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PRELIMINARY NOTE

Ligand Exchange Reactions of Bis(trifluoromethyl)mercury; The Preparation of $(CF_3)_4Ge$ and $(CF_3)_2SnBr_2$ from $(CF_3)_2Hg$.

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ABSTRACT

In sealed tube reactions bis(trifluoromethyl)mercury has been shown to exchange ligands with halogenated compounds such as $GeBr_4$ and $SnBr_4$ to produce a series of trifluoromethyl containing germanium and tin compounds including $Ge(CF_3)_4$ and $Sn(CF_3)_2Br_2$. These exchange reactions are shown to be synthetically useful provided the desired products are stable at the required reaction temperatures.

INTRODUCTION

The properties of a trifluoromethyl group attached to an organometallic compound have been of interest for many reasons, not the least of which is that this substituted alkyl group has an electronegativity of about 3.5 on the Pauling scale, an electronegativity higher than that of chlorine[2]. The trifluoromethyl group is thus not only a substituted alkyl, but it is also an analog of the halogens. Many reactions of the CF_3 group have been interpreted in terms of a "pseudohalogen" character of the trifluoromethyl group[3]. One type of reaction common to both halogenated and alkylated inorganic compounds is the ligand exchange reaction which has been used for many years as a preparative route to new compounds of note[4,5]. Both mercury halides and mercury alkyls have been used synthetically as reagents for the preparation of halogenated or alkylated metallic species; however, reactions of bis(trifluoromethyl)mercury with inorganic halides have not generally resulted in the isolation of new trifluoromethyl substituted species. Rather the results of these reactions have been summarized as follows:"The reaction of bis(perfluoroalkyl)mercury derivatives with metal or metalloid halides does not yield the perfluoroalkyl derivatives expected by analogy with the corresponding alkylmercury derivatives."[6] "All attempts to prepare new perfluoroalkyl organo-metallics from the mercury compounds have been unsuccessful."[3] "In its . . . reluctance to undergo exchange with inorganic halides, bistrifluoromethylmercury is unlike its simple methyl analogue."[7]

In order to learn the reasons behind this anomalous behavior, we have studied the reactions of the compound $(CF_3)_2Hg$ with the metal halides of one representative group of the Periodic Table, Group IVA. We find that bis(trifluoromethyl)mercury easily exchanges ligands with these halides and that this reaction affords a very convenient preparation of many trifluoromethyl substituted derivatives of germanium and tin.

EXPERIMENTAL

The reactions were carried out by placing measured amounts of the reagents in 10 mm Pyrex tubing, evacuating the air with a standard vacuum line, and sealing the tubes with a torch. After the vessels had remained in an oven which was maintained at the indicated temperatures, they were opened under vacuum and the contents were separated by fractional condensation or gas liquid chromatography (10% SE-30 on Chromasorb P column). Spectroscopic data were obtained by conventional means: ^{19}FMR spectra from a Perkin-Elmer R-20-B spectrometer operating at 56.46 MHz; mass spectra at 70 eV. with an Hitachi RMU-6E machine; gas phase infrared spectra by means of a Beckman IR-20-A spectrophotometer. The Group IVA tetrahalides were commercially supplied; bis(trifluoromethyl)mercury was prepared either by the reaction of HgI_2 with the products formed in a radio frequency discharge of C_2F_6[8], or by the thermal decarboxylation of $(CF_3CO_2)_2Hg$[9].

Reaction of $(CF_3)_2Hg$ with $GeBr_4$. A 1.98 g (5.05 mmol.) sample of $GeBr_4$ was sealed with 1.69 g (4.95 mmol.) of $(CF_3)_2Hg$ and heated to 110^o for 18 hours. The volatile contents of the tube were then analyzed by ^{19}FMR (see Table I) and found to consist of CF_3GeBr_3, 55%; $(CF_3)_2GeBr_2$, 22%; $(CF_3)_3GeBr$, 18%; and $(CF_3)_4Ge$, 4%. These products were accompanied by small amounts of SiF_4 (δ = 86.8 ppm) and cyclo-C_3F_6 (δ = 83.2 ppm). Separation yielded the pure compounds which were further characterized by mass spectral data (see Table I). The infra-red spectra[8,10] were characterized by very strong absorptions at ca 1165 cm^{-1} (C-F stretch) and 735 cm^{-1} (symmetric CF_3 deformation) and are characteristic of trifluoromethyl substituted germanes. (Trifluoromethyl)mercurybromide was identified by its fluorine nmr spectrum in etherial extracts of the involatile residue remaining in the vessel. At 150^o with a molar ratio of mercurial to germane of 2:1 the yield of $(CF_3)_4$ was 20%; the yield of $(CF_3)_3GeBr$ was 65%; and the yield of $(CF_3)_2GeBr_2$ was 10%. The yield of $(CF_3)_4Ge$, based on $GeBr_4$, could be raised to 40% if the less substituted germanium species were separated and "recycled" by further reaction with more $(CF_3)_2Hg$. In diethyl ether (5 ml) at 50^o the reaction yielded only monosubstituted CF_3GeBr_3 during a reaction time of 7 days.

