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New partially fluorinated epoxides by oxidation of olefins with sodium hypohalites under phase transfer catalysis☆

Viacheslav A. Petrov[a,*], Will J. Marshall[a], Carl. G. Krespan[a], Victor F. Cherstkov[b], Era A. Avetisian[b]

[a]*Experimental Station, DuPont Central Research and Development (CRD), P.O.Box 80328 Wilmington, DE 19880-0328, USA*
[b]*INEOS RAN, ul. Vavilova 28, Moscow 117813, Russia*

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Abstract

Partially fluorinated epoxides can be readily prepared by oxidation of the corresponding olefins by NaOCl (or NaOBr) under phase transfer catalysis (PTC) conditions. Oxidation of CH_2=$C(CF_3)_2$ at 0–5 °C leads to the formation of 2,2-bis(trifluoromethyl)oxirane in 65–75% yield. $(CF_3)_2C$=$CHCH_2X$ (X = Cl or Br) were converted into the corresponding epoxides in 24–31% yield by the action of NaOCl and NaOBr, respectively. Baylis–Hillman adducts of fluorinated ketones and esters of acrylic acid CH_2=C[C(OH)(CF_2X)Y][C(O)OR] [X = F or Cl, Y = CF_3, CF_2Cl or C(O)OCH_3 and R = CH_3 or $C(CH_3)_3$] were converted into α-hydroxyepoxides in 47–84% yield under action of NaOCl in the presence of PT catalyst. Oxidation of *tert*-butyl ester of α-trifluoromethylacrylic acid by NaOCl rapidly proceeds at ambient temperature with formation of epoxide in 75% yield. Oxidation of $(C_2F_5)_2C$=CHC_3F_7 results in the high yield formation of trisubstituted epoxide.

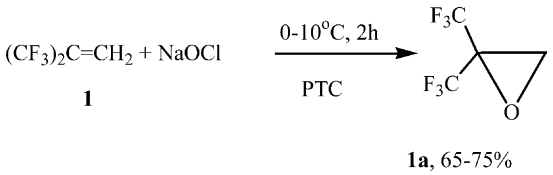
Keywords: Fluorinated epoxides; Oxidation under phase transfer catalysis conditions; Sodium hypochlorite; Sodium hypobromite

1. Introduction

Fluorinated epoxides can be prepared by a variety of methods, including synthesis based on halohydrines, carbene addition to ketones or aldehydes, oxidation of olefins by oxygen, ozone, hydrogen peroxide, *m*-chloroperbenzoic acid, complex of HOF with CH_3CN, NaOCl in CH_3CN/H_2O mixture. A comprehensive overview of the methods can be found in Ref. [1]. In the last decade a method based on the oxidation of fluorolefins under phase transfer catalysis (PTC) conditions was introduced. PTC was successfully used for oxidation of perfluorofluoroolefins and perfluoroallyl chloride by H_2O_2 [2,3] and preparation of SF_5-containing fluoroepoxides [4]. In this paper the preparation of partially fluorinated epoxides by oxidation of the corresponding olefins by NaOX (X = Cl or Br) in water is reported.

2. Results and discussion

Hexafluoroisobutene (**1**) reacts with the solution of sodium hypochlorite in the water at 0–10 °C giving the corresponding epoxide **1a** in a 65–70% yield.



(1)

PTC= Aliquat^R 336 or $(C_4H_9)_4NHSO_4$

The reaction proceeds rapidly only in the presence of the catalyst—Aliquat^R-336 (Aldrich, tricaprylyl methylammonium chloride) or tetrabutylammonium hydrogen sulfate. Both the temperature and the reaction time are critical, since at higher temperature and longer reaction time the yield of the epoxide decreases, due to polymerization of **1a** [5].

2-(Trifluoromethyl)-4,4,3,3,3-pentafluorobuten-1-ene (**2**) reacts with NaOCl under similar conditions producing epoxide **2a**, isolated in 46% yield.

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* Corresponding author. Tel.: +1-302-695-1958; fax: +1-302-695-8281.
E-mail address: viacheslav.a.petrov@usa.dupont.com (V.A. Petrov).

