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# Synthesis of Perfluoro- and 2-Trifluoromethylpentafluoro-dihydrofurans and Their Epoxy Derivatives

## T. I. Filyakova, M. I. Kodess, A. Ya. Zapevalov, and V. I. Saloutin

*Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences,*
*ul. S. Kovalevskoi 20, Yekaterinburg, 620219 Russia*
*e-mail: saloutin@ios.uran.ru*

**Abstract**—Perfluorotetrahydrofuran-2-carboxylic acid was converted through a series of transformations into perfluoro-2,3-dihydrofuran and perfluoro-2,5-dihydrofuran; likewise, from (2-perfluorotetrahydrofuryl)difluoroacetic acid 2-trifluoromethylpentafluoro-2,3-dihydrofuran was obtained. Perfluoro-2,3-dihydrofuran and 2-trifluoromethylpentafluoro-2,3-dihydrofuran underwent isomerization into perfluoro-2,5-dihydrofuran and 2-trifluoromethylpentafluoro-2,5-dihydrofuran by the action of cesium fluoride. Treatment of perfluoro-2,5-dihydrofuran with $SbF_5$ resulted in ring opening and formation of *cis*-perfluoro-2-butenoyl fluoride, while 2-trifluoromethylpentafluoro-2,3-dihydrofuran was converted into 2-trifluoromethylpentafluoro-2,5-dihydrofuran under the same conditions. Perfluoro-3,4-epoxytetrahydrofuran and 2-trifluoromethyl-3,4-epoxypentafluorotetrahydrofuran containing fused oxirane and tetrahydrofuran rings were synthesized by reactions of perfluoro-2,5-dihydrofuran and 2-trifluoromethylpentafluoro-2,5-dihydrofuran, respectively, with sodium hypochlorite.

Polyfluorinated heterocyclic compounds attract researchers' attention from both theoretical and practical viewpoints. Methods of their synthesis are based mainly on fluorination of hydrocarbons and chlorinated heterocycles [1–5]. In the present work we used as starting compounds perfluorotetrahydrofuran-2-carboxylic acid and (perfluorotetrahydro-2-furyl)difluoroacetic acid which are formed as by-products in the electrochemical synthesis of perfluoroadipic acid. The goal of our study was to obtain perfluorinated dihydrofurans and their epoxy derivatives and examine their properties.

Pyrolysis of potassium salts **II** and **IV** in the presence of potassium carbonate gave, respectively, a 1:9 mixture of perfluoro-2,3-dihydrofuran (**Ia**) and per-fluoro-2,5-dihydrofuran (**Ib**) and 2-trifluoromethyl-pentafluoro-2,3-dihydrofuran (**IIIa**) (Scheme 1). Compounds **Ib** and **IIIa** were synthesized previously by other methods [1, 4]. It was shown that perfluoro-2,5-dihydrofuran (**Ib**) can be used as starting compound in the synthesis of perfluoro-3-oxaglutaric acid [1]. However, the properties of perfluorinated dihydrofurans have been studied insufficiently.

We examined nucleophilic and electrophilic isomerization of perfluoro derivatives **Ia/Ib** and **IIIa**. Treatment of mixture **Ia/Ib** with cesium fluoride in

**Scheme 1.**



**Scheme 2.**



**Ia**, **Ib**, X = F; **IIIa**, **IIIb**, X = CF₃.
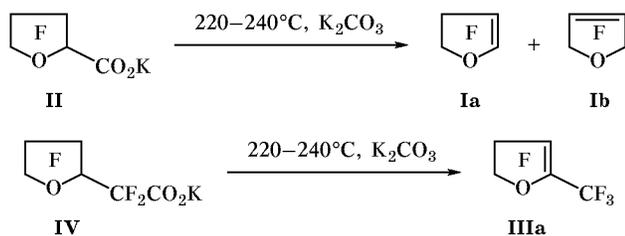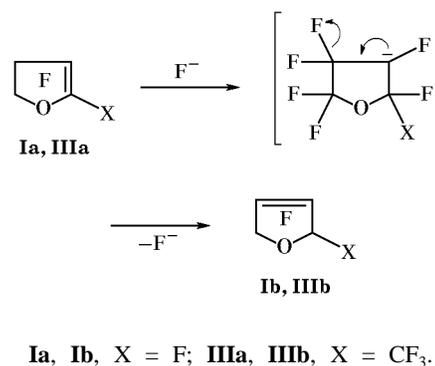
diethylene glycol dimethyl ether gave compound **Ib** which is likely to be thermodynamically more stable. Likewise, from perfluorinated 2,3-dihydrofuran **IIIa** we obtained perfluorinated 2,5-dihydrofuran **IIIb** (Scheme 2).

