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Fluorinated epoxides 5. Highly selective synthesis of diepoxides from α,ω-diiodoperfluoroalkanes. Regioselectivity of nucleophilic epoxide-ring opening and new amphiphilic compounds and monomers☆

Vladimír Církva, Manuel Gaboyard[1], Oldřich Paleta*

Department of Organic Chemistry, Prague Institute of Chemical Technology, Technická 5, 16628 Prague 6, Czech Republic

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Dedicated to Professor Paul Tarrant on the occasion of his 85th birthday

Abstract

An improved procedure for the radical addition of α,ω-diiodoperfluoroalkanes I–$(CF_2CF_2)_n$–I ($n = 2, 3$) to allyl acetate that afford the corresponding bis-adducts $AcOCH_2CHICH_2(CF_2CF_2)_nCH_2CHI–CH_2OAc$ (**2a–2b**) has been developed. The primary bis-adducts **2a–2b** suffered a subsequent rearrangement in the addition mixture to afford semi-rearranged adducts $AcOCH_2CHICH_2–(CF_2CF_2)_n–CH_2CH–(OAc)CH_2I$ (**3a–3b**) in an amount of ca. 15% rel. at reaction temperatures. Both adducts **2a–2b** and rearranged adducts **3a–3b** were converted to diepoxides $CH_2(–O–)CHCH_2(CF_2CF_2)_nCH_2CH–(–O–)CH_2$ (**4a–4b**) with high chemoselectivity in two ways: the selectivity of the direct epoxidation of **2a–2b** and/or **3a–3b** with potassium hydroxide was extremely dependent on the solvent; the second method included hydrolysis of **2a–2b** and/or **3a–3b** to bis-iodohydrins **5a–5b** and **6a–6b** that were easily transformed to the diepoxides **4a–4b**. Ring-opening reactions of bis-epoxides **4a–4b** with hydroxy compounds in the presence of boron trifluoride etherate took place at the terminal carbon atom of both epoxide rings with complete regioselectivity. A convenient transformation of the diepoxides to the corresponding amphiphilic tetrols (**14a–14b**) via dioxolane intermediates was accomplished with overall yields of 57–65% . Base-catalyzed ring-opening by methacrylic acid was not completely regioselective (89% terminal attack on both oxirane rings) and afforded a mixture of regioisomeric bis-methacrylates (**16a–16b** and **17a–17b**) bearing two hydroxyl groups. In contrast, epoxide ring-opening with morpholine was completely regioselective in both diepoxides **4a** and **4b**.

Keywords: Radical addition of α,ω-diiodoperfluoroalkanes; Rearrangement of α-iodoacetates; Bis-iodohydrins; Epoxidation; Nucleophilic rearrangement of fluoroalkyloxiranes; Diepoxyfluoroalkanes; Nucleophilic oxirane ring opening; Amphiphilic compounds; α,ω-Bis(2,2-dimethyl-1,3-dioxolan-4-yl)fluoroalkanes; Fluoroalkanetetrols; Dihydroxyfluoroalkane-α,ω-diyl bis-methacrylates; α,ω-Bis(morpholin-4-yl)fluoroalkanediols

1. Introduction

Some years ago, P. Tarrant had emphasized in a review [3] that fluorocarbon iodides have been useful reagents for the preparation of a variety compounds by several fundamental reactions including radical additions. Recently, N.O. Brace summarized in a recent review [4] free radical chemistry of perfluoroalkyl iodides in the synthesis of organic substances of a large variety of structures with emphasis on practical applications. Unfortunately, this review has not included a series of recent papers [5–13] from the Journal of Fluorine Chemistry which correct some previous results [5,10], improve procedures to some important synthetic intermediates [6–11,13] and extend variety of useful products for potential practical applications prepared on the basis of the radical additions [9,12,14,15]. A careful spectral analysis of the reaction mixture in additions of perfluoroalkyl iodides to allyl acetate, that were originally carried out previously [4,16–18], led to the discovery of a novel rearrangement [5,8]. The new and improved knowledge presented in the recent papers [5,8–12] were employed with advantage in this paper.

Analogously to the chemistry of perfluoroalkyl iodides [3,4], the chemistry of diiodoperfluoroalkanes can lead to a

☆ Part 1, [1]. Part 2, [2]. Part 3, [11]. Part 4, [12].

* Corresponding author. Fax: +42-2-2431-1082.
E-mail address: oldrich.paleta@vscht.cz (O. Paleta).
[1] Present address: École Nationale Supérieure de Chimie de Montpellier, 34296 Montpellier Cedex 5, France.

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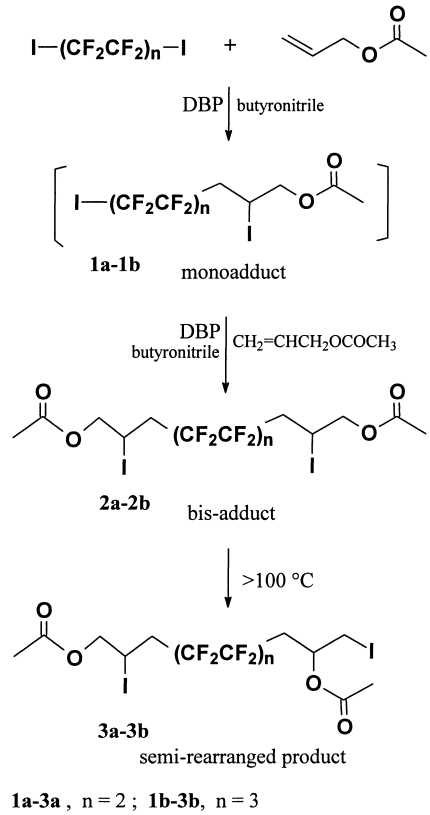
variety of mono- and bifunctional compounds, e.g. special amphiphilic compounds, substituted diols for polyesters or polyurethanes [14,15,19–21], bifunctional monomers and curing and crosslinking agents for polymers including coatings [22]. While the chemistry of perfluoroalkyl iodides has been extensively studied [4,8 and references therein], the reports on the chemistry of α,ω-diiodoperfluoroalkanes are relatively scarce. Among radical additions of the reagents to olefins, e.g. the additions to ethylene and propene [7,23], β-bromostyrene [24], vinyl acetate [25] or allyl-substituted steroide compound [26] have been published. In addition, several papers have reported additions of diiodoperfluoroalkanes to allyl acetate: the addition reaction of some α,ω-diiodoperfluoro-alkanes [16,17,25] has been described previously, but the structures of products were assigned, as usual in that time, only on the basis of elemental analyses and refractive indexes and/or boiling points; in a more recent study [7], the addition products were not purified and characterized; recently, the additions with diiodoperfluoroalkanes were described [8] in details and main and by-products were characterized. The last reaction afforded mixtures of mono- and bis-adducts. In this paper, a procedure has been developed affording almost pure bis-adducts.

Diepoxides, in which the oxirane rings are connected by a fluorinated or perfluorinated alkane-α,ω-diyl, i.e. $-(CH_2)_n(CF_2)_m(CH_2)_n-$ ($n = 0, 1$; $m = 4, 6, 8$), are quite rarely reported in the literature: the first type ($n = 0$, $m = 4$) was obtained by a several-step synthesis from perfluorodicarboxylate [27], while the second type ($n = 1$, $m = 4$) was obtained by a direct epoxidation of the bis-adduct to allyl acetate [16]. Concerning reactions of these diepoxides, we have not found any characterized compound prepared from the diepoxides.

2. Results and discussion

2.1. Radical additions of α,ω-diiodoperfluoroalkanes to allyl acetate

The reactions of diiodides $I-(CF_2)_n-I$ ($n = 4, 6$) were initiated with dibenzoyl peroxide [7,8,16]. They are stepwise processes in which mono-adducts **1a–1b** are formed initially and subsequently react with the second molecule of allyl acetate to form bis-adducts **2a–2b** (Scheme 1) [8]. The relative amount of mono- and bis-adducts can be strongly influenced by a solvent: the reaction in butyronitrile leads to almost exclusive formation of bis-adducts, while without solvent the end reaction mixture contained 25–33% of mono-adducts **1a–1b** (Table 1). In contrast to previous report [8], no 2 : 1 telomers were detected in the mixture probably owing to a lower reaction temperature and lower reactivity of relatively bigger molecules **2a–2b**. The primary adducts **1a–1b** and **2a–2b** undergo a subsequent rearrangement [5,8]. The amount of rearranged products is dependent on reaction temperature, but after some time an equilibrium is established [5]. In this study the content of semi-rear-



Scheme 1. Products of radical addition of diiodoperfluoroalkanes to allyl acetate.

Table 1
Composition of mono- and bis-adducts obtained in the radical addition of diiodoperfluoroalkanes to allyl acetate

Starting diiodide	Solvent	Conversion (%)	Composition of adducts (%)[b]						Ratio of bis-adducts **2/3** (% rel.)
			Mono-adduct		Bis-adducts				
			1		**2**		**3**		
$I-(CF_2CF_2)_2-I$	–[a]	98	**1a**	33	**2a**	67		0	
	Butyronitrile	98	**1a**	4	**2a**	82.5	**3a**	13.5	86/14
$I-(CF_2CF_2)_3-I$	–[a]	98	**1b**	25	**2b**	75		0	
	Butyronitrile	98	**1b**	2	**2b**	82.5	**3b**	15.5	84/16

[a] [8].
[b] Calculated from ^{19}F NMR spectra.

