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# Highly selective synthesis of [(perfluoroalkyl)methyl]oxiranes (by the addition of iodoperfluoroalkanes to allyl acetate)

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## Abstract

Mixtures of regioisomeric adducts of monoiodoperfluoroalkanes $R_F$–I ($R_F = C_4F_9$, $C_6F_{13}$, $C_8F_{17}$) with allyl acetate, $R_FCH_2CHICH_2OAc$ (1a–1c) and rearranged adducts $R_FCH_2CH(OAc)–CH_2I$ (2a–2c), were converted chemoselectively to the corresponding oxiranes $R_FCH_2CH(–O–)CH_2$ (3a–3c) in yields of 94–96% (total yields of the two-step synthesis starting from $R_F$–I were 85–87%). The chemoselectivity of the oxirane formation appeared to be very dependent on the solvent used. Dependence on the reaction conditions on formation of byproducts $R_FCH=CHCH_2OAc$ (4a–4c) and $R_FCH=CHCH_2OH$ (5a–5c) in the epoxidation reaction was studied. © 1997 Elsevier Science S.A.

## 1. Introduction

Oxiranes are very important synthetic and industrial intermediates. Fluorinated oxiranes have been also a subject of much interest because such compounds are versatile and valuable intermediates for special products and various polymeric materials. For example, fluorinated oxiranes can be transformed to new alkenes [1,2], polyhalogenated fluorohydrins [3] and to new surfactants [4–6]. They are used in the preparation of polymeric materials as telechelic diols or polyethers with fluorinated side chains for water uptake [7,8], novel acrylates for adhesive compositions [9], coatings [10] including ones of low surface tension [11], and telechelic epoxides [12] with particular naval applications [12].

The literature describes several synthetic ways to fluoroalkyl oxiranes, as previously reviewed [13]. Most authors started the syntheses of epoxides from addition products of perfluoroalkyl iodides to allyl alcohol [14–23] or to allyl acetate [24–28] followed by cyclisation. Several authors described syntheses of perfluoroalkyloxiranes starting from perfluoroalkyl ethylenes [29–31] or from branched 3-(perfluoroalkyl)propenes [32]. There was also developed a direct epoxidation of 3-(perfluoralkyl)propenes with the flu-

orine–water agent [33,34]. In addition, the reaction of fluorinated hydroxyderivatives with epichlorohydrin led to an epoxy compound with an ether bridge [35].

In our previous papers we reported syntheses of a series of perfluoroalkyl oxiranes from adducts of perfluoroalkyl iodides [36] to allylic hydroxy compounds and from individual adducts of the iodides to allyl acetate [37]. As described in a preliminary communication [38], we wish to report here a convenient synthesis of (perfluoroalkylmethyl)oxiranes, based on our previously described addition reaction of perfluoroalkyl iodides to allyl acetate [39] in which mixtures of regioisomeric products were formed. Previous yields of epoxides prepared from individual adducts were not very high (52% [24], 48% [27], 32–75% [36]) with the exception of tertiary perfluoroalkyl (82–96% [32]). However, we have observed a strong influence of solvents on the epoxide yield [37] and, in addition, we found the formation of byproducts in the epoxidation reaction that were not reported in the former papers [18,24,27] or were not formed due to a steric hindrance of tert. perfluoroalkyl ([32]). Therefore, we directed our efforts to find conditions for high chemoselective conversion of the adducts to the corresponding epoxides and we now present the influence of reaction conditions on the yields of epoxides 3a–3c and on the formation of byproducts.

