

# Reaction of $(\text{CF}_3)_2\text{Hg}$ with Group 4A Tetrahalides. Preparation and Stabilities of (Trifluoromethyl)germanium and (Trifluoromethyl)tin Compounds

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**Abstract:** Bis(trifluoromethyl)mercury,  $(\text{CF}_3)_2\text{Hg}$ , is found to react with  $\text{GeBr}_4$ ,  $\text{GeI}_4$ , and  $\text{SnBr}_4$  to produce all of the trifluoromethyl halides,  $(\text{CF}_3)_n\text{MX}_{4-n}$ ,  $n = 1-4$  when M is germanium and  $n = 1, 2$  when M is tin. The perfluoroalkylgermanium halides are shown to be reactive, and a number of derivatives have been synthesized by reactions in which the trifluoromethyl-germanium bond is retained while the halogen ligand is replaced by other substituents. The tris(trifluoromethyl)germanium compounds,  $\text{Ge}_2(\text{CF}_3)_6$ ,  $\text{Ge}(\text{CF}_3)_3\text{-O-Ge}(\text{CF}_3)_3$ ,  $(\text{CF}_3)_3\text{GeX}$  where  $X = \text{H, I, Br, Cl, F, and CH}_3$ , the disubstituted species  $(\text{CF}_3)_2\text{GeH}_2$  and  $(\text{CF}_3)_2\text{Ge}(\text{CH}_3)_2$ , and monosubstituted pentafluoroethyl derivatives  $\text{C}_2\text{F}_5\text{GeX}_3$  where  $X = \text{I, Br, and CH}_3$  have all been newly synthesized and their properties determined. The tin-containing compounds  $\text{CF}_3\text{SnBr}_3$  and  $(\text{CF}_3)_2\text{SnBr}_2$  have also been prepared and characterized. Thermal stability studies indicate that the (trifluoromethyl)germanium iodides undergo redistribution reactions at  $155^\circ\text{C}$  and that the germanium-containing compounds, such as  $(\text{CF}_3)_4\text{Ge}$ , are more stable than their tin-containing counterparts, e.g.,  $(\text{CF}_3)_4\text{Sn}$ .

## Introduction

The reactions, properties, and stabilities of perfluoroalkyl-containing organometallic compounds have provided a rich and diverse chemistry, particularly for the group 5A elements such as phosphorus. Preparative reactions which yield compounds that contain trifluoromethyl groups and any of a wide variety of other substituents bonded to group 5A atoms are known for both the trivalent and pentavalent states.<sup>3</sup> The properties of, for example, trifluoromethyl-substituted phosphoranes have been of interest for many reasons including their stereochemistry and the fluxional behavior exhibited by many of these pentacoordinate species. The chemistry of perfluoroalkyl derivatives of the more electropositive group 4A elements may well prove to be equally interesting, but very little is known about these species because reactions suitable for the preparation of a number of representative (perfluoroalkyl)group 4A derivatives have not been developed.

Previous syntheses of trifluoromethyl-substituted group 4A compounds have utilized the interaction of  $\text{CF}_3\text{I}$  with the divalent silicon or germanium species  $\text{SiF}_2$  or  $\text{GeI}_2$  to give  $\text{CF}_3\text{SiF}_2\text{I}^4$  or  $\text{CF}_3\text{GeI}_3$ .<sup>5</sup> Trifluoromethyl iodide also reacts with hexamethyldistannane,  $(\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3$ , to cleave the metal-metal bond and produce trimethyl(trifluoromethyl)tin,  $\text{CF}_3\text{Sn}(\text{CH}_3)_3$ .<sup>6</sup> These reactions are quite specific. The reaction of the divalent tin species  $\text{SnI}_2$  with  $\text{CF}_3\text{I}$ , for example, does not provide  $\text{CF}_3\text{SnI}_3$ ;<sup>5</sup> and  $\text{CF}_3\text{I}$  cleaves the metal-metal bond in neither  $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$  nor  $(\text{CH}_3)_3\text{GeGe}(\text{CH}_3)_3$ .<sup>5</sup> Moreover, while the reaction of  $\text{GeI}_2$  with  $\text{CF}_3\text{I}$  does produce minor amounts of the disubstituted compound,  $(\text{CF}_3)_2\text{GeI}_2$ ,<sup>5,7</sup> none of these reactions yields the more fully substituted group 4A halides such as  $(\text{CF}_3)_3\text{GeI}$  or  $(\text{CF}_3)_3\text{SnBr}_2$ . Recently the reactions of metal halides like  $\text{GeBr}_4$  with the intermediates produced in the radio-frequency discharge of  $\text{C}_2\text{F}_6$  have been shown to result in  $(\text{CF}_3)_4\text{Ge}$  and  $(\text{CF}_3)_4\text{Sn}$ ,<sup>8</sup> the first group 4A compounds to be prepared in which the metallic atoms were highly substituted with trifluoromethyl groups. While this discharge reaction has been very successful for the preparation of completely substituted species, the yields of partially substituted compounds, like  $(\text{CF}_3)_2\text{SnI}_2$ , are quite low. Additionally, this plasma reaction requires equipment not readily accessible to many laboratories. Therefore, an alternative type of reaction which required only readily available materials was investigated.

