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PERFLUOROALKYL MERCURIALS AS A SOURCE OF PERFLUOROCARBANIONS

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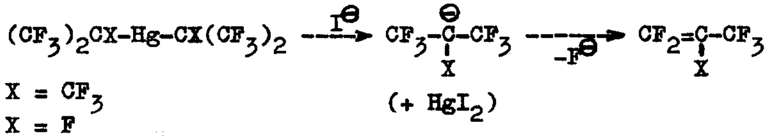
The perfluoroalkyl mercurials are known to be very stable to electrophilic attack. They survive at high temperatures in anhydrous HF[1] and they sublime from concentrated H_2SO_4 without decomposition.[2] As a rule, these compounds react under more vigorous conditions than non-fluorinated mercurials. For example, dissymmetrization of $(CF_3)_2Hg$ by treating it with HgI_2 requires heating to 175°C[3], the reaction with halogens is conducted at a high temperature[4], and the interaction with sulphur takes place at 200 - 220°C[5].

It seemed probable that nucleophilic catalysis could play an essential part for many reactions of perfluoroalkyl mercury compounds with electrophilic agents. In 1965 Seyferth proved that the first stage of forming dichlorocarbene by treating phenyltrichloromethyl mercury with NaI was the displacement of $CCl_3^{\ominus}$ by iodide ion.[6] The halide ion catalysis may be supposed to be a method for generation of perfluoroalkyl carbanions from perfluoroalkyl mercurials.

Our experiments showed alkali metal iodides to react with both bis-perfluoro-t-butyl mercury (I) and bis-perfluoroisopropyl mercury (II) in aprotic polar solvents giving HgI_2 and perfluoroisobutene or perfluoropropene respectively:



$$(CF_3)_2CX\text{-}Hg\text{-}CX(CF_3)_2 \xrightarrow{I^\ominus} CF_3\text{-}\overset{\ominus}{\underset{X}{C}}\text{-}CF_3 \xrightarrow[-F^\ominus]{} CF_2{=}\underset{X}{C}\text{-}CF_3$$

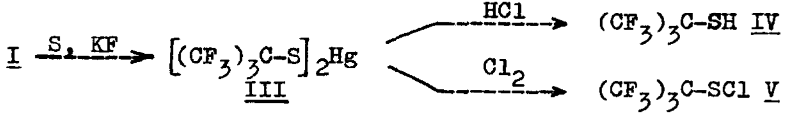
$(+ HgI_2)$

I, $X = CF_3$

II, $X = F$

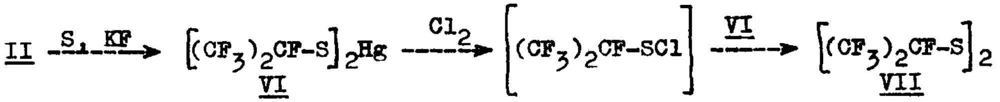
Intermediate carbanions may be trapped by electrophilic agents, but usually a fluoride ion is eliminated and fluoroolefines are produced.

The using of alkali metal fluorides gives quite different results. In this case we have not observed the formation of fluoroolefines. At the same time the lability of the perfluoroalkyl groups sharply increases. Thus, when 19.1g of I, 6,1 g of powdered sulphur and 50 ml of anhydrous dimethylformamide (DMF) are stirred at 70°C for 3 hrs, no reaction takes place. The NMR ^{19}F spectrum signalled only I, i.e. the singlet at -22 p.p.m. (from external CF_3COOH) with mercury satellites, $J_{^{199}Hg-^{19}F} = 151$ cps. After adding 1 g of freshly calcined and ground KF, a rapid reaction occured under the same conditions. After 20 minutes the NMR ^{19}F spectrum contained only a new singlet at -10 p.p.m. The reaction mixture was filtered and decomposed with water. Crystallization of the precipitate from hexane gave complex of mercury bis-perfluoro-t-butyl mercaptide (III) with 0.5 mol of DMF (17.3 g; 79%), which, after sublimation at 100°C (bath temperature) and 2.5 mm Hg, had m.p. 78.5-79.5°C. Found % C 15.48; H 0.51; F 46.30; S 8.66.Calcd for $C_8F_{18}S_2Hg \cdot 0.5$ DMF % C 15.44; H 0.61; F 45.62; S 8.67. Mass spectrum (m/e, %, fragment): 702, 5.5, $C_8F_{18}S_2Hg$ (M); 633, 2.7, M-CF_3; 483, 1.2, M-CF_3-CF_2; 451, 18.3, $(CF_3)_3CSHg$; 251, 8.2, $(CF_3)_3CS$; 232, 4.1, 251-F; 182, 5.9, C_3F_6S; 181, 4.8, C_4F_7; 163, 18.3, C_3F_5S; 113, 26.8, C_2F_3S; 73, 24.0, $(CH_3)_2NCHO$; 69, 100, CF_3; 64, 68, S_2; 44, 22.5, $(CH_3)_2N$ and CS. Reaction of $(CF_3)_3C\text{-}HgCl$ with S and KF (DMF, 15 hrs, 70°C) yielded 68% of III·0.5 DMF. Treatment of III·0.5 DMF with HCl yielded 96% of IV, m.p. 63.5-64°C (in a sealed capillary; highly volatile). Chlorination of III·0.5 DMF at -45°C in CHF_2Cl solution gave 52.5% of V, b.p.78-79°C (crystallizes at room temperature).



