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Preliminary communication

The formation of mercury–carbon bonds by sulphur trioxide elimination

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The insertion of sulphur trioxide into metal–carbon bonds to give metal sulphonates is well-established[1,2], but the formation of metal–carbon bonds by sulphur trioxide elimination, has apparently not been observed. We now report the preparation

$$-\mathrm{M(O_3SR)} \rightarrow -\mathrm{MR} + \mathrm{SO_3}$$

of bis(pentafluorophenyl)-, bis(2,3,5,6-tetrafluorophenyl)-, and bis(pentachlorophenyl)-mercury by sulphur trioxide elimination reactions of the corresponding mercuric arenesulphonates.

Mercuric pentafluorobenzenesulphonate and 2,3,5,6-tetrafluorobenzenesulphonate were prepared by reaction between stoichiometric amounts of mercuric acetate and the polyfluorobenzenesulphonic acids in water, and were isolated by evaporation to dryness, whilst mercuric pentachlorobenzenesulphonate was precipitated on reaction of an excess of pentachlorobenzenesulphonic acid with mercuric acetate in water. The mercuric polyhalogenobenzenesulphonates were isolated as hydrates, were characterized by intense infrared absorption attributable[3] to sulphur–oxygen stretching at 1270–1185 and 1070–1040 cm^{-1}, and were used in the thermal decomposition reactions without purification. Aqueous pentafluorobenzenesulphonic acid was obtained by treatment of the commercially available barium salt with an equimolar amount of sulphuric acid in water. Pentachlorobenzenesulphonic acid and 2,3,5,6-tetrafluorobenzenesulphonic acid were prepared by reaction of sulphur trioxide with pentachlorobenzene[4] and 1,2,4,5-tetrafluorobenzene[5], respectively.

Thermal decomposition of mercuric pentafluorobenzenesulphonate (ca. 210°; 4 h) and mercuric 2,3,5,6-tetrafluorobenzenesulphonate (from 160–270° over 2 h) under vacuum gave oily sublimates, which, on treatment with water, yielded bis(pentafluorophenyl)mercury (m.p. 142°; lit. [6] m.p. 142°; 49% yield after recrystallization from aqueous methanol) and bis(2,3,5,6-tetrafluorophenyl)mercury (m.p. 147–148°; lit. [7] m.p. 146–147°; 7% yield after recrystallization from hexane) respectively, and aqueous sulphuric acid. The infrared spectra of the mercurials were identical with those of authentic samples prepared by mercuration under basic conditions[7]. Mercuric pentachlorobenzenesulphonate was heated from 160–230° over 2 h under vacuum. The residue, after being washed with concentrated hydrochloric acid (to remove mercuric salts), water, and acetone, was bis(pentachlorophenyl)mercury, m.p. ca. 380°, lit.[8] m.p. 383° (51% yield). The infrared spectrum was identical with that of a sample obtained by the Grignard method[8]. An oily sublimate, which gave sulphuric acid on treatment with water, was also obtained.

Studies are in progress to establish the scope of sulphur trioxide elimination, and, in particular, the possibility of extending the reaction to derivatives of other elements.

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