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Polyfluoro *N*-aryloxaziridines. Synthesis and thermal rearrangement

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Abstract

Previously unknown perfluoroaryl imines of polyfluoroketones were prepared in 60%–70% yield by reaction of the imines of hexafluoroacetone, chloropentafluoroacetone and 1,3-dichlorotetrafluoroacetone with pentafluoropyridine or perfluorotoluene. Oxidation of these *N*-perfluoroaryl imines by *m*-chloroperoxybenzoic acid (MCPBA) in sulfolane leads to the formation of the corresponding oxaziridines in 60%–90% yield. At elevated temperature the *N*-aryloxaziridines readily rearrange into the respective *N*-arylamides of chlorodifluoro- and trifluoro-acetic acid.

Keywords: Polyfluoro *N*-aryloxaziridines; Synthesis; Thermal rearrangement; NMR spectroscopy; IR spectroscopy; Mass spectrometry

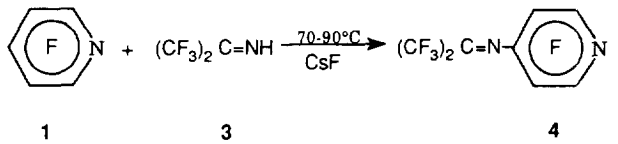
1. Introduction

Oxaziridines are an important class of heterocyclic compounds which have been intensively studied for more than 35 years [1,2] but the numbers of fluorooxaziridines are still very limited. Perfluoro-2-azapropene oxide [3], $SF_5\overline{N-O-CF_2}$ [4], $\overline{CF_2-O-NCFXCF_2Y}$ [5] and $CF_3\overline{N-O-C}(CF_3)_2$ [6] have been prepared by the reaction of CF_3OOH with the corresponding imines. More recently, $CF_3\overline{N-O-CFN}(CF_3)_2$ [7] was prepared by the oxidation of the dimer of perfluoro-2-azapropene with H_2O_2 and $(CF_3)_2CF\overline{N-O-C}(CF_3)_2$ [8] by oxidation of the imine with chlorine gas in the presence of metal carbonate. Other methods for the preparation of fluorooxaziridines include the condensation of $(CF_3)_3CN{=}O$ with Ph_2N_2 resulting in the formation of 2-perfluoro-t-butyl-3,3-diphenyloxaziridine [9], photochemical cyclization of the corresponding nitrones leading to 2,3,3-fluorotriaryloxaziridines [10] and the use of *m*-chloroperoxybenzoic acid (MCPBA) for the preparation of partially fluorinated *N*-sulfonyl–oxaziridines $RSO_2\overline{N-O-CHC_6F_5}$ [11] and *N*-(phenylsulfonyl) (3,3-difluorocamphoryl) oxaziridine [12].

Recently, a general route for the oxidation of per- and polyfluoroazaalkenes was developed using MCPBA in appropriate polar solvents [13–15]. To further explore the scope of this procedure, a new simple procedure for the preparation of polyfluoro-*N*-arylimines from fluoroacetones was developed. Oxidation with MCPBA in sulfolane provided the corresponding *N*-aryloxaziridines in excellent yield.

2. Results and discussion

The azaanion of hexafluoroacetone imine is a strong nucleophile and is effective in replacing activated halogen atoms in acyl halides and the chlorides of silicon, phosphorus, arsenic and sulfur [16]. We have extended these reactions to include nucleophilic substitution of fluoroaromatics. Pentafluoropyridine (**1**) and perfluorotoluene (**2**) react with the imine of hexafluoroacetone (**3**) in sulfolane in the presence of an excess of CsF, giving the corresponding arylimines **4** and **5** in 60% yield.



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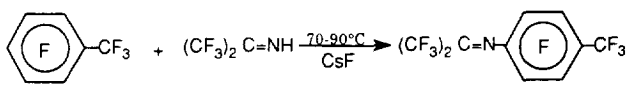

2 3 5

Under similar conditions the imines of chloropentafluoro- (**6**) and 1,3-dichlorotetrafluoro acetone (**7**) also react with **1** and **2** producing imines **8** and **9**, respectively.

