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Chemistry of [(perfluoroalkyl)methyl] oxiranes. Regioselectivity of ring opening with O-nucleophiles and the preparation of amphiphilic monomers

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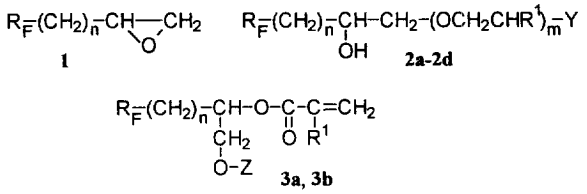
Abstract

The reactions of oxiranes $R_FCH_2CH(-O-)CH_2$ ($R_F \equiv C_4F_9$, C_6F_{13}, C_8F_{17}; **4a–4c**) with a series of alkanols in the presence of a Lewis acid took place at the terminal carbon atom with complete regioselectivity. 2-Hydroxyethyl methacrylate and acrylate reacted similarly. The reaction with alkane diols was controlled to proceed with one or two molecules of the oxiranes chemoselectively. Non-regioselective, base-catalysed ring opening by methacrylic acid (83% terminal attack) was discussed on the basis of the hard and soft acids and bases (HSAB) concept. A convenient transformation of the oxiranes to the corresponding diols **13a–13c** via dioxolane intermediates, and their conversion to bis-methacrylates, was accomplished with overall yields of 75%–79%. Thiourea converted the oxiranes into the corresponding thiiranes (**15a–15c**). The reactions afforded products generally in yields of 82%–98%. © 1997 Elsevier Science S.A.

Keywords: Amphiphilic fluoroalkyl (meth)acrylates; Fluoroalkane-1,2-diols; Fluoroalkane-1,2-diyl-bis-methacrylates; 4-Fluoroalkyl-2,2-dimethyl-1,3-dioxolanes; Fluoroalkyl thiiranes; Nucleophilic oxirane ring opening

1. Introduction

Chemical transformations of fluoroalkyl oxiranes provide good possibilities for the preparation of interesting intermediates and products of practical importance. Therefore the applied chemistry of fluoroalkyl oxiranes **1** has been the subject of much industrial interest as it may yield a series of advanced technical applications. Epoxides have been employed as polymers for special purposes and as surfactants with the general structures **2** and **3** (Scheme 1). In the polymer area, oxiranes **1** are used in the preparation of amphiphilic monomethacrylates of perfluoroalkyl diols (**2a**) [1,2], materials for optical fibres (**2a** and **3a**) [3–5], polymers for contact lenses with improved oxygen transport (**3b**) [5], hydrophobic coatings and surface property modifiers for polymers (**2a** and **3a**) [6,7], oleophobic copolymers (**2d** and **3a**) [7,8] and polyacrylates containing perfluoro pendant chains which display very low surface tensions (**2a**) [9]. The epoxides **1** can be transformed to 1,2-diols, which are then used for new polyurethane resins for different purposes [4,10]. In the area of surface-active compounds, new non-



n = 0, 1; m - undefined; R_F = perfluoroalkyl; R^1 = H, CH_3

Y = (meth)acrylate group (**2a**), non-ionogenic group (alkyl, polyoxaalkyl, **2b**), ionogen group (**2c**) (e.g. $^{(+)}NR_3\ X^{(-)}$ $PO(OH)O^{(-)}\ M^{(+)}$ $NR_2(CH_2)_x\ CO_2^{(-)}\ M^{(+)}$ $O\text{-}C_6H_4\text{-}SO_3^{(-)}\ M^{(+)}$) alkyl or polyoxaalkyl (**2d**)

Z = alkyl, polyoxaalkyl (**3a**), perfluoroacyl (**3b**)

Scheme 1. General structures of (meth)acrylate monomers and hydroxyl-containing surfactants.

ionogenic (**2b**) and ionogenic (**2c**) surfactants have been prepared [11–14], together with oil dispersants (**2d**) [15].

Fluoroalkyl oxiranes **1** are versatile intermediates which can be transformed into various products [1–15]; the first reactions in syntheses and preparations involve nucleophilic ring opening. Several reactions of perfluoroalkylated oxiranes **1** with O- and S-nucleophiles have been reported in the literature. The nucleophilic reagents reported in the reactions

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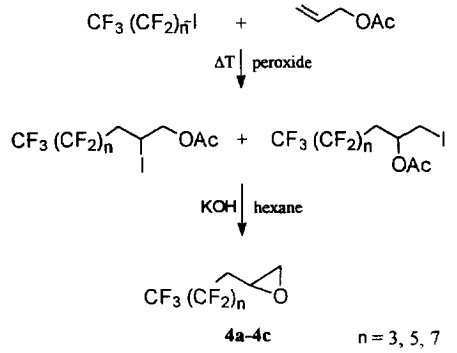


Scheme 2. Two-step preparation of perfluoroalkyl epoxides from perfluoroalkyl iodides.

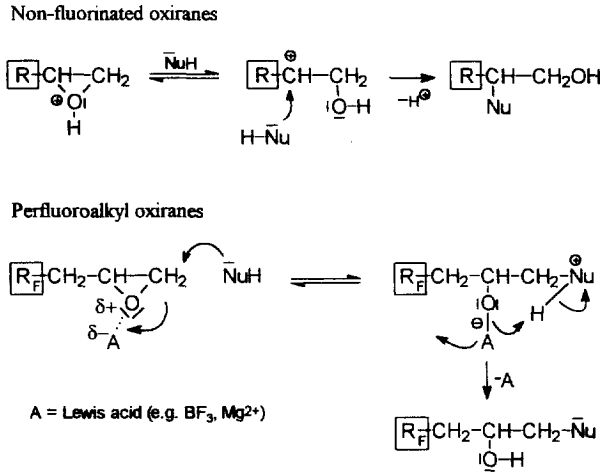
of oxiranes **1** include water [16–18], alkali metal hydroxides [19], acrylic or methacrylic acid [2,20], monoethers of poly(ethylene glycols) [20,21], monomethacrylates of poly(ethylene glycols) [6,7] and thiourea [19]. Reactions of perfluoroalkylated oxirane with potassium hydroxide [19] lead to an unsaturated product.

Previously [22,23], we have developed a convenient two-step preparation of perfluoroalkyl oxiranes **4a–4c**, based on the radical addition of perfluoroalkyl iodides onto allyl acetate (Scheme 2), with overall yields of 85%–87%. In this paper, we present the ring-opening reactions of these epoxides with a series of O-nucleophiles and thiourea. The purpose has been to obtain basic and comparative information about the reactivity of the epoxides and about the regioselectivity of the ring opening with alkanols, as models for reactions of more complicated hydroxy compounds; in addition, the aim has been to develop a preparative method for amphiphilic (meth)acrylate monomers and perfluoroalkylated ethane-1,2-diol bis-methacrylates.

