

Leone-Bay and P. L. Huesmann and enlightening discussions with Professor F. W. Fowler are greatly appreciated. The 200-MHz spectrometer used in this research was purchased by funds derived in part from an NSF grant.

**Registry No.** ( $\pm$ )-8 ( $R_2$  = dioxolane), 87420-64-2; ( $\pm$ )-8 ( $R_1$  = dioxolane), 87420-66-4; ( $\pm$ )-9en, 87371-63-9; 11, 87371-65-1; 12,

87371-64-0; 13, 87371-72-0; 14, 87371-67-3; 15, 87393-28-0; ( $\pm$ )-endo-16, 87371-68-4; ( $\pm$ )-exo-16, 87420-63-1; ( $\pm$ )-17, 87371-69-5; ( $\pm$ )-18, 87393-29-1; ( $\pm$ )-20, 87371-70-8; 24 ( $R^1$  = H;  $R''$  = *t*-Bu), 87393-27-9; ( $\pm$ )-26, 87371-71-9; ( $\pm$ )-27, 87420-65-3; 2-[(trichloroethoxy)carbonyl]-6-carbomethoxy-7-(1,1-(ethylenedioxy)ethyl)-2-azabicyclo[2.2.2]oct-5-ene, 87371-66-2; tryptophyl bromide, 55982-76-8; methyl vinyl ketone, 78-94-4; ethyl propiolate, 623-47-2; *tert*-butyl propiolate, 13831-03-3; methyl nicotinate, 93-60-7.

## Protonation of Anion Intermediates in Metal-Ammonia Reduction: 1,2- vs. 1,4-Dihydro Aromatic Products

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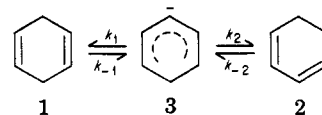
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The competition between 1,3-cyclohexadienes and 1,4-cyclohexadienes during metal-ammonia reduction has been examined. The former is usually regarded as a thermodynamic product and the latter as a kinetic product although, in actuality, little thermodynamic difference exists between these two isomers. 1,4-Cyclohexadiene was found to undergo proton abstraction with potassium or sodium amide in ammonia at  $-50^\circ\text{C}$  but not with lithium amide. Similarly, 1,3-cyclohexadiene reacts only with potassium amide and not with sodium or lithium amide. Consequences relating to the formation of conjugated and nonconjugated products during metal-ammonia reduction are discussed. The reaction of dihydronaphthalenes with various amides is also presented and again there is considerable variation in behavior. This has led to improved synthetic schemes for the selective production of 1,2-dihydro- and 1,4-dihydronaphthalenes as well as tetralins. Finally, protonation sites in pentadienyl type anions are considered.

The Birch reduction and related metal-ammonia processes have become important methods for the preparation of dienes and dihydro aromatics<sup>1</sup> (Figure 1). Benzene itself affords 1,4-cyclohexadiene (1), which is regarded as a kinetic product, whereas 1,3-cyclohexadiene (2) has been considered to be the thermodynamic product<sup>2,3</sup> since it is a conjugated diene. It has been suggested<sup>3</sup> that conjugated products may result under equilibrium conditions such as illustrated in Scheme I (regioselectivity is determined by protonation of the final monoanion in Figure 1). However, Dewar has pointed out<sup>4</sup> that 1,3-cyclohexadiene cannot exist in an unstrained, planar conformation, and, in fact, experimental results<sup>5,6</sup> support little difference in thermodynamic stability between these dienes. We will show that thermodynamic arguments<sup>3</sup> may be unnecessary to explain conjugated products in light of additional information regarding the kinetics of these processes.

Protonation of the cyclohexadienyl anion (3) occurs most readily at the 3-position to produce 1 although a small amount ( $\sim 1\%$ ) of 2 is also formed (i.e.,  $k_1 \gg k_2$ ). It becomes obvious from Scheme I that the relative amounts of 1 and 2 will be greatly affected by the values of  $k_{-1}$  and  $k_{-2}$ . For example, if protonation to form one isomer is reversible, and the other not, buildup of the latter may

Scheme I



occur. It is enlightening to consider the possible pathways 1-3. With pathway 1, an equilibrium exists and the ratio

$$\text{nonconjugated product} \rightleftharpoons \text{anion} \rightleftharpoons \text{conjugated product} \quad (1)$$

$$\text{nonconjugated product} \rightleftharpoons \text{anion} \rightarrow \text{conjugated product} \quad (2)$$

$$\text{nonconjugated product} \leftarrow \text{anion} \rightarrow \text{conjugated product} \quad (3)$$

of products will indeed be dictated by the relative thermodynamic stabilities. In contrast, path 3 will produce products that simply reflect the relative protonation rates ( $k_1/k_2$  in Scheme I). Path 2, however, will provide the conjugated product exclusively. As we will show below, it is, in fact, paths 2 and 3 that are most important for metal-ammonia reduction, and attention must be focused on the reverse (deprotonation) steps.

