solutions of the ketyl anions were handled with microsyringes lubricated with parafin oil and previously flashed with argon and the ketyl solution. The difficulty of reading accurately the volume of dark solutions was overcome by measuring the length of the plunger of the syringe with a pair of calipers, preset when the syringe was empty.

The shift vs. concentration relationships have been determined as follows. An aliquot of the ketyl solution, 0.50 mL, was added to the NMR tube containing the capillary with the external markers and having been filled with argon. The resonances due to the markers and the two THF bands were recorded at 35 ± 1 °C. In order to observe solvent resonances in concentrated solutions it was necessary to apply very fast spinning to the sample, otherwise the signals were too broad to be seen. Dilution of the sample with argon-saturated solvent (or cosolvent), by adding 100–300 μL at a time, and recording the respective shift gave the data points from which the curve shift vs. concentration could be constructed. Molar paramagnetic solvent shifts were calculated by analytical extrapolation, using the shift vs. concentration linear regression equations. These equations had a correlation coefficient better than 0.998. The reported $\Delta\nu_m^\alpha$ and $\Delta\nu_m^\beta$ values have been corrected for the difference in the chemical shifts between the external marker and the THF bands. Namely, there was sub-

tracted from the α shift 4.5 Hz and from the β shift 5.0 Hz.

Tetrahydrofuran was purified as described previously.[2e] Dioxane, triethylamine, and TMEDA were distilled from lithium aluminum hydride under argon shortly before use. Benzophenone and fluorenone were products of Merck, 99% pure, and were used after recrystallization from ethanol. The naphthyl phenyl ketones were prepared from the corresponding naphthyl bromides via naphthyllithium and naphthylphenylcarbinol. Finally the carbinols were oxidized with potassium permanganate in benzene, using tetrabutylammonium bromide as a phase-transfer catalyst.[14] The ketones after two recrystallizations from hexane melted as follows: 1-naphthylphenyl ketone, 74–76 °C (lit.[15] mp 75.5–76 °C); 2-naphthylphenyl ketone, 80–81 °C (lit.[15] mp 82 °C).

(14) Starks, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 195.
(15) "Dictionary of Organic Compounds"; Eyre and Spottiswoode: London, 1965; Vol. 1, p 362.

Theoretical Study of the Methylsilyl and Silylmethyl Cations and Anions

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Ab initio molecular orbital calculations with a double-ζ basis set have been used to optimize geometries for methylsilane, the methylsilyl and silylmethyl anions and cations, and their carbon analogues. Silicon is more effective than carbon at supporting both positive and negative charges. There is a barrier of ~60 kcal/mol to the interconversion of the methylsilyl and silylmethyl anions while on the $CSiH_5^+$ surface only the methylsilyl cation is at a minimum at the highest level of calculation. In carbenium ions the α-silyl group is stabilizing relative to hydrogen but destabilizing relative to an α-methyl group. In carbanions the α-methyl group is weakly destabilizing while the α-silyl group is strongly stabilizing. An α-methyl group destabilizes both methyl and silyl anions relative to hydrogen but stabilizes both the methyl and silyl cations. Inclusion of polarization functions (d orbitals on Si and C, p orbitals on H) does not significantly change the results.

The structure of the ethyl cation, $C_2H_5^+$, has been the subject of considerable experimental[1,2] and theoretical[3–7] investigation. Ab initio molecular orbital calculations with small basis sets predict the ion to have the classical primary carbenium structure **1**, while inclusion of d functions

1   2
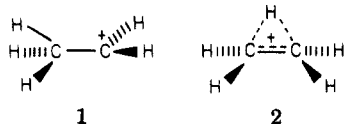
on the carbon atoms results in the nonclassical bridged structure **2** being the more stable. Inclusion of correlation energy corrections results in a further relative stabilization of **2**. Calculations on the vinyl cation, $C_2H_3^+$, have produced similar conclusions, with small basis set calculations favoring the classical or open cation and the bridged nonclassical ion becoming progressively more stable as the basis set is improved and correlation effects are included.[3–5,8]

There have been few reports of calculations on the analogous $CSiH_5^+$ and $CSiH_3^+$ surfaces,[9–12] even though $CSiH_5^+$ is a well characterized ion in the gas phase.[13,14]

(1) J. H. Vorachek, G. G. Meisels, R. A. Geanangel, and R. H. Emmel, *J. Am. Chem. Soc.*, **95**, 4078 (1973).
(2) A. S. Fiaux, D. L. Smith, and J. H. Futrell, *J. Am. Chem. Soc.*, **98**, 5773 (1976).
(3) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971).
(4) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971).
(5) B. Zurawski, R. Ahlrichs, and W. Kutzelnigg, *Chem. Phys. Lett.*, **21**, 309 (1973).
(6) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).
(7) J. E. Williams, J. V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **92**, 2141 (1970).

