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Features of Catalysis in the Reaction of Polyfluoroalkyl Chlorosulfites with Saturated Monohydric Alcohols

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Abstract—Synthetic opportunities and mechanism of catalysis of the reaction of polyfluororalkylchlorosulfites with saturated monohydric alcohols are considered. Kinetic measurements and quantum-chemical calculations showed that polyfluoroalkylation of these compounds proceeded through the step of complex formation involving reagents and catalyst followed by liberation of hydrogen chloride and sulfur dioxide and formation of polyfluoroalkyl ethers.

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We have shown earlier that polyfluoroalkyl chlorosulfites enter into a reaction with alcohols in the presence of triethylamine affording polyfluoroalkyl alkyl ethers in 41–52 % yield [1, 2]. This method is disadvantageous in several respects: low yields and a contamination by triethylammonium salt of the ether formed.

We developed a catalytic method for the synthesis of such ethers that is attractive by technology and affords product of higher purity.

The most suitable catalyst for the reaction of polyfluoroalkyl chlorosulfites with monohydric alcohols is *N,N*-dimethylformamide (DMF): the polyfluoroalkyl alkyl ethers were obtained in the yield up to 90%. The reaction proceeds along the scheme:

$$\underset{\textbf{Ia–Ic}}{H(CF_2)_nCH_2OS(O)Cl} + ROH \xrightarrow{HC(O)N(CH_3)_2} \underset{\textbf{II–XII}}{H(CF_2)_nCH_2OR} + SO_2 + HCl,$$

n = 2 (**Ia**), n = 4 (**Ib**), n = 6 (**Ic**); R = *p*-Pr, n = 4 (**II**); R = *p*-Bu, n = 2 (**IIIa**), n = 4 (**IIIb**); R = *i*-Bu, n = 2 (**IVa**), n = 4 (**IVb**); R = *n*-C_5H_{11}, n = 2 (**V**); R = *i*-C_5H_{11}, n = 2 (**VIa**), n = 4 (**VIb**); R = *p*-C_6H_{13}, n = 2 (**VIIa**), n = 4 (**VIIb**); R = C_6H_{11} (cyclohexyl), n = 2 (**VIIIa**), n = 4 (**VIIIb**), n = 6 (**VIIIc**); R = $PhCH_2$, n = 2 (**IXa**), n = 4 (**IXb**); R = *p*-Cl-$PhCH_2$, n = 2 (**Xa**), n = 4 (**Xb**); R = *p*-CH_3O–$PhCH_2$, n = 2 (**XIa**), n = 4 (**XIb**); R = *m*-NO_2–$PhCH_2$, n = 2 (**XIIa**), n = 4 (**XIIb**).

The alcohols were introduced into the reaction as complexes with DMF. A solution of polyfluoroalkyl chlorosulfite was charged into a mixture containing alcohol and DMF in the ratio 1 : (0.005–0.01) mol at the temperature –10 to –5°C. Then reaction was performed at 40–50°C for 4–6 h, the sulfur dioxide and hydrogen chloride liberated were flushed with an inert gas or dry air. Physicochemical characteristics and yields of the polyfluoroalkyl alkyl ethers are listed in Table 1.

By the study of influence of the reaction conditions on its occurrence we found that elevating the temperature above 50°C did not lead in the increase in

Table 1. Phisicochemical characteristics of polyfluoroalkyl compounds

Comp. no.	Yield, %	bp, °C (*p*, mm Hg)	d_4^{20}	n_D^{20}
II	87.9	104 (13)	1.4234	1.3705
IIIa	90.0	95 (4)	1.2770	1.4180
IIIv	85.0	102 (4)	1.4165	1.3700
IVa	60.0	95 (3)	1.1020	1.3450
IVb	56.0	106 (3)	1.3040	1.3520
V	80.0[49a]	88 (2)	1.0371	1.3996
VIa	70.0	100 (3)	1.0990	1.3550
VIb	71.0	113 (3)	1.2990	1.3600
VIIa	60.0	100 (2)	1.0870	1.3650
VIIb	55.0	120 (2)	1.2130	1.3480
VIIIa	82.3	95 (3)	1.1005	1.3798
VIIIb	75.5	105 (3)	1.3733	1.3865
VIIIc	65.2	123 (3)	1.4067	1.3891
IXa	85.4	120 (3)	1.5065	1.3580
IXb	83.1	125 (3)	1.6382	1.3730
Xa	90.2	130 (3)	1.4025	1.4580
Xb	85.3	135 (3)	1.5002	1.4100
XIa	70.4	110 (3)	1.2856	1.4440
XIb	63.7	116 (3)	1.3643	1.3995
XIIa	90.0	130 (3)	1.3570	1.4760
XIIb	84.1	140 (3)	1.5002	1.4310

