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Synthesis of oxiranes based on 1,1,2,3,3-pentafluoro-1,5-hexadiene

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Interaction of 1,1,2,3,3-pentafluoro-1,5-hexadiene with Br_2 in a MeCOOH medium results in the product of selective bromination of the hydrocarbon double bond, *i.e.*, 5,6-dibromo-1,1,2,3,3-pentafluoro-1-hexene. Epoxidation of the latter with H_2O_2 in an alkaline medium followed by debromination afforded 5,6-epoxy-4,4,5,6,6-pentafluoro-1-hexene for the first time.

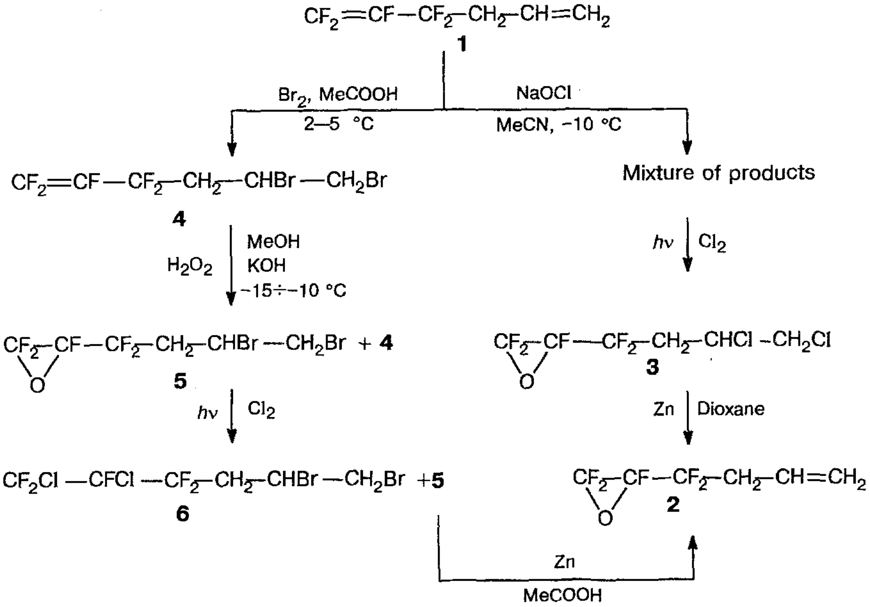
Key words: perfluorinated and partially fluorinated nonconjugated dienes, epoxidation, oxiranes, dioxiranes.

Continuing our studies on the chemical properties of partially fluorinated unconjugated dienes, in this communication we investigated the possibility of epoxidation of 1,1,2,3,3-pentafluoro-1,5-hexadiene (**1**), which was obtained earlier,[1] for the purpose of preparation of functionally substituted oxiranes, which are promising monomers and intermediates for fine organic synthesis. Scheme 1 represents the results of this work.

There is no literature information concerning the oxiranes of partially fluorinated dienes. The presence of two double bonds in compound **1** (perfluorinated and hydrocarbon) and their mutual influence[2] significantly impedes the possibilities of preparative synthesis of oxiranes. This circumstance is complicated[2,3] by the predominant rearrangement processes in the molecule of **1**.

For perfluorinated unconjugated dienes, very few oxiranes and dioxiranes are known[4,5] that can be obtained by photochemical epoxidation of perfluorodienes with oxygen in the presence of catalytic amounts of Cl_2. In this case, epoxidation proceeds sequentially: one double bond is oxidized at the first stage followed by the second one, which enables isolation of both oxirane and dioxirane from the reaction mixture; unreacted perfluorodiene always remains with the epoxidation products.

Scheme 1



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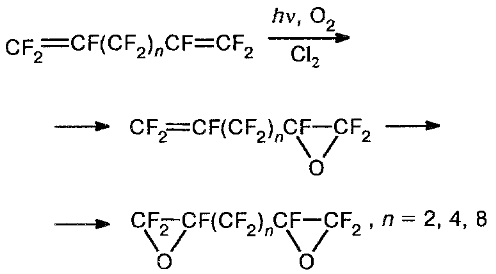


