volytic condition employed. The structure of **9** formulated as shown in Scheme II stands on secure spectral evidence similar to that utilized for **6**.[6]

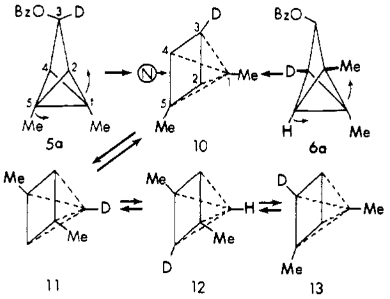
Use of the 3-deuterio compound **5a** in the above experiments clearly demonstrated that the label atom appeared at specific positions of the products (**6a**, **7a**, **8a**, and **9a**) as indicated and that there was no scrambling of the deuterium within the limit of the spectral analysis. Experiments employing methanol-*4-d* and **5** provided **6**, **7b**, **8b**, and **9b** and demonstrated the manner of protonation of the tricyclo system leading to the cyclopentene system, the process being analogous to that observed for protonation of the bicyclobutane system.[9]

We have established first that the solvolysis proceeds enormously fast[10] *not* because of the relief of strain involved in the system, but because of the unique anchimeric assistance brought about by delocalization of the positive charge within the system. Second, we have defined the type of solvolytic rearrangement of the homotetrahedrane system. There are 18 possible isomeric monodeuteriodimethylhydroxyhomotetrahedranes of which 12 are *d,l* pairs and any types of processes leading to all the isomers must be nonstereospecific at least at some stages. In contrast, if the stereospecificity analogous to that observed for the cyclopropylcarbinyl system[11] is rigorously held during the formal 1,2 (but not 1,3) carbon sigmatropic rearrangement, then **5a** can lead to only two other isomers (**6a**, **9a**) which was observed.[12] The above findings appear to be explained simply by invoking well-known bicyclobutonium cations of type **3a** or their equivalents[3,11] (without their interconversion at each step), the formation of the ions and the attack of the nucleophiles (benzoate ion and methanol) being stereospecific as defined above.

Finally, we wish to examine briefly the results in terms of Hoffmann's square pyramid intermediates by imposing some restriction to meet the observed stereochemistry. Suppose that the stereochemistry of the leaving group decides, in the manner shown in Scheme III, which carbon atom will occupy the C-apical position of **10** and that the nucleophile attacks the cation from the bottom side of the pyramid. Then compounds **5a** and **6a** will lead to exactly the same square pyramid **10** which benzoate ion and methanol must attack at different positions, C-2 and C-4, in order to obtain **6a** and **9a**, respectively. Although **6a** resulted from ion-pair return and **9a** formed through capture by the solvent molecule, methanol and benzoate ion rarely choose different sites of attack, unlike methoxide and hydride. If this is the case, **10** appears unlikely to be the intermediate. On the other hand, it is not impossible that the nucleophiles may attack different sites because of the extremely high reactivity of the system and the benzoate corresponding to **9** would be too reactive to be isolated. Then the above solvolysis results are consistent with the involvement of **10**. In any event, the absence of deuterium scrambling eliminates the possibility of interconversions such as **10** → **11** → **12** → **13** during the solvolytic reaction.

In conclusion, the results obtained by the solvolytic studies tend to indicate that the mechanism similar to that now apparently accepted for the cyclopropylcarbinyl system[11] is operating in the present system, and whether or not C_{4v} is energetically favorable, it appears not to have fully developed. At least the experimental results using the dimethyl derivatives and the conditions specified above appear not to demand such a species.[13]

Scheme III



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[9] For instance, K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1971), and ref 1d, pp 200–201.

[10] Using the Foote–Schleyer treatment [C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854 (1964)] and proper correction factors to estimate the rate of the tosylate of **6** in acetic acid at 25° [S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961); H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953); and ref 1], one obtains a factor of 21 powers of 10 in rate of acceleration attributable to the neighboring participation. While this number bears little meaning except that it is very large, it is extremely difficult to find a suitable model compound for comparison.

[11] Z. Majerski and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 663 (1971), and references quoted therein.

[12] Note that the bicyclobutonium cations formally derived from **9a** are exactly the same as those from **6a**. Therefore, **5a**, **6a**, and **9a** form a closed circuit.

[13] 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, Abstract PETR 24.

