

Formation of fluorosulfatodimerization products in reactions of perfluoroaliphatic α,β -unsaturated carbonyl compounds and conjugated dienes with electrochemically generated peroxydisulfuryldifluoride

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Reactions of fluoroaliphatic α,β -unsaturated carbonyl compounds and perfluoro-2,7-dimethylocta-3,5-diene with electrochemically generated peroxydisulfuryldifluoride proceed to give both 1 : 1 adducts and fluorosulfatodimerization products, whose formation is explained by generation of heteroallyl and allyl radicals due to the addition of a fluorosulfonyloxy radical to the sterically hindered vinyl carbon atom.

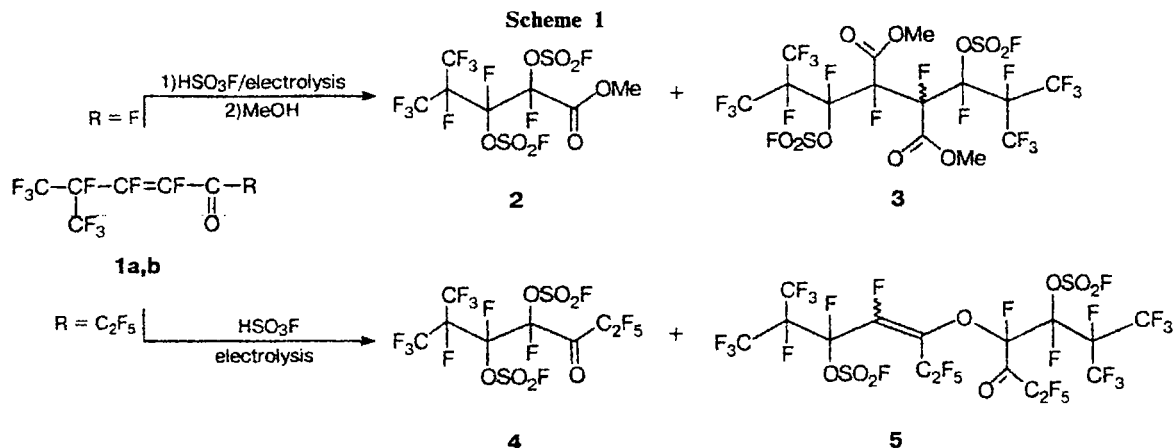
Key words: perfluorovinylketones, perfluoro-1,3-dienes, peroxydisulfuryldifluoride, fluorosulfatodimerization, fluoroaliphatic allyl and α -keto radicals.

Previously,¹ it was found that perfluorinated α,β -unsaturated carbonyl compounds, namely, perfluoro-4-methylpent-2-enoic acid fluoride (**1a**) and perfluoro-6-methylhept-4-en-3-one (**1b**), under conditions of electrolysis in HSO_3F (on gradual addition of **1a** and **1b** to the electrolyte) react with electrochemically generated peroxydisulfuryldifluoride to form corresponding vicinal bis-fluorosulfates (**2** and **3**). Further investigations have shown that the composition of reaction products is to a great extent dependent on the experimental procedure employed. For instance, addition of the whole amount of the starting unsaturated compound (**1a,b**) to the electrolyte before starting electrolysis in HSO_3F results not only in vicinal bis-fluorosulfates **2** and **4**, but also in fluorosulfatodimers **3** and **5** (Scheme 1, products **2** and **3** were isolated as methyl esters).

It should be noted that the reaction of peroxydisulfuryldifluoride with perfluoro-4-methylpent-2-ene

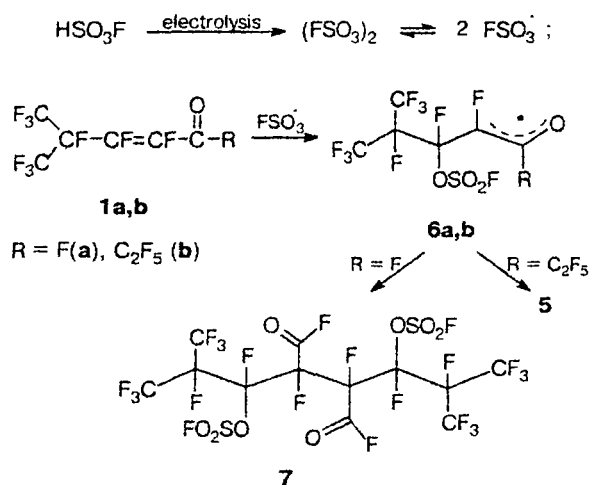
(structural analogy of the latter with compounds **1a,b** is determined by the presence of the perfluoroisopropylvinyl group) gives only a vicinal bis-fluorosulfate; the formation of a fluorosulfatodimer has never been observed in this case irrespective of the order of mixing the reagents.² This fact, as well as the results of investigations of conjugated radical fluorosulfatohalogenation of perfluoro-4-methylpent-2-ene,³ makes it possible to assume that the addition of fluorosulfonyloxy radical to this olefin proceeds under kinetic conditions and is regioselective. The α -fluorosulfonyloxytetrafluoroethyl-perfluoroisopropylmethyl radical that is formed in this case is incapable of dimerizing.

