A New General Synthesis for Trifluoromethyl Organometallic Compounds

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Abstract: A new general synthesis for trifluoromethyl organometallic compounds using very reactive trifluoromethyl radicals obtained from the glow discharge of hexafluoroethane is reported. Reaction of these trifluoromethyl radicals with metal halides produces trifluoromethyl organometallic compounds in high yields. In most cases, substitution of trifluoromethyl radicals for halogen atoms is effected more easily as one proceeds from chlorine to iodine in accordance with decreasing metal–halogen bond strengths. Novel syntheses for bis(trifluoromethyl)mercury, $Hg(CF_3)_2$, the trifluoromethylmercuric halides, CF_3HgX, and bis(trifluoromethyl)ditelluride, $(CF_3)_2Te_2$, are reported. The new compounds bis(trifluoromethyl)tellurium, $(CF_3)_2Te$, tetrakis(trifluoromethyl)tin, $Sn(CF_3)_4$, and tetrakis(trifluoromethyl)germanium, $Ge(CF_3)_4$, have been prepared.

A substantial amount of work has been done on the synthesis of trifluoromethyl organometallic compounds over the past 25 years. Many interesting chemical species such as bis(trifluoromethyl)mercury, tris(trifluoromethyl)phosphorus, and perfluorotrimethylamine have been prepared and characterized and their chemistry thoroughly investigated. However, the synthesis of many highly substituted metal trifluoromethyl compounds has not yet been possible using conventional synthetic techniques. For example, the most highly substituted trifluoromethyltin or -germanium compounds which have been previously reported are $CF_3Sn(CH_3)_3$[2a] and $(CF_3)_2GeX_2$.[2b] Many important trifluoromethyl organometallic compounds which are potentially fairly stable when isolated have yet to be prepared. A new general synthesis using a plasma source for generation of reactive trifluoromethyl radicals is being developed in our laboratory for such trifluoromethyl organometallic compounds

$$n\mathrm{CF_3}\cdot + \mathrm{M(X)}_n \longrightarrow \mathrm{M(CF_3)}_n + n/2\mathrm{X_2}$$

where X = I, Br, or Cl.

The low temperature glow discharge is a convenient source of highly reactive radicals. These radicals are likely to be formed in excited electronic states and be vibrationally and rotationally excited but have very little translational energy compared with a similar radical which has been thermally generated. The apparent gas temperature in such a low energy glow discharge is often only slightly above ambient temperature and usually less than 50°. This "gentle" type of discharge, therefore, offers the advantage of highly energetic reactive species at temperatures where, for most organic or inorganic reactants of average stability, reactions can be designed such that they occur without degradation as a major problem.

The generation of trifluoromethyl radicals is a particularly interesting case. The carbon–carbon bond in hexafluoroethane is relatively weak due to the strong electron withdrawing effect of the six fluorine atoms. The actual bond strength has been a subject of controversy,[3-5] but presently the best estimate is 60–75 kcal/mol[6] as compared to 86–88 kcal/mol for the average carbon–carbon bond. The average carbon–fluorine bond energies in hexafluoroethane are 117–119 kcal/mol, and thus one has a difference in bond energy of 42–59 kcal/mol between the two types of bonds in the compound. If the minimum amount of radiofrequency power necessary to maintain a glow discharge in hexafluoroethane (22 W at 10 MHz) is applied to the reactor, a very clean source of reactive trifluoromethyl radicals is obtained. Under these conditions the population of other species such as fluorine atoms and CF_2 radicals is chemically negligible. If the power were increased significantly above this level, fluorination of the metal halide was observed experimentally. In the case of the reaction of HgI_2 with such a hexafluoroethane plasma, a nonreactive film of HgF_2 which was characterized by powder pattern X-ray was observed on the surface of the metal halide when the power level was increased. The production of trifluoromethyl radicals in this manner is very similar mechanistically to mass spectral fragmentation patterns, which produce very intense specific ions and radicals under conditions of relatively low electron beam energy. There are several available processes by which fragmentation may occur in hexafluoroethane, and, while the most energetic electrons in the plasma have sufficient energy to break even the carbon–fluorine bonds, one would expect to obtain a statistical distribution of bonds broken. Cleavage of the relatively weak carbon–carbon bond in hexafluoroethane is definitely the lowest energy bond breaking process for obtaining a radical or ion in this system. Under conditions of minimum power to maintain a glow discharge, the lowest energy process, as one might expect, is the most highly populated level of such a Botzmann distribution.

A crucial consideration is that the reactant metal halide should not be introduced into the main body of the plasma, but a solid metal halide be allowed only to contact the tail of the plasma or a volatile metal halide be vaporized into the tail of the plasma. To vaporize the metal halide through the discharge, results in decomposition of the metal halide and much lower yields of trifluoromethyl organometallic compounds.