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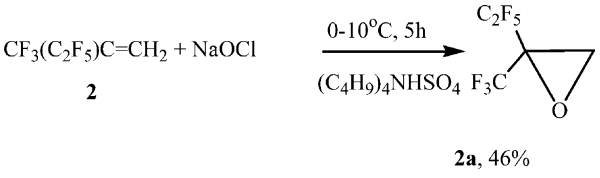
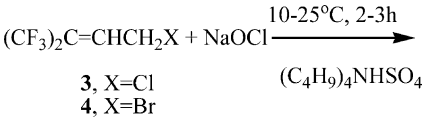
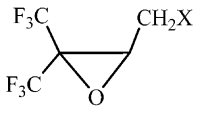


(2)

Despite the fact that olefins **3** and **4** were reported to isomerize rapidly under action of base [6] epoxidation of **3** and **4** by either NaOCl or NaOBr in water under basic conditions and in the presence of PTC successfully competes with isomerization, producing mostly epoxide **3a** or **4a**, along with smaller amount (~15–20% in crude product) of the corresponding olefins $(CF_3)_2CHCH{=}CHX$ (X = Cl, Br) [6,7].



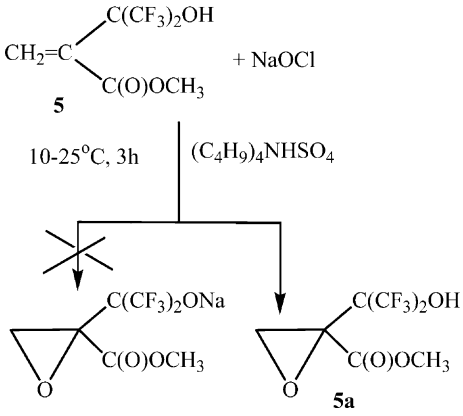


(3)

3a, X=Cl, 24%;
4a, X=Br, 31%

It should be pointed out that both reactions are exceptionally clean and have low isolated yields of **3a** and **4a** resulted from the necessity of the separating epoxides **3a** and **4a** (bp 88.5 and 102.5 °C, respectively) from byproducts—$(CF_3)_2$-CHCH=CHX (bp 84.5 °C for X = Cl and 96–98 °C for X = Br [6], respectively) by fractionation.

The reaction of the olefin **5** (Baylis–Hillman adduct of methylacrylate and hexafluoroacetone [8]) with NaOCl in water catalyzed by tetrabutylammonium hydrogen sulfate leads to an unexpected result. Despite the fact that fluorinated secondary alcohols are known to be relatively acidic (hexafluoroisopropanol has roughly the acidity of phenol) high yield formation of the hydroxyepoxide **5a** (instead of the expected sodium salt of compound **5a**) was observed in the reaction carried out at pH~14.



(4)

The formation of the solid compound **5a** in the reaction was confirmed by NMR, IR and elemental analysis data of the sample isolated by filtration of the reaction mixture prior acidification. Both olefins **6** and **7** behave similarly in the reaction with NaOCl, giving the corresponding hydroxyepoxides **6a** and **7a** in 84 and 55% yield (Eq. (5)). Additional evidence supporting the formation **6a** in protonated form was provided by single crystal X-ray diffraction of the crystalline **6a**, isolated directly from the reaction **6** and NaOCl. The structure is shown in Fig. 1. Not surprisingly the hydroxy group (O1–H1) forms a hydrogen bond to the oxy (O4) group of an adjacent molecule. The molecules form an infinite hydrogen bonded chain which propagates along the crystallographic *b*-axis. Details of the single crystal results are given in the experimental section.

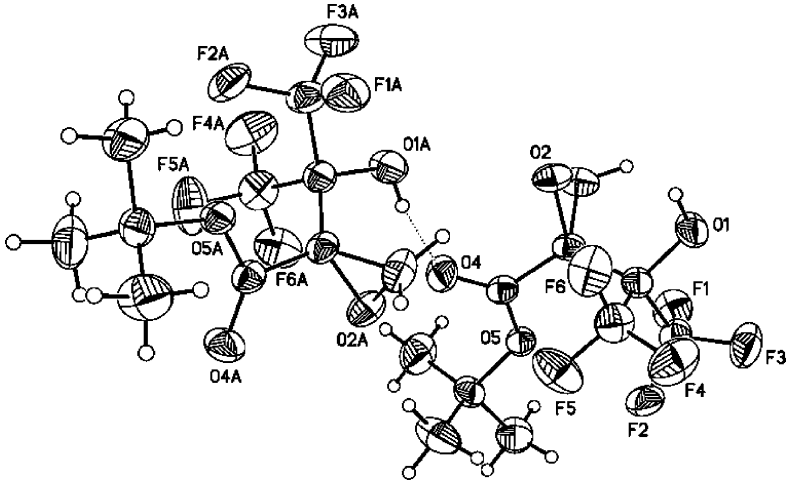
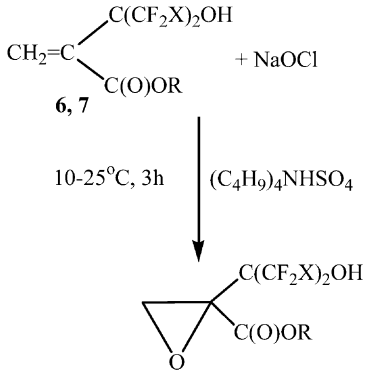


