chloride. The methylene chloride extracts were dried over MgSO₄, concentrated, and purified by preparative TLC. The major product (R_f = 0.68) isolated was a slightly impure sample, mp 73–75 °C, of 2-methoxy-1-naphthaldehyde (9a) whose ¹H NMR (CDCl₃) and IR (Nujol) spectra were identical with those of a known sample (Aldrich) of this aldehyde. There was no evidence for the formation of any 2a upon treatment of 8a with an equimolar amount of methoxide ion.

Formation of 8a from 2a in CD₃O⁻/CD₃OD. An amount of a 1.44 M solution of CD₃O⁻ in methanol-d_4 sufficient to give the desired concentration (0.03–0.05 M) of CD₃O⁻ was added to 3.0 mL of CD₃OD contained in a 1-cm cell in the thermostated cell compartment of a UV/visible spectrophotometer. After the solution had reached thermal equilibrium, a 25-μL aliquot of a 0.009 16 M stock solution of 2a in CD₃OD was added by micro-

syringe with good mixing, and the absorbance of the solution was monitored as a function of time at 398 nm, the wavelength where 8a has its long-wavelength maximum. The absorbance at 398 nm first increased from 0.00 to about 0.06 and then declined. The maximum absorbance achieved was independent of [CD₃O⁻], but the time to reach the maximum was not, being shorter the higher the concentration of CD₃O⁻. The data were analyzed using the expressions[9] for the behavior of the concentration of an intermediate during two consecutive pseudo-first-order reactions.

Competition between Birch Reduction and Bond Cleavage in 1,2-Bis(4-methyl-1-naphthyl)ethane

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The reaction of 1,2-bis(4-methyl-1-naphthyl)ethane with Li, Na, and K in ammonia, THF, and HMPA, or mixtures thereof, has been examined with respect to the factors favoring Birch reduction of the aromatic ring and cleavage of the ethane carbon–carbon bond. Bond cleavage was found to increase relative to ring reduction in the series Li < Na < K and with the solvents NH₃ < THF < HMPA. However, the latter position of ammonia may be due to the necessarily restricted low-reaction temperature since only ring reduction was observed at temperatures at or below the boiling point of ammonia (−33 °C). A number of reduction and cleavage products were isolated and identified, and the mechanistic pathways for their formation is discussed.

A discussion of the cleavage of 1,2-diarylethanes by alkali metals, together with a historical perspective, has been provided recently by Grovenstein et al.[2] Pentaphenyl-

$$Ar_nCH_m–CH_{m'}Ar_{n'} \xrightarrow{M} Ar_nCH_m^- \, M^+ + Ar_{n'}CH_m^- \, M^+$$

ethane is cleaved[3] by potassium sand in ether[3] while 1,1,2,2-tetraphenylethane may be cleaved with Na–K alloy.[4] 1,2-Diphenylethane, on the other hand, is not reactive under these conditions.[5] As noted by Grovenstein,[2] the ease of cleavage increases with increasing number of aryl groups and/or increasing stabilization of the cleavage products (benzyl anions). This was also demonstrated by Eisch[6] who found 1,1,2,2- and 1,1,1,2-tetraphenylethane to be cleaved by lithium–biphenyl in THF while 1,1,1-triphenylethane was unreactive. However, 1,2-diphenylethane reacts with Na–K alloy in glyme–triglyme at 0 °C, and so solvaton effects are also expected to be important.[5] Grovenstein also points out that cleavage of 1,2-diarylethanes should increase throughout the series aryl = anthracene < naphthalene < benzene due to the corresponding decrease in π-resonance energies between the

radical anions (or dianions) and the respective arylmethyl anions.

