Interaction of perfluorinated α-fluorosulfatocarbonyl compounds with nucleophilic reagents

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Abstract

α-Perfluorosulfatoperfluorocarbonyl compounds interact with alkaline metals halogenides to form the corresponding α-halo derivatives as a result of the direct nucleophilic substitution of the FSO_3 group. Through the action of halogenide anions on perfluorinated α,β-bis-fluorosulfatocarbonyl compounds, substitution by halogen of the FSO_3 group in the α-position to the carbonyl takes place. However, the FSO_3 group in the β-position is cleaved, which allows α-substituted β-dicarbonyl derivatives to be obtained.

Introduction

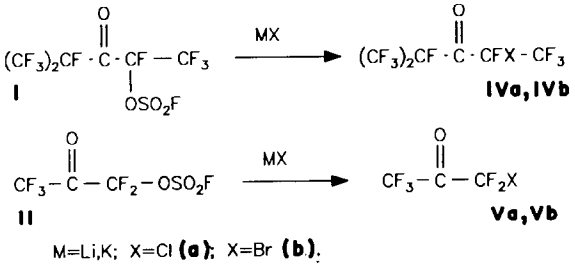
Nucleophilic substitution reactions leading to the replacement of the FSO_3 group by a nucleophile are not typical for perfluoroalkyl-1-fluorosulfates, since attack by a nucleophile is directed towards a sulfur atom [1]. At the same time, soft nucleophiles readily interact with esters of fluorosulfatodifluoroacetic acid (compounds containing a carbonyl group in the α-position to an FSO_3 group) and substitute the FSO_3 group via S_N2 type reactions [2]. Perfluorinated α-ketofluorosulfates (KFS) are similar to alkylfluorosulfatodifluoroacetates in structure, leading to the assumption that KFS would also react with nucleophiles via FSO_3 group substitution. Examples of the interaction between KFS and nucleophiles reported in literature did not confirm this assumption. For instance, although the reaction of ketone **I** with CsF leads to the perfluoroisopropylketone **III**, it occurs in two stages via the intermediate formation of 2-trifluoromethylperfluoropent-2-ene oxide, i.e. substitution of the FSO_3 group proceeds according to an S_Ni mechanism [3], and ketone **II** is isomerized to α-fluorosulfatotetrafluoropropanoyl fluoride by the action of NaI [4]. Thus the question as to how direct nucleophilic substitution of the FSO_3 group is achieved has remained open until now.

Results and discussion

The interaction of compounds **I** and **II** with halogenide anions has been studied in this work. Under mild conditions, compounds **I** and **II** react with LiCl and KBr to give the corresponding α-haloketones (Scheme 1).

We may assume that haloketones **IVa,b** like ketone **III** are also formed as a result of ring-opening in the intermediate α-oxide. However, this assumption is undermined by the formation of the isomeric α-chloroketones **IVa** and **VIII** (as a mixture) in the reaction of the mixture of ketofluorosulfates with LiCl. This follows because if α-oxide **VII** is formed as an intermediate, the products of its ring-opening by the chloride anion must contain the α,α-dichloroketone **IX**; however, **IX** was not found (Scheme 2).

Hence, we may conclude that the α-haloketones **IVa** and **IVb** are formed as a result of the direct nucleophilic substitution of the FSO_3 group in **I** by halogen. The synthesis of ketones **Va** and **Vb** is conducted in the same manner; intermediate formation of hexafluoropropene oxide should be excluded, however, because ring-opening by halogenide anions must produce α-halotetrafluoropropanoyl fluorides, not **Va** and **Vb**.



Scheme 1.

