

Fluorinated epoxides

6. Chemoselectivity in the preparation of 2-[(heptafluoroisopropyl)methyl]oxirane from iodoacetate and iodohydrin precursors

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Abstract

Fluorinated iodoacetate $(\text{CF}_3)_2\text{CFCH}_2\text{CHICH}_2\text{OAc}$ (**1**) (prepared by radical addition of perfluoroisopropyl iodide to allyl acetate) and fluorinated iodohydrin $(\text{CF}_3)_2\text{CFCH}_2\text{CHICH}_2\text{OH}$ (**2**) (prepared from **1**) were converted to the corresponding perfluoroalkylated oxirane $(\text{CF}_3)_2\text{CFCH}_2\text{CH}(\text{O})\text{CH}_2$ (**3**) in the yield of 62%. The chemoselectivity of the oxirane formation appeared to be strongly dependent on the starting compound **1** or **2** and solvent used. Byproducts $(\text{CF}_3)_2\text{CFCH}=\text{CHCH}_2\text{OH}$ (**4**) and $(\text{CF}_3)_2\text{CFCH}=\text{CHCH}_2\text{OAc}$ (**5**) can form a major part of the products in the formation of epoxide **3**.

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1. Introduction

Fluorinated oxiranes are very important synthetic and industrial intermediates for special amphiphilic products (surfactants [1]), various polymeric materials (telechelic diols or polyethers [2], adhesive acrylates [3,4], coatings [5], epoxy resin compositions [6]) or amphiphilic perfluoroalkylated triols [7].

Several synthetic ways to fluoroalkyl oxiranes described in the literature [5,8–12] include, among others, transformations of iodoacetates and iodohydrins. In our recent papers, we have reported syntheses of a series of perfluoroalkylated oxiranes from individual adducts of the perfluoroalkyl iodides with allyl acetate [13–16] followed by epoxide formation. In contrast to the former report [9], we have found [15] that the formation of perfluoroalkylated epoxides was accompanied by the formation of unsaturated byproducts whose amount was strongly dependent on the polarity of solvent used. In diethyl ether, e.g. the amount of unsaturated byproducts exceeded the amount of the target epoxide [15]. These results have fundamentally corrected the former report [9].

Unfortunately, these corrections were not included in the recent review [17] which has dealt with the chemistry of perfluoroalkylated epoxides.

The aim of the research presented here has been to verify whether recent findings on the chemoselectivity in the formation of perfluoroalkylated epoxides [15,20] are also valid for analogous compounds with branched perfluoroalkyl, i.e. in the conversion of iodoacetate **1** [9] or iodohydrin **2** [10] to the [(heptafluoroisopropyl)methyl]oxirane (**3**).

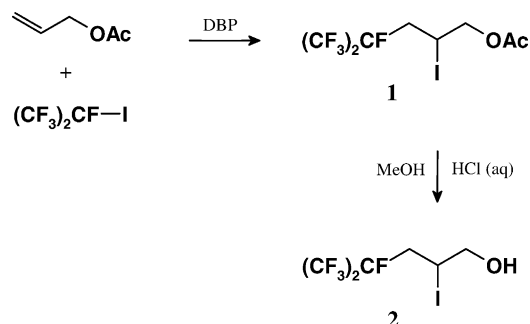
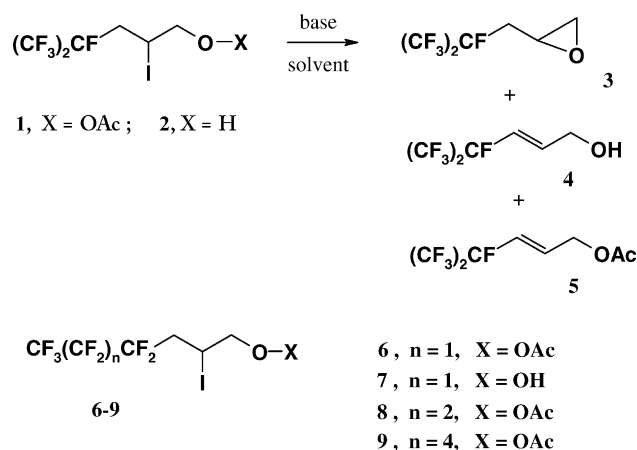
2. Results and discussion

