Rearrangement of Nascent α-Silyl-Substituted Carbenium Ions in the Gas Phase. 1,2-Hydrogen versus 1,2-Methyl versus 1,2-Phenyl Migration

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Abstract: The unimolecular rearrangement of incipient α-silyl-substituted carbenium ions ((CH_3)$_2$HSi-$^+CH_2$ (**5**), (CH_3)$_3$Si-$^+CH_2$ (**6**), (CH_3)$_3$Si-$^+CHCH_3$ (**7**), (C_6H_5)(CH_3)HSi-$^+CH_2$ (**8**)) in the gas phase has been studied by using Fourier transform mass spectrometry (FTMS). Incipient α-silyl-substituted carbenium ions were formed by chloride elimination from the corresponding α-chloroalkylsilanes. These nascent carbenium ions rearrange to the corresponding silylenium ions by direct 1,2-group migration (H, CH_3, C_6H_5) from silicon to carbon. The structures of the resulting silylenium ions were determined by specific ion/molecule reactions with methanol and isotopically labeled ethene. The driving force for this rearrangement (1,2-group migration) is the increased thermodynamic stability of the silylenium ion. **5** undergoes exclusive 1,2-hydrogen migration, whereas **6** yields specific 1,2-methyl migration. **7** undergoes rearrangement by both 1,2-methyl and 1,2-hydrogen migration. For **7**, 1,2-hydrogen migration involves the transfer of a hydrogen atom from the methyl group bound to the carbenium center yielding (CH_3)$_3$Si(CH_2CH_2)$^+$. The incipient carbenium ion, **8**, yields competitive 1,2-phenyl (0.94) and 1,2-hydrogen (0.06) migration with *no* methyl migration observed. These results suggest the following relative migratory aptitude: phenyl > hydrogen ≫ methyl.

Introduction

The Lewis acid induced intramolecular rearrangement of α-chloroalkylsilanes (e.g., eq 1) was first reported by Whitmore,

$$(CH_3)_3SiCH_2Cl \xrightarrow{\text{AlCl}_3} (CH_3)_2(Cl)Si\text{-}CH_2CH_3 \qquad (1)$$

Sommer, and Gold.[1] It was assumed that this reaction proceeded in a manner analogous to Wagner–Meerwein rearrangements of organic systems with chloride abstraction yielding carbenium ion **1**, subsequent methyl migration generating silylenium ion, **2**, followed by chloride quenching (Scheme I). Several groups have been found to migrate, and this process (reaction 1) has often been employed in syntheses.[2]

The mechanism of process 1 was explored by Eaborn and co-workers by studying the kinetics of the $AlCl_3$ induced rearrangement of (p-XC_6H_4)(CH_3)$_2$SiCH$_2$Cl (X = CH_3, H, and Cl).[3] The reactions were first order in silane with *exclusive* aryl migration. The relative reactivities [(CH_3) 1.7:(H) 1.0:(Cl) 0.02] established that rearrangement was dramatically retarded by an electron-withdrawing group. They proposed that the rearrangement was concerted, involving a four-centered transition state, **3**, with significant positive charge on the migrating carbon atom.

R
/⁺·
Me₂Si——CH₂
\ ·⁻·/
Cl
AlCl₃

3

Steward et al.[4] studied the migratory aptitude of various organic groups in the $AlCl_3$-catalyzed rearrangement of (chloromethyl)trialkylsilanes and found the following relative aptitudes: (Me) 1.00:(Et) 2.07:(n-Pr) 2.97:(i-Pr) ≪ 1.00:(ClCH₂) ≪ 1.00. Kumada and co-workers[5] also reported exclusive methyl migration

Scheme I

$$(CH_3)_3SiCH_2Cl \xrightarrow{\text{AlCl}_3} (CH_3)_3Si\overset{+}{C}H_2 \quad + \quad AlCl_4^-$$

1

$$\Big\downarrow \sim CH_3$$

$$(CH_3)_2ClSi(CH_2CH_3) \xleftarrow{\text{AlCl}_4^-} (CH_3)_2\overset{+}{Si}(CH_2CH_3)$$

2

for (*tert*-butyl)(CH_3)$_2$SiCH$_2$Cl when stirred with $AlCl_3$. Hence, migration is facilitated by electron release and inhibited, relative to methyl, by branching at the α-carbon. Steward et al. proposed a concerted mechanism similar to Eaborn's; however, they suggested that **3** was an intermediate and not a transition state for the rearrangement.[4] They proposed an initial transition state for formation of **3** and a second transition state for conversion to products. The first transition state was believed to have developed significant carbanion character; hence primary alkyl group migration forming intermediate **3** is favored over secondary or tertiary alkyl group migration (carbanion stability: primary > secondary > tertiary).[6] The transition state for conversion of **3** to products was believed to develop considerable carbonium ion character, and this process was assumed to be the rate limiting step.[4]

Tamao and Kumada[7] studied the $AlCl_3$ induced intramolecular rearrangement of a series of chloromethyl- and dichloromethyl-substituted disilanes. They favored a mechanism involving an initial slow, rate-determining step of ionization of the carbon-halogen bond, followed by a fast step involving synchronous nucleophilic attack by halide on silicon and migration from silicon to carbon. Brook et al.[8] suggested a similar mechanism for the rearrangement of (α-hydroxyalkyl)triphenylsilanes with boron trifluoride. Hairston and O'Brien[9] supported this view in a study

(1) Whitmore, F. C.; Sommer, L. H.; Gold, J. *J. Am. Chem. Soc.* 1947, *69*, 1976.
(2) (a) Sommer, L. H.; Baily, D. L.; Gould, J. R.; Whitmore, F. C. *J. Am. Chem. Soc.* 1954, *76*, 801. (b) Nametkin, N. S.; Vdovin, V. M.; Pushchevaya, K. S.; Egorochkin, A. N. *Izv. Akad. Nauk SSR, Ser. Khim.* 1967, *11*, 2530. (c) Kumada, M.; Nakajima, J.; Ishikawa, M.; Yamamoto, Y. *J. Org. Chem.* 1958, *23*, 292. (d) Sakurai, H.; Yamamori, H.; Kumada, M. *J. Org. Chem.* 1968, *33*, 1527.
(3) Bott, R. W.; Eaborn, C.; Rushton, B. M. *J. Organomet. Chem.* 1965, *3*, 455.
(4) Steward, O. W.; Uhl, W. J.; Sands, B. W. *J. Organomet. Chem.* 1968, *15*, 329.

(5) Kumada, M.; Ishikawa, M.; Maeda, S.; Ikura, K. *J. Organomet. Chem.* 1964, *2*, 146.
(6) Cram, D. C. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965; p 21.
(7) Tamao, K.; Kumada, M. *J. Organomet. Chem.* 1971, *30*, 339.
(8) Brook, A. G.; Pannell, K. H.; LeGrow, G. E.; Shuto, J. J. *J. Organomet. Chem.* 1964, *2*, 491.
(9) (a) Hairston, T. J.; O'Brien, D. H. *J. Organomet. Chem.* 1970, *23*, C41. (b) Hairston, T. J.; O'Brien, D. H. *J. Organomet. Chem.* 1971, *29*, 79.
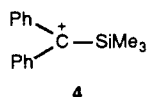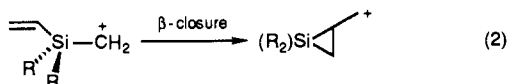
of the rearrangement of 2-(trimethylsilyl)-2-chloropropane with SbF$_5$ where an initially formed tertiary carbocation was observed by ^{1}H NMR. Olah et al.[10] reported formation of a stable α-silyl carbenium ion, **4** (stable at -78 °C for 2 days), that rearranged,
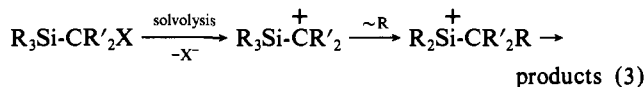
$$\underset{\text{Ph}}{\overset{\text{Ph}}{>}}\overset{+}{C}\text{—SiMe}_3$$

4

upon warming in FSO$_3$H to 0 °C, by methyl migration from silicon to carbon with nucleophilic quenching of the developing silicon cation yielding the corresponding fluorosulfate.

Consequently, there is support for both concerted and stepwise mechanisms for these rearrangements. Organosilylenium ions (R$_3$Si$^+$) were not featured in any of the above mechanisms. This, no doubt, was due to the inability to detect organosilylenium ions in solution under conditions where analogous carbenium ions are long lived.[11] Organosilylenium ions have recently been observed directly in solution[12,13] and are becoming increasingly implicated as reactive intermediates in solvolytic processes.[14-17] The difficulty in observing silylenium ions in solution is open to debate; however, their high reactivity with Lewis bases is certainly an important contributing factor.[12]

Recently, Barton and co-workers[18] provided strong support for the involvement of silylenium ions in the AlCl$_3$-induced intramolecular rearrangement of various (chloromethyl)vinylsilanes. These reactions were viewed as involving initial ionization of the carbon–halogen bond yielding α-silyl-substituted carbenium ions. Subsequent β-closure, process 2, yields silacyclopropylcarbinyl

$$\underset{\underset{R}{\overset{|}{R}}}{\overset{}{\equiv}}\text{Si}\overset{+}{-}\text{CH}_2 \xrightarrow{\beta\text{-closure}} (\text{R}_2)\text{Si}\overset{+}{\triangleleft} \qquad (2)$$

ions which either rearrange to cyclopropylsilylenium ions or are quenched directly by chloride to yield allylic chlorosilanes.[18] Apeloig and Stanger[19] have provided convincing evidence for a direct, solvent *unassisted* 1,2-methyl migration of a solvolytically produced α-silyl-substituted carbenium ion, process 3.

$$\text{R}_3\text{Si-CR}'_2\text{X} \xrightarrow[-\text{X}^-]{\text{solvolysis}} \text{R}_3\text{Si-}\overset{+}{\text{CR}}'_2 \xrightarrow{\sim\text{R}} \text{R}_2\text{Si-}\overset{+}{\text{CR}}'_2\text{R} \rightarrow$$

$$\text{products} \qquad (3)$$

The unimolecular rearrangements of α-silyl-substituted carbenium ions in the absence of complicating solvation effects have recently been studied by both theory[20-22] and experiment.[21,22] Hopkinson and Lien found that there is essentially no barrier for the strongly ($\sim$40 kcal/mol) exothermic rearrangement, process 4.[20] Schwarz, Apeloig, and co-workers, employing elegant gas

$$\text{H}_3\text{Si-}\overset{+}{\text{CH}}_2 \rightarrow \text{H}_2\text{Si(CH}_3)^+ \qquad (4)$$
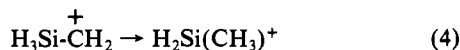
phase ion techniques[23] combined with theory, have studied the mechanism of unimolecular dissociation of nascent α-silyl-substituted carbenium ions.[21,22] Their results indicate little or no barrier for the highly exothermic 1,2-methyl and 1,2-hydrogen migrations from silicon to an α-carbenium ion center (e.g., process 4). These results are in accord with the high reactivity of cationic organo-silicon species where a number of interesting facile rearrangements have been proposed.[24-26] These results clearly demonstrate that α-silyl-substituted carbenium ions may indeed play an important role in solvolytic rearrangements of α-functionalized silanes.