2. Results and discussion

2.1. Regioselectivity of the acid-catalysed ring-opening reactions

All previously reported reactions of epoxides with hydroxy compounds, carried out under acid catalysis [6,7,16–21], have proceeded with complete regioselectivity. We tested the reactivity of epoxides **4a–4c** with a series of hydroxy compounds (Schemes 4 and 5) in the presence of Lewis acid catalysts (boron trifluoride etherate, magnesium perchlorate). All the reactions took place with complete regioselectivity independent of the structure and branching of the alkanols (see below). Non-fluorinated alkyloxiranes are usually cleaved at the C2 carbon atom of the oxirane ring [24] (Scheme 3); the reason for this regioselectivity is the formation of an intermediate carbocation-like reactant which is stabilized by the attached alkyl. In the case of the fluoroalkylated epoxides **4a–4c**, our observations have confirmed complete nucleophilic attack at C1, as depicted in Scheme 3 and Scheme 4. The reversed regioselectivity in this case can

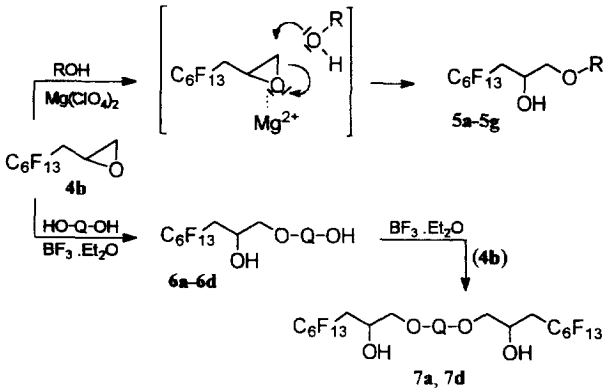


Scheme 3. Mechanisms of nucleophilic oxirane ring opening under acid catalysis.

be explained by the destabilizing effect of β-perfluoroalkyl on the potentially formed intermediate carbocation.

2.2. Acid-catalysed reactions with alkanols, α,ω-alkane diols and hydroxyalkyl (meth)acrylates

The reactions of alkanols with the epoxide **4b** were carried out in the presence of magnesium perchlorate (Scheme 4, **5a–5g**). We did not observe the formation of the epoxide **4b** oligomers. The results in Table 2 also reveal no apparent decrease in yield with branching of the alkanol chain, as demonstrated for the series of 1- and 2-propanol (products **5c** and **5d**) and primary, secondary and tertiary butyl alcohols (products **5e–5g**); however, the reaction times were longer for branched alkanols to achieve complete conversion of the epoxides (Table 2). On this basis, the reactions of polyhydroxy compounds with the epoxides **4a–4c** were successfully carried out during the synthesis of potential biosurfactants as reported previously [12]. All reactions with alkanols took place with 100% regioselectivity of ring opening and no regioisomers were found in the reaction mixtures.



R = CH_3 (5a), CH_3CH_2 (5b), $CH_3CH_2CH_2$ (5c), $(CH_3)_2CH$ (5d), $CH_3(CH_2)_3$ (5e), $CH_3CH_2CH(CH_3)$ (5f), $(CH_3)_3C$ (5g)

Q = $(CH_2)_n$, n = 2, 3, 4 (6a - 6c), $(CH_2CH_2)_2O$ (6d)

Scheme 4. Reaction of epoxide (**4b**) with alcohols and diols.

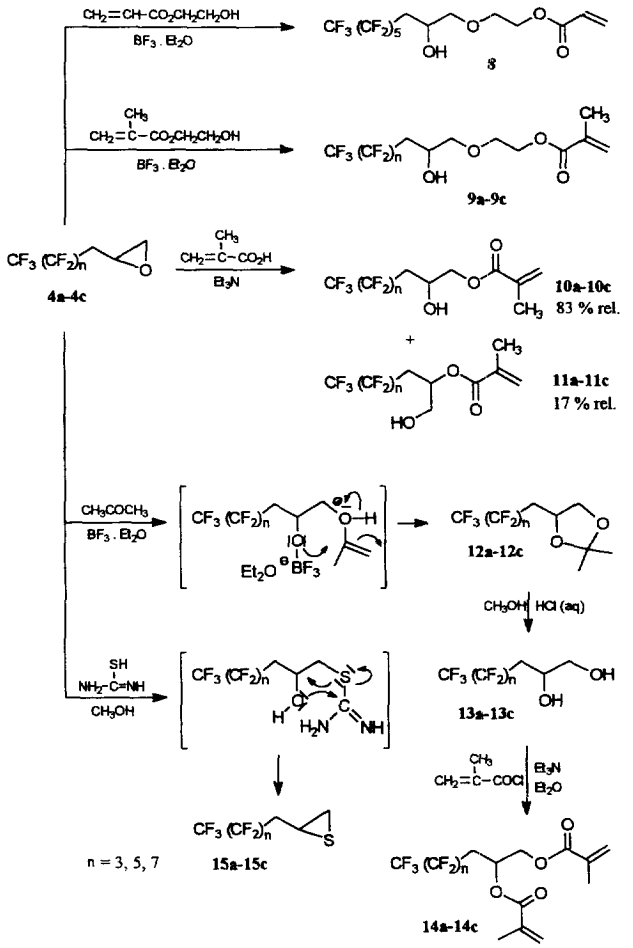
The reactions of the epoxide **4b** with aliphatic diols were carried out in the presence of boron trifluoride etherate (Scheme 4). We have developed reaction conditions under which only one hydroxyl group reacts with the epoxide to afford monofluoroalkylated products **6a–6d**. These compounds can be converted subsequently to the bis-fluoroalkylated diols (**7a** and **7d**), which can also be obtained directly from the diols with an excess of the epoxide.

As a continuation of the study of oxirane **4b** ring-opening reactions, we carried out reactions of the epoxides **4a–4c** with 2-hydroxyethyl acrylate or methacrylate (Scheme 5). The reactions afforded the corresponding amphiphilic acrylate **8** and methacrylates **9a–9c** in 92% yield (Table 2). These compounds have been obtained previously [20] by the direct reaction of iodohydrins with potassium (meth)acrylate in octafluoropentanol in yields of approximately 9.2%. An analogous ring opening of epoxides **4a–4c** with methacrylic acid in the presence or absence of boron trifluoride etherate or magnesium perchlorate did not take place, probably due to the low nucleophilicity of the acid hydroxylic oxygen; the polymerization of the starting epoxides was observed as the only reaction.

2.3. *Regioselectivity of base-catalysed reactions with methacrylic acid*

Tertiary amines have been used as catalysts for the ring opening of non-fluorinated epoxides [25–28] with methacrylic acid, whereas the reaction of fluoroalkyl epoxide **4b** was accomplished in the presence of potassium methacrylate [2] or triphenylphosphine [2]. We carried out the reaction of epoxides **4a–4c** in the presence of triethylamine to generate a quasi-methacrylate anion ($CH_2=C(CH_3)CO–O^{(-)}HEt_3N^{(+)}$) as a stronger nucleophile of the free acid (Scheme 5). The reaction took place readily, but the nucleophilic attack was not regioselective as previously reported [29]: the main attack of quasi-methacrylate anion took place at C1 (83% terminal attack) in oxiranes **4a–4c**; the regioisomeric products **10** and **11** were not separated and the minor products were identified by nuclear magnetic resonance (NMR) spectroscopy. The regioselectivity results are listed in Table 1. A very similar regioselectivity of ring opening was reported previously [2].