We have observed a considerable variation in the behavior of 1 and 2 toward deprotonation by amide in ammonia.<sup>8</sup> Moreover, we have noted substantial differences between lithium, sodium, and potassium as counterions<sup>8b</sup> (see Table I).  $\text{KNH}_2$  is most effective at proton ab-

(1) (a) Birch, A. J. *Q. Rev.* 1950, 4, 69. (b) Birch, A. J.; Subba Rao, G. "Advances in Organic Chemistry, Methods and Results"; Taylor, E. C., Ed.; Wiley-Interscience: New York, 1972. (c) Harvey, R. G. *Synthesis* 1970, 161. (d) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; pp 150-151.

(2) For example, see Harris, J. M.; Wamser, C. C. "Fundamentals of Organic Reaction Mechanisms"; Wiley: New York, 1976; p 292.

(3) Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* 1981, 103, 284.

(4) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.





(5) Bates, R. B.; Carnighan, R. H.; Staples, C. E. *J. Am. Chem. Soc.* 1963, 85, 3032.

(6) Turner, R. B.; Mallon, B. J.; Tichy, M.; Doering, W. von E.; Roth, W. R.; Schroder, G. *J. Am. Chem. Soc.* 1973, 95, 8605.

(7) A difference in reactivity between the 1,3- and 1,4-dienes toward *n*-BuLi/THF has been noted. Bates, R. B.; Gosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* 1967, 199.

(8) The nature of ion pairing may have profound effect on proton-transfer reactions. For a general discussion, see "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley-Interscience: New York, 1974 (especially Vol. 2, Chapter 2 by Szwarc, M.; Streitwieser, A.; Mowery, P. C.).

Table I. Reaction of Cyclohexadienes with Amide in Ammonia<sup>a</sup>

diene	amide	temp, °C	% composition <sup>b</sup>			
						
1	KNH <sub>2</sub>	-50	1	91	1	7
1	NaNH <sub>2</sub>	-50	1	84	4	11
1	LiNH <sub>2</sub>	-50		96 <sup>c</sup>		4 <sup>d</sup>
2	KNH <sub>2</sub>	-50 (-60)	3 (65)	43 (6)	26 (15)	31 (14)
2	NaNH <sub>2</sub>	-50	86		7	7
2	LiNH <sub>2</sub>	-50	100 <sup>c</sup>			

<sup>a</sup> Diene (8 mmol) reacted with excess amide (15.3 mmol) in 12 mL of NH<sub>3</sub> for 3 h followed by addition of aqueous NH<sub>4</sub>Cl. <sup>b</sup> By VPC on a 10% OV-101 column (fid). <sup>c</sup> Lack of color change and failure of reaction with acetone or methyl iodide indicate that no anion had formed. <sup>d</sup> Present in starting material.

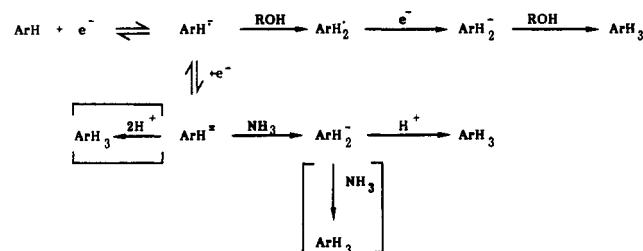


Figure 1. Birch reduction (upper pathway, benzene and derivatives) and related metal-ammonia reduction (lower pathway, polynuclear compounds; less common routes in parentheses). Proton source added later indicated by H<sup>+</sup>.

straction, although reaction with 2 becomes slow at temperatures below -60 °C. Neither 1 or 2 react to any appreciable extent with LiNH<sub>2</sub> in NH<sub>3</sub> at -50 °C.<sup>7</sup> Although NaNH<sub>2</sub> is effective with 1, reaction with 2 is rather slow (~15% after 3 h at -50 °C). These results are particularly significant since most metal-ammonia reductions are carried out with lithium or sodium, not potassium. We would anticipate that, with lithium and sodium, conditions could exist where  $k_1$ ,  $k_2$ , and  $k_{-1}$  have values much greater than  $k_{-2}$  (see Scheme I), and these circumstances would indeed produce 2 but on kinetic grounds, not thermodynamics.