Fig. 1. Thermal ellipsoid drawing of **6a**. Thermal ellipsoids are drawn to the 50% probability level.

experimental section.

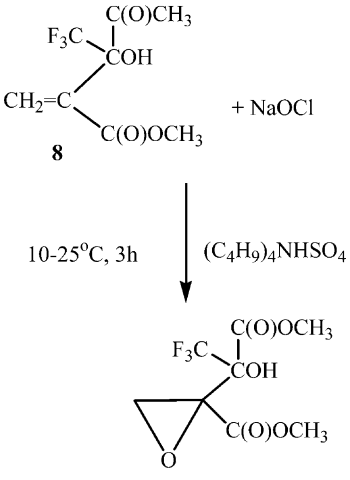


(5)

6a, X=F, R=C(CH$_3$)$_3$, 84%

7a, X=Cl, R=CH$_3$, 55%

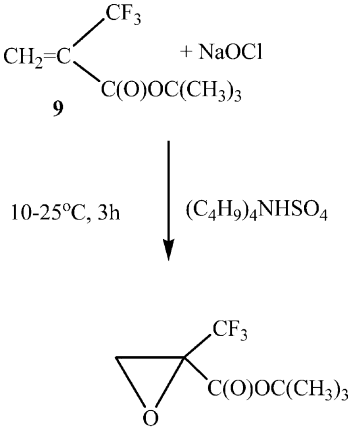
Compound **8** under similar conditions was converted into epoxide **8a**.



(6)

8a, 47% (6)

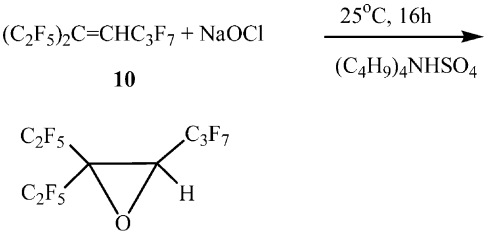
Tert-butyl ester of α-trifluoromethylacrylic acid (**9**) rapidly reacts with NaOCl under PTC conditions giving epoxide **9a**.



(7)

9a, 75%

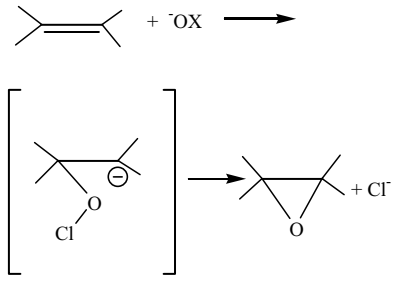
The reactivity of partially fluorinated olefins towards NaOCl strongly depends on the electrophilicity of the double bond. For example, $C_4F_9CH{=}CH_2$ does not produces the corresponding epoxide in reaction with solution of NaOCl in the presence of tetrabutylammonium hydrogen sulfate (25 °C, 16 h), however, trisubstituted olefin **10** under similar conditions was converted into the epoxide **10a** in high yield.



(8)

10a, 86%

Oxidation of fluoroolefins by NaOX under basic conditions is a typical nucleophilic reaction [9], which proceeds through the attack of hypohalite anion (generated in water phase and delivered into organic phase by the cation of transfer catalyst [10]) on the electron-deficient double bond of olefin and is followed by intramolecular cyclization (Scheme 1).

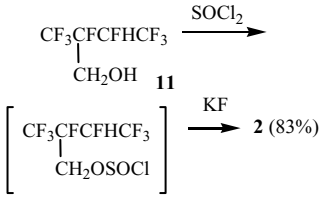


Scheme 1.

