

One-Step Synthesis of Epoxy(perfluoroalkyl)alkenes

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Abstract—Epoxy(perfluoroalkyl)alkenes were synthesized in one step by reaction of perfluoroalkyl iodides with 2-(allyloxymethyl)oxirane and 2-(oct-7-en-1-yl)oxirane in the presence of sodium dithionite and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under mild conditions.

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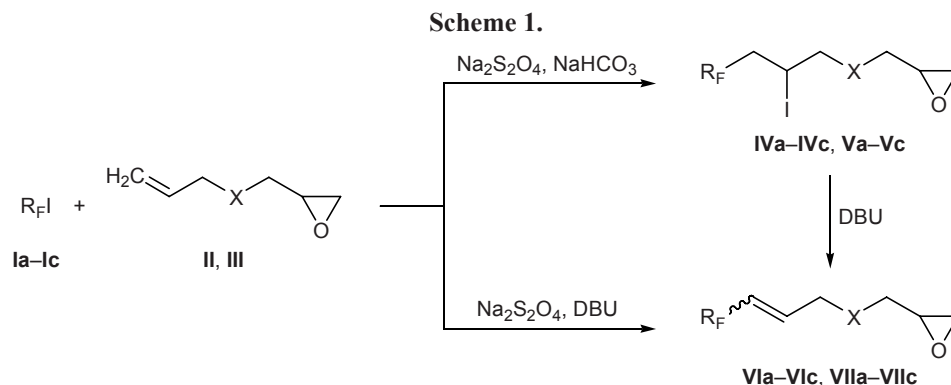
Epoxyalkanes are known to be potential monomers, and polyethers derived therefrom are widely used in industry as lubricants, dielectrics, and solvents [1]. Introduction of fluoroalkyl groups into epoxyalkane molecules could give rise to polymers possessing practically important properties, such as frost- and heat-resistance, chemical stability, and oleo- and hydrophobicity [2–10]. In the recent years, polymers containing fluoroalkyl substituents with functional groups have attracted considerable interest due to their potential applications in modern nanotechnologies [11, 12], medicine [13, 14], and electronics [15–17].

Yang et al. [18, 19] and Legov et al. [20] previously proposed a synthetic approach to functionalized epoxy-fluoroalkanes via introduction of perfluoroalkyl groups into compounds having an oxirane ring. 3-Iodo-4-(perfluoroalkyl)butyloxiranes were synthesized from 5,6-epoxyhex-1-ene and a series of perfluoroalkyl iodides (R_FI) under conditions of radical initiation (Cu, 60°C). We tried to follow analogous approach and carried reactions of 2-(allyloxymethyl)oxirane with perfluoroalkyl iodides R_FI under milder conditions using $Na_2S_2O_4$ in aqueous acetonitrile at room temperature in the presence of $NaHCO_3$ [21]. We showed in [22] that [2-iodo-3-(perfluoroalkyl)propoxymethyl]oxiranes thus formed undergo mild dehydroiodination by the action of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the oxirane ring remaining intact. We also noted that the use of other bases, such as triethylamine, ethyl(diisopropyl)amine, and pyridine, gave no desired result [22].

With the goal of obtaining epoxy(perfluoroalkyl)alkenes in one step we examined reactions of per-

fluoroalkyl iodides **Ia–Ic** with 2-(allyloxymethyl)oxirane (**II**) and 2-(oct-7-en-1-yl)oxirane (**III**) in aqueous acetonitrile in the presence of $Na_2S_2O_4$ using DBU as a base. Patrik and Cahard [23] previously described radical trifluoromethylation of ammonium salts derived from some 1,3-dicarbonyl compounds in the presence of $Na_2S_2O_4$ in aqueous acetonitrile. Ammonium salts were generated *in situ* with the use of nitrogen-centered bases such as Et_3N , $Et(i-Pr)_2N$, or DBU. The authors noted that 2 equiv of DBU is necessary for the process to be successful. In the initial step DBU promotes formation of unsaturated compound (enol form) which is then involved in radical addition of CF_3I . The second equivalent of DBU enhances the reactivity of trifluoromethyl iodide via activation of the carbon–iodine bond due to effect of the electron-withdrawing nitrogen atom. The yield of the target product also depended on the solvent [23]. However, among all bases used in [23], only DBU turned out to be suitable in our case due to its selectivity at the dehydroiodination step. The reactions were carried out in aprotic solvents to enhance basic properties of DBU [24–28].

