

of the band gap on going from Γ to X at the edge of the BZ. The band gap at X is, however, much larger than the gap for the BC-8 structure at H. At Γ the HOMOs and LUMOs are both doubly degenerate. The short (1.87 Å) C--C distance results in a significant destabilization of the a_2'' band (which has σ -antibonding character with respect to the C--C contact) at X, so that it becomes the HOMO. The LUMO's (e'') however, are not significantly affected, so the band gap at X remains quite large (≈ 8 eV). In the alternative geometry (b; C--C = 2.18 Å), the destabilization of the a_2'' band at X is smaller so it remains below the e' pair.

The difference between the propellane and BC-8 band patterns can be rationalized as follows. The pyramidal distortion of the bridgehead carbon atoms in polypropylene takes the form of an elongation of the tetrahedron. This results in a local orbital splitting pattern and hybridization similar to that of supercubane (see Figure 7).

Acknowledgment. The impetus for this work came from correspondence with J. C. Angus, which in turn arose from a controversial statement made by one of us in ref 14e. We thank Dr. Angus for his stimulating correspondence. We also thank one of the reviewers for helpful comments. R.L.J. is grateful to the Science and Engineering Research Council of Great Britain

(SERC) for the award of a NATO postdoctoral fellowship. He also thanks all the members of the group, especially Marja Zonneville and Jing Li, for sharing their expertise and for many helpful discussions. We thank Jane Jorgensen and Elisabeth Fields for their expert drawings. The research was supported by the National Science Foundation through research Grants CHE84064119 and DMR84722702.

Appendix

All calculations were of the extended Hückel type,³⁰ within the tight-binding approach,³¹ with standard atomic parameters for carbon and hydrogen.³⁰

The following bond lengths were used (unless otherwise stated in the text): C-C = 1.54 Å; C-H = 1.09 Å.

For the calculation of average properties, cubic unit cells ($Z = 16$) were taken for the supercubane and BC-8 allotropes. The irreducible wedges for supercubane and BC-8 are $1/48$ and $1/24$ of the cubic BZ, respectively. The k point sets were chosen according to the geometrical method of Ramirez and Böhm.⁴³

Registry No. C, 7440-44-0.

(43) Ramirez, R.; Böhm, M. C. *Int. J. Quantum. Chem.* **1986**, *30*, 391.

(44) Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232.

Ab Initio Investigations of the β -Silicon Effect on Alkyl and Cyclopropyl Carbenium Ions and Radicals

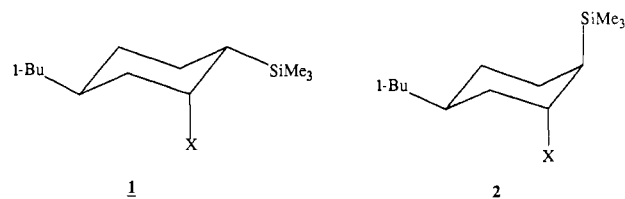
Mustafa R. Ibrahim and William L. Jorgensen*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received July 5, 1988

Abstract: Ab initio molecular orbital calculations have been applied to study the effects of β -silicon and β -carbon substitution vs β -hydrogen on the stabilities of secondary and tertiary alkyl carbenium ions, primary, secondary, and tertiary alkyl radicals, and secondary cyclopropyl carbenium ions and radicals. The computations consisted of geometry optimizations with the 6-31G(d) basis set followed by single-point calculations for the correlation energy with second-order Møller-Plesset theory [MP2/6-31G(d)]. The influence of a β -SiH₃ group is pronounced for the cations providing 22.1 and 15.9 kcal/mol stabilization for the secondary and tertiary alkyl species relative to hydrogen, while the corresponding stabilization energies for a β -methyl substituent are 6.6 and 5.0 kcal/mol. A SiH₃-bridged form for the secondary cation, H₃SiCH₂CHCH₃⁺, was considered, but appears to be ca. 4 kcal/mol higher in energy than the bisected, open form. For the secondary cyclopropyl cations, the hyperconjugative component of the β -silicon effect is diminished by the less optimal orbital alignment. The results for the β effects on the radical stabilities are in sharp contrast with those for the carbenium ions. The influences of β -SiH₃ and β -CH₃ are now nearly identical and yield only 1-4 kcal/mol of stabilization relative to β -hydrogen. The findings are compared with recent experimental results for β -silyl carbenium ions and radicals and provide a quantitative guide to directing effects for synthetic transformations.

The utility of silicon in organic synthesis is much enhanced by the directing effects of silyl groups.¹⁻³ Some well-known generalizations have emerged, such as silicon stabilizes an adjacent negative charge and a β positive charge relative to hydrogen, though quantification of the corresponding energetic effects has been limited from a physical organic perspective. However, progress is being made along both experimental and theoretical lines. The recent solvolysis work of several groups is particularly notable. Apeloig and Stanger established that in 2-adamantyl derivatives an α -Si(CH₃)₃ group stabilizes the carbenium ion center by 12-14 kcal/mol more than hydrogen and by several kilocalories per mole less than α -CH₃. They also reported results of ab initio calculations that α -SiH₃-substituted carbenium ions are less stable than their CH₃-substituted counterparts in the gas

phase by ca. 18, 14, and 9 kcal/mol for the parent primary, secondary, and tertiary cations.⁴ Furthermore, the recent studies of Lambert et al. have yielded important data on the magnitude of the β -silicon effect.^{5,6} Specifically, they solvolyzed the conformationally constrained **1** and **2** (X = OCOCF₃) and found rate



(4) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.

