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REACTIONS OF PERFLUOROALKYLCARBANIONS WITH SULPHUR

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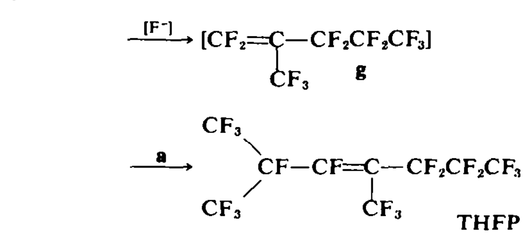
Abstract – The interaction of perfluoroalkylcarbanions generated (a) by the addition of the fluoride ion to fluoro-olefines and (b) from bis-perfluoroalkyl mercurials in the presence of the fluoride ion with elementary sulphur has been investigated and various transformations of the resulting perfluoroalkylmercaptide anions are shown.

The syntheses of perfluoroalkyl derivatives of bivalent sulphur have been achieved by the reactions of elementary sulphur with perfluoroalkyliodides,[1,2] perfluoroalkyl mercurials,[3,4] and fluoro-olefines[5,6] giving perfluoroalkylsulphides, -polysulphides and -thiocarbonyl compounds. The conditions of these reactions suggest that they are homolytic in character. Perfluoroalkyl iodides react with sulphur at 250 to 300°, perfluoroalkyl mercurials and fluoro-olefines – at 220 to 444° (b.p. of sulphur). At such high temperatures cyclic octoatomic molecules of sulphur are transformed into linear fragments of a different length, these fragments, according to ESR data, being biradicals.[7] Perfluoroalkyl iodides, as a rule, enter only into reactions that are accompanied by the homolytic breakage of the C—I bond. Fluoro-olefines also readily undergo homolytic addition. It has been noted that reactions of fluoro-olefines with sulphur are accelerated by iodine:[8] in this case vicinal perfluoroalkylenediiodides may participate in the reaction.

Elementary sulphur reacts with Grignard compounds to give the corresponding magnesium mercaptides and transformations products. Perfluoro carbanions generated from fluoro-olefines and fluorides of alkali metals in polar aprotic solvents,[9] in many cases react like Grignard reagents, and therefore should react with sulphur to give perfluoroalkyl mercaptides. The further transformation of the products formed would depend on the structure of the perfluoroalkyl radical and also on the reaction conditions. We have investigated the reaction of fluoro-olefines with sulphur in the presence of alkali metal fluorides. The results partly published earlier (*cf* 10, 11) are reported in the present paper.

Hexafluoropropylene

Equimolar proportions of hexafluoropropylene (HFP) and sulphur react in the presence of a catalytic quantity of potassium fluoride to give mainly a dimer of hexafluorothioacetone – 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (**1**).* The addition of the fluoride ion to HFP gave the hexafluoroisopropyl anion **a** which, interacting with sulphur, formed perfluoroisopropylmercaptide anion **b**. The latter, as a result of α-elimination of the fluoride ion, gave hexafluorothioacetone **c** which under the reaction conditions dimerized into **1**. Isolated as by-products were: bis-heptafluoroisopropyldisulphide **2**, dimers and trimers of herxafluoropropylene (DHFP and THFP respectively) and also compound **3** for which the structure of perfluoroisopropyl(2-propyl-2-methylpenten-1-yl)sulphide is suggested. The formation of compound **2** is, evidently, the consequence of oxidation of anion **b** by sulphur. Oligomerization of HFP in the presence of F^- has been investigated earlier. We suggest that the formation and structure of compound **3** are analogous with the formation and the structure of THFP established by Haszeldine *et al.*[12]: indeed, if THFP is formed as a result of nucleophilic substitution of the fluorine atom in DHFP with the terminal double bond **g** by perfluoroisopropyl anion **a**, then the formation of



