shielding of the methine protons relative to the neutral species[6,7] (as indicated in **3**) eliminate a charge-localized structure such as **9**, even though the cationic center is tertiary. The evidence thus strongly indicates that the correct representation of X is either a mixture of rapidly equilibrating ions such as **8a–d** or a single, highly charge-delocalized species expressed by square pyramid **10**.[4]

Before we accept these structures (**8a–d**) or **10**, however, the remarkable, high-field (δ −23) absorption due to a quaternary carbon must be accounted for. Assignment of this signal to a carbon atom of the square (*e.g.*, C-1 of **8a**) should be rejected on several grounds. First, in order to achieve equivalence of C-2 and C-4 without putting a positive charge on C-1, the above assignment requires equilibration of only **8a** and **8b**, which seems unreasonable. Second, equilibration of **8a** and **8b** leads to the conclusion that the chemical shift (δ 73) of C-2 (and C-4) should be between those of C-1 (−23) and C-3 (61), which is not observed. Third, the proton chemical shifts of all three CH groups are virtually identical, and, finally, the quenching experiment appears inconsistent with **8a** and **8b**. In contrast, assigning the δ −23 signal to C-5 brings the chemical shifts of all C-1. . .-4 into a region expected for complete equilibration of **8a–d** or for **10**. Then the only remaining question is: is the δ value −23 reasonable for C-5?

The chemical shift demands that this unique C-5 atom carry very little charge, if any. This demand can be at least formally fulfilled in a rather naive way if it is justified to interpret Hoffmann's square pyramid,[4] **10** in the present case, in terms of the resonance hybrid of structures **11a–d**, as shown above.[8] (One would obviously expect that **11a** contributes more than **11b–d** due to its tertiary character and accordingly **10** should have more positive charge density at C_1 than C_2–C_4.) The even higher field absorption of C-5 in X than that of any atom in the starting homotetrahedrane derivatives can be attributed to the specially constrained geometry of this C-5 position. For comparison purposes the ^{13}C chemical shifts of several pertinent compounds are shown in Table I (compare C-1 with C-2). A clear trend is evident in which increasing strain causes an upfield shift.[9] Methyl substitution effects a normal downfield shift of approximately 5–10 ppm.[10]

In conclusion, the spectral data of the long-lived cation X are compatible with the theoretically predicted structure **10** or an equilibrating set of **8a–d**, indicating that the calculations should give a very low positive charge at the apex. These two sets of structures are equivalent on the nmr time scale and are distinguished only by a subtle difference in spatial arrangement. Since both are extensively charge-delocalized cations, the chemical-shift argument does not provide a clear distinction between them.[11,12]

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(6) G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Amer. Chem. Soc.*, **93**, 464 (1971).

(7) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 5123 (1965).

(8) If **8a** represents the resonance hybrid of two structures similar to but slightly different in geometry from **11a** and **11b**, then rapid equilibration of **8a–d** becomes equivalent to **10** on the nmr time scale. See ref 2, footnote 3, for the relationship of **8a** with the bicyclobutonium cation.

(9) Comparison of the chemical shifts of C-1 with those of C-5 demonstrates the significant deshielding effect of the C-3–O bond on C-5, which substantiates the stereochemical assignment of the C-3 substituent previously made (ref 2).

(10) For example, see: D. M. Grant and E. G. Paul, *ibid.*, **86**, 2984 (1964); D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967); B. V. Cheney and D. M. Grant, *ibid.*, **89**, 5319 (1967).

(11) The authors thank the National Research Council of Canada for financial support. This work was presented before the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 12, 1972, Abstracts, PETR 24.