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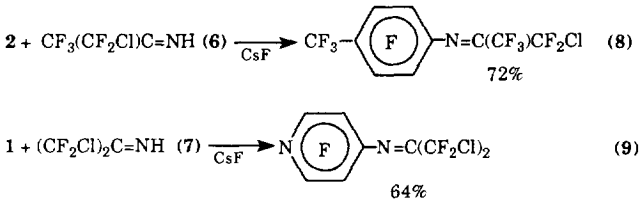
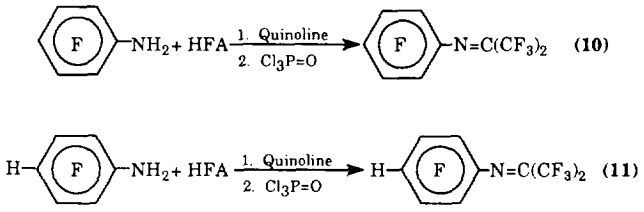


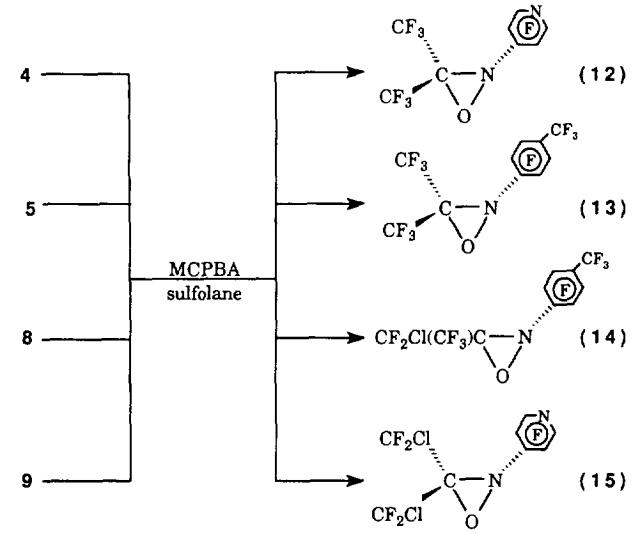
In the preparation of the pentafluoro- (**10**) and tetrafluorophenyllimines (**11**) of hexafluoroacetone by reaction of the corresponding anilines with hexafluoroacetone, the conditions previously used for the preparation of acylimines of hexafluoroacetone were employed [16].



Compounds **4, 5** and **8–11** are pale yellow liquids and highly soluble in polar organic solvents. The IR spectra exhibit absorptions within the range 1750–1725 cm^{-1} (C=N) and the MS (CI) contain M + 1 ions of high intensity in each case. The ^{19}F NMR spectra of these compounds are in good agreement with the structure of the imines and are discussed below.

2.1. Preparation of N-aryloxaziridines

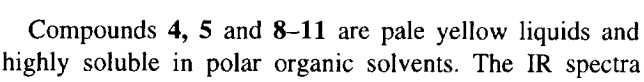
The reaction of imines **4, 5, 8** and **9** with MCPBA at 22 °C in CH_3CN or sulfolane results in the formation of the corresponding oxaziridines in 60%–89% yield. Sulfolane is a more suitable solvent for this reaction because the low solubility of the target compounds facilitates their isolation. No evidence for the formation of the corresponding isomeric nitrones was found in these oxidations.



The formation of the oxaziridines **12–15** in this reaction is in sharp contrast with other data where the oxidation of polyfluorotriarylimines by CF_3COOOH resulted in the formation of the corresponding nitrones exclusively [17]. Perhaps these contrasting results are due to the greater oxidizing power of the peracid and the higher acidity of the trifluoroacetic acid. Attempts to oxidize imines **10** and **11** with MCPBA gave a complex mixture of unidentified compounds with no evidence for the formation of oxaziridines.

Compounds **12–15** are colorless liquids, stable at 22 °C for several days. The IR spectra exhibit weak to moderate absorptions at 1420 cm^{-1} and strong absorptions at 1500 and 1640 cm^{-1} assigned to vibrations of the oxaziridine and aromatic rings. Mass spectra (CI) exhibit intense M + 1 ions in each case. ^{19}F NMR spectra are discussed in the next section of this paper.

