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Synthesis of new polyfluorinated oxaziridines

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(1*S*,6*S*,7*R*,8*R*,10*S*)-3-(perfluoroalkyl)-4,9-dioxapentacyclo[5.3.1.02,6.03,5.08,10]undecanes
Reduction
Oxygen transfer

ABSTRACT

The article describes a synthesis of new per- and polyfluorinated oxaziridines along with some reactions of these materials.

1. Introduction

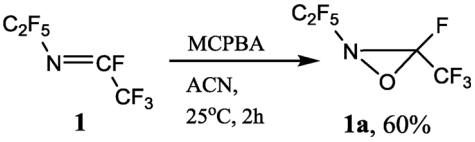
The first representative of polyfluorinated oxaziridines −oxide of perfluoro-2-azapropene [1], was shown to have an unusual and interesting reactivity [2]. The development of simple and general synthesis of perfluorinated oxaziridines, based on the reaction of dry *m*-chloroperoxybenzoic acid (MCPBA) with the corresponding perfluorinated imidoyl fluorides and imines [3,4] resulted in preparation of large number of perfluorinated oxaziridines, including $CF_3N(O)CFCF_3$ [5], $R_fN(O)CFR_f'$ [4], $Ar_fN(O)C(CF_2X)_2$ [6], $R_fSO_2N(O)C(CF_2X)_2$ [7], rapid development chemistry of these materials [2] and their application as neutral, potent oxidants for olefins [8], hydrocarbons [9,10], adamantanes [11], steroids [12], alcohols [13], sulfur- [14] and nitrogen containing compounds [15].

This article describes a synthesis of several new representatives of per- and poly- fluorinated oxaziridines and some reactions of these materials.

2. Results and discussion

Commercially available perfluorinated tertiary amines can be readily converted into the corresponding imidoyl fluorides $R_fN{=}CFR_f'$ through the reaction with catalytic amount of strong Lewis acid – antimony pentafluoride [16–18]. This reaction was also shown to be applicable to perfluorinated secondary amines [19]. For example, the cleavage of $(CF_3)CFN(F)C_2F_5$ was reported to proceed selectively under action of SbF_5, leading to the formation of $CF_3N{=}CFCF_3$ [19]. This process was successfully used for the preparation of $CF_3N{=}CFCF_3$ and it's oxide by Mlsna and DesMarteau [5].

Despite the fact, that a substantial number of perfluorinated oxaziridines was prepared at this point, the corresponding oxide of readily available [16] $C_2F_5N{=}CFCF_3$ (**1**) was never reported. In this study oxaziridine **1a** was prepared by oxidation of **1** with MCPBA in acetonitrile (ACN) solvent (Eq. (1))



1 **1a**, 60% (1)

Compound **1a** was isolated in 60% yield after vacuum transfer at low temperature and removal of residual solvent by washing with water. New oxaziridine was fully characterized by ^{19}F NMR, IR and mass- spectroscopy (Table 1).

The ^{19}F spectrum of oxaziridine **1a** exhibits A:B quartet (-CF_2 group, J = 204.5 Hz) due to magnetic non-equivalent fluorine substituents of CF_2- group and substantially shifted downfield signal of unique fluorine (δ = −146.00 ppm in **1a** vs. −29.3 ppm in **1**), along with signals of two CF_3- groups (Table 1). Additional evidence for correct assignment of oxaziridine structure came from IR spectrum, which exhibited a band at

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Table 1
NMR, IR and MS Data for New Compounds.

