A Facile Synthesis of Partly-fluorinated Ethers Using Perfluoropropoxyethylene and Aliphatic Alcohols

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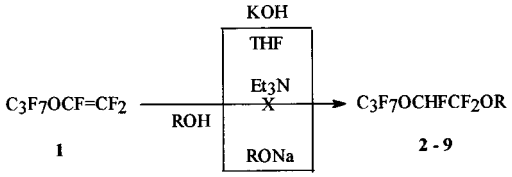
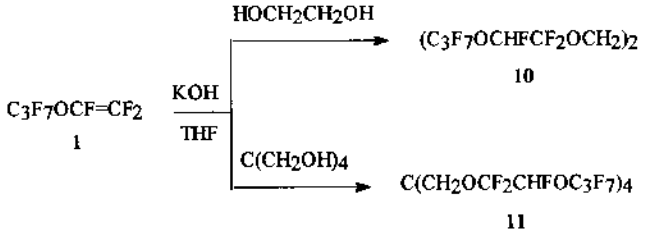
Perfluorinated dialkyl ethers have been classified as a nonflammable and/or lubricating substance with an excellent thermal and oxidative stability, a low melting point and a good temperature-viscosity characteristic.[1-3] These liquids are useful for the preservation of internal organs due to their high oxygen content and also good for a solvent in electronic industry. In addition, low molecular weight perfluorinated ethers are used for various applications such as vapor phase soldering fluids, thermal shock fluids and inert fluids. However, it has not been easy to prepare perfluorinated ethers since direct fluorination of hydrocarbon precursors with F_2 or by electrochemical fluorination method produced perfluorinated ethers in poor yields.[4,5] Only recently, highly-branched perfluoroethers, perfluorocrown ethers and perfluorocryptands were successfu-ly prepared by liquid-phase direct fluorination with elemental fluorine.[6] Unfortunately, the liquid-phase fluorination method also has some restriction on the versatility and solubility of precursors. It should be underscored, however, that perfluorination of partly-fluorinated precursors has a number of advantages over perfluorination of non-fluorinated ones. With partly-fluorinated compounds, it has been known that reduction of decomposition as well as control for the extent of fluorination is possible during a perfluorination process. Thus, partly-fluorinated compounds must be potential precursors for the effective synthesis of perfluorinated materials. On the other hand, partly-fluorinated compounds are not readily accessible either since only few general methods have been published for their synthesis.[7,1b]

In this paper, we would like to report a new method for the synthesis of partly-fluorinated dialkyl ethers starting with commercially available perfluoropropoxyethylene (**1**)[8,9] and aliphatic alcohols. Reactions of **1** with various alcohols (methanol, ethanol, 2,2,2-trifluoroethanol, propanol, iso-propanol, n-butanol, iso-butanol, 2-methoxyethanol) in the presence of KOH in THF effectively provide the partly-fluorinated ethers **2-9** in good yields. Dioxane or acetonitrile can be substituted for THF as a solvent in this reaction. The similar result is also obtained by the treatment of **1** with sodium alkoxide in the excess amount of a corresponding alcohol. Our methods are easier and more convenient than previous methods with potassium *tert*-butoxide[10] in DMF or NaH[11] in an alcohol. However, triethylamine is not effective as a base to produce an addition product starting with **1** and alcohols.

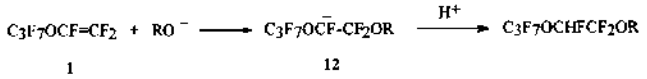
This method can be also applicable for the synthesis of partly-fluorinated ethers with ethylene glycol or pentaerythritol. The change of alkyl group in alcohols has practically no effect on the composition of reaction products.