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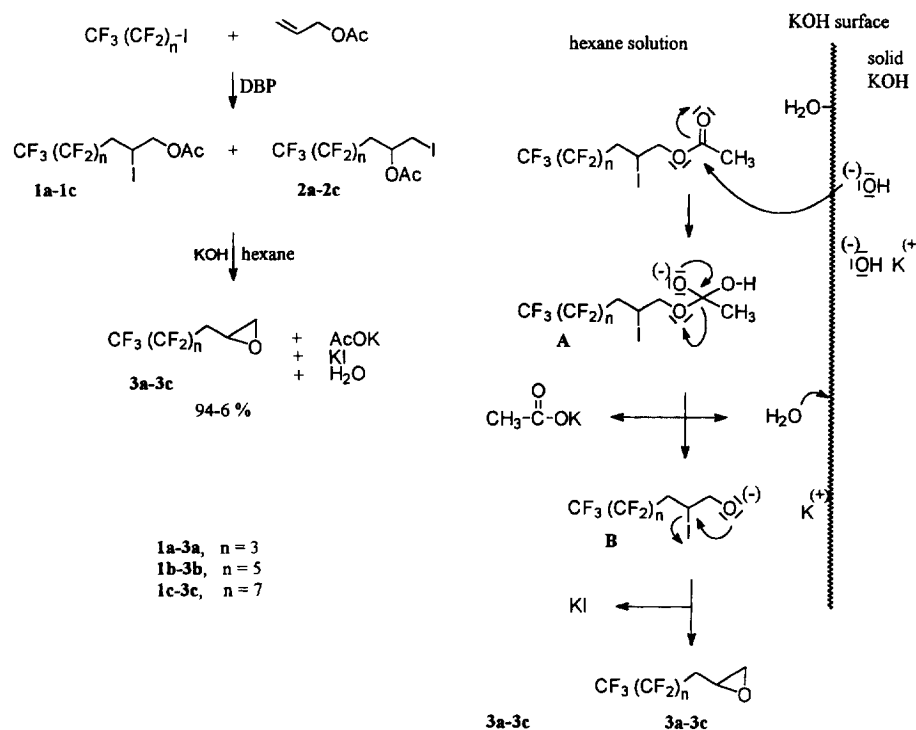
Scheme 1. Chemo selective preparation of fluoroalkyloxiranes.

## 2. Results and discussion

### 2.1. Preparation of epoxides

The peroxide-induced addition of monoiodoperfluoroalkanes 1a–1c to allyl acetate usually affords [39] a mixture of regioisomeric adducts 1a–1c and 2a–2c (Scheme 1) because the primary adducts 1a–1c partially rearrange in a subsequent thermal reaction [40] to regioisomers 2a–2c. In a larger preparative scale, relative yields of rearranged products 2a–2c were 4–15% [39], but at higher temperatures the yields can achieve 89% [40]. Therefore it was important to know if both regioisomers 1 and 2 can be transformed to the same epoxide 3 as reported previously [32] for a mixture of similar bromoacetates (but with tert. perfluoroalkyl in the molecule). We have found that such a conversion is possible (Scheme 1) and that the epoxidation reaction can be carried out with high yields (Table 1). The epoxidation was carried out in a quasi-heterogenous system in an aprotic solvent with solid potassium hydroxide as base.

Owing to insolubility of alkali metal hydroxide in aprotic solvents, the reaction probably took place on the surface of hydroxide particles. The suggested mechanism is depicted in Scheme 1: water, which is formed stoichiometrically in the reaction, is absorbed on the hydroxide surface and in this layer, base hydrolysis of the acetates 1a–1c or 2a–2c can proceed; intermediate A is transformed to iodohydrin salt (intermediate B) from which epoxides 3a–3c are formed by an intramolecular substitution reaction [14–23].

Rearranged adducts 2a–2c are acetates of secondary alcohols. Therefore, their base hydrolyses according to Scheme 1

will generally proceed more slowly than hydrolyses of primary acetates 1a–1c [41]. We verified these relative rates on an equimolar mixture of acetates 1b and 2b. The relative amount of the isomer 2b in the reaction mixture increased in time and reached 60% rel. in 2 h under 68% conversion. Thus, the slower hydrolysis of the secondary acetate 2b was confirmed.

The potassium hydroxide promoted epoxidations of both individual adducts 1a–1c and their mixtures with regioisomers 2a–2c in refluxing hexane took place with complete conversion, with a selectivity of 98% and with yields of 94–96% (Table 2, vide infra). In contrast to these results, the epoxidation reaction with sodium hydroxide was slower and the yields of epoxides were lower (in the earlier report [27] the yield was 48%). The results of the epoxidation with sodium hydroxide in different solvents are summarised in Table 1 (byproducts were not analysed). It can be seen that the yields of epoxide 3a were increased with decreasing solubility of water in an ether: the lowest yield was obtained in tetrahydrofuran while the highest yield was achieved in dibutyl ether. Non-polar hexane appeared to be the best solvent, but potassium hydroxide gave better yields of the epoxides 3a–3c than sodium hydroxide (Table 2) and in a shorter time.

