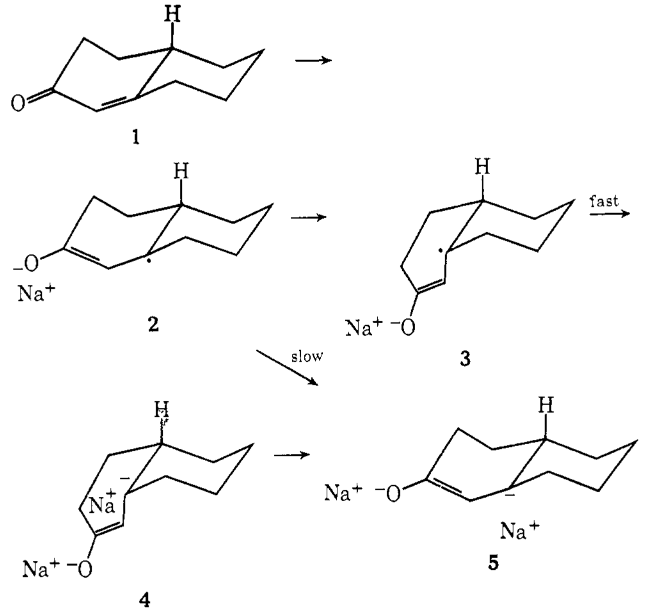
Scheme I



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.

Acknowledgment. This research was supported by Grant No. GM 15955 from the National Institutes of Health.

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[15] H. H. Glaze, C. M. Selman, A. L. Ball, Jr., and L. E. Bray, *J. Org. Chem.*, **34**, 641 (1969).

[16] Lithium may actually form an organometallic compound as suggested by D. H. R. Barton and G. A. Morrison, *Fortschr. Chem. Org. Naturstoffe*, **19**, 225 (1961); see ref 7c.

[17] N. Hirota in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, p 57.

[18] L. D. McKeever, R. Haack, M. A. Doran, and E. B. Baker, *J. Amer. Chem. Soc.*, **90**, 3244 (1968); M. T. Rogers and A. Young, *ibid.*, **68**, 2748 (1946).

[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.

[20] U. Schindewolf, *Angew. Chem. Intern. Ed. Engl.*, 7, 190 (1968).

[21] S. I. Weissman and H. van Willigen, *J. Amer. Chem. Soc.*, **87**, 2285 (1965).

[22] R. L. Augustine, *J. Org. Chem.*, **23**, 1853 (1958).

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

[24] Dimer formation does not always occur during reduction: J. A. Hoffman and J. T. Charles, *J. Amer. Chem. Soc.*, **90**, 6486 (1968).

[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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Received July 23, 1969

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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[1] S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Jap.*, **29**, 322 (1956).

[2] R. A. Benkeser and W. E. Smith, *J. Amer. Chem. Soc.*, **90**, 5307 (1968).

[3] R. A. Benkeser and W. E. Smith, *ibid.*, **91**, 1556 (1969); R. A. Benkeser, J. M. Gaul, and W. E. Smith, *ibid.*, **91**, 3666 (1969); R. A. Benkeser, K. M. Foley, J. M. Gaul, G. S. Li, and W. E. Smith, *ibid.*, **91**, 4578 (1969).

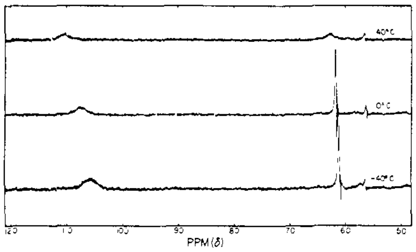

Figure 1. Nmr spectra at various temperatures. Solution contained 20 mmol of Cl_3SiH and 10 mmol of n-Pr_3N in 3 ml of acetonitrile. Spectra were recorded on a Varian A-60 spectrometer. The relative areas for the trichlorosilane and tripropylammonium ion peaks are essentially 1:1 at each of the temperatures indicated.

in the spectrum of *either* trichlorosilane *or* tri-*n*-propylamine in acetonitrile and can be assigned[4] to the tri-*n*-propylammonium ion.

When the nmr spectrum of a solution of trichlorosilane and tri-*n*-propylamine (2:1 ratio) in acetonitrile is run at progressively lower temperatures, the broad Cl_3SiH resonance becomes a sharp singlet (Figure 1).

The Forsen–Hoffman[5] saturation technique has been used to show that the broadening of the trichlorosilane proton is due to rapid exchange with the tri-*n*-propylammonium ion. It was not possible to observe exchange broadening of the N–H proton directly because of quadrupolar broadening already present. Irradiation of the N–H proton with a strong decoupling field caused the Cl_3SiH resonance to disappear (Figure 2). Likewise, irradiation of the trichlorosilane resonance greatly diminishes the N–H signal (Figure 2). When the frequency of the decoupler is shifted away from resonance (at the same power level) both signals rapidly return to normal intensity (Figure 2).

