SODIUM-AMINE REACTIONS OF NAPHTHALENE I. EFFECT OF TYPES OF SODIUM DISPERSION II. EFFECT OF COSOLVENTS III. SELECTIVE 1,2'-DIMERIZATION

By

Lawrence Eugene Harris

Bachelor of Science
Kansas State College
Pittsburg, Kansas
1966

Master of Science
Kansas State College
Pittsburg, Kansas
1968

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Thesis Approved:

E J Eisenbraun
Thesis Adviser

S. E. Scheppele

O. C. Dermer

L. Herbert Bruneau

D. Durham
Dean of the Graduate College

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SODIUM-AMINE REACTIONS OF NAPHTHALENE

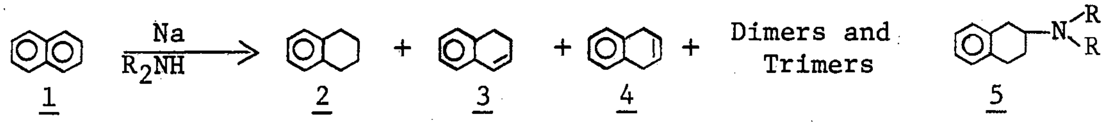
PART I. EFFECT OF TYPES OF SODIUM DISPERSION

CHAPTER I

INTRODUCTION AND HISTORICAL

The reduction of unsaturated hydrocarbons with sodium using amines as a solvent medium was first reported by Ziegler and co-workers.[1a] However, the use of metal-amine reducing agents in organic chemistry is mainly due to the work of Benkeser and co-workers.[1b] They found that more extensive reduction resulted when low-molecular-weight amines such as methylamine, ethylamine, and propylamine were used instead of ammonia. These results were attributed to an increase in solubility of organic molecules in amines and the higher reaction temperatures attainable. Reggel and co-workers showed that lithium in ethylenediamine is one of the most powerful metal-amine reducing systems, which can reduce aromatic hydrocarbons to saturated hydrocarbons.[2a,b]

The reduction of naphthalenes with sodium in several higher-molecular-weight primary and secondary amines has been extensively investigated by Eisenbraun and co-workers.[3a-g] They found that in addition to the familiar Birch-type reduction products 2, 3, and 4, reductive amination of naphthalene (1) occurs, and in many cases, it is the preferred course of reaction.[3a-d] However, examples were



observed in which reductive dimerization and trimerization is the predominant reaction.[3e-g]

CHAPTER II

RESULTS AND DISCUSSION

Some control of the product distribution in the reaction of <u>1</u> with sodium has been achieved by selection of the appropriate amine solvent. Reductive amination is the favored course of the reaction when certain secondary amines such as pyrrolidine and N-methylpiperazine are used. In low-molecular-weight diamines[3g] and sterically hindered amines, reductive dimerization is the principal reaction pathway.

Recently we have found that much higher yields of reductive amination products result when finely divided sodium metal and short reaction times are used (Table I) for the reduction of <u>1</u> in secondary amines. The finely divided sodium was generated in situ using the stirring (1650 rpm) and shredding device[4] shown in Figures 1, 2, and 3. In Figure 2 is shown a detailed drawing of the assembly which shreds the sodium into small pieces. The apparatus is constructed of stainless steel and consists of a stationary cage containing a rotating shaft fitted with three chopping blades. The circulating sodium metal (1/16" to 1/4" spheres) enters the bottom of the cage and is swept upward by the lift blade. As it encounters the chopping blades, the metal is thrown outward and is shredded on the exhaust separator slots. The exhaust ports provide another exit from the cage and allow the sodium to recirculate until finely divided metal results.

TABLE I

REDUCTIVE AMINATION OF NAPHTHALENE WITH USE OF A STIR-SHREDDING DEVICE

Amine	Reaction Time,[a] hr	Reductive Amination Products, %[b]	Naphthalene Recovered, %	Yield of Hydrocarbon, %[b]			
				2	3	4	Dimers (Major)
N-Methylpiperazine	3	95	..	<1	1	<1	1 (8)
Piperidine	3	79	<1	<1	2	2	2 (7)
Pyrrolidine	3	78	<1	4	<1	<1	8 (10)
Butylmethylamine	3	78	<1	2	5	2	9 (7)
Diethylamine	3	13	2	13	13	2	56 (8,7)
Ethylenediamine	3	c	5	2	3	13	42 (6,7,11)
2-Methylpiperidine	3	13[d]	33	2	15	9	50 (8)
2,6-Dimethylpiperidine	3	e	25	5	17	..	63 (9)

N-Methylpiperazine	6	57	1	1	..	1	1 (8)
Pyrrolidine	20	64	..	6	..	..	13 (10)
Dipropylamine	23	12[f]	49	6	..	..	62 (9)
Diisopropylamine	27	..	61	4	..	..	65 (9,7)

[a] At room temperature. [b] Yield based on consumed naphthalene. [c] Consisted of several products (1.6 g). [d] Consisted of two major products, 79% of the expected one and 17% of one with the same glc retention time as the amination product from piperidine. [e] Two products (1.3 g) which showed molecular ion *m/e* 229 in their mass spectra and not 243 as expected for the amination product. [f] Consisted of several unidentified products.

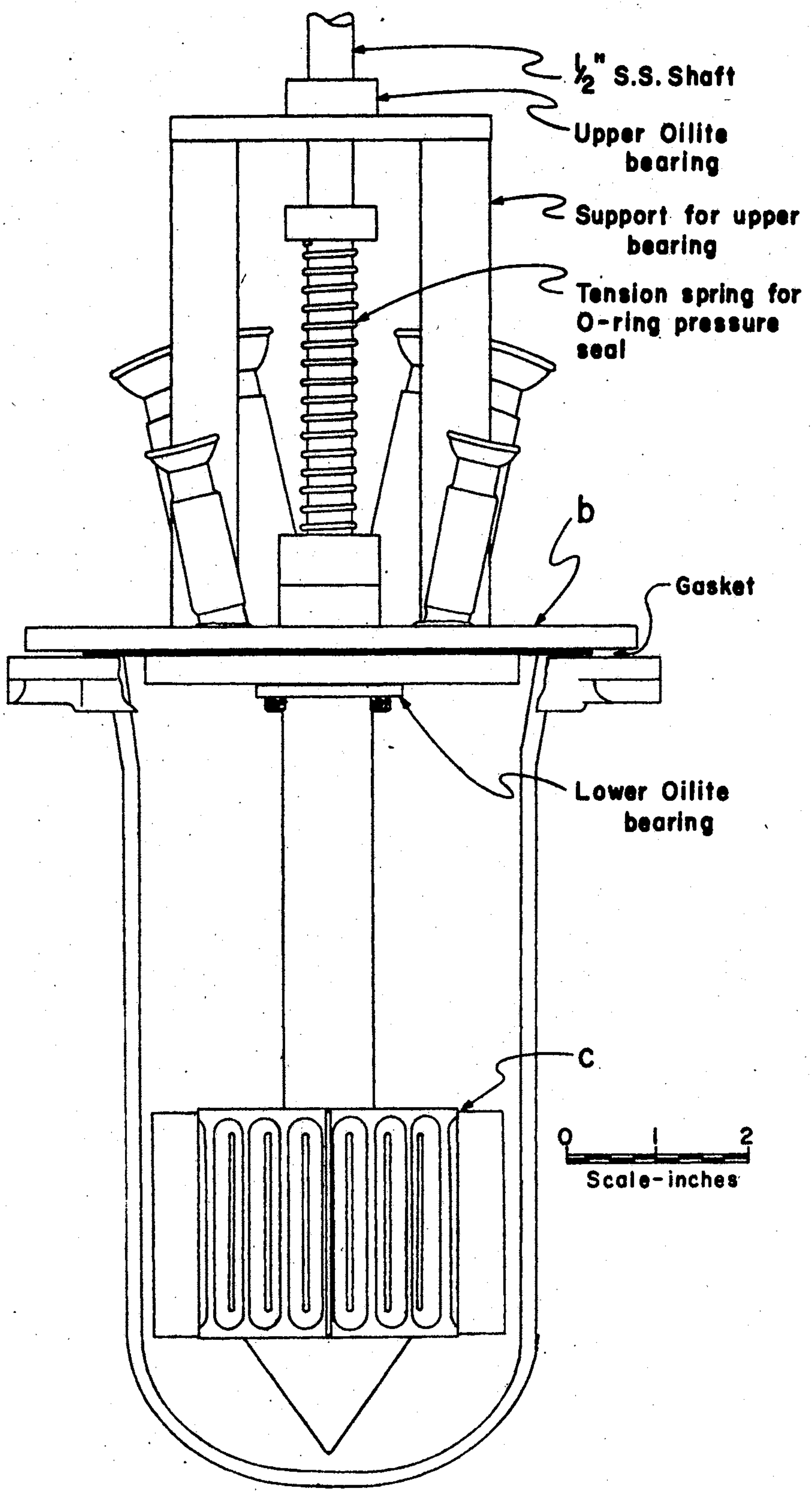


Figure 1. Apparatus for Sodium-Amine Reactions

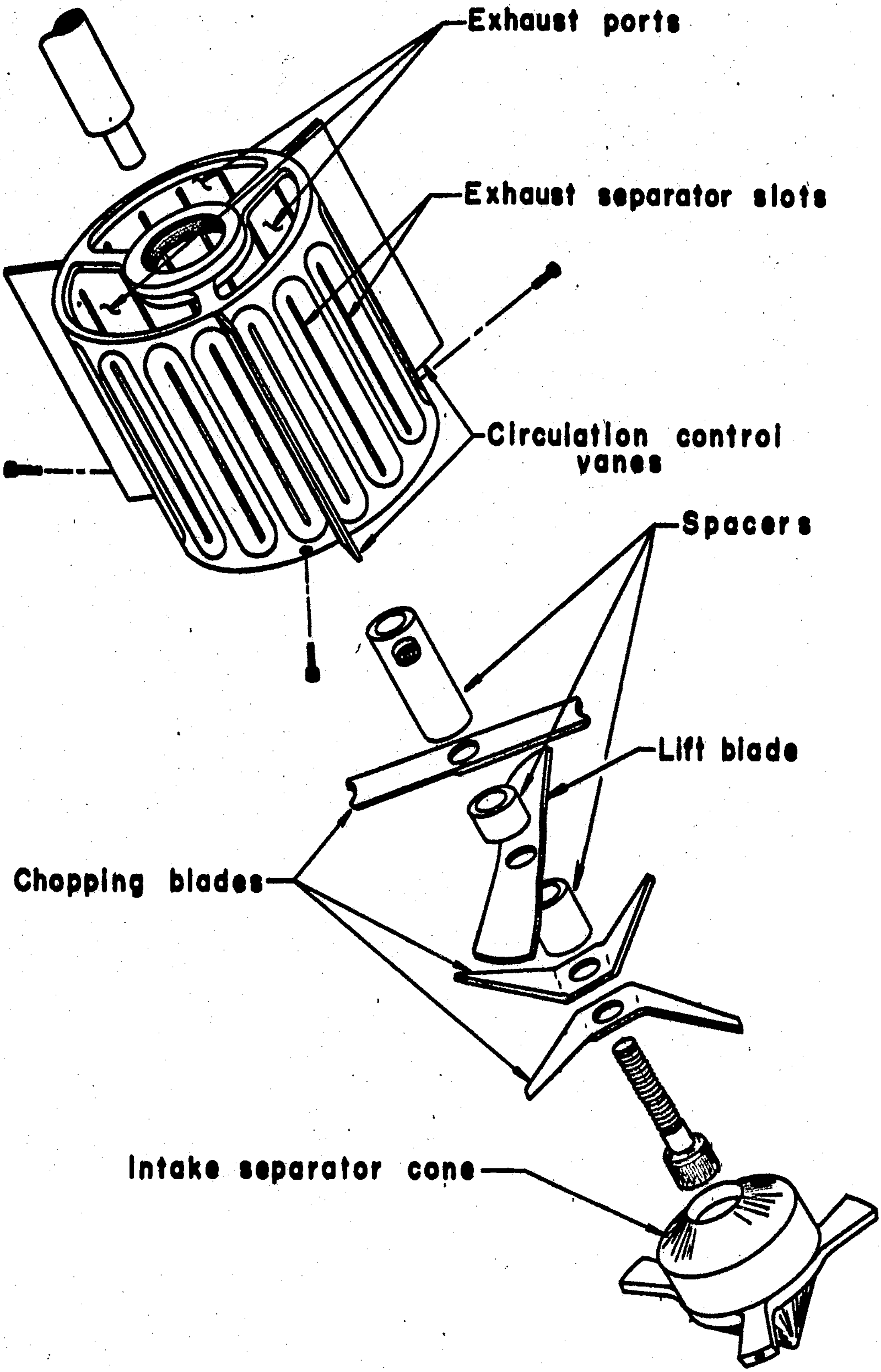


Figure 2. Stirring and Shredding Device for Sodium-Amine Reactions

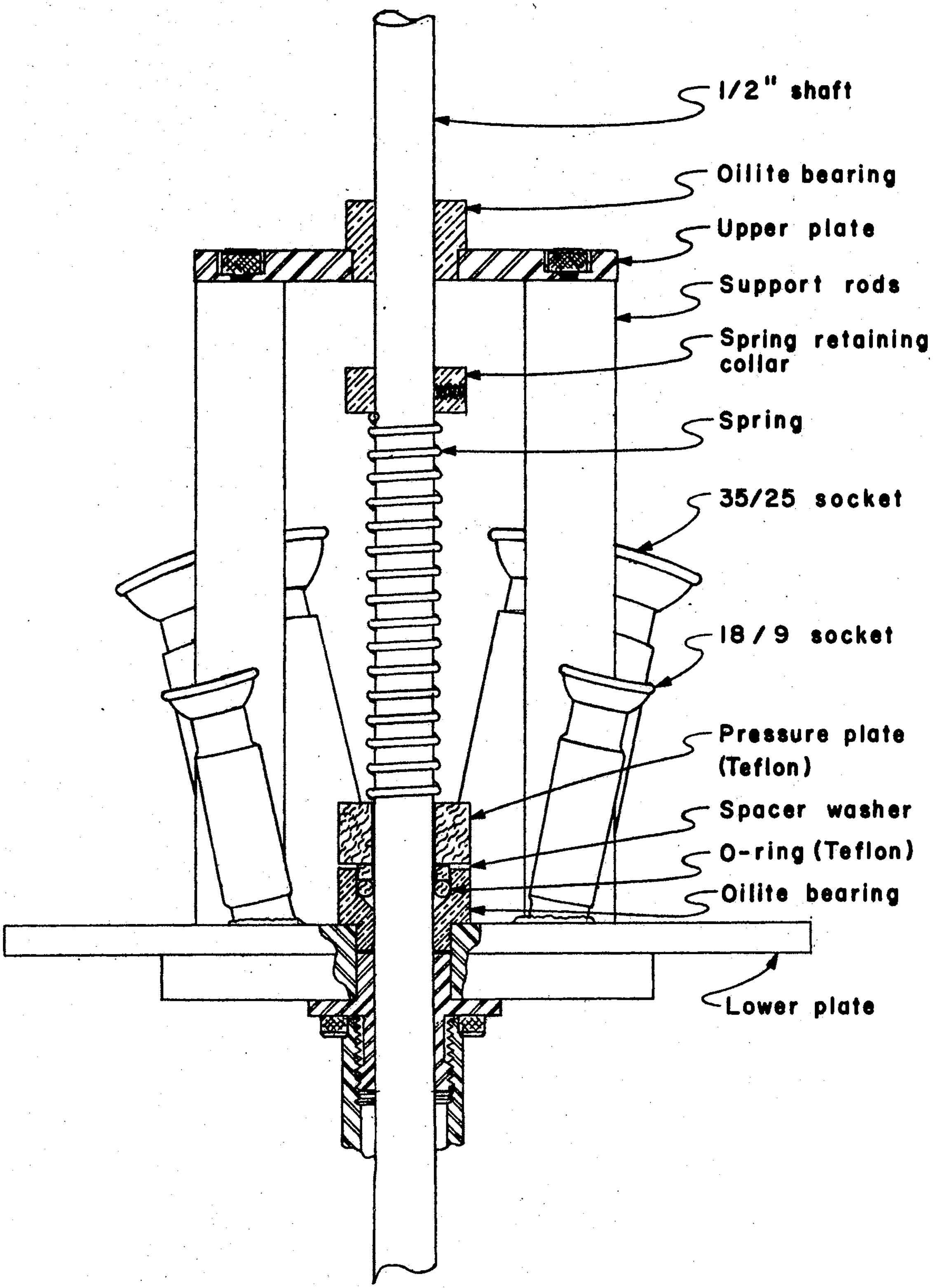


Figure 3. Top Deck of Stir-Shredder Assembly

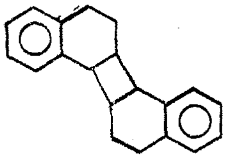
Much of the original reductive amination and reductive dimerization work was carried out using finely dispersed sodium which was prepared by high-speed stirring of sodium in boiling xylene.[3g] The hydrocarbon dissolved in amine was then added to the dispersed sodium and the mixture was magnetically stirred for 12 hours. The sodium usually agglomerated into a ball within an hour, so the exposed sodium surface available for reaction was minimal during most of the reaction. In contrast, the stir-shredding device described above continuously regenerates fresh metal surface throughout the reaction period. The addition of talc to the reaction seemed to have no effect on the agglomeration of sodium into larger pieces nor was there an effect on product distribution.