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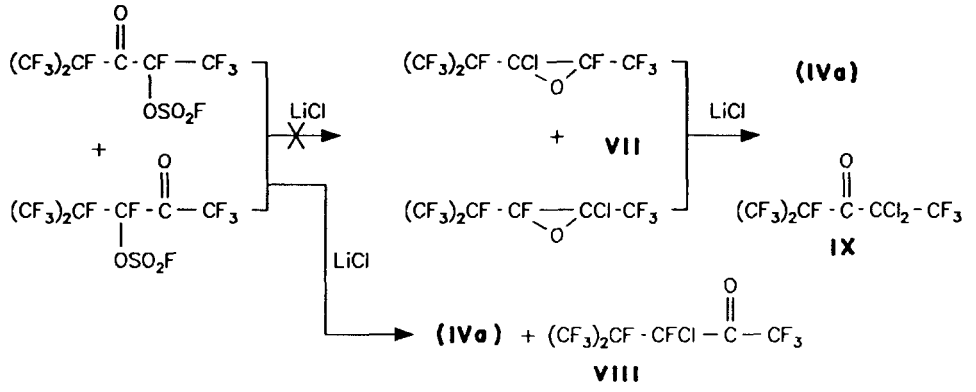
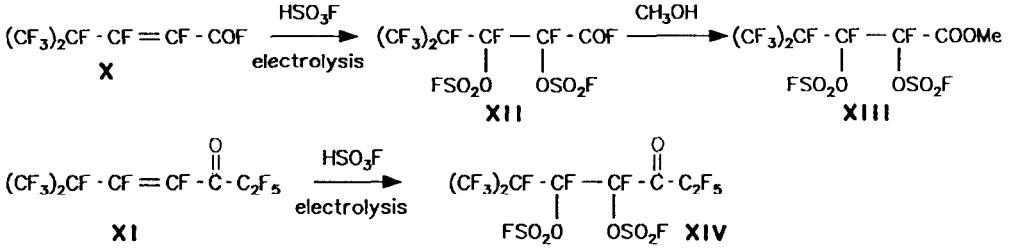


Scheme 2.



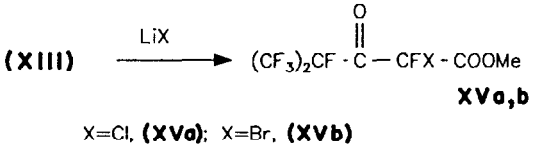
Scheme 3.

The results obtained allow us to suggest that in the reactions of α,β-bis-fluorosulfatocarbonyl compounds with nucleophiles, both routes (a) substitution of the FSO_3 group in the α-position to a carbonyl group and (b) cleavage of such a group in the β-position, would be followed to allow the synthesis of perfluorinated α-substituted β-dicarbonyl compounds.

To verify this conclusion we have prepared the bis-fluorosulfatoanhydride **XII** (which is converted into ester **XIII** by esterification) and the bis-fluorosulfatoketone **XIV** by electrochemical fluorosulfatation of carbonyl fluoride **X** and ketone **XI**, respectively (Scheme 3), and have studied the interaction of **XII** and **XIII** with halogenide ions.

Ester **XIII** interacts readily with LiCl and LiBr to give the α-halo-β-ketoesters **XVa,b** in good yield (Scheme 4).

Depending on the nature of the solvent, the reaction of **XIII** with CsF follows two routes: (a) in DMF medium, the diketoester **XVI** is formed in high yield; (b) in dioxan, the reaction results in a mixture of the epoxide **XVII** and the β-ketoester **XVIII**. Evidently, the formation of product **XVII** includes steps involving the generation



Scheme 4.

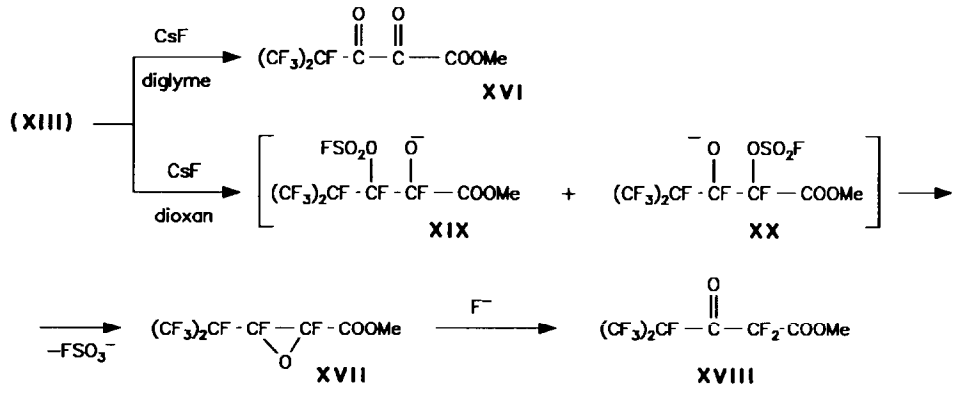
of alkoxy anions and intramolecular substitution of the FSO_3 group*; ring-opening of the epoxy ring via the action of the fluoride anion gives **XVIII** (Scheme 5).