[a] Yield of ether in the presence of triethylamine as catalyst [1].

the product yield, but, on the contrary, decreased it. This is due to a side reaction proceeding at elevated temperature and resulting in a symmetrical polyfluorinated ether:

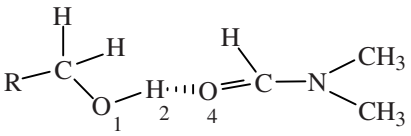
$$2H(CF_2)_nCH_2OS(O)Cl \rightarrow H(CF_2)_nCH_2OCH_2(CF_2)_nH + SO_2 + SOCl_2.$$

This reaction pathway becomes predominant when copper(I) chloride is used as a catalyst [3].

A particular feature of the reaction of chlorosulfites **Ia–Ic** with alcohols is the nucleophilic substitution of the chlorosulfite group by the alkoxy group of the alcohol with simultaneous liberation of hydrogen chloride and sulfur dioxide and formation of polyfluoroalkyl alkyl ether.

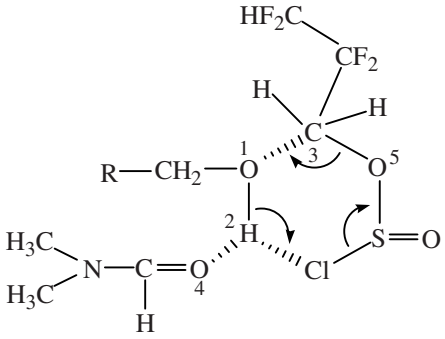
Alcohols possess weak acidic properties, and form with weak base DMF a donor–acceptor complex (associate **XIII**) stable at low temperature.

In the associate **XIII** due to formation of hydrogen bonds the H_2–O_1 bond is polarized. This bond elongates and the proton becomes more labile.



XIII

First step of reaction includes interaction of associate **XIII** with molecule **I**. This results in formation of six-membered complex **XIV** on account of interactions between the atoms $O_1\cdots C_3$ and $H_2\cdots Cl$. The formation of the complex is favored by a high electron density on the chlorine atom and a significant positive charge on the proton in the hydroxy group of the alcohol:



XIV

In the second step complex **XIV** decomposes with H_2 proton transfer from the alcohol to the polar chlorine atom with simultaneous cleavage of C_3–O_5 and S–Cl bonds and the liberation of SO_2 and HCl, regeneration of DMF molecule and the formation of ether:

$$\mathbf{XIV} \rightarrow ROCH_2CF_2CF_2H + (CH_3)_2NCHO + SO_2 + HCl.$$

Introducing to the alcohol molecule of phenyl or another substituent with electron–acceptor effect leads to increase in lability (acidity) of the proton on account of stronger polarization of H_2–O_1 bond. This should result in increased reactivity of the alcohol in the reaction with polyfluoroalkyl chlorosulfite.

The initial reaction rate of the nucleophilic substitution was measured by the rate of formation of hydrogen chloride and sulfur dioxide: by differentiation of the curves of hydrogen chloride and sulfur dioxide evolution at the time $\tau \rightarrow 0$ we determined initial reaction rates of 1,1,5-trihydroperfluoropentyl chlorosulfite (**Ib**) with aliphatic (C_4H_9OH, $C_5H_{11}OH$, $C_6H_{13}OH$), alicyclic (cyclohexanol), and benzyl ($C_6H_5CH_2OH$ and its *p*-CH_3O-, *p*-Cl-, and *m*-NO_2-derivatives) alcohols at 25, 30 and 35°C (Table 2) [4].

