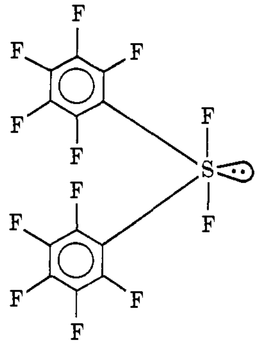
at −80° in its ^{19}F nmr spectrum at −19.4, +130, +133, +142, and +155 in the ratio 2:2:2:2:4. Such a spectrum could arise from **11** if the ortho fluorines



11

are nonequivalent, which is not unreasonable.[6] Further work on these compounds and related materials is in progress and details will be reported in a subsequent publication.

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(6) The difluorosulfurane **11** has also been prepared by W. A. Sheppard, Du Pont Central Research Department, from reaction of pentafluorophenyllithium and sulfur tetrafluoride. A detailed ^{19}F nmr study of compound **11** will be published by Sheppard, Ovenall, Meakin, Jesson, and Read of Du Pont. By private communication with Dr. Sheppard, our preliminary observations agree with their detailed studies.

Donald B. Denney,* Dorothy Z. Denney, Y. F. Hsu
Department of Chemistry, Rutgers University
New Brunswick, New Jersey 08903

Received March 3, 1973

Consecutive 1,2- and 1,4-Trimethylsilyl Shifts in the Anionic Rearrangement of 1,1-Bis(trimethylsilyl)-1,2-diphenylethane[1]

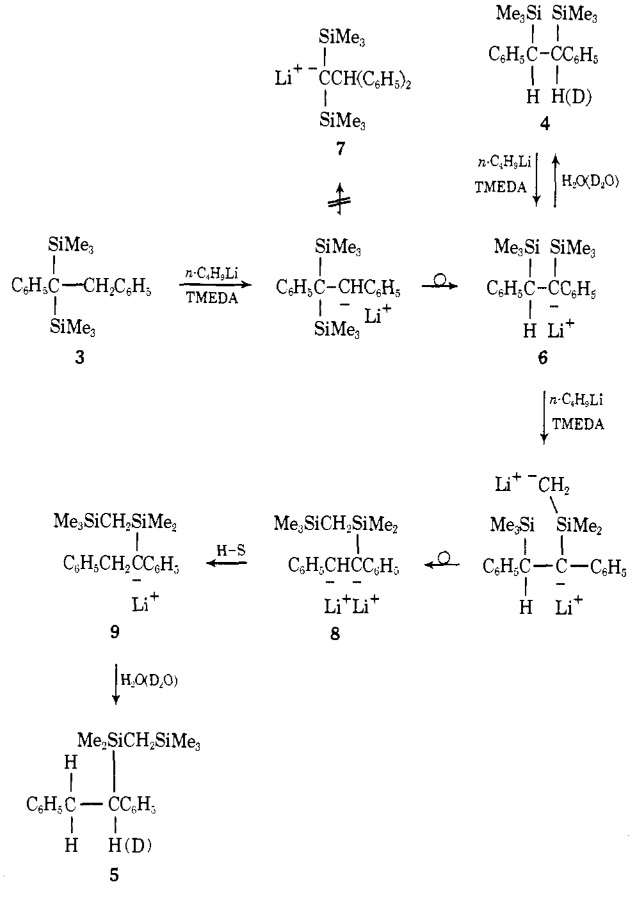
Sir:

Although 1,2 shifts of trialkylsilyl groups between anionic nitrogen centers have been amply established by the excellent studies of West and coworkers,[2] little is known about such shifts between carbanionic sites.[3] Even though treatment of $(Cl_3Si)_2CHCH_3$ with either methyllithium or methyl Grignard reagents leads to a mixture of $[(CH_3)_3Si]_2CHCH_3$ (**1**) and $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ (**2**), it was shown that **1** and **2** are not interconverted by the action of the methyl organometallic reagents.[4] Consequently, a cationic 1,2 silyl shift, induced by metallic halides, seems to be a more reasonable cause of this rearrangement,[3] rather than a 1,2 shift involving carbanions.

As part of our interest in 1,2-carbanionic shifts,[5] therefore, we undertook a search for a genuine carbanionic 1,2-trialkylsilyl rearrangement. Investigation of the behavior of 1,1-bis(trimethylsilyl)-1,2-diphenylethane (**3**) toward butyllithium not only uncovered a genuine carbanionic 1,2-trialkylsilyl shift but a subsequent 1,4-trialkylsilyl shift as well. Thus, treatment of a solution of **3** in *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) with a fourfold excess of butyllithium in hexane gave, after 4 days at 25°, 5% of 1,2-bis(trimethylsilyl)-1,2-diphenylethane (**4**) and, unexpectedly, 90% of 1-[dimethyl(trimethylsilylmethyl)-silyl]-1,2-diphenylethane (**5**). Work-up of a similar reaction mixture with deuterium oxide and nmr spectral examination showed that both **4** and **5** were deuterated only at the benzylic position. The structural assignment of **5** follows from (a) elemental and mass spectral analysis (prominent *m/e* peaks at 70 eV, 326 parent, 180 ($C_6H_5CH{=}CHC_6H_5$) and 145 ($Me_3SiCH_2SiMe_2$)), (b) cleavage with alcoholic KOH solution[6] to yield bibenzyl, and (c) nmr spectral data (δ relative to Me_3Si of **5** as 0, neat) −0.29, 2 H (Si-CH_2-Si); 0, 15 H (Me_3Si,Me_2Si); 2.30, 1 H (t) (1-CH-$SiMe_3$); 3.30, 2 H (d) (2-CH_2); and 7.00, 10 H (s) (2-C_6H_5). The identity of **4** was established by comparison with an authentic sample prepared in a well-established manner.[7]

