Petroleum Research Fund, administered by the American Chemical Society, for grants in support of this work. The junior author gratefully acknowledges fellowship support at different times from the Woodrow Wilson Foundation, the National Science Foundation, and the National Institutes of Health.

# Stable Carbonium Ions. LXVIII.[1] Protonation and Ionization of Cyclopropyl Halides. Measurement of Rotational Barriers in Substituted Allyl Cations

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**Abstract:** Cyclopropyl halides were found to give, in fluorosulfuric acid–antimony pentafluoride–sulfur dioxide solution, either, by protonation, the corresponding halonium ions or, by ionization, substituted allylic cations, two of which exhibited temperature-dependent nmr spectra. Activation parameters were measured for these ions for rotation about the partial double bond.

We have previously reported the behavior of cyclopropanes in strong acid solutions.[2] We felt it of interest to continue these studies by examining the behavior of cyclopropyl halides in these systems as a possible pathway to both allylic cations and halonium ions.

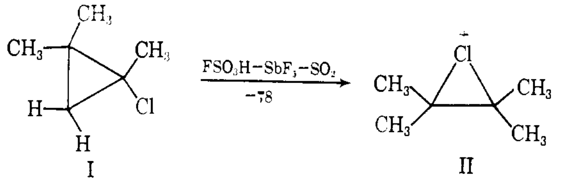
There are a large number of reports of the protolytic cleavage of cyclopropane bonds.[3] The cleavage of cyclopropanols is usually a clean reaction since the hydroxyl stabilizes positive charges.[4] Cyclopropyl halides ought to show some of the characteristics of the cyclopropanols, since halogen stabilizes positive charges in these systems.

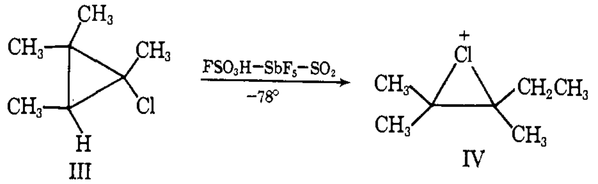
DePuy and coworkers[5] isolated allylic products from solvolysis of cyclopropyl tosylates. Schleyer[6] has also recently reported concerted ring opening during the solvolysis of cyclopropyl tosylates. Recent reports,[7–9] on the other hand, indicate that ring opening may not always be concerted with ionization as demonstrated by the isolation of species derived from cyclopropyl cations.

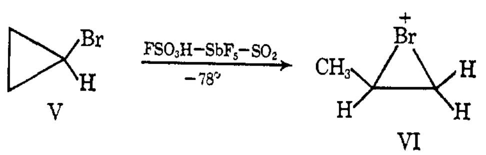
We hoped to learn about the timing of the ring opening in the solvent fluorosulfuric acid–antimony pentafluoride–sulfur dioxide. According to the observations of Peterson,[10] anchimeric assistance to ionization becomes more pronounced as the nucleophilicity of the solvent decreases. This predicts that concerted ionization should take place in this extremely nonnucleophilic solvent. Unfortunately, we were unable to come to any conclusion as to whether or not the cyclopropyl halide ionizations were concerted.

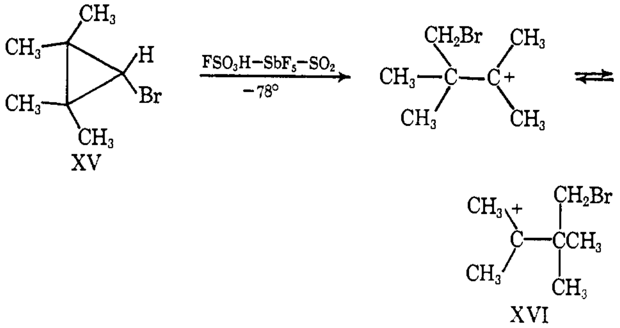
## Results and Discussion

Addition of the cyclopropyl halides, I, III, and V, to a solution of fluorosulfuric acid–antimony pentafluoride–sulfur dioxide at −78° resulted in protolytic cleavage of a carbon–carbon bond with formation of the halonium ions, II, IV, and VI, respectively (ions II









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[1] Part LXVII: G. A. Olah and P. E. Peterson, *J. Amer. Chem. Soc.*, **90**, 4675 (1968).

