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## Metal-Ammonia Reduction and Reductive Alkylation of Polycyclic Aromatic Compounds: Nature of the Anionic Intermediates

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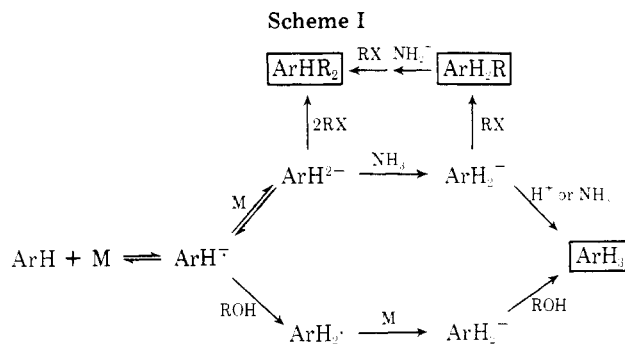
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A scheme of metal-ammonia reduction is presented which categorizes the behavior of aromatic and polynuclear aromatic compounds according to the nature of the intermediate radical anions, monoanions, and dianions. It is found that the outcome of many reductions and reductive alkylations is, in fact, a result of secondary reactions that occur during the quenching process, and a dramatic difference is found in many cases by the introduction of an inverse quench procedure. That is, the ammonia solution is poured into the quenching agent, which may be a proton source (water, saturated ammonium chloride) or an alkyl halide solution. The results of a series of such experiments are presented and indicate that common hydrocarbons such as anthracene and naphthalene react with Li or Na in ammonia to form dianions which are quickly protonated by ammonia to form dianions which are quickly protonated by ammonia to form monoanions. The alkylation of these monoanions is studied under a variety of conditions, and both monoalkylation and dialkylation (via a subsequent reaction) can occur. This behavior is contrasted to dibenzocyclooctatetraene, which is shown to form a dianion resistant to protonation by ammonia.

The reduction of polycyclic aromatic compounds by solutions of alkali metals in liquid ammonia has received considerable attention,<sup>1</sup> and a wide variety of experimental procedures have been developed. For example, the metals employed are usually lithium or sodium, but also include potassium and calcium. Protonating agents range from moderately acidic, such as ammonium chloride and water, to weakly acidic, like ethanol and 2-methyl-2-propanol. A wide range of cosolvents is also employed (usually but not always ethers), and iron salts are sometimes added to limit reduction. In addition, polynuclear compounds often lead to stable anionic intermediates which can be alkylated by suitable alkylating agents, but once again the results are variable, leading to the incorporation of zero to three alkyl groups depending on the compound reduced as well as reaction conditions such as choice of metal and/or cosolvent.

Thus, it has become generally concluded that this reaction must be carried out with meticulous care, since it has been shown that the selection of reaction conditions can afford a wide range of results. For example, the reduction of anthracene<sup>1c</sup> can result in dihydro, tetrahydro, or further reduced products depending on the level of alkali metal employed, cosolvents, and the presence of iron impurities. To our surprise, however, we have found that anthracene can be reduced quantitatively to 9,10-dihydroanthracene (in 10 min) with no prior purification of ammonia or cosolvents, and with a wide variation in alkali metal concentration as well as stoichiometry (1.2–5 equiv of metal). These results were accomplished by inverse quenching (i.e., hydrocarbon/metal/ammonia solution poured into a large volume of water) and, although not applicable to all polycyclic hydrocarbons, should be useful in many cases. Of greater importance, however, are the mechanistic implications of this result and the fact that the quenching procedure is by far the most significant factor in this particular reaction.



Thus, a general understanding of the overall reaction mechanism should allow for predictions concerning which experimental variables should be of greatest importance. With this in mind, we would like to present Scheme I for reduction and reductive alkylation and categorize aromatic compounds according to their particular position within this system.

**a. Only Radical Anions Generated.** In this case, the initial equilibrium usually lies to the left and  $\text{ArH}^{\bullet-}$  is the only anionic species present. In order to effect reduction, a proton source must be added to shift the equilibrium by protonation of the radical anion, which then accepts another electron, resulting in a monoanion which is protonated to form the reduced product,  $\text{ArH}_3$ . It is important that the proton source not be too strong, or metal will be destroyed rapidly, shifting the equilibrium back to the left. Alcohols are most commonly used for this purpose, and this method represents the procedure known as the Birch reduction. Monobenzenoid compounds most frequently fall into this category, and reductive alkylation is not possible due to the low nucleophilicity of radical anions and the much more rapid electron-transfer reaction.<sup>4</sup>

**b. Dianions Resistant to Protonation by Ammonia.** In

the case where dianions ( $\text{ArH}_2^{2-}$ ) are formed which are resistant to protonation by ammonia (probably very few polycyclic aromatic compounds fit into this category; see discussion below), simple reduction is best accomplished by rapid quench with a strong proton source such as ammonium chloride or water. It should be noted, however, that in this case alcohols *should not be used* as a quenching agent (a common error), since the metal is not rapidly consumed under these conditions, and any excess metal/ammonia/alcohol can reduce  $\text{ArH}_3$  as it is formed, leading to overreduction of the original compound (the exception is when  $\text{ArH}_3$  is nonreactive). Alkylation is expected to give  $\text{ArHR}_2$  provided  $\text{ArHR}^-$  is not protonated by ammonia before the second alkylation takes place.

