Onium Ions. VII.[1a] Dialkylhalonium Ions[1b]

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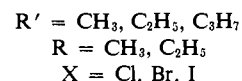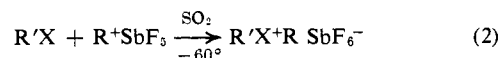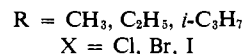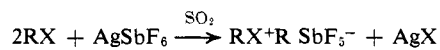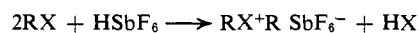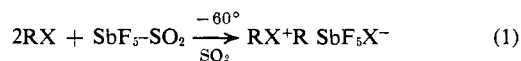Cleveland, Ohio 44106. Received April 27, 1973*

Abstract: The preparation of dialkylhalonium ions from alkyl halides and antimony pentafluoride (or fluoro-antimonic acid) or by alkylation of alkyl halides with alkyl fluoroantimonates in SO_2 solution at low temperature is described. The structure of dialkylhalonium ions is based on their nmr (^1H and ^{13}C), laser Raman, and ir spectroscopic studies. Isolation of dimethylhalonium fluoroantimonate salts (1–3) was also achieved. It is also shown that in methyl (ethyl) bromide–aluminum bromide complexes dimethyl- (diethyl-) bromonium bromo-aluminates play a significant role. The alkylating ability of dialkylhalonium ions in alkylation of aromatics and heteroorganic compounds was studied and their possible role in Friedel–Crafts alkylations evaluated.

Halonium ions represent a significant class of onium compounds and their role in electrophilic halogenation reactions is well recognized.[3] We have previously reported observation of a series of stable, long-lived three- and five-membered ring halonium ions[4] generated through halogen participation in ionization of dihalides, haloalkoxides, haloacetates, etc., in SbF_5–SO_2, FSO_3–SbF_5, and other superacid solutions. Some of these ions were also observed subsequently by direct halogenation of alkenes with cyanogen iodide and bromide, respectively, in SbF_5–SO_2 solution.[5] Open-chain diarylhalonium ions have been obtained from reaction of aryldiazonium compounds with halobenzenes and aryliodoso compounds with aromatics.[6] Recently, alkylarylhalonium ions have also been prepared and investigated by Olah and Melby.[7] More recently, di- and trihalonium ions have also been prepared and studied by Olah and Peterson and their coworkers.[8] Dialkylhalonium ions were first reported in a preliminary way in a series of communications by Olah and DeMember.[1b] We now report the detailed study of the preparation of dialkylhalonium ions, their nmr (^1H and ^{13}C), laser Raman, and ir spectroscopic studies, as well as investigation of their chemical reactivity.
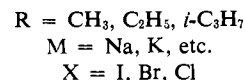
Results and Discussion

Preparation and Pmr Study. We have developed two general methods of preparations of dialkylhalo-

nium ions, namely: (1) the reaction of excess primary and secondary alkyl halides with SbF_5–SO_2, anhydrous fluoroantimonic acid (HF–SbF_5), or anhydrous silver hexafluoroantimonate (and related complex fluoro silver salts) in SO_2 solution, and (2) alkylation of alkyl halides with methyl or ethyl fluoroantimonate[9] in SO_2

$$2RX + SbF_5\text{-}SO_2 \xrightarrow[SO_2]{-60°} RX^+R\ SbF_5X^- \qquad (1)$$

$$2RX + HSbF_6 \longrightarrow RX^+R\ SbF_6^- + HX$$

$$2RX + AgSbF_6 \xrightarrow{SO_2} RX^+R\ SbF_5^- + AgX$$

$$R = CH_3,\ C_2H_5,\ i\text{-}C_3H_7$$
$$X = Cl,\ Br,\ I$$

$$R'X + R^+SbF_5 \xrightarrow[-60°]{SO_2} R'X^+R\ SbF_6^- \qquad (2)$$

$$R' = CH_3,\ C_2H_5,\ C_3H_7$$
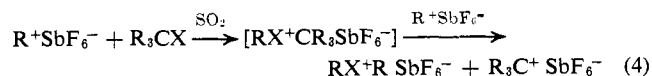$$R = CH_3,\ C_2H_5$$
$$X = Cl,\ Br,\ I$$

solution. The first method is only suitable for the preparation of symmetrical dialkylhalonium ion, while the second is adaptable for both symmetrical and unsymmetrical dialkylhalonium ions.

We have also found additional reactions which give dialkylhalonium ion (eq 3–7). However, these have less practical value because they usually also form by-product ions. (a) The reaction of alkyl fluoroantimonates with alkali halides in SO_2 solution gave the corresponding dialkylhalonium ions (eq 3). Dimethyl-, di-

$$2R^+SbF_6^- + MX \xrightarrow{SO_2} RX^+RSbF_6^- + MSbF_6^- \qquad (3)$$

$$R = CH_3,\ C_2H_5,\ i\text{-}C_3H_7$$
$$M = Na,\ K,\ etc.$$
$$X = I,\ Br,\ Cl$$

ethyl-, and diisopropylhalonium ions can be prepared by this method. (b) Tertiary alkyl halides reacted with alkyl fluoroantimonate to give the corresponding tertiary alkylcarbenium ions and a symmetrical dialkylhalonium ion (eq 4). The initially formed primary (secondary)-

$$R^+SbF_6^- + R_3CX \xrightarrow{SO_2} [RX^+CR_3SbF_6^-] \xrightarrow{R^+SbF_6^-}$$
$$RX^+R\ SbF_6^- + R_3C^+\ SbF_6^- \qquad (4)$$

(1) (a) Part VI: G. A. Olah and J. J. Sovboda, *Synthesis*, 203 (1973). (b) Reported in part in a series of Communications to the Editor: G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2113 (1969); **92**, 718, 2562 (1970).

(2) (a) Postdoctoral Research Associate, 1968–1970; (b) Postdoctoral Research Associate, 1972–1973; (c) Postdoctoral Research Associate, 1970–1972.

(3) See, for example, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969.

(4) (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); **90**, 947, 2587, 6988 (1968); (b) G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968).

(5) G. A. Olah, P. Schilling, P. W. Westerman, and H. C. Lin, *J. Amer. Chem. Soc.*, in press.

(6) (a) A. N. Nesmeyanov, L. G. Makarova, and T. P. Tolstaya, *Tetrahedron*, **1**, 145 (1957), and references therein; (b) I. Masson and E. Race, *J. Chem. Soc.*, 1718 (1937); I. Masson and C. Argument, *ibid.*, 1702 (1938).

(7) G. A. Olah and E. G. Melby, *J. Amer. Chem. Soc.*, **94**, 6220 (1972).
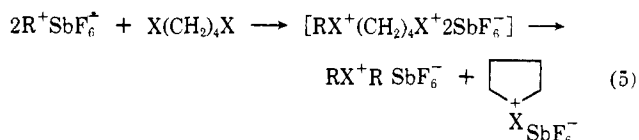
(8) (a) G. A. Olah, Y. K. Mo, E. G. Melby, and H. Lin, *J. Org. Chem.*, **38**, 367 (1973); (b) P. E. Peterson, B. R. Bonazza, and P. M. Henrichs, *J. Amer. Chem. Soc.*, **95**, 2222 (1973).

(9) (a) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **92**, 2112 (1970); (b) G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *ibid.*, **94**, 156 (1972).