Table 2
Selectivity of the formation of epoxides **4a–4b** from diacetates **2a–2b** ($AcOCH_2CHICH_2–Q_F–CH_2CHI–CH_2OAc$), **3a–3b** or diiodohydrins **5a–5b**, **6a–6b** by potassium hydroxide in solvents

Starting compound			Solvent[a]	Time (h)	Conversion (%)	Reaction mixture composition[b] (% rel.)			Diepoxide yield (%)	
	Q_F	Purity				Diepoxide **4a–4b**	Unsaturated ester **11a–11b**	Unsaturated alcohol **9a–9b**		
2a	C_4F_8	100	Hexane	5	0	–	–	–	**4a**	0
2a	C_4F_8	100	Et_2O	5	98	25	51	24	**4a**	15
2a	C_4F_8	100	Hexane/Et_2O (1 : 1)	5	98	62	25	13	**4a**	50
2a	C_4F_8	100	Hexane/Et_2O (4 : 1)	5	99	86	9	5	**4a**	71[h]
2a	C_4F_8	86[c]	Hexane/Et_2O (4 : 1)	5	99	88	8	4	**4a**	72
2b	C_6F_{12}	100	Hexane	5	98	25	50[e]	25[e]	**4b**	10
2b	C_6F_{12}	100	Hexane/Et_2O (4 : 1)	5	99	86	9[e]	5[e]	**4b**	72[h]
2b	C_6F_{12}	84[d]	Hexane/Et_2O (4 : 1)	5	99	87	8[e]	5[e]	**4b**	72
5a	C_4F_8	100	Et_2O	0.5	98	95	–	5	**4a**	73[h]
5a	C_4F_8	86[f]	Et_2O	0.5	98	94	–	6	**4a**	74
5b	C_6F_{12}	100	Et_2O	0.5	98	95	–	5[e]	**4b**	76[h]
5b	C_6F_{12}	84[g]	Et_2O	0.5	98	94	–	6[e]	**4b**	76

[a] Mixing at room temperature.
[b] GC analyses with calibration.
[c] Isomer **3a**, 14% rel.
[d] Isomer **3b**,16% rel.
[e] The structures of **9b** and **11b** were not confirmed.
[f] Isomer **6a**, 14% rel.
[g] Isomer **6b**, 16% rel.
[h] Purity 99%.

Table 3
Optimization of the solvent mixture for epoxidation of diiododiacetates **2a–2b** and **3a–3b**

Solvent mixture	Vol. : Vol.	Reaction mixture composition (%)	
		Diepoxide **4a**	Diacetates **2a**, **3a**
Petroleum ether/diethyl ether			
	4 : 1	82	0
	5 : 1	84	0
	6 : 1	80	<1
	7 : 1	74	ca. 2
	8 : 1	66	14
Hexane/diethyl ether			
	1 : 1	62	0
	2 : 1	60	5
	3 : 1	74	0
	4 : 1	86	0
	5 : 1	67	0
	6 : 1	69	0

ranged compounds **3a–3b** was relatively low (14 and 16% rel.) owing to a lower reaction temperature and short reaction time. When the reaction was carried out below 100°C no rearranged product was observed during 1 h reaction time (Section 3.2).

2.2. Preparation of diepoxides *4a–4b* and formation of by-products *9* and *11*

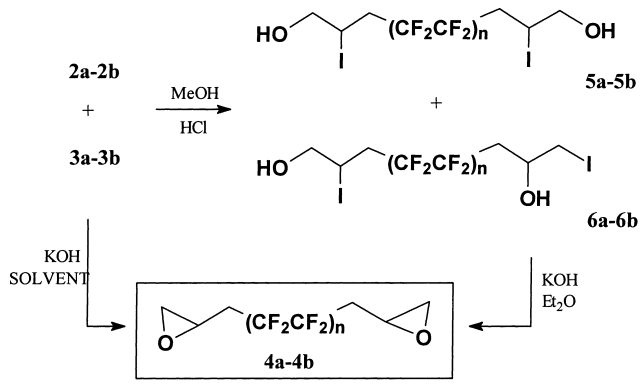
2.2.1. From diiodoalkanediyl diacetates *2a–2b* and *3a–3b*

We have reported in our recent paper [11] that the chemoselectivity of the transformation of perfluoroalkyl iodide adducts onto allyl acetate to the corresponding epoxides is extremely dependent on the solvent used. The amount of by-products formed in diethyl ether, that was found as the least convenient solvent [11], was up to 75% rel. The previous papers using this procedure [18,25] have not mentioned the formation of any amount of by-products. We have also found [11] that the chemoselectivity of epoxidation is the best in hexane giving only ca. 2% rel. of by-product. No by-products have been reported in previous papers using pentane or hexane [9,16].

We employed our experience [11] in the optimization of a solvent system for the preparation of diepoxides **4a–4b** using powdered potassium hydroxide (Tables 2 and 3, Scheme 2) that appeared to be a better base than sodium hydroxide in the epoxidations [11]. However, solvent-chemoselectivity relation appeared to be rather different from that observed in the preparation of perfluoroalkylated oxiranes on the basis of additions of perfluoroalkyl iodides [11]: diethyl ether again caused the formation of about 75% rel. of by-products **9a** and **11a** in the epoxidation, but epoxidation in hexane, the best solvent for the preparation of monoepoxides from the iodoacetates [11] gave surprisingly no product or low yield (Table 2). Therefore, a mixed solvent containing diethyl ether was optimized (Table 3). Petroleum ether and hexane as the main component appeared to be the best among other hydrocarbons, but the latter gave better chemoselectivity (Tables 2 and 3). By this methodology, the amount of the by-products **9** and **11** was reduced to about 13% rel. (Table 2), which is a more worse result than that for the preparation of monoepoxides where the relative amount of by-products was suppressed to about 2% rel. [11]. Both initial bis-adducts **2a–2b** and rearranged bis-adducts **3a–3b** were converted to the diepoxides **4a–4b** which is an analogous observation to that for the formation of monoepoxides [11].

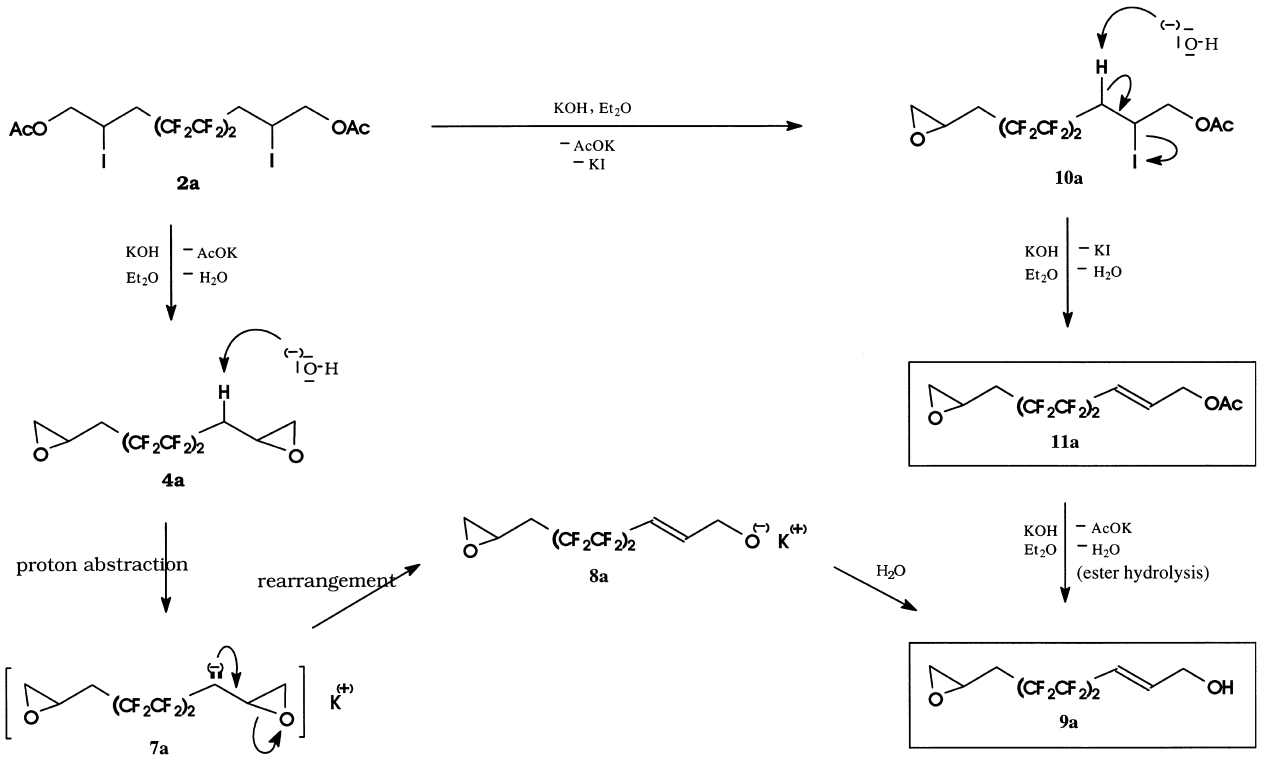
2.2.2. From diiododiols *5a–5b* and *6a–6b*

To avoid the formation of by-products and to obtain pure diepoxides, a two step synthesis of the diepoxides was accomplished. The mixtures of products **2** and **3** were first converted to the corresponding iodohydrins **5** and **6** (Scheme 2) in 84–86% preparative yields by reesterification with acidic methanol. The iodohydrins **5** and **6** (Scheme 2) were subsequently epoxidized in 64–74% preparative yields using powdered potassium hydroxide in diethyl ether, i.e. by analogous procedure previously reported [25] for the preparation of monoepoxides. By using iodohydrins **5** and **6** as



2a-6a , n = 2 ; **2b-6b** , n = 3

Scheme 2. Preparation of diepoxides **4a–4b** from bis-adducts **2a–2b** and rearranged bis-adducts **3a–3b**.



