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Synthesis of novel perfluoroalkyl-containing polyethers

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ABSTRACT

The synthesis of iodo(perfluoroalkyl)epoxides by radical addition of perfluoroalkyl iodides to allyl glycidyl ether and 1,2-epoxydec-9-ene is described. Dehydroiodination of additional products upon treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gives unsaturated products. The use of Bu_3SnH/Bz_2O_2 as a reduction reagent of iodo(perfluoroalkyl)allyl glycidyl ethers allows to save oxirane ring. Cationic polymerization of saturated or functional (with iodine or double bond) fluoroalkyl oxiranes under action of catalytic amount of $BF_3 \cdot Et_2O$ proceeds only on epoxide group. In case of poly(9-iod-10-(perfluoroalkyl)-1,2-epoxyalkane) iodine atoms are removed by standard zinc reduction.

1. Introduction

It is well known that perfluoropolymers exhibit excellent chemical and thermal stability, low activities of surface energy, refractive index, dielectric constant and friction coefficient [1–6]. However, these compounds, in general, reveal extremely low solubility in organic medium. Synthesis of partially fluorinated (macro)molecules extends the opportunity of their application [7–17]. Recent results obtained in the fields of biotechnologies [18,19] and nanotechnologies [20–22], fluorous phase chemistry [23] are represented in literature.

Partially fluorinated macromolecules preparation ways include the use of fluoroalkyl (co)monomers such as acrylates [19,24–28], epoxides [29–36], alkenes [37,38], vinyl ethers [39]. Another approach to these compounds is introduction of perfluoroalkyl groups into organic (macro)molecules. As an example, the selective modification of functional polymers using perfluoroalkenes [40], perfluoroalkyl iodides [41] or fluorinated glycidyl ethers [42] is described.

As far as we know, only few examples of reactions between perfluoroalkyl iodides and unsaturated epoxides have been reported in works [43–46]. This approach was extended by us for allyl glycidyl ether [47]. Earlier we also demonstrated further dehydroiodination of adducts by the use of DBU [48]. This type of epoxides containing perfluorinated aliphatic chain and functional group (iodine or double bond) are interesting intermediates, in particularly, for the synthesis of fluorinated polyethers. In this study we report the results of block-type fluorinated polyethers preparation from iodo(perfluoroalkyl)epoxides and their derivatives.

2. Results and discussion

2.1. Synthesis of epoxy monomers

Sodium dithionite effectively promotes the addition of polyfluoro(oxa)alkyl iodides **1a–e** to allyl glycidyl ether **2** [47] and 1,2-epoxydec-9-ene **3** in 72–85% yields (Scheme 1). The treatment of addition products **4a–d**, **5a–c, e** with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in CH_2Cl_2 gave unsaturated compounds **6a**, **c**, **d**, **7a–c, e** with the predominate of *E*-configuration as a result of elimination of hydrogen iodide in 81–87% yields (Table 1).

Use of Bu_3SnH/Bz_2O_2 in dehalogenation process of iodo(perfluoroalkyl)allyl glycidyl ethers **4b**, **c** is chosen for selective reduction of iodine according to work [49,50] (Scheme 2). This approach is more perspective than 'standard' zinc reduction. In this reaction instead of replacing the iodine by hydrogen in $R^FCH_2CHICH_2OR$, a cleavage of the adjacent OR groups occurs to form $R^FCH_2CH{=}CH_2$ [50].

2.2. Polymerization of fluorinated epoxides

It is known that polymerization of fluoroalkyl epoxides can be carried out with the help of Al(*i*-Bu)$_3$, $AlEt_3$ [24,29], $FeCl_3$ [34], organozinc compounds [51]. To obtain polyethers from saturated

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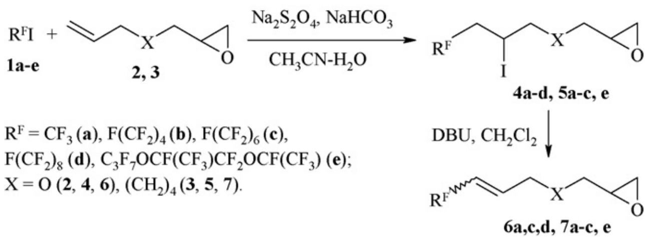
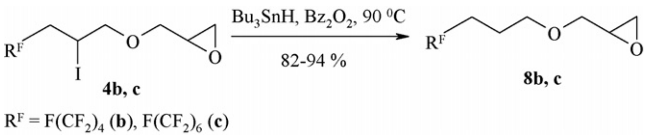


Scheme 1. Preparation of iodo(perfluoroalkyl)epoxides and their dehydroiodination products.

Table 1
The isomeric ratio *E*/*Z* of unsaturated epoxides **6a**, **d** and **7a–c, e**.

R^F	Compounds	*E*/*Z*
CF_3	**6a**, **7a**	15/1
$F(CF_2)_n$, *n* = 4, 6, 8	**6d**, **7b**,**c**	25/1
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	**7e**	50/1



Scheme 2. Reduction of iodo(perfluoroalkyl)allyl glycidyl ethers.

Table 2
Molecular parameters determined by light scattering, water repellency of aluminum foil treated with polyethers **11c**, **12c**, **13c**, **14c**.

Polymer	M_w, g/mol	A_2 (($\times 10^{-4}$ ml mol)/g^2)	d*n*/d*c*	Contact angle, θ
11c	7600[a]	(0.203 ± 0.021)	0.064	128
11c	7900[b]	(-6.50 ± 0.14)	0.073	–
12c	5600[a]	(0.620 ± 0.023)	0.067	126
12c	6000[b]	(-5.32 ± 0.02)	0.078	–
13c	6900[a]	(0.228 ± 0.015)	0.063	130
14c	8500[a]	(1.95 ± 0.01)	0.065	127

[a] In CCl_4.
[b] In toluene.

or functional fluorinated epoxides **4c**, **5c**, **6c**, **7c**, **8c** we have used $BF_3 \cdot Et_2O$ (Scheme 3) accordingly to the described procedure of allyl glycidyl ether oligomerization [52]. Using the molar ratio $[oxirane]/[BF_3Et_2O] \approx 100:1$ we were able to obtain low weight polymers, which molar weights are shown (Table 2). The polyethers obtained are very soluble in organic solvents ($CHCl_3$, acetone, toluene, THF) and easily combine with c industrial oil I-20A, which fact we have used for improvement of tribological properties of the latter. Further reduction of fluoroalkyl polyether **11c** without ether group adjacent to CHI fragment was carried out by zinc in acidic medium in good yield (Scheme 3).