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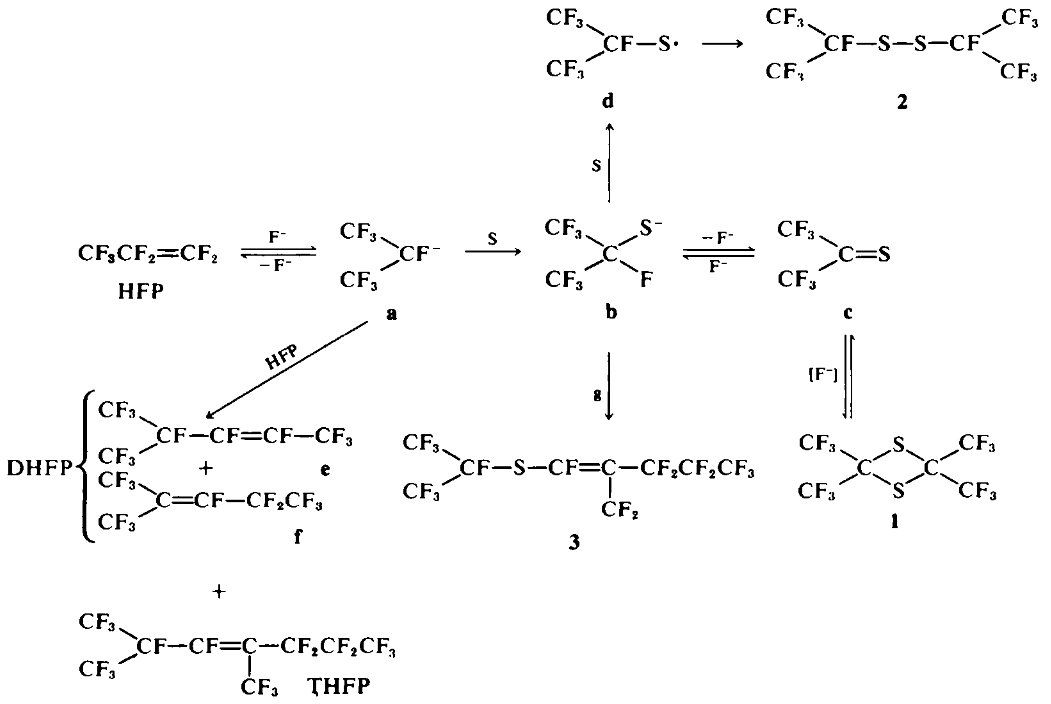
*Compound **1** was obtained by Middleton *et al.* by dimerization of hexafluorothioacetone formed by the action of boiling sulphur on bis-hexafluoroisopropylmercury.[4]

compound **3** can be regarded as the interaction of **g** with anion **b** also according to a scheme of vinyl substitution. Under the conditions of catalysis with potassium fluoride the interaction of HFP with S leads to compound **1** with a yield of 70%; the amounts of compounds **2** and **3** are negligible. The general scheme of the reaction is as follows:



SCHEME 1

Variation in the ratios of the reagents determines the composition of the products. The results of some experiments are given in Tables 1–4.*

According to Scheme 1, an increase in the quantity of potassium fluoride, with the HFP:S ratio remaining equimolar, should lead to an increase in the amount of the products containing the perfluoroisopropylthio-group, i.e. disulphide **2** and sulphide **3** (as a result of the sequence of reactions HFP → **a** → **b** → **d** → **2**, HFP → **a** → **b** → **3** and also as a result of the **b** ⇄ **c** equilibrium shifting to the left) and the perfluoroisopropyl group—DHFP and THFP (on account of an increase in the concentration of **a**). Indeed, while with the HFP:S:KF molar ratio equal to 1:1:0·06 the main S-containing product is dithietane **1** (98% of the total quantity of **1**, **2** and **3**), with the HFP:S:KF ratio equal to 1:1:0·65 the quantity of compound **1** is only 33% and that of disulphide **2** and sulphide **3** increases to 67%; the yield of DHFP and THFP is somewhat augmented. A further increase in the amount of potassium fluoride, however, again leads to the predominant formation of dithietane **1**, to 69% with the equimolar ratio of HFP, sulphur and KF, and to 92% with the HFP:S:KF ratio equal to 1:1:5; a monotonic decrease in the yield of the S-containing products and a corresponding increase in the yield of DHFP and THFP are observed (Table 1).

Evidently, an increase in the concentration of anion **a** (due to the shift of the equilibrium HFP ⇄ **a** to the right with an increasing concentration of the fluoride ion) reveals more regarding the formation of DHFP and THFP than the formation of disulphide **2** and sulphide **3**.

As a result of an increase in the yield of HFP oligomers, the actual HFP:S ratio shifts towards an increase in the relative quantity of sulphur, which, in turn, must lead to an increase in the proportion of disulphide **2** in the reaction products (on account of the transformations **b** → **d** → **2**). If greater quantities of sulphur are used, the main S-containing product is dithietane **1**; no clear-cut explanation of this phenomenon has been found (Table 2).

Consideration of reactions HFP → **a** → **b**, HFP → **a** → **b** and **b** → **3** (Table 3), indicates that if less than equimolar quantities of sulphur are used with excess of potassium fluoride, a notice-

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*The data given in Tables 1–4 should not be regarded as the absolute characteristics of the investigated reactions but only as an illustration of their general pathway.