(1) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

(2) Fleming, I. *Chem. Soc. Rev.* **1981**, *10*, 83.

(3) Birkofer, L.; Stuhol, O. *Top. Curr. Chem.* **1980**, *88*, 33.

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

(6) (a) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020.

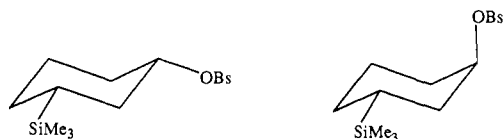
(b) Lambert, J. B.; Wang, G.-T. *J. Phys. Org. Chem.* **1988**, *1*, 169.

Table I. Total and Stabilization Energies for Primary and Secondary Carbenium Ions from RHF Calculations^a

XR ⁺	sym	-E _{tot} , au		ΔE ^b , kcal/mol	
		6-31G(d)	MP2/6-31G(d)	6-31G(d)	MP2/6-31G(d)
CH ₃ C ⁺ HCH ₃ (7)	C _{2v}	117.380 76 ^c	117.745 03	0.0	0.0
b-CH ₃ CH ₂ C ⁺ HCH ₃ (8)	C ₁	156.420 80	156.917 58	4.05	6.58
b-SiH ₃ CH ₂ C ⁺ HCH ₃ (9a)	C ₁	407.481 63	407.932 89	14.83	22.13
e-SiH ₃ CH ₂ C ⁺ HCH ₃ (9b)	C ₁	407.456 10	407.897 52	-1.19	-0.07
c-SiH ₃ CH ₂ C ⁺ HCH ₃ (9c)	C ₁	407.470 70	407.926 57	7.97	18.16
10	C _{2v}	116.132 19 ^c	116.484 23	0.0	0.0
11	C ₁	155.176 25 ^d	155.660 06	6.58	8.64
12	C ₁	406.226 22 ^d	406.664 69	10.54	17.48
(CH ₃) ₃ C ⁺ (13)	C _{3h}	156.442 41 ^e	156.939 55	0.0	0.0
b-CH ₃ CH ₂ C ⁺ (CH ₃) ₂ (14)	C _s	195.480 41	196.109 56	2.77	4.99
b-SiH ₃ CH ₂ C ⁺ (CH ₃) ₂ (15)	C _s	446.535 42	447.117 44	9.90	15.87

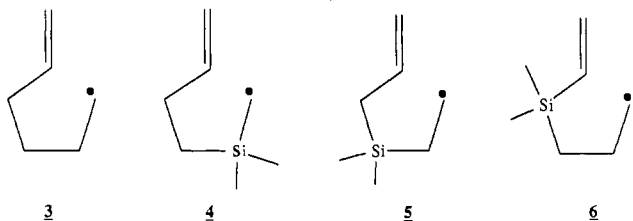
^a Prefixes b, e, and c refer to bisected, eclipsed, and cyclic (bridged) structures. All geometries were optimized with the 6-31G(d) basis set. ^b ΔE for the equation XR⁺ + CH₄ → HR⁺ + XCH₃. ^c Reference 27. ^d Constraints were employed to avoid ring opening. See the text. ^e Reference 28.

accelerations relative to cyclohexyl trifluoroacetate of 4.0×10^4 and 2.4×10^{12} , respectively, in 97% trifluoroethanol at 25 °C.⁵ The latter figure implies stabilization of the incipient carbenium ion of **2** by at least 18 kcal/mol from the β-SiMe₃ group. The results for **1** and **2** also clearly illustrate the conformational dependence of the p-σ_{CSi} hyperconjugative interaction that is maximized when the developing p orbital on the cationic carbon and the C-Si σ-bond orbital are parallel, as for **2**. These authors noted the ab initio results [MP3/6-31G(d)] of Wierschke et al. that predicted stabilization of the bisected ethyl cation by 38 kcal/mol upon β-SiH₃ substitution.⁷ This level of stabilization has been supported by recent gas-phase experiments.⁸ The greater stabilization than observed for **2** is attributable primarily to the enhanced substituent effect for a primary compared to a secondary carbenium ion, and to the leveling effect of the solvolysis medium as well as to incomplete charge development on carbon in the solvolysis transition state. Even a γ-silicon effect has now been discovered by Shiner and co-workers in the solvolyses of *cis*- and *trans*-3-(trimethylsilyl)cyclohexyl brosylates.^{9a} The rate accel-



eration of 452 for the *cis* isomer over *trans*-4-*tert*-butylcyclohexyl brosylate in 97% trifluoroethanol indicates participation by the γ-silyl group. Interaction between C_α and C_γ with transfer of positive charge to the silyl group was supported by a subsequent quantum mechanical study.^{9b}

There is also much current interest in the use of silyl-substituted radicals as synthetic intermediates.¹⁰ The emphasis has been on cyclization reactions¹⁰⁻¹² for which silyl substituents have provided some interesting variations in the preferred mode of ring closure. The extensive studies of Wilt, Ingold, and co-workers on **3-6** are



(7) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.

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

(9) (a) Shiner, V. J., Jr.; Ensinger, M. W.; Kriz, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 842. (b) Davidson, E. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 3135.