Hence it follows that fluorosulfatodimers **3** and **5** can be formed only if the FSO_3^\cdot radical adds to the sterically hindered vinyl carbon atom in the β -position with respect to the carbonyl group. Such a direction of the radical attack can be explained by the formation of



relatively stable heteroallyl radicals **6a,b** which recombine to give fluorosulfatodimers **5** and **7** (Scheme 2).

Scheme 2



Fluorosulfatodimers **3** and **5** are mixtures of not only diastereoisomers but also stable conformers, which makes interpretation of their ^{19}F NMR spectra difficult. The structure of dimers **3** and **5** was suggested on the basis of molecular spectroscopy data: the Raman spectrum of **3** contains absorption bands of sulfonyl and alkoxycarbonyl groups only (at 1491 and 1886 cm^{-1} , respectively), whereas a strong $\text{C}=\text{C}$ absorption band at 1674 cm^{-1} is observed in the Raman spectrum of **5** in addition to absorption bands of SO_2 and CO groups (at 1491 and 1791 cm^{-1} , respectively).

The capability of heteroallyl radicals **6a,b** to enter recombination in the form of C- or O-centered radicals is determined mainly by the size of the substituent R at the carbonyl group. As is known, the unpaired electron density in α -carbonylalkyl radicals is mainly (~80%) localized on the carbon atom⁴; therefore the formation of dimer **7**, a product of recombination of two C-centered

radicals **6a**, seems to be quite natural. However, in the case of radicals **6b** the bulky pentafluoroethyl group produces steric hindrances to the formation of the $\text{C}-\text{C}$ bond, so these radicals enter the recombination in the form of O- and C-centered radicals.

The possibility of adding the bulky fluorosulfonyloxy radical to the sterically hindered carbon atom is confirmed by the composition of the products of electrochemical fluorosulfation of perfluoro-2,7-dimethyloct-3,5-diene (**8**). Electrolysis of this compound resulted in a mixture of perfluoro-2,7-dimethyl-3,6-bis(fluoro-sulfonyloxy)oct-4-ene (**9**) (a mixture of diastereoisomers; the chemical shifts of vinyl fluorine atoms suggest the formation of *Z*-isomers (cf. Ref. 5)) and fluorosulfatodimer (**10**, Scheme 3).

The structure of **9** as well as the absence of vicinal bis-fluorosulfate (**11**) among the reaction products are unambiguous evidence for regiospecificity of the addition of a fluorosulfonyloxy radical, resulting in the formation of the corresponding allyl radical; hence in this case a thermodynamically controlled radical attack proceeds.

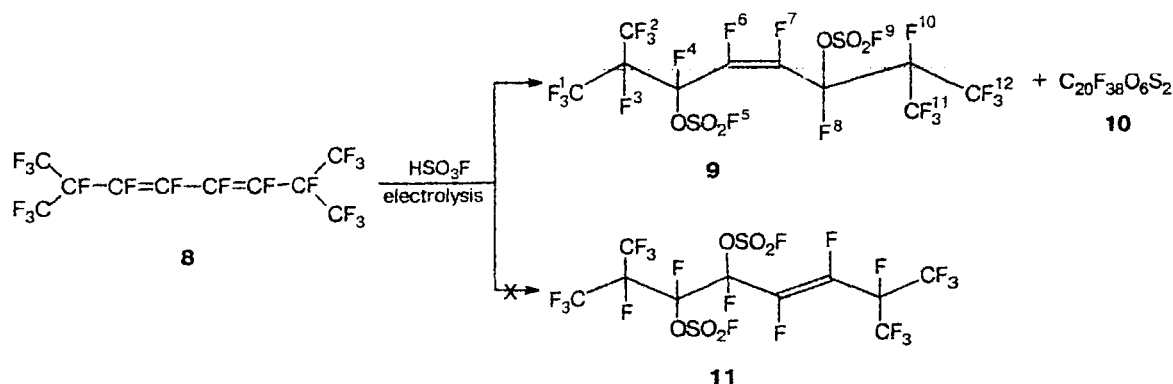
Experimental

Electrochemical fluorosulfation of compounds **1a,b**, and **8** was carried out in a undivided glass cell electrolyzer cooled with running water at 27–32 °C using an SU 2000 glassy-carbon anode and a titanium cathode.