Compounds **12–15** are thermally less stable than perfluoro-2,3-dialkyloxaziridines [15] and at 70–90 °C they rapidly rearrange into the amides **16–19**.



(**16**) X = Y = F, $Ar_f = p\text{-}NC_5F_4$

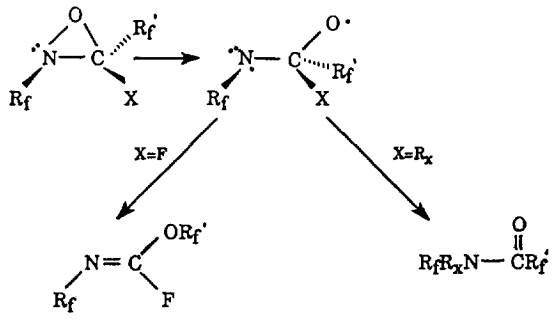
(**17**) X = Y = F, $Ar_f = p\text{-}CF_3C_6F_4$

(**18**) X = F, Y = Cl, $Ar_f = p\text{-}CF_3C_6F_4$

(**19**) X = Y = Cl, $Ar_f = p\text{-}NC_5F_4$

Surprisingly, this process is regiospecific. In the case of the unsymmetrical oxaziridine **14**, only the CF_2Cl group migrates to the nitrogen.

This thermal rearrangement is similar to that of 2,3,3-tris(trifluoromethyl)oxaziridine [6] and is typical for hydrocarbon oxaziridines [1,2]. In contrast, all the 2,3-bis-(perfluoroalkyl)-3-fluorooxaziridines observed to data undergo thermal rearrangement to the respective imidates $R_fN{=}CFOR'_f$ [15]. The presence of a fluorine atom on C-3 clearly has a dramatic effect on the thermal rearrangement path. If we assume a common diradical intermediate for both rearrangements, the two rearrangements are depicted in Scheme 1.



Scheme 1.

Table 1
Free energy of activation for equivalent methyl groups in imines

Compound	T_c (K)	δ (Hz)	$\Delta G^{\ddagger}$ (kcal mol^{-1})
4	320	526	14.28
5	333	534	14.88
10	321	378	14.54
11	326	488	14.61

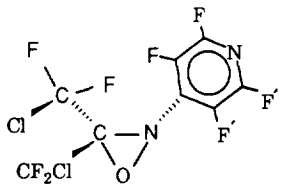
2.2. NMR spectra of N-arylimines and N-aryloxaziridines

The ^{19}F NMR spectra of compounds **4, 5** and **8–11** at room temperature are in good agreement with the imine structure, but the signals belonging to the CF_3 or CF_2Cl resonances are broad. However, at low temperature, the NMR spectra of compounds **4, 5** and **11** change to well-resolved multiplets exhibiting $^4J_{FF}$ coupling of the trifluoromethyl groups and $^6J_{FF}$ coupling of the low-field CF_3 group with *ortho*-fluorines in the aromatic ring. At 40–60 °C, the signals of the CF_3 groups collapse to one broad signal. Coalescence points (T_c) for solutions of these compounds in $CDCl_3$ (Table 1) have been determined and the activation energies for the dynamic process calculated using a literature procedure [2] (Table 1).

The calculated free energies are in good agreement with values reported for the rotational barriers about the C=N bond in the *p*-substituted *N*-phenylimines of hexafluoroacetone [19]. However, in the case of imines **5, 10** and **11**, it is impossible to distinguish the process (nitrogen inversion or rotation around the C=N bond) responsible for the temperature-dependent NMR.