Ligand exchange reactions which involve the interchange

of electronegative substituents between compounds of the group 4A elements are well known and have frequently been used as synthetic tools, as have the reactions between compounds of these elements with silver or mercury salts.<sup>9</sup> The trifluoromethyl group is an especially interesting ligand in that it is a substituted alkyl group which often appears to react as if it were a pseudohalogen.<sup>3-8,10</sup> Indeed, the electronegativity of the  $\text{CF}_3$  group has been calculated to be between 3.2 and 3.55, or substantially higher than the electronegativity of chlorine.<sup>3b,10,11</sup> However, ligand exchange reactions which result in the transfer of a  $\text{CF}_3$  group from one metallic element to another appear to have been little investigated as a synthetic procedure, perhaps because of an early report which indicated that bis(trifluoromethyl)mercury is very reluctant to exchange ligands with inorganic halides.<sup>12</sup> The only preparation of a highly substituted, (trifluoromethyl)organometallic species by a reaction of this type that we are aware of is a recent report of a reaction between dimethylcadmium and bis(trifluoromethyl)mercury. In that study no compounds were isolated, but new resonances in the fluorine NMR were ascribed to the formation of  $\text{CF}_3\text{CdCH}_3$  and  $(\text{CF}_3)_2\text{Cd}$ .<sup>13</sup>

In the present study the potential usefulness of ligand exchange reactions between the mercurial  $(\text{CF}_3)_2\text{Hg}$  and halides of the group 4A elements was investigated by sealed tube reactions to determine if (trifluoromethyl)group 4A halides could be prepared in synthetically useful amounts. The reactions of the higher homologue,  $(\text{C}_2\text{F}_5)_2\text{Hg}$ , with the germanium halides were followed to observe the effect of a change in the perfluoroalkyl group. The chemical stability of the germanium-trifluoromethyl linkage was assessed by reaction of the (trifluoromethyl)germanium halides with a number of reagents to find whether a series of trifluoromethyl containing germanium compounds could be prepared or if these species decomposed upon substitution of the halogen atom attached to the germanium. Finally, the thermal stability of a number of the (trifluoromethyl)group 4A compounds was studied by heating small samples to temperatures between 100 and  $200^\circ\text{C}$ .

## Experimental Section

**General.** All volatile materials were manipulated in a standard vacuum line; nonvolatile solids were handled in an inert atmosphere bag. Reagents were obtained from commercial sources (Alfa Inorganics, PCR Inc.). The solid group 4A tetrahalides were purified by sublimation; other reagents were used as received. Purification of the

**Table I.** NMR Parameters and Infrared Absorptions of (Trifluoromethyl)germanes<sup>a</sup>

New compds	<sup>19</sup> F NMR, δ ppm <sup>b</sup>	<sup>1</sup> H NMR, δ ppm	J <sub>FF</sub> , J <sub>HF</sub> , Hz	IR, cm <sup>-1</sup>
(CF <sub>3</sub> ) <sub>3</sub> GeH	-26.4	5.23	<sup>3</sup> J <sub>HF</sub> = 6.7	2155 (s), 1167 (vvs), 734 (s)
(CF <sub>3</sub> ) <sub>2</sub> GeH <sub>2</sub> <sup>c</sup>	-26.2	4.55	<sup>3</sup> J <sub>HF</sub> = 7.8	2155 (s), 1168 (vs), 1137 (vvs), 722 (s)
(CF <sub>3</sub> ) <sub>3</sub> GeF	-22.1 <sup>d</sup>		<sup>3</sup> J <sub>FF</sub> = 3.7 <sup>e</sup>	1263 (s), 1176 (vs), 725 (s)
(CF <sub>3</sub> ) <sub>3</sub> GeCl	-22.6			1193 (s), 1168 (vs), 736 (s)
(CF <sub>3</sub> ) <sub>3</sub> GeBr	-23.1			1256 (s), 1164 (vs), 737 (s)
(CF <sub>3</sub> ) <sub>3</sub> GeI	-23.9			1258 (s), 1165 (vs), 735 (s)
(CF <sub>3</sub> ) <sub>3</sub> GeCH <sub>3</sub>	-23.0	0.61	<sup>1</sup> J <sub>CF</sub> = 135	2960 (w), 1172 (vvs), 727 (s)
(CF <sub>3</sub> ) <sub>2</sub> Ge(CH <sub>3</sub> ) <sub>2</sub>	-19.4	0.35	<sup>1</sup> J <sub>CF</sub> = 131.4	2930 (m), 1170 (vvs), 721 (m)
(CF <sub>3</sub> ) <sub>3</sub> GeGe(CF <sub>3</sub> ) <sub>3</sub>	-22.1 <sup>f</sup>			1170 (vs), 1135 (s), 737 (s)
(CF <sub>3</sub> ) <sub>3</sub> GeOGe(CF <sub>3</sub> ) <sub>3</sub>	-21.8			1175 (vs), 1155 (vs), 735 (vs)

<sup>a</sup> C<sub>2</sub>F<sub>5</sub>Ge(CH<sub>3</sub>)<sub>3</sub>: The <sup>19</sup>F NMR consists of unresolved resonances at 5.4 (CF<sub>3</sub>) and 50.7 ppm (CF<sub>2</sub>); the <sup>1</sup>H NMR spectrum is a singlet at 0.15 ppm. Infrared absorptions: 2985 (m), 1330 (s), 1202 (vs), 1116 (s), 1075 (s), 960 (s), and 837 cm<sup>-1</sup> (s). <sup>b</sup> Neat compounds vs. external CF<sub>3</sub>COOH; negative sign is deshielded. Also see ref 7. <sup>c</sup> For comparison, δ (GeH<sub>3</sub>) 4.13 ppm; <sup>3</sup>J<sub>HF</sub> = 8.6 Hz for the related compound CF<sub>3</sub>GeH<sub>3</sub>.<sup>18</sup> <sup>d</sup> δ (GeF) 142.6 ppm. <sup>e</sup> See Discussion. <sup>f</sup> Solution in (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O.

products was achieved by trap-to-trap fractionation followed, if necessary, by gas chromatography using a Bendix 2300 temperature programmed gas chromatograph equipped with a 3/8 in. × 24 ft. column 10% SE-30 on Chromosorb P. Gas-phase infrared spectra were obtained from a Beckman IR-20A spectrophotometer with 10-cm cells which had KBr windows. Nuclear magnetic resonance spectra are from a Perkin-Elmer R-20-B spectrometer operating at 60.0 MHz for protons (<sup>1</sup>H NMR) and 56.46 MHz for fluorine (<sup>19</sup>F NMR). Coupling constants and chemical shifts were measured by a Takeda-Riken 3824X frequency counter. Chemical shifts for fluorine and hydrogen are referenced to external trifluoroacetic acid (TFA) and tetramethylsilane (Me<sub>4</sub>Si), respectively. Positive fluorine chemical shifts indicate a resonance which is shielded relative to the reference. Positive proton chemical shifts are *deshielded* relative to Me<sub>4</sub>Si in accordance with the historical convention. Mass spectra at 70 eV were recorded using a Hitachi RMU-6E spectrometer which was operated at room temperature. All reported ions were contained in an envelope of the appropriate intensities and distributions corresponding to the normal isotopic composition for that ion. Satisfactory elemental analyses were obtained for the germanium-containing products prepared from the (trifluoromethyl)germanium halides by Schwartzkopf Laboratories, Woodside, N.Y.