(10) See, for example: Stork, G.; Kahn, M. *J. Am. Chem. Soc.* **1985**, *107*, 500. Stork, G.; Sofla, M. *J. Am. Chem. Soc.* **1986**, *108*, 6826.

(11) (a) Wilt, J. W. *Tetrahedron* **1985**, *41*, 3979. (b) Wilt, J. W.; Luszyk, J.; Peeran, M.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 281.

(12) Saigo, K.; Tateishi, K.; Adachi, H.; Saotome, Y. *J. Org. Chem.* **1988**, *53*, 1572.

especially notable.¹¹ While **3** and **6** predominantly exhibit exo closure in accord with the Baldwin-Beckwith rules, **4** prefers the endo alternative by a 2:1 ratio and the β-silyl radical **5** gives only endo closure. The investigators propose that a combination of varying transition-state polarization by silicon and the preference of β-silyl radicals to adopt the bisected configuration¹³ can rationalize the observations.¹¹

In order to provide additional quantitative data on substituent effects for silyl groups, the present theoretical study was initiated. Since our earlier work only considered β effects on primary alkyl and vinyl cations,⁷ a principal aim of the present effort was to provide high-level ab initio results on the β-silicon effect for secondary and tertiary carbenium ions. This greatly facilitates direct comparisons with experimental data because the primary cations are either unstable or have bridged structures,⁷ whereas the secondary and tertiary ions are experimentally accessible and have open structures. In addition, the study was extended to examine β-silicon effects for primary, secondary, and tertiary alkyl radicals as well as secondary cyclopropyl radicals and cations. As shown below, the contrast between the findings for the cations and radicals is striking. Other prior ab initio studies on α- and β-silicon effects should also be noted, though only primary carbenium ions, primary radicals, and vinyl cations have been considered.¹⁴⁻²¹ Most of the calculations involved small basis sets with no treatment of the correlation energy except for the recent work by Coolidge and Borden on α-substituted methyl and silyl radicals.²¹

Computational Details

The geometry optimizations were carried out by gradient methods for all neutral molecules, ions, and radicals with the 6-31G(d) basis set^{22,23} which includes a set of d orbitals on all non-hydrogen atoms. These geometries and basis set were then utilized in calculations that incorporated second-order Møller-Plesset perturbation theory to include the effects of electron correlation.^{24,25} The standard designation for the calculations is then MP2/6-31G(d)//6-31G(d).²⁵ In the present treatment, the frozen-core approximation was made such that the Møller-Plesset calculations did not include contributions from the 1s orbitals of

(13) (a) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846. (b) Chen, K. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1383.

(14) Eaborn, C.; Feichtmayr, F.; Horn, M.; Murrell, J. N. *J. Organomet. Chem.* **1974**, *77*, 39.

(15) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291.

(16) Clark, T.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, 4641.

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

(18) Apeloig, Y.; Stanger, A. *J. Org. Chem.* **1982**, *47*, 1462.

(19) Pople, J. A.; Apeloig, Y.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *85*, 489.

(20) Bernardi, F.; Bottoni, A. *Tetrahedron* **1986**, *42*, 5567.

(21) Coolidge, M. B.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 2298.

(22) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 203.

(23) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1983**, *77*, 3054.

(24) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(25) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 38, 96, 208-215, 381-390.

Table II. Total and Stabilization Energies for Primary, Secondary, and Tertiary Radicals from UHF Calculations^a

XR*	sym	$-E_e$, au		ΔE , ^b kcal/mol	
		6-31G(d)	UMP2/6-31G(d)	6-31G(d)	UMP2/6-31G(d)
CH ₃ ĊH ₂ (16)	C ₁	78.597 15	78.835 36	0.0	0.0
b-CH ₃ CH ₂ ĊH ₂ (17a)	C ₁	117.631 43	117.999 80	0.44	1.49
e-CH ₃ CH ₂ ĊH ₂ (17b)	C _s	117.631 44	117.999 82	0.45	1.51
b-SiH ₃ CH ₂ ĊH ₂ (18a)	C ₁	368.674 00	368.990 66	-0.24	1.69
e-SiH ₃ CH ₂ ĊH ₂ (18b)	C _s	368.671 29	368.986 74	-1.95	-0.77
CH ₃ ĊHCH ₃ (19)	C ₁	117.634 38	118.003 06	0.0	0.0
b-CH ₃ CH ₂ ĊHCH ₃ (20a)	C ₁	156.669 00	157.168 37	0.65	2.04
e-CH ₃ CH ₂ ĊHCH ₃ (20b)	C _s	156.669 57	157.168 67	1.01	2.23
b-SiH ₃ CH ₂ ĊHCH ₃ (21a)	C ₁	407.711 41	408.159 21	-0.13	2.23
e-SiH ₃ CH ₂ ĊHCH ₃ (21b)	C _s	407.709 53	408.155 99	-1.31	0.21
22	C _s	116.415 54	116.777 51	0.0	0.0
23	C ₁	155.452 54 ^c	155.946 00	2.15	4.03
24	C ₁	155.452 76 ^c	155.946 43	2.28	4.30
25	C ₁	406.495 28 ^c	406.936 57	1.57	4.05
26	C ₁	406.494 89 ^c	406.936 13	1.32	3.78
(CH ₃) ₃ Ċ (27)	C ₁	156.672 99	157.173 88	0.0	0.0
b-CH ₃ CH ₂ Ċ(CH ₃) ₂ (28)	C _s	195.707 19	196.339 30	0.39	2.11
b-SiH ₃ CH ₂ Ċ(CH ₃) ₂ (29)	C _s	446.750 08	447.330 83	-0.09	2.73

^a The prefixes b and e refer to the bisected and eclipsed structures. All geometries were optimized with the 6-31G(d) basis set. ^b ΔE for the equation $\text{XR}^* + \text{CH}_4 \rightarrow \text{HR}^* + \text{XCH}_3$. ^c The length of the C-C bond opposite to the radical center was fixed. See the text.

