Dehydroiodination of 2-iodo-3-(polyfluoroalkyl)propoxymethyloxiranes

D. N. Bazhin, T. I. Gorbunova, A. Ya. Zapevalov, and V. I. Saloutin*

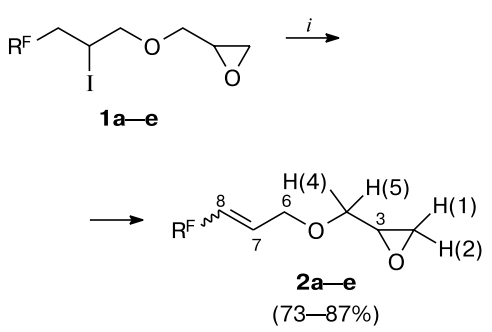
I. Ya. Postovskii Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 22 ul. S. Kovalevskoi, 620041 Ekaterinburg, Russian Federation. Fax: +7 (343) 362 3105. E-mail: bazhin@ios.uran.ru

Dehydroiodination of 2-iodo-3-(polyfluoroalkyl)propoxymethyloxiranes upon treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded (polyfluoroalk-2-enyl)oxymethyloxiranes as *E*- and *Z*-isomers in ratio depending on the nature of the fluoroalkyl substituent.

Key words: glycidyl ethers, dehydroiodination, olefins, organofluorine compounds.

Earlier,[1] we performed an addition of polyfluoroalkyl iodides to allyl glycidyl ether under mild conditions. A specific feature of the functionalized fluorine-containing glycidyl ethers consist in the possibility of its further chemical transformations with the oxirane ring retention. The present work is aimed at the synthesis of unsaturated glycidyl ethers by dehydroiodination of derivatives **1a—d** (Scheme 1).

Scheme 1



R^F = $F(CF_2)_3$ (**a**), $F(CF_2)_4$ (**b**), $F(CF_2)_6$ (**c**), $Cl(CF_2)_6$ (**d**), $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$ (**e**)

Reagents and conditions: *i*. DBU, CH_2Cl_2, ~20 °C.

It is known[2] that triethylamine, tributylamine, and pyridine, used as the dehydroiodination agents for 1-iodo-1,1,2,2-tetrahydroperfluoroalkanes, allow one to synthesize terminal alkenes in 82, 80, and 12% yield, respectively. In similar conditions, the action of these agents (including diisopropylethylamine) on compounds **1a—d** led to the resinification of the reaction mixture.

The use of DBU as the base, which often shows high effectivity and selectivity in elimination reactions under mild conditions,[3—6] allowed us to successfully solve the indicated problem. In our experiments, the dehydroiodination of compounds **1a—d** with DBU afforded the target compounds **2a—d** in high yields (see Scheme 1). It was reasonable to carry out the process in dichloromethane, which allowed one to control the reaction temperature and decreased the resinification.

In the IR spectra of (polyfluoroalk-2-enyl)oxymethyloxiranes **2a—d**, a characteristic absorption band in the region 1680 cm^{-1}, responsible for the C=C bond vibrations, was registered. The ^1H NMR spectra of compounds **2a—d** have a number of features due to the presence of the internal double bond together with the epoxide ring. In contrast to the oxirane ring protons, having only one set of signals, the rest of the protons have two sets of signals, responsible for the *E*- and *Z*-isomers. The assignment of isomers was made on the basis of the spin-spin coupling constant values of olefin protons, equal to 15.8 and 12.5 Hz for *E*- and *Z*-isomers, respectively.[7] (Polyfluoroalk-2-enyl)oxymethyloxiranes **2a—d** were formed predominantly in *E*-configuration (ratio $E : Z = 10 : 1$).

In order to study the influence of the nature of polyfluoroalkyl substituent on the isomeric composition of the dehydroiodination products, compound **1e** was synthesized, the subsequent treatment of which with DBU led to product **2e**. Compound **2e** is also a mixture of *E*- and *Z*-isomers in ratio 50 : 1, which confirms a decisive influence of sterical factor on the isomeric composition of the products obtained.

In conclusion, dehydroiodination of 2-iodo-3-(polyfluoroalkyl)propyl glycidyl ethers **1a—e** upon treatment with DBU, possessing strong basicity and low nucleophilicity, allowed us to synthesize the earlier unknown (polyfluoroalk-2-enyl)oxymethyloxiranes **2a—e**, which may serve as promising monomers for the synthesis of functional fluorinated polymers.