In liquid ammonia the alkali metals dissolve reversibly to give solvated electrons.[5a-d] Even in low-molecular-weight amines the alkali metal dissolves to some extent[5b,e,f] to form blue solutions which show one or both of two electronic absorption bands in the visible (~6500 Å) and infrared (~15,000 Å) regions due to diamagnetic and paramagnetic species.[5f] The absorption spectra of solutions of alkali metals in ammonia, methylamine, and ethylamine have been measured.[5g]

In the higher-molecular-weight amines which have relatively low dielectric constants, such as diethylamine ($\varepsilon = 3.7$), the solubility of sodium is expected to be quite low. In our reductions at room temperature, the reaction appears to take place at the sodium surface. Increasing the amount of metal surface by using the stir-shredding device would then be expected to have a pronounced effect on the course of the reaction.

Comparison of our results (Table I) obtained by use of the stir-shredding device for a 3-hour reaction time with those reported previously using xylene-dispersed sodium (Table II),[3a] illustrates the complexity of this reaction and the changes in the yields of products due to the change in technique. The change in product composition reflects the relative rates of the various competing reactions. At high sodium-surface concentrations (stir-shredding device) and short reaction times, reductive amination is the predominant reaction for some amines. At lower sodium-surface concentrations (magnetic stirring) and longer reaction times, the amount of reductive dimerization increases. The amination step is reversible[3b] and at longer reaction times the yields of reductive amination products decrease as shown in the latter part of Table I.

The reductive amination products, e.g. 5, are the 2-substituted tetrahydronaphthyl derivatives except as noted. The reductive dimerization products are complex mixtures, in which dimers 6,[3b,d-g] 7,[6] 8,[3g] 9,[6] 10[3b,d-g,7] and 11[3b,d-g,7] predominate.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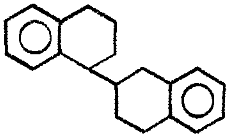
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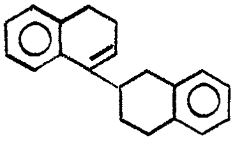
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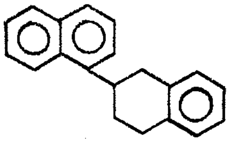
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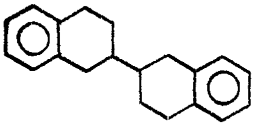
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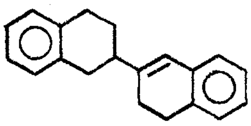
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TABLE II

REDUCTIVE AMINATION OF NAPHTHALENE WITH USE OF PREDISPERSED SODIUM[3a]

Amine	Reaction Time,[a] hr	Reductive Amination Products, %[b]	Yield of Hydrocarbons, %[b]		
			<u>2</u>	<u>3</u>	Dimers
N-Methylpiperazine	12	64	6	<1	5
Piperidine	12	46	4	<1	11
Pyrrolidine	12	35	20	..	36
2-Methylpiperidine	12	5	42	..	36
2,6-Dimethylpiperidine	12	..	5	4	85

[a] At room temperature. [b] Yield based on consumed naphthalene.

CHAPTER III

EXPERIMENTAL[8]

<u>General Reaction Conditions</u>.— All reductions were carried out in a similar manner using the stir-shredding device shown in Fig. 1, 2, and 3. The equipment was dried before assembling and a flow of dry lamp-grade nitrogen gas was employed to flush the system for 10 min before any reactants were added. A thermocouple (inserted through one of the large openings at the top) immersed in the solution was used to monitor the temperature. A rubber cooling tube[9] wrapped around the outer wall of the reaction flask was used to maintain the reaction at room temperature.

The amine and <u>1</u> were introduced through a port at the top of the flask and stirred until solution was complete. Sodium was then added slowly over a period of 1-2 hr from a flask attached by Gooch tubing to one of the addition ports. The sodium addition was slow enough to allow the metal spheres of each portion to be shredded into small pieces before more was added. A yellow-orange color usually developed in less than 10 min with most amine solvents. This color rapidly darkened to red and then to a red-brown color within 1-2 min and the solution became opaque. The solution usually remained a dark red-brown to brown color with a muddy appearance for the rest of the 3-hr reaction period.

Reduction of 1 with Sodium and Butylmethylamine.— To 12.8 g (0.1 mol) of 1 and 250 ml of butylmethylamine (bp 88-90°) contained in the reaction flask was added 9.2 g (0.4 g-atom) of sodium over a period of 1.5 hr. A yellow color developed on the metal surface immediately and the solution turned red-orange in *ca*. 2 min. This color quickly darkened to red-brown in 30 sec and after 8 min the solution had gradually darkened to an opaque brown solution. This color remained until the reaction mixture was decanted from the unreacted sodium at the end of 3 hr and poured cautiously over 400 ml of crushed ice. The resulting orange solution was extracted with 500 ml ether in 3 portions and the ether layer was washed with water, and then twice with 10% aqueous HCl. The ether layer, which retained the hydrocarbons, was then washed with water until neutral. The acidic extracts and water washings were combined, made basic with NaOH, and extracted with ether. The amine-carrying ether layer was washed with water, dried (Na_2SO_4) and concentrated to yield 17.9 g of amines. Distillation at reduced pressure yielded 16.7 g (78%) of N-butyl-N-methyl-1,2,3,4-tetrahydro-2-naphthylamine which appeared pure by glc analysis: bp 86° (0.2 mm); mass spectrum (70 eV) *m/e* (rel intensity) 217 (25), 174 (100), 131 (71), 70 (20), 44 (35), 42 (33); nmr (CCl_4) four aromatic protons at δ 6.92 (singlet) and 19 aliphatic protons at δ 0.8-3.1 (several overlapping multiplets) with a singlet at δ 2.21.

Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.45. Found: C, 82.90; H, 10.61; N, 6.78.

The ether layer containing the hydrocarbons was concentrated and steam distilled. Both pot residue and distillate were extracted with ether and dried (Na_2SO_4). Distillation of the ether from the extract of the distillate yielded 1.3 g of steam-volatile hydrocarbons. These were shown by glc analysis to be a mixture of 1:2:3:4 (8:20:50:22).

The ether extract of the pot residue was concentrated (rotary evaporator) to yield 1.2 g of a dark viscous oil. This was shown by glc analysis to be a mixture of dimers 7, 8, 9, and 10 in which dimer 7 is the major one.

The reaction procedure and product analysis techniques given above are identical to those used for the other amine solvents shown in Table I. The other reductive amination products were shown by instrumental methods to be identical in structure with authentic samples of the expected amines.

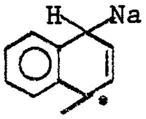
SODIUM-AMINE REACTIONS OF NAPHTHALENE

PART II. EFFECT OF COSOLVENTS

CHAPTER I

INTRODUCTION AND HISTORICAL

The reaction of naphthalene (1) with alkali metals was first reported by Berthelot[10] over one hundred years ago. He described the formation of a black addition product on fusing metallic potassium with 1 in a closed tube. Since then, extensive investigations of the reaction of alkali metals with aromatic hydrocarbons have been carried out beginning with the work of Schlenk[11,12] in 1914. He reported the formation of two distinct products: 1:1 and 2:1 adducts of sodium:anthracene.[11] The radical nature of these compounds was stressed; consequently sodium-naphthalene was described by early investigators as 12, a formula which represents the molecule as electrically neutral.[13a]



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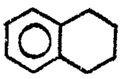

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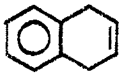

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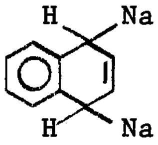
In 1914 Lebeau and Picon[14] first observed the formation of 1,2,3,4-tetrahydronaphthalene (2) and sodium amide in the reduction of 1 by sodium in liquid ammonia. Wooster and Smith confirmed the formation of 2 at -33° C and established that the reaction involves only four atoms of sodium even when a large excess of sodium is present.[15a] They concluded, incorrectly, that reduction proceeded by formation and protonolysis of a tetrasodium adduct.

The first objection to the formulation of the alkali adducts was raised by Hückel and Bretschneider,[16] who noted that the reduction by an alkaline earth metal such as calcium should closely resemble the reaction with sodium; and indeed, both metals reduce 1 to 1,4-dihydronaphthalene (4) in liquid ammonia at -75° to -65°. However, had the proposed structure 13 been correct, the calcium adduct should be represented by the improbably structure 14 and might, therefore, exhibit different properties than those of the sodium adduct. Since this is contrary to observations, they proposed that reduction involves an electron transfer, producing a heteropolar $C^{-}Na^{+}$ bond as shown below.



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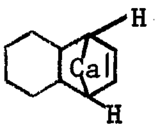

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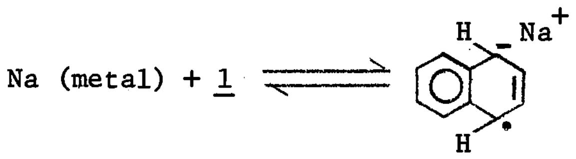


Here for the first time, the concept of an electron-transfer process was explicitly expressed in interpreting this class of reactions.

Considerable progress was made in studying the reaction after Scott and co-workers[17] introduced the use of methyl ether and 1,2-dimethoxyethane (DME) as a medium for the reaction. They found that the characteristic green color of sodium naphthalene adduct rapidly appeared when the reaction took place in these solvents, but no reaction occurred in diethyl ether or benzene. Also, addition of benzene to the green solution of the adduct in tetrahydrofuran (THF), followed by removal of THF by distillation, led to the reverse reaction. That is, sodium naphthalene decomposed to <u>1</u> and sodium dust. All these observations indicated that the sodium naphthalene adduct had an ionic character. Indeed, Scott, et al.,[17a,b] stated that the green solution showed electric conductance.

Birch has suggested that the reactive intermediate is formed by the transfer of one or two electrons to the aromatic nucleus yielding a radical-anion or a dianion, respectively.[18a,b] Evidence for the radical-anion nature of some of the alkali metal adducts was elegantly demonstrated in the United States by the studies of Weissman and colleagues,[19] who reported and extensively discussed the paramagnetic properties of these compounds, and in the Netherlands by Hoijtink and colleagues[20] using polarography and potentiometric titrations.

The investigation of a mechanism for many of these reductions is not easy since the processes are often carried out at the surface of a metal dissolving, sometimes with evolution of hydrogen gas, in an excess of an "acid" (amine or alcohol). The alkali metals are often insoluble in many of the solvents used in these reductions. Sodium is insoluble in THF[21b] and DME;[21b] whereas potassium forms dilute solutions in DME at low temperature.

The mechanism by which sodium reacts with 1 has been studied extensively by several workers, and the mechanism which is now commonly accepted for this reaction is shown in Fig. 4. The essential step is the addition of one electron to a molecule to give a radical-anion or addition of two electrons to give a dianion. The charged molecules are associated with positive counterions, usually derived from the metal supplying electrons, so ionized salts may be considered to act as intermediates. These salts, even radical-anions, can be isolated as stable compounds or in other cases they may exist momentarily as part of a transition complex.[18a,c] The reductions are usually represented in terms of free anions, because these ions are the reactive species and there is uncertainty as to where the sodium cations are attached.[18a]

It is important to distinguish between one-electron and two-electron addition as the rate-determining step. Often the uptake of the first electron requires the highest potential. A second electron is then rapidly taken up and the products are those derived from the anions 19 and 20, rather than the radicals 17 and 18.[18a] The polarographic reduction of polycyclic hydrocarbons shows this clearly.[22] A characteristic reaction of radical-anions is protonation, i.e., they act as bases;[23a] however, it has been estimated that protonation of the anions 19 and 20 is 150 times as fast as that of the radical-anion.[23b] Also, proton transfer from water to the radical-anion in THF is many orders of magnitude slower than typical electron-transfer reactions.[23b] The radical initially formed is usually more easily