In contrast to ester **XIII** (in which substitution of the FSO_3 group only occurs in the position α to the carbonyl by the action of chloride or bromide anions), similar reactions of ketone **XIV** result in the formation of two isomeric diketohalogenides, i.e. derivatives of the β-diketones **XXIa** and **XXIb** and of the α-diketones **XXIIIa** and **XXIIIb**. This appears to be connected with the alkylating properties of **XIV** which are not as pronounced as those of **XIII**; a nucleophilic attack at the sulfur atom then takes place (the extent of this direction of attack is greater in the case of the harder Cl^- nucleophile), together with attack at the carbon atom leading to the formation of **XXIa** and **XXIb**.

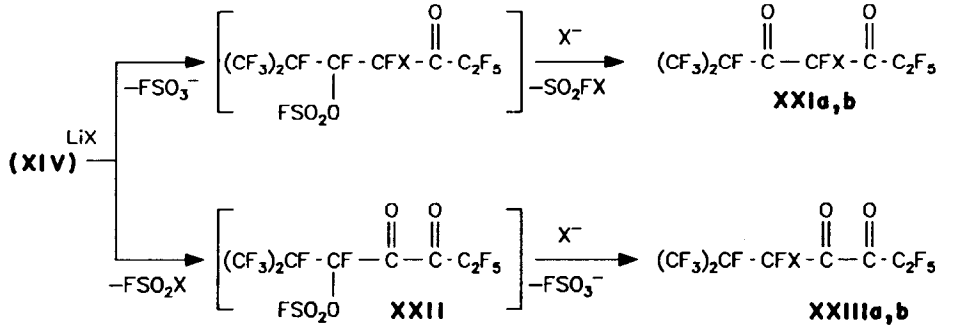
Attack at the sulfur atom results in the formation of the fluorosulfato-α-diketone **XXII** as an intermediate, leading to the generation of the α-diketones **XIIIa** and **XIIIb** through nucleophilic reaction with halogenide ions (Scheme 6).

The composition of the products formed in the reaction between **XIV** and CsF depends on the nature of the solvent as in the case of **XIII**. As a result of the action of the fluoride anion in diglyme at 25 °C, product **XIV** undergoes reaction (isomerization) to give a mixture of the bis-fluorosulfatoketones **XXIV** and

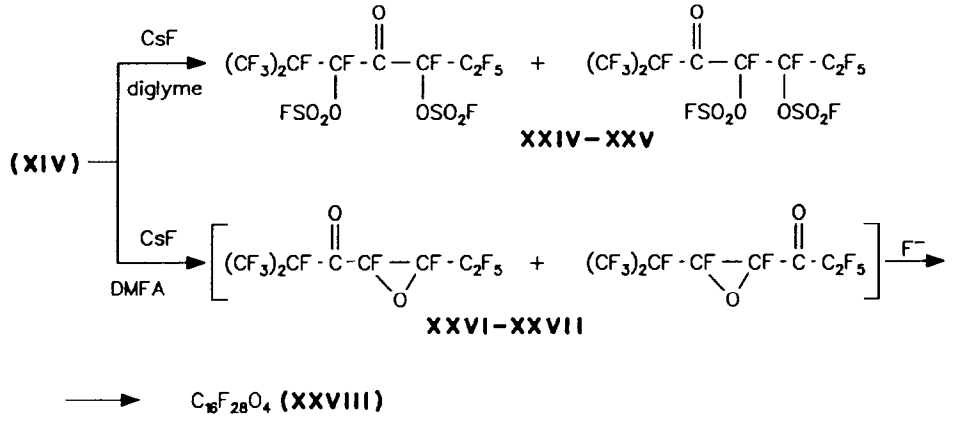
*The formation of perfluorinated α-oxides from α-fluorosulfonyloxyketones via the action of KF has been reported [3].



