silcarbane substrates containing the requisite Si–CH$_3$ and SiCH$_2$Si moieties are readily prepared.[10]

Our preliminary efforts to convert (Me$_2$SiCH$_2$)$_3$ to the desired cage structure with modest amounts of AlBr$_3$ (*i.e.*, 1–5% of substrate weight) were disappointing. Noting that Schleyer's adamantane syntheses often employed quite massive amounts of aluminum halide catalysts, we evaluated the effect of larger amounts (*i.e.*, 20–200% of substrate weight) in the present system and this did indeed afford facile redistribution at moderate temperatures (*e.g.*, 80–100°) producing Me$_4$Si and the desired cage structure (I, X = Me). Moreover, the "catalyst" is apparently a reactant and also gives rise to a substantial number of silicon-functional sites; *i.e.*, depending on the conditions, cage structures are formed in which one or more of the methyl substituents have been replaced by Cl or Br.

Thus when a mixture of (Me$_2$SiCH$_2$)$_3$ (130.0 g; 0.61 mol) and AlBr$_3$ (22.5 g; 0.085 mol) was heated, the temperature rose to approximately 100°, then decreased as Me$_4$Si gradually formed; an 85% yield of Me$_4$Si (45 g) was distilled from the system during the ensuing 2-hr period. After the reaction product was diluted with benzene and washed with water to remove the aluminum salts, the organic layer was dried and examined *via* tandem glc–mass spectrometry. The overall yield of volatile tetrasilaadamantanes in this particular run was approximately 27% (in some recent runs, yields as high as 80% have been achieved); the major component was the Me$_4$ derivative admixed with lesser amounts of the Me$_3$Br and Me$_2$Br$_2$ derivatives. The individual components were resolved by preparative glc and characterized by nmr and/or mass spectroscopy. Like the substituted adamantane hydrocarbons, these silicon analogs exhibit very characteristic cracking phenomena;[11,12] thus, their mass spectra generally show a parent-ion line accompanied by a very intense line corresponding to a fragment produced by the loss of one bridgehead substituent (or several such lines if more than one type of substituent is present) and little else of comparable intensity. To illustrate, the monobromide shows parent lines of moderate intensity (12%, relative intensity) at *m/e* values of 320 and 322 (corresponding to the two almost equally distributed isotopes of Br), very intense lines (100%) at 305 and 307 (parents − methyl), and a weak line (2%) at 241 (parents − bromine). The nmr spectrum (CCl$_4$ solution) of this species consists of three lines at τ 9.62 (BrSiCH_2SiCH$_3$), 9.84 (SiCH_3), and 10.19 (CH$_3$SiCH_2SiCH$_3$) in the expected intensity ratio of 6:9:6.

The above ligand exchange method thus constitutes a versatile route to a variety of 1,3,5,7-tetrasilaadamantanes (*i.e.*, I, X = Cl, Br, Me). The derivative chemistry of these functional cages is currently under study, and will be described at an early date. Redistribution[13] of organic ligands for the synthesis of polycyclic heteroatom cage systems appears to be without precedent and should facilitate future studies of such systems. Thus, this general method may well be applicable to the synthesis of polycyclic heteroatom cages containing components such as SiCH$_2$CH$_2$Si, Si$_3$CH, GeCH$_2$, SnCH$_2$, etc.

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(10) W. A. Kriner, *J. Org. Chem.*, 29, 1601 (1964).

(11) Z. Dolejsek, S. Hala, V. Hanus, and S. Landa, *Collect. Czech. Chem. Commun.*, 31, 435 (1966).

(12) However, see R. S. Gohlke and R. J. Robinson (*Org. Mass Spectrom.*, 3 (7), 967 (1970)), for the details of an interesting skeletal rearrangement which "carborundanes" undergo in a mass spectrometer.

(13) Lest our analogy to Schleyer's work be misinterpreted, we emphasize that we are dealing here with the conceptually much simpler redistribution reactions in which the organic moieties undergo changes in their relative position but not with respect to their total number or formal character.[14] In contrast to the adamantane work in which deep-seated carbonium ion rearrangements are involved, the aluminum halide catalyzed redistribution of *n*-Pr$_{1-x}$SiEt$_x$ was shown *not* to involve carbonium ion intermediates (*i.e.*, the equilibrium mixture contained no *i*-Pr moiety).[15]

(14) H. A. Skinner and T. F. S. Tees, *J. Chem. Soc.*, 3378 (1953).

