ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 5, pp. 656–659. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © D.N. Bazhin, T.I. Gorbunova, A.Ya. Zapevalov, V.E. Kirichenko, V.I. Saloutin, 2007, published in Zhurnal Organicheskoi Khimii, 2007, Vol. 43, No. 5, pp. 661–664.

Features of Reaction between Fluorine-Containing Glycidyl Ethers and Alcohols in Basic Medium

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

Postovskii Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, Yekaterinburg, 620219 Russia
e-mail: zapevalov@ios.uran.ru

Received April 6, 2006

Abstract—The reaction of fluorine-containing glycidyl ethers with various alcohols (*i*-PrOH, MeOH, PhOH, 2,2,3,3-tetrafluoropropanol) in basic medium resulted in products of regioselective opening of the oxirane ring. In reaction of 2,2,3,3-tetrafluoropropyloxymethyloxirane with 2-propanol under conditions of phase-transfer catalysis the main product was the corresponding 1,2-diol (yield 42%).

DOI: 10.1134/S1070428007050041

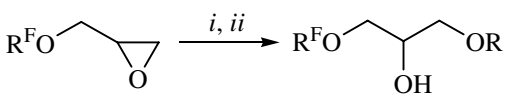
Fluorine-containing glycidyl ethers are promising monomers for production of polymer materials of low surface energy, high thermal stability, and resistance against aggressive media [1], and they are also interesting from the viewpoint of oxirane ring transformation under treatment with diverse reagents.

The hydrocarbon nature of the oxirane ring in the glycidyl ethers suggests that in the presence of bases it should undrgo opening in keeping with Krasussky rule. However the presence of fluorine-containing substituents in the oxiranes may change the direction of the reaction.

The aim of this study is the comparison of reactivity with respect to alcohols in basic media of glycidyl ethers with fluorinated substituents of various structure.

We chose as objects of investigation oxiranes **I** and **II** (Scheme 1) obtained by reaction of fluorinated alcohols with epichlorohydrin under the conditions of phase-transfer catalysis [2]. In the preparation of oxirane **I** a commercial telomer alcohol, 2,2,3,3-tetrafluoropropanol, was used, and in the synthesis of compound **II** a reduction product of carbonyl fluoride group in the hexafluoropropylene oxide trimer was applied [3].

Scheme 1.



I, II **IIIa–IIId, IVa–IVd**

$R^F = H(CF_2)_2CH_2$ (**I, III**), $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CH_2$ (**II, IV**); R = Me (**a**), Ph (**b**), $H(CF_2)_2CH_2$ (**c**), *i*-Pr (**d**); *i*: RONa, ROH, dioxane, heating, 2 h; *ii*: H_2O, HCl.

Reactions were described for fluorine-containing oxiranes with nucleophilic reagents where these substrates were prone to hydrolysis and oligomerization [2, 4]. This behavior of oxiranes was caused both by the reaction conditions (temperature, time, solvent character, order of reagents introduction) and by the nucleophile nature.

In this study we used as reagents alcoholates whose basicity decreased in the series *i*-PrO^-, MeO^-, PhO^-, $H(CF_2)_2CH_2O^-$.

The opening of oxirane ring in compounds **I** and **II** under the treatment of alcoholates prepared in situ was performed in the environment of the corresponding anhydrous alcohol. To strengthen the nucleophilic properties of alcoholates we used dioxane as additional solvent. The processes conditions and results of reactions are given in Scheme 1 (see EXPERIMENTAL, procedure *a*).

Notwithstanding the difference in basic and nucleophilic characteristics of the alcoholates used the isolated hydroxypolyethers **IIIa–IIId** and **IVa–IVd** resulted from the regioselective opening of the oxirane ring in compounds **I** and **II**.

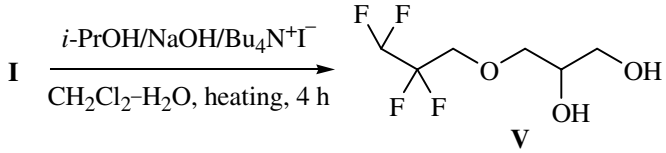
Nowadays the procedure of the phase transfer catalysis of various reactions finds more and more

application in the practice of organic synthesis. In the processes involving organofluorine compounds the application of the phase transfer catalysis is limited to epoxidation, dehydrohalogenation, and isomerization [4]. In the ring opening of fluorine-containing oxiranes the phase transfer catalysis is not a frequently used procedure. Yet the application of the phase transfer catalysts in this type reactions is a convenient method and does not require drying of the reagents.

