

results of statistical mechanics simulations for pure liquid formamide, NMA, and DMF and for dilute aqueous solutions of these same amides. The thermodynamic and structural results for the pure amides were found to be in excellent agreement with experimental data.⁵ For the aqueous solutions, few direct experimental structural data are available; however, the computed results, particularly for the numbers of hydrogen bonds, appear reasonable. The computed heats of solution for the amides of ca. -20 kcal/mol are also in the correct range. In addition, these studies have yielded detailed descriptions of the structure in pure liquid amides and of the hydration of amides. At this point, the

OPLS functions have been extensively tested and have revealed no significant flaws. This includes Monte Carlo simulations of over 30 pure liquids and dilute solutions. Coupled with their simplicity, the functions are highly suitable for use in computer simulations of a broad range of chemical and biochemical systems.

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Registry No. NMA, 79-16-3; DMF, 68-12-2; formamide, 75-12-7.

Magnitude and Origin of the β -Silicon Effect on Carbenium Ions

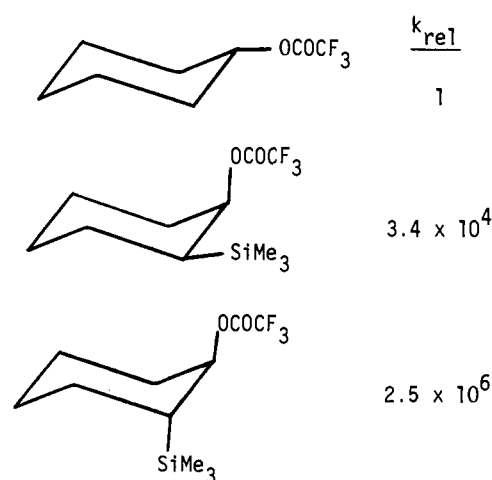
Scott G. Wierschke, Jayaraman Chandrasekhar,* and William L. Jorgensen*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received November 16, 1984

Abstract: Ab initio molecular orbital calculations have been carried out on α - and β -substituted methyl and vinyl cations to obtain a quantitative measure of the substituent effect of a silyl group relative to a methyl group and hydrogen. Geometries optimized with the 3-21G(*) basis set were used in calculations at the MP3/6-31G* level. The stabilization energies due to various substituents were determined by means of isodesmic reactions involving the parent methyl and classical vinyl cations. α -Methyl substitution of the methyl cation leads to a stabilization energy of 34.0 kcal/mol compared to 17.8 kcal/mol obtained through α -silyl substitution. The stabilization due to α -methyl and α -silyl groups is comparable for the vinyl cation (27.2 and 24.1 kcal/mol), suggesting that the inductive effect of silicon is more effective in this case. The β stabilization due to a methyl group consists of 4 kcal/mol due to induction and polarization effects and ca. 9 kcal/mol due to C-C hyperconjugation. Silyl groups lead to a significantly larger β stabilization (38 kcal/mol). The principal contribution to the β effect arises from Si-C hyperconjugation (ca. 29 kcal/mol) with only about 9 kcal/mol resulting from induction and polarization. The β effect on vinyl cations is also similar; a methyl group leads to a stabilization energy of only 8 kcal/mol compared to 28.6 kcal/mol for a silyl group. Ions **12** and **17** with α -alkyl and β -silyl substitution are particularly stabilized vinyl cations. The calculated results are in accord with available experimental evidence and place the conventional explanations of the β -silicon effect on a quantitative basis. However, the data are not consistent with a recent interpretation of the solvolysis of silyl-substituted cyclohexyl trifluoroacetates.

