1942 Russian Chemical Bulletin, International Edition, Vol. 54, No. 8, pp. 1942—1947, August, 2005

Electrochemical fluorosulfation of perfluoroalkyl vinyl ethers

V. A. Grinberg[a] *and S. R. Sterlin*[b]★

[a]*A. N. Frumkin Institute of Electrochemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 952 0846. E-mail: grinberg@phyche.ac.ru
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 6549. E-mail: lsg@ineos.ac.ru

The reaction of perfluoroalkyl vinyl ethers with electrochemically generated peroxydisulfuryl difluoride produces a mixture of α,ω-bis-fluorosulfonyloxy(perfluoroalkoxyalkanes). The fluorosulfate dimers of the starting vinyl ethers prevailing in the reaction mixture were transformed into perfluoro-2,3-dialkoxysuccinyl difluorides. High stability of intermediate radicals, in which the radical center is adjacent to the oxygen atom, is one of the factors determining the compositions of the reaction products.

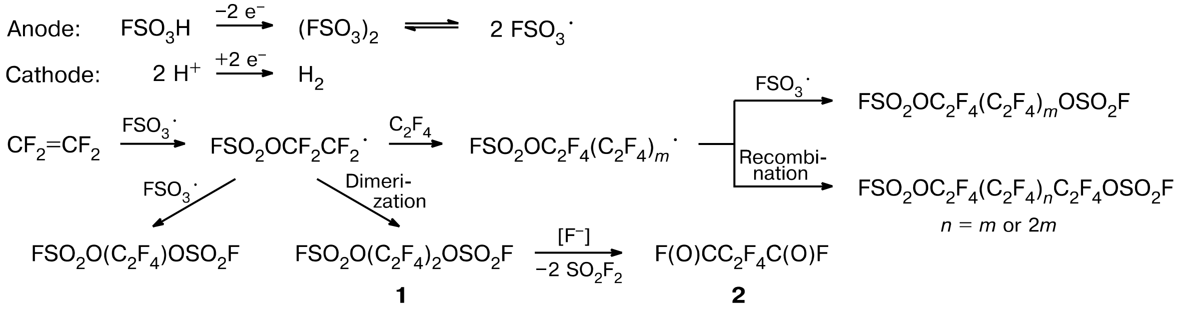
Key words: perfluoroalkyl vinyl ethers, fluorosulfonic acid, electrolysis, peroxydisulfuryl difluoride, perfluoro-α-alkoxyalkyl radicals, perfluoroalkyl fluorosulfates, perfluoro-2,3-dialkoxysuccinyl difluorides.

Fluoroaliphatic esters of fluorosulfonic acid can serve as precursors of the corresponding carboxylic acid fluorides due to which the synthesis of this class of compounds has attracted keen interest. Galvanostatic electrolysis of fluorosulfonic acid in the presence of fluoroolefins is one of the most convenient preparative methods for the synthesis of these compounds. The anodic generation of peroxydisulfuryl difluoride (PDF) is the major electrochemical pathway of this reaction. This peroxide is rather stable and, at the same time, readily dissociates into radicals (the energy of O—O bond homolysis is ~37 kcal mol^{-1}). The reaction products are formed mostly due to addition of the $FSO_3^{\bullet}$ radical to fluoroolefin. This can be illustrated by electrochemical fluorosulfation of tetrafluoroethylene[1] (Scheme 1).

This reaction affords the fluorosulfate dimer of tetrafluoroethylene (**1**) as the major product, which can easily be transformed into perfluorosuccinyl difluoride (**2**) by the reaction with alkali metal fluorides. It should be noted that tetrafluoroethylene, like other fluoroolefins, can undergo anodic oxidation[2] to give, under these conditions, virtually the same set of reaction products but in a principally different ratio. In the case of galvanostatic electrolysis, this reaction pathway is not the major one, and it is not considered in the present study.

The composition of the products prepared by galvanostatic electrolysis with the use of monosubstituted fluoroolefin, *viz.*, hexafluoropropylene (HFP), is substantially more complicated compared to that synthesized in the presence of tetrafluoroethylene (Scheme 2). This process

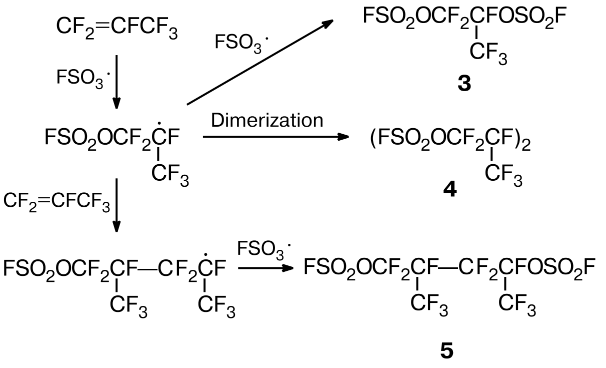
Scheme 1



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1884—1889, August, 2005.

afforded a considerable amount of head-to-tail dimer **5** along with vicinal bis-fluorosulfate **3** and head-to-head fluorosulfate dimer **4** in the **4** : **5** molar ratio of *ca.* 2 : 1, whereas higher oligomeric bis-fluorosulfates were not formed at all.[1,3]