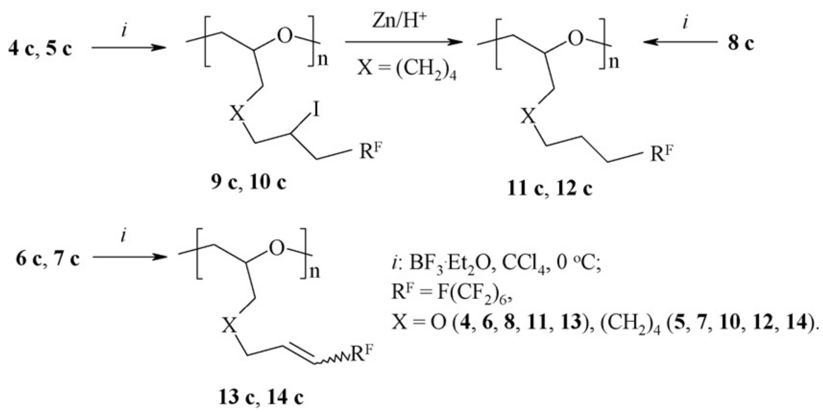
The fluorinated epoxides polymerization leads to disappearance of epoxide ring protons in their ^1H NMR spectra. The ^1H NMR analysis of the unsaturated polyethers **13c**, **14c** showed the existence of broad signals at 5.9 ppm and 6.4 ppm of olefinic protons. This fact demonstrates the occurrence of a double bond in the polymers **13c**, **14c**. Moreover, the ratio of the integral intensities of these NMR signals to the total integral intensity of protons in the range of 3.5–4.0 ppm indicates that there is one double bond per unit. For iodocontaining polyethers, signals of CHI and CF_2CH_2 groups do not undergo any changes during polymerization. The reduction of **11c**, leads to disappearance of CHI and CF_2CH_2 groups at 4.3 ppm and 2.84–3.05 ppm, respectively. After removal of iodine atom in polyether **11c** protons of CF_2CH_2 group appeared in the range of 2.0–2.1 ppm.

2.3. Characterization and properties of fluorinated polyethers

The M_w of prepared oligomers was measured by static light scattering according to work [53]. The weight-average molecular weight M_w and second virial coefficient A_2 were calculated from the concentration dependence of the reciprocal scattering at straight angle ($\theta = 90°$) in the usual manner $K_C/R_\theta = 1/M_w + 2A_2c$, where R_θ is the measured Rayleigh factor for a solution of concentration *c* at a scattering angle θ, $K = [4\pi^2n^2(dn/dc)^2]/(\lambda^4N_A)$ with d*n*/d*c* the refractive index increment, *n* is the refractive index, and λ the wavelength of light (656 nm). The slope of the straight line, which is obtained by measuring of refractive index at different concentrations of polymers in the correspondent solvent, is represented by d*n*/d*c* ratio for every particular pair of polymer–solvent (Table 2). At $A_2 < 0$ it means that the solvent chosen (toluene) is thermodynamically poor solvent. In its turn, $A_2 > 0$ (in case with CCl_4) indicates favorable interaction of polymer with solvent. Close values M_w at positive and negative values A_2 shows, that regardless of the nature of solvents there is no aggregation of polymeric molecules with each other.

The hydrophobic properties of obtained polyethers **11c**, **12c**, **13c**, **14c** were evaluated by measuring the contact angles of water. To obtain surface layers of compounds **11c**, **12c**, **13c**, **14c**, we used their 2 or 4% solutions in $CFCl_2CH_3$; aluminum foil was used as support.

Polyethers **11c**, **12c**, **13c**, **14c** show good water repellent property but no oil repellent property (dodecane immediately spreads over on the aluminum foil having been treated by



Scheme 3. Synthesis of fluorinated polyethers.

Table 3
Results of tribological tests using fluorinated polyethers **11c**, **12c**[a] as additives to industrial oil I-20A.

Type of additive polyether in oil	Load (N), *H*	Friction coefficient		Wear-and-tear intensity (I_h)
		μ[b]	μ[c]	
–	294	0.50	0.33	1.6×10^{-8}
11c	294	0.13	0.07	1.6×10^{-9}
12c	294	0.10	0.05	0
11c	686	0.19	0.08	1.6×10^{-9}
12c	686	0.14	0.06	1.6×10^{-9}
11c	1666	0.15	0.08	1.6×10^{-9}
12c	1666	0.16	0.06	1.6×10^{-9}

[a] Velocity of sliding V = 0.07 m/s.

[b] Maximum value of friction coefficient during first 100 cycles of finger stroke on plate.

[c] The established friction coefficient equals to the value of this parameter after 100 cycles stroke of the finger on plate, which is the same during the whole further process of measuring.

polyethers) (Table 3). Such properties of partially fluorinated polymers were described earlier [13], which depends on proportion of perfluoroalkyl and hydrocarbon polymer parts length. The given behavior of the received compounds allows their use as additives to industrial oil I-20A for the purpose of improvement of tribological properties of the given oil.

To define the quantity of friction coefficient (μ) and wear-and-tear intensity (I_h) we carried out test of 18/9 stainless steel by "finger-plate" scheme in friction slip condition at reciprocating motion of finger on plate at room temperature. The finger and и plate are parallelepipeds, made of steels of the same brand. The finger's dimensions are – 7 × 7 × 20 mm, dimensions of plate – 60 mm × 40 mm × 10 mm. Sliding face of the finger – 7 mm × 7 mm, the surface of plate slip – 60 mm × 40 mm. The velocity of finger's slide on the plate – 0.07 m/s, the total distance covered by a finger – 80 m, which equals to 1000 cycles (double strokes of the finger on plate). Before the test fingers and plates were thoroughly degreased. Before the start of the movement of the finger a drop of 100 mcl by volume is put on plate. This drop contains 4% of fluorinated polyether in industrial iol I-20A.

