Friedel–Crafts Chemistry. V.[1a] Isolation and Carbon-13 Nuclear Magnetic Resonance and Laser Raman Spectroscopic Study of Dimethylhalonium Fluoroantimonates[1b]

Sir:

The physical properties and behavior of diphenyliodonium salts have been extensively investigated and include ultraviolet,[2] infrared,[3] and pmr spectra,[4] ion association,[5] acidity and basicity,[6] polarographic reduction,[7] and crystallographic[8] studies. Iodonium betaines[9] and acetylinic iodonium salts[10] have also been synthesized and studied. However, previous attempts to prepare aliphatic iodonium salts[11] were unsuccessful and Dence and Roberts[11b] suggested that this may reflect "an inherent reactivity or thermodynamic instability of these systems" that is not obvious in the aromatic series. They also described alternate and unattempted pathways to alkyliodonium salts that could possibly be used to overcome the suspected barriers to stability. Among those routes mentioned, the reaction of a carbonium ion with an appropriate iodide seemed to be the most tenable.

Since we have reported already[1] the pmr spectroscopic detection of dialkylhalonium ions prepared in a similar fashion in solution by alkylation reactions 1 and 2, and have suggested their possible importance in Friedel–Crafts reactions, we were intrigued with the possibility of isolating stable dialkylhalonium ion salts.

$$\mathrm{RX} + \mathrm{SbF_5{\leftarrow}SO_2} \rightleftharpoons [\mathrm{RX{\rightarrow}SbF_5}] + \mathrm{RX{\rightarrow}RXR^+\,(SO_2)} + \mathrm{SbF_5X^-\,(SO_2)} \quad (1)$$

$$\mathrm{CH_3FSbF_5} + \mathrm{RX} \longrightarrow \mathrm{CH_3XR^+\,(SO_2)} + \mathrm{SbF_6^-\,(SO_2)} \quad (2)$$

We now wish to report the isolation and characterization of dimethyliodonium (**1**), -bromonium (**2**), and -chloronium (**3**) fluoroantimonate salts.

$CH_3ICH_3^+SbF_6^-$	$CH_3BrCH_3^+Sb_2F_{11}^-$	$CH_3ClCH_3^+Sb_2F_{11}^-$
1	**2**	**3**

Solutions of the ions were prepared by adding a slight excess of methyl halide[12] (1.1–1 mol ratio) in SO_2 at −78° to a solution of the $CF_3F–SbF_5$ complex[13] in SO_2 at −78° under dry nitrogen in a controlled atmosphere drybox. After addition of the excess alkyl halide the solutions were stirred at −40° for ~5 min at which point they were clear, colorless, and shown by nmr,[1] Raman, and ir spectra (*vide infra*) to contain only the desired dialkylhalonium ions and a small excess of alkyl halide. On standing, evaporation of the SO_2 and excess halides leaves fluffy white crystalline $[CH_3–X–CH_3]^+[SbF_6^-]$ salt in the I case and a mixture of $[CH_3–X–CH_3]^+[SbF_6^-]$ and predominantly $[CH_3–X–CH_3]^+[Sb_2F_{11}^-]$ in the cases of **2** and **3**.[14]

The dimethylhalonium ion salts are stable in a dry nitrogen atmosphere at room temperature and when redissolved in SO_2 they yield nmr spectra identical with those previously described[1] for dimethylhalonium ions. The fluoroantimonate salts **1–3** are very hygroscopic and exposure to atmospheric moisture leads to immediate hydrolysis. As expected, dimethylhalonium salts are insoluble in many nonpolar organic solvents but, with solvents of increased polarity [*e.g.*, CH_3NO_2, $(CH_3)_2C{=}O$, etc.], the irreversible reactions of the halonium ion with the solvent appear to predominate at 25°. They are soluble in and apparently unreactive toward SO_2 which was used in most of their studies. To pursue our study on the structure of the isolated dimethylhalonium ions we have obtained the carbon-13 nmr spectra in SO_2 solution.