Comp. No	^{1}H NMR (δ, ppm, J, Hz)[a]	^{19}F NMR (δ, ppm, J, Hz)[a]	^{13}C NMR (δ, ppm, J, Hz)[a]	IR(cm^{-1})[b]	MS (*mz*)[c]
1a	–	-81.22(3F, s), −84.39(3F,s), −104.5 (1F,dd, 204.5, 23.8), −110.10 (1F, dd, 204.5, 30.5), −146.02, 1F, dd, 30.5, 23.8)	–	1448[d]	250 (M+1,$C_4HF_9NO^+$)[e]
1c	–	-74.74 (1F, dddt, 164.0, 15.2, 7.4, 2.1), −74.91(1F, ddtt, 164.0, 13.7, 4.1, 1.3), −76.05(1F, dtt, 151.9, 17.6, 5.0) −84.07(1F, dddt, 151.9, 17.9, 8.1, 2.9) −97.83 (1F, dt, 235.2, 18.5) −102.78(1F, ddd, 235.2, 16.9, 9.6), −132.63 (1F, t, 14.8)	96.72 (ddd, 303.1, 43.0, 8.2), 108.8o-116.40(3 overlapped multiplets)	–	227(M^+, $C_4F_7NO_2^+$), 228 (M+1,$C_4HF_7NO_2^+$)
2a	1.08 (2H,m), 1.19 (1H, d quint., 11.0, 1.1), 1.26(1H, d quint., 11.0, 2.1), 1.63(2H,m), 2.21 (1H, m), 2.41(1H, dq, 4.6, 1.5), 3.11(1H, dd, 3.4, 0.9), 3.97(1H, m, 2.3)	-74.32 (d, 1.6)	24.64, 26.15, 29.66, 31.50, 34.52, 51.39, 69.80, 116.75(q, 277.0), 176.20(q, 38.2)	1611 (C═N)	189 (M^+, $C_9H_{10}F_3N^+$)
2b	1.50(1H, dm, 11.6), 1.57(1H, dm, 11.6), 2.89(1H, m, 1.5), 2.91(1H, m, 1.2), 2.99(1H, dt, 3.7, 0.5), 3.03(1H, dd, 3.4, 0.9), 3.15(1H, dm, 3.7, 0.9), 3.48(1H, dd, 3.5, 1.5)	-74.10 (s)	17.55, 34.17, 36.37, 44.33, 45.38, 47.70, 70.63, 77.00(q, 41.7), 118.40(q, 277.0),	1466	218 [(M-H)$^+$, $C_9H_7F_3NO_2^+$]
2c	0.79(1H, d, 11.3), 1.36(1H,dm, 11.3, 1.8), 2.54(1H, quint., 1.5), 2.71(1H, quint., 1.5), 3.28(1H, dm, 3.7, 0.6), 3.54(1H,m), 4.22(1H,m), 1.5)	−74.74 (d, 1.7)	–	–	–
3a	1.59(2H, s), 2.93(2H, m), 3.00(1H, d, 3.7), 3.04(1H, dd, 3.7, 0.5), 3.13(1H, dd, 3.7, 1.5), 3.53(1H, dd, 3.7, 1.2)	-88.99(3F, t, 1.7), −123.47(1F, d, 288.0), −127.33(1F, d, 288.0)	17.39, 34.16, 36.31, 45.29, 45.40, 47.48, 47.50, 77.03(dd, 37.8, 28.1), 108.20(tq, 261.0, 38.8), 115.93(qt, 285.8, 34.9)	1467	269(M^+, $C_{10}H_8F_5NO_2^+$)
4a	1.58(1H, dm, 12.5), 1.61(1H, dm, 12.5), 2.90(2H, m), 2.95(1H, d, 3.7), 3.05(1H, dd, 3.4, 1.2), 3.15(1H, dd, 3.7, 1.2), 3.52(1H, dt, 3.4, 1.2)	-81.40(3F, t, 3.0), −122.00(1F, dm, 291.4), −126.52(1F dm, 291.4), −127.501F, dt, 294.3, 4.3), −128.23(1F, dt, 294.3, 4.3)	17.30, 34.25, 36.28, 45.25, 45.72, 47.44, 70.93 77.00(dd, 37.8, 24.9), 107.76(tt, 266.0, 38.8), 109.69(tt, 254.0, 32.0) 115.28(qt, 282.0, 32.9)	1467	318 [(M-H)$^+$, $C_{11}H_7F_7NO_2^+$]
4b[f]	1.85(1H,dm, ~12), 2.10(1H,dm, ~12), 2.80 (1H,m), 3.15 (1H,m), 3.19 (1H, s), 3.43(1H, dt, 4.2, 1.5), 6.10 (1H, m), 6.28(1H,m)	–	–	–	303 (M^+, $C_{11}H_8F_7NO^+$)

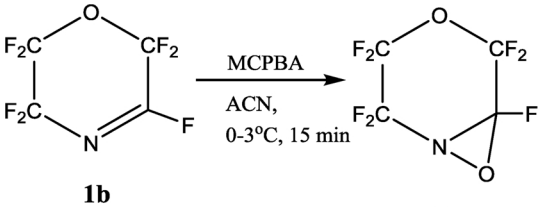
[a] $CDCl_3$ as a lock solvent, unless indicated otherwise; ^{13}C {H} spectra.
[b] liquid film, KCl plates, unless indicated otherwise; band for oxaziridine ring.
[c] electronic ionization (EI), unless indicated otherwise.
[d] Gas-phase IR.
[e] Chemical ionization (methane).
[f] Characterized in mixture with **4a**.