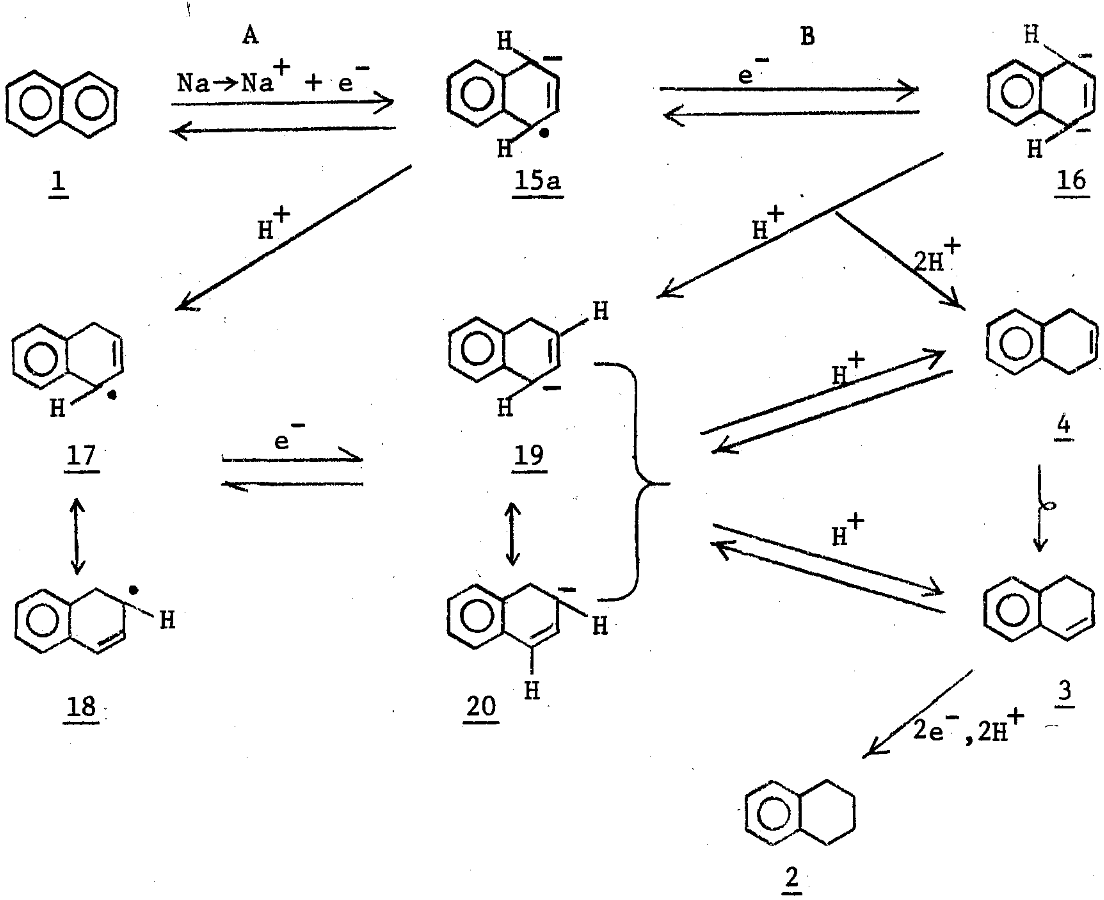


Figure 4. Mechanism for the Reduction of Naphthalene With Sodium

reduced than starting material and is reduced before it can undergo other reactions, e.g., dimerizations.[24] The addition of a second electron to the radical-anion to form the dianion 16 probably represents an irreversible process. The dianion, because of the enhanced reactivity of the dinegative ion toward protons, is rapidly destroyed.[13b]

Important factors to consider in sodium reductions of 1 are the position of the equilibrium A (Fig. 4), whether equilibrium B can be established at all, and whether a sufficiently acidic proton source (alcohol or amine) is present to protonate the radical-anion. There is considerable evidence for the reversibility of A.[17a,b,21a,c] Equilibria such as A depend on a number of factors[25] including: (1) the resonance possibilities for distributing the charge or charges over the molecule, (2) the specific solvating capacity of the solvent for the anions, (3) the extent to which the counterions may be solvated[19a,26] or held in ion-pairs with the negatively charged species, and (4) the temperature.[21a]

In liquid ammonia, 1 readily takes up two atoms of an alkali metal per molecule,[16] forming the dianion 16. The reducing power of sodium is thus seen to vary with the ability of the solvent to stabilize the electron-addition products by solvation: in general, the higher its polarity the further to the right the equilibria A and B lie.[18a] Ammonia is thus polar enough to stabilize the resulting dianions by solvation; this explains the favorable influence of ammonia on the reduction process in general.

Generally, ammonia cannot provide protons to the anions formed from 1 (below -50° C) because of the low acidity (pK~34) of this solvent.[21c] However, in 1937, Wooster reported that aromatic compounds are hydrogenated by sodium and a proton donor in liquid ammonia solution.[15b] Birch, in the early 1940's, greatly extended Wooster's observations, and as a result, the "Birch" reduction has found considerable utility in synthetic organic chemistry.[27,28] Birch routinely included alcohols (pK~16-18) in his reaction mixtures. These were considered to be the source of protons for the reduction of aromatic systems. The reduction of organic compounds by alkali or alkaline earth metals dissolved in liquid ammonia has been discussed extensively and is the subject of several excellent reviews.[18a,29]

Another important modification of the Birch reduction can be attributed to Benkeser and co-workers, who used low-molecular-weight amines such as methylamine, ethylamine, and propylamine, instead of liquid ammonia.[1b] More extensive reduction results when these amines are substituted for ammonia since they are more effective solvents for organic molecules and their higher boiling points permit higher reaction temperatures. Reggel and co-workers showed that lithium in ethylenediamine can reduce aromatic hydrocarbons to saturated hydrocarbons,[2] and appears to be the most powerful reducing metal-amine system. The use of various higher-molecular-weight primary and secondary amines as a solvent medium for the reduction of several naphthalenes with sodium has been studied extensively by Eisenbraun, et al.[3] They have shown that an amine can provide the protons for the reduction.

That alcohols and amines can supply protons to the anions formed from 1 is supported by the fact that even anions of the type ArH^- have basicity of the same order as NH_2^-.[21c] Sodium reacts surprisingly slowly with alcohols in liquid ammonia to give hydrogen gas,[21c,30] but anions react very rapidly so it is possible that the reaction is forced to the right by removal of the ions as the conjugate "acids" even though the instantaneous concentration of ions is small. If the product is the strongest "acid" in the solution, it is unchanged because it is protected as its sodium salt until a stronger acid is added on work-up. The differences between ammonia and other solvents are usually in degree, due to the difference in the solvation energies of ions, rather than in kinds of solvation.

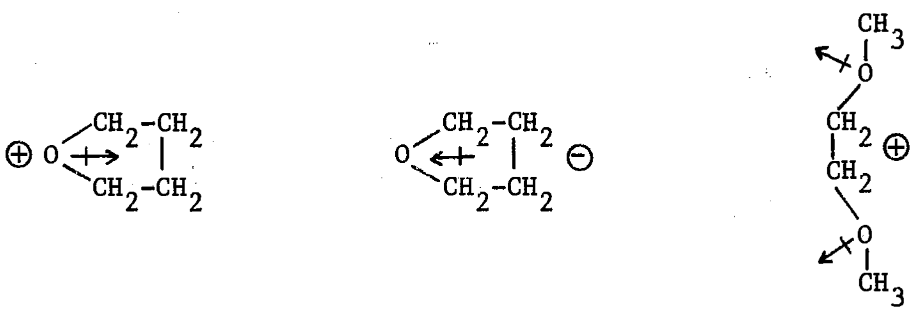
Since the pioneering work of Scott, Walker, and co-workers,[17] much of the reported work dealing with the metal-ammonia reactions stresses the necessity of employing a "cosolvent" such as ether, DME, THF, or dioxane (DIOX) in order to improve the poor solubility of many organic compounds in ammonia at -33° C.[31] These reagents have generally been considered to be inert and to have little effect on the course of the reaction. While this is probably true for certain reductions in liquid ammonia, the exact nature of the "cosolvent" has been found to have a decisive role in determining the product distribution using alcohols as proton sources.[32,33]

Studies of the effect of several solvents on the reaction of sodium with 1 have been carried out in dilute solutions. When 1 in THF solution is allowed to react with sodium at 25°, a green solution results which gives rise to electron spin resonance (esr) absorption.[19a-c,34] The green color, attributed to the radical-anion, cannot be altered by addition of more sodium.[25] From the esr spectra, Atherton and Weissman[34] have concluded that the radical-anion and sodium cation exist almost entirely in the form of tight ion pairs in THF. Similar conclusions have been made by other investigators using esr[35a] and conductometric measurements.[36a,b] Disproportionation of the radical-anion in THF to form the dianion and 1 occurs on standing at room temperature. This process takes place rapidly in concentrated solutions.[36c]

Some other ethers (DME, DIOX, and methyl ether), but not diethyl ether, can supply the solvation energy required for addition of an electron to 1 to form the radical-anion; however, these solvents cannot sufficiently solvate the cation to permit formation of the dianion.

For the reaction of 1 with sodium at 25° C a higher proportion of solvent-separated ion pairs is observed in DME, which acts as a bidentate solvating agent,[21b] than in THF.[13c] At room temperature, the latter solvent has a slightly higher dielectric constant (7.4) than DME (7.2). This clearly indicates that factors other than dielectric constant are of paramount importance in determining the coordinating power of the solvent. Other factors which must be considered include basicity and steric effects. Surprisingly, no solvent-separated ion pairs are detected in DIOX. Under normal conditions, a molecule of DIOX exists in a chair form in which the C-O-C dipoles oppose each other and, therefore, the bulk dielectric constant of this solvent is quite low (2.4) so the degree of dissociation into free ions is expected to be small.[13d,36d,37] However, the polar boat form is apparently favored in the vicinity of ions and this should increase the effective dielectric constant of DIOX.[37] The association of ion-pairs into higher agglomerates is also negligible because, in spite of its low dielectric constant, DIOX is a powerful solvating agent which interacts with at least one member of the pairs and prevents their association.

Neither THF nor DME seem to be coordinated with negative ions.[26,36d,e] This is not surprising because reversing the orientation of the ether displaces the oxygen atoms (seats of the dipole) from the inner layer of its solvation shell to its outside. Experimental evidence supporting this conclusion is given by Slates and Szwarc.[36a,b] Studies of the conductance of aromatic radical-anions showed that their mobilities have the values expected on the basis of the diffusion coefficients of the respective neutral aromatic hydrocarbons. The latter are obviously not coordinated with the solvent molecules.[13e]



Closer to charge--greater coordination energy

Anion separated by -CH$_2$- groups

Bidentate solvating agent

Figure 5. Models for Solvation in THF and DME

Orientation is particularly important when coordination involves the solvent, e.g., THF. This is clearly shown by the perhaps oversimplified models shown in Fig. 5. The dipole of THF is located at the oxygen atom of the ether. It may, therefore, closely approach a cation, but it remains separated from the anion by aliphatic -CH$_2$- groups. This difference in distance greatly reduces the respective coordination energy, making it substantial for a cation and insignificant for an anion of the same radius.[13f] This solvation of the cation in organoalkali compounds is well-known and has been observed in solvent mixtures of hydrocarbons with ethereal solvents, amines, and other solvating agents.[38] Often the effect amounts to an increase in the ionic character of the organoalkali compound.

Recently it was shown that sodium salts of radical ions are virtually completely dissociated in hexamethylphosphoramide (HMPA).[39a,b] Also reported is the reduction of olefins to saturated hydrocarbons using sodium and _tert_-butyl alcohol in HMPA.[40] Various other ionic reactions have been carried out in this solvent, each of which confirms that dissociation into free ions is complete.[39b,c,41] In HMPA only one solvent molecule is coordinated with the alkali metal cation in the solvent-separated ion pairs, at least at low solvent concentrations.[35b]

The use of tetramethylethylenediamine (TMEDA), which also solvates the cation in organoalkali compounds, has a pronounced effect on the ionic character of compounds such as butyllithium.[35b,42,43] A new addition to the list of solvents used for alkali metal reductions is trimesitylborane, a nonpolar aprotic medium.[44] A new series of alkali metal complexing agents has also been introduced by Pedersen[45] which should exhibit special effects in sodium-amine reactions.

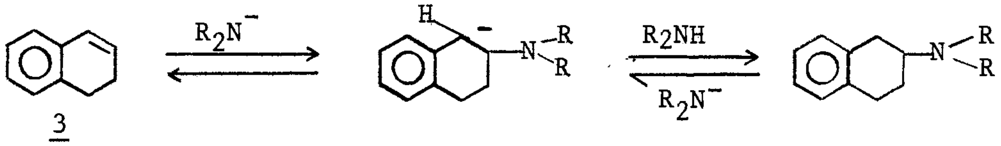
CHAPTER II

RESULTS AND DISCUSSION

During our investigation of the reductive amination of 1 with sodium in amines,[46] it became of interest to study certain solid, primary and secondary amines and certain expensive liquid amines or ones that are available only in limited quantities. Since there have been a number of cosolvents used in sodium-ammonia reductions, we decided to include some of these solvents in our metal-amine systems to provide reaction media. Use of these solvents would then allow us to add only the calculated amount of amine needed as a proton source.

We were particularly interested in applying the reaction to synthesis of the novel secondary and tertiary amines and C_{20} dimeric hydrocarbons which are often major sodium-amine reaction products of 1.[3,6,7,46] Several cosolvent-amine systems were investigated and the product distributions were determined, either by isolation and identification, or by glc comparison with authentic samples. These include THF, DME, HMPA, TMEDA, and DIOX. As mentioned previously, most of these cosolvents are generally considered to be inert and do not participate in sodium reductions of 1 in liquid ammonia; however, the product distribution in our studies was found to depend considerably on the solvent system employed. Besides the reduced C_{10} hydrocarbons and reductive amination products, reductive dimerization of 1 in these solvent systems may produce any of the compounds whose structures are shown on page 10[46] as a major product or part of a more complex mixture.

In order to discuss any trends in the course which a particular reaction follows, it is essential to include a mechanism by which the products are formed and to distinguish between radical and ionic processes. The reduced C_{10} hydrocarbons are probably formed as shown previously in Fig. 4. A proposed mechanism for formation of reductive amination products is shown below and supporting evidence for the addition of the alkyl amide anion to 3 has been presented.[3b]



Mechanistic pathways by which reductive dimerization occurs are less certain. The probability of a radical coupling of the naphthalene radical-anions (15a), is quite low because the substantial loss of resonance stability of the aromatic system, which arises from the formation of a new covalent carbon-carbon bond, prevents such a process.[13g] The probability of a radical coupling of the intermediate radicals formed by protonation of the radical-anion is also low since the radical has a much higher electron affinity than 1, so proton transfer is followed instantaneously by electron transfer to form an allylic anion.[24] Indeed, no 1,1'-coupled dimers, which would arise from radical coupling of 15a or 17, have yet been identified as products in the reductive dimerization of 1 with sodium in protic solvents. Evidence for the absence of any 1,1'-coupled dimers was obtained by gas chromatography studies and by dehydrogenation of reaction mixtures with palladium on carbon (Pd/C). The glc retention times of several C_{20} dimers of naphthalene are shown in Fig. 6. The glc peaks shown are used only as reference points for the purpose of illustration. It should be noted that the sodium-diethylamine reduction products of 1,1'-binaphthyl show a retention time of 23-24 min. None of the dimer fractions from the systems investigated contain any compounds which would correspond to this retention time. Dehydrogenation of the reduced 1,1'-binaphthyls with Pd/C at 310° yielded only 1,1'-binaphthyl with no rearrangement occurring.

A mechanism for ionic dimerization has been proposed which accounts for the formation of dimers 6, 7, 8, 10, and 11[3e-g] in metal-amine systems. Evidence supporting this ionic mechanism comes from base-catalyzed reactions of 3,[3g] 4,[3g,47] and 8[6] to give mixtures of the dimers mentioned previously.

