Reaction of Plasma-generated Trifluoromethyl Radicals with Carbon Tetraiodide and with Bromobenzene; a New Synthesis for Trifluoromethyl Organic Compounds

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Summary The reaction of plasma-generated trifluoromethyl radicals with carbon tetraiodide leads to a mixture of perfluoroneopentane and perfluoro-t-butyl iodide in 97% total yield; bromobenzene reacts with trifluoromethyl radicals to give a 10–15% yield of trifluoromethylbenzene.

OVER the last several years a new general synthesis for trifluoromethyl organometallic compounds has been developed in our laboratory.[1–5] Extremely reactive trifluoromethyl radicals are generated in a low temperature radio frequency discharge, at 1–3 mmHg pressure and a radio frequency of 10 MHz at 20 W power level, from cleavage of hexafluoroethane, admitted to the reactor at *ca.* 15 cm³/min. The species produced in these low-pressure discharges are vibrationally and electronically excited, but almost in thermal equilibrium with the surroundings (T_g *ca.* 40 °C). Thus the trifluoromethyl radical is very reactive but any molecules synthesized by interaction with a second substrate are formed at or near room temperature. For details of the apparatus see ref. 2. Trifluoromethyl radicals will react easily with metal halides[1–5] to produce a general route to trifluoromethyl organometallic compounds [reaction (1)]. The new trifluoromethyl compounds are recovered downstream from the plasma reactor in a trap at cryogenic temperatures.

$$CF_3\cdot + MX_n \rightarrow M(CF_3)_n + n/2\ X_2 \text{ where } X = I, Br, \text{ or } Cl \qquad (1)$$

Recently we have found that this reaction occurs readily not only with metal halides but also with compounds containing carbon–halogen bonds. Initially, the reaction of carbon tetraiodide, the organic halide most similar in structure to the previously studied metal halides, with trifluoromethyl radicals was studied. Carbon tetraiodide (2 g) and plasma-generated trifluoromethyl radicals reacted during 4 h to give a 97% yield of a 1:3 mixture of perfluoroneopentane and perfluoro-t-butyl iodide [reaction (2)]. The perfluoroneopentane was a white waxy solid m.p. 72·5—73 °C, and its mass spectrum contained an $(M - 19)^+$ ion (*m/e* 269) in agreement with previously reported values.[6] The ^{19}F n.m.r. spectrum consisted of a singlet at −13·92 p.p.m. from external trifluoroacetic acid.[6] The i.r. spectrum contained absorptions at 3000, (1190), (980), and (720) cm⁻¹. Perfluoro-t-butyl iodide was characterized by its ^{19}F n.m.r. spectrum which consisted of a singlet at −13·5 p.p.m. from external trifluoroacetic acid. The mass spectrum showed M^+ (*m/e* 346) and $(M - 19)^+$ (*m/e* 327) ions and its i.r. spectrum had absorptions at (1270), (960), and (725) cm⁻¹. Satisfactory elemental analyses were obtained.

$$\underset{}{CF_3\cdot} + CI_4 \rightarrow \underset{(24\%)}{C(CF_3)_4} + \underset{(73\%)}{(CF_3)_3CI} + I_2 \qquad (2)$$

Under the same plasma conditions, bromobenzene and trifluoromethyl radicals gave a 10—15% yield of trifluoromethylbenzene [reaction (3)]. Hexafluoroethane was admitted to the reactor at a rate of *ca.* 4 mmol/h while the bromobenzene was admitted at a rate of 0·11 mmol/h. A mixture of trifluoromethylbenzene, fluorobenzene, and a small amount of benzene was collected in a −78 °C trap downstream. The origin of the fluorobenzene is not clear. Previously we had reported that under excess power conditions fluorination of mercuric iodide is observed.[1] However, the plasma conditions used in this experiment were not sufficient to produce fluorination of mercuric iodide and perhaps the isolation of fluorobenzene is due to an elimination of difluorocarbene from a vibrationally excited trifluoromethyl compound. Trifluoromethylbenzene was characterized by its ^1H and ^{19}F n.m.r. spectra, the latter consisting of a peak at +63 p.p.m. from trifluoroacetic acid. It was further characterized by comparison of its g.l.c. retention time with a genuine sample and by mass spectroscopy. Fluorobenzene was characterized by its ^1H and ^{19}F n.m.r. spectra, by its g.l.c. retention time, and its mass spectrum. Similarly, the reaction of 1-iodoheptane with trifluoromethyl radicals produces 1,1,1-trifluoro-octane in 20% yield, characterized by its mass, ^{19}F n.m.r., and i.r. spectra.

$$PhBr + CF_3\cdot \rightarrow \underset{15\%}{PhCF_3} + \underset{60\%}{PhF} \qquad (3)$$

These reactions illustrate the possibility of preparing compounds substituted with trifluoromethyl groups or trifluoromethyl organic compounds which are difficult to obtain by other means. This should prove to be a valuable alternative method for syntheses which are not possible using such methods as sulphur tetrafluoride reactions.

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