lead ultimately to the very stable *t*-butyl cation (I). The tendency to cleave increases with the length and branching of alkanes. Butanes form the *t*-butyl cation (I) which is stable to 150° (boiling point of FSO_3H-SbF_5). Pentanes give the *t*-amyl cation IV which cleaves slowly to ion I at 150°, the hexyl cations cleave at +80°, the heptyl cations at −10°, and the octyl cations even at −80°.

In compounds with only primary hydrogen atoms (neopentane and 2,2,3,3-tetramethylbutane) a carbon–carbon bond is broken rather than a carbon–hydrogen bond. In ethane the fragmentation product would be CH_3^+, obviously less stable than $CH_3CH_2^+$, therefore a hydride ion is abstracted. The unstable ethyl cation then undergoes polymerization and cleavage. The difference with temperature in the fragmentation pattern of neopentane is striking. At low temperatures in a slow process, a primary hydrogen atom is abstracted. Above 0° a methide ion is abstracted (from a tertiary position) much faster than hydride ion (from a primary position).

The fate of the abstracted hydride ion is not yet fully determined in the reactions. In all probability it partly forms molecular hydrogen by adding to proton, part of which is observed escaping from the reaction mixture. The bulk of the nascent hydrogen, however, seems to reduce fluorosulfonic or fluoroantimonysulfonic acid.

Probably the most surprising observation of our work is that salts of the alkyl cations I, II, and V can be obtained and crystallized from SO_2 or SO_2ClF solutions at low temperature (−60 to −100°). They are stable at least to room temperature. Redissolved in SO_2 or SO_2ClF they give the unchanged nmr spectra of the ions. Attempts are in progress (with Professor M. Sundaralingam) for the X-ray crystallographic investigation of these alkylcarbonium salts.

Experimental Section

All nmr spectra were obtained on a Varian Associates Model A-56-60A nmr spectrometer. Spin–spin decoupling experiments were done on a Varian Associates Model HA-60 IL nmr spectrometer. External capillary TMS was used as reference.

Generation of Alkylcarbonium Ions in Neat FSO_3H-SbF_5 or $HF-SbF_3$. In a typical experiment, the alkane and a tenfold (weight) excess of acid (1:1 FSO_3H-SbF_5 or $HF-SbF_5$) were vigorously stirred at room temperature until they formed a homogeneous colorless mixture. The reaction is carried out with exclusion of moisture and is generally completed in 10–30 min. When using gaseous alkanes they are bubbled through the acid mixture in a slow stream.

Generation of Alkylcarbonium Ions in $FSO_3H-SbF_5-SO_2ClF$. To a 1:1 mixture of SO_2ClF with FSO_3H-SbF_5 or $HF-SbF_5$, the alkane is added. On mixing, it will generally ionize at temperatures above −120°. Nonionized material will be supernatant. If the acid concentration is decreased, nonionized alkane will be present in solution together with the carbonium ion.

Acknowledgment. Generous support of the work by grants of the National Institutes of Health and the National Science Foundation is gratefully acknowledged

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Stable Carbonium Ions. XLVIII.[1a] Halonium Ion Formation *via* Neighboring Halogen Participation. Tetramethylethylene Halonium Ions

George A. Olah and J. Martin Bollinger[1b]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received April 21, 1967*

Abstract: Bridged halonium ions were observed to arise on ionization of 2,3-dihalo-2,3-dimethylbutanes in antimony pentafluoride–sulfur dioxide solution at −60°, when the participating halogen atom is chlorine, bromine, or iodine. 2,3-Difluoro-2,3-dimethylbutane, on the other hand, gave α-fluoroisopropyldimethylcarbonium ion in which the fluorine atom is rapidly exchanging intramolecularly between the two equivalent sites. 2-Halo-3-acetoxy-2,3-dimethylbutanes and 2-halo-3-methoxy-2,3-dimethylbutanes also ionize in antimony pentafluoride–sulfur dioxide solution to similar ions. Bridged acetoxonium ion formation but not bridged methyloxonium ion formation is accompanying these ionizations.

Bromonium ion (I) formation in certain electrophilic additions of bromine to olefins is the generally accepted explanation for the complete stereospecificity observed.[2,3] This concept has been criticized because it assumes that molecular rotation in a carbonium ion is much more rapid than attack by an external nucleophile, an assumption that was questioned.[4] Moreover, it has been suggested that rapidly equilibrating ions such as IIa and b could also lead to stereospecificity.[5] Similarly, from results of rate measurements and stereochemistry, bromine has been suggested as a good neighboring group, participating through the

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[1] (a) Part XLVI: G. A. Olah and M. Calin, *J. Am. Chem. Soc.*, **89**, 4736 (1967). (b) National Science Foundation Postdoctoral Research Investigator, 1966–1967.

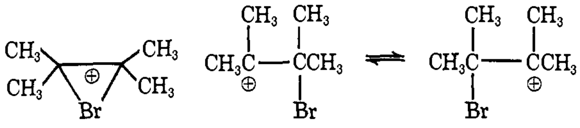
[2] We do not intend this brief introduction to be a comprehensive review of the literature on the mechanism of halogenation or neighboring halogen; for a more complete review on the latter, see B. Capone, *Quart. Rev.* (London), **18**, 45 (1964).

[3] Credit for this proposition is generally given to I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).

[4] B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *ibid.*, **79**, 6160 (1957).

[5] S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952).

same type of bridged bromium ions as suggested for bromination of olefins.[6]



I IIa IIb

Iodonium ions have been similarly suggested for iodination reactions,[7] and in reactions involving neighboring iodine.[8] The kinetic and stereochemical arguments are strong for a bridged intermediate.

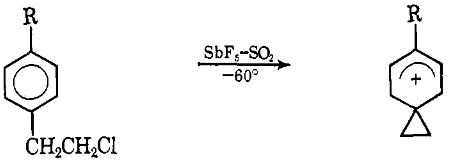
It has been suggested that polar chlorination proceeds through a bridged chloronium ion,[9] although evidence has been presented that classical chlorocarbonium ions are also involved.[10] There seems to be no evidence that chlorine can give appreciable anchimeric assistance.[11]

Work on fluorination of olefins has led to the suggestion of classical fluorocarbonium ion intermediates.[12] A recent publication has also reported a 1,4-fluorine migration where a cyclic fluoronium ion has been proposed as either an intermediate or a transition state.[13] Generally, however, there is little indication of bridged fluoronium ion formation.

We wish now to report our results on the direct observation of tetramethylethylenehalonium ions in antimony pentafluoride-sulfur dioxide solution. We believe our results give the first direct experimental observation of halonium ions in solution.