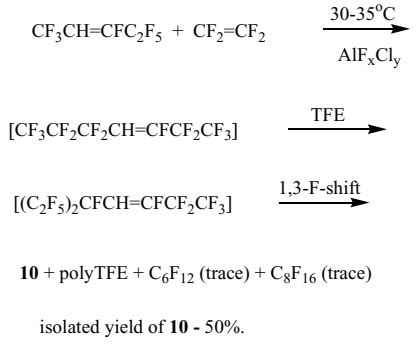
The major difference (and at the same time the advantage) of the method involving the PT catalyst over reported earlier oxidation of fluorolefins using NaOX (X = Cl, Br) in water/acetonitrile mixture [11–13] is the absence of organic solvent in the system. That helps to minimize side reactions, such as basic hydrolysis of olefins, ring opening or polymerization of epoxide [5] simplifies the isolation and improves yields of epoxides.

3. Synthesis of starting fluoroolefins

Some of the fluoroolefins used in this study such as hexafluoroisobutene (**1**) were commercially available, but some of them were made by reported methods. For example, compounds **3**, **4** were synthesized by reaction of $(CF_3)_2$-CFCH=CH$_2$ with either aluminum chloride of aluminum bromide [6]; Ballis–Hillman adducts **5**–**8** [8] were prepared by the base catalyzed reaction of methyl- or *tert*-butyl acrylates with hexafluoroacetone, 1,3-dichlorotetrafluoroacetone or methyltrifluoropyruvate. Compound **2** was



Scheme 2.



Scheme 3.

prepared by a modified literature procedure [14]) in a two step process. The first step involved the reaction of alcohol **11** [15] with $SOCl_2$, followed by the treatment of crude product with an excess of dry KF in *N*-methylpyrrolidone (see Scheme 2).

Olefin **10** was prepared by the reaction of 2-*H*-*F*-pentene-2 with tetrafluoroethylene (TFE) under mild conditions (30–35 °C.; 5.8–6.4 atm) catalyzed by aluminum chlorofluoride (ACF) [16]. In sharp contrast to the ACF catalyzed reaction of *F*-pentene-2 with an excess of TFE leading to the formation of a complex mixture of higher oligomers [17], the reaction of 2-*H*-*F*-pentene-2 with TFE resulted in a surprisingly regioselective addition of two equivalents of TFE to the 1,1,1-trifluoromethyl end group of pentene (after which further addition was strongly inhibited) and led to the high yield formation of olefin **10** (76% calculated and 50% isolated yield). The probable mechanism formation of olefin **10** is presented by Scheme 3.

Successive additions of TFE to some systems containing allylic fluorine atoms are known to occur. Thus, 4-*H*-*F*-heptene-3 was shown earlier to be formed along with 2-*H*-*F*-pentene-2 from reaction of TFE with 2-*H*-*F*-propene [17]. In the present case, we show that addition of a third equivalent of TFE occurs to give the olefin **10** after a 1,3-fluorine shift and double bond migration.

4. Experimental

^{19}F and ^{1}H NMR spectra were recorded on a QE-300 (General Electric, 200 MHz) or a Bruker DRX-400 instrument (400.5524 and 376.8485 MHz, respectively) using $CDCl_3$ or TMS as internal standards and chloroform-d as a lock solvent. IR spectra were recorded on a Perkin–Elmer 1600 FT spectrometer in a liquid film or in KBr pellets. GC analysis and GC/MS were carried out on an HP 6890 instrument using HP FFAP capillary column (30 m) and TC (GC) or mass-selective (GC/MS) detectors. Sodium hydroxide (VWR) (50 wt.%) solution, sodium hypochlorite (10–13% chlorine available), Aliquat-336^{R}, $(C_4H_9)_4NHSO_4$, diazabicyclooctane (Aldrich), hexafluoroacetone, 1,3-dichlorotetrafluoroacetone (Synquest), $CH_2{=}C(CF_3)_2$ (DuPont) were commercially available and used without further purification. Aluminum chlorofluoride [17], methyltrifluoropyruvate [19], olefins **3** and **4** [6] were prepared using reported procedures. Olefins $(CF_3)_2CHCH{=}CHX$ (X = Cl and Br) were identified based on boiling points, NMR and IR data [6,7]. Deionized water was used for the preparation of NaOCl and NaOBr.

