

# Stable Carbonium Ions. XLVII.<sup>1</sup> Alkylcarbonium Ion Formation from Alkanes *via* Hydride (Alkide) Ion Abstraction in Fluorosulfonic Acid–Antimony Pentafluoride–Sulfuryl Chlorofluoride Solution<sup>2</sup>

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

**Abstract:** Alkylcarbonium ions are formed at temperatures between  $-125$  and  $+25^\circ$  from alkanes *via* hydride (alkide) ion abstraction in fluorosulfonic acid–antimony pentafluoride solution (diluted at lower temperatures with sulfuryl chlorofluoride). All alkylcarbonium ions convert ultimately on heating through isomerization, fragmentation, and dimerization to the *t*-butyl cation which was found to be stable in the acid solution up to  $150^\circ$ .

Hydride ion abstraction is primarily known as transfer of a hydride ion between a hydrocarbon and a carbonium ion. This could occur intramolecularly in a rearrangement or intermolecularly as in the case of the formation of tropylium ion from triphenylcarbonium ion and tropyliene.<sup>4</sup> Isomerizations of saturated hydrocarbons catalyzed by Friedel–Crafts catalysts ( $\text{HF–BF}_3$ ,  $\text{HCl–AlCl}_3$ ) show evidence (evolution of  $\text{H}_2$ , rate dependence on  $H_0$ ) of hydride ion abstraction as initiating steps.<sup>5</sup> Claims that Lewis acid halides themselves are capable of effecting hydride ion abstraction in the absence of proton sources were disproved by Nenitzescu.<sup>6</sup>

A more recent claim of the ability of antimony pentachloride to abstract hydride ion<sup>7</sup> may also find its explanation in traces of proton impurities in the reaction medium.<sup>8</sup>

We have previously reported the generation of stable alkylcarbonium ions from alkyl halides in  $\text{SbF}_5$  and  $\text{SbF}_5\text{–SO}_2$  solutions<sup>9</sup> and from alcohols in  $\text{FSO}_3\text{H–SbF}_5$  solution.<sup>10</sup> We would like now to report our observations relating to the generation of alkylcarbonium ions from alkanes *via* hydride (alkide) ion abstraction with the extremely strong acid  $\text{FSO}_3\text{H–SbF}_5$ .



## Results and Discussion

*n*-Butane and isobutane both form exclusively the *t*-butyl cation (I) (sharp singlet at  $-4.50$  ppm<sup>9</sup>) when

(1) Part XLVI: G. A. Olah and M. Calin, *J. Am. Chem. Soc.*, **89**, 4736 (1967).

(2) For a preliminary communication see G. A. Olah and J. Lukas, *ibid.*, **89**, 2227 (1967).

(3) National Institutes of Health Postdoctoral Research Investigator, 1965–1967.

(4) For a comprehensive review on intermolecular hydride abstraction, see (a) N. C. Deno, J. Peterson, and George S. Saines, *Chem. Rev.*, **60**, 7 (1960); (b) C. D. Nenitzescu in "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, Inc., New York, N. Y., 1967.

(5) "Friedel–Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Interscience Publishers Inc., New York, N. Y., 1963, p 86.

(6) C. D. Nenitzescu and J. P. Cantuniari, *Ber.*, **66**, 1097 (1933).

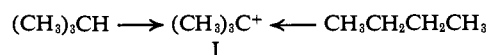
(7) J. Holms and R. Pettit, *J. Org. Chem.*, **28**, 1695 (1963).

(8) Observations of Dr. Paul Kreienbühl in our laboratories.

(9) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastian, *J. Am. Chem. Soc.*, **86**, 1360 (1964); G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *ibid.*, **87**, 2997 (1965).

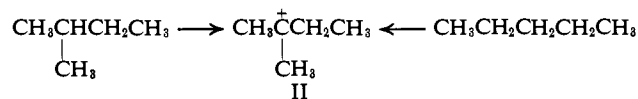
(10) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *ibid.*, **87**, 2997 (1965).

dissolved in  $\text{FSO}_3\text{H–SbF}_5$  solution. The *t*-butyl cation is, in our experience, the most stable alkylcarbonium ion. When generated in  $\text{FSO}_3\text{H–SbF}_5$  solution *via* hydride ion abstraction, the solution of I is unchanged even after having been heated to  $150^\circ$ . All other investigated alkylcarbonium ions were observed to convert to ion I at higher temperatures through various fragmentation (and isomerization) pathways.