Table 1

Reaction temp	Weight of HFP, g	HFP:S:KF molar ratio	**1:2:3** ratio (in per cent according to GLC data)	Yield of sulphur-containing products, g	Yield of HFP oligomers, g
120°	8	1:1:0·06	98:1:1	6·8	2·0
120°	8	1:1:0·65	33:31:36	6·7	2·15
120°	8	1:1:1:	69:15:16	5·7	2·9
120°	8	1:1:5	92:6:2	4·8	4·0

Table 2

Reaction temp	Weight of HFP, g	HFP:S:KF molar ratio	**1:2:3** ratio (in per cent according to GLC data)	Yield of sulphur-containing products, g	Yield of HFP oligomers, g
120°	8	1:1:1	69:15:16	5·7	2·9
120°	8	1:2:1	82:11:7	4·0	4·1
120°	8	1:2·5:2·5	95:2:3	4·1	3·8

Table 3

Reaction temp	Weight of HFP, g	HFP:S:KF molar ratio	**1:2:3** ratio (in per cent according to GLC data)	Yield of sulphur-containing products, g	Yield of HFP oligomers, g
120°	8	1:2:1	82:11:7	4·0	4·1
120°	8	1:1:1	69:15:16	5·7	2·9
120°	8	1:0·5:1	27:33:40	5·0	3·5
120°	8	1:0·5:2	16:37:47	4·7	4·0

able increase in the yield of sulphide **3** should result.

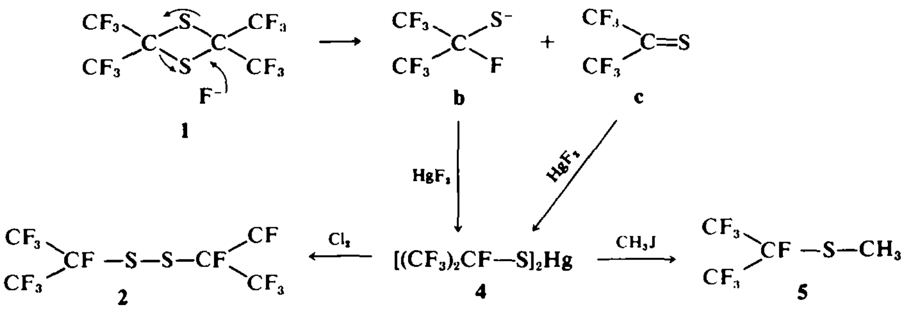
The composition of the products depends also on the reaction conditions. While with the molar ratio of HFP:S:KF = 1:1:0·65 and a reaction temperature of 120°, dithietane **1** makes up 33% of the total quantity of the S-containing products, with the temperature drop by 30 to 50° the content of compound **1** increases to 85% and over.

The complexity of the reaction of hexafluoropropylene with sulphur is due, on the one hand, to the several interconnected transformations and, on the other hand, by the heterogeneity of the process. Nevertheless, it is possible to obtain dithietane **1** and sulphide **3** in satisfactory yields.

Middleton and Sharkey reported that dithiethane **1** and monomeric hexafluorothioacetone **c** give the same products by interaction with nucleophilic agents.[3] Therefore we assumed that the conversion **c** → **1** in the presence of potassium fluoride is reversible and that dithiethane **1** can be a source of the anion **b**.

Indeed, the heating of dithietane **1** with mercury fluoride and potassium fluoride in dimethylformamide leads to the formation of mercury bis-perfluoroisopropylmercaptide **4**. Without the potassium fluoride the reaction does not take place. The structure of compound **4** was proved by the ^{19}F NMR spectrum and also by interaction with methyl iodide, which leads to methylperfluoroisopropylsulphide **5**, and by chlorination with the formation of bis-heptafluoroisopropyldisulphide **2**.

In a special experiment, however, dithietane with sulphur in the presence of potassium fluoride was shown not to form disulphide **2** under the conditions of the investigated reaction (sulpholane, 120°). The formation of compound **2** from compound **1** and sulphur was observed only at 170°

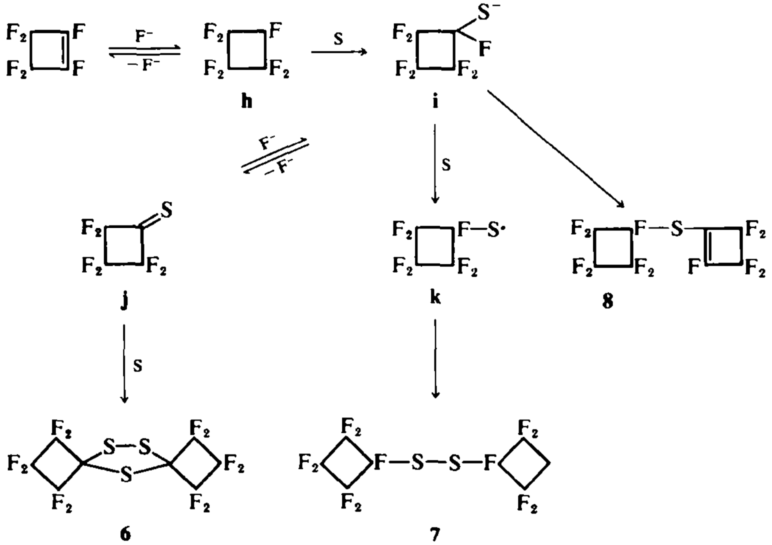


SCHEME 2

in the presence of caesium fluoride, the yield of compound **2** being very small. Thus, in the given case the equilibrium **c** ⇄ **1** is almost completely shifted to the right, and the formation of disulphide **2** takes place mainly as a result of the sequence of reactions HFP → **a** → **b** → **2**.