2.1. Preparation of fluorinated iodoacetate **1** and iodohydrin **2**

The dibenzoyl peroxide (DBP) induced addition of perfluoroisopropyl iodide to allyl acetate afforded [11,14] regioselectively iodoacetate **1** (Scheme 1). In contrast to our previous report [14], no rearranged adduct or 2:1 telomer were detected in the mixture probably owing to a lower reaction temperature and a shorter reaction time.

The iodoacetate **1** was converted to the corresponding iodohydrin **2** (Scheme 1) in 86% preparative yield by reesterification with acidic methanol.

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Scheme 1. Preparation of iodoacetate **1** and iodohydrin **2**.Scheme 2. Preparation of epoxide **3** from iodoacetate **1** or iodohydrin **2**.

2.2. Preparation of epoxide **3** and formation of byproducts **4** and **5**

2.2.1. From iodoacetate **1**

On the basis of our recent findings [15], it could be expected that the formation of epoxide **3** from iodoacetate

1 and a hydroxide (Scheme 2) would be highly chemoselective in hexane while in more polar diethyl ether byproducts **4** and **5** could predominate. The results in this paper with branched iodoacetate **1** are in accord with our previous observations [14]. The chemoselectivity of epoxide formation was best in hexane, but 12% of unsaturated alcohol **4** (Table 1, entry 1) was formed as a byproduct, which is a higher amount than that for unbranched iodoacetates (Table 1, entries 6 and 8).

In diethyl ether (Table 1, entry 2) we used the same reaction conditions and reactant ratios as reported [9] (Table 1, entry 4) and obtained the following results: the amount of byproducts **4** and **5** (8 and 45% rel.) was higher than the relative yield of epoxide **3** (Table 1, entry 2), which was almost the same result as for unbranched epoxides (Table 1, entries 7 and 9). The previous papers [9,19] using this procedure have not mentioned the formation of any amount of byproducts (Table 1, entry 4). No byproducts have also been reported in the recent paper [5] using diethyl ether as a solvent in the preparation of 2-(2,2,3,3,3-pentafluoropropyl)oxirane from the corresponding iodoacetate.

2.2.2. From iodohydrin **2**

We carried out this preparation to compare the chemoselectivity of the formation of epoxide **3** from iodohydrin **2** with that from iodoacetate **1**. The former report [10] did not mention any byproduct in the preparation of perfluoroalkylated epoxide from iodohydrin **7** (Table 1, entry 5). On the other hand, unsaturated byproducts have recently been reported in a non-selective direct transformation of allyl alcohol to perfluoroalkylated epoxides [20] and in optimized preparation of bis-epoxides from bis-iodohydrins [16]. In the preparation of **3**, we used the same reaction conditions and reactant ratios as reported [10] (Table 1, entry 5) and obtained the following results (Table 1, entry 3): the

Table 1
Selectivity of the formation of epoxide **3** from iodoacetate **1** or iodohydrin **2**

Entry	Starting compound	Solvent ^a	Conditions	Time (h)	Conversion (%)	Reaction mixture composition ^b (% rel.)			Epoxide isolated yield (%)
						Epoxide 3	Unsaturated alcohol 4	Unsaturated ester 5	
1	1	Hexane	KOH, reflux	2	83	88	12	0	62
2	1	Et ₂ O	NaOH, reflux	5	94	47	8	45	32
3	2	H ₂ O	NaOH, 25 °C	1	16	88	12	0	10
4	6^c	Et ₂ O	NaOH, reflux	5	61	100 ^c	—	—	78 ^d
5	7^d	H ₂ O	NaOH, 25 °C	1	66	100 ^c	—	—	38 ^e
6	8^e	Hexane	KOH, reflux	2.5	99	98	2	0	94 ^f
7	8^e	Et ₂ O	KOH, reflux	5	99	40	5	55	35 ^f
8	9^e	Hexane	KOH, reflux	2	99	98	2	0	95 ^f
9	9^e	Et ₂ O	KOH, reflux	6	99	31	8	61	25 ^f
10	9^e	Et ₂ O	NaOH, reflux	30	81	45	6	49	40 ^f

^a Mixing at room temperature.

