

REACTION OF PERFLUOROALKYL CARBANIONS WITH MERCURY SALTS*

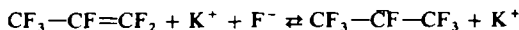
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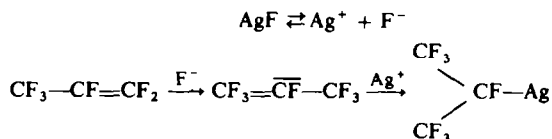
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Abstract—A method for the nucleophilic mercuration of fluoroolefines has been found. Perfluoroalkyl carbanions are shown to react with mercury salts, and depending on nature of the reactants and reaction conditions yield bis-perfluoroalkyl mercurials or perfluoroalkylmercury salts. This reaction is a new example of the reversal of the addition mechanism in the fluoroolefines series.

GREAT advances have been made in recent years in the chemistry of perfluoroalkyl carbanions generated *in situ* by the addition of the fluoride-ion to perfluoroolefines in polar aprotic solvents. The "fluoroolefine – alkali metal fluoride" system can be regarded as a perfluoroalkyl derivative of an alkali metal, e.g.:

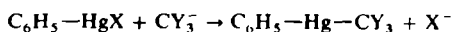
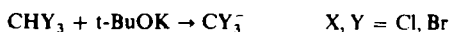


Reactions of these systems are numerous and compensate to a considerable extent for the lack of organomagnesium syntheses in the series of organofluorine compounds.¹ Silver fluoride behaves similarly to fluorides of alkali metals and has been shown by Miller and Burnard to add in acetonitrile to perfluoropropene with the formation of perfluoroisopropyl silver:



As a complex with a solvent, perfluoroisopropyl silver was isolated and characterized².

It seemed possible to synthesize perfluoroalkyl mercurials through perfluoro carbanions, this reaction being analogous to the well known method of synthesizing organomercuric compounds by interacting Grignard reagents with mercury salts. On the other hand, Seyferth and Burlitch showed³ that trihalomethyl anions, generated by the action of bases on haloforms, substitute the halogen atom in phenylmercury halides:



Fluoroolefines react in the presence of alkali metal fluorides with mercury salts, and depending on the nature of the reactants and reaction conditions, yield either completely substituted or mixed perfluoroalkyl mercury derivatives. In accordance with the previous discussion the scheme of the reaction can be represented as follows:

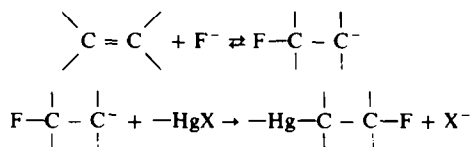
* Preliminary communication cf. B. L. Dyatkin, S. R. Sterlin, B. I. Martynov and I. L. Knunyants, *Tetrahedron Letters* 1385 (1970).

