Russian Journal of Applied Chemistry, Vol. 77, No. 9, 2004, pp. 1561-1563. Translated from Zhurnal Prikladnoi Khimii, Vol. 77, No. 9, 2004, pp. 1573-1574.

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## BRIEF **COMMUNICATIONS**

# Synthesis of Di(polyfluoroalkyl) Ethers

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Received July 6, 2004

Abstract—New procedures for preparing di(polyfluoroalkyl) ethers by reactions of polyfluoropropyl chlorosulfonites with polyfluorinated alcohols were tested.

Polyfluorinated dialkyl ethers are promising ozonefriendly and moderately toxic solvents [1]. In particular, tetrafluoroethyl difluoromethyl ether and its closest homolog, di(tetrafluoropropyl) ether can be used instead of perfluorohydrocarbons for dry etching in microelectronics [2], and, with subsequent electrochemical afterfluorination in anhydrous HF, these compounds can be recommended for cleaning of electronic circuits and as polymerization media [3-5]. Polyfluorinated ethers of higher molecular weight are used as compression, motor, and vacuum oils [6].

Alkyl polyfluoroalkyl ethers are prepared by addition of polyfluorinated alcohols to alkenes and fluoroalkenes [1, 7] and by alkylation of alcoholates derived from polyfluorinated alcohols with alkyl halides [8, 9].

We suggest a procedure for preparing polyfluorinated ethers from available raw materials, polyfluorinated alcohols and thionyl chloride, via intermediate polyfluoroalkyl chlorosulfonites [10]. This procedure is environmentally safe and economically attractive, as its cost is determined by the cost of polyfluorinated alcohols (some of them are production wastes) and thionyl choride and by small production expenditures.

With the aim to extend the homologous series of symmetrical and unsymmetrical di(polyfluoroalkyl) ethers, we suggested catalytic and noncatalytic procedures based on reactions of polyfluoroalkyl chlorosulfonites with polyfluorinated alcohols. The catalytic reaction (1) is performed in the presence of dimethylformamide (DMF) as catalyst, and the noncatalytic reaction (2), in the presence of triethylamine:

$$R_{F}CH_{2}OS(O)Cl + R_{F}'CH_{2}OH \xrightarrow{DMF} R_{F}CH_{2}OCH_{2}R_{F}' + SO_{2}$$
  
+ HCl, (1)

$$R_{F}CH_{2}OS(O)Cl + R'_{F}CH_{2}OH \xrightarrow{NEt_{3}} R_{F}CH_{2}OCH_{2}R'_{F} + SO_{2}$$
$$+ NEt_{3} \cdot HCl, \qquad (2)$$

where  $R_F = R'_F = H(CF_2CF_2)_2$  (I),  $HCF_2CF_2$  (II),  $H(CF_2CF_2)_3$  (III),  $R_F = HCF_2CF_2$ ,  $R'_F = H(CF_2CF_2)_2$ (IV),  $\mathbf{R}_{F} = \mathbf{H}\mathbf{C}\mathbf{F}_{2}\mathbf{C}\mathbf{F}_{2}$ ,  $\mathbf{R}_{F} = \mathbf{H}(\mathbf{C}\mathbf{F}_{2}\mathbf{C}\mathbf{F}_{2})_{3}$  (V),  $\mathbf{R}_{F} =$  $HCF_2CF_2$ ,  $R'_F = H(CF_2CF_2)_4$  (VI),  $R_F = H(CF_2CF_2)_2$ ,  $R_F = H(CF_2CF_2)_3$  (VII).

In procedure (1), a solution of polyfluoroalkyl chlorosulfonite was added to appropriate alcohol containing DMF (molar ratio from 1: 0.005 to 1: 0.01) at -10°C; the mixture was allowed to stand for 24 h at room temperature. After distilling off the solvent (chloroform, diethyl ether), the product was distilled; yield 59-98%.

In procedure (2), a solution of polyfluoroalkyl chlorosulfonite was added at -10°C to a complex of alcohol with triethylamine, prepared in advance; the resulting mixture (solvent pentane or hexane) was allowed to stand for 24 h at room temperature. The triethylammonium chloride precipitate was filtered off, and the fluorinated ether was distilled; yield 52-85%.

Symmetrical ethers I-III were prepared by reactions of polyfluoroalkyl chlorosulfonites with the related alcohols. The highest yield (98%) was attained with the most reactive tetrafluoropropyl chlorosulfonite in the presence of DMF. With increasing length of the fluorocarbon chain, the yield of di(polyfluoroalkyl) ethers decreases. Tetrafluoropropyl octafluoropentyl ether was obtained in 85% yield, and the yields of the ethers with longer fluorocarbon chains were still lower.

Although both procedures allow preparation of the ethers in similar yields, the catalytic process is preferable because of lower production cost and higher purity of the target product; the triethylammonium salt formed in reaction (2) appreciably contaminates the resulting ether.

#### EXPERIMENTAL

The structures of ethers **I**–**VII** were proved by IR and <sup>1</sup>H NMR spectroscopy. The IR spectra were recorded on a Specord-M82 spectrometer (thin films). The <sup>1</sup>H NMR spectra were taken on a Varian Mercury-300 spectrometer (working frequency 300 MHz, internal reference tetramethylsilane, solvent  $CCl_{\Delta}$ ).