(12) Professor Hoffmann informed us recently (Aug 11, 1972) that some calculations on dimethyl-substituted $(CH)_5^+$ species show that the most stable one is indeed **10** rather than that with two basal methyl groups. Twofold symmetry for X has been demonstrated: if the two methyl groups were missing, fourfold symmetry would be attained. The complete absence of deuterium scrambling can be rationalized by the presence of the methyl group which probably suppresses interconversion of the ions through the process discussed.[2]

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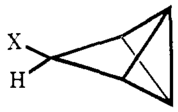
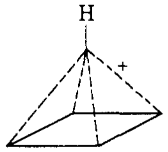
Evidence Concerning the Structure of $(CH)_5^+$-Type Carbonium Ions

Sir:

Stohrer and Hoffmann[1] made the imaginative suggestion that $(CH)_5^+$ formed by loss of X^- from **1** (and perhaps in other ways) may attain an energy minimum with the square pyramidal geometry **2**. In a formal sense, **2** could arise by bringing CH^+ toward the center of the face of square cyclobutadiene, as in **3**. We present here evidence for a bishomo analog of **2**, with a structure which can be visualized by bringing CH^+ along the symmetry axis which passes through C-7, to the open face of the double bonds in octamethylnorbornadiene, as in **4**.



1



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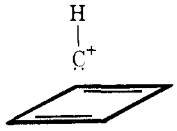

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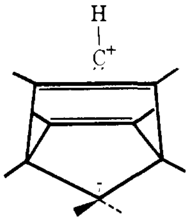

4

Reduction of ketone **5**[2] with lithium aluminum hydride gave the colorless, crystalline alcohol **6** in 90% yield.[3] The geometry of **6** is clear from the large Eu-shift slope[4] of the methyl singlet at δ 1.05. Jones' oxidation of **6** gave **5**, showing that no skeletal rearrangement occurred during the reduction.

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(1) W-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

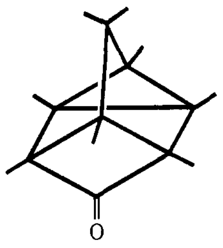
(2) H. Hart and G. M. Love, *ibid.*, **93**, 6266 (1971).

(3) A satisfactory elemental analysis was obtained.

(4) The formulas show proton chemical shifts in parts per million from TMS and, in parentheses, the relative extents to which these signals were shifted downfield by $Eu(fod)_3$.[5,6] The solvent was carbon tetrachloride.

(5) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

(6) D. R. Kelsey, *ibid.*, **94**, 1764 (1972).



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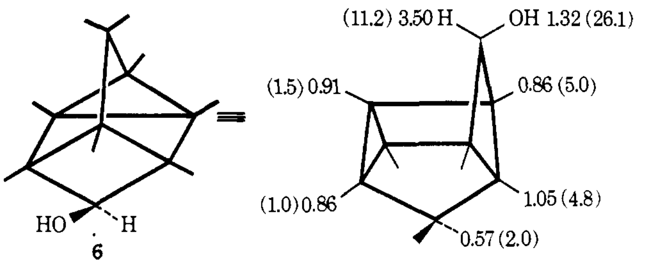
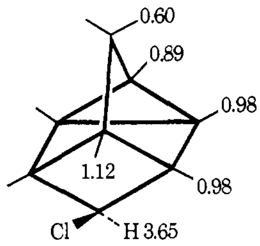
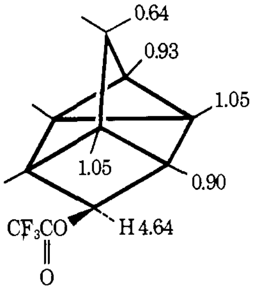


6

Treatment of **6** with hydrogen chloride in ether (0°, 5 min) or with trifluoroacetic acid in carbon tetrachloride (room temperature, 1 min) gave the secondary chloride **7** or trifluoroacetate **8**. No rearrangement to the tertiary dicyclopropylcarbinyl structure **9** was observed.[7] Chromatography of **7** (silica gel or alumina, methylene chloride eluent) afforded **6** in high yield.