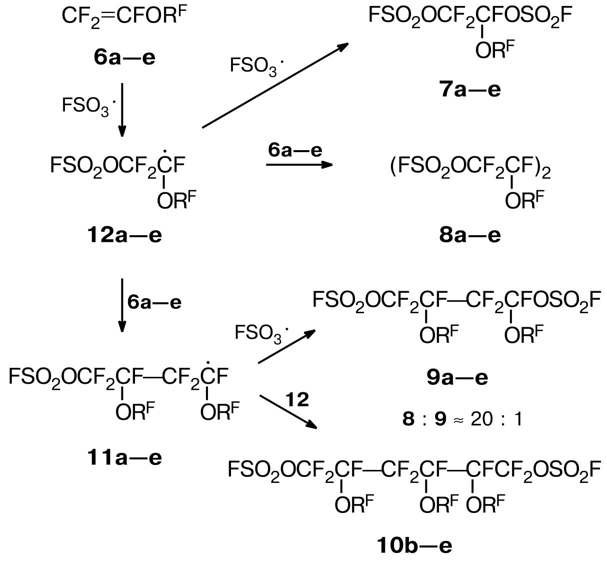
Scheme 2



The addition of peroxydisulfuryl difluoride to perfluoroalkyl vinyl ethers (PVE) has not been investigated earlier. When we initiated studies of electrochemical fluorosulfation of ethers **6a—e** under the conditions of anodic generation of PDF, we expected that, since PVE (like HFP) are monosubstituted fluoroolefins, the composition of the reaction products would be similar to that prepared by galvanostatic fluorosulfation of HFP. From the practical standpoint, fluorosulfatodimerization products of PVE are of particular interest, because they can serve as precursors of perfluoro-2,3-dialkoxysuccinyl difluorides.

However, it appeared that fluorosulfation of PVE afforded a mixture of products, whose composition differs from that prepared from HFP and is typical of this class of compounds (Scheme 3, Table 1). In addition to vicinal bis-fluorosulfates **7a—e**, a mixture of head-to-head fluorosulfate dimers **8a—e** and head-to-tail dimers **9a—e** was obtained. In this mixture, the percentage of dimers **8a—e** was an order of magnitude higher than that present in a mixture of the related compounds synthesized from HFP. In addition, fluorosulfate trimers **10** were isolated in most cases. The latter, like head-to-tail dimers, are recombination products of radicals **11**. The difference is that this recombination involves the initially formed radicals **12** rather than the fluorosulfonyloxy radical.

Scheme 3



$R^F = CF_3$ (**a**), $CF_3O(CF_2)_3$ (**b**), $FSO_2(CF_2)_2OCF(CF_3)CF_2$ (**c**), n-C_3F_7 (**d**), $FSO_2(CF_2)_2$ (**e**)

It should be noted that in both cases (both with HFP and PVE), head-to-tail fluorosulfate dimers **5** and **9** are generated as a result of the attack of secondary radicals **12** on the C_α atom of the double bond of the starting fluoroolefin followed by the reaction with the fluorosulfonyloxy radical. An alternative pathway of the forma-

Table 1. Results of electrochemical fluorosulfation of fluoroolefins $R^FCF=CF_2$

Compound	R^F	Composition of the reaction mixture (mol.%)		
		Vicinal bis-fluorosulfates	Fluorosulfate dimers	Fluorosulfate trimers
6a	CF_3O	29	71 [a]	0
6b	$CF_3O(CF_2)_3O$	31	64 [b]	5
6c	$FSO_2(CF_2)_2OCF(CF_3)CF_2O$	29	62 [b]	10
6d	$CF_3(CF_2)_2O$	19	70 [b]	11
6e	$FSO_2(CF_2)_2O$	23	64 [b]	13
HFP	CF_3	30	70 [c]	—

[a] The head-to-head dimer : head-to-tail dimer ratio is 98 : 2.
[b] The head-to-head dimer : head-to-tail dimer ratio is 93—95 : 7—5.
[c] The head-to-head dimer : head-to-tail dimer ratio is 67 : 33.

tion of these compounds by recombination of the primary radicals $FSO_2OC(R)FCF_2^{\bullet}$ (R = CF_3 or OR^F), which are generated through the addition of the $FSO_3^{\bullet}$ radical at the C_β atom of the double bond, with the corresponding secondary radicals **12** should be rejected because tail-to-tail fluorosulfate dimers were never detected in any of these two processes.

Evidently, regiospecificity of the radical addition of monosubstituted fluoroolefins at the α-carbon atom is determined by the steric factor, *i.e.*, the large size of the $FSO_3^{\bullet}$ radical or carbon-centered radicals **12**. If the size of the attacking radical is small, the radical attack follows both pathways. For example, fluorination of perfluoroallyl fluorosulfate affords all three possible fluorodimerization products.[4]

It can be seen from Table 1 that, in spite of the identical reaction conditions (the addition of PVE or HFP to the electrolyte in a ~2 : 1 molar ratio with respect to the current concentration of PDF), the reactions afford different mixtures of products. As mentioned above, galvanostatic electrolysis of fluoroolefins in fluorosulfonic acid occurs predominantly as a radical process, and the contribution of direct anodic oxidation of the double bond is relatively small. Presumably, the causes of the difference in the composition of fluorosulfation products of HFP and vinyl ethers should be searched for primarily in the difference in the reactivity of the secondary radicals derived from propylene and vinyl ethers. In our opinion, both the relatively low percentage of the head-to-tail fluorosulfate dimer and the formation of fluorosulfate trimers are associated with an increase in stability and, correspondingly, with a decrease in the reactivity of the α-fluoroalkoxy radicals $R^F{-}O{-}C^{\bullet}(R^F)_2$. The stabilizing effect of the oxygen atoms in the α position with respect to the paramagnetic center of radicals of a hydrocarbon series has been noted earlier.[5] By analogy with the scheme reported in the study,[5] high stability of radicals **11** and **12** is also accounted for by the possibility of the formation of the mesomeric form $R^FO^{\bullet+}{-}C^{-}(R^F)_2$.

