hydrogen atoms are minimized. Table X contains the bonding parameters of the four independent DMF ligands. Large thermal parameters, associated with the atoms of these ligands, possibly in part due to the partial decomposition of the sample crystals observed during data collection, have seriously affected the determination of accurate bonding parameters. A Fourier synthesis reveals regions of diffuse electron density for all atoms except the carbonyl oxygen atom in the DMF ligands.

Intermolecular contact distances are normal, with only two methyl–methyl group distances less than 4.0 Å. The distance from $C_{\alpha AM5}$ to $C_{\beta CM5}$ in an adjacent unit cell is 3.87 (2) Å, and the distance from $C_{\beta BM1}$ to $C_{\beta DMFM1}$ of a centrosymmetrically related molecule is 3.85 (2) Å.

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Formation and Reactions of the (Trifluoromethyl)tin Bromides CF_3SnBr_3 and $(CF_3)_2SnBr_2$

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The formation of CF_3SnBr_3 and $(CF_3)_2SnBr_2$ from the reaction of $(CF_3)_2Hg$ and $SnBr_4$ at temperatures of 112, 121, and 130 °C has been followed in a semikinetic manner. The data indicate that the (trifluoromethyl)tin bromides are easily formed in reactions that proceed to equilibria, but the decomposition of more fully substituted species, e.g., $(CF_3)_3SnBr$, is almost immediate and severely limits the temperature range that can be utilized. The methylated compounds $CF_3Sn(CH_3)_3$ and $(CF_3)_2Sn(CH_3)_2$ are easily formed in high yield. The latter reacts with excess $Cd(CH_3)_2$ to yield $CF_3Sn(CH_3)_3$ while the former reacts with CH_3Li to yield $Sn(CH_3)_4$. The formation of an unstable hydride, CF_3SnH_3, is also demonstrated.

Introduction

Since the preparation of the first perfluorinated analogue of an organometallic compound, $(CF_3)_2Hg$,[1] the properties and stabilities of compounds that contain trifluoromethyl–metal or –metalloid linkages have been the subject of many investigations. The most stable of the perfluoromethyl compounds appear to be formed by the smaller, relatively electronegative group 5- and 6A elements. They react with CF_3I at temperatures between 165 and 250 °C to form mononuclear compounds either by direct means or upon UV irradiation.[2] Much less is known about the trifluoromethyl-containing derivatives of the remaining elements, however. In group 3A, for example, although the compound CF_3BF_2 has been prepared and described as "enduringly metastable",[3] trifluoromethyl derivatives of the other elements are unknown, as are boranes containing more than one CF_3 group.

As might be expected the group 4A elements are very representative of the trends observed throughout the periodic table. The fully substituted compounds of the most electronegative elements of this group, $(CF_3)_4C$ and $(CF_3)_4Ge$, have been easily synthesized by a number of methods,[4,5] while the fully substituted derivative of tin has, as yet, been prepared only by means of discharge reactions.[6] The corresponding compound of the more electropositive[7] element silicon is currently unknown.

While mercuric halides, pseudohalides, and alkyls have all been used extensively in ligand-exchange reactions directed toward the preparation of new inorganic or organometallic species, bis(trifluoromethyl)mercury had been thought to be a very poor ligand-exchange reagent.[8] In a recent study, however, the reactions of $GeBr_4$ and $SnBr_4$ with $(CF_3)_2Hg$ were shown to produce the trifluoromethyl-substituted derivatives $(CF_3)_nMBr_{4-n}$, where $n = 1$ or 2 for M = Sn and $n = 1$–4 for M = Ge.[9] The chemistry of the germanium-containing trifluoromethyl compounds was later examined, and the CF_3–Ge linkage was shown to be very stable chemically when the (trifluoromethyl)germanium halides were shown to react with a variety of reagents to form, e.g., $(CF_3)_3GeH$, $[(CF_3)_3Ge]_2O$, and $(CF_3)_3GeCH_3$ nearly quantitatively.[10]

The present study is directed toward an assessement of the trifluoromethyl–tin linkage. In this study three main areas of interest were investigated: First, since no information about the rates of reaction between $(CF_3)_2Hg$ and a group 4A tetrahalide or any perhalide is available, we have followed the reaction of $SnBr_4$ with $(CF_3)_2Hg$ in a semikinetic manner to determine approximately how quickly the (trifluoromethyl)tin bromides are formed. Second, we have studied the reaction of these bromides with two methylating agents, $(CH_3)_2Cd$ and CH_3Li, to determine the stability of the CF_3–Sn bond toward representative alkylating agents. Finally, because the (trifluoromethyl)germanium hydrides had been synthesized in high (95%) yield, several attempts were made to isolate the currently unknown (trifluoromethyl)tin hydrides.

