744. *Polyfluoroalkylmercuric Fluorides.*

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The reaction between chlorotrifluoroethylene and mercuric fluoride provides a convenient route to the mercurial $CF_3 \cdot CFCl \cdot HgF$, the structure of which has been demonstrated by various cleavage reactions.

The reaction between mercuric fluoride and fluoro-olefins, $CF_2{=}CXY + HgF_2 \longrightarrow CF_3 \cdot CXY \cdot HgF$, has been investigated as a potential route to polyfluoroalkyl derivatives of mercury, the synthetic uses of which have already been demonstrated.[1]

The reaction between chlorotrifluoroethylene and mercuric fluoride gave satisfactory yields of the crystalline mercurial C_2ClF_5Hg. Of the two possible structures for the product, $CF_3 \cdot CFCl \cdot HgF$ or $CF_2Cl \cdot CF_2 \cdot HgF$, the former was shown to be correct in the following ways. Cleavage by aqueous sodium stannite gave the halogenoalkane $CF_3 \cdot CHFCl$, which on photochemical chlorination gave the known compound $CF_3 \cdot CFCl_2$, readily distinguished from its isomer $CF_2Cl \cdot CF_2Cl$. Cleavage of the mercurial by chlorine gave an excellent yield of the same compound $CF_3 \cdot CFCl_2$, and reaction of the mercurial with iodine gave over 80% of the iodo-compound $CF_3 \cdot CFClI$. The ultraviolet spectrum of this iodo-compound is consistent with its proposed structure. It has been shown [2] that compounds containing a $-CFClI$ group show absorption maxima, either in the vapour state or in light petroleum, in the region 280—290 mμ, whereas compounds containing a

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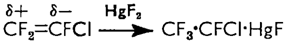
[1] Emeléus and Haszeldine, *J.*, 1949, 2948, 2953; Banus, Emeléus, and Haszeldine, *J.*, 1950, 3041.
[2] Haszeldine, *J.*, 1953, 1764.

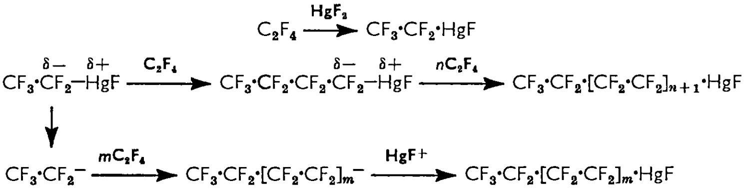
$-CF_2I$ group usually have an absorption maximum in the region of 270 mμ.[3] The new iodo-compound has an absorption maximum at 282 mμ, both in the vapour state and in light petroleum, and thus clearly contains the $-CFClI$ group. The reaction of mercuric fluoride with chlorotrifluoroethylene is thus probably an ionic process:



$$\overset{\delta+}{CF_2}{=}\overset{\delta-}{CFCl} \xrightarrow{HgF_2} CF_3{\cdot}CFCl{\cdot}HgF$$

with fluoride ion attack on the CF_2 group as for other nucleophilic additions.

Tetrafluoroethylene reacted readily with mercuric fluoride at moderately elevated temperatures and pressures, but the main product was a polymer, probably arising by anionic polymerisation of the olefin:



$$C_2F_4 \xrightarrow{HgF_2} CF_3{\cdot}CF_2{\cdot}HgF$$

$$\begin{tikzcd} CF_3{\cdot}\overset{\delta-}{CF_2}\text{–}\overset{\delta+}{HgF} \arrow[r, "C_2F_4"] \arrow[d] & CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}\overset{\delta-}{CF_2}\text{–}\overset{\delta+}{HgF} \arrow[r, "nC_2F_4"] & CF_3{\cdot}CF_2{\cdot}[CF_2{\cdot}CF_2]_{n+1}{\cdot}HgF \\ CF_3{\cdot}CF_2^- \arrow[r, "mC_2F_4"] & CF_3{\cdot}CF_2{\cdot}[CF_2{\cdot}CF_2]_m^- \arrow[r, "HgF^+"] & CF_3{\cdot}CF_2{\cdot}[CF_2{\cdot}CF_2]_m{\cdot}HgF \end{tikzcd}$$

Small amounts of a compound identified as probably $C_2F_5{\cdot}HgF$ were obtained from the reaction, but the yields were too low to be useful. Polyfluoroalkylmercuric fluorides do not decompose to yield radicals at the temperatures used in these mercuric fluoride additions, so that polymerisation of tetrafluoroethylene initiated by free radicals is unlikely.