Despite the widespread use of silicon compounds in organic synthesis,^{1,2} the effect of silyl groups on the stability of common reactive intermediates is not fully understood. For example, there is virtually no quantitative measurement in the gas phase of the stabilization energy for a carbenium ion resulting from a silyl substituent. Even the qualitative description of the origin of the β -silicon effect (the ability of silyl groups to promote the formation or development of carbenium ions at the β position)¹⁻³ is currently controversial. The inductive effect of electropositive silicon is not usually considered to be responsible for the unusual β stabilization since the silyl group is not effective in stabilizing a carbenium ion at the α position where the inductive effect should operate to a greater extent.¹⁻⁴ In fact, early solvolysis work and various chemical evidence show that α -silyl groups are less stabilizing than α -alkyl groups toward incipient carbenium ion centers.⁴ Thus,

Scheme I



(i) $(\text{CH}_3)_3\text{SiC}(\text{CH}_3)_2\text{Br}$ solvolyzes slower than $(\text{CH}_3)_3\text{CC}(\text{C}-\text{H}_3)_2\text{Br}$ and (ii) the trimethylsilyl group exerts little directing influence on the regioselectivity of cycloaddition reactions.⁵ The origin of the β effect is more commonly attributed to the stabilizing interaction between the C-Si bond orbital and the empty p_π orbital

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Table I. Calculated Total Energies (au)^a

molecule	3-21G ^(*) //3-21G ^(*)	6-31G ^(*) //3-21G ^(*)	MP2/6-31G [*]	MP3/6-31G [*]
CH ₄	39.976 88	40.195 17	40.332 42	40.348 44
CH ₃ ⁺ (1)	39.009 13	39.230 64	39.325 11	39.341 54
CH ₃ CH ₃	78.793 95	79.228 61	79.494 29	79.520 42
b-CH ₃ CH ₂ ⁺ (2a)	77.872 60	78.310 82	78.541 86	78.567 64
e-CH ₃ CH ₂ ⁺ (2b)	77.872 16	78.310 11	78.541 07	78.566 88
SiH ₃ CH ₃	328.622 74	330.272 41	330.495 55	330.523 71
b-SiH ₃ CH ₂ ⁺ (3a)	327.681 20	329.333 57	329.514 79	329.545 10
e-SiH ₃ CH ₂ ⁺ (3b)	327.680 86	329.333 31	329.513 92	329.544 29
CH ₂ CH ₂ CH ₃	117.613 30	118.263 99	118.659 63	118.695 35
b-CH ₃ CH ₂ CH ₂ ⁺ (4a)	116.705 26	117.356 14	117.730 42	117.762 36
e-CH ₃ CH ₂ CH ₂ ⁺ (4b)	116.697 31	117.350 86	117.712 56	117.747 98
SiH ₃ CH ₂ CH ₃	367.437 67	369.302 63	369.656 82	369.694 49
b-SiH ₃ CH ₂ CH ₂ ⁺ (5a)	366.555 97	368.425 40	368.757 19	368.791 76
e-SiH ₃ CH ₂ CH ₂ ⁺ (5b)	366.518 54	368.388 27	368.707 08	368.744 61
c-SiH ₃ CH ₂ CH ₂ ⁺ (5c)	366.555 12	368.427 32	368.761 09	368.795 71
CH ₂ CH ₂	77.600 99	78.031 70	78.284 10	78.305 12
CH ₂ CH ⁺ (6)	76.655 77	77.086 64	77.306 55	77.327 41
CH ₃ CHCH ₂	116.424 01	117.071 40	117.454 41	117.484 68
CH ₃ CCH ₂ ⁺ (7)	115.518 73	116.166 48	116.520 85	116.550 28
SiH ₃ CHCH ₂	366.250 86	368.112 48	368.452 77	368.484 78
SiH ₃ CCH ₂ ⁺ (8)	365.344 45	367.205 83	367.511 88	367.545 41
CH ₃ CHCH ⁺ (9)	115.494 00	116.140 78	116.490 35	116.519 92
SiH ₃ CHCH ⁺ (10)	365.341 65	367.203 93	367.525 92	367.552 57
CH ₃ CH ₂ CHCH ₂	155.241 95	156.104 78	156.623 50	156.653 50
CH ₃ CH ₂ CCH ₂ ⁺ (11)	154.345 60	155.206 68	155.693 39	155.723 39
SiH ₃ CH ₂ CHCH ₂	405.066 25	407.143 97	407.143 97	407.143 97
SiH ₃ CH ₂ CCH ₂ ⁺ (12)	404.189 33	406.267 16	406.267 16	406.267 16