S. Masamune,* M. Sakai, H. Ona
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

Received May 17, 1972

Nature of the $(CH)_5^+$ Species. II. Direct Observation of the Carbonium Ion of 3-Hydroxyhomotetrehedrane Derivatives

Sir:

Olah's remarkable success[1] in the direct observation of ionic species has led us to investigate the behavior of some 3-hydroxyhomotetrahedrane derivatives[2] in superacid media. We have observed well-defined ^1H and ^{13}C nmr spectra of the cationic species derived from the above compounds, and wish to present extraordinary features of the long-lived carbonium ion, in contrast to those involved in the solvolysis.[2]

Solutions of a set of isomeric dimethylhomotetrahedranes **1**, **2**, and **3**[2] in a 3:2 mixture of SO_2ClF and FSO_3H at $-78°$ all provided identical pmr and cmr spectra (Figures 1 and 2), which remained unchanged at least for several hours. An off-resonance spectrum allowed assignment of the cmr signals to two CH_3, two equivalent CH, one CH, and two quaternary carbons as indicated. Use of the specifically deuterium labeled

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[1] (a) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972); (b) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, **94**, 146 (1972), and references quoted therein.

[2] See the preceding communication: S. Masamune, M. Sakai, and H. Ona, *ibid.*, **94**, 8955 (1972).

Table I. ^{13}C Chemical Shifts of Some Homotetrahedrane Derivatives[a,b]

Substituents	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Ref
1,5-Dimethyl-3-hydroxy	CS_2	12.9	33.6	84.4	33.6	27.5	6.4	8.5	
1,5-Dimethyl-3-benzoxy	CS_2	14.8	28.6	85.5	28.6	28.1	6.4	7.9	
1,2-Dimethyl-3-benzoxy	CD_2Cl_2	14.2	32.0	86.1	23.1	22.5	6.1	8.6	
1,5-Dimethyl-3-keto	CD_2Cl_2	14.6	42.3	185.3	42.30	14.6	5.8	5.8	
1,5-Diphenyl-3-hydroxy	$(CD_3)_2CO$	~30	40.1	84.1	40.1	44.9	125–136		*c*
1,5-Diphenyl-3-benzoxy	$(CD_3)_2CO$	~30	35.9	84.9	35.9	44.0	126–134		*c*
1,5-Diphenyl-3-keto	$(CD_3)_2CO$	25.6	46.8	181.7	46.8	25.6	127–130		*c*
Bicyclobutane		−4.5	31.5						*d*

[a] The substituent of C-3 is cis oriented to that at C-5 (see **2** for numbering). [b] Positive numbers indicate parts per million downfield from TMS and the chemical shift of $^{13}CS_2$ is 192.82.[5] [c] M. Suda and S. Masamune, unpublished. [d] K. Wüthrick, S. Meilboom, and L. C. Snyder, *J. Chem. Phys.*, **52**, 230 (1970).

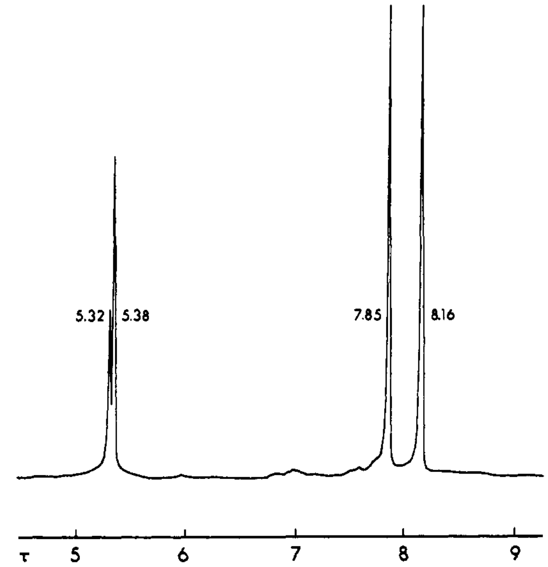


Figure 1. A pmr spectrum (100 MHz) of cation X in $SO_2ClF-FSO_3H$ at −78°.

