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Thermal Desulfurization of (Alkoxymethyl)thiiranes

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Abstract—Reaction of (alkoxymethyl)oxiranes with thiourea in methanol has afforded the corresponding thiiranes, and catalyst-free thermal desulfurization of the products has been studied. The major products of desulfurization are alcohols and alkenes, both in the cases of (polyfluoroalkyloxymethyl)thiiranes and their non-fluorinated analogs. Longer alkyl chain in thiiranes favors formation of alcohols over alkenes formation in the course of desulfurization.

Keywords: thiiranes, desulfurization, extrusion of sulfur, alcohol, alkene

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Three-membered heterocycles oxiranes and thiiranes are structural analogs. However, the studies of oxiranes chemistry are far more numerous. The scarcity of studies on thiiranes is mainly due to their lower availability and stability. The thiirane ring is less strained than the oxirane ring, but energy of the C–S bond is of 66 kcal/mol as compared with 91 kcal/mol for the C–O bond; hence, reactivity of thiiranes is higher [1]. This has been confirmed by possibility of spontaneous (photo) oligo- and polymerization of thiiranes even at room temperature, as distinct from oxiranes, as well as by studies of typical reactions of three-membered heterocycles (regioselective ring opening under the action of various reagents) [1, 2].

Another striking example of the difference between thiiranes and oxiranes is thermal destruction of thiiranes accompanied by extrusion of sulfur and formation of the corresponding alkenes. The mechanism of desulfurization of thiiranes is still questionable. According to Chew and Harpp [3], it can involve either mono- or bimolecular ionic mechanism, whereas quantum-chemical simulation has suggested the radical mechanism of thiiranes desulfurization to be energetically preferable [4].

Detailed data on desulfurization of thiiranes have been presented in monograph [2] and reviews [1, 5]. Desulfurization can occur under the conditions of pyrolysis, photolysis, in the presence of radicals or catalysts. Thiiranes with aromatic substituents at carbon atoms of the three-membered ring are the most prone to desulfurization. The process is of practical importance for synthesis of sterically hindered alkenes [6].

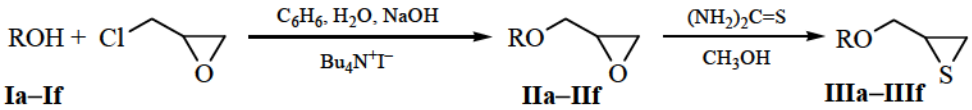
No data on desulfurization of thiiranes with substituents containing ether bonds has been found in the literature. Studies of desulfurization of thiiranes with oxygen-containing groups have been limited to compounds with carbonyl- or hydroxyl-containing substituents; it has been demonstrated that after the extrusion of sulfur the substituents remain intact [7].

The present work aimed at comparative study of thermal desulfurization of fluorinated and non-fluorinated (alkoxymethyl)thiiranes in the open system.

The studied compounds were prepared via a modified Williamson reaction: the reaction of alcohols (**Ia**–**If**) with epichlorohydrin under conditions of phase-transfer catalysis gave oxiranes **IIa**–**IIf** (Scheme 1) [8–10]; treatment of compounds **IIa**–**IIf** with thiourea in methanol afforded the corresponding thiiranes **IIIa**–**IIIf** in moderate yields [11]. Fluorinated thiiranes **IIIb**–**IIId** have never been synthesized before.

Thermal desulfurization of thiiranes **IIIa**–**IIIf** was performed in an open system with simultaneous distillation of low-boiling fractions; the latter were studied by GC–MS. Conversion of compounds **IIIa**–**IIIf** was of 99% to give the corresponding alcohols **Ia**–

Scheme 1.



Ia–If **IIa–IIf** **IIIa–IIIf**

R = $H(CF_2)_2CH_2$ (**a**), $H(CF_2)_4CH_2$ (**b**), $C_6F_{13}CH_2$ (**c**), $C_8F_{13}CH_2$ (**d**), C_4H_9 (**e**), C_6H_{13} (**f**).

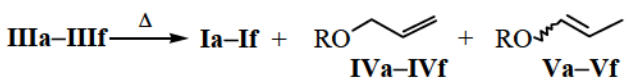
If, alkenes **IVa–IVf**, and their internal analogs **Va–Vf** (Scheme 2). Compounds **Va** and **Ve** exist as mixtures of the *Z*- and *E*-isomers.