The reactions of perfluoroalkyl iodides **Ia–Ic** with alkenyloxiranes **II** and **III** in aqueous acetonitrile in the presence of $Na_2S_2O_4$ and 2 equiv of DBU at room temperature were accompanied by strong self-heating of the reaction mixture and tarring. It is known that both radical addition of R_FI to unsaturated compounds [29, 30] and dehydroiodination [22] are exothermic processes, and heat evolution is likely to favor side reactions, such as oxirane ring opening and oligomerization. We examined temperature effect on the



$\text{R}_F = \text{CF}_3$ (**a**), $\text{CF}_3(\text{CF}_2)_3$ (**b**), $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)$ (**c**); **II, IV, VI, X = O**; **III, V, VII, X = (CH₂)₄**.

overall process and its particular steps. For this purpose, the reactions of perfluoroalkyl iodides **Ia–Ic** with alkenyloxiranes **II** and **III** were carried out in the presence of $\text{Na}_2\text{S}_2\text{O}_4$ and NaHCO_3 in aqueous acetonitrile at lower temperature (0–5°C). We thus isolated compounds **IVa–IVc** and **Va–Vc** in 69–75% yield (Scheme 1); the results were comparable with those reported by us previously [21] for the reaction performed at room temperature. The second step, i.e., dehydroiodination of **IVa–IVc** and **Va–Vc** by the action of DBU, was also performed at 0–5°C in aqueous acetonitrile, but the complete conversion of adducts **IVa–IVc** and **Va–Vc** was reached only in the presence of a larger than stoichiometric amount of DBU (see Experimental, method *a*). The yield of polyfluoroalkenyloxiranes **VIa–VIc** and **VIIa–VIIc** was 83–87%, despite the use of aqueous–organic solvent. The *E/Z*-isomer ratio was 15:1, 25:1, and 50:1 for $\text{R}_F = \text{CF}_3$, C_4F_9 , and $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)$, respectively. We previously synthesized compounds **IVb** and **IVc** (DBU, CH_2Cl_2 , room temperature) in 73 (*E/Z* = 10:1) and 82% yield (*E/Z* = 50:1), respectively [22]. In support of our results on the dehydroiodination [22], the *E/Z* ratio depended on the length and degree of branching of the fluoroalkyl substituent. As shown in [24], reduction of temperature in analogous processes leads to increased fraction of the *E* isomer. A similar tendency is observed for compound **IVb** (see above), despite different properties of reaction medium. The overall yields of compounds **VIa–VIc** and **VIIa–VIIc** in two steps did not exceed 65%.

We tried to synthesize epoxy(perfluoroalkyl)alkenes in one step in an open system at 0–5°C by gradually adding $\text{Na}_2\text{S}_2\text{O}_4$ to a mixture of perfluoroalkyl iodide **Ia–Ic**, epoxyalkene **II** or **III**, and DBU in aqueous acetonitrile. As a result, compounds **VIa–VIc** and **VIIa–VIIc** were isolated in 81–87% yield. When

perfluoroalkyl iodide **Ia–Ic** was added last to the reaction mixture, the yield of **VIa–VIc** and **VIIa–VIIc** was lower. Presumably, in this case compounds **Ia–Ic** were partially converted into $\text{R}_F\text{SO}_2\text{Na}$ [23]. Here, the use of 2.2 equiv of DBU is important. As noted in [31], the role of NaHCO_3 in the addition of perfluoroalkyl halides to unsaturated compounds is to neutralize liberated hydrogen halide. In the proposed one-step procedure, 1 equiv of DBU substitutes for NaHCO_3 . The remaining amount of DBU is consumed for dehydroiodination of intermediately formed epoxyiodo(perfluoroalkyl)alkanes **IVa–IVc** and **Va–Vc** (Scheme 1).

