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Regioselective ring opening of [(perfluoroalkyl)methyl] oxiranes with *N*-nucleophiles

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Abstract

The reactions of $C_8F_{17}CH_2\overline{CHCH_2O}$ with some primary and secondary aliphatic amines affording selective ring opening at C_β are reported. The reactions with secondary amines HNR^1R^2 ($R^1 = R^2 = Et$; $R^1 = Bu^t$, $R^2 = CH_2CH_2O(CO)C(CH_3){=}CH_2$; $R^1 = Et$, $R^2 = CH_2CH_2OH$; $R^1 = R^2 = CH_2CH_2OH$) gave the corresponding $C_8F_{17}CH_2$–CH(OH)–CH_2–NR^1R^2 derivatives. For $R^1 = Et$, $R^2 = CH_2CH_2OH$; $R^1 = R^2 = CH_2CH_2OH$, the reactions proceed through the selective nucleophilic attack of the NH moiety with no evidence of reactivity of the OH group. The reactions with the primary amines, allylamine and *n*-hexamethylenediamine, gave different products depending on reaction conditions.

Keywords: [(Perfuoroalkyl)methyl]oxiranes; *F*-Alkyl oxiranes; Ring opening; Primary and secondary aliphatic amines; Aminoalcohols; Fluorinated surfactants

1. Introduction

Fluorinated oxiranes [1] are very important industrial intermediates for various polymeric materials employed for a wide variety of special purposes, from polymers for contact lenses with improved oxygen transport, to hydrophobic coatings and surface property modifiers [2]. Fluoroalkyloxiranes can be easily transformed into various products through nucleophilic ring opening processes [1].

O- and *S*-nucleophiles have been reported to react under acid and base catalysis conditions with complete regioselectivity of ring opening [1b]. Alkanols, alkane diols and hydroxyalkyl (meth)acrylates are reported to give ring opening of (perfluoroalkyl)methyl oxiranes in the presence of Lewis acids [1b]. Thiourea reacts with perfluoroalkyl epoxides under non-catalysed conditions to afford thiiranes with complete regioselectivity [1b]. *F*-Alkyl α-hydroxy acids are prepared by ring opening oxidative reaction of *F*-alkyl oxiranes in the presence of HNO_3 [3].

To our knowledge, only few reactions of perfluoroalkyl epoxides have been reported with *N*-nucleophiles: (i) morpholine, possessing a strongly nucleophilic nitrogen, gave nucleophilic attack selectively at both the terminal C-atoms in diepoxides of the type $\overline{OCH_2CHCH_2}(CF_2CF_2)n\overline{CH_2CHCH_2O}$ ($n = 4$, 6) to yield the corresponding dihydroxylated bis morpholinyl derivatives [4]; (ii) hydrazine hydrate reacted with $C_8F_{17}CH_2\overline{CHCH_2O}$ at −10 °C and at room temperature to give the monoalkylated hydrazinoalcohol derivative $C_8F_{17}CH_2CH(OH)CH_2NHNH_2$, as the major product [5]; and (iii) aqueous ammonia (28%) reacted with *F*-alkylated oxiranes to give the corresponding aminodiol derivatives $R_FCH_2CH(OH)CH_2NHCH_2CH(OH)CH_2R_F$, formed by the action of NH_2 on the primary carbon atom of the starting *F*-alkyl oxirane, followed by the action of –NH_2 of the

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aminoalcohol intermediate, on the primary carbon atom of an another starting *F*-alkyl oxirane [6].

Recently, highly efficient cleavage of aliphatic epoxides with alcohols, aniline and thiophenol in the presence of catalytic amount of BPh_3 [7], with aromatic and aliphatic amines in the presence of Zn(II) chloride [8] and of ruthenium catalysts [9] have been reported.

Steric, polar and resonance effects can contribute to the regioselectivity that is observed in the ring cleavage reactions of unsymmetrical-substituted oxiranes [10a–c]. In the case of a monoalkyl-substituted oxirane, such as 2-methyl oxirane, basic reagents such as sodium methoxide or ammonia yield, predominantly, products of nucleophilic attack at C_β (i.e. the least substituted carbon), while under acidic conditions a greater proportion of attack occurs at C_α. On the contrary, 2-phenyl oxiran is preferentially attacked at the primary position by methoxide anion, while in the case of attack by amines, both products can be obtained [10d–f].

1-Perfluoroalkyl epoxy ethers of the type $(CF_3)(OEt)\overline{CCHRO}$ are reported to react with Lewis acids to give different ring opening products, depending upon the structure and the experimental conditions. In all cases, except when a phenyl group stabilizes, the C_β secondary carbenium ion, the C_α–O bond is broken leading to additon, trasposition or cyclization products [11]. Consistent with the above mechanistic concepts are the observations that in an oxirane an electron withdrawing group with no conjugative effect, such as a trifluoromethyl group, inhibits reaction at that carbon to which it is attached [12].

Recently, the mild cleavage of aliphatic epoxides with substituted anilines over alumina was reported in a completely regioselective fashion affording the compound formed by C_β attack as the only product [13]. Mild and efficient aminolysis of oxiranes was reported to occur in the presence of metal salts (such as $LiClO_4$, $Mg(ClO_4)_2$, $NaClO_4$, $CaCl_2$, $ZnCl_2$, $LiBF_4$) as catalysts at room temperature [14].

Here we report the ring opening in (perfluoroalkyl)methyl oxirane $C_8F_{17}CH_2\overline{CHCH_2O}$ with some primary and secondary aliphatic amines in order to prepare new amphiphilic compounds suitable for paper treatment, capable of imparting water repelling and oil resistance [15]. As a matter of fact, aliphatic amines can be considered as models for polymeric systems of technological interest as coatings, such as polyethylenimines $H–(NHCH_2CH_2)_n–NH_2$ and $–(NHCH_2CH_2)_x–[N(CH_2CH_2NH_2)CH_2CH_2]_y–$. Furthermore, the experimental conditions suitable to perform addition of one or more fluorinated moieties to primary amines are discussed.