Results and Discussion

Recently we succeeded in showing that β-anisylethyl, β-mesityethyl, and β-(pentamethylphenyl)ethyl chloride ionize in antimony pentafluoride-sulfur dioxide solution at low temperature (−60°) *via* strong aryl participation to form the bridged arylonium (substituted phenonium) ions.



These arylonium ions were the first direct observation of bridged ions formed *via* π-neighboring group participation.

We now extend our investigations to bridged ions formed *via* n-neighboring group participation. When 2,3-dihalo-2,3-dimethylbutanes are ionized in antimony pentafluoride-sulfur dioxide solution at −60°, stable solutions of tetramethylethylenehalonium ions are obtained with chlorine, bromine, and iodine acting as donor-participating atoms. Fluorine in our experiments showed no similar ability and only rapidly equilibrating, open-chain classical fluorinated ions are obtained even at −90°.

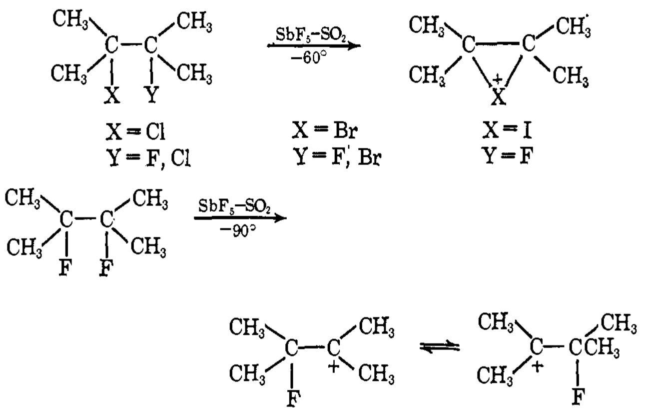


Table I summarizes pmr spectral data for the ions observed in antimony pentafluoride-sulfur dioxide solution. The covalent precursors and the products of methanolysis were observed in carbon tetrachloride solution.

The ionic nature of the halonium ions observed in the strong acid system is substantiated on the following basis: (1) downfield shifts of methyl groups of 0.8–1.8 ppm (donor-acceptor complexes would not be expected to be as strongly deshielded),[14] (2) disappearance of fluorine-proton coupling, (3) appearance of protonated methanol or acetic acid when the halonium ions are prepared by protonation of the appropriate methoxyl or acetyl derivatives (see subsequent discussion), and (4) solvolysis of the solutions which gives high yields of the expected quenched products.

Data of Table I apparently indicate that deshielding increases in going from chloronium to iodonium ion. This is the reverse of the expected trend based on the electronegativity of the halogen atoms. One would anticipate that iodine would better be able to bear positive charge and would, in the absence of other effects, be the least deshielded ion.[15] The comparison of the observed methyl deshielding effects, however, can be very misleading if one does not consider the effect of halogen atom on the methyl protons. That a large effect is operative is evident from the chemical shifts of the covalent starting halides. The effect is probably due to steric deshielding caused by the crowding introduced by the larger halogen atoms.[16] In Table II, therefore, we have presented differences in chemical shifts between the observed ions and covalent starting materials. In this comparison we have attempted to eliminate steric deshielding by comparing the ion with a suitable halogenated precursor. From

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(6) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 1576, 2845 (1939).

(7) K. R. Wood, P. W. Kent, and D. Fisher, *J. Chem. Soc.*, 910 (1966); see also A. Hassner and C. Heathcock, *J. Org. Chem.*, 30, 1748 (1965).

(8) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, 70, 821 (1948).

(9) P. Ballinger and P. B. D. de la Mare, *J. Chem. Soc.*, 1481 (1957).

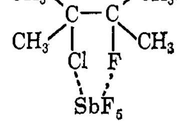
(10) P. B. D. de la Mare and A. Salama, *ibid.*, 3337 (1956).

(11) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **73**, 5458 (1951), and earlier papers; H. C. Brown, *Chem. Eng. News*, **45**, 87 (Feb 13, 1967).

(12) R. F. Merritt, *J. Am. Chem. Soc.*, **89**, 609 (1967).

(13) P. E. Peterson and R. J. Bopp, *ibid.*, **89**, 1283 (1967).

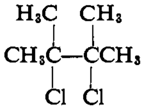
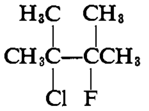
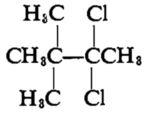
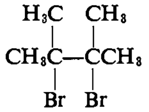
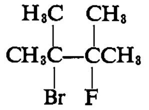
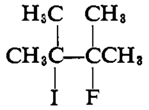
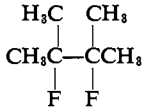
(14) Starting from unsymmetrical precursors rules out such a species as



(15) The methyl resonances of ethyl halides show the same trend, *i.e.*, increased deshielding from F to I: H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

(16) T. Schaefer, W. F. Reynolds, and T. Yonemoto, *Can. J. Chem.*, **41**, 2969 (1963).

Table I. Pmr Resonance Data of Tetramethylethylene Halonium Ions and Their Dihalide Precursors and Methanolysis Products

Compound	Starting material in CCl_4, intern. TMS	Ion in SbF_5–SO_2 at −60°, extern. TMS in $DCCl_3$	MeOH-quenched product in CCl_4, intern. TMS
 $CH_3\overset{H_3C}{\underset{Cl}{C}}-\overset{CH_3}{\underset{Cl}{C}}CH_3$	−1.77(s)	−2.72(s)	−1.28(s) −1.52(s) −3.20(s)
 $CH_3\overset{H_3C}{\underset{Cl}{C}}-\overset{CH_3}{\underset{F}{C}}CH_3$	−1.54(d) J = 21 Hz −1.57(d) J = 1.1 Hz	−2.72(s)	−1.28(s) −1.52(s) −3.20(s)
 $CH_3\overset{H_3C}{\underset{H_3C}{C}}-\overset{Cl}{\underset{Cl}{C}}CH_3$	−1.21(s) −2.12(s)	−2.72(s)	−1.28(s) −1.52(s) −3.20(s)
 $CH_3\overset{H_3C}{\underset{Br}{C}}-\overset{CH_3}{\underset{Br}{C}}CH_3$	−2.00(s)	−2.86(s)	−1.35(s) −1.80(s) −3.24(s)
 $CH_3\overset{H_3C}{\underset{Br}{C}}-\overset{CH_3}{\underset{F}{C}}CH_3$	−1.52(d) J = 21 Hz −1.78(d) J = 1.0 Hz	−2.86(s)	−1.35(s) −1.80(s) −3.24(s)
 $CH_3\overset{H_3C}{\underset{I}{C}}-\overset{CH_3}{\underset{F}{C}}CH_3$	−1.54(d) J = 21 Hz −2.00(s)	−3.05(s)	−1.37(s) −1.87(s) −3.26(s)
 $CH_3\overset{H_3C}{\underset{F}{C}}-\overset{CH_3}{\underset{F}{C}}CH_3$	−1.34 J = 23 Hz[a]	−3.10(d) J = 11 Hz	Complex mixture[b]

[a] This spectrum is that of an $A_3A_3'XX'$ system; the "coupling constant" represents the distance between the major spikes of the absorption. [b] See Experimental Section.