^b GC analyses with calibration.

^c As assumed from [9,10].

^d Yield related to the conversion [9].

^e From [10].

^f From [14].

conversion of branched **2** was approximately four times lower than that for the non-branched analog **7** [10] and the mixture contained 12% of the unsaturated alcohol **4**. Thus, the chemoselectivity was approximately the same as in the preparation of epoxide **3** from iodoacetate **1**. Sodium hydroxide appeared to be a less reactive in epoxide reaction than potassium hydroxide (Table 1, entries 9 and 10). For that reason, potassium hydroxide was preferred in preparative runs [15,16].

3. Conclusions

Transformations of branched iodoacetate **1** and iodohydrin **2** to the corresponding perfluoroalkylated epoxide **3** were accompanied with the formation of byproducts. The new results complete our recent findings [15,16] on the chemoselectivity of the preparations of 2-[(perfluoroalkyl)methyl]oxiranes.

4. Experimental details

4.1. General comments

The temperature data were not corrected. Distillations of high boiling compounds were carried out on a Vacuubrand RC5 high vacuum oil pump. Boiling points were not corrected. GC analyses were performed on Micromat HRGC 412 (Nordion Analytical; 25 m glass capillary column, SE-30) instrument; nitrogen was used as carrier gas, detector/injector temperatures were 260/255 °C. NMR spectra were recorded on a Bruker 400 AM (FT, ¹⁹F at 376.5 MHz) and Varian Gemini 300 HC (FT, ¹H at 300 MHz) instruments using TMS and CFCl₃ as the internal standards. Chemical shifts are quoted in ppm (s, singlet; bs, broad singlet; d, doublet; t, triplet; qi, quintuplet; m, multiplet), coupling constants *J* in Hz, and solvent is CDCl₃. Mass spectra were obtained using a Finnigan MAT-44S (single focus, 70 eV, direct head inlet) apparatus.

The chemicals used were as follows: perfluoroisopropyl iodide (Aldrich), was distilled before use; dibenzoyl peroxide was precipitated from its chloroform solution by methanol and dried in vacuum [18]; allyl acetate (Aldrich) was used without purification; sodium and potassium hydroxide pellets were powdered before use; diethyl ether, hexane, chloroform and methanol were purified according to standard laboratory procedures.

4.2. Radical addition of perfluoroisopropyl iodide to allyl acetate

The reaction was carried out according to our procedure [13]. The round-bottomed flask (100 ml) equipped with a water condenser and a magnetic stirrer was charged under nitrogen with a mixture of perfluoroisopropyl iodide

(32.75 g, 0.11 mol) and allyl acetate (11.09 g, 0.11 mol) that was heated up to reflux. Then, dibenzoyl peroxide (0.53 g, 2.19 mmol) was added portionwise to the mixture and the temperature in flask was increasing spontaneously. The mixture was stirred for 10 min until the temperature fell down. The product of the addition (iodoacetate **1**) was isolated by distillation under reduced pressure to afford 36.39 g (83%) of (4,5,5,5-tetrafluoro-2-iodo-4-trifluoromethyl)pentyl acetate (**1**), bp 90–92 °C at 50 mmHg (literature value [10]: 80–85 °C at 30 mmHg), purity 99%.

