$$C_3 + \text{hydrogen-containing substrates} \longrightarrow \begin{array}{l} CH_3CH_2CH_3 \\ CH_3CH{=}CH_2 \\ CH_2{=}C{=}CH_2 \\ CH_3C{\equiv}CH \end{array}$$

strates is analogous to the hydrogenation of C_2[18] and C_4,[19] which lead to C_2 and C_4 hydrocarbons, respectively.

Formation of the C_3 hydrocarbons from a variety of partially deuterated substrates is being studied; detailed mechanistic conclusions will be discussed elsewhere.

The C_3 hydrocarbons allene and propyne result from attack of excited-state C_3 on the substrate. This was demonstrated by carrying out the reaction with carbon vapor from resistively heated carbon (no arcing) and methanol and ethanol: allene and propyne *are not* reaction products, virtually the sole product being the propargyl aldehyde acetal. From this experiment it follows that excited-state C_3 is the precursor of allene and propyne. Whether the excited state is one of the singlets or the previously studied triplet cannot be specified at present.

Experimental Section

The reaction system has been described.[4] The C_3 molecules are generated, along with C_1, C_2, and C_4, from a 16-V (ac) carbon arc under vacuum ($\sim 1 \times 10^{-4}$ mm). Reactions occur in condensed phase near 77°K. Products were isolated by vapor phase chromatography and the retention times and infrared and mass spectra of the C_3 hydrocarbons, hexachloropropene, and octachloropropane[20] were compared with those of known compounds. The propargyl aldehyde acetals were identified by consistent infrared and mass spectra and confirmed by nmr (Table IV).

Table IV. Nmr of 3,3-Dialkoxypropynes[a]

δ	Area	Multiplicity	Assignment
		$(CH_3O)_2CHC{\equiv}CH$	
2.41	1.0_0	Doublet (*J* = 2)	HC≡C-
3.25	6.0_0	Singlet	CH_3O-
4.95	1.00	Doublet (*J* = 2)	-OCHO-
		$(CH_3CH_2)O_2CHC{\equiv}CH$	
1.16	6.0_2	Triplet (*J* = 7)	CH_3-
2.39[b]	1.00	Doublet (*J* = 2)	HC≡C-
3.55	4.0_2	Multiplet	-OCH_2-
5.07	1.00	Doublet (*J* = 2)	-OCHO-
		$(CH_3CH_2CH_2O)_2CHC{\equiv}CH$	
0.92	6.0_2	Triplet (*J* = 7)	CH_3-
1.55	4.0_0	Multiplet	-CH_2-
2.36	1.00	Doublet (*J* = 2)	HC≡C-
3.44	4.0_0	Multiplet	-OCH_2-
5.06	1.00	Doublet (*J* = 2)	-OCHO-

[a] Microtubes (25 μl). [b] Literature values: δ 2.39 in CCl_4 (M. M. Kreevoy, H. B. Charman, and D. R. Vinard, *J. Amer. Chem. Soc.*, **83**, 1978 (1961)) and δ 2.33 in CCl_4 (P. Jouve, *C. R. Acad. Sci. Paris*, **256**, 1497 (1963)).

Thermally vaporized carbon vapor was obtained by replacing the upper electrode with a thin (~1 mm) graphite slice and heating resistively (~2800°). Carbon vapor enriched in carbon-14 was obtained by replacing one graphite electrode with a graphite rod enriched in carbon-14 (~0.01 Ci/g).

Acknowledgment. The financial support of the Air Force Office of Scientific Research is gratefully acknowledged.

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(18) P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **88**, 5933 (1966).

(19) R. F. Harris and P. S. Skell, *ibid.*, **90**, 4172 (1968).

(20) A. L. Henne and E. C. Ladd, *ibid.*, **60**, 2491 (1938).

Stable Carbonium Ions. LXXIV.[1a] Protonated Alkoxysilanes and Disiloxanes and Their Cleavage in Fluorosulfuric Acid–Antimony Pentafluoride Solution

George A. Olah, Daniel H. O'Brien,[1b] and Christine Y. Lui

Contribution from the Department of Chemistry,
Case Western Reserve University, Cleveland, Ohio 44106.
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Abstract: Several alkoxysilanes and disiloxanes have been examined in the extremely strong acid system, fluorosulfuric acid–antimony pentafluoride at low temperatures by nuclear magnetic resonance spectroscopy. For trimethylmethoxysilane and hexamethyldisiloxane it was possible to directly observe the protonated species with the proton on oxygen. For the other siloxanes studied it was possible to observe the stepwise cleavage of alkoxy and alkyl groups from silicon. The mechanism of the cleavage reactions is discussed. No experimental evidence was found for the intermediacy of trivalent siliconium ion intermediates.