Scheme 3. Probable reaction sequence in the formation of by-products in the epoxidation of adducts **2a–2b** and **3a–3b**.

substrates instead of iodoacetates **2** and **3**, the relative amount of by-products **9** was suppressed to 5–6% rel. (Table 2) and unsaturated esters **11** were not detected in the reaction mixture at all. No unsaturated by-products were reported in the previous paper [25] for an analogous reaction.

2.2.3. *Formation of by-products **9** and **11***

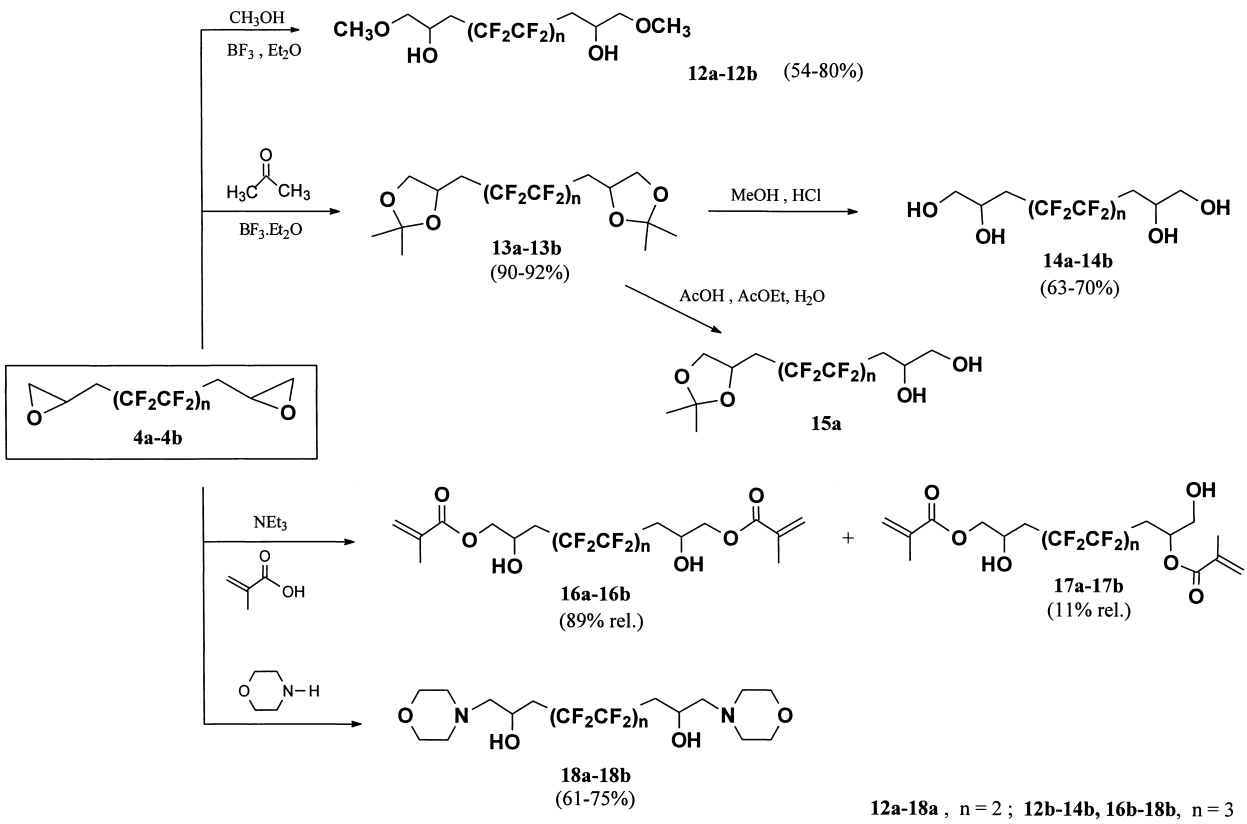
The amount of by-products **9** and **11** is strongly dependent on the substrate and solvent used (Table 3): in diethyl ether or hexane the by-products strongly dominate when diiododiacetates are used as substrates (Table 2), which is a sharp contrast to the preparation of monoepoxides from iodoacetates reported recently [11]. The amounts of by-products are strongly reduced when bis-iodohydrins **5** are employed in diethyl ether. The reason of the formation of by-products **9** and **11** (Scheme 3) is the acidity of the α-bond C–H relatively to the perfluorinated chain (for a discussion on the reactions by which the by-products are formed see the preceding paper [11]).This bond can be attacked directly in the iodoacetate **2** (as well as in rearranged adduct **3** [11]) to afford unsaturated epoxyacetate **11** that subsequently affords allylic epoxyalkenol **9** by hydrolysis. The α-bond C–H is also attacked by hydroxyl anion in the diepoxides **4** to start a rearrangement leading to epoxyalkenol **9** (Scheme 3). This subsequent side transformation of diepoxides **4** to the corresponding epoxyalkenols **9** is much slower than the formation of the diepoxides **4**, but cannot be completely suppressed in the reaction system even when bis-iodohydrins **5** are used as substrates and short reaction time applied (Table 2). Thus, unsaturated by-products generally accompany diepoxides **4** prepared by the above reactions in higher relative amount than in structurally analogous monoepoxides [11]. As the formation of the by-products was studied in our preceding paper [11], we verified the by-products only for one of the bis-adducts, i.e. **2a** (Scheme 3).

2.3. *Nucleophilic ring-opening reactions in diepoxides **4a–4b***

It has been shown in our preceding paper ([12] and references therein) that the regioselectivity of the epoxide-ring opening in 2-[(perfluoroalkyl)methyl]oxiranes is dependent on the type of a catalyst applied. Both mechanisms for acid-catalyzed (boron trifluoride etherate, magnesium perchlorate) and triethylamine-catalyzed reactions were discussed to explain different regioselectivity. As diepoxides **4a–4b** are two-fold analogues of 2-[(perfluoroalkyl)methyl]oxiranes, a similar reactivity toward nucleophiles and similar regioselectivity [12] of reactions can be expected.

2.3.1. *Acid-catalyzed ring opening, reaction with alkanols*

The reported Lewis-acid catalyzed reactions of perfluoroalkylated epoxides with hydroxy compounds have proceeded with complete regioselectivity [12,28–30]. The same result has been observed for the reactions of



Scheme 4. Nucleophilic reactions of diepoxides **4a–4b**.

diepoxides **4a–4b** with methanol in the presence of boron trifluoride etherate (Scheme 4): the oxygen of hydroxy groups attacked both terminal carbon atoms at the epoxide rings with complete regioselectivity to afford dihydroxy bis-ethers **12a–12b**; no regioisomers were found in the reaction mixtures by ^{19}F NMR (the sensitivity of the method is about 1% rel. [31,32]. α,ω-Dialkoxydiols **12a–12b** can further be transformed to bifunctional monomers as bis-(meth)-acrylates [9,12,14] or used directly for poly(urethanes), bis-(meth)acrylates etc. As the ring opening in the diepoxides **4a–4b** can be performed with monohydroxy compounds of different structure ([12] and references therein), e.g. oligoethylene glycol monoalkyl ethers or hydroxyalkyl (meth)acrylates [12], the synthesis that starts from α,ω-diiodoperfluoroakanes can afford a number of interesting compounds for various practical applications including hydrophilic biocompatible polymers.

2.3.2. *Transformation to tetrols **14a–14b***

We have recently developed a novel method for the transformation of fluoroalkylated epoxides to the corresponding vicinal diols [12,14,15], because the yields of the direct acid-catalyzed reaction or were not very satisfactory [28,33,34], or required special conditions [35–38]. In this method, the epoxides **4a–4b** were first transformed to the corresponding bis-1,3-dioxolanyl derivatives **13a–13b** by acid-catalyzed reaction with acetone [12] in 90–92% yields and subsequently re-acetalized with methanol and hydrochloric acid to tetrols **14a–14b** in 63–70% preparative yields. The tetrols **14a–14b** can be applied for the preparation of new dendrimeric compounds, or as crosslinking agents for polymers. Heating of bis-dioxolanyl derivative **13a** in wet ethyl acetate caused partial hydrolysis to dioxolanyldiol **15a**.

2.3.3. *Ring opening in the presence of a base and with morpholine, preparation of amphiphilic bis-methacrylates **16** and **17***

It has been known [12] that the nucleophilicity of hydroxylic oxygen in (meth)acrylic acids is low to cause a ring opening in perfluoroalkyl epoxides under acid catalysis. A similar reactivity was observed for non-fluorinated epoxides, where tertiary amines were used as catalysts [39–41]. In the case of fluoroalkyl epoxides, the ring opening was performed in the presence of potassium methacrylate [42,43], triphenylphosphane [42,43] or triethylamine [12,44]. Before base-catalyzed ring opening the reaction was not regioselective with 10–17% rel. of the inner carbon attack [12,42–44]. According to the previous experience, we used triethyl amine as a catalyst for the ring opening. As previously observed for monoepoxides [12,42–44], the ring opening in the diepoxides **4a–4b** was also not completely regioselective (Scheme 4): the attack of the terminal carbons occurred from 89% rel. to afford major regioisomers

16a–16b. The attack at the inner carbon atom (11% rel., products **17a–17b**) has been previously explained in the terms of the HSAB concept [12]. Thus, base-catalyzed ring opening of fluoroalkylated epoxides [12] or diepoxides prepared by the addition to allyl acetate or allylic alcohol afford mixture of the corresponding amphiphilic methacrylates [12] or bis-methacrylates with the regioisomers formed by the terminal attack highly prevailing (83–90% rel.). Amphiphilic bis-methacrylates as mixtures of **16a–16b** and **17a–17b** can be used as special crosslinking agents including hydrophilic biocompatible copolymers.