¹H NMR (CDCl₃) δ (ppm): 2.11 (s, 3H, CH₃); 2.7–3.1 (m, 2H, CH₂CF); 4.23 (m, 1H, CHI); 4.38 (m, 2H, CH₂O). ¹⁹F NMR (CDCl₃) δ (ppm): –77.03, –77.59 (2× qi, 3F, ³*J*_{FF} = ⁴*J*_{FF} = 7.6, CF₃); –186.88 (m, 1F, ³*J*_{FF} = 7.6, CF). MS *m/z* (%): 396 (1, *M*⁺); 336 (8); 269 (40); 127 (7); 69 (10); 43 (100).

4.3. Preparation of epoxide **3** from iodoacetate **1**

4.3.1. Reaction of iodoacetate **1** with potassium hydroxide in hexane

The reaction was carried out according to our procedure [14]. Powdered potassium hydroxide (5.11 g, 0.091 mol) was added to a vigorously stirred solution of iodoacetate **1** (15.05 g, 0.038 mol) in hexane (60 ml) placed in a 100 ml round-bottomed flask, equipped with magnetic spinbar and a Dimroth reflux condenser connected to the atmosphere through a drying tube (NaOH). The mixture was then refluxed for 2 h, after cooling, the solid was filtered off and solvent was then distilled off. The residual mixture contained 17% of the starting iodoacetate **1**, 73% of epoxide **3** and 10% of unsaturated alcohol **4** (checked by GC). The pure epoxide **3** was obtained by distillation under reduced pressure to afford 5.33 g (62%) of [(heptafluoroisopropyl)methyl]oxirane (**3**), bp 66–68 °C at 150 mmHg, purity 99%. The pure unsaturated alcohol **4** was separated from the distillation residue by fractional distillation on a rectification column to afford 0.65 g (8%) of 4,5,5,5-tetrafluoro-4-trifluoromethylpent-2-en-1-ol (**4**), bp 71–73 °C at 50 mmHg, purity 99%.

The spectral data of **3**—¹H NMR (CDCl₃) δ (ppm): 2.2, 2.5 (2× ddd, 2H, ²*J*_{HH} = 15.4, CH₂CF); 2.58 (dd, 1H (a), ²*J*_{HH} = 4.4, ³*J*_{HH} = 2.2, CH₂); 2.89 (t, 1H (b), ²*J*_{HH} = ³*J*_{HH} = 4.4, CH₂); 3.19 (m, 1H, CH). ¹⁹F NMR (CDCl₃) δ (ppm): –77.3, –76.9 (2× m, 3F, CF₃); –184.0 to –183.8 (m, 1F, CFCH₂). MS *m/z* (%): 227 (1, *M*⁺ + 1); 213 (100); 193 (9); 173 (4); 165 (9); 145 (10); 127 (8); 95 (80); 79 (24); 69 (75); 51 (37).

The spectral data of **4**—¹H NMR (CDCl₃) δ (ppm): 1.67 (s, 1H, OH); 4.35 (m, 2H, CH₂O); 5.94 (m, 1H, CFCH=); 6.47 (dt, 1H, ³*J*_{HH} = 3.84 (t), CH₂CH=). ¹⁹F NMR (CDCl₃) δ (ppm): –77.81 (d, 6F, ³*J*_{FF} = 7.63, CF₃); –186.53 (m, 1F, ³*J*_{FF} = 7.63, CFCH=). MS *m/z* (%): 225 (2, *M*⁺ – 1); 207 (5); 158 (6); 139 (28); 69 (64); 57 (100); 31 (56); 29 (61).

4.3.2. Reaction of iodoacetate **1** with sodium hydroxide in diethyl ether

The reaction was carried out according to procedure [9]. Powdered sodium hydroxide (1.16 g, 0.029 mol) was added