1448 cm^{-1} (previously also observed in IR spectra of perfluorinated oxaziridines $R_fN(O)CFR_f$' [2,4]), while strong C=N band of starting material was absent in IR spectrum. The mass of observed in mass spectrum (CI) M = 250 was consistent with protonated parent ions of **1a** $[M+H]^+$,$C_4F_9NOH^+$, 100%).

Previously reported longer chain bis(perfluoroalkyl) oxaziridines $R_fN(O)CFR_f$' were estimated to have relatively high (> 25 kcal/mol) nitrogen inversion barrier [2], so it is not surprising that structurally similar compound **1a** was found to be configurationally stable on NMR time scale. No evidence for nitrogen inversion in this material was obtained by ^{19}F NMR at ambient temperature (in $CDCl_3$ as a solvent) indicating relatively high nitrogen inversion barrier. However, further investigation of the behavior of this material at elevated temperature by NMR spectroscopy was not attempted in this study.

Similar to other fluorinated substrates such as fluoroolefins [20] or fluorinated imidoyl fluorides [4], the oxidation of **1** proceeded with complete retention of the *anti*- geometry of starting material, resulting in exclusive formation of oxaziridine with *trans*- orientation of two perfluoroalkyl groups. This conclusion was made based on the presence in ^{19}F NMR spectrum of **1a** a large through space J^4 coupling constants between magnetically non-equivalent fluorines of $-CF_2$- and single fluorine of C-**F** group (J^4 = 30.5 and J^4 = 23.4 Hz), which agreed with *cis*- orientation of C_2F_5- and C-**F**-groups.

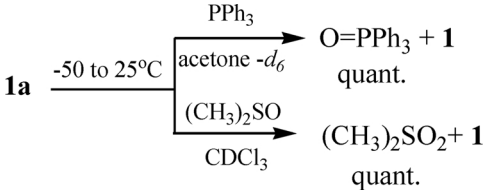
Cyclic perfluorinated imidoyl fluoride **1b** [21] was also converted into the corresponding oxaziridine **1c** under mild conditions (Eq. (2))



1b **1c**, yield 52% (2)

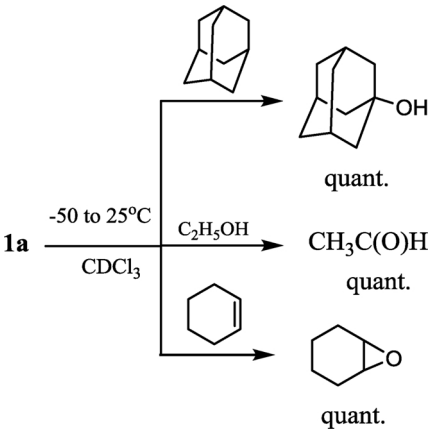
Compound **1c** was characterized by ^{19}F NMR spectroscopy and mass-spectrometry (Table 1). It should be pointed out that **1c** is significantly less stable and undergoes decomposition under reaction conditions. So, in case of the reaction of **1b** with MCPBA it should be carried out at lower temperature and the product should be isolated as soon as complete conversion of the starting material was achieved.

Compound **1a** possesses oxidative properties reported for other perfluorinated oxaziridines [2]. Being a strong oxidant it reacts with solution of KI liberating iodine and readily transfers oxygen to substrates, such as Ph_3P and DMSO, resulting in formation of Ph_3P = O or $(CH_3)_2SO_2$ and starting imidoyl fluoride **1** (Eq. (3), NMR experiments)



(3)

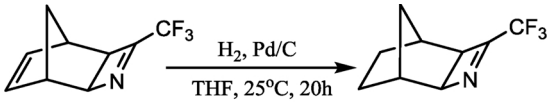
Similar to other perfluorinated oxaziridines [8,9,13] compound **1a** was demonstrated to oxidize adamantane into 1-adamantanol; ethanol into acetaldehyde and cyclohexene into the corresponding *cis*-oxide (Eq. (4))



(4)

Recently we reported a synthesis of new group of materials – *exo*-3-aza-4-perfluoroalkyl-tricyclo[4.2.1.02,5]non-3,7-dienes – derived from the cycloaddition reaction of quadricyclane and perfluorinated nitriles [22]. These unique group of new materials has only one hydrocarbon analog, isolated from Diels-Alder reaction of tris(*t*-butyl)azet and cyclopentadiene [23] and reported to have *endo*- orientation of four membered ring.