The regioselectivity of base-catalysed ring opening in perfluoroalkyl epoxides **4a–4c** is surprising when compared with non-fluorinated alkyloxiranes in which ring opening with alkoxides is completely regioselective [24]. On the other hand, the opening reaction of epoxides **4a–4c** is similar to the partly selective acid-catalysed ring opening of non-fluorinated epoxides [24]. The unexpected result can be explained using the hard and soft acids and bases (HSAB) concept [30–32] as depicted in Scheme 6: under acid catalysis, the complex of oxirane and the acid (**16**) is attacked by a softer nucleophile at a softer (delocalized) centre; the reaction of the charged nucleophile, which is a harder agent than oxygen in the hydroxyl group [30–32], can take place at a harder



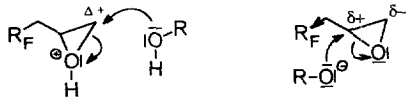
Scheme 5. Reaction of epoxides **4a–4c** with nucleophiles.

centre at the oxirane ring, i.e. at the carbon, which is closer to the perfluoroalkyl group having strong electron-withdrawing properties (**17**). The smaller yield of the product of this

Table 1
Regioselectivity of oxirane ring opening in **4a–4c** with methacrylic acid in the presence of NEt_3

Epoxide	R_F	Regioisomeric products[a] (% rel.)			
		$R_FCH_2CH(OH)CH_2OMA$		$R_FCH_2CH(OMA)CH_2OH$	
4a	C_4F_9	**10a**	83	**11a**	17
4b	C_6F_{13}	**10b**	85–90[b]	**11b**	10–15[b]
4b	C_6F_{13}	**10b**	83	**11b**	17
4c	C_8F_{17}	**10c**	83	**11c**	17

[a]The formation of regioisomers has also been mentioned in the presence of Me_4NCl as the catalyst [1].
[b]In the presence of potassium methacrylate or triphenylphosphine [2].



16 17

Scheme 6. Hard and soft attack in oxirane ring opening.

attack (**11**) than expected may be caused by a repulsive interaction between the perfluoroalkyl group and the charged nucleophile in this S_N2 reaction.

2.4. Preparation of perfluoroalkylated 1,2-diols; (meth)acrylate monomers

The transformation of fluoroalkyl epoxides to the corresponding 1,2-diols under acid catalysis has been described previously [16,17,33,34]. The yields were not very satisfactory [16,17] or required special conditions [33,34]. We have developed a procedure in which the epoxides **4a–4c** are first converted into the dioxolanes **12a–12c** (Scheme 5) in yields of approximately 95%, and then easily hydrolysed to the corresponding diols **13a–13c** in aqueous methanol in the presence of hydrochloric acid in mean yields of 96% (Table 2). We assume that the attack of epoxides **4a–4c** proceeds by the enol form of acetone (Scheme 5).

The diols **13a–13c** can be converted to the bis-methacrylates **14a–14c**, which are examples of bifunctional monomers that can be used to modify the properties of highly hydrophilic and water-soluble poly(methacrylates). The mono-fluoroalkylated (**13a–13c**) and bis-fluoroalkylated (**7a** and **7d**) diols are potential intermediates for well-defined structured polymers, such as polyurethanes or polyesters, and for poly(meth)acrylate compositions as cross-linking agents. Acrylate **8** and methacrylates **9** and **10** represent types of amphiphilic monomer which can be used as biocompatible materials, enabling better oxygen transport [35].

2.5. Reaction with thiourea

According to the previously described procedure [19], we carried out the reaction of the epoxides **4a–4c** with thiourea in a non-catalysed reaction. The nucleophilicity of the thiol form of thiourea, as depicted in Scheme 5, was sufficient to attack the oxirane ring of fluoroalkyl epoxides to afford thiiranes (Table 2) in much higher yields (86%–89%) than those reported previously [19] for a branched perfluoroalkyl oxirane **1** (yield below 20%).

The structures of the compounds prepared were elucidated on the basis of elemental analyses and ^1H, ^{13}C and ^{19}F NMR spectra. A detailed study of the ^{13}C NMR spectra of the epoxide **4b** and similar compounds has been published previously [36]. In a preceding paper [37], we reported the ^1H and ^{13}C NMR spectra of the individual epoxides **4a–4c**. The chemical shifts of the corresponding individual atoms and groups in the ^{19}F NMR spectra of the reaction products appear to be similar to those in the starting epoxides **4a–4c** and therefore are presented briefly (see Section 4).

Compounds **5a–5g**, **6a–6d**, **7a**, **7d**, **8**, **9a–9c**, **10a**, **11a**, **11c**, **12a–12c**, **14a–14c** and **15a–15c** are new.

3. Conclusions

The regioselectivity of the ring opening of the fluoroalkyl oxiranes **4a–4c** with different O-nucleophiles and thiourea was studied: the ring opening with alkanols and 2-hydroxyethyl acrylate or methacrylate in the presence of a Lewis acid catalyst took place at the terminal carbon atom with complete regioselectivity. Branching of the alkyl chain of the alkanols prolonged the reaction times, but did not influence the complete epoxide conversion. The reaction of the epoxides with hydroxyalkyl (meth)acrylates afforded new amphiphilic fluoroalkyl (meth)acrylates in 81%–92% yield; contrary to this selective reaction, the oxirane ring opening with methacrylic acid in the presence of triethylamine was not completely selective (terminal attack of 83%).

The epoxides were easily converted to the corresponding diols in a two-step synthesis via 1,3-dioxolane intermediates with overall yields of approximately 91%. The reaction of the epoxides with thiourea afforded the corresponding thiiranes in 86%–89% yield.

4. Experimental details

4.1. General comments

The temperature data were uncorrected. Distillations of high boiling compounds were carried out on a Vacuubrand RC5 high vacuum oil pump. Gas chromatography (GC) analyses were performed on a Chrom 5 instrument (Laboratorní přístroje, Prague; FID, 380 cm × 0.3 cm packed column, silicone elastomer E-301 on Chromaton N-AW-DMCS (Lachema, Brno), nitrogen) and on a Delsi apparatus (model 330, equipped with SE30 column, 100 cm × 1/8 in (i.d.), nitrogen, temperature programme in the range 50–250 °C); the GC apparatus was connected to a Hewlett-Packard integrator (model 33990). NMR spectra were recorded on Bruker 400 AM (FT, ^{19}F at 376.5 MHz) and Bruker WP 80 SY (FT, ^{19}F at 75 MHz) instruments; tetramethylsilane (TMS) and $CFCl_3$ were used as internal standards and the chemical shifts are given in parts per million (s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quadruplet; qi, quintuplet; sex, sextuplet; sep, septuplet; m, multiplet); the coupling constants J are given in hertz and the solvents used were $CDCl_3$, acetone-d_6 and dimethylsulphoxide-d_6 (DMSO-d_6).