Experimental Section

General. Except where noted all manipulations were carried out by using a standard vacuum line to ensure the absence of air and water. Proton NMR spectra were obtained from a Varian A-60A spectrometer operating at 60 MHz; positive chemical shifts are deshielded

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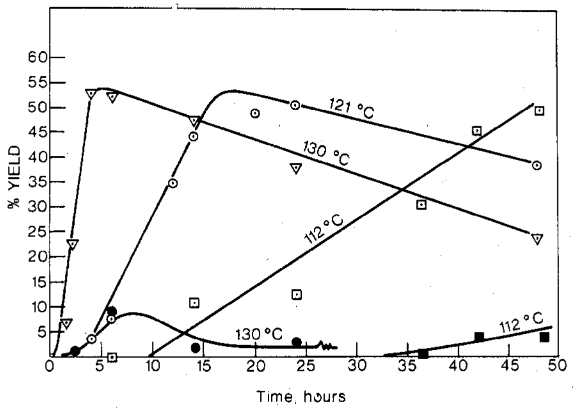

Figure 1. Yields of CF_3SnBr_3 and $(CF_3)_2SnBr_2$ as functions of time and temperature: ▼, CF_3SnBr_3 at 130 °C; ⊙, CF_3SnBr_3 at 121 °C; ⊡, CF_3SnBr_3 at 112 °C; ●, $(CF_3)_2SnBr_2$ at 130 °C; ■, $(CF_3)_2SnBr_2$ at 112 °C.

Table I. ^1H NMR and ^{19}F NMR Parameters[a]

compd	$\delta(F)$	$^2J_{Sn-F}$, Hz	$\delta(H)$	$^2J_{Sn-H}$, Hz
CF_3SnBr_3	−31.2	875/831		
$(CF_3)_2SnBr_2$	−33.3	721/689		
$CF_3Sn(CH_3)_3$	−29.5	273/260	0.37	60/56.8
$(CF_3)_2Sn(CH_3)_2$	−32.3	346/329	0.66	66.2/63.2
$Sn(CH_3)_4$			0.05	54.2/51.5
$CF_3SnBr(CH_3)_2$	−29.16[b]	391/372	1.34	65/62
$CF_3SnBr_2CH_3$	−29.57[b]	583/557	1.70	79.6/75.6

[a] Neat samples; ^1H NMR vs. external standard Me_4Si, positive values deshielded; ^{19}F NMR vs. external standard trifluoroacetic acid, negative values deshielded. See ref 10 and 13 for previous values obtained. [b] In CCl_4 solution.

relative to the external standard tetramethylsilane. Fluorine magnetic resonance data are from a Bruker HFX-90 FT spectrometer operating at 84.7 MHz; positive chemical shifts are shielded relative to the external standard, neat trifluoroacetic acid. Mass spectral data were recorded on an AEI 30 instrument operating at an ionization potential of 70 eV and ambient temperature. Tin tetrabromide, methyllithium, 1.6 M in diethyl ether, dimethylcadmium, and trimethylaluminum were obtained commercially and used as received. Di-*n*-butyl ether and diethyl ether were dried over sodium benzophenone ketyl.

Reaction of $(CF_3)_2Hg$ with $SnBr_4$. Freshly sublimed bis(trifluoromethyl)mercury,[10] 2.91 g (8.61 mmol), and stannic bromide, 2.00 g (4.54 mmol), were placed (drybag) in each of several 12 × 20 mm Pyrex tubes which were then attached to the vacuum system and evacuated while the contents were held at −196 °C. The tubes were sealed with a torch and placed for the indicated lengths of time (Figure 1) in an oven maintained (±2 °C) at 112, 121, or 130 °C. After the reaction period the ampules were opened while the contents were at −196 °C and reconnected to the vacuum line. The material that was volatile at room temperature was distilled into the line. The mixture obtained was then purified by fractional condensation.