(8) A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, **55**, 3835 (1971).
(9) A. C. Hopkinson and M. H. Lien, *J. Chem. Soc., Chem. Commun.*, 107 (1980).
(10) Y. Apeloig, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **99**, 1291 (1977).
(11) Y. Apeloig and P. v. R. Schleyer, *Tetrahedron Lett.*, 4647 (1977).
(12) C. Eaborn, F. Feichtmayr, M. Horn, and J. N. Murrell, *J. Organomet. Chem.*, **77**, 39 (1974).
(13) T. H. Mayer and F. W. Lampe, *J. Phys. Chem.*, **78**, 2422 (1974); *ibid.*, **78**, 2645 (1974).

Eaborn et al.[12] have examined the effect of a silyl group in the α or β position relative to a carbenium ion center using a minimal basis of Slater orbitals and assumed structures. Apeloig and Schleyer[11] have reported a theoretical study of α-substituent effects in silicenium ions using an STO-3G basis set and geometry optimizations. Recently we optimized the structures of cations on the $CSiH_3^+$ surface using a double-ζ basis set and found that H_3CSi^+ is the most stable tautomer.[9] This unexpected result prompted us to examine the $CSiH_5^+$ surface in more detail than previous authors. We have subjected the silylmethyl (3) and methylsilyl (4) cations to geometry optimizations and have investigated the profile to their interconversion by optimizing the geometry of the bridged ion 5.

3   **4**   **5**
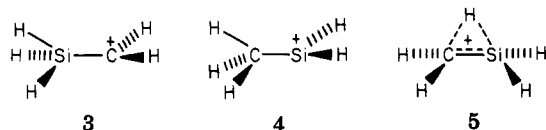
The structures of the silylmethyl (6) and methylsilyl (7)

7
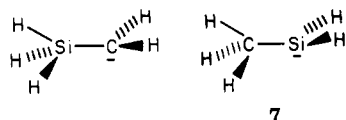
anions have not previously been examined by the ab initio method. Silicon is larger than carbon and is, therefore, more capable of accommodating a negative charge. Hence, with the assumption of deprotonation at silicon, methylsilane should be more acidic than ethane, with 7 being formed. However, carbanions are stabilized by a silicon atom adjacent to the carbanion center.[15-17] This substituent effect is usually explained in terms of delocalizing the negative charge from the carbanion center into the low-lying empty d orbitals on the silicon. There are, then, reasons to expect both anions 6 and 7 to be formed more easily from methylsilane than $C_2H_5^-$ is formed from ethane. We now report that we have optimized geometries for both these anions and examined the profile to their interconversion.

Methods

All calculations were for closed-shell singlets. The primitive Gaussian basis set used throughout the geometry optimizations consists of 11^s7^p on Si, 9^s5^p on C, and 4^s on H, all contracted to a double-ζ basis set.[18,19] For critical points on the hypersurfaces the following exponents were used for polarization orbitals:[20] d on C, 0.7; d on Si, 0.4; p on H attached to C, 0.75; p on H attached to Si, 0.433. All geometry optimizations used the gradient method[21,22] incorporated in the MONSTERGAUSS 80 program.[23]

(14) G. W. Stewart, J. M. S. Henis, and P. P. Gaspar, *J. Chem. Phys.*, **57**, 1990 (1972).

(15) D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968); *Organomet. Chem. Rev., Sect. A*, **7**, 295 (1972).

(16) C. Burford, F. Cooke, E. Ehlinger, and P. Magnus, *J. Am. Chem. Soc.*, **99**, 4537 (1977).

(17) C. Eaborn, R. Eidenschink, P. M. Jackson, and D. R. M. Walton, *J. Organomet. Chem.*, **101**, C40 (1975).

(18) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).

(19) T. H. Dunning and P. J. Hay, "Modern Theoretical Chemistry", Vol. 3, H. F. Schaefer, Ed., Plenum, New York, 1977, pp 1–37.

(20) R. Ahlrichs and R. Heinzmann, *J. Am. Chem. Soc.*, **99**, 7452 (1977).

(21) H. B. Schlegel, S. Wolfe, and F. Bernardi, *J. Chem. Phys.*, **63**, 3632 (1975).

