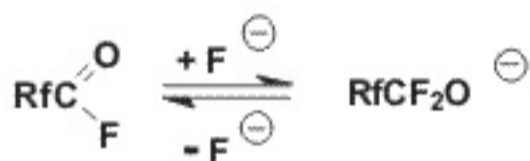


REACTIVITY OF PERFLUORINATED O-ANION

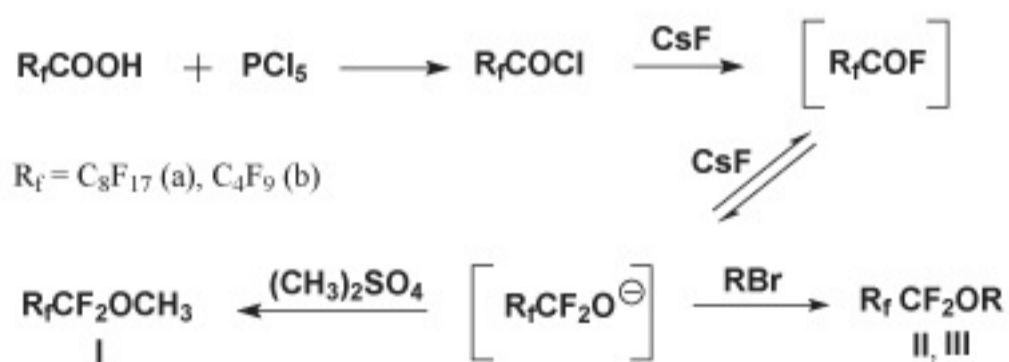
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Hydrofluoroethers (HFEs), as a class, are very promising candidates for substitution oz because of their zero ozonedepleting potentials, but also because they exhibit superior solvent synthesis of hydrofluoroethers are alkylation of an acid fluoride [1]. Very good known, that the to anhydrides of perfluoronated acids leads to formation of perfluoroalkoxy anions [2,3,4].



We used both C₈F₁₇COOH and C₃F₇COOH as the sources of perfluorinated O-anions. Th obtained from these acids by the action of PCl₅. For alkylation of O-anions we used the set o that C₈F₁₇CF₂O⁻ anion could be prepared from the corresponding chloride by a one-step proce and with no step of isolation of perfluorononanoyl fluoride. Actually, we obtained methyl perfluor the reaction of nonanoyl chloride with two moles of CsF in diglyme followed by addition of dimet

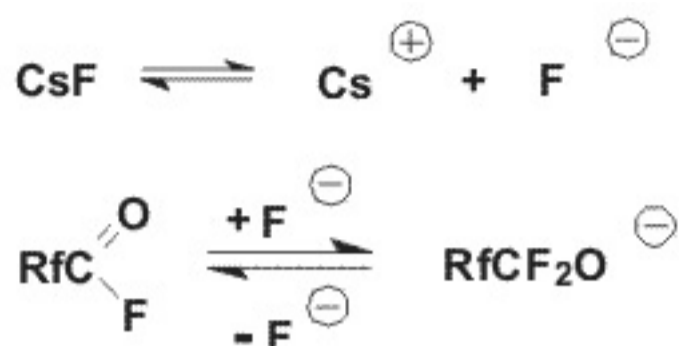


Reactions of O-anions obtained from perfluorononylic and perfluorobutyric acids with others a ethyl bromoacetate and epibromohydrine proceed very slowly with low conversions and in poor