2, R = Me; **3**, R = Et; **4**, R = n-Pr;
5, R = i-Pr; **6**, R = n-Bu; **7**; R = i-Bu;
8, R = CF_3CH_2; **9**, R = $CH_3OCH_2CH_2$;



It is quite plausible to assume the following reaction mechanism for the addition process. An alkoxide anion attacks on the terminal carbon of **1** to form the carbanion **12**. In the presence of a proton source, the carbanion **12** reacts with a proton to end up with an addition product.



In short, reactions of perfluoropropoxyethylene with aliphatic alcohols in the presence of equimolar amounts of KOH in THF or with sodium alkoxides in corresponding alcohols effectively provide various partly-fluorinated ethers. The partly-fluorinated ethers **2-11** are expected to be used as excellent precursors for a perfluorination reaction.

Experimental Section

^{19}F NMR spectra were recorded at 282.2 MHz with a Varian UNITYplus-300 spectrometer and obtained in the presence of C_6F_6 as an internal standard. ^{13}C and ^{1}H NMR spectra were measured with a Bruker AM-300 spectrometer (75.4 and 300.1 MHz, respectively) in ppm using tetramethylsilane as an external standard in neat liquids (J_{CH} not recorded). IR spectra were obtained on a Mattson 5000 FTIR (NICAM) spectrometer (5% in CCl_4). Mass spectra were run on a JEOL LMS-DX 303 spectrometer. GC/MS data were checked using a 4.8 cm x 0.32 cm column packed

Table 1. Yields, Boiling Points, and Elemental Analysis Data of the Partly-fluorinated Ethers **2-11**

Compound	Yield.* %	b.p., °C	Found, % C H F	Fumula	Calculated, % C H F
2	65(79)	79-80	24.01 1.44 63.56	$C_6H_4F_{10}O_2$	24.16 1.34 63.75
3	92(80)	92-93	27.31 1.93 60.72	$C_7H_6F_{10}O_2$	26.92 1.92 60.90
4	95(84)	113-114	29.48 2.38 58.14	$C_8H_8F_{10}O_2$	29.44 2.45 58.28
5	96(82)	105-106	29.68 2.46 58.20	$C_8H_8F_{10}O_2$	29.44 2.45 58.28
6	92(77)	109-110	32.05 3.17 56.34	$C_9H_{10}F_{10}O_2$	31.76 2.94 55.88
7	94(85)	120-121	31.77 3.05 55.63	$C_9H_{10}F_{10}O_2$	31.76 2.94 55.88
8	93(94)	95-96	22.98 0.96 67.95	$C_7H_5F_{13}O_2$	22.95 0.82 67.49
9	95(98)	134-135	28.42 2.56 55.34	$C_{10}H_{10}F_{10}O_3$	28.07 2.34 55.56
10	(78)	154-155	24.24 1.29 63.21	$C_{12}H_6F_{20}O_4$	24.24 1.01 63.97
11	(75)	130-132 0.3	25.45 1.01 63.38	$C_{25}H_{12}F_{40}O_8$	25.00 1.01 63.33

* Method A(Method B).

