

The infrared spectrum, as in the case of adamantane and hexamethylenetetramine⁴ is relatively simple, and is given in Table I. It is significant

TABLE I

Wave length, microns	Interpretation
3.42 (VW)	C-H stretch
7.38 (M)	CH ₂ scissors
9.70 (S)	CH ₂ wag
12.58 (M)	SiC stretch
14.0 (W)	CH ₂ rock
19.0 (S)	SiCl stretch

that only bands characteristic of SiCH₂Si are present in the 2–12 micron region, and that no SiCH₃ or SiCH₂Cl bands are observed.⁵ A band of variable intensity at 12.23 microns is ascribed to impurity. X-Ray studies show a molecular weight of 335. A nuclear magnetic resonance spectrum on a benzene solution of the material shows a single strong line at $\delta = -0.265$ parts per million referred to (CH₃)₄Si, plus three small impurity lines.

The most striking property of this molecule is the resistance to hydrolysis of its SiCl bond. On numerous occasions crystals have been dissolved in diethyl ether (in which they are sparingly soluble) or dioxane, water added, and the bulk of the material recovered unchanged upon evaporation of the solvent. Such behavior seems inconsistent with the well-known rapid hydrolysis of the SiCl bond. Sommer,¹ however, recently has proved that the hydrolysis of chlorosilanes is highly stereospecific and proceeds with inversion of configuration. Thus, a backside attack must be involved in hydrolysis. Molecular models of 1,3,5,7-tetrachloro-1,3,5,7-tetrasiladamantane show that it fits together rigidly without appreciable strain, and with no opportunity for other than a frontal attack on the SiCl linkages.⁶

Attempts to methylate the compound with CH₃MgCl were unsuccessful, and only partial reaction, if any, was observed.

(4) R. Mecke and H. Spiesecke, *Spectrochim. Acta*, **7**, 387 (1956).

(5) A. L. Smith, *ibid.*, **16**, 87 (1960).

(6) One of the referees, L. H. Sommer, had these comments: "At first sight, the results appear inconsistent with previous reactivity data for bridgehead silicon. Actually, they afford strong support for the previously advanced concept of Si(5) intermediates in which the entering and leaving groups may be at 90° to each other in the trigonal bipyramidal addition complex (see L. H. Sommer and O. F. Bennett, *J. Am. Chem. Soc.*, **79**, 1008 (1957) and subsequent publications on bridgehead silicon). The order of reactivity with LiAlH₄ for I, 1-chloro-1-silabicyclo[2.2.1]heptane, II, *n*-Bu₃SiCl, and III, 1-chloro-1-silabicyclo[2.2.2]octane, is: I >> II > III (M. C. Musolf, Ph.D. Thesis, The Pennsylvania State University, 1960), and the tetrasiladamantane system, IV, should have less reactive SiCl than III on the grounds that formation of Si(5) from IV would necessarily involve: (i) serious angular distortion of the tetrahedral O-Si-C bond angles of all four ring-locked silicon atoms, because of the nature of the ring-system in IV—a very unfavorable I-strain factor would obtain since IV is a perfectly symmetrical unstrained structure; (ii) serious steric hindrance, due to the fact that each silicon atom in IV bears three substituents that are highly substituted at the β -position (*i.e.*, Cl(CH₂)₂-Si(CH₂)₂), a situation that does not obtain for III. It is noteworthy that bridgehead reactivity for Si(5) mechanisms (addition intermediates, sp³ bonding) and for carbonium ion mechanisms (dissociation or ionization intermediates, sp² bonding) turn out to have (a not expected) inverse structure dependence; for the preparative hydrolysis of 1-bromoadamantane see: H. Stetter, M. Schwarz and A. Hirschhorn, *Ber.*, **92**, 1629 (1959)."

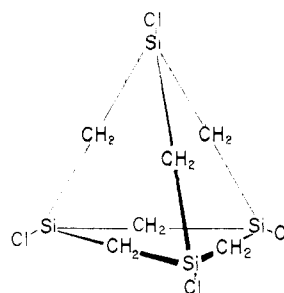


Fig. 1

We are indebted to Dr. E. B. Baker of the Dow Chemical Company for the n.m.r. spectrum.