TABLE 1. MASS SPECTRA OF PERFLUOROALKYL MERCURIALS

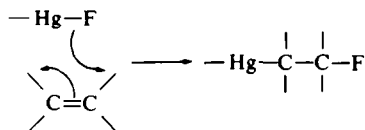
Ions	m/e	Compounds						
		(i-C ₃ F ₇) ₂ Hg	(t-C ₄ F ₉) ₂ Hg	(c-C ₄ F ₇) ₂ Hg	i-C ₃ F ₇ HgCl	t-C ₄ F ₉ HgCl	c-C ₄ F ₇ HgCl	t-C ₄ F ₉ HgC ₆ H ₅
CF	31	4.0	1.8	15.6	21.4	5.9	47.8	1.7
CF ₂ (C ₄ H ₂)	50	0.4	0.5		2.4	1.0	4.5	14.1
C ₄ H ₃	51							37.5
CF ₃	69	48.4	37.1	12.9	53.4	63.5	18.4	20.9
C ₃ F ₂ (C ₆ H ₂)	74	0.24	0.3	3.9	0.8	0.8	6.8	4.5
C ₆ H ₃	75							4.4
C ₆ H ₄	76							6.6
C ₆ H ₅	77							100
C ₆ H ₆	78							9.1
C ₂ F ₃	81	1.6	0.8	13.3	4.3	1.3	13.5	0.8
C ₃ F ₃	93	2.4	9.6	50.8	6.6	18.1	54.2	3.1
C ₂ F ₄	100	12.5	3.7	7.0	62.1	4.1	13.5	1.5
C ₃ F ₄	112	0.7	3.4	10.6	2.7	8.2	9.0	1.2
C ₂ F ₅	119	3.6	0.2	0.8	4.2			0.07
C ₃ F ₅	131	8.8	5.1	100	100	18.1	32.9	1.2
C ₄ F ₅	143			7.0			42.3	0.1
C ₃ F ₆	150	2.3	1.8		84.5	6.7		1.9
C ₄ F ₆	162		0.16	20.7			100	0.2

C ₃ F ₇	169	45.5	0.13		1.9			0.04
C ₄ F ₇	181		75.8	59.4		100	1.7	6.2
C ₄ F ₈	200		1			19.2	0.1	1.6
C ₄ F ₉	219		0.25			0.07		
Hg~	< 202 >	16.6	63.1	17.0	42.8	40.8	18.4	7.9
CFHg~	< 233 >	1.3	0.5	5.1			1.9	
C ₆ H ₃ Hg~	< 279 >							38
C ₂ F ₃ Hg~	< 283 >	0.8		12.2			5.7	
C ₂ F ₄ Hg~	< 302 >			6.7				
C ₃ F ₃ Hg~	< 333 >	0.9	3.3					
C ₃ F ₆ Hg~	< 352 >		0.7					
C ₃ F ₇ Hg~	< 371 >	100	2.8		0.8			
C ₄ F ₇ Hg~	< 383 >			54.1			0.3	
C ₄ F ₉ Hg~	< 421 >		100			3.6		0.9
HgCl~	< 237 >				45.6	70.2	9.2	
CF ₂ HgCl~	< 287 >				8.5		3.2	
C ₂ F ₃ HgCl~	< 318 >						12.8	
M-F~		0.05	0.5		1.1	0.4		
M~		0.5	0.5	2.7	82.7	51.1	0.2	8.1

Spectra are obtained on "Varian" CH-8 mass-spectrometer. Recording was made with the help of a loop oscillograph with line scanning without ionic current integration. Relative heights of corresponding peaks are tabulated with the maximum peak taken as 100; in case of isotopes the sums of the heights of isotope peaks corresponding to said ion are tabulated; given in brackets are mass numbers corresponding to the most intensive isotope peaks. Ionic current, corresponding to the ions tabulated ranges from 88 to 100% of the total ionic current.

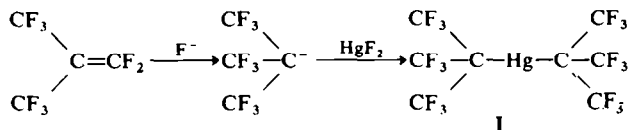


The first step of the reaction consists in nucleophilic addition of the fluoride-ion on the double bond of the fluoroolefine with the formation of a perfluoro carbanion, the second step is the substitution of the acid radical X by the perfluoro carbanion. Thus, easy formation of the carbanion, determined by its stability, on the one hand, and its activity, on the other hand, are essential here; with a change in the anion structure these factors, naturally, change in opposite directions. The nature of the Hg-X bond is also of great importance, since the more ionic this bond is, the easier the substitution proceeds. Compounds with a Hg-F bond, such as mercuric fluoride, phenylmercuric fluoride, react most easily; mercuric chloride also reacts, and, in some cases, mercuric nitrate does. We have not succeeded, however, to react mercuric bromide or mercuric iodide with perfluoro carbanions. Accordingly, the reaction is facilitated in solvents which favour ionization of the Hg-X bond. As regards mercuric fluoride and phenylmercuric fluoride, they add to perfluoroisobutene and to some other fluoroolefines without potassium fluoride. Mercuric fluorides themselves can be a source of a fluoride-ion; for such reactions a cyclic mechanism is also possible:

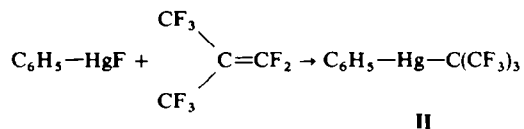


The anionoid attack of the F atom on the relatively positively charged C atom of the double bond is essential in this case.

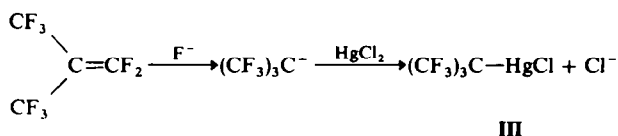
The reaction of perfluoroisobutene with HgF_2 in dimethylformamide (DMFA) is exothermic and results in a good yield of bis-perfluoro-t-butyl mercury (I):



Phenylmercuric fluoride adds to perfluoroisobutene in ether, giving phenylperfluoro-t-butyl mercury (II):

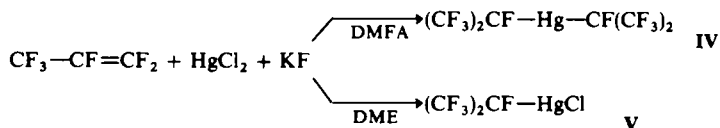


Mercuric chloride reacts with perfluoroisobutene in the presence of potassium fluoride in THF, giving perfluoro-t-butylmercuric chloride (III):



III

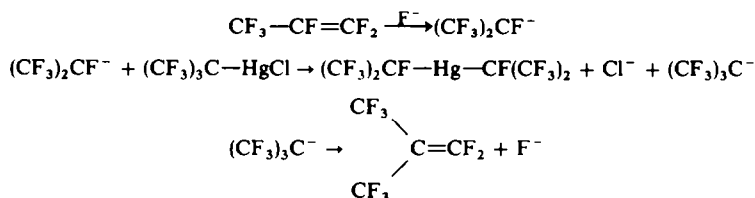
Perfluoropropene, potassium fluoride and mercuric chloride in DMFA give bis-perfluoroisopropyl mercury (IV); when the reaction is carried out in 1,2-dimethoxyethane (DME), perfluoroisopropylmercuric chloride (V) can be isolated.



IV

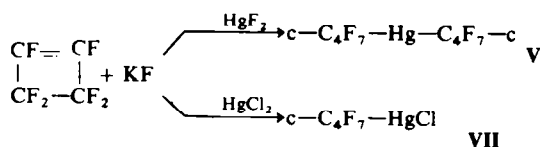
V

Perfluoropropene in the presence of KF in DMFA reacts with perfluoro-*t*-butylmercuric chloride giving bis-perfluoroisopropyl mercury; thus, the perfluoroisopropyl anion displaces not only Cl^- , but also the perfluoro-*t*-butyl anion:



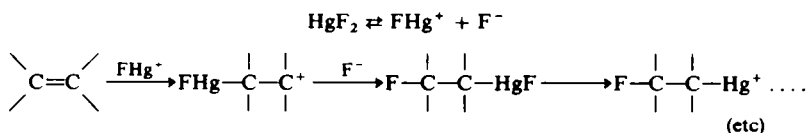
This reaction demonstrates the greater activity of the perfluoroisopropyl anion.