We demonstrated that in a binary system dichloromethane–water in the presence of sodium hydroxide and tetrabutylammonium iodide the reaction of oxiranes **I** and **II** with the above alcohols led to the formation of the same hydroxypolyethers **IIIa–IIId** and **IVa–IVd** (see EXPERIMENTAL, procedure *b*).

An unexpected result was obtained in the reaction of oxirane **I** with 2-propanol. Here the main product was 1,2-diol **V** obtained in 42% yield (Scheme 2). The rest of the reaction mixture was tarry products.

Scheme 2.



The corresponding 1,2-diol was formerly obtained under similar conditions (25°C, 20 h) as a side product of the reaction between 2,2-bis(trifluoromethyl)oxirane with 2-propanol [4] in about 4% yield, while the main reaction product was a dimer of the initial oxirane.

We carried out reactions of oxiranes **I** and **II** with 2-propanol at room temperature under phase transfer catalysis and obtained 1,2-diol **V** in 7% yield and hydroxypolyether **IVd** in 10% yield at a low conversion of initial compounds.

It is presumable that in reactions of compounds **I** and **II** with the isopropylate anion the basic and nucleophilic properties of the latter are of the main importance, and the prevalence of one characteristic over the other depends apparently on the structure of the fluorine-containing fragment in oxiranes **I** and **II**.

Demonstrating its basic qualities in reaction with oxirane **I** the sodium isopropylate acts like a weak nucleophile leading to the formation of the base hydrolysis product **V**. In the second case, with oxirane **II**, the nucleophilic properties of the isopropylate anion dominate, and the product results from the regioselective opening of the oxirane ring (**IVd**).

Probably this strengthening of the nucleophilic properties of the sodium isopropylate occurs partially due to its specific solvation with compound **II** itself, for it has a sufficiently long polyether chain and may act like a podand [5]. Owing to the structure of the polyfluoroetheralkyl substituent of oxirane **II** the reaction mixture gets richer in free isopropylate anions resulting in prevailing formation of compound **IVd**.

Note in conclusion that reactions of compounds **I** and **II** with alcohols in basic medium are insensitive to the replacement of one bipolar aprotic solvent (dioxane) by another (diglyme). The change in the reaction temperature is essential: At higher temperature increases the probability of oligomerization.

EXPERIMENTAL

IR spectra were registered on a spectrophotometer Perkin Elmer Spectrum One from thin film, ^1H and ^{19}F NMR spectra, on a spectrometer Bruker DRX-400 from solutions in $CDCl_3$ or $(CD_3)_2CO$, internal references TMS and hexafluorobenzene respectively. A mass spectrum of compound **V** was measured on a GC-MS instrument Fisons (electron impact, 70 eV).

General procedure of reactions. *a.* To 0.35 mol of anhydrous alcohol 0.81 g (0.035 mol) of metal Na was added, 30 ml of dioxane was charged at stirring, and the mixture was heated to boiling. Within 30 min 0.01 mol of oxirane **I** or **II** was added, and stirring was continued for 2 h at the same temperature. On cooling the mixture was diluted with 100 ml of water, acidified with HCl till weakly acidic reaction, the products were extracted into ethyl ether, the extract was dried with $MgSO_4$, ether was removed, and the residue was distilled.

b. To a mixture of 50 ml CH_2Cl_2, 50 ml of 50% water solution of NaOH, 0.35 mol of alcohol, and 0.1 g (2 mol%) of $Bu_4N^+I^-$ was added at 40°C while stirring 0.01 mol of oxirane **I** or **II**. After 4 h the mixture was cooled, the organic layer was separated, and the water layer was extracted with CH_2Cl_2 (2×20 ml). The combined organic solution was washed with a solution of HCl, dried with $MgSO_4$, CH_2Cl_2 was removed, and the residue was distilled.

IR spectra of compounds **IIIa–IIId** contained common characteristic absorption bands in the regions, ν, cm^{-1}: 3392–3431 (O–H), 2963–2965, 2918–2920, 2892–2893, 2857–2859 (C–H), 1120–1122 (C–O-C, C–F); of hydroxypolyethers **IVa–IVd**: 3398–3436 (O–H),

2962–2966, 2938–2943, 2858–2861 (C–H), 1247–1249, 1202–1205, 1160–1162, 1119–1121 (C–O–C, C–F).