Unlike perfluorodienes, photochemical epoxidation of **1** does not give positive results. Unsatisfactory result is also given by the common hypochlorite epoxidation of **1** due to the low yield of 5,6-epoxy-4,4,5,6,6-pentafluoro-1-hexene (**2**): the reaction results in a complex mixture of products (see Scheme 1), chlorination of which and subsequent distillation enables isolation of 1,2-epoxy-5,6-dichloro-1,1,2,3,3-pentafluorohexane (**3**) in 20 % yield. Dechlorination of **3** with zinc in dioxane[6] affords only trace amounts of compound **2** since the process seems to be accompanied by isomerization of the epoxide cycle in both compounds (**2** and **3**) under the action of a nascent Lewis acid ($ZnCl_2$). It should be noted that the epoxidation reaction under the influence of NaOCl involves exclusively the perfluorinated double bond that indicates the possibility of separate epoxidation of the perfluorinated and hydrocarbon fragments of the molecule of **1**. This possibility is accounted for by the fact that nucleophilic OCl^- acts as an attacking particle, and the perfluorinated double bond is depleted in electron density unlike the hydrocarbon bond due to the strong negative *I*-effect of the fluorine atoms. It follows then that the OCl^- attack is directed just to the perfluorinated double bond. In order to increase the yield of compound **2** and suppress the possible rearrangement processes, it became necessary to protect the hydrocarbon double bond having the enhanced electron density. The successful attempt of electrophilic bromination of nonfluorinated fragment of the molecule of **1** in the MeCOOH medium afforded 5,6-dibromo-1,1,2,3,3-pentafluoro-1-hexene (**4**) in 90 % yield. Use of a protic solvent deactivates the γ-CF_2 group, which has nucleophilic and basic properties and takes part in the rearrangement processes.[2] The attempts of bromination of compound **1** with Br_2 under an incandescent lamp resulted in unidentifiable mixtures of products of numerous rearrangements and strong resinification of the reaction mixture.

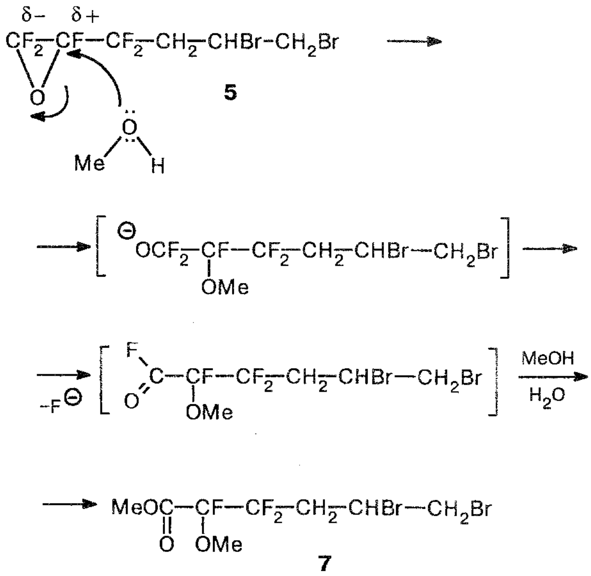
Similar to compound **4**, 1,2-dichloroperfluoro-ω-olefins were epoxidized earlier[6] by H_2O_2 in an alkaline medium. The peroxide epoxidation afforded the 2:3 mixture of compounds **4** and **5**, which were separated by a common technique, *i.e.*, by chlorination of the perfluorinated double bond in **4** resulting in product **6**. Epoxide **5** isolated by distillation was treated with Zn in MeCOOH. As a result, compound **2** was obtained in 83 % yield.

Note that epoxidation of **4** carried out at a temperature above −10 °C affords the methyl ester of 2-methoxy-5,6-dibromo-2,3,3-trifluorocaproic acid (**7**). Compound **7** results from cleavage of the epoxide cycle formed in the reaction mass of product **5** under the action of nucleophilic MeOH (Scheme 2).

Similar processes for perfluorooxiranes are described in literature.[7]

The structures of the compounds synthesized were confirmed by ^{19}F and ^1H NMR and IR spectra and elemental analyses (Tables 1 and 2).

Scheme 2



Experimental

IR spectra (thin layer) were recorded using a Specord IR-75 spectrophotometer. ^1H (100 MHz) and ^{19}F (75.3 MHz) NMR spectra were recorded with TMS and HFB internal standards using a Tesla BS-567A spectrometer. The fluorine shifts are given relative to $CFCl_3$; higher-field shifts are considered as positive. GLC was carried out using a LKhM-72 chromatograph with helium as the carrier gas and a steel column (6000×4 mm) containing 20 % SKTFT-50 on Chromosorb W.

5,6-Dibromo-1,1,2,3,3-pentafluoro-1-hexene (4). Upon stirring and cooling to 2 to 5 °C, a solution of 80.0 g (0.5 mol) of Br_2 in 200 mL of glacial MeCOOH was added dropwise to 86.0 g (0.5 mol) of **1** in 100 mL of glacial MeCOOH. The reaction mixture was warmed to room temperature, and the lower layer was separated, washed with H_2O, and dried over $MgSO_4$. After distillation, 149.5 g (90 %) of compound **4** was obtained, b.p. 82 °C (2—3 Torr). IR spectrum (ν/cm^{-1}): 1780 (C=C).