Table 2. ^{19}F and ^1H NMR Data of the Partly-fluorinated Ether **2-11**

1 2 3 4 5
$CF_3CF_2CF_2OCHFCF_2OR$

R	F^1	F^2	F^3 AB-system	F^4	F^5 AB-system	H^4	H^6	H^7	H^8	H^9
	($^2J_{FF}$)		($^1J_{FF}$)	($^1J_{FH}$, $^2J_{FF}$)	($^1J^{FF}$)	(^1J, $^2J_{HF}$)	(J_{HH})			
6 CH_3	82.2 (7)	34.1	79.0 76.8 (145)	19.3 (53, 7)	70.7	5.85 (53, 3)	3.62			
6 7 CH_2CH_3	82.4 (7)	34.0	79.0 76.7 (149)	19.2 (53, 7)	73.8 73.3 (149)	5.84 (53, 3)	4.05 (7)	1.32		
6 7 8 $CH_2CH_2CH_3$	82.1 (7)	33.9	78.8 76.5 (145)	19.0 (54, 7)	74.0 73.1 (145)	5.77 (54, 3)	3.94 (7)	1.69	0.95	
6 7 $CH(CH_3)_2$	82.1 (7)	33.8	76.9 78.4 (149)	19.0 (57, 7)	76.2 74.7 (148)	5.75 (57, 3)	4.62 (7)	1.27		
6 7 8 9 $CH_2CH_2CH_2CH_3$	82.0 (7)	33.8	78.8 75.6 (149)	19.2 (54, 7)	73.8 73.0 (149)	5.78 (54, 3)	3.95 (7)	1.61	1.41	0.93
6 7 8 $CH_2CH(CH_3)_2$	82.5 (7)	34.2	79.1 76.9 (149)	19.5 (54, 7)	74.6 73.3 (145)	5.78 (54, 3)	3.71 (6)	1.91	0.93	
6 7 CH_2CF_3	82.3 (7)	34.2	79.1 76.7 (141)	19.1 (50, 7)	73.8 72.4 (151)	5.96 (50, 3)	4.29 (8)	88.5		
6 7 8 $CH_2CH_2OCH_3$	82.2 (7)	34.0	79.0 77.0 (149)	19.1 (54, 7)	73.5	6.00 (54, 3)	4.06 (7)	3.54	3.30	
6 CH_2CH_2	82.3 (7)	34.1	79.0 76.7 (149)	19.3 (54, 7)	73.7 73.0 (153)	5.85 (54, 3)	4.14 (7)			
6 7 $(CH_2)_4C$	81.6 (7)	33.4	78.2 76.2 (149)	18.6 (54, 7)	73.1 71.5 (149)	5.91 (54, 3)	4.07			

with 10% OV-202 on 100-200 mesh Gas Chrom RZ. Reactions were routinely monitored with the aid of ^{19}F NMR spectroscopy. All chemicals were of analytical grade and used without further purification. Tetrahydrofuran was distilled from sodium benzophenone ketyl. The yields, boiling points and elemental analysis data of the new ethers **2-11** are shown in Table 1. The ^1H, ^{19}F and ^{13}C NMR spectral data of the new products **2-11** are also shown in Table 2 and 3. In ^{19}F NMR spectra, there are 5 signals from the structure of $CF_3CF_2CF_2O$-$CHFCF_2$ with 3 : 2 : 2 : 1 : 2 intensity. And the signals of F^3 and F^5 atoms represent AB-system; F^{3a}-dtt (145-149 Hz for J with F^{3b}, 7 Hz for J with F^4 and H^4, 7 Hz for J with F^5), F^{3b}-dqt (145-149 Hz for J with F^{3a}, 7 Hz for J with F^4, 7 Hz for J with F^4 and H^4), F^2-singlet, F^4-dtt (53-57 Hz for J with F^4 and H^4, 7 Hz for J with F^5, 7 Hz for J with F^3), F^1-t (7 Hz for J with F^3).

Typical procedures for the preparation of partly-fluorinated ethers. Method A: To a solution of 1 (10.0 g, 0.037 mol) in THF (15 mL) at 0 °C was slowly added 1 M solution of C_2H_5ONa in ethanol (38 mL) for 0.5 h. The reaction mixture was stirred at 25 °C overnight and the resulting solution was diluted with water (200 mL). The organic phase was separated, washed with water (50 mL) and dried over anhydrous $MgSO_4$. The crude product was distilled to give 3 (10.8 g, 92%) as a colorless liquid: b.p. 92-93 °C; IR (5% in CCl_4) 2995, 2985 (saturated CH), 1240-1091 (C-F) cm^{-1}; GC/MS 311 $[M-H]^+$, 297 $[M-CH_3]^+$, 293 $[M-F]^+$, 169 $[C_3F_7]^+$, 127 $[M-OC_3F_7]^+$, 95 $[CF_2OC_2H_5]^+$, 69 $[CF_3]^+$, 45