#### c. Monoanions Resistant to Protonation by Ammonia.

In this case we envision the major anionic species to be the monoanion ( $\text{ArH}_2^-$ ) resulting from protonation of the more basic dianion ( $\text{ArH}_2^{2-}$ ) by ammonia, and probably a number of polycyclic aromatic compounds fall into this category. Methods of reduction in these cases are identical with those discussed above for dianion formation for the same reasons. Although reductive alkylation may provide good yields of  $\text{ArH}_2\text{R}$  under certain conditions,  $\text{ArHR}_2$  as well as  $\text{ArR}_3$  (see below) can also be formed and have often complicated reaction mixtures in the past.

#### d. Neutral Compounds Produced by Complete Protonation by Ammonia.

In some cases, the monoanions produced by protonation of dianions by ammonia may be sufficiently basic themselves so as also to be protonated by the ammonia. This can lead to two results: (1) the compound produced ( $\text{ArH}_3$ ) is resistant to further reduction; or (2) the compound may be reduced by any of the pathways described previously. It is the latter case in which removal of surplus metal becomes important, and we would like to examine the use of ferric chloride to limit reduction in light of Scheme I.

For example, although the first efficient reduction of anthracene to 9,10-dihydroanthracene involved the use of added ferric chloride with extended reaction periods,<sup>1c</sup> the importance of rapid quenching has since been realized for several polycyclic systems.<sup>5</sup> It is evident from alkylation behavior (see below) that anthracene forms monoanions<sup>6</sup> (Scheme I) and that overreduction occurs during the quenching process. That is, excess metal<sup>7</sup> reacts with the product as it is formed, and the iron simply consumes this surplus metal.<sup>8</sup> However, the use of ferric chloride involves relatively long reaction times and is unnecessary in cases where monoanions are formed. As mentioned above, anthracene can be reduced quantitatively under almost any conditions provided the quenching process is rapid with a strong proton source ( $\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$ ). With small quantities (1–2 g) and a controlled amount of metal (1.3 equiv) this can be done conveniently by simply adding saturated ammonium chloride as fast as possible, whereas with larger amounts (e.g., 10 g) quantitative results can still be obtained by pouring the ammonia solution into a large volume of saturated ammonium chloride. In either case, the anions are protonated and excess metal is destroyed at such a rate as to make overreduction impossible.

The use of iron is necessary in some cases, however, and according to Scheme I it is evident that surplus metal will be an important factor when the product  $\text{ArH}_3$  is generated by protonation from ammonia (i.e., metal not yet quenched) and is *itself* reducible. A notable example of this situation is found

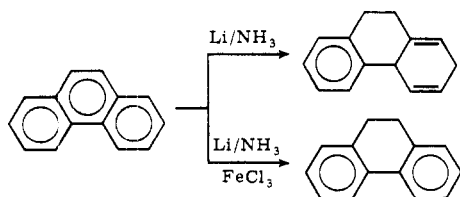


Table I. Metal–Ammonia Reduction of Naphthalene<sup>a</sup>

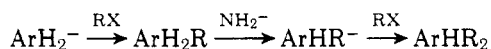
metal	temp, °C	quench <sup>b</sup>	1,2,3,4-tetrahydronaphthalene <sup>c</sup>	1,4-dihydronaphthalene <sup>c</sup>	naphthalene <sup>c</sup>
Na	-33	normal	17	83	
Na	-33	inverse	18	72	10
Na	-78	normal	2	98 <sup>d</sup>	
Li	-78	normal	14	81	5
Li	-33	inverse	55	40	5

<sup>a</sup> Metal added to naphthalene in  $\text{NH}_3/\text{ether}$  (2:1), and reaction stirred for  $\sim 15$  min. <sup>b</sup> Either excess aqueous ammonium chloride solution added rapidly (normal), or ammonia solution poured into excess ammonium chloride (inverse). <sup>c</sup> By GLC on a 6 ft  $\times$   $\frac{1}{8}$  in W-98 (silicon) column, corroborated by relative NMR integrations. <sup>d</sup> Examination on a 4; 15% Carbowax column indicated a very small shoulder, and (coupled with NMR) this suggests the presence of the 1,2-dihydro isomer (1–2%).

with the reduction of phenanthrene,<sup>9</sup> which proceeds smoothly to the tetrahydro stage with adequate metal concentration, but can be limited to the formation of 9,10-dihydrophenanthrene by the use of less metal and added ferric chloride.