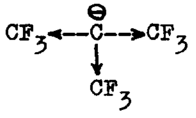
$$I \xrightarrow{S,\ KF} \underset{III}{[(CF_3)_3C\text{-}S]_2Hg} \begin{cases} \xrightarrow{HCl} (CF_3)_3C\text{-}SH \ \ IV \\ \xrightarrow{Cl_2} (CF_3)_3C\text{-}SCl \ \ V \end{cases}$$

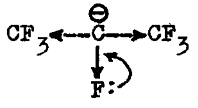
The bis-perfluoroisopropylmercury I is less reactive than I. Thus a mixture of 15.0 g of II, 3.5 g of sulphur and 2 g of KF in 40 ml of DMF was heated under stirring up to 90-100°C (water bath). II completely converted into mercury bis-perfluoroisopropyl mercaptide (VI) during 15 hrs (control by NMR ^{19}F spectra). The reaction mixture was cooled to -20°C and excess of chlorine was bubbled through it. 6.5 g (58%) of bis-perfluoroisopropyldisulphide (VII) were obtained and identified by mass and NMR ^{19}F spectra, as well as by GLC.



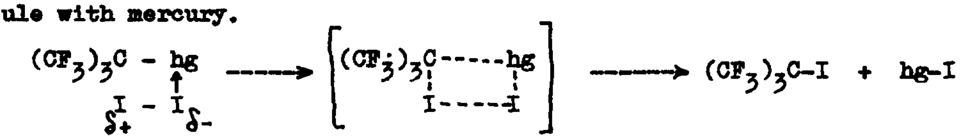
$$\underline{II} \xrightarrow{S,\ KF} \underset{\underline{VI}}{\left[(CF_3)_2CF\text{-}S\right]_2Hg} \xrightarrow{Cl_2} \left[(CF_3)_2CF\text{-}SCl\right] \xrightarrow{\underline{VI}} \underset{\underline{VII}}{\left[(CF_3)_2CF\text{-}S\right]_2}$$

Potassium fluoride shows catalytic activity for the dissymmetrization of some bis-perfluoroalkyl mercurials by $HgCl_2$ and for the reaction with I_2. It is interesting to note that I can react with I_2 in DMF without a catalyst, though less rapidly; the reaction ends at room temperature in half an hour, while in the presence of KF the reaction is practically instantaneous. The enhanced lability of perfluoroalkyl groups of mercury derivatives in the presence of alkali metal halides could be explained by the nucleophilic coordination of halide ion with mercury, which in extreme cases leads to the displacement of perfluoroalkyl carbanions. This is just the case with KI, and the resulting carbanions undergo mainly β-elimination of the fluoride ion. In case of KF, however, the displacement of the carbanion is debatable, but, rather, the coordination of $F^{\ominus}$ with the Hg atom enhances the anionoid properties of the Hg-bonded carbon atom. Even if the displacement of the carbanion is really the case, it is reversible, since the perfluorocarbanions, as we have shown[6], react with mercury fluorides giving perfluoroalkyl mercurials. Mercury iodides do not react in this manner. The fact that I is more reactive than II may be explained by a higher stability of perfluoro-t-butyl carbanion as compared with perfluoroisopropyl carbanion.





Nucleophilic assistance may be suggested for the reaction of I with I_2 without a catalyst due to coordination of the anionic centre of the iodine molecule with mercury.



It is likely to be a reason for the less difficult interaction of perfluoroalkyl mercurials with ClNO reported earlier[7]. The role of the nucleophilic assistance in reactions of organometallic compounds is known to be essential[8,9]

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