### 2.2. Formation of byproducts in the preparation of epoxides 3a–3c

The yields of epoxides 3a–3c are extremely sensitive to the solvents used. It was shown in the preceding paper [37] that even the change of pentane for hexane can increase the yields dramatically (Table 2). Moreover, we discovered that

Table 1

Yields of the reaction of iodopolyfluoroalkyl acetates $R_F–CH_2–CHX–CH_2Y$ (X, Y = I, OAc; **Xa**, $C_4F_9$; **Xb**, $C_6F_{13}$; **Xc**, $C_6F_{17}$) with sodium hydroxide

| Starting compound | | | Solvent [a] | Time (h) | Conversion (%) | Epoxide yield | | |
|---|---|---|---|---|---|---|---|---|
| | Purity (%) | (g/mmol) | | | | | (g) | (%) |
| 1a | 100 | 66.5/150 | THF | 10 | 100 | 3a | 11.2 | 27 |
| 1a | 100 | 66.5/150 | Et₂O | 25 | 82 | 3a | 16.5 | 40 |
| 1a | 100 | 66.5/150 | (iPr)₂O | 10 | 78 | 3a | 23.9 | 58 |
| 1a | 100 | 66.5/150 | Bu₂O | 5 | 89 | 3a | 25.5 | 62 |
| 1b | 96 [b] | 58.8/108 | Hexane | 3 | 100 | 3b | 33.6 | 94 [c] |
| 1b | 96 [b] | 58.8/108 | Hexane [d] | 8 | 98 | 3b | 33.2 | 93 [c] |
| 1b | 96 [b] | 56.4/103 | Et₂O | 30 | 81 | 3b | 15.1 | 40 |

[a] Refluxing mixture.
[b] 6% of regioisomer 2b.
[c] Purity 99%.
[d] Room temperature.

a solvent can have a dramatic influence on the formation of byproducts in the epoxidation reaction. In the previous papers [18,24,27], the formation of byproducts in the preparation of the epoxides from iodoacetates **1a–1c** has not been mentioned.

It is known from the literature that iodohydrin acetates **1a–1c** or bromohydrin acetates of a similar structure eliminated hydrogen iodide or bromide [18,42–44] when reacted with a hydroxide in a polar solvent, but in a protic solvent such as methanol, together with elimination, hydrolysis of the ester took place [18,43,44] to give exclusively (3-perfluoral-

kyl)allyl alcohols (**5a–5c**, Scheme 2). To our surprise, we observed the formation of unsaturated byproducts **4** and **5** also when diethyl ether was used as the solvent (Scheme 2). This solvent has been used formerly [18,24,27] for the transformation of adducts **1a–1c** to the epoxides **3a–3c**, but the formation of byproducts has not been reported. We have found that regioisomeric iodohydrin acetates **1** and **2** give a different pattern of byproducts (Table 2): in the reaction of primary adducts **1a–1c** the reaction mixtures contained acetates of unsaturated alcohols **4a–4c** as major components (55–63%, vs. 0–8% for rearranged **2a–2c** in diethyl ether),

Table 2

Selectivity of the reaction of iodopolyfluoroalkyl acetates $R_F–CH_2–CHX–CH_2Y$ (X, Y = I, OAc) with potassium hydroxide in various solvents

| Starting compound | | | | KOH/R-I [b] | Solvent [c] | Time (h) | Reaction mixture composition [a] (%rel.) | | | Epoxide yield (%) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | R_F | X | Y | (mol/mol) | | | Epoxide 3a–3c | Unsaturated ester 4a–4c | Unsaturated alcohol 5a–5c | | |
| 1a | C₄F₉ | I | OAc | 2.4 | hexane [d] | 5 | – | – | – | 3a | 55 |
| 1a | C₄F₉ | I | OAc | 2.4 | hexane | 2.5 | 98 | 0 | 2 | 3a | 94 |
| 1a | C₄F₉ | I | OAc | 2.4 | ether [e] | 5 | 40 | 55 | 5 | 3a | 35 |
| 1a | C₄F₉ | I | OAc | 2.4 | tetraglyme | 6 | – | – | – | 3a | 10 |
| 1a | C₄F₉ | I | OAc | 2.4 | decalin | 7 | – | – | – | 3a | 74 |
| 2a | C₄F₉ | OAc | I [f] | 2.4 | ether [e] | 5 | 52 | 0 | 48 | 3a | 42 |
| 1b | C₆F₁₃ | I | OAc | 2.0 | hexane [d] | 16 | – | – | – | 3b | 57 |
| 1b | C₆F₁₃ | I | OAc | 2.4 | hexane | 2 | 98 | 0 | 2 | 3b | 95 |
| 1b | C₆F₁₃ | I | OAc | 2.4 | ether [e] | 6 | 31 | 61 | 8 | 3b | 25 |
| 1b | C₆F₁₃ | OAc | I [g] | 2.4 | ether [e] | 6 | 41 | 8 | 51 | 3b | 36 |
| 1c | C₈F₁₇ | I | OAc | 2.5 | pentane [d] | 5 | – | – | – | 3c | 30 |
| 1c | C₈F₁₇ | I | OAc | 2.0 | hexane [d] | 5 | – | – | – | 3c | 80 |
| 1c | C₈F₁₇ | I | OAc | 2.4 | hexane | 2 | 98 | 0 | 2 | 3c | 96 |
| 1c | C₈F₁₇ | I | OAc | 2.4 | ether [e] | 7 | 25 | 63 | 12 | 3c | 17 |
| 2c | C₈F₁₇ | OAc | I [h] | 2.4 | ether [e] | 7 | 36 | 8 | 56 | 3c | 29 |