Fragmentation of molecular ions (MI) of non-fluorinated alkenes **IVe, IVf, Ve,** and **Vf** was in line with the reference data [12]. Intensity of the MI peak in the mass spectra of alkenes **IVe** and **IVf** was of 0.1% and 0.02%, respectively; intensity of the MI peak in the mass spectra of alkenes **Ve** and **Vf** was of 11% and 0.7%, respectively. That is, the longer alkyl substituent decreased intensity of the MI peak. In the mass spectra of alkenes **IVe, IVf** the base peak was that of the ion with *m/z* 41 $[C_3H_5]^+$, in the case of alkenes **IVa–IVf** and **Va–Vf** the base peak corresponded to *m/z* 29 $[C_2H_5]^+$.

Similarly, intensity of the MI peak in the mass spectra of fluorinated alkenes **IVa–IVc** and **Va–Vc** decreased for longer fluoroalkyl groups. The MI peak intensity was as follows: 1.2% for alkenes **IVc** and **Vc**, 4–5% for alkenes **IVb** and **Vb**, and 8–9% for alkenes **IVa** and **Va**. Fragmentation of the MI peak was similar for all the fluorinated alkenes **IVa–IVc** and **Va–Vc**. The base peak was the one with *m/z* 41 $[C_3H_5]^+$. All the mass spectra contained the peaks typical of ions appeared via fragmentation of the fluorinated substituents, their intensity being of 2–15%. The main difference between the mass spectra of alkenes **IVa–IVc** and **Va–Vc** was intensity of the peak with *m/z* 29 $[C_2H_5]^+$: in the mass spectra of alkenes **IVa–IVc** it was of 20–30%, whereas for alkenes **Va–Vc** it was increased to 60–75%.

The ratio of the products **Ia–If**, **IVa–IVf**, and **Va–Vf** was determined by internal normalization from the peaks area in the chromatograms. The data are given in the table.

Scheme 2.



IVa–IVf **Va–Vf**

R = $H(CF_2)_2CH_2$ (**a**), $H(CF_2)_4CH_2$ (**b**), $C_6F_{13}CH_2$ (**c**), $C_8F_{13}CH_2$ (**d**), C_4H_9 (**e**), C_6H_{13} (**f**).

The tabulated data were consistent with the known reference data: the major products of desulfurization of thiiranes **IIIa–IIIf** were the corresponding alkenes **IVa–IVf**. However, the presence of ether bond in the substituent of the thiirane ring favored formation of alcohols **Ia–If** under thermolysis conditions. To get a better insight into the mechanism of desulfurization, a series of experiments was performed; the composition of the gas phase evolving during thermal destruction of thiiranes **IIIa–IIIf** was analyzed using the GC–MS technique. It was shown that the thermolysis yielded propene, hydrogen sulfide, and sulfur dioxide besides the previously detected products (**I, IV,** and **V**). Therefore, the overall reaction of desulfurization of thiiranes **IIIa–IIIf** could be presented by the following scheme:

$$2\mathbf{III} + [O] \rightarrow \mathbf{I} + \mathbf{IV} + \mathbf{V} + CH_2{=}CHCH_3 + H_2S + SO_2.$$

Since hydrogen sulfide (with reductive properties) and sulfur dioxide (with oxidative properties) were formed in the course of desulfurization, the process could be considered as a disproportionation reaction proceeding via ionic or free-radical mechanism.

A specific feature of thermal desulfurization of thiiranes **IIIa–IIIf** was that the longer alkyl substituent increased the amount of the corresponding alcohol, and simultaneously less of the corresponding alkene **IVa–IVf, Va–Vf** was formed. On top of that, thermolysis of the fluorinated thiiranes **IIIa–IIId** gave notably more of the alcohols **Ia–Id** than the non-fluorinated compounds **IIIe** and **IIIf**.