Table I. Carbon-13 Nuclear Magnetic Resonance Shifts of Methyl Halides and Dialkylhalonium Ion[a]

Ion	δ ^{13}C halonium ion ($J_{^{13}C-H}$, Hz)	δ ^{13}C CH_3X precursor ($J_{^{13}C-H}$, Hz)	$\Delta\delta$ ^{13}C ($\Delta J_{^{13}C-H}$, Hz)
1	184.3 (158)	213.3 (155)	29.0 (3)
2	156.2 (162)	182.0 (152)	25.8 (10)
3	144.9 (169)	167.5 (154)	23.5 (6)

[a] In parts per million relative to CS_2; ^{13}C nmr spectra were recorded from enriched (25%) samples, prepared by reaction 2, by the indor method. Chemical shifts of excess CH_3X precursor observed in solutions of the dialkylhalonium ions were used in computing $\Delta\delta$.

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(1) (a) Friedel–Crafts Chemistry. IV: G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2113 (1969); (b) presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969; Abstract No. ORGN 110.

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(7) (a) T. L. Khotsyanova, *Kristallografiya*, **2**, 51 (1957); (b) *Chem. Abstr.*, **82**, 1704 (1958); (c) T. L. Khotsyanova, *Kristallografiya*, **2**, 384 (1957); (d) *Chem. Abstr.*, **52**, 3457 (1958); (e) Yu. T. Struchkov and T. L. Khotsyanova, *Bull. Acad. Sci. USSR, Div. Chem. Sci., Engl. Trans.*, 771 (1960).

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(9) (a) O. Neilands and G. Vanage, *Proc. Acad. Sci. USSR*, **129**, 983 (1959); **131**, 425 (1960); **141**, 1232 (1961); (b) O. Neilands and B. Karele, *J. Org. Chem. USSR*, **2**, 491 (1966).

(10) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **30**, 1930 (1965).

(11) (a) V. A. Lachman, *Amer. Chem. J.*, **18**, 374 (1896); (b) J. B. Dence and J. D. Roberts, *J. Org. Chem.*, **33**, 1251 (1968).

(12) Solutions prepared in SO_2 by the addition of $CH_3–X$ to $SbF_5{\leftarrow}SO_2$ (reaction 1) at −78° show the formation of some of the free halogen Br_2 and I_2 with CH_3Br and CH_3I, respectively. We attribute these results to side reactions of the SbF_5X^- anions. When reaction 2 is used, the formation of the stable SbF_6^- and/or $Sb_2F_{11}^-$ anions occurs leading to relatively high purity solutions of the halonium ion fluoroantimonate salts in SO_2.

(13) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91**, 2112 (1969).

(14) **Elemental Analysis.** Compound **1** 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. Compound **3** had mp 108–113° dec at 116° with the evolution of a gas. *Anal.* Calcd for $C_2H_6Sb_2F_{11}Cl$: C, 4.64; H, 1.16; Sb, 47.00; F, 40.34; 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 **2** and **3** 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. The problem of the gegenion formed upon ionization in SbF_5 was recently clarified by Gillespie [J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, **47**, 1655 (1969)] as well as in our continued work [A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **90**, 2929 (1968)]. In the case of salt **1**, the presence of large excess nucleophile, CH_3I, throughout the evaporation step prevents the formation of the $Sb_2F_{11}^-$ anion.

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

Compd	ν_7 C–X–C deformation	ν_6 [ν_{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)
$(CH_3)TeCH_3$ (neat)[d]	198	526 (dp)	2810, 2923 (p), 3000 (dp)
$CH_3CH_2SCH_2CH_3$ (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,
(SO_2)		706 [$\delta(\Delta\nu)$ = 25 cm^{-1}]	2869, 2969
CH_3Br (neat)[e]		611	2861, 2972, 3055.8,
(SO_2)		595 [$\delta(\Delta\nu)$ = 15 cm^{-1}]	2869, 2969, ?
CH_3I (neat)[e]		532.8	2861, 2969.8, 3060.6,
(SO_2)		527 [$\delta(\Delta\nu)$ = 6 cm^{-1}]	2867, 2968, ?