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Experimental

IR spectra were recorded on a Perkin—Elmer Spectrum One spectrometer for neat samples. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker DRX 400 spectrometer in $CDCl_3$ (400.1 (^{1}H) and 376.5 MHz (^{19}F)) relatively to Me_4Si and C_6F_6 as the internal standards, respectively.

Compound **1e** was synthesized according to the known procedure.[1] The ^{1}H NMR spectrum of glycidyl ether **1e** is similar to the spectra of compounds **1a**—**d**.[1] Yields, boiling points, and elemental analysis data of compound **1e** are given in Table 1.

Synthesis of compounds 2a—e (general procedure). 1,8-Diazabicyclo[5.4.0]undec-7-ene (12.2 g, 0.08 mol) was slowly added to a solution of compound **1a**—**e** (0.08 mol) in CH_2Cl_2 (30 mL). The mixture was stirred for 20 min at ~20 °C, after this, water (100 mL) was added, the organic layer was sequentially washed with 2 *M* aqueous H_2SO_4 and Na_2CO_3 aqueous solution, dried with $MgSO_4$, and concentrated. Individual compounds **2a**—**e** were isolated by distillation *in vacuo*.

Yields, boiling points, and elemental analysis data of compounds **2a**—**e** are given in Table 1, ^{1}H and ^{19}F NMR spectroscopy data, in Tables 2 and 3.

Table 1. Yields, boiling points, and elemental analysis data of compounds **1e** and **2a**—**e**

Compound	Yield (%)	B.p./°C (p/Torr)	Found / Calculated (%)			Molecular formula
			C	H	F	
6-Iodo-8,11-bis(trifluoromethyl)-8,10,10,11,13,13,14,14,15,15,15-undecafluoro-1,2-epoxy-4,9,12-trioxapentadecane (**1e**)	79	119—120 (5)	24.42 24.30	1.51 1.46	46.80 46.66	$C_{14}H_{10}F_{17}IO_4$
(4,4,5,5,6,6,6-Heptafluorohex-2-en-1-yl)oxymethyloxirane (**2a**)	75	83—84 (10)	38.28 38.31	3.15 3.22	47.02 47.13	$C_9H_9F_7O_2$
(4,4,5,5,6,6,7,7,7-Nonafluorohept-2-en-1-yl)oxymethyloxirane (**2b**)	73	89—90 (5)	36.29 36.16	2.78 2.73	51.55 51.48	$C_{10}H_9F_9O_2$
(4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononon-2-en-1-yl)oxymethyloxirane (**2c**)	85	109—110 (10)	33.38 33.35	2.15 2.10	57.26 57.15	$C_{12}H_9F_{13}O_2$
(9-Chloro-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorononon-2-en-1-yl)oxymethyloxirane (**2d**)	87	120—121 (10)	32.20 32.13	2.09 2.02	50.96 50.82	$C_{12}H_9ClF_{12}O_2$
8,11-Bis(trifluoromethyl)-8,10,10,11,13,13,14,14,15,15,15-undecafluoro-1,2-epoxy-4,9,12-trioxapentadec-6-ene (**2e**)	82	110—111 (5)	29.93 29.80	1.63 1.61	57.41 57.24	$C_{14}H_9F_{17}O_4$