2. Results and discussion

2.1. Synthesis of the epoxide

The [(perfluoroalkyl)methyl] oxirane $C_8F_{17}CH_2\overline{CHCH_2O}$, **1**, was prepared according to Scheme 1 by reaction of the perfluoroalkyl iodide $C_8F_{17}I$ with allyl alcohol in the presence of $Na_2S_2O_5$ and AIBN [2,2′-azobis(2-methylpropionitrile)] as initiators in a biphasic system forming the corresponding iodo-alcohol according to the procedure reported by Brace for the addition of perfluoroalkyl iodides to allylic compounds [16]. Free radical addition of R_FI to allylic compounds requires longer reaction time and more initiator with respect to terminal alkenes and norbornene, in order to obtain a high conversion avoiding "degradative chain transfer" processes that represent a termination step. In spite of these difficulties, the experimental conditions suitable to obtain quite good conversion and yields have been previously studied [17]. Subsequent epoxidation of the iodo-alcohol mediated by NaOH gives the corresponding oxirane in high yield [18] (Scheme 1).

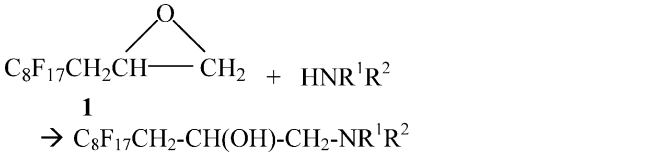
The preparation of [(perfluoroalkyl)methyl] oxiranes was previously reported to occur from 2-bromo-2-*F*-alkylethyl acetates and from 2-bromo-2-*F*-alkylethanols by reactions with concentrated NaOH and a phase transfer catalyst or with KF in triethylene glycol [19a]. The one step synthesis of perfluoroalkyl oxiranes was reported to occur starting from perfluoroalkyl halides and allylic alcohols (in the presence of K_2CO_3) catalyzed by $PdCl_2(PPh_3)_2$ [19b].

The synthesis here described can be performed with very good yield and was tested even with significantly large reactant quantities. Furthermore, the high yield results guaranteed by the use of the isopropyl alcohol, were significantly reduced if the reaction is performed in the presence of methanol or ethanol.

Recently, the chemoselective preparation of perfluoroalkylated epoxides from branched iodoacetate and iodohydrin precursors was also reported [20].

2.2. Reactions of $C_8F_{17}CH_2\overline{CHCH_2O}$ with amines

The epoxide **1** was reacted with some primary and secondary aliphatic amines with complete regioselectivity in the ring opening according to Eq. (1) giving rise to the corresponding amino alcohol derivatives **2**–**6**.

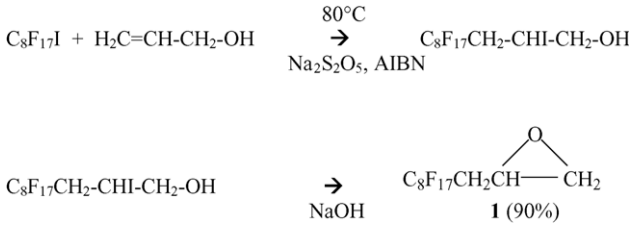


$C_8F_{17}CH_2CH(O)CH_2 + HNR^1R^2$ (**1**) → $C_8F_{17}CH_2$-CH(OH)-CH_2-NR^1R^2

$R^1 = R^2 = Et$ (**2**) (79%)
$R^1 = Bu^t$, $R^2 = CH_2CH_2O(CO)C(CH_3)=CH_2$ (**3**) (84%)
$R^1 = H$, $R^2 = CH_2CH=CH_2$ (**4**) (67%)
$R^1 = Et$, $R^2 = CH_2CH_2OH$ (**5**) (92%)
$R^1 = R^2 = CH_2CH_2OH$ (**6**) (98%) (1)

The reaction of **1** with diethylamine and 2-(*t*-butylamino)ethyl methacrylate occurred only by mixing upon heating to afford the corresponding products **2** and **3** in good yields.

Compounds **2** and **3** have been characterised by elemental analysis, IR and NMR spectroscopic determinations. In



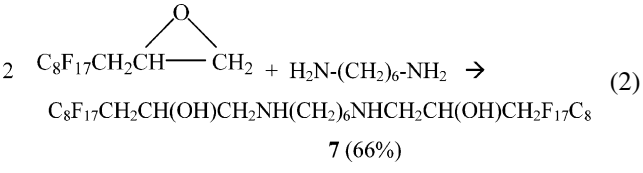
Scheme 1.

particular, the ^{13}C NMR data confirmed the selective formation of the product obtained by regioselective attack of the amine moiety to the C_β atom of the epoxide ring. The reaction with 2-(*t*-butylamino)ethyl methacrylate was performed in the presence of a catalytic amount of hydroquinone in order to avoid polymerization processes of the amine.

The reaction of **1** with allylamine was performed by heating at 90 °C for 5 h; GC/MS analysis of the reaction mixture indicates the formation of two products in about 60/35 ratio, corresponding to **4** and $[C_8F_{17}CH_2–CH(OH)–CH_2]_2NCH_2CH=CH_2$, **4′**, the latter being obtained by subsequent addition of two epoxide moieties to the primary amine. The formation of $[C_8F_{17}CH_2–CH(OH)–CH_2]_2$-$NCH_2CH=CH_2$ was confirmed by mass spectrometric analysis of the reaction mixture.