The ^{19}F NMR spectra of oxaziridines **12–15** are equally interesting. For example, the NMR spectrum of compound **15** at 22 °C shows seven different resonances with relative areas 1:2:1:1:1:1:1. The presence of the asymmetric nitrogen causes magnetic nonequivalence of the fluorines in both CF_2Cl groups. Four broad signals are observed for the fluorines in the aromatic ring at 22 °C, but they are resolved at −30 °C and the spectrum can be analyzed as first order (see Fig. 1). Values of the coupling constants in the aromatic ring are in good agreement with values reported in the literature for monosubstituted tetrafluoropyridines [20]. The magnetic nonequivalence of the fluorines in the aromatic ring can be explained in terms of restricted rotation of the tetrafluoropyridine ring around the C–N bond leading to a strong interaction of one of the *ortho* fluorines on the aromatic ring with the *cis*-alkyl group at C-3. This is reasonable based on work with *cis*-2,3-bis(perfluoroalkyl)-3-fluorooxaziridines where large long-range ^4J couplings between the C-3 fluorine and the *cis*-*N*-alkyl groups are observed, indicating a close juxtaposition in the molecule [1].

[2] $\Delta G^{\ddagger} = aT[9.972 + \log(T/\Delta\delta)]$ ($a = 4.575 \times 10^{-3}$, ΔG in kcal mol^{-1}) [18].



Experimental data derived from the variable-temperature NMR spectra of the compounds are in good agreement with this hypothesis. The signals of the *m,m'*- and *o,o'*-fluorine atoms in the spectrum of compound **15** exhibit a reversible temperature dependence and collapse into one broad signal at approximately 60 °C. However heating to 60 °C results in the formation of a small amount of the corresponding amide **19** (< 15%) as a result of the thermal rearrangement mentioned earlier. In the NMR spectra of **12** and **13** at 22 °C, *m*- and *m'*-fluorines are nonequivalent and have different chemical shifts, whereas the signals of the *o*- and *o'*- overlap. At elevated temperatures, both compounds behave similarly to **15** and the signals of the *m*- and *m'*-fluorines collapse into one broad signal within the temperature range 45–60 °C. Coalescence points were determined for oxaziridines **12, 13** and **15** and the free energies of rotation of the aryl group were calculated [18]. The data are summarized in Table 2.

The free energy values are in good agreement with the proposed restricted rotation of the aryl group around the C–N bond because the barrier depends on the size of the fluoromethyl group (compounds **12** and **15**). However, it is necessary to stress that calculated values obtained by the method used in this work are approximate and can be significantly different from values found by other methods [21].

3. Experimental details

3.1. General methods

All volatile compounds were handled in a Pyrex vacuum system equipped with glass–Teflon valves. Pressures were measured with a Wallace and Tiernan series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by *PVT* measurements. Temperatures were measured using a digital indicating iron–constantan thermocouple. ^{19}F and ^1H NMR spectra were recorded on an IBM NR 200 AF instrument in $CDCl_3$ with $CFCl_3$ or TMS as internal reference. Coalescence temperatures were determined for 10% solutions of the imines and oxaziridines in $CDCl_3$. The samples were prepared as described in Ref. [19]. Infrared spectra were recorded on a Perkin–Elmer model 1430 instrument with a data station (liquid film, KCl). Mass spectra were recorded on a Hewlett–Packard 5985-B spectrometer at 70 eV for both EI and CI (CH_4). Samples were introduced by direct injection. Boiling points of amides **16–19** were determined by Sivoloboff's [22] method and are uncorrected.