The single crystal X-ray structure of **6a** ($C_{10}H_{12}F_6O_4$) was obtained from a colorless crystal with approximate dimensions of 0.36 mm × 0.34 mm × 0.30 mm grown from hexanes. Data were collected at −100 °C using a Bruker Smart 1 K CCD detector equipped with Mo radiation and indexed monoclinic, $P21/n$, $a = 12.9508(13)$ Å, $b = 8.5835(9)$ Å, $c = 13.2733(13)$ Å, beta = 117.523(2)°, volume = 1308.5(2) Å^3, $Z = 4$, formula weight = 310.20, density = 1.575 g/cm^3, μ(Mo) = 0.17 mm^{-1}. A SADABS correction was applied after integration yielded 5802 reflections, 2912 unique with a 2θ-range of 3.64–56.54°. The structure was solved and refined with the SHELXTL software package, refinement by full-matrix least squares on F^2, scattering factors from International Table, Vol. C Tables 4.2.6.8 and 6.1.1.4, number of parameters = 196, data/parameter ratio = 14.86, goodness-of-fit on $F^2 = 1.03$, R indices-$[I > 4\sigma(I)]$ $R_1 = 0.0363$, $wR_2 = 0.0978$, R indices(all data) $R_1 = 0.0459$, $wR_2 = 0.1060$, max difference peak and hole = 0.284 and −0.210 e/Å^3. All of the hydrogen atoms except H1, H3 and H3′ were idealized using a riding model. The rotations of the methyl groups were refined. Complete crystallographic data are available from the Cambridge Crystallographic Data Center (CCDC No. 220280).

4.1. Synthesis of fluoroolefins

4.1.1. Synthesis of 4-H-3-pentafluoroethylperfluorhept-3-ene (*10*)

A 1 l metal autoclave was purged with dry nitrogen, charged with 80 g (0.31 mol) of 90% pure 2-*H*-*F*-pentene-2 and 25 g of ACF, then stirred at 30–35 °C for 5.5 h while being pressured with tetrafluoroethylene at a rate to maintain internal pressure at 5.8–6.4 atm. A total of 108 g (1.08 mol) of TFE had been added to this point, when the rate of pressure drop had greatly slowed. During another 14.5 h an additional 35 g (0.35 mol) of TFE was added and stirring was continued for another 12 h while the pressure fell slowly to 55 psig. The reaction mixture consisted of 125 g of liquid and 73 g of solid. Analysis of the liquid by GC/MS indicated the major product to be 76.7% (96.1 g.) of

10 along with 4.8% of known C_6F_{12} isomers, 9.6% of known C_8F_{16} isomers, and smaller amounts of higher boilers. Fractionation afforded 66.5 g (50%) of **10**, bp 106–107.5 °C. ^{1}H NMR (δ, ppm): 6.6 (t, 16 Hz); ^{19}F NMR (δ, ppm): −80.8 (3F, m), −82.4 (3F, m), −83.9 (3F, m), −108.9 (2F, m), −110.1 (2F, m), −111.2 (2F, m), −127.2 (2F, m); IR (neat) (cm^{-1}): 3105 + 3034 (unsat. CH), 1674 (C=C), 1250–1100 (CF).

*4.1.2. Synthesis of Baylis–Hillman adducts **6–8** [8]*

The procedure published in [8] was used for the preparation of compounds **6–8**. Reactions of hexafluoroacetone and 1,3-dichlorotetrafluoroacetone with methyl acrylate were carried out at ambient temperature, although better conversions and yield of the product the reaction of *tert*-butylacrylate and hexafluoroacetone were achieved when it was carried out at 80 °C (16 h).

Compound **6**: Reaction conditions: solvent THF, 80 °C, 16 h; yield of **6**—58%, bp 32–34 at 0.27 mmHg; ^{1}H NMR (δ, ppm): 2.2 (9H, s), 6.5 (1H, s), 7.0 (1H, s), 8.4 (1H, s); ^{19}F (δ, ppm): −76.9 (s); IR (liquid, KBr; cm^{-1}): 3144 (OH), 1730 (C=O), 1618 (C=C); GC/MS (*m/e*): 295 [$M+1$, $C_{10}H_{13}F_6O_3^+$].