However, electrophilic isomerization of perfluoro-dihydrofurans by the action of antimony pentafluoride takes different pathways. Compound **IIIa**, as in the reaction with cesium fluoride, isomerizes into 2,5-di-hydro derivative **IIIb**. Treatment of compounds **Ia** and **Ib** with SbF$_5$ leads to opening of the dihydrofuran ring with formation of unsaturated perfluoro-2-bute-noyl fluoride (**V**). According to the $^{19}$F NMR data, the product has *cis* configuration of the double C=C bond. Presumably, the transformation **Ia** → **V** involves intermediate formation of isomer **Ib** (Scheme 3).

**Scheme 3.**
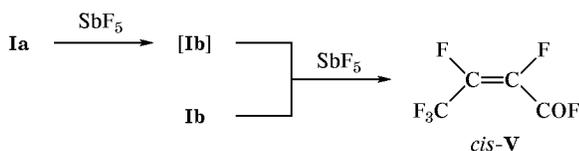


The driving force for the above process is likely to be rearrangement of carbocation **A** (which is the primary product of electrophilic attack on **Ib** by SbF$_5$) into more stable difluoromethyl cation **B**. The latter gives rise to vinylacylium ion **C**. The stability of such cations and their acylating ability were demonstrated in [6, 7]. Complex **C** decomposes on distillation of the reaction mixture with concentrated sulfuric acid, yielding acyl fluoride **V** (Scheme 4).

**Scheme 4.**
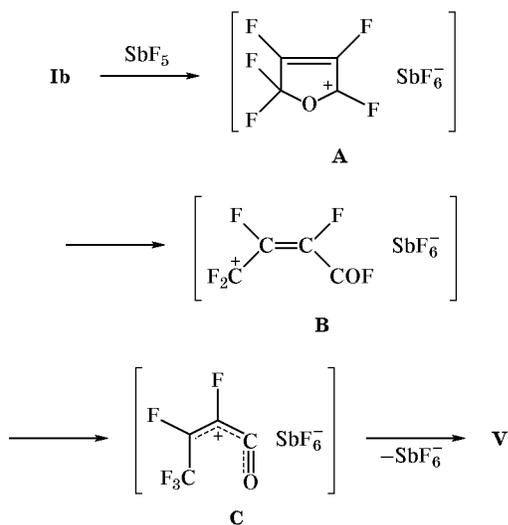


Perfluorocycloalkenes are known to react with bromine at a very low rate. As a rule, the process requires prolonged UV irradiation in a quartz tube [8]. We have found that isomer **Ia** readily reacts with bromine. On exposure to light, the process is accompanied by heat evolution. The bromination of compound **Ib** requires UV irradiation and yields 3,4-di-bromohexafluorotetrahydrofuran (**VIb**). By treatment of isomer mixture **Ia/Ib** with a stoichiometric amount of bromine we succeeded in obtaining and isolating 2,3-dibromohexafluorotetrahydrofuran (**VIa**). According to the $^{19}$F NMR data, dibromo derivatives **VIa** and **VIb** were formed as a single stereoisomer. Likewise, trifluoromethyl-substituted compounds **IIIa** and **IIIb** reacted with bromine to afford the corresponding dibromides **VIIa** and **VIIb** (Scheme 5).

**Scheme 5.**
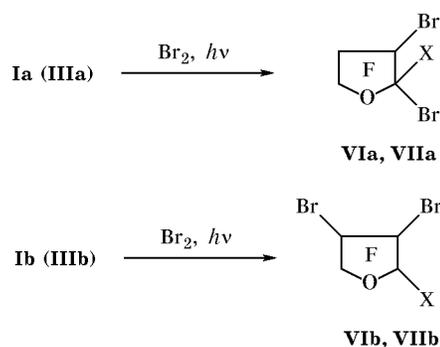


**VI**, X = F; **VII**, X = CF$_3$.

The ease of bromination of **Ia** and **IIIa** may be explained by the presence of oxygen atom at the double bond, i.e., the substrates can be regarded as perfluorinated cyclic vinyl ethers. Dibromo derivatives **VI** and **VII** are readily debrominated to give the initial dihydrofurans by the action of zinc in acetic acid. In such a way we obtained pure isomer **Ia**.