The mechanism of formation of **4** from **3** can be readily depicted in an anionic fashion, as shown in Scheme I: metalation of **3** at the benzylic position and the 1,2 shift of the trimethyl group to yield the anion **6** of **4**. The absence of any sign of **7** shows, as a bonus,

Scheme I



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(1) Part IX of a series devoted to "Rearrangements of Organometallic Compounds"; the following reports are considered as predecessors: J. J. Eisch and G. R. Husk, *J. Organometal. Chem.*, **4**, 415 (1965); **14**, P13 (1968); **25**, C33 (1970); **26**, C1 (1971); **30**, C97 (1971); **30**, 167 (1971); **38**, 209 (1972); **43**, C17 (1972).

(2) *Cf.* R. West and B. Bichlmeir, *J. Amer. Chem. Soc.*, **94**, 1649 (1972), and references cited therein.

(3) The 1,2 shifts of trichlorosilyl groups between carbon centers have been described previously; *cf.* V. F. Mironov and V. V. Nepomnina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1795 (1961); *Chem. Abstr.*, **56**, 8735 (1962). However, such shifts are effected by $AlCl_3$ and HCl and thus presumably involve carbenium ionic intermediates.

(4) (a) S. Nozakura, *Bull. Chem. Soc. Jap.*, **29**, 660 (1956), and (b) G. Fritz and G. Sonntag, *Z. Anorg. Allg. Chem.*, **332**, 41 (1963).

(5) J. J. Eisch and C. A. Kovacs, *J. Organometal. Chem.*, **25**, C33 (1970); **30**, C97 (1971).

(6) M. C. Musolf and J. L. Speier, *J. Org. Chem.*, **29**, 2519 (1964).

(7) C. R. Hauser and C. R. Hance, *J. Amer. Chem. Soc.*, **74**, 5091 (1952).

that a 1,2-phenyl shift cannot compete with the ready migration of the trimethylsilyl group.[8] However, the formation of **5** as the principal rearrangement product is, at first consideration, explicable in more than one way: (a) **5** could be formed directly from **3** by way of metalation at one of the six CH_3Si groups,[9] followed by 1,3-trimethylsilyl shift (path a); or (b) **5** could be formed indirectly from **3** by way of **4** in which either **6** or **4** undergoes metalation at one of the six CH_3Si groups and subsequently undergoes a 1,4-trimethylsilyl shift to yield anion **8** (path b). If path b obtains, anion **8** would have to be subsequently transformed into anion **9**, in order to fit the finding that the isolated, deuterated **5** is only the 1-deuterio isomer.

Subsequent experiments strongly favor the principal formation of **5** by a 1,4 shift, rather than a 1,3 shift. First of all, treatment of **4** in TMEDA with butyllithium leads, upon hydrolysis, exclusively to **5**; at no time during the reaction did withdrawn aliquots reveal any trace of **3**. Hence, it is improbable that **4** reverts to the anion of **3**, in order to yield **5** by a 1,3 shift. Secondly, a time study of the reaction of **3** in TMEDA with butyllithium shows that **3**, **4**, and **5** are all present throughout the reaction; as conversion to **5** reaches >98%, small traces of **3** and **4** persist. From the foregoing, we cannot as yet rule out that some of the rearrangement of **3** to **5** does occur *via* a 1,3 shift,[10] but there is no doubt that a considerable portion of the reaction involves a 1,2 shift, converting **3** into **4**, followed by a relatively more rapid 1,4 shift, converting **4** into **5**. Ongoing research aims at defining the relative importance of such novel competing 1,*n* anionic shifts in carbosilanes.

Acknowledgment. The research support of the Public Health Service through Grant CA-10743, both at The Catholic University of America and at The State University of New York at Binghamton, is gratefully recorded.

[8] *Cf.* R. West, *Pure Appl. Chem.*, **19**, 301 (1969).

[9] (a) D. J. Peterson, *J. Organometal. Chem.*, **9**, 373 (1967); (b) G. A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, **90**, 4478 (1968).

