FLUOROALIPHATIC ESTERS OF FLUOROSULFONIC ACID. 1. REACTIONS OF HIGHER FLUOROOLEFINS WITH ELECTROCHEMICALLY GENERATED PEROXYDISULFURYL DIFLUORIDE

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The electrolysis of fluorosulfonic acid in the presence of perfluoro-2-alkenes in an electrolyzer without a diaphragm results in the formation of a mixture of products, whose composition is determined by both the anodic and cathodic processes.

The reactions of electrochemically generated peroxydisulfuryl difluoride I with fluoroolefins [1, 2], hydroperfluoroalkanes, α,α -dihydroperfluoro alcohols, and fluoroaliphatic carboxylic and sulfonic acids [3, 4] provide convenient paths for the synthesis of fluoroaliphatic esters of fluorosulfonic acid. According to [1, 4], the contribution of the electrochemical step in these reactions, which are carried out in electrolyzers without diaphragms, is determined exclusively by the anodic process, i.e., by the oxidation of the FSO₃⁻ anion to an FSO₃⁻ radical.

Studying the reaction of perfluoro-4-methyl-2-pentene II with I during the electrolysis of HSO_3F in an electrolyzer without a diaphragm (the anode was a glassy carbon electrode, the cathode was Ti, and the supporting electrolyte was 4% NaSO₃F), we found that the formation of the main reaction product, viz., 2,3-bi(fluorosulfato)perfluoro-4-methylpentane III, was accompanied by the formation of small quantities of isomeric keto fluorosulfates IV and V and perfluoroisohexene sulfate VI [III:(IV + V):VI = 90:7:2].

 $\begin{array}{cccc} (CF_3)_2CFCF = CFCF_3 & \xrightarrow{HSO_3F;} & (CF_3)_2CFCFCFCF_3 + (CF_3)_2CFCCFCF_3 + \\ & electrolysis & & | & | \\ & & fSO_2O & OSO_2F & OOSO_2F \\ (11) & & (111) & (1V) \\ & + (CF_3)_2CFCFCCF_3 + (CF_3)_2CFCF - CFCF_3 \\ & & fSO_2O & O & O \\ & & & SO_2 \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & &$

It might have been postulated that the formation of IV-VI is determined by the presence of H_2SO_4 in the reaction mixture as a result of the partial hydrolysis of HSO_3F : the anodic oxidation of H_2SO_4 gives persulfuric acid, whose addition to II produces cyclic sulfate VI, and the combined addition of this compound and I to II gives keto fluorosulfates IV-V.

A. N. Nesmeyanov Institute of Organometallic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2048-2056, September, 1990. Original article submitted July 7, 1989.

	Olefin, g (mole)	Quant- ity of elec- tric- ity,F	A 11	Composition of reaction products (GLC), %				
USOF, ml			reac- tion pro- duct, g	vicinal bis(fluoro- sulfates)	keto fluoro- sulfates (mixture of iso- mers)	cyclic sulfates	dimers C _{2n} F _{4n} (OSO ₂ F) ₂	
.30	(11) 35,4 $(0,12)$	0.242	45,2	(111) 91,6	(IV), (V) 6,5	(VI) 1.9	_	
×0	(XIII) 50(0,46)	0.778	ee e	(XIV) 09.5	(XV)	(XVI)		
		0,110	00,0	55,5	0,5			
20	(XVII)			(XVIII)	(XIX).	(XXI)		
	7,4(0.02)	0,046	9,8	93	(XX) 3,5	3,5		
:30 *	(XXIIa)			(XX111a)	(XXIVa), (XXIVa)	(XXVIa)	(XXVIIa)	
	30(0,12)	0,177	38	59,9	(XXVa) 3,3	1.0	35,8	
30*+	(XXHa) 30 (0,42)	0,204	37,7	(XX111a) 35,3		-	(XXVIIa) 64,7	
30	(XXIIP)			(XXHIÞ)	(XXIVb),	(XXV b)	(XXVIIb)	
	20 (0,067)	0,453	21	71.2	2.5	0,5	25,8	
30 +	(XXIIЪ) 15 (0,05)	0,112	17,2	(XX111b) 55.4	_		(XXVIIb) 44.6	
16	(XXHc)		1	(XXII)C)	(XXIVc.),	(XXVIC)	(XXVH¢)	
	17 (0,043)	0,068	20	42,9	(XXVC) 1.5	0,5	55.1	
30	(XXVIII) 23(0,088)	0.177	26,8	(XXIX) 56.6	-	_	(XXX) 43,4	

TABLE 1. Electrolysis of HSO₃F in the Presence of Fluoroolefins

*The electrolysis temperature was 18-20°C. †The HSO₃F contained 15.6% NaSO₃F.

