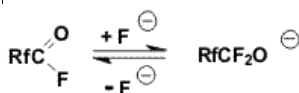


REACTIVITY OF PERFLUORINATED O-ANIONES

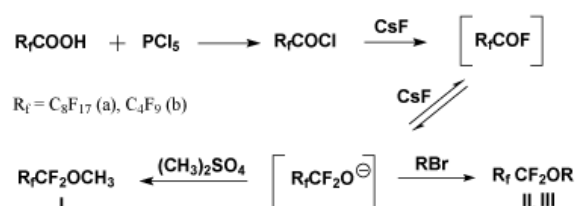
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Hydrofluoroethers (HFEs), as a class, are very promising candidates for substitution ozone-depleting solvents not only because of their zero ozonedepleting potentials, but also because they exhibit superior solvent properties. One of the routes for synthesis of hydrofluoroethers are alkylation of an acid fluoride [1]. Very good known, that the reversible addition of fluoride-ion to anhydrides of perfluoronated acids leads to formation of perfluoroalkoxy anions [2,3,4].



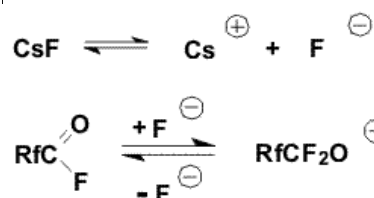
We used both $\text{C}_8\text{F}_{17}\text{COOH}$ and $\text{C}_3\text{F}_7\text{COOH}$ as the sources of perfluorinated O-anions. The corresponding chlorides were obtained from these acids by the action of PCl_5 . For alkylation of O-anions we used the set of alkylating agents. We assumed that $\text{C}_8\text{F}_{17}\text{CF}_2\text{O}^-$ anion could be prepared from the corresponding chloride by a one-step procedure with CsF used as a reagent and with no step of isolation of perfluorononanyl fluoride. Actually, we obtained methyl perfluorononyl ether (**Ia**) in 78% yield by the reaction of nonanoyl chloride with two moles of CsF in diglyme followed by addition of dimethylsulfate.



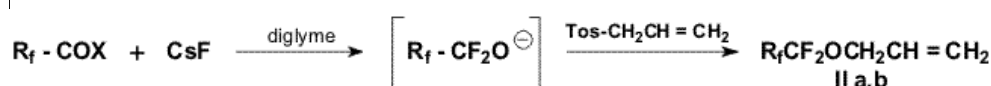
Reactions of O-anions obtained from perfluorononylic and perfluorobutyric acids with others alkylation agents like allyl bromide, ethyl bromoacetate and epibromohydrine proceed very slowly with low conversions and in poor yields.

RBr	C3F7CF2O-		C8F17CF2O-	
	Time of reaction, h	Yield, %	Time of reaction, h	Yield, %
BrCH ₂ CH=CH ₂	100	44 (IIb)	100	28 (IIa)
BrCH ₂ COOEt	100	18 (IIIb)	75	12 (IIIa)
BrCH ₂ CH-CH ₂ O	15 days	No reaction products	15 days	No reaction products

Obviously, equilibrium in the addition reactions of fluoride-ion to the carbonyl group of an acid fluoride and stabilization of O-anion by elimination of fluoride-ion is shifted to the left.



Additionally, the solubility of the corresponding cesium salt in diglyme is likely to decrease, as the alkyl chain length in the fluoride increases. Therefore, the rate of alkylation will depend mainly on the alkylating agent activity. A raise of temperature of the reaction mixture increases the activity of O-anion, on one hand, but, obviously, at the same time, additionally shifts the equilibrium to the left, and the anion concentrations decreases. Under these conditions the fluoride-ion which presents in the reaction mixture is alkylated to a greater extent than the O-anion. This is especially pronounced when halogen-containing compounds are used as alkylating agents. In order to avoid occurring the reactions of halogen exchange and increase the activity of an alkylating agents we used a derivative of p-toluenesulfonic acid, allyl tosylate as the alkylating agents.



R_f = C₈F₁₇ (a); C₃F₇ (b)

X = F (a); Cl (b)

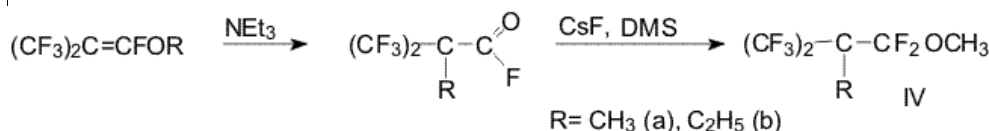
Yield : a = 40% ; b = 64%

Methylation of perfluorobutoxy-anion with various methylating agents was carried out at 20°C with the ratio of the starting reagents being equal.