[10] NOTE ADDED IN PROOF. Subsequent experiments with α,α-bis(trimethylsilyl)ethylbenzene and butyllithium in TMEDA have now shown that a 1,3-trimethylsilyl shift can occur in such a system. In this case, the observed formation of α-[dimethyl(trimethylsilylmethyl)silyl]ethylbenzene cannot be reasonably ascribed to consecutive 1,2 and 1,4 shifts.

John J. Eisch,* Miin-Rong Tsai
Department of Chemistry
State University of New York at Binghamton
Binghamton, New York 13901

Received March 3, 1973

Formation and Relative Stability of Chloride Ion Clusters in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

Sir:

High-pressure mass spectrometry has been extensively used in recent years by Kebarle to study positive and negative ions "solvated" by neutrals in the gas phase.[1-5] For example, the relevant thermodynamic quantities have been obtained for Cl^- clustered by hydrogen bonding neutrals[4] and by CH_3CN.[5] Such studies are of extreme importance in relating the intrinsic chemical behavior of ionic species under solvent-free conditions (gas phase) with that usually observed in condensed phases. Such traditional concepts as acidities and basicities are by now well illustrated examples of significant differences between gas-phase and solution chemistry.[6-10]

The advantages of ion cyclotron resonance spectroscopy have been used in our present investigations to introduce a new and general method for the formation of chloride ion clusters in the gas phase. This method is based on the reaction of $COCl^-$ with neutral species according to reaction 1 at pressures as low as 5×10^{-6}

$$COCl^- + M \longrightarrow Cl^-(M) + CO \qquad (1)$$

Torr.[11] This reaction has been initially studied with a series of alkyl halides, and related compounds, to yield $Cl^-(CH_3Cl)$, $Cl^-(C_2H_5Cl)$, $Cl^-(i\text{-}C_3H_7Cl)$, $Cl^-(t\text{-}C_4H_9Cl)$, $Cl^-(CH_3F)$, $Cl^-(CH_2F_2)$, $Cl^-(CHF_3)$, $Cl^-(CF_4)$, $Cl^-(CH_3Br)$, $Cl^-(CH_3OH)$, $Cl^-(CH_3NO_2)$, $Cl^-(CH_3CN)$, and $Cl^-(CH_3CF_3)$.[12]

Several binary mixtures of neutrals were studied in the presence of $COCl^-$ to determine relative clustering ability. Since $COCl^-$ was found to react completely above 10^{-5} Torr, reaction 2 was probed under these conditions

$$Cl^-(A) + B \rightleftharpoons A + Cl^-(B) \qquad (2)$$

by pressure dependence of the relative intensities of the cluster ions and pulsed double resonance in both directions to establish the preferred "solvent" molecule. This technique is analogous to that used for relative proton affinities.[8] For example, at pressures above 3×10^{-5} Torr the species $Cl^-(CH_3NO_2)$ clearly predominates over $Cl^-(C_2H_5Cl)$ in an approximately equimolar mixture of CH_3NO_2 and C_2H_5Cl, although at lower pressures the intensities are roughly the same. On the other hand, no appreciable relative variation is observed with pressures up to 8×10^{-5} Torr for $Cl^-(CH_3OH)$ and $Cl^-(CH_3NO_2)$ in a CH_3OH and CH_3NO_2 mixture with phosgene. Pulsed double resonance experiments with fields as low as 0.01 V/cm establish that reaction 3 proceeds in both directions under the conditions present in the experiment

$$Cl^-(CH_3NO_2) + CH_3OH \rightleftharpoons Cl^-(CH_3OH) + CH_3NO_2 \qquad (3)$$

Experiments of this nature performed on selected pairs of compounds yield the following relative gas phase "solvating" ability: (a) $CH_3Cl < C_2H_5Cl < (CH_3)_2$-

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[1] M. Arshadi, R. Yamdagni, and P. Kebarle, *J. Phys. Chem.*, **74**, 1475 (1970).

[2] I. Dzidic and P. Kebarle, *ibid.*, **74**, 1466 (1970).

[3] J. D. Payzant, R. Yamdagni, and P. Kebarle, *Can. J. Chem.*, **49**, 3308 (1971).

[4] R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, **93**, 7139 (1971).

[5] R. Yamdagni and P. Kebarle, *ibid.*, **94**, 2940 (1972).

[6] J. I. Brauman and L. K. Blair, *ibid.*, **92**, 5986 (1970).

[7] J. I. Brauman, J. R. Eyler, L. K. Blair, M. J. White, M. B. Comisarow, and K. C. Smyth, *ibid.*, **93**, 6360 (1971).

[8] J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971).

[9] M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *ibid.*, **93**, 4314 (1971).

[10] E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *ibid.*, **94**, 4724 (1972).

[11] Experiments were carried out in a Varian V-5900 ICR spectrometer provided with a dual inlet system. The reacting ion, $COCl^-$, was obtained by electron impact of phosgene at 25 eV. The pressure of phosgene was kept constant in the experiments at 2.5×10^{-6} Torr.

[12] For species like $Cl^-(CCl_4)$ see: P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *Advan. Mass Spectrom.*, **4**, 621 (1968).