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[20] H. Harm and C. S. Rupert, *Mutat. Res.*, **10**, 291 (1970).

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Received May 12, 1971

Organometallic Chemistry. III.[1] Attempted Preparation of Trivalent Silicocations (Silicenium Ions).[2] The Exchange Reaction of Methylfluorosilanes with Antimony Pentafluoride

Sir:

Long-lived stable trivalent carbenium ions have been extensively studied in our laboratories.[3] The analogous trivalent silicocations (trivalent silicenium ions) were proposed as a reaction intermediate in many organosilicon chemical reactions.[4] Furthermore, silicocations have been observed as high-abundance fragment ions in the mass spectra of organosilicon compounds.[5] Attempts to prepare silicenium ions for direct observation in solution were unsuccessful.[6] We presently wish to report our attempts to prepare silicenium ion in extremely low nucleophilicity superacid media in which trivalent carbenium ions are stable and can be directly observed.

The pmr spectrum of trimethylfluorosilane (**1**) in an excess of SbF_5–SO_2ClF at −78° shows a sole singlet absorption at δ 1.35. Compound **1** in SO_2ClF at −78° has a doublet at δ 0.23 (J_{HF} = 8 Hz). The absence of the proton–fluorine coupling in the former indicates the formation of either the trimethylsilicenium ion, $(CH_3)_3{}^+Si$, or the exchanging donor–acceptor complex, $(CH_3)_3SiF \rightarrow SbF_5$. The chemical shift of the observed singlet absorption is relatively shielded compared to that of the *tert*-butyl cation (by 2.7 ppm).[7] In the ^{19}F nmr spectrum, the resonance of **1** is not present any more and only shows a broadened fluoroantimonate absorption at ϕ 110 (1000 ppm width, from $CFCl_3$).[8] Adding more SbF_5 to the above solution did not change either the ^1H or ^{19}F nmr spectra. On the other hand, when excess **1** was added to the solution, the proton singlet absorption became slightly more shielded. The shielded proton shift is proportional to the amount of **1** added. The ^{19}F nmr spectrum is essentially unchanged. But, when **1** was about four times in excess of SbF_5 in SO_2ClF at −80°, the nmr spectrum showed a doublet at δ 0.30 (J_{HF} = 8 Hz) and an overlapping singlet at δ 0.40. The ^{19}F nmr spectrum showed a resonance similar to that of **1** (at ϕ 122.7) and the broadened fluoroantimonate absorption still remained at ϕ 110.0. The nmr spectra of the above solutions were temperature independent ranging from −50 to −80°. Above −50°, a protolytic cleavage reaction occurred (see subsequent discussion).

The above observations indicate that an exchanging donor–acceptor complex of **1** with SbF_5 was formed. Similar complexes were previously found when methyl fluoride, ethyl fluoride, and 1,1-difluoroethane were treated with SbF_5–$SO_2(SO_2ClF)$ solution.[9] The complex formation can explain the absence of proton–fluorine coupling and the observed chemical shifts which depend on the relative ratio of **1** and SbF_5. In the case when **1** was present in fourfold excess to SbF_5, both the exchanging complex, $(CH_3)_3SiF \rightarrow SbF_5$, and **1** were observed. This is also the case in the methyl fluoride–antimony pentafluoride system where an excess of methyl fluoride is observed not to be exchanging with the $CH_3F \rightarrow SbF_5$ complex.[9a]

The solution of dimethyldifluorosilane (**2**) in excess of SbF_5–SO_2ClF gave again a singlet absorption at δ 1.20 in the pmr spectrum and no observable fluorine resonance–resonance corresponding to **2** in the ^{19}F nmr spectrum. If the dimethylfluorosilicenium ion, $(CH_3)_2{}^+SiF$, were formed, the pmr spectrum should show a deshielded doublet. Also, a substantially deshielded fluorine resonance will be expected, as in the case of dimethylfluorocarbenium ion, $(CH_3)_2{}^+CF$.[10] The formation of the donor–acceptor complex, $(CH_3)_2SiF_2 \rightarrow SbF_5$, seems best to explain all experimental observation. By adding more **2** to the above solution, the singlet absorption is shifted to higher field. In the specific case when the molar ratio of **2** to SbF_5 was 2:1, temperature-dependent ^1H and ^{19}F nmr spectra were obtained. In the pmr spectra, the triplet of **2** observed at lower temperature collapsed to a singlet at higher temperature (Figure 1). Similar behavior of pmr spectra has been observed when 2,2-difluoropropane was treated with HF–SbF_5–SO_2ClF superacid system.[9b] In Figure 1 there are also shown the theoretical computed spectra. The lifetimes, τ, of exchanging **2** were obtained from the best fit of experimental and calculated spectra.[11] The energy of activation of the exchange process is estimated to be 6.3 ± 0.8 kcal/mol.