With the goal of synthesizing the corresponding epoxy derivatives, we examined oxidation of **Ib** and

**Scheme 6.**
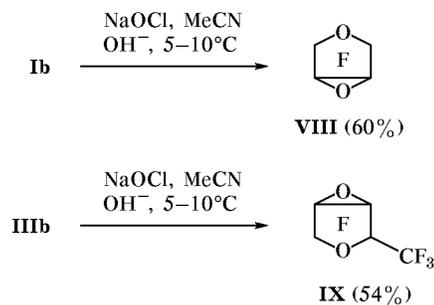
**Scheme 7.**
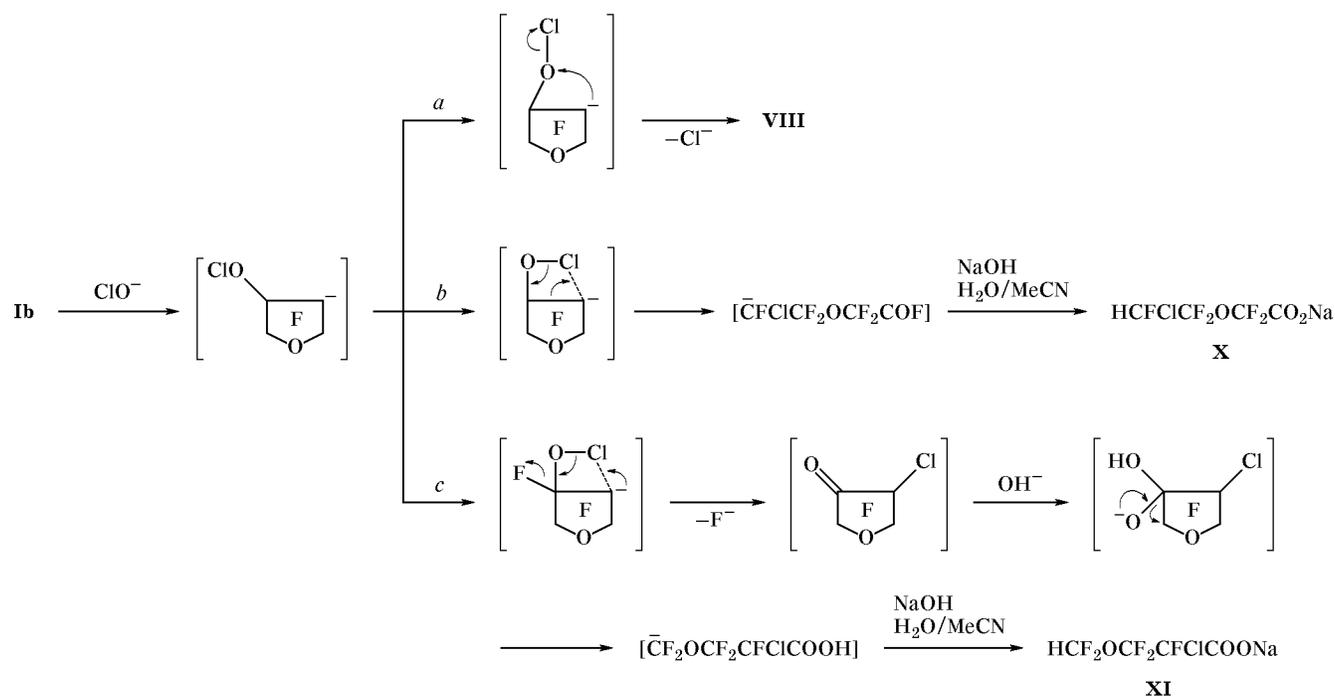


**IIIb**. These compounds turned out to react with aqueous sodium hypochlorite in the presence of acetonitrile, affording bicyclic products with fused oxirane and tetrahydrofuran rings: perfluoro-3,4-epoxytetrahydrofuran (**VIII**) and 2-trifluoromethylpentafluoro-3,4-epoxytetrahydrofuran (**IX**) (Scheme 6).

