel intensity) 218 (100), 217 (44), 215 (23), 202 (20), 141 (11), and 115 (10).

B. From 54.— A 2.00-g sample of 54 and 0.20 g of 10% Pd/C were placed in a 4-ml flask equipped with a condenser. The system was flushed with helium for 5 minutes and the flask was slowly lowered into a molten metal bath at 325° C. Heating was continued until hydrogen evolution ceased (17 min).

The mixture was cooled, ether was added, and the catalyst was filtered out. Glc showed 3 and 54 formed in the ratio of 98 to 2.

C. From 53.— The above procedure was applied to 53 and glc studies showed the 3:53 ratio to be 99:1.

2-Benzyl-3,4-dihydro-1(2H)-naphthalenone (57).— A 234-g (1 mol) sample of 56 dissolved in 500 ml of 95% ethanol was hydrogenated in the presence of 5.9 g (2.5%) of 10% Pd/C catalyst at 33° and 55 psi for 2 hr. The hydrogenation was stopped when glc studies showed absence of 56. The crude product was filtered out and recrystallized from 95% ethanol to give 221 g of 57 (94%): mp 53.5-54° [lit.[36] 53-54°]; bp 150-155° (0.04 mm) [lit.[36] 155-159° (0.01 mm)]; nmr (CCl_4)

δ 7.96 (m, 1, Ar<u>H</u> peri to carbonyl), 7.13 (m, 8, Ar<u>H</u>), 3.40 (m, 1, C<u>H</u>-C=O), 2.4-3.0 (m, 4, ArCH_2), 1.3-2.3 (m, 2, -CH_2- β to aromatic ring); mass spectrum (70 eV) <u>m/e</u> (rel intensity) 236 (59), 145 (48), 118 (22), 117 (20), 115 (18), and 91 (100).

<u>2-Benzyl-1,2,3,4-tetrahydronaphthalene (54)</u>.

<u>A. From 56.</u>— A 234-g (1-mol) sample of <u>56</u> dissolved in 500 ml acetic acid was hydrogenated in the presence of 23 g of 10% Pd/C catalyst at 66° for 19 hr at which time glc studies showed that all <u>56</u> was consumed. The catalyst was filtered out and the crude product was distilled to give <u>54</u> (92%); mp 38-39°, bp 133° (0.04 mm) [lit.[57] bp 194-195° (13 mm)]; nmr (CCl_4) δ 7.13 (s, 5, C_6H_5), 6.92 (s, 4, C_6H_4) 2.58 (m, 6, ArCH_2-), 1.0-2.4 (m, 3, β -C<u>H</u>CH_2): mass spectrum (70 eV) <u>m/e</u> (rel intensity) 222 (72), 132 (59), 131 (100), 130 (62), 129 (34), and 92 (99).

<u>B. From 57.</u>— The application of the above procedure to <u>57</u> yielded <u>54</u> (97%).

<u>2-Benzyl-1,2,3,4-tetrahydro-1-naphthol (58)</u>.— A 493-g (2.1-mol) sample of <u>57</u> dissolved in 1200 ml of dry benzene was added dropwise over a 2.5-hr period to a well-stirred solution of 371 g (2.6 mol) of diisobutylaluminum hydride[58a] in 1 l. of benzene at room temperature in a nitrogen atmosphere.[58b] The solution was withdrawn and cautiously poured onto several liters of crushed ice. The mixture was acidified to pH 3 with conc. hydrochloric acid. Additional benzene (2 l.) was added, the layers were separated, and the organic phase was dried ($MgSO_4$) and concentrated to give 450 g (90%) of crude <u>58</u>, which was recrystallized from petroleum ether (bp 60-68°): mp 118-119° [lit.[36] 119-120°]; nmr ($CDCl_3$) δ 7.35 (m, 1, Ar<u>H</u> peri to hydroxyl), 7.05-7.30

(m, 8, ArH), 4.40 (d, 1, >CH-O), 2.2-3.2 (m, 4, ArCH), 1.1-2.2 (m, 3, -CHCH_2- β to aromatic ring), 2.09 (s, 1, OH); mass spectrum (70 eV) *m/e* (rel intensity) 220 (51), 147 (25), 146 (62), 129 (100), 128 (37), and 91 (80).