Thus the use of DBU in the addition of perfluoroalkyl iodides **Ia–Ic** to unsaturated epoxy derivatives **II** and **III** in the presence of $\text{Na}_2\text{S}_2\text{O}_4$ as radical initiator ensures highly effective one-step synthesis of epoxy(perfluoroalkyl)alkenes **VIa–VIc** and **VIIa–VIIc**.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer from samples prepared as thin films. The ^1H and ^{19}F NMR spectra were measured from solutions in CDCl_3 on a Bruker DRX 400 spectrometer at 400.1 and 376.5 MHz, respectively; the chemical shifts were determined relative to tetramethylsilane (^1H) and hexafluorobenzene (^{19}F) as internal references.

Epoxyiodo(perfluoroalkyl)alkanes IVa–IVc and Va–Vc (general procedure). Perfluoroalkyl iodide **Ia–Ic**, 0.12 mol, was added to a mixture of 0.1 mol NaHCO_3 , 24 ml of oxygen-free water, and 24 ml of acetonitrile under stirring at 0–5°C in an argon atmosphere [trifluoromethyl iodide (**Ia**) was bubbled through that mixture], 0.1 mol of compound **II** or **III** and 0.07 mol of $\text{Na}_2\text{S}_2\text{O}_4$ were then added in succession, and the mixture was stirred for 1 h. The mixture was

treated with 150 ml of water, and the organic phase was separated, dried over CaCl_2 , and distilled under reduced pressure. The IR spectra of **IVa–IVc** and **Va–Vc** characteristically contained absorption bands in the following regions, ν , cm^{-1} : 2963–2965, 2918–2920, 2892–2893 (C–H); 1120–1122 (C–O–C, C–F).

2-(4,4,4-Trifluoro-2-iodobutoxymethyl)oxirane (IVa). Yield 75%, bp 120–121°C (5 mm). ^1H NMR spectrum, δ , ppm: 2.62 t.d (1H, 3-H, $J = 5.1, 2.6$ Hz), 2.71 m (1H, 3-H), 2.81 d.d.d (1H, 3'-H, $J = 5.3, 4.2, 1.3$ Hz), 3.03 m (1H, 2-H), 3.16 m (1H, 3'-H), 3.43 d.d.d (1H, 2- CH_2 , $J = 11.8, 6.0, 2.4$ Hz), 3.73 d.d.d (1H, 1'-H, $J = 17.6, 10.6, 5.9$ Hz), 3.75 d.d (1H, 1'-H, $J = 6.1, 2.3$ Hz), 3.87 d.d.d (1H, 2- CH_2 , $J = 11.8, 2.6, 1.2$ Hz), 4.23 m (1H, 2'-H). ^{19}F NMR spectrum: δ_{F} 97.60 ppm, q (CF_3 , $J = 10.4$ Hz). Found, %: C 27.01; H 3.16; F 18.15. $\text{C}_7\text{H}_{10}\text{F}_3\text{IO}_2$. Calculated, %: C 27.12; H 3.25; F 18.38.

2-(4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptyloxy-methyl)oxirane (IVb). Yield 73%, bp 110–112°C (5 mm). ^1H NMR spectrum, δ , ppm: 2.63 m (1H, 3-H), 2.74 d.d (1H, 3-H, $J = 5.2, 4.2$ Hz), 2.85 t.d.d (1H, 3'-H, $J = 29.3, 16.5, 8.1$ Hz), 3.13 m (1H, 2-H), 3.23 m (1H, 3'-H), 3.43 d.d.d (1H, 2- CH_2 , $J = 11.7, 6.2, 5.3$ Hz), 3.73 d.d.d (1H, 1'-H, $J = 17.6, 10.6, 5.9$ Hz), 3.75 d.d (1H, 1'-H, $J = 6.1, 2.3$ Hz), 3.87 d.d.d (1H, 2- CH_2 , $J = 11.8, 2.6, 1.2$ Hz), 4.23 m (1H, 2'-H). ^{19}F NMR spectrum, δ_{F} , ppm: 37.98 m (2F, 6'-F), 39.35 m (2F, 5'-F), 49.64 m (1F, 4'-F), 50.87 m (1F, 4'-F), 82.60 t.t (3F, 7'-F, $J = 9.7, 3.3$ Hz). Found, %: C 26.02; H 2.10; F 37.07. $\text{C}_{10}\text{H}_{10}\text{F}_9\text{IO}_2$. Calculated, %: C 26.12; H 2.17; F 37.16.