Olah et al.<sup>9</sup> have also reported the generation of the cyclohexadienyl anion from either 1 or 2 with KND<sub>2</sub>/ND<sub>3</sub> and observed decomposition of 3 into benzene at temperatures above -40 °C. We confirm the presence of benzene and also observed the formation of cyclohexene that is substantial under some conditions. This is consistent with an earlier report that indicates both benzene and cyclohexene formation from anion 3 and cyclohexadiene isomers in Me<sub>2</sub>SO at 55 °C.<sup>10a</sup> The fact that we observe more benzene than cyclohexene in some cases indicates that the presence of 1,3-cyclohexadiene as an acceptor is not a requirement for hydride loss<sup>10</sup> although it certainly appears to accelerate it.

In the typical Birch reduction of benzene and many of its derivatives (Figure 1, upper pathway), amide ion is not present due to the addition of alcohols, and alkoxides will not lead to deprotonation of the products. This corresponds to pathway 3, and conjugated products are generally not observed. Hence the consequences of our observations noted above will not be important in this case but will become apparent under conditions where an anion

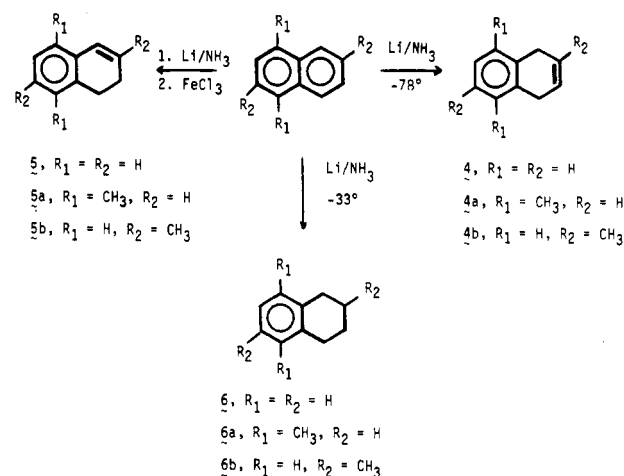
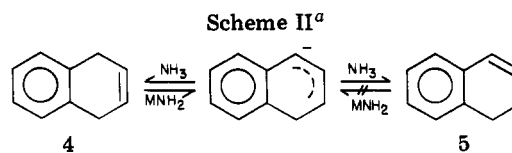


Figure 2. Selected reduction of naphthalene and methylated naphthalenes.



<sup>a</sup> M = Li, Na.

is present that may be reversibly protonated by ammonia, and under these circumstances, reduction reactions may be quite sensitive to metal and temperature effects. Naphthalene serves as a case in point. Naphthalene reacts with Li or Na in ammonia to form a dianion that is protonated by ammonia, resulting in a monoanion.<sup>11</sup> At higher temperatures the monoanion itself is slowly protonated by ammonia (see Figure 1) so that reduction at the boiling point of ammonia (-33 °C) affords a mixture of products.<sup>12,13</sup> To better understand these processes, we examined the behavior of 1,4-dihydronaphthalene (4) and 1,2-dihydronaphthalene (5) with amide in ammonia and the results are presented in Table II. Thus 4 reacts smoothly with LiNH<sub>2</sub>, NaNH<sub>2</sub>, and KNH<sub>2</sub> at -78 °C, whereas 5 reacts only with KNH<sub>2</sub> (as evidenced by success or failure of reaction with methyl iodide). The conversion of 4 to 5 under certain conditions may be understood in terms of pathway 2. Protonation of the dihydronaphthalene monoanion affords 4 and 1-2% 5.<sup>11</sup> Hence at -33 °C (especially with LiNH<sub>2</sub>) an equilibrium is set up

(9) Olah, G. A.; Asensio, G.; Mayr, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1978, 100, 4347.

(10) (a) Paul, R.; Tchelitcheff, S. C. R. *Hebd. Seances Acad. Sci.* 1954, 239, 1222. (b) Hofman, J. E.; Argabright, P. A.; Schreishheim, A. *Tetrahedron Lett.* 1964, 1005. (c) Kloosterziel, H.; Van Drunen, J. A. A. *Recl. Trav. Chim. Pays-Bas* 1970, 89, 368.