Exo-3-aza-4-perfluoroalkyl-tricyclo[4.2.1.02,5]non-3,7-dienes [**2,**R_f = CF_3, **3,** R_f = C_2F_5, **4,** R_f = *n*-C_3F_7] have two double bonds (C=C and C=N), having very different reactivity. By choosing a proper reagents it was possible selectively involve one or another into a reaction. For example, a catalytic hydrogenation of **2** resulted in exclusive hydrogenation of C=C, while C=N bond stayed intact and the *exo*-orientation of four membered ring was preserved in **2a** (NMR). (Eq. (5))

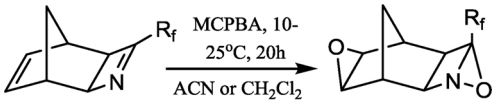


2 **2a**, 64% (5)

NMR analysis of crude reaction mixture confirmed high selectivity of the process, since only one sets of signals attributed to compound **2a** was observed in ^1H, ^{19}F NMR spectra. The assigned structure **2a** is consistent with data of ^1H, ^{13}C and ^{19}F NMR spectroscopy and mass-spectrometry.

On the other hand, 3-aza-4-perfluoroalkyl-tricyclo[4.2.1.02,5]non-3,7-dienes*exo*-3-aza-4-perfluoroalkyl-tricyclo[4.2.1.02,5]non-3,7-dienes (**2-4**) have a highly electrophilic C=N double bond, since they were reported to add R_f $Si(CH_3)_3$ across C=N bond under action of CsF catalyst [22].

The ability of **2-4** readily react with nucleophiles prompted us to attempt oxidation of C=N bond by MCPBA, since in contrast to the Prilezhaev reaction, which usually proceeds through the protonation of electron rich C=C bond, the reaction of **1** (and other imidoyl fluorides R_fN=CFR_f') with MCPBA involves *nucleophilic* attack peroxy-anion on electron deficient C=N bond [2]. Indeed, the oxidation of **2-4** by MCPBA proceeded at 10–30 °C in either ACN or CH_2Cl_2 solvent, leading to the oxidation of both double bonds and the formation of the corresponding epoxy-oxaziridines **2b, 3a** and **4a** (Eq.(6))



2 R_f=CF_3 **2b**, 54%
3 R_f=C_2F_5 **3a**, 72%
4 R_f=C_3F_7 **4a**, 24% (6)

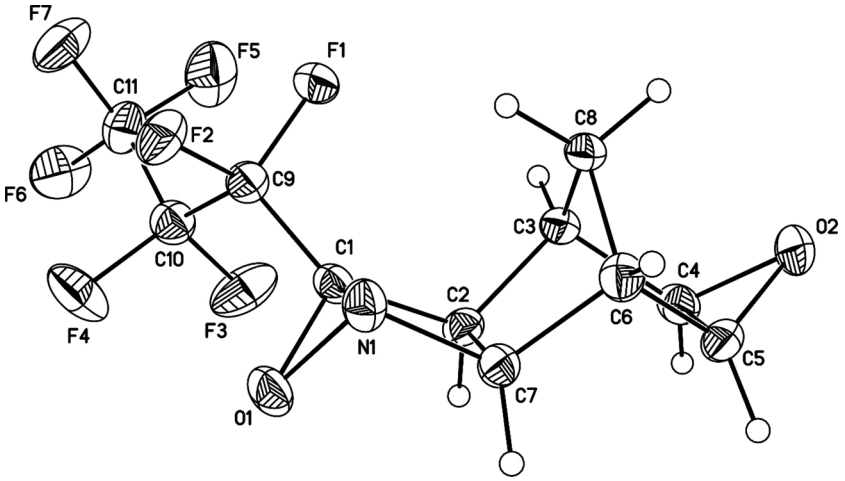
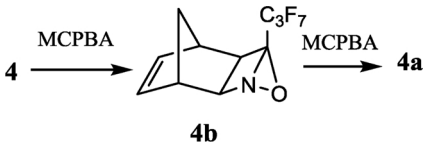


Fig. 1. Crystal structure of **4a** with thermal ellipsoids drawn to the 30% probability level. Only one enantiomer is shown.