Results of mathematical treatment of the obtained kinetic curves [4] are listed in Table 3.

Study of reaction of polyfluoroalkyl chlorosulfites with benzyl alcohols showed that introducing an electron-donor substituent to aromatic ring decreases initial reaction rate considerably as compared with unsubstituted benzyl alcohol (Table 2). The maximal yield is achieved in the case of *m*-nitrobenzyl alcohol (90%), the lowest one with *p*-methoxybenzyl alcohol (70.4%). As seen from Table 3, in going from benzyl alcohol to *m*-nitrobenzyl derivative the reaction rate constant grows 1.5-fold and activation energy falls by 5 kcal mol^{-1} that indicates higher reactivity of the latter compound. The chlorine substituent in the aromatic ring also increases reaction rate constant and decreases the activation barrier. The introduction of a methoxy group, on the contrary, decreases reaction rate constant and increases the activation energy. Thus, it seems obvious, that introducing electron-acceptor substituents to the aromatic ring increases both initial rate and yield of ether as compared with unsubstituted benzyl alcohol on account of increase in the alcohol acidity, while electron–donor substituents, on the contrary, decrease the initial rate and product yield.

Higher acidity of hydroxy group in *m*-nitrobenzyl alcohol as compared with benzyl alcohol leads to higher polarization of H–O bond and to easier formation of associate with DMF that causes the transfer of more labile proton and liberation of HCl and SO_2 molecules at the decomposition of complex **XIV**. Electron-releasing methoxy group, on the contrary, reduces the acidity of the alcohol hydroxy group, that is, decreases the proton mobility and retards the formation of complex **XIV**.

Thus, activation energy is maximal for cyclohexanol and minimal for *m*-nitrobenzyl alcohol.

Table 2. Initial reaction rates of polyfluoroalkyl chlorosulfites with alcohols, v_0, min^{-1}

Alcohol	Polyfluoroalkyl chlorosulfite	Reaction temperature, °C		
		25	30	35
Butan-1-ol	**Ia**	–	0.0326	–
	Ib	0.0189	0.0249	0.0279
Pentan-1-ol	**Ia**	–	0.0235	–
	Ib	0.0140	0.0169	0.0234
Hexan-1-ol	**Ia**	–	0.0128	–
	Ib	0.0087	0.0094	0.0101
Cyclohexanol	**Ia**	–	0.0098	–
	Ib	–	0.0088	–
Benzyl	**Ib**	–	0.0211	–
p-Metoxybenzyl	**Ib**	–	0.0158	–
p-Chlorobenzyl	**Ib**	–	0.0230	–
m-Nitrobenzyl	**Ib**	–	0.0260	–

Hence, the kinetics study confirms the assumption that introducing to alcohol molecule electron-withdrawing groups leads to increase in the reaction rate and decrease in the activation barrier. However, on the one hand, introducing electron–acceptor groups decreases electron density on the oxygen atom that leads to a decrease in the alcohol nucleophilicity and thus retards its association with the carbon atom in polyfluoroalkyl chlorosulfite, and on the other hand, introducing the electron–acceptor group leads to a significant increase in the positive charge on the hydroxy hydrogen atom and to increase in polarity of H–O bond in the alcohol–DMF associate **XIII**, which in turn leads to increase in the proton mobility. Thus, the more mobile proton of the alcohol hydroxy group, the easier its association with chlorine atom, and the reaction proceeds faster.

Table 3. Kinetic parameters of reaction of alcohols with 1,1,5-trihydroperfluoropentyl chlorosulfite

Alcohol	$k\times10^3$, mol l^{-1} s^{-1}			E_a, kcal mol^{-1}	$E_{a(calc)}$, kcal mol^{-1} [a]	*n*
	25°C	30°C	35°C			
Butan-1-ol	0.06	0.21	0.33	31.0	37.05	1.87
Pentan-1-ol	0.04	0.18	0.25	32.2	–	1.69
Hexan-1-ol	0.03	0.14	0.21	33.0	41.53	2.01
Cyclohexanol	0.02	0.08	0.12	42.9	–	–
Benzyl alcohol	0.08	0.25	0.38	25.5	25.3	2.3
p-Metoxybenzyl	0.05	0.21	0.32	28.6	–	–
p-Chlorobenzyl	0.10	0.29	0.40	21.4	–	–
m-Nitrobenzyl	0.10	0.31	0.41	21.05	–	–

[a] Calculated by quantum-chemical ab initio method.