Reaction of **1** with 2-(ethylamino)ethan-1-ol gave selectively product **5** obtained by addition of the NH moiety, not OH, to the C_β carbon of the epoxide. The reaction occurred only upon heating the reagents obtaining the desired product in very good yield. Also reaction of **1** with diethanolamine occurred through the selective attach of the NH moiety, affording quantitatively the product **6**, bearing three OH groups, suitable for interaction with hydrophilic surfaces.

1 reacted also with the diamine hexamethylenediamine yielding the corresponding diamino-dialcohol derivative **7** (Eq. (2)).



(2)

Compound **7** was characterized by elemental analysis, IR spectroscopy and NMR spectrometry. The mass spectrometric analysis by MALDI technique confirmed the formation of **7** accompanied by a small (<10%) amount of the ter-adduct $[C_8F_{17}CH_2CH(OH)CH_2]_2N(CH_2)_6NHCH_2CH$-$(OH)CH_2F_{17}C_8$, **7′**, characterized by the presence of the signals at *m*/*z* 1544 in the MALDI determination.

Compound $[C_8F_{17}CH_2CH(OH)CH_2]_2N(CH_2)_6N[CH_2$-$CH(OH)CH_2F_{17}C_8]_2$, **7″** is the only product formed when the reaction of the diamine $H_2N–(CH_2)_6–NH_2$, is performed at 120 °C and for longer time (8 h) in the presence of four equivalents of **1**, as clearly indicated by the MALDI analysis of the solid product obtained.

The values of contact angles and surface tension for **7″** have been determined. Surface free energy of the solid was calculated using the contact angles according to the method proposed by Owens and Wendt [219b] who extended the Fowkes concept [21a]. The Θ_{H_2O} and $\Theta_{CH_2I_2}$ for **7″** are, respectively, 114.7 ± 2° and 108.3 ± 7°. The dispersion and the polar components of the surface free energy of water are 26.0 and 48.5 mN m^{-1}, respectively, and those of diiodomethane are 46.8 and 2.3 mN m^{-1}, respectively [21b], with a total surface energy of 6.92 mN m^{-1}. These values must be compared with the corresponding Θ_{H_2O} and $\Theta_{CH_2I_2}$ values obtained for poly(tetrafluoroethylene), which are 108° and 88°, respectively, with a total surface energy of 19.1 mN m^{-1}, significantly higher than the value calculated for **7″**. The contact angle values must be as large as possible to indicate hydrophobic and oleophobic properties (in any case larger than 90°; $\Theta_{H_2O} \geq 150°$ corresponds to superhydrophobic behavior) while the total surface energy value must be as small as possible.

3. Experimental

3.1. General

Perfluorooctyl iodide was a commercial grade reagent (Elf Atochem S.A.). Diethylamine, 2-(*t*-butylamino)ethyl-methacrilate, allylamine, 2-(ethylamino)ethan-1-ol, diethanolamine, hexamethylenediamine and AIBN [2,2′-azobis(2-methylpropionitrile)] were purchased from Aldrich Chemical Co. All other reagents employed were common laboratory materials. All the chemical reagents were used as received. Reactions were performed under inert atmosphere (N_2). GLC analyses of the reaction mixtures were performed using a Carlo Erba GC6000 VEGA2 instrument (2.5 m × 2 mm stainless steel column packed with RTZ 100 Silicoport P200-20). Typical operative conditions were: temperature programme 50°, 20° min^{-1} to 250 °C; He as gas carrier 24 ml min^{-1}.

GCMS spectra were measured on a Carlo Erba Instruments MFC 500/QMD1000 using a silica fused capillary PS264 column (30 m × 0.2 mm) and on a Finnigan Mat TSQ7000 (capillary column 30 m × 0.3 mm). Typical conditions were: temperature programme 60° for 2 min, 10° min^{-1} to 280 °C; He as gas carrier 1 ml min^{-1}.

FT IR spectra were measured using a Nicolet Avatar spectrophotometer.

^1H and ^{13}C {^1H} NMR spectra were recorded on a Bruker 200 AC spectrometer operating at 200.1 and 50.3 MHz, respectively. Peak positions are relative to Me_4Si and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). ^{19}F NMR measurements were recorded on a Bruker 200 AC spectrometer operating at 188.3 MHz. Peak positions are reported relative to $CFCl_3$.

The electrospray ionisation mass spectrum of **6** was recorded on a LCQ DECA (Finningam MAT) instrument,

operating in positive ion mode. The instrumental conditions used were the following: source potential 4 kV, capillary temperature 270 °C, sheath gas (N_2) flow rate 40 arbitrary units. One milligram of samples was dissolved in 1 ml of acetone. Five microlitres of the initial solution were diluted to 1 ml with CH_3CN. The final solution was directly introduced into the ESI ion source by a syringe pump at a flow rate of 10 μl min^{-1}.

MALDI mass measurements were performed on a REFLEX time-of-flight instrument (Bruker-Franzen Analytik, Bremen, Germany) equipped with a SCOUT ion source, operating in positive reflectron mode. Ions, formed by a pulsed UV laser beam (nitrogen laser, λ = 337 nm) were accelerated to 25 kV. Pulsed ion extraction (PIE) was obtained applying a voltage of about 14 kV to the second grid for 200 ns. 2,5-Dihydroxybenzoic acid (DHB) (10 mg ml^{-1} in acetone) was used as matrix. Five microlitres of sample solution (2 mg/mL in $CHCl_3$) was mixed with 5 μL of matrix solution. One microlitre of the resulting mixture were deposited on the stainless steel sample holder and allowed to dry before introduction into the mass spectrometer. External mass calibration was made using the $[M + H]^+$ and $[M + 2H]^{2+}$ ions of bovine insulin at *m/z* 5734 and 2867, respectively.

The surface free energies were determined using a Kruss G10/DSA10 goniometer interfaced to image-capture software. Measurements were made with de-ionised water and diiodomethane taking an average of ten 15 μL drops with each type of liquid.