Alkoxysilanes undergo facile cleavage reactions in the presence of both proton and Lewis acids. Cryoscopic studies of alkoxysilanes and polysiloxanes indicate the rapid formation of silyl hydrogen sulfates at 0° in sulfuric acid.[2] Lewis acid adducts of moderate stability have been isolated for the reaction of boron halides[3] and aluminum halides[4] with alkoxysilanes and disiloxanes. These complexes undergo further reaction to form halosilanes and oxy salts of boron and aluminum. Protonated intermediates have been proposed

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(1) (a) Part LXXIII: G. A. Olah, M. B. Comisarow, and C. F. Kim, *J. Amer. Chem. Soc.*, in press. (b) National Science Foundation Postdoctral Research Investigator, 1966–1967.

(2) (a) F. P. Price, *J. Amer. Chem. Soc.*, **70**, 872 (1948); (b) M. S. Newman, R. A. Craig, and A. B. Garrett, *ibid.*, **71**, 869 (1949); (c) H. H. Szmant, O. M. Devlin, and G. A. Brost, *ibid.*, **73**, 3059 (1951).

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on the basis of kinetic evidence for the acid-catalyzed cleavage of alkoxysilanes and the rearrangement of cyclic and linear polysiloxanes.[5]

The cleavage of silicon–carbon bonds of alkyl and aryl silanes has been frequently observed in strong acid solutions.[6] In particular, the study of the cleavage of a single methyl group from silicon for β-trimethylsilylpropionic acid and γ-trimethylsilylbutyric acid in concentrated sulfuric acid indicates that silicon–carbon cleavage is the result of electrophilic attack at carbon assisted by nucleophilic attack at silicon.[7,8] The facile cleavage of aryl groups from silicon by strong proton acids has been used to study electrophilic aromatic substitution.[9] It has been shown that electrophilic attack occurs exclusively at the ring position containing the silicon.

Results and Discussion

In view of our recent interest in protonated ethers and their cleavage in the extremely strong acid system, HSO_3F–SbF_5–SO_2,[10] we felt it of interest to study the analogous alkoxysilanes and disiloxanes to see if the proposed protonated intermediates could be observed by nmr spectroscopy. A variety of alkoxysilanes and disiloxanes were examined in the "magic acid" system at low temperatures. It was possible to observe the protonated intermediates in some cases and also to follow the stepwise cleavage of alkoxy, alkyl, and aryl groups from silicon. In general, an acidity of greater than 3:1 HSO_3F–SbF_5 (mol:mol) resulted in the rapid evolution of methane from methylalkoxysilanes and the formation of solid products in the nmr tube which consequently did not allow the observation of the products of the reaction by nmr. The use of acidities in the range of 4:1 to 8:1 HSO_3F–SbF_5 (mol:mol) allowed the observation of protonated species and their cleavage products. Acidities lower than 8:1 resulted in incomplete protonation of the alkoxysilanes and undesirable side reactions.

Protonation and Cleavage of Alkoxysilanes

Trimethylmethoxysilane when carefully added as a cooled sulfur dioxide solution at −70° to a solution of 4:1 → 8:1 FSO_3H–SbF_5 acid in sulfur dioxide, allowed the observation of the protonated species including the proton on oxygen. However, even under these conditions the spectrum contains other resonances, indicating that considerable cleavage of protonated trimethylmethoxysilane has already taken place (Figure 1). The proton on oxygen appears as a quartet at δ 8.10. The proton on oxygen for protonated hexamethyldisiloxane appears as a singlet at δ 7.23 (Figure 7). These values are consistent with the greater shielding expected from successive substitution of the more electropositive silicon atom for carbon adjacent to the proton on oxygen when compared to a value of δ 9.03 for the proton on oxygen of protonated dimethyl ether.[10]

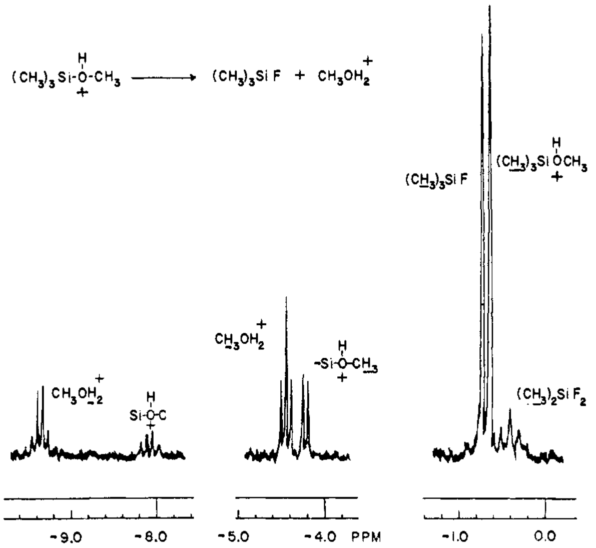

Figure 1. Pmr spectrum of the cleavage of trimethylmethoxysilane in FSO_3H–SbF_5–SO_2 solution at −70°.