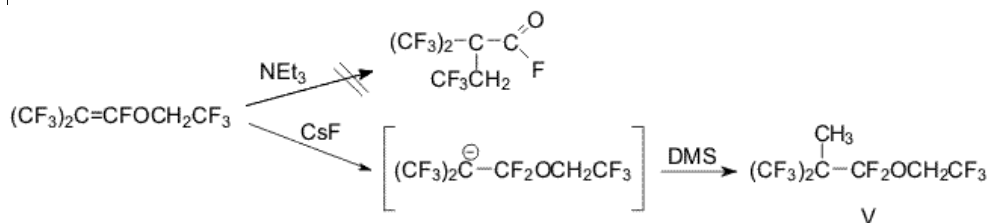
Table 1

Methylating Agent	Time, h	Yield of Ether (Ib , %)
CF ₃ SO ₄ CH ₃	6	70
CH ₃ SO ₄ CH ₃	15	64
CH ₃ -C ₄ H ₄ -SO ₃ CH ₃	40	60
CH ₃ SO ₃ CH ₃	65	51
CH ₃ I	70	37

Methyl triflate proved to be the most reactive agent. The reaction with methyl triflate is exothermic and completed for 5 to 6 h. The obtained ether (**Ib**) was isolated in 70% yield. The reaction with dimethylsulfate occurred more slowly, the disappearance of perfluorobutoxy anion (**I**) was observed in 12 to 15 h, and the yield of the methyl ether (**Ib**) was 64%. Methyl tosylate reacts much more slowly. Reactivity of methyl mesilate and methyl iodide decrease in series. In order to estimate reactivity partially fluorinated acyl fluoride we used capability of perfluoroisobutenyl ethers rearranging to carbonyl fluorides [5]. As we showed these carbonyl fluorides can add the fluoride-ion and resulted alcoholates are capable to give the ethers under the action of alkylation agent with fairly good yield.



It turned out, that trifluoroethylisobutenyl ether don't transform to corresponding carbonyl fluorides under NEt₃ influence. It's interaction with CsF lead to carbanion, whose methylation affords the corresponding ether (V).



Experimental

¹H and ¹⁹F NMR spectra were recorded on a "Bruker AC-200 X" instrument (200 MHz for ¹H and 188.3 MHz for ¹⁹F NMR, respectively) with TMS and CF₃COOH used as references, respectively. Chemical shifts are given in ppm using (¹H) and (¹⁹F) scales, the coupling constants reported in Hz. Mass-spectra were obtained on a VG 7070E spectrometer (ionizing electron energy 70 eV).

The course of the reactions was monitored by ¹⁹F NMR spectroscopy.

Synthesis of perfluoropelargonyl chloride

Perfluoropelargonyl chloride (214 g, 85%, b.p. 153 - 155 °C) was prepared from 241.6 g of perfluoropelargonic acid and 108.6 g of PCl₅ using the procedure reported in J. Am. Chem. Soc. 75, 966 (1958).

Synthesis of methylperfluorononyl ether (**Ia**)

Chloride from previous experiment (48.25 g, 0.1 mol) was added slowly dropwise to a suspension of anhydrous CsF (38 g, 0.25 mol) in 120 mL of dry diglyme. The reaction mixture was stirred at 20 °C for 16 h, then a solution of DMS (15.12 g, 0.12 mol) in 30 mL of dry diglyme was added, and the mixture was stirred for 30 h. at 20 °C (the process was monitored by ¹⁹F NMR spectroscopy). The reaction mixture was poured into ice, the lower layer was separated and dissolved in ether. The ethereal solution was washed with water and dried over MgSO₄. The ether was evaporated, and the residue was distilled to give ether (**Ia**) (39.1 g, 78.2%), b.p. 70 - 72 °C /15 mm Hg.

Anal. Calcd for C₁₀H₃F₁₉O: C, 24.00; H, 0.60; F, 72.20.

Found: C, 24.05; H, 0.63; F 72.30.

¹⁹F NMR (δ, ppm): 6.4 t (CF₃); 13.8 m (CF₂O); 46.4 m (3CF₂); 46.9 m (CF₂); 50.2 m (CF₂); 51.1 m (CF₂); ¹H NMR (δ, ppm): 3.8 s (CH₃).