[2] G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968).

[3] L. Joris, P. von R. Schleyer, and R. Gleiter, *ibid.*, **90**, 327 (1968), and references therein.

[4] C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

[5] C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Amer. Chem. Soc.*, **87**, 4006 (1965); C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966).

[6] P. von R. Schleyer, G. W. Van Dine, W. Schollkopf, and J. H. Paust, *ibid.*, **88**, 2868 (1966).

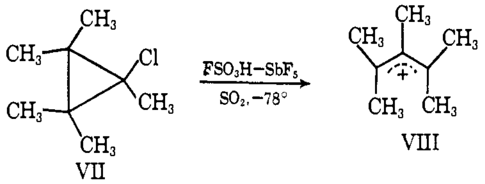
[7] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951), originally proposed nonconcerted solvolysis for cyclopropyl tosylate.

[8] W. Kirmse and H. Schutte, *ibid.*, **89**, 1284 (1967).

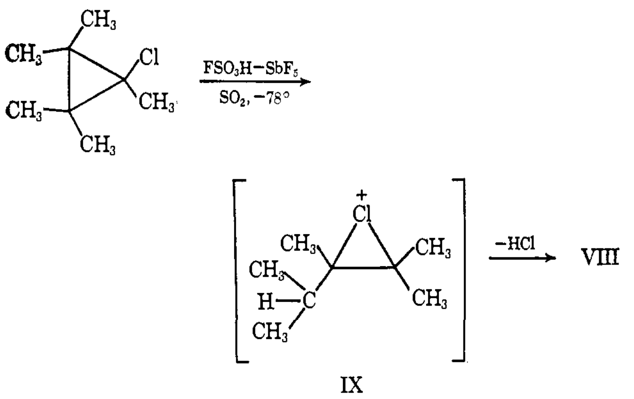
[9] J. A. Landgrebe and L. W. Becker, *ibid.*, **89**, 2505 (1967).

[10] P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Amer. Chem. Soc.*, **89**, 5092 (1967).

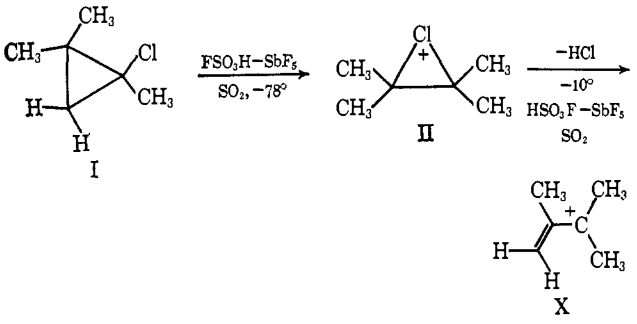
and VI had been observed in our previous work from other precursors).[11a] Protonation of XV gave a species to which we tentatively assign the structure of the equilibrating ions XVI.[11b] Pentamethylcyclopropyl chloride (VII), however, gave only the pentamethylallyl cation VIII under these conditions.[12]