Probably the proton transfer is the limiting factor defining the readiness of formation of the reaction products. For aliphatic alcohols the rate of transfer is low and elongation of aliphatic chain leads to lower acidity of the alcohol resulting in the increase in activation barrier of the reaction. Benzyl alcohols are more acidic, and reaction rate with these alcohols is higher.

Thus, the activity of alcohols falls in the series: butanol–pentanol–hexanol, the hydrocarbon chain elongation leads to the decrease in the initial reaction rate. Maximal yield is reached with butanol and pentanol: 90 and 80 %, respectively. Branching of the alcohol hydrocarbon chain retards reaction and decreases yield, probably due to steric hindrances. The chain elongation to C_6 also decreases yield considerably (to 60%).

We showed experimentally that reaction of polyfluoroalkyl chlorosulfites with secondary alcohols under the same conditions did not occur, probably due to steric hindrances. However, we found that cyclohexanol enters in the reaction affording the ether in high yield (up to 82%). That is understandable in keeping with the features of its structure. The cyclohexanol exists predominantly in a more energetically favorable *chair* conformer with equatorial hydroxy group, more accessible for the reaction with polyfluoroalkyl chlorosulfite, in contrast to the hydroxy group in aliphatic secondary alcohols. Nevertheless, reactivity of cyclohexanol is 1.3-fold below that of hexanol.

By the method of ^{1}H NMR spectroscopy we elucidated structure of six-membered complex **XIV** on the example of reactions of butanol and benzyl alcohols with 1,1,5-trihydroperfluoropentyl chlorosulfite (**Ib**) (Table 4). The spectra were registered at –30°C from solutions in $CDCl_3$, internal reference TMS. For comparison, ^{1}H NMR spectra were also registered of the parent 1,1,5-trihydroperfluoropentyl chloro-sulfites and alcohols. In the spectrum of compound **Ib** appear two triplets corresponding to the protons of methylene groups. By our assumption, the presence of two triplets can be explained by the existence of **Ib** in two conformations differing by the mutual positions of the protons of methylene group relatively to chlorine and oxygen atoms. At low temperatures the conformational transformations are frozen and the proton signals are split. Due to direct interactions of hydrogen atom H_2 in the complex **XIV** with oxygen atom of DMF and chlorine atom of 1,1,5-trihydroperfluoropentyl chlorosulfite, in ^{1}H NMR spectrum occurs downfield shift of the signal of this proton. The signal of CH_2-group protons in **Ib** at the carbon atom entering in the reaction with the oxygen atom bearing extra electron density is shifted upfield as compared with isolated molecule **Ib** evidencing the formation of the complex.

As seen from Table 4 the shifts of signals of the protons involved into formation of the complex and located at a carbon atom depend on the nature of alcohol. For the complex with butanol the shift of methylene group protons of **Ib** is 0.87 ppm, that of hydoxy group proton 0.17 ppm. In the case of benzyl alcohol these shifts are larger: for methylene protons of **Ib** 0.98 ppm, for hydroxy proton 0.29 ppm. This indicates higher polarization of the intermediate complex formed by benzyl alcohol.

The assumed reaction mechanism that includes formation of complex **XIV** allows to relate the alcohol acidity and its reactivity: the increase in the acidity of an alcohol leads to its higher reactivity.