Synthesis of methyl perfluorobutyl ether (**Ib**) (general procedure)

Perfluorobutyl chloride (0.04 mol) was added slowly dropwise to a suspension of freshly dried CsF (0.1 mol) in dry diglyme (50

mL) with stirring and ice cooling. The resulting mixture was stirred for at ca. 20°C, and in 16 h a solution of a methylating agent (0.04 mol) in dry diglyme (15 mL) was added. The reaction mixture was stirred at ca. 20°C for several hours and volatiles were distilled into a trap (-78°C) in vacuo (10 mm Hg) at 20-50°C. The content of the trap was poured into water, the lower layer was separated, washed with water, and dried over MgSO₄. Distillation afforded ether (**IIb**), b.p. 59-61°C; the yields and the reaction time are presented in Table 1.

¹⁹F NMR (CCl₄): 3.7 t (CF₃); 11.2 m (CF₂O); 48.9 m (CF₂); 49.4 m (CF₂); J (F-F) = 9.5. ¹H NMR (CCl₄): 2.98 s (CH₃). MS (m/z, assignments, intensity (%)): 249 [M-H]⁺ 2.24; 232 [M-H₂O]⁺ 1.32; 231 [M-F]⁺ 24.82; 219 [M-OCH₃]⁺ 5.15; 197 [C₄F₇O]⁺ 2.43; 181 [C₄F₇]⁺ 13.04; 170 [C₃F₇H]⁺ 1.60; 169 [C₃F₇]⁺ 47.51; 151 [C₃F₆H]⁺ 1.35; 131 [C₃F₅]⁺ 13.41; 119 [C₂F₅]⁺ 13.15; 100 [C₂F₄]⁺ 15.06; 97 [C₂F₃O]⁺ 5.17; 93 [C₃F₃]⁺ 1.71; 82 [C₂F₃H]⁺ 2.62; 81 [CF₂OCH₃]⁺ 100; 69 [CF₃]⁺ 60.95; 50 [CF₂]⁺ 2.19; 47 [CFO]⁺ 10.89; 31 [CF]⁺ 6.00; 29 [CHO]⁺ 6.37; 15 [CH₃]⁺ 73.31.

Synthesis of allylperfluorobutyl ether (IIb)

Perfluorobutyryl chloride (7 g, 0.03 mol) was added slowly dropwise to a suspension of anhydrous CsF (11.4 g, 0.075 mol) in 40 mL of dry diglyme. The reaction mixture was stirred at 20 °C for 16 h, then a solution of allylbromide (3.6 g, 0.03 mol) in 10 ml of dry diglyme was added, and the mixture was stirred for 100 h at 50 °C. The reaction mixture was poured into ice, the lower layer was separated and dissolved in ether. The ethereal solution was washed with water and dried over MgSO₄. The ether was evaporated, and the residue was distilled to give methyl perfluorobutyl ether (**IIb**) (3,7 g, 44,6%), b.p. 92 - 94 °C. ¹⁹F NMR (δ, ppm): -5.9 (CF₃) t J(CF₃-CF₂)=10 Hz; 10 m (CF₂O); 50.5 m (CF₂); 50.9 m (CF₂) ¹H NMR (δ, ppm): ABCX₂-system: 5.0 ppm. (-OCH₂) d. J (CH₂-CH) = 5.5 Hz; 5.8 ppm (=CHB) d. J (HB-CH) = 10.0 Hz; 5.91 (=CHA) d. J (HA-CH) = 17.0 Hz; 6.4 ppm (CH) ddt. J (CH-CHA) = 17.0 Hz, J (CH-CHB) = 10.0 Hz, J(CH-CH₂)=5.5 Hz. MS (m/z, intensity, %) : 276 (M⁺ C₇H₅F₉O)(16.2).

Synthesis of allylperfluorononyl ether(IIa)

1. Perfluorononanoil fluoride (30g, 0.06 mol) was added slowly dropwise to a suspension of freshly dried CsF (15,2 g, 0.1 mol) in 120 mL of dry diglyme. The reaction mixture was stirred at 20 °C for 16 h, then a solution of allyl bromide (9,3 g, 0.08 mol) in 30 mL of dry diglyme was added, and the mixture was stirred at 60 - 70 °C for 100 h. The reaction mixture was poured into ice, the lower layer was separated and dissolved in ether. The ethereal layer was washed with water and dried over MgSO₄. The ether was distilled off, and distillation of the residue afforded ether (**IIa**) (9,7 g, 28,6 %), b.p..80 - 82 °C /10 mm Hg.