Table II. Chemical Shift Differences in Tetramethylethylene Halonium Ions and Their Covalent Precursors

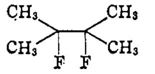
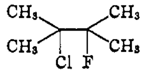
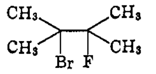
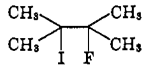
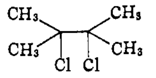
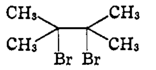
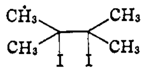
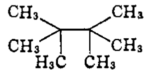
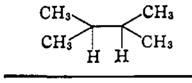
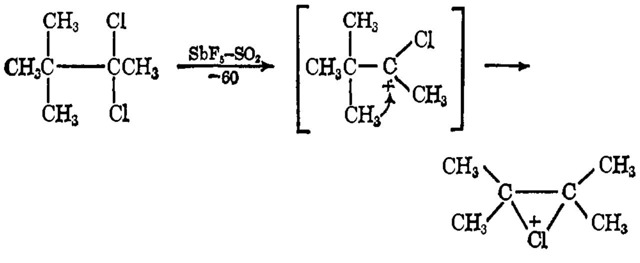
Compound	δ, ppm Covalent precursor	Ion	Δδ, ppm
	−1.34	−3.10	−1.76
	−1.57	−2.72	−1.15
	−1.78	−2.86	−1.08
	−2.00	−3.05	−1.05
	−1.77	−2.72	−0.95
	−2.00	−2.86	−0.86
	−2.30 (estimated)	−3.05	−0.75
	−0.87	−2.90	−2.03
	−0.85	−3.32	−2.47

Table II it is apparent that the expected I > Br > Cl trend in ability to bear positive charge is observed.[17] We believe that the experimental data are consistent with bridged halonium ions and not with rapidly equilibrating β-halocarbonium ions. In support of this suggestion we find no change in the spectra of the chloronium, bromonium, or iodonium ions down to −95° in sulfur dioxide–antimony pentafluoride solution. Using sulfuryl chlorofluoride as solvent we were able to attain −130° with the bromonium ion and −120° with the chloronium ion with no change in the spectrum other than slight viscosity broadening and modest, solvent-induced change in position of the absorption. Figures 1 and 2 show the pmr spectra of the tetramethylethylene-chloronium and -bromonium ions in SbF_5–SO_2 solution at −60°.

2,2-Dichloro-3,3-dimethylbutane (pinacolone dichloride) ionizes in antimony pentafluoride–sulfur dioxide solution at −60° to give the bridged tetra-



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(17) Due to the instability of 2,3-diiodo-2,3-dimethylbutane, the methyl shift could only be calculated for this compound.

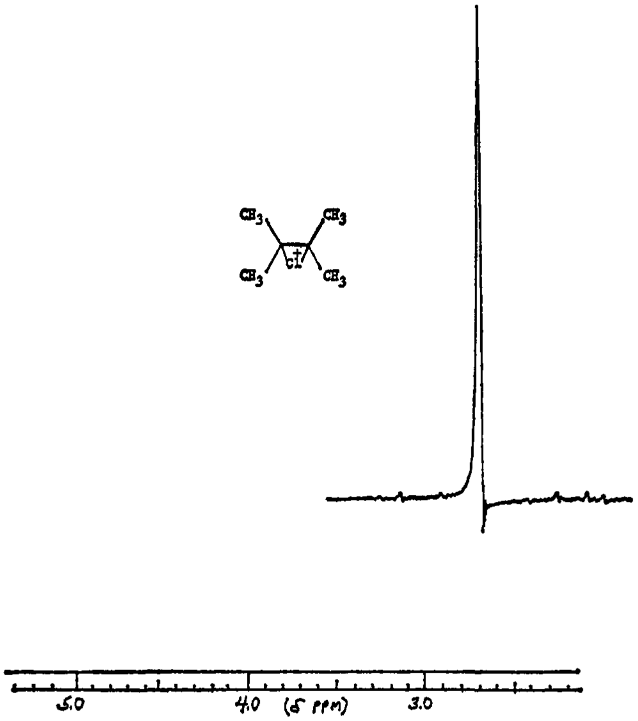

Figure 1. Tetramethylethylenechloronium ion in SbF_5–SO_2 solution at −60°.

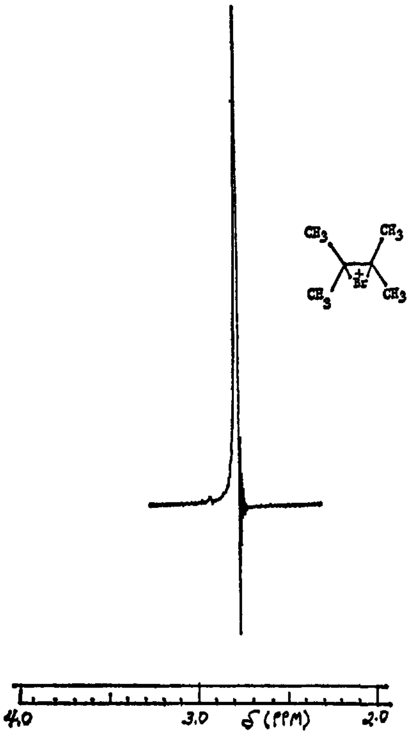

Figure 2. Tetramethylethylenebromonium ion in SbF_5–SO_2 solution at −60°.

methylethylenechloronium ion. Rapid rearrangement (*via* 1,2-methyl shift) of the intermediate unstable methyl-*t*-butylchlorocarbonium ion with simultaneous strong halogen participation to form the bridged chloronium ion must be assumed.