2-[4,6,6,7,9,9,10,10,11,11,11-Undecafluoro-2-iodo-4,7-bis(trifluoromethyl)-5,8-dioxaundecyloxy-methyl]oxirane (IVc). Yield 68%, bp 119–120°C (5 mm). ^1H NMR spectrum, δ , ppm: 2.61 m (1H, 3-H), 2.76 m (2H, 3-H, 3'-H), 3.14 m (2H, 3'-H, 2-H), 3.45 m (1H, 2- CH_2), 3.75 m (3H, 1'-H, 2- CH_2), 4.26 m (1H, 2'-H). ^{19}F NMR spectrum, δ_{F} , ppm: 17.17 m (1F, 7'-F), 30.47 m (1F, 4'-F), 32.38 m (2F, CF_2), 78.79 m (2F, 6'-F), 80.02 m (2F, 9'-F), 80.61 m (3F, 11'-F), 82.15 m (6F, 4'- CF_3 , 7'- CF_3). Found, %: C 24.42; H 1.51; F 46.80. $\text{C}_{14}\text{H}_{10}\text{F}_{17}\text{IO}_4$. Calculated, %: C 24.30; H 1.46; F 46.66.

2-(9,9,9-Trifluoro-7-iodononyl)oxirane (Va). Yield 81%, bp 175–176°C (5 mm). ^1H NMR spectrum, δ , ppm: 1.42 m (10H, CH_2), 1.77 m (2H, 6'-H), 2.46 d.d (1H, 3-H, $J = 5.0, 2.7$ Hz), 2.75 d.d (1H, 3-H, $J = 5.0, 4.0$ Hz), 2.87 m (3H, 2-H, 8'-H), 4.19 m (1H, 7'-H). ^{19}F NMR spectrum: δ_{F} 98.00 ppm, t (CF_3 , $J =$

10.3 Hz). Found, %: C 37.62; H 5.15; F 16.13. $\text{C}_{11}\text{H}_{18}\text{F}_3\text{IO}$. Calculated, %: C 37.73; H 5.18; F 16.28.

2-(9,9,10,10,11,11,12,12,12-Nonafluoro-7-iodo-dodecyl)oxirane (Vb). Yield 85%, bp 162–163°C (3 mm). ^1H NMR spectrum, δ , ppm: 1.44 m (10H, CH_2), 1.80 m (2H, 6'-H), 2.46 d.d (1H, 3-H, $J = 5.0, 2.7$ Hz), 2.74 d.d (1H, 3-H, $J = 5.0, 4.0$ Hz), 2.90 m (3H, 8'-H, 2-H), 4.33 m (1H, 7'-H). ^{19}F NMR spectrum, δ_{F} , ppm: 35.95 q.t (2F, 11'-F, $J = 12.7, 3.8$ Hz), 37.29 m (2F, 10'-F), 47.06 d.m (1F, 9'-F, $J = 270.9$ Hz), 49.86 d.m (1F, 9'-F, $J = 270.9$ Hz), 80.79 t.t (CF_3 , $J = 9.7, 3.2$ Hz). Found, %: C 33.54; H 3.55; F 34.02. $\text{C}_{14}\text{H}_{18}\text{F}_9\text{IO}$. Calculated, %: C 33.62; H 3.63; F 34.18.