The low reactivity of α-fluoroalkoxy radicals has a larger effect on the rate of their addition at the double bond of vinyl ethers than on the rate of their recombination, resulting in an increase in the percentage of head-to-head dimers.

Besides, it has been demonstrated[6] that the composition of a mixture of products prepared by electrochemical fluorosulfation is determined also by the distribution of the starting olefins and intermediate radicals between the inorganic and organic phases of the reaction mixture. For example, an increase in the concentration of the supporting electrolyte facilitating phase separation leads to a sharp increase in the percentage of fluorosulfate dimers due to an increase in the concentration of the fluorosulfonyloxyalkyl radicals in the organic phase.

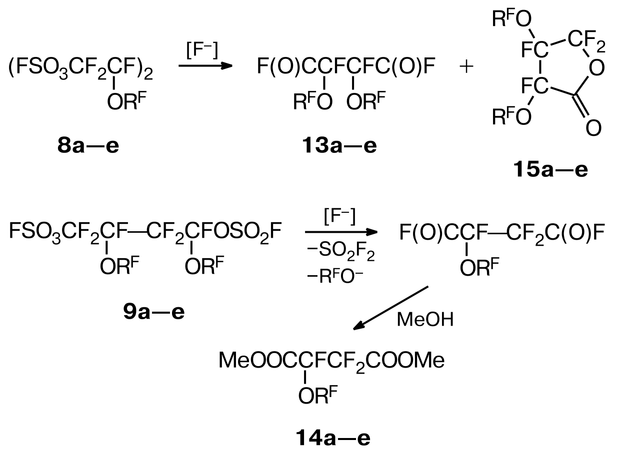
Evidently, the solubilities of both PVE and organofluorine intermediates in the electrolyte is inversely proportional to the molecular weight. At the same time, an increase in the molecular weight leads to an increase in oleophilicity, resulting in an increase in the concentration of these compounds in the organic phase. In addition, the bulky fluoroalkoxy groups in the radicals derived from higher vinyl ethers shield the paramagnetic center to a higher degree. This results in an increase in stability of these radicals, thus facilitating an increase in their current concentration in the organic phase.

Therefore, the above-mentioned three factors, *i.e.*, high stability of perfluorinated alkoxy radicals due to the stabilizing effect of the oxygen atom in the α position with respect to the paramagnetic center, the difference in solubility of perfluoroalkyl vinyl ethers and the related radicals in inorganic and organic phases of the reaction mixture, and steric shielding of the radical center by the fluoroalkoxy groups, primarily determine the composition of a mixture of products prepared by electrochemical fluorosulfation of PVE. In particular, the transformation into fluorosulfate trimers **10b—e**, whose formation is observed in all cases except for perfluoromethyl vinyl ether, most likely occurs in the organic phase. High oleophilicity of higher PVE and stable radicals **11b—e** and **12b—e** derived from these PVE provides accumulation of PVE and intermediate radicals in the organic phase at concentrations sufficiently high for the formation of trimers **10b—e** (see Scheme 3).

At the same time, the absence of fluorosulfate trimer **10a** in the case of perfluoromethyl vinyl ether (**6a**), which has the smallest molecular weight of all the compounds under study, can be attributed to both the relatively high solubility of the olefin and radicals derived from the olefin in the electrolyte and the lowest steric shielding of the radical center (and, consequently, the lowest stability of the intermediate radicals). As a result, all transformations of both vinyl ether **6a** and radicals **11a** and **12a** occur predominantly in the inorganic phase due to which the olefin and radicals are not accumulated in the organic phase in concentrations providing the formation of fluorosulfate trimers.

Despite the complex composition of the products prepared by electrochemical fluorosulfation of perfluoroalkyl vinyl ethers, isolation and purification of the target perfluoro-2,3-dialkoxysuccinyl difluorides **13** (as mentioned above, the development of procedures for the synthesis of these compounds was the practical aim of the present study) present no serious difficulties (Scheme 4). Upon treatment of a mixture of isomeric fluorosulfate dimers **8** and **9** with cesium fluoride, head-to-tail dimers **9** undergo not only desulfodefluorination but also dealkoxylation to give low-boiling products **14** (see Scheme 4). The latter can easily be separated from decomposition products of fluorosulfate dimers **8**, which are a mixture of dialkoxysuccinyl difluorides **13** and dialkoxy-γ-lactones **15**, by distillation. It should be noted that the percentage of γ-lactones increases with increasing volume of the fluoroalkoxy substituents.

Scheme 4



$R^F = CF_3$ (**a**), $CF_3O(CF_2)_3$ (**b**), $FSO_2(CF_2)_2OCF(CF_3)CF_2$ (**c**), n-C_3F_7 (**d**), $FSO_2(CF_2)_2$ (**e**)

To summarize, we developed a convenient procedure for the synthesis of perfluorinated 2,3-dialkoxy-1,4-bis(fluorosulfonyloxy)butanes, which can easily be transformed into the corresponding dialkoxysuccinyl difluorides.