In contrast to (meth)acrylate quasi-oxyanions acting in the above epoxide ring-opening reactions [12], morpholine possessing a strongly nucleophilic nitrogen reacted with complete regioselectivity: the nucleophilic attack occurred at the both terminal carbon atoms in diepoxides **4a–4b** to afford dihydroxylated bis-morpholinyl **18a–18b** (Scheme 4). The same regioselectivity has been reported [9] for the analogous reaction of morpholine with 2-[(perfluoroalkyl)-methyl]oxiranes. The different regioselectivity in ring-opening reactions of oxyanions and secondary amines can be caused by different hardness of these two nucleophilic centers, nitrogen being a softer nucleophile, as discussed in our preceding paper [12].

3. Experimental details

3.1. General comments

Boiling points were not corrected. GC analyses were performed on Micromat HRGC 412 (Nordion Analytical; 25 m glass capillary column, SE-30) and a Chrom 5 instrument (Laboratorní pøístroje, Prague; FID, 380 cm × 0.3 cm column packed with silicon elastomer E-301 on Chromaton N-AW-DMCS (Lachema, Brno); nitrogen was used as carrier gas, detector/injector temperatures were 260/255°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 $CDCl_3$.

The chemicals used were as follows: silica gel L40/100 (Merck); potassium hydroxide pellets were ground to powder before use; boron trifluoride etherate (Lachema) was distilled before use; 1,4- and 1,6-diiodoperfluoroalkanes were obtained from Asahi Glass Co., Japan, and were worked-up with alkaline thiosulphate solution; dibenzoyl peroxide (Fluka) was precipitated from its chloroform solution by methanol and dried in vacuo; 2,2-diphenyl-1-picrylhydrazyl (Aldrich); allyl acetate (Aldrich), butyronitrile (Aldrich) and were used without purification; triethylamine (Aldrich) was distilled before use (88–89°C); diethyl ether was dried with sodium and distilled over sodium; hexane (Fluka) and morpholine (Lachema) was distilled prior to use and stored over molecular sieves; methacrylic acid (Aldrich); petroleum ether, chloroform, methanol, acetone and toluene were purified according to standard procedures [45].

3.2. General procedure for the radical addition of diiodoperfluoroalkanes to allyl acetate

The reactions were carried out in a two-necked round-bottom flask (250 ml) equipped with a long reflux condenser and magnetic spinbar on a oil bath.

Method A: The flask was charged with a mixture of diiodoperfluoroalkane, allyl acetate and butyronitrile that was heated up to ca. 115°C. Then, dibenzoyl peroxide was added portionwise to the mixture through the neck and heating was stopped. A slight foam at the mixture surface appeared indicating start of the reaction, by which the temperature in flask increased up to 125°C. The amber solution became clear after 5 min reaction indicating almost completion of the reaction. The mixture was stirred for 30 min until the temperature fell down to 90°C. Volatile components were distilled off in vacuum by oil pump (0.5 mm Hg, 130°C bath temperature) to afford crude product consisting of compounds **1**, **2** and **3** (Table 1). For analytical purposes and further transformations, the mono-adducts **1** and di-adducts **2** and **3** were separated by simple column chromatography (silica gel; hexane, chloroform).

Method B: The same reactants as in Method A, but without butyronitrile as a solvent, were used and the reaction was carried out according to [8]. The mixture was warmed up to ca. 90°C and the peroxide was added in several portions to keep reaction temperature below 100°C during 1 h reaction time. After removing volatile components as above, the crude product contained compounds **1** and **2** (Table 1), which were easily separated by simple column chromatography (see Method A).

3.2.1. From 1,4-diiodoperfluorobutane

Method A: 1,4-Diiodoperfluorobutane (68.1 g, 0.15 mol), allyl acetate (30 g, 0.3 mol), dibenzoyl peroxide (1.81 g, 7.5 mmol), butyronitrile (31.1 g, 0.45 mol). On the conversion of 98%, the crude product consisted of a mixture of mono-adduct **1a** (4%) and diadducts **2a** and **3a** (96%, Table 1), yield 94.7 g (95%).

2,7-Diiodo-4,4,5,5,6,6,7,7-octafluoroheptyl acetate (**1a**): for ^{1}H and ^{19}F NMR and MS spectra see [8].

(2,9-Diiodo-4,4,5,5,6,6,7,7-octafluorodecane-1,10-diyl) diacetate (**2a**, ca. 86% rel.): for ^{1}H and ^{19}F NMR and MS spectra see [8].

(2,10-Diiodo-4,4,5,5,6,6,7,7-octafluorodecane-1,9-diyl) diacetate (**3a**, ca. 14% rel.) [$CH_3COOCH_2CHICH_2(CF_2)_4$-$CH_2CH(OCOCH_3)CH_2I$]: ^{1}H NMR ($CDCl_3$) δ: 2.07, 2.10 (2s, 6H, CH_3); 2.40–2.60 (m, 2H, CH_2CF_2); 3.25–3.45 (m,

2H, CH_2I); 4.20–4.35 (m, 2H, CH_2O); 4.35–4.50 (m, 1H, CHI); 5.12 (m, 1H, CHO) ppm.

^{19}F NMR ($CDCl_3$): The same spectrum as for **2a**.

3.2.2. From 1,6-diiodoperfluorohexane

Method A: 1,6-Diiodoperfluorohexane (68.1 g, 0.12 mol), allyl acetate (30 g, 0.3 mol), dibenzoyl peroxide (1.81 g, 7.5 mmol), butyronitrile (31.1 g, 0.45 mol). On the conversion of 98%, the crude product consisted of a mixture of mono-adduct **1b** (2%) and diadducts **2b** and **3b** (98%, Table 1), yield 88.4 g (92%).

2,9-Diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorononyl acetate (**1b**): for ^1H and ^{19}F NMR and MS spectra see [8].

(2,11-Diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane-1,12-diyl) diacetate (**2b**, ca. 84% rel.): for ^1H and ^{19}F NMR and MS spectra see [8].

(2,12-Diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane-1,11-diyl) diacetate (**3b**, ca. 16%) [CH_3COOCH_2-$CHICH_2(CF_2)_6CH_2CH(OCOCH_3)CH_2I$]: ^1H NMR ($CDCl_3$) δ: 2.07, 2.10 (2s, 6H, CH_3); 2.60–3.00 (m, 2H, CH_2CF_2); 4.20–4.35 (m, 2H, CH_2O); 4.35–4.50 (m, 1H, CHI) ppm. ^{19}F NMR ($CDCl_3$) δ: −113.75 (m, 4F, CF_2CH_2); −122.07 (m, 4F, $CH_2C_2F_4\mathit{CF}_2$); −123.93 (m, 4F, $CH_2CF_2\mathit{CF}_2$) ppm.

*3.3. Preparation of diepoxides **4a–4b** from diacetates **2a–2b**and **3a–3b***

*3.3.1. From individual non-rearranged diacetates **2a–2b** by reaction with potassium hydroxide in solvents (Table 2)*

A round-bottom flask (500 ml) was charged with diacetate **2a** or **2b** (13.1 or 15.1 g, respectively; 0.02 mol), powdered potassium hydroxide (5.6 g, 0.10 mol), hexane (200 ml) and diethyl ether (50 ml). The heterogenous mixture was refluxed while stirring by mechanic stirrer with spirals from stainless wire for 5 h (conversion 99%). Then, the mixture was filtered, solvents were evaporated on rotary evaporator, and yield of pure diepoxides (or, respectively) were obtained by distillation on oil pump: **4a**, 5.4 g (86%), purity 99%. bp 90–92°C/0.5 mm Hg (lit. value [16]: 110–112°C/5 mm Hg); **4b**: 7.1 g (85%), bp 104–106°C/0.5 mm Hg, purity 99%. The distillation residue also contained unsaturated by-products. In the reaction of the starting diacetate **2a** the following by-products were isolated and identified as mixtures of *cis* and *trans* isomers: epoxy-acetate **11a** (0.6 g, 9% rel., bp 81–83°C/0.1 mm Hg, purity 98%) and epoxy-alcohol **9a** (0.3 g, 5% rel., bp 75–78°C/0.2 mm Hg, purity 98%). In the case of diacetate **2b** the by-products epoxy-alcohol **9b** (11,12-epoxy-4,4,5,5,6,6,7,7,-8,8,9,9-dodecafluorododec-2-en-1-ol) and epoxy-acetate **11b** [(11,12-epoxy-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododec-2-ene-1-yl) acetate] were not isolated and their structures were approximately assigned on the basis of NMR spectra of reaction mixture (and their similarity with **9a**, **11a**) and similarity of gas chromatograms with the mixture of products in the reaction of **2a**.

*3.3.2. From mixtures of diacetates **2a–2b** and rearranged diacetates **3a–3b** (14 and 16% rel.) by reaction with potassium hydroxide in solvents*

Preparative reactions: The reactions were performed in the same manner as in Section 3.3.1. For results see Table 2.

Optimization of the solvent mixture for epoxidations: A round-bottom flask (50 ml) was charged with a mixture of diacetates **2a** and **2b** (1.31 g, 2 mmol), powdered potassium hydroxide (0.6 g, 10 mmol) and solvent (25 ml). The heterogenous mixture was refluxed while stirring by mechanic stirrer with spirals from stainless wire for 5 h. Then, the mixture was filtered, solvents were evaporated on rotary evaporator and the residue was analyzed by GC (for results see Table 3).1,2;9,10-Diepoxy-4,4,5,5,6,6,7,7-octafluorodecane (**4a**) [$(CH_2(O)CHCH_2CF_2CF_2)_2$]: Analysis — Found: C, 38.0; H, 3.30; F, 48.8%. $C_{10}H_{10}F_8O_2$, requires: C, 38.23; H, 3.21; F, 48.38%; M, 314.2.