Boiling points and quantitative composition of the products of desulfurization of thiiranes **IIIa–IIIf**

Comp. no.	R	bp, °C	Ratio of products (from peaks area) **I** : **IV** : **V**, %
IIIa	$H(CF_2)_2CH_2$	108–121	5.64 : 87.15 : 6.37
IIIb	$H(CF_2)_4CH_2$	149–165	9.65 : 87.38 : 2.22
IIIc	*n*-$C_6F_{13}CH_2$	162–175	30.95 : 68.54 : 0.31
IIId	*n*-$C_8F_{17}CH_2$	189–195	37.70 : 61.69 : 0
IIIe	*n*-C_4H_9	118–127	2.26 : 93.45 : 2.98
IIIf	*n*-C_6H_{13}	164–185	8.34 : 90.39 : 0.27

The mixtures of the products of desulfurization of thiiranes **IIIa–IIIf** were separated either via chemical method or by means of chromatography. Noteworthily, alkenes **Va–Vf** could not be isolated as individual compounds due to the low content in the mixtures and also because their retention times were close to those of the corresponding alkenes **IVa–IVf**.

Bromination of the mixtures of compounds **Ib, IVb** and **Id, IVd** allowed conversion of the alkenes into the corresponding mixtures 1,2-dibromoalkanes [$H(CF_2)_4CH_2OCH_2CHBrCH_2Br$ **VIb** and $C_8F_{17}CH_2O{\cdot}CH_2CHBrCH_2Br$ **VId**). Dibromoalkanes **VIb** and **VId** could be separated from alcohols **Ib** and **Id** by fractional distillation and gave individual alkenes **IVb** and **IVd** after debromination. Other alkenes **IVa, IVc, IVe, IVf** were separated from alcohols **Ia, Ic, Ie, If** using the preparative HPLC method.

To conclude, thermal desulfurization of thiiranes containing substituents with ether bond was performed in the open system, and formation of alcohols was observed besides the typical products of thiiranes thermolysis (alkenes). Composition of the products mixture was affected by length of the alkyl substituent: longer alkyl present in the molecule favored formation of the alcohol.

EXPERIMENTAL

IR spectra were recorded with a Perkin–Elmer Spectrum One spectrophotometer. Elemental analysis was performed using a Perkin–Elmer CHN PE 2400 automatic analyzer. NMR spectra were registered with a Bruker DRX-400 spectrometer [400 MHz (^{1}H), with referenced to Me_4Si; 376 MHz (^{19}F), referenced to C_6F_6] in $CDCl_3$ solutions.

Chromatograms and mass spectra were recorded with a Trace GC Ultra DSQ II Thermo Scientific chromatograph equipped with mass spectrometric detector. Conditions: quartz capillary column Thermo TR-5ms of 30 m length, 0.25 mm diameter, 0.25 μm polydimethylsiloxane film (5 wt % of grafted phenyl groups); quadrupole mass detector, scanning by total ionic current in the range of masses 20–1000 amu, electronic ionization (70 eV). Starting temperature of the column 40°C (3 min), heating at 10°C/min, final temperature of the column 280°C. Temperature of the injector 250°C, of the detector 200°C, of the transition chamber 200°C. Gas-carrier was helium, flow splitting of 1 : 50, flow rate through the column 1.0 mL/min.

Preparative HPLC was performed using a semi-preparative liquid chromatograph Agilent 1200 Series (Agilent Technologies) equipped with autosampler (900 μL), diode-matrix detector (analytical wavelength 200 nm), and a fraction collector. Column: ZORBAX Eclipse XDB-C18 Semi-Preparative 9.4 × 250 mm, particle size 5 μm, room temperature. Acetonitrile–water 75 : 25 was used as a mobile phase, isocratic regime, the flow rate of 4 mL/min,.

Synthesis of oxiranes IIa–IIf was performed as described in [8–10].

2,2,3,3-Tetrafluoropropyloxymethyloxirane (IIa). Yield 55%, colorless liquid, bp 175–177°C. Spectral data were consistent with the reference ones [8].

2,2,3,3,4,4,5,5-Octafluoropentyloxymethyloxirane (IIb). Yield 57%, colorless liquid, bp 85–89°C (12 mmHg). Spectral data were consistent with the reference ones [8].