In fact, sulfate VI was obtained as a result of the electrolysis of H_2SO_4 in the presence of II.* Apparently, this result confirms the role of H_2SO_4 in the formation of IV-VI during the electrolysis of HSO_3F in the presence of olefin II, but the attempts to simulate the conditions for the synthesis of these compounds by carrying out the electrolysis in HSO_3F with an addition of 5-15 vol. % H_2SO_4 did not lead to an increase in the yields of IV-VI. At the same time, the composition of the reaction products remained unchanged when freshly distilled HSO_3F and thoroughly dried equipment were used, ruling out the possibility of the formation of H_2SO_4 as a result of the hydrolysis of HSO_3F . Thus, the data obtained attest to the fact that the synthesis of compounds IV-VI is not associated with the presence of H_2SO_4 in the original mixture. We assume that the processes resulting in the formation of IV-VI have an endogenous character and are based on the cathodic reduction of HSO_3F .

It has been noted that the electrochemical reduction of HSO_3F results in the formation of SO_2 [5]. During the cycling of a glassy carbon electrode at potentials ranging from -1.1 to 2.2 V relative to a reference Pd/H₂ electrode, we observed peaks corresponding to the oxidation of compounds of sulfur in its lower valence states (Fig. 1, curve 1) at E = 0.6, 0.9, and 1.4-1.8 V, whose intensity increases when SO_2 is introduced into the electrolyte and the electrode is held at the potential for the reduction of $SO_2 E = -0.45$ V (Fig. 1, curve 2). The possibility of the generation of SO_2 as a result of the electrolysis of HSO_3F allows us to represent the formation of IV-VI by the following sequence of reduction, oxidation, and hydrolysis reactions

^{*}The yield of VI in this reaction was only 14%; the bulk of the products consists of nonvolatile compounds, which decomposed during an attempt at vacuum distillation.



Fig. 1. Cyclic voltammogram of a glassy carbon electrode: 1, 1') forward and reverse courses in a solution of HSO_3F in 1 mole KSO_3F ; 2) anodic polarization curve after the introduction of SO_2 into the solution and maintenance of the electrode at the reduction potential of SO_2 (-0.45 V) over the course of 3 min. The scanning rate of the potential was 80 mV/sec. The area of the glassy carbon electrode was $3.1 \cdot 10^{-2}$ cm².



The proposed scheme is confirmed by the significant increase in the percentage content of IV-VI in the reaction products when the electrolysis is carried out in the presence of SO_3 , which attests to the decisive role of VII in the formation of these compounds. The yield of IV-VI also increases, although not so appreciably, when the Ti cathode is replaced by Ni, which has a high electrocatalytic activity in cathodic processes [6]. In the latter case, the influence of the cathodic process on the composition of the electrolysis products is demonstrated not only by the increase in the yield of IV-VI, but also by the formation of derivatives of divalent sulfur, for which the structures of sulfide X, disulfide XI, and trisulfide XII were proposed on the basis of the data from gas-chromatographic-mass spectrometry:

$$(11) \xrightarrow{(11)} (CF_3)_2 CF \dot{C}F CF CF_3 \xrightarrow{S} (CF_3)_2 CF CF CF CF_3 \xrightarrow{I} OSO_2 F \xrightarrow{I} OSO_2 F$$



TABLE 2. Boiling Points and Results of the Elemental Analysis of the Compounds Obtained

	bp, °C (p, mm	Foun	d, %	Empirical	Calculated, %	
Compound	Hg)	с	F	formula	С	F
(VI) (XIV) (XVIII) (XXVIIa) (XXVIIa) (XXVIIa) (XXVIIa) (XXVIIa) (XXIX)	$\begin{array}{c} 33-35\ (50)\\ 48-50\ (20)\\ 80-83\ (15)\\ 55-56\ (2-3)\\ 90-92\ (2-3)\\ 62-65\ (10)\\ 103-105\ (2-3)\\ 26-27\ (2-3)\\ 90-92\ (2-3)\end{array}$	17,9714,1915,2616,8517,6315,9819,1715,5219,95	57,4754,2455,4759,4661,3457,0264,9349,8458,38	$ \begin{bmatrix} C_6F_{12}O_4S\\ C_6F_{13}O_6S_2\\ C_7F_{16}O_6S_2\\ C_{16}F_{22}O_6S_2\\ C_{16}F_{22}O_6S_2\\ C_{6}F_{12}S_{26}O_8S_2\\ C_{6}F_{12}O_6S_2\\ C_{6}F_{12}O_6S_2\\ C_{6}F_{12}O_6S_2\\ C_{12}F_{22}O_6S_2 \end{bmatrix} $	18,1914,4615,3417,2018,0516,0519,2415,6519,95	$57,56 \\ 53,39 \\ 55,46 \\ 59,87 \\ 61,88 \\ 57,18 \\ 64,73 \\ 49,54 \\ 57,87 \\$