The pyrolysis of hexafluoroethane at temperatures in the range of 1200° could also be used as a source of trifluoromethyl radicals. However, the high translation energies of such species would heat the reactant upon collision beyond the decomposition temperature of many metal halide or organic compounds, and one would not expect as selective production of trifluoromethyl radicals.

The trifluoromethyl radical is of interest because it has a pseudohalogen character and forms many inert and stable compounds. Most of the known chemistry of CF_3 radicals has involved expensive starting materials such as perfluoroalkyl halides, and hexafluoroacetone. None of these are very clean sources of CF_3 radicals and most of the procedures involved require more than 1 day for the synthesis.

The original synthesis of bis(trifluoromethyl)mercury by Haszeldine and Emeléus involved the reaction of trifluoromethylmercuric iodide with cadmium or silver amalgams.[7] Griffiths and Burg have also developed a synthesis where tris(trifluoromethylphosphine) is heated with mercuric oxide in a sealed tube.[8] Bis(trifluoromethyl)ditelluride

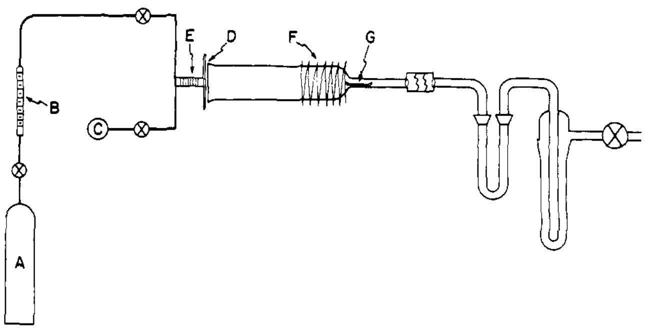

Figure 1. Diagram of plasma apparatus.

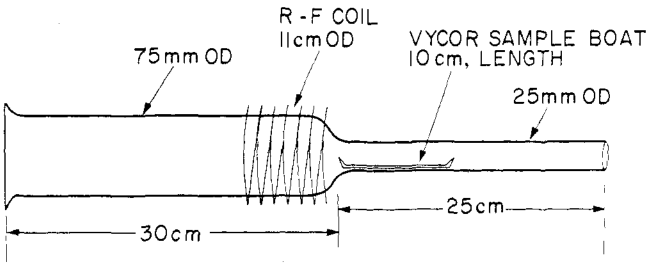

Figure 2. Quartz reaction chamber.

has been previously prepared by the reaction of trifluoromethyl radicals with a tellurium mirror.[9]

Experimental Section

Materials, Analyses, and Physical Measurements. The mercuric halide starting materials were Mallinckrodt Analytical Reagents. The tin, germanium, and tellurium halides were obtained from Alfa Inorganics. The hexafluoroethane used was Matheson high purity Freon 116. The elemental analyses were performed by Galbraith Laboratories, Inc., of Knoxville, Tenn., or Schwarzkopf Laboratories of Woodside, N.Y. Infrared spectra were obtained with a Beckman IR-20A spectrometer utilizing Nujol mull, KBr disk samples, or gas phase cells with KBr windows. Fluorine nmr spectra were obtained with a Perkin-Elmer R-20B spectrometer operating at a frequency of 56.47 MHz. Chemical shifts and coupling constants were measured with a Takeda-Riken TR3824X frequency counter. Mass spectra were obtained with a Hitachi RMU 6E mass spectrometer.

Apparatus. The radiofrequency power source was a Lepel 2.5-KW high frequency generator modified for variable frequency. The operating frequencies were between 4.8 and 10 MHz as measured with a Millen grid-dip meter. With the plasma on, the usual power level in the coil was measured as 22 W with a Thruline directional wattmeter, Model 43 (Bird Electronic Corporation). The wattmeter was connected between the second turn of the coil and a 25-ohm, 100-W dummy load. In addition the power was calculated by measuring the voltage across the coil and the current between the blocking and tank capacitor. These measurements gave a power value of 22.9 W.

The apparatus in which the syntheses were carried out is shown in Figure 1. Cyclinder (A) contains hexafluoroethane. The gas lines consist of copper tubing and Nupro fine metering valves connected with Swagelok fittings. Matheson 150-mm flowmeters (B), No. 600, with stainless steel floats and a Hastings thermocouple vacuum gauge, Model SP-1, (C) are used to monitor the system pressure. A Viton O-ring junction (D) connects a brass plate with the quartz reactor. The brass plate is somewhat mobile due to a flexible Swagelok fitting (E). The helical coil (F) consists of seven turns of $^3/_{16}$ in. copper tubing and is connected to the rf oscillator. For products which are highly moisture sensitive, a more dependable vacuum may be obtained in an all glass system of similar design.