Perfluorocyclobutene reacts with KF and sulphur in tetramethylenesulphone at 130°. The main products are: a derivative of perfluorothiocyclobutanone – trithiane **6**; bis-perfluorocyclobutylsulphide **7** and perfluorocyclobutylcyclobuten-1-yl-sulphide **8**. The formation of these compounds can be the result of transformations of the perfluorocyclobutylmercaptide ion **i** (Scheme 3).

The ratio between the products also depends on the ratio between the reagents. The results of some experiments are given in Table 4.



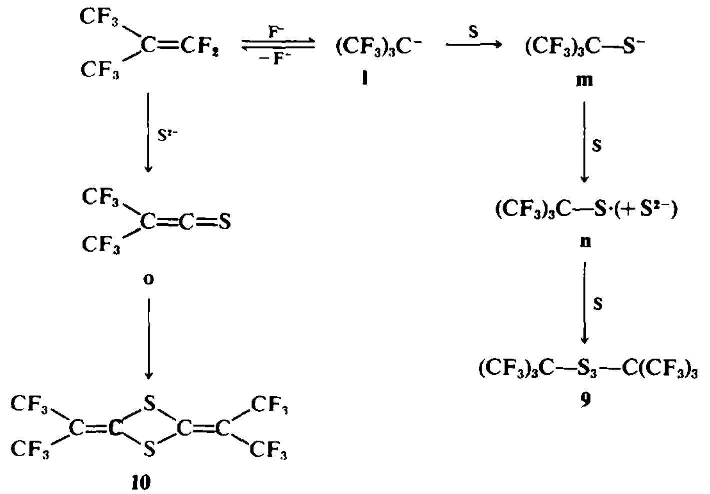
SCHEME 3

Table 4

Nos.	Reaction temp	Weight of perfluoro-cyclobutene, g	Perfluoro-cyclo-butene : S : KF molar ratio	**6**:**7**:**8** ratio (in per cent according to GLC data)	Yield of sulphur-containing products, g
1	130°	11·5	1 : 1·3 : 0·2	78 : 19 : 3	10·5
2	130°	33	1 : 1 : 1	60 : 35 : 5	32·4
3	130°	12	1 : 1·9 : 1·1	57 : 37 : 6	9·6
4	130°	12	1 : 0·5 : 1·5	20 : 45 : 35	7·1

In view of a comparatively low activity of perfluorocyclobutene, a more complete conversion of the olefine by interaction with sulphur required the presence of at least 0·2 mole of KF.

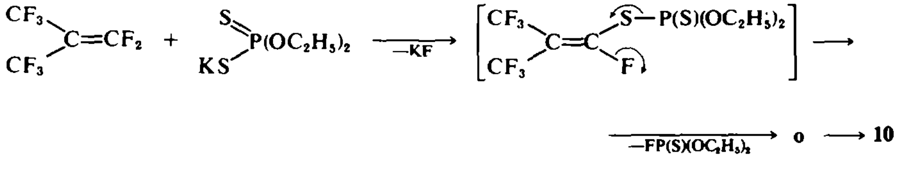
Perfluoroisobutylene which is highly electrophilic and, hence, easily forms perfluoro-t-butyl carbanion l, reacts with sulphur and potassium fluoride in tetramethylenesulphone under milder conditions—at 80 to 90°—giving mainly two compounds—bis-perfluoro-t-butyltrisulphide **9** and a dimer of bis-trifluoromethylthioketene **10**.* Evidently, the initially formed perfluoro-t-butylmercaptide anion **m** is oxidized by sulphur and the resulting sulphide ion reacts with perfluoroisobutylene by a vinyl substitution mechanism (Scheme 4).



SCHEME 4

A similar result was obtained by Krespan and England[15] in the action of potassium sulphide on perfluoroisobutylene in DMF: the chief product was compound **10** and by-product was compound **9**, evidently, because of an admixture of sulphur in potassium sulphide. Compound **9** was also produced by Krespan and England through the interaction of perfluoroisobutylene with CsF and sulphur in DMF.

This scheme for the formation of compound **10** suggested the synthesis by reacting perfluoroisobutylene with thiolic acid salts. Actually, compound **10** is formed in the reaction of perfluoroisobutylene with potassium thiocyanate, sodium thiosulphate, sodium hydrosulphide and other salts of thiolic acids. By using potassium diethyldithiophosphate, the yield of compound **10** was higher than 75% (Scheme 5).[16,17]



SCHEME 5

This reaction is, evidently, the most convenient preparative method for producing compound **10** and, consequently, of bis-trifluoromethylthioketene **o**, since the preparation of potassium sulphide free from water or alcohol is not an easy matter.