TABLE 3. ¹⁹F NMR Spectra of Compounds Obtained

Compound	ô, ppm; J, Hz
$\begin{array}{c} 1 \\ CF_{3} - CF \\ 0 \\ 0 \\ SO_{*} \end{array} \xrightarrow{2} CF - CF(CF_{3})_{*} (VI) \\ 0 \\ SO_{*} \end{array}$	1.6 m (3F ¹). 37,3 m, 45,7 m (F ² +F ³), 107,1m (F ⁴), $-4,0$ m, $-5,1$ m (6F ⁵)
$ \begin{array}{c} 1 \\ CF_{3}CF_{2}CF_{-}CF_{-}C \\ i \\ FSO_{2}O \\ 0 \\ SO_{2}F \\ 6 \\ 5 \end{array} $	2.5 m (3F ¹), AB AB quartet with a center at 38.9 J_{AB} =291,4 (2F ²), 48,4m ⁻ (F ³), -11,9 m (6F ⁴), -128.9 m, -131,1 m (F ⁵ +F ⁶)
$\begin{array}{c}1&2&3\\ CF_{s}CF-CF-CF-C (CF_{s})_{s}&(XVIII)\\ I&I\\ FSO_{s}O&OSO_{2}F\\ 6&5\end{array}$	-0.8 m (3F ⁴), 38.2 m, 40.7 m, 49.8 m (F ² +F ³), -16.5 m (9F ⁴), -130.4 m, -132.5 m (F ⁵ +F ⁶)
$\begin{array}{c}1&2&3&4-7\\ CF_{s}CF-CF-C_{s}-C_{s}F_{s}-CF_{s}&(XXIIIb)\\ FSO_{s}0&OSO_{s}F\\ 10&9\end{array}$	0.13 m, 0.7 m, (3F ¹), 55,8 m, 56,9 m (F ² +F ³), 40,2 m, 43,6 m, 45,3 m, 49,3 m (2F ¹ +2F ⁵ +2F ⁶ + +2F ⁷), 6.3 m (3F ⁸), -129,5 m, -130,7 m (F ⁵ +F ¹⁰)

Despite the variety of secondary products of the reaction of II and I, their total yield is low when a Ti cathode is used, and the content of III in the mixture of products formed reaches 88-90%. High yields of bis(fluorosulfates) XIV and XVIII were obtained as a result of the electrolysis of HSO_3F in the presence of perfluoro-2-methyl-2pentene XIII and perfluoro-4,4-dimethyl-2-pentene XVII; the secondary products of these reactions form in insignificant amounts. Thus, the reaction of high fluorosulfato)perfluoroalkanes.



In contrast to the foregoing examples, the reaction of unbranched perfluoro-2-alkenes and perfluorocyclohexene with electrochemically generated I results in the formation of significant amounts of the products of the fluorosulfatodimerization of these olefins along with the vicinal bis(fluorosulfates), keto fluorosulfates, and cyclic sulfates:*

	Rel. intensity, % for R _F					
<i>m/:</i>	C ₂ F ₅ (XX111a)	C ₃ F ₇ (XXIIIb)	i-C ₄ F ₇ (111)	t-C4F5 (XVIII)	$\begin{array}{c} C_{5}F_{11}\\ (XXIIIC) \end{array}$	
M_F	_	_	0.1		_	
M-CF ₂	-	19		-	-	
M-SO ₂ F			0.4	0.1	0,6	
RFCFOSO2F	9,9	10,8	12.1	5,9	12,8	
CF ₃ CFOSO ₂ F	10,0	10,1	12,8	4.6	16,8	
R _F CO	14.7	3.7	30,2	25,0		
CF ₅ CO	26,0	24,5	25,2	14,2	31,8	
$C_{0}F_{0}O$	14.7	3,9	5,5	4.1	7.2	
C_3F_3O	-	10.6	1,4	_	2,2	
RF	57.5	47.9	22.4		16,8	
CF ₂	100,0	100,0	83,5	100,0	100.0	
SO_2F	53,7	69,0	100,0	72,3	100.0	

