Synthesis of Tetrakistrifluoromethyltin

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Summary Tetrakistrifluoromethyltin, $Sn(CF_3)_4$, has been prepared by the reaction of tin(IV) iodide with trifluoromethyl radicals in a radio-frequency discharge.

THE synthesis of many highly substituted metal trifluoromethyl compounds has not been possible using conventional synthetic techniques. We report here a new general technique for the preparation of a number of previously unknown tin trifluoromethyl compounds, *e.g.* $Sn(CF_3)_4$.

A hexafluoroethane discharge has been found to be an excellent source of highly reactive CF_3 radicals. The carbon–carbon bond in hexafluoroethane is relatively weak (60—70 kcal mol^{-1}) due to the electron-withdrawing effect of the fluorine and the carbon–fluorine bonds are in the 115—120 kcal mol^{-1} range. If the minimum amount of r.f. power necessary to maintain the discharge (22 W at 6 MHz) is applied through the copper coils around the reactor, the lowest energy process, the production of CF_3

radicals, predominates, and the population of other species such as fluorine atoms and CF_2 radicals is negligible.

A 3 in. O.D. quartz vessel which tapered sharply to 1 in. O.D. quartz tube was used as a reactor. A quartz boat containing SnI_4 was placed in the 1 in. O.D. tube and the r.f. coils were positioned so that the tail of the plasma, which was violet, 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^{-1}.

The volatile $Sn(CF_3)_4$ was recovered in two traps downstream from the reactor. A trap at −78 °C contained a small amount of nearly pure $Sn(CF_3)_4$ and most of the $Sn(CF_3)_4$, a volatile colourless liquid, was recovered in a subsequent −196 °C trap along with fluorocarbons. The products were extracted with benzene and $Sn(CF_3)_4$ was separated from the extract by g.l.c. The yield was over 90% based on SnI_4 and a typical 4 h run yielded 19 mg $Sn(CF_3)_4$ (0·048 mmol). The product had a correct C and F analysis. The 56·47 MHz ^{19}F n.m.r. spectrum of neat $Sn(CF_3)_4$ consisted of a singlet at −21 ± 1 p.p.m. from external trifluoromethylbenzene, and symmetrical double satellites due to tin isotope coupling [$I = 1/2$, ^{117}Sn, ^{119}Sn; J (^{119}Sn–F) 9·4 ± 0·1, J (^{117}Sn–F) 8·9 ± 0·1 p.p.m.]. The chemical shift of $Sn(CF_3)_4$ in benzene is −18 ± 1 p.p.m. The mass spectrum consisted of $Sn(CF_3)_n$ ($n = 1,2,3$) species and fluorocarbon fragments and an isotopically correct pattern around 327 for $^{120}Sn(CF_3)_3$ was of highest molecular weight. A peak at 377 ($P - 19$) was observed of insufficient intensity to determine the isotope distribution. The i.r. 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.

If the SnI_4 were positioned in the reactor to promote partial reaction, the new compounds $Sn(CF_3)_3I$ [−19·8 p.p.m., J (^{119}Sn–F) 10·3 ± 0·1, J (^{117}Sn–F) 9·8 ± 0·1 p.p.m.] and $Sn(CF_3)_2I_2$ [−16·4 p.p.m., J (^{119}Sn–F) 10·9 ± 0·1, J (^{117}Sn–F) 10·4 ± 0·1 p.p.m.] are produced. The use of other tin halides, produces other new $Sn(CF_3)_nX_{4-n}$ species but lower yields of $Sn(CF_3)_4$ are observed with about the same total yield.

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