Unlike internal and cyclic perfluoroalkenes whose epoxidation with sodium hypochlorite occurs almost quantitatively [9, 10], the reaction of NaOCl with compounds **Ib** and **IIIb** does not come to completion. The product isolated from the organic phase is a mixture of the initial dihydrofuran and the corresponding epoxy derivative. This may be explained by reduced electrophilicity of fluorinated dihydrofuran ring, as compared to perfluorocycloalkenes, due to the presence of oxygen atom. Moreover, the reaction with NaOCl is complicated by side processes leading to cleavage of the dihydrofuran ring (via alternative paths of stabilization of the carbanionic intermediate), so that the temperature conditions should be strictly met. As by-products, sodium salts of polyfluorooxacarboxylic acids are mainly formed; they reside in the aqueous phase. Scheme 7 shows a probable mechanism of the process with the reaction of compound **Ib** with NaOCl as an example.

The boiling points of epoxy derivatives **VIII** and **IX** and the initial dihydrofurans are very similar; therefore, compounds **VIII** and **IX** were subjected to bromination or chlorination in a quartz tube under UV irradiation, and the halogenation products were isolated by fractional distillation. According to the $^{19}F$ NMR data, epoxytetrahydrofuran **IX** is formed as a mixture of diastereoisomers at a ratio of 65:35.

### EXPERIMENTAL

The $^{19}F$ NMR spectra were recorded on Tesla BS-567A (94.1 MHz), Tesla BS-587A (75.3 MHz), and Bruker DRX-400 spectrometers (376 MHz) using $C_6F_6$ as internal reference. The $^{19}F$ chemical shifts are given relative to $CFCl_3$ (positive values correspond to increasing field strength). The $^1H$ NMR spectra were obtained on a Bruker DRX-400 instrument at 400 MHz using TMS as internal reference. The NMR data of the obtained compounds are given in table. The IR spectra were measured on a Specord 75IR spectrometer from samples prepared as thin films or gaseous samples. GLC analysis was performed on an LKhM-72 chromatograph equipped with a thermal conductivity detector; carrier gas helium; steel columns, $6500 \times 4$ mm, packed with 15% of SKTFT-100 on Chromosorb W. A solution of sodium hypochlorite was prepared as described in [11].

**Perfluoro-2,5-dihydrofuran (Ib).** *a. Pyrolysis of potassium perfluorotetrahydrofuran-2-carboxylate (II).* A mixture of 84 g (0.3 mol) of salt **II** and 48 g

$^{19}$F and $^1$H NMR spectra of compounds **Ia**, **Ib**, **IIIa**, **IIIb**, **V**, **VIa**, **VIb**, **VIIa**, and **VIII–XI**