In this report we study the rearrangement of nascent α-silyl-substituted carbenium ions (CH$_3$)$_2$HSi–$^+$CH$_2$ (**5**), (CH$_3$)$_3$Si–$^+$CH$_2$ (**6**), (CH$_3$)$_3$Si-$^+$CHCH$_3$ (**7**), and (C$_6$H$_5$)(CH$_3$)HSi-$^+$CH$_2$ (**8**) in the gas phase. Each of these ions should undergo facile rearrangement yielding more stable (thermodynamically) silylenium ions.[20-22] **5** may rearrange by either a 1,2-hydrogen or a 1,2-methyl migration, process 5, with each migration forming a distinct

$$(\text{CH}_3)_2\text{HSi}\overset{+}{-}\text{CH}_2 \left\{ \begin{array}{ll} \rightarrow (\text{CH}_3)_2\text{Si(CH}_3)^+ & (5a) \\ \rightarrow (\text{CH}_3)\text{HSi(C}_2\text{H}_5)^+ & (5b) \end{array}\right.$$

5
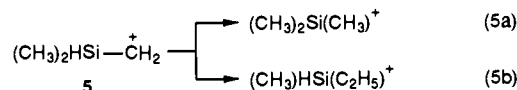
silylenium ion structure. Rearrangement of **6** will proceed by only a 1,2-methyl migration yielding the corresponding dimethylethylsilylenium ion, process 6.   **7** may rearrange by either a

$$(\text{CH}_3)_3\text{Si-}\overset{+}{\text{CH}}_2 \rightarrow (\text{CH}_3)_2\text{Si(C}_2\text{H}_5)^+ \qquad (6)$$

6
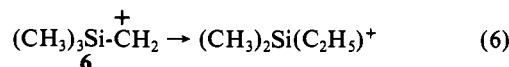
1,2-methyl or a 1,2-hydrogen migration, process 7. In this case,

$$(\text{CH}_3)_3\text{Si}\overset{+}{-}\text{CHCH}_3 \left\{ \begin{array}{ll} \rightarrow (\text{CH}_3)_2\text{Si(i-C}_3\text{H}_7)^+ & (7a) \\ \rightarrow (\text{CH}_3)_3\text{Si(CH}_2\text{CH}_2)^+ & (7b) \end{array}\right.$$

7
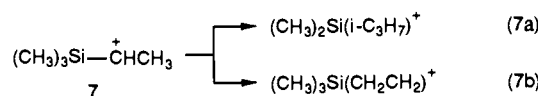
1,2-hydrogen migration generates a complex containing a labile ethene, process 7b.[21,22,27,28] The product of process 7b may exist in either a cyclic form (π-ethene complex), **9**, or an unbridged (open) form (β-silyl cation), **10**.[29] Finally, **8** may rearrange by

$$(\text{R}_3)\overset{+}{\text{Si}}\triangleleft \qquad \qquad \underset{\text{CH}_2-\overset{+}{\text{CH}}_2}{\overset{\text{R}_3\text{Si}}{\diagdown}}$$

9   **10**
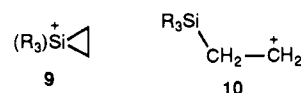
competitive 1,2-phenyl, -methyl, and -hydrogen migrations, process 8.

$$(\text{C}_6\text{H}_5)(\text{CH}_3)(\text{H})\text{Si}\overset{+}{-}\text{CH}_2 \left\{ \begin{array}{ll} \rightarrow (\text{CH}_3)\text{HSi(CH}_2\text{C}_6\text{H}_5)^+ & (8a) \\ \rightarrow (\text{C}_6\text{H}_5)\text{HSi(C}_2\text{H}_5)^+ & (8b) \\ \rightarrow (\text{C}_6\text{H}_5)(\text{CH}_3)\text{Si(CH}_3)^+ & (8c) \end{array}\right.$$

8
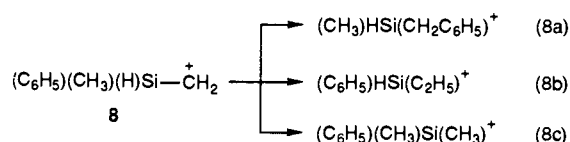
Studying these competing processes by using gas phase ion techniques is challenging, requiring the ability to distinguish the structure of isomeric organosilylenium ions. Collision-activated dissociation (CAD) is commonly employed for ion structure determination,[30] but the propensity for organosilylenium ions toward rearrangement renders CAD a less than definitive probe of ion

(10) Olah, G. A.; Berrier, A. L.; Field, L. D.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 1349.

(11) (a) Sommer, L. H. *Stereochemistry, Mechanism, and Silicon*; McGraw-Hill: New York, 1965. (b) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1, and references cited therein. (c) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 624, and references cited therein.

(12) (a) Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schiff, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201. (b) Lambert, J. B.; McConnell, J. A.; Schilf, W.; Schulz, W. J., Jr. *J. Chem. Soc., Chem. Commun.* **1988**, 455.

(13) Lambert, J. B.; Kania, L.; Schilf, W.; McConnel, J. A. *Organometallics* **1991**, *10*, 2578.

(14) Chojnowski, J.; Stanczk, W. *Adv. Organomet. Chem.* **1990**, *30*, 243.

(15) Eaborn, C.; Lickiss, P. D.; Nafin, S. T.; Romanelli, M. N. *J. Chem. Soc., Chem. Commun.* **1985**, 1754.

(16) Chojnowski, J.; Fortuniak, W.; Stanzayk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776.

(17) Chen, Y.-L.; Barton, T. J. *Organometallics* **1987**, *6*, 2590.

(18) Robinson, L. R.; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3935.

(19) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1987**, *109*, 272.

(20) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998.

(21) Apeloig, Y.; Karni, M.; Stanger, A.; Schwarz, H.; Drewello, T.; Czekay, G. *J. Chem. Soc., Chem. Commun.* **1987**, 989.

(22) Drewello, T.; Burgers, P. C.; Zummack, W.; Apeloig, Y.; Schwarz, H. *Organometallics* **1990**, *9*, 1161.

(23) For a review of gas phase ion principles and techniques, see: *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vols. 1 and 2.

(24) Oppenstein, A.; Lampe, F. W. *Review of Chemical Intermediates*; Strausz, O. P., Ed.; Elsevier: Amsterdam, 1986; Vol. 6, p 275.

(25) Schwarz, H. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rapport, Z., Eds.; Wiley: New York, 1989; p 445.

(26) Depuy, C. H.; Damrauer, R.; Bowie, J. H.; Sheldon, J. C. *Acc. Chem. Res.* **1989**, *20*, 127.

(27) Hajdasz, D.; Squires, R. *J. Chem. Soc., Chem. Commun.* **1988**, 1212.

(28) Li, X.; Stone, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 5586.

(29) For discussions on the cyclic versus open forms of (CH$_3$)$_3$Si-(CH$_2$CH$_2$)$^+$, see: (a) Wierschke, S. G.; Chandraskhar, J.; Jorgenson, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) Ibrahim, M. R.; Jorgenson, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819. (c) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.

(30) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/ Mass Spectrometry*; VCH: New York, 1988.

structure.[21,22] Specific ion/molecule reactions can, however, be quite selective probes of ion structure.[31,32] In this case, neutral reagents are selected that exploit the characteristic reactivity of an ion. For example, Hajdasz and Squires were able to distinguish the $Si(C_5H_{13})^+$ isomers ($(CH_3)_2Si(C_3H_7)^+$ and $(CH_3)_3Si-(CH_2CH_2)^+$) by reaction with methanol in a flowing afterglow-triple quadrupole instrument.[27] We have expanded upon these results and have recently demonstrated that specific ion/molecule reactions (methanol and isotopically labeled ethene as reagents) can distinguish isomeric silylenium ion structures.[33] By employing these techniques the simple 1,2-migration processes for α-silyl-substituted carbenium ions (5-8) were explored.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry[34] and Fourier transform mass spectrometry (FTMS)[35,36] have been discussed at length elsewhere. All experiments were performed by using a modified Nicolet FTMS-1000 Fourier transform mass spectrometer equipped with a 5.08 cm cubic trapping cell and 3.0 T superconducting magnet.[37] A Bayard/Alpert type ionization gauge was used to monitor pressure and was calibrated by using reactions with well-known rate constants. Pressures of reagent neutrals were subsequently corrected by using ionization cross sections.[38] Absolute pressure uncertainties are believed to be <30% with relative uncertainties <10%. Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensable gases. Ethene-d_4 and ethene-$^{13}C_2$ were obtained from MSD Isotopes with >98% isotopic purity. $(CD_3)_3Si-CHClCH_3$ was prepared by reaction of the corresponding trichlorosilane, $(Cl)_3Si-CH-ClCH_3$, with CD_3MgI[39] and the product purity confirmed by NMR. Finally, $(C_6H_5)(CH_3)HSiCH_2Cl$[40] and $(CH_3)_3Si(CH_2C_6H_5)$[41] were prepared by standard methods.