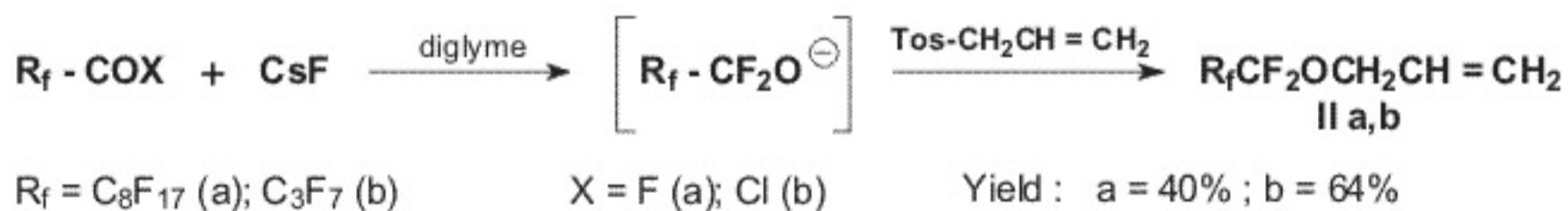
| RBr | C3F7CF ₂ O ⁻ | | C8F17CF ₂ O ⁻ |
|--------------------------------------|------------------------------------|-----------|-------------------------------------|
| | Time of reaction, h | Yield, % | Time of reaction, h |
| BrCH ₂ CH=CH ₂ | 100 | 44 (IIb) | 100 |
| BrCH ₂ COOEt | 100 | 18 (IIIb) | 75 |

| | | | | |
|---|---------|----------------------|---------|----|
| $\text{BrCH}_2\text{CH}(\text{O})\text{CH}_2$ | 15 days | No reaction products | 15 days | pr |
|---|---------|----------------------|---------|----|

Obviously, equilibrium in the addition reactions of fluoride-ion to the carbonyl group of an acyl 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 fluoride increases. Therefore, the rate of alkylation will depend mainly on the alkylating agent as the reaction mixture increases the activity of O-anion, on one hand, but, obviously, at the same time equilibrium is shifted to the left, and the anion concentrations decrease. Under these conditions the acyl anion reaction mixture is alkylated to a greater extent than the O-anion. This is especially pronounced when perfluorinated compounds are used as alkylating agents. In order to avoid occurring the reactions of haloalkylating agents we used a derivative of p-toluenesulfonic acid, allyl tosylate as the alkylating agent.

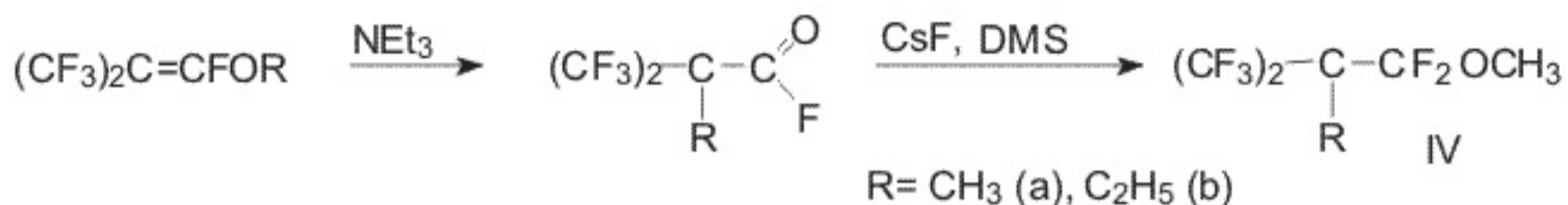


Methylation of perfluorobutoxy-anion with various methylating agents was carried out at 20°C, the reagents being equal.