Table I. Pmr Parameters of Dialkylhalonium Ions[a]

Ion	Method of preparation (eq)	CH₃X⁺	CH₂X⁺	CHX⁺	CH₃CX⁺	CH₂CX⁺	CH₃CCX⁺
CH₃Cl⁺CH₃, 1	(1)	4.20 (s)					
CH₃Br⁺CH₃, 2	(1)	4.13 (s)					
CH₃I⁺CH₃, 3	(1)	3.60 (s)					
CH₃Cl⁺CH₂CH₃, 4	(2)	4.41 (s)	5.23 (q, J = 7)		1.98 (t, J = 7)		
CH₃Br⁺CH₂CH₃, 5	(2)	4.09 (s)	5.10 (q, J = 7)		2.14 (t, J = 7)		
CH₃I⁺CH₂CH₃, 6	(2)	3.57 (s)	4.60 (q, J = 7)		2.17 (t, J = 7)		
(CH₃CH₂)₂Cl⁺, 7	(1)		5.20 (q, J = 7)		1.93 (t, J = 7)		
(CH₃CH₂)₂Br⁺, 8	(1)		5.20 (q, J = 7)		2.20 (t, J = 7)		
(CH₃CH₂)₂I⁺, 9	(1)		4.74 (q, J = 7.5)		2.30 (t, J = 7.5)		
CH₃Br⁺CH₂CH₂CH₃, 11	(2)	4.21 (s)	5.11 (t, J = 7)			2.3 (m)	1.34 (t, J = 7)
CH₃I⁺CH₂CH₂CH₃, 12	(2)	3.60 (s)	4.70 (t, J = 7)			2.33 (sex, J = 7)	1.33 (t, J = 7)
CH₃Cl⁺CH(CH₃)₂, 13	(2)	4.48 (s)		6.20 (hep, J = 6)	2.18 (d, J = 6)		
CH₃Br⁺CH(CH₃)₂, 14	(2)	4.18 (s)		6.21 (hep, J = 6)	2.23 (d, J = 6)		
CH₃I⁺CH(CH₃)₂, 15	(2)	3.69 (s)		5.90 (hep, J = 6.5)	2.40 (d, J = 6.5)		
CH₃CH₂Br⁺CH₂CH₂CH₃, 17	(2)		5.13 (q, J = 7) 5.13 (t, J = 7)		2.30 (t, J = 7)	2.32 (m)	1.30 (t, J = 7)
CH₃CH₂I⁺CH₂CH₂CH₃, 18	(2)		4.67 (q, J = 7) 4.70 (t, J = 7)		2.24 (t, J = 7)	2.38 (sex, J = 7)	1.30 (t, J = 7)
CH₃CH₂Cl⁺CH(CH₃)₂, 19	(2)		5.10 (q, J = 7.5)	6.23 (hep, J = 6)	2.03 (t, J = 7.5) 2.19 (d, J = 6)		
CH₃CH₂Br⁺CH(CH₃)₂, 20	(2)		4.94 (q, J = 7)	6.21 (hep, J = 7)	2.09 (t, J = 7) 2.25 (d, J = 7)		
CH₃CH₂I⁺CH(CH₃)₂, 21	(2)		4.70 (q, J = 7.5)	5.90 (hep, J = 7)	2.30 (t, J = 7) 2.37 (d, J = 7)		
(CH₃CH₂CH₂)₂Br⁺, 23	(1)		5.23 (t, J = 7)			2.3 (m)	1.31 (t, J = 7)
(CH₃CH₂CH₂)₂I⁺, 24	(1)		4.61 (t, J = 7)			2.4 (m)	1.18 (t, J = 7)
((CH₃)₂CH)₂Br⁺, 26	(1)			6.30 (hep, J = 7)	2.30 (d, J = 7)		
((CH₃)₂CH)₂I⁺, 27	(1)			5.84 (hep, J = 7)	2.10 (d, J = 7)		

[a] From external capillary TMS. Spectra were recorded in SO₂ solution at 60 MHz. J values are given in hertz.

tertiary dialkylhalonium ions were not observed, presumably due to further reaction with another mole of alkyl fluoroantimonate to give the thermodynamically more stable product. (c) When excess alkyl fluoroantimonate was treated with some of the alkylene dihalides (e.g. 1,4-dihalobutanes), the initially formed dihalonium ions were cleaved to give the five-membered ring halonium ions and dialkylhalonium ion.[8a] (d) When a

$$2R^+SbF_6^- + X(CH_2)_4X \longrightarrow [RX^+(CH_2)_4X^+2SbF_6^-] \longrightarrow$$

$$RX^+R\ SbF_6^- + \underset{X\ SbF_6^-}{\boxed{\ \ +\ \ }} \qquad (5)$$

haloalkylcarbenium ion, such as dimethylchlorocarbenium ion, was treated with the analogous alkanes (propane in this case), rapidly exchanging diisopropylchloronium ion was obtained (vide infra). (e) Further-

$$CH_3^+CClCH_3 + CH_3CH_2CH_3 \rightleftharpoons CH_3CHClCH_3 +$$
$$CH_3^+CHCH_3 \rightleftharpoons [(CH_3)_2CH]_2Cl^+ \qquad (6)$$
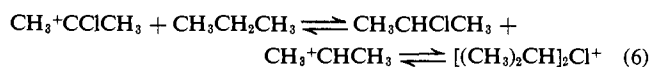
more, we found that dialkylchloronium ions can be directly obtained from alkanes and SbF₅-Cl₂-SO₂ClF solution at -78°.[10] For example, ethane reacted with this powerful chlorinating reagent (SbF₅-Cl₂-SO₂ClF) to give dimethylchloronium ion.

$$CH_3CH_3 + SbF_5\text{-}Cl_2\text{-}SO_2ClF \longrightarrow CH_3Cl^+CH_3\ SbF_5Cl^- \qquad (7)$$
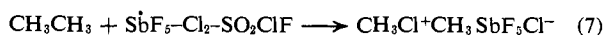
The pmr data of the prepared dialkylhalonium ions are tabulated in Table I. The simple first-order spectra showing expected multiplicities do not necessitate further discussion.

(10) G. A. Olah and Y. K. Mo, J. Amer. Chem. Soc., **94**, 6864 (1972).

It is interesting, however, to discuss the pmr spectra of 60% ¹³C enriched (¹³⁽¹²⁾CH₃)₂Br⁺Sb₂F₁₁⁻ (prepared from the corresponding 60% enriched ¹³CH₃Br). An exactly

¹³CH₃Br⁺¹³CH₃ Sb₂F₁₁⁻   ¹²CH₃Br⁺¹³CH₃ Sb₂F₁₁⁻
36%   48%
¹²CH₃Br⁺¹²CH₃ Sb₂F₁₁⁻
16%
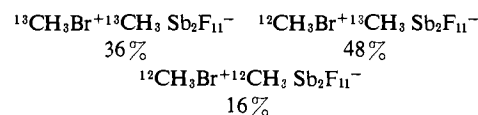
statistical distribution of three ions was obtained (based on relative peak areas). The spectrum of the ¹³CH₃-Br⁺¹³CH₃ ion was characterized by a doublet of doublets ($J_{H^{13}C}$ = 162.2 Hz; $J_{H^{13}C}$ = 1.5 Hz) centered at δ 4.13. The pmr spectrum of the ¹²C₃Br⁺¹³CH₃ ion was observed as two doublets: one centered at δ 4.13 ($J_{H^{13}CBr^{13}C}$ = 1.5 Hz) and another centered at δ 4.13 ($J_{H^{13}C}$ = 162.2 Hz). The pmr spectrum of the ¹²CH₃-Br⁺¹²CH₃ ion in this solution was observed as a singlet at δ 4.13. The long range H-¹²C-Br-¹³C coupling constant of 1.5 Hz is consistent with the coupling in analogous dimethyl selenide. The formation of dimethylbromonium ions is the only consistent explanation that can account for these ¹³C enriched pmr spectral data. Furthermore, the lack of methyl exchange on the pmr time scale at -78° was evident since each of these three ions was observed as a distinct entity with no decrease in $J_{HCX^{13}C}$ due to the methyl scrambling with ¹³⁽¹²⁾CH₃Br. Generally, the preparation of symmetrical dialkylhalonium ions is very clean. For example, dialkylhalonium ions prepared by the first method (eq 1) are not contaminated with any by-products. The decreasing order of stability of dimethylhalonium ions is (CH₃)₂I⁺ > (CH₃)₂Br⁺ > (CH₃)₂Cl⁺, based on the trend of their decomposition temperature. Unsymmetrical dialkylhalonium ions are susceptible

to disproportionation and subsequent self-condensation even at low temperature (ca. $-30°$). The decreasing order of stability of the methylethylhalonium ions is again $R_2I^+ > R_3Br^+ > R_2Cl^+$ and the increasing tendency for disproportionation is $R_2Cl^+ > R_2Br^+ > R_2I^+$.