The methyl resonances for protonated trimethylmethoxysilane and its initial cleavage product appear as singlets at δ 0.67 and 0.76. Warming the reaction mixture to approximately −50° resulted in the disappearance of the resonance at δ 0.76 and the simultaneous appearance of a sharp triplet centered at δ 0.42 in the proton spectrum (J_{HF} = 7.1 Hz; Figure 2) and a septet in the fluorine-19 spectrum at ϕ +129.7 (from CCl_3F [J_{HF} = 7.1 Hz]). The fluorine-19 chemical shift is identical with that of dimethyldifluorosilane in the same solvent system and compares well with the reported value of ϕ +132.7 for the fluorines in dimethyldifluorosilane in carbon tetrachloride.[11] Since resonances due to protonated methanol (CH_3 triplet: δ 4.43 OH_2^+; quartet: δ 9.37)[12] appear in the initial spectrum (Figure 1) it is clear that the initial reaction of protonated trimethylmethoxysilane is the cleavage of the silicon–oxygen bond with the formation of a trimethylsilyl species which gives a singlet at δ 0.76. Further reaction of this trimethylsilyl species results in the cleavage of a methyl group from silicon and the formation of dimethyldifluorosilane.

The singlet at δ 0.76 arising from the initial cleavage of protonated trimethylmethoxysilane is not considered to be the trimethylsiliconium ion[13] but rather can be, best explained by being trimethylfluorosilane whose fluorine atom undergoes rapid exchange with available fluoride ion in the acid system. Substantiation for this assignment is obtained when trimethylfluorosilane itself is treated in the same acid system. Trimethylfluorosilane gives a methyl doublet at δ 0.37 in the proton spectrum and a fluorine-19 decet at ϕ +153.3 (J_{HF} = 7.2 Hz).

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(5) (a) S. W. Kantor, W. R. Grubb, and R. C. Osthoff, *J. Amer. Chem. Soc.*, 76, 5190 (1954); (b) D. T. Hurd, *ibid.*, 77, 2998 (1955); (c) E. Akerman, *Acta Chem. Scand.*, 10, 298 (1956); 11, 373 (1957).

(6) V. Bazant, V. Chvalovsky, and J. Rathousky, "Organosilicon Compounds," Vol. I, Academic Press, New York, N. Y., 1965, p 212–233, and references therein.

(7) L. H. Sommer, W. P. Barie, and J. R. Gould, *J. Amer. Chem. Soc.*, 75, 3765 (1953).

(8) L. M. Shorr, H. Freiser, and J. L. Speier, *ibid.*, 77, 547 (1955).

(9) (a) C. Eaborn, *J. Chem. Soc.*, 3148 (1953); (b) R. A. Benkeser, R. A. Hickner, and D. I. Hoke, *J. Amer. Chem. Soc.*, 80, 2279 (1958); (c) R. A. Benkeser and H. R. Krysiak., *ibid.*, 76, 6363 (1954).

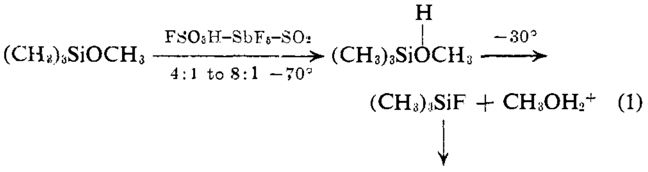
(10) G. A. Olah and D. H. O'Brien, *ibid.*, 89, 1723 (1967).

(11) E. Schnell and E. G. Rochow, *ibid.*, 78, 4178 (1956).

(12) G. A. Olah and E. Namanworth, *ibid.*, 88, 5327 (1966).

(13) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 28–37.

In 8:1 FSO_3–SbF_5 acid diluted with sulfur dioxide at −70°, it shows a singlet at δ 0.76 which is replaced by a triplet centered at δ 0.42 upon slight warming. This indicates that the species resulting from the initial cleavage of protonated trimethylmethoxysilane and from trimethylfluorosilane in the acid system are the same but does not unequivocally prove that this species is not the trimethylsiliconium ion. The resonance at δ 0.76 is, however, not significantly deshielding when compared to that of trimethylfluorosilane ($[CH_3]_3SiF$ = δ 0.37). Although it must be considered that the deshielding in a siliconium ion would likely not be as great as for a comparable carbon system (*e.g.*, the trimethylcarbonium ion[14]) because of the larger size of the silicon atom, a considerably larger downfield shift than that observed still should be expected. A suitable explanation appears therefore to be that the singlet at δ 0.76 is due to trimethylfluorosilane which is undergoing rapid fluoride exchange under the conditions of the reaction, while dimethyldifluorosilane does not. Indeed, it was found that dimethyldifluorosilane began to undergo exchange as the temperature was increased. The triplet at δ 0.42 became significantly broadened when the temperature was raised to about −20°. Such an explanation would imply an increase in silicon–fluorine bond strength in going from trimethylfluorosilane to dimethyldifluorosilane. This is consistent with dipole moment studies of ethylfluorosilanes[15] and methylbromosilanes[16] and microwave studies of methylchlorosilanes[17] and fluorosilanes.[18] which indicate the apparent increase in silicon–halogen bond strength with increased halogen substitution. This increase in bond strength has been attributed to an increase in the donation of electrons to silicon's d orbitals with increasing number of silicon–halogen bonds. From the evidence which has been discussed, the reaction of trimethylmethylmethoxysilane in the super acid system is summarized in (1). The resonance δ 0.67, which can be