(22) P. Pulay, *Mol. Phys.*, **17**, 197 (1969); **18**, 473 (1970).

(23) M. R. Peterson, R. A. Poirier and I. G. Csizmadia, "MONSTERGAUSS 80", University of Toronto, 1980.
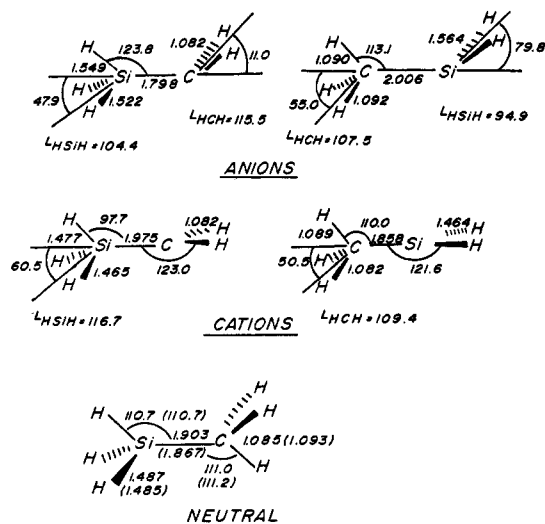

Figure 1. Geometries as optimized with the double-ζ basis set for $CSiH_5^+$, $CSiH_5^-$, and $CSiH_6$. Bond lengths are in angstroms and angles in degrees. The experimental geometry of methylsilane is in parentheses.

Results

(a) Geometries. Silaethane (8) was subjected to a full geometry optimization in both the eclipsed and staggered conformations. The latter was the more stable, with the rotational barrier being 1.2 kcal/mol[24] (experimental value 1.67 kcal/mol[25,26]). The computed and experimental geometries are in excellent agreement (Figure 1), except for the C–Si bond where the computed value is longer by 0.036 Å.

8
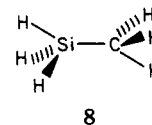
Removal of a hydride ion from the methyl group of methylsilane to form the silylmethyl cation, 3, results in an elongation of the C–Si bond (by 0.072 Å). Similar elongations of C–X bonds have been noted previously in the deprotonation of substituted methanes, CH_3X, in which the substituent X is more electropositive than carbon (e.g., X = Li, BeH, and BH_2).[27] Conversely, in the methylsilyl cation, 4, where a more electronegative substituent is attached to the cationic center, the C–Si bond is shorter (by 0.045 Å) than in silaethane. Both cations 3 and 4 are planar at the trigonal atoms. Geometry optimizations for both the eclipsed (3a) and bisected (3b) conformations of both 3 and 4 established that both cations have rotational barriers of less than 0.1 kcal/mol.

3a   **3b**
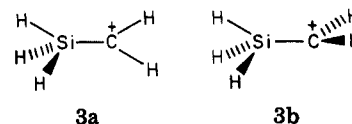
Deprotonation of silaethane leads to anions 6 and 7. Both prefer the staggered conformation, and their barriers to rotation are 8.0 and 1.6 kcal/mol, respectively. [In order

(24) Other ab initio calculations on the structure and rotational barrier of methylsilane include the following: (a) A. Veillard, *Chem. Phys. Lett.*, **3**, 128 (1969); (b) D. H. Liskow and H. F. Schaefer III, *J. Am. Chem. Soc.*, **94**, 6641 (1972). (c) G. Nicolas, J. C. Barthelat, and P. Durand, *ibid.*, **98**, 1346 (1976); (d) F. Bernardi and A. Bottoni, *Theor. Chim. Acta*, **53**, 37 (1979); (e) P. H. Blustin, *J. Organomet. Chem.*, **105**, 161 (1978).

(25) R. D. Herschbach, *J. Chem. Phys.*, **31**, 91 (1959).

(26) R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957).

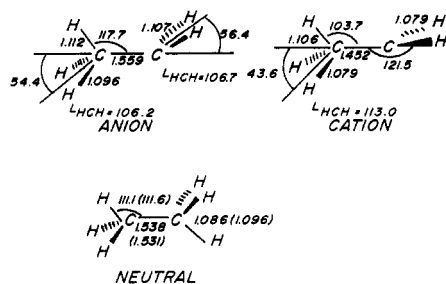(27) A. C. Hopkinson and M. H. Lien, *Int. J. Quantum Chem.*, in press.

Figure 2. Geometries as optimized with double-ζ basis set for $C_2H_5^+$, $C_2H_5^-$ and C_2H_6. Bond lengths are in angstroms and angles in degrees. The experimental geometry of ethane is in parentheses.