Reaction of $(CF_3)_2Hg$ with $SnBr_4$. Under a variety of conditions the reaction of $SnBr_4$ with $(CF_3)_2Hg$ resulted in the formation of CF_3SnBr_3 and $(CF_3)_2SnBr_2$ as the only volatile tin containing products. For example, 2.9 grams of $SnBr_4$ and 6.74 grams of $(CF_3)_2Hg$ were reacted for 67 hours at 125^0 resulting in a 54% yield of CF_3SnBr_3 and a 19% yield of $(CF_3)SnBr_2$, based on $SnBr_4$. (Trifluoromethyl)tin tribromide passes through a -30^0 trap and is held in a trap maintained at -45^0. The infrared spectrum of this new compound contains absorptions at 1212(w), 1142(s), 1130(vs), 1091(w), 1070(sh), 1040(w), and 730(w) cm^{-1}. Bis-(trifluoromethyl)tin dibromide, also a new compound, passes through a trap held at -45^0, and is retained in a trap maintained at -78^0. The infrared spectrum is characterized by absorptions at 1180(sh), 1140(vs), 1114(m), 1095(sh), 1040(vw), and 730(w) cm^{-1}. The ^{19}F NMR and mass spectral data for these compounds are presented in Table I. Attempts to produce more fully substituted compounds by further reacting $(CF_3)_2SnBr_2$ with $(CF_3)_2Hg$ failed. At 80^0 there was no reaction; at 100^0 the $(CF_3)_2SnBr_2$ decomposed very slowly. To gain some insight into the stability of the more fully substituted trifluoromethyl derivatives of tin, $(CF_3)_4Sn$ was synthesized and a 0.3 gram sample was heated to 100^0. After 24 hours, the sample had completely decomposed with the evolution of CF_2 which had trimerized to yield the observed cycle-C_3F_6.

Reaction of $(CF_3)_2Hg$ with $SiBr_4$. Under a wide variety of conditions $SiBr_4$, 1-20 mmol., was reacted with $(CF_3)_2Hg$, 5 mmol.; large amounts of SiF_4 and cyclo-C_3F_6 were recovered, but in no case were trifluoromethyl substituted silanes observed.

TABLE I

Fluorine nmr and mass spectral data of trifluoromethyl germanium and tin compounds.

Compound	^{19}NMR, ppm[a]	Mass[a] Spectrum[d]
(Trifluoromethyl)germanes		
CF_3GeBr_3	-13.3	$CF_3GeBr_3^+$, $FBeBr_3^+$. $CF_3GeBr_2^+$
$(CF_3)_2GeBr_2$	-19.1	$(CF_3)_2GeBr_2^+$, $CF_3GeCF_2Br_2^+$, $CF_3GeBr_2^+$
$(CF_3)_3GeBr$	-23.1	$(CF_3)_3GeBr^+$, $(CF_3)_2GeBr^+$, $(CF_3)_3Ge^+$
$(CF_3)_4Ge$	-27.6	$(CF_3)_3GeCF_2^+$, $(CF_3)_3Ge^+$, $(CF_3)_2GeCF_2^+$
(Trifluoromethyl)stannanes		
CF_3SnBr_3	-30.8[b]	$SnBr_3^+$, $CF_3SnBr_2^+$, CF_3SnBr^+
$(CF_3)_2SnBr_2$	-34.7[c]	$CF_3SnBr_2^+$, $(CF_3)_2SnBr^+$, $SnBr_2^+$

a. Neat compounds vs ext. CF_3COOH; negative chemical shifts are deshielded.

b. $^2J(Sn\text{-}F) = 871/835$ Hz.

c. $^2J(Sn\text{-}F) = 717/689$ Hz.

d. All of these ions exhibited the expected envelope corresponding to the normal isotopic distribution of the metal.

DISCUSSION

These preliminary results illustrate that $(CF_3)_2Hg$ does exchange ligands with the inorganic halides of the Group IVA elements, and that this reaction is a very convenient preparation of trifluoromethyl substituted germanium and tin compounds. The two trifluoromethyl tin halides reported here have not been previously prepared. The first step of the reaction sequence is shown in Equation 1.

$$(CF_3)_2Hg + MBr_4 \longrightarrow CF_3MBr_3 + CF_3HgBr$$
$$M = Ge,\ Sn;\ M \neq Si \qquad (1)$$

The second step of the reaction, which produces $(CF_3)_2MBr_2$, also proceeds for both germanium and tin, but the next step, to produce tris-(trifluoromethyl)MBr, (Equation 2) progresses only for germanium; presumably any $(CF_3)_3SnBr$ formed decomposes immediately. As shown above, the related compound $(CF_3)_4Sn$ is also unstable at 100-150°, the temperatures required for the exchange reaction.

$$(CF_3)_2Hg + (CF_3)_2MBr_2 \longrightarrow (CF_3)_3MBr + CF_3HgBr$$
$$M = Ge;\ M \neq Sn \qquad (2)$$

In the reaction of silicon tetrabromide with $(CF_3)_2Hg$, no trifluoromethyl substituted silicon compounds were discerned although the observed SiF_4 could have come from the decomposition of such a species. In this connection, one should note that the half-life of CF_3SiF_2I at 100° is only 7 minutes.

In conclusion, perhaps a better summary of the reaction of $(CF_3)_2Hg$ with inorganic halides than those referred to previously[3,6,7] is that bis(trifluoromethyl)mercury exchanges ligands easily with inorganic halides and this reaction affords a very convenient synthesis of trifluoromethyl organometallic species provided that the compounds prepared are stable at the temperatures required for their formation.

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