TABLE 4. Mass Spectra of the Vicinal Bis(fluorosulfates) $R_F CF(OSO_2F)CF(OSO_2F)CF_3$



	Rel. intensity, % for R _F						
fn/z	C ₂ F ₅ (XXVIa)	C ₃ F ₇ (XXV1b)	i-C ₅ F ₇ (VI)	f-C.F. (XX1)	(XXV1c)		
M-F	0.3	1.2		2.2	_		
M-CFa	2.0	-	5.0	-	- 1		
M-RF	-	17.5	1.2	-	15.6		
M-SO ₃ F	1,9	1,9	_	3,0	0,9		
R _F CFOSO ₂ F	1,6	-	1 1.7	_	-		
CF ₃ CFOSO ₂ F	8,1	12,2	1.8		11,0		
RFCFCF	-	-	1.3	5.1	- 1		
RF	62,2	21.7	2.2	-	6,0		
RFCO	1	3,0	7,0	5,4	_		
$C_{3}F_{5}O$	24,6	11,3	15.0	9.5	13,3		
CF ₃ CO	30,0	32,8	7,3	3,1	35,6		
C_3F_3O	1.3	1,0	1,6		- 1		
CFa	100.0	100,0	100.0	100,0	100,0		
SO_2	[18,6	12,7	16,7	13,5	4,9		

^{*}According to the data in [7], the reaction of unbranched perfluoro-2-alkenes with I results in the formation of only 2,3-bi(fluorosulfato)perfluoroalkanes.



Dimers XXVIIa-c were obtained in the form of a mixture of isomers, and the presence of several asymmetric centers in them makes it difficult to establish their structure by means of ¹⁹F NMR.

By comparing the results of the reactions of fluoroolefins with I considered above, we can evaluate the influence of different fluoroalkyl groups on the reactivity of α -fluorosulfatoperfluoroalkyl radicals. The absence of fluorosulfatodimerization products in the case of olefins II and XVII, which have iso structures, is clearly a consequence of the steric hindrances created by the branched fluoroalkyl groups in the α position to the radical center (at least in the case of II, the regioselective character of the addition of the FSO₃⁻ radical at the double bond is confirmed by the structures of sulfides X-XII). Such radicals can add a second FSO₃⁻ radical, but they are not capable of undergoing dimerization.

In the case of olefins XXIIa-c, the unbranched fluoroalkyl groups do not place such rigid restrictions on the addition of fluorosulfate radicals at the double bond or on the subsequent dimerization of the fluoroalkyl radicals formed practically regardless of their size, as is evidenced by the formation of a mixture of isomeric fluorosulfatodimerization products. It should also be noted that along the series of olefins XXIIa-c the relative yield of the dimeric products (in millimoles per mole of the corresponding adducts) at first decreases and then increases again, being equal to 0.39, 0.23, and 0.76 for XXVIIa, XXVIIb, and XXVIIc, respectively.

The fact that the variation of the yield of the dimers does not have a monotonic character is apparently due to the different distributions of the original fluoroolefins and the fluorosulfatoperfluoroalkyl radicals formed in the organic and inorganic phases of the reaction mixture, depending on the size of the molecule. Assuming that the solubility of the fluoroolefins in HSO₃F is inversely proportional to the molecular weight, we may postulate that the relatively high yield of XXVIIa observed in the case of perfluoro-2-pentene XXIIa is stipulated by the comparatively high solubility of XXIIa in HSO₃F. The concentration of XXIIa apparently reaches values exceeding the current concentration of I ($\sim 1.10^{-5}$ mole/liter.sec).‡ Thus, the conditions for competition between the dimerization of the fluorosulfatoperfluoropentyl radicals formed and the addition of I to XXIIa are created in a medium of HSO₃F.

In the case of perfluoro-2-octene XXIIc, the solubility of the olefin in HSO_3F should clearly be significantly lower, and it may be expected that its reaction with I will take place predominantly on the phase boundary. The fluorosulfatoperfluorooctyl radicals formed are concentrated in the organic phase owing to their high solubility in perfluorooctene, and this fact contributes to the relatively high yield of dimer XXVIIc.

If this conception is correct, the yield of the fluorosulfatodimerization products formed when fluoroalkenes react with electrochemically generated I can clearly be increased by concentrating the fluorosulfatoperfluoroalkyl radicals in one of the phases, for example, by creating conditions which promote separation of the organic phase.