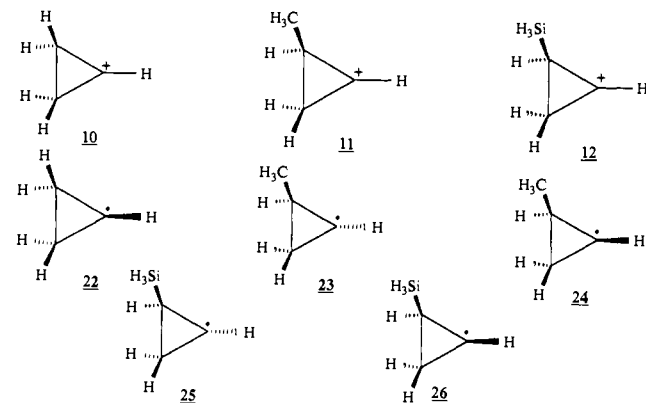
Table III. Calculated Total Energies (au) of Neutral Molecules^a

molecule	sym	6-31G(d)	MP2/6-31G(d)
methane	T _d	-40.195 17 ^b	-40.332 44
ethane	D _{3d}	-79.228 75 ^b	-79.4945 ^c
methylsilane	C _{3v}	-330.272 41	-330.485 04
cyclopropane	D _{3h}	-117.058 87 ^b	-117.4482 ^c
methylcyclopropane	C _s	-156.095 93	-156.617 01
silylcyclopropane	C _s	-407.137 55	-407.606 19

^a Geometries optimized with the 6-31G(d) basis set. ^b Reference 27. ^c Reference 39.

non-hydrogen atoms.²⁵ The self-consistent field (SCF) calculations used restricted Hartree-Fock (RHF) theory for the neutral molecules and ions and unrestricted Hartree-Fock (UHF) theory for the radicals. Based on extensive experience, the errors in computed bond lengths and bond angles are anticipated to be less than 0.02 Å and 2° at the level of theory used here.²⁵ All computations were carried out with the GAUSSIAN/82 program on a Gould 32/8750 computer.²⁶

The principal calculations were for the carbenium ions and radicals, 7-29, listed in Tables I and II including the cyclopropyl species illustrated. For reference, the total electronic energies, E_e , were also needed



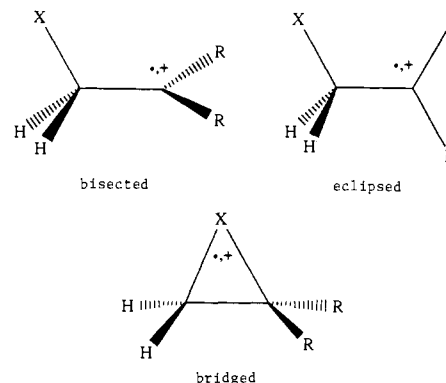
for the neutral molecules listed in Table III. In most cases the geometry optimizations were performed with no constraints in C₁ symmetry. However, to avoid ring opening to allyl cations, the optimizations for **11** and **12** kept the C2-C3 bond length fixed at 1.512 Å and the hydrogen on C1 in the plane of the ring, as obtained in an earlier optimization for **10** in C_{2v} symmetry.²⁷ Similarly, the C2-C3 bonds in **23-26** were fixed

(26) Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. R. *GAUSSIAN 82 Release H*; Carnegie Mellon University: Pittsburgh, PA, 1982. Converted to the Gould 32/8750 by J. D. Madura and J. F. Blake.

(27) Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Carnegie-Mellon University: Pittsburgh, PA, 1983.

at 1.517 Å, as found in the present optimization for **22** in C_s symmetry.

For several of the acyclic carbenium ions and radicals, both bisected and eclipsed conformations were considered. Since the bisected forms

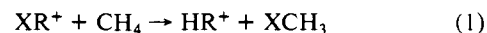


are often lower in energy,^{7,13,14,20,30} a C_s symmetry constraint was used to optimize some of the eclipsed structures. In addition, for the 4-sila-2-butyl cation (**9**), optimizations were performed for the bisected (**9a**), eclipsed (**9b**) and bridged (**9c**) forms. Without constraints the latter two reverted to the bisected ion. Consequently, for **9b**, the H-C-C-Si dihedral angle was fixed at 0°. And, for **9c**, the structure was first optimized with one C-C-Si angle fixed at 60°, after which this angle was optimized with the other variables fixed at their previously optimized values.

Results and Discussion

Carbenium Ions. The computed structures for the ions optimized in this work are shown in Figure 1. The quantitative results for some of the key geometrical variables are given in the figure, while complete details for each structure are provided in the supplementary material in symbolic Z-matrix format.²⁵ The structural results are discussed below along with the energetic results for the different ions.