**Preparation of the Perfluoroalkyl Mercurials.** Bis(trifluoromethyl)mercury, (CF<sub>3</sub>)<sub>2</sub>Hg, was originally prepared by the reaction of C<sub>2</sub>F<sub>6</sub> with HgI<sub>2</sub> in a discharge as previously reported;<sup>8</sup> the yield was 8 g/day. An alternative procedure, originally developed by Knunyants,<sup>14</sup> utilized the reaction of HgO which was added to the stoichiometric amount of aqueous CF<sub>3</sub>COOH, 50% by volume in H<sub>2</sub>O, to yield (CF<sub>3</sub>COO)<sub>2</sub>Hg. After the solvent was removed under vacuum, the mercurial (50 g, 0.11 mol) was mixed with potassium carbonate (30 g, 0.22 mol) and placed in a 500-mL flask which was equipped with a side arm 30 mm in diameter. With the pressure maintained at 20 mmHg by an external fore pump, the mercuric trifluoroacetate smoothly decarboxylated at temperatures of 140–200 °C to afford (CF<sub>3</sub>)<sub>2</sub>Hg which sublimed from the vessel; the yield was 28 g (74%). Bis(trifluoromethyl)mercury was identified by its NMR and mass spectra.

Bis(pentafluoroethyl)mercury was prepared by an adaptation of the decarboxylation reaction described above. Stoichiometric amounts of mercuric oxide were added to a solution of perfluoropropionic acid, 50% by volume in H<sub>2</sub>O. The solvent was evaporated under vacuum to yield a white powder, presumably (CF<sub>3</sub>CF<sub>2</sub>COO)<sub>2</sub>Hg, which was dried under vacuum at 100 °C. The thermal decarboxylation of this salt, even in the presence of a twofold molar excess of K<sub>2</sub>CO<sub>3</sub>, requires temperatures of 200–220 °C. At these temperatures the formation of the acid anhydride, (C<sub>2</sub>F<sub>5</sub>CO)<sub>2</sub>O, mercury metal, and oxygen predominates and the yield of (C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>Hg does not exceed 10%. The <sup>19</sup>F NMR spectrum of (C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>Hg in diethyl ether consists of a triplet at 6.5 ppm, <sup>3</sup>J<sub>Hg-F</sub> = 76 Hz, and a quartet at 32.5 ppm, <sup>2</sup>J<sub>Hg-F</sub> = 751 Hz; the fluorine-fluorine coupling constant is 1.4 Hz. The mass spectrum contains peaks at *m/e* 440, HgC<sub>4</sub>F<sub>10</sub><sup>+</sup>, and 371, HgC<sub>3</sub>F<sub>7</sub><sup>+</sup>. The base peak of the spectra occurs at *m/e* 321, HgC<sub>2</sub>F<sub>5</sub><sup>+</sup>.

**Preparation of the (Perfluoroalkyl)group 4A Halides. Reaction Conditions.** Measured amounts of approximately 1–3 g of the indicated reagents were placed in 10-mm Pyrex tubes and degassed under

**Table II.** Characterization of the (Trifluoromethyl)germanium Species

Compd	Mp, °C	Bp, °C	Mass spectra <sup>e</sup>
(CF <sub>3</sub> ) <sub>3</sub> GeH <sup>a</sup>	-102	31.6 <sup>c</sup>	(CF <sub>3</sub> ) <sub>2</sub> GeCF <sub>2</sub> H <sup>+</sup> , (CF <sub>3</sub> ) <sub>2</sub> GeH <sup>+</sup>
(CF <sub>3</sub> ) <sub>2</sub> GeH <sub>2</sub>			CF <sub>3</sub> GeCF <sub>2</sub> H <sub>2</sub> <sup>+</sup> , CF <sub>3</sub> GeFH <sub>2</sub> <sup>+</sup>
(CF <sub>3</sub> ) <sub>4</sub> Ge <sup>a</sup>	-19.7	31.7 <sup>c</sup>	(CF <sub>3</sub> ) <sub>3</sub> GeCF <sub>2</sub> <sup>+</sup> , (CF <sub>3</sub> ) <sub>3</sub> Ge <sup>+</sup>
(CF <sub>3</sub> ) <sub>3</sub> GeF <sup>a</sup>	27–30 <sup>b</sup>	19.1 <sup>c</sup>	(CF <sub>3</sub> ) <sub>3</sub> Ge <sup>+</sup> , (CF <sub>3</sub> ) <sub>2</sub> GeF <sup>+</sup>
(CF <sub>3</sub> ) <sub>3</sub> GeCl <sup>a</sup>	-98	37	(CF <sub>3</sub> ) <sub>2</sub> GeClCF <sub>2</sub> <sup>+</sup> , (CF <sub>3</sub> ) <sub>3</sub> Ge <sup>+</sup>
(CF <sub>3</sub> ) <sub>3</sub> GeBr <sup>a</sup>	-63	49	(CF <sub>3</sub> ) <sub>3</sub> GeBr <sup>+</sup> , (CF <sub>3</sub> ) <sub>2</sub> GeBrCF <sub>2</sub> <sup>+</sup>
(CF <sub>3</sub> ) <sub>3</sub> GeI <sup>a</sup>	-39.8	72	(CF <sub>3</sub> ) <sub>3</sub> GeI <sup>+</sup> , (CF <sub>3</sub> ) <sub>2</sub> GeICF <sub>2</sub> <sup>+</sup>
(CF <sub>3</sub> ) <sub>3</sub> GeCH <sub>3</sub> <sup>a</sup>	-48.5	57.5	(CF <sub>3</sub> ) <sub>2</sub> GeCF <sub>2</sub> CH <sub>3</sub> <sup>+</sup> , (CF <sub>3</sub> ) <sub>2</sub> GeCH <sub>3</sub> <sup>+</sup>
(CF <sub>3</sub> ) <sub>2</sub> Ge(CH <sub>3</sub> ) <sub>2</sub> <sup>a</sup>		78	CF <sub>3</sub> GeCF <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup> , CF <sub>3</sub> Ge(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>
(CF <sub>3</sub> ) <sub>3</sub> GeGe(CF <sub>3</sub> ) <sub>3</sub>	72–74	<i>d</i>	(CF <sub>3</sub> ) <sub>5</sub> Ge <sub>2</sub> CF <sub>2</sub> <sup>+</sup> , (CF <sub>3</sub> ) <sub>5</sub> Ge <sub>2</sub> <sup>+</sup>
(CF <sub>3</sub> ) <sub>3</sub> GeOGe- (CF <sub>3</sub> ) <sub>3</sub> <sup>a</sup>		98	(CF <sub>3</sub> ) <sub>5</sub> Ge <sub>2</sub> O <sup>+</sup> , (CF <sub>3</sub> ) <sub>4</sub> Ge <sub>2</sub> O <sup>+</sup>

