Addition of polyfluoroalkyl iodides to allyl glycidyl ether

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Addition of polyfluoroalkyl iodides to the double bond of allyl glycidyl ether occurred under mild conditions (20—25 °C, $MeCN/H_2O$, $Na_2S_2O_4$, $NaHCO_3$) with retention of the oxirane ring.

Key words: glycidyl ethers, polyfluoroalkyl iodides, sodium dithionite, oxiranes, olefins, organofluorine compounds, free-radical processes.

Fluorine-containing glycidyl ethers are important intermediates in the synthesis of various polymeric materials that exhibit unique physicochemical properties (chemical and thermal stability, low surface tension, and optical and electrical properties).[1—3] A search for routes to compounds of this chemotype and improvement of appropriate synthetic procedures still remain of current interest.

It is known that monofunctional fluorine-containing glycidyl ethers are synthesized in three main ways: (1) epoxidation of allyl ethers prepared from fluorine-containing alcohols and allyl halides,[4] (2) addition of glycidol to polyfluoroalkenes,[5,6] and (3) base-catalyzed reactions of fluorine-containing alcohols with epichlorohydrin.[1—3,7—10] The use of a basic medium in the last two ways initiates side processes such as oligomerization and hydrolysis, thus substantially lowering the yields of the target compounds.[2,8,9]

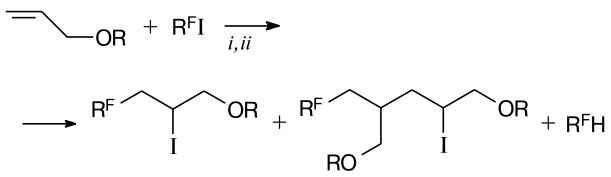
Here we proposed an alternative route to fluorine-containing glycidyl ethers starting from allyl glycidyl ether **1** and polyfluoroalkyl iodides (R^FI) **2a—d**.

Results and Discussion

The structure of compound **1** (the presence of two reactive sites: the oxirane ring and the double bond) makes it more difficult to achieve our purpose and requires relatively mild conditions for free-radical reactions. For instance, reactions of R^FI with allyl phenyl ether and allyl alcohol in the presence of Bz_2O_2 or AIBN occur with a low conversion of the iodides, giving rise to large amounts of by-products[11,12] (Scheme 1).

We found that free-radical addition of R^FI (**2a,b**) to compound **1** with Bz_2O_2 as an initiator is also characterized by low yields (30—40%) of fluorine-containing glycidyl ethers **3a,b**. Known[13] compounds **4a,b** were identified as by-products (Scheme 2).

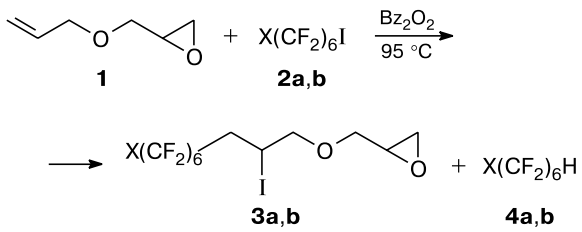
Scheme 1



R = H, Ph

i. Bz_2O_2, 90 °C; *ii*. AIBN, 70 °C

Scheme 2



X = F (**a**), Cl (**b**)

Fluoroalkyl radicals can be generated from fluoroalkyl halides under the action of various redox systems, which allows addition to the double bond of nonfluorinated objects under milder conditions.[14—19] For compound **1**, the use of $FeCl_3/CuCl_2$ in an addition reaction with CF_3CCl_3 has been reported only.[14] The sole reaction product was $ClCFClCF_2CCl_3$, while the starting compound **1** remained unchanged.

Earlier,[20,21] good yields of adducts R^FI with a number of olefins have been attained in an open system at 20—25 °C with the use of $Na_2S_2O_4$ in aqueous acetonitrile in the presence of $NaHCO_3$.

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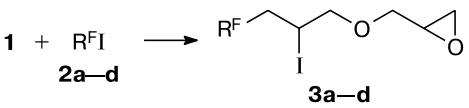
The application of the above system reagents to substrates **1** and **2a—d** afforded the target fluorine-containing glycidyl ethers **3a—d** in high (67—78%) yields (Scheme 3). No other products were detected in the reaction mixtures. The absence of strong nucleophiles, the mild reaction conditions, and the weakly basic medium favor the retention of the oxirane ring.