Carbon-13 Nmr Study. Carbon-13 nuclear magnetic resonance spectroscopy is an extremely powerful tool for the study of organic cations. In order to obtain more information about the structure of dialkylhalonium ions, in particular relating to charge distribution at the carbon atoms, we undertook a study of their carbon-13 nmr (cmr) spectra. The Fourier transform (FT) carbon-13 nmr data of ten dialkylhalonium ions are summarized in Table II.

Table II. Carbon-13 Nmr Shifts of Dialkylhalonium Ions[a]

Ion	CH_2X^+	CH_2X^+	CH_3CX^+ $-CH_2CX^+$	CH_3CCX^+
1	144.9			
2	156.2			
3	184.3			
4	145.8	120.3	176.9	
5	157.7	126.9	177.1	
6	185.8	155.9	176.5	
7		120.7	173.3	
8		129.4	175.7	
9		156.9	175.1	
12	167.5	144.9	176.7	184.3

[a] In parts per million from $^{13}CS_2$. For detailed discussion on carbon-13 nmr study of halonium ions in general, see G. A. Olah, P. W. Westerman, E. G. Melby, and Y. K. Mo, J. Amer. Chem. Soc., submitted for publication.

The relative stability (thermal) of dialkylhalonium ions was observed in the order I > Br > Cl, whereas their reactivity gave the opposite sequence Cl > Br > I, as observed in their alkylation reactions (see subsequent discussion). These observations and nmr data are in good accordance.

Raman and Infrared Spectroscopic Studies. Raman data of the dimethylhalonium ions studied are shown in Table III along with data observed for isoelectronic model compounds (both neat[11] and in SO_2 solution). An additional intense line at ~600 cm^{-1} is observed in all solutions of ions 1–3 (in excess CH_3X and SO_2) and is characteristic of the SbF_6^- anion. Dimethylhalonium ions ($CH_3X^+CH_3$) could exist in either a linear or bent conformation. On the basis of energetic considerations and the well-established geometry of the isoelectronic dimethyl chalcides[11d] it is expected that dialkylhalonium ions contain an sp^3-hybridized halogen atom resulting in approximate tetrahedral geometry. Furthermore, the point group can be expected to be C_{2v} if the methyl groups assume the preferred chalcide-like conformations, as anticipated.[11a,b,d,12] Such an arrangement would lead to three skeletal vibrations that are both ir and Raman active. Two of the vibrations are totally symmetric, A_1 in character, and one asymmetric of the B_1 type. Thus, two polarized and one depolarized Raman active and three ir active modes are theoretically predicted for the fundamental skeletal vibrations of a C_{2v} dimethylhalonium ion.[13]

The strong, polarized lines assigned to the ν_7 and ν_6 vibrations of the dimethylbromonium ion correlate very

Table III. Raman Spectra of Dialkylhalonium Ions, Their Isoelectronic Models, and Methyl Halides[a]

Compd	C–X–C deformation	$\nu_6[\nu_{17}]$ C–X stretching	C–H stretching
$CH_3^+ClCH_3$ (SO_2)	392 (0.31)	610 (0.36)	2865, 2950, 2980, 3080
$CH_3Br^+CH_3$ (SO_2)	282 (0.46)	544 (0.31) [561 (dp)]	2865 (0.70), 2950, 2978 (0.23), 3100
$CH_3I^+CH_3$ (SO_2)	?	511 (0.33)	2872, 2952, 2973
$CH_3CH_2Cl^+CH_2CH_3$ (SO_2)	390 (0.27)	610 (0.35), 545 (0.36), 527 (dp)	2860 (0.70), 2945 (0.24), 2987 (0.65), 3060
CH_3SCH_3 (neat)[b,d]	282 (p)	691 (p) [742 (dp)]	2832 (p), 2910 (p), 2966 (p), 2982 (dp)
CH_3SeCH_3 (neat)[b,c]	236 (dp)	587 (p) [602 (dp)]	2823 (p), 2919 (p), 2996 (dp)
CH_3TeCH_3 (neat)[d]	198	526 (dp)	2810, 2923 (p), 3000 (dp)
$CH_3CH_2SCH_3CH_3$ (SO_2)	340 (0.54)	693 (0.82), 656 (0.34), 638 (0.82)	2946
CH_3Cl (neat)[e]		731.2	2878.8, 2966.2, 3041.8, 2869, 2969
(SO_2)		706 [$\delta(\Delta\nu) = 25$ cm^{-1}]	
CH_3Br (neat)[e]		611	2861, 2972, 3055.8, 2869, 2969, ?
(SO_2)		595 [$\delta(\Delta\nu) = 15$ cm^{-1}]	
CH_3I (neat)[e]		532.8	2861, 2969.8, 3060.6, 2867, 2978, ?
(SO_2)		527 [$\delta(\Delta\nu) = 6$ cm^{-1}]	

[a] Spectra reported were recorded at $-40°$. For detailed experimental conditions, see G. A. Olah and A. Commeyras, J. Amer. Chem. Soc., 91, 2929 (1969). Parenthetical values are the depolarization factors taken as an average for three runs and are uncorrected; p, indicates polarized; dp, indicates depolarized. [b] Reference 12a. [c] Reference 12b. [d] Reference 12d. [e] Reference 12c.

The cmr shifts of the methyl carbons of ions 1–3 indicate that little charge is introduced into these carbons. The deshielding from their precursors (methyl chloride, bromide, and iodide) is 29.0, 25.8 and 23.0 ppm, respectively. These carbons are clearly remaining sp^3 hybridized. Thus most of the positive charge in dialkylhalonium ions is located at the halogen centers.

It is interesting to note that carbons attached to chlorine are more deshielded than those attached to bromine and iodine in homolog dialkylhalonium ions. This is probably because the larger halogen (e.g., iodine) can accommodate more charge than the smaller (e.g., chlorine) and also due to related magnetic shielding effects.

well with those shown in Table II for dimethyl selenide. When the Raman polarizer is arranged so that it passes only the perpendicular component of the incident beam, another depolarized signal at 561 cm^{-1} is observed due

(11) (a) R. Vogel-Högler, Acta Phys. Aust., 1, 311 (1947); (b) H. Siebert, Z. Anorg. Allg. Chem., 271, 65 (1953); (c) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, Van Nostrand, Princeton, N. J., 1945, p 315; (d) D. R. Allkins and P. J. Hendra, Spectrochim. Acta, 22, 2075 (1966).

(12) It is generally accepted that torsional barriers will lead to preferred C_{2v} conformations for molecules of the $(CH_3)_2X$ type. Furthermore, the molecular distribution of conformers is such that ir and Raman spectra for only those molecules at or near the torsional minima are observed (see, for example, ref 11c, pp 353-354).

(13) See ref 11c, pp 168-172.

Table IV. Alkylation of Benzene and Toluene (Ethylbenzne) with Dimethyl- and Diethylhalonium Fluoroantimonates in SO$_2$ClF

Alkylating agent	Aromatic	Temp, °C	Time, min	k_T/k_B	Isomer distribution (%)			Ortho/para
					Ortho	Meta	Para	
1	Toluene	25	10		46.6	27.2	26.7	1.75
		0	1		51.8	16.2	32.1	1.61
		−50	5		52.3	15.7	32.0	1.63
		−50	2		58.6	13.0	28.4	2.06
2	Toluene	−50	5		57.8	9.5	32.7	1.76
		−50	2		59.0	8.6	32.4	1.82
3	Toluene	25	10		46.2	15.6	38.1	1.27
		0	10		53.9	11.8	34.3	1.57
		−20	60		No reaction			
7	Benzene	−78	1	4.9	33.4	28.1	38.5	0.86
	Toluene	−78	2.5	4.8	31.4	24.6	44.0	0.75
	Ethylbenzene–toluene	−78	2.5	1.10	31.9	19.3	48.8	0.62
8	Benzene	−78	1	4.0	38.7	19.3	42.0	0.92
	Toluene	−78	5	4.5	36.0	18.2	45.8	0.78
	Ethylbenzene–toluene	−78	5	1.2	32.8	14.5	52.8	0.62
					(25.2)	(19.4)	(55.4)	(0.45)
9	Benzene	−45	5	4.1	44.0	10.2	45.8	0.96
	Toluene							

to the significant decrease in the intensity of the polarized line at 544 cm^{-1}. This signal correlates with the depolarized line at 602 cm^{-1} in the Raman spectrum of (CH$_3$)$_2$Se and, therefore, is assigned to the ν_{17} asymmetric C–Br–C stretching vibration of the dimethylbromonium ion. The ir spectrum displays four strong absorptions in the 700–200-cm^{-1} region. The ν_6 and ν_{17} absorptions were observed as strong bands at 551 and 535 cm^{-1}, respectively. The C–Br–C symmetric skeletal vibration ν_7 is observed at 285 cm^{-1} and the fluoroantimonate anions yield a broad band at 632 cm^{-1}.