Specific organosilane ions were generated by either electron impact on the corresponding organosilane or by specific ion/molecule reactions with an appropriate organosilane. All precursor organosilanes as well as chemical ionization reagents were introduced into the vacuum chamber via a pulsed solenoid inlet valve[42] in order to prevent complicating side reactions with background organosilane.[24-26] The pulsed valve was triggered off the quench pulse with the valve duration varied (typically between 2 and 3 ms) in order to control the amount of pulsed reagents. The ballast pressure in the pulsed valve assembly was <1 Torr. A 50 ms delay follows the valve pulse prior to electron impact ionization (typically 50 ms beam duration, -70 eV). A variable delay following ionization (ca. 1.0 s) is employed to allow the pulsed reagents to be pumped from the vacuum chamber followed by isolation of the desired ions by swept ejection pulses.[36] The isolated ions are subsequently allowed to react with a static pressure of specific reagents or are collisionally activated. A static pressure of 1×10^{-5} Torr of Ar was employed throughout these experiments and serves both to facilitate ion thermalization prior to reaction and as the target for collision-activated dissociation (CAD).[43]

Details for CAD in conjunction with FTMS have been described elsewhere.[44-46] CAD breakdown curves were obtained by varying the

kinetic energy of the ions (typically between 1 and 100 eV) by adjusting the duration of CAD electric field pulse (typically between 100 and 600 μs). The maximum kinetic energy acquired by an irradiated ion (in excess of thermal energy) was calculated by using the following relationship

$$E_{tr(max)} = (E_{Rf})^2 e^2 t^2 / 8m \qquad (9)$$

where E_{Rf} is the electric field amplitude, e is the electric charge, t is the duration of the electric field pulse, and m is the mass of the ion.[34a,47] CAD fragment ion intensities are plotted as a fraction of the initial parent ion intensity (no excitation) versus kinetic energy. This allows both the energy dependency for fragmentation as well as the fragmentation efficiency to be compared directly for related systems. The CAD breakdown curves are very reproducible with less than ±3% absolute variation in ion abundances for replicate curves. The spread in ion kinetic energy is dependent on the total average kinetic energy and is 65% at 1 eV, 19% at 10 eV, 11% at 30 eV, and 6% at 100 eV.[48]

In addition to conventional FTMS-CAD, CAD by application of an "off-resonance" electric field pulse was investigated where the translational energy of an irradiated ion is given by

$$E_{tr} = \{(E_{Rf})^2 e^2 / [2m(\omega_1 - \omega_c)^2]\} \sin^2 (\omega_1 - \omega_c)t/2 \qquad (10)$$

where ω_1 (rad·s⁻¹) is the excitation frequency and ω_c is the natural cyclotron frequency of the ion.[34a,47] A consequence of "off-resonance" irradiation is that the ion undergoes acceleration-deceleration cycles throughout the duration of the electric field pulse. Hence, ions can be irradiated for a long duration without ejection from the cell. By employing a long duration (500 ms) off-resonance pulse and an appropriate $\Delta\omega$ ($\Delta\omega = |\omega_1 - \omega_c|$) an ion can be slowly collisionally activated by sequential, inelastic collisions prior to fragmentation.[49] This activation technique is analogous to infrared multiphoton dissociation (IRMPD) for probing the lowest energy pathway for ion dissociation.[50] The lowest energy pathway for dissociation of $SiC_5H_{13}^+$ ions was studied by using "off-resonance" irradiation for CAD employing a 500 ms pulse and appropriate $\Delta\omega$.

Results

$(CH_3)_2HSi-^+CH_2$. Nascent carbenium ion **5**, $(CH_3)_2HSi-^+-CH_2$, is generated by protonolysis with a $CH_5^+/C_2H_5^+$ mixture (obtained from EI of methane), reaction 11. Some $SiC_3H_8Cl^+$

$$(CH_3)_2HSi-CH_2Cl + CH_5^+/C_2H_5^+ \rightarrow$$
$$\begin{array}{c} + \\ (CH_3)_2HSi-CH_2 + HCl + CH_4/C_2H_4 \quad (11) \\ \mathbf{5} \end{array}$$
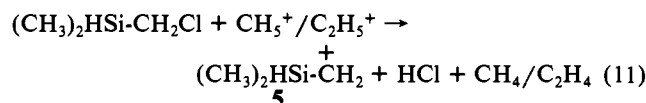
and $SiC_2H_6Cl^+$ are also generated by this protonolysis process. The nascent carbenium ion, **5**, may rearrange by either a 1,2-hydrogen or a 1,2-methyl migration, process 5. The authentic isomers ($Si(CH_3)_3^+$ and $SiH(CH_3)(C_2H_5)^+$) yield nearly identical CAD breakdown curves (identical products with similar energy dependency); however, these two $SiC_3H_9^+$ isomers are readily distinguished by specific ion/molecule reactions involving methanol and isotopically labeled ethene.[33] $Si(CH_3)_3^+$ reacts with methanol yielding elimination of methane generating a dimethylmethoxy-silylenium ion along with adduct formation,[33,51] reaction 12, with

$$Si(CH_3)_3^+ + CH_3OH \begin{array}{c} \xrightarrow{0.90} Si(CH_3)_2(OCH_3)^+ + CH_4 \quad (12a) \\ \xrightarrow{0.10} Si(CH_3)_3(HOCH_3)^+ \quad (12b) \end{array}$$
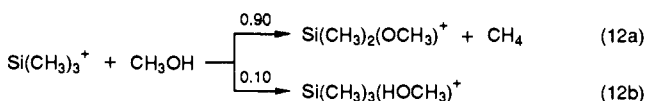
a rate constant (k) of 6.1 (1.8) $\times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.[52] In contrast, $SiH(CH_3)(C_2H_5)^+$ yields three competitive neutral losses

(31) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

(32) Kascheres, C.; Cooks, R. G. *Anal. Chim. Acta* **1988**, *215*, 223.

(33) Holznagel, C. M.; Bakhtiar, R.; Jacobson, D. B. *J. Am. Soc. Mass Spectrom.* **1991**, *2*, 278.

(34) For reviews on ICR, see: (a) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527. (b) Lehman, T. A.; Bursey, M. M. *Ion Cyclotron Resonance Spectrometry*; Wiley-Interscience: New York, 1976.

(35) For reviews on FTMS methodology, see: (a) Gross, M. L.; Rempel, D. L. *Science (Washington, D.C.)* **1984**, *226*, 26. (b) Wanczek, K. P. *Int. J. Mass Spectrom. Ion Processes* **1984**, *60*, 11. (c) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316. (d) Comisarow, M. B. *Anal. Chim. Acta* **1985**, *178*, 1.

(36) *Fourier Transform Mass Spectrometry*; Buchanan, M. V., Ed.; American Chemical Society: Washington, D.C., 1987.

(37) A complete description of the instrument can be found in: Jacobson, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 1626.

(38) Bartmess, J. E.; Geordiadis, R. M. *Vacuum*, **1983**, *33*, 149.

(39) Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 485.

(40) Belyakove, Z. V.; Golubtsov, S. A. *Zh. Khim.* **1961**, *31*, 3178.

(41) Steward, O. W.; Pierce, O. R. *J. Am. Chem. Soc.* **1961**, *83*, 1916.

(42) A detailed description of pulsed valve introduction of reagent gases in conjunction with FTMS can be found in: Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

(43) Cooks, R. G. *Collision Spectroscopy*; Plenum Press: New York, 1978.

(44) (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Processes* **1982**, *41*, 199. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96. (c) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436.

(45) McIver, R. T., Jr.; Bowers, W. D. *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; Wiley: New York, 1983; p 287.

(46) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736, 7484.

(47) It has been suggested that the kinetic energy obtained by an irradiated ion is much less than that calculated from eq 8: Grosshans, P. B.; Marshall, A. G. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 347.

(48) Comisarow, M. B. *J. Chem. Phys.* **1971**, *55*, 187.

(49) Gauthier, J. W.; Trautman, T. R.; Jacobson, D. B. *Anal. Chim. Acta* **1991**, *246*, 211.

(50) Thorne, L. R.; Beauchamp, J. L. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 3, p 41.
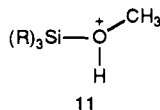
(51) Blair, I. A.; Philipou, G.; Bowie, J. H. *Aust. J. Chem.* **1979**, *32*, 59.

(52) Uncertainties in reaction rate constants are in parentheses and are primarily a consequence of pressure uncertainties.

with methanol,[33] reaction 13, along with some adduct formation
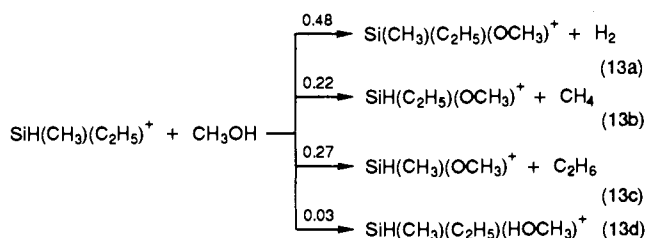
$(k = 1.43\ (0.43) \times 10^{-9}\ cm^3\ molecule^{-1}\ s^{-1})$. Reactions 12 and 13 presumably involve initial formation of an oxonium ion, **11**,
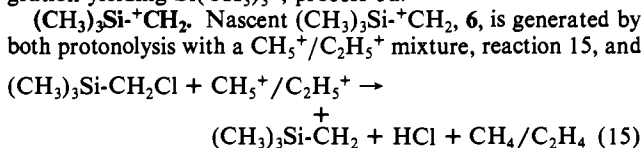

that subsequently decomposes.[51] Observation of adduct formation, processes 12b and 13d, suggests that the ion/molecule collision complex is long lived and, consequently, is stabilized by either infrared radiative emission[53] or collisional stabilization with argon (ca. 6 ms/collision).