(11) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* 1978, 43, 4283.

(12) The presence of naphthalene in these previous cases as well as the reactions herein is due to loss of hydride from the monoanion. This also occurs more readily at higher temperatures (see Table II).

(13) The lithium salt is protonated more readily than the sodium salt.

Table II. Reaction of Isomeric Dihydronaphthalenes with Amide in Ammonia<sup>a</sup>

diene	amide	temp, °C	% composition <sup>b</sup>			
			6	4	5	8
4	LiNH <sub>2</sub>	-33	3	2	93	2
4	LiNH <sub>2</sub>	-78	1	90 <sup>c</sup>	1	8
4	NaNH <sub>2</sub>	-33	2	69 <sup>c</sup>	14	15
4	NaNH <sub>2</sub>	-78	2	91 <sup>c</sup>	2	5
4	KNH <sub>2</sub>	-33	2	1	82	15
5	KNH <sub>2</sub>	-78		80	1	9
5	NaNH <sub>2</sub> or LiNH <sub>2</sub>	-78			100 <sup>d</sup>	

<sup>a</sup> Reaction time of 30 min. <sup>b</sup> By VPC on a 10% OV-101 column. <sup>c</sup> The fact that an anion had, in fact, been formed was confirmed by reaction with methyl iodide. <sup>d</sup> Recovered starting material. Anion was not formed under these conditions.

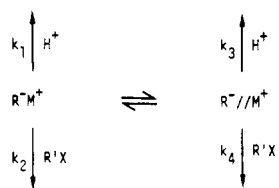


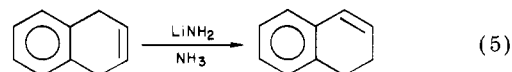
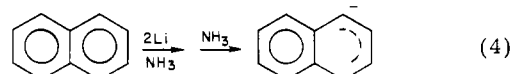
Figure 3. Alkylation and protonation of ion pairs.

between this anion and 4 (Scheme II). However, since neither LiNH<sub>2</sub> or NaNH<sub>2</sub> will abstract a proton from 5 under these conditions, it eventually becomes the exclusive product. If this process occurs under reduction conditions (i.e., free metal present), the conjugated diene 5 will be easily reduced. Hence metal-ammonia reduction of naphthalenes at -33 °C (particularly with lithium) should provide considerable overreduction, and this is what is actually observed.<sup>11,14</sup>

These results allowed us to devise a simple synthetic scheme for the selective production of tetralins, 1,2- or 1,4-dihydronaphthalenes (Table III). Thus, treatment of naphthalenes with lithium at -78 °C affords excellent yields of 1,4-dihydronaphthalenes, since the monoanion is resistant to protonation under these conditions (Figure 2). Knowing that the protonation/deprotonation mechanism taking place at -33 °C with lithium converts the monoanion to neutral 1,2-dihydronaphthalene, reduction with excess lithium at this temperature affords tetralin in 98% yield. With 1,4-dimethyl- and 2,6-dimethylnaphthalene, however, longer reaction periods were necessary for complete conversion. This is due to slow isomerization of 4a and 4b to the conjugated isomers 5a and 5b, which can be attributed to steric hindrance of proton abstraction from 4a and 4b by amide due to the presence of an adjacent methyl group. This could be demonstrated in separate experiments beginning with 4a (or 4b) wherein several hours were required to effect the isomerization process as opposed to 15–30 min for the parent compound. We should also note that the formation of 5b is accompanied by 10–15% of the other possible isomer, 2,6-dimethyl-1,2-dihydronaphthalene. In any event, this procedure should provide an excellent one-step route to a variety of tetralins, avoiding multistep, ring closure type procedures.

Since we knew that reaction of naphthalene(s) with Li at -78 °C results in an anion resistant to protonation (eq 4), and that LiNH<sub>2</sub> causes isomerization to the conjugated

isomer (eq 5), and FeCl<sub>3</sub> causes the conversion of lithium metal to its salt (eq 6), we were able to effect the smooth










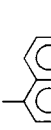
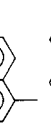
conversion of naphthalene and methylated naphthalenes to their 1,2-dihydro structures. This is accomplished by reaction of the naphthalene with Li/NH<sub>3</sub> at -78 °C for 30 min, followed by the addition of FeCl<sub>3</sub> and allowing the reaction mixture to warm to -33 °C. This method produced good to excellent yields of the 1,2-dihydro compounds, and, of course, since there is no metal present during the isomerization step, overreduction is minimized.