Table I. Energies (hartrees) of all Species at Double-ζ Optimized Geometries

species	double ζ	double ζ plus d on Si	double ζ plus d on Si and C and p on H
CH_4	$-40.185\,61^a$		$-40.206\,13$
CH_3^+	$-39.220\,32^b$		$-39.240\,90$
CH_3^-	$-39.475\,22^c$		$-39.496\,30$
SiH_4	$-291.180\,71^d$		$-291.233\,88$
SiH_3^+	$-290.290\,27^e$		$-290.335\,76$
SiH_3^-	$-290.574\,12^f$	$-290.602\,17$	$-290.605\,98$
CH_3CH_3	$-79.206\,41$		$-79.246\,92$
$CH_3CH_2^+$	$-78.287\,33$		$-78.328\,56$
$CH_3CH_2^-$	$-78.491\,61$		$-78.533\,56$
CH_3SiH_3	$-330.220\,93$	$-330.267\,64$	$-330.289\,587$
$CH_3SiH_2^+$	$-329.352\,52$	$-329.392\,59$	$-329.413\,70$
$^+CH_2SiH_3$	$-329.278\,65$	$-329.326\,63$	$-329.348\,39$
$CH_3SiH_2^-$	$-329.604\,35$	$-329.631\,21$	$-329.651\,47$
$^-CH_2SiH_3$	$-329.558\,69$	$-329.609\,77$	$-329.626\,35$

^{a} C-H 1.083 A. ^{b} Planar, C-H 1.080 A. ^{c} Pyramidal, C-H 1.105 A; $\angle$HCH 108.4°. ^{d} Si-H 1.483 A. ^{e} Planar, Si-H 1.460 A. ^{f} Pyramidal, Si-H 1.559 A; $\angle$HSiH 95.3°.

to estimate the rotational barriers, the geometries optimized for the staggered conformations were used.] Both anions are pyramidal with out-of-plane angles α of 11.0° and 79.8° (for the definition of α see structure **9**). Re-

9
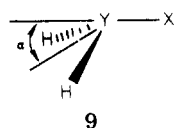
moval of a proton from monosubstituted methanes, CH_3X, where the substituent is more electronegative than carbon, results in a slight increase of the C-X bond length and values of α from 60° to 75°.[27] In this respect the methylsilyl anion **7** behaves typically. In the silylmethyl anion, **6**, however, the substituent is less electronegative than carbon, and the bond length is shorter than in silaethane, showing that the dependency of bond length variations on substituents in anions is exactly the converse of that in cations. In carbanions, electronegative substituents increase the out-of-plane angle, α, and electropositive substituents might therefore be expected to decrease this angle. In the ethyl anion, $C_2H_5^-$, α is 56.4 (see Figure 2), and the value of 15.5° for the silylmethyl anion deviates in the anticipated direction but is surprisingly low for a saturated anion (for a tetrahedral carbon $\alpha = 54.4°$).

(b) Relative Thermodynamic Stabilities of Tautomers. The total energies listed in Table I permit calculation of the relative energies of pairs of tautomers and also the assessment of relative abilities of carbon and silicon to accommodate charges.

(1) Cations. The methylsilyl cation (**4**) is more stable than the silylmethyl cation (**3**) by 46.4 kcal/mol at the double-ζ level, and this energy difference is decreased to
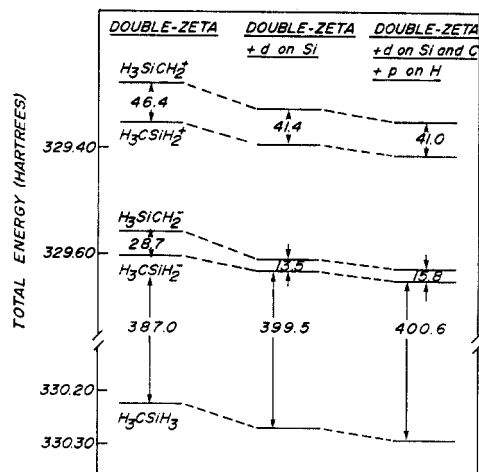

Figure 3. Relative energies of tautomers of $CSiH_5^+$ and of $CSiH_5^-$ and of $CSiH_6$ as a function of basis set. The energy differences on the diagram are in kilocalories/mole.