^1H NMR ($CDCl_3$) δ: 2.1–2.45 (m, 2H, CH_2CF_2); 2.55 (dd, H_A, CH_2O, $^2J_{HH} = 5$, $^3J_{HH} = 2$); 2.83 (t, H_B, CH_2O, $^2J_{HH} = {}^3J_{HH} = 4$); 3.17–3.21 (m, 1H,CHO) ppm.

^{13}C NMR ($CDCl_3$) δ: 35.19 (t, CH_2CF_2,$^2J_{CF} = 22$); 44.82 (t, $CHCH_2CF_2$, $^2J_{CF} = 5$); 45.75 (s, CH_2O) ppm.^{19}F NMR ($CDCl_3$) δ: −112.99 (m, 4F, CF_2CH_2); −123.89 (m, 4F, $CH_2CF_2CF_2$) ppm. 1,2;11,12-Diepoxy-4,4,5,5,6,6,7,7,8,8,-9,9-dodecafluorododecane (**4b**) [$(CH_2(O)CHCH_2CF_2CF_2$-$CF_2)_2$]: Analysis — Found: C, 34.4; H, 2.52; F, 55.3%. $C_{12}H_{10}F_{12}O_2$, requires: C, 34.80; H, 2.43; F, 55.04%; M, 414.2.

^1H NMR ($CDCl_3$) δ: 2.10–2.45 (m, 2H, CH_2CF_2); 2.52 (dd, H_A, CH_2O, $^2J_{HH} = 5$, $^3J_{HH} = 2$); 2.81 (t, H_B, CH_2O, $^2J_{HH} = {}^3J_{HH} = 4$); 3.13–3.21 (m, 1H, CHO) ppm.

^{19}F NMR ($CDCl_3$) δ: −113.83 (m, 4F, CF_2CH_2); −122.12 (m, 4F, $CH_2C_2F_4CF_2$); −124.04 (m, 4F, $CH_2CF_2CF_2$) ppm.

9,10-Epoxy-4,4,5,5,6,6,7,7-octafluorodec-2-en-1-ol (**9a**) [$CH_2(O)CHCH_2CF_2CF_2$-CF_2CF_2CH=$CHCH_2OH$]: Analysis — Found: C, 38.1; H, 3.2; F, 48.5%. $C_{10}H_{10}F_8O_2$, requires: C, 38.23; H, 3.21; F, 48.38%; M, 314.18.

trans isomer (89% rel.): ^1H NMR ($CDCl_3$) δ: 2.02 (s, 3H, CH_3); 2.10–2.40 (m, 2H, CH_2CF_2); 2.52 (q, 2H, CH_2O); 2.79 (s, 1H,OH); 3.15 (m, 1H, CHO); 4.21 (m, 2H, CH_2OH); 6.30–6.38 (m, H_A, CH=CH); 6.38–6.45 (m, H_B, CH=CH) ppm. ^{13}C NMR ($CDCl_3$) δ: 35.09 (t, CH_2CF_2, $^2J_{CF} = 22$); 44.80 (t, CHO, $^3J_{CF} = 5$); 45.60 (s, CH_2O); 60.88 (s, CH_2OH); 141.09 (t, $CHCF_2$, $^2J_{CF} = 22$ Hz); 170.16 (s, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ: −108.25 (m, 1F, CF_2CH); −112.20 (m, 1F, CF_2CH); −112.90 (m, 2F, CF_2CH_2); −113.15 (m, 2F, CF_2CH_2); −123.86 (m, 4F, $CH_2CF_2CF_2$) ppm.

cis isomer (11% rel.): ^1H NMR ($CDCl_3$) δ: 2.02 (s, 3H, CH_3); 2.10–2.40 (m, 2H, CH_2CF_2); 2.52 (q, 2H, CH_2O); 2.79 (s, 1H, OH); 3.15 (m, 1H, CHO); 4.35 (m, 2H, CH_2OH); 6.49 (m, 2H, CH=CH) ppm. ^{13}C NMR ($CDCl_3$) δ: 20.21 (s, CH_3); 35.09 (t, CH_2CF_2,$^2J_{CF} = 22$); 44.80 (t, CHO,$^3J_{CF} = 5$); 45.60 (s, CH_2O); 61.92 (s, CH_2OAc); 144.50 (t, $CHCF_2$, $^2J_{CF} = 22$ H); 170.16 (s, C=O) ppm. ^{19}F NMR ($CDCl_3$): the same as for the *trans* isomer.

(9, 10-Epoxy-4, 4, 5, 5, 6, 6, 7, 7-octafluorodec-2-ene-1-yl) acetate (**11a**) [$CH_2(O)CHCH_2CF_2CF_2CF_2CF_2CH$=CH-$CH_2OCOCH_3$]: Analysis — Found: C, 40.4; H, 3.43; F, 43.0%. $C_{12}H_{12}F_8O_3$, requires: C, 40.46; H, 3.40; F, 42.67%; M, 356.2.

trans isomer (81% rel): ^{1}H NMR ($CDCl_3$) δ: 2.05 (s, 3H, CH_3); 2.10–2.40 (m, 2H, CH_2CF_2); 2.79 (q, 2H, CH_2O); 3.15 (m, 1H, CHO); 4.65 (m, 2H, CH_2OAc); 5.70–6.00 (m, 2H, CH=CH) ppm. ^{13}C NMR ($CDCl_3$) δ: 20.21 (s, CH_3); 35.09 (t, CH_2CF_2, $^2J_{CF} = 22$); 44.80 (t, CHO, $^3J_{CF} = 5$); 45.60 (s, CH_2O); 61.92 (s, CH_2OAc); 135.46 (t, $CHCF_2$, $^2J_{CF} = 22$); 170.16 (s, C=O) ppm. ^{19}F NMR ($CDCl_3$) δ: −108.90 (m, 1F, CF_2CH); −112.90 (m, 1F, CF_2CH_2); −113.15 (m, 2F, CF_2 CH_2); −123.86 (m, 4F, $CH_2CF_2CF_2$) ppm.

cis isomer (19% rel.): ^{1}H NMR ($CDCl_3$) δ: 2.05 (s, 3H, CH_3); 2.10–2.40 (m, 2H, CH_2CF_2); 2.79 (q, 2H, CH_2O); 3.15 (m, 1H, CHO); 4.80 (m, 2H, CH_2OAc); 6.05–6.20 (m, 2H, CH=CH) ppm. ^{13}C NMR ($CDCl_3$) δ: 20.21 (s, CH_3); 35.09 (t, CH_2CF_2, $^2J_{CF} = 22$); 44.80 (t, CHO, $^3J_{CF} = 5$); 45.60 (s, CH_2O); 61.92 (s, CH_2OAc); 138.58 (t, $CHCF_2$, $^2J_{CF} = 22$); 170.16 (s, C=O) ppm. ^{19}F NMR ($CDCl_3$): the same as for the *trans* isomer.

*3.4. Preparation of diepoxides **4a–4b** from diiodohydrins **5a–5b** and **6a–6b** (Table 2)*

*3.4.1. Preparation of diiodohydrins **5a–5b** and **6a–6b** from mixtures of diacetates **2a–2b** and rearranged diacetates **3a–3b** (14 and 16% rel.) by acid reesterification with methanol*

*3.4.1.1. Diiodo-4,4,5,5,6,6,7,7-octafluorodecanediols (**5a** and **6a**).* A mixture of diiododiacetates **2a** and **3a** (86 and 14% rel. 13.1 g, 20 mmol), methanol (39.5 g, 1.2 mol) and concentrated hydrochloric acid (4 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 mm Hg) on a distillation apparatus with oil pump to give almost pure mixture (ca. 97%) of **5a** and **6a** in an yield of 9.25 g (86%) was obtained. For analytical purposes the mixture of products was purified by column chromatography (silica gel, toluene/methylene chloride).

Analysis (**5a** and **6a**) — Found: C, 21.2.1; H, 2.24; I, 44.1%. $C_{10}H_{12}F_8I_2O_2$, requires: C, 21.07; H, 12.08; I, 44.51%; M, 570.0.

2, 9-Diiodo-4, 4, 5, 5, 6, 6, 7, 7-octafluorodecane-1,10-diol (86% rel., **5a**) [$(HOCH_2CHICH_2$–$CF_2CF_2)_2$]: ^{1}H NMR ($CDCl_3$) δ: 2.57 (s, 1H, OH); 2.60–2.87 (m, 1H, CH_2CF_2); 2.87–3.10 (m, 1H, CH_2CF_2); 3.80 (m, 2H, CH_2O); 4.40 (m, 1H, CHI) ppm. ^{19}F NMR ($CDCl_3$) δ: −113.54 (m, 4F, CF_2CH_2); −123.89 (m, 4F, $CH_2CF_2CF_2$) ppm.

2, 10-Diiodo-4, 4, 5, 5, 6, 6, 7, 7-octafluorodecane-1,9-diol (14% rel., **6a**) ($HOCH_2CHICH_2$–$(CF_2)_4CH_2CHOHCH_2I$): ^{1}H NMR ($CDCl_3$) δ: 2.30–2.60 (2m, 2H, CH_2CF_2); 2.57 (s, 1H, OH); 2.60–2.87 (m, 1H, CH_2CF_2); 2.87–3.10 (m, 1H, CH_2CF_2); 3.31 (dd, H_A, CH_2I, $^2J_{HH} = 10$ Hz, $^3J_{HH} = 6$ Hz); 3.42 (dd, H_B, CH_2I, $^2J_{HH} = 10$ Hz, $^3J_{HH} = 4$ Hz); 3.80 (m, 2H, CH_2O); 4.00–4.10 (m, 1H, CHO); 4.40 (m, 1H, CHI) ppm. ^{19}F NMR ($CDCl_3$) δ: the same as for **5a**.