The observation of three Raman and three ir active skeletal vibrations for 2, with two totally symmetric and one asymmetric, in accordance with the selection rules for the C_{2v} point group, and the correlation with the skeletal frequencies of dimethyl selenide indicate that the halogen atom in bromonium ion 2 is sp^3 hybridized and that the methyl groups maintain preferred conformations with torsional minima at a C_{2v} arrangement. The calculated C–Br–C bond angle using force constants obtained by Siebert[11b] for dimethyl selenide and the valence force equations of a triatomic molecule[14] is 108° 50′.

The Raman spectrum of dimethylchloronium ion does not parallel that observed for dimethyl sulfide well enough to suggest a significant correlation between their molecular symmetry.

The low energy of the symmetric bending vibration ν_7 (197 cm^{-1} for (CH$_3$)$_2$Te^{11d}) allows the observation of only the symmetric stretching vibration ν_6 for ion 3. However, the depolarized line observed for ion 3 at 511 cm^{-1} is nearly identical with that observed for the ν_6 skeletal mode of (CH$_3$)$_2$Te (526 cm^{-1}). This excellent correlation allows the assignment of this peak in the spectrum of ion 3 to the symmetric stretching vibration ν_6 for the C–I$^+$–C skeleton.

Isolation of Dimethylhalonium Fluoroantimonate Salts. Dimethylhalonium fluoroantimonate salts can be isolated under careful experimental conditions. Solutions of the ions were prepared by adding a slight excess of methyl halide[15] (1.1 : 1 mol ratio) in SO$_2$ at −78° to a

solution of the CH$_3$F→SbF$_5$ complex in SO$_2$ at −78° under dry nitrogen in a controlled atmosphere drybox. After addition of the excess methyl halide the solutions were stirred at −40° for 5 min at which point they were clear, colorless, and shown by nmr, Raman, and ir spectra (previously discussed) to contain only the desired dimethylhalonium ions and a small excess of the methyl halide. Subsequent evaporation of SO$_2$ and excess methyl halides leaves the fluffy, white crystalline (CH$_3$X$^+$CH$_3$)(SbF$_6^-$) salt in case of 3 (containing some CH$_3$X$^+$CH$_3$Sb$_2$F$_{11}^-$) and predominantly CH$_3$X$^+$CH$_3$ Sb$_2$F$_{11}^-$ in the case of 1 and 2.

A more convenient preparation of halonium salts was found by the reaction of alkyl halides, such as methyl bromide, with anhydrous fluoroantimonic acid (see Experimental Section). Dimethylbromonium fluoro-

$$CH_3Br(excess) + HF\text{-}SbF_5 \longrightarrow CH_3Br^+CH_3SbF_6^- + HBr$$

antimonate is a particularly stable halonium salt suitable for preparative use as a selective methylating agent (*vide infra*).

The dimethylhalonium ion salts are stable in a dry nitrogen atmosphere at room temperature and when redissolved in SO$_2$ they give nmr spectra identical with those previously described for dimethylhalonium ions prepared in solution. The fluoroantimonate salts 1–3 are very hygroscopic and exposure to atmospheric moisture leads to immediate hydrolysis. SO$_2$ and SO$_2$ClF seem to be the most convenient solvents for dialkylhalonium ions. As expected, dimethylhalonium salts are insoluble in many nonpolar organic solvents. With solvents of increased polarity (*e.g.*, CH$_3$NO$_2$, (CH$_3$)$_2$CO, etc.), the reactions of the halonium ion with the solvent appear to predominate at 25° (*vide infra*).

Alkylation of Aromatics with Dialkylhalonium Ions and Their Possible Role in Friedel–Crafts Alkylations. Alkylation of aromatic hydrocarbons, such as benzene, toluene, and ethylbenzene, with dimethyl- and diethylhalonium hexafluoroantimonates 1–3 and 7–9 in SO$_2$ClF solution takes place with ease. (Data are summarized in Table IV. All data are the average of at least three parallel experiments.) Ions 1 and 2 give similar results

(14) (a) V. A. Lachman, *J. Amer. Chem. Soc.*, 18, 374 (1986); (b) J. B. Dence and J. D. Roberts, *J. Org. Chem.*, 33, 1251 (1968).

(15) Solutions prepared in SO$_2$ by the addition of CH$_3$X to SbF$_5$–SO$_2$

(method 2) at −78° show the formation of some of the free halogen Br$_2$ and I$_2$ with CH$_3$Br and CH$_3$I, respectively.

Table V. Comparative Friedel–Crafts Methylation of Toluene

Methylating agent	Catalyst	Temp, °C	Time, min	Solvent	Isomer distribution, %			Ortho/para
					Ortho	Meta	Para	
CH_3F		25	10	SO_2ClF	44.3	29.4	26.3	1.68
		−78	10	SO_2ClF	47.2	21.8	31.1	1.52
		−78	5	SO_2ClF	47.6	22.4	30.0	1.53
		−78	0.2	SO_2ClF	53.6	18.5	27.9	1.92
CH_3OSO_2F		0	5	SO_2ClF	68.1	13.1	28.8	2.01
			10		52.3	17.2	30.5	1.21
			30		48.1	20.5	31.4	1.53
CH_3Cl	$AlCl_3$	13	78	CH_3NO_2	52	16	32	1.62
	$AlCl_3$	13	40	CH_3NO_2	53	15	32	1.66
	$SnCl_4$	17	102	CH_3NO_2	55	14	31	1.77
	$FeCl_3$	17	78		55	16	29	1.89
	$TiCl_4$	17	108		54	14	32	1.69
	$SbCl_5$	13	60		52	18	30	1.74
CH_3Br	$AlBr_3$	0	1		54	17	29	1.86
CH_3I	$AlBr_3$	0	900		48	12	40	1.21
CH_3I	$AgBF_4$	25	20	CH_3NO_2	56.8	11.8	31.4	1.81

Table VI. Comparative Friedel–Crafts Ethylation of Benzene and Toluene

Aromatic substrate	Ethylating agent	Catalyst	Temp, °C	Time, min	Solvent	k_T/k_B	% isomer distribution			Ortho/para
							Ortho	Meta	Para	
Toluene–benzene	EtF	SbF_5	−78	0.08	SO_2ClF	2.0	39.2	29.0	31.8	1.28
Toluene–benzene	CH_3CH_2-OSO_2F	SbF_5	0	0.5	SO_2ClF	2.1	41.2	32.5	26.3	1.56
	CH_3CH_2-OSO_2F	SbF_5	−78	0.5	SO_2ClF	2.5	43.1	28.9	28.0	1.53
Toluene	EtF	$FeCl_3$-CH_3NO_2	25	1440			52.5	18.5	29.0	1.81
Toluene–benzene	EtI	AgBF	25	0.2	CH_3NO_2	2.6	39.8	24.5	35.7	1.12
Toluene	EtI	$AgBF_4$	25	18	CH_3NO_2		39.3	24.5	36.2	1.09
	EtI	$FeCl_3$-CH_3NO_2	25	1440			45.5	15.5	39.0	1.17
Toluene	EtCl	$FeCl_3$-CH_3NO_2		1440			50.0	18.4	31.6	1.61
Toluene	EtBr	$FeCl_3$-CH_3NO_2	25	1440			55.7	14.4	29.9	1.86
	EtBr	$FeCl_3$-CH_3NO_2	Reflux	60			51.0	19.0	30.0	1.70
	EtBr	$FeCl_3$	Reflux	60			53.0	18.0	29.0	1.84
Toluene–benzene	$CH_2{=}CH_2$	$AlCl_3$	25	20	CH_3NO_2	1.7	47.4	27.4	28.8	1.64
Ethylbenzene–toluene	$CH_2{=}CH_2$	$AlCl_3$	25	20	CH_3NO_2	2.0	39.9	29.0	31.1	1.28
Toluene	$CH_2{=}CH_2$	$AlCl_3$	25	18	CH_3NO_2		47.4	27.8	28.4	1.64

