Russian Journal of Applied Chemistry, Vol. 77, No. 1, 2004, pp. 98–101. Translated from Zhurnal Prikladnoi Khimii, Vol. 77, No. 1, 2004, pp. 102–105.
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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis and Use of Partially Fluorinated Dialkyl Ethers Derived from Hexafluoropropylene

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Received June 19, 2003

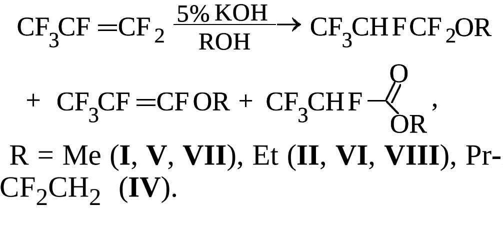
Abstract—A procedure was developed for preparing partially fluorinated dialkyl ethers by the reaction of hexafluoropropylene with aliphatic and polyfluorinated alcohols in the presence of KOH. On treatment with concentrated sulfuric acid, these ethers form alkyl esters of acids, and on treatment with KOH, alkenyl ethers.

The problems in development of new ozone-friendly solvents are largely determined by the need in replacement of Freon 113, widely used as solvent. The main drawback of this Freon is that hydrocarbon oils are limitedly or poorly soluble in it, and organofluorine and organosilicon liquids are insoluble. Major efforts in this direction have not led to success. Orlov *et al.* [1] suggested as one of alternatives hexafluorocyclobutane, which is an efficient solvent for various azeotropic compositions. This compound can be prepared on the commercial scale from dichlorohexafluorocyclobutane, which, in turn, is obtained by dimerization of trifluorochloroethylene. At the same time, partially fluorinated dialkyl ethers are also of interest. The 3M company developed Freon HFE 7110, $CH_3OCF_2CF_2CF_2CF_3$, but it also has certain drawbacks, whereas tetrafluoroethyl difluoromethyl ether $CHF_2CF_2OCHF_2$ can replace Freon 11 as a foaming agent in production of foamed plastics and can be used in microelectronics in dry etching instead of perfluorocarbons [2]. Ethers like $C_4F_9OCH_3$ (bp 61°C), $(CF_3)_2CFCF_2OC_2H_5$, and others, used for extraction of lavender essential oils, showed good performance with respect to the quality of the extracted product and the purity of the oils obtained therefrom [3]. These ethers were used as solvents in chemical reactions, in particular, in synthesis of amides derived from fluoropolyalkyl ethers for magnetic reproducing media [4] and in oxidation of tetrafluoroethylene [5].

Partially fluorinated ethers were prepared by reactions of hexafluoropropylene with alcohols in the presence of alkali [6, 7] or with metal alcoholates in toluene [8], dioxane [9], or methanol [10]. Polyoxaalkylene glycols add to hexafluoropropylene in the presence of water traces across the olefin double bond; the resulting adducts are used as compression, motor, and vacuum oils [11]. Fully fluorinated dialkyl ethers prepared by reactions of octafluoroisobutylene with alcohols, followed by further electrochemical fluorination in anhydrous HF, e.g., $(CF_3)_2CFCF_2OC_nF_{2n+1}$, are used as solvents for cleaning electronic circuits, as refrigerants, as foaming agents, and as polymerization media [12–14].

The goal of this study was to develop a commercially acceptable procedure for synthesis of partially fluorinated dialkyl ethers from available and relatively cheap hexafluoropropylene and to examine the possibilities of using these ethers as ozone-friendly solvents and as intermediates in organofluorine synthesis.

When gaseous hexafluoropropylene is passed at 20–40°C through alcohols containing catalytic amounts of sodium alcoholates or alkalis (the reaction can also be performed in a pressure vessel), the alcohol adds across the double bond. The reaction pathway only slightly depends on the conditions. The by-products are alkenyl ethers formed by substitution of the terminal fluorine atom at the double bond by alkoxy groups and alkyl 2,3,3,3-tetrafluoropropionates; their amount does not exceed 5% (cf. data from [15]):



$$CF_3CF{=}CF_2 \xrightarrow[ROH]{5\%\,KOH} CF_3CHFCF_2OR + CF_3CF{=}CFOR + CF_3CHF{-}C(=O)OR,$$

where R = Me (**I**, **V**, **VII**), Et (**II**, **VI**, **VIII**), Pr-*i* (**III**), $CHF_2CF_2CH_2$ (**IV**).