Further support for the bridged nature of the chloronium, bromonium, and iodonium ions is derived from the contrasting behavior of the fluorinated species,

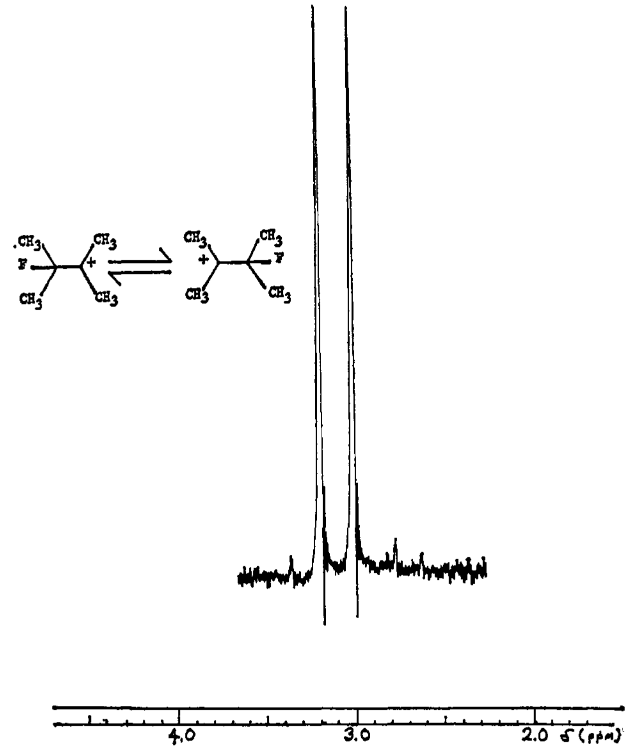

Figure 3. Equilibrating dimethylfluoroisopropylcarbonium ion in SbF_5–SO_2 solution at −90°.

where additional information can be obtained, specifically, spin–spin coupling and direct measurement of a chemical shift for the halogen atom (Figure 3).

From Table II it is evident that the deshielding effect on methyl groups is greatest for the fluorinated ion. This is expected on the basis of electronegativity, but since the deshielding (1.76 ppm) is nearly twice that of the chloronium ion (0.95 ppm) we suggest that a change in behavior is indicated, *i.e.*, *a change from a static bridged species to equilibrating β-fluorocarbonium ions.* In Table II, we have included Δδ's for the pentamethylethyl cation which is not bridged, since it shows, even at −170°, only one kind of methyl group,[18] and the dimethylisopropylcarbonium ion, which also is a rapidly equilibrating but not bridged ion.[18] These equilibrating ions have Δδ's falling in the same general order of magnitude as the dimethyl-α-fluoroisopropylcarbonium ion.

Strong support for the equilibrating β-fluorocarbonium ion is also found in the chemical shift of the fluorine atom. Initially, difficulty was experienced in locating the fluorine spectrum because of the high degree of coupling. The fluorine resonance was located by heteronuclear spin–spin decoupling, *i.e.*, by observing the proton spectrum while irradiating the fluorine region. (We used benzyl fluoride to correlate the positions of the fluorine resonance with the decoupling frequency.) The fluorine in the carbonium ion is found at about +119 ppm, only 31 ppm downfield from the starting difluoride (ϕ = +150 ppm in CCl_4 from external CCl_3F). This is the region where antimony–fluorine resonances are observed so that in our solvent systems we could not directly determine the chemical shift for this fluorine atom. It is quite clear, however,

[18] G. A. Olah and J. Lukas, *J. Am. Chem. Soc.*, **89**, 4739 (1967).

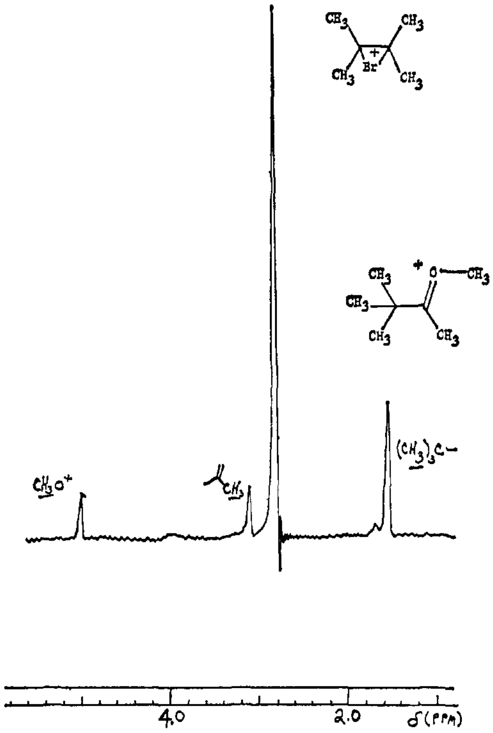

Figure 4. Ionization of 2-bromo-3-methoxy-2,3-dimethylbutane in FSO_3H-SbF_5-SO_2 solution at −60°.

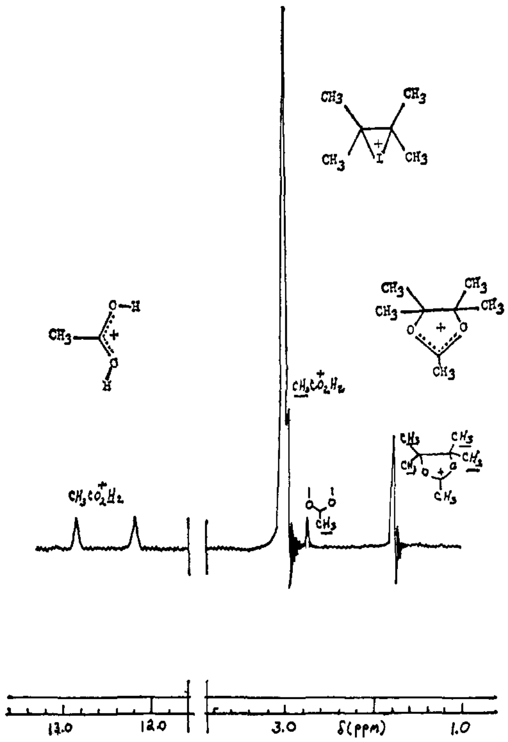

Figure 5. Ionization of 2-iodo-3-acetoxy-2,3-dimethylbutane in FSO_3H-SbF_5-SO_2 solution at −60°.

that the fluorine resonance appears in the region expected for a fluorine atom β to a positively charged carbon atom[19] and quite far from the region expected for fluorine on a positive carbon atom.[20] We suggest also that this shift is inconsistent with that expected for a bridged fluorine ion, where at least partial positive charge would be expected on fluorine. The measured spin–spin coupling of J_{H-F} = 11 Hz is consistent with equilibrating ions where one would expect an average of the three-bond coupling (21–22 Hz), and the four-bond coupling (1.2 Hz). It is, of course not obvious what one should expect for the coupling in a bridged fluoronium ion.[21]

We attempted to freeze out the two different kinds of methyl groups, but this did not occur even at −95°. Poor solubility prevented us from attaining lower temperatures.