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MIDLAND, MICHIGAN

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SILICONIUM IONS AND CARBONIUM IONS AS REACTION INTERMEDIATES

Sir:

Despite the gradually emerging outlines of a better general understanding of the mechanisms of organosilicon reactions *via* studies of kinetics and stereochemistry, the situation with regard to the status of siliconium ions as reaction intermediates has remained exceedingly obscure (*vide infra*). On the basis of earlier qualitative studies of aliphatic organosilicon compounds, we had attributed certain remarkably rapid reactions of the aliphatic carbon-silicon bond to: "electron-release from silicon to electronically-deficient beta carbon."¹ However, it was not possible to decide—on the basis of the qualitative data then available—whether or not such electron-release was assisted by simultaneous nucleophilic attack on silicon, even with electrophilic reagents such as aluminum chloride or mineral acids.

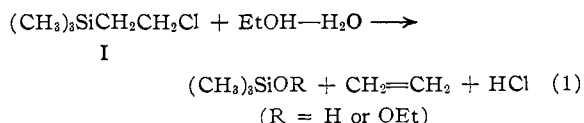
From the (personal) conviction that *trialkyl* silicon cations, R₃Si⁺, and *trialkyl* carbon cations, R₃C⁺, may, in certain circumstances, be of comparable stability relative to their precursors²; and that a siliconium ion mechanism would be isolable, provided that due care was exercised in the choice of reactant and reagent structures for the purpose of decreasing the probability of reaction by direct displacement or Si(5) mechanism paths,^{2,3} we have been led to undertake quantita-

(1) L. H. Sommer, D. L. Bailey and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2869 (1948); L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948); L. H. Sommer and N. S. Marans, *ibid.*, **72**, 1935 (1950); L. H. Sommer and R. P. Pioch, *ibid.*, **76**, 1606 (1954).

(2) Use of the term "stability" as applied to cations is, of course, extremely hazardous unless it is recognized—as we have tried to do herein—that relative equilibria and relative rates depend upon differences between reactant states and product states for the former, and between reactant states and transition states for the latter. See the basic Hammett equations for relative rates and relative equilibria: L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 78; F. P. Price and L. P. Hammett, *J. Am. Chem. Soc.*, **63**, 2387 (1941).

(3) For example, if it is known that Me₃SiCl and Me₃CCl solvolyse by different mechanisms, but it is also known that the former is far more reactive than the latter in solvolysis (*cf.*, A. D. Allen and G. Modena, *J. Chem. Soc.*, 3671 (1957)), then the data do not compel

tive studies of the kinetics of β -eliminations involving silicon in which the leaving group is β -chloroethyl and the silicon bears three organic groups as substituents.



Solvolysis of I (% Si, 20.3; % Cl, 26.2⁴) in aqueous ethanol at 30.0° follows a first-order rate-law with excellent precision (as measured by ethylene evolution); gives excellent correlation of variation in rate constant with variation in solvent composition over the range 50% ethanol to 80% ethanol—20% water by volume, according to the Winstein–Grunwald equation, $\log(k/k_0) = mY^5$ and yields a value of m , 1.02, which indicates that I and *t*-butyl chloride are about equally susceptible to “ionizing power” of the solvolysis medium: rate constants for I at 30.0° vary from 2.9×10^{-3} sec.⁻¹ in 50% ethanol to 6.1×10^{-5} sec.⁻¹ in 80% ethanol; at 25°, the rate constants for *t*-butyl chloride⁵ in corresponding solvent compositions are 3.7×10^{-4} sec.⁻¹ and 9.2×10^{-6} sec.⁻¹. In formic acid, I reacts more rapidly, by a factor of 2.7, than would be predicted by m . For I in formic acid at 30°, $k_1 = 2.0 \times 10^{-2}$ sec.⁻¹; for *t*-butyl chloride⁵ in the same solvent at 25°, $k_1 = 1.1 \times 10^{-3}$ sec.⁻¹.

These data clearly show that: (1) solvolysis rates of I are not sensitive to the nucleophilic character of the solvent, but are strongly dependent on its ionizing power—even more so, perhaps, than *t*-butyl chloride solvolyses; (2) approximately equal rate constants in corresponding media for I, a primary chloride, and for *t*-butyl chloride, a tertiary chloride, argue convincingly for strong participation of electron-release from silicon in the rate-controlling transition state, without simultaneous nucleophilic attack by solvent at the silicon atom. On these grounds, and from the rate-retarding effects of electron-withdrawing substituents (e.g., in 70% ethanol at 50.0°, the rate constant of $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{Cl}$ relative to $m\text{-CF}_3\text{-C}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{Cl}$ corresponds to $\rho = -2.15$), reaction (1) is properly described as proceeding by a limiting siliconium ion mechanism in the designated solvents in the absence of added lyate ion.