Similarily, when methyltrifluorosilane (**3**) was complexed with SbF_5–SO_2ClF solution, a slightly broadened singlet absorption at δ 0.95 was observed in the nmr spectrum (0.5 ppm deshielded from the precursor). The ^{19}F nmr spectrum shows only the fluoroantimonate resonance. These results do not agree with formation of methyldifluorosilicenium ion, $CH_3{}^+SiF_2$, although

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[1] Part II: G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **93**, 2320 (1971).

[2] The term "silicocations" is used in a manner analogous to the use of the term "carbocations," for the corresponding cations of carbon. For a discussion of the general concept of carbocations and differentiation of trivalent carbenium ions from penta- (or tetra-) coordinated carbonium ions, see G. A. Olah, *ibid.*, in press.

[3] G. A. Olah, *Science*, **168**, 1298 (1970); *Chem. Eng. News*, **45**, 76 (Mar 27, 1967).

[4] (a) M. S. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968); (b) R. West, *Int. Symp. Organosilicon Chem., Sci. Commun., 1965*, 1 (1965); (c) L. H. Sommer and F. J. Evans, *J. Amer. Chem. Soc.*, **76**, 1186 (1954); (d) L. H. Sommer, D. L. Bailey, J. R. Coulf, and F. C. Whitmore, *ibid.*, **76**, 801 (1954).

[5] W. P. Weber, R. A. Felix, and A. K. Willare, *Tetrahedron Lett.*, 907 (1970), and references therein.

[6] A. G. Brook and K. H. Pannell, *Can. J. Chem.*, **48**, 3679 (1970).

[7] *tert*-Butyl cation generated from *tert*-butyl chloride and SbF_5–SO_2ClF solution has a proton singlet at δ 4.05 (also see G. A. Olah, E. B. Baker, T. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien (*J. Amer. Chem. Soc.*, **86**, 1360 (1964)) who reported the proton shift of *tert*-butyl cation at δ 4.35).

[8] The ^{19}F nmr spectrum of HF–SbF_5(1:1 mol:mol)–SO_2ClF shows a broadened resonance at ϕ 100 (500–600 ppm width); G. A. Olah and Y. K. Mo, unpublished results.

[9] (a) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91**, 2133 (1969); (b) G. A. Olah, Y. K. Mo, and Y. Halpern, *ibid.*, in press; (c) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *ibid.*, in press.

[10] G. A. Olah and M. B. Comisarow, *ibid.*, **91**, 2955 (1969).

[11] C. S. Johnson, *Advan. Magn. Resonance*, **1**, 33 (1965).

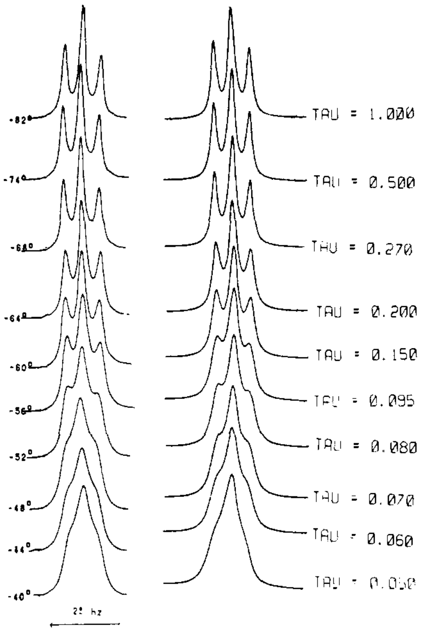


Figure 1. Temperature-dependent pmr spectra of exchanging complex, $(CH_3)_2SiF_2 \rightarrow SbF_5$, in SO_2ClF (left) and calculated spectra (right).

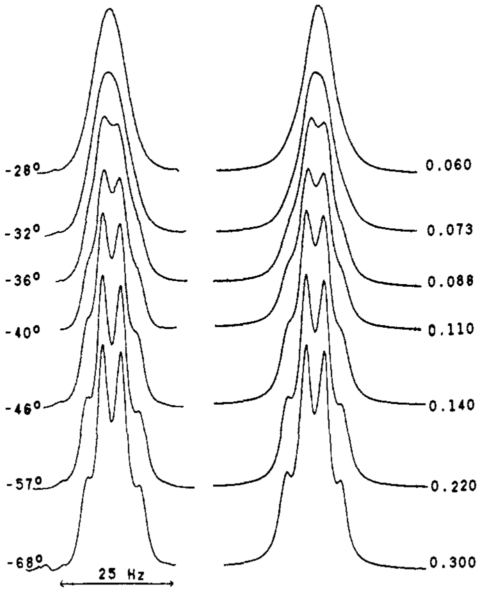
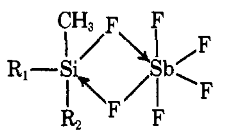


Figure 2. Temperature-dependent pmr spectra of exchanging complex, $CH_3SiF_3 \rightarrow SbF_5$, in SO_2ClF (left) and calculated spectra (right).