The computed total energies and stabilization energies are summarized in Table I. The stabilization energy for a substituent X (H, CH₃, SiH₃) is defined by the ΔE for eq 1. The results



are grouped separately for the 2-propyl, cyclopropyl, and *tert*-butyl derivatives. Comparisons can be made with experimental data for two cases, specifically the stabilization of the 2-propyl and

(28) Jorgensen, W. L.; Buckner, J. K.; Huston, S. E.; Rosicky, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 1891.

(29) Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1904.

(30) Schultz, J. C.; Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3917.

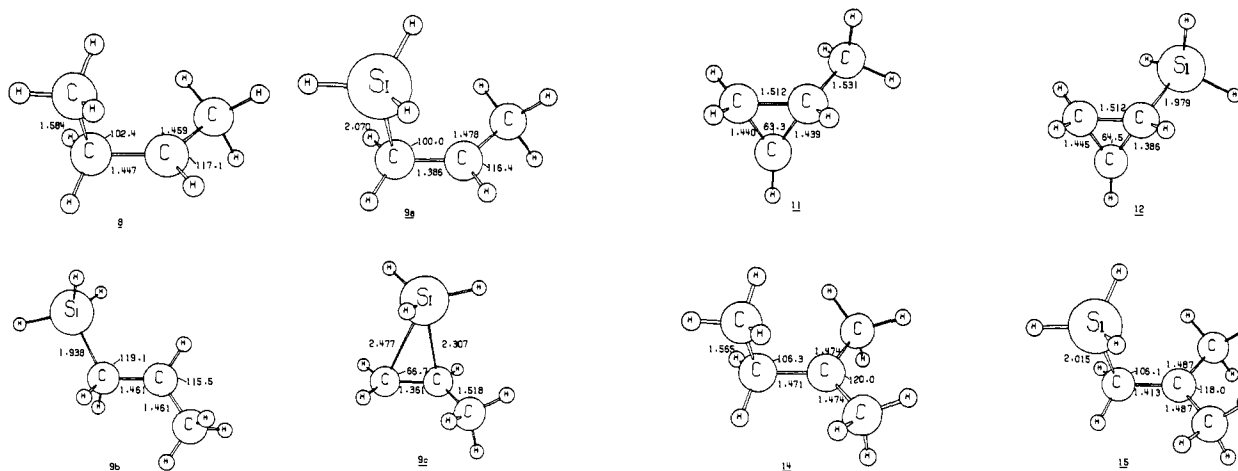
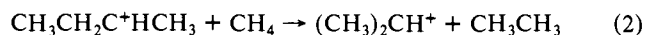
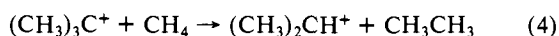


Figure 1.

tert-butyl cations by replacement of a β -hydrogen by a methyl group. The experimental ΔH s for eq 2 and 3 are 6.3 and 5.6



kcal/mol, as obtained from the heats of formation reported for the ions by Beauchamp and co-workers.^{30,31} The corresponding ΔE s of 6.6 and 5.0 kcal/mol at the MP2/6-31G(d) level in Table I are in good accord. It should be noted that the agreement with experiment is significantly improved by inclusion of the correlation energy. There are two more points of comparison available with experimental data. From Table I, the difference in energy for the 2-butyl and *tert*-butyl cations is 13.8 kcal/mol at the MP2/6-31G(d) level, while the difference in experimental heats of formation is 16.2 kcal/mol.³⁰ In addition, from Tables I and III the ΔE for eq 4 is 20.4 kcal/mol with the correlation energy



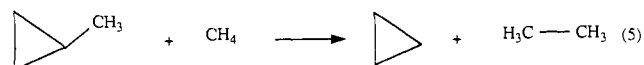
included, while the experimental ΔH is 22.5 kcal/mol.³⁰ These comparisons show that the MP2/6-31G(d) calculations provide accurate estimates of the β -CH₃ substituent effects as well as the energy differences between secondary and tertiary carbocations. The remaining discrepancies with experiment have several origins, including the lack of treatment of the vibrational energy changes in the calculations and the fact that the uncertainties in the experimental heats of formation of the ions are ca. ± 1 kcal/mol.³⁰ Extending the treatment of the correlation energy to the MP3 or MP4 levels is expected to have little effect on the results; previous findings show variations of 0–1 kcal/mol for the relative energies of isomeric cations such as 1-propyl and 2-propyl or 1-propenyl and 2-propenyl on progressing from MP2/6-31G(d) to MP4/6-31G(d).²⁵ With the reliability of the approach having been demonstrated, the key results in Table I can now be considered.