Friction coefficient (μ) calculated as ratio of frictional force (F) to normal load (N):

$$\mu = \frac{F}{N}$$

Friction (F) is measured with resilient member (steel ring) with tensometric sensors assembled on it, the readings of which are recorded on output type of electronic recording potentiometer.

Wear-and-tear intensity (I_h) of fingers calculated by formula: $I_h = \Delta Q/\rho{\cdot}L{\cdot}S$, where ΔQ – mass lose of finger sample, g; ρ – density of sample material, g/cm^3; L – friction way, cm; S – geometric area of contact, cm^2. The mass loss (ΔQ) are determined by weighting of finger samples which were degreased after tests on the analytical balances Shimadzu AUX-220 with accuracy of 0.0001 g.

It is noted that the friction coefficients for industrial oil with additives of fluorinated polyethers are six times less than in use of industrial oil only (Table 3), and the high efficiency keeps in contact load increase. Thus, performance characteristics of industrial oil, being used for reduction of friction and wearing of metal surfaces in different industrial constructions, can be improved due to addition to it partially fluorinated polyethers **11c**, **12c**.

In conclusion, we have developed methods of fluoroalkyl-containing polyethers synthesis based on additional products from perfluoroalkyl iodides to unsaturated epoxides. The advantage of the described approach is an opportunity of preparative preparation of oxiranes and polyethers with long perfluoroalkyl groups which is hardly possible in case of applying other methods of partially fluorinated epoxides synthesis in basic conditions [31,54–56]. The obtained fluoroalkyl-containing polyethers possess hydrophobicity as well as oleophility. We consider that these properties extend their application areas. One of such directions is shown to be the improvement of tribological properties of industrial oil.

3. Experimental

Boiling points were not corrected. GC analyses were measured by Shimadzu GC-17A instrument. ^{1}H NMR spectra were recorded on a Brucker DRX 400 (400.1 MHz) spectrometer using TMS as an internal standard. ^{19}F NMR spectra were recorded with Brucker DRX 400 (376.5 MHz) spectrometer with CFCl$_3$ as internal standard. All chemical shifts are reported in ppm, the coupling constants J being in Hz. Infrared spectra were obtained on a "Perkin-Elmer Spectrum One" spectrometer. Molecular parameters of polyethers obtained are determined by measuring of static light scattering of polymer solution by device 90 Plus Brookhoven Instrument Corporation (USA). Static contact angles were measured with a contact goniometer (Erma Contact Anglement, Model G-1,13-100-0, Japan) by the sessile drop method with a micro-syringe at 25 °C. More than 10 contact angle values were averaged to get a reliable value for each sample.

DBU was obtained from Acrās and sodium dithionite from Merck.

Compounds **1a**–**e** were synthesized employing methods from works [57,58]. The compounds **4b**, **c** were obtained using the methods [47].

3.1. Radical addition of perfluoroalkyl iodides **1a–e** *to unsaturated epoxides* **2**, **3**

General procedure. Perfluorinated iodide (**1a**–**e**) (0.14 mol), allyl glycidyl ether **2** or 1,2-epoxydec-9-ene **3** (0.14 mol) and NaHCO$_3$ 10.0 g (0.08 mol) were added in 15 ml acetonitrile and 30 ml water with magnetic stirrer. Then, Na$_2$S$_2$O$_4$ (0.08 mol) was added dropwised for an hour. The mixture was stirred at room temperature for 4 h. After that mixture was diluted with 100 ml water, extracted with ether 2× 50 ml. The combined extracts were dried over MgSO$_4$. After evaporation of ether, the pure compounds (**4a**–**d**, **5a**–**c**, **e**) were obtained by distillation under reduced pressure.

*3.1.1. 4,4,4-Trifluoro-2-iodobutyloxymethyloxirane (***4a***)*

Colorless liquid: yield 83%; bp, 90–91 °C/5 Torr. IR υ (cm^{-1}): 2963–2965, 2918–2920, 2892–2893 (C–H), 1120–1122 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, CDCl$_3$), δ: 2.62 (1H, td, $^2J_{H,H}$ = 5.1 Hz, $^3J_{H,H}$ = 2.6 Hz, CH(O)CH*H*), 2.71 (1H, m, CF$_3$CH*H*), 2.81 (1H, dd, $^2J_{H,H}$ = 5.3 Hz, ^2J_H,H = 4.2 Hz, CH(O)C*H*H), 3.03 (1H, m, CF$_3$C*H*H), 3.16 (1H, m, C*H*(O)CH$_2$), 3.43 (1H, dd, ^2J_H,H 11.8 Hz, $^3J_{H,H}$ 6.0 Hz, CH*H*CH(O)CH$_2$), 3.73 (1H, m, CHICH*H*O), 3.75 (1H, dd, $^2J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 2.3 Hz, CHIC*H*HO), 3.87 (1H, dd, $^2J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 2.6 Hz, C*H*HCH(O)CH$_2$), 4.23 (1H, m, C*H*I); ^{19}F NMR (376.5 MHz, CDCl$_3$), δ: −65.30 (3F, q, $^3J_{F,F}$ = 10.4 Hz, CF$_3$). Analysis: Calc. for C$_7$H$_{10}$F$_3$IO$_2$: C, 27.12; H, 3.25; F, 18.38%. Found: C, 27.01; H, 3.16; F, 18.15%.

*3.1.2. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-2-iodoundecyloxymethyl-oxirane (***4d***)*

Colorless liquid: yield 75%; bp, 125–126 °C/3 Torr. IR υ (cm^{-1}): 2962–2965, 2919–2921, 2891–2892 (C–H), 1120–1122 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, CDCl$_3$), δ: 2.63 (1H, m, CH(O)CH*H*), 2.72 (1H, m, CF$_2$CH*H*), 2.82 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.2 Hz, CH(O)C*H*H), 3.05 (1H, m, CF$_2$C*H*H), 3.17 (1H, m, C*H*(O)CH$_2$), 3.45

(1H, dd, $^2J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 6.0 Hz, CH*H*CH(O)CH$_2$), 3.80 (3H, m, CHICH$_2$OCHH), 4.38 (1H, m, C*H*I); ^{19}F NMR (376.5 MHz, CDCl$_3$), δ: −126.42 (2F, m, CF$_{2\omega}$), −123.63 (6F, m, CF$_{2\delta}$CF$_{2\lambda}$CF$_{2\chi}$), −122.79 (2F, m, CF$_{2\beta}$), −122.43 (2F, m, CF$_{2\gamma}$), −114.62 (2F, m, CF$_{2\alpha}$), −81.85 (3F, t, $^3J_{F,F}$ = 10.1 Hz, CF$_3$). Analysis: Calc. for $C_{14}H_{10}F_{17}IO_2$: C, 25.47; H, 1.53; F, 48.93%. Found: C, 25.50; H, 1.59; F, 49.04%.