$$
\begin{array}{l}
(CH_3)_3SiOCH_3 \xrightarrow[4:1\text{ to }8:1\ -70^\circ]{FSO_3H\text{–}SbF_5\text{–}SO_2} (CH_3)_3Si\overset{\overset{H}{|}}{O}CH_3 \xrightarrow{-30^\circ} \\
\qquad\qquad\qquad\qquad\qquad (CH_3)_3SiF + CH_3OH_2^+ \quad (1) \\
\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\
\qquad\qquad\qquad\qquad\qquad (CH_3)_2SiF_2 + CH_4
\end{array}
$$

assigned to the methyl groups of protonated trimethylmethoxysilane, shows no significant change in intensity upon warming to about −30° (Figure 2). This indicates that protonated trimethylmethoxysilane is more stable than the exchanging trimethylfluorosilane and that the initial decomposition displayed in Figure 1 was probably due to local heating during sample preparation. At about −30° protonated trimethylmethoxysilane (the peak at δ 0.67) disappeared with a corresponding increase in the triplet due to dimethyldifluorosilane. Under more forceful heating, dimethyldifluorosilane undergoes further protolytic cleavage eventually yielding silicon tetrafluoride and methane.

$$
\begin{array}{ccc}
(CH_3)_2SiF_2 \longrightarrow & CH_3SiF_3 + CH_4 \\
 & \downarrow \\
 & SiF_4 + CH_4
\end{array}
$$

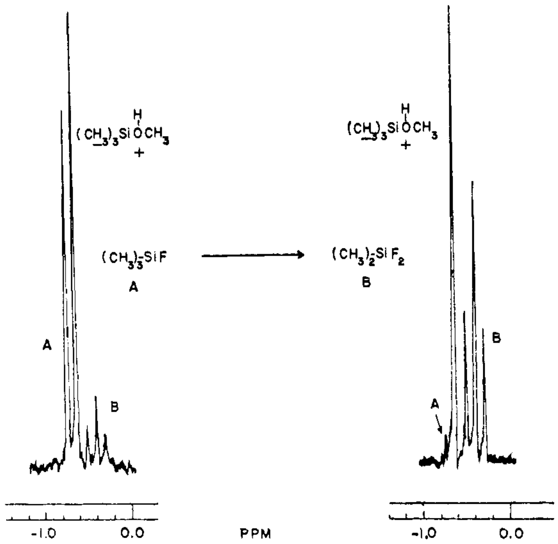


Figure 2. Pmr spectrum of the cleavage of trimethylmethoxysilane showing subsequent transformation of trimethylfluorosilane to dimethyldifluorosilane by heating from −70 to −50°.

Triethylmethoxysilane in a manner similar to trimethylmethoxysilane, cleaves first to triethylfluorosilane, which in turn can cleave to diethyldifluorosilane (giving side products derived from the ionization of ethane found as by-product). Triethylfluorosilane exchanges rapidly in the reaction medium, similar to trimethylfluorosilane. In this case, the intermediate protonated siloxane could not be directly observed.

$$
\begin{array}{ll}
(CH_3CH_2)_3SiOCH_3 \xrightarrow[-70^\circ]{FSO_3H\text{–}SbF_5\text{–}SO_2} & (CH_3CH_2)_3SiF + CH_3OH_2^+ \\
 & \qquad \downarrow \Delta \\
 & (CH_3CH_2)_2SiF_2,\ \text{etc.}
\end{array}
$$

Several other alkosysilanes were also examined in the same acid system. None of the protonated intermediates were stable enough to be observed by nmr even when the spectra were recorded less than 2 min after sample preparation, with care taken to ensure that the temperature was maintained below −70°. In all cases the reactions had proceeded beyond the initial protonation stage and only the products of the initial cleavage could be observed.

Dimethyldiethoxysilane and Phenyldimethylmethoxysilane. Comparison of the reaction products for dimethyldiethoxysilane and phenyldimethylmethoxysilane in the super acid system indicates again that cleavage takes place without the observed intermediacy of the siliconium ion. Dimethyldiethoxysilane reacted rapidly even in 8:1 acid at −70° to give a quantitative conversion (Figure 3) to protonated ethanol and dimethyldifluorosilane. If the nmr spectrum is taken quickly, a doublet can be seen at δ 0.70, slightly downfield from the dimethyldifluorosilane triplet. We assign this doublet to the formation of dimethylethoxy-

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(14) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964).