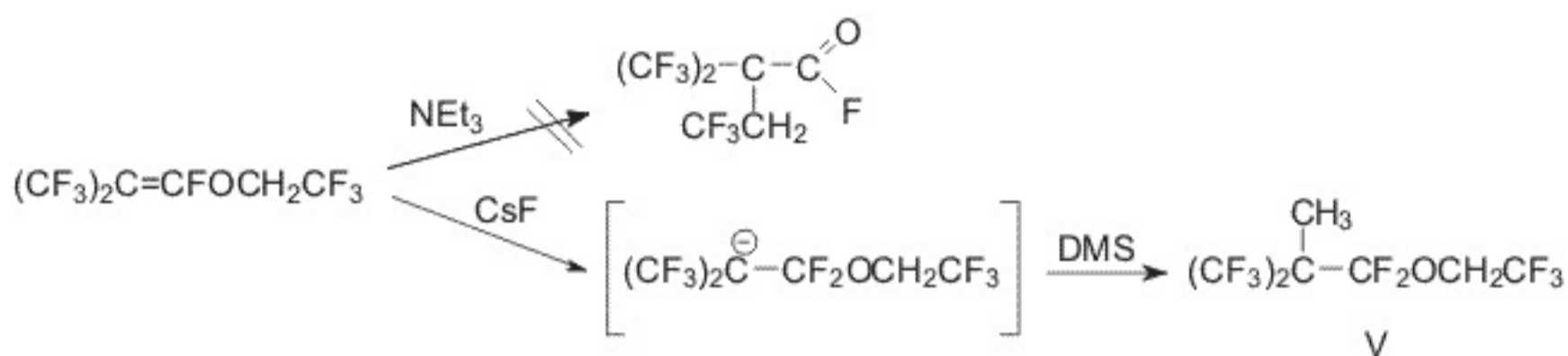
Table 1

| Methylating Agent | Time, h | Yield of Ether (%) |
|---|---------|--------------------|
| $\text{CF}_3\text{SO}_4\text{CH}_3$ | 6 | 70 |
| $\text{CH}_3\text{SO}_4\text{CH}_3$ | 15 | 64 |
| $\text{CH}_3\text{-C}_6\text{H}_4\text{-SO}_3\text{CH}_3$ | 40 | 60 |
| $\text{CH}_3\text{SO}_3\text{CH}_3$ | 65 | 51 |
| CH_3I | 70 | 37 |

Methyl triflate proved to be the most reactive agent. The reaction with methyl triflate is exothermic. The obtained ether (**1b**) was isolated in 70% yield. The reaction with dimethylsulfate occurred of perfluorobutoxy anion (**I**) was observed in 12 to 15 h, and the yield of the methyl ether (**1b**) much more slowly. Reactivity of methyl mesilate and methyl iodide decrease in series. In order to synthesize fluorinated acyl fluoride we used capability of perfluoroisobutenyl ethers rearranging to carbonyl fluorides. These carbonyl fluorides can add the fluoride-ion and resulted alcoholates are capable to give alkylation agent with fairly good yield.



It turned out, that trifluoroethylisobutenyl ether don't transform to corresponding carbonyl fluoride. Interaction with CsF lead to carbanion, whose methylation affords the corresponding ether (**V**).



Experimental

^1H and ^{19}F NMR spectra were recorded on a "Bruker AC-200 X" instrument (200 MHz for ^1H and 252 MHz for ^{19}F respectively) with TMS and CF_3COOH used as references, respectively. Chemical shifts are given in ppm, the coupling constants reported in Hz. Mass-spectra were obtained on a VG 7070E instrument (ionization energy 70 eV).

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

Synthesis of perfluoropelargonyl chloride

Perfluoropelargonyl chloride (214 g, 85%, b.p. 153 - 155 °C) was prepared from 241.6 g of perfluoropelargonyl fluoride and 100 g of PCl_5 using the procedure reported in J. Am. Chem. Soc. 75, 966 (1958).

Synthesis of methylperfluorononyl ether (**1a**)

Perfluoropelargonyl chloride from previous experiment (48.25 g, 0.1 mol) was added slowly dropwise to a suspension of 0.25 mol of Mg in 120 mL of dry diglyme. The reaction mixture was stirred at 20 °C for 16 h, then 0.25 mol of Mg in 30 mL of dry diglyme was added, and the mixture was stirred for 30 h. at 20 °C (monitored by ^{19}F NMR spectroscopy). The reaction mixture was poured into ice, the lower layer was separated, the etheral solution was washed with water and dried over MgSO_4 . The ether was evaporated, give ether (**1a**) (39.1 g, 78.2%), b.p. 70 - 72 °C /15 mm Hg.

Anal. Calcd for $\text{C}_{10}\text{H}_3\text{F}_{19}\text{O}$: C, 24.00; H, 0.60; F, 72.20.