7



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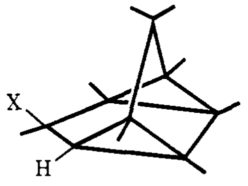
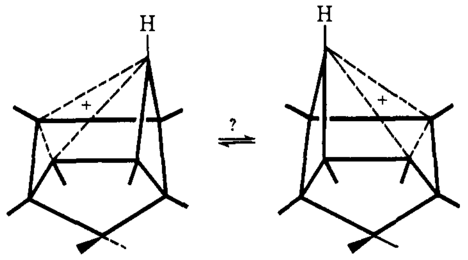


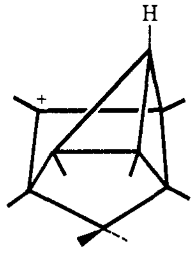
9, X = Cl or $OCOCF_3$

Lack of structural rearrangement in the conversion of **6** to **7** or **8** suggested the possible intervention of a trishomocyclopropenyl cation[8] such as **10** which might react with nucleophile preferentially at the secondary carbon atom. Further, one could imagine the conversion of **10** to its enantiomer **10′**, *via* delocalized intermediates or classical ions such as **10″**, etc. To test this possibility, labeled alcohol **11** was synthesized.[2,9] Treatment of **11** with trifluoroacetic acid gave the ester **12** with the label scrambled (nmr) as shown. Similarly, conversion of **11** to the chloride followed by hydrolysis gave scrambled alcohol **13**.[10,11]

To test the possibility that the ion responsible for the scrambling would have greater symmetry than **10**, as, for example, the symmetric pyramidal delocalized



10 **10′**



10″

structure **14**, we examined the proton nmr spectrum of **6** in FSO_3H-SO_2ClF (*ca.* 1:3 v/v) at low temperatures. The spectrum consisted of four very sharp singlets at δ 1.80, 1.33, 0.77, and 0.76 with relative areas 12:6:6 + 1.[12,13] This spectrum is consistent with structure **14**, with most of the positive charge distributed over the base of the pyramid. The high-field position of the apical proton is noteworthy. The spectrum was un-

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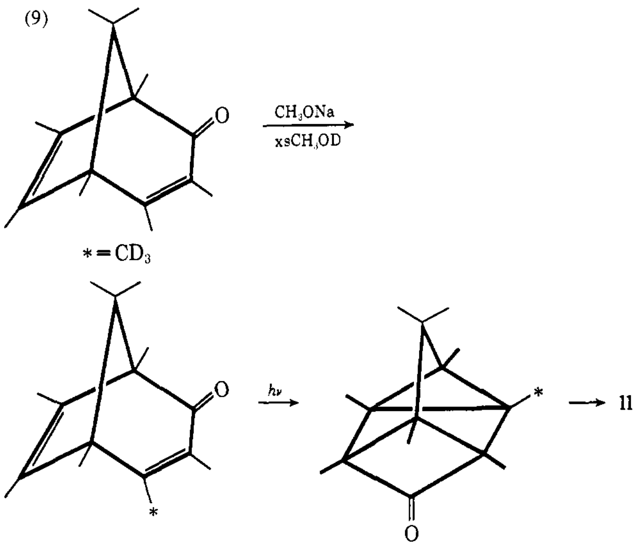
(7) Retention of configuration of **6**, **7**, and **8** is assumed, but not yet conclusively proved.

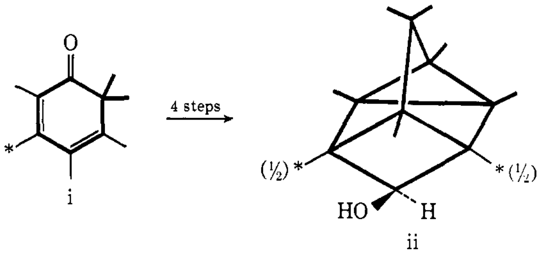
(8) S. Winstein, J. Sonnenberg, and L. de Vries, *J. Amer. Chem. Soc.*, **81**, 6523 (1959).