Electrolysis of perfluoro-4-methylpent-2-enoic acid fluoride (1a) in HSO_3F . Electrolysis of a mixture of acid fluoride **1** (27.8, g 0.1 mol), HSO_3F (30 mL), and NaSO_3F (2.3 g) was carried out over a period of 10 h ($I = 0.5 \text{ A}$; 1.86 F mol^{-1}). After electrolysis, the lower organic layer was separated, 30 mL of cooled MeOH was added with stirring, the methanolic solution was washed with water, and the organic layer was separated and distilled to give 26.4 g (54%) of methyl perfluoro-[2,3-bis-(4-methylfluorosulfonyloxy)]pentanoate (**2**),¹ b.p. 55–56 °C (2 Torr) (cf. Ref. 1), and 4.6 g (12%) of dimethyl perfluoro-2,3-bis(3-methylfluorosulfonyloxybutyl)succinate (**3**) (a mixture of diastereomers, b.p. 114–115 °C (2 Torr). Found (%): F, 49.22. $\text{C}_{14}\text{H}_6\text{F}_{20}\text{O}_{10}\text{S}_2$. Calculated (%): F, 48.83. Raman spectrum ($\nu_{\text{max}}/\text{cm}^{-1}$): 1491 (SO_2); 1886 (CO).

Electrolysis of perfluoro-6-methylhept-4-en-3-one (1b) in HSO_3F . Electrolysis of a mixture of vinyl ketone **1b** (19.8 g,

Scheme 3



0.05 mol), HSO_3F (20 mL), and NaSO_3F (1.5 g) was carried out over a period of 5.5 h ($I = 1$ A; 4.08 F mol^{-1}). After electrolysis, the reaction mass was poured on ice, and the organic layer was separated, washed with water, and distilled to give 12 g (41%) of perfluoro-6-methyl-4,5-bis(fluorosulfonyloxy)heptan-3-one (4), b.p. $52-54^\circ\text{C}$ (10 Torr) (identified by comparison with the specimen obtained by independent synthesis according to the known procedure¹), and 6.2 g (26%) of perfluoro-6-methyl-4-(6-methyl-5-fluorosulfonyloxyhept-3-en-3-yloxy)-5-fluorosulfonyloxyheptan-3-one (5), b.p. $92-94^\circ\text{C}$ (2 Torr). Found (%): C, 19.57; F, 59.56. $\text{C}_{16}\text{F}_{30}\text{O}_8\text{S}_2$. Calculated (%): C, 20.13; F, 59.73. MS, m/z (I_{rel} (%)): 954 $[\text{M}]^+$ (0.04); 935 $[\text{M} - \text{F}]^+$ (0.24); 855 $[\text{M} - \text{FSO}_2]^+$ (0.35); 807 $[\text{M} - \text{C}_3\text{F}_5\text{O}]^+$ (3.13); 785 $[\text{M} - \text{C}_3\text{F}_7]^+$ (0.75); 769 $[\text{C}_{13}\text{F}_{23}\text{O}_7\text{S}_2]^+$ (0.31); 689 $[\text{C}_{13}\text{F}_{23}\text{O}_4\text{S}]^+$ (6.46); 686 $[\text{C}_{11}\text{F}_{18}\text{O}_5\text{S}]^+$ (1.25); 609 $[\text{C}_{13}\text{F}_{23}\text{O}]^+$ (2.17); 605 $[\text{C}_{11}\text{F}_{19}\text{O}_4\text{S}]^+$ (2.48); 560 $[\text{C}_{11}\text{F}_{20}\text{O}_3]^+$ (1.04); 477 $[\text{C}_8\text{F}_{15}\text{O}_4\text{S}]^+$ (2.25); 449 $[\text{C}_7\text{F}_{15}\text{O}_3\text{S}]^+$ (1.34); 381 $[\text{C}_8\text{F}_{15}]^+$ (4.15); 359 $[\text{C}_8\text{F}_{13}\text{O}]^+$ (2.97); 349 $[\text{C}_5\text{F}_{11}\text{O}_3\text{S}]^+$ (4.52); 339 $[\text{C}_6\text{F}_9\text{O}_4\text{S}]^+$ (1.52); 330 $[\text{C}_5\text{F}_{10}\text{O}_3\text{S}]^+$ (8.89); 309 $[\text{C}_7\text{F}_{11}\text{O}]^+$ (2.33); 299 $[\text{C}_4\text{F}_9\text{O}_3\text{S}]^+$ (2.47); 259 $[\text{C}_6\text{F}_9\text{O}]^+$ (66.50); 219 $[\text{C}_4\text{F}_9]^+$ (64.91); 199 $[\text{C}_2\text{F}_5\text{O}_3\text{S}]^+$ (13.11); 147 $[\text{C}_3\text{F}_5\text{O}]^+$ (100); 131 $[\text{C}_3\text{F}_5]^+$ (43.23); 119 $[\text{C}_2\text{F}_5]^+$ (100); 83 $[\text{FSO}_2]^+$ (74.41); 69 $[\text{CF}_3]^+$ (100); 67 $[\text{FOS}]^+$ (17.79); 47 $[\text{CFO}]^+$ (12.01); 31 $[\text{CF}]^+$ (8.71).