3.1.3. 11,11,11-Trifluoro-9-iodo-1,2-epoxyundecane (**5a**)

Colorless liquid: yield 81%; bp, 175–176 °C/5 Torr. IR υ (cm^{-1}): 2963–2965, 2919–2921, 2892–2893 (C–H), 1120–1123 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, CDCl$_3$), δ: 1.42 (10H, m, (CH$_2$)$_5$), 1.77 (2H, m, CHIC*H*$_2$), 2.46 (1H, dd, CH(O)CH*H*, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz), 2.75 (1H, dd, CH(O)C*H*H, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.0 Hz), 2.87 (3H, m, CF$_2$C*H*$_2$, C*H*(O)CH$_2$), 4.19 (1H, m, C*H*I); ^{19}F NMR (376.5 MHz, CDCl$_3$), δ: −64.90 (3F, t, $^3J_{F,F}$ = 10.3 Hz, CF$_3$). Analysis: Calc. for $C_{11}H_{18}F_3IO$: C, 37.73; H, 5.18; F, 16.28%. Found: C, 37.62; H, 5.15; F, 16.13%.

3.1.4. 11,11,12,12,13,13,14,14,14-Nonafluoro-9-iodo-1,2-epoxytetradecane (**5b**)

Colorless liquid: yield 85%; bp, 163–164 °C/3 Torr. IR υ (cm^{-1}): 2962–2964, 2919–2922, 2892–2893 (C–H), 1120–1122 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, CDCl$_3$), δ: 1.44 (10H, m, (CH$_2$)$_5$), 1.80 (2H, m, CHIC*H*$_2$), 2.46 (1H, dd, CH(O)CH*H*, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz), 2.74 (1H, dd, CH(O)C*H*H, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.0 Hz), 2.90 (3H, m, CF$_2$C*H*$_2$, C*H*(O)CH$_2$), 4.33 (1H, m, CHI); ^{19}F NMR (376.5 MHz, CDCl$_3$), δ: −126.95 (2F, m, CF$_3$C*F*$_2$), −125.61 (2F, m, C*F*$_2$CF$_2$CH$_2$), −115.84 (1F, dm, $^2J_{F,F}$ = 270.9 Hz, CF*F*CH$_2$), −113.04 (1F, dm, $^2J_{F,F}$ = 270.9 Hz, C*F*FCH$_2$), −82.11 (3F, tt, $^3J_{F,F}$ = 9.7 Hz, $^4J_{F,F}$ = 3.2 Hz, CF$_3$). Analysis: Calc. for $C_{14}H_{18}F_9IO$: C, 33.62; H, 3.63; F, 34.18%. Found: C, 33.54; H, 3.55; F, 34.02%.

3.1.5. 11,11,12,12,13,13,14,14,15,15,16,16,16-Tridecafluoro-9-iodo-1,2-epoxyhexadecane (**5c**)

Colorless liquid: yield 84%; bp, 179–180 °C/3 Torr. IR υ (cm^{-1}): 2963–2966, 2918–2921, 2893–2895 (C–H), 1121–1124 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, CDCl$_3$), δ: 1.44 (10H, m, (CH$_2$)$_5$), 1.80 (2H, m, CHIC*H*$_2$), 2.46 (1H, dd, CH(O)CH*H*, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz), 2.74 (1H, dd, CH(O)C*H*H, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.0 Hz), 2.90 (3H, m, CF$_2$C*H*$_2$, C*H*(O)CH$_2$), 4.33 (1H, m, C*H*I). ^{19}F NMR (376.5 MHz, CDCl$_3$), δ: −126.23 (2F, m, CF$_{2\omega}$), −122.69 (2F, m, CF$_{2\delta}$), −121.87 (2F, m, CF$_{2\beta}$), −120.79 (2F, m, CF$_{2\gamma}$), −113.58 (1F, m, CF*F*CH$_2$), −112.68 (1F, m, C*F*FCH$_2$), −81.78 (3F, tt, $^3J_{F,F}$ = 10.2 Hz, $^4J_{F,F}$ = 2.5 Hz, CF$_3$). Analysis: Calc. for $C_{18}H_{18}F_{17}IO$: C, 30.88; H, 2.59; F, 46.12%. Found: C, 30.73; H, 2.43; F, 45.98%.

3.1.6. 11,14-Bis(trifluoromethyl)-12,15-dioxa-9-iodo-11,13,13,14,16,16,17,17,18,18,18-undecafluoro-1,2-epoxyoctadecane (**5e**)

Colorless liquid: yield 84%; bp, 130–131 °C/1 Torr. IR υ (cm^{-1}): 2962–2965, 2919–2922, 2893–2895 (C–H), 1119–1123 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, CDCl$_3$), δ: 1.43 M (10H, (CH$_2$)$_5$), 1.75 (2H, m, CHIC*H*$_2$), 2.46 (1H, dd, CH(O)CH*H*, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz), 2.75 (1H, CH(O)C*H*H, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.0 Hz), 2.92 (3H, m, CF$_2$C*H*$_2$, C*H*(O)CH$_2$), 4.22 (1H, m, C*H*I). ^{19}F NMR (376.5 MHz, CDCl$_3$), δ: −145.77 (1F, m, C*F*), −132.47 (1F, m, C*F*CH$_2$), −130.56 (2F, m, CF$_2$), −84.15 (2F, m, CFC*F*$_2$O), −82.92 (2F, m, CF$_2$C*F*$_2$O), −82.33 (3F, m, C*F*$_3$CF$_2$), −80.79 (6F, m, 2C*F*$_3$CF). Analysis: Calc. for $C_{18}H_{18}F_{17}IO_3$: C, 29.53; H, 2.48; F, 44.11%. Found: C, 29.42; H, 2.36; F, 43.97%.