The increasing viscosity of the neat fluorosulfonic acid–antimony pentafluoride mixture puts a lower limit of  $0$ – $10^\circ$  on the heterogeneous reaction. It therefore was necessary to use a solvent to dilute the solution and also to lower the freezing point. Sulfur dioxide was used extensively in stable carbonium ion chemistry previously as solvent, but had its disadvantages. The melting point is, in some cases, too high ( $-75^\circ$ ); the carbonium ions are considerably less stable in solutions diluted with  $\text{SO}_2$  than in undiluted acid. In some cases carbonium ions react with  $\text{SO}_2$  to give sulfinic acids. Sulfuryl chlorofluoride ( $\text{SO}_2\text{ClF}$ ) was found to be a more suitable solvent. It dissolves hydrocarbons to a certain extent, and solutions of carbonium ions in  $\text{FSO}_3\text{H–SbF}_5$  diluted with it are stable even at higher temperatures ( $-30$  to  $0^\circ$ ). The solutions are colorless. However, compared to similar solutions in  $\text{SO}_2$ , the spectra of carbonium ions in  $\text{SO}_2\text{ClF}$  do not show the same degree of resolution. The melting point of  $\text{SO}_2\text{ClF}$  is  $-125^\circ$ ,  $50^\circ$  lower than that of  $\text{SO}_2$ . Carbonium ion chemical shifts show dependence on solvent and acidity of the system. In the case of trimethylcarbonium ion, its nmr singlet moves downfield with increasing acid concentration ( $-4.2$  ppm in  $1:1 \text{SO}_2\text{ClF}:\text{FSO}_3\text{H–SbF}_5$  and  $-4.5$  ppm in neat  $\text{FSO}_3\text{H–SbF}_5$ ).

*n*-Pentane and isopentane are ionized in  $\text{FSO}_3\text{H–SbF}_5$  to the *t*-amyl cation<sup>9</sup> II. At  $-30^\circ$  the pmr spectrum shows a methyl triplet at  $-4.42$  ppm (with the large long-range coupling  $^4J_{\text{H–H}} = 5.0$  Hz through the  $\text{sp}^2$ -hybridized carbonium ion carbon atom), methylene multiplet at  $-4.75$  ppm, and the methyl triplet at  $-2.17$  ppm ( $^3J_{\text{H–H}} = 5.6$  Hz).



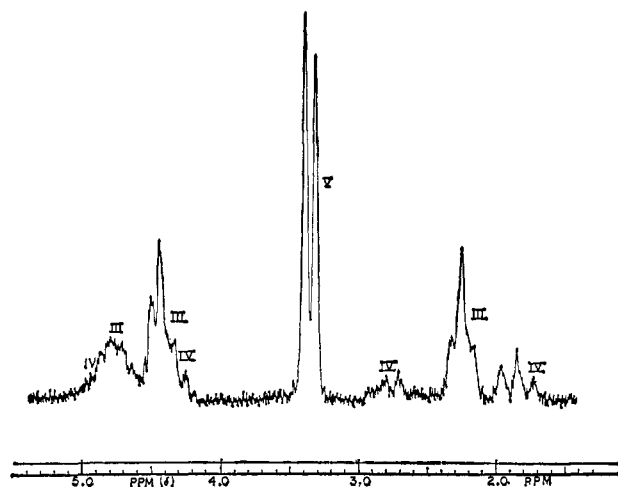
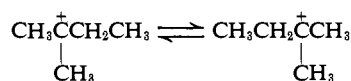
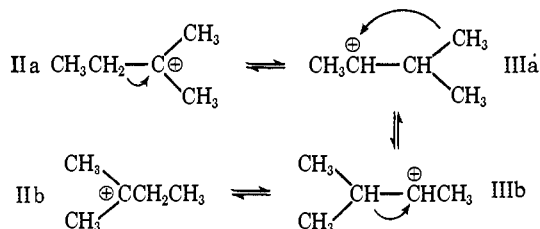


Figure 1. Mixture of *t*-hexyl cations: methyldiethylcarbonium ion (III), dimethyl-*n*-propylcarbonium ion (IV), and dimethylisopropylcarbonium ion (V).