Although both double bonds get oxidized in this process, the reaction of C=N bond with MCPBA seems to be faster, since transient formation of unsaturated oxaziridine **4b** was observed in the reaction mixture by NMR at early stages of oxidation of compound **4** (Eq. (7)).



(7)

While the oxidation of imines **3** and **4** was highly selective and led to the formation of a single isomer in each case, the reaction of compound **2** led to the formation of small amount (~5%) of isomeric material. Although the structure of second isomer was not established, the elemental analysis of fraction containing unknown impurity was satisfactory, confirming isomeric nature of the impurity.

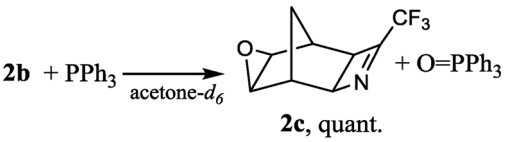
Oxaziridines **2b, 3a** and **4a** were isolated by distillation under reduced pressure and fully characterized by spectroscopic methods and all isolated materials gave satisfactory elemental analysis. Similar to reported perfluorinated oxaziridines [2], IR spectra of compounds **2b, 3a, 4a** contained a new band at 1466–1467 cm^{-1}, assigned to oxaziridine ring, while bands related to either C=C or C=N bonds were absent in IR-spectra of all new materials. Data of ^{1}H, ^{13}C and ^{19}F NMR spectroscopy were consistent with proposed structures. MS spectrum (EI) of **3a** exhibited a parent ion, while MS spectra of **2b** and **4a** contained $[M-H]^+$ ion.

Although both **2b** and **3a** were liquids at ambient temperature, compound **4a** crystallized at ambient temperature after purification and its structure was established by X-ray diffraction (Fig. 1)

Compound **4a** forms as a mixture as mixture of two enantiomers, since reaction didn't involve chiral oxidizing agent. Isolated crystals of compound **4a** used for X-ray diffraction experiment were a racemic mixture of two enantiomers and Fig. 1 depicts the structure of one enantiomer, while no separation or characterization of pure enantiomers was attempted in this study.

Based on the structure of **4a** it is clear, that the oxidation of the C=C bond of *exo*-3-aza-4-perfluoroalkyl-tricyclo[4.2.1.02,5]non-3,7-dienes [**2-4**, $R_f = CF_3$ (**2**), $R_f = C_2F_5$ (**3**), $R_f = n\text{-}C_3F_7$ (**4**)] was stereoselective and proceeded from *exo*- side in case of C=C bond (which is typical for oxidation of norbornenes. For example, the oxidation structurally similar 5,5-bis(trifluoromethyl)-6-thia-bicyclo[2.2.1]hept-2-ene by MCPBA led to selective formation of the corresponding *exo*-epoxide [24]). On the other hand the oxidation of the C=N bond of compounds **2-4** was *endo*- selective, which is consistent with other reactions of these materials, such as fluoride-ion catalyzed addition of R_fSiMe_3 [22].

Compounds **2b, 3a** and **4a** were found to be significantly less potent oxidizing agents compared to perfluorinated oxaziridine **1a.** Although, all of them were able to oxidize KI solution, liberating iodine, no oxidation of cyclohexene was observed in reaction with **3a** (NMR, 20 °C, 16 h). On the other hand, compound **2b** was demonstrated to convert triphenylphosine into oxide, producing imine **2c** (Eq.8), which was characterized in solution by ^{19}F and ^{1}H NMR spectroscopy. While the changes in ^{19}F NMR spectrum of the reaction mixture were insignificant (**2b,** δ = -74.10(s); **2c,** δ = -74.74 (d, 1,7 Hz, Table 1), an appearance of new set of signals was observed in the proton spectrum (Table 1), consistent with the structure of imine **2c** (Eq. (8), Table 1).



(8)

While **2c** was not isolated, but characterized in the solution, the formation of $Ph_3P = O$ (confirmed by ^{31}P NMR) and the absence of signals of compound **2** in ^{1}H NMR spectrum of crude reaction mixture agreed with selective transfer of oxygen from oxaziridine moiety.

3. Conclusion

Several new polyfluorinated oxaziridines were synthesized using dry MCPBA as an oxidizing agent. All oxidations were found to be stereoselective, leading to the formation of only one stereoisomer of oxaziridine in each case and new oxaziridines were found to be configurationally stable at ambient temperature.