3.2. General procedure for the dehydrohalogenation of iod-F-alkylated epoxides **4a, c, d, 5a–c, e**

DBU 12.2 g (0.08 mol) was added dropwised to compound (**4a, c, d, 5a–c, e**) (0.08 mol) in 30 ml CH$_2$Cl$_2$. Then mixture was stirred at room temperature for 20 min. After that mixture was diluted with 100 ml water. The organic layer was washed with 2 M H$_2$SO$_4$ to pH ≈ 5, then with aqueous K$_2$CO$_3$. After drying (MgSO$_4$), the solvent was evaporation, the pure compound (**6a–e**, **7a–c**, **e**) was obtained by distillation under reduced pressure.

3.2.1. 4,4,4-Trifluorobut-2-enyloxymethyloxirane (**6a**)

Colorless liquid: yield 84%; bp, 110–112 °C/3 Torr. IR υ (cm^{-1}): 2963–2965, 2920–2922, 2892–2894 (C–H), 1680 (C=C), 1121–1123 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, CDCl$_3$), δ: 2.62 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz, CH(O)CH*H*), 2.81 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.2 Hz, CH(O)C*H*H), 3.17 (1H, tdd, $^3J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 4.2 Hz, $^3J_{H,H}$ = 2.7 Hz, C*H*(O)CH$_2$), 3.40 (1H, dd, $^2J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 6.1 Hz, CH*H*CH(O)CH$_2$), 3.84 (1H, dd, $^2J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 2.6 Hz, C*H*HCH(O)CH$_2$), 4.20 (2H, m, CH=CHC*H*$_2$), 5.70 (1H-*Z*, m, CF$_3$C*H*), 6.00 (1H-*E*, dqt, $^3J_{H,H}$ = 15.8 Hz, $^3J_{H,F}$ = 6.6 Hz, $^4J_{H,H}$ = 2.1 Hz, CF$_3$C*H*), 6.15 (1H-*Z*, dt, $^3J_{H,H}$ = 12.1 Hz, $^3J_{H,H}$ = 5.9 Hz, CF$_3$CH = C*H*), 6.42 (1H-*E*, dtq, $^3J_{H,H}$ = 15.8 Hz, $^3J_{H,H}$ = 4.1 Hz, $^4J_{H,F}$ = 2.1 Hz, CF$_3$CH=C*H*); ^{19}F NMR (376.5 MHz, CDCl$_3$), δ: −65.23 (3F-*E*, ddd, $^3J_{F,H}$ = 6.3 Hz, $^4J_{F,H}$ = 5.2 Hz, $^5J_{F,H}$ = 2.9 Hz, CF$_3$), −60.10 (3F-*Z*, td, $^3J_{F,H}$ = 8.7 Hz, $^4J_{F,H}$ = 2.6 Hz, CF$_3$). Analysis: Calc. for $C_7H_9F_3O_2$: C, 46.16; H, 4.98; F, 31.29%. Found: C, 46.04; H, 4.87; F, 31.13%.

3.2.2. 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoronon-2-enyloxymethyloxirane (**6c**)

Colorless liquid: yield 85%; bp, 109–110 °C/5 Torr. IR υ (cm^{-1}): 2962–2964, 2921–2923, 2892–2894 (C–H), 1680 (C=C), 1120–1123 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, CDCl$_3$), δ: 2.62 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz, CH(O)CH*H*), 2.82 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.2 Hz, CH(O)C*H*H), 3.18 (1H, tdd, $^3J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 4.2 Hz, $^3J_{H,H}$ = 2.7 Hz, C*H*(O)CH$_2$), 3.39 (1H-*Z*, dd, $^2J_{H,H}$ = 11.4 Hz, $^3J_{H,H}$ = 6.0 Hz, CH*H*CH(O)CH$_2$), 3.41 (1H-*E*, dd, $^2J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 6.1 Hz, CH*H*CH(O)CH$_2$), 3.78 (1H-*Z*, dd, $^2J_{H,H}$ = 11.4 Hz, $^3J_{H,H}$ = 2.8 Hz, C*H*HCH(O)CH$_2$), 3.85 (1H-*E*, dd, $^2J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 2.6 Hz, C*H*HCH(O)CH$_2$), 4.22 (2H-*E*, m, CH = CHC*H*$_2$), 4.35 (2H-*Z*, m, CH=CHC*H*$_2$), 5.61 (1H-*Z*, m, CF$_2$C*H*), 5.96 (1H-*E*, m, CF$_2$C*H*), 6.30 (1H-*Z*, dm, $^3J_{H,H}$ = 12.1 Hz, CF$_2$CH=C*H*), 6.45 (1H-*E*, dm, $^3J_{H,H}$ = 15.8 Hz, CF$_2$CH=C*H*); ^{19}F NMR (376.5 MHz, CDCl$_3$), δ: −127.02 (2F, m, CF$_{2\omega}$), −124.19 (2F, m, CF$_{2\delta}$), −123.72 (2F, m, CF$_{2\beta}$), −122.46 (2F, m, CF$_{2\gamma}$), −112.59 (2F-*E*, m, CF$_{2\alpha}$), −108.77 (2F-*Z*, m, CF$_{2\alpha}$), −81.78 (3F, tt, $^3J_{F,F}$ = 10.1 Hz, $^4J_{F,F}$ = 2.4 Hz, CF$_3$). Analysis: Calc. for $C_{12}H_9F_{13}O_2$: C, 33.35; H, 2.10; F, 57.15%. Found: C, 33.38; H, 2.15; F, 57.26%.