2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyloxymethyloxirane (IIc). Yield 48%, colorless liquid, bp 114–117°C (25 mmHg). IR spectrum, ν, cm^{-1}: 3060, 3005, 2939, 2889 (C–H), 1239, 1202, 1144 (C–F, C–O). ^{1}H NMR spectrum, δ, ppm: 2.64 d.d [1H, CH(O)C<u>H</u>H, *J* 4.9 and *J* 2.7 Hz], 2.82 m [1H, CH(O)CH<u>H</u>], 3.18 m [1H, C<u>H</u>(O)CH_2], 3.53 d.d [1H, OC<u>H</u>HCH(O)CH_2, *J* 11.9 and *J* 5.9 Hz], 4.03 m (3H, $CF_2C\underline{H_2}OCH\underline{H}$). ^{19}F NMR spectrum, δ, ppm: 35.64 m (2F, CF_2), 38.37 m (2F, CF_2), 38.94 m (2F, CF_2), 39.56 m (2F, CF_2), 41.95 m (2F, CF_2), 80.99 t.t (3F, CF_3, *J* 9.9 and *J* 2.3 Hz). Found, %: C 29.89; H 1.73; F 60.45. $C_{10}H_7F_{13}O_2$. Calculated, %: C 29.57; H 1.74; F 60.81.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyloxymethyloxirane (IId). Yield 43%, colorless liquid, bp 137–141°C (12 mmHg). Spectral data were consistent with the reference ones [9].

Butoxymethyloxirane (IIe). Yield 60%, colorless liquid, bp 163–165°C. IR spectrum, ν, cm^{-1}: 2959, 2934, 2871 (C–H), 1107 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.92 t (3H, CH_3, *J* 7.4 Hz), 1.38 m (2H $CH_3C\underline{H_2}$), 1.58 m (2H, $CH_3CH_2C\underline{H_2}$), 2.61 d.d [1H, CH(O)C<u>H</u>H, *J* 5.1 and *J* 2.7 Hz], 2.79 m [1H, CH(O)CH<u>H</u>], 3.14 m [1H, C<u>H</u>(O)CH_2], 3.38 d.d [1H, OC<u>H</u>HCH(O)CH_2, *J* 11.5 and *J* 5.8 Hz], 3.50 m [2H, $C\underline{H_2}OCH_2CH(O)$], 3.71 d.d [1H, OC<u>H</u>HCH(O)CH_2, *J* 11.5 and *J* 3.1 Hz]. Found, %: C 64.18; H 10.47. $C_7H_{14}O_2$. Calculated, %: C 64.58; H 10.84.

Hexyloxymethyloxirane (IIf). Yield 52%, colorless liquid, bp 95–97°C (12 mmHg). IR spectrum, ν, cm^{-1}: 2956, 2931, 2860 (C–H), 1108 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.90 m (3H, CH_3), 1.32 m (6H,

$CH_3C\underline{H}_2C\underline{H}_2C\underline{H}_2$), 1.58 m (2H, $CH_2C\underline{H}_2CH_2O$), 2.61 d.d [1H, $CH(O)C\underline{H}H$, *J* 5.4 and *J* 2.7 Hz], 2.80 m [1H, $CH(O)CH\underline{H}$], 3.15 m [1H, $C\underline{H}(O)CH_2$], 3.38 d.d [1H, $OC\underline{H}HCH(O)CH_2$, *J* 11.5 and *J* 5.8 Hz], 3.49 m [2H, $C\underline{H}_2OCH_2CH(O)$], 3.71 d.d [1H, $OC\underline{H}HCH(O)CH_2$, *J* 11.5 and *J* 3.1 Hz]. Found, %: C 68.38; H 11.44. $C_9H_{18}O_2$. Calculated, %; C 68.31; H 11.47.

Synthesis of thiiranes IIIa–IIIf was performed as described elsewhere [11].

2,2,3,3-Tetrafluoropropyloxymethylthiirane (IIIa). Yield 63%, colorless liquid, bp 81–82°C (12 mmHg). Spectral data were consistent with the reference ones [13].