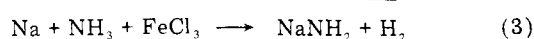
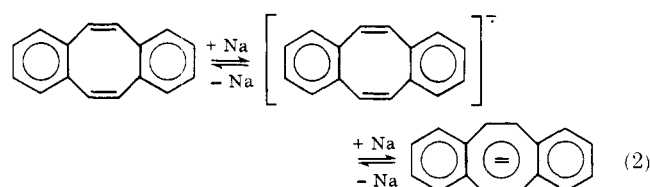
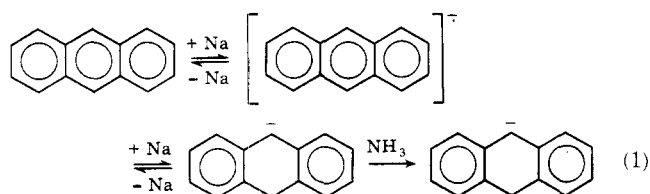
Another case of single-stage reduction that deserves special attention is naphthalene. Quite to our surprise, although a considerable amount of work has been reported on the reduction of naphthalene derivatives,<sup>1c</sup> a perusal of the literature has not uncovered an efficient synthesis of 1,4-dihydronaphthalene by metal/ammonia reduction of the parent hydrocarbon. As it turns out, the metal/ammonia reduction of naphthalene is quite sensitive to reaction conditions as is indicated by the data in Table I. Although reduction is essentially quantitative with the use of sodium metal at  $-78$  °C followed by a *rapid* quench with ammonium chloride solution, the use of lithium metal results in significant overreduction. Since overreduction occurs even with an inverse quench procedure, we conclude that naphthalene leads to a monoanion according to Scheme I, which itself undergoes significant protonation by ammonia at either higher temperatures, or when lithium is the counterion. These results seem reasonable, however, since radical anions formed from lithium are more easily protonated than those from sodium, and the more easily protonated tight ion pairs are expected to be more abundant at higher temperatures.<sup>4</sup>

**Reductive Alkylation.** The formation of stable dianions from the reaction of anthracene and other polycyclic hydrocarbons with alkali metals in liquid ammonia had been accepted for over 30 years in accordance with Wooster's rule<sup>1b</sup> (see also ref 8 and references therein), and the presence of such intermediates seemed to be confirmed by the fact that dialkyl derivatives are produced by the addition of alkyl halides to alkali metal solutions of these hydrocarbons in anhydrous ammonia.<sup>1,9</sup> However, it has since been recognized<sup>9</sup> that dialkylated products could also arise by alkylation of a monoanion followed by reaction with amide (formed from protonation of the dianion by ammonia) to generate a second monoanion, which is in turn alkylated.<sup>11</sup>

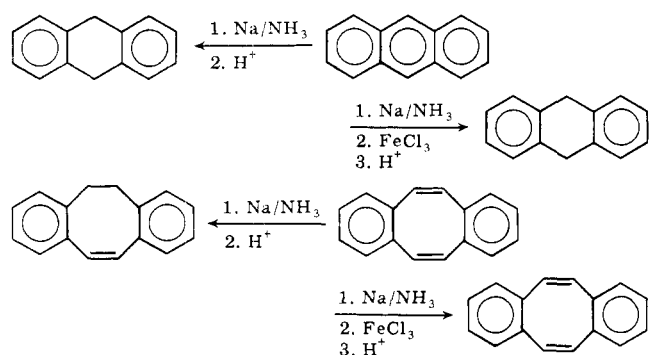


Harvey et al. concluded that this is indeed the case with biphenyl<sup>5</sup> and suggested that this process should be examined for anthracene as well as other polynuclear systems. They also suggested that in the reduction of anthracene, dianions are indeed formed and are protonated rapidly in the case of lithium or calcium, but more slowly with sodium. Our results, however, indicate that protonation is rapid with both lithium

and sodium, and that both systems result in essentially irreversible monoanion formation. This can be demonstrated in the following manner. Equation 1 depicts our proposal that the anthracene radical anion accepts a second electron, resulting in the reversible formation of a dianion. However, we

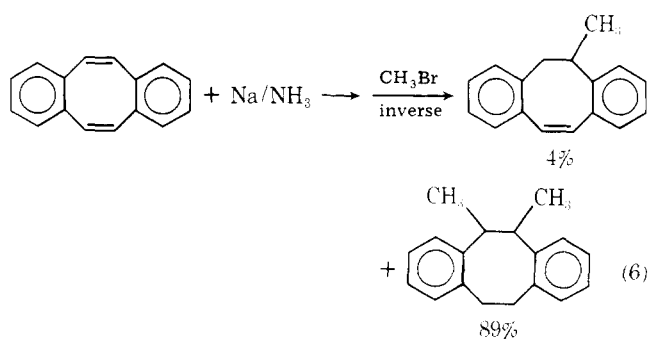
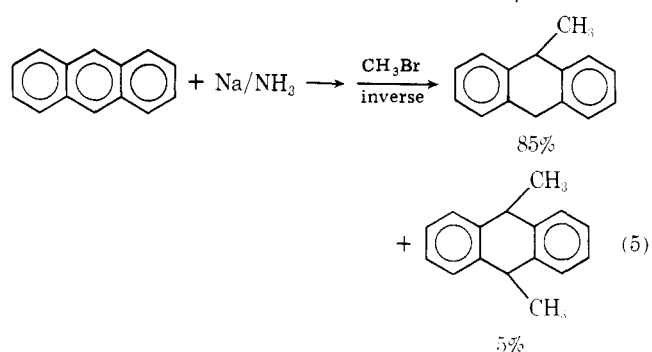
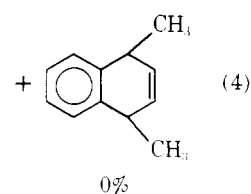
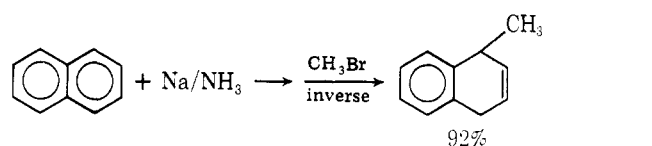