3.2.3. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundec-2-enyloxymethyl-oxirane (**6d**)

Colorless liquid: yield 84%; bp, 130–132 °C/5 Torr. IR υ (cm^{-1}): 2963–2965, 2920–2922, 2892–2894 (C–H), 1680 (C=C), 1121–1123 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, CDCl$_3$), δ: 2.62 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz, CH(O)CH*H*), 2.82 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.2 Hz, CH(O)C*H*H), 3.18 (1H, tdd, $^3J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 4.2 Hz, $^3J_{H,H}$ = 2.7 Hz, C*H*(O)CH$_2$), 3.39 (1H-*Z*, dd, $^2J_{H,H}$ = 11.4 Hz, $^3J_{H,H}$ = 6.0 Hz, CH*H*CH(O)CH$_2$), 3.41 (1H-*E*, dd, $^2J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 6.1 Hz, CH*H*CH(O)CH$_2$), 3.78 (1H-*Z*, dd, $^2J_{H,H}$ = 11.4 Hz, $^3J_{H,H}$ = 2.8 Hz, C*H*HCH(O)CH$_2$), 3.86 (1H-*E*, dd, $^2J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 2.6 Hz, C*H*HCH(O)CH$_2$), 4.23 (2H-*E*, m, CH = CHC*H*$_2$), 4.36 (2H-*Z*, m, CH=CHC*H*$_2$), 5.61 (1H-*Z*, m, CF$_2$C*H*), 5.96 (1H-*E*, m, CF$_2$C*H*), 6.30 (1H-*Z*, dm, $^3J_{H,H}$ = 12.0 Hz, CF$_2$CH=C*H*), 6.45 (1H-*E*, dm, $^3J_{H,H}$ = 15.7 Hz, CF$_2$CH=C*H*); ^{19}F NMR (376.5 MHz, CDCl$_3$), δ: −126.74 (2F, m, CF$_{2\omega}$), −123.78 (6F, m, CF$_{2\delta}$CF$_{2\lambda}$CF$_{2\chi}$), −122.40 (2F, m, CF$_{2\beta}$), −121.88 (2F, m, CF$_{2\gamma}$), −112.27 (2F-*E*, m, CF$_{2\alpha}$), −108.42 (2F-*Z*, m, CF$_{2\alpha}$), −81.61 (3F, t, $^3J_{F,F}$ = 10.1 Hz, CF$_3$). Analysis: Calc. for $C_{14}H_9F_{17}O_2$: C, 31.60; H, 1.70; F, 60.69%. Found: C, 31.65; H, 1.75; F, 60.72%.

3.2.4. 11,11,11-Trifluoro-1,2-epoxyundec-9-ene (**7a**)

Colorless liquid: yield 81%; bp, 112–113 °C/1 Torr. IR υ (cm^{-1}): 2962–2965, 2921–2924, 2892–2894 (C–H), 1682 (C═C), 1120–1122 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 1.44 (10H, m, $(CH_2)_5$), 2.15 (2H, m, CH = CHC*H*$_2$), 2.46 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz, CH(O)CH*H*), 2.75 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.0 Hz, CH(O)C*H*H), 2.90 (1 H, m, C*H*(O)CH$_2$), 5.58 (1H-*Z*, m, CF$_2$C*H*), 5.60 (1H-*E*, dqt, $^3J_{H,H}$ = 15.8 Hz, $^3J_{H,F}$ = 6.5 Hz, $^4J_{H,H}$ = 1.6 Hz, CF$_2$C*H*), 6.00 (1H-*Z*, dt, $^3J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 7.9 Hz, CF$_2$CH═C*H*), 6.37 (1H-*E*, dtq, $^3J_{H,H}$ = 15.8 Hz, $^4J_{H,F}$ = 6.7 Hz, $^3J_{H,H}$ = 2.2 Hz, CF$_2$CH═C*H*); ^{19}F NMR (376.5 MHz, $CDCl_3$), δ: − 64.90 (3F-*E*, m, C*F*$_3$), − 59.10 (3F-*Z*, td, $^4J_{F,H}$ = 8.6, $^3J_{F,H}$ = 2.3, C*F*$_3$). Analysis: Calc. for $C_{11}H_{17}F_3O$: C, 59.45; H, 7.71; F, 25.64%. Found: C, 59.36; H, 7.63; F, 25.55%.

3.2.5. 11,11,12,12,13,13,14,14,14-Nonafluoro-1,2-epoxytetradec-9-ene (**7b**)

Colorless liquid: yield 87%; bp, 130–131 °C/3 Torr. IR υ (cm^{-1}): 2962–2964, 2920–2922, 2892–2894 (C–H), 1681 (C═C), 1120–1123 (C–O–C, C–F).^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 1.43 (10H, m, $(CH_2)_5$), 2.20 (2H, m, CH = CHC*H*$_2$), 2.46 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz, CH(O)CH*H*), 2.74 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.0 Hz, CH(O)C*H*H), 2.90 (1H, m, C*H*(O)CH$_2$), 5.57 (1H-*Z*, m, CF$_2$C*H*), 5.63 (1H-*E*, dt, $^3J_{H,H}$ = 15.7 Hz, $^3J_{H,F}$ = 12.5 Hz, CF$_2$C*H*), 6.12 (1H-*Z*, dt, $^3J_{H,H}$ = 12.0 Hz, $^3J_{H,H}$ = 7.8 Hz, CF$_2$CH═C*H*), 6.44 (1H-*E*, dtt, $^3J_{H,H}$ = 15.7 Hz, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,F}$ = 2.3 Hz, CF$_2$CH═C*H*); ^{19}F NMR (376.5 MHz, $CDCl_3$), δ: −126.77 (2F-*Z*, m, C*F*$_{2\gamma}$), −126.50 (2F-*E*, m, C*F*$_{2\gamma}$), −125.38 (2F-*Z*, C*F*$_{2\beta}$), −124.99 (2F-*E*, m, C*F*$_{2\beta}$), −112.69 (2F-*E*, m, C*F*$_{2\alpha}$), −108.83 (2F-*Z*, m, C*F*$_{2\alpha}$), −81.91 (3F, tt, $^3J_{F,F}$ = 9.7 Hz, $^4J_{F,F}$ = 3.3 Hz, C*F*$_3$). Analysis: Calc. for $C_{14}H_{17}F_9O$: C, 45.17; H, 4.60; F, 45.93%. Found: C, 45.06; H, 4.49; F, 45.81%.