Taken as a composite, all the experimental data cited above are consistent with the equilibrium shown below and postulated previously.[1-3]

$$n\text{-}Pr_3N + HSiCl_3 \rightleftharpoons n\text{-}Pr_3NH^+ + SiCl_3^-$$

When equimolar amounts of tertiary amine and trichlorosilane are allowed to interact in acetonitrile, the nmr spectrum of this solution *shows no detectable signal in the SiH region* (indicating less than 2% SiH) which suggests that the above equilibrium lies far to the right. However, such a solution, despite its lack of an SiH signal, *does effect the hydrosilylation of phenylacetylene to give the usual diadduct.*[6]

The small peak at δ 5.65 (see Figures 1 and 2) has a chemical shift very close to that of pentachlorodisilane[7] ($Cl_3SiSiCl_2H$). If, indeed, the latter compound is responsible for this peak, its presence could be rationalized by the existence of an equilibrium like the following.

$$Cl_3Si^- + Cl_3SiH \rightleftharpoons Cl_3SiSiCl_2H + Cl^-$$

In any event, it is obvious that the material responsible for the peak at δ 5.65 is a minor component at best and is not participating in the rapid proton exchange.

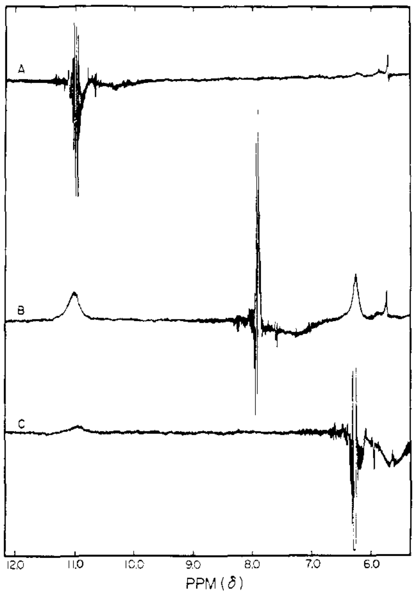

Figure 2. Decoupling experiments: (A) NH irradiated, (B) irradiation between NHa nd SiH, (C) SiH irradiated. Solutions contained 20 mmol of Cl_3SiH and 10 mmol of n-Pr_3N in 2 ml of acetonitrile. Spectra were recorded on a Varian T-60 spectrometer.

The normal nmr spectrum of a solution containing equimolar amounts of tri-*n*-propylammonium chloride and trichlorosilane in acetonitrile shows the typical sharp singlet characteristic of the Cl_3SiH[8] proton at δ 6.32 and the unperturbed spectrum of tri-*n*-propylammonium chloride. In addition the α-methylene protons of the salt show coupling (J = 5.6 Hz) with the N–H proton. Only when such a solution is heated to about 80° does one observe a peak broadening of the SiH signal comparable to that observed at 20° with an acetonitrile solution containing a 2:1 ratio of trichlorosilane to tri-*n*-propylamine.

The latter data strongly suggest that the dominant anion in the 2:1 trichlorosilane amine combination in acetonitrile is *not* Cl^-. In addition it is consistent with the concept that it is the free amine and not its hydrochloride which is the true catalyst in hydrosilylation reactions.

In conclusion it might be noted that an equimolar mixture of tri-*n*-propylamine and methyldichlorosilane in acetonitrile exhibits an unperturbed quartet for the SiH proton, centered at δ 5.63, and no absorption whatsoever downfield attributable to the tri-*n*-propylammonium ion. Consistent with this observation, we have not found such solutions to exhibit the chemistry of similar tertiary amine–trichlorosilane combinations.

Acknowledgment. The authors are grateful to the National Science Foundation whose financial assistance made this work possible.

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Received October 27, 1969

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[4] Tri-*n*-propylammonium chloride in acetonitrile gives a broad NH resonance at δ 11.48. The difference in chemical shift observed in this solution and the one containing Cl_3SiH-n-Pr_3N (11.03 *vs.* δ 11.48) is not unexpected in view of the difference in anions in the two cases.

[5] S. Forsen and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963).

[6] R. A. Benkeser, S. Dunny, and P. R. Jones, *J. Organometal. Chem.*, **4**, 338 (1965).

[7] This compound has a chemical shift of δ 5.71 in hexachlorodisilane.

[8] We deem it significant that hydrosilylation of phenylacetylene is *not* achieved over a 24-hr period by heating equimolar quantities of the latter to 57° with trichlorosilane in the presence of tri-*n*-butylammonium chloride.