Table 4. ^{1}H NMR spectrum of **XIV**

Complex	Chemical shift, δ and spin–spin coupling constant, *J*					
	HCF_2		$O–CH_2–CF_2$		HO–	Ph–
	δ, ppm	*J*, Hz	δ, ppm	*J*, Hz	δ, ppm	δ, ppm
Complex with butan-1-ol	5.735 t.t	51.9 5.4	3.850 t 3.645 t	14.6 12.6	3.10 s	–
Complex with benzyl alcohol	5.611 t.t	53.1 3.9	3.995 t 3.532 t	15.3 13.2	4.209 s	7.16 m
Ib	5.907 t.t	52.5 3.9	4.065 t 4.515 t	12.0 12.3	–	–
Butan-1-ol	–	–	–	–	2.93 s	–
Benzyl alcohol	–	–	–	–	3.92 s	7.15 m

By quantum-chemical ab initio method with 3-21G basis (from H to Ar) [5] we calculated a model of reaction of 1,1,3-trihydroperfluoropropyl chlorosulfite with various alcohols in the presence of DMF.

Association of alcohol with DMF (**XIII**) proceeds on account of formation of hydrogen bonds between the atoms H_1–O_2 and H_2–O_2 and is energetically advantageous because leads to energy gain matching the value known for hydrogen bonding: ΔE = –3.12 kcal mol^{-1} (butanol), ΔE = –6.10 kcal mol^{-1} (benzyl alcohol).

Formation of six-membered complex **XIV** that includes polyfluoroalkyl chlorosulfite, alcohol and DMF proceeds via interaction between the atoms: H_1–Cl, O_1–C_3. The oxygen atom of alcohol involved into attack at the carbon atom of CH_2-group bears higher electron density than in the parent alcohol, that is, an energy gain is achieved: ΔE = –1.94 kcal mol^{-1} (butanol), ΔE = –2.88 kcal mol^{-1} (benzyl alcohol).

At the thermolysis of six-membered complex the proton of alcohol is transferred to the negatively charged chlorine atom and simultaneously C–O and S–Cl bonds are ruptured with liberation of SO_2 and HCl molecules and regeneration of DMF molecule. This step has an energetic barrier E_a = 38.058 kcal mol^{-1} (butanol) or 25.341 kcal mol^{-1} (benzyl alcohol).

Table 5 shows changes in charges on the atoms involved in the formation of complex **XIV**.

As seen from Table 5 in going from butanol to benzyl alcohol the positive charge on the hydroxy group hydrogen atom rises leading to elongation of H–O bond and increased proton mobility. Simultaneously in going from butanol to benzyl alcohol rises the electron density on the chlorine atom of polyfluoroalkyl chlorosulfite that makes easier association of the hydroxy group proton with the chlorine atom, and this association in turn promotes proton transfer with formation of the hydrogen chloride molecule.

Thus, the quantum-chemical calculation also confirms that introducing electron-acceptor group to the alcohol molecule diminishes considerably energetic barriers and stipulates reaction proceeding on account of increased polarization of O–H bond and the formation of stronger associates with DMF. Reactivity of butanol is much lower owing to weak polarization of O–H bond. Calculated and experimental activation energies (Table 3) are close by value pointing to high probability of the proposed mechanism.

On the basis of these quantum-chemical calculations and kinetic investigations we may conclude that the reaction of polyfluoroalkyl chlorosulfites with alcohols evidently proceeds along the bimolecular mechanism of nucleophilic substitution of chlorosulfite group by alkoxy anion. Introducing electron-acceptor substituents to the alcohol molecule increases the reaction rate and decreases the activation energy. Thus, when the alcohol acidity is higher its reactivity in the catalytic reaction with polyfluoroalkyl chlorosulfite grows.

EXPERIMENTAL

The ^{1}H NMR spectra (300 MHz) were registered on a Varian Mercury-300 instrument, solvents $CDCl_3$ and CCl_4, internal reference tetramethylsilane. IR spectra were registered on a Specord-M82 spectrophotometer from thin liquid film.