(15) P. D. George, L. H. Sommer, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 77, 1677 (1955).

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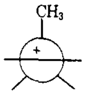
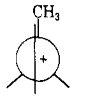
Rotational Barriers of Alkyl Cations

Sir:

The structures and stabilities of carbonium ions are subjects of continuing interest.[1] Although a great deal of information has been obtained from spectroscopic and mechanistic evidence, quantum mechanical calculations provide insights not yet accessible experimentally.[2–10] Semiempirical molecular orbital methods have already been used to study rotational barriers in a number of carbonium ions.[11–15] How-

Table I. Extended *ab initio* Energies for the Propyl Cation[a]

Compd	Conformation[b]	Total energy	Relative energy
1a		−117.25566	0.0
1b		−117.25206	2.26

[a] Absolute energies in hartrees, relative energies in kilocalories per mole. [b] Bond lengths: d(CH), 1.096; d(C$^+$H), 1.084; d(CC), 1.534; d(C$^+$C), 1.48 Å. Bond angles: CH$_3$ and CH$_2$ tetrahedral and staggered; CH$_2{}^+$ planar.

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(1) See *e.g.*, "Carbonium Ions," Vol. I, G. Olah and P. von R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1968; Vol. 2, 1970; D. Bethell and V. Gold, "Carbonium Ions. An Introduction," Academic Press, New York, N. Y., 1967.

(2) J. E. Williams, R. Sustmann, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 91, 1037 (1969).

(3) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *ibid.*, 91, 5350 (1969).

(4) J. E. Williams, V. Buss, and L. C. Allen, submitted for publication.

(5) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, in press.

(6) J. E. Williams, V. Buss, L. C. Allen, P. von R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, 92, 2141 (1970), and references therein cited.

(7) G. V. Pfeiffer and J. G. Jewett, *ibid.*, 92, 2143 (1970).

(8) D. T. Clark and D. M. J. Lilley, *Chem. Commun.*, 549 (1970).

(9) D. T. Clark and D. M. J. Lilley, *ibid.*, 603 (1970).

(10) V. Buss, P. von R. Schleyer, and L. C. Allen, to be published.

(11) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

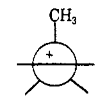
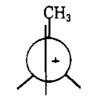
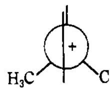
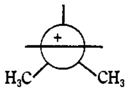
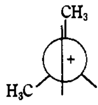
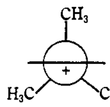
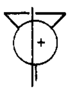
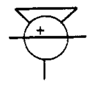
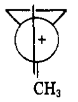
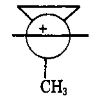
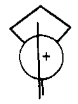
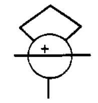
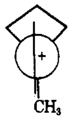
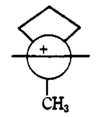
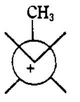
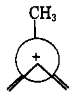
(12) H. Kollmar and H. O. Smith, *Tetrahedron Lett.*, 1833 (1970).

(13) R. Hoffmann, *J. Chem. Phys.*, 40, 2480 (1964).

(14) T. Yonezawa, H. Hakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, 90, 1239 (1968).

(15) V. Buss, unpublished results.

Table II. STO-3G Energies for Some Carbonium Ions[a]

Cation	No.	Conformation[b]	Total energy	Relative energy
n-Propyl	**2a**		−115.99294	0.0
	2b		−115.98893	2.52
Isobutyl	**3a**		−154.57747	0.0
	3b		−154.57320	2.68
Neopentyl	**4a**		−193.15889	0.0
	4b		−193.15890	0.0
Cyclopropylcarbinyl	**5a**		−153.37722	0.0
	5b		−153.34926	17.54
1-Methylcyclopropylcarbinyl	**6a**		−191.96189	0.0
	6b		−191.93640	16.00
Cyclobutylcarbinyl	**7a**		−191.96654	0.0
	7b		−191.96003	4.08
1-Methylcyclobutylcarbinyl	**8a**		−230.55015	0.0
	8b		−230.54646	2.32
Tetrahedral *n*-propyl	**9a**		−115.94602	0.0
	9b		−115.93635	6.04