With increasing temperature the methyl peaks start to coalesce until they collapse at 90° to give a single broad peak at -3.60 ppm. The methylene peak is unchanged. The observed temperature dependence of the spectrum of II indicates equilibration at elevated temperatures.



To explain equilibration, an equilibrium between the *t*-amyl cation (dimethylethylcarbonium ion) (IIa) and the secondary methylisopropylcarbonium ion (IIIa) must exist through a 1,2-hydride shift. The latter (IIIa) can react by reversing the hydride shift (IIIa → IIa) or by undergoing a methyl shift to give the equilibrating methylisopropylcarbonium ion (IIIa ⇌ IIIb). A 1,2-hydride shift of IIIb gives a *t*-amyl cation in which scrambling of the methyl groups has occurred.



The temperature of collapse of the two methyl peaks is -10° in SO<sub>2</sub><sup>9</sup> or SO<sub>2</sub>ClF solution, thus 100° lower than in undiluted acid (+90°). Obviously ion pairing is more intimate in the latter case, thus obstructing methyl and hydride shifts.

At 150° the rate of decomposition of II to I is still slow. These observations seem to indicate remarkable stabilization of alkylcarbonium ions in the highly acidic solvent, involving in all probability solvation of tight ion pairs.

The ionization pattern of neopentane differs sharply with temperature. At -20° in FSO<sub>3</sub>H-SbF<sub>5</sub>-SO<sub>2</sub>ClF, it slowly loses a primary hydrogen. The incipient primary carbonium ion rearranges immediately to the *t*-amyl cation (II). At +25° however, without solvent, the *t*-butyl ion (I) is formed exclusively while methane is liberated (as proved by mass spectroscopic analysis).

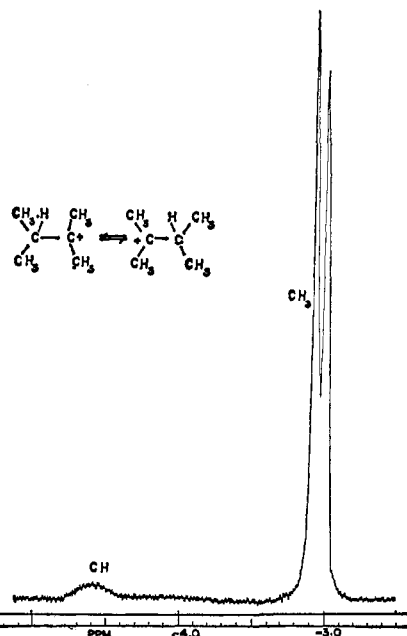
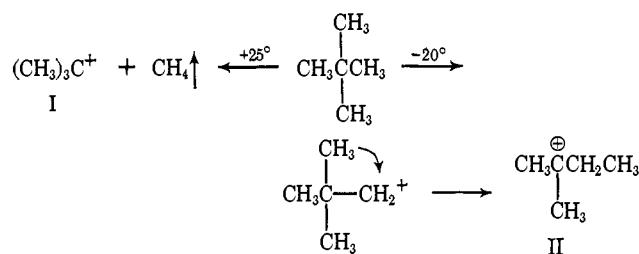


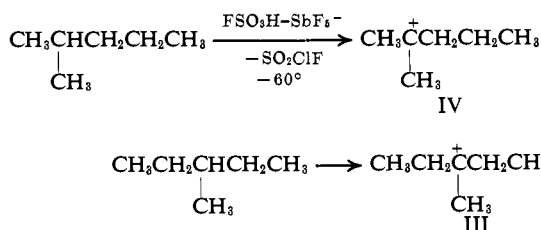
Figure 2. Dimethylisopropylcarbonium ion (V).

Thus at higher temperatures abstraction of methide ion giving the *t*-butyl cation is favored over hydride ion abstraction. That ion I was not formed *via* ion II is seen from the fact that II is stable up to 150°.



*n*-Hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane all show in FSO<sub>3</sub>H-SbF<sub>5</sub> solution at room temperature a spectrum (Figure 1) consisting of all three isomeric tertiary hexyl cations: the methyldiethylcarbonium ion (III), the dimethyl-*n*-propylcarbonium ion (IV), and the dimethylisopropylcarbonium ion (V) (see Scheme I). On heating, ions III and IV are increasingly converted into ion V, which seems to be the most stable hexyl cation. The *t*-hexyl cations convert to the *t*-butyl cation (I) above 80°.