Di(1,1,5-trihydroperfluoropentyl) ether I. (a) A 4.4-g portion of 1,1,5-trihydroperfluoro-1-pentanol was mixed with 0.015 ml of DMF in 15 ml of chloroform and cooled to  $-10^{\circ}$ C; a solution of 5.9 g of 1,1,5-trihydroperfluoropentyl chlorosulfonite in 10 ml of chloroform was added with stirring, with the temperature maintained at  $-10^{\circ}$ C. Then the mixture was allowed to warm up to 20°C and was kept at this temperature for 2 h, with bubbling of dry air to remove the released hydrogen chloride. After that, the mixture was allowed to stand for 24 h at room temperature. The solvent was distilled off, and the product was distilled in a vacuum. Yield of I 4.5 g (59%), bp 103°C (2 mm Hg),  $n_D^{20}$  1.3385,  $d_4^{20}$  1.7344. IR spectrum, v, cm<sup>-1</sup>: 1137 s (vC–O–C), 1176 s (vCF<sub>2</sub>), 2860 w, 2946 m (vCH<sub>2</sub>), 3016 w (vCHF<sub>2</sub>).

(b) A 5.0-g portion of 1,1,5-trihydroperfluoro-1pentanol was mixed with 2.1 of triethylamine in 15 ml of hexane and cooled to  $-10^{\circ}$ C; a solution of 6.7 g of 1,1,5-trihydroperfluoropentyl chlorosulfonite in 10 ml of hexane was gradually added with stirring, with the temperature maintained at  $-10^{\circ}$ C. Then the mixture was allowed to warm up to 20°C and to stand at this temperature for 24 h. The precipitated salt was filtered off, the solvent was distilled off, and the product was vacuum-distilled. Yield of **I** 5.2 g (52%).

Compounds **II**–**VII** were prepared similarly to **I** by procedure (a) or (b).

**Di**(1,1,3-trihydroperfluoropropyl) ether II. Procedure (a). Yield 98%, bp 65°C (1 mm Hg),  $n_D^{20}$  1.3575,  $d_4^{20}$  1.6251. IR spectrum, v, cm<sup>-1</sup>: 1111 s.br (vC–O–C), 1223 s (vCF<sub>2</sub>), 2850 m, 2920 m, 2960 m (vCH<sub>2</sub>), 3008 w (vCHF<sub>2</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm (*J*, Hz): 5.803 t.d (H<sup>1</sup>, H<sup>6</sup>; *J* 52.8, 3.3), 4.274 q (H<sup>3</sup>, H<sup>4</sup>, *J* 13.2).

**Di**(1,1,7-trihydroperfluoroheptyl) ether III. Procedure (a). Yield 57%, bp 130°C (1 mm Hg),  $n_D^{20}$  1.3370,  $d_4^{20}$  1.8014. IR spectrum, v, cm<sup>-1</sup>: 1124 s (vC–O–C), 1249 s (vCF<sub>2</sub>), 2860 w, 2980 m (vCH<sub>2</sub>), 3024 w (vCHF<sub>2</sub>).

1,1,5-Trihydroperfluoro-1-(1,1,3-trihydroperfluoropropyloxy)pentane IV. Procedure (b). Yield 85%, bp 83°C (2 mm Hg),  $n_D^{20}$  1.3500,  $d_4^{20}$  1.6790. IR spectrum, v, cm<sup>-1</sup>: 1116 s (vC–O–C), 1242 s (vCF<sub>2</sub>), 2860 w, 2934 w, 2980 m (vCH<sub>2</sub>), 3017 w (vCHF<sub>2</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm (*J*, Hz): 5.966 t.t (H<sup>8</sup>, *J* 51.6, 5.4), 5.810 t.t (H<sup>1</sup>, *J* 52.1, 3.8), 4.432 t (H<sup>3</sup>, *J* 13.2), 4.255 t (H<sup>4</sup>, *J* 12.6).

**1,1,7-Trihydroperfluoro-1-(1,1,3-trihydroperfluoropropyloxy)heptane V.** Procedure (b). Yield 51%, bp 95°C (1 mm Hg),  $n_D^{20}$  1.3450,  $d_4^{20}$  1.7310. IR spectrum, v, cm<sup>-1</sup>: 1116 s (vC–O–C), 1223 s (vCF<sub>2</sub>), 2868 w, 2937 w, 2968 m (vCH<sub>2</sub>), 3014 w (vCHF<sub>2</sub>).

**1,1,9-Trihydroperfluoro-1-(1,1,3-trihydroperfluoropropyloxy)nonane VI.** Procedure (a). Yield 34%, mp 49°C, bp 130°C (1 mm Hg). IR spectrum, v, cm<sup>-1</sup>: 1120 s (vC–O–C), 1216 s (vCF<sub>2</sub>), 2856 m, 2894 w, 2932 m (vCH<sub>2</sub>), 2954 w (vCHF<sub>2</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm (*J*, Hz): 5.975 t.t (H<sup>1</sup>, H<sup>12</sup>, *J* 52, 5.1), 4.359 t (*J* 16.6) and 4.331 t (*J* 12.3) (H<sup>3</sup>, H<sup>4</sup>).

**1,1,7-Trihydroperfluoro-1-(1,1,5-trihydroperfluoropentyloxy)heptane VII.** Procedure (a). Yield 62%, bp 110°C (1 mm Hg),  $n_D^{20}$  1.3380,  $d_4^{20}$  1.7647. IR spectrum, v, cm<sup>-1</sup>: 1120 s (vC–O–C), 1220 s (vCF<sub>2</sub>), 2864 w, 2932 m, 2961 m (vCH<sub>2</sub>), 3009 w (vCHF<sub>2</sub>).

### CONCLUSION

A catalytic reaction of polyfluorinated alcohols with polyfluoroalkyl chlorosulfonites in the presence of DMF allows preparation of the corresponding di(polyfluoroalkyl) ethers in 59–98% yield.

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