to a vigorously stirred (magnetic spinbar) solution of iodoacetate **1** (5.52 g, 0.014 mol) in diethyl ether (15 ml) placed in a 50 ml round-bottomed flask, equipped with a Dimroth reflux condenser connected to the atmosphere through a drying tube (NaOH). The mixture was then refluxed for 5 h, after cooling, the solid was filtered off and solvent was then distilled off. The mixture of the residue contained 6% of the starting iodoacetate **1**, 44% of epoxide **3**, 8% of unsaturated alcohol **4** and 42% of unsaturated ester **5** (checked by GC). The pure epoxide **3** was obtained by distillation under reduced pressure to afford 1.01 g (32%) of [(heptafluoroisopropyl)methyl]oxirane (**3**), bp 66–68 °C at 150 mmHg, purity 99%. Pure unsaturated alcohol **4** was separated by fractional distillation on a rectification column to afford 0.16 g (5%) of 4,5,5,5-tetrafluoro-4-trifluoromethyl-pent-2-en-1-ol (**4**), bp 71–73 °C at 50 mmHg, purity 99%. Pure unsaturated ester **5** was obtained as a fraction by distillation on the same rectification column to afford 0.98 g (31%) of (4,5,5,5-tetrafluoro-4-trifluoromethyl-pent-2-enyl) acetate (**5**), bp 87–89 °C at 50 mmHg, purity 99%.

The spectral data of **5**—¹H NMR (CDCl₃) δ (ppm): 2.13 (s, 3H, CH₃); 4.72 (d, 2H, ³J_{HH} = 4.39, CH₂O); 5.82 (m, 1H, ³J_{HH} = 15.38, CFCH=); 6.41 (dt, 1H, ³J_{HH} = 15.38 (d) and 4.39, CH₂CH=). ¹⁹F NMR (CDCl₃) δ (ppm): –77.69 (d, 6F, ³J_{FF} = 7.63, CF₃); –186.92 (m, 1F, ³J_{FF} = 7.63, CFCH=). MS *m/z* (%): 268 (1, *M*⁺); 225 (1); 209 (1); 189 (3); 169 (1); 69 (15); 43 (100).

4.4. Preparation of iodohydrin **2** from iodoacetate **1** by acid reesterification with methanol

A mixture of iodoacetate **1** (10.69 g, 0.027 mol), methanol (86.5 g, 2.7 mol) and concentrated hydrochloric acid (four drops) was refluxed for 6 h when the conversion was ca. 98% (checked by GC). Then, volatile components were distilled off in vacuum (0.5 mmHg) with oil pump to give almost pure iodohydrin **2** as 4,5,5,5-tetrafluoro-2-iodo-4-trifluoromethylpentan-1-ol (**2**), bp 82–84 °C at 20 mmHg, in a yield of 8.22 g (86%), purity 99%.

The spectral data of **2**—¹H NMR (CDCl₃) δ (ppm): 2.04 (bs, 1H, OH); 2.65–3.16 (m, 2H, CH₂CF); 3.77 (m, 2H, CH₂O); 4.44 (m, 1H, CHI). ¹⁹F NMR (CDCl₃) δ (ppm): –76.82, –77.60 (2× qi, 3F, ³J_{FF} = ⁴J_{FF} = 7.5, CF₃); –186.58 (m, 1F, ³J_{FF} = 7.5, CF). MS *m/z* (%): 353 (1, *M*⁺ – 1); 337 (20); 227 (100); 207 (8); 159 (12); 139 (12); 121 (15); 95 (18); 69 (30); 57 (35); 43 (16); 31 (33).

4.5. Preparation of epoxide **3** from iodohydrin **2**

To a round-bottomed flask (50 ml) fitted with a magnetic stirrer and Dimroth condenser were charged iodohydrin **2** (8.14 g, 0.023 mol) and an aqueous sodium hydroxide

solution (1.16 g in 5.3 ml of water). The mixture was stirred at room temperature for 1 h, after which time the organic layer was separated and dried over magnesium sulfate overnight. Vacuum distillation gave 7.6 g of crude mixture which contained 84% of the starting iodohydrin **2**, 14% of epoxide **3** and 2% of unsaturated alcohol **4** (checked by GC). Pure epoxide **3** and unsaturated alcohol **4** were separated by distillation on a rectification column to afford 0.52 g (10%) of **3** and 0.07 g (1%) of **4**.

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