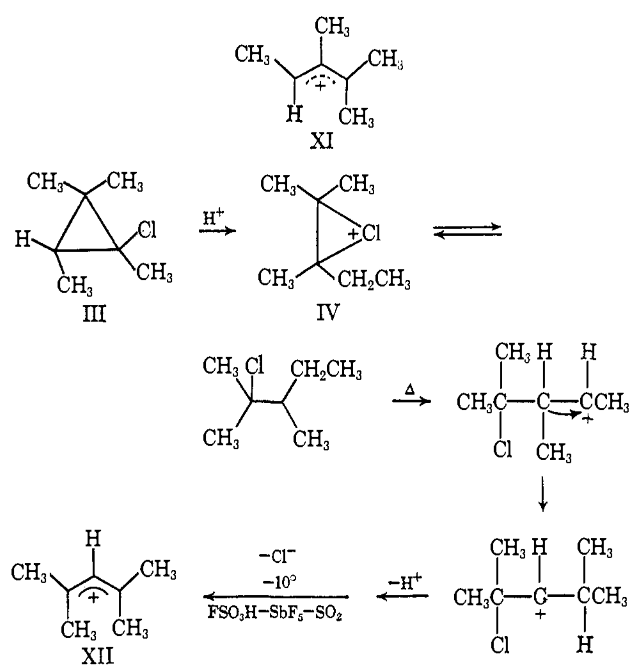
In our experience, fluorosulfuric acid-antimony pentafluoride ionizes alkyl and acyl halides readily. Ion VIII could then have been produced by direct concerted ionization with ring opening. However, protonation giving the intermediate trimethylisopropylethylenechloronium ion (IX), followed by loss of HCl, would also yield VIII. This latter pathway has been observed in the case of ion II to lead to the 1,1,2-trimethylallyl cation (X) (see subsequent discussion), and we consider this latter pathway more probable.



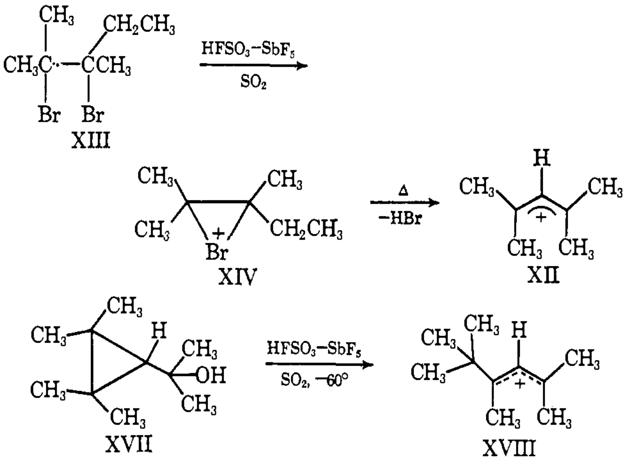
This type reaction scheme was definitely shown for the conversion of I to ion X by quenching the intermediate tetramethylethylenechloronium ion (II) in methanol at −78° to yield the known 2-methoxy-3-chloro-2,3-dimethylbutane.[11a] We had previously noted an elimination scheme of the same kind for 2-methoxy-3-fluoro-2,3-dimethylbutane in this medium.[11,13] The preparation of ion X was readily accomplished by preparing II, either by protonation of I or by ionization of 2,3-dichloro-2,3-dimethylbutane in fluorosulfuric acid-antimony pentafluoride-sulfur dioxide and warming the solution to the boiling point briefly.



In the same way, warming the halonium ion IV, which is prepared by protonation of III, might be expected to yield the 1,1,2,3-tetramethylallyl cation XI (or an isomer). However, warming ion IV produced cleanly ion XII.[13,14] Although other paths are possible, the most reasonable explanation for the formation of XII from IV is



The identity of XII was confirmed by mixing samples prepared from 2,4-dimethyl-2-chloro-4-pentene with



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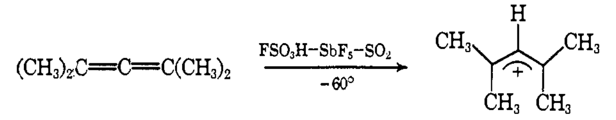
(11) (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967). (b) The nmr spectrum of this ion in fluorosulfuric acid-antimony pentafluoride-sulfur dioxide solution consists of a sharp singlet at δ (from external TMS) 2.85 (12 H) and 4.13 (2H) ppm.

(12) The 1,1,3,3-tetramethylallyl cation and pentamethylallyl cation were first prepared by N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, **85**, 2991 (1963), in sulfuric acid. The nmr chemical shifts reported by these authors are surprisingly similar, considering the difference in solvent, to those measured by us.