3.2.6. 11,11,12,12,13,13,14,14,15,15,16,16,16-Tridecafluoro-1,2-epoxytetradec-9-ene (**7c**)

Colorless liquid: yield 83%; bp, 153–155 °C/3 Torr. IR υ (cm^{-1}): 2962–2964, 2921–2923, 2892–2894 (C–H), 1680 (C═C), 1120–1124 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 1.43 (10H, m, $(CH_2)_5$), 2.20 (2H, m, CH = CHC*H*$_2$), 2.46 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz, CH(O)CH*H*), 2.74 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^2J_{H,H}$ = 4.0 Hz, CH(O)C*H*H), 2.90 (1H, m, C*H*(O)CH$_2$), 5.57 (1H-*Z*, m, CF$_2$C*H*), 5.63 (1H-*E*, dt, $^3J_{H,H}$ = 15.7 Hz, $^3J_{H,F}$ = 12.5 Hz, CF$_2$C*H*), 6.12 (1H-*Z*, dt, $^3J_{H,H}$ = 12.0 Hz, $^3J_{H,H}$ = 7.8 Hz, CF$_2$CH═C*H*), 6.44 (1H-*E*, dtt, $^3J_{H,H}$ = 15.7 Hz, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,F}$ = 2.3 Hz, CF$_2$CH═C*H*); ^{19}F NMR (376.5 MHz, $CDCl_3$), δ: −127.89 (2F, m, C*F*$_{2\omega}$), −124.97 (2F, m, C*F*$_{2\delta}$), −123.87 (2F, m, C*F*$_{2\beta}$), −122.46 (2F, m, C*F*$_{2\gamma}$), −112.59 (2F-*E*, m, C*F*$_{2\alpha}$), −108.77 (2F-*Z*, m, C*F*$_{2\alpha}$), −81.78 (3F, tt, $^3J_{F,F}$ = 10.1 Hz, $^4J_{F,F}$ = 2.4 Hz, C*F*$_3$).

3.2.7. 11,14-Bis(trifluoromethyl)-12,15-dioxa-11,13,13,14,16,16,17,17,18,18,18-undecafluoro-1,2-epoxyoctadec-9-ene (**7e**)

Colorless liquid: yield 85%; bp, 139–140 °C/1 Torr. IR υ (cm^{-1}): 2963–2965, 2920–2922, 2892–2894 (C–H), 1682 (C═C), 1119–1124 (C–O–C, C–F). ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 1.42 (10H, m, $(CH_2)_5$), 2.22 (2H, m, CHC*H*$_2$), 2.46 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz, CH(O)CH*H*), 2.74 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.0 Hz, CH(O)C*H*H), 2.91 (1H, m, C*H*(O)CH$_2$), 5.32 (1H-*Z*, m, CFC*H*), 5.63 (1H-*E*, dd, $^3J_{H,H}$ = 15.8 Hz, $^3J_{H,F}$ = 12.2 Hz, CFC*H*), 6.11 (1H-*Z*, m, CFCH═C*H*), 6.45 (1H-*E*, dm, $^3J_{H,H}$ = 15.8 Hz, CFCH═C*H*); ^{19}F NMR (376.5 MHz, $CDCl_3$), δ: −145.84 (1F, m, C*F*), −130.37 (2F, m, C*F*$_2$), −129.40 (1F, m, C*F*CH$_2$), −85.71 (2F, m, CFC*F*$_2$O), −82.89 (2F, m, CF$_2$C*F*$_2$O), −82.13 (3F, m, C*F*$_3$CF$_2$), −80.75 (6F, m, 2C*F*$_3$CF). Analysis: Calc. for $C_{18}H_{17}F_{17}O_3$: C, 35.78; H, 2.84; F, 53.45%. Found: C, 35.65; H, 2.75; F, 53.31%.

3.3. Tributyltin hydride reduction of iodo(perfluoroalkyl)allyl glycidyl ethers 4*b*, c

Tributyltin hydride was prepared by $LiAlH_4$ reduction of tributyltin chloride and distilled, bp 101–104 °C/5 Torr. Tributyltin hydride (0.052 mol) and 0.05 mol of compound (**4b**, **4c**), kept under nitrogen, was stirred by magnet bar at 95 °C, as Bz_2O_2 (2.5 mmol) was added dropwise during 4 h. In case of compound **4b** further distillation under reduced pressure gave pure compound **8b** (analysis according to GC) (the first fraction of distillation) (see bp). In case of compound **4c** after distillation of the substance at lowered pressure the obtained product can contain unreacted tributyltin hydride (analysis according to GC), in that case the substance is treated by saturated solution KF at ambient temperature. Then extracted by Et_2O (30 ml × 3), and combined organic phase was dried over anhydrous $MgSO_4$. The pure compound **8c** was obtained by distillation under reduced pressure.

3.3.1. 4,4,5,5,6,6,7,7,7-Nonafluoroheptyloxymethyloxirane (**8b**)

Colorless liquid: yield 94%; bp, 94–95 °C/3 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 1.89 (2H, m, CF$_2$CH$_2$C*H*$_2$), 2.21 (2H, m, CF$_2$C*H*$_2$), 2.60 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 2.7 Hz, CH(O)CH*H*), 2.80 (1H, dd, $^2J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.2 Hz, CH(O)C*H*H), 3.15 (1H, m, C*H*(O)CH$_2$), 3.36 (1H, dd, $^2J_{H,H}$ = 12.6 Hz, $^3J_{H,H}$ = 6.0 Hz, C*H*HCH(O)CH$_2$), 3.58 (2H, m, CH$_2$C*H*$_2$O), 3.77 (1H, dd, $^2J_{H,H}$ = 12.0 Hz, $^3J_{H,H}$ = 2.7 Hz, CH*H*CH(O)CH$_2$); ^{19}F NMR (376.5 MHz, $CDCl_3$), δ: − 126.92 (2F, m, CF$_3$C*F*$_2$), − 125.29 (2F, m, CF$_2$C*F*$_2$CH$_2$), − 115.48 (2F, m, C*F*$_2$CH$_2$), − 82.00 (3F, tt, $^3J_{F,F}$ = 10.0 Hz, $^4J_{F,F}$ = 3.4 Hz, C*F*$_3$). Analysis: Calc. for $C_{10}H_{11}F_9O_2$: C, 35.94; H, 3.32; F, 51.17%. Found: C, 35.83; H, 3.24; F, 51.02%.