Scheme 5.



Scheme 6.



Scheme 7.

XXV. When reaction with XIV is carried out in DMF at 0–5 °C, compound XXVIII is formed; according to elemental analysis and GC–MS data, the latter is probably the product of the dimerization of the oxides XXVI and XXVII (mixture of isomers) (Scheme 7).

Experimental

^{19}F NMR spectra were recorded with a Perkin-Elmer R-32 spectrometer (84.6 MHz) and a Bruker WP-200 SY spectrometer (188.3 MHz). Chemical shifts are reported downfield from CF_3COOH as an external standard and given in parts per million. Mass spectra were obtained with a VG 7070E instrument using an ionization potential of 70 eV (*m/z*, relative intensity listed).

Interaction of α-fluorosulfatotetrafluoroethylheptafluoroisopropylketone (I) [3] with LiCl. (General procedure A)

Ketone I (10.0 g) was added dropwise to a mixture of anhydrous LiCl (1.8 g) and 15 ml absolute diglyme with stirring (20 °C). The reaction mixture was stirred

for 2 h at 20 °C and then the lower layer separated. The upper layer was poured into water; the organic layer and the layer which separated from the reaction were combined and distilled over conc. H_2SO_4. A fraction (b.p. 30 °C/40 mmHg, 6.7 g) was obtained which contained 4.4% **I**, 63.6% ketone **IVa** [5] and 31.9% perfluoro-4-methylpentadi-2,3-one (PFD) [6] (GLC, ^{19}F NMR methods).

Interaction of α-fluorosulfatotetrafluoroethylheptafluoro-isopropylketone (I) with LiBr

According to the GLC and ^{19}F NMR data, a mixture (4.1 g) containing 11% PFD and 89% ketone **IVb** (b.p. 94 °C) was obtained from LiBr (2.4 g) and ketone **I** (6.9 g) in 15 ml absolute diglyme (by Procedure A). Analysis: Found: C, 18.96; F, 55.49; Br, 21.15%. $C_6F_{11}BrO$ requires: C, 19.10; F, 55.44; Br, 21.22%. ^{19}F NMR δ: −4.1 (br s, $(CF_3)_2$; −0.2 (br s, CF_3); 68.5 (br d, CFBr); 108 (br d, CF, J(CF–CFBr) = 47 Hz) ppm.

Interaction of fluorosulfatopentafluoroacetone (II) with LiCl

The reaction of 4.5 g **II** with 1 g LiCl in 15 ml diglyme was carried out according to Procedure A. The reaction products were then distilled off from the reaction mixture at 20 °C (50 mmHg) when a low-boiling fraction was collected in the trap (−78 °C). Following distillation this gave 2.9 g (88%) ketone **Va**, b.p. 10 °C (GLC, ^{19}F NMR methods) [7].

Interaction of fluorosulfatopentafluoroacetone (II) with LiBr

Ketone **Vb** (5.2 g, 80%) was obtained from 3 g LiBr and 7 g **II** in 15 ml diglyme (25 °C, 1 h) via Procedure A. Compound **Vb**: b.p. 31–33 °C (GLC, ^{19}F NMR methods) [7].

Interaction of ketofluorosulfates I and VI with LiCl

Reaction of a mixture of **I** + **VI** (3 g) with 0.5 g LiCl in 15 ml diglyme (10 °C, 1 h) was carried out via Procedure A. Distillation of the organic layer obtained over conc. H_2SO_4 gave 1.7 g of a fraction (b.p. < 30 °C/ 40 mmHg) containing 76.6% **IVa**, 5.8% **VIII** [5] and 17.6% **VI** (GLC, ^{19}F NMR methods).

