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METAL-AMMONIA REDUCTION. IX. A NOVEL METAL EFFECT IN THE REDUCTIVE METHYLATION OF NAPHTHALENE[1]

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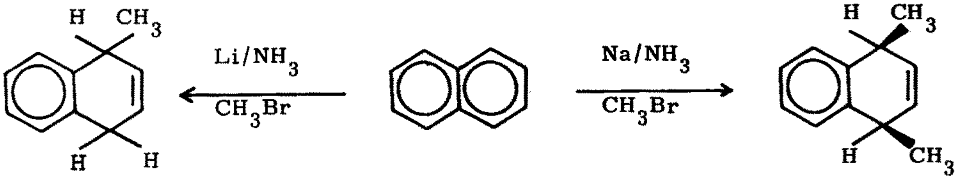
We wish to report a dramatic difference between sodium and lithium in the reductive methylation of naphthalene. Treatment of a solution of naphthalene (0.02M) in liquid ammonia-tetrahydrofuran at -78° with lithium (2.5 g-atom) followed by excess methyl bromide afforded 1-methyl-1,4-dihydronaphthalene (1)[2] in high yield (95%). In contrast, analogous reaction with sodium metal furnished the dimethyl homolog of 1, *cis*-1,4-dimethyl-1,4-dihydronaphthalene (2), as the major product. The latter reaction was reported earlier by Hückel and Wolfering[3] without mention of the stereochemistry[4]. Repetition of both lithium and sodium reactions under Hückel conditions (-78°, ether as cosolvent, 0.4M) led to formation of the same products in somewhat lower yields (Table 1). Product structure is clearly dependent primarily on the choice of metal.



1

2

Dianionic intermediates appear probable, since alkylation of the naphthalene radical anion is known to provide a complex mixture of alkylation and reduction products[5], including a large proportion of recovered naphthalene (not detected herein).

To determine whether monoprotonation of the dilithio dianion occurs prior or subsequent to alkylation, anthracene followed by methyl bromide was introduced into a solution of dilithionaphthalenide in ammonia. 9, 10-Dimethyl-9, 10-dihydroanthracene and naphthalene were the major products[6], indicative of electron transfer from the naphthalene dianion to anthracene, and clearcut evidence against protonation prior to methylation.

The observed metal effect is explicable as a consequence of: (1) the greater tendency of lithium than sodium to form solvent-separated rather than contact ion pairs in solution[7]; and (2) more facile protonation of the former by the medium[8]. In this hypothesis, the monolithio anion ($Li^+\|\bar{N}CH_3$) formed on initial alkylation of the dilithio dianion[9] ($2Li^+, N^=$) is solvent-separated and susceptible to protonation by ammonia to form 1 (eq. 2), whereas the corresponding monosodio anion exists as an intimate ion pair ($Na^+, \bar{N}CH_3$) able to persist in the medium sufficiently long to undergo a second alkylation, leading to formation of 2 (eq. 1).

$$\begin{tikzcd} 2M^+, N^= \arrow[r, "RX"] & M^+, \bar{N}R \arrow[r, "RX"] \arrow[d, shift right] & \underset{2}{NR_2} + MX & (1) \\ & MX + M^+\|\bar{N}R \arrow[u, shift right] \arrow[r, "NH_3"] & \underset{1}{HNR} + MNH_2 & (2) \end{tikzcd}$$

M^+ = Na, Li; N = naphthalene; R = CH_3.

Solvating agents more powerful than THF might be expected to further enhance the ratio of protonated to methylated products. In agreement, reductive methylation of naphthalene with sodium in ammonia-dimethoxyethane at -78° afforded 1 and 2 in approximately equal ratio. By contrast, analogous reaction with lithium in the presence of dimethoxyethane provided only 1 together with recovered naphthalene (3:1 by nmr). A temperature dependence was also apparent in that lower yields and more extensive reduction characterized reactions

Table 1. The Reductive Methylation of Naphthalene[a]

Hydrocarbon mmole	Metal, equiv	Ammonia, ml	Cosolvent, ml	% Yield[b]	
				1	**2**
5	Li, 3.5	150	THF, 75	95	2
5	Na, 3.5	150	THF, 75	0	93
30	Li, 2.5	60	Ether, 20	91	4
30	Na, 2.5	60	Ether, 20	0	85

a. A solution of the hydrocarbon in the cosolvent was added to the ammonia at -78° followed by the metal. After 10 min, methyl bromide was introduced into the solution through a column of activated silica gel; in the Li-THF reaction optimum results were obtained by addition of the metal in 5-6 pieces, a minute apart.

b. Yields were determined by glpc with 1-methylnaphthalene as internal standard on a 1/4" x 6' 10% DEGS column at 80° (**1** and **2**, 2 min; naphthalene, 3 min; 1-methylnaphthalene 3.5 min); the relative amounts of **1** and **2** were determined on a 1/4" x 6' polyphenyl ether column at 110° (**1**, 8.0 min; **2**, 8.7 min) under which conditions naphthalene was not separable from **2**.

conducted at higher temperature (-33°).

The foregoing results represent, to our knowledge, the first evidence for solvation as a major product determining factor for reactions conducted in liquid ammonia.

REFERENCES

1. Part X: R. G. Harvey and P. W. Rabideau, *Tetrahedron Lett.*, in press.
2. All new products gave satisfactory spectra and analysis.
3. W. Hückel and J. Wolfering, *Ann.*, *686*, 34 (1965).
4. The *cis* structure was assigned by Jones and Levin to whom the authors are indebted for nmr spectra of the authentic *cis* and *trans* compounds; cf M. Jones, Jr., and R. H. Levin, *J. Amer. Chem. Soc.*, *91*, 6411 (1969).
5. J. F. Garst; J. T. Barbas; F. E. Barton II, *ibid.*, *90*, 7159 (1968).
6. R. G. Harvey and L. Arzadon, *Tetrahedron*, *25*, 4887 (1969).
7. (a) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, *90*, 4654 (1968);
   (b) N. H. Velthorst and G. J. Hoijtink, *ibid.*, *87*, 4529 (1965).
8. Solvent-separated ion pairs, according to the available experimental evidence[7a], exhibit generally greater reactivity than contact ion pairs.
9. The dilithio dianion is represented as a contact ion pair $(2\mathrm{Li}^{+}, \mathrm{N}^{=})$, consistent with its demonstrated resistance to protonation by the medium. However, at this stage of our knowledge, it is not possible to conclusively rule out solvent-separated dianionic ion pairs $(2\mathrm{M}^{+}||\mathrm{N}^{=})$ resistant to protonation by ammonia under these conditions.