Stable Carbonium Ions. LVII.[1a] Halonium Ion Formation *via* Neighboring Halogen Participation. Trimethyl- and 1,1-Dimethylethylenehalonium Ions

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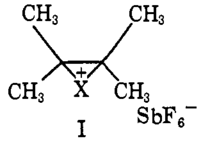
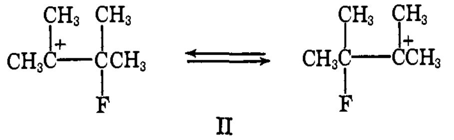
Abstract: Trimethylethylenehalonium ions were prepared from 2-fluoro-3-halo-2-methylbutanes in antimony pentafluoride–sulfur dioxide solution at −60° when the participating halogen atom was chlorine, bromine, or iodine. 1,1-Dimethylethylenehalonium ions were prepared on ionization of 1-halo-2-fluoro-2-methylpropanes in antimony pentafluoride–sulfur dioxide solution between −60 and −80° when the participating halogen atom was bromine or iodine. 1-Chloro-2-fluoro-2-methylpropane, on the other hand, ionized to an open-chain ion, the chloro-*t*-butyl cation, which exhibited long-range coupling similar to that observed in the *t*-amyl cation. Stable protonated tertiary alcohols and methyl ethers from 1-fluoro(chloro)-2-methyl-2-propanol and their methyl ethers were obtained in antimony pentafluoride–fluorosulfonic acid–sulfur dioxide solution. Fluoro-*t*-butyl alcohol ionized with rearrangement in this medium to the methylethylfluorocarbonium ion.

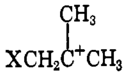
We have recently reported nmr observation of tetramethylethylenechloronium, -bromonium, and -iodonium ions (I).[2] The corresponding fluorine-containing ion exists as a rapidly equilibrating β-fluorocarbonium ion (II).[2] We now wish to report nmr observations of unsymmetrically substituted ethylenehalonium ions which provide additional strong support for the bridged halonium ion structures.


I

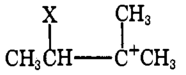
X = Br, Cl, I


II

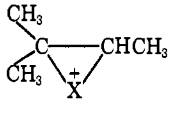
Rate data of base-catalyzed epoxide formation from the corresponding chlorohydrins[3] indicate that halonium ions would be stabilized with increasing methyl substitution. Our previous work concerning the observation of tetramethylethylenehalonium ions justified this expectation. It seemed of interest in continuation of our work to see whether a change from bridged to open-chain halonium ion would occur on changing from bromine to chlorine as participating halogen atoms by decreasing the number of methyl substituents. Therefore, we examined the ionization of vicinal dihalides in the trimethylethylene and 1,1-dimethylethylene (isobutylene) series. These systems could be expected to provide additional evidence as to the nature of the derived ions. Open-chain ions III and IV should show long-range coupling through sp^2-hybridized carbonium ion carbon atoms, as in the *t*-amyl cation,[4] and bridged ions V and VI should show very small or no measurable long-range coupling due to lack of sp^2 hybridization, as in cyclopropyl compounds.[5]

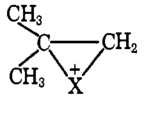

$XCH_2\overset{CH_3}{C^+}CH_3$

III


$CH_3\overset{X}{C}H{-}\overset{CH_3}{C^+}CH_3$

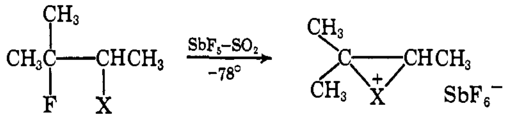
IV


V


VI

Results and Discussion

When 2-fluoro-3-chloro(bromo or iodo)-2-methylbutane was ionized in antimony pentafluoride–sulfur dioxide solution at −78° stable solutions of trimethylethylenehalonium ions were obtained (Figures 1–3).


X = Cl, Br, I

V

Examination of the pmr data of the trimethylethylenehalonium ions and their precursors indicates that participating chlorine, bromine, and iodine all form bridged ions. Data are summarized in Table I. This conclusion follows from the lack of long-range coupling between the methyl and methine protons and the deshielding effects (Δδ) observed. The methine hydrogen is the most highly deshielded proton, as is observed for the methylene protons in the dimethylethylenehalonium ions

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(1) (a) Part LVI: G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 943 (1968); (b) National Science Foundation Postdoctoral Research Investigator, 1966–1967.

(2) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967).

(3) H. Nilsson and L. Smith, *Z. Physik. Chem.*, **166A**, 136 (1933).

(4) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and L. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964); see also J. M. Bollinger, C. A. Cupas, K. J. Friday, M. Woolfe, and G. A. Olah, *ibid.*, **89**, 156 (1967).

(5) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960), report 0.7 Hz coupling in 1,1-dimethylcyclopropane. We have prepared 2-chloro-1,1,2-trimethylcyclopropane and 2-chloro-1,1,2,3-tetramethylcyclopropane and observe no measurable long-range coupling (G. A. Olah and J. M. Bollinger, unpublished results).