(15) C. Curran, R. M. Witucki, and P. A. McCusker, *ibid.*, **72**, 4771 (1950).

(16) E. L. Reilly, C. Curran, and P. A. McCusker, *ibid.*, **76**, 3311 (1954).

(17) R. C. Mockler, J. H. Bailey, and W. Gordy, *J. Chem. Phys.*, **21**, 1710 (1953).

(18) L. Sheridan and W. Gordy, *ibid.*, **19**, 965 (1951).

fluorosilane which then cleaves to dimethyldifluorosilane.

The spectrum of phenyldimethylmethoxysilane in 8 : 1 acid presented in Figure 4 was recorded less than 2 min after sample preparation and contains several interesting features. Integration of the protonated methanol triplet (δ 4.40)[12] and the silicon–methyl doublet (δ 0.70) shows that the cleavage of the methoxy group is already complete. The sharp singlet in the aromatic region at δ 7.4 and the aliphatic singlet at δ 1.0 may be due to the intermediacy of the ring protonated species, *I*, indicating that phenyl cleavage is taking place (**3**).

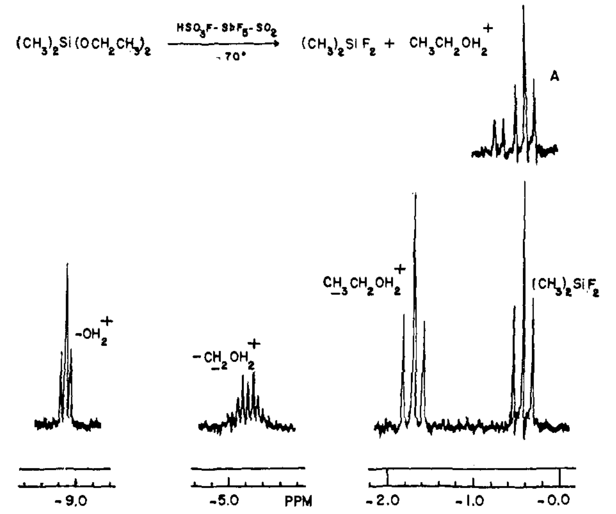


Figure 3. Pmr spectrum of the cleavage of dimethyldiethoxysilane.

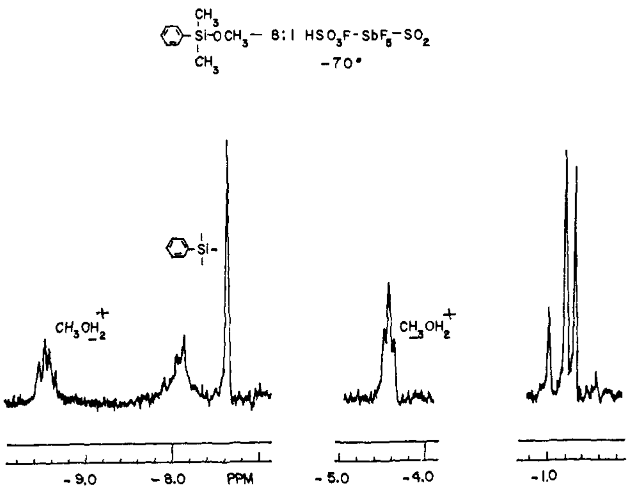


Figure 4. Pmr spectrum of the cleaveage of phenyldimethylmethoxysilane.

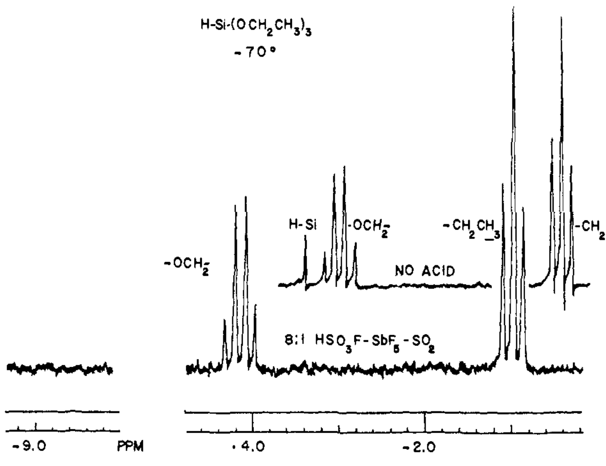
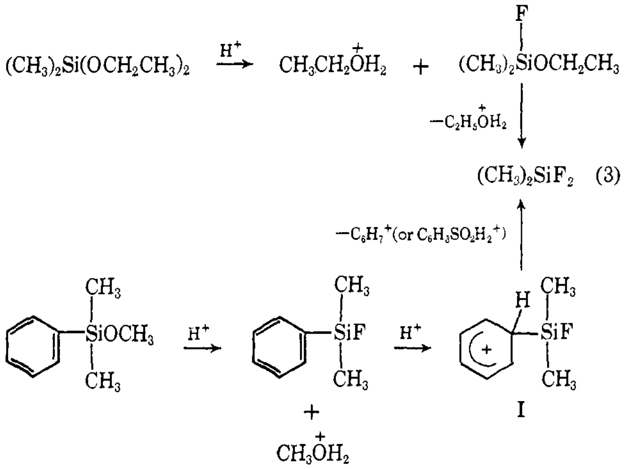
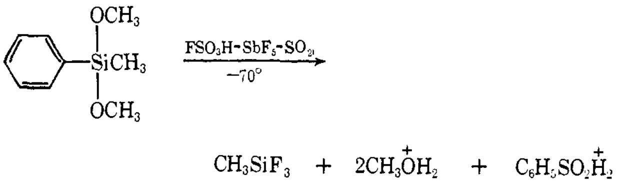