Although the identification of the actual intermediate undergoing cleavage has been addressed in several investigations, radical anions have often been suggested without detailed kinetic evidence.[2] Szwarc et al.[8] studied the cleavage of 1,2-bis(1-naphthyl)ethane and found a rate law second order in the radical anion (at least for Li⁺, Na⁺, and K⁺). This is consistent with the dianion as the species
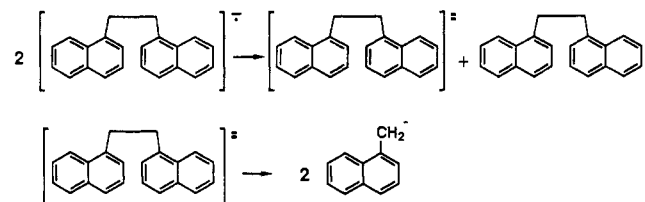
undergoing cleavage. Groverstein[2] studied a number of 1,2-diarylethanes and also concluded the dianion to be the responsible intermediate. Moreover, he suggested the importance of a stereoelectronic effect that involves the alignment of the p orbitals of the benzene rings with the sp³–sp³ bond so as to allow interaction with the σ orbitals (this also allows maximum overlap with the developing, benzylic anionic center).

Thus it appears that dianions are the likely intermediates undergoing cleavage in the treatment of 1,2-diarylethanes with alkali metals. However, radical anions appear to play an important role in the similar reaction of diarylmethanes where sp²–sp³ bonds are undergoing

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(2) Grovenstein, E., Jr.; Bhatti, A. M.; Quest, D. E.; Sengupta, D.; VanDerveer, D. *J. Am. Chem. Soc.* **1983**, *105*, 6290.
(3) Bachmann, W. E. *J. Am. Chem. Soc.* **1933**, *55*, 3005.
(4) Ziegler, K.; Thielmann, F. *Chem. Ber.* **1953**, *56*, 1740.
(5) Conant, J. B.; Garvey, B. S., Jr. *J. Am. Chem. Soc.* **1927**, *49*, 2599.
(6) Eisch, J. J. *J. Org. Chem.* **1963**, *28*, 707.
(7) Collins, C. J.; Hombach, H.-P.; Maxwell, B.; Woody, M. C.; Benjamin, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 851. Collins, C. J.; Hombach, H.-P.; Maxwell, B. E.; Benjamin, B. M.; McKamey, D. *J. Am. Chem. Soc.* **1981**, *103*, 1213.

(8) Lagendijk, A.; Szwarc, M. *J. Am. Chem. Soc.* **1971**, *93*, 5359.

**Table I. Major Reduction Products of 1,2-Bis(4-methyl-1-naphthyl)ethane[a]**

entry	Na,[b] mmol	NH₃:THF[c]	temp, °C	method[d]	% composition[e]		
					2	3	4
1	15	3:2	−78	A	1	98	−
2	15	2:3	−78	A	21	71	−
3	15	1:9	−78	A	56	34	−
4	5	2:3	−78	A	1	54	−
5	5	2:3	−78	B	4	47	−
6	15	1:9	−78	B	71	27	−
7	7.5	1:9	−78	B	86	8	−
8	10	2:3	−33	A	1	10[f]	84[f]
9	15	1:1	−33	A	2[f]	81[f]	
10	15	1:4	−33	A	−	45[f]	4[f]
11	15	1:9	−33	A	−	24[f]	10[f]
12	15	1:1 (NH₃/HMPA)	−33	A	2	81	−

[a] Reactions quenched after 1 h by pumping into aqueous ammonium chloride. [b] Millimoles metal per millimole hydrocarbon. [c] Total volume of solvent = 50 mL. [d] Method A is metal added last. Method B is hydrocarbon in THF added last to sodium/ammonium solution. [e] By GC; difference from 100% represents unreacted starting material unless otherwise indicated. [f] Difference from 100% represent unidentified reduction product(s) with molecular weight = 316 (by GC–MS).

scission. The interesting studies on diphenylmethanes by Collins and co-workers[9] and by Walsh[10] on 9,9-diphenylfluorene have provided considerable insight into these processes.