[a] Absolute energies in hartrees, relative energies in kilocalories per mole. [b] Structural parameters based on the ethyl cations.[6] Throughout **2**-**8**: $d(CC)$, 1.54; $d(C^+C)$, 1.49; $d(CH)$, 1.09; $d(C^+H)$, 1.12 Å. The ring structure for **5** and **6** taken from R. H. Schwendeman, G. D. Jacobs, and T. M. Krigas, *J. Chem. Phys.*, **40**, 1022 (1964); for **7** and **8** from R. C. Lord and B. P. Stoicheff, *Can. J. Phys.*, **40**, 725 (1962). In **9**, all carbons are tetrahedral, with bond lengths $d(CC)$, 1.534; $d(C^+C)$, 1.488; $d(CH)$, 1.096; $d(C^+H)$, 1.084 Å.

ever, such methods have serious limitations when applied to charged species,[3] and there is a wide divergence in the results which have been found.[16] It is therefore desirable to carry out *ab initio* studies on such systems.

The use of a minimal Gaussian type orbital basis set appears promising since this combines the advantages of an *ab initio* calculation with the feasibility of performing calculations on systems with more than three heavy atoms. The STO-3G basis set[17] which we use here has already been shown to produce geometries[5,18] and rotational barriers[19] in close agreement with experiment. It is also of interest to compare STO-3G basis set results with those obtained from the extended basis set described earlier[3] which has given threefold rotational barriers with an accuracy of ±0.4 kcal/mol.[20] In this communication we wish to report our calculations of the rotational barrier in the *n*-propyl cation, both with the extended and STO-3G basis sets, and in addition STO-3G calculations of the rotational barriers in the isobutyl, neopentyl, cyclopropylcarbinyl, 1-methylcyclopropylcarbinyl, cyclobutylcarbinyl, 1-methylcyclobutylcarbinyl, and tetrahedral *n*-propyl cations.

Table I presents the results obtained with the extended basis set for the barrier to internal rotation about the C+–C bond in the *n*-propyl cation. This rotational barrier is twofold and therefore on general grounds[21] expected to be higher than the sixfold barrier in the ethyl cation (calculated to be close to zero).[6] We find that the conformation in which the "empty" p lobe is coplanar with the C–C bond is favored by 2.3 kcal/mol. This indicates that C–C hyperconjugation which is most effective in this conformation is stronger than hyperconjugation involving the β hydrogens.[22,23]

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[16] Of the semiempirical methods, CNDO seems to give the best results[11] when compared to our *ab initio* calculations. However, with a reparametrized CNDO scheme, Kollmar and Smith[12] got no more than 0.9 kcal/mol for the rotational barrier of $n\text{-Pr}^+$.

[17] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

[18] M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **52**, 4064 (1970).

[19] L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

[20] L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968); W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967).

[21] J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).

[22] The cause of this effect, of considerable interest, will be discussed in detail in forthcoming papers.

[23] For a critical review of the literature, see M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

The STO-3G results for the same barrier but using a geometry derived from the optimized geometry of the ethyl cation are shown in Table II (**2a**, **2b**). The barriers obtained with the two basis sets (2.52 and 2.26 kcal/mol) are in close agreement. Since the STO-3G calculations require about one-tenth the computer time of the extended basis set, the remaining calculations were performed at the STO-3G level.

The rotational barriers for four more carbonium ions held in their planar[24] conformations are presented in Table II. If the preference for the C–CH_3 bond to be coplanar with the "empty" p orbital in the *n*-propyl cation follows a simple twofold cosine potential function, *i.e.*, $V(\theta) = (V_2/2)(1 - \cos 2\theta)$, where V_2 is the twofold barrier, it is easy to show that the same function applied to the isobutyl cation predicts the conformation (**3a**) which has both C–CH_3 bonds forming dihedral angles of 30° with the "empty" p orbital to have the lowest energy and the barrier to be the same as in the *n*-propyl cation. Our calculated barrier and lowest energy conformation are in agreement with these predictions. As expected, the sixfold barrier in the planar[24] neopentyl cation (**4**) is indistinguishable from zero.

Incorporation of the two methyl groups of the isobutyl cation into increasingly smaller ring systems leads to an increasing preference of the cations for the "bisected" conformations (**5a** and **7a**), the energy difference being 4.08 kcal mol^{-1} in the cyclobutylcarbinyl (**7**) and 17.54 kcal/mol in the cyclopropylcarbinyl (**5**) systems. In going from the cyclopropyl- (**5**) to the 1-methylcyclopropylcarbinyl (**6**) cation this rotational barrier is reduced[25] by 1.54 kcal/mol, analogous to the 1.77- and 2.68-kcal/mol drops in barriers in going from the cyclobutylcarbinyl to the 1-methylcyclobutylcarbinyl, and from the isobutyl to neopentyl cations, respectively. The preference of the cyclopropylcarbinyl cation for the bisected conformation has been shown in many ways.[26] Recent nuclear magnetic double resonance studies[27] have suggested the bisected conformation for the dimethylcyclopropylcarbinyl cation and a barrier to rotation of 13.7 kcal/mol in this tertiary system.