Epoxidation of 4. The solution of 17.0 g (0.3 mol) of KOH in 35 mL of H_2O was added dropwise upon stirring during 45 min to the mixture of 63 mL of MeOH, 63 mL of 30 % H_2O_2, and 33.4 g (0.1 mol) of **2** cooled to −15 °C. The

Table 1. ^{19}F and ^{1}H NMR spectra of compounds **2—7**

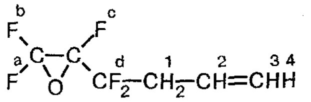
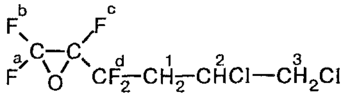
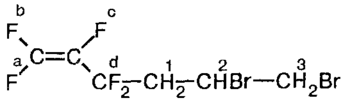
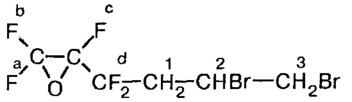
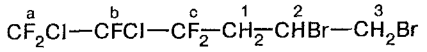
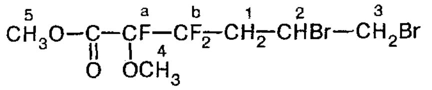
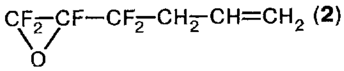
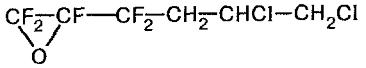
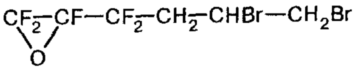
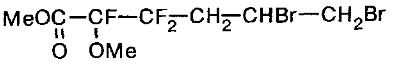
Compound	^{19}F NMR, δ	^{1}H NMR, δ	J/Hz
 (**2**)	96.28 (ddt, F^a); 63.09 (ddt, F^b); 130.96 (tdd, F^c); 107.52 (ndtdd, 2 F^d)	2.93 (ddt, 2 H-1); 5.69 (ddt, H-2); 5.22 (dd, H-3); 5.36 (dd, H-4)	J_{a-b} = 36.0; J_{a-c} = 69.5; J_{a-d} = 4.9; J_{c-d} = 15.6; J_{1-2} = 6.6; J_{1-d} = 17.4; J_{3-4} = 1.4; J_{3-2} = 6.5
 (**3**)	107.59 (nm, F^a); 63.24 (nm, F^b); 131.79 (nm, F^c); 110.03 (nm, 2 F^d)	2.89 (dt, 2 H-1); 4.41 (tt, H-2); 3.72 (d, 2 H-3)	J_{1-2} = 6.3; J_{1-d} = 11.8; J_{2-3} = 4.7
 (**4**)	99.90 (ddt, F^a); 92.67 (ddt, F^b); 187.78 (ddt, F^c); 107.29 (ndddt, 2 F^d)	3.11 (td, 2 H-1); 4.31 (ntt, H-2); 3.75 (nm, 2 H-3)	J_{a-b} = 62.5; J_{b-c} = 36.9; J_{b-d} = 4.8; J_{a-c} = 172.9; J_{c-d} = 14.5; J_{1-2} = 16.7; J_{1-d} = 3.8; J_{2-3} = 23.0
 (**5**)	102.59 (nm, F^a); 63.24 (nm, F^b); 131.79 (nm, F^c); 110.03 (nm, 2 F^d)	2.89 (dt, 2 H-1); 4.41 (tt, H-2); 3.72 (d, 2 H-3)	J_{1-2} = 6.3; J_{1-d} = 11.9; J_{2-3} = 4.7
 (**6**) $\overset{a}{C}F_2Cl-\overset{b}{C}FCl-\overset{c}{C}F_2-\overset{1}{C}H_2-\overset{2}{C}HBr-\overset{3}{C}H_2Br$	60.96 (ndt, 2 F^a); 131.37 (ntt, F^b); 106.70 (ntd, 2 F^c)	3.04 (dt, 2 H-1); 4.37 (tt, H-2); 3.77 (d, 2 H-3)	J_{1-2} = 17.0; J_{a-b} = 12.8; J_{b-c} = 12.8; J_{c-1} = 24.1
 (**7**) $\overset{5}{C}H_3O-\underset{\displaystyle O}{\overset{\Vert}{C}}-\underset{\displaystyle O\overset{4}{C}H_3}{\overset{a}{C}F}-\overset{b}{C}F_2-\overset{1}{C}H_2-\overset{2}{C}HBr-\overset{3}{C}H_2Br$	103.01 (ntt, F^a); 104.68 (ntd, 2 F^b)	2.96 (dtd, 2 H-1); 4.27 (ntt, H-2); 3.76 (nm, 2 H-3); 1.75 (td, 3 H-4); 0.97 (td, 3 H-5)	J_{a-b} = 14.5; J_{b-1} = 16.0; J_{1-a} = 2.1; J_{4-a} = 7.3; J_{4-b} = 18.9; J_{5-b} = 7.5

