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Oxidation of Elemental Mercury with Trifluoromethyl Radicals. Synthesis for Bis(trifluoromethyl)mercury

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We have recently developed in our laboratory a general synthesis for trifluoromethyl organometallic compounds.[2] Trifluoromethyl radicals generated from C_2F_6 in a glow discharge were shown to react with metal halides to produce completely substituted trifluoromethyl organometallic compounds in high yields. The preparation of $Hg(CF_3)_2$ by this method[2] is a facile synthesis which is now operable in our laboratory on a scale of 8 g/4 hr. Haszeldine and Emeleus, in the first preparation of trifluoromethylmercury compounds, established that CF_3I reacts on heating and/or irradiation with mercury metal to yield only CF_3HgI[3] and that the use of amalgams was necessary to produce $(CF_3)_2Hg$.[4] We have found trifluoromethyl radicals generated from C_2F_6 in radiofrequency discharge are capable of oxidizing mercury metal directly to bis(trifluoromethyl)mercury.

A glow discharge is a convenient source of reactive radicals which are likely to be formed in excited electronic vibrational states and rotational states but have little translational energy. The reaction of trifluoromethyl radicals with Hg appears to take place in the gas phase. The elemental mercury is placed on the bottom surface of the plasma reactor and vaporized through the plasma zone. The presence of electronically excited mercury atoms, established by the characteristic lines in the visible spectrum, definitely increases the reaction rate and is probably essential for this reaction. If metallic mercury is placed in a boat or container slightly ahead of the recombination zone of the plasma, no reaction occurs. Gentle heating of the mercury to 45°C increases the concentration of excited mercury atoms in the plasma and markedly increases the overall yield. The use of cadmium amalgam does not influence the reaction.

If a mixture of C_2F_6 (95%) and CF_3I (5%) is used, CF_3HgI and $(CF_3)_2Hg$ are formed in a ratio of about 2:1. With pure CF_3I, nearly quantitative conversion to C_2F_6 and HgI_2 with the formation of only traces of $(CF_3)_2Hg$ is observed. The reaction sequence of eq 1–9 is probable.

$$C_2F_6 \overset{rf}{\rightleftarrows} 2CF_3\cdot \tag{1}$$

$$CF_3I \overset{rf}{\rightleftarrows} CF_3\cdot + I\cdot \tag{2}$$

$$Hg + I\cdot \rightarrow \cdot HgI \tag{3}$$

$$Hg^* + CF_3\cdot \rightarrow \cdot HgCF_3 \tag{4}$$

$$\cdot HgCF_3 + I\cdot \rightleftarrows \cdot HgI + CF_3\cdot \tag{5}$$

$$\cdot HgI + CF_3\cdot \rightleftarrows CF_3HgI \tag{6}$$

$$\cdot HgI + I\cdot \rightleftarrows HgI_2 \tag{7}$$

$$\cdot HgCF_3 + I\cdot \rightarrow IHgCF_3 \tag{8}$$

$$\cdot HgCF_3 + CF_3\cdot \rightarrow Hg(CF_3)_2 \tag{9}$$

The results indicate that the high CF_3 radical recombination rate k_{-1} and the abstraction of iodine atoms by mercury and/or Hg–CF_3 compounds are limiting factors for the yields of $(CF_3)_2Hg$ or CF_3HgI. The absence or nearly negligible formation of CF_3HgI in the plasma reactions of CF_3I with Hg or C_2F_6 with HgI_2[2] may be due to its low volatility and therefore long exposure time to the reactive plasma. Pure CF_3Br in a radiofrequency discharge over mercury does not yield trifluoromethylmercury compounds.

These results raise the possibility of the synthesis of other trifluoromethyl organometallic compounds via reactions of trifluoromethyl radicals with metallic substrates.

Experimental Section

In a typical experiment about 30 ml of Hg was placed in a reactor similar to that described previously.[2] The C_2F_6 flow rate was adjusted to 8 mmol/hr; the radiofrequency power level (13.6 MHz, inductive coupling) was adjusted to about 25 W allowing the mercury to warm up to 35–40°C. The operating pressure was approximately 2 mm. Bis(trifluoromethyl)mercury was collected downstream at −78°, dissolved in ether, separated from elementary mercury by filtration, and purified by sublimation. The average yield was 0.25 mmol/hr (80 mg/hr). The products were identified by their characteristic ^{19}F NMR spectra: for $Hg(CF_3)_2$, δ −40.5 ppm, $J_{^{199}HgF}$ = 1287 Hz; for $HgCF_3I$; δ −43.5 ppm, $J_{^{199}HgF}$ = 1760 Hz (in ether, vs. external TFA). Parent ions in the mass spectrum were at *m/e* 336–342 and 394–400, respectively.

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Registry No. Hg, 7439-97-6; C_2F_6, 76-16-4; $Hg(CF_3)_2$, 371-76-6.

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Crystal Structure of β-Zirconium Tribromide

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The structures of zirconium trichloride, tribromide, and triiodide were first deduced from powder data and shown to consist of linear chains of face-sharing ZrX_6 octahedra.[1-3] There was disagreement, however, on the space group assignment and therefore disagreement on whether the metal ions are paired[1] or equally spaced along the chain.[2,3] Sub-