The liquid that passed through a trap held at −30 °C but was held in a trap maintained at −45 °C was identified as CF_3SnBr_3 while the liquid that passed a −45 °C trap but was retained at −78 °C was found to be $(CF_3)_2SnBr_2$ as shown in Tables I and II. Fluorine-19 resonances that might have been ascribed to $(CF_3)_3SnBr$ or $(CF_3)_4Sn$ were not observed. Figure 1 presents the recovered yields, based on $SnBr_4$, of CF_3SnBr_3 and $(CF_3)_2SnBr_2$ as functions of time and temperature. Although each sample was prepared in a seemingly identical manner, the yield obtained after a given reaction was occasionally found to vary slightly, ca. 10%.

After one typical reaction, which had been carried out for 42 h at 112 °C, the more volatile products which consisted of CF_3SnBr_3 and $(CF_3)_2SnBr_2$, separated in 46% and 3% yields, respectively, along with fluorocarbons and small amounts of SiF_4, were removed. The material which had been retained in the −30 °C trap along with the nonvolatile solids remaining in the tube was reacted with excess dimethylcadmium. The volatile material resulting from this reaction, ca. 1 g, contained a small amount of $(CH_3)_2Hg$ as well as $(CF_3)_2Sn(CH_3)_2$, $CF_3Sn(CH_3)_3$, and $Sn(CH_3)_4$, the last three in a 36:24:40 molar ratio as determined by ^1H NMR.

Table II. Mass Spectral Data [*m*/*e*, Ion (Abundance)][a]

CF_3SnBr_3	413, CF_2SnBr_3 (11%); 363, $SnBr_3$ (100%); 282, $SnBr_2$ (11%); 201, SnBr (77%); 139, SnF (33%); 120, Sn (88%)
$(CF_3)_2SnBr_2$	399, $(CF_3)CF_2SnBr_2$ (2%); 351, CF_3SnBr_2 (81%); 337, $(CF_3)_2SnBr$ (32%); 299, $FSnBr_2$ (23%); 280, $SnBr_2$ (27%); 201, SnBr (100%); 139, SnF (68%); 120, Sn (64%)
$CF_3SnBr_2(CH_3)$	347, CF_3SnBr_2 (8%); 343, $CF_2SnBr_2CH_3$ (10%); 293, $SnBr_2CH_3$ (77%); 278, $SnBr_2$ (8%); 249, CF_2SnBr (6%); 214, $SnBrCH_3$ (9%); 199, SnBr (100%); 139, SnF (46%); 135, $SnCH_3$ (62%); 120, Sn (77%)
$CF_3SnBr(CH_3)_2$	249, CF_2SnBr (15%); 229, $(CH_3)_2SnBr$ (54%); 214, CH_3SnBr (12%); 199, SnBr (38%); 185, CF_2SnCH_3 (100%); 150, $Sn(CH_3)_2$ (31%); 139, SnF (23%); 135, $SnCH_3$ (46%); 120, Sn (45%)
$CF_3Sn(CH_3)_3$	215, $CF_2Sn(CH_3)_3$ (23%); 219, $CF_3Sn(CH_3)_2$ (23%); 185, CF_2SnCH_3 (3%); 169, $FSn(CH_3)_3$ (100%); 165, $Sn(CH_3)_3$ (100%); 150, $Sn(CH_3)_2$ (23%); 139, SnF (38%); 135, $SnCH_3$ (38%); 120, Sn (77%)
$(CF_3)_2Sn(CH_3)_2$	273, $(CF_3)_2SnCH_3$ (8%); 223, $(CF_3)FSnCH_3$ (25%); 219, $CF_3Sn(CH_3)_2$ (100%); 189, CF_3Sn (8%); 173, F_2SnCH_3 (25%); 169, FSn-$(CH_3)_2$ (92%); 150, $Sn(CH_3)_2$ (10%); 139, FSn (45%); 135, $SnCH_3$ (30%); 120, Sn (25%)

[a] At 70 eV. Percentages refer to the peak height relative to base peak.

A small sample, 0.10 g, of neat $(CF_3)_2SnBr_2$ which had been sealed into a 4-mm tube under vacuum was placed into an oven which was maintained at 125 °C for 72 h. At the end of this time the sample had totally decomposed.