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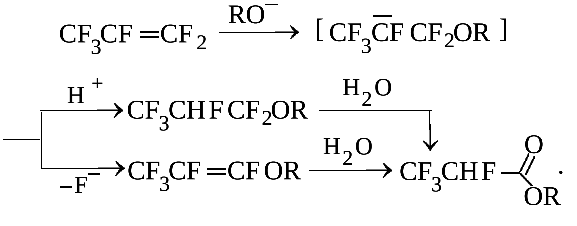
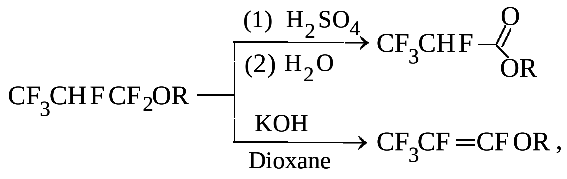
Table 1. ^{1}H, ^{13}C, and ^{19}F NMR spectra of new partially fluorinated dialkyl ethers

Compound	^{1}H NMR spectrum, δ_{H}, ppm (*J*, Hz)	^{13}C NMR spectrum, δ_{C}, ppm ($J_{\mathrm{C-F}}$, Hz)	^{19}F NMR spectrum, δ_{F}, ppm (*J*, Hz)
I	4.72 td (H^2, 36.4, 9.2), 3.63 (H^4)	120.4 (C^1, $^{1}J_{\mathrm{CF}}$ 255.9, $^{2}J_{\mathrm{CF}}$ 25.5), 118.8 (C^3, $^{1}J_{\mathrm{CF}}$ 249.9, $^{2}J_{\mathrm{CF}}$ 45.1), 87.6 (C^2, $^{1}J_{\mathrm{CF}}$ 200.6, $^{2}J_{\mathrm{CF}}$ 35.9), 50.0 (C^4, $^{3}J_{\mathrm{CF}}$ 7.1)	88.4 (F^1), *AB* system (F^3) 80.4 and 77.7 (J_{FF} 151.6), –48.2 (F^2)
II	4.71 td (H^2, 43.2, 5.5), 4.03 (H^4, 7.1), 1.29 (H^5, 7.1)	120.3 (C^1, $^{1}J_{\mathrm{CF}}$ 280.0, $^{2}J_{\mathrm{CF}}$ 25.4), 118.7 (C^3, $^{1}J_{\mathrm{CF}}$ 265.9, $^{2}J_{\mathrm{CF}}$ 25.4), 85.1 (C^2, $^{1}J_{\mathrm{CF}}$ 200.0, $^{2}J_{\mathrm{CF}}$ 35.7), 60.7 (C^4, $^{2}J_{\mathrm{CF}}$ 6.2), 14.2 (C^5)	87.5 (F^1), *AB* system 83.5 and 80.5 (J_{FF} 153.4), –48.3 (F^2)
III	4.66 (H^2, 50), 4.65 (H^4, 6.5), 1.29 (H^{5,6}, 6.5)	120.1 (C^1, $^{1}J_{\mathrm{CF}}$ 309.8, $^{2}J_{\mathrm{CF}}$ 26.0), 118.7 (C^3, $^{1}J_{\mathrm{CF}}$ 277.3, $^{2}J_{\mathrm{CF}}$ 21.9), 85.2 (C^2, $^{1}J_{\mathrm{CF}}$ 200.3, $^{2}J_{\mathrm{CF}}$ 37.6), 77.7 (C^4), 22.8 (C^{5,6})	88.2 (F^4), *AB* system 85.9 and 82.1 (J_{FF} 152.5), –48.1 (F^2, J_{FH} 40, J_{FF} 12.5)
IV	4.29 t (H^4, 50), 4.65 (H^2, 6.5), 1.29 (H^{5,6}, 6.5)	119.9 (C^1, $^{1}J_{\mathrm{CF}}$ 281.4, $^{2}J_{\mathrm{CF}}$ 27.6), 114.1 (C^6, $^{1}J_{\mathrm{CF}}$ 220.6, $^{2}J_{\mathrm{CF}}$ 28.0), 109.1 (C^{3,5}, $^{1}J_{\mathrm{CF}}$ 250.1, $^{2}J_{\mathrm{CF}}$ 35.8), 85.0 (C^2, $^{1}J_{\mathrm{CF}}$ 201.9, $^{2}J_{\mathrm{CF}}$ 34.9), 60.5 (C^4, $^{2}J_{\mathrm{CF}}$ 30.8),	88.4 (F^1), *AB* system 38.8 (F^5) and 25.2 (F^6) (J_{FF} 149.7), *AB* system (F^3) 82 and 79.8 (J_{FF} 148.9), –48.4 (F^2)
VII	5.27 (H^2, 44.0, 6), 3.88 (H^4), 1.33 (H^5)	120.5 (C^1, $^{1}J_{\mathrm{CF}}$ 281.9, $^{2}J_{\mathrm{CF}}$ 25.8), 84.1 (C^2, $^{1}J_{\mathrm{CF}}$ 199.5, $^{2}J_{\mathrm{CF}}$ 35.8), 53.3 (C^4)	87.6 (F^1, 8, 12), –41.2 (F^2, 32, 10)
VIII	5.10 (H^2, $^{1}J_{\mathrm{HF}}$ 45, $^{2}J_{\mathrm{HF}}$ 7) 4.36 (H^4, $^{2}J_{\mathrm{HH}}$ 7.1), 1.34 (H^5, $^{2}J_{\mathrm{HH}}$ 7.1)	120.5 (C^1, $^{1}J_{\mathrm{CF}}$ 281.9, $^{2}J_{\mathrm{CF}}$ 27.8), 84.1 (C^2, $^{1}J_{\mathrm{CF}}$ 199.2, $^{2}J_{\mathrm{CF}}$ 35.6), 63.0 (C^4), 13.2 (C^5)	86.5 (F^1, 8, 12), –42.2 (F^2, 45, 10)