The chemicals used were as follows: fluoroalkyloxiranes **4a–4c** were prepared according to the procedure described in Ref. [22]; iodoperfluoroalkanes were obtained from Elf Atochem and were distilled before use; silica gel L40/100 (Merck); magnesium perchlorate (Aldrich); boron trifluoride etherate (Aldrich); triethylamine (Aldrich) was distilled before use (88–89 °C); thiourea (Aldrich); methacrylic acid (Aldrich); 2-hydroxyethyl acrylate (Aldrich); 2-hydroxyethyl methacrylate (Aldrich); 1-propanol, 2-propanol, 1-butanol, 2-butanol, tert-butyl alcohol (all Fluka) and acetone were dried and purified according to standard procedures

Table 2
Yields, physical properties and elemental analyses of compounds **5–15**

Starting compound	Time (h)	Product	Yield		Purity (%)	B.p. (m.p.) (°C/mmHg; °C)	Formula	M.W.	Analysis: found/calculated (%)		
			(g)	(%)					C	H	F or (S)
4b	3	**5a**	3.91	96	99	58–59/1.5	$C_{10}H_9F_{13}O_2$	408.2	29.4/29.4	2.33/2.22	59.9/60.5
4b	4	**5b**	4.03	95	98	66–68/1.5	$C_{11}H_{11}F_{13}O_2$	422.2	31.2/31.3	2.73/2.63	57.0/58.5
4b	4	**5c**	4.10	94	98	72–73/1.5	$C_{12}H_{13}F_{13}O_2$	436.2	32.9/33.0	3.03/3.00	57.1/56.6
4b	4	**5d**	4.12	94	98	67–69/1.5	$C_{12}H_{13}F_{13}O_2$	436.2	32.7/33.0	3.04/3.00	56.1/56.6
4b	4	**5e**	4.33	96	99	78–79/1.5	$C_{13}H_{15}F_{13}O_2$	450.2	34.3/34.7	3.39/3.36	55.9/54.9
4b	4	**5f**	4.30	96	99	77–78/1.5	$C_{13}H_{15}F_{13}O_2$	450.2	34.8/34.7	3.64/3.36	54.9/54.9
4b	5	**5g**	4.28	95	98	78–79/1.5	$C_{13}H_{15}F_{13}O_2$	450.2	34.4/34.7	3.50/3.36	54.4/54.9
4b	1	**6a**	23.1	88	98	88–89/0.025	$C_{11}H_{11}F_{13}O_3$	438.2	30.65/30.15	2.71/2.53	55.3/56.4
4b	1	**6b**	24.2	89	98	105–107/0.03	$C_{12}H_{13}F_{13}O_3$	452.2	32.3/31.9	3.11/2.90	55.3/54.6
4b	1	**6c**	25.2	90	99	113–115/0.04	$C_{13}H_{15}F_{13}O_3$	466.2	33.7/33.5	3.39/3.24	51.89/53.0
4b	1	**6d**	26.6	92	99	122–124/0.03	$C_{13}H_{15}F_{13}O_4$	482.2	33.16/32.4	3.51/3.14	50.6/51.2
6a	1	**7a**	6.68	82	96	105–107/0.015	$C_{20}H_{16}F_{26}O_4$	814.3	29.7/29.5	1.91/1.98	59.9/60.7
6d	1	**7d**	7.30	85	96	131–133/0.012	$C_{22}H_{20}F_{26}O_5$	858.4	30.2/30.8	2.71/2.35	56.8/57.5
4b	2	**8**	12.0	81	98	95–98/0.005	$C_{14}H_{13}F_{13}O_4$	492.2	34.25/34.2	2.79/2.66	50.5/50.2
4a	2	**9a**	18.7	92	98	100–102/0.08	$C_{13}H_{15}F_9O_4$	406.25	38.1/38.4	3.46/3.72	41.8/42.1
4b	2	**9b**	23.3	92	98	100–103/0.02	$C_{15}H_{15}F_{13}O_4$	506.2	35.9/35.6	3.35/2.99	47.7/48.7
4c	2	**9c**	27.9	92	98	102–104/0.003	$C_{17}H_{15}F_{17}O_4$	606.3	33.3/33.7	2.62/2.49	53.0/53.3
4a	2	**10a**[a]	35.5	98	98	73–75/0.8	$C_{11}H_{11}F_9O_3$	362.2	36.3/36.5	2.89/3.06	46.9/47.2
4b	2	**10b**[a]	44.4	96	98	77–79/0.08[b]	$C_{13}H_{11}F_{13}O_3$	462.2	33.3/33.8	2.65/2.40	54.2/53.4
4c	2	**10c**[a]	52.9	94	98	93–95/0.01[c]	$C_{15}H_{11}F_{17}O_3$	562.2	32.2/32.05	1.93/1.97	57.35/57.45
4a	0.5	**12a**	6.35	95	98	70–72/15	$C_{10}H_{11}F_9O_2$	334.2	35.7/35.9	3.33/3.32	51.4/51.2
4b	0.5	**12b**	8.25	95	98	77–79/5	$C_{12}H_{11}F_{13}O_2$	434.2	32.9/33.2	2.62/2.55	57.2/56.9
4c	0.5	**12c**	10.2	95	98	81–83/1 (32–33)	$C_{14}H_{11}F_{17}O_2$	534.2	30.5/31.5	1.99/2.08	60.0/60.5
12a	2	**13a**	2.82	96	99	104–106/5	$C_7H_7F_9O_2$	294.1	28.8/28.6	2.51/2.40	57.8/58.1
12b	2	**13b**	3.78	96	99	108–109/1 (62–63)	$C_9H_7F_{13}O_2$	394.1	27.1/27.4	1.80/1.79	63.4/62.7
12c	2	**13c**	4.74	96	99	125–129/0.8 (114–115)	$C_{11}H_7F_{17}O_2$	494.15	26.9/26.7	1.55/1.43	65.7/65.4
13a	2	**14a**	1.74	81	98	84–85/0.12	$C_{15}H_{15}F_{13}O_4$	430.3	42.0/41.9	3.59/3.51	39.9/39.7
13b	2	**14b**	2.20	83	98	90–91/0.06	$C_{17}H_{15}F_{13}O_4$	530.3	38.7/38.5	2.98/2.85	46.7/46.6
13c	2	**14c**	2.71	86	98	95–97/0.005 (31–32)	$C_{19}H_{15}F_{17}O_4$	630.3	36.2/36.2	2.55/2.40	51.3/51.2
4a	4	**15a**	2.51	86	98	71–73/50	$C_7H_5F_9S$	292.2	28.1/28.8	1.91/1.72	(10.4/11.0)[d]
4b	4	**15b**	3.41	87	98	73–75/20	$C_9H_5F_{13}S$	392.2	27.3/27.6	1.44/1.29	(8.25/8.17)[d]
4c	4	**15c**	4.38	89	98	85–87/10 (33–34)	$C_{11}H_5F_{17}S$	492.2	26.6/26.8	1.06/1.02	(6.40/6.51)[d]

[a]Content of 17% of the corresponding regioisomer **11a**, **11b** or **11c**.
[b]Literature value [20]: 108–112 °C/1.0–1.2 mmHg.
[c]Literature value [20]: 127–130 °C/2.5–2.8 mmHg.
[d]Sulphur content; the fluorine content could not be determined in the presence of sulphur.

[38]; ethane-1,2-diol, propane-1,3-diol, butane-1,4-diol and diethylene glycol (all Aldrich) were dried with sodium and further purified by distillation or according to standard procedures [38].

4.2. Reactions of epoxide **4b** with hydroxy compounds

The summarized NMR spectra of **4a–4c** [23] are as follows. ^{1}H NMR ($CDCl_3$) δ: 2.18, 2.29 (2×dm, 2H, CH_2CF_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_2CF_2, $^2J_{CF}=21$), 44.11–44.19 (t, 1C, CHO, $^3J_{CF}=5$), 44.94–45.08 (s, 1C, CH_2O), 109–119 (m, 4–8C, CF_2 and CF_3) ppm. ^{19}F NMR ($CDCl_3$) δ: 81.35–82.77 (t, 3F, CF_3, $^3J_{FF}=10$), 113.02–114.22 (m, 2F, CF_2CH_2), 122.15–125.63 (m, 2–10F, 1–5CF_2), 126.34–127.67 (m, 2F, CF_2CF_3) ppm.