A number of processes are associated with the fact that the system fluoride ion + fluoro-olefine ⇄ perfluoroalkylcarbanion is an equilibrium and the reactions of the carbanion are always competing with those of the fluoro-olefine itself. Evidently, the results of the reaction may be different with some other method of the carbanion generation, for instance, if the source of the carbanion is not a fluoro-olefine, but an organometallic compound. In fact, we succeeded in proving that some perfluoroalkyl mercurials can be convenient for the generation of perfluoroalkyl carbanions.

Perfluoroalkyl mercurials, in contrast to their alkyl analogues, are stable to electrophilic agents, which is analogous with the properties of fluoro-

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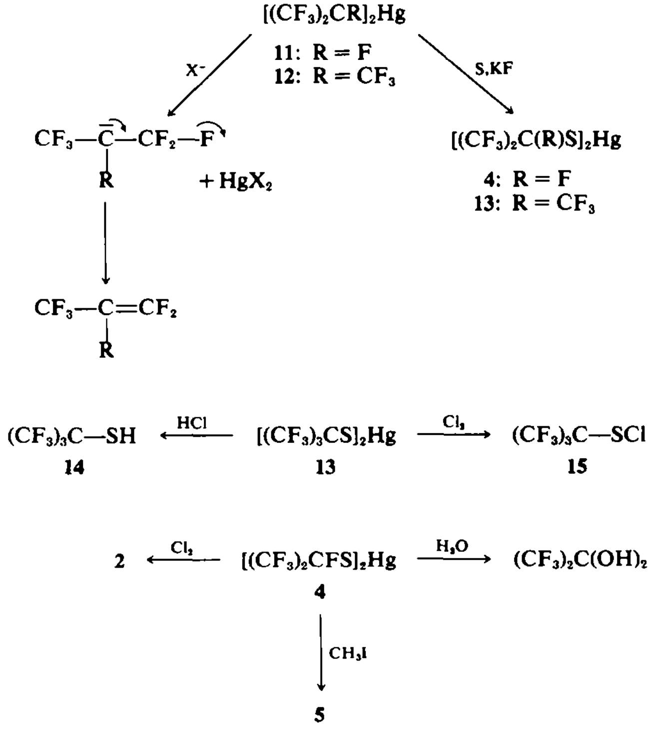
*This compound was first obtained by Raasch by a multistage synthesis.[14]

olefines as compared to olefines. At the same time an increased tendency of perfluoroalkyl mercurials to react with nucleophilic agents has been noted (complexation, haloform decomposition, etc.[18–20]). Consequently, nucleophilic catalysis and nucleophilic assistance which play an essential role in the reactions of organometallic compounds in general,[21,22] can be used for the generation of perfluoroalkyl carbanions from bisperfluoroalkyl mercurials.

Seyferth has shown[23] the replacement of the trichloromethyl anion by the iodide ion to be the first stage in the generation of dichlorocarbene from phenyltrichloromethyl mercury in the presence of sodium iodide. But in our attempts in the use of iodide, bromide and chloride ions for the generation of perfluoroalkyl carbanions from bis-perfluoro-t-butylmercury **11** and bis-perfluoroisopropylmercury **12** we observed only the formation of perfluoroisobutylene and perfluoropropylene, respectively.

A convenient nucleophilic catalyst for the generation of perfluoroalkyl carbanions in this case proved to be the fluoride ion.[24] The heating of bisperfluoroalkyl mercurials **11** and **12** with sulphur in DMF in the presence of potassium fluoride to 70–100° yields the corresponding bisperfluoroalkylmercaptides **13** and **4** and is not accompanied by the evolution of fluoro-olefine or other side processes. Mercaptide **13** can be isolated as a complex with 0·5 mole of DMF. Its acidulation with hydrochloric acid gives bis-perfluoro-t-butylmercaptan **14**, and chlorination – a corresponding sulphenylchloride **15**.