^aNegatives of total energies are given. b, e, and c refer to bisected, eclipsed, and cyclic structures. All calculations employ 3-21G^(*) optimized geometries. Vinyl cations have the linear (classical) geometry.

of the carbenium ion.¹ In contrast to inductive stabilization, hyperconjugative stabilization must necessarily be direction dependent; parallel alignment of the C–Si bond and the p_π orbital leads to maximum stabilization, while hyperconjugation is impossible when the orbitals are perpendicular. A critical evaluation of the orientation dependence of the β effect in the solvolysis of suitably chosen cyclic compounds has been carried out recently with surprising results (Scheme I).⁶ The rate enhancement of over 6 orders of magnitude due to silyl substitution reflects the β effect, but the orientation dependence is modest. The optimal hyperconjugation possible in the trans isomer leads only to a factor of 75 over the cis isomer in which the C–Si bond and the developing empty orbital are expected to be gauche to each other. Inductive stabilization is therefore implicated as the major contributor contrary to earlier explanations.

The discrepancy can be resolved through a knowledge of the energies of carefully chosen model systems with appropriate conformations and fully developed charged centers in the absence of any medium effects. Since gas-phase data are lacking, theory can be used to obtain these results. In fact, there have been several theoretical investigations of the α and β effects of silyl and methyl groups on simple carbenium ions.^{7–9} The α effect has been studied especially thoroughly.⁷ However, in order to resolve the relative importance of inductive stabilization and of Si–C and Si–H hyperconjugation, it is essential to examine both α - and β -substituted systems at uniformly high levels of theory. Such results are reported in this paper, which features ab initio calculations including significant electron correlation on substituted methyl and vinyl cations. For several ions, two conformations were considered in which the hyperconjugating bond of interest, X–H or X–C, was

Table II. Calculated Stabilization Energies (kcal/mol) for XCH₂⁺ + CH₄ → XCH₃ + CH₃⁺

XCH ₂ ⁺	3-21G ^(*) //3-21G ^(*)	6-31G ^(*) //3-21G ^(*)	MP2/6-31G [*]	MP3/6-31G [*]
CH ₃ ⁺ (1)	0.0	0.0	0.0	0.0
b-CH ₃ CH ₂ ⁺ (2a)	29.1	29.2	34.4	34.0
e-CH ₃ CH ₂ ⁺ (2b)	28.9	28.8	33.9	33.5
b-SiH ₃ CH ₂ ⁺ (3a)	16.5	16.1	16.7	17.8
e-SiH ₃ CH ₂ ⁺ (3b)	16.2	16.0	16.1	17.2
b-CH ₃ CH ₂ CH ₂ ⁺ (4a)	37.5	35.8	49.0	46.4
e-CH ₃ CH ₂ CH ₂ ⁺ (4b)	32.5	32.5	37.8	37.4
b-SiH ₃ CH ₂ CH ₂ ⁺ (5a)	54.0	54.8	67.6	72.0
e-SiH ₃ CH ₂ CH ₂ ⁺ (5b)	30.5	31.5	36.1	42.4
c-SiH ₃ CH ₂ CH ₂ ⁺ (5c)	53.5	56.0	70.0	74.4

Table III. Calculated Stabilization Energies (kcal/mol) for X⁺ + CH₂CH₂ → XH + CH₂CH⁺