<sup>a</sup> A satisfactory elemental analysis was obtained. <sup>b</sup> Sealed capillary; see Discussion. <sup>c</sup> Extrapolated. <sup>d</sup> The vapor pressure is 20 mm at 20 °C. <sup>e</sup> C<sub>2</sub>F<sub>5</sub>Ge(CH<sub>3</sub>)<sub>3</sub>: C<sub>2</sub>F<sub>5</sub>Ge(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>, Ge(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>.

dynamic vacuum. The vessels were then sealed with a torch, placed in an oven, and maintained at the temperatures reported below. After the reaction was terminated the products were separated by fractional condensation or GLC and identified by their properties. The mercury-containing products were the least volatile and were separated by vacuum sublimation. <sup>19</sup>F NMR spectra of the ethereal solutions of these solids indicated the presence of the trifluoromethylmercuric halide, CF<sub>3</sub>HgBr or CF<sub>3</sub>HgI, as well as unreacted (CF<sub>3</sub>)<sub>2</sub>Hg.<sup>8</sup> Mercuric iodide was identified among the reaction products by mass spectrometry.

**Reaction of Germanium Tetrabromide with Perfluoroalkyl Mercurials.** Germanium tetrabromide (1.98 g, 5.05 mmol) and (CF<sub>3</sub>)<sub>2</sub>Hg (1.69 g, 4.95 mmol) were reacted at 110 °C for 18 h. The tube was opened and the volatile contents removed at -22 °C for analysis by <sup>19</sup>F NMR (see Table I) which indicated the presence of CF<sub>3</sub>GeBr<sub>3</sub>, 55%; (CF<sub>3</sub>)<sub>2</sub>GeBr<sub>2</sub>, 22%; (CF<sub>3</sub>)<sub>3</sub>GeBr, 18%; and (CF<sub>3</sub>)<sub>4</sub>Ge, 4%; accompanied by very small amounts of SiF<sub>4</sub> (δ 86.8 ppm) and *c*-C<sub>3</sub>F<sub>6</sub> (δ 83.2 ppm). Separation by GLC yielded the pure compounds, which were further characterized by mass spectrometry (see Table II). The infrared spectra of each compound contained strong absorptions at ca. 1165 cm<sup>-1</sup> (C–F stretch) and 735 cm<sup>-1</sup> (symmetric CF<sub>3</sub> defor-

**Table III.** Typical Product Distribution from the Reaction of GeI<sub>4</sub> + Hg(CF<sub>3</sub>)<sub>2</sub> at 120 °C for 120 h

Initial molar ratio <sup>c</sup>	Yields <sup>a</sup> of products, %				
	CF <sub>3</sub> GeI <sub>3</sub>	(CF <sub>3</sub> ) <sub>2</sub> -GeI <sub>2</sub>	(CF <sub>3</sub> ) <sub>3</sub> -GeI	(CF <sub>3</sub> ) <sub>4</sub> Ge	(CF <sub>3</sub> ) <sub>3</sub> -GeF <sup>b</sup>
0.55	90	5			
0.98	13	53	16		
1.72			72	22	
2.00			72	15	11

<sup>a</sup> Based on GeI<sub>4</sub>. <sup>b</sup> See Discussion. <sup>c</sup> (CF<sub>3</sub>)<sub>2</sub>Hg/GeI<sub>4</sub>.

mation) and were in accord with the spectra of the known (trifluoromethyl)germanium compounds.<sup>5,8,15</sup>

A sample containing 5 mmol of GeBr<sub>4</sub> and 10 mmol of (CF<sub>3</sub>)<sub>2</sub>Hg was held at 150 °C for 24 h. Upon separation the yield of (CF<sub>4</sub>)<sub>4</sub>Ge was 20%, based on GeBr<sub>4</sub>; (CF<sub>3</sub>)<sub>3</sub>GeBr was 65%; and (CF<sub>3</sub>)<sub>2</sub>GeBr<sub>2</sub> was 10%. If the less substituted germanium species were "recycled" several times by fractionating the products of the reaction at -112 or -119 °C and reacting the material retained in the trap [CF<sub>3</sub>GeBr<sub>3</sub>, (CF<sub>3</sub>)<sub>2</sub>GeBr<sub>2</sub>, and much of the (CF<sub>3</sub>)<sub>3</sub>GeBr] with more (CF<sub>3</sub>)<sub>3</sub>Hg, the yields of (CF<sub>3</sub>)<sub>4</sub>Ge could be increased to 40%. In contrast the yield of the less substituted (trifluoromethyl)germanium tribromide was enhanced if dry ethyl ether, (5 mL) was used as solvent and a temperature of only 50 °C was maintained. Under these conditions equimolar amounts of GeBr<sub>4</sub> and (CF<sub>3</sub>)<sub>2</sub>Hg were reacted for 7 days and yielded only the monosubstituted CF<sub>3</sub>GeBr<sub>3</sub>.