The Vycor sample boat (G) is placed so that one end just enters the large diameter portion of the quartz reactor. A Teflon-coated stirring bar or other magnet may be placed behind the boat and subsequently used to move the boat forward as the reaction proceeds by using another magnet outside the reactor. The coil is positioned so that the plasma will overlap the boat by not more than 3 cm. The two Pyrex traps before the vacuum pump are cooled to the desired temperatures using slush baths or liquid nitrogen. The dimensions of the quartz reactor, sample boat, and rf coil are shown in Figure 2. The reactor was constructed in the configuration illustrated in an attempt to concentrate the radical population at the site of the reactant by creating favorable flow dynamics.

General Procedure. The Vycor boat was filled with enough finely powdered metal halide to cover the bottom to a depth of at least 3 mm then weighed, or the metal halide was vaporized into the tail of the plasma through a tube at approximately the same site as the illustrated boat. A dewar containing liquid nitrogen was placed around the trap before the vacuum pump, and the system was evacuated to 0.1 Torr or less. A bath of a selectd temperature was then placed on the U-trap. The flow rate of hexafluoroethane was adjusted to approximately 15 cm^3/min which corresponds to a system pressure of 0.5 Torr as measured with the thermocouple vacuum gauge. Small deviations from this flow rate are inconsequential, but best results were obtained with a flow rate in the range of 11–17 cm^3/min. The plasma was then initiated.

Reaction of Mercuric Halides. After a 5-hr run, the U-trap (acetone–Dry Ice) was weighed, and the contents were extracted with benzene. Fluorine^{19} nmr spectra were taken on the crude extracts as well as the purified compounds. The extracts contained the soluble bis(trifluoromethyl)mercury, the trifluoromethylmercuric halides, and free halogen species. The volatile benzene and iodine were separated from the mercurials on the vacuum line. The crude bis(trifluoromethyl)mercury was then easily purified by high vacuum sublimation at 35° and gas chromatography. The respective trifluoromethylmercuric halides were subsequently recovered by vacuum sublimation at 70–100° and purified by gas chromatography.

Bis(trifluoromethyl)mercury, $(CF_3)_2Hg$. Bis(trifluoromethyl)mercury was obtained in all of the reactions of trifluoromethyl radicals with mercuric halides but is produced in highest yield (95% based on the amount of HgI_2 consumed) from the reaction of CF_3 with mercuric iodide. The infrared spectrum (Nujol mull) had absorptions at 1148 (vs), 1077 (vs), 1051 (vs), 715 (m), and 523 (w) cm^{-1}, in agreement with literature values. The ^{19}F nmr spectrum showed a singlet at −42.1 ppm in benzene (external trifluoroacetic acid (TFA)) with $J_{^{199}Hg-F} = 1264$ Hz. Peaks were observed in the mass spectrum corresponding to the molecular ion, $(P - F)^+$ and $(P - CF_3)^+$, which contained the appropriate Hg isotopic pattern. The amount of $Hg(CF_3)_2$ obtained in a 5-hr run is in excess of 0.8 g corresponding to a yield of over 95% based on HgI_2.

Anal. Calcd for $Hg(CF_3)_2$: C, 7.10; Hg, 59.25; F, 33.67. Found: C, 7.07; Hg, 59.21; F, 33.47.

Trifluoromethylmercuric Iodide, CF_3HgI. Trifluoromethylmercuric iodide was obtained in low yields (0.02 g) from reaction of CF_3 with mercuric iodide. The ^{19}F spectrum consisted of a singlet at −44.5 ppm in benzene (external TFA) with $J_{^{199}Hg-F} = 1705$ Hz. In the mass spectrum, parent and $(P - F)^+$ ions were observed with the appropriate Hg isotopic pattern. The yield was >3%.

Trifluoromethylmercuric Bromide, CF_3HgBr. Trifluoromethylmercuric bromide (0.3 g) was obtained from the reaction of CF_3 with mercuric bromide. The ^{19}F nmr spectrum in benzene was a singlet at −45.6 ppm (external TFA) with $J_{^{199}Hg-F} = 1807$ Hz. The mass spectrum showed a parent ion and a $(P - F)^+$ ion with the appropriate Hg isotopic pattern. The yield was 46%.

Trifluoromethylmercuric Chloride, CF_3HgCl. Trifluoromethylmercuric chloride (0.4 g) was obtained from the reaction of CF_3 radicals with mercuric chloride. The ^{19}F nmr spectrum in benzene was a singlet at −45.8 ppm (external TFA) with $J_{^{199}Hg-F} = 1869$ Hz. A parent ion and a $(P - F)^+$ ion were observed in the mass spectrum with the appropriate Hg isotopic pattern. The yield was 9%.