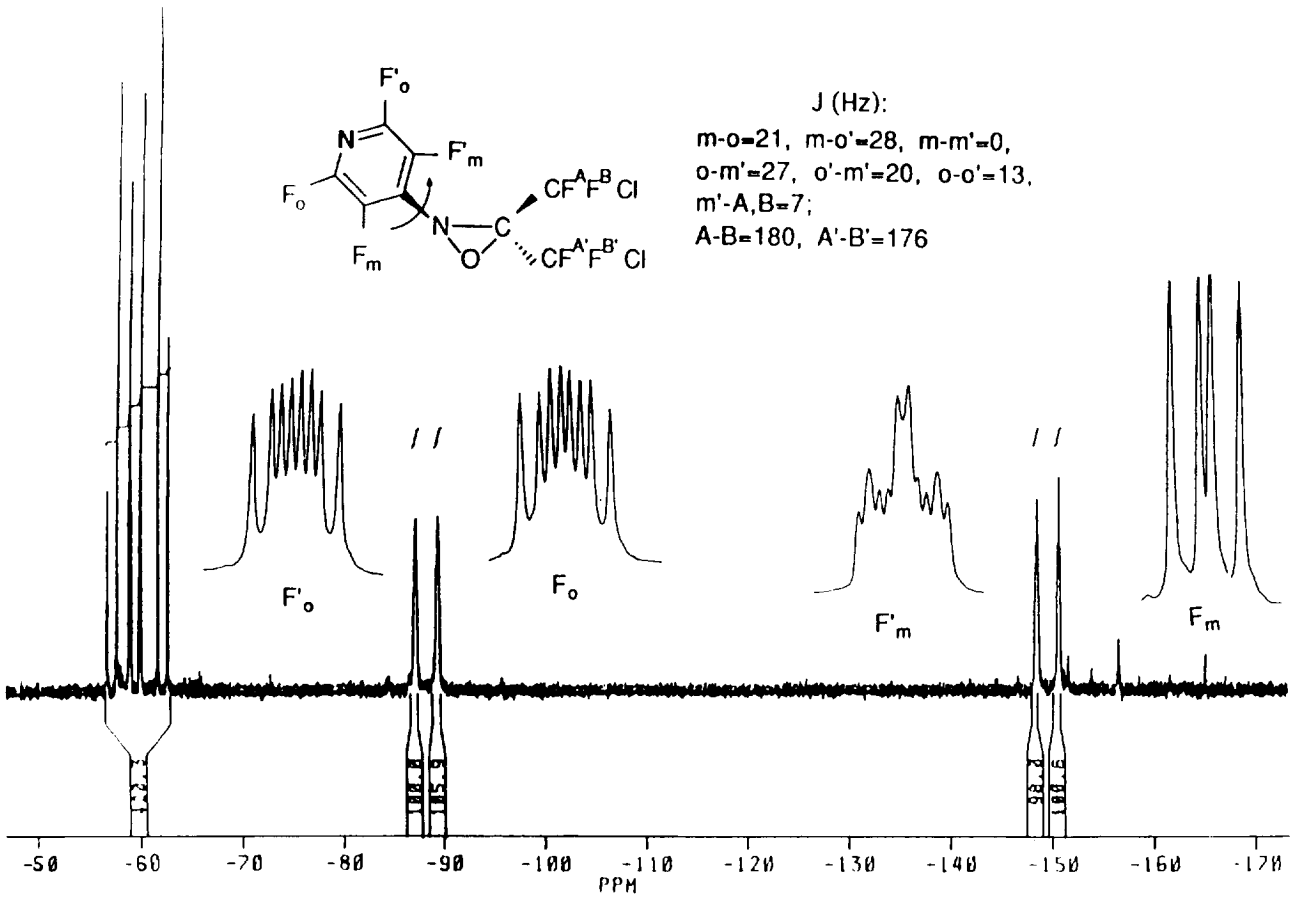


Fig. 1. ^{19}F spectrum of oxaziridine **15** at −30 °C.

Table 2
Free energies of activation for equivalent *m*-fluorine atoms

Compound	T_c [a,b] (K)	δ (Hz)	$\Delta G^{\ddagger}$ (kcal mol^{-1})
12	319	420	14.33
13	304	465	13.61
15	333	520	14.90

[a] Coalescence points for signals of *m,m'*-fluorines.
[b] ±1 K.

The purity of the new compounds was established by ^{19}F NMR spectroscopy. Spectra were generally free of fluorine-containing impurities or contained only trace amounts of impurities.

3.2. Reagents

Pentafluoropyridine (**1**), perfluorotoluene (**2**), polyfluoroketones, ammonia, cesium fluoride, MCPBA and sulfolane were obtained from commercial sources. Cesium fluoride was heated for 2 h with the flame of Bunsen burner in a porcelain dish and used directly after heating. MCPBA (60%–80%, Aldrich) was washed three times with a buffer solution of pH 7–8 and dried in a vacuum desiccator over P_4O_{10} for 5–10 h at 22 °C. Compound **10** was identified by comparison of the ^{19}F NMR and IR data with literature values [23]. Imines **3, 6** and **7** were synthesized by a literature method [24].