We also examined the ionization of 2-halo-2-methoxy- and 2-halo-3-acetoxy-2,3-dimethylbutanes in both antimony pentafluoride–sulfur dioxide and in antimony pentafluoride–fluorosulfonic acid–sulfur dioxide solution. Besides the bridged halonium ions we obtained bridged acetoxonium ions, examples of which are well known,[22] but not bridged ethyleneoxonium ions.[23] The pmr data are summarized in Table III. Figures 4 and 5 show representative examples of the spectra.

Interestingly, 2-chloro-2-acetoxy-2,3-dimethylbutane in FSO_3H-SbF_5-SO_2 solution gave 95% bridged acetate, whereas the iodo and bromo derivatives gave 80–90% bridged halonium ion. Methoxy is a good leaving group in antimony pentafluoride–sulfur dioxide solution as evidenced by the formation of high yields of tetramethylethylenehalonium ions from 1-halo-2-methoxy-2,3-dimethylbutanes. Protonated methanol[24] and protonated acetic acid[25] formed through protonation of the leaving groups are stable in the acid system and were known from previous work.

The quenching of all ions with cold methanol in the presence of potassium carbonate was straightforward in every case except that of the ion formed from 2,3-difluoro-2,3-dimethylbutane, giving high yields of the expected methoxy derivatives. In the latter case, a mixture consisting of pinacolone, 2-fluoro-2-methoxy-2,3-dimethylbutene-1, and 2-methoxy-2,3-dimethylbutene-1 (major product) was obtained. It seemed possible that the elimination occurred in work-up because of the excess carbonate, and so a second quench was performed in the presence of sodium bicarbonate. Again the same mixture was obtained, but now pinacolone was the major product. In both cases, there were several unidentified components present in small amounts. We have not rationalized the behavior of this ion, but it is another example of the contrasting behavior exhibited by the fluorine member of the series. The solutions of ions obtained by ionization of oxygenated precursors were not quenched since they invariably contained a mixture of species.

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(19) G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **88**, 3310 (1966), report $\Delta\phi$ = −24.8 ppm for $(CF_3)CH_3C^+C_6H_5$ (compared with the covalent precursors) in FSO_3H-SbF_5-SO_2 solution, which compares favorably with $\Delta\phi$ = −31 ppm observed in this work.

(20) G. A. Olah, M. B. Comisarow, and R. D. Chambers, *ibid.*, **89**, 1268 (1967), report a chemical shift of ϕ = −182.0 ppm for CH_3-C^+FCH_3. This rules out rapid scrambling of methyl groups as in $(CH_3)_3CC^+FCH_3$.

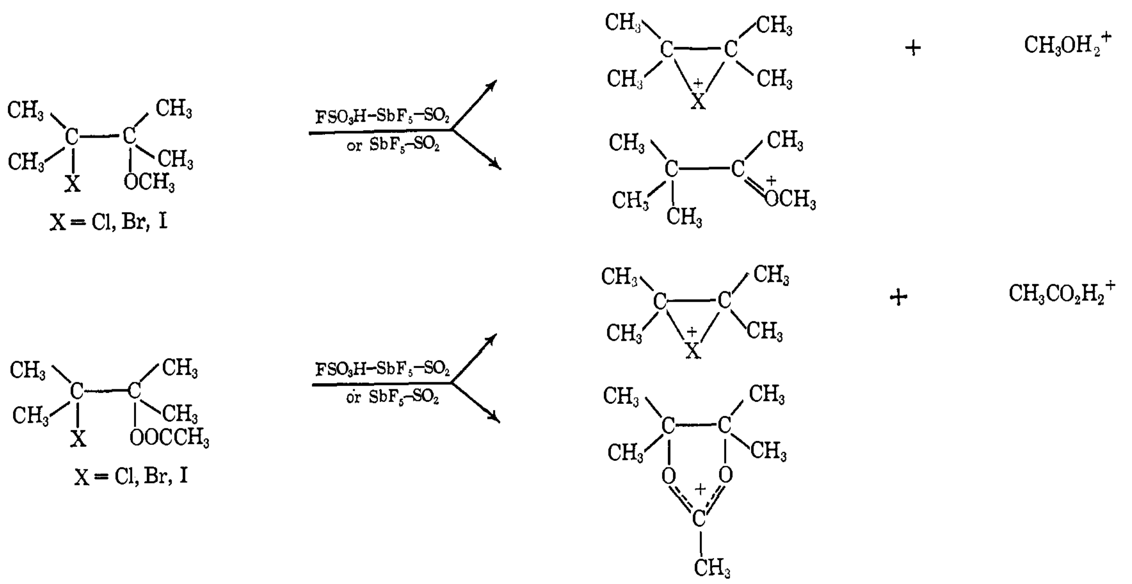
(21) We intuitively feel that the coupling constant would be considerably larger for a cyclic species. We know of no pertinent evidence to cite.

(22) H. Hart and D. Tomalia, *Tetrahedron Letters*, 3383, 3389 (1966); C. B Anderson, E. C. Liedluch, and S. Winstein, *ibid.*, 2037 (1963); H. Meerwein, V. Hederick, V. Morschel, and K. Wunderlich, *Ann.*, **635**, 1 (1960), and references therein.

(23) This is not unexpected, since this group is known to cause rate decreases rather than rate enhancements in the β position.

(24) G. A. Olah and E. Namanworth, *J. Am. Chem. Soc.*, **88**, 5327 (1966); G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

(25) G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).



Finally, it should be mentioned that in contrast to other members of this series, the β-fluorocarbonium ion completely decomposes at Dry Ice temperature in antimony pentafluoride–sulfur dioxide solution within a week. The tetramethylenehalonium ions under similar conditions are stable for long periods of time (no decomposition was noted after several weeks at −78°).

Experimental Section

Preparation of Ions. Solutions of the ions were obtained in the following way. A saturated solution of antimony pentafluoride in sulfur dioxide was prepared (at −10°). Two-milliliter portions 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 (methoxy-, acetoxy halide). 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. This procedure provides a simple way to generate carbonium ions in a highly reproducible manner.