 $[\]pm$ The electrolysis of HSO₃F in the presence of fluoroolefins was carried out at a volumetric current density equal to 10-15 mA/ml and a potential of the glassy carbon anode E > 2.1 V (Fig. 1).

In fact, it was found that an increase in the concentration of the supporting electrolyte (from 4 to 15%) in the case of the electrolysis of HSO_3F in the presence of XXIIa and XXIIb results in increases in the yields of dimers XXVIIa and XXVIIb by factors of 1.7 and 1.8, respectively. At the same time, by carrying out the reactions of XXIIa and XXIIb with an excess of I, for example, by gradually adding the olefins to the electrolyte over the course of the electrolysis process (1 mole of the olefin per quantity of electricity equal to 2.8-3.2 F), we can almost completely eliminate the formation of dimers. In this case, the yields of adducts XXIIa and XXIIb are equal to 80-95%, allowing us to propose this procedure as a preparative method for the synthesis of unbranched 2,3-bis(fluorosulfato)perfluoroalkanes.

EXPERIMENTAL

The ¹⁹F NMR spectra were recorded on a Perkin–Elmer R-32 spectrometer (84.6 MHz). The chemical shifts are given in parts per million relative to CF_3COOH (an external reference). The mass spectra were recorded on a VGMS 70-70e spectrometer. Compounds III, XXIIIa, XXIIIb [7], IV, V, XXIVa, XXIVb, XXVa, XXVb [8], XV [9], and XVI [10] were identified by ¹⁹F NMR and GLC by comparison with known samples. The polarization curves were recorded on a P-5848 potentiostat with a rate of application of the potential equal to 80 mV/sec in a Teflon cell according to a three-electrode scheme. The potentials were measured and are given relative to a Pd/H₂ reference electrode in fluorosulfonic acid. Working and auxiliary electrodes of appropriate materials were modeled in Teflon. Fluorosulfonic acid was distilled twice before the measurements and protected from moisture. Potassium fluorosulfate was obtained according to a standard method and dried at 80°C in a vacuum.

Electrolysis of HSO_3F in the Presence of Fluoroolefins (Variant A). Typical Experiment. A mixture of HSO_3F containing 4% $NaSO_3F$ and the entire portion of the fluoroolefin was placed in a glass electrolyzer without a diaphragm, which was cooled by running water (the anode was an SU-2000 glassy carbon electrode, and the cathode was Ti). the electrolysis was carried out with stirring of the reaction mixture at a temperature of 22-25°C to 95-98% conversion of the olefin (GLC). The mixture was poured onto ice, and the organic layer was washed with water, dried by $MgSO_4$, and distilled. The conditions of the experiments and the results are presented in Table 1. The boiling points and the results of the elemental analysis of the compounds obtained are presented in Table 2, and the ¹⁹F NMR spectra are presented in Table 3.

The electrolysis of an HSO_3F/H_2SO_4 mixture in the presence of II was carried out under the conditions of the typical experiment a current of 1.5 A over the course of 8 h: 80 ml of HSO_3F , 7.3 g (74.8 mmoles) of H_2SO_4 , and 60 g (200 mmoles) of II. Distillation gave 66.8 g of III and 4.8 g of a mixture containing (GLC) 70.8% IV and V and 29.2% VI.

The electrolysis of HSO_3F in the presence of II and an Ni cathode was carried out under the conditions of the typical experiment at a current of 0.5 A over the course of 21.5 h: 80 ml of HSO_3F in the presence of 50 g (160 mmoles) of II. Treatment of the reaction mass gave 52.5 g of a mixture, whose rectification resulted in the recovery of 39 g of III, 10 g of a mixture containing (GLC) 40.2% II, 44.4% IV and V, 15.4% of VI, and 2.7 g of a mixture with bp 107-110°C (3-3.5 mm Hg) containing (GLC) 11.8% X, 47.9% XI, and 40.3% XII.

The electrolysis of H_2SO_4 in the presence of II was carried out under the conditions of the typical experiment at a current of 1.5 A over the course of 13 h: 70 ml of H_2SO_4 in the presence of 50 g (160 mmoles) of II. Treatment of the reaction mass gave 25 g of a mixture, from which 9.6 g (14.5%) of VI were recovered by rectification. An attempt to rectify the residue at 90-100°C (1.5-2 mm Hg) resulted in the intense decomposition of the substance.