$Si(CH_3)_3^+$ is inert toward isotopically labeled ethene whereas $SiH(CH_3)(C_2H_5)^+$ reacts with ethene-$^{13}C_2$ yielding thermoneutral displacement of an *unlabeled* ethene, process 14 ($k = 3.5\ (1.1) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$).[33]

$$SiH(CH_3)(C_2H_5)^+ + {}^{13}C_2H_4 \rightarrow$$
$$SiH(CH_3)({}^{13}C_2H_5)^+ + C_2H_4 \quad (14)$$
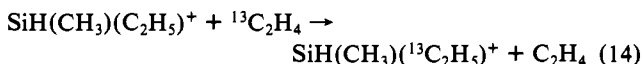
The nascent carbenium ion, **5**, formed in reaction 11 yields only methane elimination with methanol along with adduct formation in a 0.93:0.07 ratio ($k = 5.8\ (1.8) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$). In addition, incipient carbenium ion **5** is inert with ethene-$^{13}C_2$. These results clearly demonstrate that the nascent carbenium ion formed by process 11 undergoes exclusively 1,2-hydrogen migration yielding $Si(CH_3)_3^+$, process 5a.

$(CH_3)_3Si^{-+}CH_2$. Nascent $(CH_3)_3Si^{-+}CH_2$, **6**, is generated by both protonolysis with a $CH_5^+/C_2H_5^+$ mixture, reaction 15, and

$$(CH_3)_3Si\text{-}CH_2Cl + CH_5^+/C_2H_5^+ \rightarrow$$
$$\overset{+}{(CH_3)_3Si\text{-}CH_2} + HCl + CH_4/C_2H_4 \quad (15)$$

by chloride abstraction with $Si(CH_3)_3^+$, reaction 16. In addition

$$(CH_3)_3Si\text{-}CH_2Cl + Si(CH_3)_3^+ \rightarrow$$
$$\overset{+}{(CH_3)_3Si\text{-}CH_2} + Si(CH_3)_3Cl \quad (16)$$
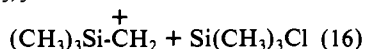
to reaction 15, small amounts of $SiC_2H_7^+$, $SiC_3H_9^+$, and $SiC_3H_8Cl^+$ are also produced by protonolysis. The nascent carbenium ion, **6**, can rearrange by a 1,2-methyl migration, process 6, yielding $Si(CH_3)_2(C_2H_5)^+$. Authentic $Si(CH_3)_2(C_2H_5)^+$, produced by EI of $Si(CH_3)_3(C_2H_5)$, reacts with methanol by competitive methane/ethane eliminations along with adduct formation, reaction 17 ($k = 7.8\ (2.3) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$).[33]
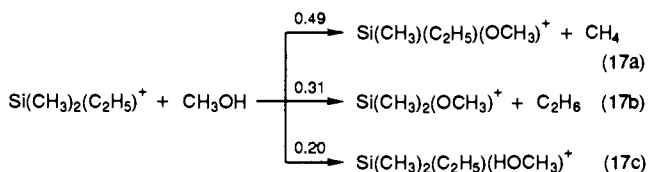
Furthermore, ethene-d_4 reacts with $Si(CH_3)_2(C_2H_5)^+$ yielding exclusive slow ($k = 4.2\ (1.3) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$) thermoneutral displacement of *unlabeled* ethene, process 18.

$$Si(CH_3)_2(C_2H_5)^+ + C_2D_4 \rightarrow$$
$$Si(CH_3)_2(C_2D_4H)^+ + C_2H_4 \quad (18)$$

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(53) (a) Woodin, R. L.; Beauchamp, J. L. *Chem. Phys.* **1979**, *41*, 1. (b) Dunbar, R. C. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *54*, 109.
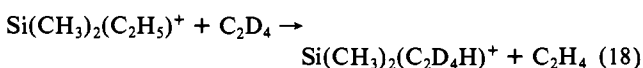
Nascent carbenium ion **6**, formed by either processes 15 or 16, reacts with methanol by competitive methane/ethane eliminations along with adduct formation, reaction 19 ($k = 7.2\ (2.2) \times 10^{-10}$
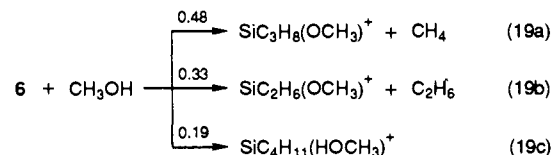
$cm^3\ molecule^{-1}\ s^{-1}$). Moreover, ethene-$d_4$ yields exclusive displacement of unlabeled ethene with **6** (e.g., process 18) with a rate constant of $4.5\ (1.4) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$. These results suggest that **6** has undergone a 1,2-methyl migration yielding $Si(CH_3)_2(C_2H_5)^+$. Nascent carbenium ion **6**, formed by either process 15 or 16, yields identical results, indicating that rearrangement is independent of the method of carbenium ion generation.

$(CH_3)_3Si^{-+}CHCH_3$ and $(CD_3)_3Si^{-+}CHCH_3$. Nascent $(CH_3)_3Si^{-+}CHCH_3$, **7**, is generated by both chloride abstraction of the corresponding chloromethyl species with $Si(CH_3)_3^+$, process 20, as well as by protonolysis with a $CH_5^+/C_2H_5^+$ mixture, reaction 21. Also, a small amount of $SiC_2H_6Cl^+$ is observed by
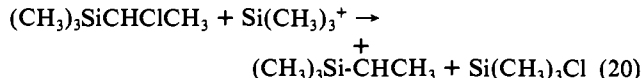
$$(CH_3)_3SiCHClCH_3 + Si(CH_3)_3^+ \rightarrow$$
$$\overset{+}{(CH_3)_3Si\text{-}CHCH_3} + Si(CH_3)_3Cl \quad (20)$$

$$B = CH_4/C_2H_4$$
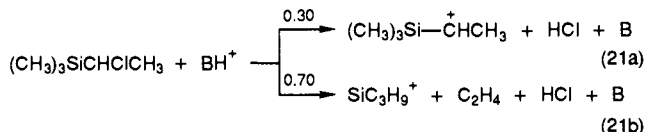
protonolysis. Nascent carbenium ion **7**, formed in processes 20 and 21a, may rearrange by a 1,2-methyl migration to yield $Si(CH_3)_2(i\text{-}C_3H_7)^+$ (process 7a) or by a 1,2-hydrogen migration generating $(CH_3)_3Si(CH_2CH_2)^+$ (process 7b).[21,22]

Authentic $Si(CH_3)_2(i\text{-}C_3H_7)^+$, produced by chloride abstraction of the corresponding chloro species by $Si(CH_3)_3^+$, reacts with methanol to yield competitive CH_4/C_3H_8 eliminations, process 22 ($k = 6.6\ (2.0) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$).[33] Ethene-$^{13}C_2$ yields
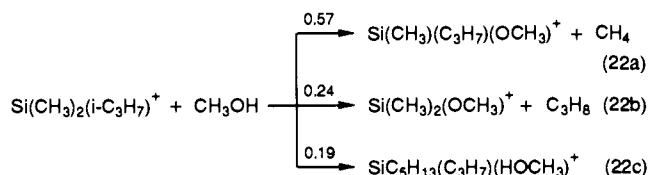

exclusively slow ($k = 4.7\ (1.4) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$) displacement of C_3H_6 (no isotopic scrambling) with authentic $Si(CH_3)_2(i\text{-}C_3H_7)^+$. Authentic $Si(CH_3)_3(CH_2CH_2)^+$, formed by process 23, reacts exclusively with methanol by elimination of

$$(CH_3)_3SiCH_2CH_2OH + CH_5^+/C_2H_5^+ \rightarrow$$
$$(CH_3)_3Si(C_2H_4)^+ + H_2O + CH_4/C_2H_4 \quad (23)$$

ethene, process 24.[27,33]

$$(CH_3)_3Si(C_2H_4)^+ + CH_3OH \rightarrow$$
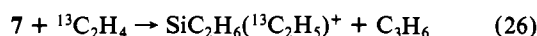$$(CH_3)_3Si(HOCH_3)^+ + C_2H_4 \quad (24)$$
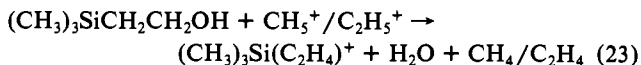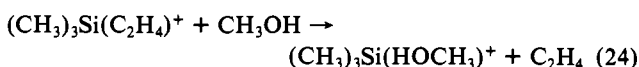
The incipient carbenium ion, **7**, formed by either process 20 or 21a, reacts with methanol by competitive methane/propane eliminations along with some adduct formation, process 25 ($k =$
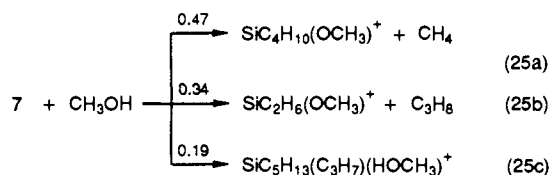
6.9 (2.1) $\times$ 10^{-10} cm³ molecule⁻¹ s⁻¹). Furthermore, ethene-$^{13}C_2$ gives *exclusive* displacement of C_3H_6 with 7, process 26; however,

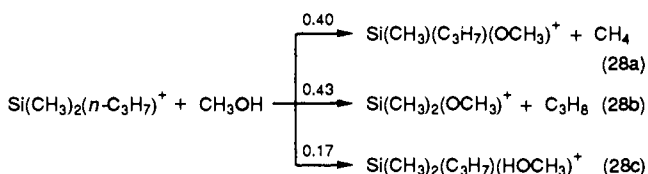$$7 + {}^{13}C_2H_4 \rightarrow SiC_2H_6({}^{13}C_2H_5)^+ + C_3H_6 \qquad (26)$$

this reaction yields nonlinear kinetics. These results clearly indicate that *stable* $SiC_5H_{13}^+$ ions formed from nascent carbenium ion 7, consist *exclusively* of a dimethylpropylsilylenium ion structure, presumably formed by 1,2-methyl migration, process 7a. These results are in contrast to a flowing afterglow study where nascent carbenium ion 7, formed by protonolysis of the corresponding chloro species, yields both an isopropyl species (1,2-methyl migration, process 7a) as well as $Si(CH_3)_3(CH_2CH_2)^+$ (1,2-hydrogen migration, process 7b) in a 4:1 ratio.[27] The disparity between the flowing afterglow and FTMS results is probably a consequence of the difference in buffer gas pressure (ca. 1 Torr in the flowing afterglow versus 1 $\times$ 10^{-5} Torr in the FTMS). Presumably, reaction 19b proceeds by initial 1,2-hydrogen migration, process 7b, yielding $Si(CH_3)_3(CH_2CH_2)^+$, but this complex must be stabilized by collisions with the buffer gas and this stabilization is much more likely in the high pressure conditions of the flowing afterglow. Hence, the above results indicate that nascent carbenium ion 7 undergoes rearrangement by both processes 7a and 7b; however, rearrangement by process 7b is followed by ethene extrusion yielding $Si(CH_3)_3^+$.