suggest that this dianion is rapidly protonated by ammonia to form a monoanion and amide ion. In an effort to detect this chemically, we sought a model system for comparison that would form a stabilized dianion. Hence, we selected *sym*-dibenzocyclooctatetraene, since the addition of two electrons (eq 2) would result in an aromatic dianion which we felt may be resistant to protonation by ammonia. Thus, the validity of eq 1 and 2 can be tested by taking into account the effect of added iron salts. As indicated in eq 3, ferric chloride catalyzes the reaction of sodium with ammonia (resulting in amide and hydrogen), which effectively removes the metal from metal-ammonia solutions. It is expected that removal of metal (i.e., FeCl<sub>3</sub> addition) from the *sym*-dibenzocyclooctatetraene dianion solution would shift the equilibrium back to the hydrocarbon (it is well established that dianions exist in equilibrium with their radical anions<sup>4a</sup>), whereas, according to eq 1, there would be no effect in the anthracene case. In fact,



when metal-ammonia solutions of both hydrocarbons are generated, protonation of aliquots after 10 min gives reduction products in both cases. However, if ferric chloride is then added and the reactions quenched with water after 2 h, anthracene still gives the reduction product exclusively, whereas *sym*-dibenzocyclooctatetraene is *itself* recovered from the latter reaction.

A similar contrast in behavior is noted with reductive alkylations. Thus, all three systems, naphthalene, anthracene, and *sym*-dibenzocyclooctatetraene, provide good yields of dialkylated, dihydro products when alkyl halides are added to their metal-ammonia solutions, but only *sym*-dibenzocyclooctatetraene produces dimethylation (see eq 4-6) upon inverse addition to an ethereal solution (or neat) of methyl bromide or iodide. Thus, this rapid quenching process is able to "trap" the dianion in the latter case, but does not allow



enough time for secondary reactions, and the monoanions that result in the first two cases result in monomethylation.

A more detailed description of the reductive alkylation behavior of naphthalene<sup>13</sup> and anthracene is presented in Tables II-IV. Thus, in contrast to *sym*-dibenzocyclooctatetraene, naphthalene and anthracene provide monoalkylation as the chief product in most cases involving a reverse quench procedure (in many cases >90%), and, as mentioned previously, these results support the intermediacy of monoanions. The possibility that the anthracene/Na/NH<sub>3</sub> system results in dianions that are slowly protonated<sup>5</sup> was examined by inverse quenching of several samples over a period of 30 min (Table III). Our results show very little variation in dialkylation with time and do not support this possibility. Thus, we conclude that the dialkylated products are due to the back reaction with amide even under inverse quench conditions. That this back reaction *can* occur with inverse quench procedures is demonstrated by the use of added sodium amide (1 equiv) during reduction followed by an inverse quench. As indicated in Table III, dialkylation goes up to 94% with added amide ion as compared to 42% in its absence. These results are in substantial agreement with previous studies on the reductive alkylation of biphenyl and anthracene<sup>5</sup> and a clear pattern now emerges. Conditions which result in a slower quenching process (i.e., lower vs. higher temperatures, gaseous vs. liquid methyl bromide, alkyl bromides vs. alkyl iodides, and ethyl vs. methyl bromide) lead to a greater proportion of di- and trialkylated products. This is, of course, consistent with our hypothesis that the amide back reaction is responsible for di- and trialkylation, since slowing the quench allows time for this reaction to occur.

We should also note that our results show a substantial

Table II. Reductive Methylation of Anthracene (ArH)

R-X	metal	temp, °C	quench procedure	% composition <sup>a</sup>	
				ArH <sub>2</sub> R <sup>b</sup>	ArHR <sub>2</sub> <sup>c</sup>
MeBr	Na	-78	inverse <sup>d</sup>	88	12
MeBr	Na	-78	normal <sup>e</sup>	15 <sup>f</sup>	80 <sup>f</sup>
MeBr (liq)	Na	-33	inverse	89	11
MeBr (liq)	Na	-33	normal	6	85
MeI	Na	-33	inverse	95	5
MeI	Na	-33	normal	14 <sup>g</sup>	64 <sup>g</sup>
MeI	Li	-78	inverse	97	3
MeI	Li	-78	normal	58	42

<sup>a</sup> By relative NMR integrations and/or GLC on a 6 ft W-98 (silicon) column at 165 °C. <sup>b</sup> 9-Methyl-9,10-dihydroanthracene. <sup>c</sup> 9,10-Dimethyl-9,10-dihydroanthracene. <sup>d</sup> Metal added to anthracene in NH<sub>3</sub>/ether (2:1), and reaction mixture pumped under inert gas into alkyl halide under inert gas (MeBr was condensed to a liquid for inverse quenches and added as a gas for normal quenches). <sup>e</sup> As above except after the time period (~15 min) the alkyl halide was added to the reaction mixture. <sup>f</sup> ~5% ArR<sub>3</sub>. <sup>g</sup> ~23% ArR<sub>3</sub>.