Table 2. Elemental analysis of compounds **2—7**

Compound	Found/Calculated (%)					Molecular formula
	C	H	Br	Cl	F	
 (**2**)	38.45 38.31	2.72 2.68	—	—	50.11 50.50	$C_6H_5F_5O$
 (**3**)	27.83 27.82	2.01 1.95	—	27.20 27.38	36.34 36.68	$C_6H_5Cl_2F_5O$
$CF_2=CF-CF_2-CH_2-CHBr-CH_2Br$ (**4**)	21.77 21.71	1.57 1.52	48.95 48.15	—	28.23 28.62	$C_6H_5Br_2F_5$
 (**5**)	20.79 20.71	1.50 1.45	45.99 45.93	—	27.03 27.30	$C_6H_5Br_2F_5O$
$CF_2Cl-CFCl-CF_2-CH_2-CHBr-CH_2Br$ (**6**)	17.98 17.89	1.28 1.25	39.79 39.67	17.38 17.60	23.35 23.58	$C_6H_5Br_2Cl_2F_5$
 (**7**) $MeO\underset{\displaystyle O}{\overset{\Vert}{C}}-\underset{\displaystyle OMe}{\overset{\vert}{C}F}-CF_2-CH_2-CHBr-CH_2Br$	25.91 25.83	3.01 2.98	42.97 42.96	—	15.10 15.32	$C_8H_{11}Br_2F_3O_3$

reaction mixture was kept at a temperature below −10 °C and was stirred further for 1 h; the lower layer was separated and dried over $MgSO_4$. Distillation afforded 25.1 g of a mixture containing **4** and **5** (~40 : 60), b.p. 78—92 °C (2—3 Torr). IR spectrum (ν/cm^{-1}): 1780 (C=C); 1535 ($\underline{O-CF-C}F_2$).

Separation of mixture of 4 and 5. Clorine flow was passed into the mixture of **4** and **5** (25.1 g) placed in a quartz reactor cooled with solid CO_2 upon irradiation of a PRK-2M mercury lamp placed at the distance of 10 cm from the reactor. After finishing Cl_2 absorption, the reaction mixture was distilled.

12.8 g of compound **5** with b.p. of 79 to 80 °C (2—3 Torr) and 9.0 g of compound **6** with b.p. of 132 to 134 °C (2—3 Torr) were obtained. IR spectrum of **5** (ν/cm^{-1}): 1535 $(\underbrace{O{-}CF{-}C}F_2)$. IR spectrum of **6** contains no absorption band of the C=C bond.

5,6-Epoxy-4,4,5,6,6-pentafluoro-1-hexene (2). Dibromide **5** (12.8 g, 0.037 mol) was added dropwise upon stirring during 30 min to the mixture of 9.6 g (0.148 mol) of Zn and 50 mL of glacial MeCOOH with simultaneous separation of **2** at the head of complete condensation. 5.8 g (83 %) of **2** was obtained, b.p. 64—65 °C. IR spectrum of **3** (ν/cm^{-1}): 1675 (C=C); 1535 $(\underbrace{O{-}CF{-}C}F_2)$.

Methyl 2-methoxy-5,6-dibromo-2,3,3-trifluorocaproate (7). The solution of 17.0 g (0.3 mol) of KOH in 35 mL of H_2O was added dropwise upon stirring during 45 min at ~20 °C to the mixture of 63 mL of MeOH, 63 mL of 30 % H_2O_2, and 33.4 g (0.1 mol) of **4**. After further stirring for 1 h, the lower layer was separated and dried over $MgSO_4$. Distillation afforded 34.0 g (91 %) of **7**, b.p. 149—152 °C (5—6 Torr). IR spectrum of **7** (ν/cm^{-1}): 1435 (OMe); 1755 (COOMe); 2950 (C—H).

Epoxidation of 1. Solution of NaOCl (145 mL) obtained by the known technique[8] was added dropwise over 1.5 h to a mixture of 17.2 g (0.1 mol) of **1** and 10 mL of MeCN cooled to −10 °C; after further stirring for 2 h, the lower layer was separated and dried over $MgSO_4$. Distillation afforded 12.2 g of mixture of **1** and **2** in the ratio of 1 : 1, b.p. 64—68 °C. IR spectrum (ν/cm^{-1}): 1675, 1780 (C=C); 1540 $(\underbrace{O{-}CF{-}C}F_2)$.

Separation of the mixture of 1 and 2 was carried out as in the case of the mixture of **4** and **5**. 1.7 g (20 %) of **3** was obtained, b.p. 126—128 °C. IR spectrum (ν/cm^{-1}): 1540 $(\underbrace{O{-}CF{-}C}F_2)$. Treatment of 10.5 g (0.041 mol) of **3** with zinc in dioxane afforded 0.2 g (2.6 %) of **2**.

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