Perfluorinated oxaziridine **1a** was demonstrated to be a potent oxidizer, able to transfer oxygen to a number of organic substrates, while partially fluorinated oxaziridines **2b**, **3a**, **4a** were found to be to be significantly less potent oxidizing agents.

4. Experimental

^{19}F NMR spectra were recorded on GE QE Plus (283.11 MHz, compounds **1a, 1c**) ^{1}H NMR and ^{19}F NMR Bruker DRX-500 (499.87 MHz, compounds **2a–c, 3, 4a–c**) instrument using $CFCl_3$ or TMS as an internal standards. Unless stated otherwise, $CDCl_3$ was used as a lock solvent. GC and GC/MS analyses were carried out on a HP-6890 instrument, using HP FFAP capillary column and either TCD (GC) and mass selective (GS/MS) detectors, respectively. Dry ACN and all hydrocarbon starting materials were obtained from commercial sources (Aldrich) and used without further purification. Perfluoro-N-methylmorpholine (3 M) was distilled before it was used for the preparation of **1b**.

For all oxidations dry MCPBA [4] was used, which was obtained by

washing commercially available MCPBA (Aldrich, 55–70%) with buffer pH 7 and drying in desiccator under vacuum, over P_2O_5 Compound **1** [16,18], **1b** [21] and **2–4** [22] was prepared according reported procedures.

4.1. Crystallography

X-ray data for 4a were collected at −100° C using a Bruker 1 K CCD system equipped with a sealed tube molybdenum source and a graphite monochromator. The structure was solved and refined using the Shelxtl [25] software package, refinement by full-matrix least squares on F2, scattering factors from Int. Table Vol. C Tables 4.2.6.8 and 6.1.1.4. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC #1584646. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e mail: deposit@ccdc cam ac uk

4.1.1. Preparation of oxaziridines 1a and 1c

Into 50 ml three-neck round bottomed flask, equipped with thermocouple, dry ice condenser, addition funnel and magnetic stir bar it was placed 3–5 g of dry MCPBA and 20–30 ml of dry acetonitrile (ACN) was added to the flask using syringe. The mixture was agitated for 5 min at ambient temperature, precooled to ~5 °C and the corresponding imidoyl fluoride (2–3 g) was added dropwise as a liquid. Agitated reaction mixture was allowed to warm to ambient temperature. After 2 h at 22–25 °C (15 min at 0–3 °C in case oxidation of **1b**) the dry ice condenser and addition funnel were removed and the reaction vessel was connected to vacuum source through cold (–78 °C) trap. The mixture of the product and ACN was collected in cold trap at 50–300 mm Hg. It was washed with iced water (100 ml x 2) to remove ACN, organic layer was separated and dried over $MgSO_4$.

Compound **1a:** Using 5 g of **1.** It was isolated 3 g (60% yield) of **1a** (purity 98%, 2% of ACN, NMR, and GC); NMR, MS and IR data are given in Table 1.

Compound **1c**: yield 52%; Prepared using 2 g of **1b** at 0–3 °C for 15 min, followed by vacuum transfer in −78 °C cold trap at 150 to 50 mm Hg, ~20 min); after washing and drying by $MgSO_4$ it was isolated 1.1 g (52%) of **1c** (99% purity, 1% ACN) NMR, MS and IR data for **1a** and **1c** can be found in Table 1.

4.1.2. Preparation of oxaziridines 2b, 3a and 4a

Into a 250 ml three-neck round bottomed flask (equipped with thermocouple, dry ice condenser, addition funnel and magnetic stir bar it was placed 8–24 g of MCPBA and 70–110 ml of the corresponding solvent was added (ACN for oxidation of **4** and CH_2Cl_2 for oxidation of **2** and **3**). The reaction mixture was agitated for 5 min at ambient temperature, precooled to 10–15 °C and the corresponding imine (6–9 g) was added dropwise as a liquid. Agitated reaction mixture was allowed to warm to ambient temperature and temperature was kept under 29 °C by occasional cooling of the reaction mixture. After 18–20 h at 22–25 °C, the conversion of the imine was checked by NMR and another portion of MCPBA (3–9 g) was added in case, if the oxidation was not competed. The reaction mixture was agitated at ambient temperature for another 5–6 h. The reaction mixture was cooled down to 5 °C, filtered, washed several times with sodium thiosulfate, until peroxide test was negative (starch paper; in case of **2b** the reaction mixture after water addition was extracted by CH_2Cl_2), 10% solution of sodium bicarbonate (100mlx3) and dried over $MgSO_4$. Solvent was removed under reduced pressure affording crude product, which typically contained 1–3% of m-chlorobenzoic acid. Pure **2b, 3a** and **4a** were isolated by distillation under reduced pressure.