Table III. Reductive Ethylation of Anthracene (ArH)

metal	temp, °C	quench procedure	time	temp of EtBr, °C	% composition <sup>a</sup>	
					ArH <sub>2</sub> R <sup>b</sup>	ArHR <sub>2</sub> <sup>c</sup>
Li	-33	inverse <sup>d</sup>	10	ambient	97	3
Li	-33	normal <sup>e</sup>	10	ambient	40	60
Li	-78	inverse	10	ambient	81	9
Li	-78	normal	10	ambient	32	68
Na	-33	inverse	10	ambient	82	18
Na	-33	normal	10	ambient		80 <sup>f</sup>
Na	-78	inverse	10	-78	40	60
Na	-78	inverse	10	ambient	60	40
Na	-78	inverse	20	-78	48	52
Na	-78	inverse	20	ambient	58	42
Na	-78	inverse	30	-78	37	63
Na	-78	inverse	30	ambient	63	37
Na	-78	normal	30	ambient	27	75
Na (+NaNH <sub>2</sub> )	-78	inverse	20	ambient	6	94

<sup>a</sup> Relative amounts determined by NMR integration and corroborated in many cases by GLC on a 6 ft × 1/8 in. W-98 (silicon) column at 165 °C. <sup>b</sup> 9-Ethyl-9,10-dihydroanthracene. <sup>c</sup> *cis*-9,10-Diethyl-9,10-dihydroanthracene. <sup>d</sup> See footnote *d*, Table II. <sup>e</sup> See footnote *e*, Table II. <sup>f</sup> ~15% ArR<sub>3</sub>. In substantial agreement with previous results: R. G. Harvey and L. Arzadon, *Tetrahedron*, **25**, 4887 (1969).

Table IV. Reductive Alkylation of Naphthalene (ArH)<sup>a</sup>

R-X	temp, °C	quench procedure	% composition <sup>b</sup>	
			ArH <sub>2</sub> R <sup>c</sup>	ArHR <sub>2</sub> <sup>d</sup>
EtBr	-78	inverse <sup>e</sup>	90	9
EtBr	-78	normal <sup>f</sup>	25	75
MeI	-78	inverse <sup>g</sup>	82 <sup>h</sup>	
MeI	-78	normal	33 <sup>h</sup>	51 <sup>h</sup>
MeI	-33	inverse	85 <sup>i</sup>	1 <sup>i</sup>
MeI	-33	normal	18 <sup>i</sup>	55 <sup>i</sup>
MeBr (liq)	-78	inverse	90 <sup>h</sup>	
MeBr (liq)	-78	normal	20	80
MeBr (gas)	-78	normal		85 <sup>j</sup>

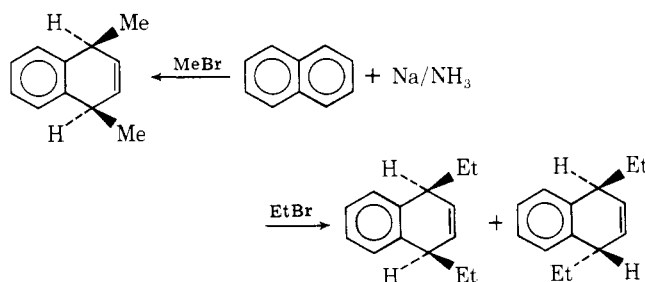
<sup>a</sup> Reaction with Na in NH<sub>3</sub>/THF (2:1). <sup>b</sup> By GLC on a 6 ft × 1/8 in. W-98 (silicon) column, corroborated by NMR peak intensities. <sup>c</sup> 1-Alkyl-1,4-dihydronaphthalene. <sup>d</sup> *cis*-1,4-Dimethyl-1,4-dihydronaphthalene (in the case of MeX), or a mixture of *cis*- and *trans*-1,4-diethyl-1,4-dihydronaphthalene (in the case of EtX). <sup>e</sup> See footnote *d*, Table II. <sup>f</sup> See footnote *e*, Table II. <sup>g</sup> A change in MeI temperature from ambient to -78 °C produced no significant change in results. <sup>h</sup> Contained some overreduction products and naphthalene. <sup>i</sup> Contained overreduction products. <sup>j</sup> In agreement with data of ref 14.

difference between lithium and sodium. This effect has been noted previously<sup>5,14</sup> and the increased amount of dialkylation with sodium has been attributed to the greater solubility of sodium amide in ammonia.<sup>5</sup>

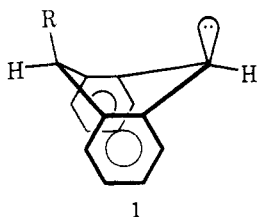
It should be noted that the earlier observation<sup>14</sup> that reductive methylation of naphthalene with sodium and methyl

bromide gas gives dimethylation exclusively, whereas the use of lithium provides monomethylation, is quite dependent on the choice of alkyl halide in that these results are not general for all alkyl halides. In fact, these results are dependent on the use of a gaseous alkyl halide which leads to a relatively slow quench. When the sodium/naphthalene solution is quenched inversely into liquid methyl bromide at -78 °C under inert gas, only monomethylation results (see Table III). However, a normal quench with liquid methyl bromide produces a considerable amount of dimethylation, whereas the use of methyl bromide gas gives dimethylation exclusively (as previously reported<sup>14</sup>). This is, of course, all quite consistent with the scheme provided herein, since once again the back reaction with amide ion is expected to be more efficient with slower quenching. This reaction appears to be of little importance when lithium is used due to the limited solubility of lithium amide in ammonia.<sup>5</sup>