Our results indicate potential problems with investigations concerning protonation sites of anions in amide/ammonia systems. As we have demonstrated, protonation of pentadienyl type anions by ammonia may take place, providing a nonconjugated and a conjugated isomer, and buildup of the latter may take place due to slow proton abstraction by amide. This process appears most common in the order LiNH<sub>2</sub> > NaNH<sub>2</sub> > KNH<sub>2</sub>, and the use of potassium amide at low temperatures (-78 °C) appears to be the most reliable method for the efficient generation of anions not protonated by ammonia (as deduced from good yields in reverse alkylations). We were particularly intrigued with an earlier study<sup>15</sup> involving the allylbenzene anion, since an unusually large amount of conjugated product was produced when ammonia was used as a solvent. It was reported that the reaction of amylsodium/pentane with allylbenzene followed by protonation gave a higher proportion of the nonconjugated isomer (74:26), whereas a similar process with NaNH<sub>2</sub>/NH<sub>3</sub> afforded the conjugated propenylbenzene (cis and trans) almost exclusively (93%). It seemed likely to us that the protonation/isomerization process described herein was responsible for the predominance of the conjugated isomer in ammonia, and so we were quite surprised to learn that treatment of allylbenzene with KNH<sub>2</sub>/NH<sub>3</sub> followed by methylation produces the nonconjugated isomer 8, whereas protonation affords 1-phenylpropane (9). We wanted to

(14) The intermediacy of 1,2-dihydronaphthalene in tetralin formation has been recognized previously by Birch.<sup>1a</sup>

(15) (a) Mixer, R. Y.; Young, G. *J. Am. Chem. Soc.* 1956, 78, 3379. (b) Herbrandson, H. F.; Mooney, D. S. *Ibid.* 1957, 79, 5809.

Table III. Lithium-Ammonia Reduction of Naphthalene and Methylated Naphthalenes

substrate	method	Li, equiv	time, h	substn	99	1	98	94	1	4	11	93	5	2	91
	A	2.5	1/2	R <sub>1</sub> = R <sub>2</sub> = H	99	1	1	1	1	4	11	93	5	2	91
	B	1.25	3/4	R <sub>1</sub> = R <sub>2</sub> = H	1	98	98	94	1	4	11	93	5	2	91
	C	1.25	1/3	R <sub>1</sub> = R <sub>2</sub> = H	3	94	94	94	1	4	11	93	5	2	91
	A	3.8	2 1/2	R <sub>1</sub> = CH <sub>3</sub> , R <sub>2</sub> = H	95	1	1	1	1	4	11	93	5	2	91
	B	1.25	2 1/2	R <sub>1</sub> = CH <sub>3</sub> , R <sub>2</sub> = H	4	1	1	1	1	4	11	93	5	2	91
	C	1.25	1/3	R <sub>1</sub> = CH <sub>3</sub> , R <sub>2</sub> = H	2	1	1	1	1	4	11	93	5	2	91
	A	5.0	2 1/2	R <sub>1</sub> = H, R <sub>2</sub> = CH <sub>3</sub>	94	1	1	1	1	4	11	93	5	2	91
	B	1.25	2 1/2	R <sub>1</sub> = H, R <sub>2</sub> = CH <sub>3</sub>	8	1	1	1	1	4	11	93	5	2	91
	C	1.25	1/3	R <sub>1</sub> = H, R <sub>2</sub> = CH <sub>3</sub>	8	1	1	1	1	4	11	93	5	2	91

<sup>a</sup> GLC values, corrected with internal standards. Difference between product total and 100% represents unreacted starting material.

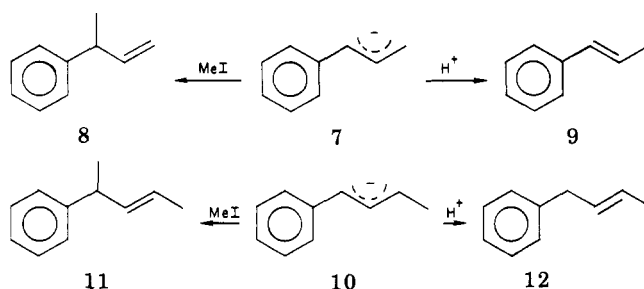
Table IV. Protonation and Alkylation of Pentadienyl Type Anions