Perfluorocyclobutene, HgF_2 and KF in DMFA give bis-perfluorocyclobutyl mercury (VI); the reaction with HgCl_2 gives perfluorocyclobutylmercuric chloride (VII):



VII

One method for synthesizing bis-perfluoroalkyl mercurials consists in reacting fluoroolefines with mercuric fluoride in arsenic trifluoride or in anhydrous HF^4 . An electrophilic mechanism has been proved for this reaction, including a mercurinium cation attack to the double bond^{4d}.



(etc)

In principle, this is the same reaction as the addition of mercury salts to non-fluorinated olefines. The reaction found by us, that is, nucleophilic mercuriation, is specific

for fluoroolefines (though other unsaturated compounds with an electrophilic double bond may also possibly enter into it). As has been pointed out⁵, many reactions of fluoroolefines (addition of HF, FNO, acylation, alkylation) can proceed both by electrophilic and nucleophilic paths. Reversal of the mechanism is demonstrated now for mercuration of fluoroolefines. In contradistinction to electrophilic mercuration, where fluoroethylenes react easier than other fluoroolefines, perfluoroisobutene reacts nucleophilically very easily (whereas the addition of HgF_2 to it in HF takes place only at 200°). Perfluorocyclobutene does not add mercury salts under the conditions of electrophilic reaction^{4b}, although it is nucleophilically mercured. Nucleophilic mercuration makes it possible to obtain organomercuric compounds, where one of the radicals is perfluorinated, and the other does not contain fluorine (e.g. II). Thus, not only theoretical, but also preparative aspects of these two types of reactions are different. The nucleophilic type was proposed earlier⁶ for the addition of mercuric fluoride to tetrafluoroethylene and trifluorochloroethylene without solvent and catalyst under heating in an autoclave with the formation of $\text{CF}_3\text{CF}_2\text{—HgF}$ (2%) and $\text{CF}_3\text{CFCl—HgF}$ (24%), respectively, and of polymer products. The conditions employed, however, do not favour the formation of carbanions; besides, as compared to other fluoroolefines, it is only fluoroethylenes which are less liable to enter into reactions with nucleophilic and more liable to react with electrophilic agents. These circumstances being taken into account, the results reported⁶ can be explained within the framework of the electrophilic addition scheme.

EXPERIMENTAL

1. *Bis-perfluoro-butyl mercury* (I). A 100 ml 3-necked flask provided with a stirrer, a gas inlet tube and a reflux condenser cooled down to -78° was charged with mercuric fluoride (13.5 g, 0.057 mole) and abs. DMFA (40 ml). Perfluoroisobutene (22.6 g, 0.113 mole) was introduced under stirring. The gas absorption was exothermic. On completion of the reaction the mixture was filtered, the filtrate was decomposed with water, the lower layer was separated and distilled from H_2SO_4 , collecting the substance within the temp range of $120\text{--}140^\circ$. The yield was 24 g of a crystalline product which according to NMR F^{19} spectrum and GLC data was practically pure I, yield 66.5%. After sublimation, m.p. $64\text{--}65.5^\circ$; the substance showed no m.p. depression when mixed with an authentic sample^{4a} having m.p. $65\text{--}65.5$.

2. *Phenylperfluoro-t-butyl mercury* (II). A 100 ml 3-necked flask provided with a gas inlet tube, a stirrer and a reflux condenser cooled down to -78° was charged with phenylmercuric fluoride (14 g, 0.047 mole) and abs. ether (40 ml). Perfluoroisobutene (10.5 g, 0.05 mole) was added under stirring (exothermic absorption). On completion of the reaction the ether was distilled off under small rarefaction, and the residue was vacuum-distilled, yielding II (15.8 g, 61%), b.p. $59\text{--}61^\circ/1.5$ mm (crystallizes at room temp). (Found: C, 24.00; H, 1.59; F, 34.36. $\text{C}_{10}\text{H}_5\text{F}_9\text{Hg}$ requires: C, 24.18; H, 1.02; F, 34.42%).

