Communications to the Editor

Trimesitylborane Solutions. A Nonpolar Aprotic Medium for Dissolving Metal Reductions[1]

Sir:

We wish to report that trimesitylborane (TMB) can be used to mediate the transfer of electrons to organic systems in a variety of aprotic media. This allows a much greater range of reaction conditions than have been available with the highly polar hexamethylphosphoramide.[2]

Treatment of TMB with sodium has been observed to produce blue paramagnetic solutions which remained unchanged for extended periods of time.[8] Such radical anions suggested a novel method for the production of "solvated electrons" in an aprotic environment where the proton donor can be rigorously controlled. The mesityl group of TMB serves to impede dimerization of the radical anion as well as inhibit formation of quaternary boron compounds[9] and rapid reaction with alcohols. Radical anions such as sodium naphthalenide which have been used in reductive cyclizations[10] would be expected to undergo protonation rapidly by alcohols and may conceivably form carbon–carbon bonds with the substrate. Thus, TMB, lacking these complications, serves only as a conductor of electrons as demonstrated by its complete recovery from the reaction.

Reduction of $\Delta^{1,9}$-octalone-2 (**1**) was performed in a nitrogen atmosphere at room temperature with 5 g of TMB and 1 g of shaved sodium in 400 ml[11] of anhydrous 1,2-dimethoxyethane. Rapid stirring with a glass-coated magnetic bar produced a pervading blue solution after 30 min. When a deep blue-black color was obtained after 1 or 2 hr of additional stirring, a solution of 1 g of $\Delta^{1,9}$-octalone-2 in 1 g of *t*-butyl alcohol[12] was added dropwise over 15–30 min so as to maintain the color. The reaction was usually 90% complete after the addition but was often allowed to stir for 3–36 hr. After removing the surplus metal, the excess reagent was destroyed with absolute alcohol. Addition of 200 g of ice, 50 ml of methyl alcohol, and acidification precipitated the TMB which was recovered by filtration for reuse. The solid was washed with a 1:1 methanol–water solution and the product obtained in high yield (85–95%). Overreduction to the alcohol was negligible.

Under the above reaction conditions the product consisted of 70% *trans*-2-decalone and 30% *cis*-2-decalone.[13] This appears to be an equilibrium point for this reduction.[14] If a sample was removed immediately after the addition of the enone, 48–59% *cis*-2-decalone was found.

A study of the effects of changing the solvent or metal suggests the nature of the reaction intermediate. The equilibration results obtained after 24 hr are summarized in Tables I and II.

Table I. Effect of Solvent on $\Delta^{1,9}$-Octalone-2 TMB Reduction

Solvent[a]	% *cis*	% *trans*	% enone
Diethyl ether	42	58	34
Diglyme	29	71	4
Tetrahydrofuran	30	70	0
Glyme	30	70	0
n-Propylamine	25	75	32
Isopropylamine	31	69	16
Ammonia	12	88	14

[a] The metal was sodium; proton source *t*-BuOH.

Table II. Effect of Metal on $\Delta^{1,9}$-Octalone-2 TMB Reduction

Solvent	Metal	% *cis*	% *trans*	% enone
Glyme	Li[a]	57	43	12
	Na	30	70	0
	Ba	50	41	27
n-Propylamine	Li	51	49	7
	Na	25	75	32
	Ba	44	56	0
	Et_4N^+ [b]	42	58	48
Ammonia	Li	13	87	7
	Na	12	88	8
	Ba[c]	6	94	2
	Et_4N^+ [b–d]	9	91	44
	Na[c]	5	95	8

[a] A red solution, indicating ion pair association, was formed instead of the usual blue coloration. [b] Produced from barium and tetraethylammonium chloride: A. Coulombeau and R. Rassat, *Chem. Commun.*, 1587 (1968). [c] No TMB present. [d] Proton source was ethyl alcohol.

A possible reaction path is outlined in Scheme I. The initial intermediate **2** is radical-like because of the tight ion pair formed in the electron-transfer step. Equilibration of the radical leads to *cis*-**3** and *trans*-**2** forms. Kinetic formation of the *cis*-ion pair **4** would be expected from further reaction with additional boron radical anion. Steric hindrance in the electron-transfer step should be minimized in **3**. Although some of the *trans*-ion pair **5** may arise directly from reduction of **2**, much of **5** is derived from equilibration of **4**. Protona-

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[1] S. D. Darling, O. N. Devgan, and R. E. Cosgrove, presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[2] Solvated electrons have been used in solvents such as ammonia,[3] primary amines,[4] diamines,[5] and the aprotic solvent hexamethylphosphoramide.[6] Reductions of enones in these solvents are stereoselective but appear insensitive to changes in reagents and conditions.[7]

[3] A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950); H. S. Smith, "Organic Reactions in Liquid Ammonia," Interscience Publishers, Inc., New York, N. Y., 1963.

[4] R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Amer. Chem. Soc.*, **77**, 3230 (1955).

[5] L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891, (1957).

[6] G. Fraenkel, S. H. Ellis, and D. T. Dix, *J. Amer. Chem. Soc.*, **87**, 1406 (1965).

[7] (a) G. Stork and S. D. Darling, *ibid.*, **86**, 1761 (1964); (b) M. J. T. Robinson, *Tetrahedron*, **21**, 2475 (1965); (c) D. H. R. Barton and C. H. Robinson, *J. Chem. Soc.*, 3045 (1954); (d) M. Fetizon and J. Gore, *Tetrahedron Lett.*, 471 (1966).

[8] T. L. Chu and T. J. Weismann, *J. Amer. Chem. Soc.*, **78**, 23 (1956).