The branching ratio for reaction of methanol with 7 is markedly different from that for authentic $Si(CH_3)_2(i\text{-}C_3H_7)^+$; vide supra. Furthermore, ethene yields linear kinetics with authentic $Si(CH_3)_2(i\text{-}C_3H_7)^{+,33}$ whereas 7 yields nonlinear kinetics with ethene. These results suggest that 7 has not simply isomerized to $Si(CH_3)_2(i\text{-}C_3H_7)^+$, yet the results are consistent with a dimethylpropylsilylenium ion structure. Ab initio calculations indicate that 1,2-methyl migration, process 7a, is roughly 32 kcal/mol exothermic.[21,22] Hence, $(CH_3)_2Si(i\text{-}C_3H_7)^+$ formed by process 7a may have sufficient internal energy to isomerize further. One possible isomerization process involves reversible β-hydrogen migration/olefin insertion, process 27, interconverting an isopropyl

$$Si(CH_3)_2(i\text{-}C_3H_7)^+ \rightleftharpoons Si(CH_3)_2(H)(C_3H_6)^+ \rightleftharpoons$$
$$Si(CH_3)_2(n\text{-}C_3H_7)^+ \qquad (27)$$
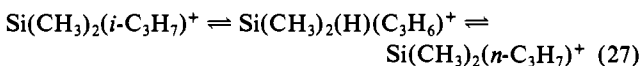
with an *n*-propyl complex.[54-59] To test this hypothesis, reaction of methanol and ethene with an authentic $Si(CH_3)_2(n\text{-}C_3H_7)^+$ isomer was studied. Methanol reacts with the *n*-propyl isomer by process 28 ($k = 8.2$ (2.5) $\times$ 10^{-10} cm³ molecule⁻¹ s⁻¹). Also,

$$Si(CH_3)_2(n\text{-}C_3H_7)^+ + CH_3OH \longrightarrow$$

$$\overset{0.40}{\longrightarrow} Si(CH_3)(C_3H_7)(OCH_3)^+ + CH_4 \qquad (28a)$$
$$\overset{0.43}{\longrightarrow} Si(CH_3)_2(OCH_3)^+ + C_3H_8 \qquad (28b)$$
$$\overset{0.17}{\longrightarrow} Si(CH_3)_2(C_3H_7)(HOCH_3)^+ \qquad (28c)$$

ethene-$^{13}C_2$ reacts with the *n*-propyl isomer exclusively by C_3H_6 displacement with a rate constant of 1.8 (0.5) $\times$ 10^{-11} cm³ molecule⁻¹ s⁻¹. Considering only the methane/propane elimination ratios with methanol, processes 22, 25, and 28 suggest that nascent carbenium ion 7 has rearranged (presumably by reversible β-hydrogen migration/olefin insertion, process 27), yielding approximately 31% of the isopropyl isomer and 69% of the *n*-propyl isomer. This isomer distribution also explains the nonlinear kinetics with ethene where the *n*-propyl isomer reacts ca. 2.6 times faster than the corresponding isopropyl isomer.[33] Consequently, a distribution of the two isomeric structures would yield nonlinear

(54) Reuter, K. A.; Jacobson, D. B. *Organometallics* **1989**, *8*, 1126.

(55) Abernathy, R. N.; Lampe, F. W. *J. Am. Chem. Soc.* **1981**, *103*, 2573.

(56) Barton, T. J.; Tillman, N. *J. Am. Chem. Soc.* **1987**, *109*, 6711.

(57) (a) Rogers, D. S.; Walker, K. L.; Ring, M. A.; O'Neal, H. E. *Organometallics* **1987**, *6*, 2313. (b) Dickinson, A. P.; Nares, K. E.; Ring, M. A.; O'Neal, H. E. *Ibid.* **1987**, *6*, 2596.

(58) Welsh, K. M.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1988**, *110*, 6689.

(59) Gaspar, P. P. *Reactive Intermediates*; Jones, M. J., Moss, R. A., Eds.; Wiley: New York, 1978; Vol. 3, p 333.
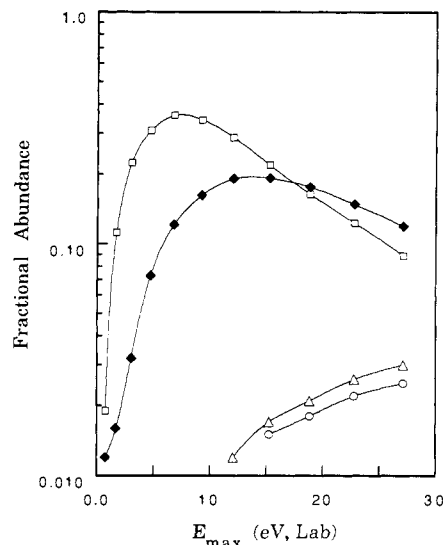

Figure 1. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of nascent carbenium ion 7, produced in reaction 20: $SiC_3H_9^+$ (□), $SiC_2H_7^+$ (◆) $SiCH_5^+$, (△), SiH_3^+ (○).
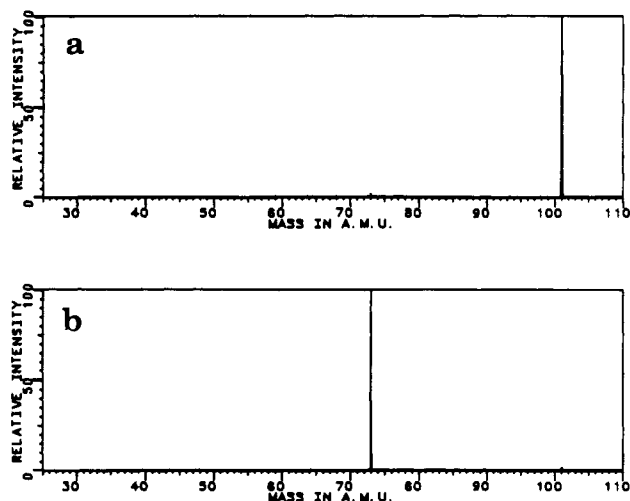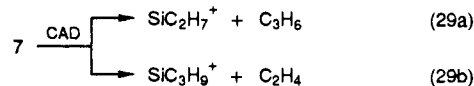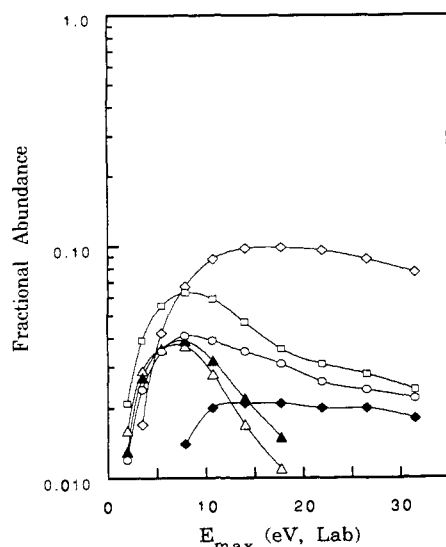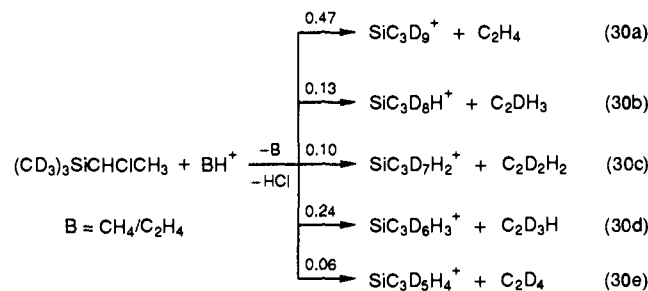

Figure 2. Sustained "off-resonance" irradiation for CAD of nascent carbenium ion 7, produced by reaction 20. CAD involves application of a 500 ms, 1.02 V electric field pulse 1.90 kHz lower than the natural cyclotron frequency of $SiC_5H_{13}^+$: (a) isolation of $SiC_5H_{13}^+$ followed by a 500 ms trap; (b) same as (a) except $SiC_5H_{13}^+$ is irradiated for 500 ms.

kinetics with ethene as observed.

The breakdown curve for CAD of 7 (a dimethylpropylsilylenium ion), formed in reaction 20, is illustrated in Figure 1 and agrees well with CAD breakdown curves for authentic $Si(CH_3)_2(C_3H_7)^{+}.33$ The two dominant fragmentation channels are elimination of C_3H_6 and C_2H_4, process 29, with C_2H_4 elimination

$$7 \xrightarrow{CAD} \begin{array}{l} \longrightarrow SiC_2H_7^+ + C_3H_6 \qquad (29a) \\ \longrightarrow SiC_3H_9^+ + C_2H_4 \qquad (29b) \end{array}$$

dominating at low kinetic energy. Process 29a probably involves simple β-hydrogen migration from a propyl group (process 27) with propene extrusion. Elimination of C_2H_4 may involve initial 1,2-methyl migration from an isopropyl group to Si regenerating carbenium ion 7 followed by 1,2-hydrogen migration (process 7b) with C_2H_4 extrusion.[21,22] The lowest energy pathway for decomposition of 7 was investigated by application of a sustained (500 ms) off-resonance electric field pulse for CAD.[49] This CAD procedure is analogous to infrared multiphoton dissociation (IRMPD) for investigating the lowest energy channel for ion decomposition.[50] 7 undergoes exclusive elimination of C_2H_4,

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Figure 3. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of nascent carbenium ion **7a**, produced by chloride abstraction of $(CD_3)_3SiCHClCH_3$ by $Si(CH_3)_3^+$: $SiC_3D_9^+$ (O), $SiC_3D_8H^+$ (▲), $SiC_3D_7H_2^+$ (△), $SiC_3D_6H_3^+$ (□), $SiC_2D_7^+$ (◆), $SiC_2D_6H^+$ (◇).

process 29b, upon off-resonance irradiation for CAD (Figure 2), indicating that this process is the lowest energy channel for decomposition of **7**. In addition, CAD by "off-resonance" irradiation of authentic $Si(CH_3)_3(i\text{-}C_3H_7)^+$ yields results identical with those for CAD of **7** (i.e., exclusive C_2H_4 elimination).