3.2. Synthesis of $C_8F_{17}CH_2\overline{CHCH_2O}$

In a 2-L round-bottomed flask equipped with a reflux condenser connected with the atmosphere through a drying tube and a mechanic stirrer, 1000 g (1.8 mol) of $C_8F_{17}I$, 800 g of a 24% water solution of $Na_2S_2O_5$ and 9.0 g of AIBN were introduced. When the temperature of the reaction mixture reached 80 °C, 150 g (2.6 mol) of allyl alcohol were added dropwise in an hour. The reaction mixture was heated for additional 2 h at 80 °C. Then the reaction mixture was cooled to room temperature and 500 g of water were added. A white solid formed, which was filtered off, washed with water and identified as $C_8F_{17}CH_2CHICH_2OH$.

The undried product (1350 g) was reacted with 380 g of 40% NaOH water solution containing 230 g of isopropyl alcohol at room temperature for 45 min under stirring.

Then 300 g of water and 300 g of $CHCl_3$ were added. From the organic phase after three extractions (3 × 100 ml), the final epoxide was distilled at 100 °C (17 mbar). Yield: 783.0 g (90%). A GC/MS analysis of the product showed a unique peak at retention time of 4.9 min.

El. Anal. Calcd. for $C_{11}H_5F_{17}O$: C, 27.7; H, 1.1; Found: C, 27.5; H, 1.1. Mass spectrum (*m/z*, rel.ab%): 476 ($[C_8F_{17}CH_2CH(O)CH_2]^{\bullet+}$, 5); 57 ($[CH_2CH(O)CH_2]^+$, 70); 107 ($[CF_2CH_2CH(O)CH_2]^+$, 100).

IR (neat): ν_{CH} 3058 m, 3011 m, 2925 m; ν_{CF} 1205 s; ν_{COC} 908 cm^{-1}.

^1H NMR (CD_3COCD_3): δ 3.2 (m, CHO, 1H); 2.5 (m, CF_2CH_2, 2H); 3.0 (m, CH_2O, 1H); 3.3 (m, CH_2O, 1H).

^{19}F NMR (CD_3COCD_3): δ −82.8 (t, CF_3, $^3J_{FF}$ = 10.0 Hz); −113.9 (m, CF_2CH_2); −123.3, −124.2, −124.7, −127.8 (m, CF_2). ^{13}C NMR (CD_3COCD_3): δ 45.1 (s, CH_2), 44.6 (t, CH, $^3J_{CF}$ = 5.6 Hz), 35.2 (t, CH_2CF_2, $^2J_{CF}$ = 21.7 Hz), 115–125 (m, CF_2, CF_3).

3.3. Reaction of $C_8F_{17}CH_2\overline{CHCH_2O}$ with diethylamine

57.2 g of **1** (0.1 mol) were reacted with diethylamine at 85 °C for 12 h. Diethylamine (8.8 g, 0.1 mol) was added into three steps (3 g at the beginning, 3 g after 7 h and 3 g after a further hour). Residual diethylamine was distilled at 55 °C. The GC/MS analysis of the reaction mixture showed the presence of a unique peak at retention time of 9.4 min. Compound **2** was distilled at 108–110 °C, 4–7 mbar. M.P. 45 °C. Yield: 52.1 g (79%).

El. Anal. Calcd. for $C_{15}H_{16}F_{17}ON$, C, 32.8; H, 2.9; N, 2.5. Found: C, 33.0; H, 2.9; N, 2.6.

Mass spectrum (*m/z*, rel.ab%): 549 ($[C_8F_{17}CH_2CH(OH)CH_2N(C_2H_5)_2]^{\bullet+}$, 5); 534 ($[C_8F_{17}CH_2CH(OH)CH_2N(C_2H_5)CH_2]^+$, 5); 531 ($[C_8F_{17}CH{=}CHCH_2N(C_2H_5)_2]^{\bullet+}$, 2); 520 ($[C_8F_{17}CH_2CH(OH)CH_2N(C_2H_5)]^+$, 2); 116 ($[CH(OH)CH_2N(C_2H_5)_2]^+$, 20); 86 ($[(C_2H_5)_2NCH_2]^+$, 100); 58 ($[(C_2H_5)CH_3N]^+$, 20).

IR (neat): ν_{OH} 3431 s br; ν_{CF} 1205 s cm^{-1}.

^1H NMR (CD_3COCD_3): δ 1.6 (t, CH_3, $^3J_{HH}$ = 6.2 Hz, 6H); 2.7–3.2 (m, CH_2, 8H); 4.6 (m, CH, 1H); 5.0 (s, OH, 1H).

^{19}F NMR (CD_3COCD_3): δ −82.3 (t, CF_3, $^3J_{FF}$ = 9.4 Hz); −113.1 (t, CF_2CH_2); −122.3, −122.8, −122.5, −124.3, −127.2 (m, CF_2).

^{13}C NMR (CD_3COCD_3): δ 11.0 (s, CH_3), 47.1 (s, NCH_2), 59.8 (s, NCH_2), 61.6 (CH), 35.5 (t, CH_2CF_2, $^2J_{CF}$ = 21.0 Hz), 102–128 (m, CF_2, CF_3).

3.4. Reaction of $C_8F_{17}CH_2\overline{CHCH_2O}$ with 2-(t-butylamino)ethyl methacrilate

2-(*t*-Butylamino)ethyl methacrilate (11.2 g, 0.1 mol) have been reacted with 28.5 g (0.1 mol) of **1** at 150 °C for 17 h in the presence of a catalytic amount of hydroquinone. The reaction mixture turned to brown. The product was distilled at 140–145 °C (1 mbar). The GC/MS analysis of the reaction mixture showed the presence a unique peak at retention time of 29.2 min.