For the 2-propyl cation, a β -silyl group in the bisected orientation provides 22.1 kcal/mol of stabilization. The large increase over the 6.6 kcal/mol for a β -methyl group is reflected in the structural results in Figure 1. For the 2-butyl cation (8), hyperconjugation, which features the p - σ_{CC} orbital mixing, causes some shortening of the C2–C3 bond, narrowing of the C2–C3–C4 angle, and lengthening of the C3–C4 bond; however, the effects are much greater for the sila analogue 9a. In particular, the C2–C3 bond is 0.06 Å shorter in 9a and the C–Si bond has lengthened by 0.18 Å relative to methylsilane, while the C3–C4 bond in 8 is only 0.06 Å longer than the C–C bond in ethane. The results in Table I also show that the β -silyl stabilization is completely shut off upon rotation to the eclipsed form 9b in which the p and σ_{CS} orbitals are orthogonal. The lack of interaction

is clearly reflected in the structural results (Figure 1). Thus, the two C–C bonds in 9b are both 1.46 Å long, the C–C–Si angle has widened to 119°, and the C–Si bond is only 0.05 Å longer than in methylsilane. The energetic results for 9b indicate that the β -SiH₃ group does not inductively stabilize the cation, and consequently, the β -silyl effect for secondary carbenium ions results entirely from hyperconjugation in the bisected form. As noted above, the bridged alternative 9c, like 9b, is not an energy minimum at the 6-31G(d) level and could only be optimized with geometric constraints. The energy difference between 9a and 9c decreases from 6.9 to 4.0 kcal/mol upon inclusion of the correlation energy. The gap is still sufficiently large that it is unlikely that the bridged form is preferred at higher levels of theory. It should be noted that the effects of including the correlation energy are particularly important for the bisected and bridged silyl-substituted ions, as found previously.⁷ The electronic reorganization is substantial in these cases and requires inclusion of electron correlation to properly account for the mixing between the p orbital on the carbenium carbon and the C–Si bond orbitals.

The present results for the secondary carbenium ions can now be directly compared with Lambert's solvolytic data for 1 and 2.⁵ The β -silyl effect found here of 22 kcal/mol should represent an upper limit, since it is in the gas phase and reflects optimal orbital alignment and complete charge development. Some differences are also expected for a SiH₃ group and Si(CH₃)₃, the usual experimental choice. Nevertheless, the 18 kcal/mol difference in activation energies for the solvolyses of 2 and cyclohexyl trifluoroacetate is nicely consistent with the present result. In addition, the current findings suggest that the rate acceleration of 4×10^4 for 1 is not due to induction, but rather to weak hyperconjugation between the developing p orbital and the poorly, but not orthogonally, aligned C–Si bond orbital. From their analyses, Lambert et al. conclude that hyperconjugation is responsible for 10^{10} of the 10^{12} acceleration for 2 and 10^2 of the 10^4 for 1, while both solvolyses benefit by a factor of 10^2 from induction. The small discrepancy between theory and experiment can be attributed to the detailed differences between the systems and conditions that have been studied. This reassuring level of accord did not always exist.^{6a,7}

For the cyclopropyl cations, β -methyl and β -silyl groups yield stabilizations of 8.6 and 17.5 kcal/mol (Table I). These figures are, respectively, greater and less than the β effects for the 2-propyl cation. The result for β -methyl seems surprising at first since the p orbital on C1 cannot perfectly eclipse the C2–C4 bond; the computed dihedral angle is 22°. However, alkyl groups are well-known to stabilize small rings as reflected in the ΔE of 4.2 kcal/mol from MP2/6-31G(d) calculations for eq 5. The cor-



responding effect for *n*-alkanes is 2–3 kcal/mol. Thus, when

(31) Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162.

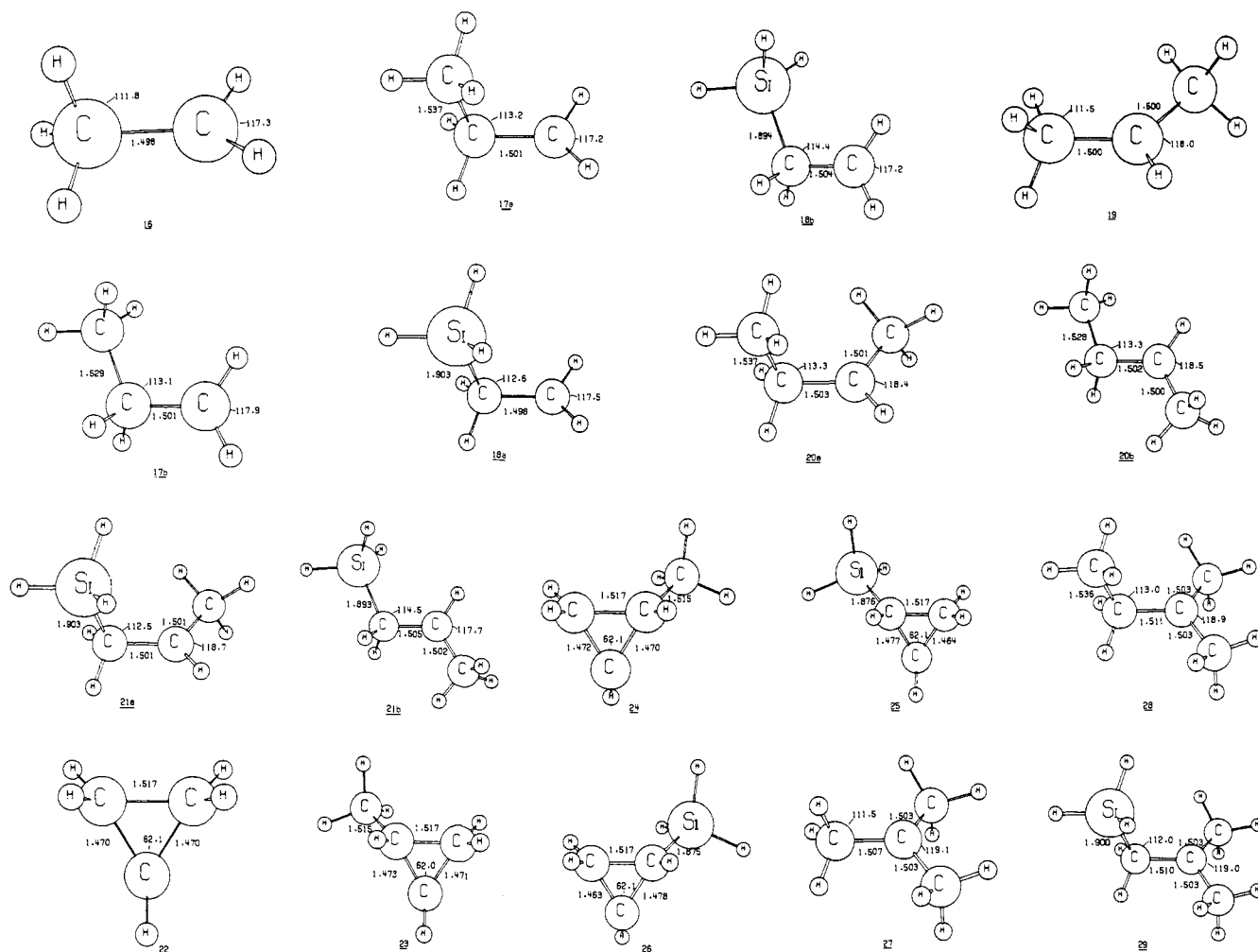
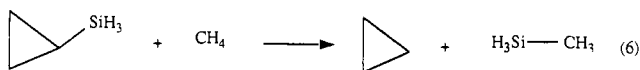