Solutions of the ions in FSO_3H-SbF_5-SO_2 solutions were prepared in the following way. Approximately 1.5 ml of HSO_3F-SbF_5 (1:1 *M* solution) in an equal volume of sulfur dioxide was cooled to −78°. The precursor (approximately 0.2 ml) was dissolved in 1 ml of sulfur dioxide, cooled to −78°, and with vigorous agitation, slowly added to the acid solution.

Very low temperature spectra (−130 to −100°) were obtained in sulfuryl chlorofluoride (Allied Chemical) solution. In this solvent, solubility of the ions was generally less than in sulfur dioxide, and solid material, if present in the samples, was removed by centrifuging.

Spectra were recorded either on a Varian Model A-56-60A spectrometer with external TMS in deuteriochloroform as reference (0.5 ppm has been added to these chemical shifts to correct them to TMS in a capillary as reference) or on a Varian Model HA-60 spectrometer with TMS in a capillary as reference. The nmr spectrometers were equipped with low-temperature probes (on the HA-60 model we used a special low-temperature probe enabling work down to −180°).

The fluorine-decoupling experiment was performed, using an NMR Specialties Model SD-60B spin–spin decoupler to generate the 56.4-MHz signal. Integrated areas were consistent with assigned structures.

Methanolysis of the 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. Identification of products was made by glpc comparison of retention times with authentic samples and by nmr and infrared spectroscopy.

Preparation of 2-Chloro-3-fluoro-2,3-dimethylbutane. To a solution of 25 g of anhydrous hydrogen fluoride and 50 ml of dry ether were alternately added, at −78°, 4.2 g (0.05 mole) of tetramethylethylene (Aldrich) and 5.6 g (0.051 mole) of *t*-butyl hypochlorite (Frinton Laboratories) over a period of 5 min. The reaction mixture was stirred for 1 hr at −78° and an additional 1 hr at 0°, and then poured into ice water containing excess potassium carbonate. An additional 60 ml of ether was added, and the layers separated. Removal of solvent left an oil, which after flash distillation at 1 mm partially crystallized. The yield was 3.6 g, 46% of material containing small amounts of an unknown contaminant. The analytical sample was purified by preparative gas chromatography on an Apiezon L on Chromosorb W column. It had mp 63–64°.

Anal. Calcd for $C_6H_{12}ClF$: C, 51.99; H, 8.73; Cl, 25.57; F, 13.70. Found: C, 52.25; H, 8.81; Cl, 25.69; F, 13.25.

Preparation of 2-Bromo-3-fluoro-2,3-dimethylbutane. This material was prepared by the procedure of Kent and Freeman.[26] From 25.2 g (0.3 mole) of tetramethylethylene and 53.4 g (0.3 mole) of N-bromosuccinide in 70 g of anhhydrous hydrogen fluoride diluted with 140 ml of dry ether, there was obtained 33.0 g of compound, 60%, mp 85–87°, after sublimation. The analytical sample was prepared by recrystallization from hexane followed by sublimation and had mp 87–89°.

Anal. Calcd for $C_6H_{12}BrF$: C, 39.36; H, 6.61; Br, 43.65; F, 10.38. Found: C, 39.60; H, 6.68; Br, 43.38; F, 10.62.

Preparation of 2-Fluoro-3-iodo-2,3-dimethylbutane. This compound was prepared by the method of Wood, Kent, and Fisher.[27] From 8.4 g (0.1 mole) of tetramethylethylene and 22.5 g (0.1 mole) of N-iodosuccinimide in 20 g of anhydrous hydrogen fluoride diluted with 100 ml of anhydrous ether, there was obtained 12.7 g, 55% of material, mp 63–65° after sublimation. This compound decomposed readily and was not analyzed.

Preparation of 2,3-Difluoro-2,3-dimethylbutane. 2-Bromo-3-fluoro-2,3-dimethylbutane (33 g, 0.18 mole) was dissolved in 150 ml of anhydrous acetonitrile. To this solution, cooled to −20° (Dry Ice–carbon tetrachloride), was added in portions with stirring 63.5 g (0.5 mole) of silver fluoride (argentous, Harshaw) over a 10-min period. The solution was stirred 4 hr at −20° and then for 24 hr at 0°. The reaction mixture was filtered and poured into ice water. The organic layer was washed ten times with 50-ml portions of ice water and dried over sodium sulfate. The reaction mixture was flash distilled at about 10 mm (no heating) which allowed the recovery of 9.5 g of starting material. The more volatile components of the mixture consisted of the desired 2,3-difluoro-2,3-dimethylbutane, isolated yield (by preparative vpc, Apiezon L on Chromosorb W column) 1.2 g, 5%, 3-fluoro-2,3-dimethylbutene, 43%, and unreacted starting material. (The yields are based on total starting material.) The separation of the reaction mixture was unsuccessful due to decomposition with attempted distillation

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[26] P. W. Kent and M. R. Freeman, *J. Chem. Soc.*, 912 (1966); P. W. Kent, F. O. Robson, and V. A. Welch, *ibid.*, 3273 (1963); P. W. Kent and J. E. G. Barnett, *ibid.*, 6196 (1964).

[27] K. R. Wood, P. W. Kent, and D. Fisher, *ibid.*, 912 (1966).

Table III. Pmr Data of 2-Halo-3-methoxy- (-acetoxy-) 2,3-dimethylbutanes and Their Ions in FSO_3H–SbF_5–SO_2 and SbF_5–SO_2 Solutions