Preparation of 2,3-bis-fluorosulfatoperfluoro-4-methyl-pentanoyl fluoride (XII)

Acid HSO_3F (80 ml), containing 4% $NaSO_3F$, was placed in an unseparated glass cell cooled by running water (anode, glass carbon CU-2000; cathode, steel 8X13). Electrolysis was conducted at 20 °C using a current of 1 A for 14 h; 60 g (216 mmol) **X** [9] was added dropwise during the course of the experiment. The organic layer obtained was separated and distilled over conc. H_2SO_4. Product **XII** (85.3 g, 83%, b.p. 54–55 °C/10 mmHg) was obtained. Analysis: Found: C, 14.72; F, 47.73; S, 13.34%. $C_6F_{12}S_2O_7$ requires: C, 15.13; F, 47.87; S, 13.46%. MS: 429 $[M-COF]^+$ (1.13); 377 $[M-OSO_2F]^+$ (0.30); 330 $[C_5F_{10}O_3S]^+$ (0.13); 307 $[M-C_3F_7]^+$ (0.19); 299 $[C_4F_9O_3S]^+$ (11.3); 219 $[C_4F_9]^+$ (17.11); 197 $[C_4F_7O]^+$ (35.50); 177 $[C_2F_3O_4S]^+$ (263); 169 $[C_3F_7]^+$ (24.76); 131 $[C_3F_5]^+$ (13.87); 83 $[SO_2F]^+$ (100.0); 69 $[CF_3]^+$ (81.18); 67 $[SOF]^+$ (13.62); 47 $[COF]^+$ (23.88).

Preparation of 4,5-bis-fluorosulfatoperfluoro-6-methyl-heptan-3-one (XIV)

With the same conditions as employed in the previous experiment, electrolysis of 60 ml HSO_3F was conducted for 7 h, and **XI** [10] (40 g, 105 mmol) was added dropwise. The reaction mixture was poured into crushed ice, the organic layer obtained washed with water and distilled over conc. H_2SO_4. Distillation gave 46 g (75%) of product **XIV** (b.p. 68–70 °C/10 mmHg). MS: 429 $[M-C_3F_5O]^+$ (4.2); 330 $[C_5F_{10}]^+$ (10.4); 299 $[C_4F_9O_3S]^+$ (1.6); 259 $[C_6F_9O]^+$ (4.5); 228 $[C_5F_8O]^+$ (5.2); 219 $[C_4F_9]^+$ (35.5); 197 $[C_4F_7O]^+$ (10.2); 169 $[C_3F_7]$ (8.3); 147 $[C_3F_5O]^+$ (28.5); 131 $[C_3F_5]^+$ (18.6); 119 $[C_2F_5]^+$ (93.6); 100 $[C_2F_4]^+$ (4.4); 97 $[C_2F_3O]^+$ (4.9); 83 $[SO_2F]^+$ (53.9); 69 $[CF_3]^+$ (100.0); 67 $[SOF]^+$ (8.9).

Preparation of methyl-1,2-bisfluorosulfatoperfluoro-3-methylpentanoate (XIII)

To 150 ml of methanol, **XII** (136 g, 280 mmol) was added dropwise at 0 °C with stirring. The mixture was stirred for a further 30 min and poured into water; the organic layer obtained was separated and dried over $CaCl_2$. Distillation gave product **XIII** (130 g, 93%, b.p. 53–55 °C/2 mmHg). Analysis: Found: C, 17.16; H, 0.62; F, 43.60%. $C_7H_3F_{11}S_2O_8$ requires: C, 17.22; H, 0.61; F, 42.81%. MS: 469 $[M-F]^+$ (0.65); 429 $[M-COOCH_3]^+$ (0.28); 389 $[M-SO_2F]^+$ (0.19); 330 $[C_5F_{10}O_3S]^+$ (4.10); 219 $[C_4F_9]^+$ (4.47); 197 $[C_4F_7O]^+$ (4.26); 169 $[C_3F_7]^+$ (2.99); 131 $[C_3F_5]^+$ (5.63); 83 $[SO_2F]^+$ (21.06); 69 $[CF_3]^+$ (31.71); 67 $[SOF]^+$ (6.30); 59 $[COOCH_3]^+$ (100.0); 15 $[CH_3]^+$ (48.47).