(13) G. A. Olah and J. Sommer, *ibid.*, **90**, 931 (1968), prepared the 1,3-dimethylallyl cation by decomposition of a difunctional saturated precursor.

(14) The 1,1,3,3-tetramethylallyl cation was also prepared by Olah and Schlosberg (unpublished results, to be reported) by the protonation of tetramethylallene.



Work is also in progress on the preparation of other allylic cations by protonation of allenes.

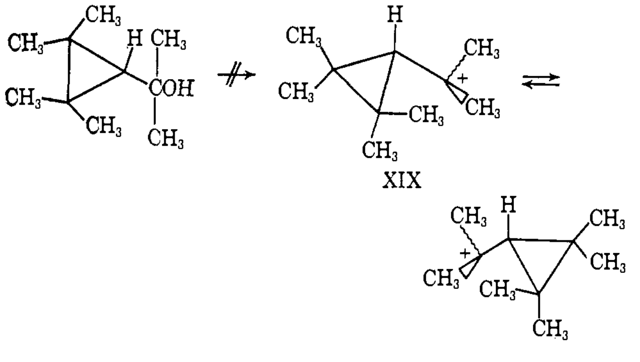
**Table I.** Nmr Chemical Shifts[a] of Allylic Cations at −60°

| Cation | Solvent | $C_1$-methyl (H) | $C_2$-methyl (H) | $C_3$-methyl (H) |
|---|---|---|---|---|
| Pentamethylallyl | $SbF_5$–$SO_2$ | 2.94<br>3.10 | 2.30 | 2.94<br>3.10 |
| 1,1,3,3-Tetramethylallyl | $SbF_5$–$SO_2$ | 2.91 | 7.83 | 2.91 |
| 1,1,2-Trimethylallyl | $HFSO_3$–$SbF_5$–$SO_2$ | 3.41<br>3.53 | 2.38 | 7.72<br>8.27 |
| 1,3-Dimethylallyl[b] | $HFSO_3$–$SbF_5$–$SO_2$ | 3.45[c]<br>10.10[d] | 8.30[e] | 3.45[c]<br>10.10[d] |
| Dimethyleneallyl[f] (cyclopentenyl) | $SbF_5$–$SO_2$ | 4.04[g]<br>11.10[h] | 8.46[i] | 4.04<br>11.10 |
| 1-*t*-Butyl-1,3,3-trimethylallyl[j] | $HFSO_3$–$SbF_5$–$SO_2$ | 3.15<br>1.72[k] | 8.10 | 3.15 |

[a] δ Values in parts per million from external TMS. [b] Reference 13. [c] Doublet, $J$ = 7 Hz. [d] Multiplet. [e] Triplet, $J$ = 14 Hz. [f] Prepared from 1,2-dibromocyclopentane. [g] Doublet, $J$ = 1.9 Hz. [h] Overlapping triplets. Triplet, $J$ = 3.8 Hz. [j] Prepared from 1,1,2,2-tetramethylcyclopropyldimethylcarbinol. [k] *t*-Butyl group.

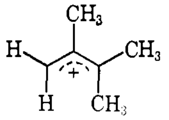
that from the cyclopropyl halide. Ion XII could also be prepared *via* the bromonium ion XIV (prepared from dibromide XIII).

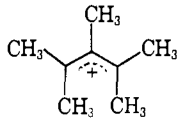
We were surprised to find the cyclopropylcarbinol XVII went cleanly to the allylic ion XVIII. We expected the stable degenerate cyclopropylcarbinyl cation XIX to be produced. Apparently, the methyl groups on the cyclopropane ring prevent the ion from attaining the "bisected" geometry required for the charge delocalization by the rings.