Polyfluoroalkyl ethers (II–XII). 0.023 mol of alcohol was mixed with 0.00023 mol of DMF in 20 ml of a solvent (hexane, chloroform, or, in the case of benzyl alcohols, benzene), the mixture was cooled to –5°C and 0.024 mol of polyfluoroalkyl chlorosulfite **Ia–Ic** in 15 ml of solvent was added by portions to the solution at vigorous stirring, maintaining the temperature –5°C. After mixing the reagents, the mixture temperature was increased to 45–50°C, and the mixture was kept for 6 h at continuous passage of inert

Table 5. Changes in atomic charges of the atoms involved in formation of **XIV**

Complex		Charge value				Bond length, Å	
		–C– –CH_2 in **Ia**	–O– of alcohol	–H HO-group of alcohol	–Cl in **Ia**	O–H In alcohol	–S–Cl in **Ia**
With butan-1-ol	initial	–0.004	–0.330	+0.197	–0.361	0.9637	2.0111
	in the complex	–0.007	–0.363	+0.223	–0.393	0.9678	2.0237
With benzyl	initial	–0.004	–0.325	+0.197	–0.361	0.9641	2.0111
alcohol	in the complex	–0.005	–0.380	+0.235	–0.398	0.9825	2.0285

gas (nitrogen). Then solvent was distilled off, and the product was distilled in a vacuum.

1-(2,2,3,3,4,4,5,5-Octafluoro)pentoxypropane (II). Yield 87.9%, bp 104°C (13 mm Hg), n_D^{20} 1.3705, d_{20}^4 1.4234. IR spectrum, ν, cm^{-1}: 1154 (C–O–C), 1180 (CF_2), 2892 (CH_2–O), 2980 (CH_2, CH_3).

1-(2,2,3,3-Tetrafluoro)propyloxybutane (IIIa). Yield 90.0%, bp 95°C (4 mm Hg), n_D^{20} 1.4180, d_{20}^4 1.2770. IR spectrum, ν, cm^{-1}: 1171 (C–O–C), 1206 (CF_2), 2912 (O–CH_2), 2963 (CH_2), 2997 (CH_3).

1-(2,2,3,3,4,4,5,5-Octafluoro)pentoxybutane (IIIb). Yield 85.0%, bp 102°C (4 mm Hg), n_D^{20} 1.3700, d_{20}^4 1.4165. IR spectrum, ν, cm^{-1}: 1179 (C–O–C), 1216 (CF_2), 2928, 2966 (CH_2), 3004 (CF_2H).

1-(2,2,3,3-Tetrafluoropropyloxy)-2-methylpropane (IVa). Yield 60.0%, bp 95°C (3 mm Hg), n_D^{20} 1.3450, d_{20}^4 1.1020. IR spectrum, ν, cm^{-1}: 1170 (C–O–C), 1210 (CF_2), 2930, 2966 (CH_2), 3001 (CF_2H).

1-(2,2,3,3,4,4,5,5-Octafluoropentoxy)-2-methylpropane (IVb). Yield 56.0%, bp 106°C (3 mm Hg), n_D^{20} 1.3520, d_{20}^4 1.3040. IR spectrum, ν, cm^{-1}: 1169 (C–O–C), 1215 (CF_2), 2930, 2968 (CH_2), 3009 (CF_2H).

1-(2,2,3,3-Tetrafluoropropyloxy)pentane (V). Yield 80%, bp 88°C (2 mm Hg), n_D^{20} 1.3996, d_{20}^4 1.0371. IR spectrum, ν, cm^{-1}: 1169 (C–O–C), 1214 (CF_2), 2885 (CH_2), 2963 (CF_2H).

1-(2,2,3,3-Tetrafluoropropyloxy)-3-methylbutane (VIa). Yield 70.0%, bp 113°C (3 mm Hg), n_D^{20} 1.3550, d_{20}^4 1.0990. IR spectrum, ν, cm^{-1}: 1171 (C–O–C), 1210 (CF_2), 2885 (CH_2), 2965 (CF_2H).

1-(2,2,3,3,4,4,5,5-Octafluoropentoxy)-3-methylbutane (VIb). Yield 71.0%, bp 100°C (2 mm Hg), n_D^{20} 1.3600, d_{20}^4 1.2990. IR spectrum, ν, cm^{-1}: 1175 (C–O–C), 1210 (CF_2), 2890 (CH_2), 2969 (CF_2H).