Experimental

Electrolysis was carried out in an undivided electrochemical cell equipped with a water-cooled jacket using a GC-2000 glassy carbon anode (10 cm^2) and a stainless-steel cathode; the ratio of the anode to cathode surface areas was 10 : 1, the anode current density was 75—150 mA cm^{-2}; a 3% KSO_3F solution in HSO_3F was used as the electrolyte; the electrolysis temperature was 28±2 °C. Electrolysis was carried out at a $(FSO_3)_2$ current yield of 65—68%. Vinyl ethers **6a—e** were added to the electrolyte at a rate of 2.1—2.2 mol per mole of $(FSO_3)_2$ (with respect to the current concentration of PDF). After completion of electrolysis, the electrolyte was poured onto ice. The organic products were separated, washed with cold water and a 5% aqueous $KHCO_3$ solution, dried over $MgSO_4$, and distilled.

The mass spectra were recorded on a VGMS 70-70c spectrometer (70 eV). The ^{19}F NMR spectra were measured on a Bruker WP-200 SY instrument (188 MHz); the chemical shifts are given on the δ scale relative to CF_3COOH as the internal standard.

Electrolysis of vinyl ether 6a. Ether **6a** was bubbled through an electrolyte at a rate given above (21 g of compound **6a** was absorbed). After treatment of the reaction mixture, a mixture of compounds **7a—9a** was isolated in a yield of 32.0 g. Pure samples of the products were isolated by rectification.

1,2-Bis(fluorosulfonyloxy)-1-trifluoromethoxy-1,2,2-trifluoroethane (**7a**). B.p. 76—78 °C. Found (%): C, 9.87; F, 41.81; S, 17.40. $C_3F_8O_7S_2$. Calculated (%): C, 9.89; F, 41.76; S, 17.58. ^{19}F NMR, δ: −126.6 (m, 1 F, $CFOSO_2\underline{F}$); −126.6 (t, 1 F, $CF_2OSO_2\underline{F}$, J = 8.0 Hz); −21.5 (d, 3 F, CF_3O, J = 10.0 Hz, J = 3.5 Hz); 11.0 (m, 2 F, CF_2); 21.0 (q, 1 F, CF, J = 8.0 Hz).

1,4-Bis(fluorosulfonyloxy)-2,3-di(trifluoromethoxy)-1,1,2,3,4,4-hexafluorobutane (**8a**),* a mixture of diastereomers. B.p. 101—105 °C (95 Torr). Found (%): C, 13.39; F, 50.00; S, 12.20. $C_6F_{14}O_8S_2$. Calculated (%): C, 13.58; F, 50.19; S, 12.07. ^{19}F NMR, δ: −127.0 (m, 2 F, 2 $CF_2OSO_2\underline{F}$); −23.5 and −23.0 (both m, 3 F each, 2 CF_3O); 3.2 (AB system, 2 F, $CFC\underline{F}_2$, $J_{A,B}$ = 134.0 Hz); 4.5 (br.s, 2 F, $CFC\underline{F}_2$); 61.0 and 63.1 (both m, 1 F each, 2 CF).

Electrolysis of vinyl ether 6b. Ether **6b** (20 g) was added to an electrolyte at a rate given above. After treatment of the reaction mixture, a mixture of compounds **7b—10b** was obtained in a yield of 17.3 g. Pure samples of the products were isolated by rectification.

1,2-Bis(fluorosulfonyloxy)perfluoro[1-(3-methoxypropoxy)ethane] (**7b**). B.p. 58—59 °C (12 Torr). Found (%): C, 13.57; F, 50.33; S, 11.77. $C_6F_{14}O_8S_2$. Calculated (%): C, 13.58; F, 50.19; S, 12.07. ^{19}F NMR, δ: −126.6 (m, 1 F, $CFOSO_2\underline{F}$); −126.4 (m, 1 F, $CF_2OSO_2\underline{F}$); −20.5 (br.t, 3 F, CF_3O, J = 10.0 Hz); 5.5 (AB system, 2 F, $CF_3O(CF_2)_2C\underline{F}_2$, $J_{A,B}$ = 145.0 Hz); 9.2 (d, 2 F, $CF_3OC\underline{F}_2$, J = 19.0 Hz); 10.7 (br.t, 2 F, $CFC\underline{F}_2O$, J = 8.5 Hz); 19.8 (td, 1 F, CF, J = 8.5 Hz, J = 18.0 Hz); 52.5 (br.s, 2 F, $CF_3OCF_2C\underline{F}_2$).

1,4-Bis(fluorosulfonyloxy)perfluoro[2,3-di(3-methoxypropoxy)butane] (**8b**), a mixture of diastereomers. B.p. 78—80 °C (0.5—1 Torr). Found (%): C, 16.63; F, 57.41; S, 7.25. $C_{12}F_{26}O_{10}S_2$. Calculated (%): C, 16.70; F, 57.31; S, 7.42. ^{19}F NMR, δ: −127.0 (m, 2 F, $CF_2OSO_2\underline{F}$); −20.0 (m, 6 F, 2 CF_3O); 3.2—5.5 (group of signals, 8 F, 2 $CF_3OC\underline{F}_2CF_2C\underline{F}_2$); 10.0 (m, 4 F, 2 $CFC\underline{F}_2$); 52.6 and 52.7 (both m, 2 F each, 2 $CF_3OCF_2C\underline{F}_2CF_2$); 61.5 and 63.0 (both m, 1 F each, 2 CF).