*3.4.1.2. Diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecanediols (**5b** and **6b**).* The same procedure as in Section 3.4.1.1 was used; a mixture of diiododiacetates **2b** (84% rel.) and **3b** (15.1 g, 20 mmol) was reacted. The mixture of products **5b** and **6b** (purity ca. 96%) was obtained in an yield of 10.2 g (85%). For analytical purposes the mixture of products was purified by column chromatography (silica gel, toluene/methylene chloride).

Analysis (**5b** and **6b**) — Found: C, 21.8.1; H, 1.83; F, 34.7; I, 38.0%. $C_{12}H_{12}F_{12}I_2O_2$, requires: C, 21.51; H, 1.80; F, 34.0; I, 37.9%; M, 670.0.2,11-Diiodo-4,4,5,5,6,6,7,7,8,-8,9,9-dodecafluorododecane-1,12-diol (84% rel., **5b**) [$(HOCH_2CHICH_2CF_2CF_2CF_2)_2$]: ^{13}C NMR ($CDCl_3$) δ: 22.68 (s, CHI); 38.30 (t, CH_2Q_F, $^2J_{CF} = 21$ Hz); 68.64 (s, CH_2O) ppm. ^{1}H NMR ($CDCl_3$) δ: 2.15 (s, 1H, OH); 2.69–2.84 (m, 1H, CH_2CF_2); 2.93–3.08 (m, 1H, CH_2CF_2); 3.78 (dd, H_A, CH_2O, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 5$ Hz); 3.83 (dd, H_B, CH_2O, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 5$ Hz); 4.44 (kv, 1H, CHI) ppm. ^{19}F NMR ($CDCl_3$) δ: −113.83 (m, 4F, CF_2CH_2); −122.12 (m, 4F, $CH_2C_2F_4CF_2$); −124.04 (m, 4F, $CH_2CF_2CF_2$) ppm.1,12-Diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane-2,11-diol (16% rel., **6b**) ($HOCH_2CHICH_2(CF_2)_6CH_2CHOH$-$CH_2I$): ^{13}C NMR ($CDCl_3$) δ: 14.76 (s, CH_2I); 38.30 (t, CH_2Q_F, $^2J_{CF} = 21$ Hz); 65.45 (s, CHO); 68.64 (s, CH_2O) ppm. ^{1}H NMR ($CDCl_3$) δ: 2.15 (s, 1H, OH); 2.30–2.50 (m, 2H, CH_2CF_2); 3.32–3.40 (m, 1H, CH_2I); 4.05–4.12 (m, 1H, CHO); 4.44 (q, 1H, CHI) ppm. ^{19}F NMR ($CDCl_3$) δ: the same as for **5b**

*3.4.2. Preparation of diiodohydrins **5a–5b** from diacetates **2a–2b** by acid reesterification with methanol (Table 2)*

*3.4.2.1. 2,9-Diiodo-4,4,5,5,6,6,7,7-octafluorodecane-1,10-diol (**5a**).* The same procedure as in Section 3.4.1.1 was applied; a mixture of diiododiacetate **2a** (4.6 g, 7 mmol), methanol (13.2 g, 0.4 mol) and concentrated hydrochloric acid (2 drops) was refluxed for 6 h when the conversion was ca. 98% (checked by GC). After removing volatile components, almost pure mixture (ca. 95%) of **5a** in an yield of 3.05 g (83%) was obtained. For analytical purposes the product was purified by column chromatography (silica gel, toluene/methylene chloride).

*3.4.2.2. 1,12-Diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane-2,11-diol (**5b**).* The same procedure as in Section 3.4.2.1 was applied; a mixture of diiododiacetate **2b** (5.1 g, 6.8 mmol), methanol (13.2 g, 0.4 mol) and concentrated hydrochloric acid (2 drops) was refluxed for 6 h when the conversion was ca. 98% (checked by GC). After removing volatile components, almost pure mixture (ca. 95%) of **5b** in an yield of 3.25 g (82%) was obtained.

For analytical purposes the product was purified by column chromatography (silica gel, toluene/methylene chloride).

*3.4.3. Preparation of diepoxides **4a–4b** from diiodohydrins **5a–5b** and **6a–6b** by reaction with potassium hydroxide (Table 2)*

*3.4.3.1. 1,2;9,10-diepoxy-4,4,5,5,6,6,7,7-octafluorodecane (**4a**).* In a round-bottom flask equipped with a reflux condenser with a drying tube, a mixture of diiodohydrins **5a** (86% rel.) and **6a** (2.2 g, 4 mmol), powdered potassium hydroxide (1.2 g, 0.02 mol) and diethyl ether (20 ml) was refluxed while stirring intensively with magnetic spinbar for 30 min when the conversion was ca. 98% (checked by GC). After filtration, the ether was removed from the filtrate under reduced pressure and the residue was distilled in vacuum to afford diepoxide **4a** in an yield of 0.95 g (74%), bp 88–90°C/0.5 mm Hg, which contained unsaturated alcohol **11a** (ca. 6%, GC and ^{19}F NMR).

*3.4.3.2. 1,2;11,12-Diepoxy-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane (**4b**).* The same procedure as above [diiodohydrins **5b** (84% rel.) and **6b** (2.92 g, 4 mmol)] was applied to obtain diepoxide **4b** in an yield of 1.16 g (66%), bp 103–105°C/0.5 mm Hg, which contained unsaturated alcohol **11b** (ca. 6%, GC and ^{19}F NMR).

*3.4.4. Preparation of diepoxides **4a–4b** from diiodohydrins **5a–5b** by reaction with potassium hydroxide (Table 2)*

The same procedures and same amounts of reactants were employed as in Section 3.4.3. For results see Table 2.

*3.5. Ring opening of diepoxides **4a** and **4b** with methanol (products **12a** and **12b**)*

*3.5.1. 1,10-dimethoxy-4,4,5,5,6,6,7,7-octafluorodecane-2,9-diol (**12a**)*

In a round-bottom flask equipped with a reflux condenser with a drying tube ($MgSO_4$), a mixture of diepoxide **4a** (0.325 g, 1.03 mmol), methanol (7.9 g, 0.25 mol) and boron trifluoride etherate (2 drops) was refluxed while stirring intensively with magnetic spinbar for 4 h when the conversion was complete (checked by GC). After evaporation of methanol on rotary evaporation, crude **12a** as a white solid was obtained that was dissolved in boiling toluene and precipitated with petroleum ether to afford pure dimethoxydiol **12a** in an yield of 0.21 g (54%), mp 87–89°C. Analysis — Found: C, 37.8; H, 4.70; F, 39.7%. $C_{12}H_{18}F_8O_4$, requires: C, 38.10; H, 4.80; F, 40.16%; M, 378.25. ^{13}C NMR ($CDCl_3$) δ: 35.42 (t, CH_2CF_2, $^2J_{CF} = 21$ Hz); 59.75 (s, CH_3O); 64.68 (s, CHO); 76.64 (s, CH_2O) ppm. ^{1}H NMR ($CDCl_3$) δ: 2.20–2.40 (2m, 2H, CH_2CF_2); 2.76 (s, 1H, OH); 3.37 (dd, H_A, CH_2O, $^2J_{HH} = 10$ Hz, $^3J_{HH} = 6.5$ Hz); 3.41 (s, 3H, CH_3); 3.48 (dd, H_B, CH_2O, $^2J_{HH} = 10$ Hz, $^3J_{HH} = 4$ Hz); 4.26 (m, 1H, CHO) ppm. ^{19}F NMR ($CDCl_3$) δ: −113.33 (m, 4F, CF_2CH_2); −124.06 (m, 4F, $CH_2CF_2CF_2$) ppm.

*3.5.2. 1,12-Dimethoxy-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane-2,11-diol (**12b**)*

The same procedure as in Section 3.5.1 was applied; diepoxide **4b** (0.434 g, 1.05 mmol), boron trifluoride etherate (4 drops). With the complete conversion of the starting diepoxide and after precipitation from toluene solution the product **12b** was obtained in an yield of 0.40 g (80%), mp 90–92°C. Analysis — Found: C, 34.8; H, 3.70; F, 48.0%. $C_{14}H_{18}F_{12}O_4$, requires: C, 35.15; H, 3.79; F, 47.65%; M, 478.3. ^{13}C NMR ($CDCl_3$) δ: 35.43 (t, CH_2CF_2, $^2J_{CF} = 21$ Hz); 59.84 (s, CH_3O); 64.92 (s, CHO); 76.53 (s, CH_2O) ppm. ^{1}H NMR ($CDCl_3$) δ: 2.20–2.40 (2m, 2H, CH_2CF_2); 2.47 (s, 1H, OH); 3.40 (dd, H_A, CH_2O, $^2J_{HH} = 9.5$ Hz, $^3J_{HH} = 6$ Hz); 3.42 (s, 3H, CH_3); 3.50 (dd, H_B, CH_2O, $^2J_{HH} = 9.5$ Hz, $^3J_{HH} = 4$ Hz); 4.29 (m, 1H, CHO) ppm. ^{19}F NMR ($CDCl_3$) δ: −113.22 (m, 4F, CF_2CH_2); −122.12 (m, 4F, $CH_2C_2F_4CF_2$); −124.18 (m, 4F, $CH_2CF_2CF_2$) ppm.