2-[9,11,11,12,14,14,15,15,16,16,16-Undecafluoro-7-iodo-9,12-bis(trifluoromethyl)-10,13-dioxa-hexadecyl]oxirane (Vc). Yield 75%, bp 130–131°C (1 mm). ^1H NMR spectrum, δ , ppm: 1.43 m (10H, CH_2), 1.75 m (2H, 6'-H), 2.46 d.d (1H, 3-H, $J = 5.0, 2.7$ Hz), 2.75 m (1H, 3-H, $J = 5.0, 4.0$ Hz), 2.92 m (3H, 2-H, 8'-H), 4.22 m (1H, 7'-H). ^{19}F NMR spectrum, δ , ppm: 17.17 m (1F, 12'-F), 30.47 m (1F, 9'-F), 32.38 m (2F, 15'-F), 78.79 m (2F, 11'-F), 80.02 m (2F, 14'-F), 80.61 m (3F, 16'-F), 82.15 m (6F, 9'- CF_3 , 12'- CF_3). Found, %: C 29.42; H 2.36; F 43.97. $\text{C}_{18}\text{H}_{18}\text{F}_{17}\text{IO}_3$. Calculated, %: C 29.53; H 2.48; F 44.11.

Epoxy(perfluoroalkyl)alkenes VIa–VIc and VIIa–VIIc (general procedure). a. 1,8-Diazabicyclo[5.4.0]undec-7-ene, 12.2 g (0.1 mol), was added under stirring to a mixture of 0.08 mol of compound **IVa–IVc** or **Va–Vc**, 15 ml of acetonitrile, and 15 ml of water, cooled to 0–5°C. The mixture was stirred for 20 min, 100 ml of water was added, the organic phase was separated, washed with 2 M sulfuric acid and aqueous sodium carbonate, and dried over CaCl_2 , the solvent was distilled off, and the residue was distilled under reduced pressure (oil pump).

b. Perfluoroalkyl iodide **Ia–Ic**, 0.12 mol, was added to a mixture of 24 ml of oxygen-free water and 24 ml of acetonitrile under stirring at 0–5°C in an argon atmosphere [trifluoromethyl iodide (**Ia**) was bubbled through that mixture], 0.1 mol of compound **II** or **III** and 0.07 mol of $\text{Na}_2\text{S}_2\text{O}_4$ were then added in succession, and the mixture was stirred for 1 h. The mixture was treated with 150 ml of water, and the organic phase was separated, dried over CaCl_2 , and distilled under reduced pressure. The IR spectra of compounds **VIa–VIc** and **VIIa–VIIc** characteristically contained the following absorption bands, ν , cm^{-1} : 2963–2965, 2918–2920, 2892–2893 (C–H); 1680–1682 (C=C); 1120–1122 (C–O–C, C–F).

2-(4,4,4-Trifluorobut-2-en-1-yloxymethyl)oxirane (VIa). Yield 84% (*b*), bp 110–112°C (3 mm). ¹H NMR spectrum, δ , ppm: 2.62 d.d (1H, 3-H, $J = 5.0$, 2.7 Hz), 2.81 d.d (1H, 3-H, $J = 5.0$, 4.2 Hz), 3.17 t.d.d (1H, 2-H, $J = 6.1$, 4.2, 2.7 Hz), 3.40 d.d (1H, 2-CH₂, $J = 11.6$, 6.1 Hz), 3.84 d.d (1H, 2-CH₂, $J = 11.6$, 2.6 Hz), 4.20 m (2H, 1'-H), 5.70 m (1H, 3'-H, *Z* isomer), 6.00 d.q.t (1H, 3'-H, *E* isomer, $J = 15.8$, 6.6, 2.1 Hz), 6.15 d.t (1H, 2'-H, *Z* isomer, $J = 12.1$, 5.9 Hz), 6.42 d.t.q (1H, 2'-H, *E* isomer, $J = 15.8$, 4.1, 2.1 Hz). ¹⁹F NMR spectrum, δ_F , ppm: 97.67 d.d.d (CF₃, *E* isomer, $J = 6.3$, 5.2, 2.9 Hz), 102.80 t.d (CF₃, *Z* isomer, $J = 8.7$, 2.6 Hz). Found, %: C 46.04; H 4.87; F 31.13. C₇H₉F₃O₂. Calculated, %: C 46.16; H 4.98; F 31.29.