Many of the intriguing features of ionic reactions, particularly those in low dielectric media, must be attributed to the variety of forms in which the reactive species can exist. Ionic species may exist as free ions, ion pairs, triple ions, quadruples, and as still higher aggregates in media of low polarity, and in solutions where strong specific solvent-solute interactions are important, often more than one solvation state of each of these species can be realized.[48a,b] This is especially true in the mixed solvent systems which were investigated. The nature of the solvent determines the type of solvation, so

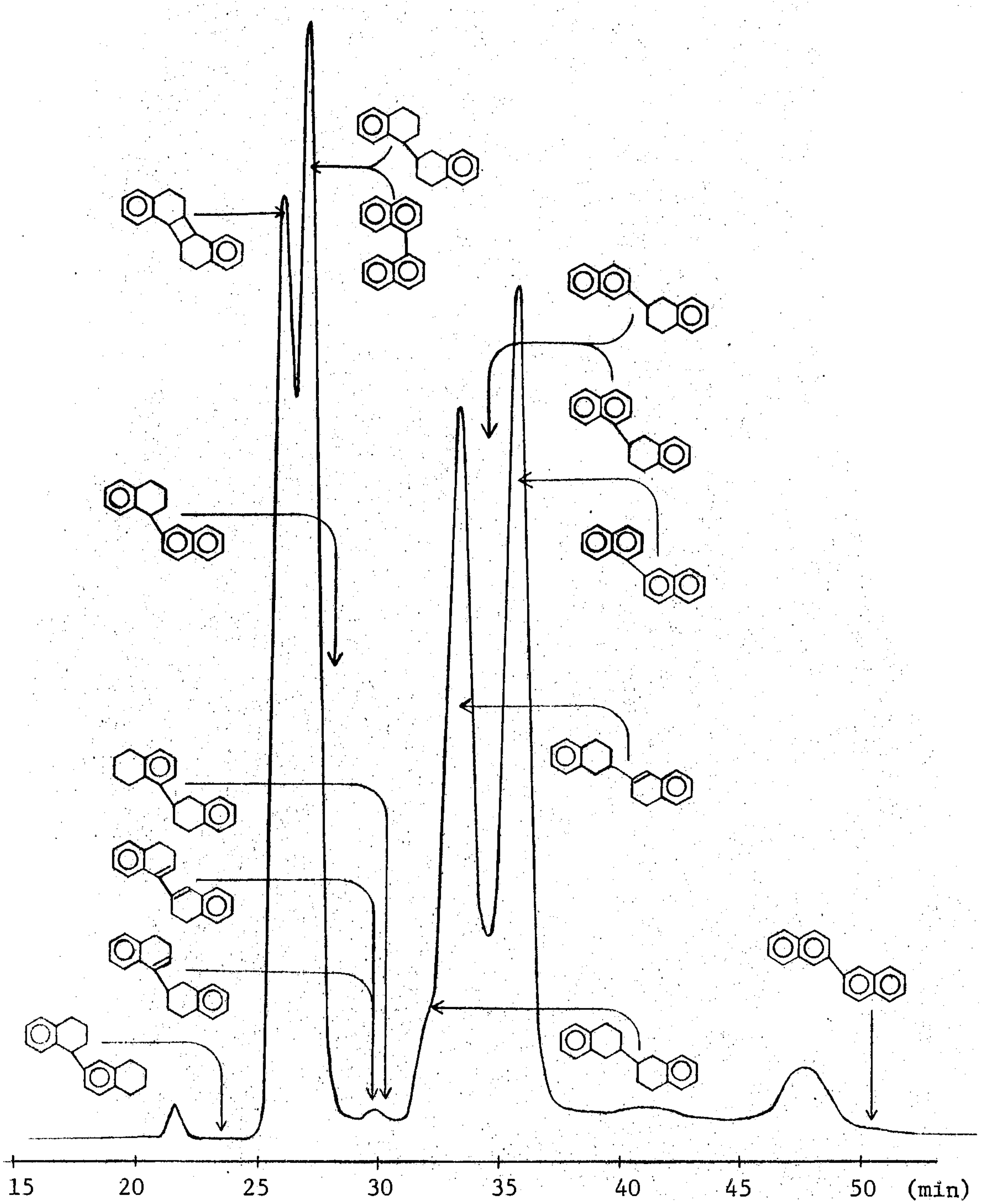


Figure 6. GLC Retention Times of Dimers

that a change in medium may profoundly affect the course of ionic reactions.

The complexity of the reaction of sodium with <u>1</u> in amines and cosolvents can best be illustrated by citing the change in product composition with change in amine and/or cosolvent as shown in Table III. This change in product composition appears to reflect the success of various competing reactions in the different solvents. These trends are summarized by comparison of yields in Table IV.

When cosolvents are used with an amine, e.g. N-methylpiperazine (N-MPZ), in which reductive amination is favored, the yield of reductive amination product usually decreases in the order TMEDA>THF>DIOX>DME>HMPA. In cosolvents the yields of reductive amination product are usually lower than in neat amine; however, a higher yield of tertiary amine is obtained using TMEDA as a cosolvent in the reaction of pyrrolidine with <u>1</u>. The reductive amination of <u>1</u> with several amines in TMEDA demonstrates that this reaction can be extended to other amines using cosolvents. The limiting factor appears to be the degree of steric hindrance in the alkylamide anion.

The reaction of <u>1</u> with sodium and sterically hindered amines, e.g. dipropylamine (DPA), appears to occur faster in cosolvents than in neat amine as evidenced by the smaller amount of recovered starting material, although there is not an accompanying increase in the amount of reductive amination. The increase in solvation effects with cosolvents is reflected as increases in the amount of dimerization and/or reduction. In THF and DME reductive dimerization predominates and in DIOX and TMEDA reduction predominates with DPA as a proton source.

TABLE III

REDUCTION OF NAPHTHALENE[a,b] WITH SODIUM, SECONDARY AMINES, AND COSOLVENTS

Proton Source	Cosolvent	Reductive Amination Yield, %[c]	Naphthalene Recovered, %	Yield of Hydrocarbons, %[c]			
				2	3	4	Dimers (Major)
...	TMEDA	...	68	3	4	24	29 d
...	DME	...	73	<1	<1	89	10 d
...	THF	...	52	2	10	70	3 d
...	DIOX	...	91	..	..	9	86 d
...	HMPA	...	99	..	..	..	..
N-Methylpiperazine	TMEDA	81	4	<1	5	<1	1 (8)
Dipropylamine	TMEDA	8[d]	8	1	19	49	23 (7)
Piperidine	TMEDA	56	2	2	9	8	19 (7,8)
Pyrrolidine	TMEDA	90	1	2	2	<1	2 (7,10)
2-Methylpiperidine	TMEDA	8[d]	33	1	29	38	20 (7,8)
2,6-Dimethylpiperidine	TMEDA	5[d]	68	..	41	28	12 (7,8.9)
N,N,N'-Trimethylethylenediamine	TMEDA	19	3	2	31	4	32 (10,11)
Dibenzylamine	TMEDA	e	3	5	63	..	f (8)
3-Azabicyclo[3.2.2]nonane	TMEDA	17	10	3	10	21	31 (7,9)
Piperidine hydrochloride[g]	TMEDA	3[d]	..	11	40	27	15 (7)
N-Methylpiperazine	DME	27	..	1	14	..	55 (10,11)
Dipropylamine	DME	h	4	2	5	1	73 (9)
3-Azabicyclo[3.2.2]nonane	DME	i	62	3	17	..	42 (8,9)
Piperidine hydrochloride	DME	5	16	10	5	63	12 (11,7)
N-Methylpiperazine	THF[n]	69	4	..	5	1	16 (11)

TABLE III (Continued)

Proton Source	Cosolvent	Reductive Amination Yield, %[c]	Naphthalene Recovered, %	Yield of Hydrocarbons, %[c]			
				2	3	4	Dimers (Major)
Dipropylamine	THF	j	25	2	3	4	75[m] (7)
N-Methylpiperazine	DIOX	40	5	1	46	1	7 (8)
Dipropylamine	DIOX	k	56	7	35	25	23 (9)
N-Methylpiperazine	HMPA	...	69	14	..	55	25 (6,10,11)

[a] Reaction time of 3 hr unless otherwise stated. [b] At room temperature. [c] Yield based on consumed 1. [d] Included several unidentified products. [e] Consisted of 2 major components, 5.8 g. [f] Major product was identified as N-benzylbenzamide (2.6 g crude product). [g] Reaction time of 7.5 hr. [h] Several unidentified products, 1.5 g. [i] See h, 3.8 g. [j] See h, 0.9 g. [k] See h, 1.1 g. [m] Approximate yield because *ca.* 30% of nonvolatile fraction was lower-molecular-weight fraction which showed OH absorption in ir (bp 145-155° at 0.2 mm). [n] Approximately 12% of the steam-volatile hydrocarbon fraction was composed of unidentified products.

TABLE IV

SUMMARY OF TABLE III

Reaction Products	Amine	Comparison of Yields in Cosolvents
Reductive Amination	N-MPZ	TMEDA>THF>DIOX>DME>HMPA
Reductive Dimerization	N-MPZ	DME>HMPA>THF>DIOX>TMEDA
Reduction	N-MPZ	HMPA>DIOX>DME>THF, TMEDA
Recovered <u>1</u>	N-MPZ	HMPA>>DIOX, THF, TMEDA, DME
Reductive Amination	DPA	All about equal
Reductive Dimerization	DPA	DME, THF>DIOX, TMEDA
Reduction	DPA	TMEDA, DIOX>THF, DME
Recovered <u>1</u>	DPA	DIOX>THF>TMEDA, DME
Reductive Dimerization	...	DIOX>TMEDA>DME>THF, HMPA
Reduction	...	THF>TMEDA>DME>DIOX>HMPA
Recovered <u>1</u>	...	HMPA>DIOX>TMEDA>THF>DME

In general, the use of DME as a cosolvent in these reductions results in a large increase in the amount of dimerization in the presence of an amine as a proton source. However, the addition of a stronger acid (amine hydrochloride) results in reduction as the major reaction pathway in DME. This solvent is apparently the most effective in solvating the intermediates which lead to dimer formation.

In DIOX reductive dimerization is minimal and reduction is the predominant reaction. Apparently, this solvent is ineffective in solvating the intermediates in dimer formation. In THF, amination (N-MPZ) or dimerization (DPA) are the predominant reactions, depending on the amine, with very little reduction in either case. However, some side reactions resulted in THF.[48c] These side-products (bp 145-155° at 0.2 mm) absorb in the O-H stretch region of the infrared and apparently arise from ring opening of THF because the amount of products isolated exceeds the theoretical yield.

The reduction in HMPA with N-MPZ gave mostly reduced hydrocarbons with some dimerization. No amination was observed. The amount of recovered 1 using HMPA seems to indicate that this solvent is a much less effective cosolvent for solvating the intermediates in this reaction. Normant[41b] has suggested that the solvating properties of HMPA are greatly superior to those of DME and THF in this type of reduction. In the absence of an added proton source in HMPA, the solution remained dark green for most of the reaction time; however, at the end of 3 hr, the solution was red-orange. After the reaction was quenched in ice, work-up yielded 99% of the recovered starting material unchanged. Normant reports that the blue color of 1M solutions of sodium in HMPA disappears after 6 hr as the sodium reacts with the solvent.[41b] In our reaction there was no sodium left after 3 hr and no reaction with 1 was observed so the sodium undoubtedly reacted completely with the cosolvent.

The dimers formed in these reactions are predominantly reduced 1,2'-binaphthyls. The systems in which reduced 2,2'-binaphthyls appear as major dimers are those in which N-MPZ and trimethylethylenediamine are used in cosolvents. The dimer formation apparently depends on both the proton source used and the cosolvent; however, 1,2'-binaphthyls are the major dimers when sterically hindered amines are added as proton sources. Since a mixed solvent system was employed in these reactions, it is difficult to evaluate the product distribution in terms of the types of solvation involved.

With the exception of HMPA, in cosolvents with no added proton source, 4 is the major reduced C_{10} hydrocarbon formed when the reaction is quenched in water. A mechanism for the formation of 4 has been presented by Bank and Bockrath.[23b] A typical gas chromatogram of the C_{20} dimeric fraction formed in the reaction of 1 with sodium in a cosolvent is shown in Fig. 7 (a). The mass spectrum of this mixture shows a molecular ion *m/e* 260. The mixture shown in the second curve (b) was obtained by treatment of the dimer fraction (a) with Pd/C in boiling toluene. The major dimers in (b) were identified as 7 and 9 (42:53) by isolation and comparison with authentic samples. Dehydrogenation (Pd/C) of the mixture shown in (a) gave 1,2'-binaphthyl as the major product as shown in Fig. 7 (c). The composition of the mixture in (a) and the mechanism by which the 1,2'-coupling occurs is being investigated. Hydrogen abstraction from the solvents, DME and THF, has been reported[49] and could account for a partially reduced dimer in these systems.

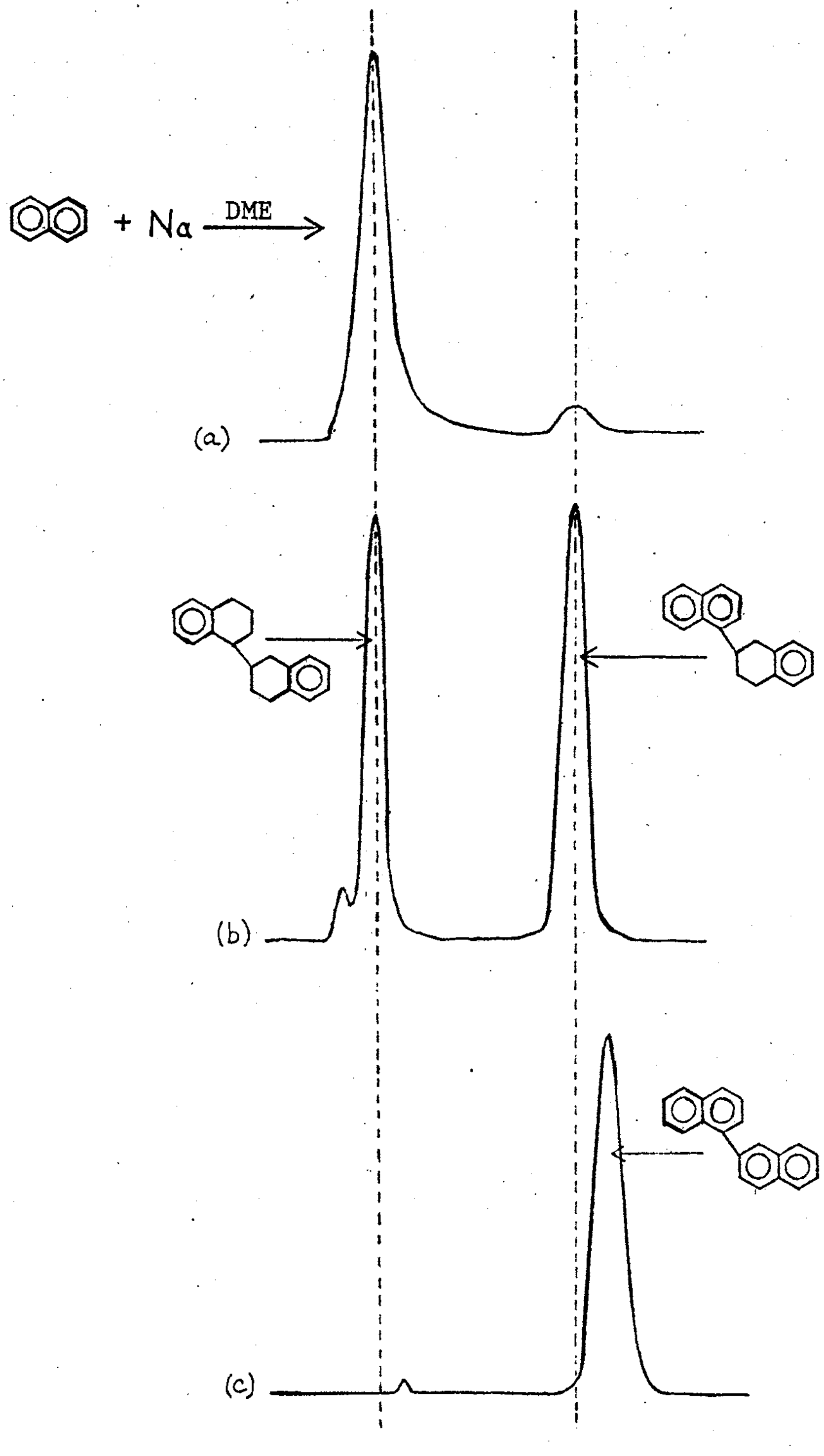


Figure 7. Gas Chromatograms of Dimers (a) Sodium and 1 in DME (b) After Treatment with Pd/C in Toluene (c) After Treatment With Pd/C at 310°

CHAPTER III

EXPERIMENTAL[8]

The solid amine was recrystallized from ethanol and sublimed. The amine hydrochloride was prepared by bubbling HCl gas through an ether solution of the amine and filtering out the resulting precipitate. The HCl was generated by treating NaCl with concentrated H_2SO_4.