An even more curious feature of the reaction is the fact that



reductive methylation of naphthalene leads only to *cis* products, whereas reductive ethylation provides a mixture of both *cis* and *trans* products. These results are quite significant, since it has always been puzzling as to why the reductive alkylation of naphthalene should be more stereoselective than anthracene. The arguments presented for the stereochemical outcome in anthracene<sup>15</sup> suggest that "peri" interactions in



the anion **1** force a pseudoaxial position for the substituent with the electron pair also pseudoaxial (for maximum overlap with aromatic rings). Thus, the second alkylation occurs from the same side, resulting in overall *cis* dialkylation. However, although this reaction is stereospecific for many R groups, it is not for methyl, presumably due to its smaller size. We should also note that isomerization of alkylated dihydroanthracenes and dihydronaphthalenes has never been observed by ammonia. Thus, the alkylation behavior of naphthalene warrants further study and is currently under investigation.

### Experimental Section

**General Procedures.** (1) **Preparation of Metal-Ammonia Solutions.** The hydrocarbon was added to a solution of 1 part dry THF (or anhydrous ether where specified) in 2 parts ammonia at  $-78^{\circ}\text{C}$  (or  $-33^{\circ}\text{C}$  where specified), followed by the addition of 1.25 equiv of sodium or lithium metal, and stirred under helium for 20 min. (2) **Reduction/Normal Quench.** Saturated ammonium chloride solution was added as rapidly as possible to discharge the deep color.<sup>16</sup> (3) **Reduction/Inverse Quench.** The reaction mixture was pumped (helium pressure) through a glass tube into a large volume of saturated ammonium chloride solution (**Caution:** some spattering occurs).<sup>16,17</sup> (4) **Reductive Alkylation/Normal Quench.** An excess of alkyl halide dissolved in dry THF was added from a dropping funnel (or in the case of  $\text{CH}_3\text{Br}$  introduced as the gas) at a reasonable rate until the discharge of the deep color. This was followed immediately by the addition of saturated ammonium chloride solution.<sup>16</sup> (5) **Reductive Alkylation/Inverse Quench.** The reaction mixture was pumped (helium pressure) through a glass tube which was immersed in a large excess of alkyl halide (under helium) which was cooled to the same temperature as the reaction mixture (**Caution:** this must be done carefully to avoid frothing).<sup>16,17</sup>

**Anthracenes.** All of the reduced products from anthracene (see Table II) are known compounds and were compared with authentic spectral data.<sup>15,18</sup> 9,10-Dihydroanthracene can be prepared from anthracene in essentially quantitative yield by either procedure 2 or 3. As mentioned previously, procedure 3 is much less sensitive to experimental conditions and precautions.

**Naphthalenes.** The reduction products of naphthalene are known compounds, although to the best of our knowledge the data in Table I represent the only efficient (98%) preparation of 1,4-dihydronaphthalene from naphthalene via metal-ammonia reduction. 1-Methyl-1,4-dihydronaphthalene and *cis*-1,4-dimethyl-1,4-dihydronaphthalene are known compounds and identification was made by comparison with authentic spectral data.<sup>14</sup>

**1-Ethyl-1,4-dihydronaphthalene** was obtained as a colorless liquid by the above procedures followed by spinning band distillation (bp  $79^{\circ}\text{C}$ ): NMR ( $\text{CCl}_4$ )  $\delta$  7.0 (m, 4 H), 5.8 (complex d, 2), 3.3 (m, 3), 1.6 (complex q, 2), 0.8 (t, 3).

Anal. Calcd for  $\text{C}_{12}\text{H}_{14}$ : C, 91.14; H, 8.86. Found, C, 91.27; H, 8.82.

***cis*-1,4-Diethyl-1,4-dihydronaphthalene**<sup>19</sup> was prepared according to the above procedures and trapped off GLC (5 ft, 7% DEGS at  $135^{\circ}\text{C}$ , retention time 7.8 min) to yield a colorless oil: NMR ( $\text{CCl}_4$ )  $\delta$  7.1 (s, 4 H), 5.9 (complex d, 2), 3.4 (bm, 2), 1.7 (complex q, 4), 0.9 (t, 6).

Anal. Calcd for  $\text{C}_{14}\text{H}_{18}$ : C, 90.32; H, 9.68. Found, 89.32 H, 9.95.<sup>19b</sup>

***trans*-1,4-Diethyl-1,4-dihydronaphthalene**<sup>19</sup> was isolated in the same fashion as the *cis* isomer (retention time 6.2 min): NMR ( $\text{CCl}_4$ )  $\delta$  7.1 (bs, 4 H), 5.8 (d, 2), 3.4 (bm, 2), 1.8 (m, 4), 0.75 (t, 6).