Reaction of Tellurium Halides. The sample boat contained 2.6 g of $TeBr_4$. After evacuation of the system to approximately 2 μ, the pressure in the reactor was adjusted to 0.2–0.5 Torr with a C_2F_6 flow of 4 mmol/hr. After the reaction was terminated, the sample boat was reweighed, and the products which had been collected downstream in two cold traps maintained at −78 and −196° were separated under vacuum and analyzed. At the end of 46 hr, 1.5 g (3.3 mmol) of $TeBr_4$ had been consumed in the reaction.

In order to free the products from unreacted C_2F_6 and other low molecular weight fluorocarbons produced in the reaction, the products were first subjected to trap to trap fractionation. All material which passed a trap held at −104° was discarded. The contents of the −104° trap were then further fractionated at −63 and −78°. Each of the three fractions was then separately condensed on Porapak P contained in a trap on the vacuum line. The contents of this trap were allowed to warm slowly to room temperature and fractions collected as they distilled out of the Porapak. The first compounds to emerge were colorless fluorocarbons which were discarded. These fractions were followed by yellow colored Te-containing products which appeared as the Porapak reached room temperature. If necessary, overnight pumping and gentle heating (50°) were used to recover all of the material from the Porapak. This process was repeated until no contaminants could be seen in either the nmr or mass spectra of the Te-containing fractions. The products were then further separated and purified using a Dobson low temperature distillation apparatus. The major tellurium-containing products identified from the above process were $(CF_3)_2Te_2$ and $(CF_3)_2Te$.

Bis(trifluoromethyl)ditelluride, $(CF_3)_2Te_2$. Pure bis(trifluoromethyl)ditelluride distilled at −53° as a red-brown liquid in 33% yield based upon $TeBr_4$ consumed, and had an ir spectrum and melting point in agreement with those previously reported.[9] The ^{19}F nmr spectrum of $(CF_3)_2Te_2$ consisted of a singlet at −49.8 ppm from external TFA with $J_{^{125}Te-F} = 92.6$ Hz. The mass spectrum of the ditelluride had a base peak at *m/e* 69 (CF_3^+) and the following comparative abundances of ^{130}Te in fragments having the expected isotopic ratios for 1 and 2 tellurium atoms: Te^+ (100%), FTe^+ (16%), $CFTe^+$ (7%), CF_2Te^+ (50%), CF_3Te^+ (56%), Te_2^+ (49%), $CF_3Te_2^+$ (66%), $C_2F_6Te_2^+$ (74%).

Bis(trifluoromethyl)tellurium, $(CF_3)_2Te$. Bis(trifluoromethyl)monotelluride distilled at −98° in approximately 20% yield based upon the $TeBr_4$ consumed in the reaction. $Te(CF_3)_2$ is a yellow-green liquid with a melting point below −160° as determined with a Stock magnetic plunger. Major bands in the gas phase ir were found at 1178 (s), 1143 (s), 1126 (s), 1072 (s), 782 (m), and 740 cm^{-1} (s). The ^{19}F nmr spectrum of $(CF_3)_2Te$ consisted of a singlet at −54 ppm from external TFA with $J_{^{125}Te-F} = 22$ Hz. The mass spectrum of the monotelluride had a base peak at *m/e* 69 (CF_3^+) and the following comparative abundances of the ^{130}Te isotope (each envelope possessed the expected peak ratios for tellurium isotopes): Te^+ (70%), FTe^+ (23%), $CFTe^+$ (11%), CF_2Te^+ (60%), CF_3Te^+ (100%), $C_2F_5Te^+$ (20%), $C_2F_6Te^+$ (90%). $(CF_3)_2Te$ reacted with bromine in the gas phase to form a bright yellow powder having the correct analysis for $(CF_3)_2TeBr_2$, and which decomposed in air above 150°. As expected, bis(trifluoromethyl)telluride was extremely air sensitive.

Anal. Calcd for $(CF_3)_2Te$: C, 9.04; F, 42.92. Found: C, 9.1; F, 43.1.

In the −78° trap on the plasma line, a yellow solid was found which sublimed *in vacuo* at 50°, and which represented a 36% yield based upon the $TeBr_4$ used in the reaction. With the mass spectrometer cooled to room temperature and operating at 10 eV, this solid gave a mass spectrum similar to that of $(CF_3)_2Te$ with additional peaks corresponding to $TeC_2F_5Br^+$. The yellow solid was sparingly soluble in methylene chloride, benzene, carbon tetrachloride, ethanol, fluorobenzene, and acetone and precipitated a white solid from solution upon standing. In several attempts to obtain ^{19}F nmr data only a small peak at −27.1 (external TFA) in C_6H_5F and −29.0 (external TFA) in benzene could be seen. An infrared spectrum (KBr pellet) consisted of two broad bands centered at 1200 and 650 cm^{-1}, and two sharp intense peaks at 1052 and 745 cm^{-1}. The compound is air sensitive and formed a white solid upon exposure to air for several hours. A sample contained in an evacuated tube and placed in an oven at 130° for 2 days yielded primarily $(CF_3)_2Te$, and small amounts of SiF_4, metallic Te, and HCF_3. No satisfactory analysis of the yellow solid could be obtained, however.