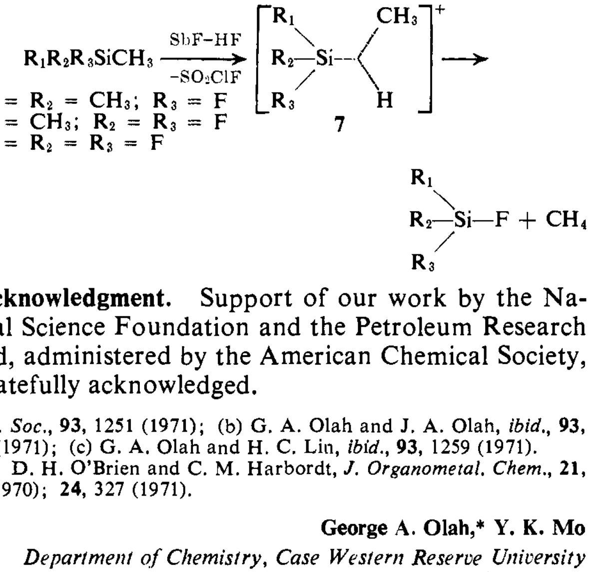
the analogous carbenium ion, $CH_3{}^+CF_2$, has been recently directly observed.[12] Again, the formation of a donor-acceptor complex, $CH_3SiF_3 \rightarrow SbF_5$, is indicated by the above observations. Temperature-dependent ^1H and ^{19}F nmr spectra were obtained when equal molar amounts of 3 and SbF_5 were mixed in SO_2ClF (Figure 2). Theoretical spectra were calculated to fit the experimental proton spectra. The energy of activation, E_a, of this exchange process was estimated to be 4.3 ± 0.9 kcal/mol.

The direct observation of a silicenium ion was not achieved even in the low nucleophilicity SbF_5-SO_2ClF media used in this study. In comparison to the chemistry of carbocations, the available empty 3d orbitals of the silicon atom seem to be responsible for the failure to directly observe silicenium ions. This is because the empty 3d orbital of silicon is capable of changing the tetrahedral sp^3 hybridization to the trigonal pyramidal sp^3 d hybridization. Consequently, we conclude that the rapidly exchanging complexes of **1**–**3** with SbF_5 could have structures **4**–**6** as shown (or containing dimeric antimony pentafluoride, *i.e.*, $R_1R_2CH_3SiF$, Sb_2F_{10}).



4, $R_1 = R_2 = CH_3$
5, $R_1 = CH_3$; $R_2 = F$
6, $R_1 = R_2 = F$

We have also studied the behavior of the methylfluorosilanes (**1**–**3**) in SbF_5-HF-SO_2ClF solution. Silicocations were not observed. Instead, protolytic cleavage of Si–C single bonds (assumed through a three-center bound[13] transition state **7**, a pentacoordinated siliconium ion) took place to give methane and the higher homologous methylfluorosilanes. Similar types of Si–C single bond cleavage reactions in strong acid have been observed by O'Brien.[14]



1, $R_1 = R_2 = CH_3$; $R_3 = F$
2, $R_2 = CH_3$; $R_2 = R_3 = F$
3, $R_1 = R_2 = R_3 = F$

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[12] G. A. Olah and Y. K. Mo, *J. Org. Chem.*, in press.

[13] (a) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 1251 (1971); (b) G. A. Olah and J. A. Olah, *ibid.*, **93**, 1256 (1971); (c) G. A. Olah and H. C. Lin, *ibid.*, **93**, 1259 (1971).

[14] D. H. O'Brien and C. M. Harbordt, *J. Organometal. Chem.*, **21**, 321 (1970); **24**, 327 (1971).

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Received June 17, 1971

Tirandamycin. I. Structure Assignment

Sir:

Tirandamycin, a new antibacterial agent isolated from the culture broth of *Streptomyces tirandis* sp. n.,[1] has been the subject of two recent reports describing its mode of action.[2,3] The compound shows potent inhibition of RNA polymerase in bacterial cell-free systems[2] and interferes with oxidative phosphorylation

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[1] C. E. Meyer, *J. Antibiot.*, **24**, 558 (1971).

[2] F. Reusser, *Infec. Immun.*, **2**, 77 (1970).

[3] F. Reusser, *ibid.*, **2**, 82 (1970).