[a] GC analyses with calibration.
[b] R-I as $R_F–CH_2–CHX–CH_2Y$ (see above).
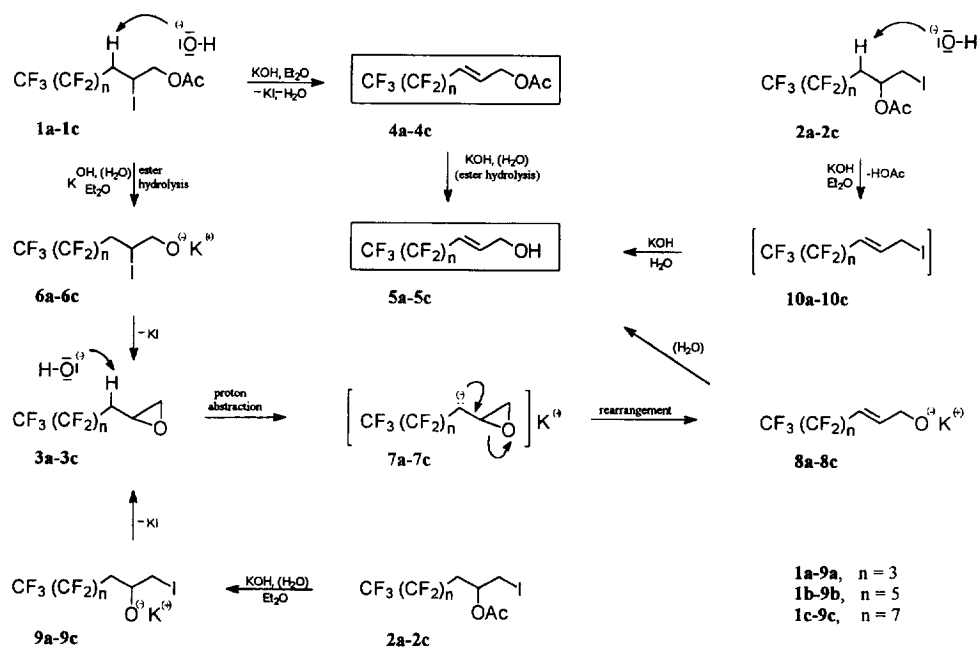[c] Reflux, complete conversion of starting compounds.
[d] Ref. [24].
[e] Diethyl ether.
[f] 14% of the isomer 1a.
[g] 13% of the isomer 1b.
[h] 15% of the isomer 1c.

Scheme 2. Formation of byproducts in diethyl ether.

while rearranged adducts 2a–2c are mainly transformed to the corresponding alkenols 5a–5c (48–56%, vs. 5–12% for 1a–1c). The relative amount of the unsaturated products 4 and 5 increased with the perfluoro-alkyl chain length for both non-rearranged (1) and rearranged (2) substrates (Table 2, reactions in diethyl ether). The mechanism of the formation of the unsaturated compounds 4 or 5 is probably the same (Scheme 2): the elimination of hydrogen iodide is induced by the attack of hydroxide ion on the acidic C–H bond at C3; b-elimination reactions probably proceed through a highly polar transition state (E1cb-like, [46,47]) and diethyl ether that dissolves water (which is formed by the reaction) is probably able to solvate the transition state. In the case of the adducts 1a–1c, the corresponding acetates 4a–4c were formed in one step (Scheme 2); their subsequent hydrolysis to the alkenols 5a–5c has to be comparatively slow as their content was high in the mixture (55–63% rel., Table 2, reactions in diethyl ether). In contrast to 1a–1c, the elimination of acetic acid from the rearranged adducts 2a–2c leads to the corresponding allylic iodides 10a–10c (Scheme 2), which are probably rapidly converted to allylic alcohols 5a–5c as we have not found the intermediates 10a–10c in the reaction

mixtures. Small amounts of unsaturated acetates 4a–4c can be formed from the corresponding isomers 1a–1c, which are present in the starting 2a–2c. Thus, the results in Table 2 reveal different behaviour of primary adducts 1a–1c and rearranged adducts 2a–2c in side reactions in diethyl ether.