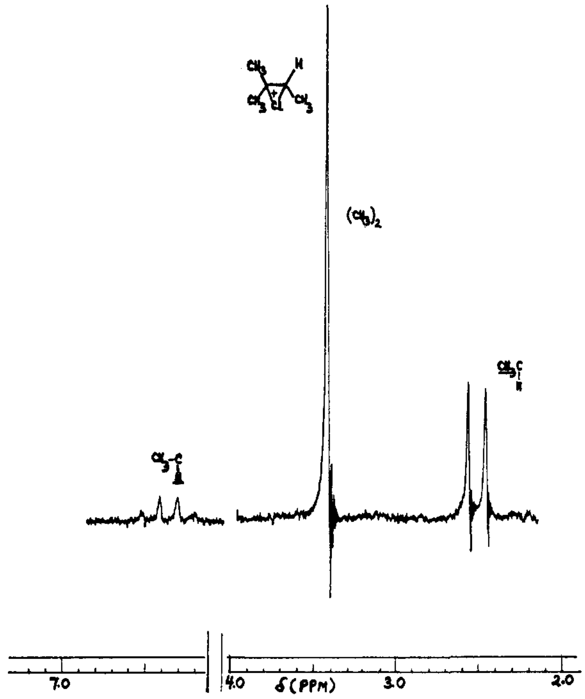


Figure 1.

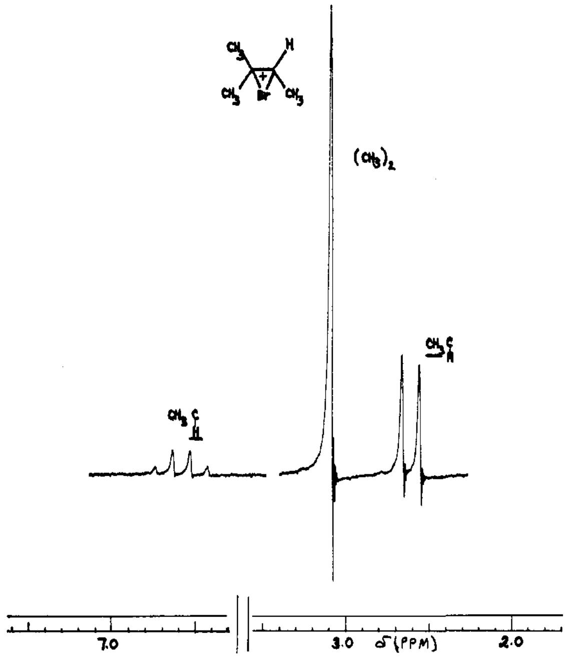


Figure 2.

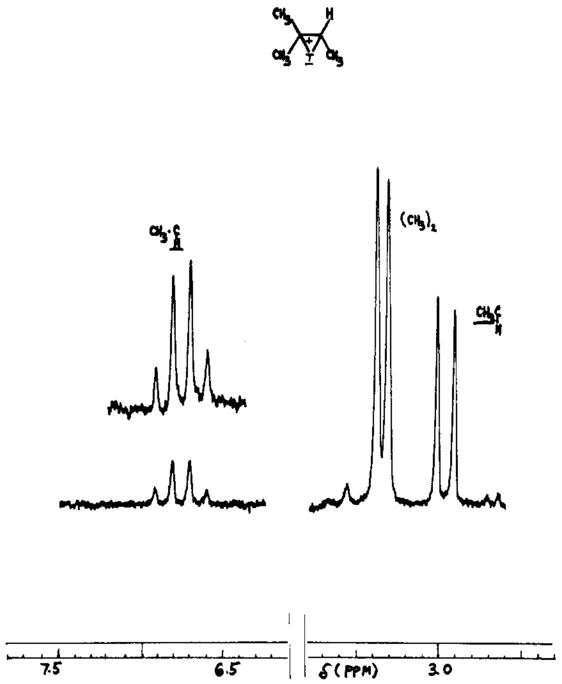
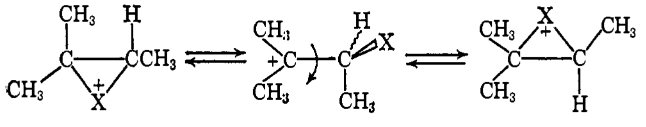


Figure 3.

(see subsequent discussion) and as one would expect for a cyclic species. The deshielding effects of both the methyl and methine protons decrease going from chlorine to iodine indicating that the charge is localized on the halogen atom. The unsymmetrical nature of the carbon–halogen bonding is shown by the large difference in deshielding of the single methyl compared to the geminal methyl groups.

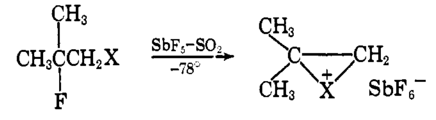
In the spectra of trimethylethylenebromonium and -chloronium ions equivalence of the geminal methyl groups is observed. This could be suggestive of a rapid equilibration of the type



From the lack of a measurable long-range coupling, it can be concluded that the concentration of open ion is relatively small. The lack of variation of the spectra of these species with temperature suggests that the chemical shifts of the geminal methyl groups are accidentally equivalent in the case of the trimethylethylenechloronium and -bromonium ions. We prefer the latter explanation for the observed equivalence. When the bridging atom is iodine the methyl groups are somewhat sterically compressed resulting in deshielding of the interfering groups and nonequivalence of the geminal methyl chemical shifts.