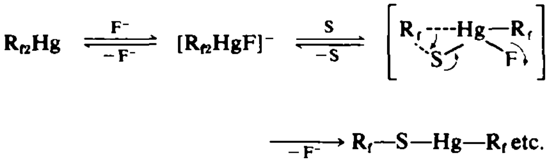
Mercaptide **4** could not be isolated, evidently due to its hydrolysis. The compound was identified by its ^{19}F NMR spectrum which corresponded to the expected one and coincided with the spectrum of the compound obtained by the reaction of dithiethane **1** with mercury fluoride (*cf* above) (the signal of trifluoromethyl groups: a doublet, $\delta = -1{\cdot}43$ ppm, $J_{F-C-C-F} = 12{\cdot}9$ Hz). The addition of water to the solution of compound **4** in DMF caused a very rapid change in the ^{19}F NMR spectrum: the spectrum became a singlet at 3·5 ppm, which corresponds to a signal of hexafluoroacetone hydrate. The chlorination of the solution of **4** yielded bis-perfluoroisopropyldisulphide **2**, and the action of methyl iodide – to methylperfluoroisopropylsulphide **5**. Probably, similar to other halide ions, the fluoride ion is coordinated by its unshared electron pair with the mercury atom and replaces the perfluoro carbanion. However, the presence of the fluoride ion in the reaction medium to a certain extent suppresses the decomposition of the perfluorocarbanion into fluoro-olefine and the fluoride ion; besides, the replacement of the carbanion leads to the formation of mercury fluoride which has



SCHEME 6

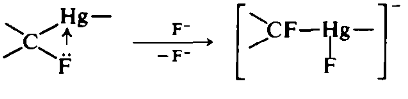
been shown[25,26] to react easily with perfluorocarbanions forming perfluoroalkyl mercurials.

On the other hand, it is not unlikely that in case of the fluoride ion its coordination with the mercury atom does not lead to a complete displacement of the carbanion, but only enhances the carbanion character of the C atom bonded with mercury, so that not the free carbanion but this complex enters into the reaction.



SCHEME 7

It should be pointed out that bis-perfluoroisoprepylmercury **12** in this reaction is much less active than bis-perfluoro-t-butylmercury **11**. The reaction of compound **12** with sulphur + KF in DMF is completed only in 15 hr with heating on a boiling water bath, whereas compound **11** reacts completely in 10 to 15 min at 70°. In our opinion, this difference can be accounted for by the intramolecular coordination of the α-atom of fluorine with the mercury atom, competing with the intermolecular coordination with the fluoride ion and thus contributing to the strengthening of the C—Hg bond.



The existence of such an intramolecular α-coordination is supported by the reduction in the constant of the spin–spin splitting $J_{^{199}Hg\text{-}C\text{-}^{19}F}$ with an increase in the basicity of the solvent.[27]

EXPERIMENTAL

The ^{19}F NMR spectra were recorded on a "Hitachi" H-60 NMR spectrometer. Chemical shifts are given in ppm from CF_3COOH as the external standard. The IR spectra were recorded on a UR-20 IR spectrometer.

Interaction of perfluoropropylene with sulphur and potassium fluoride (Typical experiment).

In a 100 ml capacity steel autoclave, perfluoropropylene, (8 g; 0·053 mole), S (1·72 g; 0·054 g-at.), KF (2·0 g; 0·034 mole) and 25 ml tetramethylenesulphone were heated with constant shaking at 120° for 12 hr. The distillation gave 6·7 g of a fraction with a b.p. of 106–118° composed of, according to GLC data, **1**, **2** and **3** in a ratio of 33 : 31 : 36. By further rectification pure **1** was isolated, b.p. 110–111°, $n_D^{25} = 1{\cdot}3342$, ^{19}F NMR spectrum: singlet, $\delta = -8{\cdot}0$ ppm. Disulphide **2** was identified by the GLC method by comparison with a reference specimen prepared by a different method.* Sulphide **3** was isolated by the method of preparative GLC on a "Carlo Erba" chromatography (20% E-301 on chromosorb G).

IR spectrum: $\nu_{max} = 1645\ cm^{-1}$; Mass spectrum: 482 M, 463 M-F, 413 M-CF_3, 313 M-C_3F_7, 313 M-C_3F_7, 294 M-C_3F_8, 275 M-C_3F_9, 263 C_5F_9S, 244 C_5F_8S, 231 C_5F_9, 225 C_5F_7S, 219 C_4F_9, 213 C_4F_7S, 206 C_5F_6S, 201 C_3F_7S, 193 C_5F_7, 187 C_5F_5S, 181 C_4F_7, 175 C_4F_5S, 169 C_3F_7, 163 C_3F_5S, 156 C_4F_4S, 150 C_3F_6, 144 C_3F_4S, 137 C_4F_3S, 131 C_3F_5, 125 C_3F_3S, 119 C_2F_5, 113 C_2F_3S, 106 C_3F_2S, 100 C_2F_4, 93 C_3F_3, 87 C_3FS, 81 C_2F_3, 75 C_2FS, 69 CF_3, 63 CFS, 50 CF_2, 43 C_2F, 32 S. (Found: C, 22·31; F, 70·99; S, 6·31. $C_9F_{18}S$ requires: C, 22·40; F, 70·95; S, 6·64%).

Interaction of perfluorocyclobutene with sulphur and potassium fluoride (Typical experiment).