2-(4,4,5,5,6,6,7,7,7-Nonafluorohept-2-en-1-yloxymethyl)oxirane (VIb). Yield 73% (*b*), bp 89–90°C (5 mm). ¹H NMR spectrum, δ , ppm: 2.62 d.d (1H, 3-H, $J = 5.0$, 2.7 Hz), 2.82 d.d (1H, 3-H, $J = 5.0$, 4.2 Hz), 3.18 t.d.d (1H, 2-H, $J = 6.1$, 4.2, 2.7 Hz), 3.39 d.d (1H, 2-CH₂, *Z* isomer, $J = 11.4$, 6.0 Hz), 3.41 d.d (1H, 2-CH₂, *E* isomer, $J = 11.6$, 6.1 Hz), 3.78 d.d (1H, 2-CH₂, *Z* isomer, $J = 11.4$, 2.8 Hz), 3.85 d.d (1H, 2-CH₂, *E* isomer, $J = 11.6$, 2.6 Hz), 4.22 m (2H, 1'-H, *E* isomer), 4.27 m (2H, 1'-H, *Z* isomer), 5.61 m (1H, 3'-H, *Z* isomer), 5.96 m (1H, 3'-H, *E* isomer), 6.30 d.m (1H, 2'-H, *Z* isomer, $J = 12.5$ Hz), 6.46 d.m (1H, 2'-H, *E* isomer, $J = 15.8$ Hz). ¹⁹F NMR spectrum, δ_F , ppm: 36.17 m (2F, 6'-F, *Z* isomer), 36.44 m (2F, 6'-F, *E* isomer), 37.56 m (2F, 5'-F, *Z* isomer), 37.95 m (2F, 5'-F, *E* isomer), 50.25 m (2F, 4'-F, *E* isomer), 54.11 m (2F, 4'-F, *Z* isomer), 81.03 t.t (3F, 7'-F, $J = 9.7$, 3.3 Hz). Found, %: C 37.29; H 2.78; F 51.55. C₁₀H₉F₉O₂. Calculated, %: C 36.16; H 2.73; F 51.48.

2-[4,6,6,7,9,9,10,10,11,11,11-Undecafluoro-4,7-bis(trifluoromethyl)-5,8-dioxundec-2-en-1-yloxymethyl]oxirane (VIc). Yield 82%, bp 110–111°C (5 mm). ¹H NMR spectrum, δ , ppm: 2.61 d.d (1H, 3-H, $J = 4.9$, 2.7 Hz), 2.81 d.d (1H, 3-H, $J = 4.9$, 4.2 Hz), 3.18 t.d.d (1H, 2-H, $J = 6.5$, 4.2, 2.7 Hz), 3.37 d.d (1H, 2-CH₂, *Z* isomer, $J = 11.7$, 6.0 Hz), 3.41 d.d (1H, 2-CH₂, *E* isomer, $J = 11.7$, 6.1 Hz), 3.64 d.d (1H, 2-CH₂, *Z* isomer, $J = 11.7$, 2.8 Hz), 3.85 d.d (1H, 2-CH₂, *E* isomer, $J = 11.7$, 2.6 Hz), 4.22 m (2H, 1'-H, *E* isomer), 4.37 m (2H, 1'-H, *Z* isomer), 5.60 m (1H, 3'-H, *Z* isomer), 6.01 m (1H, 3'-H, *E* isomer), 6.40 d.m (1H, 2'-H, *Z* isomer, $J = 11.8$ Hz), 6.50 d.m (1H, 2'-H, *E* isomer, $J = 15.8$ Hz). ¹⁹F NMR spectrum, δ_F , ppm: 17.10 m (1F, 7'-F), 32.57 m (2F, 10'-F), 33.54 m (1F, 4'-F), 77.23 m (2F, 6'-F), 80.05 m (2F, 9'-F), 80.81 m (3F, 11'-F), 82.19 m (6F, 4'-CF₃, 7'-CF₃). Found, %:

C 29.93; H 1.63; F 57.41. C₁₄H₉F₁₇O₄. Calculated, %: C 29.80; H 1.61; F 57.24.