The alcohols 5a–5c can also be formed from epoxides 3a–3c in a subsequent reaction (Scheme 2): the mechanism is the same as in the formation of unsaturated products—the attack of the acidic C–H bond at C3 by hydroxide anion followed by a rearrangement of the carbanion intermediate 7 and hydrolysis of the alkoxide 8. There is evidence in the literature for such reactions [44,45,48,49]. To confirm the assumption of the formation of alkenols 5a–5c from epoxides 3a–3c in a subsequent reaction (Scheme 2), we carried out the reactions of pure epoxides with potassium hydroxide in hexane and in diethyl ether. The results are summarised in Table 3 and showed that in hexane no unsaturated byproducts were formed.

In a non-polar solvent such as hexane the formation of unsaturated products 4a–4c, 5a–5c was suppressed to a minimum, but unsaturated alcohols 5a–5c were detected in all reaction mixtures in amount up to 2% (Table 2). Table 3

Table 3
Reactions of epoxides $R_F$–$CH_2$–CH(–O–)$CH_2$ (3a–3c) with KOH in solvents [a]

| Epoxide | | Content of $R_F$–CH=CH–CH$_2$OH in the reaction mixture [b] | | |
|---------|---------|-----|--------|--------------|
| | | | Hexane | Diethyl ether |
| 3a | $C_4F_9$ | 5a | 0 | 11 |
| 3b | $C_6F_{13}$ | 5b | 0 | 17 |
| 3c | $C_8F_{17}$ | 5c | 0 | 21 |

[a] For reaction conditions see Section 4.
[b] GC analysis with calibration.

shows that these small amounts of allylic alcohols 5a–5c that appeared even in the epoxidation in hexane (Table 2) were not formed from epoxides 3a–3c, but very probably from the starting iodoacetates 1a–1c or 2a–2c by the sequence of reactions as depicted in Scheme 2.

Structures of the compounds prepared were elucidated on the basis of elemental analyses and $^1$H, $^{13}$C and $^{19}$F NMR spectra. A detailed study of the $^{13}$C NMR spectra of the epoxide 3b and similar compounds has been published [50]. In the preceding paper [37], $^1$H and $^{13}$C NMR spectra of individual epoxides 3a–3c were given. The chemical shifts of the corresponding individual atoms and groups appeared to be similar one to another in the compounds 3a–3c, 4a–4c and 5a–5c, and therefore we present the data in a overlapped form (see Experimental details).

## 3. Conclusions

An optimised and highly selective synthesis of [(perfluoroalkyl)methyl]oxiranes from adducts of iodoperfluoroalkanes with allyl acetate was developed. On total conversion of adducts, the chemoselectivity was 98% and epoxide yields were 94–96%. The formation of byproducts in the epoxidation reaction was studied and explained by a set of chemical reactions. It has been shown that the change of solvent from hexane to diethyl ether can dramatically decrease the chemoselectivity of the epoxide formation. Unsaturated byproducts formed were characterised for first time. The fluorinated oxiranes obtained are precursors of new functional and telechelic derivatives and amphiphilic monomers which are under investigation.

## 4. Experimental details

### 4.1. General comments

Boiling points were not corrected. GC analyses were performed on a Chrom 5 instrument (Laboratorní pøístroje, Prague; FID, 380 × 0.3 cm column packed with silicon elastomer E-301 on Chromaton N-AW-DMCS (Lachema, Brno), nitrogen) and on Delsi apparatus (model 330, equipped with SE30 column, 100 cm × 1/8 in. (i.d.); nitrogen was used as carrier gas, detector/injector temperatures were 260/255 °C, temperature programme in the range 50–250 °C); the GC apparatus was connected to a Hewlett-Packard integrator (model 3390). NMR spectra were recorded on a Bruker 400 AM (FT, $^{19}$F at 376.5 MHz) and a Bruker WP 80 SY (FT, $^{19}$F at 75 MHz) instruments using TMS and CFCl$_3$ as the internal standards. Chemical shifts are quoted in ppm (s singlet, bs broad singlet, d doublet, t triplet, q quadruplet, m multiplet), coupling constants *J* in Hz, solvent CDCl$_3$.

Chemicals used were as follows. Silicagel L40/100 (Merck), potassium hydroxide pellets were ground to pow-

der before use; iodoperfluoroalkanes were obtained from Elf Atochem and distilled before use. Dibenzoyl peroxide was precipitated from its chloroform solution by methanol and dried in vacuo. Allyl acetate (Aldrich) was used without purification. Diethyl ether, diisopropyl ether and dibutyl ether were dried with sodium and distilled over sodium, hexane (Fluka) was distilled prior to use and stored over molecular sieves; tetrahydrofuran (Fluka) was dried with sodium and distilled over sodium [51].