4.2.1. Reactions with alkanols (products **5a–5g**)

In a round-bottomed flask (25 ml), equipped with a Dimroth reflux condenser connected to the atmosphere through a drying tube (potassium hydroxide) and a magnetic spinbar, a mixture of alkanol (0.1 mol), epoxide **4b** (3.76 g, 0.01 mol) and magnesium perchlorate (1.12 g, 5 mmol) was heated at 70 °C for 3–5 h (complete conversion of **4b**) with stirring. After cooling to room temperature, water (25 ml) was added to the mixture and the lower oily yellow-coloured

layer was separated, diluted with diethyl ether (10 ml) and dried with magnesium sulphate. After filtering off the drier, the solvent was evaporated and the residue was distilled in vacuo (oil pump) (for boiling points (b.p.), yields, purity of products **5a–5g** and elemental analyses, see Table 2; **5a**, 6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-2-oxaundecan-4-ol; **5b**, 7,7,8,8,9,9,10,10,11,11,12,12,12,-tridecafluoro-3-oxadodecan-5-ol; **5c**, 8,8,9,9,10,10,11,11,12,12,13,13,13-tridecafluoro-4-oxatridecan-6-ol; **5d**, 7,7,8,8,9,9,10,10,-11,11,12,12,12-tridecafluoro-2-methyl-3-oxadodecan-5-ol; **5e**, 9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-5-oxatetradecan-7-ol; **5f**, 8,8,9,9,10,10,11,11,12,12,13,13,13-tridecafluoro-3-methyl-4-oxatridecan-6-ol; **5g**, 7,7,8,8,-9,9,10,10,11,11,12,12,12-tridecafluoro-2,2-dimethyl-3-oxadodecan-5-ol).

^{1}H NMR ($CDCl_3$) δ, common signals of **5a–5g**: 2.20, 2.32 (2×dm, 2H, CH_2CF_2, $^2J_{HH}=19$), 3.31 and 3.45 (2×dd, 2H, CH_2O, $^2J_{HH}=9.5$, $^3J_{HH}=5$), 3.15–3.50 (bs, 1H, OH), 4.20–4.23 (m, 1H, C*H*OH) ppm.

^{1}H NMR ($CDCl_3$) δ, individual signals of **5a–5g**: **5a**: 3.37 (s, 3H, CH_3O) ppm; **5b**: 1.14 (t, 3H, CH_3, $^3J_{HH}=7$), 3.48 (q, 2H, CH_2CH_3, $^3J_{HH}=7$) ppm; **5c**: 0.90 (t, 3H, CH_3, $^3J_{HH}=7$), 1.59 (sex, 2H, CH_2CH_3, $^3J_{HH}=7$), 3.42 (t, 2H, CH_2O, $^3J_{HH}=7$) ppm; **5d**: 1.15 (d, 6H, $2CH_3$, $^3J_{HH}=6$), 3.60 (sep, 1H, CHO, $^3J_{HH}=6$) ppm; **5e**: 0.90 (t, 3H, CH_3, $^3J_{HH}=7$), 1.35 (sex, 2H, CH_2CH_3, $^3J_{HH}=7$), 1.55 (qi, 2H, CH_2CH_2O, $^3J_{HH}=7$), 3.46 (t, 2H, CH_2O, $^3J_{HH}=7$) ppm; **5f**, 2 diastereoisomers, A (50% rel.), B (50% rel.): 0.91 (t, 3H, CH_3CH_2, $^3J_{HH}=7.4$), 1.14, 1.15 (2×d, 3H(A, B), CH_3CH, $^3J_{HH}=6.2$), 1.44, 1.48 (2×dqi, 2H(A), CH_2CH_3, $^2J_{HH}=14$, $^3J_{HH}=7$), 1.55, 1.59 (2×dqi, 2H(B), CH_2CH_3, $^2J_{HH}=14$, $^3J_{HH}=7$), 3.58 (m, 1H, CHO) ppm; **5g**: 1.15 (s, 9H, $3CH_3$) ppm.

^{13}C NMR ($CDCl_3$) δ, common signals of **5a–5g**: 34.27–34.39 (t, 1C, CH_2CF_2, $^2J_{CF}=21$), 63.87–64.29 (s, 1C, CHOH), 72.26–75.81 (s, 1C, CH_2O), 110–120 (m, 6C, CF_2 and CF_3) ppm.

^{13}C NMR ($CDCl_3$) δ, individual signals of **5a–5g**: **5a**: 58.60 (s, 1C, CH_3O) ppm; **5b**: 14.07 (s, 1C, CH_3), 66.46 (s, 1C, CH_2CH_3) ppm; **5c**: 9.83 (s, 1C, CH_3), 22.39 (s, 1C, CH_2CH_3), 72.97 (s, 1C, OCH_2CH_2) ppm; **5d**: 21.50 and 21.61 (2×s, 2C, $2CH_3$), 71.23 (s, 1C, CHO) ppm; **5e**: 13.19 (s, 1C, CH_3), 18.87 (s, 1C, CH_2CH_3), 31.29 (s, 1C, CH_2CH_2O), 71.11 (s, 1C, CH_2O) ppm; **5f**: 10.30 (s, 1C, CH_3CH_2), 19.63, 19.78 (2×s, 1C(A, B), CH_3CH), 29.76, 29.78 (2×s, 1C(A, B), CH_2), 78.28, 78.40 (2×s, 1C(A, B), CHO) ppm; **5g**: 26.78 (s, 3C, $3CH_3$), 64.97 (s, 1C, C) ppm.

^{19}F NMR ($CDCl_3$) of **5a–5g**: the same as for **4a–4c**.

4.2.2. *Reactions with diols*

4.2.2.1. *Monoperfluoroalkylated diols 6a–6d*

In a round-bottomed flask (100 ml), equipped with a Dimroth reflux condenser connected to the atmosphere through a drying tube (potassium hydroxide) and a magnetic spinbar, a mixture of α,ω-diol (1.2 mol), epoxide **4b** (22.6 g, 60 mmol) and boron trifluoride etherate (0.21 g, 1.5 mmol) was heated at 90 °C for 1 h with stirring (complete conversion of **4b**, the mixture becomes clear). The unreacted diol was distilled off in vacuo (oil pump) and the distillation was continued to obtain products **6a–6d** (for b.p., yields, purity of products and elemental analyses, see Table 2; **6a**, 7,7,-8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-3-oxadodecan-1,5-diol; **6b**, 8,8,9,9,10,10,11,11,12,12,13,13,13-tridecafluoro-4-oxatridecan-1,6-diol; **6c**, 9,9,10,10,11,11,-12,12,13,13,14,14,14-tridecafluoro-5-oxatetradecan-1,7-diol; **6d**, 9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-3,5-dioxatetradecan-1,7-diol).

^{1}H NMR ($CDCl_3$) δ, common signals of **6a–6d**: 2.18, 2.28 (2×dm, 2H, CH_2CF_2, $^2J_{HH}=19$), 3.38 and 3.45 (2×dd, 2H, CH_2O, $^2J_{HH}=10$, $^3J_{HH}=5$), 3.72–4.78 (bs, 2H, 2OH), 4.18–4.26 (m, 1H, C*H*OH) ppm.