The electrolysis of an HSO_3F/SO_3 mixture in the presence of II was carried out under the conditions of the typical experiment at a current of 0.5 A over the course of 4 h: 30 ml of HSO_3F in the presence of 0.8 g (10 mmoles) of SO₃ and 7.0 g (25 mmoles) of II. Treatment of the reaction mass gave 6.4 g of a mixture containing (GLC) 19% III, 48.9% IV and V, and 32.1% VI.

Electrolysis of HSO_3F in the Presence of Fluoroolefins (Variant B). The electrolysis of 80 ml of HSO_3F was carried out under the conditions of variant A (2.5 A, 10 h) with the dropwise addition of 75 g (250 mmoles) of olefin XXIIb over the course of the electrolysis. Treatment of the reaction mass (variant A) gave 116.3 g of a mixture, whose rectification yielded 1.7 g of the original olefin and 113.3 g of XXIIIb (91%).

A similar procedure employing 30 ml of HSO_3F (0.5 A, 5 h) and 15.4 g (30 mmoles) of XXIIc gave 17.9 g of a mixture whose rectification resulted in the recovery of 0.5 g of a mixture containing (GLC) 75% XXIVc and XXVc and 25% XXVIc, 12.7 g (55.2%) XXIIIc, and 2.2 g XXVIIc.

Mass spectra of the compounds obtained (the masses for the principal isotopes of C and S are given) m/z (relative intensity, %).

Mixture of XXIVa and XXVa: 249 $[C_3F_7O_3S]^+$ (3.4), 199 $[C_2F_5O_3S]^+$ (28.4), 147 $[C_3F_5O]^+$ (31.7), 128 $[C_3F_4O]^+$ (4), 119 $[C_2F_5]^+$ (100), 109 $[C_3F_3O]^+$ (3.5), 100 $[C_2F_4]^+$ (8.5), 97 $[C_2F_3O]^+$ (57.7), 83 $[SO_2F]^+$ (92), 69 $[CF_3]^+$ (100).

Mixture of XXIVb and XXVb: 377 [M – F]⁺ (1.2), 299 [C₄F₉O₃S]⁺ (0.9), 247 [C₃F₇O₃]⁺ (1.3), 199 [C₂F₅O₃S]⁺ (20.6), 197 [C₄F₇O]⁺ (21), 169 [C₃F₇]⁺ (85.2), 147 [C₃F₅O]⁺ (1.8), 128 [C₃F₄O]⁺ (3.5), 119 [C₂F₅]⁺ (9.1), 109 [C₃F₃O]⁺ (4.3), 100 [C₂F₄]⁺ (9.9), 97 [C₂F₃O]⁺ (39.9), 83 [SO₂F]⁺ (63.6), 69 [CF₃]⁺ (100).

Mixture of IV and V: 377 $[M - F]^+$ (0.2), 299 $[C_4F_9O_3S]^+$ (6), 199 $[C_2F_5O_3S]^+$ (6.9), 197 $[C_4F_7O]^+$ (19.8), 181 $[C_4F_7]^+$ (1.2), 169 $[C_3F_7]^+$ (17.8), 159 $[C_4F_5O]^+$ (8.8), 131 $[C_3F_5]^+$ (4.5), 119 $[C_2F_5]^+$ (2.5), 109 $[C_3F_3O]^+$ (1.5), 100 $[C_2F_4]^+$ (2.8), 97 $[C_2F_3O]^+$ (23.8), 83 $[SO_2F]^+$ (48.4), 69 $[CF_3]^+$ (100).

XIX: 349 $[C_5F_{11}O_3S]^+$ (4.2), 281 $[C_6F_{11}]^+$ (2.5), 259 $[C_6F_9O]^+$ (1.8), 249 $[C_3F_7O_3S]^+$ (1.8), 247 $[C_5F_9O]^+$ (9.5), 181 $[C_4F_7]^+$ (12.2), 159 $[C_4F_5O]^+$ (9.3), 97 $[C_2F_3O]^+$ (15.1), 83 $[SO_2F]^+$ (28.4), 69 $[CF_3]^+$ (100).

XX: 247 $[C_5F_9O]^+$ (37.5), 199 $[C_2F_5O_3S]^+$ (40.5), 181 $[C_4F_7]^+$ (3.2), 159 $[C_4F_5O]^+$ (23.7), 128 $[C_3F_4O]^+$ (1), 119 $[C_2F_5]^+$ (12.1), 97 $[C_2F_3O]^+$ (26.9), 83 $[SO_2F]^+$ (46.2), 69 $[CF_3]^+$ (100).