### 4.2. Preparation of epoxides 3a–3c

#### 4.2.1. From individual non-rearranged acetates 1a–1c by reaction with potassium hydroxide

Powdered potassium hydroxide (13.5 g, 0.24 mol) was added to a vigorously stirred solution of acetate 1a–1c (0.1 mol) in hexane (150 ml, 1.15 mol) placed in a 250 ml round-bottomed flask, equipped with a Dimroth reflux condenser connected to the atmosphere through a drying tube (sodium hydroxide) and with magnetic stirrer. The mixture was then refluxed for 2–3 h; after cooling, the solid (potassium iodide and hydroxide) was filtered off and solvent was then distilled off on a rectification column (Vigreux-type, 50 cm). The composition of the residue, which was a raw epoxide, was checked by GC (SE30, 180 °C) and pure epoxide (3a–3c) was obtained by distillation under reduced pressure (for b.p., yields and elemental analyses see Table 4).

#### 4.2.2. From acetate 1a or 1b by reaction with sodium hydroxide

Heterogenous mixture of acetates 1a or 1b (for amounts see Table 1), powdered sodium hydroxide (hydroxide/acetate, 2.4 mol/mol), and a solvent (150 ml) was refluxed while stirring in the apparatus as in Section 4.2.1. (a flask of 250 ml). The epoxide 3a or 3b was obtained by the treatment of the reaction mixture as in Section 4.2.1. (for yields see Table 1, for b.p. see Table 4).

#### 4.2.3. From mixtures of acetates 1 and rearranged acetates 2 (2–15% rel.) by reaction with potassium hydroxide

In the apparatus as in Section 4.2.1. (a flask of 1000 ml), a heterogenous mixture of potassium hydroxide (53.9 g, 0.96 mol), acetate 1a or 1b or 1c and rearranged acetate 2a or 2b or 2c (0.4 mol) in hexane (600 ml, 4.59 mol) was refluxed for 2–3 h while stirring. The epoxides (3a–3c) were obtained by the treatment of the reaction mixture as in Section 4.2.1. (for b.p. see Table 4).

Yields: a mixture of isomers 1a and 2a (0.4 mol together, 98% mol of 1a, 2% mol of 2b) afforded 103.8 g (94%) of 3a, purity 99%; a mixture of isomers 1b and 2b (0.4 mol together, 94% mol of 1b, 6% mol of 2b) gave 142.9 g (95%) of 3b, purity 99%; a mixture of isomers 1c and 2c (0.4 mol together, 85% mol of 1c, 15% mol of 2c) yielded 182.8 g (96%) of 3c, purity 99% (viz Table 4).

Table 4
Physical properties and elemental analyses of compounds 3–5

| Starting compounds | Product | Yield | | Purity (%) | B.p. (°C/mmHg) | Formula | MW | Analysis: found/calculated (%) | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | (g) | (%) | | | | | C | H | F |
| 1a | 3a | 26.0 | 94 | 99 | 84–86/150 | $C_7H_5F_9O$ | 276.10 | 30.22/30.45 | 1.95/1.83 | 62.15/61.93 |
| 1b | 3b | 35.7 | 95 | 99 | 88–89/60 | $C_9H_5F_{13}O$ | 376.12 | 28.45/28.74 | 1.41/1.34 | 65.81/65.67 |
| 1c | 3c | 45.7 | 96 | 99 | 92–93/25 | $C_{11}H_5F_{17}O$ | 476.13 | 27.58/27.75 | 1.13/1.06 | 67.97/67.83 |
| 2a (13% 1a) | 3a | 12.8 | 93 | 99 | 95–96/200 | | | | | |
| 2b (13% 1b) | 3b | 17.7 | 94 | 99 | 98–99/100 | | | | | |
| 2c (13% 1c) | 3c | 22.6 | 95 | 99 | 96–98/30 | | | | | |
| 1a (2% 2a) | 3a | 103.8 | 94 | 99 | 75–77/100 | | | | | |
| 1b (6% 2b) | 3b | 142.9 | 95 | 99 | 77–79/40 | | | | | |
| 1c (15% 2c) | 3c | 182.8 | 96 | 99 | 85–87/20 | | | | | |
| 1a | 4a | 6.36 | 50 | 98 | 63–65/20 | $C_9H_7F_9O_2$ | 318.14 | 33.85/33.98 | 2.37/2.22 | 54.12/53.75 |
| 1b | 4b | 9.20 | 55 | 98 | 83–85/10 | $C_{11}H_7F_{13}O_2$ | 418.15 | 31.78/31.60 | 1.82/1.69 | 59.42/59.06 |
| 1c | 4c | 12.4 | 60 | 98 | 77–79/1 | $C_{13}H_7F_{17}O_2$ | 518.17 | 30.23/30.13 | 1.42/1.36 | 62.87/62.33 |
| 2a (13% 1a) | 5a | 4.42 | 40 | 98 | 57–59/30 | $C_7H_5F_9O$ | 276.10 | 30.37/30.45 | 1.94/1.83 | 62.18/61.93 |
| 2b (13% 1b) | 5b | 7.22 | 48 | 98 | 72–74/20 | $C_9H_5F_{13}O$ | 376.12 | 28.87/28.74 | 1.42/1.34 | 65.91/65.67 |
| 2c (13% 1c) | 5c | 10.1 | 53 | 98 | 87–89/10 | $C_{11}H_5F_{17}O$ | 476.13 | 27.91/27.75 | 1.15/1.06 | 68.05/67.83 |
| 3a | 5a | 0.25 | 9 | 97 | 52–54/20 | | | | | |
| 3b | 5b | 0.56 | 15 | 97 | 65–67/10 | | | | | |
| 3c | 5c | 0.86 | 18 | 99 | 80–82/5 | | | | | |