Electrolysis of perfluoro-2,7-dimethylocta-3,5-diene (8) in HSO_3F . Electrolysis of a mixture of octadiene 8 (18.1 g, 0.04 mol), HSO_3F (30 mL), and NaSO_3F (2.2 g) was carried out over a period of 10 h ($I = 0.3$ A; 2.85 F mol^{-1}). After electrolysis, the mixture was poured onto ice, the organic layer was extracted with Freon 13, the extract was dried with MgSO_4 and concentrated, and the residue was distilled to give 3.2 g (12%) of perfluoro-2,7-dimethyl-3,6-bis(fluorosulfonyloxy)oct-4-ene (9) (a mixture of diastereomers; the chemical shifts of vinyl fluorine atoms suggest formation of *Z*-isomers (cf. Ref. 5)), b.p. $100-101^\circ\text{C}$ (23 Torr), and 10.2 g (46%) fluorosulfatodimer 10, b.p. $115-120^\circ\text{C}$ (2 Torr) (part. decomp. upon distillation).

Compound 9. Found (%): C, 17.96; F, 57.99. $\text{C}_{10}\text{F}_{20}\text{O}_6\text{S}_2$. Calculated (%): C, 18.19; F, 57.55. Raman spectrum: ($\nu_{\text{max}}/\text{cm}^{-1}$): 1488 (SO_2); 1716 ($\text{C}=\text{C}$). ^{19}F NMR (δ): -125.5

(2 F, F(5), F(9)); -6.0 and -5.5 (12 F, F(1), F(2), F(11), F(12)); 46.5 (2 F, F(4), F(8)); 65.5 and 66.2 (2 F, F(6), F(7)), 105.9 (2 F, F(3), F(10)).

Compound 10. Found (%): C, 20.48; F, 62.97. $\text{C}_{20}\text{F}_{38}\text{O}_6\text{S}_2$. Calculated (%): C, 21.40; F, 64.33. Raman spectrum ($\nu_{\text{max}}/\text{cm}^{-1}$): 1489 (SO_2); 1703 ($\text{C}=\text{C}$).

MS, m/z (I_{rel} (%)): 561 $[\text{C}_{10}\text{F}_{19}\text{O}_3\text{S}]^+$ (59); 459 $[\text{C}_{10}\text{F}_{17}\text{O}]^+$ (18); 431 $[\text{C}_9\text{F}_{17}]^+$ (7); 393 $[\text{C}_9\text{F}_{15}]^+$ (8); 355 $[\text{C}_9\text{F}_{13}]^+$ (1); 309 $[\text{C}_7\text{F}_{11}\text{O}]^+$ (23); 293 $[\text{C}_7\text{F}_{11}]^+$ (10); 281 $[\text{C}_6\text{F}_{11}]^+$ (23); 255 $[\text{C}_7\text{F}_9]^+$ (3); 243 $[\text{C}_6\text{F}_9]^+$ (11); 197 $[\text{C}_4\text{F}_7\text{O}]^+$ (3); 181 $[\text{C}_4\text{F}_7]^+$ (1); 159 $[\text{C}_4\text{F}_5\text{O}]^+$ (2); 131 $[\text{C}_3\text{F}_5]^+$ (2); 83 $[\text{FSO}_2]^+$ (30); 69 $[\text{CF}_3]^+$ (100); 67 $[\text{FOS}]^+$ (1); 47 $[\text{CFO}]^+$ (1).

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