[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 15a. [c] Reference 15b. [d] Reference 15d. [e] Reference 15c.

Table I shows the ^{13}C nmr shifts for halonium ions **1**–**3** with related $\Delta\delta$'s for precursor methyl halides.

Long-range H_1–C_2–X–$^{13}C_3$ coupling was observed in each case ($J_{^{13}C_3-H_1} \sim$ 1–2 Hz) with spectral patterns for ^{13}C enriched samples of **1** and **3** nearly identical with that described previously for **2**.

The nmr data indicate that although the methyl carbons are deshielded by 23–29 ppm relative to the precursors there is no significant variation in $\Delta\delta$ ^{13}C for the dimethylhalonium ions *vs.* their methyl halide precursors. Thus the methyl groups of halonium ions **1**–**3** share approximately the same increase in positive charge relative to CH_3X regardless of the halogen atom. The order of reactivity suggested by chemical shifts observed for the methyl groups in halonium ions **1**–**3**, however, is Cl > Br > I, as observed in their alkylation reactions (to be reported).

Raman data of the dialkylhalonium ions studied are shown in Table II along with data observed for isoelectronic models both neat[15] and in SO_2 solution. An additional intense line at 600 cm^{-1} is observed for solutions of ions **1**–**3** (in excess CH_3X and SO_2) and is characteristic of the $SbF_6{}^-$ anion. Ions $[CH_3XCH_3]^+$ can exist in either a linear or bent conformation. On the basis of energetic considerations and the well-established geometry of isoelectronic dimethylcalconide models[15d] it is expected that dialkylhalonium ions exist with 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 preferred conformations as anticipated.[15a,b,d,16] 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.[15a,b,d,16,17]

The strong, polarized lines assigned to the ν_7 and ν_6 vibrations of the dimethylbromonium ion correlate very well with those shown in Table II for dimethylselenide. 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 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 $(CH_3)_2Se$ 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}.[18]

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 C_{2v} point group, and the correlation with the skeletal frequencies of dimethylselenide 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[15b] for dimethylselenide and the valence force equations of a triatomic molecule[11] 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 (198 cm^{-1} for $(CH_3)_2Te$[15d]) allows the observation of only the symmetric stretching vibration ν_6 for ion **1**. However, the depolarized line observed for ion **1** at 511 cm^{-1} is nearly identical with that observed for the ν_6

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

(16) It is generally accepted that torsional barriers will lead to preferred C_{2v} conformations for molecules of the $(CH_3)_2\ddot{X}$: 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 15a,b,d, and also 15c, pp 353–354].

(17) See ref 15c, pp 168–172.

(18) Ir spectra were recorded as Nujol and Fluorolube mulls on ITRAN and KRS-5 plates with a Beckman IR-10 spectrophotometer. All manipulations were carried out in a drybox.

skeletal mode of $(CH_3)_2Te$ (526 cm^{-1}). This excellent correlation allows the assignment of this peak in the spectrum of ion **1** to the symmetric stretching vibration ν_6 for the C–I$^+$–C skeleton.

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A New Method of Forming the Carbon–Silicon Bond. Reductive Silylation of Aromatic Acids

Sir:

It is well recognized that only a limited number of chemical reagents are available which can bring about the reduction of a carboxyl group.[1] Previously[2,3] we described the potency of certain trichlorosilane–tertiary amine combinations as reducing agents. We now wish to report a novel reaction in which the latter effects the reduction of benzoic acid and certain of its derivatives to benzylic trichlorosilanes in good yields.

The overall process, which can again be termed a "reductive silylation,"[3] can be represented as follows

$$RCO_2H + SiHCl_3 + R_3N \xrightarrow[\Delta]{CH_3CN} RCH_2SiCl_3 + R_3\overset{+}{N}H\overset{-}{Cl} + (SiCl_2O)_x$$

In a typical experiment, 1 equiv of benzoic acid and 5 equiv of trichlorosilane were dissolved in 100 ml of acetonitrile and refluxed for 1 hr.[4] Two equivalents of tri-*n*-propylamine was added at this point and the resulting mixture was refluxed at 79–86° for 14 hr. Treatment with dry ether caused the precipitation of tri-*n*-propylamine hydrochloride (95%). Distillation of the filtrate gave benzyltrichlorosilane (58%) boiling at 82–84° (8 mm). The pot residue was a resinous material whose ir spectrum was dominated by Si–O absorption at 8.5–9.5 μ. Data for the transformation of a series of aromatic acids are summarized in Table I.