The cosolvents were dried as shown in Table V.

TABLE V

METHODS USED FOR DRYING COSOLVENTS

Cosolvent	Drying Agent	Distilled From	bp, °C	Supplier of Cosolvent
TMEDA	KOH	KOH	121-2	Rohm and Haas
DME	4Å Molecular Sieve	$LiAlH_4$	84-5	Ansul
THF	4Å Molecular Sieve	$LiAlH_4$	65-6	MC & B
DIOX	4Å Molecular Sieve	....	.....	MC & B
HMPA	4Å Molecular Sieve	....	86-96 (0.2 mm)	Aldrich

The general reaction conditions used are identical to those given in Part I (page 12). The cosolvent, naphthalene, proton source, and sodium were added as described. The colors which developed in many of the cosolvent-amine systems and the time required for color development are shown in Table VI.

General Reaction of 1 with Sodium and Cosolvent.— To 12.8 g (0.1 mol) of **1** dissolved in 250 ml of cosolvent was added 4.6 g (0.2 g-atom) of sodium over a period of 1-2 hr. The color changes are noted in Table VI. After 3 hr the reaction mixture was decanted from the unreacted sodium and poured cautiously over 400 ml of crushed ice. The resulting solution was extracted with 500 ml ether (3 portions) and the ether layer was washed with water and concentrated by distillation. The extract was steam distilled and both the pot residue and distillate were extracted with ether and dried (Na_2SO_4). Distillation of the ether from the extract of the distillate yielded the steam-volatile hydrocarbons and concentration of the ether extract of the pot residue yielded the dimer hydrocarbons. Analyses of the fractions were carried out using glc. The dimer fraction from the reaction using DME as cosolvent showed mass spectrum (70 eV) *m/e* (rel intensity) 260 (10), 131 (63), 130 (57), 129 (100), 128 (66), 115 (16), 91 (18).

Reduction of 1 with Sodium and N-Methylpiperazine in TMEDA.— To 12.8 g (0.1 mol) of **1**, 35 g (0.35 mol) of N-MPZ, and 215 ml of TMEDA in the reaction flask was added 9.2 g (0.4 g-atom) of sodium over a period of 1.5 hr. The color changes are given in Table VI. After 3 hr the reaction mixture was decanted from the unreacted sodium and poured cautiously over 400 ml of crushed ice. The resulting emulsion was extracted with 500 ml ether (3 portions) and the ether layer was washed with water, and then twice with 10% aqueous HCl. The ether layer which retained the hydrocarbons, was then washed with water until neutral. The acidic extracts and water washings were combined, made

TABLE VI

COLOR DEVELOPMENT IN COSOLVENT-AMINE SYSTEMS

Cosolvent	Amine	Description (Time in Min)
THF	N-MPZ	Muddy yellow-brown (1)
THF	DPA	Dark green (1); muddy yellow-brown (3)
THF	...	Blue to green (2); dark green (14)
DIOX	N-MPZ	Green (6); red (19); dark red-brown (67)
DIOX	DPA	Green (15); muddy brown (78)
DIOX	...	Orange (24); green (32)
HMPA	N-MPZ	Green (1); dark green (3)
HMPA	...	Dark green (1); color faded to red-orange between sodium additions
DME	N-MPZ	Yellow (8); red (9); red-brown (20)
DME	DPA	Dark green (0.5); muddy brown (3)
DME	...	Dark green (17)
DME	Piperidine•HCl	Milky-white throughout reaction
TMEDA	N-MPZ	Yellow (8); red (9); red-brown (20)
TMEDA	DPA	Red-brown (8); muddy yellow-brown (12)
TMEDA	...	Yellow (11); red-orange (12); muddy yellow-brown (16)
TMEDA	Piperidine•HCl	Milky-white throughout reaction

basic with NaOH, and extracted with ether. The amine-carrying ether layer was washed with water, dried (Na_2SO_4) and concentrated to yield 18.3 g of amines. Distillation at reduced pressure (bp 110° at 0.2 mm) yielded 17.7 g (81%) of reductive amination product which appeared pure by glc analysis and was shown to be identical in structure with an authentic sample.

The ether layer containing the hydrocarbons was concentrated and steam distilled. Both pot residue and distillate were extracted with ether and dried (Na_2SO_4). Distillation of the ether from the extract of the distillate yielded 1.3 g of steam-volatile hydrocarbons which were shown by glc analysis to be a mixture of <u>1</u>:<u>2</u>:<u>3</u>:<u>4</u> (43:2:52:3).

The ether extract of the pot residue was concentrated to yield 0.1 g of a dark viscous oil. This was shown by glc analysis to be a mixture of 7, 8, and 9 in which dimer 8 is the major one.

The reaction procedure and product analysis techniques given above are identical to those used for the other amines and hydrochlorides shown in Table III. The reductive amination products were shown by instrumental methods to be identical in structure with authentic samples of the expected amines. The products from amines not previously used in this type of reduction are discussed in the following procedures.

Reduction of 1 with Sodium and N,N,N'-Trimethylethylenediamine in TMEDA.— The reaction of 12.8 g (0.1 mol) of 1, 35.7 g (0.35 mol) of amine, and 9.2 g (0.4 g-atom) of sodium in 215 ml TMEDA yielded the following: 4.0 g of nonvolatile hydrocarbons containing dimers 7, 8, and 10 with the latter being the major one; 5.0 g of steam-volatile hydrocarbons containing 1:2:3:4 (7:5:78:10); and 5.7 g amines of which 4.3 g (19%) distilled (bp 78° at 0.2 mm): mass spectrum (70 eV) m/e (rel intensity) 174 (100), 131 (99), 91 (18), 58 (75), 44 (45), 42 (28); nmr ($CDCl_3$) four aromatic protons at δ 6.91 (singlet) and twenty aliphatic protons at δ 1.2-3.0 (several overlapping multiplets) with singlets at δ 2.17 and δ 2.26.

Anal. Calcd for $C_{15}H_{24}N_2$: C, 77.54; H, 10.41; N, 12.05. Found: C, 77.65; H, 10.52; N, 11.77.

Reduction of 1 with Sodium and 3-Azabicyclo[3.2.2]nonane in TMEDA.— The reaction of 12.8 g (0.1 mol) of 1, 43.8 g (0.35 mol) of secondary amine, and 9.2 g (0.4 g-atom) of sodium in 215 ml TMEDA yielded the following: 3.7 g of nonvolatile hydrocarbons containing dimers 6, 7, 8, and 9 with 7 and 9 being the major ones; 5.4 g of steam-volatile hydrocarbons containing 1:2:3:4 (25:7:22:46); and 5.9 g of non-steam-volatile amines from which 3.9 g of light brown crystals were obtained by recrystallization from ethanol: mp 91.5-92.5°; mass spectrum (70 eV) m/e (rel intensity) 255 (100), 150 (63), 131 (29), 91 (24), 44 (20), and 41 (29); nmr ($CDCl_3$) four aromatic protons at δ 6.94 (singlet), nine aliphatic protons at δ 2.5-3.2 (multiplet), and twelve aliphatic protons at δ 1.3-2.3 (multiplet).

Anal. Calcd for $C_{18}H_{25}N$: C, 84.65; H, 9.87; N, 5.48. Found: C, 84.45; H, 9.78; N, 5.47.

Reduction of 1 with Sodium and Dibenzylamine in TMEDA.— The reaction of 12.8 g (0.1 mol) of 1, 69.0 g (0.35 mol) of dibenzylamine, and 9.2 g (0.4 g-atom) of sodium in 215 ml TMEDA yielded the following: 9.8 g of steam-volatile hydrocarbons containing 1:2:3:4 (4:6:81:0) and about 9% of a compound with glc retention time slightly less than 2; 5.8 g of distilled (bp 165-178° at 0.2 mm) amines which contained at least two unidentified products; and 2.6 g of nonvolatile hydrocarbons containing dimers 7, 8, and 10 with 8 being the major one. Approximately 50% of this fraction was identified as N-benzylbenzamide: mp 103.5-104° from petroleum ether [lit.[50a] mp 105-6°], ir ($CHCl_3$) 1660 cm^{-1} (C=O) and 3043 cm^{-1} (N-H).

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.71; H, 6.35; N, 6.26.

Reduction of 1,1'-Binaphthyl with Sodium and Diethylamine.— To 12.7 g (0.05 mol) of 1,1'-binaphthyl dissolved in 250 ml of diethylamine was added 9.2 g (0.4 g-atom) of sodium over a 4-hr period in the usual manner. After a total reaction time of 7 hr, the muddy brown reaction mixture was poured onto ice and extracted with ether (4 portions). The ether layer was washed with water and extracted with 2 portions of 10% HCl to remove the amines. The ether layer, which retained the hydrocarbons, was then washed with water until neutral. After drying (Na_2SO_4), the ether was distilled to give 11.2 g of unreacted starting material and a mixture of unknown reduced 1,1'-binaphthyls (14:86) which exhibited shorter glc retention times than the former.

Dehydrogenation of Reduced 1,1'-Binaphthyls.— The reaction mixture (1.0 g) from the preceding reduction was treated with 10% Pd/C (0.1 g) at 310° for 1.5 hr. After cooling, the solid was dissolved in benzene and the solution filtered (Dicalite filter-aid) and concentrated to give 1.0 g of 1,1'-binaphthyl. No 1,2'- or 2,2'-binaphthyl was formed as shown by glc studies.

Disproportionation of a Dimer Mixture with Pd/C in Toluene.— The dimer fraction (1.0 g) from the reduction of 1 with sodium and DME (see Fig. 7, a) was heated at reflux in 20 ml of toluene with 0.1 g of 10% Pd/C for 2.5 hr. The solution was then filtered and concentrated to give 1.0 g oil which was shown by glc (see Fig. 7, b) to consist of 7, 9, and an unknown (42:53:5). Dimers 7 and 9 were separated by column chromatography and identified by comparison with authentic samples.

Dehydrogenation of a Dimer Mixture.— To 1.0 g of the same dimer fraction used above (see Fig. 7, a) was added 0.1 g of 10% Pd/C and the mixture was heated at 310° for 1.5 hr. The mixture was cooled, dissolved in benzene, filtered, and concentrated to give 0.9 g of 22 (see Fig. 7, c). Recrystallization from petroleum ether gave 0.6 g of 22: mp 76-77° [lit.[50b] mp 76°].

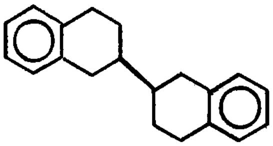
SODIUM-AMINE REACTIONS OF NAPHTHALENE

PART III. SELECTIVE 1,2'-DIMERIZATION

CHAPTER I

INTRODUCTION AND HISTORICAL

The reduction of naphthalene (1) using alkali or alkaline earth metals and amines or ammonia is known to produce products including C_{20} dimeric hydrocarbons and various other higher molecular weight compounds.[3,7] Although Lebeau and Picon[14] first studied the reduction of 1 with sodium in liquid ammonia as early as 1914, it remained for Wooster and Smith[15a] to carry out a more detailed study of the reaction. Hückel and Bretschneider,[16] in 1939, reported the formation of C_{20} hydrocarbons as side-reaction products of metal-ammonia reduction of 1,2-dihydronaphthalene (3). More recently Hückel and Wartini[51] have shown that the slow addition of sodium to 3 in liquid ammonia gives a 2,2'-octahydrobinaphthyl, (10), mp 114°. Benkeser,[52] *et al.*, probably isolated C_{20} dimeric hydrocarbons from the products of the reduction of 1 with sodium and ethylamine but did not report the composition of their "polymeric material". Reggel, *et al.*,[7] reported that 2,2'-hexahydro- and 2,2'-octahydrobinaphthyl (11, 10) were the primary products of this reaction. In contrast to previous reports,[16,51] the octahydrobinaphthyl isolated from this reaction by Reggel[7] and Eisenbraun, *et al.*,[3] melted at 85°. The latter group has also established the structure of the second product of the reaction as 5,6,6a,6b,11,12,12a,12b-octahydrodibenzo[*a*,*g*]biphenylene (6)[3b,g] and not 11 as reported by Reggel.[7]



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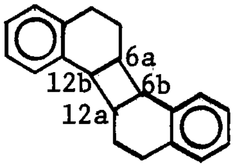

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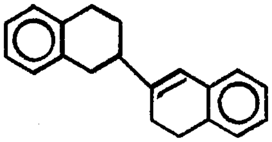

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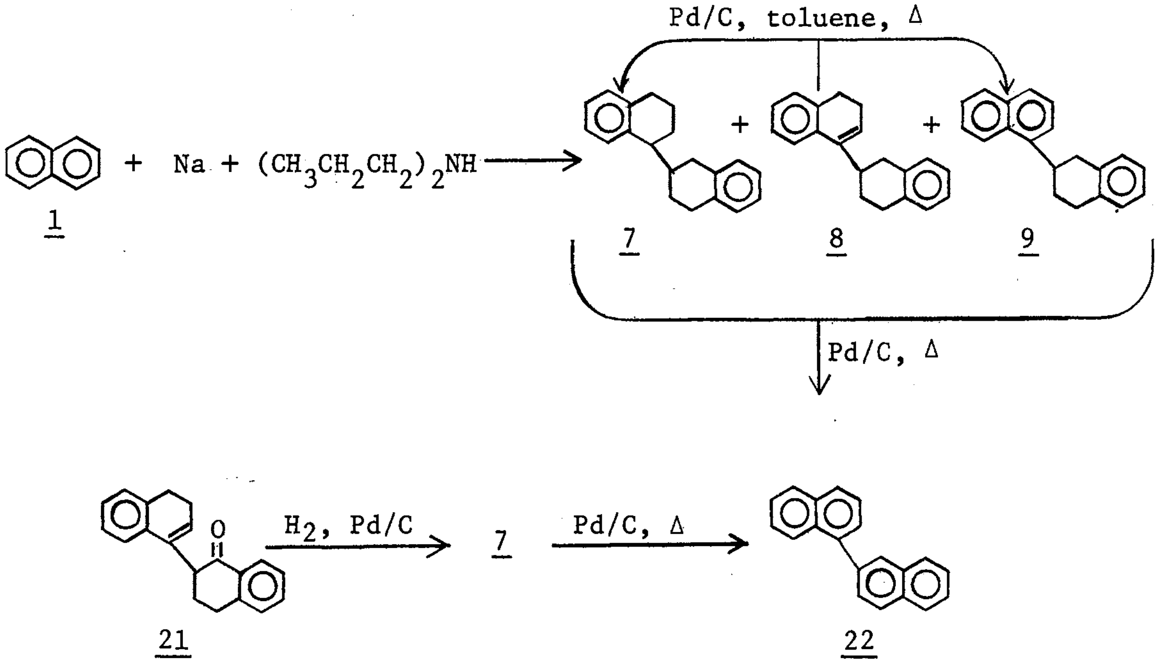
CHAPTER II