diene	base	solvent	quench	ratio of products		ref
				conjugated	nonconjugated	
1,4-cyclohexadiene	<i>n</i> -BuLi	THF	<i>n</i> -BuBr	25	75	23
1,4-cyclohexadiene	KNH <sub>2</sub>	NH <sub>3</sub> <sup>a</sup>	H <sub>2</sub> O	1	99	<i>d</i>
3,3-dimethyl-1,4-cyclohexadiene	<i>n</i> -BuLi	THF	H <sub>2</sub> O	40	60	8
1,4-dihydronaphthalene	Na <sup>b</sup>	THF	H <sub>2</sub> O	1	100	24
1,4-dihydronaphthalene	KNH <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O	1-2	98-99	<i>d</i>
1,4-dihydronaphthalene	Na <sup>b</sup>	NH <sub>3</sub>	MeBr		100	11, <i>d</i>
allylbenzene	Me(CH <sub>2</sub> ) <sub>4</sub>	pentane	H <sub>2</sub> O	26	74	15
allylbenzene	NaNH <sub>2</sub> <sup>d</sup> (KNH <sub>2</sub> ) <sup>e</sup>	NH <sub>3</sub>	H <sub>2</sub> O	93	7	15,
allylbenzene	NaNH <sub>2</sub> <sup>d</sup> (KNH <sub>2</sub> ) <sup>e</sup>	NH <sub>3</sub>	MeI	5	95	15, <i>d</i>
1-phenyl-2-butene	KNH <sub>2</sub>	NH <sub>3</sub> <sup>a</sup>	H <sub>2</sub> O	5	95	<i>d</i>
1-phenyl-2-butene	KNH <sub>2</sub>	NH <sub>3</sub> <sup>a</sup>	MeI	5	95	<i>d</i>

<sup>a</sup> Plus THF as a cosolvent. <sup>b</sup> Anion formed from electron addition to naphthalene followed by protonation of dianion.

<sup>c</sup> Normal and inverse quench give the same results. <sup>d</sup> This work. <sup>e</sup> The use of KNH<sub>2</sub> produced essentially identical results.

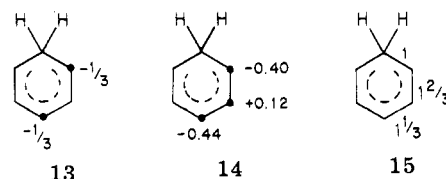
exclude the possibility that this latter conjugated product might be formed by some subsequent isomerization step. Hence, we first prepared a solution of the anion 7 and both methylated and protonated aliquots of the same reaction mixture. This did not change our results. Secondly, we subjected the nonconjugated 3-phenylpropene to the same reaction conditions but without KNH<sub>2</sub>, and no isomerization occurred.



Although the behavior of allylbenzene appears quite different from 1,4-dihydronaphthalene, this may simply be due to the fact that it does not serve as a very good model. To begin with, it has one less carbon, and Bates et al. have suggested that protonation should occur at the primary carbon for pentadienyl carbanions.<sup>16</sup> Secondly, the allyl anion is known to have a "w" conformation,<sup>17</sup> not the "u" shape necessary in the cyclic system. Thus we felt that 1-phenyl-2-butene might be a better model and, in fact, both protonation and methylation provide the nonconjugated isomers (>90%). Protonation results involving the competition between conjugated and nonconjugated products from pentadienyl type anions are presented in Table IV.

The question of protonation sites in delocalized anions has been approached in several ways,<sup>18</sup> and protonation of the cyclohexadienyl anion has become a classic example for two different methods. Charge density has been considered to be an important feature of this process with the notion that protonation should occur at the site of greatest

negative charge. The cyclohexadienyl system has received attention here<sup>18c,d</sup> since simple MO treatment predicts equal charge at three positions (13). However, more so-



phisticated treatment such as the Pople method indicates greatest charge density at the 3-position (14) and hence predicts protonation at this site resulting in the 1,4 product. A second approach has been the "principle of least motion".<sup>18a,19</sup> When average bond orders are considered for the three canonical forms of the cyclohexadienyl anion (15), it is apparent that protonation at the 3-position will produce the least change in bond order and hence the least change in atomic position and electron configuration.