3-Benzyl-1,2-dihydronaphthalene (53).— A 46.0-g sample of 58 was dissolved in 100 ml cyclohexane, 4.6 g of Amberlyst 15 was added,[38] and the mixture was stirred at reflux temperature for 1 hr. The reaction mixture was filtered and dried ($MgSO_4$), and the product was distilled through a vacuum-jacketed Vigreux column to give 41.1 g (97%) of 53: bp 125° (0.05 mm) [lit.[36] bp 126° (0.1 mm)]; nmr (CCl_4) δ 7.11 (s, 5, C_6H_5-), 6.93 (m, 4, C_6H_4=), 6.14 (m, 1, vinylic), 3.32 (s, 2, ArCH_2C=C), 2.61 (m, 2, ArCH_2), 2.01 (m, 2, allylic); mass spectrum (70 eV) *m/e* (rel intensity) 220 (59), 141 (25), 129 (100), 128 (36), 115 (14), and 91 (31).

Phenyl 5,6,7,8-Tetrahydro-2-naphthyl Ketone (62).— The ketone 62 was prepared[29,47] by addition of $AlCl_3$ (454 g, 3.4 mol) to a CS_2 (1.8 l.) solution of benzoyl chloride (350 g, 2.5 mol) and tetralin (350 g, 2.7 mol) at 10°. The mixture was stirred at 5° for 1 hr and the temperature was then allowed to rise to 25° during another hr. After the solvent was evaporated using a warm water bath, 2 l. of petroleum ether, bp 60-68°, were added. The mixture was acidified with 20% HCl and washed with H_2O (2 x 2 l.). The organic layer was dried ($MgSO_4$), filtered, and flash-evaporated to give 580 g of brown oil which was distilled to give a mixture of 529 g (90%) of 63 and 62 (1:7) boiling at 177° (0.01 mm). Methanol (2.5 l.) and then H_2O (0.1 l.) were added with stirring and the suspension was refrigerated. Filtration yielded 427 g (72%) of 62. An additional recrystallization from methanol gave pure 62: mp 40-41° [lit.[29b] 40.4-41.2°, lit.[29a] 40-41°]; ir (KBr) 690, 723, 787, 821, 837, and 1660 (C=O) cm^{-1}; nmr (CCl_4) δ 6.85-7.7 (m, 8, Ar$\underline{H}$), 2.5-2.9 (broad m, 4, Ar$C\underline{H}_2$), 1.6-1.9 (broad quintet, 4, β -$C\underline{H}_2C\underline{H}_2$); uv max (95% C_2H_5OH) 201 mμ (ε 35,000) and 268 mμ (ε 17,000).

The orange 2,4-dinitrophenylhydrazone was prepared: mp 197-198°.

Anal. Calcd for $C_{23}H_{20}N_4O_4$: C, 66.33; H, 4.84; N, 13.46. Found: C, 66.09; H, 4.74; N, 13.66.