### 4.2.4. From rearranged acetates 2a–2c by reaction with potassium hydroxide

The reactions were carried out as in Section 4.2.1. Heterogeneous mixture of acetate 2a–2c (13% rel. of 1, 50 mmol), potassium hydroxide (6.74 g; 120 mmol) and hexane (75 ml) was reacted for 2–3 h and treated as in Section 4.2.1. (for yields and b.p. see Table 4).

### 4.2.5. Relative reaction rate of isomers 1b and 2b with potassium hydroxide

In the apparatus as in Section 4.2.1. (a three-necked flask of 100 ml), a heterogenous mixture of potassium hydroxide (4.5 g, 80 mmol), acetate 1b and rearranged acetate 2b (15 mmol and 15 mmol) in hexane (50 ml) was stirred at 20 °C. The conversion was monitored by GC (E301, 80 °C) by taking periodically samples of the reaction mixture (ca. 1 ml). The samples were filtered through a short column of silica (1 ml hexane added), the solvent and most of epoxide were removed on a rotary evaporator and the residue was analysed by $^1$H NMR by which the contents of the isomers of 1b and 2b were determined.

Results (time–2b content (%rel.)/conversion (%)): 0 min–50/0, 30 min–56/42, 1 h–59/51, 1.5 h–59/60, 2 h–60/68, 2.5 h–60/75, 3 h–60/81.

Overlapped NMR spectra of 3a–3c:

$^1$H NMR (CDCl$_3$) δ: 2.18, 2.29 (2×dm, 2H, CH$_2$CF$_2$, $^2J_{HH}$ = 12); 2.45 (dd, 1H(a), CH$_2$, $^2J_{HH}$ = 4, $^3J_{HH}$ = 6); 2.75 (t, 1H(b), CH$_2$, $^2J_{HH}$ = $^3J_{HH}$ = 4); 3.12 (dq, 1H, CH, $^3J_{HH}$ = 6(q) and 4) ppm.

$^{13}$C NMR (CDCl$_3$) δ: 34.74–34.89 (t, 1C, CH$_2$CF$_2$, $^2J_{CF}$ = 21); 44.11–44.19 (t, 1C, CHO, $^3J_{CF}$ = 5); 44.94–45.08 (s, 1C, CH$_2$O); 109–119 (m, 4–8C, CF$_2$ and CF$_3$) ppm.

$^{19}$F NMR (CDCl$_3$) δ: −81.35 to −82.77 (t, 3F, CF$_3$, $^3J_{FF}$ = 10); −113.02 to −114.22 (m, 2F, CF$_2$CH$_2$); −122.15 to −125.63 (m, 2–10F, 1–5 CF$_2$); −126.34 to −127.67 (m, 2F, CF$_2$CF$_3$) ppm.