X ⁺	3-21G ^(*) //3-21G ^(*)	6-31G ^(*) //3-21G ^(*)	MP2/6-31G [*]	MP3/6-31G [*]
CH ₂ CH ⁺ (6)	0.0	0.0	0.0	0.0
CH ₃ CCH ₂ ⁺ (7)	25.1	25.2	27.6	27.2
SiH ₃ CCH ₂ ⁺ (8)	24.4	24.1	23.0	24.1
CH ₃ CHCH ⁺ (9)	9.5	9.1	8.5	8.1
SiH ₃ CHCH ⁺ (10)	22.6	22.9	31.8	28.6
CH ₃ CH ₂ CCH ₂ ⁺ (11)	30.7	29.5	29.8	29.8
SiH ₃ CH ₂ CCH ₂ ⁺ (12)	42.9	42.8	42.8	42.8

held parallel and perpendicular to the vacant p_π orbital on the carbenium ion center. The results provide a quantitative estimate of the β -silicon effect and also elucidate its origins.

Computational Details

Geometry optimizations were carried out on all molecules and ions by using the 3-21G^(*) basis set which is a split-valence basis including d-type polarization functions on silicon atoms.¹⁰ On systems containing only carbon and hydrogen, the basis reduces to the familiar 3-21G set.¹¹ Symmetry constraints were employed as indicated in Figure 1 in order to probe the conformational dependence of the substituent effect. Ana-

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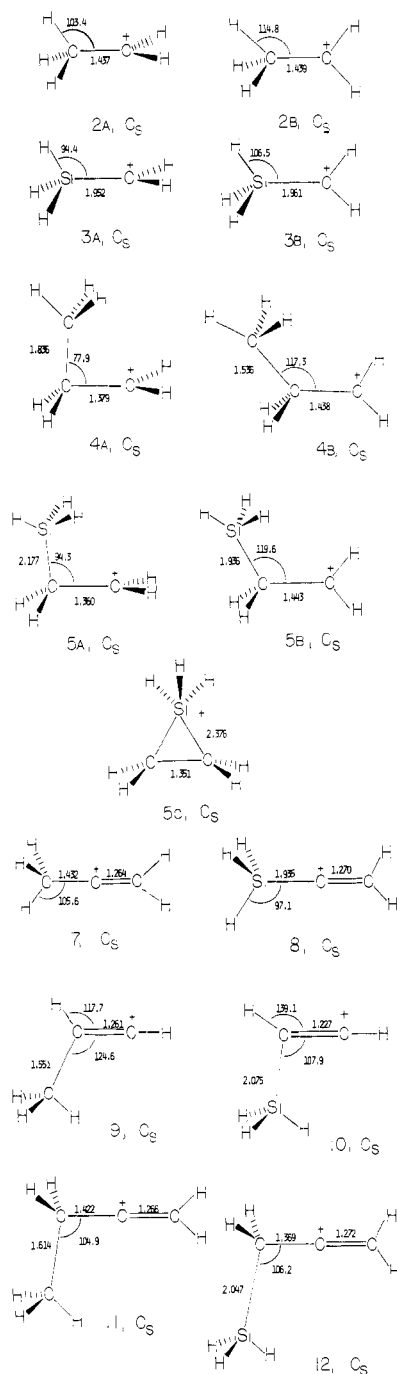


Figure 1. Selected geometrical parameters computed for the ions with the 3-21G(*) basis set. Distances in angstroms; angles in degrees.

lytical gradients and multiparameter searches were used to obtain the optimum geometries.¹² These geometries were utilized in higher level calculations by using Møller-Plesset perturbation theory to second and third orders to include the effects of electron correlation.¹³ In these computations, the 6-31G* basis set containing d functions on all non-hydrogen atoms was employed.¹⁴ The correlation calculations did not include the contribution of 1s core orbitals of heavy atoms. All calculations were carried out by using the GAUSSIAN 80 series of programs.¹⁵

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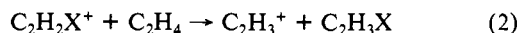
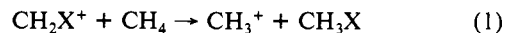
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Results

Some of the key geometrical parameters optimized for the ions are shown in Figure 1. The full geometry specifications for all ions and neutral molecules considered in this paper are included as supplementary material. The calculated total energies are given in Table I. The stabilization energies resulting from substitution of the methyl and classical vinyl cations were evaluated by means of two isodesmic reactions, eq 1 and 2, and are indicated in Tables II and III, respectively.