Preparation of methyl-2-chloro-3-oxo-4-trifluoromethyl-perfluoropentanoate (XVa)

Ester **XIII** (10 g) was added to a stirred mixture consisting of 2.5 g LiCl and 10 ml absolute diglyme at 0 °C and then the reaction mixture was stirred for 2 h at 10 °C. When the reaction had ceased, the mixture was poured into aqueous HCl, the organic layer separated and distilled over conc. H_2SO_4. Product **XVa** (4.2 g, 64%, b.p. 43–44 °C/15 mmHg) was obtained. Analysis: Found: C, 26.10; H, 1.06; Cl, 10.62; F, 46.40%. $C_7H_3F_8ClO_3$ requires: C, 26.10; H, 0.93; F, 47.13; Cl, 11.01%.

Preparation of methyl-2-bromo-3-oxo-4-trifluoromethyl-perfluoropentanoate (XVb)

Methyl ester **XIII** (9.0 g) was added to 4 g of LiBr and 10 ml of absolute diglyme at 0 °C with stirring. The mixture was stirred for a further 2 h at 10 °C and poured into aqueous HCl; the organic layer obtained was separated and distilled over conc. H_2SO_4. Product **XVb** (4.6 g, 68%, b.p. 82–84 °C/49 mmHg) was obtained. Analysis: Found: C, 22.74; H, 0.81; F, 41.41; Br, 20.86%. $C_7H_3F_8BrO_3$ requires: C, 22.87; H, 0.82; F, 41.42; Br, 21.80%

Preparation of methyl-2,3-dioxo-4-trifluoromethyl-perfluoropentanoate (XVI)

Methyl ester **XIII** (5 g) was gradually added to 1.5 g of rapidly desiccated CsF and 8 ml of absolute DMF at 5–10 °C with stirring. The reaction mixture was then stirred for 1 h at 20 °C and poured into aqueous HCl; the organic layer obtained was separated, the aqueous layer extracted with ether, the extract added to the organic layer and washed with water after removal of the ether, and the residue distilled over conc. H_2SO_4. Distillation gave 2.1 g (78%) **XVI**, b.p. 50 °C/20 mmHg (cf. ref. 8).

Interaction of methyl 2,3-bis-fluorosulfonyloxy-4-trifluoromethylperfluoropentanoate (XIII) with CsF in dioxan

Ester **XIII** (5 g) was added to 3.0 g of CsF and 10 ml of absolute dioxan at 20 °C and stirred for 3 h. The reaction mixture was then stirred for 3 h at 20 °C, poured into water, the organic layer obtained separated and distilled over conc. H_2SO_4. The resulting mixture (2.3 g, 75%) contained 63% oxide **XVII** and 37% ketoester **XVIII** (GLC methods). Compound **XVII**: MS: 259 $[M-CFO]^+$ (11); 231 $[C_5F_9]^+$ (33); 219 $[C_4F_9]^+$(28); 197 $[C_4F_7O]^+$ (7.8); 168 $[C_3F_7]^+$ (9.6); 159 $[C_2F_4COOCH_3]^+$ (6); 150 $[C_3F_6]^+$ (2.9); 131 $[C_3F_5]^+$ (12.4); 109 $[CF_2COOCH_3]^+$ (9.4); 90 $[CF_3COOCH_3]^+$ (51); 69 $[CF_3]^+$ (73.9); 59 $[CH_3OCO]^+$ (100); 47 $[CFO]^+$ (29.6); 43 $[CH_3CO]^+$ (28.6); 31 $[CF]^+$ (20.6); 15 $[CH_3]^+$ (91.5).