When a mixture of *p*-nitrobenzoic acid, trichlorosilane, and tri-*n*-propylamine was refluxed for 2 hr, a gelatinous colored material was formed which did not contain *p*-nitrobenzyltrichlorosilane. Further work is presently underway to delineate the effects of aromatic substituents on the course of the reaction as well as to ascertain whether it can be extended to aliphatic acids.

Since it is well known that benzylic silanes are readily cleaved by base,[5] the method herein described holds promise as a procedure for converting benzoic acids to substituted toluenes. It has already been shown that the benzyltrichlorosilane resulting from run 1 (Table I) can be cleaved readily to toluene.[6] Further experiments are currently underway in our laboratory to determine the generality and feasibility of such a two-step process for reducing a carboxyl group to methyl.

We must reemphasize that the mechanism of "reductive silylations," such as described here and previously,[3] remains speculative. The current thrust of our program has been directed solely at illustrating the preparative value of the method.

Table I. Reductive Silylation of Aromatic Acids by Trichlorosilane–Tri-*n*-propylamine

Run	Reactants[a]	Conditions[b]	Products[c,d]	
1	$C_6H_5CO_2H$	14 hr, 77–82°	$C_6H_5CH_2SiCl_3$	(58%)
2	p-$ClC_6H_4CO_2H$	16 hr, 73–77°	p-$ClC_6H_4CH_2SiCl_3$[e]	(69%)
3	p-$BrC_6H_4CO_2H$	15 hr, 72–79°	p-$BrC_6H_4CH_2SiCl_3$	(58%)
4	p-$CH_3C_6H_4CO_2H$	16 hr, 71–77°	p-$CH_3C_6H_4CH_2SiCl_3$	(56%)
5	3,5-$(CH_3)_2C_6H_3CO_2H$	18 hr, 75–82°	3,5-$(CH_3)_2C_6H_3CH_2SiCl_3$	(51%)

[a] In every case, the mole ratio of acid:$SiHCl_3$:$(n$-$C_3H_7)_3N$ was 1:5:2. [b] In all cases, about 100 ml of acetonitrile was used as solvent. [c] In every instance, the percentage given in parentheses represents the *isolated* yield of organosilane based upon the weight of the starting acid. In addition, isolated yields of tri-*n*-propylamine hydrochloride ranging from 86 to 98% were obtained. [d] In the case of the silanes resulting from runs 1, 2, and 4, identification was made by matching their spectra (ir and nmr) with authentic samples. Satisfactory elemental analyses and spectral data (ir and nmr) were obtained for the silanes resulting from runs 3 and 5. [e] It is likely that tri-*n*-butylamine can be substituted for the tri-*n*-propylamine in every case. A 65% yield of *p*-chlorobenzyltrichlorosilane was realized when such a substitution was made in this run.

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(2) R. A. Benkeser and W. E. Smith, *ibid.*, **90**, 5307 (1968).

(3) R. A. Benkeser and W. E. Smith, *ibid.*, **91**, 1556 (1969).

(4) It should be emphasized that the stoichiometry of the reactants has not been ascertained nor any attempt made to optimize reaction conditions.

(5) C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, pp 143–146.

(6) Unpublished studies by J. M. Gaul and K. M. Foley of these laboratories.

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Fluxional Behavior in *Tetrahapto*benzene–Rhodium and –Iridium Complexes

Sir:

We report the first example of fluxional behavior in a benzene–metal complex. Fluxional behavior in cyclic π- and σ-bonded organometallic systems, where the metal atom usually moves along the periphery of a ring by a series of 1,2 shifts, is a well-established phenomenon.[1] It has been observed for cyclooctatetraene[1]

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(1) This topic has recently been reviewed: F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).