While this investigation was in progress, a report appeared[4] of a related study in which fluoro-olefins were treated with mercuric fluoride *in the presence of a solvent* such as arsenic trifluoride, good conversions into the bispolyfluoroalkylmercury compounds [*e.g.*, $Hg(C_2F_5)_2$; $Hg(CFCl{\cdot}CF_3)_2$] being obtained. Use of a solvent thus changes the course of the reaction, possibly by facilitating heterolytic cleavage of the Hg–F bond of the polyfluoroalkylmercuric fluoride formed as an intermediate.

EXPERIMENTAL

Materials.—Mercuric fluoride was a commercial sample containing 93% of mercuric fluoride (by determination of its fluorine content). Tetrafluoroethylene and chlorotrifluoroethylene, both commercial products, were distilled *in vacuo* to remove inhibitors before they were used.

Reaction of Mercuric Fluoride with Chlorotrifluoroethylene.—Mercuric fluoride (20·0 g., 0·078 mole of HgF_2) and chlorotrifluoroethylene (17·5 g., 0·150 mole) were heated together in an autoclave of 100 ml. capacity for 10 hr. at 100°. The autoclave was then cooled and unchanged chlorotrifluoroethylene (14·0 g.) was withdrawn. The solid product, which fumed vigorously in moist air, was extracted with carbon disulphide. The extract was evaporated, and the residue was sublimed at 85°/1 atm., to yield 1-*chloro*-1,2,2,2-*tetrafluoroethylmercuric fluoride* (2·5 g., 24%), m. p. 118° (Found: C, 6·7; Hg, 54·9. C_2ClF_5Hg requires C, 6·7; Hg, 56·4%).

The mercurial was water-soluble and was recovered unchanged from aqueous solution. It was stable in air and had a penetrating, very disagreeable smell.

Cleavage of the Mercurial by Sodium Stannite.—1-Chloro-1,2,2,2-tetrafluoroethylmercuric fluoride (1·00 g., 2·82 mmoles) was cleaved by dropping on to it an excess of alkaline 0·5N-sodium stannite (50 ml.). The volatile products were distilled, to give 1-*chloro*-1,2,2,2-*tetrafluoroethane* (0·340 g., 89%), b. p. −8° (isoteniscope) (Found: C, 17·6; H, 0·6; *M*, 134·9. C_2HClF_4 requires C, 17·5; H, 0·7%; *M*, 136·5). Its infrared spectrum was quite different from that of the known 1-chloro-1,1,2,2-tetrafluoroethane. In particular 1-chloro-1,2,2,2-tetrafluoroethane has strong absorption bands at 11·25, 11·33, 11·38 (triplet), 12·23, and 14·26, 14·37,

[3] Haszeldine and Osborne, *J.*, 1956, 61.

[4] Krespan, *J. Org. Chem.*, 1960, **25**, 105.

14·53 (triplet) μ, where 1-chloro-1,1,2,2-tetrafluoroethane is relatively transparent, while the latter ethane shows strong absorption at 10·0 and 12·0 μ which is absent from the spectrum of the present product.

The ethane (0·122 g., 0·89 mmole) and chlorine (0·127 g., 1·8 mmoles) were exposed to ultraviolet light for one month (probably an excessive length of time) at room temperature. The product (0·114 g., 75%) (Found: *M*, 168. Calc. for $C_2Cl_2F_4$: *M*, 171) was found to be identical, by comparison of their infrared spectra, with an authentic sample of 1,1-dichloro-1,2,2,2-tetrafluoroethane.