Preparation of methyl-3-oxo-4-trifluoromethyl-perfluoropentanoate (XVIII)

To 0.5 g of CsF in 5 ml of absolute diglyme, 2.3 g of the mixture of **XVII** (63%) and **XVIII** (37%) was added with stirring; when addition was over, the reaction mixture was stirred for 0.5 h at 20 °C and then poured into water when the organic layer was distilled over H_2SO_4. Ketoester **XVIII** (2.0 g, b.p. 55–57 °C/110 mmHg) was obtained. Analysis: Found: C, 27.21; H, 0.99; F, 55.85%. $C_7H_3F_9O_3$ requires: C, 27.45; H, 0.98; F, 55.88%.

Interaction of 4,5-bis-persulfonyloxy-6-trifluoromethyl-perfluoroheptan-3-one (XIV) with LiCl

Bis-fluorosulfate **XIV** (5.0 g) was added to 1 g of LiCl in 5 ml of absolute diglyme at 0 °C, the reaction mixture was then stirred for 2 h at 20 °C, the lower layer separated and distilled over conc. H_2SO_4. The resulting mixture (3.0 g, 83%, b.p. 116–117 °C) contained 69% **XXIa** and 31% **XXIIIa** (GLC methods). Analysis: Found: C, 22.85; F, 59.38; Cl, 8.82%. $C_8F_{13}ClO_2$ requires: C, 23.39; F, 60.17; Cl, 8.65%.

Compound **XXIa**: MS: 410 $[M]^+$ (0.84), (0.29); 382 $[M-CO]^+$ (3.52); 263 $[M-C_2F_5CO]^+$ (3.4); 213 $[C_2F_5COCFCl]^+$ (19.5); 197 $[C_3F_7CO]^+$ (95.4); 169 $[C_3F_7]^+$ (49); 147 $[C_2F_5CO]^+$ (29.5); 119 $[C_2F_5]^+$ (100); 100 $[C_2F_4]^+$ (90); 97 $[C_2F_3O]^+$ (25); 85, 87 $[CF_2Cl]^+$ (46.9), (28.9); 69 $[CF_3]^+$ (92.6); 31 $[CF]^+$ (14.1).

Compound **XXIIIa**: MS: 410 $[M]^+$ (0.1); 347 $[M-COCl]^+$ (0.1); 309 $[M-CF_2OCl]^+$ (0.1); 263 $[M-C_2F_5CO]^+$ (1.2); 235, 237 $[C_3F_7CFCl]^+$ (23.5), (7.5); 159 $[C_4F_5O]^+$ (9.6); 147 $[C_2F_5CO]^+$ (38.6); 119 $[C_2F_5]^+$ (100); 85, 87 $[CF_2Cl]^+$ (22.2), (7.2); 69 $[CF_3]^+$ (49); 50 $[CF_2]^+$ (1.8); 31 $[CF]^+$ (6.1).

Interaction of 4,5-bis-fluorosulfonyloxy-6-trifluoromethyl-perfluoroheptan-3-one (XIV) with LiBr

Absolute diglyme (10 ml) was added to 4.0 g of LiBr at 0 °C and then bis-fluorosulfate **XIV** (5 g) was added with stirring; the reaction mixture was further stirred for 0.5 h at 10 °C and for 1 h at 20 °C. The lower layer was then separated and distilled over H_2SO_4. A mixture (3.0 g, 77%, b.p. 65–67 °C/70 mmHg), containing 80.7% **XXIb** and 19.3% **XXIIIb** (GLC methods), was obtained. Analysis: Found: C, 21.22; F, 54.96%. $C_8F_{13}BrO_2$ requires: C, 21.10; F, 54.28%.