The reaction of 0.4 mmol of GeBr<sub>4</sub> with 1.5 mmol of the perfluoroethyl mercurial, (C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>Hg, required much higher temperatures, 195 °C, before proceeding and gave only the monosubstituted C<sub>2</sub>F<sub>5</sub>GeBr<sub>3</sub> in 45% yield. <sup>19</sup>F NMR δ (CF<sub>3</sub>) -1.0 ppm; δ (CF<sub>2</sub>) 38.8 ppm; <sup>3</sup>J<sub>F-F</sub> = 2.9 Hz. Perfluoroethyl bromide was also produced in this reaction in 20% yield.

#### Reaction of Germanium Tetraiodide with Perfluoroalkyl Mercurials.

The reaction of GeI<sub>4</sub> with the perfluoroalkyl mercurials (CF<sub>3</sub>)<sub>2</sub>Hg and (C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>Hg was investigated in sealed tube reactions as described above. For the reactions of (CF<sub>3</sub>)<sub>2</sub>Hg with GeI<sub>4</sub> the effect of varying the ratio of (CF<sub>3</sub>)<sub>2</sub>Hg to GeI<sub>4</sub> was investigated. Germanium tetraiodide (3 g) and sufficient (CF<sub>3</sub>)<sub>2</sub>Hg to form molar ratios of mercurial to germane of 0.55, 0.98, 1.72, and 2.00 were placed in 10-mm tubes, degassed, sealed, and placed in an oven held at 120 °C. After 120 h the tubes were opened and the contents separated by fractionation. (Trifluoromethyl)germanium triiodide was found in a trap maintained at 0 °C, (CF<sub>3</sub>)<sub>2</sub>GeI<sub>2</sub> was held at -45 °C, (CF<sub>3</sub>)<sub>3</sub>GeI was retained at -96 °C, and (CF<sub>3</sub>)<sub>4</sub>Ge was in a trap cooled to -126 °C. Tris(trifluoromethyl)germanium fluoride stops in a -78 °C trap. The yields based on GeI<sub>4</sub> of each of the (trifluoromethyl)germanium halides isolated from these reactions are presented in Table III as a function of the molar ratio of the reagents employed. The properties of the (trifluoromethyl)germanium iodides prepared are summarized in Tables I and II.

Reaction of GeI<sub>4</sub> (0.360 g, 0.61 mmol) with (C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>Hg (0.245 g, 0.56 mmol) gave a 53% yield of a yellow liquid, C<sub>2</sub>F<sub>5</sub>GeI<sub>3</sub>, as the only (perfluoroalkyl)germanium product even after 21 days at 135 °C. The <sup>19</sup>F NMR of this compound in diethyl ether consists of a quartet at 41.3 ppm and a triplet at -0.9 ppm, <sup>3</sup>J<sub>F-F</sub> = 2.2 Hz. The mass spectrum of C<sub>2</sub>F<sub>5</sub>GeI<sub>3</sub> contains ions due to C<sub>2</sub>F<sub>5</sub>GeI<sub>3</sub><sup>+</sup>, FGeI<sub>3</sub><sup>+</sup>, and GeI<sub>3</sub><sup>+</sup>. Perfluoroethyl iodide was also produced in 30% yield.

#### Reaction of Tin Tetrabromide with Bis(trifluoromethyl)mercury.

Under a variety of conditions the reaction of SnBr<sub>4</sub> with (CF<sub>3</sub>)<sub>2</sub>Hg resulted in the formation of CF<sub>3</sub>SnBr<sub>3</sub> and (CF<sub>3</sub>)<sub>2</sub>SnBr<sub>2</sub> as the only volatile tin-containing products. For example, 2.9 g of SnBr<sub>4</sub> (6.62 mmol) and 6.74 g of (CF<sub>3</sub>)<sub>2</sub>Hg (19.9 mmol) were held at 125 °C for 67 h. This reaction produced a 54% yield of CF<sub>3</sub>SnBr<sub>3</sub> and a 19% yield of (CF<sub>3</sub>)<sub>2</sub>SnBr<sub>2</sub>.

(Trifluoromethyl)tin tribromide passes through a trap maintained at -30 °C and is held in a trap which is at -45 °C. The <sup>19</sup>F NMR spectrum is a singlet at -30.8 ppm symmetrically surrounded by satellites due to the tin 110 and 117 isotopes, <sup>2</sup>J<sub>Sn-F</sub> = 871/835 Hz. The infrared spectrum contains absorptions at 1212 (w), 1142 (s), 1130 (vs), 1091 (w), 1070 (sh), 1040 (w), and 730 cm<sup>-1</sup> (w). The mass spectrum contains ions due to SnBr<sub>3</sub><sup>+</sup>, CF<sub>3</sub>SnBr<sub>2</sub><sup>+</sup>, CF<sub>3</sub>SnBr<sup>+</sup>, and CF<sub>3</sub>Sn<sup>+</sup>, the first two being the most intense.

Bis(trifluoromethyl)tin dibromide passes through a trap held at

-45 °C and is held in a trap maintained at -78 °C. The <sup>19</sup>F NMR is a singlet at -34.7 ppm, <sup>2</sup>J<sub>Sn-F</sub> = 717/689 Hz. The infrared spectrum is characterized by absorptions at 1180 (sh), 1140 (vs), 1114 (m), 1095 (sh), 1040 (vw), and 730 cm<sup>-1</sup> (w). The mass spectrum contains ions due to CF<sub>3</sub>SnBr<sub>2</sub><sup>+</sup>, (CF<sub>3</sub>)<sub>2</sub>SnBr<sup>+</sup>, SnBr<sub>2</sub><sup>+</sup>, and SnBr<sup>+</sup>; the base peak is CF<sub>3</sub>SnBr<sub>2</sub><sup>+</sup>. Attempts to produce more fully substituted (trifluoromethyl)tin compounds by further reacting (CF<sub>3</sub>)<sub>2</sub>SnBr<sub>2</sub> with more (CF<sub>3</sub>)<sub>2</sub>Hg failed. At 80 °C there was no reaction; at 100 °C the (CF<sub>3</sub>)<sub>2</sub>SnBr<sub>2</sub> decomposed.