Reaction of (Trifluoromethyl)tin Bromides with Dimethylcadmium. (Trifluoromethyl)tin tribromide, 0.545 g (1.3 mmol), and dimethylcadmium, 0.270 g (1.9 mmol), were separately condensed into a 20 mL reactor held at −196 °C. The contents of the vessel were allowed to react for 15 min at room temperature, and then the volatile products were removed and analyzed. (Trifluoromethyl)trimethylstannane, $CF_3Sn(CH_3)_3$, 0.281 g (1.2 mmol), 92% yield, was isolated and identified by NMR and mass spectral data. Bis(trifluoromethyl)tin dibromide, 0.187 g (0.45 mmol), and dimethylcadmium, 0.064 g (0.45 mmol), were reacted in an identical manner to produce $(CF_3)_2Sn(CH_3)_2$, 0.118 g (0.41 mmol), 91% yield. Magnetic resonance and mass spectral data for these compounds are contained in Tables I and II.

The reaction of (trifluoromethyl)tin tribromide, 0.816 g (1.91 mmol), with substoichiometric amounts of $(CH_3)_2Cd$, 0.26 g (1.8 mmol), yielded $CF_3Sn(CH_3)_3$, in 58% yield, as well as the new compounds $CF_3(CH_3)_2SnBr$ and $CF_3(CH_3)SnBr_2$ in 8% and 11% yields, respectively. Unreacted CF_3SnBr_3, 17%, was also recovered. Properties of these compounds are in Tables I and II.

The reaction of excess dimethylcadmium with the (trifluoromethyl)tin bromides was also assessed. Dimethylcadmium in ca. 10-fold excess was reacted with CF_3SnBr_3, 0.35 g (0.82 mmol), in a sealed tube. The trifluoromethyl compound $CF_3Sn(CH_3)_3$ formed immediately and quantitatively. The very slow formation of $Sn(CH_3)_4$, which was only observed after 15 minutes, followed. ^1H NMR indicated the mole ratio of $CF_3Sn(CH_3)_3$ to $Sn(CH_3)_4$ to be 88:12 after 50 min. In another experiment, however, a solution containing $(CH_3)_2Cd$ and $CF_3Sn(CH_3)_3$ in a 2:1 molar ratio was allowed to stand at room temperature for 3 h. No reaction of the $CF_3Sn(CH_3)_3$ was observed. In a third experiment $(CF_3)_2SnBr_2$, 0.198 g (0.47 mmol), was reacted with $Cd(CH_3)_2$, 0.160 g (1.1 mmol). After 35 min $(CF_3)_2Sn(CH_3)_2$ and $CF_3Sn(CH_3)_3$ were found, by ^1H NMR, to be present in an 83:17 mole ratio, and after 55 min the ratio was 77:23; dimethylcadmium was present. At this point an additional 0.150 g of $Cd(CH_3)_2$ was added to the mixture and allowed to further react. After 5 min the mole ratio was still 77:23, but it decreased slowly with time, becoming 55:45 2 h later; again dimethylcadmium was still present. A very small resonance that could possibly have arisen from $Sn(CH_3)_4$ was never larger than 1% of the peak height of the resonance due to $(CF_3)_2Sn(CH_3)_2$. No resonances other than $(CF_3)_2Sn(CH_3)_2$ and $CF_3Sn(CH_3)_3$ were observed in the fluorine NMR.

Reaction of the (Trifluoromethyl)tin Bromides with Methyllithium. (Trifluoromethyl)tin tribromide, 1.02 g (2.38 mmol), was condensed onto 4.5 mL (7.17 mmol) of an ethereal solution of methyllithium. The solution was warmed to room temperature and allowed to react for 3 min while being magnetically stirred. The volatile material resulting was removed from the white precipitate and then fractionated to remove the solvent. The remaining material, 0.395 g (1.69 mmol), was identified by proton NMR as $CF_3Sn(CH_3)_3$, isolated in 71% yield. Tetramethylstannane was not observed. In a second experiment 0.255 g (0.59 mmol) of CF_3SnBr_3 was reacted with a large excess of CH_3Li, 4.8 mmol. (Trifluoromethyl)trimethylstannane and $Sn(CH_3)_4$ were isolated from this reaction in 31% and 70% yields, respectively. The further addition of 1.6 mmol of methyllithium to the tin-containing species resulted in complete methylation as the resonance due to $CF_3Sn(CH_3)_3$ was not present, and $Sn(CH_3)_4$, isolated in 91% yield, was the only tin-containing compound observed.