The use of $TeCl_4$ as starting material gives $(CF_3)_2Te_2$ and $(CF_3)_2Te$ as before, and in approximately the same yields. The solid which stopped in the −78° trap on the plasma line with $TeCl_4$ as reactant, however, was white and readily sublimable at room temperature. It, too, gave a mass spectrum nearly identical with $(CF_3)_2Te$, with additional peaks corresponding to $C_2F_5ClTe^+$ and CF_2Cl^+. The ^{19}F nmr spectrum in CH_2Cl_2 consisted of a rather weak peak at −32.6 ppm (external T.F.A.). The gas phase infrared spectrum consisted of a broad band centered at 1258 cm^{-1} and fairly intense peaks at 1180, 1075, and 1038 cm^{-1}. Gentle heating of the compound in an evacuated tube gave $(CF_3)_2Te$ as the major volatile product.

Tetrakis(trifluoromethyl)tin, $(SnCF_3)_4$. A quartz boat containing SnI_4 was placed in the 1-in. o.d. tube, and the rf coils were positioned so that the tail of the plasma, which was violet in color, would extend out of the larger chamber and half the length of the boat. After evacuation, the hexafluoroethane pressure was adjusted to 0.5–1 mm pressure with a flow rate of 15 cm^3/min.

The volatile $Sn(CF_3)_4$ was recovered in two traps downstream from the reactor. A trap at −78° contained a small amount of nearly pure $Sn(CF_3)_4$ and the majority of the $Sn(CF_3)_4$, a very volatile colorless solid, was recovered in a subsequent −196° trap along with fluorocarbons. The products were extracted with benzene, and $Sn(CF_3)_4$ was separated from the extract by vpc (retention time 28 min on ¼ in. × 10 ft S.E. 30 column, −30° with a programmed heating rate of 2°/min, 60 cm^3/min He). The yield was over 90% based on SnI_4 and a typical 4-hr run yielded 29 mg of $Sn(CF_3)_4$ (0.073 mmol).

The 56.47-MHz F^{19} nmr spectra of neat $Sn(CF_3)_4$ consisted of a singlet at −21 ± 1 ppm from external trifluoromethylbenzene, with symmetrical double satellites due to tin isotope coupling $J_{^{119}Sn-F} = 531$, $J_{^{117}Sn-F} = 503$ Hz. The chemical shift of $Sn(CF_3)_4$ in benzene was −18 ± 1 ppm. The mass spectrum consisted of $Sn(CF_3)_n^+$ species and fluorocarbon fragments, and an isotopically correct pattern around 327 corresponding to $Sn(CF_3)_3^+$ was of highest molecular weight. A peak at 377 (P − 19) was observed of insufficient intensity to determine the isotope distribution. The infrared spectrum contained carbon–fluorine stretches at 1150 and 1238 cm^{-1} and a band at 744 cm^{-1} which is probably a CF_3 deformation.

Anal. Calcd for $Sn(CF_3)_4$: C, 12.17; F, 57.76. Found: C, 12.33; F, 56.15.

Tetrakis(trifluoromethyl)germanium, $Ge(CF_3)_4$. The quartz boat was replaced by a side arm connected through a stopcock to a bulb of $GeBr_4$, and the reactor was evacuated. Hexafluoroethane was admitted at a flow rate of 5 mmol/hr, and the plasma initiated. Shortly thereafter, gaseous $GeBr_4$ was allowed to flow into the tail of the plasma at a rate of 3.1 mg/hr. The very volatile $Ge(CF_3)_4$ was vacuum distilled from the −196° trap and separated by a combination of fractionation and gas chromatography. The compound slowly passed through a trap held at −119° and remained in a trap maintained at −130°. The retention time on a ¼ in. × 30 ft, 15% fluorosilicone QF-1-0065 column was 28 min when the column was held at −8° with a He flow rate of 30 cm^3/min. The yield was 64% based on the amount of $GeBr_4$ used.