The rearrangement of nascent carbenium ion **7** was further probed by investigating the deuterium labeled analogue, $(CD_3)_3Si\text{-}^+CHCH_3$ (**7a**), produced by either chloride abstraction with $Si(CH_3)_3^+$ or by protonolysis. Ethene elimination upon protonolysis yields significant isotopic scrambling, process 30. This

$$(CD_3)_3SiCHClCH_3 + BH^+ \xrightarrow[-HCl]{-B}$$

$\xrightarrow{0.47}$ $SiC_3D_9^+$ + C_2H_4	(30a)
$\xrightarrow{0.13}$ $SiC_3D_8H^+$ + C_2DH_3	(30b)
$\xrightarrow{0.10}$ $SiC_3D_7H_2^+$ + $C_2D_2H_2$	(30c)
$\xrightarrow{0.24}$ $SiC_3D_6H_3^+$ + C_2D_3H	(30d)
$\xrightarrow{0.06}$ $SiC_3D_5H_4^+$ + C_2D_4	(30e)

$B = CH_4/C_2H_4$

isotopic distribution is in qualitative agreement with ethene elimination from the unimolecular dissociation of $(CD_3)_3Si\text{-}^+\text{-}CHCH_3$.[22] Decomposition of **7a** by direct 1,2-hydrogen migration (process 7b) would yield ethene elimination exclusively as C_2H_4. The isotopic scrambling for processes 30b–e suggests that initial 1,2-methyl migration occurs (process 7a) generating a dimethylisopropylsilylenium ion. H/D scrambling can occur by process 27 followed by 1,2-methyl migration regenerating the carbenium ion **7** with subsequent 1,2-hydrogen migration and ethene extrusion. The elimination of C_2D_4 (process 30e) requires reversible 1,2-methyl migration prior to ethene elimination.

Methanol reacts with **7a**, produced by chloride abstraction with $Si(CH_3)_3^+$, yielding methane elimination exclusively as CD_3H and propane elimination exclusively as $C_3H_5D_3$, process 31. The

$$7a + CH_3OH \longrightarrow$$

$\xrightarrow{0.42}$ $Si(CD_3)(C_3D_3H_4)(OCH_3)^+$ + CD_3H	(31a)
$\xrightarrow{0.37}$ $Si(CD_3)_2(OCH_3)^+$ + $C_3D_3H_5$	(31b)
$\xrightarrow{0.21}$ $Si(CD_3)_2(C_3D_3H_4)(HOCH_3)^+$	(31c)
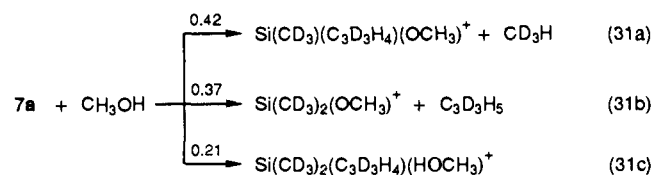
complete absence of methane elimination as CH_4 or propane elimination as $C_3D_6H_2$ indicates that a simple 1,2-methyl migration
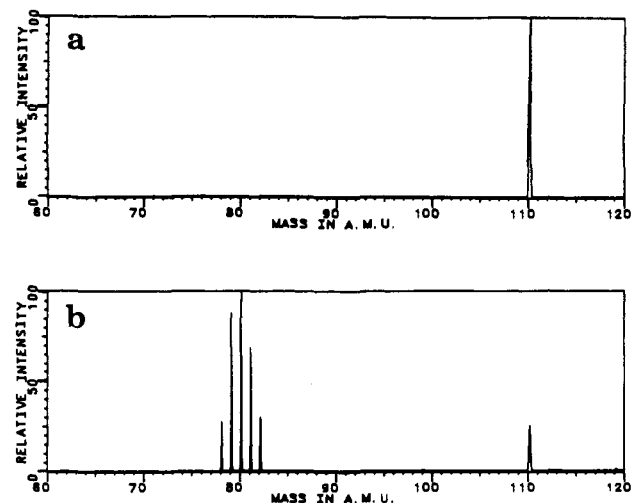

Figure 4. Sustained "off-resonance" irradiation for CAD of nascent carbenium ion **7a**, produced by chloride abstraction of $(CD_3)_3SiCHCl\text{-}CH_3$ by $Si(CH_3)_3^+$. CAD involves application of a 500 ms, 1.02 V electric field pulse 1.80 kHz lower than the natural cyclotron frequency of $SiC_5D_9H_4^+$: (a) isolation of $SiC_5D_9H_4$ followed by a 500 ms trap; (b) same as (a) except $SiC_5D_9H_4^+$ is irradiated for 500 ms.

Table I. Isotopic Distribution for Ethene Isotopomer Elimination for "Off-Resonance" Irradiation for CAD of Nascent Carbenium Ion **7a**[a]

ethene isotopomers	exptl results	random H/D scrambling
C_2H_4	8.8	0.2
C_2DH_3	22.1	6.6
$C_2D_2H_2$	32.1	39.5
C_2D_3H	28.3	30.7
C_2D_4	8.7	23.0

[a] See Figure 4 for conditions.

has occurred for **7a**. Ethene reacts with carbenium ion **7a**, yielding propene elimination as $C_3D_3H_3$ (0.77) and $C_3D_2H_4$ (0.23) (cf. process 26). Random scrambling of the label in the propyl group by process 27 would yield a 4:3 ratio for $C_3D_3H_3:C_3D_2H_4$ displacement. The actual distribution suggests that either random scrambling has not occurred or that kinetic isotope effects favor migration of H over D from the propyl group upon reaction with ethene.
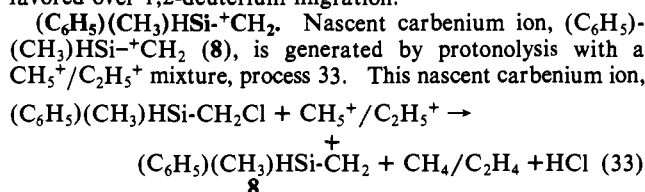
Further insights into the rearrangement of **7** is provided by probing CAD of **7a** formed by chloride abstraction with $Si(CH_3)_3^+$. Figure 3 illustrates the fragment ion abundances versus kinetic energy for CAD of **7a**. As with **7**, competitive propene/ethene eliminations are observed. Ethene elimination yields considerable isotopic scrambling at low kinetic energy; however, at high kinetic energy eliminations of C_2D_3H and C_2H_4 are the dominant isotopomer ethene losses. Hence, less scrambling is observed at high collision energy as expected. For propene elimination, loss of $C_3D_3H_3$ dominates over $C_3D_2H_4$ elimination and is consistent with the isotopic distribution for propene elimination upon reaction of **7a** with ethene; vide supra. The isotopic distribution for ethene elimination upon CAD by off-resonance irradiation of **7a** is illustrated in Figure 4. This off-resonance irradiation for CAD yields exclusive elimination of ethene, and the isotopic distribution is listed in Table I along with the distribution for random H/D scrambling. The actual isotopic distribution favors elimination of ethene isotopomers containing hydrogen.

The potential energy surface for rearrangement of **7** has been examined by ab initio MO theory.[21,22] These results indicate a barrier of ca. 10 kcal/mol for 1,2-hydrogen migration, process 7b, although this migration is highly exothermic (~27 kcal/mol). This barrier is unusual for exothermic 1,2-hydrogen shifts which are generally facile processes. The barrier for process 7b is attributed to stereoelectronic factors.[21,22] The transition state for process 7b lies approximately 15 kcal/mol higher in energy than

the separated species $(Si(CH_3)_3^+$ and $C_2H_4)$.[22] Consequently, rearrangement by process **7b** results in ethene elimination. The isotopic scrambling for **7a** upon ethene elimination, especially for CAD by off-resonance irradiation (Table I), suggests that reversible 1,2-methyl migrations, process 32, precede 1,2-hydrogen

$$(CH_3)_3Si\overset{+}{-}CHCH_3 \rightleftharpoons (CH_3)_2\overset{+}{Si}\text{-}CH(CH_3)_2 \qquad (32)$$
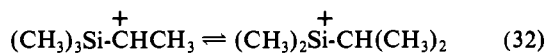
migration, process **7b**. In addition, the high abundance of isotopomer ethene elimination as $C_2D_2H_2$ and C_2DH_3 (Table I) suggests that reversible β-hydrogen migration/olefin insertion, process 27, is facile. The isotopomer distribution for ethene elimination for CAD upon off-resonance irradiation of **7a** is biased toward hydrogen products. This is consistent with a significant barrier for process **7b** where 1,2-hydrogen migration would be favored over 1,2-deuterium migration.