Table II. Improvement in Energy of Wave Function^a by Inclusion of Different Polarization Functions

	improvement by including d orbitals only on Si	improvement by including d orbitals only on C	total improvement by inclusion of polarization function
$H_3SiCH_2^+$	30.1		43.8
$H_3CSiH_2^+$	25.2		38.4
$H_3SiCH_2^-$	32.1	5.4	42.5
$H_3CSiH_2^-$	16.9	8.1	29.6
H_3CSiH_3	29.3		43.1

^{a} In kilocalories per mole.

41.0 kcal/mol by inclusion of polarization functions (see Figure 3). In agreement with this conclusion, deprotonation of methylsilane has been shown to produce only **4** in the gas phase.[13] Clearly then, the ion with the positive charge formally located on silicon is the thermodynamically more stable, consistent with the fact that silicon is larger and more electropositive than carbon.

(2) Anions. The methylsilyl anion (**7**) is more stable than the silylmethyl anion (**6**) by 28.7 kcal/mol at the double-ζ level. Inclusion of d orbitals on silicon decreases the difference to only 13.5 kcal/mol while further improvement of the basis set by including d orbitals on carbon and p orbitals on hydrogen result in a difference of 15.8 kcal/mol.

Carbanions are stabilized by an adjacent silicon atom,[15,16,28,29] and this stability has often been attributed to the ability of the empty d orbitals on silicon to delocalize the negative charge. This appears to be one of the reasons for the greater improvement of the silylmethyl anion over its tautomer, but inclusion of d orbitals produces similar improvements in the energies of methylsilane and the silylmethyl cation (Table II) where electron donation to the silicon from carbon is expected to be less important[24d] or nonexistent. The improvement in the wave functions by inclusion of d orbitals on silicon is then attributed partly to $C_\pi \rightarrow Si_{\pi^*}$ interaction and also partly to a better description of the bonding in the silyl group. In this context we have noted that the improvement in the total energy by inclusion of d orbitals on silicon is proportional to the number of hydrogen atoms attached to silicon.[30]

(28) D. Seyferth and R. E. Mammarella, *J. Organomet. Chem.*, **156**, 279 (1978).

(29) S. Bank, J. S. Sturges, D. Heyer and C. H. Bushweller, *J. Am. Chem. Soc.*, **102**, 3982 (1980).

(30) A. C. Hopkinson and M. H. Lien, *Tetrahedron*, in press.

We added the d orbitals first to silicon since we believed these would be the most important polarization functions. In order to test whether the first functions added to the double-ζ basis set would give a similar improvement in energy regardless of their location, we carried out calculations on the two anions using the double-ζ basis set augmented only with d orbitals on carbon. The total energies of **6** and **7** with this basis set are -329.567 31 and -329.617 20 hartrees, respectively, and the improvements are only 5.4 and 8.0 kcal/mol over the double-ζ calculations. Clearly then, the d orbitals on silicon are much more important than d orbitals on carbon.

In the calculations with d orbitals only on the carbon atom, there is again a larger improvement in the energy for the anion in which the d orbitals are on the atom adjacent to the formal anion center, showing that lone-pair delocalization onto the adjacent atom via the d orbitals is a small but significant factor.

(c) Relative Abilities of Silicon and Carbon to Accommodate Charges and Substituent Effects in Ions. (1) Positive Ions. The simple reaction in eq 1, where a

$$XCH_3 + XSiH_2^+ \rightarrow XCH_2^+ + XSiH_3 \qquad (1)$$

hydride ion is transferred from silicon to carbon, may be used to assess the relative abilities of these two atoms to carry a positive charge. At the highest level of calculation (i.e., double ζ plus polarization), when X = H, then ΔE = 42.1 kcal/mol, and when X = CH_3, then ΔE = 26.7 kcal/mol. Clearly then the larger and more electropositive silicon atom is the more effective atom at holding the positive charge.

The ability of the methyl group to assist in stabilizing a positive charge at silicon can be assessed from eq 2. At

$$CH_3SiH_2^+ + SiH_4 \rightarrow SiH_3^+ + CH_3SiH_3 \qquad (2)$$

the double-ζ level, ΔE = 13.8 kcal/mol, and when polarization functions are included, ΔE = 14.0 kcal/mol. These numbers should be compared with an experimental $\Delta H°$ value of 11 kcal/mol.[13] For the similar reaction at carbon (eq 3), when X = CH_3, then ΔE = 29.4 kcal/mol, and when

$$XCH_2^+ + CH_4 \rightarrow CH_3^+ + XCH_3 \qquad (3)$$
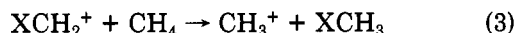
X = SiH_3, then ΔE = 15.1 kcal/mol (both at the double ζ plus polarization level). In all cases α substitution stabilizes the cation relative to hydrogen, with the carbenium ion benefiting more than the silicenium ion from substituent participation.