Figure 5. Pmr spectrum of triethoxysilane in SO_2 solution (upper spectrum) and in 8 : 1 FSO_3H-SbF_5 solution at −70° (lower spectrum).



Methylphenyldimethoxysilane cleaves rapidly at −70° in 4 : 1 acid to methyltrifluorosilane (with protonated methanol and benzenesulfinic acid as the by-products).



Methyltrimethoxysilane and methyltriethoxysilane both cleave in FSO_3H-SbF_5-SO_2 solution at −60° to give methyltrifluorosilane (methyl quartet at δ 0.5, J_{HF} = 4.5 Hz) and the characteristic spectra of the protonated alcohols.

$$CH_3Si(OR)_3 \xrightarrow[-60^\circ]{FSO_3H\text{-}SbF_5\text{-}SO_2} CH_3SiF_3 + 3ROH_2^+$$
$$R = CH_3, C_2H_5$$

Tetramethoxysilane is cleaved to trimethoxyfluorosilane, which in turn can undergo further cleavage to dimethoxyfluorosilane, methoxytrifluorosilane, and tetrafluorosilane.

Triethoxysilane. Earlier work from this laboratory has shown that alkanes undergo hydride abstraction to form carbonium ions in HSO_3F-SbF_5.[19] Hydride abstraction would be expected to be easier for silanes because of the greater hydridic nature of hydrogen attached to silicon. Therefore it is not surprising that triethoxysilane loses hydride ion to the acid system rapidly at −70°. The spectrum of triethoxysilane dissolved in sulfur dioxide shows the silicon hydrogen at δ 3.28, the methyl triplet at δ 0.30 and the methylene quartet at δ 2.90 (Figure 5). Treatment with 8 : 1 acid at −70° shows the methyl triplet at δ 0.97, the

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[19] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227, 4739 (1967).

methylene quartet at δ 4.12 and no silicon–hydrogen resonance. No evidence was found for the initial formation of protonated ethanol (methyl triplet, δ 1.9; methylene complex multiplet, δ 4.9; and OH_2^+ triplet, δ 9.3).[12] This evidence is consistent with the formation of a triethyloxysilicon species, not necessarily the triethoxysilconium ion but probably triethoxyfluorosilane which is rapidly exchanging with fluoride from the acid system. Heating the sample for about 10 min at −40° results in further cleavage of triethoxyfluorosilane giving protonated ethanol and diethoxydifluorosilane (Figure 6).

Protonation and Cleavage of Siloxanes. Hexamethyldisiloxane is protonated in $FSO_3H–SbF_5–SO_2$ solution and at −78°. The nmr spectrum is well resolved. Proton on oxygen is observed at δ 7.26 (Figure 7) thus there is no appreciable exchange with the solvent. Cleavage occurs upon warming or prolonged standing even at low temperatures (>−60°) resulting in the appearance of a singlet at δ 0.76, identical with the peak found in the cleavage of protonated trimethylmethoxysilane. At temperatures above −30° protonated hexamethyldisiloxane cleaves to dimethyldifluorosilane.

$$[(CH_3)_3Si]_2O \xrightarrow[-78°]{FSO_3H\text{–}SbF_5\text{–}SO_2} [(CH_3)_3Si]_2\overset{+}{O}H \xrightarrow{-60°}$$

$$2(CH_3)_3SiF + H_3O^+ \xrightarrow{>-30°} 2(CH_3)_2SiF_2 + 2CH_4\uparrow$$

Trimethyltriphenyldisiloxane cleaves much more readily that hexamethyldisiloxane in both 4:1 and 8:1 $FSO_3H–SbF_5$. The proton on oxygen was not observable in the intermediate protonated disiloxane, which cleaved rapidly to trimethylfluorosilane and subsequently to dimethyldifluorosilane and protonated triphenylsiloxane. The protonated triphenylsiloxane reacted further to yield triphenylfluorosilane. Figure 8 shows

$$(CH_3)_3SiOSi(C_6H_5)_3 \longrightarrow (CH_3)_3SiF + (C_6H_5)_3Si\overset{+}{O}H_2$$

$$\downarrow$$

$$(C_6H_5)_3SiF$$

the methyl region of the system as a function of time during the cleavage yielding first trimethylfluorosilane and subsequently the triplet of dimethyldifluorosilane.