Yield: 33.3 g (84%). El. Anal. Calcd. for $C_{21}H_{24}F_{17}O_3N$, C, 38.1; H, 3.7; N, 2.1. Found: C, 38.0; H, 3.5; N, 2.0.

Mass spectrum (*m/z*, rel.ab%): 661 ($[C_8F_{17}CH_2CH(OH)CH_2N(CBu^t)(CH_2CH_2OCOC(CH_3)CH_2]^{\bullet+}$, 0.1); 646 ($[C_8F_{17}CH_2CH(OH)CH_2N(CBu^t)(CH_2CH_2OCOCCH_2]^+$, 0.2); 506 ($[C_8F_{17}CH_2CH(OH)CH_2NHCH_2]^+$, 20); 198 ($[CH_2C(CH_3)CO_2CH_2CH_2NHC(CH_3)_3CH]^+$, 90); 142 ($[CH_2C(CH_3)CO_2CH_2CH_2NHCH_2]^+$, 100); 113 ($[CH_2C(CH_3)CO_2CH_2CH_2]^+$, 72); 69 ($[CH_2C(CH_3)CO]^+$, 60); 57 ($[C(CH_3)_3]^+$, 70); 41 ($[C_3H_5]^+$, 35).

IR (neat): ν_{OH} 3435 s br; ν_{CO} 1720 s; $\nu_{C=C}$ 1639 m; ν_{CF} 1206 s cm^{-1}.

^1H NMR (CD_3COCD_3): δ 1.1 (s, Bu^t, 9H); 2.0 (m, CH_3, 3H); 2.7–3.0 (m, NCH_2 and CH_2CF_2, 6H); 4.1 (m, CH and OCH_2, 3H); 6.1 and 5.6 (m, $=CH_2$, 2H), 4.7 (s, br, OH, 1H).

^{19}F NMR (CD_3COCD_3): δ −82.5 (t, $^3J_{FF}$ = 11.3 Hz, CF_3); −113.7 (t, CF_2CH_2); −122.9, −123.2, −124.1, −124.7, −127.6 (m, CF_2).

^{13}C NMR (CD_3COCD_3): δ 17.8 (s, CH_3), 55.3 (s, NCH_2), 35.8 (t, $^2J_{CF}$ = 21.1 Hz, CH_2CF_2), 26.9 (s, CCH_3), 54.0 ($CCH3$), 65.4 (s, CH_2O), 167.1 (s, CO), 137.0 (s, C=), 125.7 (s, CH_2=), 58.0 (s, NCH_2), 63.3 (CHOH), 105–110 (m, CF_2, CF_3).

3.5. Reaction of $C_8F_{17}CH_2\overline{CHCH_2O}$ with allylamine

Allylamine (2.8 g, 0.05 mol) was reacted with an equimolar amount of **1** (23.8 g, 0.05 mol) at 90 °C for 5 h. The product was distilled at 168–178 °C (1 mbar). The GC/MS analysis of the reaction mixture showed the presence of two significant peaks at 19.9 and 27.3 min, in 60/35 ratio, respectively, which were identified as product **4** and **4′** on the basis of the mass spectra. Compound **4** was purified by further distillation at 140–142 °C (1 mbar).

Yield: 184.0 g (67%). El. Anal. Calcd. for $C_{14}H_{12}F_{17}ON$, C, 31.5; H, 2.3; N, 2.6. Found: C, 33.0; H, 2.1; N, 2.5.

Mass spectrum (*m/z*, rel.ab%): 533 ($[C_8F_{17}CH_2CH(OH)CH_2NHCH_2CHCH_2]^{\bullet+}$, 2); 532 ($[C_8F_{17}CH_2CH(OH)CH_2NCH_2CHCH_2]^+$, 2); 506 ($[C_8F_{17}CH_2CH(OH)CH_2NCH_3]^+$, 2); 488 ($[C_8F_{17}CH_2CHCHNCH_3]^+$, 3); 463 ($[C_8F_{17}CH_2CH(OH)]^+$, 1); 70 ($[C_3H_5NHCH_2]^{\bullet+}$, 100); 41 ($[C_3H_5]^+$, 35).

IR (KBr): ν_{OH} 3400 br; ν_{CF} 1202 s; $\nu_{C=C}$ 1648 m cm^{-1}.

^1H NMR (CD_3COCD_3): δ 4.2 (m, CH, 1H); 4.3 (s, br, OH, 1H), 5.9 (m, CH=, 1H); 5.1 (m, CH_2=, 2H); 3.3–3.1 (m, CH_2, 4H); 2.7 (td, CH_2, $^3J_{HH}$ = 0.3 Hz, $^3J_{HF}$ = 1.0 Hz, 2H); 3.4 (br, NH, 1H).

^{19}F NMR (CD_3COCD_3): δ −82.6 (t, CF_3, $^3J_{FF}$ = 10.6 Hz); −113.9 (t, CF_2CH_2); −122.8, −123.5, −124.8, −127.5 (m, CF_2).

^{13}C NMR (CD_3COCD_3): δ 68.2 (t, CH, $^3J_{CF}$ = 2.6 Hz), 55.6 (s, NCH_2CH), 36.9 (t, $^2J_{CF}$ = 20.6 Hz, CH_2CF_2), 52.0 (CH_2), 137.3 (CH=), 116.0 (CH_2=), 100–130 (m, CF_2, CF_3). The product $[C_8F_{17}CH_2CH(OH)CH_2]_2NCH_2CH{=}CH_2$, **4′**, was distilled at 205–207 °C (1 mbar). Yield: 6.9 g (24%).