^{1}H NMR ($CDCl_3$) δ, individual signals of **6a–6d**: **6a**: 3.55 and 3.70 (2×m, 4H, $2CH_2O$) ppm; **6b**: 1.84 (qi, 2H, CH_2CH_2OH, $^3J_{HH}=6$), 3.66 and 3.68 (2×dt, 2H, CH_2O, $^2J_{HH}=4$, $^3J_{HH}=6$), 3.76 (t, 2H, CH_2OH, $^3J_{HH}=6$) ppm; **6c**: 1.60 (m, 4H, $(CH_2)_2CH_2O$), 3.46 (m, 2H, CH_2O), 3.56 (t, 2H, CH_2OH, $^3J_{HH}=6$) ppm; **6d**: 3.44–3.55 (m, 6H, $3CH_2O$), 3.57 (m, 2H, CH_2OH) ppm.

^{13}C NMR ($CDCl_3$) δ, common signals of **6a–6d**: 34.02–34.30 (t, 1C, CH_2CF_2, $^2J_{CF}=21$), 63.67–63.93 (s, 1C, CHOH), 74.07–74.67 (s, 1C, CH_2O), 110–120 (m, 6C, CF_2 and CF_3) ppm.

^{13}C NMR ($CDCl_3$) δ, individual signals of **6a–6d**: **6a**: 61.01 (s, 1C, CH_2OH), 72.17 (s, 1C, CH_2O) ppm; **6b**: 32.54 (s, 1C, CH_2), 61.30 (s, 1C, CH_2OH), 70.27 (s, 1C, CH_2O) ppm; **6c**: 25.88 and 29.11 (2×s, 2C, $2CH_2$), 61.84 (s, 1C, CH_2OH), 71.10 (s, 1C, CH_2O) ppm; **6d**: 60.91 (s, 1C, CH_2OH), 69.84 (s, 1C, CH_2CH_2OH), 70.13 (s, 1C, CH_2CH_2O), 72.27 (s, 1C, CH_2O) ppm.

^{19}F NMR ($CDCl_3$) of **6a–6d**: the same as for **4a–4c**.

4.2.2.2. *Bis-perfluoroalkylated diols 7a and 7d*

In the same equipment as above (flask, 25 ml), a mixture of diol **6a** or **6d** (20 mmol), epoxide **4b** (3.76 g, 10 mmol) and boron trifluoride etherate (85 mg, 0.6 mmol) was heated at 90 °C for 1 h with stirring (complete conversion of **4b**). The products **7a** and **7d** were obtained as above (for b.p., yields, purity of products **7a** and **7d** and elemental analyses, see Table 2; **7a**, 1,1,1,2,2,3,3,4,4,5,5,6,6,18,18,19,19,20,-20,21,21,22,22,23,23,23-hexacosafluoro-10,13-dioxadocosane-8,16-diol; **7d**, 1,1,1,2,2,3,3,4,4,5,5,6,6,20,20,21,21,22,-22,23,23,24,24,25,25,25-hexacosafluoro-10,13,16-trioxapentacosane-8,18-diol).

^{1}H NMR ($CDCl_3$) δ, common signals of **7a** and **7d**: 2.25–2.35 (m, 4H, $2CH_2CF_2$), 3.50 (m, 4H, $2CH_2O$), 3.61–3.65 (m, 4 or 8H, 2 or $4CH_2CH_2O$), 4.43–4.86 (bs, 2H, 2OH), 4.19–4.22 (m, 2H, 2CHO) ppm.

^{13}C NMR ($CDCl_3$) δ, common signals of **7a** and **7d**: 34.00–35.55 (t, 2C, $2CH_2CF_2$, $^2J_{CF}=21$), 63.70–65.04 (s,

2C, 2CHO), 70.00–71.75 (1 or 2×s, 2 or 4C, CH_2CH_2O), 74.90–75.90 (s, 2C, $2CH_2O$), 110–120 (m, 12C, CF_2 and CF_3) ppm.

^{19}F NMR ($CDCl_3$) of **7a** and **7d**: the same as for **4a–4c**.

4.3. Reactions of epoxides 4a–4c with 2-hydroxyethyl (meth)acrylates (products 8 and 9a–9c)

4.3.1. Reaction of 4b with 2-hydroxyethyl acrylate (HEA) (product 8)

In the same equipment as described in Section 4.2.1 (flask, 50 ml), a mixture of HEA (13.9 g, 120 mmol), epoxide **4b** (11.3 g, 30 mmol), boron trifluoride etherate (0.11 g, 0.76 mmol) and a stabilizer (di-tert-octylpyrocatechol; 33.5 mg, 0.1 mmol) was heated at 80 °C for 2 h with stirring (complete conversion of the epoxide). The mixture was then distilled in vacuo: the catalyst was first distilled off on a water pump, followed by unreacted HEA (oil pump) and finally product **8** as the last fraction (high vacuum pump) (for b.p., yields, purity of the product and elemental analyses, see Table 2; **8**, 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-hydroxy-3-oxadodecyl acrylate).

^1H NMR ($CDCl_3$) δ: 2.29 and 2.37 (2×dm, 2H, CH_2CF_2, $^2J_{HH}=17$), 2.81 (bs, 1H, OH), 3.50 (dd, 1H(a), CH_2O, $^2J_{HH}=9.6$, $^3J_{HH}=6.2$), 3.61 (dd, 1H(b), CH_2O, $^2J_{HH}=9.6$, $^3J_{HH}=3.8$), 3.77 and 3.78 (2×t, 2H, OCH_2CH_2, $^3J_{HH}=4$), 4.28 (m, 1H, CHO), 4.34 (t, 2H, CH_2OCO, $^3J_{HH}=4$), 5.86 (dd, 1H(cis), CH_2=, $^2J_{HH}=1.3$, $^3J_{HH}=10.4$), 6.15 (dd, 1H, –CH=, $^3J_{HH}=17.3$(trans) and 10.4(cis)), 6.44 (dd, 1H(trans), CH_2=, $^2J_{HH}=1.3$, $^3J_{HH}=17.3$) ppm.

^{13}C NMR ($CDCl_3$) δ: 35.28 (t, 1C, CH_2CF_2, $^2J_{CF}=21$), 63.95 (s, 1C, CH_2OCO), 64.94 (s, 1C, CHO), 70.11 (s, 1C, OCH_2CH_2), 75.14 (s, 1C, CH_2O), 110–120 (m, 6C, CF_2 and CF_3), 128.74 (s, 1C, –CH=), 131.88 (s, 1C, CH_2=), 166.80 (s, 1C, CO_2) ppm.

^{19}F NMR ($CDCl_3$): the same as for **4a–4c**.

4.3.2. Reactions with 2-hydroxyethyl methacrylate (HEMA) (products 9a–9c)

In the same equipment as described in Section 4.2.1 (flask, 100 ml), a mixture of HEMA (66.1 g, 0.5 mol), epoxide **4a–4c** (50 mmol), boron trifluoride etherate (0.18 g, 1.27 mmol) and a stabilizer (di-tert-octylpyrocatechol (67 mg, 0.2 mmol) or hydroquinol (44 mg, 0.4 mmol)) was heated at 80 °C for 2 h with stirring (complete conversion of the epoxides). The mixture was then distilled in vacuo: the catalyst was first distilled off on a water pump, followed by unreacted HEMA (oil pump) and finally products **9a–9c** as the last fraction on a high vacuum pump (for b.p., yields, purity of products and elemental analyses, see Table 2; **9a**, 7,7,8,8,9,9,10,10,10-nonafluoro-5-hydroxy-3-oxadecyl methacrylate; **9b**, 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-hydroxy-3-oxadodecyl methacrylate; **9c**, 7,7,8,8,-9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluoro-5-hydroxy-3-oxatetradecyl methacrylate).