It is known that aromatics also react with alkali metals in liquid ammonia to produce ring reduction in a process known as Birch reduction.[11] It may appear that one important difference between this latter process and the one discussed above is the usual presence of alcohols in the Birch reduction. However, polynuclear compounds, like
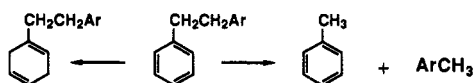
naphthalene, do not require alcohols as proton sources for ring reduction,[11] and so a comparison between the two processes would appear to be a matter of solvent. This prompted the present study aimed at an understanding of the possible competition between ring reduction and bond cleavage together with the factors that might favor one over the other.

1,2-Bis(4-methyl-1-naphthyl)ethane (1) was selected for study due to its ready availability by the reaction of 1-(bromomethyl)-4-methylnaphthalene with phenyllithium. As will be discussed below, the major compounds resulting from the ring reduction of 1 are dihydro product 2, tetrahydro product 3, and octahydro product 4, whereas reductive cleavage affords mainly 1,4-dimethylnaphthalene (5) together with its ring reduction products 6 and 7. These products are illustrated in Scheme I.

It was quickly learned that only ring reduction would be observed when ammonia was used as solvent or cosolvent. For example, treatment of 1 with an excess of sodium in NH₃/THF (3:2) at −78 °C for 1 h produced the tetrahydro isomer 3 in 98% GC yield (Table I). Interestingly, the use of less metal did not result in the production of the single ring reduction product 2 as might be expected, but rather afforded mixtures of 1 and 3; hence 1 has a propensity to reduce in both naphthalene units. Further insight may be gained from Scheme II.

After the initial electron addition, a second electron may add to produce either the bis(radical anion) ⁻•Np–Np•⁻ or the dianion Np–Np²⁻. In all likelihood these two species

Scheme I. Ring Reduction and Reductive Cleavage of 1,2-Bis(4-methyl-1-naphthyl)ethane
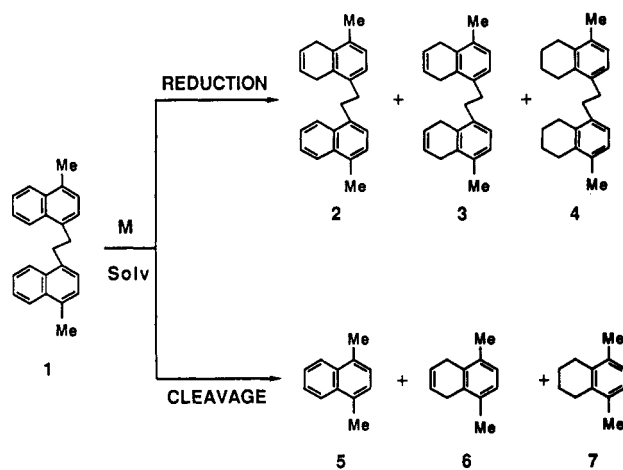
Scheme II
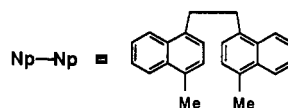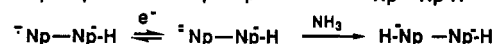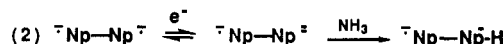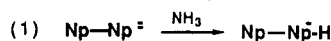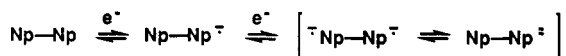
exist in equilibrium since the interconversion represents an "internal disproportionation", and such processes involving two radical anions with a dianion and a neutral molecule are well known.[12] One might expect the bis-(radical anion) to be favored since the half-wave potential for the addition of a second electron to a polynuclear aromatic is generally slightly more negative than the first.[11] However, solvation may play an important role, and moreover, the relative reactivities of these two species will be more important to product outcome than their relative concentrations.

At some point in the process, electron addition will produce an intermediate that is too basic to persist in

(9) Chambers, R. R., Jr.; Collins, C. J., Maxwell, B. E. *J. Org. Chem.* **1985**, *50*, 4960. See also ref 6.

(10) Walsh, T. D.; Megremis, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 3897. Walsh, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 1511.