| Compound no. | Formula | Chemical shifts δ and δ$_F$, ppm | Coupling constants $J$, Hz |
|---|---|---|---|
| **Ia** | (furan ring, 3-F, 4-F, O, 2, 1) | 105.82 d.t (1-F); 202.69 d.t.t (2-F); 112.58 d.d.t (3-F); 91.38 d.t (4-F) | $J_{1,2} = 20.5$, $J_{1,3} = 11.7$, $J_{2,3} = 9.1$, $J_{2,4} = 3.1$, $J_{3,4} = 1.7$ |
| **Ib** | (furan ring, 3-F, 4-F, O, 2, 1) | 77.36 d (1-F, 4-F); 153.44 t (2-F, 3-F) | $J_{1,2} = J_{3,4} = 7.3$ |
| **IIIa** | (furan ring, 3-F, 4-F, O, 2, CF$_3$ at 1) | 68.10 d.t (1-F); 167.50 q.t.t (2-F); 117.85 d.q (3-F); 90.08 d (4-F) | $J_{1,2} = 13.4$, $J_{1,3} = 2.4$, $J_{2,3} = 12.8$, $J_{2,4} = 3.6$ |
| **IIIb** | (ring, 4, 5, F, 3-F 2, O, CF$_3$ at 1) | 82.0 s (1-F); 127.42 m (2-F); 149.65 m (3-F); 150.16 m (4-F); 69.74 m (5-F$_A$); 77.53 m (5-F$_B$) | $J_{3,4} \approx J_{4,5A} \approx J_{4,5B} = 13.2$, $J_{AB} = 141.6$ |
| **V** | $^2$F–C=C–F$^3$, F$_3$C (1), COF (4) | 64.85 d.d.d (1-F); 127.90 d.d.q (2-F); 136.87 d.d.q (3-F); –25.71 d.d.q (4-F) | $J_{1,2} \approx J_{1,3} \approx 7.8$, $J_{1,4} = 11.8$, $J_{2,3} = 9.8$, $J_{2,4} = 23.6$, $J_{3,4} = 27.6$ |
| **VIa** | (ring, F$^2$ Br, F$^1$, 3 F, 4, O, Br) | 51.86 d.d.d (1-F); 121.73 d.d.d.d (2-F); 103.56 m (3-F$_A$); 126.54 d.d (3-F$_B$); 77.60 m (4-F$_A$); 85.20 d.d (4-F$_B$) | $J_{1,2} = 20.8$, $J_{1,3A} = 6.1$, $J_{1,3B} = 12.2$, $J_{2,3B} = 14.7$, $J_{2,4A} = 2.4$, $J_{3A,4A} = 14.7$, $J_{3B,4A} = 12.2$, $J_{3A,3B} = 247.8$, $J_{4A,4B} = 130.6$ |
| **VIb** | (ring, Br, Br, $^3$F 4 F O 1 F$^2$) | 65.16 (1-F$_A$, 4-F$_A$); 86.70 m (1-F$_B$, 4-F$_B$); 121.04 m (2-F, 3-F) | $J_{1A,1B} = J_{4A,4B} = 133.0$ |
| **VIIa** | (ring, F$^2$ Br, CF$_3$ at 1, 3 F, 4, O, Br) | Isomer **1** (76%): 72.36 d.d (1-F); 107.49 m (2-F); 111.84 m (3-F$_A$); 124.89 d.d (3-F$_B$); 78.80 m (4-F$_A$); 85.31 d (4-F$_B$)<br>Isomer **2** (24%): 72.16 m (1-F); 107.49 m (2-F); 104.43 m (3-F$_A$); 132.08 m (3-F$_B$); 77.29 m (4-F$_A$); 84.03 d.d (4-F$_B$) | $J_{2,3A} = 13.4$, $J_{2,3B} = 12.2$, $J_{3A,4A} = 6.1$, $J_{3A,3B} = 238.0$, $J_{4A,4B} = 133.1$<br>$J_{2,3A} \approx J_{3A,4B} = 13.4$, $J_{3A,4A} = 6.1$, $J_{3A,3B} = 246.6$, $J_{4A,4B} = 133.0$ |
| **VIII** | (ring, 4 O 1, F, 3, 2, O) | 80.65 (1-F$_A$, 4-F$_A$); 94.88 (1-F$_B$, 4-F$_B$); 182.81 (2-F, 3-F) | $J_{1A,1B} = J_{4A,4B} = 141.4$ |
| **IX** | (ring, 4 O 3 F$^2$, F, 5, O, CF$_3$ at 1) | Isomer **1** (65%): 81.76 d.d.m (1-F); 143.16 d.m (2-F); 174.72 m (3-F); 179.63 d.m (4-F); 79.74 m (5-F$_A$); 91.02 d.m (5-F$_B$)<br>Isomer **2** (35%): 79.48 m (1-F); 130.39 d.d.m (2-F); 178.17 d.m (3-F); 185.54 d.m (4-F); 78.06 d.m (5-F$_A$); 96.03 d.m (5-F$_B$) | $J_{1,2} = 1.3$, $J_{1,4} \approx J_{1,5B} \approx 3.6$, $J_{2,5A} = 2.4$, $J_{4,5A} = 14.6$, $J_{5A,5B} = 139.5$<br>$J_{1,2} = 2.4$, $J_{2,3} = 16.0$, $J_{2,5B} = 6.3$, $J_{4,5A} = 14.2$, $J_{5A,5B} = 140.8$ |
| **X** | $\overset{1}{H}\overset{2}{C}FCl\overset{3}{C}F_2O\overset{4}{C}F_2CO_2Na$ | 6.61 d.t (1-H); 154.02 d.t.m (2-F); 83.54 d.t.d (3-F$_A$); 84.44 d.t.d (3-F$_B$); 76.54 d.d.d (4-F) | $J_{1,2} = 47.2$, $J_{1,3} = 5.0$, $J_{2,3A} \approx J_{2,3B} \approx 12.0$, $J_{3A,4} \approx J_{3B,4} \approx 11.0$, $J_{2,4} = 2.8$, $J_{4A,4B} = 148.0$ |
| **XI** | $\overset{1}{H}\overset{2}{C}F_2O\overset{3}{C}F_2\overset{4}{C}FClCOONa$ | 7.04 t (1-H); 84.44 d.d.d (2-F); 79.53 d.t (3-F$_A$); 81.86 d.t (3-F$_B$); 122.66 d.d.m (4-F) | $J_{1,2} = 69.9$, $J_{2,3A} = 4.1$, $J_{2,3B} = 4.5$, $J_{2,4} = 3.4$, $J_{3B,4} = 9.0$, $J_{2A,2B} = 146.0$ |