Mass spectrum (*m/z*, rel.ab%): 573 ($[C_8F_{17}CH_2CH(OH)CH_2N(CH_2CHCH_2)_2]^+$; 546 ($[C_8F_{17}CH_2CH(OH)CH_2N(CH_2)CH_2CHCH_2]^+$, 100), 5); 490 ($[C_8F_{17}C_3H_5NO]^+$, 15); 69 ($[C_3H_5NCH_2]^{\bullet+}$, 30); 41 ($[C_3H_5]^+$, 60).

IR (KBr): ν_{OH} 3400 br; ν_{CF} 1210 s; $\nu_{C=C}$ 1644 m cm^{-1}.

^1H NMR (CD_3COCD_3): δ 5.2 (m, CH_2=, 4H); 4.2 (m, CH, 2H); 4.3 (s, br, OH, 2H), 5.9 (m, CH=, 2H); 3.3 (m, NCH_2, 4H); 2.7 (m, CH_2, 4H); 2.4 (td, CH_2, $^3J_{HH}$ = 0.4 Hz, $^3J_{HF}$ = 1.1 Hz, 4H).

^{19}F NMR (CD_3COCD_3): δ −82.5 (t, CF_3, $^3J_{FF}$ = 9.9 Hz); −114.0 (t, CF_2CH_2); −122.9, −123.2, −123.2, −125.0, −127.6 (m, CF_2).

^{13}C NMR (CD_3COCD_3): δ 63.6, 62.7, 62.0, 61.1 (s, NCH_2 e CH), 36.0 (t, $^3J_{CF}$ = 20.7 Hz, CH_2CF_2), 135.4 (CH=), 118.0 (CH_2=), 125–110 (m, CF_2, CF_3).

Product **4′** was obtained in a separate experiment by reacting 6.0 g (0.1 mol) of allylamine with **1** (23.8 g, 0.05 mol) at 90 °C for 8 h. Yield 2.5 g (87%). El. Anal. Calcd. for $C_{25}H_{17}F_{34}O_2N$, C, 29.7; H, 1.7; N, 1.4. Found: C, 30.1; H, 1.5; N, 1.2.

3.6. Reaction of $C_8F_{17}CH_2\overline{CHCH_2O}$ 2-(ethylamino)ethan-1-ol

2-(Ethylamino)ethanol (9.0 g, 0.1 mol) were heated at 85 °C and reacted with 47.6 g of **1** (0.1 mol) added dropwise during 2 h. The reaction mixture was reacted for further 3 h. Then the final product, compound **5**, was distilled at 162 °C (42 mbar). The GC/MS analysis showed the formation of a unique product at 17.6 min.

Yield: 52.2 g (92%). El. Anal. Calcd. for $C_{15}H_{16}F_{17}O_2N$, C, 31.9; H, 2.9; N, 2.5. Found: C, 32.1; H, 2.5; N, 2.2.

Mass spectrum (*m/z*, rel.ab%): 565 ($[C_8F_{17}CH_2CH(OH)CH_2N(CH_2CH_3)(CH_2CH_2OH)]^{\bullet+}$, 5); 534 ($[C_8F_{17}CH_2CH(OH)CH_2N(C_2H_5)CH_2]^+$, 15); 132 ($[C_6H_{14}NO_2]$)$]^{\bullet+}$, 15); 102 ($[C_5H_{12}NO]^{\bullet+}$, 100); 58 ($[C_3H_8N]^+$, 25).

IR (neat): ν_{OH} 3384 br; ν_{CF} 1202 s cm^{-1}.

^1H NMR (CD_3COCD_3): δ 1.0 (t, CH_3, $^3J_{HH}$ = 6.3 Hz, 3H); 2.0–2.7 (m, CH_2, 6H); 3.5 (m, CH_2, 2H); 4.0 (m, CH and CH_2, 3H), 4.5 (s, br, OH, 1H).

^{19}F NMR (CD_3COCD_3): δ −82.4 (t, $^3J_{FF}$ = 10.0 Hz, CF_3); −113.6 (t, CF_2CH_2); −122.8, −123.1, −123.9, −124.7, −127.4 (m, CF_2).

^{13}C NMR (CD_3COCD_3): δ 11.5 (CH_3), 49.0, 60.3 and 61.0 (NCH_2), 58.4 (CH_2OH), 36.4 (t, CH_2CF_2, $^2J_{CF}$ = 21.1 Hz), 62.9 (CHOH), 102–128 (m, CF_2, CF_3).

3.7. Reaction of $C_8F_{17}CH_2\overline{CHCH_2O}$ with diethanolamine

Diethanolamine (21.0 g, 0.2 mol) were heated at 85 °C and reacted with 47.6 g of 1 (0.1 mol). The reaction mixture was reacted for 6 h. A solid product formed which was identified as **6**; mp 92–93 °C.

Yield: 67.2 g (98%). El. Anal. Calcd. for $C_{15}H_{14}F_{17}O_3N$, C, 31.1; H, 2.4; N, 2.4. Found: C, 30.8; H, 2.2; N, 2.2.

Mass spectrum (ESI, *m/z*, rel.ab%): 582 ($[C_8F_{17}CH_2CH(OH)CH_2N(CH_2CH_2OH)_2H]^{\bullet+}$, 100); 564 ($[C_8F_{17}CH_2CH(OH)CH_2N(CH_2CH_2)(CH_2CH_2OH)]^{\bullet+}$, 45); 520 ($[C_8F_{17}CH_2CH(OH)CH_2N(CH_2CH_3)]^{\bullet+}$, 10).

IR (KBr): ν_{OH} 3386 br; ν_{CF} 1204 s cm^{-1}.

^1H NMR (CD_3COCD_3): δ 2.6 (m, CH_2, 6H); 3.6 (m, CH_2, 6H); 4.2 (s, br, OH and CH, 4H).