In a 100 ml capacity steel autoclave perfluorocyclobutene (33 g; 0·2 mole), S (6·4 g; 0·2 g-at.), KF (12 g; 0·21 mole) and 20 ml of tetramethylenesulphone were heated with constant shaking at 130° for 15 hr. The distillation of the mixture gave 32·4 g of a fraction with a b.p. of 60–100°/40 mm Hg composed of, according to GLC data, **6**, **7** and **8** in a ratio of 60 : 35 : 5. Pure substances were obtained by further fractionation.

Trithiane **6**, b.p. 91°/40 mm Hg, $n_D^{20} = 1{\cdot}4025$. (Found: C, 22·83; F, 54·26, $C_8F_{12}S_3$ requires: C, 22·85; F, 54·25%). The mass spectrum contains a peak of the molecular ion (*m/e* 420) and intensive peaks *m/e* 226 ($C_4F_6S_2$) and *m/e* 94 (C_2F_2S).

Bis-perfluorocyclobutyldisulphide **7**, b.p. 147°, $n_D^{20} = 1{\cdot}3635$. (Found: S, 15·53. $C_8F_{14}S_2$ requires: S, 15·02%). The mass spectrum contains a peak of the molecular ion (*m/e* 426) and intensive peaks *m/e* 213 (C_4F_6) and *m/e* 113 (C_2F_3).

Perfluorocyclobutyl-perfluorocyclobutenylsulphide **8**, b.p. 49°/43 mm Hg, $n_D^{20} = 1{\cdot}3510$; IR spectrum: $\nu_{max} = 1690\ cm^{-1}$ (C=C). (Found: C, 26·69; F, 63·69. $C_8F_{12}S$ requires: C, 26·96; F, 64·05%). The mass spectrum contains a peak of the molecular ion (*m/e* 356) and intensive peaks *m/e* 250 (M-C_2F_4), *m/e* 143 (C_4F_5) and 125 *m/e* (C_3F_3).

Interaction of perfluoroisobutylene with sulphur and potassium fluoride

In a steel 250 ml-capacity autoclave perfluoroisobutylene (80 g; 0·4 mole), S (13 g; 0·41 g-at.), KF (15 g; 0·25 mole) and 40 ml of tetramethylenesulphone were heated to 80° with constant shaking for 15 hr. The unreacted perfluoroisobutylene (20 g) was collected into a trap, the reaction mass was distilled and 45 g of a mixture was obtained, boiling within a temp range of 170 to 185° and composed of, according to GLC data, **9** and the dimer **10** in a ratio of 5 : 1. Pure **9** was isolated by further rectification; b.p. 178°, it solidified at room temp. (Found: C, 18·15; F, 63·99; S, 18·40. $C_8F_{18}S_3$ requires: C, 17·97; F, 64·05; S, 18·97%).

The compound **10** was isolated by freezing out from light petroleum and identified by the GLC method with the reference specimen produced from bis-trifluoromethylketene and triphenylphosphine thiooxide.[14]

Preparation of dimer of bis-trifluoromethylthioketene **10**

A 3-necked flask equipped with a stirrer, a condenser cooled with a mixture of acetone and dry ice and a gas inlet pipe was charged with potassium diethyldithiophosphate (18 g; 0·08 mole) and 50 ml dry acetone and

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*The specimen became available to us through the courtesy of Dr. G. G. Belen'ky.

during constant stirring perfluoroisobutylene (16 g; 0·08 mole) was introduced. On completion of the gas absorption, the mixture was stirred for 20 min, then cooled to −30°, and the resulting ppt was filtered off and extracted with ether. The ether was evaporated and the residue recrystallized from light petroleum. The product, 12 g of the compound **10** (77·7% of theory), was identified by the GLC method, by comparison with the reference specimen.

Interaction of 2,2,4,4-*tetrakis* (*trifluoromethyl*)-1,3-*dithiethane* 1 *with mercury fluoride in the presence of potassium fluoride. Bis-perfluoroisopropylmercaptide of mercury* **4**

A 4-necked flask equipped with a stirrer, a gas inlet pipe, a thermometer and a reflux condenser was charged with **1** (8·6 g; 0·024 mole), mercury fluoride (11·6 g; 0·049 mole), freshly calcined KF (4 g; 0·068 mole) and 50 ml DMF, and the mixture was stirred at 80–100° for 15–20 min. The ^{19}F NMR spectrum revealed a doublet, $\delta = -1{\cdot}43$ ppm, $J_{F-C-C-F} = 12{\cdot}9$ Hz.