Table 3. ^{13}C NMR Data of the Partly-fluorinated Ethers **2-11**

1 2 3 4 5
$CF_3CF_2CF_2OCHFCF_2OR$

R	C¹ ($^1J, ^3J_{CF}$)	C² ($^1J, ^3J_{CF}$)	C³ ($^1J, ^3J_{CF}$)	C⁴ ($^1J, ^3J_{CF}$)	C⁵ ($^1J, ^3J_{CF}$)	C⁶	C⁷ ($^1J_{CF}$)	C⁸	C⁹
6 CH_3	117.5 (311.33)	106.8 (267.39)	115.9 (280.32)	98.1 (238.42)	117.8 (266.28)	49.5			
6 7 CH_2CH_3	118.0 (286.33)	107.6 (266.39)	116.6 (280.31)	99.0 (243.42)	118.4 (266.28)	60.9	14.0		
6 7 8 $CH_2CH_2CH_3$	117.2 (283.33)	106.5 (267.39)	115.6 (283.33)	97.8 (243.42)	117.3 (266.28)	65.4	21.5	8.3	
6 7 $CH(CH_3)_2$	117.7 (286.33)	106.5 (266.38)	114.2 (287.38)	97.9 (243.43)	117.5 (266.28)	69.7	21.5		
6 7 8 9 $CH_2CH_2CH_2CH_3$	117.0 (286.33)	106.9 (267.39)	114.1 (280.30)	97.8 (243.43)	117.3 (266.28)	63.6	30.4	17.9	11.7
6 7 8 $CH_2CH(CH_3)_2$	117.0 (286.33)	106.5 (266.39)	115.6 (279.31)	97.8 (243.43)	117.3 (266.28)	69.8	27.5 17		
6 7 CH_2CF_3	117.0 (317.31)	106.8 (266.38)	115.2 (280.34)	97.6 (244.41)	117.2 (270.30)	60.7	122.1 (270)		
6 7 8 $CH_2CH_2OCH_3$	117.0 (286.33)	106.6 (267.39)	115.6 (282.30)	97.9 (243.42)	117.4 (267.29)	69.5	63.3	57.2	
6 CH_2CH_2	117.4 (313.33)	106.8 (267.39)	115.8 (280.30)	97.8 (243.41)	117.5 (268.29)	61.7			
6 7 $(CH_2)_3C$	117.9 (286.33)	107.4 (267.39)	116.5 (281.31)	98.4 (244.42)	117.9 (269.29)	61.3	43.2		

$[OC_2H_5]^+$, 29 $[C_2H_5]^+$ (100); HRMS(EI) Calcd. 311.0129 for $C_5H_5F_{10}O_2$ $[M-H]^+$ found 311.0128. **Method B:** To a solution of 1 (17.5 g, 0.066 mol) and 2,2,2-trifluoroethanol (6.6 g, 0.066 mol) in THF (45 mL) at 0 °C was added KOH (4.0 g, 0.071 mol). The reaction mixture was stirred at 25 °C overnight and the resulting solution was diluted with water (200 mL). The organic phase was separated, washed with water (50 mL) and dried over anhydrous $MgSO_4$. The crude product was distilled to give 8 (22.7 g, 94%) as a colorless liquid: b.p. 95-96 °C; GC/MS 347 $[M-F]^-$, 297 $[M-CF_3]^+$, 217 $[C_3F\text{-}OCHF]^-$, 181 $[M-OC_3F\text{-}]^+$, 169 $[C_3F\text{-}]^-$, 149 $[CF_3CH_2OCF_2]^+$, 131 $[M-CF_2, OC_3F\text{-}]^-$, 119 $[C_2F_5]^+$, 100 $[CF_2{=}CF_2]^-$, 83 $[CH_2CF_3]^-$ (100), 69 $[CF_3]^+$, 29 $[CHO]^-$.

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