^{19}F NMR (CD_3COCD_3): δ −82.5 (t, $^3J_{FF}$ = 9.8 Hz, CF_3); −113.6 (t, CF_2CH_2); −122.9, −123.2, −124.0, −124.7, −127.5 (m, CF_2).

^{13}C NMR (CD_3COCD_3): δ 59.1 (NCH_2), 61.1 (CH_2OH), 36.6 (t, CH_2CF_2, $^3J_{CF}$ = 20.5 Hz), 64.1 (CHOH), 63.4 (NCH_2), 128–106 (m, CF_2, CF_3).

3.8. Reaction of $C_8F_{17}CH_2\overline{CHCH_2O}$ with n-hexamethylendiamine

95.2 g of **1** (0.2 mol) were reacted with hexamethylendiamine (11.6 g, 0.1 mol) at 100 °C for 3 h. The obtained product was dissolved in hot THF. Upon cooling, a light yellow solid precipitated, which was filtered off and identified as compound **7**.

Yield: 70.5 g (66%). El. Anal. Calcd. for $C_{28}H_{26}F_{34}O_2N_2$, C, 31.5; H, 2.4; N, 2.6. Found: C, 30.9; H, 2.2; N, 2.7.

Mass spectrum (MALDI): 1068, $[M]^{\bullet+}$; 649 $[M - C_8F_{17}]^+$; 635 $[M - C_8F_{17}–CH_2]^{\bullet+}$; 591 $[M - C_8F_{17}–C_3H_6O]^+$; 576 $[M - C_8F_{17}–C_3H_6ONH]^{\bullet+}$; 562 $[M - C_8F_{17}–C_3H_6ONH–CH_2]^+$; 548 $[M - C_8F_{17}–C_3H_6ONH–2CH_2]^{\bullet+}$; 419 $[C_8F_{17}]^+$; 319 $[C_6F_{13}]^+$.

IR (KBr): ν_{OH} 3380 m br; ν_{NH} 3130 m br; ν_{CF} 1204 s cm^{-1}.

^{1}H NMR (CD_3COCD_3): δ 1.4 (m, CH_2, 8H); 2.4–3.2 (m, CH_2, 12H); 4.4 (m, CH, 2H); 4.2 (s, br, NH, 2H); 4.5 (s, br, OH, 2H). ^{19}F NMR (CD_3COCD_3): δ −82.3 (t, CF_3, $^3J_{FF}$ = 9.6 Hz); −113.9 (t, CF_2CH_2); −123.0, −123.9, −124.7, −127.4 (m, CF_2).

^{13}C NMR (CD_3COCD_3): δ 37.0 (t, CH_2CF_2, $^2J_{CF}$ = 20.5 Hz), 68.4 (CHOH), 55.2 (NCH_2), 48.4 (CH_2), 27.2 (CH_2); 115–125 (m, CF_2, CF_3).

From the THF solution, by taking to dryness, a yellow product was obtained, which was characterised as $[C_8F_{17}CH_2CH(OH)CH_2]_2NCH_2(CH_2)_4CH_2NHCH_2CH(OH)CH_2C_8F_{17}$, **7′**. Yield: 9.7 g (6.2%). El. Anal. Calcd. for $C_{39}H_{30}F_{51}O_3N_2$, C, 30.3; H, 2.0; N, 1.8. Found: C, 30.2; H, 1.8; N, 1.7.

Mass spectrum (MALDI): 1544, $[M]^{\bullet+}$; 1275 $[M - C_5F_{11}]^+$; 1125 $[M - C_8F_{17}]^+$; 1111 $[M - C_8F_{17}–CH_2]^{\bullet+}$; 1081 $[M - C_8F_{17}–CH_2–CHOH]^+$. IR (KBr): ν_{OH} 3420 m br; ν_{NH} 3120 m br; ν_{CF} 1204 s cm^{-1}.

^{1}H NMR (CD_3COCD_3): δ 1.4 (m, CH_2, 8H); 2.1–3.1 (m, CH_2, 16H); 4.3 (m, CH, 3H); 4.1 (s, br, OH, 3H), NH masked.

^{19}F NMR (CD_3COCD_3): δ −82.3 (t, CF_3, $^3J_{FF}$ = 9.8 Hz); −113.9 (t, CF_2CH_2); −123.1, −123.9, −124.7, −127.5 (m, CF_2).

^{13}C NMR (CD_3COCD_3): δ 36.0 (t, CH_2CF_2, $^2J_{CF}$ = 20.2 Hz), 68.4 (CHOH), 55.2 (NCH_2), 48.4 (CH_2), 27.3 (CH_2); 115–125 (m, CF_2, CF_3).

The reaction of 2.8 g (0.02 mol) of hexamethylendiamine with four equivalents of **1** at 120 °C for 8 h afforded the product $[C_8F_{17}CH_2CH(OH)CH_2]_2NCH_2(CH_2)_4CH_2N[CH_2CH(OH)CH_2C_8F_{17}]_2$, **7″**, which was purified by recrystallisation from hot THF.

Yield: 42.2 g (87%). El. Anal. Calcd. for $C_{50}H_{36}F_{34}O_4N_2$, C, 43.7; H, 2.6; N, 2.0. Found: C, 43.2; H, 2.5; N, 1.9.

Mass spectrum (MALDI): 2020, $[M]^{\bullet+}$; 1543 $[M - CH_2C(OH)CH_2C_8F_{17}]^+$. IR (KBr): ν_{OH} 3397 m br; ν_{CF} 1220 s cm^{-1}. ^{1}H NMR (CD_3COCD_3): δ 1.2 (m, CH_2, 8H); 2.0–2.6 (m, CH_2, 20H); 4.0 (m, CH, 4H); 4.2 (s, br, OH, 4H).

