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THE SYNTHESIS OF PERFLUOROALKYL MERCURY DERIVATIVES VIA PERFLUOROALKYL CARBANIONS

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The perfluoroalkyl mercurials are known to be obtained by the addition of mercuric fluoride to fluoroolefins in AsF_3 or anhydrous HF solutions. This reaction is an electrophilic addition which requires vigorous conditions, according to specifity of fluoroolefins (see review [1]). Now we have found that the mercuration of fluoroolefins can be easily carried out via perfluoroalkyl carbanions, by the interaction of fluoroolefins and mercury salts in presence of alkaly metal fluorides in aprotic polar solvents. In this way both bis-perfluoroalkyl mercurials and perfluoroalkyl mercury salts are formed. For example, perfluoropropene reacts with mercuric chloride and potassium fluoride in dimethyl formamide by bubbling at 50° giving bis-perfluoroisopropyl mercury in high yield. Similarly, an exothermal reaction of perfluoroisobutene with mercuric fluoride in dimethyl formamide gives bis-perfluorotert.-butyl mercury. The constants and NMR F^{19} spectra of the obtained perfluoroalkyl mercurials agree with the data reported[2,3]. The identity of these compounds is proved as well by GLC.

$$CF_3CR{=}CF_2 \xrightarrow{F^-} (CF_3)_2CR^- \xrightarrow{HgX_2} (CF_3)_2CR\text{-}Hg\text{-}CR(CF_3)_2$$

$$R = F;\ CF_3$$

Perfluoropropene, potassium fluoride and mercuric chloride in 1,2-dimethoxyethane at 50° give perfluoroisopropyl mercury chloride, $(CF_3)_2CF\text{-}HgCl$, m.p. 76,5–78° (lit.[4]: m.p. 77–78°).

Hence the mercuration of fluoroolefins can actually be realized both by electrophilic and nucleophilic addition reactions. The latter was postulated previously for HgF_2 addition to $CF_2{=}CF_2$ and $CF_2{=}CFCl$ [5]. The conditions described (absence of solvent and of catalyst), however, cannot be regarded as favouring the carbanion formation, and the results allow other explanation.

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