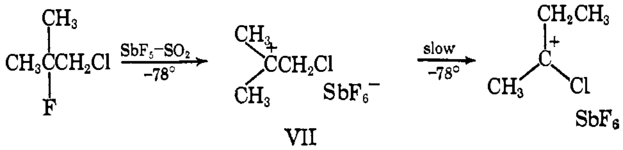
Methanolysis of the trimethylethylenehalonium ions under conditions similar to those described previously[2] gave good yields of the expected 2-halo-2-methyl-3-methoxybutanes (see Experimental Section).

When 1-halo-2-fluoro-2-methylpropanes were ionized in antimony pentafluoride–sulfur dioxide soution at −78°, solutions of dimethylethylenehalonium ions (VI) were obtained with bromine and iodine acting as donor



VI

X = Br or I



VII

VIII

Table I. Nmr Spectral Data of Trimethylethylenehalonium Ions and Their Precursors

Compound	Dihalide		Ion[a,e,f]	Methanolysis prodt[a–c,f]			
	δ (ppm) in CCl_4[a,c,f]	ϕ (ppm) in CCl_4[a,d,f]	δ (ppm) in SbF_5–SO_2	δ (ppm) in CCl_4	$\Delta\delta_{CH}$	$\Delta\delta_{CH_3}$	$\Delta\delta_{C(CH_3)_2}$
$(CH_3)_2CFCH(CH_3)Cl$	−1.37 (d), H–F 21 −1.41 (d), H–F 21 −1.46 (d) (d), H–H 7, H–F 1 −3.94 (q) (d), H–H 7, H–F 9	+141.8 (sp), H–F 21, (d) H–F 9	−2.49 (d), H–H 6 −3.41 (s) −6.35 (q), H–H 6	−1.20 (s) −1.25 (s) (48%) −1.40 (d), H–H 7 −3.16 (s) −3.97 (q), H–H 7	2.41	1.03	2.02
$(CH_3)_2CFCH(CH_3)Br$	−1.46 (d), H–F 21 −1.50 (d), H–F 21 −1.67 (d) (d), H–H 7, H–F 1 −4.03 (q) (d), H–H 7, H–F 9	+139.2 (sp), H–F 21, (d) H–F 9	−2.62 (d), H–H 6 −3.10 (s) −6.58 (q), H–H 6	−1.23 (s) (60%) −1.30 (s) −1.63 (d), H–H 7 −3.18 (s) −4.05 (q), H–H 7	2.55	0.95	1.62
$(CH_3)_2CFCH(CH_3)I$	−1.53 (d), H–F 21 −1.55 (d), H–F 21 −1.94 (d), H–H 7 −4.22 (q) (d), H–H 7, H–F 9	+135.1 (sp), H–F 21, (d) H–F 9	−2.92 (d), H–H 6.5 −3.23 (s) −3.42 (s) −6.75 (q), H–H 6.5	−1.27 (s) (66%) −1.30 (s) −1.89 (s), H–H 7 −3.16 (s) −4.22 (q), H–H 7	2.53	0.98	1.78
$(CH_3)_2CBrCH(CH_3)Br$	−1.82 (s) −1.91 (s) −1.97 (d), H–H 7 −4.41 (q), H–H 7		−2.62 (d), H–H 6 −3.10 (s) −6.58 (q), H–H 6	−1.23 (s) (62%) −1.30 (s) −1.63 (d), H–H 7 −3.18 (s), −4.05 (q), H–H 7	2.17	0.65	1.24

[a] Abbreviations used: s, singlet; t, triplet; d, doublet; q, quartet; sp, septet. [b] The figures in parenthesis are isolated yields. [c] Internal TMS. [d] Internal $FCCl_3$. [e] Internal TMS in $DCCl_3$ at −60°. [f] J values in hertz.

participating atoms (Figures 4 and 5). Chlorine and fluorine on the other hand showed no ability to bridge, and the corresponding ions exist solely as open classical ions VII and VIII in the case of chlorine (Figure 6) and IX (see subsequent discussion for its preparation) in the case of fluorine (Figure 7).

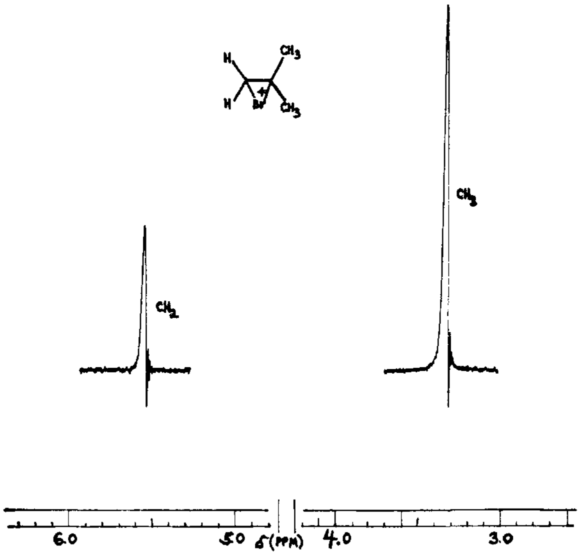


Figure 4.