The HSAB principle<sup>20</sup> may also be considered here, and we note that Murphy et al.<sup>21</sup> studied the methylation of 7 with a variety of leaving groups and reported that formation of the nonconjugated product 8 (90.5-98.6%) correlated well with the order of hardness of the leaving group (I < Br < Cl < SO<sub>4</sub> < OTs). However, we would like to point out that their yields of combined products (8 + 1-phenylbutene) ranged from 68% to 84% with the remainder attributed to dimethylation. Since they used sodium amide, our results herein suggest that dimethylation probably occurred by subsequent proton abstraction from 3-phenyl-1-butene (8) and not 1-phenyl-1-butene. In fact, when their data for MeI is corrected with the assumption that the remaining material balance (32%) comes from 8, then the nonconjugated "product" yield becomes 93.5%, which is very close to our results. This also minimizes the already small differences between leaving groups. At any rate, simple MO theory predicts no difference in charge density between C-1 and C-3 in 7<sup>22</sup> so that it is not readily apparent as to how HSAB could be applied in this case anyway.

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(20) For a discussion, see Klopman, G. In "Chemical Reactivity and Reaction Paths"; Klopman, G., ed.; Wiley: New York, 1974; p 55.

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These methods, however, do not take into account ion-pairing and solvation effects. As illustrated in Table IV, considerable differences may arise as a result of solvent changes, and alkylation sites do not always correspond to protonation sites. It has been suggested that one type of ion pair (e.g., contact ion pairs) might be most reactive toward protonation, whereas another type (e.g., solvent separated ion pairs) might alkylate fastest.<sup>18b</sup> Consider the system illustrated in Figure 3. Lets assume, for the sake of argument, that the contact ion pair  $R^-M^+$  alkylates and protonates at the same position but that this position is different from that of the solvent separated ion pair,  $R^-//M^+$  (which also protonates and alkylates at the same site). Then, if  $k_1$  were greater than  $k_3$  but  $k_4$  greater than  $k_3$ , alkylation and protonation would produce different isomers. In any event, in addition to charge control and orbital control, "solvation control" must also be considered an important possibility.

### Experimental Section

**General Procedures.** Product analysis was accomplished by <sup>1</sup>H NMR on a Varian EM-390 spectrometer and gas chromatography on Tracor 500 (fid) and Shimadzu GAPT (tc) instruments with 10% OV-1 columns. The yields of metal-ammonia reductions entered in Table I were determined by GLC, using internal standards. Products were purified by chromatography on silica gel.

**Preparation of Amide Solutions.** Ammonia was distilled through a barium oxide chamber and condensed under helium. The alkali metal was then added and, after dissolution was complete, was followed by a trace of FeCl<sub>3</sub>. Stirring was continued until the initial dark blue color gave way to a gray solution.

**Isomerization of Cyclohexadienes.** The diene (8 mmol) was added to an amide solution (ca. 12 mL) prepared as above, and the solution was stirred at -50 °C for 3 h (cf. ref 9). Aqueous NH<sub>4</sub>Cl was then added, and the products were isolated by ether partition. The results are summarized in Table I.

**Isomerization of Dihydronaphthalenes.** The dihydronaphthalene (1 g) in 10 mL of anhydrous THF (freshly distilled from benzophenone ketyl) was added to 40 mL of amide (1.5 equiv) solution prepared as above. Stirring was continued at the indicated temperature (Table II) for 30 min followed by the addition of aqueous ammonium chloride. Products were isolated by ether partition. The results are summarized in Table II.

**Alkylations.** Alkylations were performed by generating the anion according to the procedure immediately above followed by pumping the ammonia solution into cold methyl iodide in THF. Aqueous NH<sub>4</sub>Cl was then added followed by ether partition.

**Metal-Ammonia Reductions. Procedure A: 1,2,3,4-Tetrahydro Products.** The appropriate naphthalene (1 g) in 20 mL of THF was added to 40 mL of NH<sub>3</sub> at -33 °C, followed by the addition of lithium in pieces (the amount of lithium as well as reaction times are variable and are presented in Table III). The reaction mixture was quenched by pumping into an aqueous NH<sub>4</sub>Cl solution, followed by ether extraction.

**Procedure B: 1,2-Dihydro Products.** The initial steps are identical with Procedure A except that the reaction temperature was -78 °C. After stirring for 30 min, a trace of FeCl<sub>3</sub> was added and the temperature allowed to increase to reflux (ca. -33 °C) for the time indicated in Table III. Quenching was similar to above.

**Procedure C.** Reduction was carried out as above at -78 °C with the amounts of metal and reaction time indicated in Table III followed by the usual inverse quench into aqueous NH<sub>4</sub>Cl.

