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Synthesis of α-Chloropolyfluoroalkyl Ethers and Acetals Based on Them

A. I. Rakhimov, O. N. Kutyga, and A. A. Bakshaeva

Volgograd State Technical University, pr. Lenina 28, Volgograd, 400131 Russia
e-mail: rakhimov@sprint-v.com.ru

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Abstract—α-Chloropolyfluoroalkyl ethers were synthesized by the reaction of polyfluorinated alcohols $H(CF_2CF_2)_nCH_2OH$ (n=1–3) with aliphatic aldehydes (ethanal, propanal, butanal) and hydrogen chloride. Yield of α-chloroethers decreases from 71 to 61% as the number of carbon atoms in the starting reactants increases. α-Chloropolyfluoroalkyl ethers react with polyfluorinated alcohols (n = 1–3) to form acetals in yield of up to 40–61%, and with methanol and ethanol, up to 98%.

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Earlier it has been established [1] that paraform and acetaldehyde react with 1,1,3-trihydroperfluoropropanol in the presence of hydrogen chloride to give acetals, therewith, α-chloroethers are formed as intermediates.

In this paper we consider the synthesis of α-chloropolyfluoroalkyl ethers via the reaction of polyfluorinated alcohols with aliphatic aldehydes and hydrogen chloride. The reaction follows the scheme:

$$RCH{=}O + H(CF_2CF_2)_nCH_2OH$$

$$\xrightarrow{HCl} RCH(Cl)OCH_2(CF_2CF_2)_nH,$$

R = CH_3, n = 1 (**I**); R = C_2H_5, n = 1 (**II**); R = n-C_3H_7, n = 1 (**III**); R = n-C_4H_9, n = 1 (**IV**); R = CH_3, n = 2 (**V**); R = CH_3, n = 3 (**VI**); R = C_2H_5, n = 3 (**VII**).

The reaction of 1,1,3-trihydroperfluoropropanol with ethanal (**I**), propanal (**II**), butanal (**III**), pentanal (**IV**), of 1,1,5-trihydroperfluoropentanol with ethanal (**V**) and 1,1,7-trihydroperfluoroheptanol with ethanal (**VI**) and propanal (**VII**) were carried out in chloroform. An excess of dry hydrogen chloride was bubbled through the reaction mixture at –5 to +5°C. Table 1 lists the yields and physicochemical constants of α-chloropolyfluoroalkyl ethers, as well as the results of their analysis.

The highest yield (71%) was obtained for α-chloroether **I** in the case of polyfluorinated alcohol with n = 1, and the lowest yield (60%) was observed for the alcohol with n = 3 and propanal as well as for the polyfluorinated alcohol with n = 1 and pentanal.

The decrease in the yield of α-chloropolyfluoroalkyl ethers with increasing number of carbon atoms in the reagents is due, presumably, to the reaction mechanism and some steric factors. The difference should be noted in the properties of polyfluorinated alcohols as compared with the unsubstituted aliphatic monoalcohols consisting in the higher acidity of the former at the introduction of fluorine atoms [2, 3]. Thus, pK_a of 2,2-difluoropropanol is 12.00, and of 1,1,3-trihydroperfluoropropanol, 11.35, which leads to a strong association of these alcohols with carbonyl compounds [3–5]. Consequently, in the reaction system including polyfluorinated alcohols and aldehydes the associates **A** are formed. Their reaction with hydrogen chloride proceeds through a six-membered transition state **B** to give a hemiacetal **C** followed by the reaction of the latter with hydrogen chloride to form α-chloropolyfluoroalkyl ether:

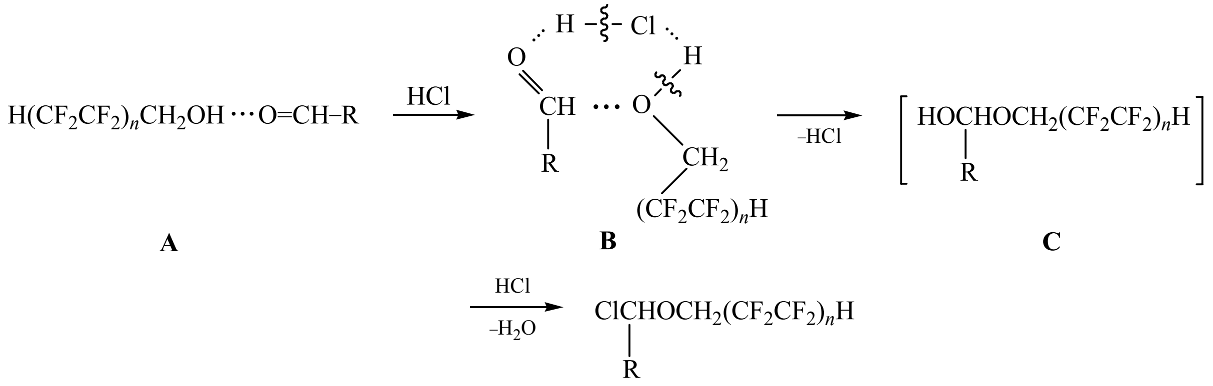
The formation of an intermediate hemiacetal **C** was proved by the tracer method: the molecule of water eliminated in the reaction contains the isotope of oxygen introduced into the starting aldehyde [6].

The structure of α-chloropolyfluoroalkyl ethers was confirmed by the ^1H NMR and IR spectra. In the ^1H NMR spectra the $H(CF_2CF_2)_nCH_2$ group is identified from the positions of the $\delta(CF_2CF_2–)$ and $\delta(–CF_2CH_2–)$ signals. The proton of HCF_2CF_2 group appears as a

Table 1. Physicochemical properties of α-chloropolyfluoroalkyl ethers $H(CF_2CF_2)_nCH_2OCH(R)Cl$[a]

Comp. no.	Yield, %	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}, g ml^{-1}	MR_D		Found, %				Formula	Calculated, %			
					found	calculated	C	H	Cl	F		C	H	Cl	F
I	71	35–37 (27)	1.3620	1.3335	32.35	32.36	29.95	3.59	18.10	36.98	$C_5H_7OF_4Cl$	30.85	3.60	18.25	38.07
II	66	47–49 (22)	1.3694	1.3155	35.80	36.01	33.91	4.39	16.99	35.41	$C_6H_9OF_4Cl$	34.53	4.32	17.03	36.45
III	62	56–59 (17)	1.3792	1.2784	40.24	40.62	37.72	7.16	15.87	32.07	$C_7H_{11}OF_4Cl$	37.75	7.19	15.95	34.16
IV	60	58–60 (15)	1.3834	1.2277	44.98	45.24	40.49	5.49	14.75	30.57	$C_8H_{13}OF_4Cl$	40.59	5.50	15.01	32.14
V	69	52–53 (15)	1.3460	1.4925	42.02	45.16	28.49	2.35	11.98	48.00	$C_7H_8OF_4Cl$	28.52	2.38	12.00	51.61
VI	66	66–68 (14)	1.3390	1.5962	51.67	51.95	27.31	1.75	8.89	56.89	$C_9H_7OF_4Cl$	27.38	1.77	9.00	57.79
VII	60	61–62 (12)	1.3452	1.5457	56.16	56.57	29.18	2.19	8.64	53.61	$C_{10}H_9OF_4Cl$	29.38	2.20	8.69	55.81

[a] **I** is 1-Chloro-1-(1,1,3-trihydroperfluoropropoxy)ethane; **II** is 1-chloro-1-(1,1,3-trihydroperfluoropropoxy)propane; **III** is 1-chloro-1-(1,1,3-trihydroperfluoropropoxy)butane; **IV** is 1-chloro-1-(1,1,3-trihydroperfluoropropoxy)pentane; **V** is 1-chloro-1-(1,1,3-trihydroperfluoropenthoxy)ethane; **VI** is 1-chloro-1-(1,1,3-trihydroperfluorohepthoxy)etane; **VII** is 1-chloro-1-(1,1,3-trihydroperfluorohepthoxy)propane.



symmetric triplet of triplets at δ = 5.72 ppm (J_{HF} 51.0, J_{CF} 5.2 Hz) due to the short- and long-range interactions with fluorine atoms. Methylene protons are observed as ABX_2 system (X = F) with δ_A 4.10 and δ_B 3.90 ppm. The CH signal is a quadruplet at δ 5.52–5.36 ppm (J_{HH} 6.0 Hz). A doublet in the strong field at δ 1.70 and 1.60 ppm belongs to the methyl protons.