XIX

We have no way of determining whether the halogen assists the carbon–carbon cleavage in the reactions of cyclopropyl halides. There was also no evidence for the formation of long-lived face- or edge-protonated cyclopropanes under our conditions. Similar results were obtained when sulfuryl chlorofluoride was used as diluent instead of $SO_2$, although the halonium ions appeared to decompose more readily in the former solvent. It is interesting to note that ion VI, which gave only two lines in the AB region in sulfur dioxide, showed three lines in sulfuryl chlorofluoride. In this solvent system a treatment of the coupling constants similar to that used on the propyleneiodonium ion[15] could be applied.

When cyclopropyl halides were treated with antimony pentafluoride in sulfur dioxide, the results were generally more complicated. In this medium VII gave VIII and XV gave XII cleanly, but I and III underwent more complicated behavior. In fact, we were unable to interpret the spectrum of III in antimony pentafluoride–sulfur dioxide although methanol solvolysis at −78° gave a satisfactory yield of 4-methoxy-2,3-dimethyl-2-pentene and 4-methoxy-3,4-dimethyl-2-pentene in equal amounts (identified by nmr spectra). We were also unable to interpret the spectrum of I in antimony pentafluoride–sulfur dioxide and, moreover, no product could be identified from methanolysis at −78°. Using $SO_2ClF$ as solvent with antimony pentafluoride, on the other hand, allowed clean preparations of ion X from I and VIII from II. Table I summarizes the nmr chemical shifts of allylic cations. Figures 1 and 2 show the nmr spectrum of ion X at −20 and −70°.


X


VIII

**Temperature Dependence of Allylic Ions.** The separation of the nonequivalent methyl groups of ions VIII and X was used in the equation for a two-site exchange to calculate the rate constants at various temperatures

$$k = \frac{1}{2\tau} = \pi\left(\frac{\delta^2 - \delta e^2}{2}\right)^{1/2}$$

$$k_{\text{coalescence}} = \frac{1}{2\tau} \frac{\pi\delta}{\sqrt{2}}$$

where δ is the separation under conditions of no exchange and δ*e* is the separation at a given exchange rate. We neglected overlap and the effects of coupling to the methyl groups. Values of $E_a$ and the frequency factor $A$ were derived from linear plots of log $k$ *vs.* $1/T$ by the method of least squares. $\Delta F^{\ddagger}$ was evaluated from the expressions $\Delta H^{\ddagger} = E_a - RT$ and $\Delta S^{\ddagger} = 2.3R[\log A - \log (kT/h)]$. As can be seen from Table II, the activation parameters are similar for the two ions in the various solvent systems and are not significantly different from each other because of the large errors involved in the method.[16] Of interest are the large unfavorable entropies of activation. White sides, Nordlander, and Roberts[17] found for allylmagnesium bromide an $E_a$ of 7 ± 3 kcal/mol (log $A$ = 3–4) for the exchange indicating that the exchange was intramolecular with a transition state resembling XX. A recent communication[18] also noted the difficulty in

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[15] G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968). This treatment yields the following values: as $J_{AB}$ varies from 0 to 12 Hz, $J_{cis}$ varies from 5.0 to 4.1 Hz, and $J_{trans}$ varies from 13.0 to 13.9 Hz. (The highest field doublet is assigned to the proton *cis* to the methyl group.)

[16] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *ibid.*, **88**, 3185 (1966).

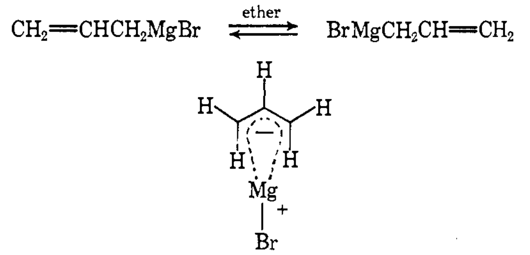
[17] G. M. Whitesides, J. E. Norlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962).

[18] V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 495 (1968), and references contained therein.