Figure 2.

adjustment is made for this component in the stabilization of the cyclopropyl cation, it appears that the hyperconjugative contribution by the β -methyl group is about the same as for the acyclic secondary cation. Analogously, the stabilization by the β -silyl group also contains an intrinsic component reflected in the ΔE of 3.4 kcal/mol (MP2/6-31G(d)) for eq 6. Consequently, the

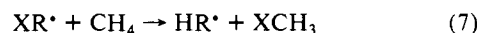


benefit of hyperconjugation by a β -silyl group decreases from 22 kcal/mol for the 2-propyl cation to ca. 15 kcal/mol for cyclopropyl cation. This is still substantial effect and is reflected in the computed structures (Figure 1). Though the difference in the C1-C2 and C1-C3 bond lengths in **11** is insignificant, the C1-C2 bond is 0.06 Å shorter in **12** and the C-Si bond is stretched to a length of nearly 2 Å. In spite of the 17.5 kcal/mol stabilization for **12**, the structure is not an energy minimum; ring opening occurred in an unconstrained geometry optimization.

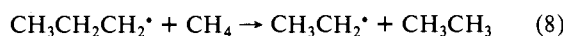
As expected, for the tertiary cations, the β effects are smaller than for the secondary ions. For β -methyl, the stabilization is reduced from 6.6 to 5.0 kcal/mol, and for β -silyl from 22.1 to 15.9 kcal/mol. The last figure provides an upper limit of 5×10^{11} for the rate acceleration that could be obtained in a solvolysis at 25 °C that leads to a β -silyl tertiary carbenium ion. The diminished hyperconjugation is again apparent in the structural results, cf. **8**, **9a**, **14**, and **15** in Figure 1. For the tertiary ions, the central C-C bond is longer, the C3-C4 bond or C-Si bond is shorter, and the C2-C3-C4 or C-C-Si angle is wider than in the secondary carbenium ions.

Radicals. The key structural results for the radicals are displayed in Figure 2 with complete details again provided in the supplementary material. The energetic results are in Table II;

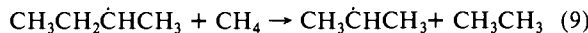
in this case, the stabilization energy for substituent X is defined by the ΔE for eq 7. Several comparisons are again possible with



experimental data.³⁰ For the β -methyl effect on the ethyl radical (eq 8), the MP2/6-31G(d) ΔE is 1.5 kcal/mol and the experi-



mental ΔH is 3.3 kcal/mol.³⁰ Next, for the β -methyl effect on the 2-propyl radical (eq 9), the computed ΔE and experimental



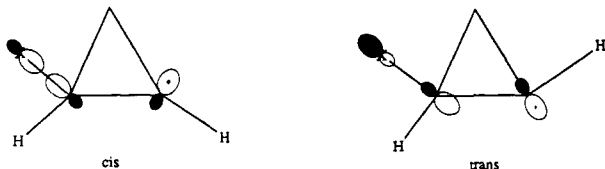
ΔH are 2.2 and 3.8 kcal/mol. Finally, the calculated ΔE and experimental ΔH are 3.3 and 3.5 kcal/mol for the isomerization of *tert*-butyl radical to 2-butyl radical. In view of the ca. 1 kcal/mol uncertainties in the experimental heats of formation, the accord between theory and experiment is excellent.

A quick scan of Table II reveals the principal finding that both the β -methyl and β -silyl effects on radical stabilities are small and nearly identical. For the acyclic radicals, the β effects increase from ca. 1.5 kcal/mol for the primary radical to 2.2 for secondary and 2.5 for tertiary radicals. This trend is curious; it is dependent on inclusion of the correlation energy and may not survive at higher levels of theory. It does agree with the experimental results for eq 8 and 9, though the difference is small compared to the uncertainties in the heats of formation. The effects are larger (4 kcal/mol) for the cyclopropyl radical; however, this can be attributed to the normal alkyl/silyl stabilization of small rings, as mentioned above for eq 5 and 6.