Reactions between the Mercurial and Halogens.—(a) *Chlorine.* The mercurial (1·00 g., 2·82 mmoles) and chlorine (0·318 g., 4·46 mmoles) were sealed in a 50-ml. Carius tube and heated at 140° for 24 hr. and then at 150° for 3 hr. The residual chlorine was absorbed in sodium hydrogen sulphite solution, and the remaining volatile products were distilled *in vacuo*, to give 1,1-dichloro-1,2,2,2-tetrafluoroethane (0·407 g., 84%) (Found: C, 14·0%; *M*, 169·5. Calc. for $C_2Cl_2F_4$: C, 14·0%; *M*, 171). The product was homogeneous on gas–liquid chromatography, and its infrared spectrum was identical with that of an authentic sample of the compound $CF_3{\cdot}CFCl_2$.

(b) *Iodine.* The mercurial (1·60 g., 4·5 mmoles) and iodine (1·50 g., 5·9 mmoles) were sealed in a 50-ml. Carius tube and heated at 100° for 1 hr. and then at 140° for 2 hr. The volatile products were distilled *in vacuo*, to give 1-*chloro*-1,2,2,2-*tetrafluoro*-1-*iodoethane* (0·95 g., 81%) (Found: C, 9·2%; *M*, 259. C_2ClF_4I requires C, 9·2%; *M*, 262·5), b. p. 53° (isoteniscope). The product was homogeneous on gas-liquid chromatography.

The ultraviolet spectra of the iodo-ethane were as follows: vapour, $\lambda_{max.}$ 282 (ε 207), $\lambda_{min.}$ 223·5 mμ (ε 12); in hexane, $\lambda_{max.}$ 282 (ε 310), $\lambda_{min.}$ 225 mμ (ε 22); in ethanol, $\lambda_{max.}$ 258 (ε 319), $\lambda_{min.}$ 232 mμ (ε 237).

Infrared Spectra.—These were determined on a Perkin–Elmer model 21 spectrophotometer with sodium chloride optics:

$CF_3{\cdot}CHFCl$ (vapour): 3·33w, 7·27m, 7·72, 7·79 (s doublet), 8·27vs, 8·54, 8·58 (s doublet), 9·05, 9·10(s doublet), 11·25, 11·33, 11·38 (s triplet), 12·23s, 14·26, 14·37, 14·53 (s triplet) μ.

$CF_3{\cdot}CFClI$ (vapour): 4·59w, 7·44w, 7·68m, 7·85s, 8·12s, 8·22s, 8·44m, 8·87m, 9·17s, 9·79w, 10·62w, 10·93s, 11·65, 11·69 (m doublet), 11·90s, 12·80, 12·85, 12·89 (m triplet), 13·85, 13·92, 13·99 (s triplet) μ.

Reaction Between Mercuric Fluoride and Tetrafluoroethylene.—Mercuric fluoride (12·0 g., 0·0465 mole of HgF_2) in an evacuated rocking autoclave of 100-ml. capacity was heated to 100°. A smaller autoclave of 20 ml. capacity containing tetrafluoroethylene (10·0 g., 0·100 mole) was then connected to the larger autoclave, and the mercuric fluoride was heated and rocked for 4 hr. at 100°. The autoclave was then cooled and unchanged tetrafluoroethylene (2·5 g.) was withdrawn. The solid product, which fumed vigorously in moist air, was extracted with carbon disulphide. The extract was evaporated, and the crystalline residue was sublimed at 80°/1 atm., to yield white crystalline pentafluoroethylmercuric fluoride (0·5 g., 2%) (Found: C, 7·5. Calc. for C_2F_6Hg: C, 7·1%), m. p. 97°. Banus, Emeléus, and Haszeldine[1] report m. p. 99—100° for the compound $C_2F_5{\cdot}HgF$.

There were also obtained 6·5 g. of a white polymer (Found: C, 18·0; F, 62·0. Calc. for $C_{16}F_{33}{\cdot}HgF$: C, 18·5; F, 62·2%). A test for mercury was positive, and the infrared spectrum of the polymer showed a general resemblance to that of polytetrafluoroethylene.

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