**Table II.** Activation Parameters for Rotations in Allylic Cations[a]

| | Solvent: $SbF_5$–$SO_2$ | | $SbF_5$–$SO_2ClF$ | | $SbF_5$–$FSO_3H$–$SO_2$ | | $SbF_5$–$FSO_3H$–$SO_2ClF$ | |
|---|---|---|---|---|---|---|---|---|
| Cation | X | VIII | X | VIII | X | VIII | X | VIII |
| $E_a$, kcal/mol | | 5.7 ± 0.1 | 4.6 ± 0.2 | | 4.4 ± 0.2 | 5.8 ± 0.3 | 4.3 ± 0.2 | 5.9 ± 0.1 |
| $A$ | | $10^{6.0 \pm 0.1}$ | $10^{5.7 \pm 0.2}$ | | $10^{5.5 \pm 0.2}$ | $10^{6.1 \pm 0.2}$ | $10^{5.4 \pm 0.2}$ | $10^{6.1 \pm 0.1}$ |
| $\Delta H^{\ddagger}$,[b] kcal/mol | | 5.2 ± 0.1 | 4.1 ± 0.2 | | 3.9 ± 0.2 | 5.3 ± 0.3 | 3.8 ± 0.2 | 5.4 ± 0.1 |
| $\Delta S^{\ddagger}$,[b] eu | | −31 ± 1 | −33 ± 1 | | +33 ± 1 | −31 ± 1 | −34 ± 1 | −31 ± 1 |
| $\Delta G^{\ddagger}$,[b] kcal/mol | | 13.7 ± 0.4 | 13.1 ± 0.5 | | 12.9 ± 0.5 | 13.8 ± 0.6 | 13.1 ± 0.5 | 13.9 ± 0.4 |
| $\Delta\nu$, Hz, of nonequiv methyl groups | | 8.7 | 8.0 | | 8.0 | 8.4 | 8.0 | 7.8 |
| $T_c$, °C (obsd) | | −13 | −48 | | −49 | −12 | −48 | −12 |

[a] Error given is the rms error from the least-squares line. [b] At 273°.



XX

choosing between a mechanism of this kind and a rotation about partial double bonds. This suggests that one mechanism for our observed exchange might be collapse of an intimate ion pair with rotation in the covalent species. This covalent species must be present in low concentration since it cannot be observed under conditions of no exchange and since under conditions of rapid exchange the spectrum observed is that to be expected of an allylic cation unmodified by averaging the chemical shifts of a covalent species with that of the ion.

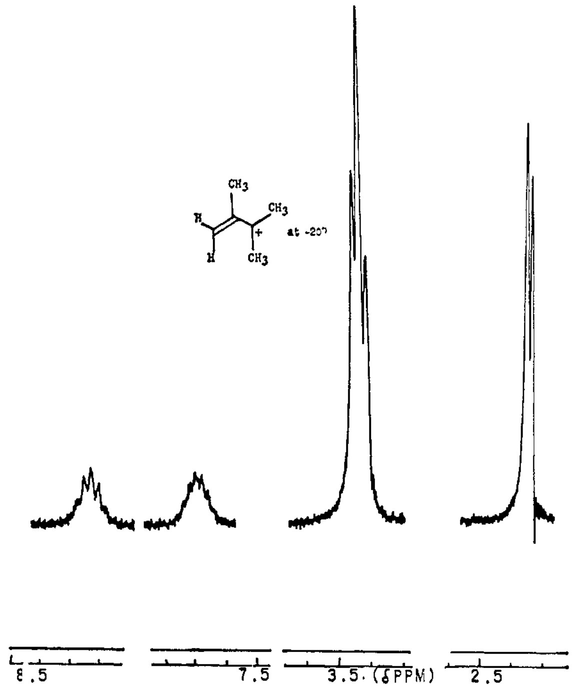
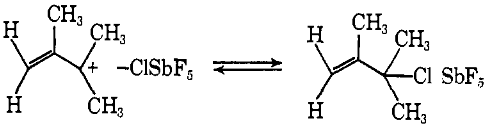


Figure 1.