The ^{19}F nmr of $Ge(CF_3)_4$ in CCl_4 was a singlet at −30.6 ppm from external TFA. With the spectrometer cooled to room temperature, the monoisotopic mass spectrum contained fragments at the following *m/e* ratios: 333, $^{76}Ge(CF_3)_3CF_2^+$ (24.6%); 283, $^{76}GeF(CF_3)_2CF_2^+$ (87.3%); 233, $^{76}GeF_2(CF_3)CF_2^+$ (31.1%); 183, $^{76}GeF_3CF_2^+$ (54.0%); 145, $^{76}GeCF_3^+$ (18.4%); 126, $^{76}GeCF_2^+$ (2.2%); 119, $C_2F_5^+$ (45.0%); 95, $^{76}GeF^+$ (100.0%); 76, $^{76}Ge^+$ (6.2%); 69, CF_3^+ (39.8%). Each of the germanium containing fragments occurred in an evelope which had the appropriate distribution and intensities for the five isotopes of germanium. In addition, the mass spectrum contained metastable ions at *m/e* ≈238, 161, 116, 61, 40, and 26.5. The gas phase infrared spectrum contained absorptions at 2253 (vw), 1338 (w), 1255 (m), 1170 (vs), 1102 (vw), 735 (m), 608 (w), and 525 (w) cm^{-1}.

Anal. Calcd for $Ge(CF_3)_4$: C, 13.78; F, 65.40. Found: C, 13.68; F, 65.58.

Results and Discussion

The reaction of trifluoromethyl radicals generated by this plasma process with metal halides provides a synthetic route to highly substituted trifluoromethyl organometallic compounds (see Chart I). The mechanism of these reactions has not been investigated, and only the final products have been characterized. The free halogen is produced as a principal by-product, and only occasionally very small amounts of CF_3X have been observed.

The reaction of mercuric iodide, mercuric bromide, and mercuric chloride with plasma-generated CF_3 radicals produces a mixture of bis(trifluoromethyl)mercury and the

Table I. Fluorine Chemical Shifts and Yields of Perfluoroorganomercurials

Compound	Chemical shift[a]	J_{Hg-F} (Hz)	Mole ratio $Hg(CF_3)_2$/$HgCF_3X$	Amount recovered (g)/5 hr $Hg(CF_3)_2$ + $HgCF_3X$
$Hg(CF_3)_2$	−42.1	1264		
CF_3HgI	−44.5	1705	43.0	0.82
CF_3HgBr	−45.6	1807	0.85	0.55
CF_3HgCl	−45.8	1869	0.11	0.44

[a] In parts per million downfield from external trifluoroacetic acid, benzene solution.

Chart I. Reaction Products

$$2CF_3\cdot + HgI_2 \longrightarrow Hg(CF_3)_2 + I_2$$
$$CF_3\cdot + HgBr_2 \longrightarrow Hg(CF_3)_2 + CF_3HgBr + Br_2$$
$$CF_3\cdot + HgCl_2 \longrightarrow Hg(CF_3)_2 + CF_3HgCl + Cl_2$$
$$4CF_3\cdot + SnI_4 \longrightarrow Sn(CF_3)_4 + 2I_2$$
$$4CF_3\cdot + GeBr_4 \longrightarrow Ge(CF_3)_4 + 2Br_2$$
$$CF_3\cdot + TeBr_4 \longrightarrow Te(CF_3)_2 + Te_2(CF_3)_2 + [Te(CF_3)_2]_n + Br_2$$

corresponding trifluoromethylmercuric halide. With mercuric iodide very little trifluoromethylmercuric iodide is produced. The nmr data for the mercury compounds, summarized in Table I, are in satisfactory agreement with the values previously reported by Rausch and Van Wazer.[10] The infrared spectra observed for $Hg(CF_3)_2$ are in agreement with the values reported by Downs.[11]

The relative and actual amounts of product produced in each reaction are reported in Table I. As might be expected, the observed distributions indicate that as the mercury–halogen bond energy increases a complete CF_3 substitution is more difficult to achieve. The amounts reported in Table I are for average 5-hr runs. The nmr spectra in Figures 3a, 3b, and 3c show the crude unseparated reaction products of the reaction of trifluoromethyl radicals with HgI_2, $HgBr_2$, and $HgCl_2$. These spectra graphically illustrate this trend. The extremely small peak to the left of the principal fluorine resonance in Figure 3a is due to the small quantity of CF_3HgI produced.

Experiments with mercurous chloride and mercurous iodide were undertaken in an attempt to prepare the mercurous compound $CF_3(Hg_2)CF_3$. These reactions were unsuccessful and mercurous chloride yielded $Hg(CF_3)_2$ and CF_3HgCl in a 4.5/1 molar ratio, plus elemental mercury. The reaction with mercurous iodide produced no elemental mercury and a 4.2/1 molar ratio of $Hg(CF_3)_2$ to CF_3HgI. There was, in addition, in the ^{19}F nmr a reproducible peak of too low an intensity for separation or characterization at −21.8 ppm from trifluoracetic acid.