The reaction involves the attack of the alkoxy anion at the carbon atom of the hexafluoropropylene double bond, with generation of the intermediate carbanion. This species abstracts the proton from the solvent to form the main reaction product **I**–**IV**. Stabilization of the carbanion by elimination of the fluoride ion from the α-position (from the CF_2 fragment) yields the product of formal substitution of fluorine at the double bond (compounds **V**, **VI**). The hydrogen fluoride released in the process reacts with the alkali, and water participates in formation of the addition product and can induce hydrolysis of both by-products **V**, **VI** and target products **I**–**IV**. This is suggested by isolation of HF from the mixture of reaction products and formation of alkyl 2,3,3,3-tetrafluoropropionates **VII** and **VIII**:



Indeed, heating of **I** and **II** with concentrated sulfuric acid at 40°C for 1 h, followed by treatment of the reaction mixture with water, causes formation of compounds **VII** [6] and **VIII** in quantitative yield, and heating with solid KOH in dioxane affords **V** and **VI**:



where R = Me or Et.

The structures of the new compounds were confirmed by ^{1}H, ^{13}C, and ^{19}F NMR (Table 1), IR, and mass spectrometry.

For partially fluorinated dialkyl ethers, telomeric alcohols, and partially fluorinated carboxylic acid ester, we evaluated the toxicological parameters. The results are listed in Table 2. It is seen that the compounds belong to hazard class III (moderately toxic) or IV (weakly toxic substances).

Table 2. Some toxicological parameters of organofluorine compounds

Compound	LD_{50}	LD_{100}	Hazard class
	mg kg^{-1}		
$CF_3CHFCF_2OCH_2CF_2CHF_2$	5000		IV
$HCF_2CF_2CH_2OCH_2CH_3$	3420	6000	III
$HCF_2CF_2CH_2OH$	2320	3000	III
$HCF_2CF_2CF_2CF_2CH_2OH$	1180	2000	III
$CF_3CHFC(O)OCH_2H_5$	5000		IV

EXPERIMENTAL

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker WP 400 SY spectrometer (400, 100, and 188 MHz, respectively) relative to internal HMDS and C_6F_6 (J_{CH} was not measured). The IR spectra were taken on a Specord M-80 spectrometer (CCl_4), and the mass spectra (ionizing electron energy 70 eV), on a Hewlett–Packard G 1800 A GCD gas chromatograph with a mass-selective detector [30 m × 0.25 mm capillary column coated with a 0.25-μm layer of 5% diphenylsiloxane–95% dimethylsiloxane copolymer (HP-5); carrier gas helium, 1 ml min^{-1}; vaporizer temperature 280°C; column temperature schedule: 50°C, 2 min; heating to 280°C at a rate of 10 deg min^{-1}; 280°C, 5 min]. The progress of all the reactions was monitored by ^{19}F NMR spectroscopy. The reaction mixtures were analyzed on an LKhM 72 chromatograph (15% SE-30, SKTF-803, QF-1 on Chromosorb W, 4000 × 4-mm column).

The characteristics of the new compounds and analytical data are listed in Table 3.

Synthesis of partially fluorinated dialkyl ethers. (1) A 100-ml flask equipped with a magnetic stirrer, a thermometer, a tube for input of gaseous reactants, and a reflux condenser was charged with 40 ml of absolute methanol, and 1 g of sodium metal was added in portions at room temperature. After complete dissolution of sodium, gaseous hexafluoropropylene was passed at a rate chosen so as to minimize the breakthrough of the gas. The process was performed for 1.5 h, after which the reaction mixture was poured into 300 ml of water and shaken; the lower organic layer was separated and dried over CaCl2. The mixture was analyzed by ^{19}F NMR spectroscopy and gas chromatography–mass spectrometry. The mixture was distilled with collection of the 54–55°C fraction (33 g).