Anal. Calcd for  $\text{C}_{14}\text{H}_{18}$ : C, 90.32; H, 9.68. Found, C, 89.56; H, 9.71.<sup>19b</sup>

**Dibenzo[*a,e*]cyclooctatetraenes.** The reduced hydrocarbon is a known compound and is easily identified by its NMR spectrum.<sup>20</sup> The presence of small amounts of monomethylated reduced hydrocarbon was suggested by GLC and NMR results for the alkylation experiments, and no attempt was made to isolate this compound.

**11,12-Dimethyldibenzo[*a,e*]cyclooctatriene**<sup>21</sup> was prepared by the above inverse quench procedure and led to a nearly quantitative yield. Recrystallization from aqueous ethanol produced white crystals: mp  $69\text{--}70^{\circ}\text{C}$ ; NMR ( $\text{CCl}_4$ )  $\delta$  7.0 (m, 8 H), 6.9 (s, 2), 3.0 (m, 2), and 1.3 (cd, 6).

Anal. Calcd for  $\text{C}_{18}\text{H}_{18}$ : C, 92.26; H, 7.74. Found: C, 92.21; H, 8.00.

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**Registry No.**—Naphthalene, 91-20-3; 1,2,3,4-tetrahydronaphthalene, 119-64-2; 1,4-dihydronaphthalene, 612-17-9; anthracene, 120-12-7; 9-methyl-9,10-dihydroanthracene, 17239-99-5; 9,10-dimethyl-9,10-dihydroanthracene, 22566-43-4; 9-ethyl-9,10-dihydroanthracene, 605-82-3; *cis*-9,10-diethyl-9,10-dihydroanthracene, 20826-55-5; 1-ethyl-1,4-dihydronaphthalene, 36789-17-0; 1-methyl-1,4-dihydronaphthalene, 21564-70-5; *cis*-1,4-dimethyl-1,4-dihydronaphthalene, 21947-40-0; *cis*-1,4-diethyl-1,4-dihydronaphthalene, 67542-20-5; *trans*-1,4-diethyl-1,4-dihydronaphthalene, 67542-21-6; dibenzo[*a,e*]cyclooctatetraene, 262-89-5; 11,12-dimethyldibenzo[*a,e*]cyclooctatriene, 67542-22-7; ammonia, 7664-41-7; sodium, 7440-23-5; lithium, 7439-93-2.

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- (2) In experiments using excess metal and short reaction times, it is not unexpected that trace iron impurities do not affect results.<sup>3</sup>
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- (5) D. F. Lindow, C. N. Cortez, and R. G. Harvey, *J. Am. Chem. Soc.*, **94**, 5406 (1972).
- (6) For example, compounds which only form radical anions in ammonia do not furnish reduction products on quenching with water (due to rapid reaction of water with metal) and normally undergo extensive electron transfer with alkyl halides.
- (7) Performing reduction without a slight excess of metal generally leads to poor results.
- (8) As has been noted previously.<sup>3</sup> See also ref 9.
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- (10) R. G. Harvey and L. Arzadon, *Tetrahedron*, **25**, 4887 (1969).
- (11) For additional discussion concerning the exclusion of radical anions as intermediates in reductive alkylation (as well as protonation by ammonia in scheme 1) see ref 5.
- (12) It is well established that dianions exist in equilibrium with their radical anions. See ref 4.
- (13) Sodium metal was used exclusively in the naphthalene reductive alkylations, since simple reduction of this system with lithium consistently gave over-reduction products (cf. previous discussion).
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- (16) In each case, the crude product was isolated by ether extraction and then purified by distillation, recrystallization, or GLC.
- (17) Although we recommend that inverse quenches be carried out with caution, our experience has been that this technique does not provide any serious safety hazard when carried out in an efficient hood.
- (18) A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, *J. Am. Chem. Soc.*, **92**, 5912 (1970).
- (19) (a) Isomer assignment is tentative (based on comparison with dihydroanthracenes<sup>15</sup>) and is currently being investigated in more detail. (b) Both of these compounds appeared somewhat unstable and several samples were submitted for microanalysis with variable results. VPC/MS was accom-

panied by substantial decomposition, but indicated strong *m/e* 186 peaks. In addition,  $^{13}\text{C}$  and off-resonance proton decoupled  $^{13}\text{C}$  NMR results were quite consistent.

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(21) Both the relatively sharp melting point and NMR spectrum suggest that we have produced a single isomer. Inspection of the models with regard to steric preferences for the first methyl group incorporated together with maximum overlap of the monocarbanion suggests that this is probably the *trans* isomer.