Table II summarizes the pmr data of the 1,1-dimethylethylenehalonium ions and their precursors, including the deshielding effects ($\Delta\delta$) observed between the ions and their covalent precursors. In previous work[2] we noted the large change in $\Delta\delta$ going from chlorine to fluorine as participating atoms. In the present work a large change (nearly 1 ppm for methyl and 0.7 ppm for methylene protons) is observed in the deshielding effects in changing from bromine to chlorine as the participating hydrogen atom. In the first instance we interpreted this large difference as indicative of a change from a bridged halonium ion to equilibrating open-chain

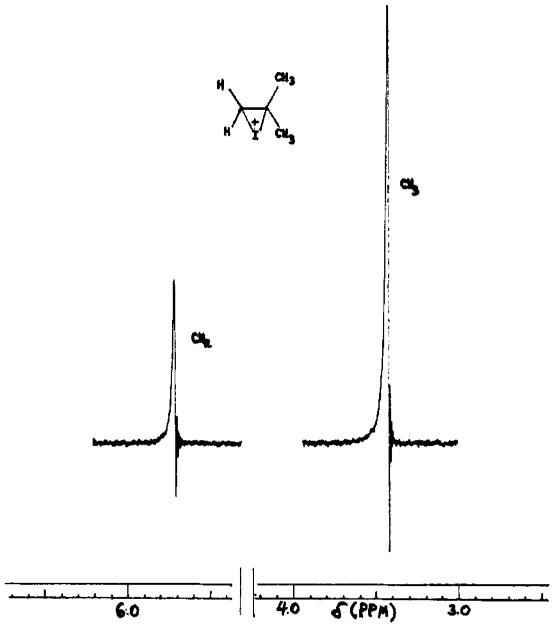


Figure 5.

Table II. Nmr Spectral Data for 1,1-Dimethylethylenehalonium Ions and Their Precursors

Dihalide	δ (ppm) in CCl_4[a,d,g]	ϕ (ppm) in CCl_4[a,e,g]	Ion[a,f] δ (ppm) in SbF_5–SO_2	Methanolysis prodt[a,b,d] δ (ppm) in CCl_4	$\Delta\delta_{CH_2}$	$\Delta\delta_{(CH_3)_2}$
$ClCH_2C(CH_3)_2F$	−1.44 (d), H–F 21 −3.54 (d), H–F 16	+140.5 (sp), H–F 21, (t) H–F 16	−4.23 (t), H–H 5 −6.24 (sp), H–H 5	−1.23 (s) −3.16 (s) (5%[c]) −3.34 (s)	2.70	2.79
$BrCH_2C(CH_3)_2F$	−1.51 (d), H–F 21 −3.45 (d), H–F 15	+137.3 (sp), H–F 21 (t) H–F 15	−3.32 (s) −5.55 (s)	−1.22 (s) −3.16 (s) (68%) −3.27 (s)	2.10	1.81
$ICH_2C(CH_3)_2F$	−1.54 (d), H–F 21 −3.63 (d), H–F 16	+132.5 (sp), H–F 21, (t) H–F 16	−3.45 (s) −5.72 (s)	−1.31 (s) −3.18 (s) (71%) −3.24 (s) (broad)	2.09	1.91
$BrCH_2C(CH_3)_2Br$	−1.87 (s) −3.88 (s)		−3.32 (s) −5.55 (s)	−1.22 (s) −3.16 (s) (63%) −3.27 (s)	1.67	1.45

[a] Abbreviations used: s, singlet; t, triplet; d, doublet; q, quartet; sp, septet. [b] The figures in parentheses are isolated yields. [c] Elimination is the main course of this solvolysis. [d] Internal TMS. [e] Internal $FCCl_3$. [f] Internal TMS in $DCCl_3$ at −70°. [g] J values in hertz.

ion pairs. In the latter case no equilibration between β-halocarbonium ions of such dissimilar stability is indicated. A change from bridged iodonium and bromonium ions to open-chain static β-chlorocarbonium ion takes place.

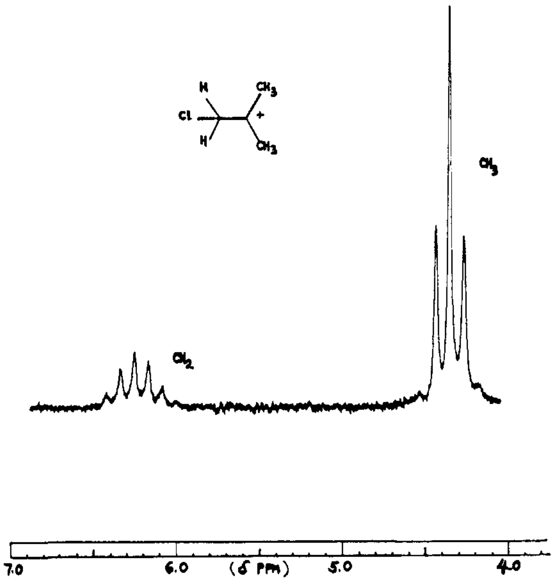
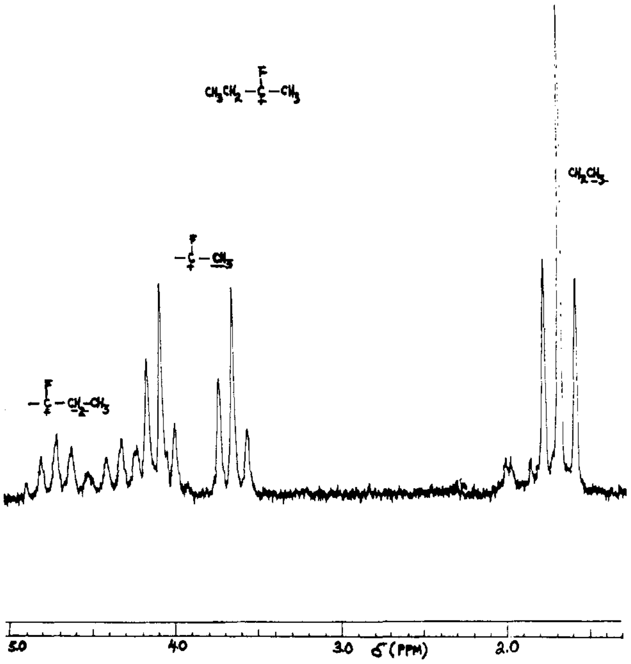


Figure 6.