2. Using the procedure of previous experiment the same ether (**IIa**) was produced (20,1 g, 44%) from perfluorononanoil fluoride (39,6 g, 0,084 mol) CsF (15,2 g, 0,1 mol) and allyl tosylate (18 g, 0,084 mol) in the 150 mL diglyme (50°C, 50 h.) ¹⁹F NMR (δ, ppm):6.1 (CF₃) t J(CF₃-CF₂)=10 Hz; 10.1 m (CF₂O); 46.1 m (CF₂); 47.1 m (CF₂); 49.7 m (CF₂); 50.8 m(CF₂). ¹H NMR (δ, ppm): ABCX₂-system: 4.7 (-OCH₂) d. J (CH₂-CH) = 5.5 Hz; 5.46 (=CHB) d. J (HB-CH) = 10.0 Hz; 5.6 (=CHA) d. J (HA-CH) = 17.0 Hz; 6.4 (CH) ddt. J (CH-CHA) = 17.0 Hz, J (CH-CHB) = 10.0 Hz, J(CH-CH₂)=5.5 Hz. MS (m/z, intensity, %) : 526 [M]⁺(19.9).

Synthesis of carboethoxymethylperfluorononyl ether (IIIa)

Perfluoropelargonyl fluoride (4.7 g, 0.01 mol) was added dropwise to a suspension of freshly dried CsF (2.3 g, 0.015 mol) in 25 ml of dry diglyme, and the mixture was stirred at 20°C for 16 h. Then a solution of 1.67 g (0.01 mol) of ethylbromoacetate in 15 ml of dry diglyme was added. The reaction mixture was stirred at 20°C for 15 h. (According to ¹⁹F NMR spectra a minor amount of the alkylation product and ethylfluoroacetate appeared in the reaction mixture). Then the reaction mixture was stirred at 50-55°C for 60 h and poured into ice water; the lower layer was separated and dissolved in ether. The ether solution was washed with a solution of NaHCO₃, and dried over MgSO₄. The ether was removed, and the residue was distilled to yield ether (**IIIa**) (0.7 g, 12%), b.p. 110-112°C/4 mm Hg.

¹H NMR (CCl₄): 1.54 t (CH₃); 4.48q (CH₂); 4.85 s (CH₂); J(H-H) = 7.6 Hz. ¹⁹F NMR (CCl₄): 5.0 t (CF₃); J(F-F)=9.9 Hz; 9.8 m (CF₂); -4 to 45.8 m (4CF₂); 46.5 m (CF₂); 49.1 m (CF₂); 50.3 m (CF₂). MS : 572 [M]⁺ 0.8; 543 [M-C₂H₅]⁺ 0.9; 529 [M-C₂H₃O]⁺ 0.8; 525 [M-F-CO]⁺ 3.2; 500 [M- COOC₂H₄]⁺ 1.6; 499[M-COOC₂H₅]⁺ 15.3; 481 [M-F-COOC₂H₄]⁺ 1.5; 480 [M-F-COO₂2H₅]⁺ 1.9; 219 [C₄F₉]⁺6.1; 181 [C₄F₇]⁺ 2; 169 [C₃F₇]⁺ 7.5; 131[C₃F₅]⁺ 9.5; 125 [M-C₉F₁₇O]⁺4.4; 119[C₂F₅]⁺5.1; 100 [C₂F₄]⁺ 4.1; 87[CH₂COOC₂H₅]⁺ 7.6; 69 [CF₃]⁺ 22; 59 [C₃H₇]⁺ 18.6; 45 [C₂H₅O]⁺ 3.1; 43[C₃H₃O]⁺ 14.6; 31 [CF]⁺; 29 [C₂H₅]⁺ 16.0; 27 [C₂H₃]⁺

Synthesis of carboethoxymethylperfluorobutyl ether (IIIb)