3.3. General procedure for the preparation of fluoroarylimines from fluoroketones

Method a

The mixture of imine, pentafluoropyridine or perfluorotoluene and excess CsF in sulfolane was heated in a 100 ml Pyrex flask closed with a glass–Teflon valve for 15–48 h at 70–90 °C. The product was collected in a trap under vacuum and then distilled at reduced pressure. The details of the reactions are given in Table 3. In the NMR data that follows, F_o and F_m refer to fluorines *ortho* and *meta* to the imine or oxaziridine nitrogen.

p-NC_5F_4–N=$C(CF_3)_2$ (**4**): b.p. 81.6–81.9 °C/160 mmHg. IR (cm^{-1}): 1753 (m); 1638 (s); 1481 (s); 1420 (w); 1335 (s); 1240 (vs); 1040 (vs); 988 (vs); 756 (m); 723 (m). MS (CI) *m/z*: 314 (M^+, 13); 295 [$(M-F)^+$, 3]; 245 [$(M-CF_3)^+$, 15]; 169 ($C_3F_7^+$, 15); 100 ($C_2F_4^+$, 14); 69 (CF_3^+, 100) ppm. ^{19}F NMR (22 °C) δ: *p*-NC_5F_4–N=$C(CF_3^A)CF_3^B$: A −67.42 (3F, br s); B −70.41 (3F, br s); F_m −88.32 (2F, hex.); F_o −152.68 (2F, hex.) ppm. ^{19}F NMR (−30 °C) δ: A −66.75 (3F, q, t.); B −69.72 (3F, q); F_m −87.48 (2F, hex.); F_o −151.12 (2F, pent) ppm; $J_{A-B}=6$ Hz, $J_{A-F_m}=3.5$ Hz.

Table 3
Reaction of imines **3**, **6** and **7** with pentafluoropyridine and perfluorotoluene

Imine [a]	Arene [a]	CsF [a]	Sulfolane (ml)	Conditions		Product (%)
				Temp. (°C)	Time (h)	
3 (10)	**1** (10)	15	5	90	15	**4** (61)
3 (25)	**2** (21)	25	10	70	48	**5** (62)
6 (21)	**2** (20)	28	10	70	15	**8** (72) [b]
7 (29)	**1** (30)	48	7	80	13	**9** (64) [c]

[a] In mmol.
[b] Conversion of **2** = 65%.
[c] Conversion of **1** = 80%.

p-CF_3–C_6F_4–N=$C(CF_3)_2$ (**5**): b.p. 78–80 °C/100 mmHg. IR (cm^{-1}): 1734 (w); 1665 (m); 1649 (m); 1510 (s); 1419 (m); 1260 (m); 1201 (s); 1156 (m); 1001 (s); 878 (m); 723 (m); 717 (m); 687 (m); 659 (m). MS (CI) *m/z*: 381 (M^+, 59); 362 [$(M-F)^+$, 100]; 312 [$(M-CF_3)^+$, 23]; 219 ($C_4F_9^+$, 10). ^{19}F NMR (22 °C) δ: *p*-CF_3^C–C_6F_4–N=$C(CF_3^A)CF_3^B$: A −67.58 (3F, br.s.); B −70.14 (3F, br.s); C −56.73 (3F, t); F_o −149.51 (2F, dd); F_m = 139.71 (2F, m) ppm. ^{19}F NMR (−30 °C) δ: A −67.08 (3F, q–t); B −69.60 (3F, q); C −56.03 (3F, t), F_o −148.23 (2F, m); F_m −138.88 (2F, m) ppm; J_{A-B} = 5 Hz, J_{C-F_m} = 21 Hz, J_{A-F_o} = 3 Hz.