1,6-Bis(fluorosulfonyloxy)perfluoro[2,4,5-tri(3-methoxypropoxy)hexane] (**10b**), a mixture of diastereomers. B.p. 107—115 °C (0.5—1 Torr). Found (%): C, 18.05; F, 61.09; S, 5.13. $C_{18}F_{38}O_{12}S_2$. Calculated (%): C, 18.09; F, 60.47; S, 5.36. ^{19}F NMR, δ: −127.0 (br.s, 2 F, $CF_2OSO_2\underline{F}$); −20.5 (m, 9 F, 3 CF_3O); 1.5—7.0 (group of signals, 16 F, 3 $CF_3OC\underline{F}_2CF_2C\underline{F}_2$ + 2 $CFC\underline{F}_2OSO_2F$); 36.0—40.0 (group of signals, 2 F, $CFC\underline{F}_2CF$); 52.5 (m, 6 F, 2 $CF_3OCF_2C\underline{F}_2CF_2$); 56.0—63.0 (group of signals, 3 F, 3 CF).

Electrolysis of vinyl ether 6c. Ether **6c** (137 g) was added to an electrolyte at a rate given above. After treatment of the reaction mixture, a mixture of compounds **7c—10c** was obtained in a yield of 121 g. Pure samples of the products were isolated by rectification.

1,2-Bis(fluorosulfonyloxy)-8-fluorosulfonylperfluoro(5-methyl-3,6-dioxaoctane) (**7c**). B.p. 58—60 °C (1 Torr). Found (%): C, 13.26; F, 47.18; S, 14.53. $C_7F_{16}O_{10}S_3$. Calculated (%):

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* Hereinafter, isomeric fluorosulfate dimers **8** and **9** cannot be separated by rectification. The structures of fluorosulfate dimers **9**, whose percentage in a mixture of **8** and **9** was 2—7%, were confirmed by isolation of perfluoro-2-alkoxysuccinyl difluorides, which were characterized as dimethyl esters of the corresponding perfluoro-2-alkoxysuccinic acids **14** (see Scheme 4).

C, 13.04; F, 47.20; S, 14.91. ^{19}F NMR, δ: −127.0 (br.s, 2 F, $CFOSO_2\underline{F}$ + $CF_2OSO_2\underline{F}$); −121.7 (br.s, 1 F, $CF_2SO_2\underline{F}$); 0.5—7.5 (group of signals, 7 F, $C\underline{F}_2OCF(C\underline{F}_3)C\underline{F}_2$); 11.0 (br.s, 2 F, $C\underline{F}_2OSO_2F$); 20.0 (br.s, 1 F, $C\underline{F}CF_2OSO_2F$); 36.2 (br.s, 2 F, $C\underline{F}_2SO_2F$); 67.5 (br.s, 1 F, $C\underline{F}CF_3$).

1,14-Bis(fluorosulfonyl)-7,8-bis[(fluorosulfonyloxy)difluoromethyl]perfluoro(4,11-dimethyl-3,6,9,12-tetraoxatetradecane) (**8c**), a mixture of diastereomers. B.p. 125—130 °C (1 Torr). Found (%): C, 15.32; F, 52.31; S, 11.43. $C_{14}F_{30}O_{14}S_4$. Calculated (%): C, 15.41; F, 52.29; S, 11.74. ^{19}F NMR, δ: −127.0 (br.s, 2 F, 2 $CF_2OSO_2\underline{F}$); −122.0 (br.s, 2 F, 2 $CF_2SO_2\underline{F}$); 1.0—5.0 (group of signals, 18 F, 2 $C\underline{F}_2OCF(C\underline{F}_3)C\underline{F}_2$ + 2 $CFC\underline{F}_2OSO_2F$); 35.8 (br.s, 4 F, 2 $C\underline{F}_2SO_2F$); 62.0 (br.s, 2 F, 2 OCF); 67.2 (br.s, 2 F, 2 $C\underline{F}CF_3$).

1,16-Bis(fluorosulfonyl)-7,10-bis[(fluorosulfonyloxy)difluoromethyl]-4,13-bis(trifluoromethyl)-8-perfluoro[2-(2-fluorosulfonylethoxy)propoxy]-3,6,11,14-tetraoxaperfluorohexadecane (**10c**). B.p. 195—203 °C (0.5—1 Torr). Found (%): C, 16.33; F, 53.63; S, 10.47. $C_{21}F_{44}O_{18}S_5$. Calculated (%): C, 16.41; F, 54.43; S, 10.42. ^{19}F NMR, δ: −129.0—−127.5 (group of signals, 2 F, 2 $CF_2OSO_2\underline{F}$); −122.0 (br.s, 3 F, 3 $CF_2SO_2\underline{F}$); −0.5—5.2 (group of signals, 25 F, 3 $C\underline{F}_2OCF(C\underline{F}_3)C\underline{F}_2$ + 2 $CFC\underline{F}_2OSO_2F$); 34.5—39.0 (group of signals, 8 F, 3 $C\underline{F}_2SO_2F$ + $CFC\underline{F}_2CF$); 55.0—67.0 (group of signals, 6 F, 6 OCF).

Electrolysis of vinyl ether 6d. Ether **6d** (166 g) was added to an electrolyte at a rate given above. After treatment of the reaction mixture, a mixture of compounds **7d**—**10d** was obtained in a yield of 190 g. Pure samples of the products were isolated by rectification.

1,2-Bis(fluorosulfonyloxy)-1-perfluoropropoxy-1,2,2-trifluoroethane (**7d**). B.p. 38—40 °C (15 Torr). Found (%): C, 12.81; F, 49.23; S, 13.40. $C_5F_{12}O_7S_2$. Calculated (%): C, 12.93; F, 49.14; S, 13.79. ^{19}F NMR, δ: −126.7 (m, 1 F, $CFOSO_2\underline{F}$); −126.5 (t, 1 F, $CF_2OSO_2\underline{F}$, J = 8.0 Hz); 4.8 (br.t, 3 F, CF_3, J = 10.0 Hz); 5.65 (AB system, 2 F, $CF_3CF_2C\underline{F}_2$, $J_{A,B}$ = 153.0 Hz); 11.0 (m, 2 F, $C\underline{F}_2OSO_2F$); 19.9 (td, 1 F, CF, J = 18.0 Hz, J = 8.0 Hz); 48.2 (br.s, 2 F, $CF_3C\underline{F}_2$).