3.3.2. 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononyloxymethyloxirane (**8c**)

Colorless liquid: yield 82%; bp, 109–110 °C/3 Torr. ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 1.90 (2H, m, CF$_2$CH$_2$C*H*$_2$), 2.21 (2H, m, CF$_2$C*H*$_2$), 2.60 (1H, dd, $^2J_{H,H}$ = 5.2 Hz, $^3J_{H,H}$ = 2.7 Hz, CH(O)CH*H*), 2.81 (1H, dd, $^2J_{H,H}$ = 5.2 Hz, $^3J_{H,H}$ = 4.2 Hz, CH(O)C*H*H), 3.15 (1H, m, C*H*(O)CH$_2$), 3.38 (1H, dd, $^2J_{H,H}$ = 12.6 Hz, $^3J_{H,H}$ = 6.0 Hz, C*H*HCH(O)CH$_2$), 3.58 (2H, m, CH$_2$C*H*$_2$O), 3.77 (1H, dd, $^2J_{H,H}$ = 12.0 Hz, $^3J_{H,H}$ = 2.7 Hz, CH*H*CH(O)CH$_2$); ^{19}F NMR (376.5 MHz, $CDCl_3$), δ: −127.29 (2F, m, CF$_{2\omega}$), −124.55 (2F, m, CF$_{2\delta}$), − 123.87 (2F, m, CF$_{2\beta}$), − 122.99 (2F, m, CF$_{2\gamma}$), − 115.51 (2F, m, CF$_{2\alpha}$), − 81.88 (3F, tt, $^3J_{F,F}$ = 10.1 Hz, $^4J_{F,F}$ = 2.4 Hz, CF$_3$). Analysis: Calc. for $C_{12}H_{11}F_{13}O_2$: C, 33.20; H, 2.55; F, 56.88%. Found: C, 33.05; H, 2.45; F, 56.74%.

3.4. Cationic polymerization of fluorinated epoxides in the presence of boron trifluoride etherate

General procedure. Fluorinated epoxide (0.03 mol) in 50 ml CCl_4 was stirred by magnet bar at 0 °C, as $2.1 \cdot 10^{-4}$ mol $BF_3 \cdot Et_2O$ was added dropwise during 20 min. Then mixture was stirred at room temperature for 1 h. After that mixture was diluted with 100 ml of water. The organic layer was washed with 2 M H_2SO_4 to pH≈5, then with aqueous K_2CO_3. After drying ($MgSO_4$), the solvent was evaporated under reduced pressure.

Data of ^{19}F NMR spectra of obtained polyethers are the same for appropriate epoxycompounds, but signals are broad.

3.4.1. Poly[4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-iodononyloxymethyloxirane] (**9c**)

Yellow oil: yield 83%; M_w = 6700 g/mol. ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 2.62–2.83 (2H, m, CF$_2$C*H*$_2$), 3.52–3.93 (7H, m, OC*H*, OC*H*$_2$), 4.32–4.44 (1H, m, C*H*I).

*3.4.2. Poly[11,11,12,12,13,13,14,14,15,15,16,16,16-tridecafluoro-9-iodo-1,2-epoxyhexadecane] (**10c**)*

Yellow oil: yield 85%; M_w = 6800 g/mol. ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 1.21–1.83 (12H, m, $(CH_2)_6$), 2.75–2.98 (2H, m, CF_2CH_2), 3.48–3.73 (3H, m, OCH, OCH_2), 4.48–4.56 (1H, m, CHI).

*3.4.3. Poly[4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyloxymethyloxirane] (**11c**)*

Colorless oil: yield 92%; M_w = 7600 g/mol. ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 1.79–1.93 (2H, m, $CF_2CH_2CH_2$), 2.02–2.27 (2H, m, CF_2CH_2), 3.39–3.79 (7H, m, OCH, OCH_2).

*3.4.4. Poly[4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoronon-2-enyloxymethyloxirane] (**13c**)*

Colorless oil: yield 84%; M_w = 6900 g/mol. ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 3.51–4.02 (7H, m, OCH, OCH_2), 5.89–5.93 (1H, m, CF_2CH), 6.41–6.45 (1H, m, $CF_2CH{=}CH$).

*3.4.5. Poly[11,11,12,12,13,13,14,14,15,15,16,16,16-tridecafluoro-1,2-epoxytetradec-9-ene] (**14c**)*

Colorless oil: yield 87%; M_w = 8500 g/mol. ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 1.38–1.45 (10H, m, $(CH_2)_5$), 2.19–2.22 (2H, m, $CH = CHCH_2$), 3.48–3.94 (3H, m, $OCHCH_2O$), 5.87–5.92 (1H, m, CF_2CH), 6.41–6.45 (1H, m, $CF_2CH{=}CH$).

3.5. Zinc reduction of iodocontaining polyether **10c**

Polyether **10c** (0.01 mol), ethanol (50 ml) and zinc (0.015 mol) were heated to 82 °C and stirred rapidly while HCl was bubbled in. After 2 hr-reaction, the total product mixture was poured into water, extracted with ether, rinsed with aqueous sodium bisulfite and dried ($MgSO_4$), the solvent was evaporated under reduced pressure.

*3.5.1. Poly[11,11,12,12,13,13,14,14,15,15,16,16,16-tridecafluoro-1,2-epoxyhexadecane] (**12c**)*

Colorless oil: yield 87%; M_w = 5600 g/mol. ^{1}H NMR (400.1 MHz, $CDCl_3$), δ: 1.24–1.67 (14H, m, $(CH_2)_7$), 1.95–2.16 (2H, m, CF_2CH_2), 3.36–3.78 (3H, m, OCH, OCH_2); ^{19}F NMR (376.5 MHz, $CDCl_3$), δ: -127.29 (2F, m, $CF_{2\omega}$), -124.55 (2F, m, $CF_{2\delta}$), -123.87 (2F, m, $CF_{2\beta}$), -122.96 (2F, m, $CF_{2\gamma}$), -115.47 (2F, m, $CF_{2\alpha}$), -81.88 (3F, m, CF_3).

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