Hexaphenyldisiloxane cleaves in a manner similar to the cleavage of trimethyltriphenyldisiloxane, to give triphenylfluorosilane. The protonated disiloxane was not observed.

Conclusions

In all the above cleavage reactions of protonated alkoxysilanes and disiloxanes, we feel that the evidence does not substantiate the formation of a trivalent siliconium ion. Such ions could be formally written to explain the cleavage pathways in analogy to the corresponding carbon systems suggesting that a trivalent siliconium ion is first formed which is, however, rather unstable even in the super acid system and extracts fluoride ion from the solvent to form the fluorosilanes. The facile formation of fluorosilanes in the super acid system can be however, reasonably explained by a pentavalent intermediate arising from nucleophilic attack by fluoride ion

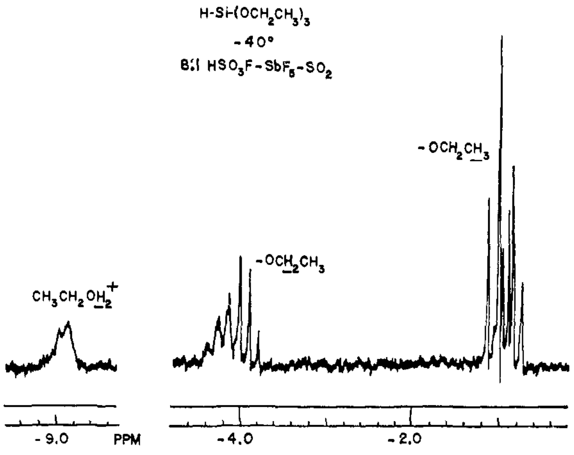


Figure 6. Pmr of cleavage of triethoxysilane in 8:1 $FSO_3H–SbF_5$ solution upon heating to −40°.

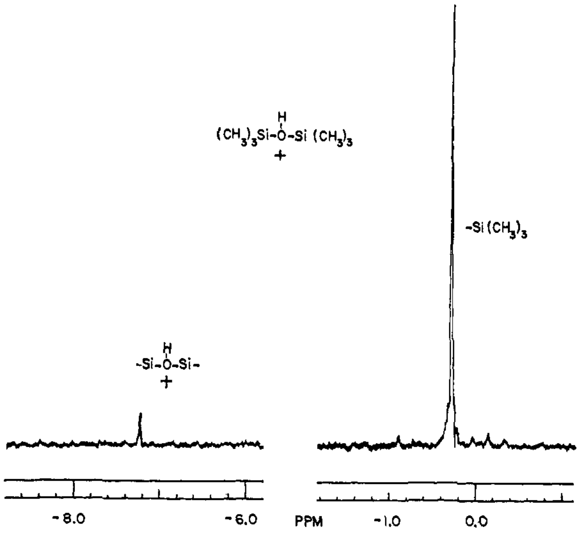


Figure 7. Pmr spectrum of protonated hexamethyldisiloxane in $FSO_3H–SbF_5–SO_2$ solution at −78°.

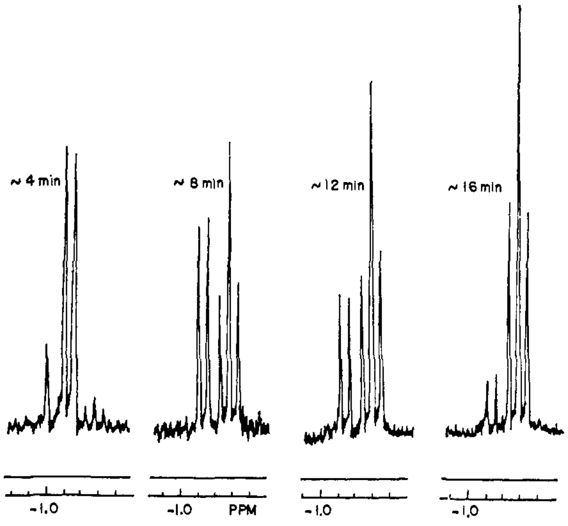
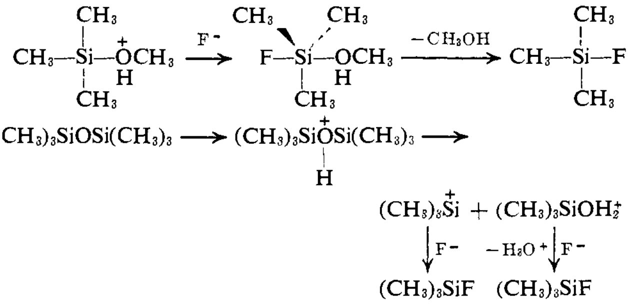


Figure 8. Methyl nmr region of cleavage of trimethyltriphenyldisiloxane in 8:1 $FSO_3H–SbF_5$ solution at −70°.

at silicon prior to the loss of methanol (direct displacement or Si(V) mechanism path[20]).