Compound **XXIb**: MS: 454 $[M]^+$ (0.5); 426 $[M-CO]^+$ (10); 375 $[M-Br]^+$ (18); 335 $[M-C_2F_5]^+$ (0.2); 307 $[M-C_3F_5O]^+$ (5); 257 $[M-C_4F_7O]^+$ (20); 197 $[C_4F_7O]^+$ (100); 169 $[C_3F_7]^+$ (43); 147 $[C_3F_5O]^+$ (33); 119 $[C_2F_5]^+$ (80); 87 $[C_3F_7O]^+$ (50); 69 $[CF_3]^+$ (98); 31 $[CF]^+$ (22).

Compound **XXIIIb**: MS: 307 $[M-C_2F_5CO]^+$ (5); 279 $[C_4F_8Br]^+$ (30); 260 $[C_4F_7Br]^+$ (3); 228 $[C_2F_4CO]^+$ (5); 209 $[C_5F_7O]^+$ (8); 191 $[C_3F_4Br]^+$ (5); 181 $[C_4F_7]^+$ (9); 159 $[C_4F_5O]^+$ (23); 147 $[C_2F_5CO]^+$ (40); 129 $[CF_2Br]^+$ (20); 119 $[C_2F_5]^+$ (100); 69 $[CF_3]^+$ (60); 31 $[CF]^+$ (5).

Interaction of 4,5-bis-fluorosulfonyloxy-6-trifluoromethyl-perfluoroheptan-3-one (XIV) with CsF in diglyme

Bis-fluorosulfate **XIV** (4.0 g) was added to 0.3 g of CsF in 3 ml of absolute diglyme at 20 °C with stirring. The reaction mixture was then stirred for 1 h and the lower layer separated. Distillation gave 2.0 g (50%) of a mixture of isomers (GLC methods), b.p. 60 °C/10 mmHg.

Compound **XXIV**: MS: 557 $[M-F]^+$ (1); 477 $[M-OSO_2F]^+$ (2); 299 $[C_3F_7CFOSO_2F]^+$ (20); 249 $[C_2F_5CFOSO_2F]^+$ (20); 197 $[C_3F_7CO]^+$ (44); 169 $[C_3F_7]^+$ (35); 119 $[C_2F_5]^+$ (60); 83 $[SO_2F]^+$ (100); 69 $[CF_3]^+$ (50).

Compound **XXV**: MS: 379 $[M-C_3F_7CO]^+$ (22); 327 $[M-C_3F_6SO_3F]^+$ (2); 280 $[M-C_4F_7SO_3F]^+$ (12); 249 $[C_3F_6SO_3F]^+$ (5); 197 $[C_3F_7CO]^+$ (66); 169 $[C_3F_7]^+$ (100); 119 $[C_2F_5]^+$ (22); 83 $[SO_2F]^+$ (55); 31 $[CF]^+$ (6).

Interaction of 4,5-bis-fluorosulfonyloxy-6-trifluoromethyl-perfluoroheptan-3-one (XIV) with CsF in DMF

Bis-fluorosulfate **XIV** (6.0 g) was added gradually to 1.8 g of CsF in 10 ml of absolute diglyme at 5 °C with stirring. The reaction mixture was then stirred for 2 h and the lower layer separated. Distillation gave 3.5 g (43%) **XXVIII**, b.p. 80 °C/10 mmHg. Analysis: Found: C, 24.27; F, 67.47%. $C_{16}F_{28}O_4$ requires: C, 24.36; F, 67.51%. MS: 591 $[M-C_3F_7CO]^+$ (9.8); 541 $[C_{11}F_{19}O_3]^+$ (20.1); 453 $[C_{10}F_{15}O_3]^+$ (5.1); 425 $[C_9F_{15}O_2]^+$ (10.2); 375 $[C_8F_{13}O_2]^+$ (0.5); 325 $[C_7F_{11}O_2]^+$ (9.8); 259 $[C_6F_9O]^+$ (0.4); 219 $[C_5F_{11}]^+$ (50); 197 $[C_3F_7CO]^+$ (100); 169 $[C_3F_7]^+$ (55); 147 $[C_2F_5CO]^+$ (30); 119 $[C_2F_5]^+$ (31); 69 $[CF_3]^+$ (83.1); 31 $[CF]^+$ (9).

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