(2) A similar flask was charged with 50 ml of an alcohol (methanol, ethanol, isopropanol, 2,2,3,3-tetrafluoropropanol) and 5 g of KOH. A flow of gaseous hexafluoropropylene was passed at atmospheric pressure; in the process, the mixture warmed up from 20 to 40°C. After the heat release ceased, passing of hexafluoropropylene was stopped, the mixture was poured into 400 ml of cold water and shaken, and the lower organic layer was separated, washed with 100 ml of water, and dried over $CaCl_2$. The products were distilled and analyzed.

(3) A 100-ml rotating autoclave was charged with 10 ml of methanol and 11.2 g of solid KOH; then the autoclave was sealed, and 30 g of hexafluoropropylene was condensed into it through a valve. The autoclave was heated at 50°C for 1 h (the pressure rose to 4 atm), cooled, and opened; the contents were poured into water. Compound **I** was obtained; yield 34.2 g (94%), bp 54–55°C.

Table 3. Characteristics of partially fluorinated dialkyl ethers and analytical data

Compound	Yield, %	T_b, °C	n_D^{20}	d_4^{20}	Found, %			m/z $[M-H]^+$	Formula	Calculated, %			M
					C	H	F			C	H	F	
I	98	54–55	1.3470	1.4200				181	$C_4H_4F_6O$				182
II	99	64–65	1.3460	1.3040	31.79 31.64	3.19 3.05	57.73 57.91	196*	$C_5H_6F_6O$	30.61	3.06	58.16	196
III	88	85–86	1.3230	1.280				210*	$C_6H_8F_6O$				210
IV	87	102–103	1.2930	1.578	26.11 25.88	1.73 1.69	67.11 67.28	282*	$C_6H_4F_{10}O$	25.53	1.42	67.38	282
VII	60	95–96	1.3200	1.358	29.78 30.08	2.46 2.31	46.86 46.61	159	$C_4H_4F_4O_2$	30.00	2.50	47.50	160
VIII	94	103–104	1.3340	1.3040	34.36 34.43	3.44 3.55	44.30 44.67	174*	$C_5H_6F_4O_2$	34.48	3.45	43.68	174

* $[M^+]$.

Hydrolysis of partially fluorinated dialkyl ethers. (1) A 20-ml flask equipped with a magnetic stirrer and a reflux condenser was charged with 15 g of **I** (with **II**, the procedure was similar), and 15 g of concentrated sulfuric acid was added. The mixture slightly warmed up. Then the mixture was heated with stirring for 1 h at 40°C and poured onto 50 g of ice; the organic layer was separated, washed with water, and dried over $CaCl_2$.

By this procedure, we prepared 10 g of compound **VIII** to be used in the subsequent studies as intermediate.

(2) A similar flask was charged with 27 g of SbF_5, and 15 g of **II** was added in portions with stirring, so as to avoid warming up above room temperature. The mixture was stirred at room temperature for 1 h and poured into 50 g of ice; the organic layer was separated, washed with cold water, and dried over $CaCl_2$. The product was distilled, with collection of the fraction boiling at 95–96°C; yield 8 g.

Reaction of KOH with partially fluorinated dialkyl ethers. A 100-ml flask equipped with a magnetic stirrer, a thermometer, and a reflux condenser was charged with 40 g of **I** (with **II**, the procedure was similar) and 50 ml of dry dioxane, after which finely divided KOH was added in portions with stirring at room temperature. The mixture warmed up. Then the mixture was heated with stirring for 2 h at 40°C, and the reaction products were distilled off. Compound **V**: yield 82%, bp 51–52°C, n_D^{20} 1.3208, d_4^{20} 1.3601 (published data [8]: bp 51.5°C/743 mm Hg, n_D^{20} 1.2970, d_4^{20} 1.3595); **VI**: yield 78%, bp 71–72°C, n_D^{20} 1.3210, d_4^{20} 1.2930 (published data [8]: bp 71–72°C/743 mm Hg, n_D^{20} 1.3103, d_4^{20} 1.2884).

CONCLUSIONS

(1) The possibility of preparing partially fluorinated dialkyl ethers by reaction of hexafluoropropylene with alcohols (methanol, ethanol, isopropanol, 2,3,3,3-tetrafluoropropanol) in the presence of KOH was examined. These ethers are formed by addition of an alcohol across the double bond in hexafluoropropylene.

(2) Partially fluorinated dialkyl ethers are converted to alkyl 2,3,3,3-tetrafluoropropionates by treatment with concentrated H_2SO_4 and to alkyl pentafluoropropenyl ethers by treatment with KOH.

ACKNOWLEDGMENTS

The study was financially supported by grant no. 47 (2002) for innovation projects of the Siberian Division, Russian Academy of Sciences.

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