Phenyl 5,6,7,8-Tetrahydro-1-naphthyl Ketone (63).— The concentrated mother liquor (74 g) from the above procedure was chromatographed on a 2" x 36" column of acidic alumina and eluted with petroleum ether, bp 60-68°. The progress of the chromatography was monitored with glc analysis[26] at 300°. After 15 x 500-ml fractions, 12.5 g of 63:62 (6:1) was obtained. This fraction was separated by preparative glc on a 0.5-in. x 4-ft column of 10% Carbowax 20M coated on acid-washed Gas Pack W (80/100 mesh) at 225°. Distillation of the collected glc fractions gave 2.5 g of 63: bp 177° (0.01 mm); ir 670, 689, 705, 724, 767, 779, 802, 817, 832, and 1670 (C=O) cm^{-1}; nmr (CCl_4) δ 6.8-7.7 (m, 8, Ar$\underline{H}$), 2.45-2.9 (broad m, 4, Ar$C\underline{H}_2$-), 1.45-1.8 (broad, quintet, 4, β -$C\underline{H}_2C\underline{H}_2$-); uv max (95% C_2H_5OH) 201 mμ (ε 40,000) and 252 mμ (ε 13,500).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.20; H, 6.87. The orange 2,4-dinitrophenylhydrazone was prepared: mp 190-191°.

Anal. Calcd for $C_{23}H_{20}N_4O_4$: C, 66.33; H, 4.84; N, 13.46. Found: C, 66.17; H, 5.03; N, 13.34.

Wolff-Kishner Reduction of Phenyl 5,6,7,8-Tetrahydro-2-naphthyl Ketone (62) to 6-Benzyl-1,2,3,4-tetrahydronaphthalene (55).— To a mixture of 47.2 g (0.20 mol) of *62*, 25 g (0.45 mol) of KOH, and 1 l. of diethylene glycol in a 1.5-l. stainless steel flask was added 30 g (0.80 mol) of 85% aqueous hydrazine. The flask was equipped with a nitrogen inlet and outlet, a thermocouple, and a Dean-Stark trap.[52] The reaction mixture was heated at a constant rate until the head temperature reached 231° (2 hr), by which time 200 ml of condensate had been collected. The reaction mixture was steam distilled until 35 l. of condensate were collected. After extracting the mixture with petroleum ether (60-68°), drying ($MgSO_4$), and concentrating the solution on a flash evaporator, the mixture was distilled at 128° (0.1 mm) to give 35.2 g (79%) of *55*: uv max (95% C_2H_5OH) 204 mμ (ε 50,000), 270 (ε 1,000), and 280 (ε 1,000); ir 694, 715, 763, 793, and 834 cm^{-1}; nmr (CCl_4) δ 6.96 (s, 5, $C_6\underline{H}_5$), 6.71 (s, 3, $ArC\underline{H}$), 3.72 (s, 2, $C_6H_5C\underline{H}_2Ar$), 2.57 (m, 4, $ArC\underline{H}_2CH_2$-), and 1.62 (m, 4, $ArCH_2$-$C\underline{H}_2$); mass spectrum (70 eV) *m/e* (rel intensity) 222 (85), 178 (18), 165 (19), 131 (100), 115 (21), and 91 (52).

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24. Nester/Faust auto-annular spinning band distillation system, Model NFA-200.

25. Mass spectra were obtained at 70 eV on a C.E.C.-110 mass spectrometer using direct probe loading in the ion source. Nmr data were obtained from a Varian HR-60 and A-60 spectrometers. Line positions are reported as ppm from internal tetramethylsilane (δ scale). The catalytic hydrogenations were carried out in a 3.5-l. stainless steel vessel using a model 3920 Parr shaker-type hydrogenator.

26. The gas chromatography studies using a Hewlett-Packard model 5750 instrument were made at 240° on an 0.25-in. x 12-ft column of 80-100 mesh Chromosorb G (acid-washed) treated with DMCS and coated with 5% silicone rubber UC W-98.

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37. We thank Dr. J. M. Springer for the direct conversion of *57* to *3*. This reaction provides a complex mixture of products.

38. Literature on the use of Amberlyst 15 resin may be obtained from the Rohm and Haas Co., Independence Mall West, Philadelphia, Pa. 19105.

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Thesis: REDUCTION OF ARYLNAPHTHALENES AND RELATED ARENES WITH SODIUM IN AMINES
I. PRODUCTS OF THE REACTION
II. SYNTHESIS OF ANCILLARY HYDROCARBONS

Major Field: Chemistry

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