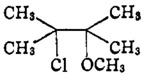
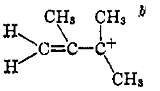
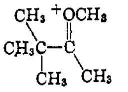
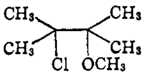
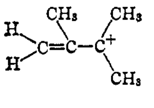
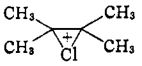
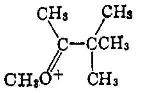
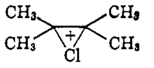
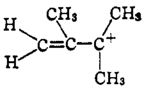
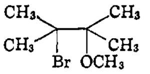
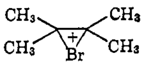
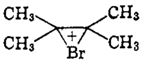
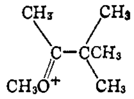
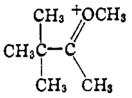
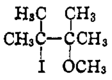
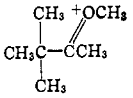
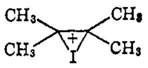
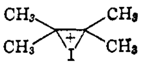
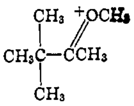
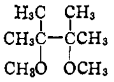
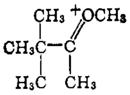
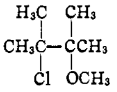
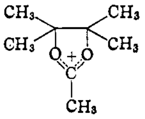
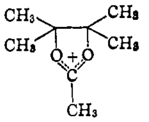
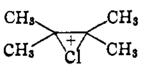
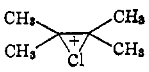
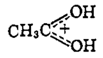
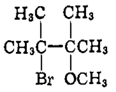
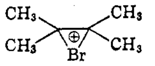
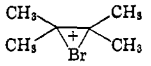
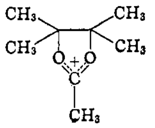
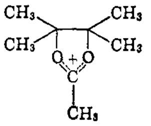
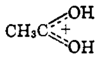
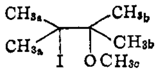
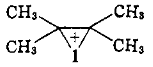
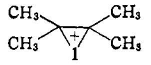
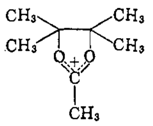
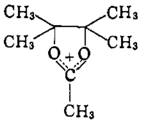
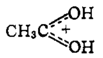
δ, ppm				
2-Halo-3-methoxy-(-acetoxy-) 2,3-dimethylbutane, intern. TMS in CCl_4[a]		Ion in SbF_5–FSO_3H–SO_2, extern. TMS in $DCCl_3$		Ion in SbF_5–SO_2, extern. TMS in $DCCl_3$
	−1.16(d) $J = 1.1$ Hz −1.28(d) $J = 2.2$ Hz −3.22(d) $J = 1.1$ Hz	$CH_3\overset{+}{O}H_2$ [c]	−4.50(t) $J = 3.9$ Hz −9.72(q) $J = 1.0$ Hz	Same ions in slightly different amounts
		 [b] 95%	−2.46(d) −3.50(m) −3.58(m) −7.90(m) −8.46(m)	
		 5%	−1.46(s) −3.02(s) −4.94(s)	
	−1.28(s) −1.52(s) −3.20(s)		(minor amount)	 75%
		$CH_3\overset{+}{O}H_2$	(major)	 25%
			−2.69(s)	Traces of $CH_3O^+H_2$
				
	−1.35(s) −1.80(s) −3.24(s)	$CH_3\overset{+}{O}H_2$		 50%
			−2.76(s)	 50%
		 Trace		
	−1.37(s) −1.84(s) −3.26(s)	 55%		 90%
		 45%	3.00(s)	 10%
		$CH_3\overset{+}{O}H_2$		
	−1.15(s) −3.18(s)			Same
	−1.57(s) −1.62(s) −1.92(s)		−1.90(s) −2.84(s)	 95%
		 Trace		 5%

Table III *continued*

2-Halo-3-methoxy-(-acetoxy-) 2,3-dimethylbutane, intern. TMS in CCl_4[a]	δ, ppm Ion in SbF_5–FSO_3H–SO_2, extern. TMS in $DCCl_3$	Ion in SbF_5–SO_2, extern. TMS in $DCCl_3$
		
 −1.70(s) −1.82(s) −1.96(s)	 90%	 70%
	 10%	 30%
		
 a −1.99(s) b −1.69(s) c −2.01(s)	 85%	 90%
	 15%	 10%
		

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[a] Abbreviations used are: d, doublet; s, singlet; m, multiplet; t, triplet; and q, quadruplet. [b] The dimethylisopropenylcarbonium ion (1,1-dimethyl-2-methylallyl cation) exhibits a temperature-dependent spectrum indicating an observable rotational barrier. We will report in a forthcoming communication in detail on this ion. [c] See ref 24.

through a short-packed column. The fluoroolefin was unstable and had to be stored over anhydrous potassium carbonate. It could not be protonated to give a stable carbonium ion.

Anal. Calcd for $C_6H_{12}F_2$: C, 58.99; H, 9.90; F, 31.10. Found: C, 58.93; H, 9.40; F, 31.00.

Preparation of 2-Chloro-3-methoxy-2,3-dimethylbutane. To 30 ml of methanol containing 0.2 ml of concentrated sulfuric acid were alternately added, in small portions, 4.2 g of tetramethylethylene (0.05 mole) and 5.5 g (0.05 mole) of *t*-butyl hypochlorite. The reaction caused the solution to warm considerably and ice-bath cooling was applied to maintain room temperature. The reaction mixture was then poured into 100 ml of water and extracted with 75 ml of pentane. Removal of solvent left an oil which was flash distilled under vacuum. The yield was 6.0 g, 40%. The analytical sample was purified by preparative vpc and had mp 43–45°.

Anal. Calcd for $C_7H_{15}ClO$: C, 55.81; H, 10.04; Cl, 23.53; O, 10.62. Found: C, 55.75; H, 10.02; Cl, 23.39; O, 10.84.

Preparation of 2-Bromo-3-methoxy-2,3-dimethylbutane. To 30 ml of methanol containing 0.2 ml of concentrated sulfuric acid were alternately added in portions 4.2 g (0.05 mole) of tetramethylethylene and 8.9 g (0.05 mole) of N-bromosuccinimide. The reaction was exothermic and ice-bath cooling was required to maintain the temperature at 25°. After pouring the reaction mixture into 100 ml of water and extracting with 75 ml of pentane, there was obtained 5.7 g (58%) of the desired compound. The analytical sample was prepared by preparative vpc and had mp 90–92°. The crude product was oily and could not be induced to crystallize even after flash distillation.

Anal. Calcd for $C_7H_{15}BrO$: C, 43.09; H, 7.75; Br, 40.96; O, 8.20. Found: C, 43.02; H, 7.56; Br, 40.73; O, 8.69.

Preparation of 2-Iodo-3-methoxy-2,3-dimethylbutane. This compound was prepared in the same way as the two previous halo ethers except that the temperature was maintained at 0°. The yield from 0.05 mole of tetramethylethylene and N-iodosuccinimide was 6.5 g, 54%, of white crystalline solid which rapidly decomposed at room temperature. No melting point or analysis could be obtained. The low-temperature pmr spectrum was completely consistent with the assigned structure. The crystalline material could be stored indefinitely at −78°.