Previous authors[11,12] have compared the silyl and methyl groups in their abilities to stabilize cationic centers by using eq 4.

$$H_3SiCH_2^+ + CH_3CH_3 \rightarrow CH_3CH_2^+ + H_3SiCH_3 \qquad (4)$$
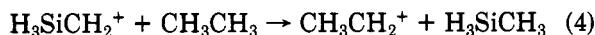
For this reaction ΔE = -14.6 kcal/mol at the double-ζ level, and when polarization functions are included, ΔE = -14.3 kcal/mol, indicating that the silyl group is considerably *less* effective at stabilizing an adjacent positive charge than the methyl group. Such a result is consistent with the experimental observations[31,32] that (i) solvolysis of (C-H$_3$)$_3$SiC(CH$_3$)$_2$Br is slower than that of (CH$_3$)$_3$CC(CH$_3$)$_2$Br and (ii) (*tert*-butyldimethylsilyl)dimethylamine is less basic than its carbon analogue in the gas phase. Our results, which included complete geometry optimizations and employed the largest basis set used to date on this reaction, are in fair agreement with one literature value (ΔE = -6.2

Table III. Proton Affinities[a]

molecule or anion	double ζ	double ζ plus d on Si	double ζ plus d on Si and C and p on H
H$_2$C=CH$_2$	172.8[b]		
H$_2$Si=CH$_2$	223.0,[c] 176.6[d]		
CH$_3^-$	445.9		445.6
C$_2$H$_5^-$	448.7		447.8
SiH$_3^-$	380.8		394.2
H$_3$SiCH$_2^-$	415.7	413.0	416.3
H$_3$CSiH$_2^-$	387.0	399.5	400.6

[a] In kilocalories per mole. [b] Geometry optimized at double-ζ level: C-C 1.334 Å, C-H 1.075 Å, and ∡CCH 121.8°. [c] C protonation. [d] Si protonation.

kcal/mol)[12] but are contrary to a minimal basis set study (ΔE = 4 kcal/mol).[10]

We have also examined the relative effects of methyl and silyl groups on an adjacent carbenium ion center by using eq 5. The geometry of silaethylene was taken from the

$$H_2C=CH_2 + H_3SiCH_2^+ \rightarrow H_2Si=CH_2 + H_3CCH_2^+ \qquad (5)$$

literature,[33] and the geometry of ethylene was optimized at the double-ζ level. For reaction 5 ΔE = 3.8 kcal/mol, which, following the reasoning above, would indicate the silyl group *stabilizes* the cation relative to the methyl group. However, this apparent reversal of the stabilizing effect of the silyl group is probably an incorrect interpretation of the structural origin of the positive energy for reaction 5. A more probable explanation is that in the products silicon is involved in a double bond whereas in the reactants it is only singly bonded. Previous studies[9,33-36] have shown the silicon has a strong tendency to avoid multiple bonds, and it is probably this feature of eq 5 which results in the positive ΔE rather than the substituent effect. Further analysis of the relative abilities of silyl and methyl groups to stabilize an adjacent carbenium center was abandoned when we found that at the highest level of calculation there is essentially no barrier to prevent the collapse of the silylmethyl cation into the more stable methylsilyl cation.

(2) Negative Ions. The relative abilities of carbon and silicon to accommodate a negative charge and the effect of substituents adjacent to the formally negatively charged center are most concisely tabulated in the form of the proton affinities of the anions (Table III). The proton affinity of the silyl anion (eq 6, X = SiH_3) is smaller than

$$X^- + H^+ \rightarrow XH \qquad (6)$$

that of the methyl anion by 65.1 kcal/mol at the double-ζ level, but this difference is decreased to 51.4 kcal/mol when polarization functions are included. Similarly, the methylsilyl anion has a lower proton affinity than the ethyl anion by 61.7 kcal/mol (double ζ) and 47.2 kcal/mol (double ζ plus polarization). Hence, the silicon atom is clearly more capable of holding a negative charge than carbon. Inclusion of polarization functions increases the proton affinities of both the silyl anions, an increase which is attributable to a greater improvement in the silane wave functions than in those of the silyl anions through a better

(31) K. J. Shea, R. Gobeille, J. Bramblett, and E. Thompson, *J. Am. Chem. Soc.*, **100**, 1611 (1978).