RESULTS AND DISCUSSION

Reductive dimerization of naphthalenes is a general reaction and has been carried out in a variety of amines.[3b] Some control of the specific dimer formation in the reaction of naphthalene with sodium can be achieved by choice of the amine. Use of ethylenediamine as a reaction medium favors the formation of the cyclobutane dimer 6,[3g] whereas dimer 10 is the major dimeric product when pyrrolidine and ethylamine are reaction solvents.[3b,7]

The use of dipropylamine and sodium in the reduction of 1 results in a remarkably selective formation of 1,2'-coupled dimers,[53,54] 7, 8, 9 (62%) in addition to tetrahydronaphthalene (2), about 12% of reductive amination product, and a small amount of trimers and tetramers. The major component of the dimer fraction, a white crystalline hydrocarbon, is shown to be 1',2',3',4'-tetrahydro-1,2'-binaphthyl (9). The new compound gives a molecular ion m/e 258.1408 and its carbon and hydrogen contents are consistent with the formula $C_{20}H_{18}$. The nmr spectrum shows 11 aromatic protons δ 6.72-8.08 (broad multiplet, m, containing a sharp singlet at δ 6.92), five benzylic protons δ 2.44-3.91 (overlapping m), and two aliphatic protons δ 1.61-2.28 (m). Hydrocarbon 9 shows uv absorption characteristic of an aliphatic-substituted naphthalene and forms a picrate which can be decomposed by stirring with petroleum ether and eluting through a column of basic alumina.[55]

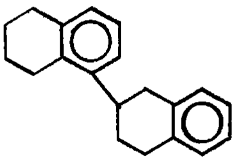
To obtain pure 7, a mixture of 7, 8, and 9 was treated with Pd/C in refluxing toluene[54] and the resulting mixture of 7 and 9 was separated by column chromatography. The ir spectrum of 7 thus prepared from 8 is very similar to that of 7 obtained by hydrogenation of 21[56] with Pd/C. The nmr spectrum of 7 shows eight aromatic protons δ 6.72-7.32 (m) and 14 aliphatic protons δ 1.12-3.08 (overlapping m).



Dimer 8 was identified by its nmr spectrum, which showed eight aromatic protons δ 6.97 (m), one vinyl proton δ 5.83 (triplet), six aliphatic benzylic protons δ 2.45-3.2 (m), and five protons δ 1.4-2.4 ($ArCH_2C\underline{H}_2$- and $>C=CH-\overset{|}{C}\underline{H}-$ as an overlapping multiplet).

Evidence for the absence of any dimers with a 1,1' or 2,2' ring system among the reaction products was obtained by dehydrogenation. On treatment of the reaction mixture of 7, 8, and 9 with Pd/C at 350°, a 92% yield of 1,2'-binaphthyl (22) was obtained. Analysis of this dehydrogenation product by glc showed that 1,1'- and 2,2'-binaphthyl were absent. A sample of 1,2'-binaphthyl prepared by Pd/C dehydrogenation of 7 from 21 was compared with 22 from the dehydrogenation of 7, 8, and 9 and these were found through melting point of a mixture and spectral comparison to be identical.

Further evidence for the structure of 9 was obtained by reducing it with sodium and diethylamine, and then treating with Pd/C in refluxing toluene.[54] This procedure yielded 7:9:23 (1:62:37). Dimer 23, shown by analysis to be $C_{20}H_{22}$, gave nmr absorption for seven aromatic protons δ 6.96 (m), nine benzylic protons δ 2.45-3.30 (m), and six aliphatic protons δ 1.45-2.12 (m). A mixture of 7, 8, and 9 was also catalytically hydrogenated in the presence of Pd/C to give 7:23 (62:38). A glc comparison of 24 with the products (7 and 23) of this hydrogenation showed that 24 was absent and therefore 25 was not a product of our metal-amine reduction of naphthalene.[57]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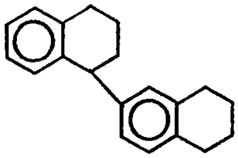
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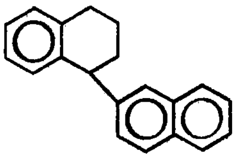
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At room temperature, dimers 7, 8, and 9 were formed in the ratio 11:16:73, respectively. At higher temperatures (40-80°) dimer 9 was the C_{20} hydrocarbon formed almost exclusively, as seen in Table VII. However, the amount of dimeric products isolated decreases as the temperature is increased. Apparently polymerization to trimers and higher molecular weight compounds takes place as the temperature is raised. Some of these C_{30} trimers and C_{40} tetramers were isolated in sufficient quantities for partial identification after treatment with Pd/C, followed by column chromatographic separation. The compounds are described in Table VIII. Two compounds (<u>26</u> and <u>27</u>) were isolated which showed molecular ions in their mass spectra <u>m/e</u> 380 with small impurities of <u>m/e</u> 506. A molecular weight of 380 corresponds to an empirical formula of $C_{30}H_{20}$. A third compound (<u>28</u>) was isolated which did not vaporize well in the mass spectrometer and did not elute from a glc column at 300°. Apparently, this compound is a tetramer ($C_{40}H_{26}$) with molecular weight of 506. The nmr of <u>26</u> shows a broad aromatic multiplet at δ 6.9-8.4 with approximately 8% aliphatic $-CH_2-$.

Since reductive dimerization of naphthalene in amines is in competition with reduction and reductive amination, it is not unexpected that changes in structure of the amine produce significant changes in product composition. The slight structural alteration in changing from hexamethyleneimine to dipropylamine is a good example of the importance of steric effect; in the latter solvent the reductive amination yield reportedly drops from 28% to 6% and reductive dimerization increases from 11% to 55%.[3b,g] Thus, we consider dipropylamine to be sterically hindered for reductive amination and a particular type of solvation to promote selective 1,2'-reductive dimerization.

A mechanistic rationalization for the formation of the C_{20} dimeric products is still uncertain. Several ionic or radical species may be

TABLE VII

REACTION OF NAPHTHALENE AND SODIUM IN DIPROPYLAMINE

Moles of Naphthalene	Moles Reacted Naphthalene	Hr Reaction Time	Temperature	g of Amination Products	g of Nonvolatile Hydrocarbons Crude (Distilled)	Ratio of Dimers		
						7	8	9
0.1	0.054	23	35°	1.7	6.4(4.3)	11	16	73
0.4	0.246	29.5	25°	3.7	19.4(11.2)	6	39	55
0.4	0.174	12	15°	11.9	16.2(8.7)	1	10	88
9.8	a	24	30°	a	229(153)	10	16	74
0.1	0.028	10	20°→80°	0.5	3.1(2.8)	2	9	89
0.1	0.027	49	80°	5.2	3.5(2.5)	3	b	89
0.1	0.099	28	20° (22 hr) 42° (6 hr)	1.3	7.2(2.3)	26	5[c]	41
0.1	a	23	80-90°	a	4.3(1.7)	b	b	98

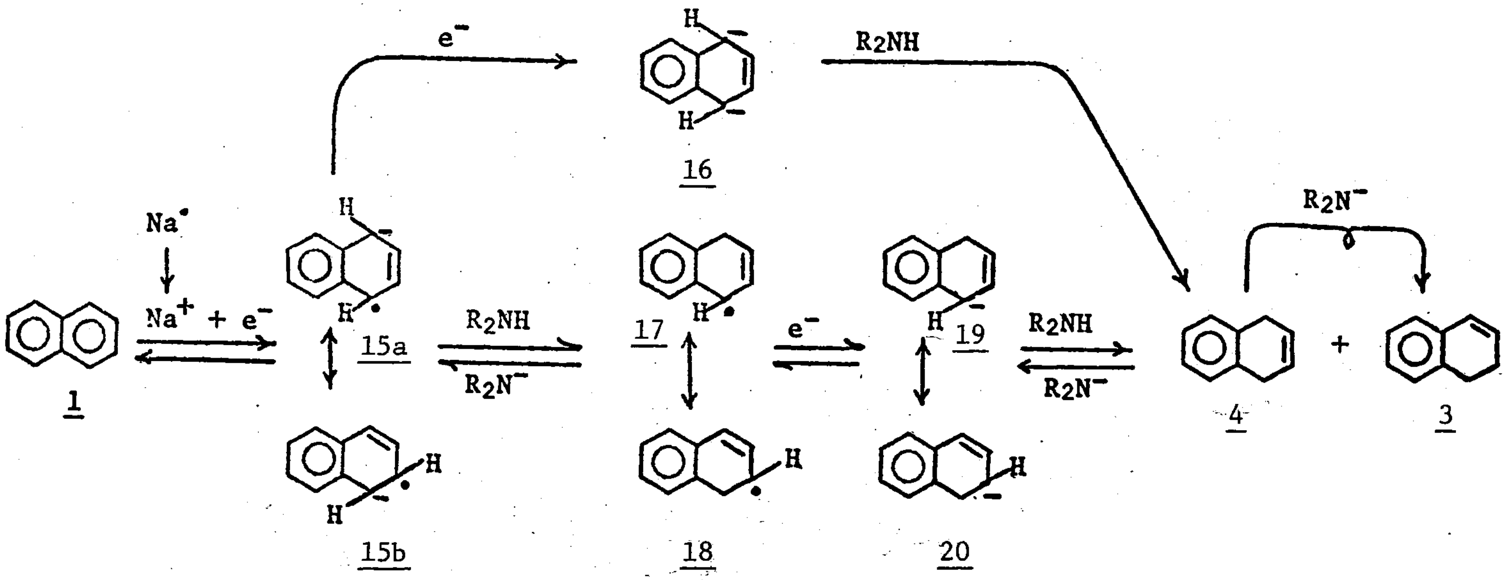
(a) Amounts were not measured. (b) Contained various other products in trace quantities. (c) 27% of dimer fraction that showed the same glc retention time as dimer 23.

TABLE VIII

DESCRIPTION OF TRIMERS AND TETRAMERS

Compound	Description	m/e (rel intensity)
26	Glass-like solid bp 275° at 0.18 mm M.W. 380, $C_{30}H_{20}$	506 (15), 381 (31), 380 (100), 379 (18), 376 (13), 253 (13), 252 (21), 188 (14), 44 (20)
27	White solid mp 243-244° M.W. 380, $C_{30}H_{20}$	380 (100), 379 (20), 378 (13), 377 (13), 376 (12), 188 (14)
28	Glass-like white solid mp 277-280° M.W. 506, $C_{40}H_{26}$	Did not vaporize adequately

responsible for dimer formation. The sequences in Figures 8, 9, and 10 show the intermediates and products which could result from nucleophilic attack of the ionic species 15a, 16, 19, and 29e on 1,2-dihydronaphthalene (3). Hertzler[3g] has proposed an ionic mechanism which involves the addition of species 19 to 3 and accounts for the formation of dimers 7 and 8 in sodium-amine reductions. The proposed mechanism does not explain the formation of 9, unless additional steps are included. Base-catalyzed disproportionation of 8 or some intermediate species could lead to 9; however, this should result in the formation of an equal amount of another product or liberation of hydrogen gas should occur. Base-catalyzed disproportionations are well documented.[2b,47,58] In a separate experiment, dimer 8, treated with potassium *tert*-butoxide in dimethyl sulfoxide, yielded a mixture of 6 and 9



R = $CH_3CH_2CH_2-$

Figure 8. Mechanism for Sodium-Amine Reduction of Naphthalene to Dihydronaphthalenes

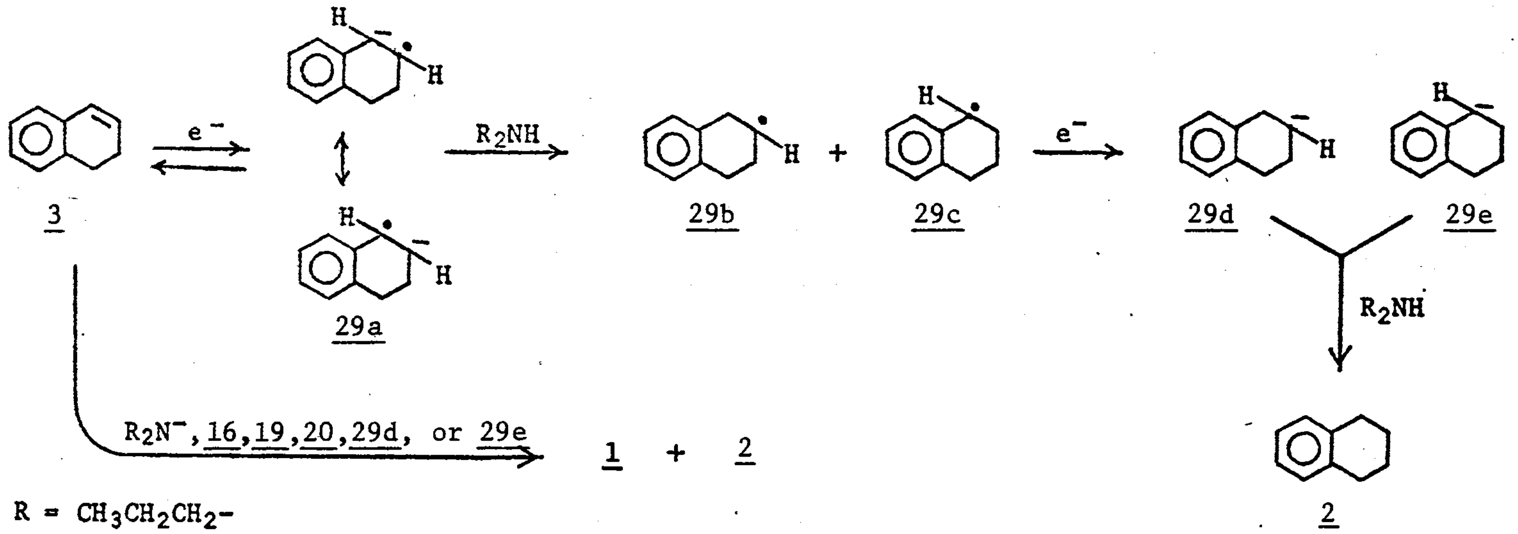


Figure 9. Mechanism for Sodium-Amine Reduction of 1,2-Dihydronaphthalene to 1,2,3,4-Tetrahydronaphthalene