Table VII. Alkylation of Benzene and Toluene with Trialkyloxonium Salts

	Solvent	Temp, °C	k_T/k_B	Ortho	Meta	Para	Ortho/para
$(CH_3)_3O^+BF_4^-$	FSO_3H-SbF_5	25		60	12	28	2.14
$(CH_3)_3O^+SbCl_6^-$		25		68	11	21	3.24
$(C_2H_5)_3O^+SbCl_6^-$		25	1.7	45	18	36	1.28

$$Ar + RX^+R\ SbF_6^- \longrightarrow ArR + RX + HSbF_6$$

1, R = CH_3; 7, R = C_2H_5, X = Cl
2, R = CH_3; 8, R = C_2H_5, X = Br
3, R = CH_3; 9, R = C_2H_5, X = I

of methylation and are quite reactive even at temperatures as low as −50°. Ion 3 is less reactive and alkylated benzene and toluene in SO_2ClF only when allowed to react at or above (under pressure) 0°. The isomer distributions in the methylation reactions with dialkylhalonium ions 1–3 show no significant differences from typical Friedel–Crafts methylations, as summarized in Tables V and VI.

Ethylation of toluene by ions 7–9 yields ethyltoluenes with ortho/para isomer ratios between 0.60 and 0.96. The ortho/para isomer ratios obtained for alkylation of toluene in all conventional Friedel–Crafts ethylations range from 1.09 to 1.84 (see Table V for data of typical reactions). A significant lowering in the ortho/para

isomer ratio in ethylations with triethylhalonium ions 7–9 is, however, observed. In electrophilic aromatic alkylations it is always difficult (or even impossible) to exclude isomerization processes affecting isomer distributions. These generally result in substantial increase of the amount of the meta isomer (at the expense of ortho and para isomers). Alkylations with dialkylhalonium salts are, however, less affected by isomerization and with the expected similar nature of the transition states (as indicated by the similarity of substrate selectivity as expressed by k_T/k_B and k_{ET}/k_T) a lowering of the ortho/para isomer ratio can be considered to reflect steric effects. Thus, for alkylation with dialkylhalonium ions 1–3 and 7–9 the decrease in the ortho/para isomer ratio is associated with increased steric hindrance at the ortho position in the alkylation reactions with dialkylhalonium fluoroantimonates.

For comparison we also found it possible to alkylate

benzene and toluene with trimethyl- and triethyloxonium salts (Meerwein salts) when carrying out the reactions in highly ionizing magic acid (FSO_3H–SbF_5) solution. Data summarized in Table VII show close similarity to those obtained with dialkylhalonium ions (Table IV).

The steric ortho effect observed for ethylation by ions **7–9** can be best interpreted as a result of displacement reaction by the aromatic on the bulky diethylhalonium ions. This can be envisioned to proceed through an S_N2 like transition state.

$$\text{ArH} + \; \overset{\displaystyle CH_3 \;\; H}{\underset{\displaystyle H}{\overset{\diagup\;\diagup}{C}}}\!\!-\!\!X^{+}\!\!\diagup^{\displaystyle Et} \quad SbF_6^{-} \;\rightleftharpoons$$

$$\left[\; HAr\text{---}\overset{\displaystyle CH_3 \;\; H}{\underset{\displaystyle H}{\overset{\diagup\;\diagup}{C}}}\text{---}X\!\!\diagdown^{\displaystyle Et} \;\right]^{+} SbF_6^{-} \;\rightleftharpoons$$

$$\left[\; Ar\!\!\diagup^{\displaystyle CH_2CH_3}_{\diagdown H} \;\right]^{+} SbF_6^{-} \; + \; CH_3CH_2X$$

$$\searrow \qquad \text{ArCH}_2\text{CH}_3 \; + \; HSbF_6$$
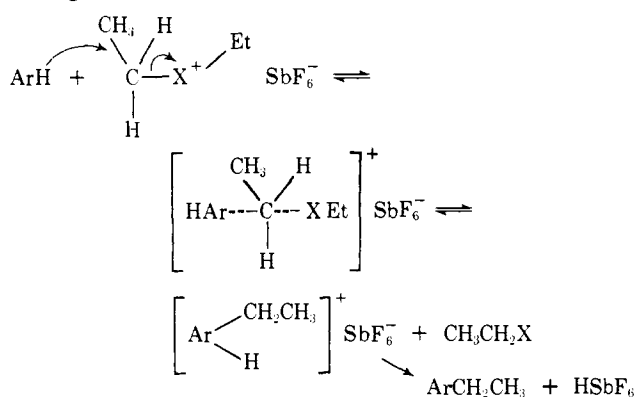
In the case of partial bond formation at a position ortho to an alkyl substituent in Ar, the transition state is subject to steric hindrance. This leads to the observed preference for the para substitution product in these ethylation reactions. The presence of an intermediate σ complex in the displacement reaction is indicated by the pmr spectra of the individual ethylation mixtures in the low nucleophilicity SO_2ClF solution at −78°. On quenching with base the ethylated aromatic is obtained in high yield.

That a steric effect is observed for the reactions of ion **7**, as compared with conventional Friedel–Crafts ethylation reactions, suggests that the active alkylating agents in the ethylation reactions of diethylhalonium ions and ethyl halides in conventional Friedel–Crafts reactions are different. It is probable that in Lewis acid halide catalyzed Friedel–Crafts ethylations, Lewis acid halide donor–acceptor complexes $C_2H_5X{\rightarrow}M_nX_z$ and/or ion pairs $C_2H_5^+M_nZ_{z+1}^-$ are the active ethylating agents. These at the same time are not significant in ethylations with diethylhalonium ions **7–9**, in SO_2ClF solution.

By analogy, the lack of variation of ortho/para isomer ratios for methylation by ions **1–3** and those of Friedel–Crafts methylation reactions indicate that steric hindrance to attack by the smaller ion $CH_3XCH_3^+$ and $CH_3^{\delta+}X{\rightarrow}M_n^{\delta-}X_z$ is similar. Alternatively, it is also possible that in all cases attack by the same methylating agent is occurring. Since the mechanism of alkylation by halonium ions **1–3** is expected to parallel that of ions **7–9**, the latter explanation is less probable. Other dialkylhalonium ions such as diisopropylbromonium and -chloronium ions also yield alkylated aromatics. In these reactions, however, dissociation equilibria play a more important role. The alkylation data obtained from the reaction of ions **1–3** and **7–9** provide evidence for *direct alkylation of aromatics by dialkylhalonium ions*. In addition, the data indicate that *dialkylhalonium ions are not necessarily involved as active alkylating agents in general Friedel–Crafts systems*, although some of the reported anomalous alkylation results, particu-
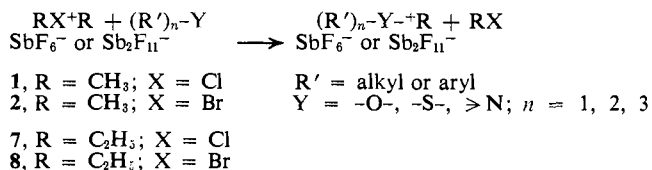
Table VIII. Onium Ions Obtained by Methylation and Ethylation of Heteroatom n-Donor Bases with Dimethyl(diethyl)halonium Fluoroantimonates[a,b]