Compound **7**: Reaction conditions: solvent ether/THF (1:1), 25 °C, 48 h; yield of **7**—66%, bp 54 at 0.1 mmHg; ^{1}H NMR (δ, ppm): 3.8 (3H, s), 6.4 (1H, m), 6.8 (1H, m), 8.4 (1H, brs, OH); ^{19}F (δ, ppm): −62.0 (2F, dm, J = 168 Hz), −62.8 (2F, dm, J = 168 Hz); IR (liquid, KBr; cm^{-1}): 3213 (OH), 1695 (C=O), 1616 (C=C). Anal. Calc. for $C_7H_6Cl_2F_4O_3$: C, 29.50; H, 2.12; F, 26.66. Found: C, 29.28; H, 2.15; F, 26.63.

Compound **8**: Reaction conditions: solvent THF, 25 °C, 5 h, yield of **8**—55%, bp 64–66 at 0.1 mmHg; ^{1}H NMR (δ, ppm): 3.8 (3H, s), 3.9 (3H, s), 4.5 (1H, brs, OH), 6.2 (1H, m), 6.6 (1H, m); ^{19}F (δ, ppm): −74.7 (s); IR (liquid, KBr; cm^{-1}): 3462 (OH), 1759, 1733 (C=O), 1636 (C=C); GC/MS (*m/e*): 243 [$M+1$, $C_8H_{10}F_3O_5^+$].

*4.1.3. Synthesis of 2-trifluoromethyl-4,4,3,3,3-pentafluoroethylbut-1-ene (**2**)*

$SOCl_2$ (30 g, 0.252 mol) was added dropwise to stirred $CF_3CF(CH_2OH)CFHCF_3$ [15] (30 g, 0.13 mol). The reaction mixture was heated at 80−90 °C for 20 min. After liberation of HCl was completed, the excess of $SOCl_2$ was distilled off. The resulting mixture was added dropwise to a suspension of dry KF (19 g, 0.39 mol) in *N*-methylpyrrolidone (50 ml) with stirring at 25–30 °C. After the completion of the exothermic reaction the agitation was continued at 35 °C. After 2 h the product was distilled out and redistilled at atmospheric pressure to give 23 g (83%) 2-trifluoromethyl-4,4,3,3,3-pentafluoroethylbut-1-ene (**2**), bp 39–40 °C; ^{1}H NMR (δ, ppm): 5.65 (1H, s), 5.85 (1H, s); ^{19}F NMR (δ, ppm): −64.9 (3F, m); −85.6 (3F, t, J = 8 Hz); −114.1 (2F, q, J = 8 Hz), MS (*m/z*, intensity %): 195 [($M-F^+$), $C_5H_2F_7^+$, 27.5], 145 ($C_4H_2F_5^+$, 100); 119 ($C_2F_5^+$, 6.3) 95 ($C_3H_2F_3^+$, 12.8), 69 (CF_3^+, 11).

*4.1.4. Oxidation of olefins **1–10** by sodium hypochlorite or sodium hypobromide under phase transfer catalysis*

*4.1.4.1. Method A: preparation of 1,1-bis(trifluoromethyl)-ethylene oxide (**1**).* Olefin **1** (25 ml, 40 g) was condensed in a flask containing a solution of NaOCl (made at −5 to −3 °C by bubbling 15 g of chlorine into a mixture of 50 ml of 50 wt.% of NaOH and 100 ml of water) and 0.5 g of phase transfer catalyst—methyltricaprylylammonium chloride (Aliquat^R-336)—was added at −2 to +2 °C under vigorous stirring. The reaction mixture was agitated at this temperature till >95% conversion of olefin (GC) was reached (∼1–1.5 h). Crude reaction product was transferred out of the reactor under vacuum at 20–30 °C (250–50 mmHg) in a cold trap (at −78 °C). The crude product was dried over $MgSO_4$ and distilled to give a 33 g (yield 75%) of **1a**, bp 41–42 °C at 760 mmHg (reported), bp 41–42 °C [5,20] and 39 °C [18].