The new compounds $Sn(CF_3)_4$ and $Ge(CF_3)_4$ are extremely volatile solids which are structurally similar but less stable than perfluoroneopentane.[12] The ^{19}F nmr spectrum of $Sn(CF_3)_4$ (Figure 4) is very distinctive due to the coupling of the tin isotopes ^{117}Sn and ^{119}Sn with fluorine. The metastable ions observed in the mass spectrum of $Ge(CF_3)_4$ are attributed to the following decompositions

$$Ge(CF_3)_3CF_2^+ \xrightarrow[m^*\ 238]{-:CF_2} GeF(CF_3)_2CF_2^+$$
$$Ge(CF_3)_3CF_2^+ \xrightarrow[m^*\ 161]{-C_2F_4} GeF_2(CF_3)CF_2^+$$
$$Ge(CF_3)_3CF_2^+ \xrightarrow[m^*\ 40]{-:Ge(CF_3)_2} C_2F_5^+$$
$$GeF_2(CF_3)CF_2^+ \xrightarrow[m^*\ 61]{-:GeF_2} C_2F_5^+$$
$$GeF(CF_3)_2CF_2^+ \xrightarrow[m^*\ 116]{-C_2F_4} GeF_3CF_2^+$$
$$GeF_3CF_2^+ \xrightarrow[m^*\ 26.5]{-:GeF_2} CF_3^+$$

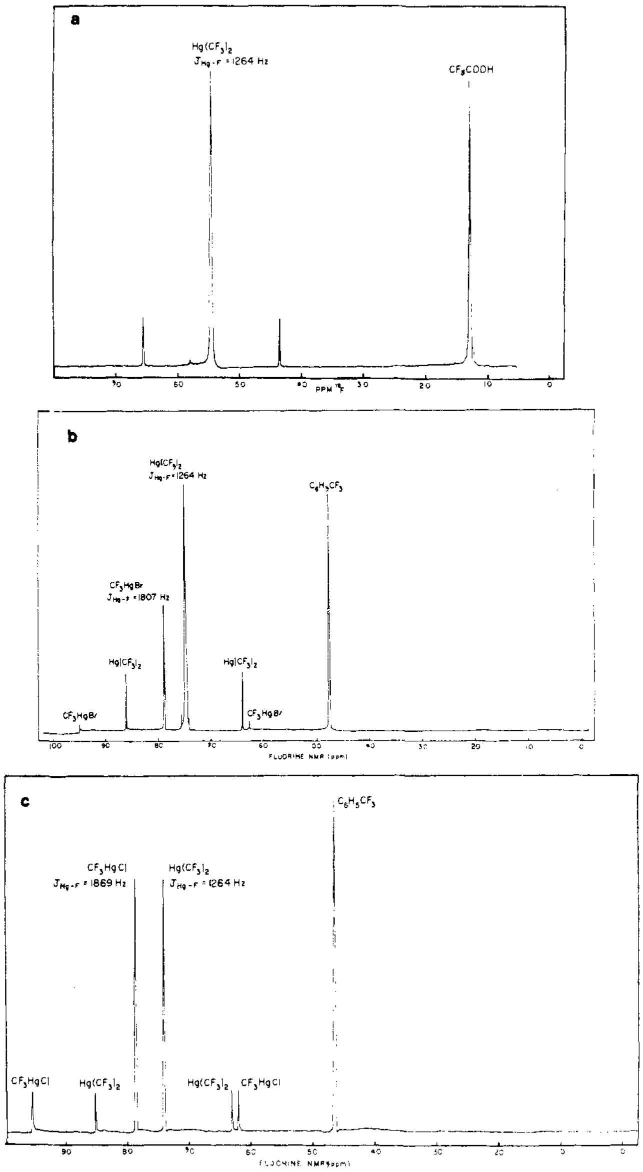

Figure 3. (a) HgI_2 reaction products, (b) $HgBr_2$ reaction products, (c) $HgCl_2$ reaction products.

The facile elimination of the methylene-like species $:GeF_2$ and $:Ge(CF_3)_2$ in the mass spectrometer indicates that, under the appropriate conditions, $Ge(CF_3)_4$ may well serve as a useful laboratory source of these divalent germanium compounds.