Preparation of 2-Fluoro-3-methoxy-2,3-dimethylbutane. To 19.5 g (0.1 mole) of 2-bromo-3-methoxy-2,3-dimethylbutane in 100 ml of anhydrous acetonitrile at 0° was added 38.1 g (0.3 mole) of silver fluoride. The reaction mixture was allowed to warm to room temperature and then stirred for 4 hr. Filtration of the mixture allowed removal of excess silver fluoride and precipitated silver bromide. The filtrate was poured into 200 ml of cold water, extracted with 100 ml of pentane, and then washed twice with 50-ml portions of cold water. Pentane was removed by distillation and the remaining oil was separated into its components by preparative vpc at 100°. There were four major components, the first of which was pinacolone, 35%, identified by its vpc retention time and pmr spectrum; the second was 3-methoxy-2,3-dimethylbutene-1 (pmr spectrum in CCl_4: δ 0.97 (s), δ 1.68 (m), δ 2.99 (s), and δ 4.83 (m), amounting to 35%; the third was the desired 2-fluoro-3-methoxy-2,3-dimethylbutane and amounted to 20%; a fourth component was unreacted starting material, 10%.

Anal. Calcd for $C_7H_{15}FO$: C, 62.65; H, 11.27; F, 14.16; O, 11.92. Found: C, 62.82; H, 11.16; F, 14.39; O, 11.63.

Preparation of 2-Chloro-3-acetoxy-2,3-dimethylbutane. To 30 ml of glacial acetic acid containing 4.2 g (0.05 mole) of tetramethylene was added dropwise with stirring 5.5 g (0.05 mole) of *t*-butylhypochlorite over a period of 15 min. Ice-bath cooling was required to keep the temperature near that of room temperature. The reaction mixture was poured into 100 ml of cold water and extracted with 100 ml of pentane. Solvent removal left an oil which was flash distilled to yield 5.3 g, 60%, of the desired compound. The analytical sample was purified by preparative vpc.

Anal. Calcd for $C_8H_{15}ClO$: C, 53.78; H, 8.46; Cl, 19.84; O, 17.91. Found: C, 54.00; H, 8.59; Cl, 20.08; O, 17.33.

Preparation of 2-Bromo-3-acetoxy-2,3-dimethylbutane. This compound was prepared in the same way as the chloro derivative using N-bromosuccinimide. From 0.05 mole of reagents there was obtained 8.6 g, 77%, of compound, bp 73–77° (9 mm). The analytical sample was a center cut, bp 74°.

Anal. Calcd for $C_8H_{15}BrO$: C, 43.07; H, 6.77; Br, 35.81; O, 14.34. Found: C, 43.31; H, 6.93; Br, 35.36; O, 14.40.

Preparation of 2-Iodo-3-acetoxy-2,3-dimethylbutane. This compound was prepared in the same way as the bromo derivative using N-iodosuccinimide and maintaining the temperature at 0°. From 0.05 mole of reagents there was obtained 7.6 g, 50%, of desired compound. This material was unstable and had to be stored at −78°. It could be stabilized with sodium sulfite. Attempted purification by vacuum distillation resulted in decomposition. This material was used without purification. The absence of appreciable extraneous absorptions in its pmr spectrum indicates better than 90% purity.

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Stable Carbonium Ions. XLIX.[1] Protonated Dicarboxylic Acids and Anhydrides and Their Cleavage to Oxocarbonium Ions

George A. Olah and Anthony M. White[2]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received April 21, 1967*

Abstract: A series of diprotonated aliphatic dicarboxylic acids (alkylenedicarboxonium ions) have been studied in HSO_3F–SbF_5–SO_2 solution. O-diprotonation was observed with negligible exchange rates at low temperature by nmr spectroscopy. Glutaric, adipic, and pimelic acids were found to cleave at higher temperatures, first to the alkylenemonooxocarbonium-monocarboxonium ions, and then to the alkylenedioxocarbonium ions. Only the monooxocarbonium ion was observed in the case of succinic acid. Protonated oxalic and malonic acids did not cleave in the acid system. Protonation of dicarboxylic acid anhydrides in FSO_3H–SbF_5–SO_2 solution, even at −90°, leads to a mixture of the corresponding monocarboxonium-monooxocarbonium ion.

The isolation of alkylenedioxocarbonium ion salts from dicarboxylic acid fluorides and antimony pentafluoride has been reported recently.[3] In continuation of our previous work on the observation of the formation of oxocarbonium ions from protonated aliphatic carboxylic acids in FSO_3H–SbF_5,[4] we now report the formation of dioxocarbonium ions from protonated aliphatic dicarboxylic acids.

Results and Discussion

The ionization of saturated dicarboxylic acids in sulfuric acids has been investigated by cryoscopy,[5] and it was concluded that succinic acid and higher members of the series are only partially ionized as diacid bases (i = 2.6). Malonic acid was reported to be only monoprotonated (i = 2.0) and oxalic acid gave an i factor of 1.3 which increased with time due to decomposition. Pittman[6] has studied the change in nmr band positions of adipic acid in H_2SO_4–oleum and found a downfield shift in the α-proton signal in 17% oleum, but was unable to assign the species under observation on the available evidence.

In the strong acid system, FSO_3H–SbF_5, all the aliphatic dicarboxylic acids studied were completely diprotonated, and we were able to observe, in certain cases, cleavage to the corresponding monocarboxonium–monooxocarbonium ion and dioxocarbonium ions.

$$HO_2C(CH_2)_nCO_2H \xrightarrow[-60^\circ]{FSO_3H\text{-}SbF_5\text{-}SO_2}$$

$$H_2\overset{+}{O}_2C(CH_2)_n\overset{+}{C}O_2H_2 \xrightarrow[\Delta(-H_2O)]{FSO_3H\text{-}SbF_5\text{-}SO_2}$$

$$H_2\overset{+}{O}_2C(CH_2)_n\overset{+}{C}O \xrightarrow[\Delta(-H_2O)]{FSO_3H\text{-}SbF_5\text{-}SO_2} \overset{+}{O}C(CH_2)_n\overset{+}{C}O$$

The following aliphatic dicarboxylic acids were examined in FSO_3H–SbF_5–SO_2 solution: oxalic, malonic, glutaric, adipic, and pimelic acids.

Diprotonated Dicarboxylic Acids (Alkylenedicarboxonium Ions). Dicarboxylic acids, with the exception of oxalic acid, gave well-resolved nmr spectra in FSO_3H–SbF_5 solution diluted with SO_2. To observe the protons on oxygen, it was necessary to record the spectra, in general, at lower temperatures (−90°) than in the case of the monocarboxylic acids[3] because of the more weakly basic nature of the diacids. At these low temperatures, the C–H protons sometimes show broadening, and the coupling constants between methylene protons were evaluated from spectra recorded at −40°. Table I summarizes the coupling constants and chemical shifts. Representative spectra are given in Figures 1–4. Integration of the peaks indicated four protons

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