*3.6. Transformation of diepoxides **4a** and **4b** to bis-dioxolanyl derivatives (products **13a–13b**)*

*3.6.1. Reaction of 1,2;9,10-diepoxy-4,4,5,5,6,6,7,7-octafluorodecane (**4a**) with acetone (product **13a**)*

In a round-bottom flask equipped with a reflux condenser with a drying tube ($MgSO_4$), a mixture of diepoxide **4a** (0.347 g, 1.10 mmol), acetone (10 ml), and boron trifluoride etherate (4 drops) was refluxed while stirring intensively with magnetic spinbar for 1 h when the conversion was ca. 98% (checked by GC). Then, acetone and volatile components were removed on rotary evaporator and crude product **13a** as a white solid was obtained (0.45 g, 94%). Recrystallization of this product was unsuccessful. For analytical purposes, **13a** was purified by simple column chromatography (silica gel; hexane, chloroform), mp 62–65°C.

An attempt of recrystallization in boiling ethyl acetate led to the formation of dioxolanyldiol **15a**, mp 95–97°C. The partial hydrolysis of the starting **13a** was caused by traces of water and acetic acid in ethyl acetate.

1,6-Bis(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2,3,3,4,4,5,5-octafluorohexane (**13a**): Analysis — Found: C, 40.2; H, 5.37; F, 36.1%. $C_{16}H_{22}F_8O_4$, requires: C, 40.65; H, 5.15; F, 35.30%; M, 430.3. ^{13}C NMR (DMSO) δ: 25.52, 26.55 (2s, CH_3); 34.31 (t, CH_2Q_F, $^2J_{CF} = 21$ Hz); 68.48 (s, CH_2O); 68.67 (s, CHO); 108.72 (s, C) ppm. ^{1}H NMR (DMSO) δ: 1.29, 1.34 (2s, 6H, CH_3); 2.30–2.60 (m, 2H, CH_2CF_2); 3.63 (dd, H_A, CH_2O, $^2J_{HH} = 8$ Hz, $^3J_{HH} = 7$ Hz); 4.09 (dd, H_B, CH_2O, $^2J_{HH} = 8$ Hz, $^3J_{HH} = 6$ Hz); 4.37 (kv, 1H, CHO) ppm. ^{19}F NMR (DMSO) δ: −112.01 (m, 4F, CF_2CH_2); −123.00 (m, 4F, $CH_2CF_2CF_2$) ppm

8-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4,4,5,5,6,6,7,7-octafluorooctane-1,2-diol (**15a**). Analysis — Found: C, 39.6; H, 4.37; F, 39.4%. $C_{13}H_{18}F_8O_4$, requires: C, 40.00; H, 4.65; F, 38.93%; M, 390.3. ^{13}C NMR (DMSO) δ: 25.58, 26.60 (2s, CH_3); 34.34 (t, CH_2Q_F, $^2J_{CF} = 21$ Hz); 65.05 (s, CHO); 65.26 (s, CH_2O); 68.54 (s, CH_2O); 68.73 (s, CHO); 108.80

(s, C) ppm. ^{1}H NMR (DMSO) δ: 1.29, 1.34 (2s, 6H, CH_3); 2.00–2.20 (m, 1H, CH_2CF_2); 2.30–2.50 (m, 1H, CH_2CF_2); 3.24 (dd, H_A, CH_2O, $^2J_{HH} = 11$ Hz, $^3J_{HH} = 7$ Hz); 3.39 (dd, H_B, CH_2O, $^2J_{HH} = 11$ Hz, $^3J_{HH} = 5$ Hz); 3.62 (t, H_A, CH_2O, $^2J_{HH} = {}^3J_{HH} = 7.5$ Hz); 3.85 (m, 1H, CHO); 4.09 (t, H_B, CH_2O, $^2J_{HH} = {}^3J_{HH} = 7.5$ Hz); 4.37 (m, 1H, CHO) ppm. ^{19}F NMR (DMSO) δ: −113.01 (m, 4F, CF_2CH_2); −123.70 (m, 4F, $CH_2CF_2CF_2$) ppm.

*3.6.2. Reaction of 1,2;11,12-diepoxy-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane (**4b**) with acetone(1,8-bis(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2,3,3,4,4,5,5,6,6,7,7-dodecafluorooctane, **13b**)*

The same procedure as in Section 3.7.1 was applied; diepoxide **4b** (0.425 g, 1.02 mmol). After removing acetone and volatile components, crude **13b** as a white solid (0.52 g, 95%) was obtained. For analytical purposes, **13b** was purified by simple column chromatography (silica gel; hexane, chloroform), mp 72–75°C. An attempt of recrystallization of the crude product in boiling ethyl acetate led to the total hydrolysis of the dioxolane rings to tetrol **14b** (see Section 3.7.2). Analysis — Found: C, 40.1; H, 4.01; F, 43.5%. $C_{18}HF_{12}O_4$, requires: C, 40.76; H, 4.18; F, 42.97%; M, 530.5. $C_{18}H_{22}O_4F_{12}$ M = 530.35) calculated/found 40.76/37.47 %C, 4.18/3.85 %H, 42.97/43.65 %F. ^{13}C NMR (DMSO) δ: 25.51, 26.52 (2s, CH_3); 34.17 (t, CH_2Q_F, $^2J_{CF} = 21$ Hz); 68.43 (s, CH_2O); 68.59 (s, CHO); 108.81 (s, C) ppm. ^{1}H NMR (DMSO) δ: 1.29, 1.34 (2s, 6H, CH_3); 2.20–2.70 (m, 2H, CH_2CF_2); 3.63 (t, H_A, CH_2O, $^2J_{HH} = {}^3J_{HH} = 7$ Hz); 4.09 (t, H_B, CH_2O, $^2J_{HH} = 8$ Hz, $^3J_{HH} = 6$ Hz); 4.37 (m, 1H, CHO) ppm. ^{19}F NMR (DMSO) δ: −112.00 (m, 4F, CF_2CH_2); −121.00 (m, 4F, $CH_2C_2F_4CF_2$); −123.50 (m, 4F, $CH_2CF_2CF_2$) ppm.

*3.7. Alcoholysis of bis-dioxolanylderivatives **13a** and **13b***

*3.7.1. 4,4,5,5,6,6,7,7-Octafluorodecane-1,2,9,10-tetrol (**14a**)*

In a round-bottom flask equipped with a reflux condenser, a mixture of crude bis-dioxolanyl derivatives **13a** (0.45 g, 1.05 mmol), methanol (10 ml) and concentrated hydrochloric acid (4 drops) was refluxed while stirring for 1 h when the conversion was ca. 98% (checked by GC). Volatile components were removed under reduced pressure on rotary evaporator to obtain crude **14a** as a white solid. This solid was dissolved in boiling ethyl acetate and precipitated with petroleum ether to obtain pure **14a** in an yield of 0.28 g (74%), mp 101–103°C. Analysis — Found: C, 33.9; H, 3.9; F, 43.1%. $C_{10}H_{14}F_8O_4$, requires: C, 34.29; H, 4.03; F, 43.38%; M, 350.2. ^{13}C NMR (DMSO) δ: 34.27 (t, CH_2Q_F, $^2J_{CF} = 21$ Hz); 65.29 (s, CHO); 65.29 (s, CH_2O) ppm.^{1}H NMR (DMSO) δ: 2.00–2.20 (m, 1H, CH_2CF_2); 2.30–2.50 (m, 1H, CH_2CF_2); 3.24 (dd, H_A, CH_2O, $^2J_{HH} = 11$ Hz, $^3J_{HH} = 7$ Hz); 3.39 (dd, H_B, CH_2O, $^2J_{HH} = 11$ Hz, $^3J_{HH} = 5$ Hz); 3.86 (m, 1H, CHO); 4.92 (2s, 2H, OH) ppm. ^{19}F NMR (DMSO) δ: −113.20 (m, 4F, CF_2CH_2); −123.79 (m, 4F, $CH_2CF_2CF_2$) ppm.

*3.7.2. 4,4,5,5,6,6,7,7,8,8,9,9-Dodecafluorododecane-1,2,11,12-tetrol (**14b**)*

The same procedure as in Section 3.7.1 was applied to crude bis-dioxolane (**13b**) (0.53 g, 1 mmol). After removing acetone and volatile components and precipitation, pure crude **14b** as a white solid (0.30 g, 67%) was obtained, mp 103–105°C. Analysis — Found: C, 31.7; H, 2.9; F, 51.1%. $C_{12}H_{14}F_{12}O_4$, requires: C, 32.01; H, 3.13; F, 50.61%; M, 450.2. ^{13}C NMR (DMSO) δ: 34.08 (t, CH_2Q_F, $^2J_{CF} = 21$ Hz); 65.01 (s, CHO); 65.18 (s, CH_2O) ppm. ^{1}H NMR (DMSO) δ: 2.00–2.20 (m, 1H, CH_2CF_2); 2.30–2.50 (m, 1H, CH_2CF_2); 3.24 (dd, H_A, CH_2O, $^2J_{HH} = 11$ Hz, $^3J_{HH} = 7$ Hz); 3.40 (dd, H_B, CH_2O, $^2J_{HH} = 11$ Hz, $^3J_{HH} = 5$ Hz); 3.85 (m, 1H, CHO); 4.45 (2s, 2H, OH) ppm. ^{19}F NMR (DMSO) δ: −112.98 (m, 4F, CF_2CH_2); −121.69 (m, 4F, $CH_2C_2F_4CF_2$); −123.75 (m, 4F, $CH_2CF_2CF_2$) ppm.