Table 1
Reactions conditions and ratio reagents for the oxidation of olefins **1–10**

Olefin (mol)	Method[a]	Catalyst[b] (mol)	Time (h)	Temperature (°C)	Product (s) (yield%)	Boiling point (°C/mmHg) (melting point)	Anal. found (calc.) or MS
1 (0.21)	A	D (0.002)	1.5	2–5	**1a** (65–75)	42	C, 26.64 (26.68); H, 1.10 (1.12)
2 (0.14)	A	E (0.001)	5	25	**2a** (46)	59–60	MS: 230 [M^+, $C_5H_2F_8O^+$][c]
3 (0.12)	A	E (0.002)	10–25	2	**3a** (24)	88.2–88.5	C, 26.44 (26.28); H, 1.31 (1.32); F, 50.03 (49.88)
4 (0.06)	C	E (0.001)	10–25	3	**4a** (31)	102.5	C, 22.02 (22.00); H, 1.11 (1.06); F, 41.57 (41.76)
5 (0.1)	A	E (0.002)	10–25	3	**5a** (75)	(56–58)	MS: 268 [M^+, $C_7H_6F_6O_4^+$][c]
6 (0.05)	B	E (0.002)	10–25	3	**6a** (84)	(80–82)	C, 38.94 (38.32); H, 4.05 (3.90); F, 37.01 (36.75)
7 (0.09)	B	E (0.002)	10–25	4	**7a** (55)	63–64/0.15	C, 27.66 (27.93); H, 2.04 (2.01); F, 25.25 (25.25)
8 (0.06)	B	E (0.002)	10–25	4	**8a** (47)	(67–69)	C, 37.03 (37.22); H, 3.64 (3.51); F, 21.91 (22.08)
9 (0.08)	B	E (0.002)	10–26	2	**9a** (75)	92/46	MS: 213 [$(M+H)^+$, $C_8H_{12}F_3O_3^+$][d]
10 (0.05)	B	E (0.002)	0–25	16	**10a** (86)	53.5–54.5/55	C, 24.03 (24.12); H, 0.22 (0.22)

[a] Method A—freshly prepared NaOCl; B—commercial NaOCl (Aldrich, 10–12% of available chlorine); C—freshly prepared sodium hypobromite.
[b] Catalyst D—Aliquat 336^R; E—$(C_4H_9)_4NHSO_4$.
[c] GC/MS, electronic ionization.
[d] GC/MS, chemical ionization.