(32) F. K. Cartledge and J. P. Jones, *Tetrahedron Lett.*, 2193 (1971).

(33) D. M. Hood and H. F. Schaefer III, *J. Chem. Phys.*, **68**, 2985 (1978).

(34) O. P. Strausz, R. K. Gosavi, G. Theodorakopoulos, and I. G. Csizmadia, *Chem. Phys. Lett.*, **58**, 43 (1978).

(35) M. S. Gordon, *Chem. Phys. Lett.*, **54**, 9 (1978).

(36) J. N. Murrell, H. W. Kroto, and M. F. Guest, *J. Chem. Soc., Chem. Commun.*, 619 (1977).

description of bonding within the SiH_3 group, as previously discussed. This conclusion is supported by the change in the proton affinity when only d orbitals are included on the silicon atom of the methylsilyl anion.

For the isodesmic proton-transfer reaction in eq 7, when

$$XCH_2^- + CH_4 \rightarrow CH_3^- + XCH_3 \qquad (7)$$
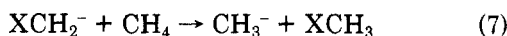
X = CH_3, then ΔE = 2.2 kcal/mol, and when X = SiH_3, then ΔE = 29.3 kcal/mol. Hence the α-methyl group weakly destabilizes the carbanion while the α-silyl group is strongly stabilizing. This stabilization of the carbanion center can, in part, be attributed to the delocalization of the "lone pair" of the carbanion center onto the adjacent silyl group. However, when only the double-ζ basis set is used for eq 7 for X = SiH_3, then ΔE = 30.2 kcal/mol, showing that essentially the same result is obtained both with and without d orbitals on silicon, thereby invalidating the argument that it is the d orbitals of silicon which are responsible for delocalizing the negative charge. This conclusion is supported by the similar charges on the silyl group of the silylmethyl anion as computed with all three basis sets (double ζ, double ζ plus d on Si, and double ζ plus polarization functions on Si, C, and H).

Introduction of a methyl substituent into the silyl anion *increases* the proton affinity by 6.4 kcal/mol. Hence an α-methyl group *destabilizes* both carbanions and silyl anions, with a slightly larger effect at silicon.

(d) Profiles to Interconversion of Tautomers. (i) Positive Ions. At the minimal STO-3G[37] and double-ζ levels both the silylmethyl and methylsilyl cations are at minima on the hypersurface. The bridged cation **5** is at a saddle point 7.7 kcal/mol (STO-3G) or 3.9 kcal/mol (double ζ) above the silylmethyl cation. These barriers are too low to permit the existence of the silylmethyl cation at room temperature. Furthermore, inclusion of polarization functions, by use of the structure for **5** as optimized with the double-ζ basis set, results in **5** being only 0.1 kcal/mol higher in energy, suggesting that optimization of the bridged ion with a basis set including polarization functions would show that this structure is not a saddle point on the surface and that the silylmethyl cation is not at a minimum. The energy of the bridged structure is high ($\sim$40 kcal/mol) above that of the methylsilyl cation, and we conclude that improvements of the wave function by further extension of the basis set and inclusion of configuration interactions is unlikely to make the bridged structure **5** the most stable. The ability of the silicon atom to accommodate a positive charge is then the dominant feature of the $CSiH_5^+$ hypersurface, and, unlike on the $C_2H_5^+$ surface, the open cation $H_3CSiH_2^+$ is at the only minimum.

(ii) Negative Ions. On the anion hypersurface both the silylmethyl (**6**) and the methylsilyl (**7**) anions are at minima with all basis sets, and a well-defined transition state occurs when one of the hydrogens is part way along the carbon–silicon bond (eq 8). The geometry of the transition state

$$7 \qquad 10 \qquad 6 \qquad (8)$$
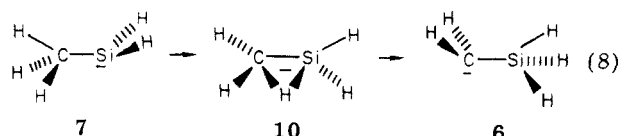
was optimized with both the STO-3G and double-ζ basis sets, and although the geometries were quite similar, the STO-3G results are not given here, as the highest occupied orbitals in this calculation had positive eigenvalues. The
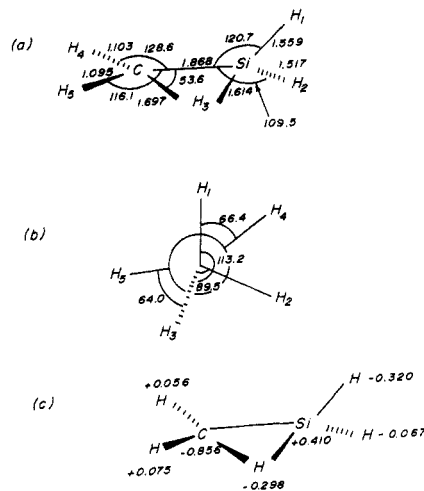
(37) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