(a) To a soln of **4** prepared from **1** (8·6 g; 0·024 mole) and mercury fluoride (7 g; 0·03 mole), MeI (14·5 g; 0·1 mole) was added. The mixture was stirred for 45 min at 85°. On completion of the reaction, the substances volatile at 60°/23 mm Hg were collected into a trap cooled down to −80°. Et_3N (20 ml) was added to the contents of the trap and the mixture allowed to stand for 24 hr, with periodic agitation. The mixture was then washed with dil HCl, and the organic layer separated and distilled over conc H_2SO_4 yielding 3·3 g of **5** (33% of theory), b.p. 60·5°, ^{19}F NMR spectrum: doublet, $\delta = -1{\cdot}9$ ppm; heptet, $\delta = -83{\cdot}7$ ppm; $J_{F-C-C-F} = 9{\cdot}5$ Hz. Mass spectrum: 216 M; 197 M-F; 163 C_3F_5S; 147 M-CF_3; 113 C_2F_3S; 97 $C_2H_3F_2S$; 78 C_2H_3FS; 69 CF_3; 63 DFS; 47 CH_3S; 45 CHS; 15 CH_3. (Found: C, 22·45; H, 1·49; F, 61·52. $C_4H_3F_7S$ requires: C, 22·22; H, 1·39; F, 61·57%).

(b) Into a soln of **4** prepared from **1** (8·6 g; 0·024 mole) and mercury fluoride (11·6 g; 0·049 mole) Cl_2 (10 g; 0·14 mole) was passed while the flask was cooled down to 5–8°. The mixture was then filtered and the lower layer of the filtrate was separated and distilled yielding 8·5 g of **2** (61% of theory). This was identified by the GLC method by comparison with the reference specimen, and also by the ^{19}F NMR data.

Preparation of bis-perfluoroisopropylmercaptide of mercury 4 *by interaction of bis-perfluoroisopropylmercury with sulphur in the presence of potassium fluoride*

A mixture of bis-perfluoroisopropylmercury (15 g; 0·025 mole), S (3·5 g; 0·11 g-at.) and KF (2 g; 0·03 mole) in 40 ml DMF was heated with stirring to 100° for 15 hr. The ^{19}F NMR spectrum was identical with that of mercaptide **4** obtained from **1** and mercury fluoride. The reaction mixture was cooled down to −20° and excess Cl_2 was passed through it yielding **2** (6·5 g) (58% of theory). The substance was identified by the GLC and ^{19}F NMR methods.

Preparation of bis-perfluoro-t-butylmercaptide of mercury 13 *by interaction of bis-perfluoro-t-butylmercury with sulphur in the presence of potassium fluoride*

A flask equipped with a stirrer and a reflux condenser was charged with bis-perfluoro-t-butylmercury (19·1 g; 0·03 mole), S (6·1 g; 0·18 g-at.) and freshly calcined KF (1 g; 0·017 mole) and heated at 70° for 20 min. Then the mixture was filtered and the filtrate decomposed with water. The ppt was recrystallized from hexane yielding 17·3 g of **13** (82% of theory), in the form of a complex with 0·5 molecule of DMF, m.p. 78·5 to 79·5°. ^{19}F NMR spectrum: singlet, $\delta = -10$ ppm; mass spectrum: 702 M; 451 $(CF_3)_3CSHg$; 251 $(CF_3)_3CS$; 182 C_3F_6S; 181 C_4E_7; 163 C_3F_5S; 113 C_2F_3S; 73 DMF; 69 CF_3; 64 S_2; 44 CS. (Found: S, 8·66. $C_8F_{18}S_2Hg{\cdot}0{\cdot}5$ DMF requires: S, 8·66%).

Preparation of perfluoro-t-butylmercaptane **14**

To **13**·0·5 DMF (17·3 g; 0·023 mole), 35 ml of conc HCl was added and the mixture was carefully heated *in vacuo* till complete disappearance of the crystals. The volatile products were passed through a Tischenko vessel with conc H_2SO_4 and collected in a trap cooled down to −78° yielding 11·4 g of **14** (92% of theory), m.p. 63·5 to 64° (in a sealed capillary). ^{19}F NMR spectrum: singlet, $\delta = -10{\cdot}5$ ppm; mass spectrum: 252 M; 233 M-F; 213 C_4F_7S; 183 C_3F_6SH; 163 C_3F_5S; 144 C_4F_4S; 131 C_3F_5; 113 C_2F_3S; 94 C_2F_2S; 69 CF_3; 63 CFS; 32 S. (Found: F, 67·54. C_4F_9SH requires: F, 67·85%).

Preparation of perfluoro-t-butylsulphenylchloride **15**

Into a soln of **13**·0·5 DMF (19·0 g; 0·026 mole) in 40 ml difluorochloromethane excess Cl_2 was passed at −45°. The resulting soln was rectified and **15** (7·8 g) was obtained (50% of theory), b.p. 78–79°. ^{19}F NMR spectrum: singlet, $\delta = -11{\cdot}0$ ppm. The substance crystallized at room temp. (Found: C, 16·59; F, 59·73; S, 11·10. C_4F_9ClS requires: C, 16·78; F, 59·79; S, 11·19%).

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