Scheme 3



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

Reagents and conditions: $Na_2S_2O_4/NaHCO_3$, $MeCN/H_2O$, 20—25 °C.

To sum up, the reactions of R^FI **2a—d** with compound **1** in the presence of $Na_2S_2O_4$ and $NaHCO_3$ in aqueous acetonitrile afforded novel fluorine-containing bifunctional glycidyl ethers **3a—d** in high yields. The products obtained can serve as promising synthons in organic synthesis.

Experimental

IR spectra were recorded on a Perkin—Elmer Spectrum One spectrophotometer (thin film). ^1H and ^{19}F NMR spectra were recorded on a Bruker DRX 400 spectrometer (400.1 (^1H) and 376.5 MHz (^{19}F)) in acetone-d_6 with Me_4Si and C_6F_6 as internal standards, respectively. The signals in the ^{19}F NMR spectra were assigned with the use of literature data.[22,23]

Compounds **2a—d** were prepared as described earlier.[24]

Synthesis of compounds 3a,b in the presence of Bz_2O_2 (general procedure). A stirred mixture of R^FI **2a** or **2b** (0.11 mol) and compound **1** (0.11 mol) was heated to 95 °C. Then Bz_2O_2 (2.19 mmol) was added in portions. The reaction mixture was kept for 6 h and then product **3a,b** was isolated by distillation under reduced pressure.

Synthesis of compounds 3a—d in the presence of $Na_2S_2O_4$ (general procedure). Compound **2a—d** (0.12 mol) and ether **1** (0.1 mol) were added under argon at ~20 °C to a stirred mixture of $NaHCO_3$ (0.1 mol), deaerated water (24 mL), and MeCN (12 mL). Then $Na_2S_2O_4$ (0.1 mol) was added and the reaction mixture was kept at room temperature for 1 h. After addition of water (150 mL), the lower organic layer was separated, dried over $CaCl_2$, and distilled *in vacuo* to give compounds **3a—d**.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-2-iodononyloxymethyloxirane (3a). Yield 75%, b.p. 125—127 °C (5 Torr). Found (%): C, 25.64; H, 1.68; F, 43.92. $C_{12}H_{10}F_{13}IO_2$. Calculated (%): C, 25.74; H, 1.79; F, 44.09. ^1H NMR (acetone-d_6), δ: 2.58 (m, 1 H, CH(O)CH<u>H</u>); 2.74 (dd, 1 H, CH(O)C<u>H</u>H, J = 5.2 Hz, J = 4.2 Hz); 2.84 (m, 1 H, $F(CF_2)_6CH\underline{H}$); 3.12 (m, 1 H, C<u>H</u>(O)CH_2); 3.23 (m, 1 H, $F(CF_2)_6C\underline{H}H$); 3.44 (ddd, 1 H, C<u>H</u>HCH(O)CH_2, J = 11.7 Hz, J = 6.2 Hz, J = 5.2 Hz); 3.83 (m, 3 H, CHIC<u>H_2</u>OCH<u>H</u>); 4.49 (m, 1 H, C<u>H</u>I). ^{19}F NMR (acetone-d_6), δ: 37.71 (m, 2 F, $CF_3C\underline{F}_2$), 40.25 (m, 2 F, $F(CF_2)_2C\underline{F}_2$), 41.07 (m, 2 F, $C\underline{F}_2CF_2CH_2$), 42.15 (m, 2 F, $F(CF_2)_3C\underline{F}_2$), 49.86 (m, 1 F, $CF\underline{F}CH_2$), 50.90 (m, 1 F, $C\underline{F}FCH_2$), 82.77 (tt, 3 F, $C\underline{F}_3$, J = 10.2 Hz, J = 2.5 Hz).