2,2,3,3,4,4,5,5-Octafluoropentyloxymethylthiirane (IIIb). Yield 70%, colorless liquid, bp 92–94°C (12 mmHg). IR spectrum, ν, cm^{-1}: 2999, 2934 (C–H), 1163, 1118 (C–F, C–O). ^{1}H NMR spectrum, δ, ppm: 2.21 d.d [1H, $CH(S)C\underline{H}H$ *J* 5.3 and *J* 1.4 Hz], 2.54 m [1H, $CH(S)CH\underline{H}$], 3.08 m [1H, $C\underline{H}(S)CH_2$], 3.72 m (2H, $CF_2CH_2OC\underline{H}_2$), 4.02 m (2H, $CF_2C\underline{H}_2$), 6.06 t.t (1H, HCF_2, *J* 52.0 and *J* 5.5 Hz). ^{19}F NMR spectrum, δ, ppm: 24.49 d.m (2F, HCF_2, *J* 52.0 Hz), 31.48 m (2F, CF_2), 36.15 t (2F, CF_2, *J* 8.2 Hz), 41.95 m (2F, CF_2). Found, %: C 31.60; H 2.59; F 49.62; S 10.27. $C_8H_8F_8OS$. Calculated, %: C 31.59; H 2.65; F 49.96; S 10.54.

2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyloxymethylthiirane (IIIc). Yield 75%, colorless liquid, bp 119–122°C (12 mmHg). IR spectrum, ν, cm^{-1}: 3000, 2879 (C–H), 1235, 1194, 1143 (C–F, C–O). ^{1}H NMR spectrum, δ, ppm: 2.22 d.d [1H, $CH(O)C\underline{H}H$, *J* 5.3 and *J* 1.4 Hz], 2.54 m [1H, $CH(O)CH\underline{H}$], 3.08 m [1H, $C\underline{H}(O)CH_2$], 3.73 m [2H, $OC\underline{H}_2CH(O)CH_2$], 4.03 m (2H, $CF_2C\underline{H}_2OCH$). ^{19}F NMR spectrum, δ, ppm: 35.63 m (2F, CF_2), 38.32 m (2F, CF_2), 39.00 m (2F, CF_2), 39.56 m (2F, CF_2), 41.94 m (2F, CF_2), 81.00 t.t (3F, CF_3, *J* 10.0 and *J* 2.3 Hz). Found, %: C 28.81; H 1.76; F 57.77; S 7.23. $C_{10}H_7F_{13}OS$. Calculated, %: C 28.45; H 1.67; F 58.50; S 7.59.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyloxymethylthiirane (IIId). Yield 65%, colorless viscous oil, bp 145–148°C (12 mmHg). IR spectrum, ν, cm^{-1}: 2993, 2929, 2883 (C–H), 1240, 1206, 1148 (C–F, C–O). ^{1}H NMR spectrum, δ, ppm: 2.22 d.d [1H, $CH(O)C\underline{H}H$, *J* 5.3 and *J* 1.3 Hz], 2.54 m [1H, $CH(O)\cdot CH\underline{H}$], 3.09 m [1H, $C\underline{H}(O)CH_2$], 3.73 m (2H, $CF_2CH_2OC\underline{H}_2$), 4.03 m (2H, $CF_2C\underline{H}_2$). ^{19}F NMR spectrum, δ, ppm: 35.64 m (2F, CF_2), 38.41 m (2F, CF_2), 39.05 m (2F, CF_2), 39.80 m (6F, CF_2), 42.15 m (2F, CF_2), 81.00 t (3F, CF_3, *J* 9.9 Hz). Found, %: C 27.95; H 1.62; F 61.43; S 6.21. $C_{12}H_7F_{17}OS$. Calculated, %: C 27.60; H 1.35; F 61.85; S 6.14.

Butyloxymethylthiirane (IIIe). Yield 60%, colorless viscous oil, bp 94–96°C (12 mmHg). IR spectrum, ν, cm^{-1}: 2958, 2933, 2866 (C–H), 1100 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H CH_3, *J* 7.4 Hz), 1.38 m (2H, $CH_3C\underline{H}_2$), 1.58 m (2H, $CH_3CH_2C\underline{H}_2$), 2.21 d.d [1H, $CH(S)C\underline{H}H$, *J* 5.4 and *J* 1.1 Hz], 2.53 m [1H, $CH(S)CH\underline{H}$], 3.07 m [1H, $C\underline{H}(S)CH_2$], 3.42 d.d [1H, $OC\underline{H}HCH(S)CH_2$, *J* 10.7 and *J* 5.8 Hz], 3.50 t [2H, $C\underline{H}_2OCH_2CH(S)$, *J* 6.7 Hz], 3.64 [1H, $OC\underline{H}HCH(S)CH_2$, *J* 10.7 and *J* 5.6 Hz]. Found, %: C 57.38; H 9.67; S 21.65. $C_7H_{14}OS$. Calculated, %: C 57.49; H 9.65; S 21.92.