^1H NMR ($CDCl_3$) δ, common signals of **9a–9c**: 1.90–1.95 (t, 3H, CH_3, $^4J_{HH}=2$), 2.28 and 2.38 (2×dm, 2H, CH_2CF_2, $^2J_{HH}=19$), 2.80–2.98 (bs, 1H, OH), 3.51 and 3.62 (2×dd, 2H, CH_2O, $^2J_{HH}=9.5$, $^3J_{HH}=4$), 3.77 and 3.78 (2×t, 2H, OCH_2CH_2, $^3J_{HH}=4$), 4.27 (m, 1H, CHO), 4.28–4.33 (t, 2H, CH_2OCO, $^3J_{HH}=4$), 5.54–5.60 (q, 1H(E), CH_2=, $^4J_{HH}=2$), 6.08–6.27 (s, 1H(Z), CH_2=) ppm.

^{13}C NMR ($CDCl_3$) δ, common signals of **9a–9c**: 17.52–17.73 (s, 1C, CH_3), 34.12–34.24 (t, 1C, CH_2CF_2, $^2J_{CF}=21$), 63.21–63.27 (s, 1C, CH_2OCO), 63.81–63.94 (s, 1C, CHO), 69.03–69.11 (s, 1C, OCH_2CH_2), 74.24–74.25 (s, 1C, CH_2O), 110–120 (m, 4–8C, CF_2 and CF_3), 125.36–126.52 (s, 1C, CH_2=), 135.80–135.84 (s, 1C, C=), 167.13–167.23 (s, 1C, CO_2) ppm.

^{19}F NMR ($CDCl_3$) of **9a–9c**: the same as for **4a–4c**.

4.4. Reactions of epoxides 4a–4c with methacrylic acid (products 10a–10c and 11a–11c)

In the same equipment as described in Section 4.2.1 (flask, 100 ml), a mixture of methacrylic acid (17.22 g, 200 mmol), epoxide **4a–4c** (100 mmol), triethylamine (2.02 g, 20 mmol) and a stabilizer (di-tert-octylpyrocatechol (67 mg, 0.2 mmol) or hydroquinol (44 mg, 0.4 mmol)) was heated at 100 °C for 2 h with stirring (complete conversion of the epoxides). The mixture was then distilled in vacuo: triethylamine was first distilled off on a water pump, followed by unreacted methacrylic acid (oil pump) and finally products **10a–10c** (high vacuum pump) (contained approximately 17% (rel.) of the corresponding regioisomers **11a–11c**) (for b.p., yields, purity of products and elemental analyses, see Table 2; **10a**, 4,4,5,5,6,6,7,7,7- nonafluoro-2-hydroxyheptan-1-yl methacrylate; **10b**, 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonan-1-yl methacrylate; **10c**, 4,4,5,5,6,6,-7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-hydroxytridecan-1-yl methacrylate; **11a**, 4,4,5,5,6,6,7,7,7-nonafluoro-1-hydroxyheptan-2-yl methacrylate; **11b**, 4,4,5,5,6,6,7,7,-8,8,9,9,9-tridecafluoro-1-hydroxynonan-2-yl methacrylate; **11c**, 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-1-hydroxytridecan-2-yl methacrylate).

^1H NMR ($CDCl_3$) δ, common signals of **10a–10c**: 1.92 (d, 3H, CH_3, $^4J_{HH}=2$), 2.29 and 2.40 (2×dm, 2H, CH_2CF_2, $^2J_{HH}=19$), 3.22–3.58 (bs, 1H, OH), 4.18 and 4.20 (2×dd, 2H, CH_2O, $^2J_{HH}=9$, $^3J_{HH}=5$), 4.32–4.39 (m, 1H, CHO), 5.54–5.60 (q, 1H(E), CH_2=, $^4J_{HH}=2$), 6.07–6.13 (s, 1H(Z), CH_2=) ppm.

^{13}C NMR ($CDCl_3$) δ, common signals of **10a–10c**: 17.75–17.91 (s, 1C, CH_3), 34.51–34.68 (t, 1C, CH_2CF_2, $^2J_{CF}=21$), 63.28–63.70 (s, 1C, CHO), 67.54–67.67 (s, 1C, CH_2O), 110–120 (m, 4–8C, CF_2 and CF_3), 126.16–126.34 (s, 1C, CH_2=), 135.51–135.69 (s, 1C, C=), 167.22–167.39 (s, 1C, CO_2) ppm.

^{19}F NMR ($CDCl_3$) of **10a–10c**: the same as for **4a–4c**.

^1H NMR ($CDCl_3$) δ, common signals of **11a–11c**: 1.92 (d, 3H, CH_3, $^4J_{HH}=2$), 2.48 and 2.58 (2×dm, 2H, CH_2CF_2, $^2J_{HH}=19$), 3.22–3.58 (bs, 1H, OH), 3.73 (dm, 2H, CH_2O,

$^3J_{HH}=5$), 5.36 (m, 1H, CHO), 5.54–5.60 (q, 1H(E), CH_2=, $^4J_{HH}=2$), 6.07–6.13 (s, 1H(Z), CH_2=) ppm.

^{13}C NMR ($CDCl_3$) δ, common signals of **11a–11c**: 17.65–17.83 (s, 1C, CH_3), 31.62–31.77 (t, 1C, CH_2CF_2, $^2J_{CF}=21$), 63.10–63.56 (s, 1C, CH_2OH), 68.01–68.24 (s, 1C, CHO), 110–120 (m, 4–8C, CF_2 and CF_3), 126.25–126.47 (s, 1C, CH_2=), 135.51–135.69 (s, 1C, C=), 166.48–166.71 (s, 1C, CO_2) ppm.

^{19}F NMR ($CDCl_3$) of **11a–11c**: the same as for **4a–4c**.

4.5. Preparation of dioxolanes 12a–12c and their transformation to polyfluoroalkan-1,2-diyl bis-methacrylates 14a–14c

4.5.1. Reactions of epoxides 4a–4c with acetone (products 12a–12c)

In the same equipment as described in Section 4.2.1 (flask, 25 ml), a mixture of epoxide **4a–4c** (20 mmol), acetone (5.81 g, 100 mmol) and boron trifluoride etherate (28 mg, 0.2 mmol) was refluxed for 0.5 h with stirring (complete conversion of the epoxides). After evaporation of acetone, the residue was distilled in vacuo (oil pump) and the products **12a–12c** were distilled as the final fractions (for b.p., yields, purity of products and elemental analyses, see Table 2; **12a**, 4-(2,2,3,3,4,4,5,5,5-nonafluoropentan-1-yl)-2,2-dimethyl-1,3-dioxolane; **12b**, 4-(2,2,3,3,4,4,5,5,6,6,-7,7,7-tridecafluoroheptan-1-yl)-2,2-dimethyl-1,3-dioxolane; **12c**, 4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoroundecan-1-yl)-2,2-dimethyl-1,3-dioxolane).