(11) For a recent review, see: Rabideau, P. W. *Tetrahedron*, **1989**, *45*, 1579.

(12) Holy, N. *Chem. Rev.* **1974**, *74*, 243.

Table II. Major Ring Reduction plus Bond Cleavage Products of 1,2-Bis(4-methyl-1-naphthyl)ethane[a]

metal	solv	temp, °C	time, h	ring reduction			cleavage			unid[b]	ratio cleavage/ reduction
				2	3	4	5	6	7		
Li	HMPA	5	6	12	49	–	1	21	5	11 (–)	27:73
Li	HMPA	20	1	7	–	–	55	36	2	–	93:07
Na	HMPA	5	1	42	14	–	3	2	–	5 (–)	5:95
Na	HMPA	5	3	11	22	3	2	35	9	14 (–)	46:54
Na	HMPA	5	6	–	6	4	30	21	–	9 (30)	81:19
Na	HMPA	20	1	–	–	–	38	37	14	– (11)	100:0
Na	HMPA	20	3	–	–	–	1	26	28	– (44)	100:0
Na	THF	–30	6	13	1	–	–	–	–	–	0:100
Na	THF	5	6	19	1	–	44	–	–	–	44:56
Na	THF	20	6	–	–	–	68	7	–	– (25)	100:0
Na	THF	20	3	–	4	–	72	2	–	– (17)	91:09
Na	THF	20	1	12	1	–	21	–	–	–	21:79
K	THF	–33	6	53	–	–	4	–	–	–	4:96
K	THF	5	6	10	–	–	85	2	–	–	87:13
Li	THF	5	6	22	3	–	29	–	–	–	29:71
Na	THF/HMPA[c]	20	1	34	5	–	1	–	–	6 (–)	0:100
Na	THF/HMPA[c]	20	6	–	–	–	–	2	73	– (25)	100:0
Na	THF/HMPA[c]	5	6	20	27	12	2	18	3	16 (–)	23:77
Na	THF/HMPA[d]	–33	6	22	3	2	–	–	–	–	0:100

[a] By GC; difference from 100% represents recovered starting material. [b] Unidentified products assigned as ring reduction or (cleavage) based on GC-MS mol wt range. [c] 1:1 ratio. [d] 1:2 ratio.

ammonia. For example ⁻•Np–Np²⁻ is expected to be protonated by ammonia to produce [⁻•Np–Np–H]⁻ which could, in turn, add an electron to form the trianion [²⁻Np–Np–H]⁻, which would be protonated by ammonia to furnish ⁻[H–Np–Np–H]⁻. This latter dianion, 8 (one of
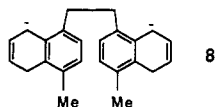
three possible isomers shown), is expected to be stable in ammonia for normal reaction periods (1 h or less) provided the temperature is kept low (–78 °C). As indicated in Table I, quenching at this stage produces 3 almost quantitatively.

If the reaction is run at higher temperature (–33 °C), the dianion 8 can also be protonated by ammonia, and this sets up a protonation/deprotonation equilibrium (i.e., NH₃/NH₂⁻) which isomerizes the nonconjugated double bonds in 3 to their conjugated counterparts (three isomers possible).[13] In the presence of excess metal, the conjugated double bonds are easily reduced, and so this provides a good method for the production of 4; that is, reduction at –33 °C with excess metal (Table I).

The formation of 2 in good yield (Table I, entry 7) is especially interesting since this compound was elusive in an earlier study where only the amount of metal and temperature were varied.[14] However, when sensitivity to solvent mixtures was examined, it was learned that 2 begins to appear as a significant product as the ratio of THF increases provided the temperature is kept low (Table I, entries 3, 6, and 7). These results are consistent with the bis(radical anion) as the principal intermediate, and there are two factors that may responsible: (1) ⁻•Np–Np•⁻ may now be favored over Np–Np²⁻, and (2) ⁻•Np–Np•⁻ may be resistant to the addition of a third electron. However, it is not clear how this explanation takes the order of addition into account: some improvement in the yield of 2 was observed when the hydrocarbon was added last (method B, Table I).