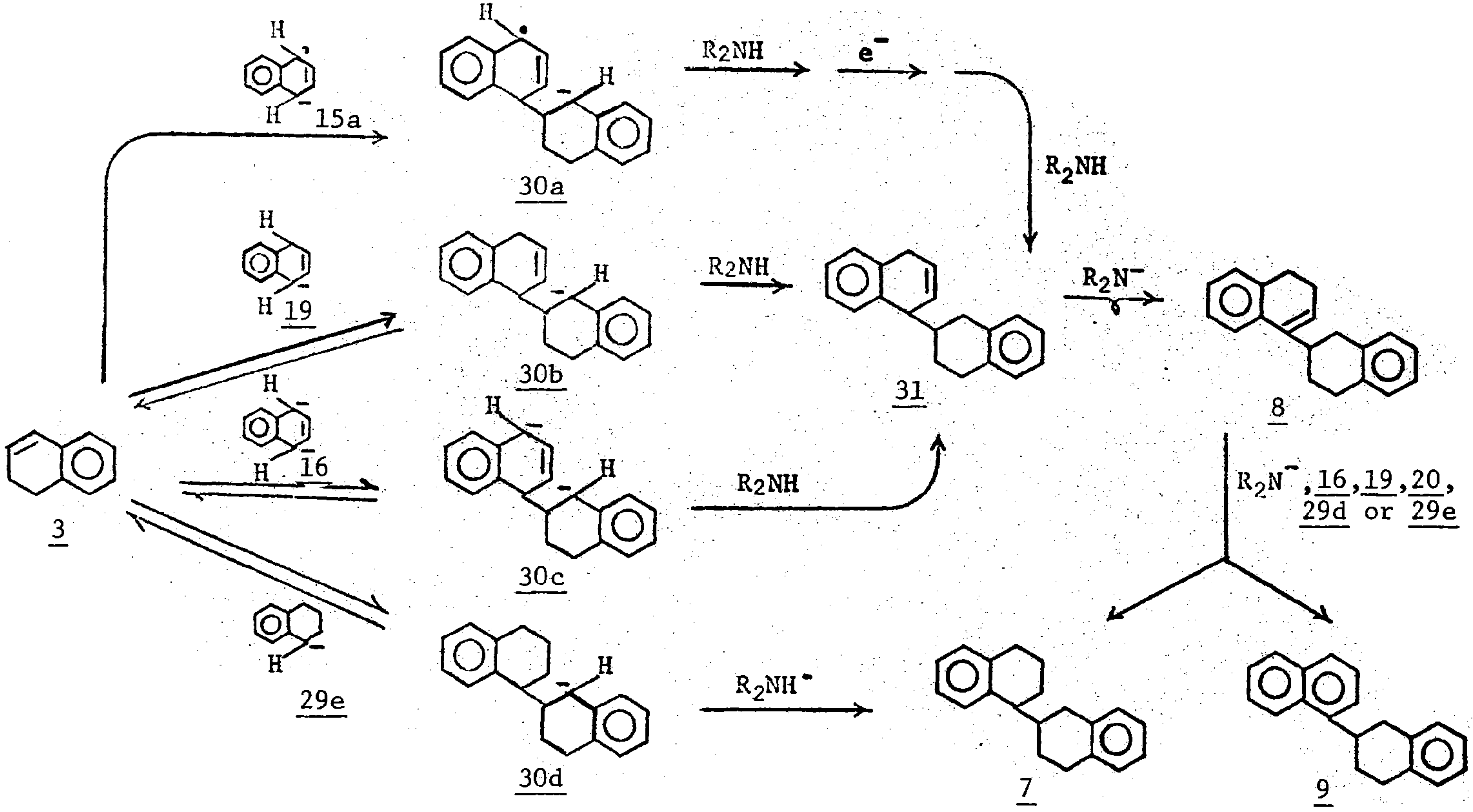
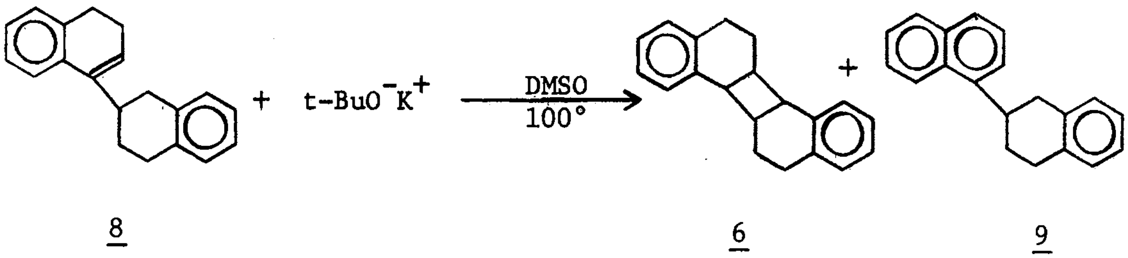
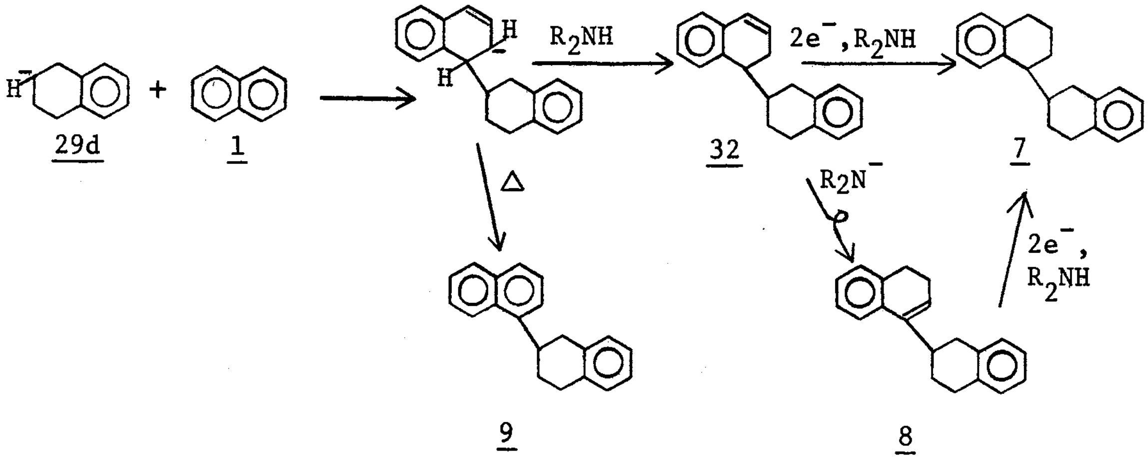


Figure 10. Possible Mechanistic Pathways for Reductive Dimerization



(46:54). In order to explain the formation of 9, it is assumed that hydride ion is transferred to the solvent or converted to hydrogen gas since disproportionation of 8 should give an equal amount of 7 and 9. The formation of 6 in this reaction suggests that 8 is a precursor to this cyclobutane dimer; thus, the latter appears to be an end-product of 1,2'-dimerization. In favor of ionic dimerization is the behavior of analogous hydrocarbons under nonreducing conditions; thus, strong bases have been shown to cause dimerization of 3 and 4 to 6, 8, and 11.[3a,g,47]

Another possible mechanistic pathway shown below involves



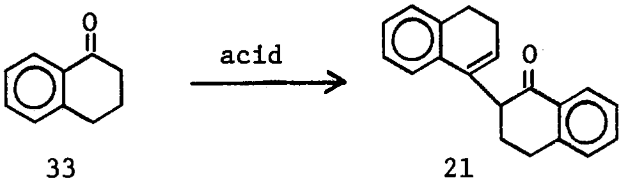
nucleophilic attack of the carbanion 29d on, and addition to, naphthalene at the 1-position. The alkylation of naphthalene with *tert*-butyllithium has been shown to favor the formation of the 1-isomer at long reaction times.[59] Wideman has suggested that the carbanion 29d is a better nucleophile than proton acceptor.[47]

The possibility of a radical dimerization involving the reactive intermediates of Figures 8 and 9 has not been ruled out completely although the failure to find 1,1'- or 2,2'-linked ring systems strongly suggests that a radical process is less likely.

Since all the mentioned reacting species of Figures 8 and 9 should be present in ammonia or amine systems, solvation and proton supply should be the major factors which influence product distribution. With sterically unhindered amines or ammonia, reductive amination or reduction is usually the predominant reaction.[3,29] With sterically hindered amines, reductive amination and reduction are minor processes and reductive dimerization is the major reaction. Hence, reduction is less favored because of limited availability of protons for reaction with anions[1b] and the slower dimerization process results.

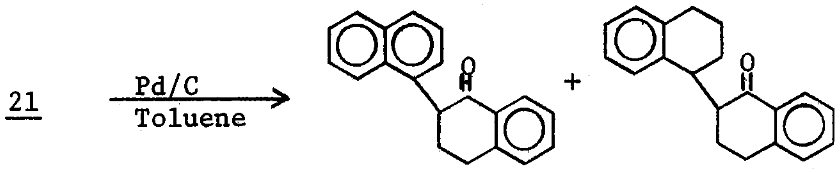
During this study, it became of interest to acquire dimer 8 in sufficient quantities to carry out investigations of proposed mechanistic pathways. In my attempts to devise a useful synthesis of 8, several interesting observations were made and some new compounds were identified. Since the dimer ketone 21 was attainable via the acid-catalyzed[56a,b,60] self-condensation of 1-tetralone (33), it appeared to be a convenient starting material for the preparation of 8.

The use of Amberlyst-15 to replace HCl gas as a catalyst[56c] had been previously shown to give 21 in refluxing xylene after several



33 21

hours. We found that a new batch of catalyst had much higher reactivity and new optimum conditions for obtaining 21 with a minimum of impurities are reported. Long reaction times and high-boiling solvents yield more dimer but the purity is considerably lower. The impurity, which could not be removed by repeated crystallizations from acetone or ether, appears to be the ketone 34, which was isolated after treatment of 21 with Pd/C in refluxing toluene.[54] The purest sample of



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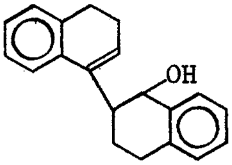
21 was obtained by a Soxhlet extraction of the crude product using petroleum ether.

Reduction of 21, prepared and purified as noted above, was attempted using several conventional methods for conversion of ketones to hydrocarbons. A modified Wolff-Kishner procedure[61] did not give 8

(M.W. 260), although the unidentified product obtained showed a molecular ion m/e 260 in the mass spectrum. This product was shown by instrumental methods to be neither 8 nor 6.

Individual reactions of the alcohol 36 with p-toluenesulfonyl chloride, methanesulfonyl chloride, and thionyl chloride followed by



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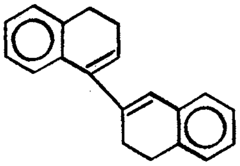

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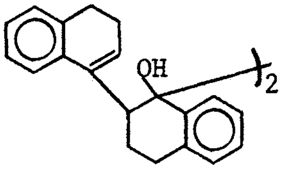

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lithium aluminum hydride reduction of each in ether gave a variety of products. The only pure product isolated was the diene 37[50b] from the methanesulfonyl chloride reaction.

The Clemmensen reduction of 21 using a conventional procedure with mossy zinc amalgam, toluene, and heating at reflux temperature yielded only minor reduction products after several days. Use of amalgams of zinc dust or granulated zinc in refluxing toluene increased the rate of reaction but gave impure product. When a Vibromix stirrer was used with zinc dust amalgam at room temperature in benzene, the reaction was faster; however, the product isolated was primarily the pinacol 38 and not the reduced hydrocarbon. At room temperature the reaction stopped when ca. 60% of the starting material was still unreacted.

The reaction conditions selected which gave the best yield of 8 in reasonable purity (93%) utilized benzene as a solvent, granulated

(20-200 mesh) zinc amalgam, and a reaction temperature of 40-60° with slow stirring of the benzene-aqueous layer. Dimer 8 was then purified further by column chromatography.

CHAPTER III

EXPERIMENTAL[8,62]

Reduction of 1 with Sodium and Dipropylamine.— To 12.8 g (0.1 mol) of naphthalene and 250 ml of dipropylamine (bp 109°) contained in the reaction flask[4,46] was added 9.2 g (0.4 g-atom) of sodium over a period of several hours. A dark brown color developed within 20 min. The mixture was stirred at room temperature for 24 hr and then decanted from the unreacted sodium. The reaction mixture was poured cautiously over 400 ml of crushed ice and an orange emulsion resulted. This was extracted with 500 ml ether (3 portions) and the ether layer, which contained the hydrocarbons, was washed with water, twice with 10% aqueous HCl, and then with water until neutral. The acidic extracts and water washings were combined, made basic with NaOH, and extracted with ether. The ether layer was washed with water, dried (Na_2SO_4) and concentrated to yield 1.7 g of amines.

The ether layer containing the amine-free hydrocarbons was dried (Na_2SO_4) and concentrated. The solution was steam distilled and both the pot residue and distillate were extracted with ether and dried (Na_2SO_4). Concentration of the extract of the distillate yielded 6.3 g steam-volatile hydrocarbons. These were shown by glc analysis to be a mixture of unreacted 1 and 2 in a 93:7 ratio.

The ether extract of the pot residue was concentrated (rotary evaporator) to yield 6.4 g of a dark viscous oil. This material was distilled (175-180° at 0.2 mm) to give 4.3 g (62%)[63] of a light yellow oil which was shown by glc analysis to be a mixture of _7_:_8_:_9_ (11:16:73).

Isolation and Identification of 1',2',3',4'-Tetrahydro-1,2'-binaphthyl (9).— A portion (1 g) of the distilled dimer mixture was dissolved in absolute ethanol and picric acid (1 g) was added. This mixture was heated until solution was complete, then allowed to cool slowly. The crystalline picrate was filtered and washed with absolute ethanol. After recrystallization from the same solvent, the yellow needles melted at 101-104°. The hydrocarbon was regenerated by stirring the picrate with petroleum ether and eluting through basic alumina. The clear oil obtained after concentration of the solution was triturated with petroleum ether until crystals formed. Recrystallization from methanol gave _9_ as white needles: mp 64-65°; mass spectrum (70 eV) _m/e_ (rel intensity) 258 (73), 154 (31), 153 (43), 130 (47), 128 (34), 104 (100); ir (melt) 3030, 2820, 1600, 1580, 1515, 1498, 1458, 1439, 1402, 1255, 951, 799, 779, 760, and 743 cm^{-1}; uv max (95% C_2H_5OH) 226 (ε 83,600), 274 (ε 7,345), and 283 mμ (ε 8,240).

Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.15; H, 7.08.

Isolation and Identification of 1,1',2,2',3,3',4,4'-Octahydro-1,2'-binaphthyl (7) and 1',2',3,3',4,4'-Hexahydro-1,2'-binaphthyl (8).— The mother liquor recovered from the picrate preparation in the previous scheme was concentrated, petroleum ether was added, and the slurry was poured onto a column containing basic alumina. Elution with petroleum ether yielded a mixture of the three dimers _7_, _8_, and _9_ in which the first two were shown by glc studies to be the major constituents.

This dimer fraction (1.5 g) was mixed with 10% Pd/C (0.15 g) and 100 ml of toluene in a 200-ml one-neck flask equipped with condenser and magnetic stirring bar. After being refluxed for two hr, the solution was filtered and concentrated to give 1.4 g of viscous oil containing 7 and 9 and none of 8.