*3.8. Base catalyzed ring opening of diepoxides **4a** and **4b** with methacrylic acid (products **16a–16b**, and **17a–17b**)*

*3.8.1. Reaction of 1,2;9,10-diepoxy-4,4,5,5,6,6,7,7-octafluorodecane (**4a**) (products **16a** and **17a**)*

In a round-bottom flask equipped with a reflux condenser with a drying tube ($MgSO_4$), a mixture of diepoxide **4a** (0.317 g, 1.01 mmol), methacrylic acid (1.70 g, 19.7 mmol), triethylamine (5 drops) and diphenyl picryl hydrazyl (15 mg) was heated to 100°C while stirring intensively with magnetic spinbar for 2 h when the conversion was ca. 98% (checked by GC). Then, the excess of methacrylic acid was distilled off in vacuum in a distillation apparatus with oil pump (0.5 mm Hg, 100°C bath temperature) to afford crude product (**16a** and **17a**) as a brown solid. Pure mixture of regioisomeric products was obtained **16a** and **17a** (89 and 11% rel.) by their precipitation from boiling toluene solution using petroleum ether, the yield was 0.205 g (41%), mp 75–78°C. Analysis (**16a** and **17a**) — Found: C, 43.8; H, 4.47; F, 31.7%. $C_{18}H_{22}F_8O_6$, requires: C, 43.45; H, 4.56; F, 31.24%; M, 486.4.

(2, 9-Dihydroxy-4, 4, 5, 5, 6, 6, 7, 7-octafluorodecan-1,10-diyl) dimethacrylate (**16a**, 89% rel.) [$(CH_2{=}C(CH_3)COOCH_2CHOHCH_2CF_2CF_2)_2$]: ^{13}C NMR ($CDCl_3$) δ: 18.83 (s, CH_3); 35.69 (t, CH_2CF_2, $^2J_{CF} = 21$ Hz); 64.75 (s, CHO); 68.50 (s, CH_2OMA); 127.19 (s, CH_2=); 136.38 (s, C=); 167.98 (s, C=O) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.97 (s, 3H, CH_3); 2.20–2.50 (m, 2H, CH_2CF_2); 2.65 (s, 1H, OH); 4.19 (dd, H_A, CH_2OMA, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 6$ Hz); 4.27 (dd, H_B, CH_2OMA, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 4$ Hz); 4.42 (m, 1H, CHO); 5.64 (s, H_{cis}, CH_2=); 6.16 (s, H_{trans}, CH_2=) ppm. ^{19}F NMR ($CDCl_3$) δ: −112.85 (m, 4F, CF_2CH_2); −123.86 (m, 4F, $CH_2CF_2CF_2$) ppm.

(2, 10-Dihydroxy-4, 4, 5, 5, 6, 6, 7, 7-octafluorodecan-1,9-diyl) dimethacrylate (**17a**, 11% rel.) ($CH_2C(CH_3)COOCH_2$-$CHOHCH_2(CF_2)_4CH_2CH(OCOC(CH_3)CH_2)CH_2OH$): ^{13}C

NMR ($CDCl_3$) δ: 18.83 (s, CH_3); 32.65 (t, CH_2CF_2, $^2J_{CF} = 21$ Hz); 35.69 (t, CH_2CF_2, $^2J_{CF} = 21$ Hz); 46.41 (s, CH_2O); 64.75 (s, CHO); 69.17 (s, CHOMA); 68.50 (s, CH_2OMA); 127.19 (s, CH_2=); 136.38 (s, C=); 167.98 (s, C=O) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.97 (s, 3H, CH_3); 2.20–2.50 (m, 2H, CH_2CF_2); 2.50–2.60 (m, 2H, CH_2CF_2); 2.65 (s, 1H, OH); 3.76 (dd, H_A, CH_2O, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 5$ Hz); 3.82 (dd, H_B, CH_2O, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 4$ Hz); 4.19 (dd, H_A, CH_2OMA, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 6$ Hz); 4.27 (dd, H_B, CH_2OMA, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 4$ Hz); 4.42 (m, 1H, CHO); 5.37 (m, 1H, CHOMA); 5.64 (s, H_{cis}, CH_2=); 6.16 (s, H_{trans}, CH_2=) ppm. ^{19}F NMR ($CDCl_3$) δ: the same as for **16a**.

*3.8.2. Reaction of 1,2;11,12-diepoxy-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane (**4b**) (products **16b** and **17b**)*

The same procedure as in Section 3.8.1 was applied; diepoxide **4b** (0.459 g, 1.11 mmol), methacrylic acid (2.0 g, 23.2 mmol), 3 h reaction at 100°C. With ca. 97% conversion of the starting diepoxide and after repeated crystallization (toluene/petroleum ether) the product (**16b** and **17b**, ca. 90% rel.) was obtained in an yield of 0.26 g (40%), mp 80–82°C. Analysis (**16b** and **17b**) — Found: F, 38.2%. $C_{20}H_{22}F_{12}O_6$, requires: F, 38.86%; M, 586.4. (2,11-Dihydroxy-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecan-1,12-diyl) dimethacrylate (**16b**, ca. 90% rel.) [$(CH_2=C(CH_3)COOCH_2CHOHCH_2CF_2CF_2CF_2)_2$]: ^{13}C NMR ($CDCl_3$) δ: 18.95 (s, CH_3); 35.64 (t, CH_2CF_2, $^2J_{CF} = 21$ Hz); 64.77 (s, CHO); 68.49 (s, CH_2OMA); 127.26 (s, CH_2=); 136.34 (s, C=); 167.96 (s, C=O) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.97 (s, 3H, CH_3); 2.20–2.50 (m, 2H, CH_2CF_2); 2.45 (s, 1H, OH); 4.19 (dd, H_A, CH_2OMA, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 6$ Hz); 4.29 (dd, H_B, CH_2OMA, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 4$ Hz); 4.42 (m, 1H, CHO); 5.65 (s, H_{cis}, CH_2=); 6.15 (s, H_{trans}, CH_2=) ppm. ^{19}F NMR (DMSO) δ: −113.00 (m, 4F, CF_2CH_2); −121.80 (m, 4F, $CH_2C_2F_4CF_2$); −124.00 (m, 4F, $CH_2CF_2CF_2$) ppm.

*3.9. Ring opening of diepoxides **4a** and **4b** with morpholine*

*3.9.1. 1,10-Bis(morpholin-4-yl)-4,4,5,5,6,6,7,7-octafluorodecane-2,9-diol (**18a**)*

In a round-bottom flask equipped with a reflux condenser with a drying tube ($MgSO_4$), a mixture of diepoxide **4a** (0.453 g, 1.44 mmol) and anhydrous morpholine (7.1 g, 81.5 mmol) was heated to 100°C while stirring intensively with magnetic spinbar for 1 h when the conversion was ca. 98% (checked by GC). Then, excess morpholine was distilled off in vacuum in a distillation apparatus with oil pump (0.5 mm Hg, 100°C bath temperature) to afford crude product (**18a**) as a brown solid. Pure product **18a** was obtained by its precipitation from boiling toluene solution using petroleum ether, the yield was 0.43 g (61%), mp 95–97°C. Analysis — Found: C, 43.9; H, 5.69; F, 31.6; N, 5.75%. $C_{18}H_{28}F_8N_2O_4$, requires: C, 44.26; H, 5.78; F, 31.10; N, 5.73%; M, 488.4. ^{13}C NMR ($CDCl_3$) δ: 36.77 (t, CH_2Q_F, $^2J_{CF} = 21$ Hz); 54.14 (s, CH_2N); 60.89 (s, CHO); 64.88 (s, CH_2N); 67.54 (s, CH_2O) ppm. ^{1}H NMR ($CDCl_3$) δ: 2.00–2.20 (m, 1H, CH_2CF_2); 2.20–2.37 (m, 1H, CH_2CF_2); 2.32–2.50 (m, 4H, CH_2N); 2.67 (m, 2H, CH_2N); 3.64 (s, 1H, OH); 3.72 (m, 4H, CH_2O); 4.14 (m, 1H, CHO) ppm. ^{19}F NMR ($CDCl_3$) δ: −112.82 (m, 4F, CF_2CH_2); −124.06 (m, 4F, $CH_2CF_2CF_2$) ppm.

*3.9.2. 1,12-Bis(morpholin-4-yl)-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane-2,11-diol (**18b**)*

The same procedure as in Section 3.9.1 was applied; diepoxide **4b** (0.453 g, 1.09 mmol), 90 min reaction. The crude **18b** as a yellow solid (0.52 g, 95%) was obtained. Pure product **18b** was obtained by its precipitation from boiling toluene solution using petroleum ether, the yield was 0.48 g (75%), mp 102–105°C. Analysis — Found: C, 40.3; H, 4.69; F, 39.2; N, 4.74%. $C_{20}H_{28}F_{12}N_2O_4$, requires: C, 40.82; H, 4.78; F, 38.73; N, 4.76%; M, 588.4. ^{13}C NMR ($CDCl_3$) δ: 36.84 (t, CH_2Q_F, $^2J_{CF} = 21$ Hz); 54.22 (s, CH_2N); 60.89 (s, CHO); 64.94 (s, CH_2N); 67.59 (s, CH_2O) ppm. ^{1}H NMR ($CDCl_3$) δ: 2.00–2.20 (m, 1H, CH_2CF_2); 2.20–2.37 (m, 1H, CH_2CF_2); 2.32–2,55 (m, 4H, CH_2N); 2.69 (m, 2H, CH_2N); 3.64 (s, 1H, OH); 3.72 (m, 4H, CH_2O); 4.15 (m, 1H, CHO) ppm. ^{19}F NMR ($CDCl_3$) δ: −112.70 (m, 4F, CF_2CH_2); −122.10 (m, 4F, $CH_2C_2F_4CF_2$); −124.10 (m, 4F, $CH_2CF_2CF_2$) ppm.

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