**1,2,3,4-Tetrahydro-, 1,2-dihydro-, and 1,4-dihydronaphthalene were prepared** from naphthalene by procedures A-C, respectively, and were identical with commercially available materials.

**5,8-Dimethyl-1,2,3,4-tetrahydronaphthalene (6a)**<sup>25</sup> was prepared from 1,4-dimethylnaphthalene in 95% GLC yield by procedure A: NMR (CCl<sub>4</sub>) δ 6.7 (s, 2 H, Ph), 2.5 (m, 4 H, Bz), 2.1 (s, 6 H, CH<sub>3</sub>), 1.75 (m, 4 H).

**2,6-Dimethyl-1,2,3,4-tetrahydronaphthalene (6b)**<sup>26</sup> was prepared from 2,6-dimethylnaphthalene in 94% GLC yield by procedure A: NMR (CCl<sub>4</sub>) δ 6.72 (s, 3 H, Ph), 2.65 and 2.2 (m, 4 H, Bz), 2.2 (s, 3 H, CH<sub>3</sub>), 1.72 (m, 2 H), 1.35 (m, 1 H), 1.0 (d, 3 H, CH<sub>3</sub>).

**3,7-Dimethyl-1,2-dihydronaphthalene (5b)**<sup>27</sup> was prepared from 2,6-dimethylnaphthalene in 86% GLC yield by procedure B: NMR<sup>28</sup> (CCl<sub>4</sub>) δ 6.72 (br s, 3 H, Ph), 6.07 (br s, 1 H, vinyl), 2.65 (m, 2 H, Bz), 2.2 (s, 3 H, CH<sub>3</sub>), 2.15 (m, 2 H, allylic), 1.8 (s, 3 H, CH<sub>3</sub>).

**5,8-Dimethyl-1,2-dihydronaphthalene (5a)**<sup>29</sup> was prepared from 1,4-dimethylnaphthalene in 82% GLC yield by procedure B: NMR (CCl<sub>4</sub>) δ 6.77 (s, 2 H, Ph), 6.7 (m, 1 H, vinyl), 6.0 (m, 1 H, vinyl), 2.6 (m, 2 H, Bz), 2.2 (s, 3 H, CH<sub>3</sub>), 2.15 (s, 3 H, CH<sub>3</sub>), 2.15 (m, 2 H, allylic).

**5,8-Dimethyl-1,4-dihydronaphthalene (4a)**<sup>30</sup> was prepared from 1,4-dimethylnaphthalene in 93% GLC yield by procedure C: NMR (CCl<sub>4</sub>) δ 6.75 (s, 2 H, Ph), 5.78 (br s, 2 H, vinyl), 3.07 (br s, 4 H, Bz), 2.1 (s, 6 H, CH<sub>3</sub>).

**2,6-Dimethyl-1,4-dihydronaphthalene (4b)**<sup>31</sup> was prepared from 2,6-dimethylnaphthalene in 91% GLC yield by procedure C: NMR (CCl<sub>4</sub>) δ 6.8 (m, 3 H, Ph), 5.5 (br s, 1 H, vinyl), 3.15 (m, 4 H, Bz), 2.12 (s, 3 H, CH<sub>3</sub>), 1.72 (s, 3 H, CH<sub>3</sub>).

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**Registry No.** 1, 628-41-1; 2, 592-57-4; 4, 612-17-9; 5, 447-53-0; KNH<sub>2</sub>, 17242-52-3; NaNH<sub>2</sub>, 7782-92-5; LiNH<sub>2</sub>, 7782-89-0; *n*-BuLi, 109-72-8; Na, 7440-23-5; Me(CH<sub>2</sub>)<sub>4</sub>Na, 1822-71-5; *n*-BuBr, 109-65-9; H<sub>2</sub>O, 7732-18-5; MeBr, 74-83-9; MeI, 74-88-4; naphthalene, 91-20-3; 1,4-dimethylnaphthalene, 571-58-4; 2,6-dimethylnaphthalene, 581-42-0; 3,3-dimethyl-1,4-cyclohexadiene, 35934-83-9; allylbenzene, 300-57-2; 1-phenyl-2-butene, 1560-06-1; 1,4-cyclohexadiene anion, 27900-34-1; 3,3-dimethyl-1,4-cyclohexadiene anion, 38095-46-4; 1,4-dihydronaphthalene anion, 67345-28-2; allylbenzene anion, 55648-04-9; 1-phenyl-2-butene anion, 12558-39-3.

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