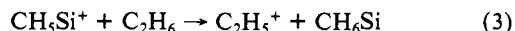


Discussion

α -Substituent Effect. The various contributions to the β effect are best analyzed by first considering α -stabilization energies of the methyl and silyl groups. These values provide an upper limit to the inductive stabilization possible from a substituent and also indicate the effectiveness of X-H hyperconjugation. Since high-level theoretical results are already available for α -stabilization energies for the methyl cation,^{7e,f} the present calculations can be calibrated as well.

As is well-known, methyl substitution results in a large stabilization of carbenium ions. The calculated stabilization energy of the classical ethyl cation, 34.0 kcal/mol (Table II) at the MP3 level is in good agreement with MP4/6-31G** calculations and experiment (33.8 and 36.4 kcal/mol, respectively).^{7f,16} The stabilization results from C-H hyperconjugation, which is effective in both conformations **2a** and **2b**, and from general charge dispersal due to polarization. It must be borne in mind that the classical structures are only convenient models for interpretation since the bridged ethyl cation is the single minimum on the C_2H_5^+ potential energy surface at higher theoretical levels.^{7f}

The silyl group is found to be much less effective in stabilizing the methyl cation at the α position (17.8 kcal/mol, MP3). The relative stabilization energies of the methyl and silyl groups were incorrectly reproduced in early theoretical work which employed small basis sets.^{7b} However, the correct trend is established even at the 3-21G level and changes little on going to larger basis sets like 6-31G*. Inclusion of electron correlation produces a significant difference in the relative stabilization energies of the methyl and silyl groups in favor of the former. In **3**, the inductive stabilization due to electropositive silicon is accompanied by the inferior hyperconjugating ability of Si-H bonds across a long Si-C bond (1.95 Å). Clearly, the inductive stabilization due to a silyl group on an alkyl cation can be no more than 17.8 kcal/mol. However, as pointed out by Pople et al., related results must be interpreted with care.^{7e} The silylenium ion isomer, $\text{CH}_3\text{SiH}_2^+$, resulting from a 1,2-hydrogen shift is calculated to be 49.1 kcal/mol more stable than **3**.^{7e} Therefore, the overall reaction (eq 3) would be endothermic and the silyl group could appear to be more stabilizing than a methyl group. However, the present



calculations do have relevance to experimentally more accessible substituted ions in which the barriers to 1,2-shifts are higher and the carbenium ion is more stable than the silylenium isomer. Thus, the relative stabilization energies are in accord with available solvolysis data and similar chemical evidence. For example, no detectable reaction of $(\text{CH}_3)_3\text{SiCH}_2\text{X}$ (X = Br, Cl) was observed in aqueous solvents at 70 °C, $\text{PhCMe}_2(\text{SiMe}_3)\text{Br}$ reacts slower than PhCMe_2Br , and $\text{Me}_3\text{SiCMe}_2\text{Br}$ solvolyzes 38 000 times slower than $\text{Me}_3\text{CCMe}_2\text{Br}$.^{1,4}

Interestingly, the difference in α -stabilization energies for methyl and silyl groups is significantly smaller for the vinyl cation. The methyl group is more stabilizing but by only 3 kcal/mol (Table III). A similar reduction in the relative stabilization energies has been noted by Apeloig and Stanger,^{9a} although the present results are likely to be more accurate due to inclusion of