9-Chloro-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluoro-2-iodononyloxymethyloxirane (3b). Yield 67%, b.p. 134—136 °C (5 Torr). Found (%): C, 24.92; H, 1.68; F, 39.35. $C_{12}H_{10}ClF_{12}IO_2$. Calculated (%): C, 25.00; H, 1.75; F, 39.54. ^1H NMR (acetone-d_6), δ: 2.58 (m, 1 H, CH(O)CH<u>H</u>); 2.74 (dd, 1 H, CH(O)C<u>H</u>H, J = 5.2 Hz, J = 4.2 Hz); 2.84 (m, 1 H, $Cl(CF_2)_6CH\underline{H}$); 3.12 (tdd, 1 H, C<u>H</u>(O)CH_2, J = 9.2 Hz, J = 4.2 Hz, J = 1.9 Hz); 3.23 (m, 1 H, $Cl(CF_2)_6C\underline{H}H$); 3.44 (ddd, 1 H, C<u>H</u>HCH(O)CH_2, J = 11.7 Hz, J = 6.2 Hz, J = 5.2 Hz); 3.82 (m, 3 H, CHIC<u>H_2</u>OCH<u>H</u>), 4.49 (m, 1 H, C<u>H</u>I). ^{19}F NMR (acetone-d_6), δ: 40.32 (m, 2 F, $ClCF_2C\underline{F}_2$), 42.35 (m, 2 F, $Cl(CF_2)_2C\underline{F}_2$), 42.73 (m, 2 F, $C\underline{F}_2CF_2CH_2$), 43.72 (m, 2 F, $Cl(CF_2)_3C\underline{F}_2$), 49.96 (m, 1 F, $CF\underline{F}CH_2$), 50.96 (m, 1 F, $C\underline{F}FCH_2$), 95.33 (m, 2 F, $ClC\underline{F}_2$).

4,4,5,5,6,6,6-Heptafluoro-2-iodohexyloxymethyloxirane (3c). Yield 72%, b.p. 87—89 °C (5 Torr). Found (%): C, 26.31; H, 2.35; F, 32.40. $C_9H_{10}F_7IO_2$. Calculated (%): C, 26.37; H, 2.44; F, 32.43. ^1H NMR (acetone-d_6), δ: 2.57 (m, 1 H, CH(O)CH<u>H</u>); 2.74 (dd, 1 H, CH(O)C<u>H</u>H, J = 5.2 Hz, J = 4.2 Hz); 2.83 (m, 1 H, $F(CF_2)_3CH\underline{H}$); 3.12 (m, 1 H, C<u>H</u>(O)CH_2); 3.21 (m, 1 H, $F(CF_2)_3C\underline{H}H$); 3.43 (ddd, 1 H, C<u>H</u>HCH(O)CH_2, J = 11.9 Hz, J = 6.2 Hz, J = 5.7 Hz); 3.83 (m, 3 H, CHIC<u>H_2</u>OCH<u>H</u>), 4.48 (m, 1 H, C<u>H</u>I). ^{19}F NMR (acetone-d_6), δ: 35.85 (m, 2 F, $CF_3C\underline{F}_2$), 48.88 (m, 1 F, $CF\underline{F}CH_2$), 49.98 (m, 1 F, $C\underline{F}FCH_2$), 83.23 (t, 3 F, $C\underline{F}_3$, J = 9.9 Hz).

4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptyloxymethyloxirane (3d). Yield 78%, b.p. 110—112 °C (5 Torr). Found (%): C, 26.02; H, 2.10; F, 37.07. $C_{10}H_{10}F_9IO_2$. Calculated (%): C, 26.12; H, 2.17; F, 37.16. ^1H NMR (acetone-d_6), δ: 2.57 (m, 1 H, CH(O)CH<u>H</u>); 2.74 (dd, 1 H, CH(O)C<u>H</u>H, J = 5.2 Hz, J = 4.2 Hz); 2.85 (tdd, 1 H, CF_2CH_2CHI, J = 29.3 Hz, J = 16.5 Hz, J = 8.1 Hz); 3.13 (m, 1 H, C<u>H</u>(O)CH_2); 3.23 (m, 1 H, $F(CF_2)_4C\underline{H}H$); 3.43 (ddd, 1 H, C<u>H</u>HCH(O)CH_2, J = 11.7 Hz, J = 6.2 Hz, J = 5.3 Hz); 3.88 (m, 3 H, CHIC<u>H_2</u>OCH<u>H</u>), 4.49 (m, 1 H, C<u>H</u>I). ^{19}F NMR (acetone-d_6), δ: 37.98 (m, 2 F, $CF_3C\underline{F}_2$), 39.35 (m, 2 F, $C\underline{F}_2CF_2CH_2$), 49.64 (m, 1 F, $CF\underline{F}CH_2$), 50.87 (m, 1 F, $C\underline{F}FCH_2$), 82.60 (tt, 3 F, $C\underline{F}_3$, J = 9.7 Hz, J = 3.3 Hz).

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