## Halocyclization of *N*-Allylbenzamide Derivatives. Effects of Halogenating Agent, Alkene Substitution, and Medium

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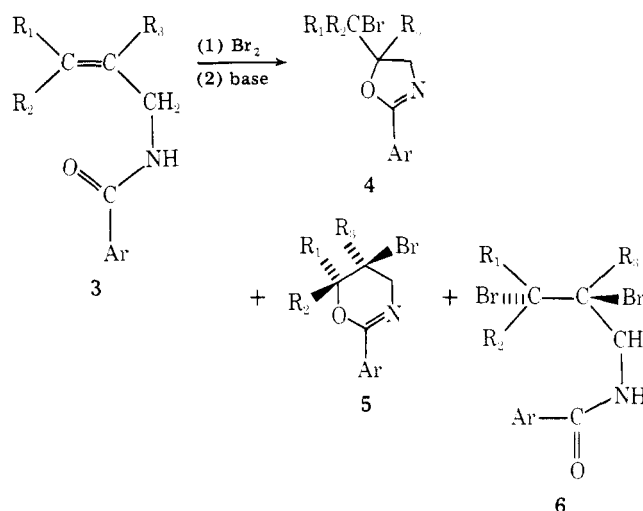
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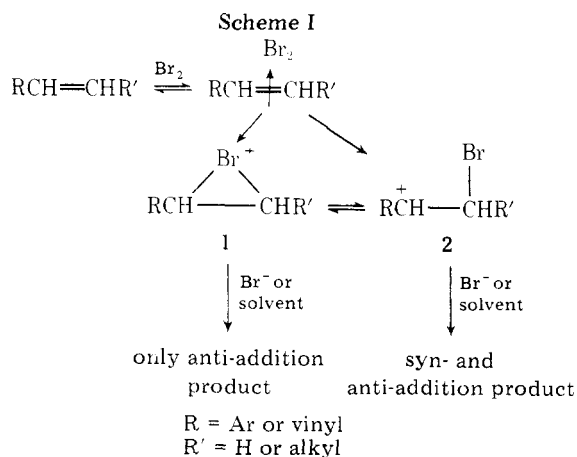
Halogenation of *N*-allylamine derivatives produces ring-closure products and addition products in varying amounts depending on the halogenating agent, the alkene structure, and the solvent. Concerted addition-cyclization does not occur in these systems when the alkene is activated by attached groups which aid in the delocalization of transition state charge. Instead, the results from the studies of these systems are best explained by invoking carbocation intermediates or carbocation-like product-forming steps. Equilibria between halonium ions and haloalkyl carbocations are probably not established in these reactions owing to the high reactivity of the carbocations in the presence of good nucleophiles. There remains the possibility that **3c-e**, like **3a** and **3b**, are brominated via a bromonium ion intermediate as the product-forming species. If this mechanism is operative, these reactions provide a rare example of fused mode cyclization in such circumstances.

Since first postulated by Roberts and Kimball,<sup>1</sup> cyclic bromonium ions have been considered important intermediates in the electrophilic bromination of most alkenes.<sup>2</sup> Evidence for ethylenebromonium ion intermediates and bromination mechanisms incorporating them seems well justified when the alkene is nonconjugated.<sup>3-10</sup> Conjugated alkenes such as styrene derivatives<sup>3,11</sup> and dienes<sup>12</sup> often behave differently.<sup>13,14</sup> The mechanistic change, which is revealed by the study of product stereochemistry and the application of linear free-energy relationships, arises because the resonance stabilized substituted  $\beta$ -bromoethyl cation **2** has an energy similar to that of its isomeric bromonium ion, Scheme I.

We began the present work with the goal of ascertaining whether or not ions **1** and **2** were both important product-forming intermediates. We chose to compare results of halogenation studies of the series of amides **3a-e** because of the neighboring amide group which should participate in these reactions thus aiding in assigning a structure to the intermediates. At the outset we assumed that there is a strong tendency of ring opening-ring closures of substances like bromonium ions to strongly prefer the spiro mode over fused mode cyclizations,<sup>15-19</sup> eq 1. Thus, one predicts that five-membered ring bromocyclization products would arise from



**3-10a**,  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{H}$ ;  $\text{Ar} = \text{phenyl}$   
**b**,  $\text{R}_1 = \text{R}_2 = \text{H}$ ;  $\text{R}_3 = \text{Me}$ ;  $\text{Ar} = \text{phenyl}$   
**c**,  $\text{R}_1 = \text{Me}$ ;  $\text{R}_2 = \text{R}_3 = \text{H}$ ;  $\text{Ar} = p\text{-nitrophenyl}$   
**d**,  $\text{R}_1 = \text{R}_2 = \text{Me}$ ;  $\text{R}_3 = \text{H}$ ;  $\text{Ar} = p\text{-nitrophenyl}$   
**e**,  $\text{R}_1 = \text{Ph}$ ;  $\text{R}_2 = \text{R}_3 = \text{H}$ ;  $\text{Ar} = p\text{-nitrophenyl}$



**3a-e** when the substrates react via amide attack on the bromonium ion, e.g., structure **7**, eq 2. However, the favored carbocation intermediates from **3d** and **3e** should be the tertiary cation **8d** and the benzylic cation **8e**, respectively, and these would cyclize only to the six-membered rings **5d** and **5e**, respectively, eq 3.<sup>20</sup> We have also investigated the effect of the medium on these addition-cyclization reactions.

### Results and Discussion

The *p*-nitrobenzamides **3c-e** ( $\text{Ar} = p\text{-nitrophenyl}$ ) were prepared and brominated in acetic acid and in carbon tetrachloride giving bromocyclization products and dibromides.<sup>21</sup> In each case, these products were isolated and their structures determined by the use of elemental analysis, IR, NMR, and mass spectroscopy. The stereochemistry of the dibromides isolated from the bromination of **3c** and **3e** was consistent with