$(C_6H_5)(CH_3)HSi\text{-}^+CH_2$. Nascent carbenium ion, (C_6H_5)-$(CH_3)HSi\text{-}^+CH_2$ (**8**), is generated by protonolysis with a $CH_5^+/C_2H_5^+$ mixture, process 33. This nascent carbenium ion,

$$(C_6H_5)(CH_3)HSi\text{-}CH_2Cl + CH_5^+/C_2H_5^+ \rightarrow$$

$$\underset{\mathbf{8}}{(C_6H_5)(CH_3)HSi\text{-}\overset{+}{C}H_2} + CH_4/C_2H_4 + HCl \quad (33)$$

8, can rearrange by 1,2-phenyl, 1,2-methyl, or 1,2-hydrogen migration to yield the corresponding silylenium ions, process 8. Authentic $(C_6H_5)(CH_3)_2Si^+$, produced by EI on $(C_6H_5)(CH_3)_3Si$, yields exclusive elimination of C_6H_6 with methanol, process 34

$$(C_6H_5)(CH_3)_2Si^+ + CH_3OH \rightarrow Si(CH_3)_2(OCH_3)^+ + C_6H_6 \quad (34)$$
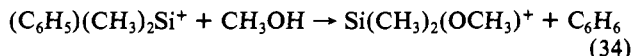
$(k = 1.1 (0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$. This high selectivity for benzene elimination is in stark contrast to the corresponding alkylsilylenium ions where competitive eliminations are observed; vide supra.[33] This highly selective benzene elimination may involve initial proton transfer of the initially formed oxonium ion (cf. **11**) from methanol to the benzenoid carbon carrying silicon facilitated by stabilization of the resulting β-carbenium ion, **12**, through

12
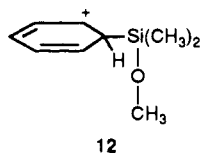
hyperconjugation.[29,60-63] Subsequent benzene elimination follows generating dimethylmethoxysilylenium, process 34. This process is analogous to benzene elimination from solvolytic protodemetalation reactions of $(C_6H_5)Si(R)_3$ (R = alkyl).[64,65] Reaction 34 is similar to the specific elimination of propene from reaction of methanol with allyldimethylsilylenium where proton transfer in the collision complex to the terminal allylic carbon generates a β-carbenium ion, stabilized by hyperconjugation,[29,60-63] followed by propene elimination.[66]

Authentic $(C_6H_5CH_2)Si(CH_3)H^+$ reacts with methanol to yield exclusive dehydrogenation, process 35 ($k = 1.8 (0.5) \times 10^{-9} \text{ cm}^3$

$$(C_6H_5CH_2)Si(CH_3)H^+ + CH_3OH \rightarrow$$

$$(C_6H_5CH_2)Si(CH_3)(OCH_3)^+ + H_2 \quad (35)$$
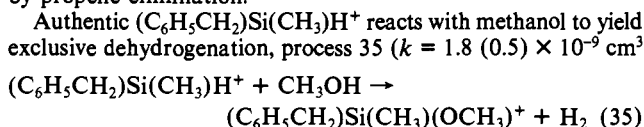
molecule^{-1} s^{-1}). The product of reaction 35 is inert with methanol. This high selectivity for dehydrogenation is surprising and not well
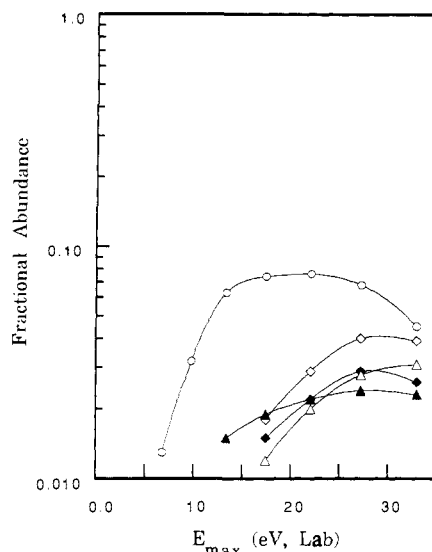
(60) Sommer, L. H.; Bailey, D. L.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 2869.

(61) Cook, M. A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 301.

(62) Lambert, J. B.; Wang, G.-T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.

(63) (a) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020. (b) Lambert, J. B.; Wang, G.-T. *J. Phys. Org. Chem.* **1988**, *1*, 169.

(64) (a) Eaborn, C. *J. Chem. Soc., Chem. Commun.* **1972**, 1255. (b) Eaborn, C.; Pande, K. C. *J. Chem. Soc.* **1960**, 1566.

(65) Berwin, H. J. *J. Chem. Soc., Chem. Commun.* **1972**, 237.

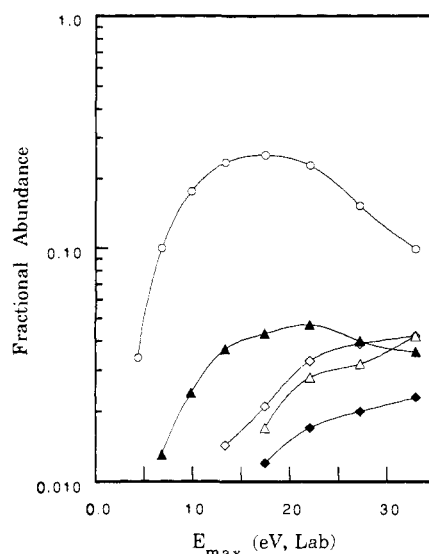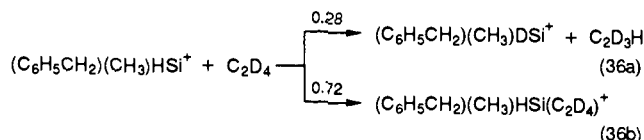(66) Blair, I. A.; Trenerry, V. C.; Bowie, J. H. *Org. Mass Spectrom.* **1980**, *15*, 15.
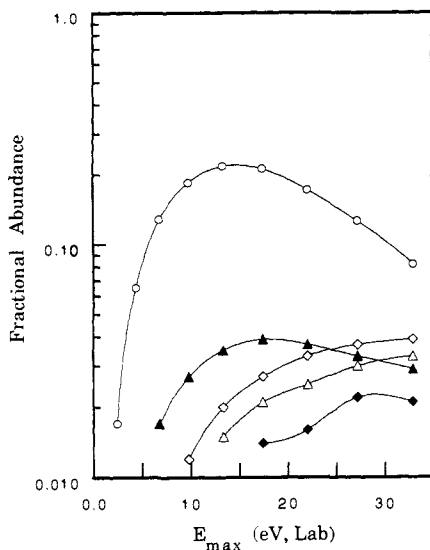
Figure 5. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of $(C_6H_5)(CH_3)_2Si^+$: $SiC_6H_7^+$ (O), $SiC_6H_5^+$ (◇), $C_7H_7^+$ (◆), $SiCH_3^+$ (▲), SiH^+ (△).

Figure 6. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of $(C_6H_5)(CH_3)HSi^+$: $SiC_6H_7^+$ (O), $SiC_6H_5^+$ (◇), $C_7H_7^+$ (◆), $SiCH_3^+$ (▲), SiH^+ (△).

understood. One possible explanation is that proton transfer to the para position of the ring in the collision complex (oxonium ion) generates β-carbenium ion, **13**, followed by dehydrogenation.

13
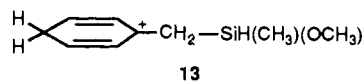
Ethene-d_4 is inert with $(C_6H_5)(CH_3)_2Si^+$; however, one slow H/D exchange is observed with $(C_6H_5CH_2)(CH_3)HSi^+$ along with condensation, reaction 36, with adduct formation, process 36b,

$$(C_6H_5CH_2)(CH_3)HSi^+ + C_2D_4 \overset{0.28}{\underset{0.72}{\longrightarrow}} \begin{cases} (C_6H_5CH_2)(CH_3)DSi^+ + C_2D_3H \quad (36a) \\ (C_6H_5CH_2)(CH_3)HSi(C_2D_4)^+ \quad (36b) \end{cases}$$

dominating over H/D exchange. CAD of the adduct (reaction 36b) yields exclusively elimination of ethene as C_2HD_3 and C_2D_4 in a 1.4:1 ratio, respectively. This suggests that ethene has inserted into the Si–H bond, yielding an ethyl complex upon adduct formation. The slow rate constant for H/D exchange of $(C_6H_5CH_2)(CH_3)HSi^+$ with ethene-d_4 contrasts with that for

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Figure 7. Variation of fractional fragment ion abundances as a function of kinetic energy (laboratory frame) for CAD of nascent carbenium ion **8**, produced in reaction 33: $SiC_6H_7^+$ (O), $SiC_6H_5^+$ (◇), $C_7H_7^+$ (◆), $SiCH_3^+$ (▲), SiH^+ (△).

$(CH_3)_2HSi^+$ where rapid H/D exchange is observed.[54] Apparently, the benzyl group inhibits reversible ethene insertion/β-hydrogen migration (e.g., process 27).

The breakdown curves for CAD of $(C_6H_5)(CH_3)_2Si^+$ and $(C_6H_5CH_2)(CH_3)HSi^+$ are illustrated in Figures 5 and 6. Both isomers yield similar fragmentations; however, there is a substantial difference in their fragmentation efficiencies. This suggests that fragmentation proceeds through a common intermediate for both isomers. For both ions, elimination of C_2H_4 is the dominant fragmentation pathway.

Methanol reactions are clearly structurally diagnostic for the $(C_6H_5)(CH_3)_2Si^+$ and $(C_6H_5CH_2)(CH_3)HSi^+$ isomers. Methanol reacts with nascent carbenium ion **8**, yielding both C_6H_6 elimination and dehydrogenation, process 37. C_6H_6 elimination is
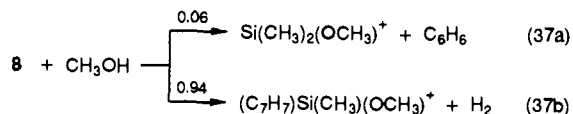
indicative of $(C_6H_5)(CH_3)_2Si^+$ and dehydrogenation is diagnostic for $(C_6H_5CH_2)(CH_3)HSi^+$. These results suggest that **8** undergoes competitive 1,2-phenyl and 1,2-hydrogen migration (processes 8a and 8c) with phenyl migration dominating. The CAD breakdown curve for nascent carbenium ion **8** is illustrated in Figure 7 and is essentially identical with that for CAD of authentic $(C_6H_5CH_2)(CH_3)HSi^+$, consistent with carbenium ion **8** rearranging primarily to that structure by a 1,2-phenyl migration.