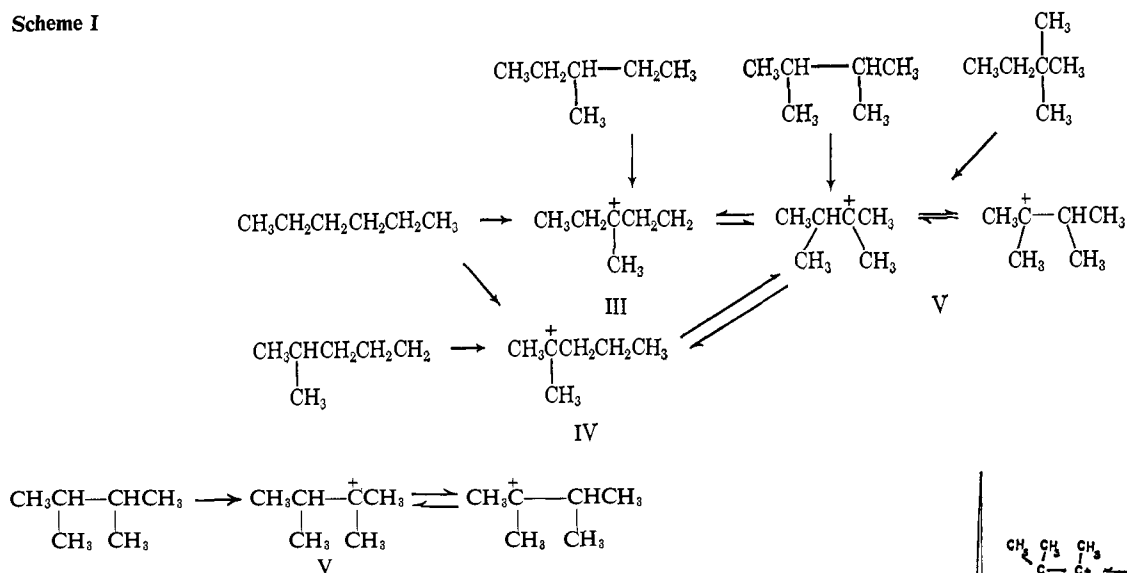
The ionization of the isomeric hexanes in FSO<sub>3</sub>H-SbF<sub>5</sub>-SO<sub>2</sub>ClF solution below -60° gives the unrearranged *t*-hexyl cations.



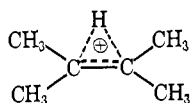
The dimethylisopropylcarbonium ion (V) is particularly interesting (Figure 2). It is an example of an acyclic equilibrating carbonium ion.<sup>11</sup>

(11) P. von R. Schleyer, W. Watts, R. C. Fort, M. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5679 (1964).

Scheme I

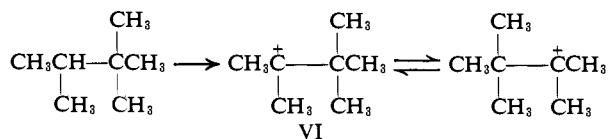


The four methyl groups are equivalent, found as a doublet at  $-3.32$  ppm ( $J_{H-H} = 4.2$  Hz). They must therefore be coupled equally to one proton. Whether the ion is equilibrating rapidly or is a static "nonclassical ion" can be determined by interpreting the observed

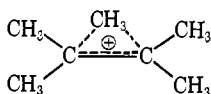


deshielding of the methyl protons and that of the methine proton in the nmr spectrum. The methine proton is at  $-4.40$  ppm, and it could be shown to be coupled to the doublet of the methyl group by spin-spin decoupling. On comparison with static carbonium ions this chemical shift is as would be expected for a tertiary hydrogen on a carbon atom  $\alpha$  to the positive center. A nonclassical structure, in which the hydrogen should be carrying part of the positive charge or in which it would be partially bonded to a positively charged carbon atom, is therefore unlikely.<sup>12</sup>

Ionization of isomeric heptanes in  $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2\text{ClF}$  resulted in the observation of three tertiary heptyl cations. 2,2,3-Trimethylbutane in  $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2\text{ClF}$  at  $-60^\circ$  gives the dimethyl-*t*-butylcarbonium ion (VI) which shows a single sharp nmr singlet ( $-2.86$  ppm). A fast 1,2-methyl shift must equilibrate all five methyl groups (Figure 3).