^{19}F NMR spectra of compounds **I, IIIa–IIId**, and **V** are of the same appearance and have a common set of signals, δ, ppm: 36.04–36.11 m (2F, $HC\underline{F}_2$), 21.49–21.52 d.m (2F, $HCF_2C\underline{F}_2$); for hydroxypolyethers **IVa–IVd**: 18.75–18.85 m [1F, $OC\underline{F}(CF_3)$], 29.17–31.11 m (1F, $C\underline{F}CH_2$), 34.23–34.24 m (2F, $CF_3C\underline{F}_2$), 81.31–81.62 m (3F, $C\underline{F}_3CF_2$), 82.35–82.44 m [6F, $2OCF(C\underline{F}_3)$], 83.78–83.79 m [2F, $2C\underline{F}_2OCF(CF_3)$].

2,2,3,3-Tetrafluoropropyloxymethyloxirane (I). Yield 35%, bp 175–176°C. IR spectrum, ν, cm^{-1}: 3069, 3010, 2933 (C–H), 1108 (C–O–C, C–F). ^{1}H [$(CD_3)_2CO$], δ, ppm: 2.58 d.d [1H, CH(–O–)C$\underline{H}$H, *J* 5.1 and 2.6 Hz], 2.74 d.d [1H, CH(–O–)CH$\underline{H}$, *J* 5.1 and 4.2 Hz], 3.13 d.d.d.d [1H, C$\underline{H}$(–O–)CH_2, *J* 6.3, 4.2, 2.6 and 1.6 Hz], 3.48 d.d [1H, OC$\underline{H}$H, *J* 11.8 and 6.3 Hz], 3.98 m (3H, $CF_2C\underline{H}_2OCH\underline{H}$), 6.30 t.t (1H, $\underline{H}CF_2$, *J* 52.6 and 5.6 Hz). Found, %: C 38.21; H 4.13; F 40.31. $C_6H_8F_4O_2$. Calculated, %: C 38.13; H 4.23; F 40.19.

2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyloxymethyloxirane (II). Yield 40%, bp 212–214°C. IR spectrum, ν, cm^{-1}: 2961, 2936, 2855 (C–H), 1247, 1200, 1159, 1118 (C–O–C, C–F). ^{1}H [$(CD_3)_2CO$], δ, ppm: 2.59 d.d [1H, CH(–O–)C$\underline{H}$H, *J* 4.9 and 2.4 Hz], 2.75 m [1H, CH(–O–)CH$\underline{H}$], 3.14 m [1H, C$\underline{H}$(–O–)CH_2], 3.53 d.d (1H, OC$\underline{H}$H, *J* 11.9 and 6.3 Hz), 4.01 t.d (1H, OCH$\underline{H}$, *J* 11.8 and 2.3 Hz), 4.32 m (2H, $CFC\underline{H}_2$). Found, %: C 26.63; H 1.37; F 60.02. $C_{12}H_7F_{17}O_4$. Calculated, %: C 26.72; H 1.30; F 59.90.

1-Methoxy-6,6,7,7-tetrafluoro-4-oxaheptan-2-ol (IIIa). Yield 48%, bp 215–216°C. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 3.30 br.s (3H, $C\underline{H}_3$), 3.38 m (2H, $C\underline{H}_2OCH_3$), 3.67 m (2H, $CF_2CH_2OC\underline{H}_2$), 3.88 m (1H, C$\underline{H}$OH), 3.98 t.t (2H, $CF_2C\underline{H}_2$, *J* 13.1 and 1.8 Hz), 6.32 t.t (1H, $\underline{H}CF_2$, *J* 52.7 and 5.7 Hz). Found, %: C 38.33; H 5.39; F 34.45. $C_7H_{12}F_4O_3$. Calculated, %: C 38.21; H 5.45; F 34.53.

1-Phenoxy-6,6,7,7-tetrafluoro-4-oxaheptan-2-ol (IIIb). Yield 44%, bp 172–174°C (30 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.45 br.s (1H, O$\underline{H}$), 3.75 d.d (1H, $C\underline{H}_AH_BOC_6H_5$, *J* 10.0 and 5.7 Hz), 3.79 d.d (1H, $CH_A\underline{H}_BOC_6H_5$, *J* 10.0 and 5.7 Hz), 3.92 t.t (2H, $CF_2C\underline{H}_2$, *J* 12.7 and 1.6 Hz), 4.01 m (2H, $C\underline{H}_2CHOH$), 4.18 m (1H, C$\underline{H}$OH), 5.91 t.t (1H, $\underline{H}CF_2$, *J* 53.2 and 4.7 Hz), 7.11 m (5H, $C_6\underline{H}_5$). Found, %: C 51.21; H 4.87; F 27.04. $C_{12}H_{14}F_4O_3$. Calculated, %: C 51.09; H 4.96; F 26.93.