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electron correlation. The smaller difference results from the combined effect of reduction in the methyl stabilization energy and an increase in the silyl stabilization energy compared to the results for the methyl cations. Unlike the methyl cation, the parent vinyl cation enjoys some C–H hyperconjugation as reflected in the negligible energy difference between the classical and bridged vinyl cations.^{7f} Demand for C–H hyperconjugation from the α -methyl group may therefore be diminished for the vinyl cations. However, since the cationic center is an sp carbon, the high electron deficiency makes the vinyl cation more susceptible to inductive effects. Electropositive silicon can respond and is more effective at stabilizing vinyl cations than alkyl cations. There has been a solvolysis study comparing trimethylsilyl and *tert*-butyl groups in stabilizing vinyl cations.¹⁷ The results were interpreted as indicating that the former was not as effective as the alkyl group in stabilizing the developing vinyl cation. Apeloig and Stanger^{9a} have argued that ground-state effects in these systems are significant and by modeling them through simple derivatives arrive at the opposite conclusion that α -Si(CH₃)₃ is more activating than *tert*-butyl. The present calculations do not provide a clear choice of interpretation since the polymethyl substituents have not been studied and due to the importance of medium effects in solvolyses. Experimental gas-phase studies would be of considerable interest.

β -Substituent Effect. 1-Propyl cation is not a true minimum on the potential energy surface but collapses without a barrier to the bridged form, viz. corner protonated cyclopropane.^{7f} However, at the 3-21G level structures **4a** and **4b** corresponding to the classical propyl cation can be obtained although **4a** is partially bridged. These can serve as models for similar structures which may exist due to medium and ion-pairing effects. The geometries can also be used in higher level calculations to obtain the magnitude of the β -substituent effect of a methyl group.

There is a modest increase in the stabilization energy (3.9 kcal/mol) on going from the eclipsed ethyl cation (**2b**) to the *n*-propyl cation (**4b**) in the conformation that does not allow C–C hyperconjugation. However, conformation **4a** is 9 kcal/mol more stable than **4b**, indicating the superiority of C–C over C–H hyperconjugation. This result found earlier supported the fact that the Baker–Nathan order of relative hyperconjugative abilities is a consequence of solvent effects.¹⁸ The calculated stabilization energy for **4b** is close to the value of 38.3 kcal/mol estimated at the MP4 level.^{7f}

Classical structures corresponding to 3-silapropyl cations could again be obtained due to the use of HF/3-21G(*) during the geometry optimization. MP3/6-31G* calculations indicate conformation **5b** to be 8.9 kcal/mol more stabilized than the ethyl cation **2b**. This is a measure of the inductive and polarization stabilization due to the β -silyl group. The value is small compared to the dramatic Si–C hyperconjugative stabilization apparent in **5a**, which has a stabilization energy 38.0 kcal/mol greater than for **2a**. Since the inductive and polarization contributions are present in this conformation also, a value of 29.1 kcal/mol can be ascribed to Si–C hyperconjugation. These results support the conventional view of the β -silicon effect but are in direct contrast to the recent solvolytic experiments on cyclohexyl derivatives which suggest that the major contribution to the β effect is a direction-independent inductive stabilization and not hyperconjugation (Scheme I).⁶ Alternative interpretations of these data suggested by the authors need to be further considered. An intriguing possibility is that the incipient cyclohexyl cation does not have the chair conformation of the starting material but rather adopts a twist boat geometry.¹⁹ This would lead to a reduced difference in the alignment of the Si–C bond and the developing vacant orbital for the *cis* and *trans* derivatives. Even if the ion adopts the chair form, the *gauche* alignment of the interacting orbitals

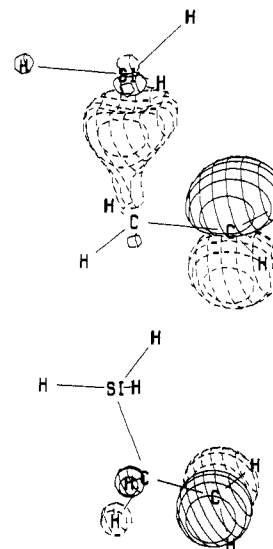


Figure 2. LUMO's for **5a** (top) and **5b** (bottom).

in the *cis* isomer may lead to some stabilization relative to the perpendicular orientation found in **5b**. Therefore, the *cis*–*trans* energy difference should be less than that found for **5b** and **5a**. The attenuation of differences in ion stabilities on going to condensed phases²⁰ must also be taken into account as well as the diminished substituent effects for secondary vs. primary ions.