**Reaction of Silicon Tetrahalides with Bis(trifluoromethyl)mercury.** Silicon tetrachloride, -bromide, or -iodide (ca. 5 mmol) was reacted with (CF<sub>3</sub>)<sub>2</sub>Hg (1-20 mmol) in a similar fashion at temperatures which varied from 0 to 100 °C. Although C<sub>3</sub>F<sub>6</sub>, SiF<sub>4</sub>, and, e.g., HgI<sub>2</sub> were produced and identified by mass spectrometry, in no case were trifluoromethyl-substituted silanes discerned.

**Chemical Integrity of the Trifluoromethyl Bond to Germanium.** The reactions of the (trifluoromethyl)germanium iodides, particularly (CF<sub>3</sub>)<sub>3</sub>GeI, with a variety of chemicals that are known to replace germanium-halogen bonds with bonds from germanium to other ligands were examined to delineate the stability of the Ge-CF<sub>3</sub> linkage toward these reagents.

**Reaction with Silver Halides.** A large excess of AgBr (1.5 g) was reacted with 0.480 g of (CF<sub>3</sub>)<sub>3</sub>GeI (1.18 mmol). After 24 h at room temperature, the sealed tube was opened and (CF<sub>3</sub>)<sub>3</sub>GeBr was recovered in 95% yield based on (CF<sub>3</sub>)<sub>3</sub>GeI. Similar reactions of (CF<sub>3</sub>)<sub>3</sub>GeI with excess AgCl and AgF yielded (CF<sub>3</sub>)<sub>3</sub>GeCl and (CF<sub>3</sub>)<sub>3</sub>GeF in 92 and 73% yield, respectively. The properties of these compounds are presented in Tables I and II.

**Reaction with Mercuric Oxide.** In a sealed tube tris(trifluoromethyl)germanium iodide (0.210 g) was reacted for 24 h with excess HgO (0.700 g) to yield the digermoxane, (CF<sub>3</sub>)<sub>3</sub>GeOGe(CF<sub>3</sub>)<sub>3</sub>, quantitatively. See Tables I and II for the properties of this compound.

**Reaction with Sodium Amalgam.** Tris(trifluoromethyl)germanium iodide (0.520 g, 0.13 mmol) was condensed onto 10 mL of 0.5% Na/Hg solution. The tube was sealed and shaken for 72 h at room temperature. This reaction after separation of the products yielded the digermene, (CF<sub>3</sub>)<sub>3</sub>GeGe(CF<sub>3</sub>)<sub>3</sub>, in 60% yield.

**Reactions with Dimethylcadmium.** A twofold excess of (CH<sub>3</sub>)<sub>2</sub>Cd, which had been prepared by the interaction of CdI<sub>2</sub> with CH<sub>3</sub>MgI in ether and purified by fractionation at -22 °C, was condensed on 1 mmol of (CF<sub>3</sub>)<sub>3</sub>GeI and allowed to react for 24 h at room temperature. After the tube was opened, (CF<sub>3</sub>)<sub>3</sub>GeCH<sub>3</sub> was separated by GLC in 90% yield. By the analogous reaction (CF<sub>3</sub>)<sub>2</sub>Ge(CH<sub>3</sub>)<sub>2</sub> was prepared from (CF<sub>3</sub>)<sub>2</sub>GeI<sub>2</sub> in 92% yield. Similarly, the reaction of 0.120 g of C<sub>2</sub>F<sub>5</sub>GeI<sub>3</sub> with 0.100 g of (CH<sub>3</sub>)<sub>2</sub>Cd yielded C<sub>2</sub>F<sub>5</sub>Ge(CH<sub>3</sub>)<sub>3</sub> quantitatively. Product characterization data are collected in Tables I and II.

**Reaction with Aqueous Solutions.** The reaction of 0.2-g samples of tris(trifluoromethyl)germanium iodide with excess 3 M hydroxide resulted in cleavage of the CF<sub>3</sub>-Ge bond and the quantitative formation of fluoroform, identified by <sup>19</sup>F NMR and mass spectrum. The reaction of (CF<sub>3</sub>)<sub>3</sub>GeI with acidic (3 M HCl) solutions, however resulted in the formation of (CF<sub>3</sub>)<sub>3</sub>geOGe(CF<sub>3</sub>)<sub>3</sub> in good yield. See Tables I and II.

**Reaction with Aqueous NaBH.** Tris(trifluoromethyl)germanium iodide (0.375 g, 0.92 mmol) was condensed onto 50 mL of 1 M HBr which was contained in a 100-mL three-necked flask. After the solution was allowed to warm to 0 °C, the vacuum system was backpressured to 1 atm with N<sub>2</sub>. The solution was then stirred while 50 mL of H<sub>2</sub>O containing 3 g of NaBH<sub>4</sub> was added over a 30-min period from a dropping funnel. The gases evolved from the reaction were passed through four traps maintained at -196 °C. After the reaction was completed the nitrogen was removed from the vacuum line and the contents of the traps were separated by fractional condensation to give 0.240 g (93%) of (CF<sub>3</sub>)<sub>3</sub>GeH. By an entirely analogous reaction, (CF<sub>3</sub>)<sub>2</sub>GeH<sub>2</sub> was prepared in 85% yield from 0.105 g of (CF<sub>3</sub>)<sub>2</sub>GeI<sub>2</sub>. Properties of these hydrides are given in Tables I and II.