Compound **2b:** Using 9 g (0.048 mol) of **2**, 22 g + 5 g of MCPBA and 150 ml of CH_2Cl_2. After distillation it was isolated 5.6 g (54% yield) of **2b**, b.p. 62.5-63/0.15 mm Hg. Calc.: C, 49.32, H, 3.68, N, 6.39, F, 26.01. $C_9H_8F_3NO_2$. Found. C, 49.09, H, 3.80, N, 6.61, F, 25.84.

Compound **3a:** Using 9 g (0.033 mol) of **3**, 24 g + 9 g of MCPBA and 150 ml of CH_2Cl_2. It was isolated 7.3 g (72% yield) of **3a**, B.P. 66.5-67.5/0.15 mm Hg. Calc. (%): C, 44.62, H, 3.00, N, 5.20, F, 35.29. $C_{10}H_8F_5NO_2$. Found. (%): C, 44.32, H, 2.88, N, 5.03, F, 35.04.

Compound **4a:** Using 6.1 g (0.021 mol) of **4**, 8 g + 3 g of MCPBA and 40 ml of acetonitrile. It was isolated 1.5 g (24% yield) of **4a**, b.p. 82–83/0.15 mm Hg, crystallized on standing at ambient temperature. Calc. (%): C, 41.39, H, 2,53, N, 4.39, F, 41.67. $C_{11}H_8F_7NO_2$. Found. (%): C, 41.17, H, 2.40, N, 4.47, F, 41.58.

4.1.3. Oxidation of hydrocarbon substrates by 1a (NMR experiments)

In 5 mm NMR tube it was placed 0.3- 0.5 ml of $CDCl_3$, ~ 0.1-0.2 g of organic substrate. NMR tube was cooled down to ~–50 °C and ~ 0.1 g of oxaziridine **1a** was added and tube allowed to warm up to ambient temperature with occasional shaking (~10 min). ^1H and ^{19}FNMR spectra were taken within 1–2 h. In all cases complete conversion of oxaziridine **1a** was observed. Oxidation products − $Ph_3P=O$, $(CH_3)_3SO_2$, 7-oxa-bicyclo[4.1.0]heptane, acetaldehyde and cyclohexene oxide were identified by comparison with authentic samples (NMR).

4.1.4. Hydrogenation of compound 2

A mixture of 20 g (0.11 mol) of **2**, 100 ml of dry THF and 2 g of 5% Pd on alumina was placed in 400 ml Hastelloy shaker tube, it was cooled down with dry ice, evacuated and pressurized with 300 psi of H_2. The reactor was warmed up to ambient temperature and was kept agitated at this temperature for 12 h. It was vented and unloaded. The reaction mixture was filtered through Celite^R to remove the catalyst. According ^1H and ^{19}F NMR only compound **2a** was present in the crude reaction mixture. The solvent was removed under reduced pressure and the residue was distilled to give 12.8 g (64% yield) of **2a**, b.p. 66 °C/14 mm Hg, purity 99.9% (GC, NMR). NMR and MS data of **2a** are given in Table 1.

4.1.5. Partial oxidation of 4

To a well agitated mixture of 1.6 g dry MCPBA and 10 ml of CH_2Cl_2 it was added 1 g of **4** at +10 °C. The reaction mixture was warmed up to ambient temperature and kept for 16 h According ^1H and ^{19}F NMR of crude reaction mixture all starting material was converted at this point. Precipitate was filtered off, organic layer was washed with sodium thiosulfate (50mlx2) and saturated solution of $NaHCO_3$ (50mlx2), dried over $MgSO_4$ and solvent was removed under reduced pressure. The residue (oil) was left at ambient temperature for 24 h, white solids which precipitated were filtered of and the residue (0.8 g) was analyzed by GC/MS and ^1H NMR and was shown to be a mixture of **4a** and **4b** in ratio 85:15. NMR and MS data of **4b** are given in Table 1.

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