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

^{19}F NMR (CDCl_3 , ppm): 6.4 t (CF_3); 13.8 m (CF_2O); 46.4 m (3CF_2); 46.9 m (CF_2); 50.2 m (CF_2); 51.5 s (CH_3).

Synthesis of methyl perfluorobutyl ether (**1b**) (general procedure)

Perfluorobutyryl chloride (0.04 mol) was added slowly dropwise to a suspension of freshly dried (15 mL) with stirring and ice cooling. The resulting mixture was stirred for at ca. 20°C, and in 16 h (0.04 mol) in dry diglyme (15 mL) was added. The reaction mixture was stirred at ca. 20°C were distilled into a trap (-78°C) in vacuo (10 mm Hg) at 20-50°C. The content of the trap v layer was separated, washed with water, and dried over MgSO₄. Distillation afforded ether (I 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 assignments, intensity (%): 249 [M-H]⁺ 2.24; 232 [M-H₂O]⁺ 1.32; 231 [M-F]⁺ 24.82; 219 2.43; 181 [C₄F₇]⁺ 13.04; 170 [C₃F₇H]⁺ 1.60; 169 [C₃F₇]⁺ 47.51; 151 [C₃F₆H]⁺ 1.35; 1 13.15; 100 [C₂F₄]⁺ 15.06; 97 [C₂F₃O]⁺ 5.17; 93 [C₃F₃]⁺ 1.71; 82 [C₂F₃H]⁺ 2.62; 81 [CF₂O [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 40 mL of dry diglyme. The reaction mixture was stirred at 20 °C for 16 h, then a solution of 10 ml of dry diglyme was added, and the mixture was stirred for 100 h at 50 °C. The reaction lower layer was separated and dissolved in ether. The ethereal solution was washed with water, ether was evaporated, and the residue was distilled to give methyl perfluorobutyl ether (**IIb**). ¹⁹F NMR (CDCl₃), ppm: -5.9 (CF₃) t J(CF₃-CF₂)=10 Hz; 10 m (CF₂O); 50.5 m (CF₂); 50.9 m (CF₂) ¹H NMR (CDCl₃), ppm: 5.0 ppm. (-OCH₂) d. J (CH₂-CH)= 5.5 Hz; 5.8 ppm (=CHB) d. J (HB- CH) = 10.0 Hz; 5.91 (=C ppm (CH) ddt. J (CH - CHA) = 17.0 Hz, J (CH - CHB)= 10.0 Hz, J(CH-CH₂)=5.5 Hz. MS (m/z, ir (16.2).

Synthesis of allylperfluorononyl ether(IIa)

1. Perfluorononanoil fluoride (30g, 0.06 mol) was added slowly dropwise to a suspension of fresh in 120 mL of dry diglyme. The reaction mixture was stirred at 20 °C for 16 h, then a solution of in 30 mL of dry diglyme was added, and the mixture was stirred at 60 - 70 °C for 100 h. The mixture was cooled in ice, the lower layer was separated and dissolved in ether. The ethereal layer was washed with water, ether was distilled off, and distillation of the residue afforded ether (**IIa**) (9,7 g, 28,6 %), b.p..8

2. Using the procedure of previous experiment the same ether (**IIa**) was produced (20,1 g) using 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 1. ¹⁹F NMR (CDCl₃), 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). ¹H NMR (CDCl₃), ppm): ABCX₂-system: 4.7 (-OCH₂) d. J (CH₂-CH)= 5.5 Hz; 5.46 (=CHB) d. J (HB- CH) = 10.0 Hz; 5.91 (=C ppm (CH) ddt. J (CH - CHA) = 17.0 Hz, J (CH - CHB)= 10.0 Hz, J(CH-CH₂)=5.5 Hz. MS (m/z, ir (19.9).