Many carbonium ions cannot achieve the preferred planar structure[2,3,10] as, *e.g.*, bridgehead cations.[28] We have reported calculations which showed that the ethyl cation barrier increases significantly if the CH_2^+ group is held in a tetrahedral geometry.[6] In the *n*-propyl cation, this deformation leads to an increase of the barrier to 6.04 kcal/mol (STO-3G) with the preferred geometry (**9a**) having the "empty" sp^3 lobe trans to the methyl group. The highest energy conformation (**9b**) has the hydrogens eclipsed.

These results have rather startling implications which should be tested experimentally. Firstly, contrary to popular assumption[29] nonsixfold barriers in simple alkylcarbonium ions may be quite appreciable, on the order of 2.5–3.0 kcal/mol. An energy difference of this magnitude corresponds to a 100-fold variation in rate or equilibrium phenomena which should be readily detectable in rigid structures where cations are locked into favorable and unfavorable conformations. However, the effects in secondary and tertiary cation systems may be smaller than these calculated here for primary systems. Secondly, the "C–C hyperconjugation" conformations are preferred over the "C–H hyperconjugation" geometries.[22] This contrasts with the usual assumption that C–H hyperconjugation is more favorable than C–C hyperconjugation.[2] Finally, the well-documented energy difference between the cyclopropylcarbinyl conformations **5a** and **5b** is revealed to be not a special case but only an extreme of a general phenomenon already present in the isobutyl cation (**3a** and **3b**). When the C–C bonds are "bent" increasing their p character (as in **5** and **7**) their C–C hyperconjugative ability increases,[30] but the enhancement in the rotational barrier only becomes really large when a three-membered ring is present.

Acknowledgments. This work was supported by the National Science Foundation (GP 9233 and GP 9338), and the Petroleum Research Fund, administered by the American Chemical Society. Some of the computer time was provided by Princeton University and by Mellon Institute. The calculations reported in Table I were carried out with computer programs developed at Princeton in the theoretical group directed by L. C. Allen and supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF49 (638)-1625.

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(24) "Planar" refers to the arrangement of bonds at the positive carbon center. Such arrangements may not represent the most stable geometries.[6]

(25) Attempts to study this barrier in super acid solution are frustrated by ready interconversion between the 1-methylcyclopropylcarbinyl and 1-methylcyclobutyl cations. See M. Saunders and J. Rosenfeld, *J. Amer. Chem. Soc.*, **92**, 2548 (1970); G. A. Olah, C. J. Jeuell, D. P. Kelley, and R. D. Porter, *ibid.*, in press.

(26) P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969); B. R. Ree and J. C. Martin, *ibid.*, **92**, (1970); G. A. Olah, D. P. Kelley, C. J. Jeuell, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

(27) D. S. Kabakoff and E. Namanworth, *ibid.*, **92**, 3234 (1970).

(28) R. C. Fort and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

(29) As was pointed out by a referee, one of the authors of this paper has been a "prime perpetrator" of the idea the barriers in alkyl cations are near zero. See P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854 (1964); G. J. Gleicher and P. v. R. Schleyer, *ibid.*, **89**, 582 (1967).

(30) *Cf.* F. R. Jensen and B. E. Smart, *ibid.*, **91**, 5686, 5688 (1969); N. A. Clinton, R. S. Brown, and T. G. Traylor, *ibid.*, **92**, 5228 (1970).

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Evidence on the Scope and Limitations of Ring-Forming Reactions of Tricarbonyliron Complexes of Functional 1,2-Disubstituted Cyclobutadienes. Synthesis of Tricarbonyliron Complexes of Cyclobutadienocycloheptatrienyl Derivatives

Sir:

Recently we reported the synthesis of a series of tricarbonyliron complexes of functional 1,2-disubstituted cyclobutadienes and commented on the potential synthetic value of the latter as precursors to complexes of theoretically interesting fused-ring cyclo-