We note the complete absence of any cleavage products in Table I even when THF or HMPA were used as co-solvents in substantial amounts relative to the ammonia. However, when ammonia was omitted altogether, reductive cleavage did take place. As indicated in Table II, the reaction of 1 with 15 mmol of sodium in HMPA at room temperature for 1 h resulted in complete conversion to cleavage products 5 (38%), 6 (37%), and 7 (14%), plus 11% of unidentified products (but cleavage products by GC/MS molecular weights). Reduction in the amount of metal to 4 mmol, while decreasing the overall extent of reaction to 57%, produced a significant change in the ratio of cleavage to ring reduction (from 100:0 to 16:84). However, lowering the temperature to 5 °C had an even greater effect since the cleavage products were lowered to 5%. It is also intersting to note that in contrast to the ammonia studies, 2 is now the predominant ring reduction product. However, under otherwise similar conditions (Table II, entries 5, 6, and 7), extension of the reaction period to 3 and 6 h leads to an increase in cleavage over ring reduction, and an increase in 3 over 2 (i.e., two rings reduced).

A question arises concerning the production of 3 in aprotic solvents. Is it being formed by the addition of more than two electrons to 1 (e.g., a tetraanion) or does it result from a second reduction of 2 during the quenching process? (As described previously,[15] a reverse quench has been used to minimize effects from the latter possibility). The observation that 3 builds up with time and the fact that the 2:3 ratio is not constant with time would seem to argue against its formation during the quench. On the other hand, the production of 3 varies inversely with the expected rates of metal destruction with aqueous solutions (K > Na > Li), and so it would not be prudent to rule out this pathway.

In any event, the following conclusions about conditions affecting the competition between cleavage and ring reduction can be drawn: (1) A reduction in temperature from room temperature to 5 °C to –33 °C produces a complete reversal from 100% cleavage and no ring reduction to 100% ring reduction. (2) Cleavage goes from the major pathway (87%) to the minor pathway (29%) in the series K, Na, Li (in THF for 6 h at 5 °C). (3) Under comparable conditions (Na, 6 h, 5 °C), 81% cleavage is observed in HMPA, but only 44% in THF (curiously, even less in a THF/HMPA mixture). Hence elevated temperatures with

(13) Rabideau, P. W.; Huser, D. L. *J. Org. Chem.* 1983, 48, 4266.
(14) Rabideau, P. W.; Marcinow, Z. *Fuel* 1985, 64, 872.

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

K in HMPA are most likely to produce cleavage. The most important factor in avoiding cleavage, in cases where ring reduction may be the desired pathway, is temperature. Although ammonia may well be a superior solvent for ring reduction, all of the ammonia reactions herein were, due to the boiling point of ammonia, necessarily carried out at temperatures where only ring reduction is observed regardless of other conditions.

These results have important implications relating to the reductive alkylation of coal. Sternberg alkylation[16] of coals involves reaction with alkali metals in THF using naphthalene as a carrier, followed by alkylation of the "coal anion" with alkyl halide. The products of the reaction are much more soluble in common solvents (e.g., benzene and hexane) than the original coal, and this provides a method for the study of coal structure (i.e., spectroscopy on the fragments in solution). The breaking of labile carbon-oxygen and carbon–carbon bonds are considered to be important steps in the solubilization process.[16] However, Stock reported[16] that the reductive butylation of coal with Na in THF at 25 °C produced a product that was 37% soluble in THF whereas similar treatment in ammonia at −78 °C afforded 32% solubility in THF. From the results of the study herein, it is clear that carbon–carbon bond cleavage should not occur under the latter conditions for ArCH$_2$CH$_2$Ar where Ar is naphthalene or any polynuclear compound with a reduction potential lower than naphthalene. Since this includes most polynuclear compounds, we must conclude that carbon–carbon bond cleavage of the type discussed here does not play a major role in coal solubilization by reductive alkylation in ammonia.[17]

Experimental Section

General. Proton NMR were obtained at 90 MHz on a Varian EM-390 spectrometer. Mass spectra were determined on a HP 5988A GC–MS at an ionization potential of 30 eV. Gas chromatographic analyses were done on a Varian 3700 (fid; split

(16) For a review, see: Stock, L. M. In *Coal Science*; Gorbaty, M. L., Larson, J. W., Wender, I., Eds.; Academic Press: New York, 1982; Vol. 1.