Hexyloxymethylthiirane (IIIf). Yield 55%, liquid viscous oil, bp 120–123°C (12 mmHg). IR spectrum, ν, cm^{-1}: 2955, 2931, 2858 (C–H), 1102 (C–O). ^{1}H NMR spectrum, δ, ppm: 0.89 m (3H, CH_3), 1.32 m (6H, $CH_3C\underline{H}_2C\underline{H}_2C\underline{H}_2$), 1.59 m (2H, $CH_2C\underline{H}_2CH_2O$), 2.21 d.d [1H $CH(O)C\underline{H}H$, *J* 5.4 and *J* 1.0 Hz], 2.52 m [1H, $CH(S)CH\underline{H}$], 3.07 m [1H, $C\underline{H}(S)CH_2$], 3.41 d.d [1H, $OC\underline{H}HCH(S)CH_2$, *J* 10.7 and *J* 6.9 Hz], 3.49 t [2H, $C\underline{H}_2OCH_2CH(S)$, *J* 6.7 Hz], 3.64 d.d [1H, $OC\underline{H}HCH(S)CH_2$, *J* 10.7 and *J* 5.6 Hz]. Found, %: C 62.14; H 10.35; S 18.33. $C_9H_{18}OS$. Calculated, %: C 62.02; H 10.41; S 18.39.

General procedure of thermal desulfurization of compounds IIIa–IIIf. 0.03 mol of thiiranes **IIIa–IIIf** was heated in the Wood alloy at 210–215°C with simultaneous distillation of the products. The data on the temperature ranges for specific fractions are given in the table.

3-(2,2,3,3-Tetrafluoropropoxy)propene-1 (IVa). Yield 51%, colorless liquid. Spectral data were consistent with the reference ones [14].

3-(2,2,3,3,4,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyloxy)propene-1 (IVc). Yield 40%, colorless liquid. Spectral data were consistent with the reference ones [15].

3-Butoxypropene-1 (IVe). Yield 48%, colorless liquid, bp 107–110°C. IR spectrum, ν, cm^{-1}: 2959, 2933, 2866 (C–H), 1647 (C=C), 1097 (C–O). ^{1}H NMR, δ, ppm: 0.92 t (3H, CH_3, *J* 7.4 Hz), 1.38 m (2H, $CH_3C\underline{H}_2$), 1.57 m (2H, $CH_3CH_2C\underline{H}_2$), 3.43 t (2H, $C\underline{H}_2OCH_2CH{=}CH_2$, *J* 6.7 Hz), 3.96 m (2H, $CH_2O\cdot C\underline{H}_2CH{=}CH_2$), 5.16 m (1H, $CH_2CH{=}C\underline{H}H$), 5.27 m (1H, $CH_2CH{=}CH\underline{H}$), 5.92 m (1H, $OCH_2C\underline{H}{=}CH_2$). Found, %: C 72.19; H 12.08. $C_7H_{14}O$. Calculated, %: C 73.63; H 12.35.

3-Hexyloxypropene-1 (IVf). Yield 41%, colorless liquid, bp 169–172°C. IR spectrum, ν, cm^{-1}: 2930,

2857 (C–H) 1647 (C=C), 1100, 919 (C–O). ^{1}H NMR, δ, ppm: 0.88 t (3H, CH_3, *J* 6.9 Hz), 1.32 m (6H, $CH_3C\underline{H_2}C\underline{H_2}C\underline{H_2}$), 1.58 m (2H, $CH_2C\underline{H_2}CH_2O$), 3.42 t (2H, $C\underline{H_2}OCH_2CH{=}CH_2$, *J* 6.7 Hz), 3.96 d.m (2H, $CH_2OC\underline{H_2}CH{=}CH_2$, *J* 5.6 Hz), 5.16 m (1H, $CH_2{\cdot}CH{=}C\underline{H}H$), 5.27 m (1H, $CH_2CH{=}CH\underline{H}$), 5.92 m (1H, $OCH_2C\underline{H}{=}CH_2$). Found, %: C 76.21; H 12.68. $C_9H_{18}O$. Calculated, %: C 76.00; H 12.76.