(9)



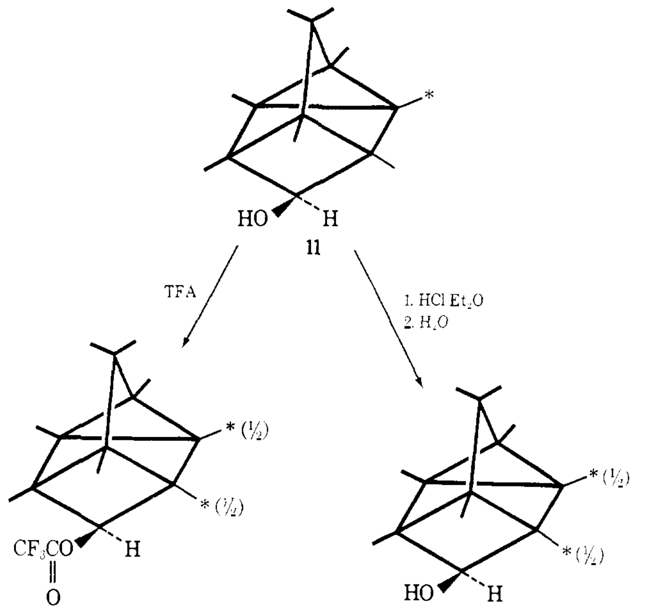
(10) Because of fortuitous coincidence of the chemical shifts in two sets of methyl groups, the chloride could not directly yield any information regarding scramble of the label.

(11) The label results were confirmed using labeled alcohol ii, prepared from i.



(12) The one-proton peak was not fully resolved from the six-proton peak and was integrated with it. Replacement of the apical H by D eliminated the peak at δ 0.76.

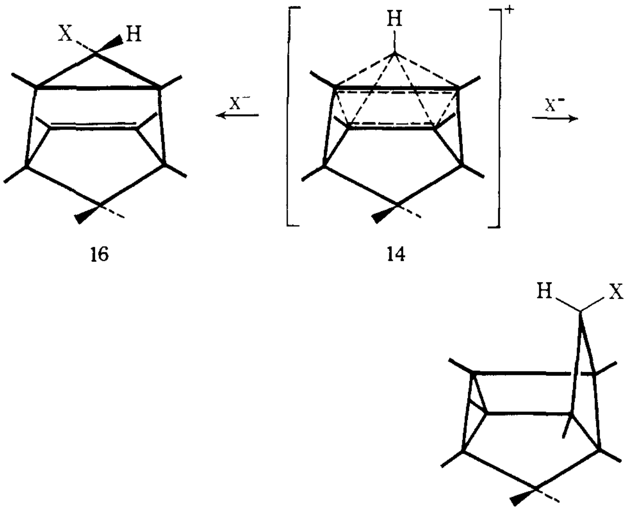
(13) The reference compound was tetramethylammonium tetrafluoroborate, δ 3.13.



11

12

13



16

14

15

changed, except for viscosity broadening, from −40 to −115°. Thus the ion shows no evidence of collapse to a less symmetric structure such as **10′** or **10″**; if the ion does not have the pyramidal structure **14**, equilibration between less symmetric structures must be rapid at −115°.

Nucleophiles could react with the apical carbon of **14** in either of two ways, giving **15** or **16**. When solutions of the ion were quenched (sodium carbonate suspension in pentane, followed by water) alcohol **6** was isolated in 60% yield; quenching with methanol gave a nearly quantitative yield of the corresponding methyl ether. The path leading to products of type **15** seems to be favored, and this result can be rationalized on energetic grounds.[14]

We are actively elaborating these initial studies.[15]

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[14] Note Added in Proof. Nucleophile could also attack **14** (or its equivalent in equilibrating ions) at a basal carbon. After this paper was submitted, R. K. Lustgarten, *J. Amer. Chem. Soc.*, **94**, 7602 (1972), described labeling results on the solvolysis of *endo*-4-psinortricyclyl tosylate which indicate that an ion analogous to **14** may be involved. However, the apical and basal carbons were all secondary, and product was derived from nucleophilic attack at basal carbon, the site of lowest electron density.