Perfluorobutyryl chloride (4.65 g, 0.02 mol) was added dropwise to a suspension of freshly dried CsF (6.8 g, 0.045 mol) in 25 ml of dry diglyme, and the mixture was stirred at 20°C for 16 h. Then a solution of 3.34 g (0.02 mol) of ethylbromoacetate in 5 ml of dry diglyme was added. The reaction mixture was stirred at 20°C for 100 h and poured into ice water; the lower layer was separated and dissolved in ether. The ether solution was washed with a NaHCO₃, water, and dried over MgSO₄. The ether was removed, and the residue was distilled to yield ether (1.2 g, 18%), b.p. 72-74°C/15 mm Hg. ¹H NMR (CCl₄): 1.67 t (CH₃); 4.61q (CH₂); 4.9 s (CH₂); J(H-H) = 7.6 Hz. ¹⁹F NMR (CCl₄): 5.0 t (CF₃); J(F-F)=9.9 Hz; 9 m (CF₂); -4.9 m (CF₂); 50.8 m (CF₂). MS (m/z, intensity,%) : 322 [M]⁺ 0.7; 293 [M-C₂F₅]⁺ 2.1; 279 [M-C₂H₃O]⁺ 3.5; 275 [M-F-CO]⁺ 1.1; 250 [M- COOC₂H₄]⁺ 2; 249[M-COOC₂H₅]⁺ 42; 231 [M-F-COOC₂H₄]⁺ 1.15; 230 [M-F-COO₂H₅]⁺ 2.4; 219 [C₄F₉]⁺ 13.6; 169 [C₃F₇]⁺ 2.1; 131[C₃F₅]⁺ 8.8; 125 [M-C₉F₁₇O]⁺ 3.2; 119[C₂F₅]⁺ 2.5; 100 [C₂F₄]⁺ 5; 87 [CH₂COOC₂H₅]⁺ 6.3; 69 [CF₃]⁺ 31.3; 59 [C₃H₇O]⁺ 2.3; 45 [C₂H₅O]⁺ 3; 43 [C₂H₃O]⁺ 10.2; 31 [CF]⁺8.8; 29 [C₂H₅]⁺ 100; 27 [C₂H₃]⁺

Synthesis of methyl 2-methylperfluoroisobutyl ether(IVa)

To a suspension of freshly calcined CsF (21,5g; 0,14 mol) in 40 ml of dry diglyme α-methyl perfluoroisobutiryl fluoride (15g, 0,07 mol) was added dropwise and stirred at ca. 20°C. After 1 h. a solution of DMS (8,9g; 0,07 mol) in 10 ml of dry diglyme was added dropwise and reaction mixture was stirred for 10 h. at 20°C. The reaction mixture was poured into ice, the lower layer was separated and washed with water and dried over MgSO₄. Distillation afforded ether (**IVa**) (9,6g, 55%) B.p. 91°C. Anal. Calcd. For C₆H₆F₈O: C 29.26: H 2.43: F 61.78%.

Found: C 29,22; H 2,43; F 61,69%.

^1H NMR: 1,29 s(CH₃); 3,38 s (OCH₃) ^{19}F NMR: -7,2 t[(CF₃)₂]; 3h(OCF₂); J F-F = 10,9 Hz.

Synthesis of methyl 2-ethylperfluoroisobutyl ether (IVb)

Using the procedure of previous experiment methyl 2-ethylperfluoroisobutyl ether was prepared from 2-ethylperfluoroisobutyryl fluoride (11,3g, 0,05 mole), CsF (15,2g, 0,1 mole) and DMS (6,3g, 0,05 mole). Reaction mixture was stirred for 40 h. at 20°C and additionally 10 h at 70°C. Distillation afforded ether (**IVb**) (4,1g; 31%) B.p. 113-114°C.

Anal. Calcd. for C₇H₈F₈O; C 32,30; H 3,07; F 58,48%.

Found: C 32,10; H 2,96; F 58,40%.

^1H NMR: 1,44 t(CH₃), 2,35 q(CH₂), 3,86 s (OCH₃); J H-H= 7,2 Hz

^{19}F NMR: -10,2 t(CF₃), 0,19 h(OCF₂), J F-F=10,8 Hz.

Synthesis of trifluoroethyl 2-methylperfluoroisobutyl ether (V)

To a suspension of freshly calcined CsF (45g,03 mole) in 80 ml of dry diglyme trifluoroethyl perfluoroisobutyryl ether (56g, 0,2 mole) was added dropwise and stirred at 20°C. After 1 h a solution of DMS (25,2g; 0,2mole) in 20 ml dry diglyme was added dropwise and reaction mixture was stirred at 20°C for 40h and poured into ice. The lower layer was separated, washed with water, dried over MgSO₄. Distillation afforded trifluoroethyl ether (V) (40,9g; 65%) B.p.105-106 °C.

Anal. Calcd. for C₇H₅F₁₁O: C 26,75; H 1,57; F 66,56%.

Found: C 26,84; H 1,70; F 66,24%. ^1H NMR: 1,9 s(CH₃); 4,5q(OCH₂), JH-F=7,5 Hz. ^{19}F NMR: 1,0h(OCF₂); -0,8t(CF₃); -7,05 t[(CF₃)₂C]; J F-F =10,5 Hz; J H-F=7,5 Hz

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