1-(2,2,3,3-Tetrafluoropropyloxy)hexane (VIIa). Yield 60.0%, bp 100°C (2 mm Hg), n_D^{20} 1.3650, d_{20}^4 1.0870. IR spectrum, ν, cm^{-1}: 1174 (C–O–C), 1211 (CF_2), 2890, 2967 (CH_2), 2970 (CF_2H).

1-(2,2,3,3,4,4,5,5-Octafluoro)pentoxyhexane (VIIb). Yield 55.0%, bp 120°C (2 mm Hg), n_D^{20} 1.3480, d_{20}^4 1.2130. IR spectrum, ν, cm^{-1}: 1170 (C–O–C), 1212 (CF_2), 2860, 2970 (CH_2), 2975 (CF_2H).

2,2,3,3-Tetrafluoropropyloxycyclohexane (VIIIa). Yield 82.3%, bp 95°C (3 mm Hg), n_D^{20} 1.3798, d_{20}^4 1.1005. IR spectrum, ν, cm^{-1}: 1170m [ν(C–O–C)]; 1170 s [ν(CF_2)]; 2878 m, 2965 m [ν(CH_2)]; 3005 w (CHF_2), 714 m, 760 m, 800 m, 1000 m (ring vibrations). ^{1}H NMR spectrum, δ, ppm: 5.95 t.t (1H, HCF_2); 3.86 t (2H, O–CH_2–CF_2), 2.85 s (CH ring), 1.74 and 1.32 (ring multiplet).

2,2,3,3,4,4,5,5-Octafluoropentoxycyclohexane (VIIIb). Yield 75.5%, bp 105°C (3 mm Hg), n_D^{20} 1.3865, d_{20}^4 1.3733. IR spectrum, ν, cm^{-1}: 1165 m [ν(C–O–C)]; 1185 s [ν(CF_2)]; 2870, 2960 [ν(CH_2)]; 3005 w (CHF_2), 716 m, 763 m, 810 m, 960 m (vibrations ring). ^{1}H NMR spectrum, δ, ppm: 5.99 t.t (1H, HCF_2); 3.95 t (2H, O–CH_2–CF_2), 2.89 s (CH ring), 1.75 and 1.31 (ring multiplet).

2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptyloxycyclohexane (VIIIc). Yield 65.2%, bp 123°C (3 mm Hg), n_D^{20} 1.3891, d_{20}^4 1.4067. IR spectrum, ν, cm^{-1}: 1165 m [ν(C–O–C)]; 1185 s [ν(CF_2)]; 2870, 2960 [ν(CH_2)]; 3005 w (CHF_2), 716 m, 763 m, 810 m, 960 m (ring vibrations).

[(2,2,3,3-Tetrafluoropropyloxy)methyl]benzene (IXa). Yield 85.4%, bp 120°C (3 mm Hg), n_D^{20} 1.3580, d_{20}^4 1.5065. IR spectrum, ν, cm^{-1}: 1160m [ν(C–O–C)]; 1200c [ν(CH_2)]; 3050 [ν(CH_2)]; 1456 m, 1500 m (Ph). ^{1}H NMR spectrum, δ, ppm: 5.96 t.t (1H, HCF_2); 4.37 t (2H, O–CH_2–CF_2), 7.39 multiplet (Ph) 4.32 s (Ph–CH_2).

[(2,2,3,3,4,4,5,5-Octafluoropentoxy)methyl]benzene (IXb). Yield 83.1%, bp 125°C (3 mm Hg), n_D^{20} 1.3730, d_{20}^4 1.6382. IR spectrum, ν, cm^{-1}: 1163m [ν(C–O–C)]; 1210s [ν(CF_2)]; 3051 [ν(CH_2)]; 1460 m, 1500 m (Ph).