### 4.3. Formation of byproducts 4 and 5 in epoxidation reactions

#### 4.3.1. Epoxidations in diethyl ether

In the apparatus as in Section 4.2.1., a heterogenous mixture of potassium hydroxide (5.39 g, 96 mmol), acetate 1a–1c or rearranged acetate 2a–2c (40 mmol together, 100% mol of 1a–1c, or 87% mol of 2a–2c) and diethyl ether (60 ml, 0.573 mol) was refluxed for 5– h while stirring. After the treatment of the reaction mixture as in Section 4.2.1. and distilling off the solvent, the composition of the residue was checked (GC, E301, 150 °C) and the residue was distilled under reduced pressure: in the case of the substrates 1a–c, epoxides 3a–3c were collected as the first fraction followed by the fraction of unsaturated acetates 4a–4c; in the case of the substrates 2a–2c, again epoxides 3a–3c were collected as the first fraction followed by the fraction of unsaturated alcohols 5a–5c; compositions of the reaction mixture are given in Table 2 (for yields, b.p. and elemental analyses see Table 4).

Overlapped NMR spectra of 4a–4c (R$_F$–CH=CH–CH$_2$–OAc):

$^1$H NMR (CDCl$_3$) δ, cis/trans = 15/85: 2.10, 2.14 (2×s, 6H(cis, trans), 2 CH$_3$); 4.74, 4.88 (2×m, 4H(trans, cis), 2 CH$_2$O); 5.67, 5.91 (2×dt, 2H(cis, trans), 2 CF$_2$CH=, $^3J_{HH}$ = 15, $^3J_{HF}$ = 13 (t)); 6.24, 6.48 (2×dm, 2H(cis, trans), 2 CH$_2$CH=, $^3J_{HH}$ = 15) ppm.

$^{13}$C NMR (CDCl$_3$) δ: 21.17, 21.22 (2×s, 2C(trans, cis),

2 CH$_3$); 61.10, 62.75 (2×s, 2C(cis, trans), 2 CH$_2$O); 105–125 (m, 4–8C, CF$_2$ and CF$_3$); 118.56, 119.18 (2×t, 2C(cis, trans), 2 CF$_2$CH=, $^2J_{CF}$=23); 136.98, 140.12 (2×t, 2C(trans, cis), 2 CH$_2$CH=, $^3J_{CF}$=9(trans), $^3J_{CF}$=5.7(cis)); 170.77, 170.83 (2×s, 2C(cis, trans), 2 CO) ppm.

$^{19}$F NMR (CDCl$_3$): as for **3a–3c**.

Overlapped NMR spectra of **5a–5c** (R$_F$–CH=CH–CH$_2$–OH):

$^1$H NMR (CDCl$_3$) $\delta$, cis/trans = 17/83: 1.55, 1.94 (2×bs, 2H(cis, trans), 2 OH); 4.36, 4.47 (2×d, 4H(trans, cis), 2 CH$_2$O, $^3J_{HH}$=3(cis), $^3J_{HH}$=2(trans)); 5.58, 5.97 (2×dt, 2H(cis, trans), 2 CF$_2$CH=, $^3J_{HH}$=15, $^3J_{HF}$=13(t)); 6.30, 6.54 (2×dm, 2H(cis, trans), 2 CH$_2$C*H*=, $^3J_{HH}$=15) ppm.

$^{13}$C NMR (CDCl$_3$) $\delta$: 59.69, 62.00 (2×s, 2C(cis, trans), 2 CH$_2$OH); 105–125 (m, 4–8C, CF$_2$ and CF$_3$); 116.92, 117.01 (2×t, 2C(cis, trans), 2 CF$_2$CH=, $^2J_{CF}$=23); 141.94, 144.96 (2×t, 2C(trans, cis), 2 CH$_2$CH=, $^3J_{CF}$=8.6(trans), $^3J_{CF}$=5.2(cis)) ppm.

$^{19}$F NMR (CDCl$_3$): as for **3a–3c**.

### 4.3.2. Reactions of epoxides *3a–3c* with potassium hydroxide

In the apparatus as in Section 4.2.1. (a two-necked round-bottomed flask, 25 ml), a heterogenous mixture of powdered potassium hydroxide (0.67 g, 12 mmol), epoxide **3a–3c** (10 mmol) and hexane or diethyl ether (15 ml) was refluxed for 2–3 h (hexane) or 5– h (diethyl ether) while stirring. Then, GC analysis (E301, 150 °C) of the mixture was carried out (Table 3).

After cooling the mixture, the solid (potassium iodide and hydroxide) was filtered off on a sintered glass filter and washed with the solvent which was then distilled off on a rectification column. The composition of the residue was checked by GC and the residue was distilled under reduced pressure: epoxides **3a–3c** were distilled as the first fraction followed by the fraction of unsaturated alcohols **5a–c** (for b.p. and yields see Table 4).

### Acknowledgements

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