Table 2. ^{1}H NMR spectroscopy data of compounds **2a**—**e**

Compound	Isomer	δ (J/Hz)							
		H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)
2a	*E*	2.62 (dd, $J_{1,2}$ = 5.0, $J_{1,3}$ = 2.7)	2.82 (dd, $J_{1,2}$ = 5.0, $J_{2,3}$ = 4.2)	3.18 (tdd, $J_{1,3}$ = 2.7, $J_{2,3}$ = 4.2, $J_{3,4}$ = 6.1, $J_{5,3}$ = 2.6)	3.41 (dd, $J_{3,4}$ = 6.1, $J_{4,5}$ = 11.6)	3.85 (dd, $J_{4,5}$ = 11.6, $J_{5,3}$ = 2.6)	4.21 (m)	6.45 (dm, $J_{7,8}$ = 15.8)	5.95 (m)
	Z	2.62 (dd, $J_{1,2}$ = 5.0, $J_{1,3}$ = 2.7)	2.82 (dd, $J_{1,2}$ = 5.0, $J_{2,3}$ = 4.2)	3.18 (tdd, $J_{1,3}$ = 2.7, $J_{2,3}$ = 4.2, $J_{4,3}$ = 6.0, $J_{5,3}$ = 2.8)	3.38 (dd, $J_{4,3}$ = 6.0, $J_{4,5}$ = 11.4)	3.78 (dd, $J_{4,5}$ = 11.4, $J_{5,3}$ = 2.8)	4.35 (m)	6.30 (dm, $J_{7,8}$ = 12.5)	5.60 (m)
2b	*E*	2.62 (dd, $J_{1,2}$ = 5.0, $J_{1,3}$ = 2.7)	2.82 (dd, $J_{1,2}$ = 5.0, $J_{2,3}$ = 4.2)	3.18 (tdd, $J_{1,3}$ = 2.7, $J_{2,3}$ = 4.2, $J_{3,4}$ = 6.1, $J_{5,3}$ = 2.6)	3.41 (dd, $J_{3,4}$ = 6.1, $J_{4,5}$ = 11.6)	3.85 (dd, $J_{4,5}$ = 11.6, $J_{5,3}$ = 2.6)	4.22 (m)	6.46 (dm, $J_{7,8}$ = 15.8)	5.96 (m)
	Z	2.62 (dd, $J_{1,2}$ = 5.0, $J_{1,3}$ = 2.7)	2.82 (dd, $J_{1,2}$ = 5.0, $J_{2,3}$ = 4.2)	3.18 (tdd, $J_{1,3}$ = 2.7, $J_{2,3}$ = 4.2, $J_{4,3}$ = 6.0, $J_{5,3}$ = 2.8)	3.39 (dd, $J_{4,3}$ = 6.0, $J_{4,5}$ = 11.4)	3.78 (dd, $J_{4,5}$ = 11.4, $J_{5,3}$ = 2.8)	4.27 (m)	6.30 (dm, $J_{7,8}$ = 12.5)	5.61 (m)
2c	*E*	2.62 (dd, $J_{1,2}$ = 5.0, $J_{1,3}$ = 2.7)	2.82 (dd, $J_{1,2}$ = 5.0, $J_{2,3}$ = 4.2)	3.18 (tdd, $J_{1,3}$ = 2.7, $J_{2,3}$ = 4.2, $J_{3,4}$ = 6.1, $J_{5,3}$ = 2.6)	3.41 (dd, $J_{3,4}$ = 6.1, $J_{4,5}$ = 11.6)	3.85 (dd, $J_{4,5}$ = 11.6, $J_{5,3}$ = 2.6)	4.22 (m)	6.45 (dm, $J_{7,8}$ = 15.8)	5.96 (m)
	Z	2.62 (dd, $J_{1,2}$ = 5.0, $J_{1,3}$ = 2.7)	2.82 (dd, $J_{1,2}$ = 5.0, $J_{2,3}$ = 4.2)	3.18 (tdd, $J_{1,3}$ = 2.7, $J_{2,3}$ = 4.2, $J_{4,3}$ = 6.0, $J_{5,3}$ = 2.8)	3.39 (dd, $J_{4,3}$ = 6.0, $J_{4,5}$ = 11.4)	3.78 (dd, $J_{5,3}$ = 2.8, $J_{4,5}$ = 11.4)	4.35 (m)	6.30 (dm, $J_{7,8}$ = 12.4)	5.61 (m)

(*to be continued*)

Table 2 (*continued*)