XXIVc: 297 $[C_6F_{11}O]^+$ (2.7), 269 $[C_5F_{11}]^+$ (32.6), 199 $[C_2F_5O_3S]^+$ (25.6), 181 $[C_4F_7]^+$ (7.1), 131 $[C_3F_5]^+$ (8.4), 128 $[C_3F_4O]^+$ (3.2), 119 $[C_2F_5]^+$ (23.8), 109 $[C_3F_3O]^+$ (7.1), 100 $[C_2F_4]^+$ (6.8), 97 $[C_2F_3O]^+$ (33.1), 83 $[SO_2F]^+$ (39.2), 69 $[CF_3]^+$ (100).

XXVc: 399 $[C_6F_{13}O_3S]^+$ (9.1), 309 $[C_7F_{11}O]^+$ (8.3), 269 $[C_5F_{11}]^+$ (11.5), 181 $[C_4F_7]^+$ (4.6), 169 $[C_3F_7]^+$ (2.6), 131 $[C_3F_5]^+$ (4.8), 119 $[C_2F_5]^+$ (13.6), 109 $[C_3F_3O]^+$ (3.7), 100 $[C_2F_4]^+$ (2.5), 97 $[C_2F_3O]^+$ (23), 83 $[SO_2F]^+$ (43.8), 69 $[CF_3]^+$ (100).

XIV: 479 $[M - F]^+$ (0.2), 429 $[M - CF_3]^+$ (0.2, 399 $[M - FSO_3]^+$ (1.9), 379 $[M - C_2F_5]^+$ (6.2), 297 $[C_6F_{11}O]^+$ (1.5), 249 $[C_3F_7O_3S]^+$ (16.6), 247 $[C_5F_9O]^+$ (3.2), 231 $[C_5F_9]^+$ (1), 197 $[C_4F_7O]^+$ (5), 181 $[C_4F_7]^+$ (2.5), 169 $[C_3F_7]^+$ (18.8), 159 $[C_4F_5O]^+$ (2.1), 147 $[C_3F_5O]^+$ (29.8), 131 $[C_3F_5]^+$ (1.1), 119 $[C_2F_5]^+$ (50.6), 109 $[C_3F_3O]^+$ (1.2), 100 $[C_2F_4]^+$ (1.8), 97 $[C_2F_3O]^+$ (11.9), 83 $[SO_2F]^+$ (100), 69 $[CF_3]^+$ (65.4), 67 $[SOF]^+$ (12.6).

X: 661 $[M - C_3H_7]^+$ (1.5), 631 $[M - C_2F_5O_3]^+$ (30.2), 531 $[C_8F_{17}O_3S_2]^+$ (1), 399 $[C_6F_{13}O_3S]^+$ (6.31), 332 $[C_6F_{12}S]^+$ (1.2), 313 $[C_6F_{11}S]^+$ (4.6), 297 $[C_5F_{11}O]^+$ (19.7), 281 $[C_6F_{11}]^+$ (1.5), 269 $[C_6F_{10}]^+$ (2.1), 263 $[C_5F_9S]^+$ (1.8), 249 $[C_3F_7O_3S]^+$ (7.4), 232 $[C_4F_8S]^+$ (3), 231 $[C_5F_9]^+$ (10.6), 219 $[C_4F_9]^+$ (11), 213 $[C_4F_7S]^+$ (4.1), 199 $[C_2F_5O_3S]^+$ (7), 197 $[C_4F_7O]^+$ (7.9), 181 $[C_4F_7]^+$ (12.9), 169 $[C_3F_7]^+$ (2.4), 163 $[C_3F_5S]^+$ (3.8), 159 $[C_4F_5O]^+$ (2.4), 147 $[C_3F_5O]^+$ (16.6), 137 $[C_4F_3S]^+$ (1), 131 $[C_3F_5]^+$ (8.2), 125 $[C_3F_3S]^+$ (1.2), 119 $[C_2F_5]^+$ (17.1), 113 $[C_2F_3S]^+$ (5.3), 100 $[C_2F_4]^+$ (1.5), 97 $[C_2F_3O]^+$ (13), 83 $[SO_2F]^+$ (100), 69 $[CF_3]^+$ (100), 63 $[CFS]^+$ (25.2).