The enhanced hyperconjugation in **5a** compared to **5b** is strikingly apparent in the orbital plots for their LUMO's shown in Figure 2.²¹ The LUMO for **5a** is primarily the p_π orbital on the carbenium carbon with an out-of-phase mixture of the eclipsing σ_{CSi} bond orbital and an in-phase mixture with the σ_{CSi}^* . The latter two components cancel on C2 and reinforce at the SiH₃ group to give the orbital the illustrated form. For **5b**, the analogous components on the CH₂ group are the π_{CH_2} and $\pi_{\text{CH}_2}^*$ group orbitals which cancel at C2 and reinforce on the hydrogens; the orbitals for the CSI bond are now in the nodal plane of the p_π orbital and cannot interact. The much stronger interaction for the bisected ion reflects the strong mixing between the p_π orbital and the high-energy σ_{CSi} bond orbital. This two-electron interaction accounts for the enhanced hyperconjugation in **5a**.

As in the case of the C₃H₇⁺ isomers, the cyclic structure **5c** (protonated silacyclopropane) is found to be a low-energy form. Both the classical structure, **5a**, and the cyclic form, **5c**, are obtained as minima with comparable energies at the 3-21G(*) level. However, inclusion of electron correlation makes the cyclic structure more stable by 2.4 kcal/mol. It is very likely that this is the only true minimum on the potential energy surface at the highest theoretical levels. The geometry of **5a** has a striking resemblance to the partially bridged structure **4a** which does not survive as a minimum on optimization with the 6-31G* basis.^{7f} Attempts to observe β -silyl carbenium ions under stable ion conditions have not been successful so far.²² However, bridged structures have been invoked by Cook et al. who observed reversible ionization and migration of the SiMe₃ group between the two carbon atoms in the solvolysis of Me₃SiCH₂CD₂Br.²³

β stabilization of the vinyl cation by methyl and silyl groups parallels the results obtained for ions **4** and **5**. Thus, the 1-propenyl cation, **9**, has a stabilization energy of 8.1 kcal/mol relative to the classical vinyl cation, **6**. Much of the stabilization can be attributed to polarization of the methyl group. The stabilization

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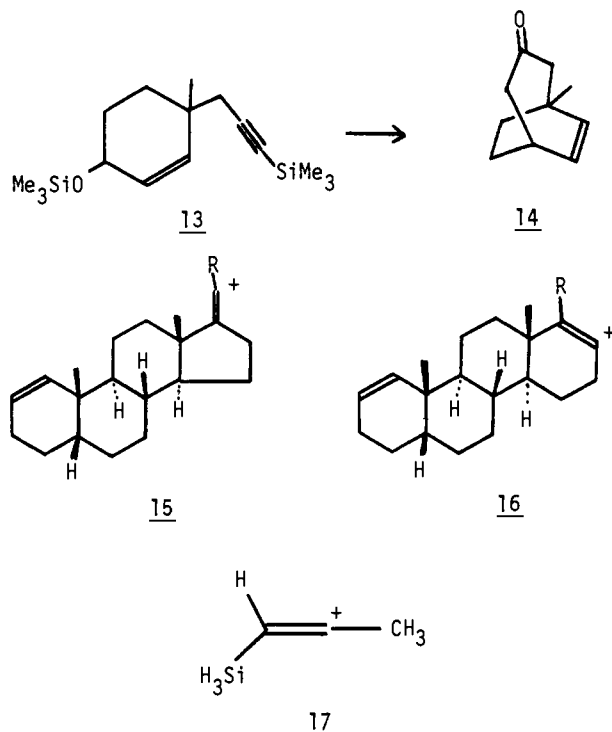
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energy remains virtually constant at all theoretical levels employed. In contrast, β -silicon substitution results in a stabilization of 28.6 kcal/mol for **10**, with electron correlation contributing as much as 6 kcal/mol (Table III). The optimized geometries reflect the differences in C–C and Si–C hyperconjugation. The CCC bond angle of 124.6° in **9** is typical of vinyl systems, while the CCSi angle is only 107.9° in **10**. The preference for formation of a vinyl cation center β to a silicon has been observed by Heathcock and co-workers in the cyclization of silyl ether **13** to give ketone **14**.²⁴