1,4-Bis(fluorosulfonyloxy)-2,3-di(perfluoropropoxy)perfluorobutane (**8d**), a mixture of diastereomers. B.p. 87—89 °C (8 Torr). Found (%): C, 16.41; F, 57.22; S, 8.69. $C_{10}F_{22}O_8S_2$. Calculated (%): C, 16.44; F, 57.26; S, 8.76. ^{19}F NMR, δ: −127.0 (m, 2 F, 2 $CF_2OSO_2\underline{F}$); 4.4 (center of a group of signals, 8 F, 2 $C\underline{F}_2OCFC\underline{F}_2$); 5.63 and 5.66 (both m, 3 F each, 2 CF_3); 52.5 (m, 4 F, 2 $CF_3C\underline{F}_2$); 61.2 and 62.6 (both m, 1 F each, 2 CF).

1,6-Bis(fluorosulfonyloxy)-2,3,5-tri(perfluoropropoxy)perfluorohexane (**10d**), a mixture of diastereomers. B.p. 122—127 °C (8 Torr). Found (%): C, 18.17; F, 60.48; S, 6.17. $C_{15}F_{32}O_9S_2$. Calculated (%): C, 18.07; F, 61.04; S, 6.43. ^{19}F NMR, δ: −126.7 (m, 2 F, $CF_2OSO_2\underline{F}$); 1.5—7.0, 14.0—15.0 (group of signals, 10 F, 3 $CF_3CF_2C\underline{F}_2$ + 2 $C\underline{F}_2OSO_2F$); 5.7 (m, 9 F, 3 CF_3); 34.5—42.5 (group of signals, 2 F, $CFC\underline{F}_2CF$); 44.0—46.0, 56.0—63.0 (group of signals, 3 F, 3 CF); 53.0 (m, 6 F, 3 $CF_3C\underline{F}_2$).

Electrolysis of vinyl ether 6e. Ether **6e** (144 g) was added to an electrolyte at a rate given above. After treatment of the reaction mixture, a mixture of compounds **7e**—**10e** was obtained in a yield of 107 g. Pure samples of the products were isolated by rectification.

1-(2-Fluorosulfonylperfluoroethoxy)-1,2-bis(fluorosulfonyloxy)-1,2,2-trifluoroethane (**7e**). B.p. 76—78 °C (98 Torr). Found (%): C, 10.12; F, 39.92; S, 19.65. $C_4F_{10}O_9S_2$. Calculated (%): C, 10.04; F, 39.75; S, 20.08. ^{19}F NMR, δ: −128.0 (br.d, 1 F, $CFOSO_2\underline{F}$); −127.5 (br.s, 1 F, $CF_2OSO_2\underline{F}$); −122.6 (br.s, 1 F, $CF_2SO_2\underline{F}$); 4.0 (AB system, 2 F, $OC\underline{F}_2CF_2SO_2F$, $J_{A,B}$ = 142.0 Hz); 10.3 (d, 2 F, $C\underline{F}_2OSO_2F$, J = 8.5 Hz); 19.0 (dd, 1 F, CF, J = 18.0 Hz, J = 8.5 Hz); 35.4 (br.s, 2 F, $C\underline{F}_2SO_2F$).

2,3-Bis(2-fluorosulfonylperfluoroethoxy)-1,4-bis(fluorosulfonyloxy)perfluorobutane (**8e**), a mixture of diastereomers. B.p. 93—94 °C (0.5—1 Torr). Found (%): C, 12.73; F, 45.49; S, 17.05. $C_8F_{18}O_{12}S_4$. Calculated (%): C, 12.66; F, 45.12; S, 16.89. ^{19}F NMR, δ: −128.0 (br.s, 2 F, 2 $CF_2OSO_2\underline{F}$); −121.7 and −121.6 (both br.s, 1 F each, 2 $CF_2SO_2\underline{F}$); 1.6 and 2.0 (both br.s, 2 F each, 2 $C\underline{F}_2CF_2SO_2F$); 3.6 and 4.4 (both br.s, 2 F each, 2 $CFC\underline{F}_2OSO_2F$); 35.6 (AB system, 4 F, 2 $C\underline{F}_2SO_2F$, $J_{A,B}$ = 252 Hz); 62.0 and 62.8 (both br.s, 1 F each, 2 CF).

1,6-Bis(fluorosulfonyloxy)-2,3,5-tris(2-fluorosulfonylperfluoroethoxy)perfluorohexane (**10e**). B.p. 130—134 °C (0.5—1 Torr). Found (%): C, 13.85; F, 47.63; S, 15.23. $C_{12}F_{26}O_{15}S_5$. Found (%): C, 13.87; F, 47.59; S, 15.41. ^{19}F NMR, δ: −128.0—−127.6 (m, 2 F, 2 $CF_2OSO_2\underline{F}$); −122.0 (br.s, 3 F, 3 $CF_2SO_2\underline{F}$); −1.0—4.5 (group of signals, 10 F, 3 $C\underline{F}_2CF_2SO_2F$ + 2 $CFC\underline{F}_2OSO_2F$); 32.5—36.5 (group of signals, 6 F, 3 $C\underline{F}_2SO_2F$); 37.5 (br.s, 2 F, $CFC\underline{F}_2CF$); 55.5—63.0 (group of signals, 3 F, 3 CF).