3. *Perfluoro-t-butylmercuric chloride* (III). Under conditions similar to these of Experiment 1, from mercuric chloride (15 g, 0.056 mole) KF (10 g, 0.018 mole) perfluoroisobutene (16 g, 0.08 mole) in THF (40 ml), III (12.5 g, 42%) was obtained, m.p. $75\text{--}76.5^\circ$. (Found: C, 10.04; F, 36.56; Cl, 7.09. $\text{C}_4\text{F}_9\text{ClHg}$ requires: C 10.56; F, 37.57; Cl, 7.79%).

4. *Bis-perfluoroisopropyl mercury* (IV). A 100 ml 3-necked flask equipped with a stirrer, a gas inlet tube and a reflux condenser was charged with mercuric chloride (27 g, 0.10 mole), KF (15 g, 0.26 mole) and DMFA (50 ml). At 40° and under stirring, perfluoropropene was passed during 8 hr and 0.31 mole of fluoroolefine was absorbed. The reaction mass was filtered, the filtrate was poured into water, the lower layer was separated, and distilled from conc H_2SO_4 yielding 37.6 g (65%) of IV, b.p. 115° . Lit.: b.p. $116\text{--}117^\circ\text{C}^{4d}$. The substance was identified by NMR F^{19} spectrum.

5. *Perfluoroisopropylmercuric chloride* (V). Under conditions similar to those of Exp. 4, from mercuric chloride (21 g, 0.078 mole), KF (15 g, 0.26 mole) and DME (60 ml) (50° , 6 hr; 0.09 mole by perfluoropropene absorbed) V was obtained (7.75 g, 25.8%), m.p. $75.5\text{--}77^\circ$ (sublimation). Lit.: m.p. $77.5\text{--}78^\circ\text{C}^{4d}$.

6. *Bis-perfluorocyclobutyl mercury* (VI). A 100 ml 3-necked flask equipped with a stirrer, a gas inlet tube and a reflux condenser cooled down to -78° was charged with mercuric fluoride (11 g, 0.046 mole), KF (1.7 g, 0.03 mole) and DMFA (40 ml). At 50° and under stirring perfluorocyclobutene (9 g, 0.055 mole) was introduced. At this temp the stirring was continued for 9 hr, after which the mixture was processed as described in Exp. 1. After recrystallization from n-heptane, VI was obtained (5.0 g, 33%), m.p. $100-101.5^{\circ}$. (Found: C, 16.61; F, 47.49. $C_8F_{14}Hg$ requires: C, 17.08; F, 47.27%).

7. *Perfluorocyclobutylmercuric chloride* (VII). A mixture of perfluorocyclobutene (30 g, 0.185 mole), mercuric chloride (54 g, 0.20 mole), KF (10 g, 0.172 mole) and DMFA (100 ml) in a sealed glass ampoule was subjected to intensive shaking at room temp during 8 days. 18 g (0.111 mole) of perfluorocyclobutene were reacted. Further processing was similar to that described in Exp. 1. After recrystallization from n-heptane, VII (14.5 g, 46.5%) was obtained, m.p. $72-74^{\circ}$. (Found: C, 11.65; F, 31.91. C_4F_7ClHg requires: C, 11.49; F, 31.89%).

8. *Reaction of perfluoro-t-butylmercuric chloride* (III) with perfluoropropene and potassium fluoride. A 100 ml 3-necked flask equipped with a stirrer, a gas inlet tube and a reflux condenser was charged with III. (5.5 g, 0.125 mole), KF (1.5 g, 0.025 mole) and DMFA (20 ml). At 50° and under stirring during 8 hr perfluoropropene was introduced and 0.078 mole was absorbed. The mixture was poured into water, the lower layer was separated and distilled from conc H_2SO_4 : IV (4.51 g, 67%) was obtained and identified by NMR F^{19} and GLC methods.

The results of the mass spectrometric analysis of the perfluoroalkyl mercurials are presented in the Table. The NMR spectrum data will be published elsewhere.

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