Johnson et al. have also described an interesting cyclization in which the linear vinyl cation intermediate **15** is preferred when R is a methyl group, but the bent vinyl cation **16** is involved when R is trimethylsilyl.²⁵ Apparently, the β stabilization afforded by the silyl group is sufficient to overcome the increase in energy due to bending at the cationic center.

We have also examined the β -substituted ions **11** and **12**, although only at the MP2/6-31G* and HF/6-31G* levels due to the larger size of the ions. These ions enjoy α -alkyl stabilization in addition to C–C and Si–C hyperconjugation, respectively. As

a result, **12** is a particularly stabilized vinyl cation. However, the hyperconjugative stabilization in **11** and **12** is less effective than in **9** and **10**, respectively, since the interaction is across a longer C–C bond. The total stabilization of **11** is about 5 kcal/mol less than the sum of the stabilization energies of **7** and **9**. Similarly, the stabilization energy of **12** is also 5 kcal/mol less than the sum of the stabilization energies of **7** and **10**. On this basis, vinyl cation **17** is likely to be even more stabilized. The ions involved in the cyclizations studied by Heathcock and Johnson correspond to precisely the same substitution pattern.^{24,25}

Conclusions

The principal conclusions from the high-level theoretical calculations carried out in the present work on α - and β -substituted methyl and vinyl cations are the following: (1) α -Alkyl groups are significantly more stabilizing than α -silyl groups for alkyl carbenium ions. The inductive stabilization due to α -silicon is significant, but C–H hyperconjugation is more effective than Si–H hyperconjugation. (2) Vinyl cations are also stabilized to a greater extent by α -alkyl groups compared to α -silyl groups, but the difference is small. Electropositive silicon is more effective in stabilizing the highly electron-deficient center of vinyl cations. (3) β Stabilization due to alkyl groups is modest for both alkyl and vinyl cations. C–C hyperconjugation leads to a greater stabilization than C–H hyperconjugation. (4) The β -stabilization due to silyl groups is large in magnitude for both alkyl and vinyl cations. The β effect is predominantly due to Si–C hyperconjugation and is correspondingly conformation dependent. Inductive and polarization effects represent a relatively minor contribution to the overall β stabilization. (5) The present results are consistent with most of the available solvolysis data and other chemical evidence and also parallel the generally accepted description of the β -silicon effect. However, the results disagree with a recent study which found inductive contributions rather than hyperconjugation to be the principal source of the β -silicon effect. (6) The stabilization energies are virtually unchanged on inclusion of d orbitals on carbon atoms. However, electron correlation produces a significant increase in the stabilization energies, especially when the hyperconjugative interaction is strong.

Finally, it must be emphasized that the calculated stabilization energies correspond to the effects of SiH₃ and CH₃ groups in the gas phase. The stabilization energies are generally reduced under usual experimental conditions due to the presence of additional substituents and the important role of the solvent.

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Supplementary Material Available: Full geometrical results for all ions and neutral molecules in this study (14 pages). Ordering information is given on any current masthead page.

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