2-(9,9,9-Trifluoronon-7-en-1-yl)oxirane (VIIa). Yield 81% (*b*), bp 112–113°C (1 mm). ¹H NMR spectrum, δ , ppm: 1.44 m (10H, CH₂), 2.15 m (2H, 6'-H), 2.46 d.d (1H, 3-H, $J = 5.0$, 2.7 Hz), 2.75 d.d (1H, 3-H, $J = 5.0$, 4.0 Hz), 2.90 m (1H, 2-H), 5.58 m (1H, 8'-H, *Z* isomer), 5.60 d.q.t (1H, 8'-H, *E* isomer, $J = 15.8$, 6.5, 1.6 Hz), 6.00 d.t (1H, 7'-H, *Z* isomer, $J = 11.8$, 7.9 Hz), 6.37 d.t.q (1H, 7'-H, *E* isomer, $J = 15.8$, 6.7, 2.2 Hz). ¹⁹F NMR spectrum, δ_F , ppm: 98.00 m (CF₃, *E* isomer), 103.84 t.d (CF₃, *Z* isomer, $J = 8.6$, 2.3 Hz). Found, %: C 59.36; H 7.63; F 25.55. C₁₁H₁₇F₃O. Calculated, %: C 59.45; H 7.71; F 25.64.

2-(9,9,10,10,11,11,12,12,12-Nonafluorododec-7-en-1-yl)oxirane (VIIb). Yield 87% (*b*), bp 130–131°C (3 mm). ¹H NMR spectrum, δ , ppm: 1.43 m (10H, CH₂), 2.20 m (2H, 6'-H), 2.46 d.d (1H, 3-H, $J = 5.0$, 2.7 Hz), 2.74 d.d (1H, 3-H, $J = 5.0$, 4.0 Hz), 2.90 m (1H, 2-H), 5.57 m (1H, 8'-H, *Z* isomer), 5.63 d.t (1H, 8'-H, *E* isomer, $J = 15.7$, 12.5 Hz), 6.12 d.t (1H, 7'-H, *Z* isomer, $J = 12.0$, 7.8, 2.4 Hz), 6.44 d.t.t (1H, 7'-H, *E* isomer, $J = 15.7$, 6.9, 2.3 Hz). ¹⁹F NMR spectrum, δ_F , ppm: 36.09 m (2F, 11'-F), 37.51 m (2F, 10'-F), 50.50 m (2F, 9'-F, *E* isomer), 55.15 m (2F, 9'-F, *Z* isomer), 80.82 t.t (3F, 12'-F, $J = 9.7$, 3.0 Hz). Found, %: C 45.06; H 4.49; F 45.81. C₁₄H₁₇F₉O. Calculated, %: C 45.17; H 4.60; F 45.93.

[9,11,11,12,14,14,15,15,16,16,16-Undecafluoro-9,12-bis(trifluoromethyl)-10,13-dioxahexadec-7-en-1-yl]oxirane (VIIc). Yield 85% (*b*), bp 139–140°C (1 mm). ¹H NMR spectrum, δ , ppm: 1.42 m (10H, CH₂), 2.22 m (2H, 1'-H), 2.46 d.d (1H, 3-H, $J = 5.0$, 2.7 Hz), 2.74 d.d (1H, 3-H, $J = 5.0$, 4.0 Hz), 2.91 m (1H, 2-H), 5.32 m (1H, 8'-H, *Z* isomer), 5.63 d.d (1H, 8'-H, *E* isomer, $J = 15.8$, 12.2 Hz), 6.11 m (1H, 7'-H, *Z* isomer), 6.45 d.m (1H, 7'-H, *E* isomer, $J = 15.8$ Hz). ¹⁹F NMR spectrum, δ_F , ppm: 17.10 m (1F, 12'-F), 32.57 m (2F, 15'-F), 33.54 m (1F, 9'-F), 77.23 m (2F, 11'-F), 80.05 m (2F, 14'-F), 80.81 m (16'-F), 82.19 m (6F, 9'-CF₃, 12'-CF₃). Found, %: C 35.65; H 2.75; F 53.31. C₁₈H₁₇F₁₇O₃. Calculated, %: C 35.78; H 2.84; F 53.45.

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