We suggest that this latter mechanism is not operative for two reasons. (1) Although the degree of solvation of ion aggregates in this medium is unknown, it would seem unreasonable to expect ions or ion pairs to have no orienting effect on the solvent; therefore, the entropy change for an ion recombination reaction should be positive,[19] not negative as we have found. (2) The constancy of the activation parameters with solvent changes suggests that there is no ion effect (in fluorosulfuric acid–antimony pentafluoride the medium must contain many more ions than in the antimony pentafluoride solution, and the possibility for recombination should be greater).

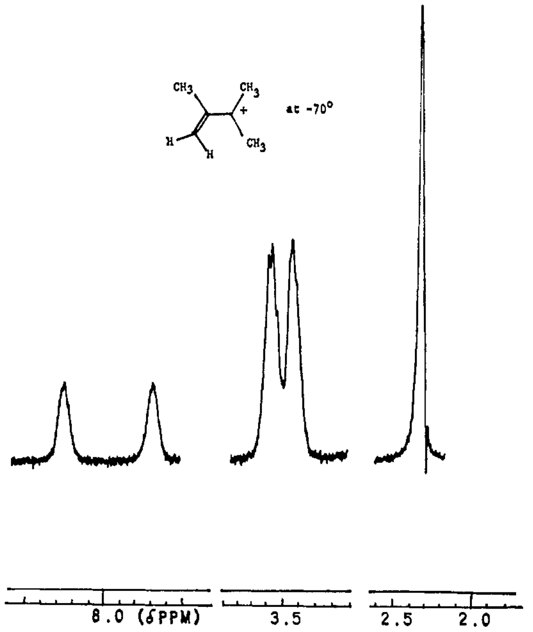


Figure 2.

It is of interest to compare the observed result of methyl substitution on the rotational barriers in these allylic cations with what might have been expected.

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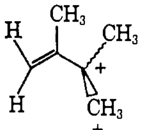
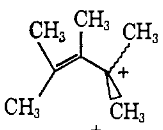
[19] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 143.

One might have expected the barrier in VIII to be lower than XI for the following reasons. (1) Substitution of the two methyl groups should not affect the energy of the transition state, but (2) substitution of the two methyl groups should increase the energy of the ground state by more than 7.6 kcal due to steric effects,[20] provided this difference is not compensated for by increase in delocalization energy caused by having the symmetrical ion.

We assume that the transition state for these rotations is an ion in which the p orbital of the carbonium ion is orthogonal to the $\pi$ orbitals of the double bond. Since the ions have nearly identical transition states, it seems reasonable to assume that the only difference in the activation energy should be due to a difference in the energy of the ground-state ion.



VIII‡



X‡

Since VIII and X have a similar barrier, we conclude that the extra delocalization energy of the symmetrical cations must compensate for the increased steric effects. A similar consideration must be responsible for the ease with which halonium ions such as IV and XIV give XII instead of the expected XI.

We have been unable to observe any change in the olefinic absorptions of X with increasing temperature. Obviously the barrier to rotation about this bond is quite large.

Our results also indicate that the equivalence of the methyl groups in the 1,1,3,3-tetramethylallyl cation (XII) is accidental and is not caused by a too low barrier to rotation. The rotational barrier in XII ought to be at least as high as that in VIII. Similarly, XVI shows slight broadening of the methyl groups, but no separation. A hydrogen atom at the 2 position does not induce nonequivalence in the methyl groups.