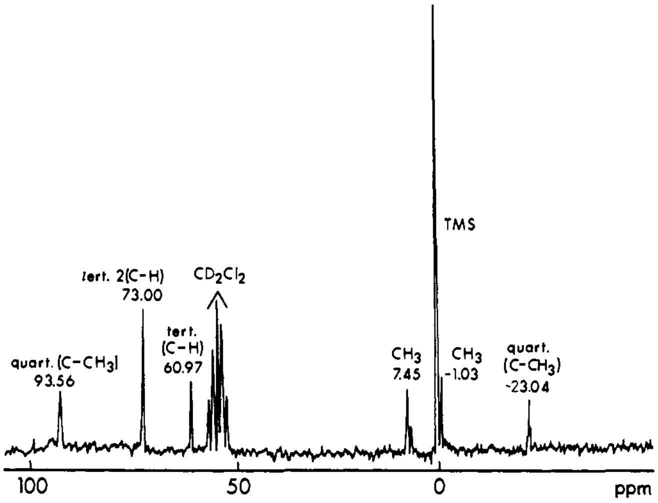
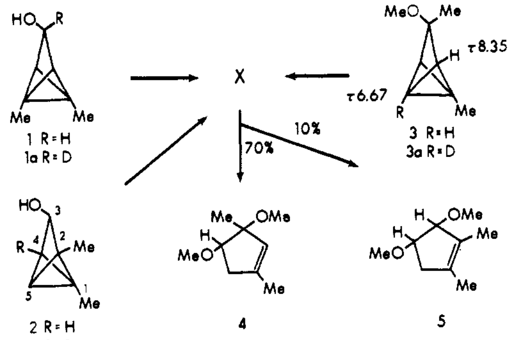
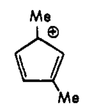


Figure 2. A cmr spectrum (22.63 MHz) of cation X in $SO_2ClF-FSO_3H$ at −78°.

compounds **1a**, **2a**, and **3a** resulted in the disappearance of the one-proton singlet at τ 5.32 in all three cases. Quenching the acidic solutions obtained from **1**, **2**, and **3** with cold (−78°) methanol containing excess sodium methoxide afforded the same mixture of dimethoxycyclopentenes **4**[2] (70% yield) and **5**[2] (10%) in addition to other unidentified minor products.

The common pmr and cmr spectra obtained from **1**, **2**, and **3** and from **1a**, **2a**, and **3a** show that the same cation X has been derived without involvement of any processes causing deuterium scrambling. The appearance of two nonequivalent CH_3 signals in the pmr and cmr spectra immediately rules out the cations expressed in **6**[3] and **7**[4] as possible structures for X. Of the three methine (CH) groups appearing at almost the same field, two are equivalent, thus excluding nonequilibrating (as compared to the nmr time scale) unsymmetrical species such as **8a**. The absence of any low-field absorptions[5] in the cmr spectrum and the de-





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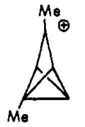

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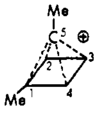

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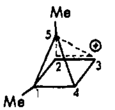
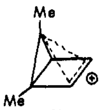
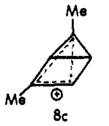


8a



8b



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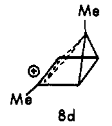
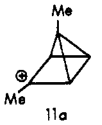
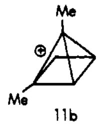


8d



11a



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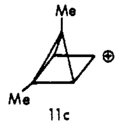

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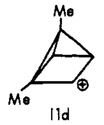

11d

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(3) R. Breslow, H. W. Chang, and W. A. Yager, *J. Amer. Chem. Soc.*, **85**, 2033 (1963); R. Breslow, R. Hill, and E. Wasserman, *ibid.*, **86**, 5349 (1964); R. Breslow and J. M. Hoffman, Jr., *ibid.*, **94**, 2110 (1972). Species **6** is obviously antiaromatic. A referee suggested that we state that "it seems unlikely that **4** or **5** should give the same spectrum in superacid media."

(4) W. D. Stohrer and R. Hoffmann, *ibid.*, **94**, 1661 (1972).

(5) G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

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]

S. Masamune,* M. Sakai, H. Ona, Alan J. Jones
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

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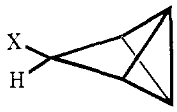
Evidence Concerning the Structure of $(CH)_5^+$-Type Carbonium Ions

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**.



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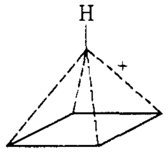

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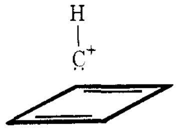

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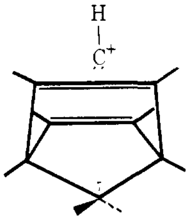

4

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).