1-Chloro-4-[(2,2,3,3-tetrafluoropropyloxy)methyl]benzene (Xa). Yield 90.2%, bp 130°C (3 mm Hg), n_D^{20} 1.4580, d_{20}^4 1.4025. IR spectrum, ν, cm^{-1}: 1168 m [ν(C–O–C)]; 1195 w [ν(CF_2)]; 3050 [ν(CH_2)]; 1470 m, 1550 m (Ph), 810 m (Cl). ^{1}H NMR spectrum, δ, ppm: 5.97 t.t (1H, HCF_2); 3.34 t (2H, O–CH_2–CF_2), 7.21 m (Ph), 4.42 s (Ph–CH_2).

1-Chloro-4-[(2,2,3,3,4,4,5,5-octafluoropentoxy)methyl]benzene (Xb). Yield 85.3%, bp 135°C (3 mm Hg), n_D^{20} 1.4100, d_{20}^4 1.5002. IR spectrum, ν, cm^{-1}: 1167 m [ν(C–O–C)]; 1190 w [ν(CF_2)]; 3055 [ν(CH_2)]; 1475 m, 1552 m (Ph), 808 m (Cl).

1-Methoxy-4-[(2,2,3,3-tetrafluoropropyloxy)methyl]benzene (XIa). Yield 70.4%, bp 110°C (3 mm Hg), n_D^{20} 1.4440, d_{20}^4 1.2856. IR spectrum, ν, cm^{-1}: 1200 m [ν(C–O–C)]; 1200 w [ν(CF_2)]; 3025 [ν(CH_2)]; 1600 m, 1516 m (Ph). ^{1}H NMR spectrum, δ, ppm: 5.94 t.t (1H, HCF_2); 4.41 t (2H, O–CH_2–CF_2), 6.73 and 7.14 d (Ph), 4.41 s (Ph–CH_2), 3.69 s (OCH_3).

1-Methoxy-4-[(2,2,3,3,4,4,5,5-octafluoropentoxy)-methyl]benzene (XIb). Yield 63.7%, bp 116°C (3 mm Hg), n_D^{20} 1.3995, d_{20}^4 1.3643. IR spectrum, ν, cm^{-1}: 1205 m [ν(C–O–C)]; 1200 w [ν(CF_2)]; 3030 [ν(CH_2)]; 1610 m, 1510 m (Ph).

1-Nitro-3-[(2,2,3,3-tetrafluoropropyloxy)methyl]-benzene (XIIa). Yield 90.0%, bp 130°C (3 mm Hg), n_D^{20} 1.4760, d_{20}^4 1.3570. IR spectrum, ν, cm^{-1}: 1170 m [ν(C–O–C)]; 1850 w [ν(CF_2)]; 3025 [ν(CH_2)]; 1450 m, 1510 m (Ph), 1320 m (NO_2). ^1H NMR spectrum, δ, ppm: 5.93 t.t (1H, HCF_2); 4.40 t (2H, O–CH_2–CF_2), 7.45 m (Ph) 4.42 s (Ph–CH_2).

1-Nitro-3-[(2,2,3,3,4,4,5,5-octafluoropentoxy)methyl]benzene (XIIb). Yield 84.1%, bp 140°C (3 mm Hg), n_D^{20} 1.4310, d_{20}^4 1.5002. IR spectrum, ν, cm^{-1}: 1175 m [ν(C–O–C)]; 1850 w [ν(CF_2)]; 3030 [ν(CH_2)]; 1455 m, 1511m (Ph), 1324 m (NO_2).

REFERENCES

1. Rakhimov, A.I., Nalesnaya, A.V. and Vostrikova, O.V., *Zh. Obshch. Khim*., 2004, vol. 74, no. 4, p. 967.
2. Rakhimov, A.I., Nalesnaya, A.V., and Vostrikova, O.V., *Zh. Prikl. Khim*., 2004, vol. 77, no. 9, p. 1573.
3. Rakhimov, A.I., Nalesnaya, A.V., Fisechko, R.V., and Vostrikova, O.V., *Zh. Obshch. Khim*., 2006, vol. 76, no. 3, p. 523.
4. Fisechko, R.V., *Candidate Sci. (Chem.) Dissertation*, Volgograd: 2007.
5. Schmidt, M.W., Baladrige, K.K., and Boatz, J.A., *J. Comput. Chem*., 1993, vol. 14, p. 1347.