^{19}F NMR (CD_3COCD_3): δ −83.2 (t, CF_3, $^3J_{FF}$ = 9.2 Hz); −114.2 (t, CF_2CH_2); −123.3, −123.7, −124.6, −125.3, −128.2 (m, CF_2).

^{13}C NMR (CD_3COCD_3): δ 36.0 (t, CH_2CF_2, $^2J_{CF}$ = 19.5 Hz), 56.0 and 55.7 (CHOH), 62.6, 63.7 and 61.6 (NCH_2), 27.4 and 27.1 (CH_2); 105–125 (m, CF_2, CF_3).

4. Conclusions

Regioselective ring opening was observed in the reactions of with some primary and secondary aliphatic amines, which can be considered as models for polymers, giving rise to the products selectively formed by nucleophilic attack on the C_β in the epoxide ring. The process could represent an interesting method for the controlled introduction of perfluorinated chains onto monomeric and polymeric systems bearing amino groups in the aim to prepare new amphiphilic compounds suitable for surface treatments.

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References

[1] (a) V. Cirkva, B. Ameduri, B. Boutevin, O. Paleta, J. Fluorine Chem. 84 (1997) 53;
(b) Idem, Ibidem 84 (1997) 151.
[2] (a) T. Deisenroth, R. Falk, J. Haase, U.S.Patent 5 585 517 (1996);
(b) M. Hariff, R. Falk, T. Deisenroth, K.F. Mueller, U.S. Patent 5 491 261 (1996).
[3] A.O. Amanetoullah, M.M. Chaabouri, A. Baklouti, J. Fluorine Chem. 84 (1997) 149.
[4] V. Cirkva, M. Gaboyard, O. Paleta, J. Fluorine Chem. 102 (2002) 349.
[5] I. Mastouri, A. Hedhli, A. Baklouti, J. Fluorine Chem. 108 (2001) 121.
[6] B. Charrada, A. Hedhli, A. Baklouti, Tetrahedron Lett. 41 (2000) 7347.
[7] S. Chandrasekhar, Ch.R. Reddy, B.N. Babu, G. Chandrasekhar, Tetrahedron Lett. 43 (2002) 3801.
[8] L.D. Pachon, P. Gamezi, J.J.M. van Brussel, J. Reedijk, Tetrahedron Lett. 44 (2003) 6025.
[9] C.S. Cho, J.H. Kim, H.-J. Choi, T.-J. Kim, S.C. Shim, Tetrahedron Lett. 44 (2003) 2975.
[10] (a) A.H. Haines, in: J.F. Stoddard (Ed.), Comprehensive Organic Chemistry, vol. 1, Pergamon Press, Oxford, 1979, p. 866Chapter 4.4;
(b) J. March, Advanced Organic Chemistry, fourth ed., Wiley/Interscinece, New York, 1992, p. 368;
(c) R. Rowiski, Chem. Heterocyclic Chem. 19 (1964) 446;
(d) R. Fusco, R. Trave, Gazz. Chim. Ital. 80 (1950) 366;
(e) C.L. Browne, R.E. Lutz, J. Org. Chem. 17 (1952) 1187;

(f) N.G. Barker, N.H. Cromwell, J. Am. Chem. Soc. 73 (1951) 1051.
[11] J.P. Beguè, F. Benayoud, D. Bonnet-Delpon, J. Org. Chem. 60 (1995) 5029.
[12] R.E. Parker, N.S. Isaacs, Chem. Rev. 59 (1959) 737.
[13] Y. Harrak, M.D. Pujol, Tetrahedron Lett. 43 (2002) 819.
[14] M. Chini, P. Crotti, F. Macchia, Tetrahedron Lett. 31 (1990) 4661.
[15] (a) L. Dainese, Facoltà di Scienze MM.FF.NN., AA 2000-2001, Thesis Dissertation;
(b) A. Deissant, FR2476097, PCUK (1981);
(c) J.M. Corpart, A. Dessaint, M.J. Lina, C. Collette, US 5439998, Elf Atochem (1996);
(d) J.M. Corpart, A. Dessaint, M.J. Lina, US 6111043, Elf Atochem S. A. (2000);
(e) F. Hiroshi, F. Shoj, R.Ryuji, US 6720371, Asahi Glass Co. LTD (2004);
(f) I. Masahiko, M. Tetsuya, Daikin Ind. LTD, WO 0157314 (2001);
(g) K. Taiji, S. Masaru, Nippon Synthetic Chemical Indu. EP 0867562 (1998);
(h) G. Michels, U. Zweering, H.A. Ahert, Bayer Ag. US 5753569 (1998);
(i) T.P. Hartjes, E. Saudstrom, K.J. Shanton, D.P. Swoboda, James River Comp. CA 2195265 (1997);
(j) U. Kuhlmann, GB 1433524 (1976);
(k) G. Michels, J. Koenig, Bayer Ag. DE 4426537 (1966).
[16] N.O. Brace, J. Fluorine Chem. 93 (1999) 1.
[17] M. Napoli, R. Bertani, J. Fluorine Chem. 111 (2001) 49.
[18] (a) N.O. Brace, U.S. Patent 3 145 222 (1964).
(b) N.O. Brace, J. Org. Chem. 27 (1962) 3033;
(c) S. Rubio, H. Blancou, A. Commeyras, J. Fluorine Chem. 106 (2000) 1.
[19] (a) M.M. Chaabouni, A. Baklouti, J. Fluorine Chem. 46 (1990) 307;
(b) T. Fuchitami, Y. Shibata, H. Urata, Chem. Lett. (1987) 521.
[20] V. Cirkva, J. Duchek, O. Paleta, J. Fluorine Chem. 121 (2003) 101.
[21] (a) F.M. Fowkes, J. Phys. Chem. 67 (1963) 2538;
(b) D.K. Owens, R.C. Wendt, J. Appl. Polym. Sci. 13 (1969) 1741.