In strong support of this conclusion is the observation of substantial long-range coupling between methyl and methylene protons through the planar sp^2-hybridized carbonium ion carbon atom in the chloro-*t*-butyl cation (J = 5 Hz) resulting in a triplet for the former and a septet for the latter. The absence of measurable coupling in the iodonium and bromonium ions (with no sp^2-hybridized carbonium ion carbon atom) is in keeping with expectations based on observations in cyclopropane chemistry. Again, if an equilibration were taking place between open ions and bridged ions our results indicate that open chloro-*t*-butyl cation and bridged 1,1-dimethyleneiodonium and -bromonium ions are the major species.

Due to difficulties in preparing 1,2-difluoro-2-methylpropane as precursor for the fluoro member of this series, we examined the ionization of 1-fluoro-2-methyl-2-propanol (as well as 1-chloro-2-methyl-2-propanol) in antimony pentafluoride–fluorosulfonic acid–sulfur dioxide solution. Both tertiary alcohols at −60° are cleanly protonated (Figures 8 and 9) losing water slowly to give the chloro-*t*-butyl cation (VII) and methylethylfluorocarbonium ion (IX), respectively. Chloro-*t*-butyl cation was unstable in this medium even at −80° and rapidly decomposed to unknown species. We also investigated the behavior of the corresponding methyl ethers (1-chloro(bromo, iodo)-2-methoxypropanes) in



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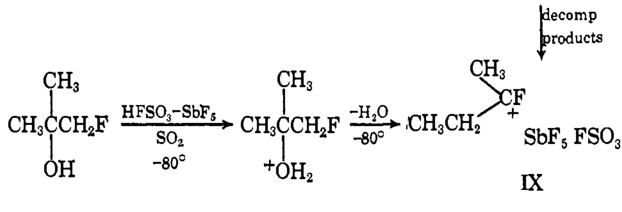


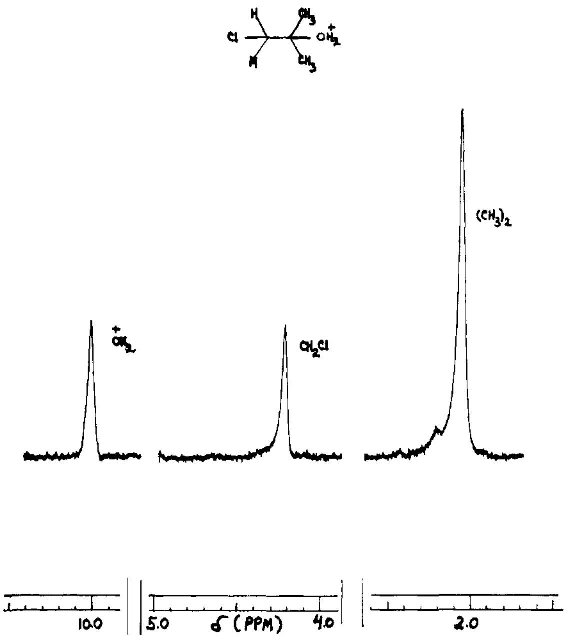
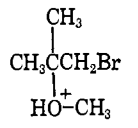


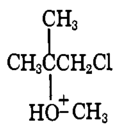
Figure 8.

the same strong acid system. Protonated methyl ethers are observed when the halogen was bromine or chlorine, but the iodine derivative cleaved too rapidly, to the iodinium ion and protonated methanol. Figure 10 is representative of the protonated species.



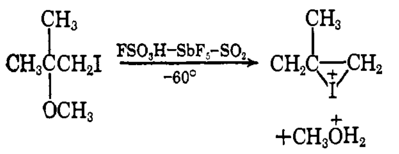
$$\mathrm{CH_3\overset{CH_3}{\underset{HO\overset{+}{-}CH_3}{C}}CH_2Br}$$

X



$$\mathrm{CH_3\overset{CH_3}{\underset{HO\overset{+}{-}CH_3}{C}}CH_2Cl}$$

XI



$$\mathrm{CH_3\overset{CH_3}{\underset{OCH_3}{C}}CH_2I \xrightarrow[-60^\circ]{FSO_3H-SbF_5-SO_2} CH_2\overset{CH_3}{C}CH_2\,(\overset{+}{I}) + CH_3\overset{+}{O}H_2}$$

Whereas protonated primary and secondary alcohols and their alkyl ethers were observed by us previously[6-10] the present observation of protonated tertiary alcohols and their methyl ethers prior to cleavage to the corresponding carbonium ions must be noted as the first observation of such tertiary species.