Figure 4. (a) Structure of the transition state in interconversion of silylmethyl and methylsilyl anions. Bond lengths are in angstroms and angles in degrees. (b) Newman projection of the structure in part a showing dihedral angles. (c) Net-charge distribution in the transition state as obtained from a Mulliken population analysis with the (double-ζ plus polarization) basis set.

geometry of the transition state **10** and its charge distribution are given in Figure 4. In **10** the migrating hydrogen atom is closer to the silicon atom (Si–H distance 1.614 Å) than to the carbon (C–H distance 1.697 Å), and since Si–H bonds are normally longer ($\sim$1.48 Å) than C–H bonds ($\sim$1.10 Å), the hydrogen is much closer to being attached to the silicon than to the carbon. Also the C–Si bond length is intermediate between those in the two anions but somewhat closer to that of the silylmethyl anion (**6**). Hence, the transition state appears to be closer in structure to **6**, the less stable species on the reaction profile.

From the Newman projection on the transition state (Figure 4) it appears that the hydrogen migrating away from the silyl group comes from the position *gauche* to the lone pair of the anion (**6a**). However, without a more

6a
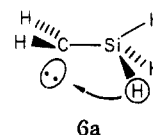
detailed study of the hypersurface no definitive conclusion can be made about the path of the migration.

The energy levels of the reactant, transition state, and product in the interconversion of methylsilyl and silylmethyl anions both at the double ζ and double ζ plus polarization levels (using double-ζ-optimized geometries) are shown in Figure 4. Initally a value of 0.6, intermediate between the exponents used for hydrogen attached to silicon (0.433) and to carbon (0.75), was used as the exponent on the migrating hydrogen. Subsequently optimization of this one exponent showed the value of 0.43 to be optimum, thereby providing further evidence that **10** is best thought of as a distorted silylmethyl anion.

The energy barriers of 61.3 kcal/mol (double ζ) and 65.0 kcal/mol (double ζ plus polarization) above the less stable tautomer, **6** indicate that interconversion of the methylsilyl and silylmethyl anions should be very slow at room temperature.

Conclusions

Comparison of ions formed by deprotonation and hydride removal from silane and methylsilane with their carbon analogues shows that silicon is more capable of

accepting positive and, more surprisingly in terms of electronegativities, negative charge than carbon. In carbenium ions an α-silyl group is destabilizing relative to an α-methyl group but is stabilizing relative to hydrogen. However, in carbanions the α-silyl group is strongly stabilizing while the methyl group is weakly destabilizing. Inclusion of d orbitals on silicon or further extension to include d orbitals on carbon and p orbitals on hydrogen does not significantly change the conclusions. Hence the interaction between a carbanion center and an adjacent silyl group is best described in terms of hyperconjugation rather than (p → d) π interaction.

Previous authors[38,39] have established that sulfur stabilizes an adjacent carbanion center by polarization rather than by d-orbital conjugation. Ab initio calculations gave the proton affinity of the thiomethyl anion, $HSCH_2^-$, to be 30 kcal/mol lower than that of the ethyl anion.[38] By comparison we find the proton affinity of the silylmethyl anion to be 33.0 kcal/mol less than that of the ethyl anion. Hence the α-silyl and α-thiol groups have a very similar effect on carbanion stability.

On the $CSiH_5^+$ hypersurface only one species, the methylsilyl cation, is at a sufficiently deep minimum to be experimentally isolable. However, on the $CSiH_5^-$ hypersurface both the silylmethyl and the methylsilyl anions are at minima. The barrier to their interconversion is ~60 kcal/mol and both should therefore be experimentally detectable.

(38) A. Streitwieser and J. E. Williams, *J. Am. Chem. Soc.*, **97**, 191 (1975).

(39) F. Bernardi, I. G. Csizmadia, A. Mangini, H. B. Schlegel, M. H. Whangbo, and S. Wolfe, *J. Am. Chem. Soc.*, **97**, 2209 (1975).