1-(2,2,3,3-Tetrafluoropropoxy)-6,6,7,7-tetrafluoro-4-oxaheptan-2-ol (IIIc). Yield 65%, bp 125–130°C. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 3.65 d.d [2H, $C\underline{H}_AH_BCH(OH)C\underline{H}_AH_B$, *J* 10.1 and 5.8 Hz], 3.69 d.d [2H, $CH_A\underline{H}_BCH(OH)CH_A\underline{H}_B$, *J* 10.1 and 4.7 Hz], 3.94 m (1H, C$\underline{H}$OH), 3.99 t.t (4H, $2CF_2C\underline{H}_2$, *J* 13.1 and 1.7 Hz), 6.32 t.t (2H, $2\underline{H}CF_2$, *J* 52.7 and 5.7 Hz). Found, %: C 33.63; H 3.84; F 47.59. $C_9H_{12}F_8O_3$. Calculated, %: C 33.78; H 3.75; F 47.48.

1-Isopropoxy-6,6,7,7-tetrafluoro-4-oxaheptan-2-ol (IIId). Yield 75%, bp 115–120°C (30 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 d (6H, $2C\underline{H}_3$, *J* 6.1 Hz), 2.51 br.s (1H, O$\underline{H}$), 3.43 d.d [1H, $C\underline{H}_AH_BOCH(CH_3)_2$, *J* 9.5 and 6.1 Hz], 3.46 d.d [1H, $CH_A\underline{H}_BOCH(CH_3)_2$, *J* 9.5 and 4.5 Hz], 3.62 m [3H, $C\underline{H}_2CH(OH)CH_2OC\underline{H}(CH_3)_2$], 3.89 m (3H, $C\underline{H}_2OCH_2C\underline{H}$), 5.92 t.t (1H, $\underline{H}CF_2$, *J* 53.2 and 4.9 Hz). Found, %: C 43.56; H 6.57; F 30.40. $C_9H_{16}F_4O_3$. Calculated, %: C 43.58; H 6.45; F 30.63.

1-Methoxy-6,8,8,9,11,11,12,12,13,13,13-undecafluoro-6,9-bis(trifluoromethyl)-4,7,10-trioxatridecan-2-ol (IVa). Yield 45%, bp 145–150°C (30 mm Hg). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 3.31 br.s (3H, $C\underline{H}_3$), 3.50 m (2H, $C\underline{H}_2OCH_3$), 3.68 m (2H, $CFCH_2OC\underline{H}_2$), 4.01 m (1H, C$\underline{H}$OH), 4.12 m (2H, $CFC\underline{H}_2$). Found, %: C 27.31; H 1.99; F 56.75. $C_{13}H_{11}F_{17}O_5$. Calculated, %: C 27.40; H 1.93; F 56.64.

1-Phenoxy-6,8,8,9,11,11,12,12,13,13,13-undecafluoro-6,9-bis(trifluoromethyl)-4,7,10-trioxatridecan-2-ol (IVb). Yield 32%, bp 210–215°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.55 br.s (1H, O$\underline{H}$), 3.79 m (2H, $C\underline{H}_2OC_6H_5$), 4.02 m (2H, $CFCH_2OC\underline{H}_2$), 4.10 d (2H, $CFC\underline{H}_2$, *J* 12.1 Hz), 4.18 m (1H, C$\underline{H}$OH), 7.08 m (5H, $C_6\underline{H}_5$). Found, %: C 34.25; H 2.01; F 51.22. $C_{18}H_{13}F_{17}O_5$. Calculated, %: C 34.21; H 2.06; F 51.08.