(0.35 mol) of potassium carbonate was heated at 220–240°C. The pyrolysis products were collected in receivers cooled with a mixture of isopropyl alcohol and solid carbon dioxide (–78°C). Distillation with concentrated sulfuric acid gave 40 g (75%) of a mixture of compounds **Ia** and **Ib** at a ratio of 1:9 (according to the GLC and $^{19}$F NMR data).

*b. Reaction of compounds Ia and Ib with cesium fluoride in diethylene glycol dimethyl ether.* A flask equipped with a magnetic stirrer and reflux condenser (–78°C) was charged with 2 g (0.013 mol) of freshly calcined CsF and 5 ml of diethylene glycol dimethyl ether (freshly distilled over lithium aluminum hydride), and 32 g of mixture **Ia/Ib** was added dropwise under stirring. The resulting mixture was stirred for 2 h at room temperature, and the products were condensed in a cooled trap (–78°C). Distillation with concentrated sulfuric acid gave 29.2 g (0.164 mol, 91%) of compound **Ib**, bp 14–15°C. IR spectrum: $\nu$ 1805 cm$^{-1}$. The physical constants and spectral parameters of the product were consistent with those reported in [1].

**2-Trifluoromethylpentafluoro-2,3-dihydrofuran (IIIa).** Pyrolysis of 82.5 g (0.25 mol) of potassium (perfluoro-2-tetrahydrofuryl)difluoroacetate (**IV**) in the presence of 50 g (0.36 mol) of K$_2$CO$_3$ at 220–240°C gave 41.6 g (73%) of compound **IIIa**, bp 27–28°C. IR spectrum: $\nu$ 1755 cm$^{-1}$. The physical constants and spectral parameters of the product were consistent with those reported in [4].

**Reaction of compound IIIa with cesium fluoride in diethylene glycol dimethyl ether.** Likewise, from 26 g (0.114 mol) of compound **IIIa**, 2 g (0.013 mol) of CsF, and 5 ml of diethylene glycol dimethyl ether (reflux, 3 h) we obtained 24 g (0.105 mol, 92%) of compound **IIIb**, bp 27°C. IR spectrum: $\nu$ 1810 cm$^{-1}$.

**Reaction of compound Ib with SbF$_5$.** A glass ampule was charged with 1.7 g (96 mmol) of compound **Ib** and 2.2 g (0.01 mol) of SbF$_5$. The ampule was sealed and kept for 6 h at room temperature. It was then cooled and opened, and the mixture was poured into concentrated sulfuric acid and distilled to isolate 1.54 g (0.086 mol, 90%) of acyl fluoride **V**, bp 36–37°C. IR spectrum, $\nu$, cm$^{-1}$: 1700 (C=C), 1860 (COF).

**Reaction of compound Ia with SbF$_5$.** Likewise, from 2.0 g (0.011 mol) of compound **Ia** and 2.4 g (0.011 mol) of SbF$_5$ we obtained 1.76 g (0.01 mol, 88%) of fluoride **V**.

**Reaction of compound IIIa** with SbF$_5$. A glass ampule was charged with 2.4 g (0.0105 mol) of compound **IIIa** and 2.2 g (0.01 mol) of SbF$_5$. The ampule was sealed and heated for 2 h at 70°C. It was then cooled and opened, and the mixture was poured into concentrated sulfuric acid and distilled to isolate 2.2 g (0.097 mol, 91%) of compound **IIIb**.