The results also now show minor dependence on conformation since the rotational barriers between the bisected and eclipsed forms are less than 2.5 kcal/mol, as found previously for alkyl

and β -silaalkyl radicals.^{13,20} ESR data in solution have been interpreted to favor the eclipsed form for the 1-propyl radical (**17**), and the 2-butyl radical (**20**), and the bisected rotamers for 2-(trialkylsilyl)alkyl radicals and the *tert*-amyl radical (**28**).¹³ In fact, the MP2/6-31G(d) calculations yield lower energies for the eclipsed form of **17** and **20** by only 0.01 and 0.19 kcal/mol, though the bisected conformers are preferred by 2.46 and 2.02 kcal/mol for the β -silyl radicals **18** and **21**. The small intrinsic rotational barriers for the alkyl radicals may make their conformations sensitive to medium effects. For example, ESR data for the 1-propyl radical in argon at 4 K are inconsistent with the eclipsed structure.³²

Furthermore, for the 2-methylcyclopropyl radicals, the *trans* isomer **24** is computed to be favored over the *cis*, **23**, by 0.3 kcal/mol, while for the silyl derivatives **25** and **26**, the preference is reversed by a similar amount. In the *cis* form, the three-electron

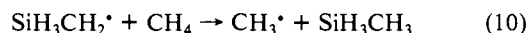


interaction between the singly occupied orbital on the radical center (*n*) and the eclipsing C2-C4 or C-Si σ -bond orbital is maximized, while the *trans* form promotes the one-electron mixing of the *n* orbital and the σ_{CC^*} or σ_{CSi^*} orbital. However, the energy gap between the orbitals in the latter case is so great that the interaction is probably inconsequential. Though the effects are small, the evidence indicates that the three-electron interaction is more favorable for the higher lying σ_{CSi^*} -bond orbital. The results are also consistent with the analyses of Bernardi and Bottoni²⁰ and with the conformational preferences observed in ESR spectra¹³ for the 2-(triethylsilyl)ethyl radical in which the bisected form permits the three-electron interaction.

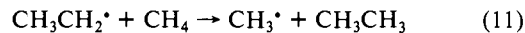
The weak β effects for the radicals are also apparent in the structural results in Figure 2 compared to Figure 1. For example, the lack of hyperconjugation is evident for **20a** and **21a**. The C1-C2 and C2-C3 bonds now have the same length, there is insignificant stretching of the C3-C4 and C-Si bonds, and the C2-C3-C4 and C-C-Si angles do not show the narrowing as in **8** and **9a**. Analogous observations can be made by comparing the results for the cyclopropyl and tertiary species in Figures 1 and 2.

It should be noted that α -silyl stabilization of an alkyl radical is actually greater than β -silyl stabilization, in sharp contrast to

the effects on carbenium ions. Thus, the high-level ab initio results of Coolidge and Borden give $\Delta E = 4.4$ kcal/mol for eq 10.²¹ They

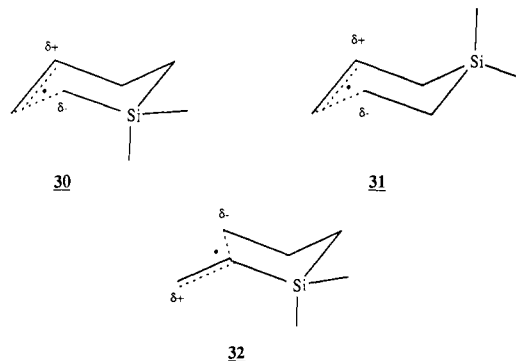


also obtained a ΔE of 3.3 kcal/mol for the α -methyl effect represented in eq 11. Thus, both the α and β effects on radical



stabilities are small and somewhat favor SiH₃ over CH₃. In comparison to the case with carbenium ions, the directing abilities of alkyl and silyl groups in the formation of radicals can be taken to be the same. For the β effect, this finding is consistent with the kinetics for bromine abstractions by *n*-Bu₃Ge[•] and *n*-Bu₃Sn[•] that show a rate increase of only a factor of 2-4 for Me₃SiCH₂CH₂Br compared to CH₃(CH₂)₃Br.^{11b}

In closing, the interesting behavior of **3-6** may be considered again. Wilt et al.¹¹ proposed that the enhanced endo cyclization for **4** is promoted by some charge development in the transition state **30** that reflects the inductive abilities of α -silicon.¹ An



analogous argument could help explain the propensities for endo and exo cyclization of **5** and **6**. The proposed transition states **31** and **32** would both benefit from stabilization of the partial positive charge by β -silicon. Conformational factors are also certainly relevant, including the preference of β -sila radicals for bisected structures¹¹ and geometrical changes due to the long C-Si bonds.¹²

Acknowledgment. Gratitude is expressed to the National Science Foundation for support of this work.

Supplementary Material Available: Complete specifications for the geometries of the carbenium ions, radicals, and neutral molecules optimized in this work provided in Z-matrix format (24 pages). Ordering information is given on any current masthead page.

(32) Adrian, F. J.; Cochran, E. L.; Bowers, V. A. *J. Chem. Phys.* **1973**, *59*, 3946.