Heteroorganic substrate	Methylated onium ion	CH_3Y^c	CH_3	CH_2	VH	HY	Aromatic	Ethylated onium ion	$CH_3\text{-}CH_2Y$	$CH_3\text{-}CH_2Y$	CH_3Y	CH_3	CH_2	CH	HY	Aromatic
$(CH_3)_2O$	$(CH_3)_3O^+$ **28**	4.30						$(CH_3)_2O^+C_2H_5$ **47**	4.12	1.27	3.98					
$(C_2H_5)_2O$	$(C_2H_5)_2O^+CH_3$ **29**	4.23	1.58	4.62				$(C_2H_5)_3O^+$ **48**	4.33	1.41						
CH_3OH	$CH_3O^+(CH_3)H$ **30**	3.68				9.42		$CH_3OH(C_2H_5)^+$ **49**	4.27	1.39	3.88				9.38	
H_2O	$CH_3OH_2^+$ **31**	4.13				9.50		$C_2H_5OH_2^+$ **50**	4.86	1.60					9.2	
$(CH_3)_2C{=}O$	$(CH_3)_2C{=}^+OCH_3$ **32**	4.80	3.94					$(CH_3)_2C{=}^+OC_2H_5$ **51**	5.02	2.05		3.92				
$(C_2H_5)_2C{=}O$	$(C_2H_5)_2C{=}^+OCH_3$ **33**	4.63	1.44	3.82				$(C_2H_5)_2C{=}^+OC_2H_5^+$ **52**	5.13	1.98		1.41				
$c\text{-}C_5H_8O^e$	$c\text{-}C_5H_8OCH_3^+$ **34**	4.86			3.18, 2.24			$c\text{-}C_5H_8OC_2H_5^+$ **53**	5.25	1.98			3.80			
$(C_6H_5)_2C{=}O$	$(C_6H_5)_2C{=}^+OCH_3{}^d$ **35**	3.83						$(C_6H_5)_2C{=}^+OC_2H_4{}^d$ **54**	4.38	1.08						7.7–8.0
CH_3CHO	$CH_3CH{=}^+OCH_3$ **36**	5.80	3.51		9.62			$CH_3CH{=}^+OC_2H_4$ **55**	5.21	1.86		3.46		9.60		
C_6H_5CHO	$C_6H_5CH{=}^+OCH_3$ **37**	4.12			9.62			$C_6H_5CH{=}^+OC_2H_4$ **56**	5.58	1.92				9.95		7.7–8.0
$HCOOH$	$HC(OCH_3^+)OH$ **38** syn	4.25			8.76	12.54		$HC(OC_2H_5^+)OH$ **57** syn	4.54	1.92				8.62	13.06	
	anti	4.18			8.70	12.54		anti	5.00	2.06				8.42	13.06	
CH_3COOH	$CH_3C(OCH_3^+)OH$ **39**	4.32	2.64			12.84		$CH_3C(OC_2H_5^+)OH$ **58**	4.95	1.48		2.75			12.47	
CH_3NO_2	$CH_3NO_2^+CH_3$ **40**	4.67	5.04					$CH_3NO_2^+C_2H_5$ **59**	5.15	1.70		5.02				
$CH_3CH_2CH_2NO_2$	$CH_3CH_2CH_2NO_2^+CH_3$ **41**	4.67	0.98	5.23, 2.18				$CH_3CH_2CH_2NO_2^+C_2H_5$ **60**	5.14	1.70		0.99	5.20, 2.16			
$C_6H_5NO_2$	$C_6H_5NO_2^+CH_3{}^d$ **42**	4.65			3.53		7.6–8.2	$C_6H_5NO_2^+C_2H_5{}^d$ **61**	5.12	1.69						7.6–8.2
$((CH_3)_2CH)_2S$	$((CH_3)CH)_2S^+CH_3$ **43**	2.52	1.38	3.18				$[(CH_3)CH]_2S^+C_2H_5$ **62**	3.03	1.45		1.33		3.57		
$(C_2H_5)_2S$	$(C_2H_5)_2S^+CH_3$ **44**	2.76	1.38					$(C_2H_5)_3S^+$ **63**	3.26	1.40						
$t\text{-}BuSH$	$t\text{-}BuS^+HCH_3$ **45**	2.99	1.62			6.16		$t\text{-}BuS^+C_2H_4$ **64**	3.58	1.54		1.63			6.08	
$(C_2H_5)_3N$	$(C_2H_5)_3N^+CH_3$ **46**	2.97	1.23	3.21				$(C_2H_5)_4N^+$ **65**	4.81	1.05						

[a] Spectra were recorded on a Varian 56/60A nmr spectrometer and are reported from external capillary TMS. Usual expected multiplicities and coupling constants are observed. Many of the ions were obtained and reported previously in our alkylation studies with methyl and ethyl fluoroantimonates: G. A. Olah, *et al.*, *J. Amer. Chem. Soc.*, **94**, 156 (1972). [b] Identical spectra were obtained from alkylations with RClR and RBrR salts. [c] Y = heteroatom. [d] Alkylation of the n-donor site occurs at low temperature. [e] $c\text{-}C_5H_8O$, cyclopentanone.

larly with alkyl iodides, could be attributed to reaction conditions favoring dialkylhalonium ion formation.

Alkylation of Heteroorganic Compounds. Dimethyl- (1-3) and diethyl- (7-9) halonium ions are a particularly effective new class of alkylating agents for heteroorganic compounds. Table VII shows the onium ions 28-66 and their pmr data, obtained from alkylation of ethers, alcohols, water, ketones, aldehydes, carboxylic acids as well as nitro, sulfur, and amino compounds with dialkylhalonium ions 1 or 2 and 7 or 8. In general, reactions were carried out by addition of an aliquot portion of halonium ion in SO₂ at ca. −60° to a

$$RX^+R + (R')_n-Y \quad\quad (R')_n-Y-^+R + RX$$
$$SbF_6^- \text{ or } Sb_2F_{11}^- \longrightarrow SbF_6^- \text{ or } Sb_2F_{11}^-$$

1, R = CH₃; X = Cl   R' = alkyl or aryl
2, R = CH₃; X = Br   Y = -O-, -S-, >N; n = 1, 2, 3
7, R = C₂H₅; X = Cl
8, R = C₂H₅; X = Br

calculated amount of the heteroorganic n-base substrate at −78°. At least two parallel experiments with each system, one with alkylating agent in excess and one with n-base substrate in excess, were carried out. Alkylation of n-donor bases by dialkylchloronium and -bromonium ions (1-2 and 7-8) appears to be indiscriminative, but mild. Dialkyliodonium ions 3 and 9 do not react with n-donor bases in SO₂ or SO₂ClF solution at temperatures varied from −78 to 0°.

Pmr spectra obtained for solutions prepared by addition of ions 1 or 2 and 7 or 8 in SO₂ to alcohols (water) and ethers are identical with spectra reported for the protonation of the corresponding ethers[16] (methanol[17]) and the alkylation of the corresponding ethers,[18] respectively. In each case alkylation leads to formation of oxonium ions quantitatively. No exchange between excess alkylating agents and oxonium ions 28-31 and 47-50 was observed on the nmr time scale between 0 and −78°.

When aldehydes, ketones, and carboxylic acids were added to SO₂ solutions of ions 1, 2, 7, and 8 immediate and exclusive alkylation on oxygen occurs with formation of oxonium ions 32-39 and 51-58. In the cases of the alkylation reactions of unsymmetrically substituted ketones, aldehydes, and carboxylic acids the formation of at least two isomeric forms of the resulting oxonium ions is observed.

The chemical shifts, multiplicities, and coupling constants of the pmr spectra of oxonium ions 32-39 and 51-58 are very similar to those obtained from protonation of the same aldehydes,[19] ketones,[20] and carboxylic acids.[21] Particularly diagnostic in the case of aldehydes is the chemical shift of the proton on the carbonyl carbon. These range from δ 9.42 to 9.95 for ions 36, 37, 55, and 56. For ions 36 and 55 these signals appear as 1 H quartets (J = 3.5 Hz). Similarly, for alkylated carboxylic acids 38 and 39 and 57 and 58 the

(16) G. A. Olah and D. H. O'Brien, J. Amer. Chem. Soc., 89, 1725 (1967).
(17) G. A. Olah, J. Sommer, and E. Namanworth, J. Amer. Chem. Soc., 89, 3574 (1967).
(18) B. M. Ramsey and R. W. Taft, J. Amer. Chem. Soc., 88, 3058 (1966), and references therein.
(19) G. A. Olah, D. H. O'Brien, and M. Calin, J. Amer. Chem. Soc., 89, 3582 (1967).
(20) G. A. Olah, M. Calin, and D. H. O'Brien, J. Amer. Chem. Soc., 89, 3586 (1967).
(21) G. A. Olah and A. M. White, J. Amer. Chem. Soc., 89, 3591 (1967).