Table 2
NMR and IR data for epoxides **1a–10a**

Compound number	^{1}H NMR[a] (δ, ppm) (J, Hz)	^{19}F NMR[a] (δ, ppm) (J, Hz)	^{13}C NMR[b] (δ, ppm) (J, Hz)	IR (cm^{-1})[c]
1a	3.3 (s)	−73.3 (s)	46.75 (s); 54.99 (sept, 37 Hz); 126.76 (q, 275 Hz)	1404, 1368[d]
2a	3.3 (s)	−72.5 (3F, hex, 6 Hz); −82.7 (3F, q, 6 Hz); −119.5 (1F, dq, J = 288, 6 Hz); −120.9 (1F, dq, J = 288, 9 Hz)	46.0 (m); 55.5 (m); 111.2 (tq, J = 258, 38 Hz); 118 (qt, J = 283, 33 Hz); 121.1 (q, J = 281 Hz)	
3a	4.0 (1H, ddm, J = 12, 6, 1 Hz); 4.1 (1H, dd, J = 12, 4 Hz); 4.2 (1H, m)[e]	−67.2 (3F, q, J = 7 Hz); −74.1 (3F, q, J = 7 Hz)	34.4 (q, 4 Hz); 58.9 (q, 3 Hz); 59.5 (sept, J = 40 Hz); 120.4 (q, J = 281 Hz); 121 (q, J = 281 Hz)	1460
4a	3.6 (2H, m); 3.9 (1H, td, J = 6, 1 Hz)	−66.2 (3F, q, J = 7 Hz); −73.2 (3F, q, J = 7 Hz)	23.6 (q, J = 4 Hz); 59.1 (q, J = 3 Hz); 61.1 (sept, J = 38 Hz); 120.7 (q, J = 280 Hz); 121 (q, J = 281)	1451
5a	3.1 (1H, d, J = 5 Hz); 3.3 (1H, d, J = 5 Hz); 3.9 (3H, s), 4.7 (1H, brs)	−73.3 (3F q, J = 9 Hz); −75.2 (3F, q, J = 9 Hz)	48.6 (m), 53.8 (s), 54.7 (s), 76.4 (sept, J = 31 Hz); 122.4 (q, J = 290 Hz); 121.7 (q, J = 290 Hz); 166.8(s)[f]	3395 (OH), 1744 (C=O), 1450[g]
6a	1.5 (9H, s); 3.1 (1H, d, J = 5 Hz); 3.3 (1H, d, J = 5 Hz); 3.5 (1H, brs)	−72.7 (3F q, J = 9 Hz); −74.7 (3F, q, J = 9 Hz)	22.8 (s), 48.6 (s), 55.0 (s), 76.0 (sept, J = 30 Hz); 86.0 (s), 121.6 (q, J = 290 Hz); 122.4 (q, J = 290 Hz); 165.0 (s)	3300 (OH), 1726 (C=O), 1460[g]
7a	3.2 (1H, d, J = 5 Hz); 3.4 (1H, d, J = 5 Hz); 3.6 (3H, s); 4.6 (1H, brs)	−56.0 (1F, ddd, J = 175, 18, 14 Hz); −56.6 (1F, ddd, J = 175, 14, 12 Hz); −58.7 (1F, dt, 170, 14, 12 Hz); −58.2 (1F, ddd, J = 170, 18, 12 Hz)	49.0 (s), 53.2 (s), 56.2 (s), 81.1 (pent, J = 25 Hz); 127.0 (t, J = 304 Hz); 127.8 (t, J = 305 Hz); 166.3 (s)	3432 (OH), 1757 (C=O), 1442
8a[h]	Major: 3.1 (1H, d, J = 5 Hz); 3.4 (1H, d, J = 5 Hz); 3.7 (3H, s); 3.9 (3H, s); 4.2 (1H, brs); minor: 3.1 (1H, d, J = 5 Hz); 3.2 (1H, d, J = 5 Hz); 3.4 (3H, s); 3.9 (3H, s); 4.2 (1H, brs)	Major: −74.2 (d, J = 2 Hz); minor: −74.1 (d, J = 1 Hz)		3438 (OH), 1756 (C=O), 1734 (C=O), 1440[g,h]
9a	1.5 (9H, s); 3.2 (1H, d, J = 6 Hz); 3.7 (1H, dq, J = 6, 1 Hz)	−72.8 (d, J = 1 Hz)	31.8 (s), 53.1 (q, J = 2 Hz); 58.7 (q, J = 37 Hz); 88.9 (s), 127.0 (q, J = 278 Hz); 167 (s)	1750 (C=O), 1480, 1460 (d)
10a	3.8 (dd, J = 11, 8 Hz)	−80.7 (3F, d); −80.9 (3F, d); −81.1 (3F, m); −110.4 (1F, dt, J = 293 Hz); −112.5 (1F, dm, J = 293 Hz); −118.0 (1F, dm, J = 283 Hz); −119.5 (1F, dm, J = 293 Hz); −119.8 (1F, dm, J = 293 Hz); −120.4 (1F, dm, J = 283 Hz); −127.6 (1F, dm, J = 292 Hz); −128.1 (1F, dm, J = 292 Hz)		

[a] In $CDCl_3$, unless indicated otherwise.
[b] Neat, unless indicated otherwise.
[c] Liquid film, KCl plates, unless stated otherwise.
[d] Gas phase [5,20].
[e] In acetone-d_6.
[f] In $CDCl_3$.
[g] In KBr pellet.
[h] Two diastereomers, ratio in isolated product—90:10.

Reaction conditions, analytical, NMR and IR data for epoxides **1a**, **2a**, **3a**, **5a** are given in Tables 1 and 2.

4.1.4.2. Method B. Sixteen grams (0.1 mol) of bromine was added slowly to the solution of 20 ml of 50% sodium hydroxide in 30 ml of water at −5 to 0 °C, followed by the addition of 0.1 g of $(C_4H_9)_4NHSO_4$ and 15 g (0.06 mol) of **4** at 0 to 3 °C. The reaction mixture was agitated at this temperature for 2 h, it was diluted with water, the organic layer was separated and dried over $MgSO_4$ and the crude product (14 g) was distilled using a short spinning band column, taking fraction bp 102–102.6 °C. It was isolated as 5 g (31%) of **4a**. Reaction conditions, analytical, NMR and IR data for **4a** are given in Tables 1 and 2.

4.1.4.3. Method C. Similar to method A, however, commercially available NaOCl (Aldrich, 10–13% chlorine available) was used instead of freshly prepared NaOCl. In the typical experiment 150 ml of the solution of NaOCl was used for oxidation of 0.05–0.09 mol of olefin in the presence of 0.002 mol of the catalyst—$(C_4H_9)_4NHSO_4$. Reaction conditions, analytical, NMR and IR data for epoxides **6a–10a** are given in Tables 1 and 2.

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