General procedure of bromination of mixtures Ib, IVb and Id, IVd. 3.2 g (0.02 mol) of Br_2 in 10 mL chloroform was added dropwise at vigorous stirring to a solution of 6.2 g of the mixture **Ib, IVb** or **Ic, IVc** in 30 mL chloroform cooled to 0–2°C; the mixture was stirred during 2 h, the solvent was distilled off, the product was fractionated under the oil pump vacuum.

1,2-Dibromo-6,6,7,7,8,8,9,9-octafluoro-4-oxanonane (VIb). Yield 70%, yellow viscous oil, bp 120–123°C (10 mmHg). IR spectrum, ν, cm^{-1}: 2940 (C–H), 1171, 1131 (C–F, C–O). ^{1}H NMR spectrum, δ, ppm: 3.80 m (2H, $CHC\underline{H_2}Br$), 4.04 m (4H, CH_2OCH_2), 4.24 m (1H, $OCH_2C\underline{H}BrCH_2$), 6.06 m (1H, HCF_2, *J* 52.0 and *J* 5.5 Hz). ^{19}F NMR spectrum, δ, ppm: 24.47 d.m (2F, HCF_2, *J* 52.0 Hz), 31.51 m (2F, CF_2), 36.23 m (2F, CF_2), 41.97 m (2F, CF_2). Found, %: C 22.16; H 1.89; F 35.16. $C_8H_8F_8OBr_2$. Calculated, %: C 22.24; H 1.87; F 35.19.

1,2-Dibromo-6,6,7,7,8,8,9,9,10,10,11,11,12,12,-13,13,13-heptadecafluoro-4-oxatridecane (VId). Yield 75%, white amorphous solid, bp 164–167°C (10 mmHg), mp 51–52°C. IR spectrum, ν, cm^{-1}: 3033, 2935 (C–H), 1234, 1200, 1144 (C–F, C–O). ^{1}H NMR spectrum, δ, ppm: 3.80 m (2H, $CHC\underline{H_2}Br$), 4.05 m (4H, CH_2OCH_2), 4.24 m (1H, $OCH_2C\underline{H}BrCH_2$). ^{19}F NMR spectrum, δ, ppm: 35.68 m (2F, CF_2), 38.51 m (2F, CF_2), 39.11 m (2F, CF_2), 39.92 m (6F, CF_2), 42.28 m (2F, CF_2), 81.01 t (3F, CF_3, *J* 10.0 Hz). Found, %: C 22.33; H 1.06; F 49.67. $C_8H_8F_8OBr_2$. Calculated, %: C 22.17; H 1.09; F 49.69.

General procedure of debromination of compounds VIb, VId. 9.3 mmol of dibromide **Vb** or **Vc** was added dropwise to a suspension of 0.8 g (12.15 mmol) of zinc powder in 20 mL of ethanol. The reaction mixture was refluxed during 1 h. The solid precipitate was filtered off, the solvent was removed, and the product was fractionated under the oil pump vacuum.

3-(2,2,3,3,4,4,5,5-Octafluoropentyloxy)propene-1 (IVb). Yield 58 %, colorless liquid. Spectral data were consistent with the reference ones [16].

3-(2,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyloxy)propene-1 (IVd). Yield 38 %, colorless liquid, bp 192–195°C. IR spectrum, ν, cm^{-1}: 1199, 1144 (C–O, C–F). ^{1}H NMR, δ, ppm: 3.93 t (2H, $CF_2C\underline{H_2}O$, *J* 13.8 Hz), 4.14 d (2H, $OC\underline{H_2}CH$, *J* 5.7 Hz), 5.31 m (2H, CH_2 $CHC\underline{H_2}$), 5.88 m (1H, HCF_2, $CH_2C\underline{H}CH_2$). ^{19}F NMR spectrum, δ, ppm: 35.68 m (2F, CF_2), 38.45 m (2F, CF_2), 39.09 m (2F, CF_2), 39.86 m (6F, CF_2), 42.26 m (2F, CF_2), 81.01 t (3F, CF_3, *J* 9.9 Hz). Found, %: C 28.48; H 1.54; F 65.70. $C_{12}H_7F_{17}O_2$. Calculated, %: C 29.40; H 1.44; F 65.89.

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