OH protons appear between δ 12.54 and 13.06. The chemical shifts of the CH₃Y methyl and CH₃CH₂Y ethyl groups in ions 32-39 and 51-58, respectively, are to slightly lower field than in the oxonium ions 28-31 and 47-49, as expected.

It should be mentioned that most tertiary oxonium ions were first prepared in the pioneering studies of Meerwein.[22,23] Secondary and primary oxonium ions were subsequently studied,[16-21] with the advent of nmr spectroscopy, mostly in solution.

The alkylation of tert-butyl mercaptan and diethyl and diisopropyl sulfides with ions 1, 2, 7, and 8 yields sulfonium ions 43-45 and 62-64, respectively. The pmr spectra of these sulfonium ions correlate very well with those reported previously for protonated mercaptans and thioethers.[24]

The reaction of triethylamine with ions 1, 2, 7, and 8 yields the corresponding tetralkylammonium ions 46 and 65, respectively. Although alkylation was obvious from the spectra of ions 46 and 65, pronounced broadening of peaks characteristic of long-range coupling is observed.

Upon addition of nitroalkyl or -aryl compounds to solutions of excess ions 1, 2, 7, and 8 pmr spectra of the solutions obtained are consistent with the formation of ions 40-42 and 59-61, respectively. These alkylalkoxyoxonium cations are isoelectronic with carboxylic acid esters and are important primarily because of their mechanistic implications for alkylation of nitroaromatic compounds.

Alkylation and Polymerization of Alkenes. Dialkylhalonium ions, as discussed, are effective alkylating agents for aromatics and various n-donor bases. A study of alkylations of olefins such as 1-butene, 2-butene, and 2-methylpropene (iosbutylene) by dimethylbromonium fluoroantimonate in sulfur dioxide solution has also been carried out. Alkylation does, indeed, take place, but under the reaction conditions, the initially formed alkylcarbenium ions are not sufficiently stable to be observed. The reaction generally proceeds rapidly yielding polymeric materials. These results and the possible involvement of dialkylhalonium ions in Friedel–Crafts polymerization of alkenes with systems such as AlBr₃–CH₃Br is reported elsewhere.[25]

Dialkylhalonium Ions in CH₃Br(I)–AlBr₃(AlI₃) Systems. The observation of dialkylhalonium ion formation in alkyl halide–antimony pentafluoride systems raises the question of their involvement in Friedel–Crafts alkylations and polymerizations. Alkyl halide–Lewis acid halide complexes (as well the related alkylcarbenium ions) can obviously alkylate not only aromatic or aliphatic hydrocarbons but also excess alkyl halides (other than fluorides) to form dialkylhalonium ions. The 1:1 or 1:2 alkyl halide–Lewis acid complexes therefore would be expected to contain 2:1 or 2:2 dialkylhalonium ion complexes.

DeHaan and Brown,[26] indeed, were able to show, based on kinetic evidence, that in the methyl bromide–

(22) H. Meerwein, Chem. Ber., 100, CV (1967), and references given therein.
(23) H. Perst, "Oxonium Ions," Verlag Chemie, Weinheim/Bergstr., Germany, 1971, and references given therein.
(24) G. A. Olah, D. H. O'Brien, and C. U. Pittman, Jr., J. Amer. Chem. Soc., 89, 2996 (1967).
(25) G. A. Olah, Makromol. Chem., in press.
(26) F. DeHaan, H. C. Brown, D. C. Conway, and M. G. Gibby, J. Amer. Chem. Soc., 91, 4854 (1969).

$$\begin{array}{cc} \overset{\delta^+}{R}\overset{\delta^-}{Cl}\rightarrow AlCl_3 & \overset{\delta^+}{R}\overset{\delta^-}{Cl}\rightarrow Al_2Cl_6 \\ 1:1 & 1:2 \\ R\bar{Cl}^+{-}R\ Cl\rightarrow AlCl_3^- & RCl^+{-}R\ Cl\rightarrow Al_2Cl_6^- \\ 2:1 & 2:2 \end{array}$$

gallium bromide (and related chloride systems) the dimethylbromonium (-chloronium) ion is involved.

Having prepared and studied a series of dialkylhalonium complexes, we therefore felt of interest to extend our studies to common Friedel–Crafts alkylation systems, such as the methyl halide–aluminum halide complexes, in order to directly determine the possible contribution of dimethylhalonium ions.

$AlBr_3$ dissolves in CH_3Br and gives a clear solution which is stable at room temperature. Walker,[27] from vapor pressure measurements, found the composition of the liquid phase to be $CH_3Br-AlBr_3:CH_3Br-Al_2Br_6 =$ 0.678:0.288 = 0.033 (at 23.8°). By the same technique Brown and Wallace[28] established at −78° the 1:1 complex. Ir spectra of this complex were recorded by Perkampus and Baumgarten[29] at −196° and Kinsella and Coward[30] at room temperature. Raman investigations were carried out by Rice and Bold.[31] However, no clear conclusions were reached from these studies.

We now studied with nmr spectroscopy the 1:1 CH_3-$Br-AlBr_3$ complex 66 and the related 1:1 AlI_3-CH_3I complex 67 (the $AlCl_3-CH_3Cl$ complex is less suitable, because of the lower boiling point of methyl chloride and difficulties to handle the 1:1 complex at atmospheric pressure).

The 1:1 $CH_3Br-AlBr_3$ complex showed (neat) a singlet pmr absorption at δ 4.0 (in SO_2ClF solution at −40° δ 3.40). The corresponding 1:1 CH_3I-AlI_3 complex showed a corresponding singlet at δ 3.65. The chemical shifts of both complexes show close resemblance to those observed for ions 2 and 3, respectively, and are different from the well-defined $CH_3F{\rightarrow}SbF_5$ donor-acceptor complex (δ 5.56 in SO_2) in which case no dimethylfluoronium ion formation is involved. These data seem to indicate that the 1:1 $CH_3Br-AlBr_3$ (or CH_3I-AlI_3) complexes, 66 and 67, contain at least substantial contribution from the corresponding dimethylhalonium ions 2 (and 3) in the equilibrating systems.

$$2CH_3Br + Al_2Br_6 \rightleftharpoons$$

$$CH_3Br{\rightarrow}Al_2Br_6 + CH_3Br \rightleftharpoons CH_3^+BrCH_3Al_2Br_7^-$$

$$2(CH_3Br{\rightarrow}AlBr_3)$$

The chemical behavior of 66 and 67 is indicative of the equilibriums systems. When treated with typical n donors such as nitromethane, acetone, methyl benzoate, or propionaldehyde, which were n alkylated with 2 or 3, 66 and 67 in sharp contrast give no alkylation products, but form the corresponding $AlBr_3$ (or AlI_3) donor-acceptor complexes. This is in accordance with transfer of aluminum halide from the methyl halide donor-acceptor complexes to the stronger n-donor bases, thus shifting the equilibrium in this direction. At the same time 66 and 67 readily alkylate aromatics (or olefins). Hexamethylbenzene, for example, with excess neat 66, forms the heptamethylbenzenium bromoaluminate 68.[32]

Conclusions

Preparation as well as spectroscopic study and investigation of the alkylating ability of dialkylhalonium ions established their structure, relative stability, as well as their chemical reactivity. In general, the relative stability of dialkylhalonium ions follows the order $RI^+R > RBr^+R > RCl^+R$, indicating that the larger halogen atom is more capable to accommodate charge. The alkylating ability, on the other hand, is generally inversely proportional to the stability of the ions.