The tosylate of demethylated **6** has been studied solvolytically (R. M. Coates and K. Yano, *Tetrahedron Lett.*, 2289 (1972)), but the possibility of an intermediate analogous to **14** was not considered. We are investigating the behavior of this parent system in strong acid.

[15] Note Added in Proof. The ^{13}C nmr spectrum of our ion has been determined and permits the following unambiguous assignment of chemical shifts, in parts per million from CS$_2$: apical carbon, 188.2; framework basal carbons, 133.5; basal methyls, 183.5; framework bridgehead carbons, 143.6; remaining framework carbon, 135.4. The remaining two sets of methyl carbons appear at 178.2 and 186.0. Long-range proton–^{13}C coupling was so extensive as to prohibit the determination of any of the coupling constants. The apical carbon is at highest field and the basal framework carbons are at lowest field, supporting the conclusion from the pmr spectrum that most of the positive charge is in the basal positions. We express our appreciation to Dr. Philip W. Westerman (Case Western Reserve University) for running the spectrum and help in interpreting it, and to Professor George A. Olah for making his facilities available to us.

Singlet Oxygen ($^1\Delta_g$) Quenching in the Liquid Phase by Metal(II) Chelates

Sir:

Relatively few classes of compounds have been shown to quench the reactions of singlet oxygen ($^1\Delta_g$), $^1O_2$. Known quenchers include various dialkyl sulfides[1] and amines,[2,3] some of which are also oxidized by $^1O_2$,[1,2b] and carotenoids.[1] Since Pfeil[4] has shown that the ^{2}E state of several Cr(III) complexes can be quenched by oxygen ($^3\Sigma_g$-) to give $^1O_2$, we have investigated the occurrence of the reverse process, $^1O_2$ quenching by metal chelates, and have found that some Ni(II) compounds are efficient $^1O_2$ quenchers.

Quenching experiments were performed with rubrene (9,10,11,12-tetraphenylnaphthacene) as the $^1O_2$ receptor; bleaching of the rubrene absorption at 520 nm was used to follow the rubrene oxidation to the *endo*-peroxide. $^1O_2$ was generated by three separate methods. In method a, air-saturated rubrene solutions were photolyzed at 520 ± 20 nm,[5] and initial rates of rubrene consumption calculated. In method b, a solution of triphenyl phosphite ozonide[6] at −70° was added to a rubrene solution (at 25°) to give an initial ozonide concentration in the range 2.4×10^{-3}–0.94×10^{-3} *M*. The rubrene solution contained small percentages of methanol and pyridine so as to catalyze a virtually instantaneous $^1O_2$ evolution.[7] In method c, oxygen (6 Torr) was fed through a microwave discharge (2450 MHz, 70 W) in a quartz tube and atomic oxygen, ozone, and $^1\Sigma_{g+}$ oxygen were removed.[8] The $^1O_2$ stream was split into two identical gas streams each of which passed over a stirred solution (2.0 ml), one with quencher and one quencher free. This procedure allowed parallel experiments to be performed

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[1] C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, **171**, 139 (1970).

[2] (a) C. Ouannès and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968); (b) W. F. Smith, *ibid.*, **94**, 186 (1972).

[3] J. P. Dalle, R. Magous, and M. Mousseron-Canet, *Photochem. Photobiol.*, **15**, 411 (1972).

[4] A. Pfeil, *J. Amer. Chem. Soc.*, **93**, 5395 (1971).

[5] T. Wilson, *ibid.*, **88**, 2898 (1966).

[6] R. W. Murray and M. L. Kaplan, *ibid.*, **91**, 5358 (1969).

[7] G. D. Mendenhall, Ph.D. Thesis, Harvard University, 1970.

[8] M. L. Kaplan and P. G. Kelleher, *Science*, **169**, 1207 (1970).