## Experimental Section[21]

**$\alpha,\alpha$-Dimethyl-1,1,2,2-tetramethylcyclopropylcarbinol** was prepared by the method of Wharton, *et al.*[22]

**1,2,2-Trimethyl-1-chlorocyclopropane.** Liquid isobutylene (25 ml, ~0.3 mol) was dissolved in a solution of 30.0 g (0.31 mol) of $CH_3CHCl_2$ (Matheson Coleman and Bell shaken with aqueous $Na_2SO_3$ and dried over $K_2CO_3$, then $Na_2SO_4$) and 100 ml of anhydrous ether cooled to −40°. To this solution was added dropwise with magnetic stirring 175 ml of $n$-$C_4H_9Li$ (1.6 *M*) in hexane, while maintaining the temperature between −30 and −40°. The addition was made over a 1-hr period. A white precipitate formed early in the addition. When all the *n*-butyllithium had been added, the reaction mixture was stirred for 0.5 hr during which time the temperature was allowed to rise to room temperature. Water (100 ml) was then added and the organic layer separated from the aqueous layer and dried over $Na_2SO_4$. Solvent was removed by distillation through a 6-in. Vigreux column. The desired product distilled at 102–103° at atmospheric pressure and amounted to 6.6 g, 20%. This material was homogeneous to vpc; nmr in $CCl_4$: 0.52 (d), $J$ = 5.8 Hz, 0.79 (d), $J$ = 5.8 Hz, 1.13 (s), 1.30 (s), and 1.62 (s).

*Anal.* Calcd for $C_6H_{11}Cl$: C, 60.76; H, 9.35; Cl, 29.89; mol wt, 118. Found: C, 60.58; H, 9.44; Cl, 29.08; mol wt, 118 (mass spectrometer).

**1,1,2,3-Tetramethyl-1-chlorocyclopropane.** An identical procedure with that described above was used, substituting 2-methyl-2-butene (Aldrich). From 21.0 g (0.3 mol) of olefin there was obtained 15.8 g of material of bp 128–132°. This material was shown by vpc to consist mostly of two components in a ratio of about 3:2. Initially these were thought to be a mixture of stereoisomers of the desired cyclopropane. Subsequent separation of these two compounds by preparative vpc on Carbowax (difficultly separable except with very small sample size) showed that the longer retained material was the desired cyclopropane of unknown stereochemistry. The material of shorter retention time remains unidentified; nmr in $CCl_4$: *ca.* 0.49 (q), $J$ = 6.0 Hz, 1.08 (d), $J$ = 6.0 Hz, 1.07 (s), 1.12 (s), and 1.61 (s); nmr of unknown impurity in $CCl_4$: 0.97 (s), 1.29 (s), and 1.47 (s) in the ratio of 2:1:1, respectively.

*Anal.* Calcd for $C_7H_{13}Cl$: C, 63.39; H, 9.88; Cl, 26.73; mol wt, 132. Found: C, 63.14; H, 9.87; Cl, 26.85; mol wt, 132 (mass spectrometer).

**1,2,2,3,3-Pentamethyl-1-chlorocyclopropane.** An identical procedure was used as described above substituting 2,3-dimethyl-2-butene (Aldrich). From 8.4 g (0.1 mol) of olefin there was obtained 3.1 g of product, bp 61–63° (30 mm) and mp *ca.* 24°, after purification by preparative vpc, mp 32–34°; nmr in $CCl_4$: 1.05 (s), 1.16 (s), and 1.56 (s).

*Anal.* Calcd for $C_8H_{15}Cl$: C, 65.52; H, 10.31; Cl, 24.17; mol wt, 146. Found: C, 65.49; H, 10.11; Cl, 24.29; mol wt, 146 (mass spectrometer).

**Nmr Spectra.** Solutions of the ions were prepared as described previously.[11,15] Spectra were recorded either on a Varian A56-60A or HA-60 IL equipped with variable-temperature probes. Temperatures were measured by means of a thermometer inserted into an nmr tube containing methanol and calibrated with the shift difference between methanol quartet and doublet. Chemical shifts of ions are referred to external TMS.

**Acknowledgment.** Support of the work by grants of the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[20] P. von R. Schleyer, G. W. Van Dine, U. Schollkopf, and J. Paust, *J. Amer. Chem. Soc.*, **88**, 2868 (1966).

[21] Nmr spectra are reported as $\delta$ in ppm relative to internal TMS. Abbreviations used are: (s) singlet; (d) doublet; (q) quartet.

[22] P. S. Wharton and T. I. Bair, *J. Org. Chem.*, 30, 1681 (1965).