No electron-deficient deshielded species (siliconium ions) were observed in the nmr studies; instead only the derived fluorosilanes were present.

We share Sommer's views[20] as to the difficulties to find an accessible pathway to trivalent siliconium ion intermediates and the present work has not succeeded to provide such. We are, however, continuing our efforts out of conviction shared with Sommer that trialkyl (triaryl) silicon cations R_3Si^+ and the corresponding carbonium ions, R_3C^+ may in certain circumstances be of comparable stability relative to their precursors. It is thus not a question of inherent instability, but lack of sufficient imagination which prevented thus far to find a pathway to trivalent siliconium ions, avoiding the much more accessible direct displacement reactions involving Si(V) intermediates.

Experimental Section

Materials. Hexamethyldisiloxane, trimethyltriphenyldisiloxane, hexaphenyldisiloxane, dimethyldiethoxysilane, triethoxysilane, methyltrimethoxysilane, and tetramethoxysilane were commercially available materials and were distilled (or recrystallized) prior to use. Trimethylmethoxysilane, triethylmethoxysilane, phenyldimethylmethoxysilane, and phenylmethyldimethoxysilane were synthesized by the addition of an equimolar solution of methanol and pyridine to the corresponding chlorosilane or dichlorosilane and purified by distillation.

Trimethylfluorosilane was synthesized by the reaction of borontrifluoride ethereate with hexamethyldisiloxane. Triphenyltrimethyldisiloxane was prepared by the reaction of sodium triphenylsilanolate with trimethylchlorosilane in ether according to the method of Gilman, Benedict, and Hartzfield.[21]

Nmr Spectra. A Varian Associates Model A56/60A spectrometer equipped with a variable-temperature probe was used for all spectra.

Sample Preparation. Samples were prepared by dissolving approximately 1.5 ml of HSO_3F-SbF_5 (4:1 to 8:1 mol:mol) in an equal volume of sulfur dioxide and cooling to −76°. Approximately 0.2 ml of the alkoxysilane was dissolved in 1 ml of sulfur dioxide, cooled to −76°, and added to the acid solution with vigorous agitation. The acid was always in large excess as indicated by the acid peak at about δ 10.9 in the nmr spectra. For simplicity this peak was deleted from the figures.

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1,3-Bisdiazopropane. Preparation and Cyclization to Pyrazole

Harold Hart and James L. Brewbaker[1]

Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48823.

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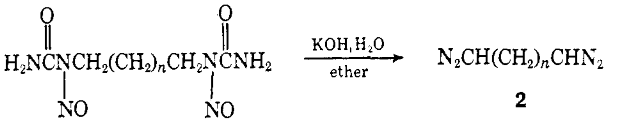
Abstract: 1,3-Bisdiazopropane was prepared by treatment of crystalline potassium propane-1,3-bisdiazotate, which is thermally stable to 168°, with protonic solvents. In cyclohexene solution, 1,3-bisdiazopropane slowly decomposed at room temperature to nitrogen and pyrazole. Kinetic studies showed that 3-diazopropene was not an intermediate, although it also cyclizes to pyrazole. The possible mechanisms are discussed.

Bisdiazoalkanes have not been extensively studied. In 1949 Lettre and Brose[2] prepared the series of bisdiazoalkanes **2c–2e** by treating ethereal solutions of the corresponding N,N′-dinitrosoureas (**1c–1e**) with aqueous potassium hydroxide. When they tried to prepare 1,3-bisdiazopropane (**2b**) by this procedure, numerous side reactions occurred and only a small amount of the yellow bisdiazo compound was extracted into the ether layer. Lieser and Beck[3] also reported the preparation of this series of compounds (**2a–2f**) using essentially the same procedure. They noted that α,ω-bisdiazoalkanes are highly unstable and that their stability decreases as the number of carbon atoms between the two diazo groups decreases.



$$H_2NC(=O)N(NO)CH_2(CH_2)_nCH_2N(NO)C(=O)NH_2 \xrightarrow[\text{ether}]{KOH,H_2O} N_2CH(CH_2)_nCHN_2$$

1 **2**

a, $n = 0$ **c**, $n = 2$ **e**, $n = 4$
b, $n = 1$ **d**, $n = 3$ **f**, $n = 5$

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[1] Michigan State University Graduate Council Fellow, 1965–1966; National Science Foundation Predoctoral Fellow, 1966–1967.

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