Synthesis of carboethoxymethylperfluorononyl ether (IIIa)

Perfluoropelargonyl fluoride (4.7 g, 0.01 mol) was added dropwise to a suspension of freshly dried diglyme (15 mL) and 15 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 dry diglyme was added. The reaction mixture was stirred at 20°C for 15 h. (According to the amount of the alkylation product and ethylfluoroacetate appeared in the reaction mixture). The mixture was stirred at 50-55°C for 60 h and poured into ice water; the lower layer was separated and dissolved in ether, and was washed with a solution of NaHCO₃, and dried over MgSO₄. The ether was removed, and the residue was distilled to give 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): 50.5 m (CF₂); -4 to 45.8 m (4CF₂); 46.5 m (CF₂); 49.1 m (CF₂); 50.3 m (CF₂). MS : 572 [M]⁺ 0.

$C_2H_3O]^+ 0.8$; $525 [M-F-CO]^+ 3.2$; $500 [M-COOC_2H_4]^+ 1.6$; $499[M-COOC_2H_5]^+ 15.3$; $481 [COO_2H_5]^+ 1.9$; $219 [C_4F_9]^+6.1$; $181 [C_4F_7]^+ 2$; $169 [C_3F_7]^+ 7.5$; $131[C_3F_5]^+ 9.5$; $125 [100 [C_2F_4]^+ 4.1$; $87[CH_2COOC_2H_5]^+ 7.6$; $69 [CF_3]^+ 22$; $59 [C_3H_7]^+ 18.6$; $45 [C_2H_5O]^+ 3.1$; $[C_2H_5]^+ 16.0$; $27 [C_2H_3]^+$

Synthesis of carboethoxymethylperfluorobutyl ether (IIIb)

Perfluorobutyryl chloride (4.65 g, 0.02 mol) was added dropwise to a suspension of freshly distilled diglyme (100 ml) and the mixture was stirred at 20°C for 16 h. Then a solution of 3.34 g (0.02 mol) of dry diglyme was added. The reaction mixture was stirred at 20°C for 100 h and poured into ice water. The ether solution was separated and dissolved in ether. The ether solution was washed with a NaHCO₃ solution, water, and the residue was removed, and the residue was distilled to yield ether (1.2 g, 18%), b.p. 72-74°C/15 mm Hg. 1H NMR (CDCl₃): 4.61 q (CH₂); 4.9 s (CH₂); J(H-H) = 7.6 Hz. ^{19}F NMR (CCl₄): 5.0 t (CF₃); J(F-F)=9.9 Hz; 9 m (C). MS (m/z, intensity, %): 322 [M]⁺ 0.7; 293 [M-C₂F₅]⁺ 2.1; 279 [M-C₂H₃O]⁺ 3.5; 275 [M-F-C₂H₅]⁺ 3.5; 249[M-COOC₂H₅]⁺ 42; 231 [M-F-COOC₂H₄]⁺ 1.15; 230 [M-F-COO₂H₅]⁺ 2.4; 219 [C₄F₉]⁺ 13.8; 125 [M-C₉F₁₇O]⁺ 3.2; 119[C₂F₅]⁺ 2.5; 100 [C₂F₄]⁺ 5; 87 [CH₂COOC₂H₅]⁺ 6.3; 69 [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 perfluoroisobutyl fluoride (11,3g; 0,05 mole) was added dropwise and stirred at ca. 20°C. After 1 h. a solution of DMS (8,9g; 0,07 mole) was added dropwise and reaction mixture was stirred for 10 h. at 20°C. The reaction mixture was separated and washed with water and dried over MgSO₄. Distillation afforded ether (IVa) (4,1g; 31%) B.p. 113-114°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 perfluoroisobutyl fluoride (11,3g, 0,05 mole), CsF (15,2g, 0,1 mole) and DMS (6,3g, 0,05 mole). Reaction mixture was stirred 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 perfluoroisobutyl fluoride (11,3g; 0,05 mole) was added dropwise and stirred at 20°C. After 1 h a solution of DMS (25,2g; 0,2mole) 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: -10,2 t[(CF₃)₂C]; J F-F =10,5 Hz; J H-F=7,5 Hz

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