(17) A significant solubilization of coal was accomplished by deprotonation with amide in ammonia followed by ethylation, a process that presumably does not involve the breaking of covalent bonds. Ignasiak, B.; Carson, D.; Gawlak, M. *Fuel* **1979**, *58*, 833.

capillary injector) using a 25 m × 0.25 mm OV-17 column. Microanalyses were performed by Galbraith Laboratories, Inc.

THF was distilled from benzophenone ketyl immediately prior to use, and HMPA was distilled from calcium hydride. 1,2-Bis(4-methyl-1-naphthyl)ethane was synthesized according to a previously described procedure.[14]

General Procedure for Metal–Ammonia Reductions. All reactions were carried out under a slight pressure of dry argon. **Method A.** The metal was added in pieces to a solution of dimer 1 (0.25 mmol) in 50 mL of ammonia/cosolvent (see Table I). After 1 h, the reaction was quenched by pumping the mixture (argon pressure) into saturated ammonium chloride solution.[15] **Method B.** Dimer 1 dissolved in THF was added dropwise (30 min) to a solution of sodium in ammonia (total volume of ammonia/THF = 50 mL; see Table I for further details). After 1 h, quenching was performed as described above for method A.

1-(4-Methyl-5,8-dihydro-1-naphthyl)-2-(4-methyl-1-naphthyl)ethane (2). An analytical sample was obtained by recrystallization of the crude product (entry 7, Table I) from methylene chloride: white needles; mp 176–178 °C; NMR (CDCl$_3$) δ 2.20 (s, 3 H), 2.67 (s, 3 H), 2.90 (m, 2 H), 3.30 (m, 6 H), 5.85 (br s, 2 H), 7.0 (s, 2 H), 7.2 (s, 2 H), 7.45 (m, 2 H), 8.0 (m, 2 H); GC–MS m/e 312 (M$^+$).

Anal. Calcd for C$_{24}$H$_{24}$: C, 92.26; H, 7.74. Found: C, 91.96; H, 7.81.

1,2-Bis(4-methyl-5,8-dihydro-1-naphthyl)ethane (3). An analytical sample was obtained as previously described:[14] mp 203–204 °C; NMR (CDCl$_3$) δ 2.20 (s, 6 H), 2.77 (s, 4 H), 3.36 (m, 8 H), 5.9 (br s, 4 H), 7.0 (s, 4 H); GC–MS m/e 314 (M$^+$).

Anal. Calcd for C$_{24}$H$_{26}$: C, 91.70; H, 8.30. Found: C, 91.34; H, 8.18.

1,2-Bis(4-methyl-5,6,7,8-tetrahydro-1-naphthyl)ethane (4). An analytical sample was isolated from the crude product (entry 8, Table I) by column chromatography followed by recrystallization from methanol: mp 139–140 °C; NMR (CDCl$_3$) δ 1.77 (m, 8 H), 2.17 (s, 3 H), 2.66 (m, 12 H), 6.93 (, 4 H); GC–MS m/e 318 (M$^+$).

Anal. Calcd for C$_{24}$H$_{30}$: C, 90.50; H, 9.50. Found: C, 90.35; H, 9.49.

Reductive Cleavage Reactions. These reactions (Table II) were performed by adding metal in pieces to a solution of dimer 1 (0.125 mmol) in 25 mL of specified solvent. After the reaction period indicated, the mixture was quenched by pumping into an ammonium chloride solution as above.[15] Cleavage products were identified by comparison of GC–MS with authentic samples.