Compound	Isomer	δ (*J*/Hz)							
		H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)
2d	*E*	2.62 (dd, $J_{1,2}$ = 5.0, $J_{1,3}$ = 2.7)	2.82 (dd, $J_{1,2}$ = 5.0, $J_{2,3}$ = 4.2)	3.18 (m)	3.41 (dd, $J_{4,3}$ = 6.1, $J_{4,5}$ = 11.6)	3.85 (dd, $J_{4,5}$ = 11.6, $J_{5,3}$ = 2.7)	4.22 (m)	6.45 (dm, $J_{7,8}$ = 15.8)	5.94 (m)
	Z	2.62 (dd, $J_{1,2}$ = 5.0, $J_{1,3}$ = 2.7)	2.82 (dd, $J_{1,2}$ = 5.0, $J_{2,3}$ = 4.2)	3.18 (m)	3.39 (dd, $J_{4,5}$ = 11.4, $J_{4,3}$ = 6.1)	3.77 (dd, $J_{4,5}$ = 11.4, $J_{5,3}$ = 2.8)	4.35 (m)	6.29 (dm, $J_{7,8}$ = 12.4)	5.63 (m)
2e	*E*	2.61 (dd, $J_{2,1}$ = 4.9, $J_{1,3}$ = 2.7)	2.81 (dd, $J_{2,1}$ = 4.9, $J_{2,3}$ = 4.2)	3.18 (dm, $J_{5,3}$ = 2.6)	3.41 (dd, $J_{3,4}$ = 6.5, $J_{4,5}$ = 11.7)	3.85 (dd, $J_{4,5}$ = 11.7, $J_{5,3}$ = 2.6)	4.22 (m)	6.50 (dm, $J_{7,8}$ = 15.8)	6.01 (m)
	Z	2.61 (dd, $J_{2,1}$ = 4.9, $J_{1,3}$ = 2.7)	2.81 (dd, $J_{2,1}$ = 4.9, $J_{2,3}$ = 4.2)	3.18 (dm, $J_{5,3}$ = 5.2)	3.37 (m)	3.64 (dd, $J_{5,3}$ = 5.2, $J_{5,4}$ = 11.8)	4.37 (m)	6.40 (m)	5.60 (m)

Table 3. ^{19}F NMR spectroscopy data of compounds **2a—e**

Compound	R^F	Isomer	δ (*J*/Hz)
2a	$CF^c_3CF^b_2CF^a_2$	*E*	34.40 (m, 2 F^b); 43.39 (m, 2 F^a); 81.69 (t, 3 F^c, $J_{c,a}$ = 4.2)
		Z	34.03 (m, 2 F^b); 53.27 (m, 2 F^a); 81.69 (t, 3 F^c, $J_{c,a}$ = 4.2)
2b	$CF^d_3CF^c_2CF^b_2CF^a_2$	*E*	36.44 (m, 2 F^c); 37.95 (m, 2 F^b); 50.25 (m, 2 F^a); 81.03 (tt, 3 F^d, $J_{d,a}$ = 9.7, $J_{d,b}$ = 3.3)
		Z	36.17 (m, 2 F^c); 37.56 (m, 2 F^b); 54.11 (m, 2 F^a); 81.03 (tt, 3 F^d, $J_{d,a}$ = 9.7, $J_{d,b}$ = 3.3)
2c	$CF^f_3CF^e_2CF^d_2CF^c_2CF^b_2CF^a_2$	*E*	35.92 (m, 2 F^e); 38.75 (m, 2 F^d); 39.22 (m, 2 F^b); 40.48 (m, 2 F^c); 50.35 (m, 2 F^a); 81.16 (tt, 3 F^f, $J_{f,c}$ = 10.7, $J_{f,d}$ = 2.4)
		Z	35.92 (m, 2 F^e); 38.75 (m, 2 F^d); 39.22 (m, 2 F^b); 40.48 (m, 2 F^c); 54.17 (m, 2 F^a); 81.16 (tt, 3 F^f, $J_{f,c}$ = 10.7, $J_{f,d}$ = 2.4)
2d	$ClCF^f_2CF^e_2CF^d_2CF^c_2CF^b_2CF^a_2$	*E*	35.54 (m, 2 F^e); 38.64 (m, 2 F^d); 40.27 (m, 2 F^b); 41.57 (m, 2 F^c); 50.16 (m, 2 F^a); 93.96 (t, 3 F^f, $J_{f,c}$ = 13.5)
		Z	35.54 (m, 2 F^e); 38.64 (m, 2 F^d); 40.27 (m, 2 F^b); 41.57 (m, 2 F^c); 54.04 (m, 2 F^a); 93.96 (t, 3 F^f, $J_{f,c}$ = 13.5)
2e	$CF^h_3CF^g_2CF^f_2OCF^d(CF^a_3)CF^c_2OCF^b(CF^a_3)$	*E*, *Z*	17.10 (m, 2 F^d); 32.57 (m, 2 F^g); 33.54 (m, 2 F^b); 77.23 (m, 2 F^c); 80.05 (m, 2 F^f); 80.81 (m, 3 F^h); 82.19 (m, 6 F^a)

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