XI: 463 $[C_6F_{13}O_3S_3]^+$ (8.4), 431 $[C_6F_{13}O_3S_2]^+$ (0.6), 399 $[C_6F_{13}O_3S]^+$ (0.5), 300 $[C_6F_{12}]^+$ (0.5), 281 $[C_6F_{11}]^+$ (1), 264 $[C_4F_8S_2]^+$ (9.6), 231 $[C_5F_9]^+$ (1.1), 213 $[C_4F_7S]^+$ (1.5), 199 $[C_2F_5O_3S]^+$ (0.5), 181 $[C_4F_7]^+$ (2.6), 163 $[C_3F_5S]^+$ (25.6), 131 $[C_3F_5]^+$ (2.7), 119 $[C_2F_5]^+$ (1.2), 113 $[C_2F_3S]^+$ (1.2), 97 $[C_2F_3O]^+$ (2.2), 83 $[SO_2F]^+$ (9.9), 69 $[CF_3]^+$ (22.5), 64 $[S_2]^+$ (100), 63 $[CFS]^+$ (8.9).

XII: 663 $[C_{10}F_{21}O_3S_3]^+$ (1.3), 463 $[C_6F_{13}O_3S_3]^+$ (5.7), 444 $[C_6F_{12}O_3S_3]^+$ (2.7), 431 $[C_6F_{13}O_3S_2]^+$ (1.5), 300 $[C_6F_{12}]^+$ (0.6), 281 $[C_6F_{11}]^+$ (1.3), 264 $[C_4F_8S_2]^+$ (5.7), 263 $[C_5F_9S]^+$ (0.6), 234 $[C_4F_8S]^+$ (10.8), 231 $[C_5F_9]^+$ (1.7), 213 $[C_4F_7S]^+$ (1.1), 199 $[C_2F_5O_3S]^+$ (0.9), 197 $[C_4F_7O]^+$ (3.7), 195 $[C_3F_5S_2]^+$ (0.8), 181 $[C_4F_7]^+$ (3), 169 $[C_3F_7]^+$ (2), 164 $[C_2F_4S_2]^+$ (8), 163 $[C_4FS_3 + C_3F_5S]^+$ (55.7), 131 $[C_3F_5]^+$ (3.4), 119 $[C_2F_5]^+$ (1.8), 113 $[C_2F_3S]^+$ (2.7), 97 $[C_2F_3O]^+$ (1.8), 96 $[S_3]^+$ (3.5), 83 $[SO_2F]^+$ (14.4), 69 $[CF_3]^+$ (32.6), 64 $[S_2]^+$ (100), 63 $[CFS]^+$ (8.8).

The mass spectra of compounds III, XVIII, and XXIIIa-c are presented in Table 4; the mass spectra of compounds VI, XXI, and XXVIa-c are presented in Table 5.

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FLUOROALIPHATIC ESTERS OF FLUOROSULFONIC ACID.

2. REACTION OF BIS(FLUOROSULFATO)PERFLUOROALKANES WITH

CESIUM FLUORIDE

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2,3-Bis(fluorosulfato)perfluoroalkanes split under the action of CsF in the absence of solvents, giving a mixture of α -fluorosulfatoperfluoro ketones, perfluoroalkene sulfates, and perfluoro α -diketones. The occurrence of these reactions in solutions results mainly in the formation of oxides of the corresponding fluoroolefins or products of their conversions. The reactions carried out are the first examples of nucleophilic substitution at a secondary carbon atom in a perfluorinated saturated chain.

Perfluorinated ketones and alkanoyl fluorides are known to add alkali metal fluorides with the formation of the alkoxides of perfluoro alcohols, which have found extensive application in syntheses [1]. We found that fluoroaliphatic esters of fluorosulfonic acid in the presence of stoichiometric quantities of KF or CsF are convenient sources of perfluoroalkoxides of these metals. For example, the reaction of α,ω -bis(fluorosulfato)perfluoroalkanes Ia-c with Me₂SO₄ in DMF in the presence of 2 moles of CsF gives dimethoxyperfluoroalkanes IVa-c. Diether IVa can be synthesized with practically the same yield on the basis of fluorosulfatodifluoroacetyl fluoride II, and diether IVc can be obtained from perfluoroadipyl difluoride acid III.



It might be expected that the analogous reaction of 2,3-bis(fluorosulfato)-4-trifluoromethylperfluoropentane V will give dimethyl ether VII, which is a derivative of α -diketone VI; the decomposition of V under the action of CsF with the formation of VI was previously demonstrated in [2]. However, it turned out that the only product of the reaction of V with Me₂SO₄/CsF is monomethyl ether VIII, which is a derivative of perfluoroethyl isopropyl ketone, whose formation from bis(fluorosulfate) V is possible only when an FSO₃ group is replaced by a fluorine atom.



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