The stability of these species is undoubtedly due to the destabilizing effect of β-halogen on the forming tertiary cation. These results suggest little anchimeric assistance by neighboring bromine or chlorine in these ionizations, although it is difficult to estimate and separate the inductive rate retardation from neighboring group acceleration. We carried out rate measurement of the cleavage of these protonated alcohols and ethers (with the exception of 1-iodo-2-methoxy-2-methylpropane) in antimony pentafluoride–fluorosulfonic acid–sulfur dioxide solution, but the extreme instability of the ions even in this medium makes the numerical values of the kinetic measurements of little value. The cleavage of the protonated alcohols and ethers to the halonium ions is generally accompanied, particularly after 10% conversion, by side reactions (polymerization) which makes the kinetic measurements of questionable value. Qualitatively, the disappearance of the protonated ethers followed the expected order I > Br > Cl. Protonated 1-fluoro- and 1-chloro-2-methyl-2-propanol cleaved at approximately the same rate at −78°, but to different kinds of ions. No trace of the fluoro-*t*-butyl cation or of the methylethylchlorocarbonium ion (which had been observed to arise from the chloro-*t*-butyl cation in SbF_5–SO_2 solution) could be detected in the FSO_3H–SbF_5–SO_2 solutions. Table III summarizes the nmr data for the investigated 1-fluoro- and 1-chloro-2-methyl-2-propanols and their methyl ethers, solvolysis products, and ions formed upon their cleavage. The

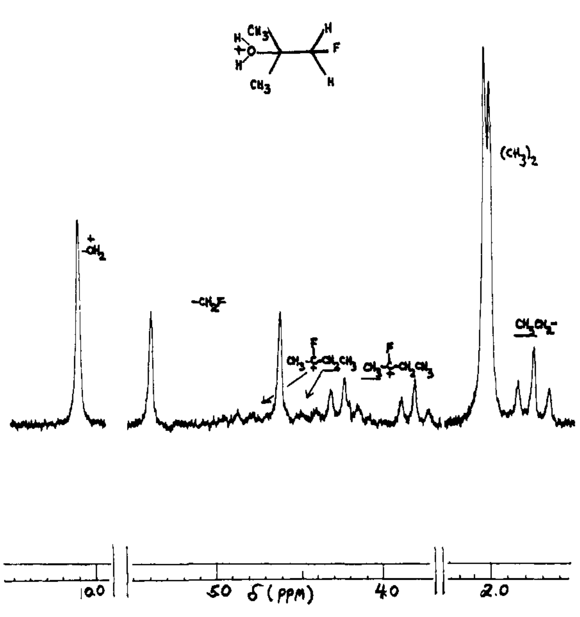


Figure 9.

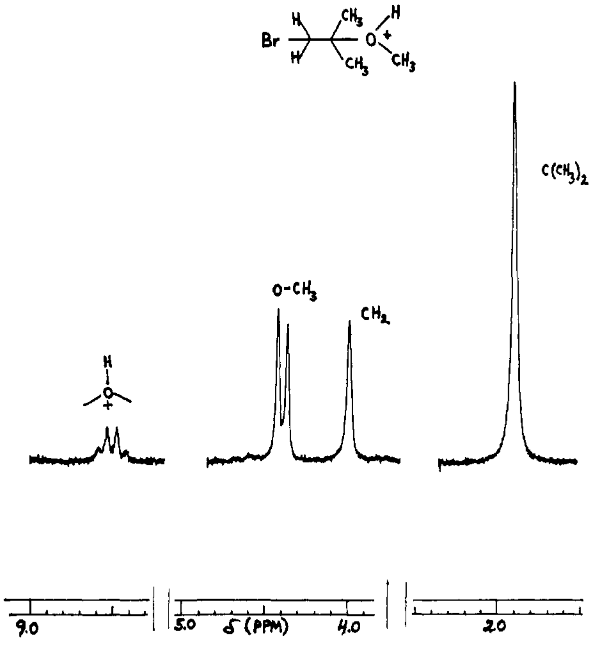


Figure 10.

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(6) G. A. Olah, C. U. Pittman, E. Namaworth, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 5571 (1966).

(7) G. A. Olah and E. Namanworth, *ibid.*, **88**, 5327 (1966).

(8) G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

(9) G. A. Olah and J. Sommer, *ibid.*, **90**, 927 (1968).

(10) G. A. Olah and D. H. O'Brien, *ibid.*, **89**, 1725 (1967).

Table III. Nmr Data of 1-Fluoro- and 1-Chloro-2-methyl-2-propanols and Their Methyl Ethers, Protonation Products, and Derived Carbonium Ions in $FSO_3H-SbF_5-SO_2$ Solution at −80°