Preparation of (Trifluoromethyl)stannane, CF_3SnH_3. The preparation of CF_3SnH_3 was attempted by several methods including the coupling of CF_3I with $NaSnH_3$ in liquid ammonia (which yields CF_3H) and ligand-exchange reactions of CF_3SnBr_3 with excess SnH_4, both in diethyl ether at −78 °C and in the absence of solvent.[11,12] In the exchange reactions carried out in ether a very small amount of a volatile, colorless gas was recovered, which decomposed much faster than stannane, which itself slowly decomposes to yield a shiny layer of metallic tin. Upon the addition of $Al(CH_3)_3$ the brown residue from the gaseous substance reacted to give $Sn(CH_3)_4$.

The reduction of CF_3SnBr_3, 1 g, with $LiAlH_4$ in butyl ether, carried out as indicated below, proceeded only at temperatures higher than −30 °C. Stannane, produced in 15% yield, was the only volatile product observed. The reduction of CF_3SnBr_3, 1.69 g (3.94 mmol) was also studied in dry ethyl ether, 5 mL, at −78 °C. A slight excess of solid $LiAlH_4$ was slowly dropped into the magnetically stirred solution over a 1.5-h period, and the very volatile material formed was periodically removed into the vacuum line to be fractionated after the reduction was concluded. The continual deposition of solids in the vacuum line was observed while the products were transferred. Proton magnetic resonance spectra of an originally clear, colorless ethereal solution of the tin-containing products were obtained at −40 °C. They indicated the presence of SnH_4 (δ 4.10), formed in 25% yield, and a small amount (ca. 10%) of a second species, CF_3SnH_3 (δ 7.00). Although SnH_4 is quite stable at −40 °C, the second compound, CF_3SnH_3, decomposes rapidly yielding brown solids similar to those noted above. All of the resonances were considerably broadened, presumably by the solids contained in the tube. While the second resonance was not inconsistent with a quartet $^3J_{HF} = 2$–3 Hz, the coupling could not be unambiguously resolved. The solids deposited in the vacuum line were reacted with $(CH_3)_3Al$ to yield $Sn(CH_3)_4$. The mass spectrum of the second species could be obtained only with great difficulty but included a series of $CF_3SnH_n^+$ ions the most intense of which was at m/e 191 (m/e for $CF_3{}^{120}SnH_2^+$ 191) with the appropriate isotopic intensities for the 10-isotopes of tin. Other ions in the spectrum included $FSnH_n^+$ and SnH_n^+. In a control reaction between $SnBr_4$ and $LiAlH_4$ carried out at −78 °C in diethyl ether, SnH_4 was prepared in 40% yield.

Results and Discussion

Preparation of (Trifluoromethyl)tin Bromides. The data presented in Figure 1 illustrate several points. The most obvious is the critical nature of the temperature regime. The temperature range reported in Figure 1 is only 18 °C, but the rate of product formation is altered substantially. For example, after 5 h the yield of CF_3SnBr_3 varies from near zero at 112 °C to about 55% at 130 °C. Similarly, the amount of $(CF_3)_2SnBr_2$ isolated after 30 h at either 112 or 130 °C is small, in the former case because the product is yet to form and in the latter because the majority of the compound had decomposed at the higher temperature employed. The extreme sensitivity of the observed yields well explains the failure of many of the previous studies directed toward the formation of trifluoromethyl-containing compounds from $(CF_3)_2Hg$ since presumably tin is not unique in this respect. The formation of trifluoromethyl-substituted derivatives of many other elements may well be equally or even more sensitive to temperature.