^{1}H NMR ($CDCl_3$) δ, common signals of **12a–12c**: 1.38, 1.43 (2×s, 6H, $2CH_3$), 2.28, 2.55 (2×m, 2H, CH_2CF_2), 3.67, 4.19 (2×dd, 2H(a, b), CH_2O, $^2J_{HH}=8$, $^3J_{HH}=7$ or 6), 4.45 (dq, 1H, CHO, $^3J_{HH}=7$ and 6(q)) ppm.

^{13}C NMR ($CDCl_3$) δ, common signals of **12a–12c**: 26.19, 27.41 (2×s, 2C, $2CH_3$), 36.06 (t, 1C, CH_2CF_2, $^2J_{CF}=21$), 69.88 (s, 1C, CHO), 70.23 (s, 1C, CH_2O), 110.10 (s, 1C, C), 110–120 (m, 4–8C, CF_2 and CF_3) ppm.

^{19}F NMR ($CDCl_3$) of **12a–12c**: the same as for **4a–4c**.

4.5.2. Methanolysis of 4-(polyfluoroalkyl)-1,3-dioxolanes to diols 13a–13c

In the same equipment as described in Section 4.2.1 (flask, 25 ml), a mixture of dioxolane **12a–12c** (10 mmol), methanol (6.4 g, 0.200 mol) and concentrated hydrochloric acid (0.5 g) was refluxed for 2 h with stirring (complete conversion of the dioxolanes). After evaporation of methanol, the residual water, together with hydrogen chloride, was removed by azeotropic fractional distillation with toluene which was distilled off. The residue was then distilled in vacuo (oil pump) and the products **13a–13c** were distilled as the final fractions (for b.p., melting points (m.p.), yields, purity of products and elemental analyses, see Table 2; **13a**, 4,4,5,5,6,6,7,7,7-nonafluoroheptane-1,2-diol; **13b**, 4,4,5,5,-6,6,7,7,8,8,9,9,9-tridecafluorononane-1,2-diol; **13c**, 4,4,5,5,-6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecane-1,2-diol).

^{1}H NMR (DMSO-d_6) δ, common signals of **13a–13c**: 2.13, 2.43 (2×m, 2H, CH_2CF_2), 3.25, 3.40 (2×dd, 2H(a, b), CH_2O, $^2J_{HH}=10.7$, $^3J_{HH}=6.7$ or 5.1), 3.86 (m, 1H, CHO), 4.86 (bs, 1H, CH_2OH), 5.06 (d, 1H, CHO*H*, $^3J_{HH}=5$) ppm.

^{13}C NMR (DMSO-d_6) δ, common signals of **13a–13c**: 33.87 (t, 1C, CH_2CF_2, $^2J_{CF}=21$), 64.97 (s, 1C, CHOH), 65.17 (s, 1C, CH_2OH), 110–120 (m, 4–8C, CF_2 and CF_3) ppm.

^{19}F NMR (DMSO-d_6) of **13a–13c**: the same as for **4a–4c**.

4.5.3. Bis-methacrylates 14a–14c

In the same equipment as described in Section 4.2.1 (flask, 50 ml), a mixture of methacryloyl chloride (3.14 g, 30 mmol), diol **13a–13c** (5 mmol), triethylamine (3.54 g, 35 mmol), diethyl ether (30 ml) and a stabilizer (di-tert-octylpyrocatechol; 33.5 mg, 0.1 mmol) was stirred at room temperature for 2 h (complete conversion of the diols). Methanol (0.64 g, 20 mmol) was then added and the mixture was stirred for an additional hour. Water (2×50 ml) was then added slowly to the mixture in a separation funnel, the ether layer was separated, the water layer was extracted with ether (20 ml), the ether solutions were combined and were dried with magnesium sulphate. After evaporation of diethyl ether, triethylamine and methyl methacrylate were removed (water pump) and the residue was distilled on a high vacuum pump (for b.p., yields, purity of products **14a–14c** and elemental analyses, see Table 2; **14a**, 4,4,5,5,6,6,7,7,7-nonafluoroheptane-1,2-diyl bis-methacrylate; **14b**, 4,4,5,5,6,6,7,7,8,8,9,-9,9-tridecafluorononane-1,2-diyl bis-methacrylate; **14c**, 4,4,-5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecane-1,2-diyl bis-methacrylate).

^{1}H NMR ($CDCl_3$) δ, common signals of **14a–14c**: 1.94, 1.95 (2×s, 6H, $2CH_3$), 2.48 and 2.58 (2×dm, 2H, CH_2CF_2, $^2J_{HH}=19$), 4.27–4.32 (dd, 1H(a), CH_2O, $^2J_{HH}=12$, $^3J_{HH}=5$), 4.43–4.48 (dd, 1H(b), CH_2O, $^2J_{HH}=12$, $^3J_{HH}=4$), 5.58–5.62 (s, 2H(E), $2CH_2$=), 5.63–5.65 (m, 1H, CHO), 6.12, 6.13 (2×m, 2H(Z), $2CH_2$=) ppm.

^{13}C NMR ($CDCl_3$) δ, common signals of **14a–14c**: 18.54, 18.62 (2×s, 2C, $2CH_3$), 32.77–32.90 (t, 1C, CH_2CF_2, $^2J_{CF}=21$), 65.19–65.25 (s, 1C, CH_2O), 65.74–65.87 (s, 1C, CHO), 110–120 (m, 4–8C, CF_2 and CF_3), 126.84, 127.03 (2×s, 2C, $2CH_2$=), 136.31, 136.36 (2×s, 2C, 2C=), 166.53, 167.21 (2×s, 2C, $2CO_2$) ppm.

^{19}F NMR ($CDCl_3$) of **14a–14c**: the same as for **4a–4c**.

4.6. Preparation of thiiranes 15a–15c

In the equipment described in Section 4.2.1, a mixture of epoxide **4a–4c** (10 mmol), thiourea (1.52 g, 20 mmol) and methanol (15 ml) was refluxed for 4 h with stirring (complete conversion of the epoxides). After cooling to room temperature, water (30 ml) was added to the mixture and the lower oily layer was diluted with diethyl ether (50 ml),

washed with water (3×30 ml) and dried with magnesium sulphate. After filtering the drier off, the solvent was evaporated and the residue was distilled in vacuo (water pump) to yield products **15a–15c** (for b.p., yields, purity of products and elemental analyses, see Table 2; **15a**, 1-(2,2,3,3,4,4,5,5,5-nonafluoropentan-1-yl) thiirane; **15b**, 1-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-yl) thiirane; **15c**, 1-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoroundecan-1-yl) thiirane).

^{1}H NMR ($CDCl_3$) δ, common signals of **15a–15c**: 2.23 and 2.61 (2×dq, 2H, CH_2CF_2, $^2J_{HH}=16$, $^3J_{HH}=8$ or 6, $^3J_{HF}=16$), 2.23 and 2.60 (2×dd, 2H, CH_2S, $^2J_{HH}=6$, $^3J_{HH}=2$), 3.03 (ddt, 1H, CHS, $^3J_{HH}=8$, 6 and 2(t)) ppm.

^{13}C NMR ($CDCl_3$) δ, common signals of **15a–15c**: 23.91 (s, 1C, CH_2S), 24.36 (t, 1C, CHS, $^3J_{CF}=5$), 38.29 (t, 1C, CH_2CF_2, $^2J_{CF}=21$), 110–120 (m, 4–8C, CF_2 and CF_3) ppm.

^{19}F NMR ($CDCl_3$) of **15a–15c**: the same as for **4a–4c**.

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