Compound	δ (ppm) in CCl_4[a,b,g]	Protonation prodt in $FSO_3H-SbF_5-SO_3$	δ (ppm)[a,c,g]	Final ion in $FSO_3H-SbF_5-SO_2$	δ (ppm)[d,g]	ϕ (ppm)[e,g]
$FCH_2C(CH_3)_2OH$	−1.20 (d), H–F 2 −4.10 (d), H–F 49 [ϕ (ppm) in $CFCl_3$] +224.8 (t), H–F 49, (sp) H–F 2	$FCH_2C(CH_3)_2\overset{+}{O}H_2$	−2.04 (d), H–F 1 −5.02 (d), H–F 49 −10.10 (d), H–F 1	$CH_3CH_2\overset{+}{C}FCH_3$	−1.72 (t), H–H 6 −4.02 (t), H–H 6 −4.56 (m)	−170.2 (t), H–F 22 (q), H–F 26
$ClCH_2C(CH_3)_2OH$	−1.18 (s) −3.36 (s) −3.82 (s)	$ClCH_2C(CH_3)_2\overset{+}{O}H_2$	−2.06 (s), CH_3 −4.22 (s), CH_2 −10.00 (s), $^+OH_2$	$CH_3CH_2\overset{+}{C}ClCH_3$[f]	−1.63 (t), H–H 5 −4.06 (t), H–H 5 −4.45 (m)	
$ClCH_2C(CH_3)_2OCH_3$	−1.23 (s) −3.16 (s) −3.34 (s)	$ClCH_2C(CH_3)_2\underset{+}{O}(H)CH_3$	−1.80 (s) 8.61 (q), H–H 4.0 −4.12 (s) −4.38 (d), H–H 4.0	Unstable		
$BrCH_2C(CH_3)_2OCH_3$	−1.22 (s) −3.16 (s) −3.27 (s)	$BrCH_2C(CH_3)_2\underset{+}{O}(H)CH_3$	−1.86 (s) 8.51 (q), H–H 4.0 −3.98 (s) −4.17 (d), H–H 4.0	Unstable		
$ICH_2C(CH_3)_2OCH_3$	−1.31 (s) −3.18 (s) −3.24 (s, broad)	Not observable		1,1-Dimethylethyleneiodonium ion		

[a] Abbreviations used: s, singlet; d, doublet; t, triplet; m, multiplet; sp, septet. [b] Internal TMS. [c] Internal TMS in $DCCl_3$ at −60°. [d] Internal TMS in $DCCl_3$. [e] In $CFCl_3$. [f] Observed only in SbF_5-SO_2 solution at −80°. [g] *J* values in hertz.

results described in this paper are in complete accord with expectations from solvolysis data[11,12] with a possible exception of the chloro-*t*-butyl cation.[13–15] We are currently examining more closely the solvolysis of this ion in various solvents.

Experimental Section

2,3-Dibromo-2-methylbutane. 2-Methyl-2-butene (Aldrich) was brominated at −10° with bromine in carbon tetrachloride in nearly quantitative yield. 2,3-Dibromo-2-methylbutane boiled from 63 to 65° (17 mm) (lit.[16] 61–64° (17 mm)).

2-Fluoro-3-chloro-2-methylbutane. To 25 g of anhydrous hydrogen fluoride and 25 ml of dry ether at −78° were alternately added 10 g (0.14 mol) of 2-methyl-2-butene and 15 g (0.14 mol) of *t*-butyl hyprochlorite (Frinton). The reaction mixture was stirred 1 hr at −78° and an additional hour at 0°, then poured onto ice. Excess acid was neutralized first with sodium hydroxide and then with sodium carbonate. The ether layer was separated, dried, and distilled. The desired product distilled from 101 to 103° and amounted to 1.9 g, 11%. The major product was an unidentified, high-boiling oil. The analytical sample was further purified by preparative vpc.

Anal. Calcd for $C_5H_{10}ClF$: C, 48.20, H, 8.09; Cl, 28.46; F, 15.25. Found: C, 48.10; H, 8.15; Cl, 28.33; F, 14.98.

2-Fluoro-3-bromo-2-methylbutane. To 5.0 g (0.021 mol) of 2,3-dibromo-2-methylbutane in 20 ml of anhydrous acetonitrile was added 8.9 g (0.07 mol) of argentous fluoride (Harshaw). The reaction mixture was stirred 1 hr, filtered, and poured into cold water. The organic material was taken up in 15 ml of pentane, washed once with water, and dried over sodium sulfate. Distillation of the pentane solution gave 1.2 g, 34%, of the desired product, bp 128–130°. The analytical sample was further purified by preparative vpc.

Anal. Calcd for $C_5H_{10}BrF$: C, 35.53; H, 5.96; F, 11.24; Br, 47.27. Found: C, 35.48; H, 5.90; F, 11.00; Br, 47.13.

2-Fluoro-3-iodo-2-methylbutane. From 10 g (0.14 mol) of 2-methyl-2-butene and 33 g (0.14 mol) of N-iodosuccinimide in 25 g of anhydrous hydrogen fluoride diluted with 50 ml of dry ether there was obtained 14.8 g, 68%, of the desired compound. Purification was achieved by flash distillation (1 mm).

1-Chloro-2-fluoro-2-methylpropane. Anhydrous hydrogen fluoride (50 g) was cooled to −78° and 50 g of methallyl chloride was added. The reaction mixture was cooled in ice and stirred magnetically for 2 hr. It was then poured onto ice and the acid neutralized with sodium carbonate. The black oil which remained was taken up in 100 ml of ether and separated from the aqueous layer, and the organic layer was dried over sodium sulfate. Distillation of the ether solution yielded 7.5 g of the desired product, bp 71–73°. It was about 95% pure by vpc. The analytical sample was further purified by preparative vpc. For a conflicting report on this reaction see ref 15.

Anal. Calcd for C_4H_8ClF: C, 43.46; H, 7.29; Cl, 32.07; F, 17.18. Found: C, 43.28; H, 7.24; Cl, 32.18; F, 17.5.