#### Characterization of the (Trifluoromethyl)germanium Compounds.

All of the new compounds gave satisfactory elemental analyses. The melting points, boiling points, and two ions of high *m/e* value from the mass spectra are presented in Table II. The <sup>19</sup>F and <sup>1</sup>H NMR data and strong infrared bands are contained in Table I. Each infrared spectrum was dominated by strong C-F stretches at ca. 1170 cm<sup>-1</sup> and CF<sub>3</sub> deformations at ca. 735 cm<sup>-1</sup>. The positions of these bands were little affected by changes in the other substituents attached to

**Table IV.** Redistribution Reaction of  $(CF_3)_3GeI$  at 155 °C, Sealed Tubes, Monitored by  $^{19}F$  NMR

Time, h	Rel amounts of		
	$(CF_3)_4Ge$	$(CF_3)_3GeI$	$(CF_3)_2GeI_2$
0	0.00	1.00	0.00
15	0.06	0.86	0.08
30	0.11	0.77	0.12
90	0.19	0.71	0.19

germanium. The complete vibrational analysis of these compounds is currently in progress.

#### Thermal Stability of (Trifluoromethyl)stannanes and -germanes.

To obtain a qualitative measure of the inherent thermal stability of some of the (trifluoromethyl)group 4A compounds which have been synthesized, small aliquots, ca. 0.25 g, of these species were introduced into 4-mm Pyrex tubes under vacuum, held at  $-196$  °C, and sealed off with a torch. The samples were then placed in an oven which was maintained at the indicated temperatures and the contents of the tubes were monitored periodically by  $^{19}F$  NMR.

**(Trifluoromethyl)stannanes.** A 0.3-g sample of tetrakis(trifluoromethyl)stannane,  $(CF_3)_4Sn$ , which had been synthesized by the plasma reaction of  $C_2F_6$  with  $SnI_4$ ,<sup>8</sup> was heated to 100 °C for 24 h. At the end of this time the sample had completely decomposed to yield 1 equiv of  $c-C_3F_6$  (identified by NMR and mass spectrum), small amounts of  $SiF_4$ , and a nonvolatile residue. Fifty-eight percent of a 0.20-g sample of  $(CF_3)_4Sn$  which had been held for 24 h at 66 °C similarly decomposed, also liberating  $C_3F_6$ , small amounts of  $SiF_4$ , and nonvolatile products which were presumably polymeric tin fluorides. In contrast,  $CF_3SnBr_3$  (0.10 g) was only very slightly affected by 24 h at 125 °C as traces of  $(CF_3)_2SnBr_2$  were observed.

**(Trifluoromethyl)germanes.** The germanium-containing compounds  $(CF_3)_4Ge$ ,  $(CF_3)_3GeI$ ,  $(CF_3)_3GeCl$ ,  $(CF_3)_2GeI_2$ ,  $(CF_3)_3GeCH_3$ , and  $(CF_3)_2Ge(CH_3)_2$  were also heated separately in 4-mm tubes which were then monitored by  $^{19}F$  NMR. All of these compounds were unchanged after 7 days at 145 °C. Even after 7 days at 190 °C the methylated derivatives,  $(CF_3)_3GeCH_3$  and  $(CF_3)_2Ge(CH_3)_2$ , were unaffected. All of the remaining samples showed slow decomposition at 190 °C to yield perfluorocyclopropane and the expected germanium fluoride, e.g.,  $(CF_3)_3GeF$  from  $(CF_3)_4Ge$ . At 155 °C the (trifluoromethyl)germanium halides were found to be stable toward the formation of  $C_3F_6$ , but redistribution (ligand scrambling) reactions slowly occur as shown in Table IV for  $(CF_3)_3GeI$ .

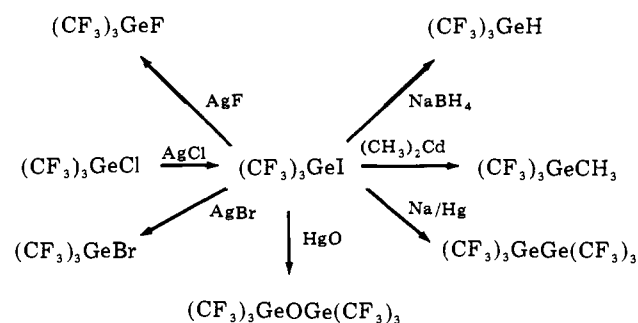
#### Results and Discussion

The reaction of the perfluoroalkyl mercurial  $(CF_3)_2Hg$  with inorganic halides has been characterized as not leading to the formation of trifluoromethyl-substituted organometallic species. For example, the statement, "The reaction of bisperfluoroalkylmercury derivatives with metal or metalloids halides does not yield the perfluoroalkyl derivatives expected by analogy with the corresponding alkylmercury compounds", appears in one review<sup>10</sup> on this subject. We find, however, that the reaction of  $(CF_3)_2Hg$  with group 4A halides provides a very convenient source of many trifluoromethyl-containing group 4A compounds and that the synthesis appears to be limited only by the thermal stability of the compounds formed. As shown in Table III, all of the (trifluoromethyl)germanium halides,  $(CF_3)_nGeI_{4-n}$  where  $n = 1-4$ , are produced in good to excellent yields, yields that can be varied to increase the amount of a desired product by the appropriate selection of the amounts of reagents used. These (trifluoromethyl)germanium halides have also been shown to be stable to temperatures of 145 °C for extended periods of time. The reaction of  $(CF_3)_2Hg$  with  $SnBr_4$  yields only  $CF_3SnBr_3$  and  $(CF_3)_3SnBr_2$ . Again this is in accord with the thermal stabilities of the (trifluoromethyl)stannanes as a sample of  $(CF_3)_4Sn$ , synthesized by an alternate route, was shown to decompose at temperatures as low as 66 °C whereas  $CF_3SnBr_3$  was shown to be stable at 125 °C. The reaction of the silicon tetrahalides did not result in the formation of detectable amounts of (trifluoromethyl)silanes under

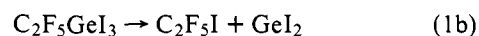
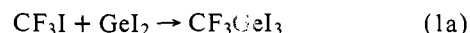
the conditions employed. The half-life, in the gas phase, of the compound  $CF_3SiF_3$  is reported to be only 7 min at 100 °C.<sup>4</sup>

The reaction of the perfluoroethylmercurial,  $(C_2F_5)_2Hg$ , with  $GeBr_4$  or  $GeI_4$  resulted in the formation of the mono-substituted  $C_2F_5GeX_3$  ( $X = Br, I$ ) only, and then only at higher temperatures or longer reaction times. Attempts to further substitute  $C_2F_5$  groups resulted in decomposition. These results imply that the activation energy for the exchange of perfluoroethyl ligands between germanium and mercury atoms is substantially higher than the activation energy for the exchange of perfluoromethyl groups.