Discussion

Nascent α-silyl-substituted carbenium ions, **5-8**, undergo rearrangement to more stable (thermodynamically) silylenium ions by 1,2-group migration from silicon to carbon. The analogous well-known 1,2-shifts for carbenium ions in organic systems will serve as a model for these rearrangements.[67] The preferred orientation for 1,2-hydrogen and 1,2-alkyl migration is coplanarity of the empty p orbital of the carbenium ion center with the σ orbital of the migration group (Z), **14**, with the transition state involving a three-center, two-electron bond. Migration can be concerted with formation of the carbocation center or may proceed
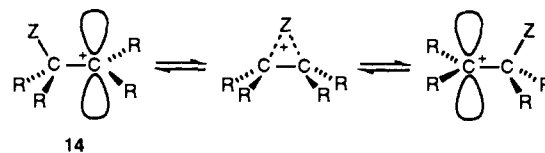
after formation of the carbenium center is complete. The question of relative preference for migration of different groups, "migratory aptitude", is a complex one, and there is no absolute order. In general, aryl groups migrate in preference to alkyl groups with the position of hydrogen often unpredictable. This low selectivity is a consequence of the low barriers for these migrations. Very often, the preferred migration involves that group which is best positioned from a stereoelectronic point of view.

The simple 1,2-migration for the incipient α-silyl-substituted carbenium ions probably involves a similar orientation to **14**. These migrations may proceed after formation of the carbenium center is complete, or migration can be concurrent with halide departure. We will assume that a fully formed carbenium ion center has developed prior to migration in the discussion.

Nascent carbenium ion, **5**, undergoes *exclusive* hydrogen migration, process 5a. Theory indicates that 1,2-hydrogen migration for the carbenium ion, $H_3Si^{-+}CH_2$, is highly exothermic (~40 kcal/mol) and proceeds with essentially no barrier.[20] Some differences are expected for methyl substitution in carbenium ion **5**, but the overall thermodynamics should be similar with process 5a highly exothermic. 1,2-Methyl migration, process 5b, is ca. 17 kcal/mol less favorable than the corresponding 1,2-hydrogen shift, process 5a,[68,69] yet both a 1,2-methyl and a 1,2-hydrogen shift for carbenium ion **5** should be highly exothermic. Nascent carbenium ion **6** undergoes 1,2-methyl migration, process 6, indicating that methyl migration occurs in the absence of the corresponding competing hydrogen shift (e.g., carbenium ion **5**). Consequently, these results suggest the following relative migratory aptitude, H ≫ Me.

The rearrangement of nascent carbenium ion **7** is complicated because two distinct rearrangements are possible, processes 7a and 7b. Labeling studies combined with CAD suggest that *reversible* 1,2-methyl migration, process 32, precedes 1,2-hydrogen migration, process 7b, for low energy ions. This suggests that 1,2-methyl migration, process 7a, has a lower barrier than the corresponding 1,2-hydrogen migration, process 7b. Ab initio MO theory reveals a barrier of ca. 10 kcal/mol for process 7b; however, no information was available concerning the barrier for 1,2-methyl migration, process 7a.[21,22] The above results, however, suggest that the barrier for 1,2-methyl migration is less than that for 1,2-hydrogen migration for nascent carbenium ion **7**.

The rearrangement of nascent carbenium ion **8** allows competitive 1,2-phenyl, -methyl, and -hydrogen migrations to be measured directly. **8** undergoes competitive phenyl (0.94) and hydrogen (0.06) migrations with *no* methyl migration observed. Competitive 1,2-aryl, -methyl, and -hydrogen migrations have been studied in detail in solution for α-aryl substituted organic carbenium ions.[71] In general, 1,2-aryl migration dominates over 1,2-methyl migration;[72] however, 1,2-hydrogen migration is competitive with 1,2-aryl migration.[73] Studies on the electronic effects of 1,2-aryl migration suggest substantial charge delocalization into the ring in the bridged (phenonium ion)[74] transition

(67) For reviews, see: (a) Fry, J. L.; Karabatsos, G. J. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1970; Vol. II, p 521. (b) Collins, C. J. *Q. Rev. Chem. Soc.* **1960**, *14*, 357. (c) Brouwer, D. M.; Hogeveen, H. *Prog. Phys. Org. Chem.* **1972**, *9*, 179. (d) McManus, S. P. *Organic Reactive Intermediates*; Academic Press: New York, 1973. (e) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper: New York, 1980; Chapter 5.

(68) $\Delta H_f°(Si(CH_3)_3^+)_g \approx 147 \pm 3$ kcal/mol from: Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 900.

(69) $\Delta H_f°(SiH(CH_3)(C_2H_5)^+)$ estimated to be 164 kcal/mol based on $\Delta H_f°(SiH(CH_3)_2^+) = 172 \pm 2$ kcal/mol[68] and assumed energy increments for replacing methyl with ethyl; cf. ref 70.

(70) Benson, S. W. *Thermochemical Kinetics*; Wiley-Interscience: New York, 1976.

(71) Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1977; Vol. 3, Chapter 27.
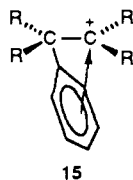
(72) Saunders, W. H., Jr.; Paine, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 882.

(73) Brookhart, M.; Anet, F. A. L.; Cram, D. J.; Winstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 5659.

(74) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6284, and references cited therein.

state leading to rearrangement.[75] Detailed studies also suggest that formation of π-bridging structures, **15**, are important in these rearrangements.[76,77]

15

1,2-Phenyl migration is a more favorable process than the corresponding 1,2-hydrogen migration for carbenium ion **8**. Although the thermodynamics of the products are not known, all three migration processes, reactions 8a–c, are probably highly exothermic. The facile nature of 1,2-phenyl migration in **8** is consistent with the AlCl$_3$ induced rearrangement of (p-XC$_6$H$_4$)(CH$_3$)$_2$SiCH$_2$Cl, where exclusive aryl migration is observed.[3] Phenyl migration is probably facilitated by initial interaction of the π electrons of the phenyl group with the developing empty 2p orbital on the carbon atom yielding a complex similar to **15**. Formal 1,2-phenyl migration then completes the process.

1,2-Hydrogen migration may precede formation of the π-bridging structure.

The results for carbenium ions, **5–8**, suggest the following relative migratory aptitude: phenyl > hydrogen ≫ methyl. Several factors, however, may contribute to the observed migration distribution. For example, the orientation of the neutral organosilane as the elimination of chloride occurs may be important. The overall thermodynamic stability of the products may also be important. Both of these effects will contribute to the observed migration distribution, but they are not part of the *intrinsic* migratory aptitude of a group.

Conclusions

The unimolecular rearrangement of simple nascent α-silyl-substituted carbenium ions in the gas phase has been explored. These incipient carbenium ions undergo 1,2-migration from silicon to carbon to yield a more stable (thermodynamically) silylenium ion with the following relative migratory aptitude: phenyl > hydrogen ≫ methyl. These results, together with recent theoretical[20–22] and experimental[18,19,21,22] findings, suggest that α-silyl-substituted carbenium ions and the corresponding silylenium ions may be important intermediates in solvolytic rearrangements of α-functionalized silanes. We are currently extending these studies to investigate the relative migratory aptitude of various groups including ethynyl, ethenyl, ethyl, *n*-propyl, isopropyl, *tert*-butyl, CH$_2$Cl, *p*-XC$_6$H$_4$, etc., in order to obtain a deeper understanding of these simple rearrangements in the gas phase.

(75) (a) Heck, R.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 3432. (b) Tanida, H.; Tsuji, T.; Ishitobi, H.; Iarie, T. *J. Org. Chem.* **1969**, *34*, 1086.
(76) (a) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1977**, *99*, 2615. (b) Brown, H. C.; Bernheimer, R.; Kim, C. J.; Scheppele, S. E. *J. Am. Chem. Soc.* **1967**, *89*, 370. (c) Brown, H. C.; Scheppele, S. E. *J. Am. Chem. Soc.* **1968**, *90*, 2082.
(77) (a) Saunders, W. H., Jr.; Asperger, S.; Edison, D. H. *J. Am. Chem. Soc.* **1958**, *80*, 2421. (b) Loukas, S. L.; Velkou, M. R.; Gregoriou, G. A. *Chem. Commun.* **1969**, 1199. (c) Loukas, S. L.; Varveri, F. S.; Velkou, M. R.; Gregoriou, G. A. *Tetrahedron Lett.* **1971**, 1803.

Homoconjugation and Transannular Orbital Interactions Detected by Photoelectron and ^{13}C-NMR Spectroscopy. Bicyclo[3.3.1]nona-3,7-diene-2,6-dione and Bicyclo[3.3.1]nonane-2,6-dione

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Abstract: Transannular orbital interactions between two ketone carbonyl groups located at positions 2 and 6 on the bicyclo[3.3.1]nonane carbocyclic framework were detected by ^{13}C-NMR and photoelectron spectroscopy (PES). Thus, an ~4.4-ppm shielding of the $\delta_{C=O}$ is observed in the ^{13}C-NMR spectra of the saturated diones (**1** and **3**) relative to the monoketones (**7** and **9**), and in the PE spectra, an ~0.15-eV splitting of the n-orbitals of the diones is detected. In the bis-enone analogues (**2** and **4**) the shieldings (relative to the corresponding mono-enones, **8** and **10**, respectively) are more than doubled, to ~10 ppm, and significant splittings are observed in the PE spectra for both n-orbitals (~0.1 eV) and π-orbitals (~0.3 eV). The origin of the electronic interaction would appear to come from orbital interaction through space and through σ-bonds.

Introduction

The phenomenon of electron delocalization through homoconjugation was described 20 years ago by Hoffmann[2] in terms of direct ("through-bond") and indirect ("through-space") interactions from localized sets of orbitals or chromophores. Orbital

interactions through a framework of σ-bonds have been studied in nonconjugated ketones, dienes, and a variety of other functional groups by photoelectron (PE)[3] and electron transmission (ET)[3c,4]

(1) (a) University of Heidelberg. (b) University of Nevada.
(2) (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499–1509. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9.

(3) Reviews: (a) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696–701. (b) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245–251. (c) Paddon-Row, M. N.; Jordan, K. D. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; Verlag Chemie: Weinheim, 1988; pp 115–194. (d) Martin, H.-D.; Mayer, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 283–310. (e) Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369–375.