This compound was also prepared in low yield (10%) by additon of *t*-butyl hypochlorite in ethereal hydrogen fluoride solution to isobutylene at low temperature.[2]

1-Bromo-2-fluoro-2-methylpropane was prepared from 11.2 g (0.2 mol) of isobutylene, 35.6 g (0.2 mol) of N-bromosuccinimide, and 50 g of anhydrous hydrogen fluoride in 50 ml of dry ether by the procedure of Kent and Wood.[17] There was obtained 12.8 g, 41%, of the desired compound, bp 95–96°. The analytical sample was purified by preparative vpc.

Anal. Calcd for C_4H_8BrF: C, 30.99; H, 5.20; Br, 51.55; F, 12.26. Found: C, 31.25; H, 5.38; Br, 51.39; F, 11.98.

1-Iodo-2-fluoro-2-methylpropane was prepared from 5.6 g (0.1 mol) of isobutylene, 22.5 g (0.1 mol) of N-iodosuccinimide, and 25 g of anhydrous hydrogen fluoride in 50 ml of dry ether by the procedure of Wood, *et al.*[18] The desired compound was isolated by removal of solvent at atmospheric pressure followed by flash distillation (1 mm). The compound readily decomposed with liberation of iodine and was not analyzed for this reason. It could be stored in the freezer over sodium bisulfite. The material prepared in this way showed the expected nmr spectrum with no extraneous absorptions.

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1-Fluoro-2-methyl-2-propanol was prepared from fluoroacetyl chloride[19] and methylmagnesium bromide, essentially by the procedure of Bergmann and Cohen.[20] From 20.0 g (0.2 mol) of fluoroacetyl chloride there was obtained 7.6 g (41%) of material, bp 94–97° (lit.[20] 96–98°). Conversion of this material to the corresponding chloride was unsuccessfully attempted with Lucas reagent, thionyl chloride in pyridine, and ethereal phosgene with a trace of pyridine.

1-Chloro-2-methyl-2-propanol was prepared according to the procedure of Burgin, *et al.*[21] The compound was obtained in about 20% yield and had bp 125–127° (lit.[21] 127°).

1-Chloro-2-methoxy-2-methylpropane was prepared from 5.6 g (0.1 mol) of isobutylene and 10.8 g (0.1 mol) of *t*-butyl hypochlorite in 30 ml of methanol at −30° with 1 ml of concentrated sulfuric acid as catalyst.[2] The yield obtained was 4.8 g, 40%, bp 115–118° (lit.[22] 117–119°). This material contained several impurities and was further purified before use by preparative vpc.

1-Bromo-2-methoxy-2-methylpropane was prepared from 5.6 g (0.1 mol) of isobutylene and 17.8 g (0.1 mol) of N-bromosuccinimide in 30 ml of methanol at −30° with 1 ml of concentrated sulfuric acid as catalyst. The yield obtained was 6.9 g, 41%, bp 45–47° (20 mm). Laughton and Robertson[23] reported a preparation of this compound but gave only the refractive index of their material.

1-Iodo-2-methoxy-2-methylpropane was prepared from 5.6 g (0.1 mol) of isobutylene and 22.5 g (0.1 mol) of N-iodosuccinimide in 30 ml of methanol at −30° with 1 ml of concentrated sulfuric acid as catalyst. There was obtained 7.2 g, 33%, of the desired compound which was purified by flash distillation. The compound decomposed readily and was not analyzed. Agreement with expected spectrum and absence of appreciable extraneous absorptions in its pmr spectrum showed that the compound was of satisfactory purity.

1,2-Dibromo-2-methylpropane. Isobutylene in carbon tetrachloride was brominated at −10° with bromine in carbon tetrachloride in nearly quantitative yield. The liquid obtained had bp 46–48° (lit.[24] 47–49° (12 mm)).

Preparation of Ions, Their Methanolysis, and Nmr Investigation. Solutions of the ions were obtained in the following way. A saturated solution of antimony pentafluoride in sulfur dioxide was prepared (at −10°). Portions (2 ml) of this solution were cooled to −78°, causing some antimony pentafluoride to crystallize from solution. To this suspension was added dropwise with stirring approximately 0.3 g of the appropriate dihalide. Slight warming was required to complete the ionization, whereupon a homogeneous solution resulted with only slight traces of color. Ion concentrations were approximately 10%. These operations were carried out in the laboratory atmosphere. When alcohols or their methyl ethers were used as precursors the same procedure was used with a solution of FSO_3H-SbF_5 (1:1) in sulfur dioxide as the acidic solvent.

Spectra were recorded on a Varian Model A56-60A spectrometer with internal TMS in deuteriochloroform as reference.[25]

Methanolysis of ions was accomplished by adding slowly the solution of the carbonium ion in sulfur dioxide to a suspension of methanol and potassium carbonate at −78°. Product isolation was accomplished by drowning the resulting suspension in water and extracting with pentane. Pentane was removed on a rotary evaporator and in all cases except the chloro-*t*-butyl cation gave a pure product (by nmr) requiring no further purification. Yields of the methanolysis products were determined by adding known weights of material to the antimony pentafluoride–sulfur dioxide solution and represent the over-all yield of the ionization and solvolysis reactions. Identification of products was made by glpc comparison of retention times with authentic samples and by nmr and ir spectroscopy.

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(25) We record the position of TMS in deuteriochloroform before and after the spectrum of the ion. On some previous work this was called "external TMS in deuteriochloroform." We have added 0.5 ppm to these shifts to make them relative to internal TMS in sulfur dioxide. Subtracting 0.25 ppm from our tabulated shifts changes the reference to external TMS (capillary).