Figure 1 further suggests that the course of the reaction may be as shown in

$$SnBr_4 + (CF_3)_2Hg = CF_3SnBr_3 + CF_3HgBr \qquad (1)$$

$$CF_3SnBr_3 + (CF_3)_2Hg = (CF_3)_2SnBr_2 + CF_3HgBr \qquad (2)$$

or

$$2CF_3SnBr_3 = (CF_3)_2SnBr_2 + SnBr_4 \qquad (2a)$$

$$(CF_3)_2SnBr_2 = (1/n)(CF_3SnBr_2F)_n + {}^1/_3C_3F_6 \qquad (3)$$

$$(CF_3)_2SnBr_2 + (CF_3)_2Hg = (CF_3)_3SnBr + CF_3HgBr \qquad (4)$$

or

$$2(CF_3)_2SnBr_2 = (CF_3)_3SnBr + CF_3SnBr_3 \qquad (4a)$$

$$(CF_3)_3SnBr = (1/n)[(CF_3)_2SnBrF]_n + {}^1/_3C_3F_6 \qquad (5)$$

$$(1/n)[(CF_3)_2SnBrF]_n + Cd(CH_3)_2 = (CF_3)_2Sn(CH_3)_2 + CdBrF \qquad (6)$$

The first step of the reaction appears to be the formation of CF_3SnBr_3 in a reaction that proceeds to equilibrium, eq 1. Extrapolation of the yield of CF_3SnBr_3 from longer reaction times back to zero time, Figure 1, implies that the equilibrium constant is slightly greater than unity.

Although CF_3SnBr_3 is stable at 125 °C, $(CF_3)_2SnBr_2$ is not. Thus the formation of compounds with more than one CF_3 group attached to tin is followed by their decomposition to nonvolatile polymeric tin fluorides, eq 3–5. Originally the rate of formation of $(CF_3)_2SnBr_2$ exceeds the rate of decomposition, but during the later stages of the reaction the amount of the compound present declines, and only a few mole percent can be recovered from the pseudo "steady-state" concentration. The concentration of $(CF_3)_3SnBr$ (if present) is much less than that of $(CF_3)_2SnBr_2$. The formation of $(CF_3)_2Sn(CH_3)_2$ from the reaction of $(CH_3)_2Cd$ with the solids present at the end of the reactions, eq 6, is most conveniently explained, however, by invoking the presence of $(CF_3)_3SnBr$ which is very unstable under the reaction conditions.

Reaction with CH_3Li and $(CH_3)_2Cd$. The preparation of the mixed methyl(trifluoromethyl)tin compounds in good to excellent yields is easily accomplished by using methyllithium or dimethylcadmium in the appropriate quantities. The procedures outlined above, for example, are currently the most efficient preparations of $(CF_3)_2Sn(CH_3)_2$, a compound that has previously been formed only in very low yields, ca. 4%.[13] Pure $CF_3Sn(CH_3)_3$ is stable in the presence of $(CH_3)_2Cd$, but if the solution contains metal salts, as from an earlier methylation of CF_3SnBr_3, $CF_3Sn(CH_3)_3$ slowly reacts with $(CH_3)_2Cd$ to form $Sn(CH_3)_4$. Presumably the first step of the sequence is the decomposition of $CF_3Sn(CH_3)_3$ to form $FSn(CH_3)_3$, a reaction that has been reported to be catalyzed by the metal salt NaI.[14] This step is followed immediately by the methylation of the tin–fluorine bond to yield $Sn(CH_3)_4$. The compound $(CF_3)_2Sn(CH_3)_2$ is much less stable toward $Cd(CH_3)_2$, and the selective replacement of one of the CF_3 groups is observed. As expected, methyllithium is found to be much more reactive, forming $Sn(CH_3)_4$ quantitatively from $CF_3Sn(CH_3)_3$ during a 3-min reaction period if sufficient $LiCH_3$ is present.

(Trifluoromethyl)stannane. Stannane, SnH_4, is reasonably stable in the absence of elemental tin, and the stability of

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organotin hydrides increases with increasing numbers of organic groups attached to the tin atom.[15] The halostannanes SnH_3X, X = Cl, Br, or I, however, are much less stable than SnH_4 and decompose upon sublimation at -35 °C.[16] Therefore, it was of some interest to attempt the preparation of CF_3SnH_3 as the trifluoromethyl group can be likened to an organic group since the linkage is through carbon, yet the ligand is very electronegative (more electronegative than Cl[17]). The experimental evidence indicates that a volatile tin compound is formed, a compound that decomposes faster than SnH_4 and has a chemical shift more deshielded than that of $ClSnH_3$ ($\delta(SnH_3Cl)$ 6.93[16]). Taken with the mass spectral data, which indicate $CF_3SnH_n^+$, $SnFH_n^+$, and SnH_n^+, these results argue strongly for the formation of CF_3SnH_3, but the compound is clearly less stable than stannane. Presumably the fact that the (trifluoromethyl)germanium hydrides are easily synthesized and stable for weeks at ambient temperatures[10,18] while the tin-containing analogues are not is a reflection of the relative electronegativities of the two central elements.