**3,4-Dibromohexafluorotetrahydrofuran (VIb).** A quartz ampule was charged with 10.0 g (0.056 mol) of compound **Ib** and 9.6 g (0.06 mol) of bromine. The ampule was sealed and irradiated with UV light over a period of 12 h. The ampule was opened, the mixture was treated with a solution of sodium thiosulfate, and the organic phase was separated, dried over MgSO$_4$, and distilled. Yield 17.4 g (0.052 mol, 92%), bp 99–101°C. Found, %: C 14.39; Br 47.62; F 34.28. C$_4$Br$_2$F$_6$O. Calculated, %: C 14.20; Br 47.34; F 33.73.

**2,3-Dibromohexafluorotetrahydrofuran (VIa).** A flask equipped with a magnetic stirred and a reflux condenser (–78°C) was charged with 80.0 g of isomer mixture **Ia/Ib** (1:9), and 7.0 g (0.044 mol) of bromine was added dropwise under stirring and irradiation with a filament lamp. The mixture was washed with water, dried over MgSO$_4$, and subjected to fractional distillation. Yield 14.2 g (0.042 mol, 93%), bp 98.5–100°C. Found, %: C 14.56; Br 47.83; F 33.24. C$_4$Br$_2$F$_6$O. Calculated, %: C 14.20; Br 47.34; F 33.73.

**2,3-Dibromo-2-trifluoromethylpentafluorotetrahydrofuran (VIIa).** Likewise, from 9.6 g (0.042 mol) of compound **IIIa** and 7.0 g (0.044 mol) of bromine we obtained 15.1 g (0.039 mol, 93%) of dibromide **VIIa**, bp 116–120°C. Found, %: C 15.25; Br 40.98; F 39.18. C$_5$Br$_2$F$_8$O. Calculated, %: C 15.46; Br 41.24; F 39.18.

**Debromination of compound VIa.** A flask equipped with a magnetic stirrer and a reflux condenser was charged with 5 g (0.077 mol) of zinc and 30 ml of acetic acid, and 12 g (0.036 mol) of compound **VIa** was added dropwise under vigorous stirring. The products were collected in a trap cooled to –78°C. Distillation over concentrated sulfuric acid gave 4.8 g (0.027 mol, 76%) of compound **Ia** with bp 15°C. IR spectrum: $\nu$ 1745 cm$^{-1}$ (C=C).

**Debromination of compound VIb.** Likewise, from 8.1 g (0.024 mol) of dibromide **VIb**, 4 g (0.061 mol) of zinc, and 25 ml of acetic acid we obtained 3.2 g (0.018 mol, 75%) of compound **Ib**.

**Debromination of compound VIIa.** Likewise, from 14.0 g (0.036 mol) of dibromide **VIIa**, 5.0 g (0.077 mol) of zinc, and 30 ml of acetic acid we obtained 6.4 g (0.028 mol, 78%) of compound **IIIa**.

**Reaction of compound Ib with sodium hypochlorite.** Compound **Ib**, 22.0 g (0.124 mol), was gradually added to a mixture of 100 ml of an aqueous solution of NaOCl and 10 ml of acetonitrile under vigorous stirring at 5–10°C. The mixture was stirred for 2 h, and the products were collected in a trap cooled to –78°C. We thus obtained 18.2 g of a mixture of epoxy derivative **VIII** and initial compound **Ib** (according to the GLC and IR data). This mixture was transferred into a quartz ampule, 1.5 ml of bromine was added, and the ampule was sealed and irradiated with UV light. The resulting mixture was treated with a solution of sodium thiosulfate, and the organic phase was separated, dried over $MgSO_4$, and subjected to fractional distillation to isolate 14.4 g (0.074 mol, 60%) of compound **VIII**, bp 14–15°C, IR spectrum, $\nu$, $cm^{-1}$: 1550, 1570 (oxirane ring), and 3.8 g (0.011 mol) of dibromide **VIb**.

The aqueous layer was evaporated, and the residue was dried, dissolved in methanol-$d_4$, and analyzed by $^{19}F$ NMR spectroscopy. It was a mixture of salts **X** and **XI** at a ratio of 31:69.

**Reaction of compound IIIb with sodium hypochlorite.** Likewise, from 16.0 g (0.07 mol) of compound **IIIb**, 80 ml of aqueous NaOCl, and 10 ml of acetonitrile we obtained 9.3 g (0.038 mol, 54%) of epoxy derivative **IX**, bp 26–28°C. IR spectrum, $\nu$, $cm^{-1}$: 1540, 1552 (oxirane ring).

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