In accord with the current structural hypothesis of limiting carbonium ion reactions,⁶ reaction (1) may be formulated as involving structures (2) and (3) as the first and second intermediates (Y is β -chloroethyl and S is a solvent molecule).⁷

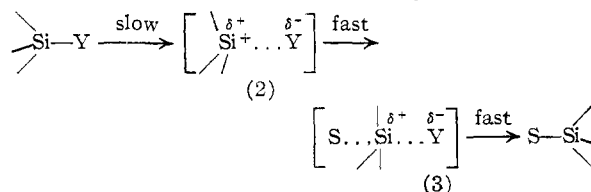
the conclusion that the stability of Me_3Si^+ relative to Me_3SiCl is less than the corresponding difference for Me_3C^+ —they only show that Me_3SiCl has a mechanism more favorable than siliconium ion available in the particular reaction studied. This statement and the one in ref. 2 seem necessary, at least in part, because of the classical-historical association of the term “carbonium ion” with tertiary organic halides.

(4) Compound I was prepared by reaction of thionyl chloride with the alcohol furnished by lithium aluminum hydride reduction of ethyl trimethylsilylacetate—J. R. Gold, L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2874 (1948).

(5) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(6) Cf. A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

In 50% ethanol at 30.0°, the addition of KOH, making the solution 0.54 *M* in lyate ion, results in a small decrease in rate (salt effects of KCl, KBr and KNO_3 are small; for 0.54 *M* concentrations, the rate factors, $k_{\text{salt}}/k_{\text{no salt}}$, are 0.8, 1.0 and 1.0); relative rate for the basic solution is 0.95. For 4.0 *M* KOH, relative rate is still only 1.45.



If the ionizing power of the solvent is decreased, thus decreasing the rate of reaction by a siliconium ion mechanism, and the solvent–reactant is again made 0.54 *M* in added KOH: at 30.0° in 70% ethanol, $k_{\text{base}}/k_{\text{neutral}} = 4.2$, but the total rate constant, for the neutral and base-catalyzed reactions, is still lower, by a factor of 3, than the rate constant for solvolysis in 50% ethanol.

We conclude that in the present case and also probably in many others, the accessibility of R_3Si^+ and R_3C^+ as intermediates is comparable; but that for the former, more favorable reaction paths may prevent a particular reaction from proceeding through a siliconium ion intermediate. For Ar_3Si^+ and Ar_3C^+ , it is clear that in equilibria the latter is far more accessible because of the large increase in resonance energy that accompanies ionization⁸; double-bonded silicon using $p_\pi-p_\pi$ bonding is still unknown, and the silicon analog of crystal violet is colorless and un-ionized.⁹

We thank Dow Corning Corporation for generous support.

(7) The alternative of a non-classical siliconium ion intermediate in which R_3Si^+ is π -bonded to the forming ethylene molecule seems more complex, but cannot be discarded on the basis of the above evidence. However, unlike the mercury case (H. J. Lucas, F. R. Hepner and S. Winstein, *J. Am. Chem. Soc.*, **61**, 3102 (1939)), the polar silylation of olefins is unknown. At this moment, it seems necessary to apply “Ocean’s Razor” to this situation.

(8) Cf. N. N. Lichtin and P. D. Bartlett, *ibid.*, **73**, 5537 (1951); A. Streitwieser, Jr., *ibid.*, **74**, 5288 (1952).

(9) U. Wannagat and F. Brandmair, *Z. anorg. Chem.*, **280**, 223 (1955); A. B. Thomas and E. G. Rochow, *J. Inorg. and Nucl. Chem.*, **4**, 205 (1957).

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A HOMOALLYLIC HYDRIDE REDUCTION WITH RING CLOSURE

Sir:

Because of its high reactivity, 7-chloronorbomadiene (I)^{1,2} seemed a natural precursor, through lithium aluminum deuteride reduction, to 7-deuterionorbomadiene, needed in a mechanism study of another reaction.³ The reaction using lithium aluminum hydride has been found to yield not only the expected norbornadiene (II) but also,

(1) S. Winstein and C. Ordroneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).

(2) P. R. Story and M. Saunders, *ibid.*, **82**, 6199 (1960).

(3) P. R. Story, *ibid.*, **82**, 2085 (1960).