In summary the sealed-tube reactions between $SnBr_4$ and $(CF_3)_2Hg$ are a very convenient method of preparing the (trifluoromethyl)tin bromides CF_3SnBr_3 and $(CF_3)_2SnBr_2$ if the appropriate times and temperatures are used. However, outside of the relatively narrow temperature ranges established here the yields drop dramatically. Further substitution of trifluoromethyl groups is also indicated, but the trisubstituted compound decomposes almost immediately. The reaction of the bromides with stoichiometric amounts of CH_3Li or $(CH_3)_2Cd$ converts these compounds to the mixed methyl(trifluoromethyl)tin compounds virtually quantitatively. On the basis of the yields and availability of the reagents, the present preparation of the alkyl(perfluoromethyl)tin compounds is the most convenient synthesis known. (Trifluoromethyl)stannane appears to be much less stable than SnH_4, as are the stannyl halides.

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Registry No. CF_3SnBr_3, 65094-19-1; $(CF_3)_2SnBr_2$, 65094-20-4; $CF_3Sn(CH_3)_3$, 754-25-6; $(CF_3)_2Sn(CH_3)_2$, 65059-36-1; $Sn(CH_3)_4$, 594-27-4; $CF_3SnBr(CH_3)_2$, 72244-71-4; $CF_3SnBr_2CH_3$, 72251-81-1; $(CF_3)_2H_9$, 371-76-6; $SnBr_4$, 7789-67-5; $(CH_3)_2Cd$, 506-82-1; CH_3Li, 917-54-4; CF_3SnH_3, 72244-72-5; SnH_4, 2406-52-2.

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Synthesis and Properties of Chlorine(I) and Bromine(I) Trifluoromethanesulfonates and Raman Spectra of CF_3SO_2X (X = F, OH, OCl)

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The synthesis and characterization of the new hypohalites CF_3SO_3Cl and CF_3SO_3Br are described. Both compounds are thermally unstable at 22 °C, decomposing to CF_3Cl and SO_3 for the hypochlorite and $CF_3SO_3CF_3$, $CF_3SO_2OSO_2OCF_3$, SO_3 and Br_2 for the hypobromite. The hypochlorite is prepared by reaction of CF_3SO_3H with ClF and the hypobromite by reaction of CF_3SO_3Cl with bromine. The low-temperature Raman spectrum of CF_3SO_3Cl suggests C_1 symmetry and assignments of 20 of the expected 21 fundamentals are given. These assignments were aided by an analysis of the Raman spectra of CF_3SO_2F and CF_3SO_2OH, which are reported for the first time.

Introduction

Halogen derivatives of strong oxyacids contain the halogen in a formal positive oxidation state.[3,4] These +1 compounds are then very useful sources of the electrophiles Cl^+, Br^+, and I^+. The potential of such compounds is apparent by considering one of the better characterized examples, $BrOSO_2F$. This reactive compound undergoes electrophilic addition to olefins, substitutive electrophilic dehalogenation reactions with various chlorides and bromides, and one-electron oxidation by Br^+ with metals and serves as a source of Br^+ in the formation of polyhalogen cations.[3]

$$BrOSO_2F + CH_2CF_2 \rightarrow BrCH_2CF_2OSO_2F$$

$$2BrOSO_2F + FCCl_3 \rightarrow 2BrCl + FCCl(OSO_2F)_2$$

$$3BrOSO_2F + Au \rightarrow Au(SO_3F)_3 + \tfrac{3}{2}Br_2$$

$$BrOSO_2F + Cl_2 \xrightarrow{SbF_5} BrCl_2^+ + FSO_3^-$$

Clearly any new compound with properties similar to those of $BrOSO_2F$ would be immediately useful in synthesis.

Halogen(I) derivatives of several strong monoprotic acids have been prepared. These include $HOSO_2F$ (Cl,[5] Br,[6] I[7]), $HOClO_3$ (Cl,[8] Br[9]), $HOSeF_5$ (Cl, Br, I[10]), $HOTeF_5$ (Cl, Br, I)[11] and $HONO_2$ (Cl,[12] Br[13]). Not all of these compounds have good thermal stability and none have been investigated to the same extent as $BrOSO_2F$. One very strong acid, for which only the iodine compound is known, is CF_3SO_2OH.[14] This acid and its organic derivatives (triflates) have been extensively investigated since its discovery in 1954.[15,16]

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