The fact that there is only one singlet and the chemical shift is similar to that of the dimethylisopropylcarbonium ion excludes a static nonclassical ion such as



This conclusion is further enhanced by the comparison of the deshielding of the methyl groups compared

(12) The  $\alpha$ -hydrogen in the isopropyl ion appears at  $-13.5$  ppm; see ref 9.

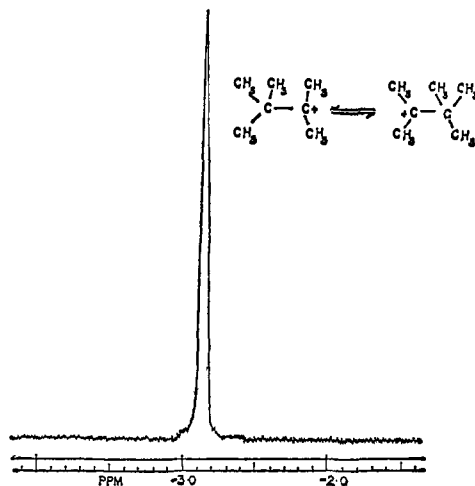
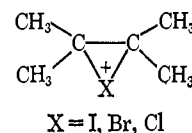


Figure 3. Dimethyl-*t*-butylcarbonium ion (VI).

with recently observed bridged tetramethylethylene halonium ions.<sup>13</sup> The deshielding of the methyl protons of ion VI compared with the methyl protons in 2,2,3,3-tetramethylbutane is 2.00 ppm. This deshielding is much larger than observed in bridged tetramethylethylene halonium ions (0.95–0.75 ppm).



If ion VI would be the bridged nonclassical ion (a protonated tetramethylcyclopropane) the four methyl groups would be expected at much higher field partly because of charge delocalization on the cyclopropane ring, partly because of the expected anisotropy effect.

It is interesting to note that the rate of the 1,2-methyl shift even at  $-180^\circ$  is still extremely fast and no change in the single line spectrum is observed.<sup>14</sup> This would mean, in comparison with our previous observation of fast shifts in the norbornyl ion,<sup>15</sup> a rate probably exceeding  $5 \times 10^8 \text{ sec}^{-1}$  and a barrier of less than 2–3 kcal/mole.<sup>16</sup>

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

(14) Observation of Dr. E. Namanworth.

(15) M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964).

(16) In cooperation with Professor E. Namanworth and Professor M. Saunders, an effort is being made to measure the rate of methyl shift by spin-echo techniques.



Table I. Nmr Shifts and Coupling Constants of Alkylcarbonium Ions

Carbonium ion	Structure	$\delta$ , ppm in $\text{SO}_2\text{ClF}$ ( $J_{\text{HH}}$ , Hz)	Temp, $^{\circ}\text{C}$	Rearr or cleaves to
Trimethyl (I)		4.20 <sup>a</sup>	+150	
Dimethylethyl (II)		a 1.94 (tr, 5.2) b 4.42 (m, 5.2), 4.42 (m, 5.2) c 4.02 (tr, 4.7), 3.60 (m)	-30 +150	I (~1 hr half-life)
Methyldiethyl (III)		a 4.16 (tr, 4.8) b 4.44 (q, 6.0) c 1.87 (tr, 6.0)	-20 +80	IV and V I
Dimethylpropyl (IV)		a 4.05 (tr, 4.8) b 4.40 (q, 6.0) c 2.58 (m) d 1.43 (tr, 7.0)	-20 +80	III and V I
Dimethylisopropyl (V)		a 3.04 (d, 4.2) b 4.55 (m)	-20 +80	III and IV I
Dimethyl- <i>t</i> -butyl (VI)		2.86 (s)	-10	I
Dimethylisobutyl (VII)		a 2.96 (d, 4.1) b 4.35 (m) c 3.30 (m) d 1.75 (tr, 6.5)	-70	VI, always present
Triethyl (VIII)		a 1.88 (m) b 4.42 (m)	-70	VI
Dimethylneopentyl (IX)		a 4.13 (br) b 4.32 (m) c 1.51 (s)	-100 -75	Rearr to X Cleaves to I
Methyldiisopropyl (X)		a 3.85 (m) b 2.64 (d)	-100 75	Rearr to IX Cleaves to I

<sup>a</sup> Abbreviations used are: s, singlet; d, doublet; tr, triplet; qu, quartet; q, quintuplet; m, multiplet; br, broad. All measured from external TMS capillary.