This oil was chromatographed (1.25-in. x 18-in. column) over silica gel (30-200 mesh) and basic and acidic alumina. Dimer 7 was eluted in the first fraction with petroleum ether. After distillation, 7 was obtained: bp 175-180° (0.2 mm); ir (film) 3010, 2925, 1700, 1670, 1490, 1450, 1435, 1040, 948, 762, and 739 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 262 (8), 132 (21), 131 (100), 130 (30), 129 (17), 115 (15), 91 (22).

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.32; H, 8.67.

Dimer 8 isolated from the mixture by preparative gas chromatography (UC W-98) on acid-washed Gas-Pack W, was a viscous liquid; mass spectrum (70 eV) m/e (rel intensity) 260 (51), 131 (63), 130 (62), 129 (100), 128 (74), 115 (43), 104 (69).

Synthesis of 1,2'-Binaphthyl (22) by Dehydrogenation of C_{20} Dimers.— The dimer fraction (4.3 g of 7, 8, and 9) was mixed with 10% Pd/C (0.5 g) in a 50-ml one-neck flask equipped with reflux condenser and gas outlet tube. As the flask was lowered into a preheated (350°) Wood's-metal bath, vigorous evolution of gas occurred. After ten min, gas evolution had subsided, but heating was continued for an hour. After cooling, the residue was dissolved in petroleum ether, filtered, and concentrated to give 4.0 g of viscous yellow oil. The latter was distilled (153-58° at 0.02 mm) to give 3.9 g (92%) of light yellow solid. This constitutes a 57% yield of 22 based on the amount of reacted naphthalene. After elution through alumina and silica gel with petroleum ether, followed by concentration of the solution, a white solid was obtained: mp 76.5-77.5° [lit.[50b] mp 76°] mmp with 22 prepared from 21, 76-77°; mass spectrum (70 eV) *m/e* (rel intensity) 254 (100), 253 (72), 252 (53), 250 (13), 127 (10), 126 (27); nmr ($CDCl_3$) δ 7.18-8.05 (m).

Reduction of 9 with Sodium and Diethylamine.— To 6.5 g (0.025 mol) of 9 in 250 ml diethylamine, bp 55°, was added 2.3 g (0.1 g-atom) Na over a period of several hours. A dark brown color developed in less than one min and persisted throughout the reaction time of 22 hr. The reaction mixture was quenched in ice and extracted with ether, and the ether solution was extracted with 10% HCl.

The ether remaining after washing with water was dried (Na_2SO_4) and concentrated to give 5.8 g hydrocarbons. The acidic and aqueous extracts were combined, made basic with NaOH, and extracted with ether, and the extract dried (Na_2SO_4) and concentrated to give 0.7 g of non-volatile amines.

The hydrocarbon fraction showed a trace of 7 and 8, 10% of 9, and 89% of an undetermined mixture. When the latter (2.5 g) was treated as before with Pd/C (0.25 g) in 100 ml of refluxing toluene for five hours,[54] a viscous oil (2.1 g) was obtained which showed the ratio 7:9:23 (1:62:37) by glc.

Isolation and Identification of 1',2',3',4',5,6,7,8-Octahydro-1,2'-binaphthyl (23).— The mixture from the preceding reduction was eluted with petroleum ether through a column of silica gel and basic, acidic, and neutral alumina. From the first fraction which eluted from the column, pure 23 was obtained; bp 175-180° (0.2 mm); ir (film) 2990, 2800, 2690, 1580, 1488, 1455, 1433, 772, 743, and 716 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 262 (50), 131 (27), 130 (100), 129 (23), 115 (21), 104 (100).

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.83; H, 8.40.

Catalytic Reduction of a Mixture of 7, 8, and 9.— A mixture (3.6 g) of the dimers 7:8:9 (18:18:64) was stirred (Teflon-covered magnet) at 25° in a 500-ml fluted flask with 0.4 g of 10% Pd/C and 150 ml of 95% ethanol. Hydrogen (1 atm.) was introduced and after 5 days, 8 and 9 had disappeared. After filtration (Dicalite filter-aid) and concentration, a viscous oil remained (3.2 g) which proved to be a mixture of 7 (62%) and 23 (38%) by glc analysis.

Dehydrogenation of Trimer and Tetramer Mixture and Isolation of 26, 27, and 28.— The undistilled pot residue (34 g) from one of the larger runs was treated with 10% Pd/C (3.4 g) at 270° for 4 hr in a 250-ml one-neck flask equipped with a reflux condenser and gas escape tube. The solid mass which remained, after cooling, was dissolved in benzene and the solution filtered to give a red-green fluorescent solution. Glc analysis at 300° on a 6' x 1/8" column (5% UC W-98 on acid-washed Chromosorb G) showed one major product and at least five minor ones.

A portion (21.9 g) of the solid in a minimum amount of benzene was added to a column (1.5 in.) of silica gel (6 in.), acidic alumina (6 in.), basic alumina (4 in.), and neutral alumina (3 in.). Elution with petroleum ether and benzene mixtures gave several fractions from which three compounds were isolated. These are described in Table VIII.

Reaction of 8 with Potassium tert-Butoxide.— To a dry 100-ml one-neck flask in a dry-box containing nitrogen was added 0.45 g (0.004 mol) of potassium tert-butoxide (free-flowing white powder) and 60 ml of reagent grade dimethyl sulfoxide (DMSO). Then 1.0 g (0.004 mol) of 8 in 10 ml of DMSO was added. An immediate red color developed which gradually faded to tan-brown in 1-2 hr. After 48 hr at room temperature the flask was heated on a steam bath for an additional 30 hr. The solution was poured into 100 ml water and extracted (three portions) with ether. The ether extract was washed with water, dried (Na_2SO_4), and concentrated to give 1.0 g viscous oil which was analyzed by glc as 6 and 9 (46:54).

When the oil was diluted with a small amount of ether and the solution kept overnight, 6 precipitated as crystals: mp 179.5-180.5 [lit.[3b] mp 179-180°]. The remaining oil (0.6 g) was chromatographed on silica gel and neutral alumina to give dimer 9. The glc retention time and ir spectrum were identical to those of an authentic sample.

Synthesis of 21 by Self-condensation of 1-Tetralone (33).— To 292 g (2 mol) of 33 and 30 g of Amberlyst-15 (Rohm and Haas Co.) in a 1-l. one-neck flask equipped with a Dean-Stark trap and condenser was added 200 ml of toluene. The mixture was heated for 1.5 hr with magnetic stirring, then cooled and filtered. Distillation of the toluene and unreacted 33 on a steam bath at reduced pressure left a viscous residue which was cooled and triturated with ether. The solid which precipitated was filtered out and washed with ether leaving 30 g of crude 21. Soxhlet extraction with petroleum ether for several hr gave 21 with <5% impurities as shown by glc studies at 280°: mp 132-134° [lit.[56a,b] 132-135°]; 2,4-dinitrophenylhydrazone, mp 249-50° (dec) [lit.[56c]

247-248°]; nmr ($CDCl_3$) eight aromatic protons at δ 6.99 (m), one vinyl proton at δ 5.68 (triplet), 3° proton alpha to ketone at δ 3.75 (triplet), and eight aliphatic protons at δ 1.9-3.1 (overlapping m).

Synthesis of 34 by Dehydrogenation of 21.— A mixture of 1 g of 21, 0.1 g of 10% Pd/C, and 50 ml toluene was heated at reflux for 5 hr in a 1-neck 100-ml flask with magnetic stirring. Filtration through Dicalite filter-aid and concentration gave 1 g crude material. Recrystallization from benzene-petroleum ether gave crystals of 34: mp 131-134°.

Wolff-Kishner Reduction[61] of 21.— To 0.55 g (0.002 mol) of 21, 6.6 g (0.132 mol) of hydrazine hydrate, and 1.7 g (0.016 mol) of hydrazine dihydrochloride was added 31.8 g (0.3 mol) of diethylene glycol in a 100-ml steel reaction pot equipped with Dean-Stark trap, condenser, and gas inlet tube. After heating at 140° for 3 hr under helium, 2.5 g of KOH (0.044 mol) was added and the temperature was increased slowly to 230°. After a total reaction time of 6 hr, the solution was cooled and extracted with ether. The ether extract was washed with water and concentrated. Elution of the viscous oil through silica gel and alumina with petroleum ether gave 0.55 g of a clear, viscous oil: bp 174-84° at 0.15 mm; mass spectrum m/e (rel intensity) 260 (61), 131 (39), 130 (100), 129 (60), 128 (42), and 115 (35); nmr ($CDCl_3$) eight aromatic protons at δ 6.4-7.7 (m), one aliphatic proton at δ 6.21 (doublet), and eleven aliphatic protons at δ 1.0-3.1 (broad m).

Reduction of 21 to 36.— To 100 ml of benzene in a 500-ml 3-neck flask equipped with magnetic stirrer and nitrogen flush was added 38 g (0.28 mol) of diisobutylaluminum hydride. The mixture was cooled to 15° and 34.3 g (0.125 mol) of 21 dissolved in 300 ml of benzene was added in 20 min. The temperature was kept below 30° by immersing in an ice bath when needed. After stirring for 1.5 hr, the solution was poured onto 800 ml crushed ice. Ether was added and then 10% aqueous HCl until the white aluminum salts dissolved. The ether layer was separated and immediately neutralized ($NaHCO_3$). Two more ether extracts were made and neutralized, and all combined, dried, and concentrated to give 32.6 of a viscous liquid (36) which would not crystallize: ir ($CHCl_3$) 3400 cm^{-1} (OH).

Isolation and Identification of 3,3',4,4'-Tetrahydro-1,2'-binaphthyl (37).— To 2.8 g (0.01 mol) of 36 and 50 ml dry pyridine cooled to 0-5° was added 1.3 g (0.011 mol) of methanesulfonyl chloride. After 18 hr at 20°, the reaction mixture was poured onto ice and extracted with 3 portions of ether. The combined ether extracts were washed with 10% HCl and water, dried (Na_2CO_3 and Na_2SO_4), and concentrated leaving a light yellow solid. This was dissolved in petroleum ether and the solution stirred with Darco and filtered (Dicalite filter-aid). The solution was concentrated at room temperature (rotary evaporator) and cooled in a dry ice-acetone bath. Filtration of the solid and recrystallization from methanol gave 1 g of 37: mp 92.0-93.5° [lit.[50b] mp 87°]; ir (CCl_4) 3010, 2930, 2870, 2810, 1483, 1450, 1430, 1040, 940, 886, and 858 cm^{-1}; nmr (CCl_4) eight aromatic protons at δ 6.7-7.3 (m), one vinylic and benzylic proton at δ 6.42 (singlet), one vinylic proton at δ 5.95 (triplet), and eight allylic and benzylic protons at δ 1.9-3.1 (m).

Clemmensen Reduction of 21: Isolation of 8 and 38.— The amalgam, prepared in a conventional method[64] using 3 g mercuric chloride, 100 g granulated zinc (60-200 mesh), 25 ml concentrated HCl, and 150 ml water, was added to a 1-l. three-neck flask containing 10 g of <u>21</u> dissolved in 500 ml of benzene. After 40 ml of concentrated HCl and 15 ml of water were added, the solution was stirred gently to cause agitation of the two liquid layers but not the amalgam. The solution was heated (50-60°) and 5-ml portions of HCl were added every 12 hr for 4.5 days.

The benzene layer was separated and the aqueous layer was extracted (2 portions) with benzene. The benzene extracts were combined, washed with $NaHCO_3$ solution, then with water, dried (Na_2SO_4), and concentrated. The residue was heated with petroleum ether and cooled. Filtration gave 4.7 g white solid, mp 165-170°. Recrystallization from mixtures of chloroform-absolute ethanol gave <u>38</u>: mp 173-174°; ir ($CHCl_3$) 3480 cm^{-1} (O-H); nmr ($CDCl_3$) sixteen aromatic protons δ 6.75-7.60 (m), two vinylic protons at δ 5.55 (triplet), two 3° allylic protons adjacent to -OH at δ 3.98 (triplet), and eighteen benzylic, hydroxylic and allylic protons at δ 1.6-3.0 (overlapping m).

<u>Anal</u>. Calcd for $C_{40}H_{38}O_2$: C, 87.23; H, 6.96. Found: C, 88.09; H, 7.00.

The petroleum ether filtrate from the above procedure was eluted through a column of silica gel and neutral alumina to give 2.6 g of a clear viscous oil which was shown by glc to be 93% of <u>8</u>. Further purification by column chromatography afforded <u>8</u> in 98% purity.

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with sulfuric acid-treated and redistilled petroleum ether, bp 60-68°, before use; (b) Melting points were determined with a Hoover-Thomas capillary tube melting point apparatus and are uncorrected; (c) The uv and ir spectra were obtained with a Cary Model 14 and with a Beckman Model IR-5A spectrophotometer respectively; (d) The nmr spectra (CCl_4) were obtained with Varian HR-60 and HA-100 instruments (TMS standard) and mass spectra with a consolidated Electrodynamics Corp. Model 21-103C mass spectrometer; (e) The elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.; (f) The glc analyses of the dimeric hydrocarbons and the reductive amination products were obtained on a Hewlett-Packard 5750 glc apparatus fitted with thermal conductivity and hydrogen flame detectors using helium as the carrier gas. For the reductive amination products, a 0.25-in. x 10-ft column of 5% polyethylenimine on base-washed fire-brick (80-120 mesh) at 190° to 230° was used. The dimer hydrocarbon mixtures were analyzed on a 0.25-in. x 11-ft column of 6% UC W-98 methyl-vinyl silicone rubber on acid-washed and DMCS-treated Chromosorb G (80-100 mesh) at 260°; (g) The glc analyses of the steam-volatile hydrocarbons were obtained on a Beckman GC-2A glc apparatus fitted with a thermal conductivity detector using a 0.25-in. x 10-ft column of 25% Carbowax 20M on Chromosorb W (30-60 mesh) at 190°.

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VITA 3

Lawrence Eugene Harris

Candidate for the Degree of

Doctor of Philosophy

Thesis: SODIUM-AMINE REACTIONS OF NAPHTHALENE
I. EFFECT OF TYPES OF SODIUM DISPERSION
II. EFFECT OF COSOLVENTS
III. SELECTIVE 1,2'-DIMERIZATION

Major Field: Chemistry

Biographical:

Personal Data: Born in Ft. Scott, Kansas, April 16, 1944, the son of Bud L. and Florence E. Harris.

Education: Graduated from Jt. Rural High School #3, Stark, Kansas, in 1962; received the Bachelor of Science degree from Kansas State College, Pittsburg, Kansas, in June, 1966, with a major in Chemistry and minor in Mathematics; received the Master of Science degree from Kansas State College in June, 1968, with a major in Organic Chemistry; completed requirements for the Doctor of Philosophy degree at Oklahoma State University in July, 1971.

Professional Experience: Chemist, W. S. Dickey Clay Mfg. Co., Pittsburg, Kansas, 1964-68; Graduate Teaching Assistant, Oklahoma State University, 1968-69; NASA Traineeship, 1969-70; Continental Oil Company Graduate Research Fellowship, 1970-71; Member of American Chemical Society, Phi Lambda Upsilon, and Phi Kappa Phi.