Dialkylhalonium ions when formed under regular Friedel–Crafts conditions exchange readily with excess alkyl halides and also dissociate according to the equilibrium

$$R-X^+{-}R\ M_xY_y^- \rightleftharpoons RX + RX \longrightarrow M_xY_{y-1}$$

The preparation and isolation of dialkylhalonium fluoroantimonate salts made available a new class of reactive onium ions. The chemical reactivity as well as synthetic application of dialkylhalonium ions have been demonstrated in alkylation of π-donor aromatics and olefins, as well a wide variety of n-donor bases. In comparison with Meerwein's trialkyloxonium ions,[33] the synthetic advantage of alkylation with dialkylhalonium lies in their greater alkylating ability and at the same selectivity, due to the possibility of changing the nature of the halogen onium centers from the more stable and therefore less reactive iodonium to bromonium to chloronium ions.

Experimental Section

Materials. All the alkyl halides were commercially available in high purity and were used without further purification. Antimony pentafluoride and anlydrous fluoroantimonic acid (Cationics) were Spectrograde quality. Sulfur dioxide was obtained from Baker Chemical.

Preparation of Dialkylhalonium Ions. (A) Solutions of the ions were prepared by adding a slight excess of alkyl halide (1.1:1 mol ratio) in SO_2 at −78° to a solution of the methyl or ethyl fluoroantimonate in SO_2 at −78°. After addition of the excess alkyl halide the solutions were stirred at −40° for 5 min at which point clear solutions were obtained. (B) Solutions of the symmetrical halonium ions were prepared by addition of excess alkyl halide in SO_2 to antimony pentafluoride in SO_2 at −78°. Upon warming, with efficient stirring, clear solutions were obtained. Dialkylhalonium fluoroantimonate salts can be isolated from these solutions by evaporating SO_2. Isolatable halonium ion salts were, however, most conveniently prepared from the corresponding halides and fluoroantimonic acid.

Isolation of Dimethylbromonium Hexafluoroantimonate Salt.

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(32) Identical with the reported spectrum by W. v. E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. E. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958), for the tetrachloroaluminate salt.
(33) H. Meerwein in "Methoden der Organischen Chemie," 4th ed, Vol. 6, No. 3, D. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1965, pp 329–363.

(All operations were conducted in an apparatus protected from atmospheric moisture.) In a flame-dried, 250-ml round-bottom flask is condensed 100 ml (170 g) of methyl bromide. The reaction flask is cooled to $-20°$. Anhydrous fluoroantimonic acid, 71 g (0.3 mol), is added dropwise with vigorous agitation over a period of 20 min. The reaction mixture is agitated an additional 40 min and excess methyl bromide is removed under vacuum through a glass tube with a frit end. The light-colored salt is washed with 50 ml of methyl bromide and dried under vacuum. The yield is 100 g, 97% of theoretical, mp $\sim110°$ dec. The product gives correct analysis and nmr spectra. It is stable at room temperature and can be stored.

Elemental Analyses. Ion salt **3** had mp 153–157° (dec with evolution of I_2). *Anal.* Calcd for $C_2H_6SbF_6I$: C, 6.12; H, 1.54; Sb, 31.00; F, 29.02; I, 32.31. Found: C, 6.58; H, 1.37; Sb, 30.57; F, 29.38; I, 32.08. Melting points determined for samples in both open and sealed capillaries were identical: **2**, mp 74–79° dec. *Anal.* Calcd for $C_2H_6Sb_2F_{11}Br$: C, 4.27; H, 1.07; Sb, 43.28; F, 37.15; Br, 14.22. Found: C, 5.61; H, 1.52, Sb, 39.84; F, 37.46; Br, 15.82. Calcd for $C_2H_6SbF_6Br$: C, 6.95; H, 1.75; Sb, 35.22; F, 32.97; Br, 23.11. Ion salt **1** had mp 108–113° (decomposing at 116° with gas evolution). *Anal.* Calcd for $C_2H_6Sb_2F_{11}Cl$: C, 4.64; H, 1.16; Sb 47.00; F, 40.43; Cl, 6.84. Found: C, 5.89; H, 1.51; Sb, 40.93; F, 37.98; Cl, 7.12. Calcd for $C_2H_6SbF_6Cl$: C, 7.97; H, 2.01; Sb, 40.41; F, 37.84; Cl, 11.77. The discrepancies in the calculated and found analysis of salts **1** and **2** are easily accounted for by considering the presence of a small amount of hexafluoroantimonate anion. The presence of $Sb_2F_{11}^-$ anions in these salts is substantiated by the ^{19}F nmr spectra of the isolated salts in SO_2 solutions in which signals characteristic of this anion are observed. This question was discussed previously in our work.[34]

Nmr Spectra. A Varian Associates Model A56/60A nmr spec-

trometer equipped with a variable-temperature probe was used for ^1H and ^{19}F nmr spectra. Proton coupling constants are believed accurate to ±0.1 Hz. Unless otherwise indicated, proton chemical shifts (δ) are in SO_2 solvent from external capillary TMS. Fourier transform carbon-13 nmr spectra were recorded on a Varian Associates Model XL-100 nmr spectrometer. Experimental details on obtaining carbon-13 spectra have been previously reported.[35]

Laser Raman and Ir Spectra. Raman spectra were obtained on a Cary 81 Raman spectrometer with laser source (50 mW gas laser using the 6328 Å He Ne line). The detailed experimental conditions have been previously reported.[34] Ir spectra were recorded as Nujol and Fluorolube mulls on ITRAN and KRS-5 plates with a Beckman IR-10 spectrometer. All manipulations were carried out in a drybox.

Alkylation of Aromatics. Solutions of the ions **1–3** and **7–9** (*ca.* 1 *M*) were prepared as described in SO_2ClF; an approximate 0.5-ml aliquot of the resulting solution was added with vigorous stirring to an approximate 10 mol excess of toluene in SO_2ClF. At the completion of the reaction, a 0.25-ml portion of the mixture was quenched with *ca.* 30 ml of a saturated solution of sodium carbonate and extracted with ether. Glc of the resulting ether solutions utilizing a Perkin-Elmer 226 gas chromatograph in conjunction with Infotronics CRS-1 Digital Chromotograph Readout System was used to obtain the isomer distribution of the xylenes formed.

Alkylation of n-Donor Substrates. In general, reactions were performed by addition of an aliquot portion of halonium ion in SO_2 at *ca.* $-60°$ to a calculated amount of the heteroorganic n-base substrate at $-78°$. The solutions then were allowed to warm up to $-15°$ for about 5 min and cooled back to $-60°$, and onium ions summarized in Table VII were identified by nmr spectroscopy.

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The Crystal Structure of Ferrocenyldiphenylcyclopropenium Tetrafluoroborate, a Stable Carbonium Ion Salt

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Abstract: The crystal and molecular structure of ferrocenyldiphenylcyclopropenium tetrafluoroborate has been determined by an X-ray diffraction study of a single crystal specimen. The monoclinic cell, space group $P2_1/c$, with $a = 8.219$ (3), $b = 14.708$ (3), and $c = 17.857$ (3) Å and $\beta = 103.60$ (5)°, contains four formula units ($C_{25}H_{19}$-$FeBF_4$); the calculated X-ray density is 1.53 g/cm.^{3} The structure was refined to a weighted R_2 factor of 0.046 and $R = 0.057$. Of the 2003 measured reflections, the number with nonzero weight was 1410. The structure consists of a $C_{25}H_{19}Fe$ cation and a BF_4 anion. The structure and stability of the cation are consistent with interaction between iron d orbitals and empty orbitals of the cyclopropenium moiety.

A lthough a wide variety of carbonium ions are known to be stable in solution, the number which have been isolated as stable solids is much smaller.[1] One such stable solid is the carbonium ion salt: ferrocenyldiphenylcyclopropenium tetrafluoroborate, the crystal and molecular structure of which we report here. The factors stabilizing the carbonium ion center in α-ferrocenyl cations have been the subject of study and debate for some time. It has been argued by some[2] that conjugation with the π electrons is the source of the un-

usual stability of α-ferrocenyl cations, while others[3–6] have suggested that direct interaction of nonbonding e_{2g} metal orbital electrons with the carbonium ion orbital leads to stabilization. The relative merits of these two points of view have been reviewed,[7] and recently the structure of the ferrocenylmethyl cation has

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