[9] H. C. Brown and V. H. Dodson, *ibid.*, **79**, 2302 (1957).

[10] C. D. Gutsche, I. Y. Tao, and J. Kozma, *J. Org. Chem.*, **32**, 1782 (1967).

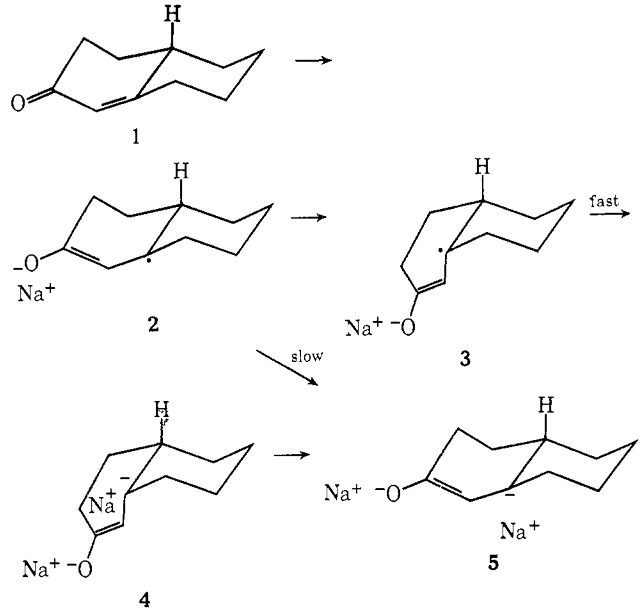
[11] Reactions conducted in 100 ml of solvent give the same results.

[12] Deuterium oxide, acetic acid, and other alcohols also had been used as a proton source.

[13] Analyzed with a 14 ft, 7% Apiezon L on Chromosorb G, glpc column.

[14] This ratio may be compared with a 1:4 *cis*:*trans* ratio obtained by S. K. Malhotra, D. F. Moakley, and F. Johnson, *J. Amer. Chem. Soc.*, **89**, 2794 (1967).

Scheme I



tion of intermediates **4** and **5** with retention leads to the product.[15]

Support for intermediate **4** is found in the early quenching of the reaction, the effect of diethyl ether, and the effect of lithium[16] (*i.e.*, association of radical ions has been observed in diethyl ether[17] and organolithium compounds are appreciably covalent[18]). Thus a *cis*-ion pair in these systems might be expected to equilibrate slowly (see Tables I and II).

The direct formation of an ion pair during the reduction is consistent with the theory of electron transfer between ions involving a bridge.[19] It is reasonable to assume that a contact bridge is required for electron transfer, as steric hindrance prevents the boron from approaching any carbon center. Moreover, the electron density around the boron radical anion probably does not extend into the solution as in the case of ammonia solvated electrons.[20]

The results of the metal–TMB reduction in liquid ammonia are especially interesting (see Table II). If the electrons were solvated by ammonia the products should be the same as those obtained in the absence of TMB.[21] Instead, more *cis*-2-decalone was produced, suggesting that the first formed intermediate had not dissociated completely before protonation.

In addition to the above conditions, the reduction was carried out in hexamethylphosphoramide with lithium. The usual extended reaction conditions gave a product which was 40% *cis*- and 60% *trans*-2-decalone. If the reaction was quenched with solid ammonium chloride, 68% *cis*-2-decalone was found. These results have interesting synthetic implications. Previously, *cis* product from **1** was available only through catalytic hydrogenation.[22]

Dissolving metal reductions in ammonia solution containing a high percentage of an ether cosolvent had previously been found to give dimeric products.[23] This side reaction is minimal in our system even with excess undissolved metal present.[24] The lack of dimer formation and relative stability of boron radical anion solutions containing proton donors should be conducive to the electrolytic generation of solvated electrons in these TMB systems.[25]

Besides the interesting stereochemical changes in the product from enone reduction, the successful use of the TMB reagent in various solvents (see Table I) is perhaps most noteworthy. Reactions involving electron transfer from metals can be studied in these many systems (*e.g.*, Wurtz coupling of 1-bromooctane occurred smoothly). Other reactions are being investigated, as well as intramolecular proton transfer, as a means of controlling stereochemistry.

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[19] J. Halpern, *Quart. Rev.* (London), **15**, 213 (1961); alkali metal bridging has been postulated in the Wurtz reaction: D. C. Ayres, "Carbanions in Synthesis," Oldbourne Press, London, 1966, p 16.

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[23] J. Fried and N. A. Abraham, *Tetrahedron Lett.*, 1879 (1964).

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[25] H. W. Sternburg, R. E. Markly, J. Wander, and D. M. Mohliner, *ibid.*, **89**, 186 (1967).

[26] National Institutes of Health Predoctoral Fellow, 1964–1968.

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Evidence for the Existence of the Trichlorosilyl Anion

Sir:

The trichlorosilyl anion has been postulated as an intermediate in a number of reactions involving trichlorosilane and tertiary amines.[1,2]

Although the concept of this anion proved very useful in suggesting experiments which have resulted in new methods of forming[3] carbon–silicon bonds, no definitive proof for its existence has ever been put forth. We wish to report physical evidence which substantiates the existence of the trichlorosilyl anion.

The nmr spectrum of a solution of trichlorosilane in acetonitrile shows a sharp singlet characteristic of the Cl_3SiH proton at δ 6.25. This singlet broadens considerably and diminishes in size as tri-*n*-propylamine is added. Simultaneously a new signal appears and grows in size at δ 11.03. The latter signal is not present

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