Once formed, the (trifluoromethyl)germanium linkage is remarkably stable to a number of chemical reagents including sodium amalgam, sodium borohydride, dimethylcadmium, and a variety of metallic salts all of which cause reaction with the germanium-halogen bonds present in the same molecule, but leave the  $CF_3-Ge$  bond unaffected. Each of these reactions, summarized in Scheme I, resulted in the preparation of new compounds in excellent yield.

Scheme I. Reactions of  $(CF_3)_3GeI$ 

The formation of perfluorocyclopropane,  $(CF_2)_3$ , in the reactions of the silicon, germanium, and tin halides with  $(CF_3)_2Hg$  and in those thermal stability studies where decomposition was noted indicates that the probable mode of decomposition for the (trifluoromethyl)group 4A halides is difluorocarbene elimination with the formation of a metal-fluorine bond. The lack of  $C_3F_6$  and the presence of, e.g.,  $C_2F_5I$  among the products when  $(C_2F_5)_2Hg$  was reacted with the germanium halides indicates that the (pentafluoroethyl)germanium halides decompose by reductive elimination of the pentafluoroethyl halide with the formation of a divalent germanium species. This is the reverse of the oxidative-addition reaction used for the original preparation of (trifluoromethyl)germanium triiodide;<sup>5</sup> these reactions are shown in the equations:

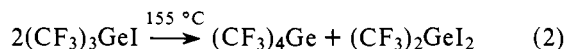


A similar reductive-elimination process was observed in the mass spectrum of  $(CF_3)_4Ge$  where the reaction  $(CF_3)_3GeCF_2^+ \rightarrow C_2F_5^+ + (CF_3)_2Ge$  was observed and supported by a metastable ion, indicating that reductive elimination is also a decomposition channel for the trifluoromethyl-substituted germanium species but the activation energy for this step is higher than that for the reaction channel leading to difluorocarbene elimination.

The mechanism for the formation of  $(CF_3)_3GeF$  in the reaction of  $(CF_3)_2Hg$  and  $GeI_4$  at 120 °C is not clear. As shown in the Experimental Section and in Table IV the (trifluoromethyl)germanes are thermally stable at these temperatures, as is the mercurial,  $(CF_3)_2Hg$ .<sup>16</sup> Presumably, formation of the fluoride is catalyzed by the Lewis acids present in the reaction mixture. The fluoride is also anomalous in that all of the other newly prepared compounds appear to be monomeric liquids or solids except  $(CF_3)_3GeF$ . As shown in Table II, the subli-

mation point of this compound is normal in comparison with the other halides, but the melting point, 30 °C, is quite abnormal, about 125 °C above the melting point of (CF<sub>3</sub>)<sub>3</sub>GeCl. This shows extensive association in the solid state, probably by means of fluorine bridging between germanium atoms. Further evidence of association comes from the <sup>19</sup>F NMR: the fluorine resonances of the neat liquid consist of two broad singlets. In a diethyl ether solution these resonances become resolved into the expected doublet and decet again indicating association in the condensed phase that is broken up (on the NMR time scale) by the intervention of solvent molecules. Similar effects have been reported for the compounds CH<sub>3</sub>GeH<sub>2</sub>F<sup>17</sup> and (CF<sub>3</sub>)<sub>2</sub>GeF<sub>2</sub>.<sup>7</sup> Thus, the properties of these fluorides indicates that the germanium fluorides occupy a middle ground between those of carbon and silicon, which are very volatile, nonassociated fluorides, and those of tin and lead, which are essentially nonvolatile at lower temperatures and are strongly associated in the solid phase.

One of the observations that led to the present study was made during the reaction of the germanium tetrahalides, GeBr<sub>4</sub> and especially GeI<sub>4</sub>, with C<sub>2</sub>F<sub>6</sub> in the discharge apparatus.<sup>8</sup> The material obtained from this reaction was fractionated at -78 °C and small amounts of (CF<sub>3</sub>)<sub>2</sub>GeI<sub>2</sub> were observed by mass spectrometry to be in the fraction retained in the -78 °C trap. After the sample had been stored at room temperature for a few days, however, these samples were shown, again by mass spectrometry, to contain all of the possible (trifluoromethyl)germanes, including (CF<sub>3</sub>)<sub>4</sub>Ge. Clearly, these products were being formed from the less volatile (trifluoromethyl)germanium halides by some exchange process, presumably involving trifluoromethyl groups migrating from one germanium atom to another. But ligand exchange reactions of pseudohalogen CF<sub>3</sub> groups attached to germanium had been reported not to proceed<sup>5</sup> even at temperatures of 190 °C. In order to resolve these two results small samples of tris(trifluoromethyl)germanium iodide were sealed into tubes and heated to 155 °C where, as shown in Table IV, the redistribution reaction was observed to occur:



In conclusion, we find that in contrast to the earlier reports, the reaction of the perfluoroalkyl mercurials with group 4A halides does provide a very convenient source of many (trifluoromethyl)group 4A compounds, especially those of germanium. The iodides and bromides can be prepared directly, and can be converted easily to other (trifluoromethyl)germanium derivatives. The reaction of other inorganic halides, including selected transition metal halides, with perfluoromethyl mercurials will be reported at a later date.

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