The IR spectrum has an absorption band at 648 cm^{-1} attributed to the stretching vibrations of C–Cl groups in α-chloroethers. Virbations of CF–, CF_2–groups give rise to multiplets in the range of 1000–1400 cm^{-1}. The absence of the starting alcohol is confirmed by the complete lack of absorption at 3300–3400 cm^{-1} characteristic for the stretching vibrations of the OH-group.

The synthesis of acetals was carried out by the reaction of α-chloropolyfluoroalkyl ethers with alcohols.

The physicochemical constants, yields, and elemental analyses of acetals **VIII–XVI** are listed in Table 2.

$$H(CF_2CF_2)nCH_2OCH(R)Cl + R'OH \xrightarrow{HCl} H(CF_2CF_2)_nCH_2OCH(R)OR',$$

R = CH_3, R' = HCF_2CF_2 (**VIII**), $H(CF_2CF_2)_2CH_2$ (**IX**), $H(CF_2CF_2)_3CH_2$ (**X**), CH_3 (**XI, XIII, XV**), C_2H_5 (**XII, XIV, XVI**); n = 1 (**VIII, XI, XII**), 2 (**IX, XIII, XIV**), 3 (**X, XV, XVI**).

The special feature of the reaction of α-chloroethers with alcohols is its reversibility owing to the reaction of the products with hydrogen chloride. Therefore, the hydrogen chloride was removed from the reaction medium. Hexane is the best medium for this reaction, since hydrogen chloride is poorly soluble in it. In the case of unsubstituted monoalcohols the high yield was obtained using the solvent-free conditions.

The structure of polyfluoroalkylacetals was confirmed by the ^1H NMR and IR spectroscopy. In the ^1H NMR spectra the proton of HCF_2CF_2 group appears as a symmetrical triplet of triplets at 5.74 ppm with the similar values of the spin–spin coupling constants (J_{HC} 53, J_{CF} 4.4 Hz). The protons of CH_2O groups are observed as a triplet at 3.65 ppm (J_{CF} 14 Hz). The alkyl protons are easily identified by their chemical shift values and the nature of the spin–spin interaction [7].

Table 2. Physicochemical properties of polyfluorinated acetals $H(CF_2CF_2)_nCH_2OCH(R)OR'$ [a]

Comp. no.	Yield, %	bp, °C (*p*, mm Hg)	n_D^{20}	d_4^{20}, g ml^{-1}	*MR*$_D$		Found, %			Formula	Calculated, %		
					found	calculated	C	H	F		C	H	F
VIII	61	61–62 (5)	1.3420	1.4058	43.52	43.55	33.06	3.43	50.21	$C_8H_{10}O_2F_8$	33.10	3.45	52.41
IX	51	91–92 (2)	1.3331	1.6011	62.97	63.14	29.32	2.01	60.71	$C_{12}H_{10}O_2F_{16}$	29.32	2.04	62.04
X	40	158–159 (5)	1.3314	1.7127	82.53	82.73	27.81	1.46	62.91	$C_{15}H_{10}O_2F_{24}$	27.83	1.50	66.09
XI	98	43–44 (30)	1.3452	1.2336	32.73	32.78	37.81	5.24	39.98	$C_6H_{10}O_2F_4$	37.89	5.26	40.00
XII	97	37–38 (30)	1.3480	1.1772	37.10	37.40	41.19	5.89	35.31	$C_7H_{12}O_2F_2$	41.18	5.88	37.25
XIII	95	50–52 (2)	1.3420	1.4891	41.04	41.61	33.08	3.43	49.98	$C_8H_{10}O_2F_8$	33.10	3.45	52.41
XIV	96	73–74 (2)	1.3430	1.4114	45.51	46.22	35.21	3.94	47.98	$C_8H_{12}O_2F_8$	35.53	3.95	50.00
XV	91	58–59 (14)	1.3380	1.6131	50.41	50.43	29.99	2.54	56.18	$C_{10}H_{10}O_2F_{12}$	30.77	2.56	58.46
XVI	89	64–65 (15)	1.3410	1.5326	55.40	55.05	32.53	2.94	53.87	$C_{11}H_{12}O_2F_{12}$	32.67	2.97	56.41