2,3-Bis(trifluoromethoxy)-2,3-difluorosuccinyl difluoride (13a). A mixture of bis-fluorosulfates **8a** and **9a** (20 g, 37.7 mmol) was gradually added at 0 °C to a mixture of CsF (0.3 g) and dry diglyme (1 mL). The reaction mixture was stirred until gas evolution ceased. Then the temperature was raised to ~20 °C, the liquid portion of the reaction mixture was decanted from the precipitate, and a mixture of compounds **13a** and **15a** (93 : 7) was isolated by distillation in a yield of 9.6 g (78%), b.p. 67.5—71 °C. Found (%): C, 22.15; F, 57.82. $C_6F_{10}O_4$. Calculated (%): C, 22.08; F, 58.28. ^{19}F NMR of compound **13a** (δ): −104.2 (m, 2 F, 2 COF); −22.2—−22.0 (m, 6 F, 2 CF_3); 49.2 and 51.5 (both br.s, 1 F each, 2 CF). The groups of unresolved multiplets at δ −2.5—7.8 and the signals at δ 58.6 and 60.7 were assigned to the CF_2O and CF groups of lactone **15a**.

2,3-Bis[perfluoro(3-methoxypropoxy)]-2,3-difluorosuccinyl difluoride (13b). A mixture of bis-fluorosulfates **8b** and **9b** (93 : 7, 25 g, 29 mmol) was gradually added to a mixture of CsF (0.5 g) and sulfolane (1 mL). The reaction mixture was stirred at ~25 °C for 6 h and at 35—45 °C for 1.5 h. Then the mixture was distilled and the fractions *A* (b.p. 39—40 °C (25 Torr)) and *B* (a mixture of **13b** and **15b** (93 : 7), b.p. 69—74 °C (15 Torr)) were obtained in yields of 1 g and 16.0 g (90%), respectively. Found (%): C, 21.82; F, 63.32. $C_{12}F_{22}O_6$. Calculated (%): C, 21.88; F, 63.53. ^{19}F NMR of compound **13b** (δ): −103.7 and −103.4 (both br.s, 1 F each, 2 COF); −20.5 (br.s, 6 F, 2 CF_3); 6.2 (two AB systems with a common center, 4 F, 2 $CFOC\underline{F}_2$, $J_{A,B}$ = 150 Hz); 9.2 (br.s, 4 F, 2 $CF_3OC\underline{F}_2$); 48.5 and 50.5 (both br.s, 1 F each, 2 COF); 52.0 and 52.1 (both br.s, 2 F each, 2 $CF_2C\underline{F}_2CF_2$). The groups of unresolved signals at δ −3.5—7.0 and two multiplets at δ 58.0 and 60.0 were assigned to the CF_2O and CF groups of lactone **15b**.

Treatment of the fraction *A* with methanol afforded **dimethyl perfluoro-2-methoxypropoxysuccinate (14b)**. ^{19}F NMR, δ: −21.8 (br.s, 3 F, CF_3); 4.9 (AB system, 2 F, $C\underline{F}_2OCF$, $J_{A,B}$ = 158.0 Hz); 8.8 (br.s, 2 F, $CF_3OC\underline{F}_2$); 41.3 (AB system, 2 F, $CFC\underline{F}_2$, $J_{A,B}$ = 270.0 Hz); 52.0 (br.s, 2 F, $CF_2C\underline{F}_2CF_2$); 53.5 (br.s, 1 F, CF). MS, m/z (I_{rel} (%)): 431 $[M - F]^+$ (0.3); 419 $[M - MeO]^+$ (0.7); 391 $[M - COOMe]^+$ (1.0); 365 $[M - CF_3O]^+$ (2.5); 199

$[C_6F_5O_2]^+$ (1.0); 171 $[C_5F_5O]^+$ (40); 109 $[C_3F_3O]^+$ (20); 93 $[C_3F_3]^+$ (10); 81 $[C_2F_3]^+$ (10); 69 $[CF_3]^+$ (90); 59 $[COOMe]^+$ (100).

1,14-Bis(fluorosulfonyl)-7,8-bis(fluorocarbonyl)-4,11-bis(trifluoromethyl)-3,6,9,12-tetraoxaperfluorotetradecane (13c). A mixture of bis-fluorosulfates **8c** and **9c** (93 : 7, 10.9 g, 10 mmol) was added to a mixture of CsF (0.8 g) and monoglyme (2 mL), and the reaction mixture was stirred until gas evolution ceased. The organofluorine layer was separated, and the fractions *A* (b.p. 38—40 °C (1 Torr)) and *B* (a mixture of **13c** and **15c** (3 : 1), b.p. 102—108 °C (1 Torr)) were isolated in yields of 0.4 g and 6.4 g (71%), respectively. Repeated distillation of the fraction *B* afforded an analytical sample of a mixture of compounds **13c** and **15c**, b.p. 104—107 °C (1 Torr). Found (%): C, 18.66; F, 55.73; S, 7.29. $C_{14}F_{13}O_{10}S_2$. Calculated (%): C, 18.96; F, 55.76; S, 7.22. ^{19}F NMR, δ: −121.8 ($CF_2SO_2\underline{F}$); −105.1—−104.9 (COF); 0—10.0, 15.0, 16.0, 18.0, 19.0 (CF_2, CF_3); 47.0—48.5, 50.5, 58.5, 59.8 (CF); 66.0—67.5 (CF).