1-(2,2,3,3-Tetrafluoropropoxy)-6,8,8,9,11,11,12,12,13,13,13-undecafluoro-6,9-bis(trifluoromethyl)-4,7,10-trioxatridecan-2-ol (IVc). Yield 57%, bp 131–134°C (30 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.32 br.s (1H, O$\underline{H}$), 3.65 m (4H, $OC\underline{H}_2CHC\underline{H}_2O$), 3.89 t.t (2H, $CF_2C\underline{H}_2$, *J* 12.7 and 1.5 Hz), 3.97 m (1H, C$\underline{H}$OH), 4.07 d (2H, $CFC\underline{H}_2$, *J* 11.8 Hz), 5.88 t.t (1H, $\underline{H}CF_2$, *J* 53.3 and 4.5 Hz). Found, %: C 26.97; H 1.55; F 59.79. $C_{15}H_{11}F_{21}O_5$. Calculated, %: C 26.89; H 1.64; F 59.63.

1-Isopropoxy-6,8,8,9,11,11,12,12,13,13,13-undecafluoro-6,9-bis(trifluoromethyl)-4,7,10-trioxatridecan-2-ol (IVd). Yield 47%, bp 120–125°C (30 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16

d (6H, $2CH_3$, *J* 6.1 Hz), 2.47 br.s (1H, OH), 3.43 d.d [1H, $CH_AH_BOCH(CH_3)_2$, *J* 9.5 and 6.2 Hz], 3.49 d.d [1H, $CH_AH_BOCH(CH_3)_2$, *J* 9.5 and 4.5 Hz], 3.64 m [3H, $CH_2CH(OH)CH_2OCH(CH_3)_2$], 4.08 d (2H, $CFCH_2$, *J* 11.9 Hz). Found, %: C 30.21; H 2.43; F 54.11. $C_{15}H_{15}F_{17}O_5$. Calculated, %: C 30.13; H 2.51; F 53.99.

6,6,7,7-Tetrafluoro-4-oxaheptan-1,2-diol (V). Yield 42%, bp 220–222°C. IR spectrum, ν, cm^{-1}: 3434 (O–H), 2980, 2926, 2892 (C–H), 1109 (C–O–C, C–F). ^1H NMR spectrum, δ, ppm: 2.65 br.s (2H, 2OH), 3.61 d.d (CH_ACH_BOH, *J* 10.8 and 5.8 Hz), 3.63 d.d (CH_ACH_BOH, *J* 10.8 and 5.1 Hz), 3.71 d (2H, CH_2CHOH, *J* 5.1 Hz), 3.92 t.t (2H, CF_2CH_2, *J* 12.7 and 1.6 Hz), 4.02 m (1H, CHOH), 5.91 t.t (1H, HCF_2, *J* 53.2 and 4.6 Hz). MaCC-Spectrum, *m/z* (I_{rel}, %): 206 $[M]^+$ (0.3), 204 $[M - H_2]^+$ (0.7), 188 $[M - H_2O]^+$ (1.3), 175 $[C_5H_7F_4O]^+$ (53), 145 $[C_4H_5F_4O]^+$ (50), 127 (8), 95 $[C_3H_5F_2O]^+$ (12), 93 (16), 81 $[C_3H_3F_2O]^+$ (27), 79 $[C_2HF_2O]^+$ (65), 65 (20), 57 $[C_3H_5O]^+$ (18), 51 $[CHF_2]^+$ (65), 45 (22), 44 $[C_2H_4O]^+$ (100), 43 $[C_2H_3O]^+$ (85), 31 [CF, $CH_3O]^+$ (43). Found, %: C 35.00; H 4.19; F 36.95. $C_6H_{10}F_4O_4$. Calculated, %: C 34.98; H 4.85; F 36.88.

The study was carried out under a financial support of the Russian Foundation for Basic Research (grant no. 04-03-96109).

REFERENCES

1. Matuszczak, S. and Feast, W. J., *J. Fluorine Chem*., 2000, vol. 102, p. 269.
2. Solov'ev, D.V., Kolomenskaya, L.V., Rodin, A.A., Zenkevich, I.G., and Lavrent'ev, A.N., *Zh. Obshch. Khim.,* 1991, 61, p. 673.
3. Ushakova, E.N., Konyushko, O.V., Glazkov, A.A., and Krukovskii, S.P., *Izv. Akad. Nauk, Ser. Khim.,* 1996, p. 1573.
4. Petrov, V.A., *J. Fluorine Chem.,* 2004, vol. 125, p. 531.
5. *Host Guest Complex Chemistry: Macrocycles: Synthesis, Structures, Applications*, Vogtle, F. and Weber, E., Eds., Berlin: Springer, 1985.