All the observed alkylcarbonium ions are tertiary. Abstraction of a secondary or primary hydrogen atom results in immediate rearrangement *via* 1,2-hydrogen or -methyl shifts or cleavage to give tertiary carbonium ions even at  $-100^{\circ}$ . No evidence was found for reversible 1,3-hydride or -methyl shifts. Ease of ionization increases in the order: primary < secondary < tertiary hydrogen atoms. The secondary and tertiary systems undergo ionization at as low a temperature as  $-100^{\circ}$ . Primary hydrogen atoms generally could not be ionized below  $-50^{\circ}$ .

*Methane* does not ionize under the reaction conditions. It reacts only at  $+140^{\circ}$  with  $\text{FSO}_3\text{H-SbF}_5$  to give, as yet, unidentified products. *Ethane* gives a mixture of 90% I and 10% V through some dimerization and trimerization pathways.

*Propane* does not give the isopropyl cation in  $\text{FSO}_3\text{H-SbF}_5$  solution, but gives immediately a mixture of the *t*-butyl ion (I) and the hexyl cations III, IV, and V. At temperatures where ionization takes place, fragmentation and isomerization are very fast.

At room temperature alkanes with seven or more carbon atoms are converted in the heterogeneous reaction with neat  $\text{FSO}_3\text{H-SbF}_5$  to the *t*-butyl cation (I). At lower temperatures, however, their ions are more stable. Investigated examples are: *n*-heptane, 2,2,3-trimethylbutane, 3-ethylpentane, 2,4-dimethylpentane, 2-methylhexane, 2,3,4-trimethylpentane, 2,2,4-trimethylpentane, *n*-nonane, *n*-undecane, *n*-dodecane, and hexadecane. Even paraffin wax and polyethylene gave ion I. Obviously complex isomerization and fragmentation processes in the strong acid solution

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<sub>3</sub>H-SbF<sub>5</sub>). 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<sub>3</sub><sup>+</sup>, obviously less stable than CH<sub>3</sub>CH<sub>2</sub><sup>+</sup>, 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 fluoroantimony sulfonic acid.

Probably the most surprising observation of our work is that salts of the alkyl cations I, II, and V can be ob-

tained and crystallized from SO<sub>2</sub> or SO<sub>2</sub>ClF solutions at low temperature (-60 to -100°). They are stable at least to room temperature. Redissolved in SO<sub>2</sub> or SO<sub>2</sub>ClF 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<sub>3</sub>H-SbF<sub>5</sub> or HF-SbF<sub>5</sub>.** In a typical experiment, the alkane and a tenfold (weight) excess of acid (1:1 FSO<sub>3</sub>H-SbF<sub>5</sub> or HF-SbF<sub>5</sub>) 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<sub>3</sub>H-SbF<sub>5</sub>-SO<sub>2</sub>ClF.** To a 1:1 mixture of SO<sub>2</sub>ClF with FSO<sub>3</sub>H-SbF<sub>5</sub> or HF-SbF<sub>5</sub>, 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

## Stable Carbonium Ions. XLVIII.<sup>1a</sup> Halonium Ion Formation via Neighboring Halogen Participation. Tetramethylethylene Halonium Ions

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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  $\alpha$ -fluoroisopropyl dimethylcarbonium 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.

**B**romonium ion (I) formation in certain electrophilic additions of bromine to olefins is the generally accepted explanation for the complete stereospecificity observed.<sup>2,3</sup> This concept has been criticized be-

(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).

cause it assumes that molecular rotation in a carbonium ion is much more rapid than attack by an external nucleophile, an assumption that was questioned.<sup>4</sup> Moreover, it has been suggested that rapidly equilibrating ions such as IIa and b could also lead to stereospecificity.<sup>5</sup> Similarly, from results of rate measurements and stereochemistry, bromine has been suggested as a good neighboring group, participating through the

(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).