[a] **VIII** is 1,1-di(1',1',3'-trihydroperfluoropropoxy)ethane; **IX** is 1,1-di(1',1',5'-trihydroperfluoropentoxy)ethane; **X** is 1,1,-di(1',1',7'-trihydroperfluoroheptoxy)ethane; **XI** is 1-methoxy-1-(1',1',3'-trihydroperfluoropropoxy)ethane; **XII** is 1-ethoxy-1-(1',1',3'-trihydroperfluoropropoxy)ethane; **XIII** is 1-methoxy-1-(1',1',5'-trihydroperfluoropentoxy)ethane; **XIV** is 1-ethoxy-1-(1',1',5'-trihydroperfluoropentoxy)ethane; **XV** is 1-methoxy-1-(1',1',7'-trihydroperfluoroheptoxy)ethane; **XVI** is 1-ethoxy-1-(1',1',7'-trihydroperfluoroheptoxy)ethane.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Mercury Varian spectrometer (300 Hz) with internal reference HMDS. The IR spectra were registered on a Specord-M82 instrument.

General procedure for the synthesis of α-chloropolyfluoroalkyl ethers. To a solution of 4.26 g (0.20 mol) of 1,1,3-trihydroperfluoropropanol in 50 ml of anhydrous chloroform cooled to –5°C was added 11.0 g (0.26 mol) of acetaldehyde in 20 ml of chloroform. Through the reaction mixture was passed 1.5–2 mol of dry hydrogen chloride over 2–2.5 h while maintaining the temperature at –5 to +5°C. After the reaction completion the reaction mixture was purged with the inert gas (nitrogen) to remove hydrogen chloride excess. The organic layer was separated, dried over magnesium sulfate, and concentrated. The residue was distilled in a vacuum. Yield 48.9 g (71%) of α-chloroether **I,** bp 35–37°C (27 mm Hg), n_D^{20} 1.3620, d_4^{20} 1.3335. Found, %: C 29.95; H 3.59; Cl 18.10; F 36.98. *MR*$_D$ 32.35. C_5H_7ClFO. Calculated, %: C 30.85; H 3.60; Cl 18.25; F 38.07. *MR*$_D$ 32.36.

General procedure for the synthesis of polyfluorinated acetals. To a solution of 9.7 g (0.05 mol) of 1-chloro-1-(1,1,3-trihydroperfluoropropoxy)ethane **I** in 50 ml of anhydrous hexane cooled to 0°C was added dropwise 6.6 g (0.05 mol) of 1,1,3-trihydroperfluoropropanol in 20 ml of anhydrous hexane. The reaction mixture was purged with an inert gas (nitrogen) to remove the liberated hydrogen chloride. The temperature was gradually raised to 30°C and the reaction mixture was stirred for 3 h. After removing the solvent, the residue was distilled in a vacuum. Yield of compound **VIII** 8.8 g (61%), bp 61–62°C (5 mm Hg), n_D^{20} 1.3420, d_4^{20} 1.4058. Found, %: C 33.06; H 3.43; F 50.21. *MR*$_D$ 43.52. $C_8H_{10}F_8O_2$. Calculated, %: C 33.10; H 3.45; F 52.41. *MR*$_D$ 43.55.

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