Treatment of the fraction *A* with methanol afforded **dimethyl perfluoro-2-(5-fluorosulfonyl-2-methyl-3-oxaamyloxy)succinate (14c)**. ^{19}F NMR, δ: −122.8 (br.s, 1 F, $CF_2SO_2\underline{F}$); −1.8—8.2 (group of signals, 7 F, $C\underline{F}_2OCF(C\underline{F}_3)C\underline{F}_2$); 34.7 (br.s, 2 F, $C\underline{F}_2SO_2F$); 41.4 (AB system, 2 F, $C\underline{F}_2CO_2Me$, $J_{A,B}$ = 262.8 Hz); 51.7, 52.8 (1 F, $C\underline{F}CF_2CO_2Me$); 66.2 (br.s, 1 F, CF). MS, m/z (I_{rel} (%)): 533 $[M - MeO]^+$ (2); 505 $[M - CO_2Me]^+$ (5); 365 $[C_5F_{11}O_4S]^+$ (6); 346 $[C_5F_{11}O_3S]^+$ (8); 285 $[C_5F_{11}O]^+$ (1); 263 $[C_5F_9O_2]^+$ (2); 199 $[C_2F_5O_3S]^+$ (10); 171 $[C_5F_9O]^+$ (60); 133 $[CF_3O_2S]^+$ (20); 140 $[C_4H_3F_3O_2]^+$ (2); 119 $[C_2F_5]^+$ (25); 109 $[C_3F_3O]^+$ (12); 100 $[C_2F_4]^+$ (15); 93 $[C_3F_3]^+$ (10); 81 $[C_2F_3]^+$ (10); 69 $[CF_3]^+$ (40); 67 $[SO_2F]^+$ (60); 59 $[C_2H_3O_2]^+$ (100); 47 $[COF]^+$ (4).

2,3-Bis(perfluoropropoxy)-2,3-difluorosuccinyl difluoride (13d). A mixture of bis-fluorosulfates **8d** and **9d** (94 : 6, 8.3 g, 11.4 mmol) was gradually added to a mixture of CsF (0.5 g) and tetraglyme (1 mL). The reaction mixture was stirred at ~25 °C for 2 h and at 35—40 °C for 30 min. Then the mixture was distilled off and the fraction with b.p. 52—55 °C (25 Torr) was collected. Repeated distillation of the distillate afforded a mixture of compounds **13d** and **15d** (9 : 1) in a yield of 4.7 g (80%), b.p. 58—60 °C (45 Torr). Found (%): C, 22.60; F, 65.00. $C_{10}F_{18}O_4$. Calculated (%): C, 22.81; F, 65.02. ^{19}F NMR of compound **13d** (δ): −103.6 (br.s, 1 F, COF); −103.3 (br.s, 1 F, COF); 5.8 (m, 6 F, 2 CF_3); 7.0 (two AB systems with a common center, 4 F, 2 $CFOC\underline{F}_2$, $J_{A,B}$ = 147.9 Hz); 48.7 (br.s, 1 F, CF); 50.5 (br.s, 1 F, CF); 53.8 (br.s, 4 F, 2 $CF_3C\underline{F}_2$). The group of unresolved signals at δ −4.0—7.5 and two multiplets at δ 58.0 and 59.7 were assigned to the CF_2O and CF groups of lactone **15d**.

2,3-Bis(2-fluorosulfonylperfluoroethoxy)-2,3-difluorosuccinyl difluoride (13e). A mixture of bis-fluorosulfates **8e** and **9e** (95 : 5, 9.2 g, 12 mmol), CsF (0.5 g), and tetraglyme (3 mL) was stirred until gas evolution ceased. The volatile products (up to 110 °C (15 Torr)) were distilled off, and the distillate was collected in a cooled receiver (0 °C). Rectification of the distillate afforded a fraction with b.p. 36—38 °C (17 Torr) in a yield of 0.6 g and a mixture of compounds **13e** and **15e** (4 : 1) in a yield of 4.5 g (74%), b.p. 88—91 °C (17 Torr). Found (%): C, 16.95; F, 48.30; S, 11.29. $C_8F_{14}O_8S_2$. Calculated (%): C, 17.33; F, 48.01; S, 11.55. ^{19}F NMR of compound **13e** (δ): −122.7 (br.s, 2 F, 2 $CF_2SO_2\underline{F}$); −105.2 (br.s, 2 F, 2 COF); 4.4 (two AB systems with a common center, 4 F, 2 $CFOC\underline{F}_2$, $J_{A,B}$ = 148.5 Hz); 36.0 (br.s, 4 F, 2 $C\underline{F}_2SO_2F$); 48.3 (br.s, 1 F, CF); 48.7 (br.s, 1 F, CF). ^{19}F NMR of lactone **15e** (δ): −122.5 (br.s, 2 F, 2 $CF_2SO_2\underline{F}$); 1.5—5.2, 14.5—15.1, 18.0, 19.0 (group of signals, 6 F, 3 CF_2); 35.5 (br.s, 4 F, 2 $C\underline{F}_2SO_2F$); 57.5 (br.s, 1 F, CF); 59.2 (br.s, 1 F, CF).

This study was financially supported by the Chemistry and Materials Science Division of the Russian Academy of Sciences (Program "Theoretical and Experimental Studies of the Nature of Chemical Bonds and Mechanisms of Important Chemical Reactions and Processes").

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Received August 16, 2004;
in revised form February 4, 2005