It is apparent from the mercuric halide reactions that the partially substituted trifluoromethyl organometallic bromides and chlorides are attainable through this plasma synthesis. One may obtain the partially substituted iodides by moving the boat or metal halide vapor inlet slightly out of the tail of the plasma such that there is greater opportunity for recombination of the trifluoromethyl radicals. Because the radical concentration is not sufficient for complete sub-

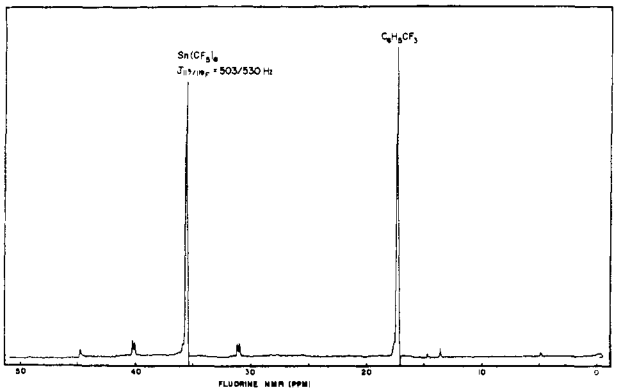

Figure 4. ^{19}F nmr spectrum of Sn(CF$_3$)$_4$.

stitution, the partially substituted iodides are obtained, If SnI_4 is positioned in the reactor to promote partial reaction, the new compounds $Sn(CF_3)_3I$ (-19.8 ppm *vs.* external $CF_3C_6H_5$, $J_{^{119}Sn-F} = 582$, $J_{^{117}Sn-F} = 553$ Hz) and $Sn(CF_3)_2I_2$ (-16.4 ppm *vs.* external $CF_3C_6H_5$, $J_{^{119}Sn-F} = 615$, $J_{^{117}Sn-F} = 587$ Hz) are produced. The new compound $Ge(CF_3)_3Br$ (chemical shift of the neat compound = -23.1 *vs.* external TFA; mass spectrum containing (P), (P $-$ F), and (P $-$ CF_3) ions) is formed from $GeBr_4$ in a similar fashion.

One of the advantages of this synthetic procedure, aside from providing a novel route to certain compounds, is that the reaction proceeds virtually unattended. Other preparations of bis(trifluoromethyl)mercury, for example, require considerably more time and effort. Although the yields based on the metal halide are excellent, the conversion in many cases is very low. A second disadvantage is the sometimes difficult separation of the desired products from perfluorocarbons of similar volatility which are produced along with hexafluoroethane from the recombination of trifluoromethyl radicals.

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(Pentafluorophenyl)sulfur Fluorides. A Detailed Analysis of Their ^{19}F Nuclear Magnetic Resonance Spectra

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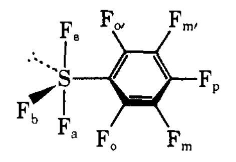
Abstract: A complete nmr line shape analysis has been carried out for the temperature-dependent ^{19}F nmr spectrum assigned to $C_6F_5SF_3$. Rate data correspond to the activation parameters $\Delta H^* = 10.5 \pm 0.4$ kcal mol^{-1}, $\Delta S^* = -7.7 \pm 1.3$ cal mol^{-1} deg^{-1}. The dynamic effects are ascribed to restricted internal rotation about the C–S bond, and no indication of loss of stereochemistry about sulfur was found. Dynamic effects were not observed for C_6F_5SOF or $C_6F_5SO_2F$; internal rotation about the C–S bond must be fast in these molecules at all temperatures investigated. The room temperature spectra for C_6F_5SOF and $C_6F_5SO_2F$ were analyzed using AA′BB′CX models. The results are in agreement with the linear relationship between the meta F–F coupling constants and the chemical shift of the para fluorine discussed by other workers. The substituent parameters σ_I and $\sigma_R{}^\circ$ were calculated for the SF_3, SOF, and SO_2F groups and compared to values determined from the *m*- and *p*-fluorophenyl system.

In a preliminary report,[1] the low-temperature ^{19}F nmr spectra of (pentafluorophenyl)sulfur trifuoride were explained by the trigonal bipyramid structure (**1**) with the pentafluorophenyl ring in the basal plane and a relatively high barrier to rotation about the C–S bond. In the presence of a hydrogen fluoride scavenger, a high barrier to intramolecular rearrangement of the sulfur fluorines about the sulfur atom was found. The single basal fluorine couples strongly with one ortho fluorine and weakly with the other, but the two apical fluorines couple equally with both ortho fluorines. A six-bond coupling between S–F and *p*-F was found in (pentafluorophenyl)sulfur trifluoride and in (pentafluorophenyl)sulfinyl fluoride. The six-bond coupling was not observed for (pentafluorophenyl)sulfonyl fluoride in the preliminary studies, but a small 0.6-Hz coupling was noted in the more detailed work.



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In the present work, the temperature-dependent ^{19}F spectra of (pentafluorophenyl)sulfur trifluoride have been measured and fitted by computer simulations. The ^{19}F spectra of (pentafluorophenyl)sulfinyl fluoride and (pentafluorophenyl)sulfonyl fluoride were measured as a function of temperature, but no changes indicative of the slowing down of internal motion were detected. A complete analysis has been made of the room temperature spectra of these molecules.