p-CF_3–C_6F_4–N=$C(CF_3)CF_2Cl$ (**8**) (1:1 mixture of *cis* and *trans* isomers): b.p. 39–40 °C/1 mmHg. IR (cm^{-1}): 1726 (w); 1659 (w); 1501 (vs); 1423 (m); 1346 (m); 1306 (m); 1239 (vs); 1173 (vs); 1001 (vs); 905 (m); 877 (m). MS (CI, ^{35}Cl) *m/z*: 398 [$(M+1)^+$, 54]; 397 (M^+, 30); 378 [$(M-F)^+$, 41]; 362 [$(M-Cl)^+$, 23). ^{19}F NMR (22 °C) δ: *p*-CF_3^C–C_6F_4–N=$C(CF_2Cl^A)CF_3^B$: A −59.60 (2F, br s); −60.31 (2F, br s); B −65.85 (3F, br s); −68.46 (3F, br s); F_o −148.63 (2F, br s); −149.59 (2F, br s); F_m −139.87 (4F, m); C −56.50 (6F, t) ppm; J_{C-F_m} = 22 Hz.

p-NC_5F_4–N=$C(CF_2Cl)_2$ (**9**): b.p. 56–57 °C/1 mmHg. IR (cm^{-1}): 1729 (m); 1635 (s); 1480 (vs); 1419 (w); 1263 (m); 1190 (s); 1135 (m); 1039 (vs); 974 (vs); 879 (vs); 828 (m). MS (CI, ^{35}Cl) *m/z*: 347 [$(M+1)^+$, 100); 346 (M^+, 62); 327 [$(M-F)^+$, 17]; 311 [$(M-Cl)^+$, 39]. ^{19}F NMR (22 °C) δ: *p*-NC_5F_4–N=$C(CF_2Cl^B)CF_2Cl^A$: A, B −58.35 (4F, br); F_o −88.85 (2F, hex.); F_m −151.63 (2F, hex.) ppm; coupling constants not readily determined.

Method b

To a solution consisting of 20–60 mmol of the corresponding aniline in 15–20 ml of quinoline, a 5% excess of hexafluoroacetone was condensed under vacuum at −196 °C. The reaction mixture was warmed to 22 °C and kept at this temperature with stirring for 3 h. The reaction mixture was then transferred into a 500 ml three-neck flask, equipped with an addition funnel and reflux condenser. Phosphoryl chloride (23 mmol) was added dropwise over 20 min. The reaction mixture was kept at 100 °C for 30 min and then the product of the reaction was distilled out at reduced pressure and further purified on a small spinning-band column.

C_6F_5–N=$C(CF_3)_2$ (**10**): yield 75%; b.p. 84–85 °C/160 mmHg (lit. value [22]: 145–148 °C). IR and NMR spectra agreed with literature values [23].

p-H–C_6F_4–N=$C(CF_3)_2$ (**11**): yield 78%; b.p. 155–156 °C. IR (cm^{-1}): 3092 (w); 1723 (m); 1638 (m); 1515 (vs); 1467 (s); 1335 (m); 1238 (s); 1195 (s); 1036 (m); 986 (m); 840 (m); 750 (m); 606 (m). ^{19}F NMR (22 °C) δ: *p*-H–C_6F_4–N=$C(CF_3^A)CF_3^B$: A −67.65 (3F, br s); B −70.00 (3F, br s); F_o −138.26 (2F, d–t); F_m −151.18 (2F, d–t) ppm. ^{19}F NMR (−53 °C) δ: A −67.58 (3F, q–t); B −69.62 (3F, q); F_o −137.72 (2F, d–t); F_m −150.25 (2F, m) ppm; J_{A-B} = 7 Hz, J_{A-F_o} = 3.5 Hz, $J_{F_o-F_m}$ = 11 Hz. ^{1}H NMR (22 °C) δ: 6.99 (t) ppm; J_{H-F_m} = 21 Hz.

3.4. General procedure for the oxidation of N-arylimines with MCPBA

The arylimine (3–4 mmol) was added at 22 °C to a stirred solution of MCPBA in sulfolane. The reaction mixture was stirred at this temperature for 15–30 min and then the lower layer was separated, washed twice with water and dried over P_4O_{10}. Details of the reactions are summarized in Table 4.

p-$NC_5F_4\overline{N-O-C}(CF_3)_2$ (**12**): IR (cm^{-1}): 1641 (m); 1489 (s); 1429 (w); 1402 (w); 1330 (m); 1262 (vs); 1217 (s); 1079 (m); 993 (m); 964 (m); 717 (m). MS (CI) *m/z*: 331 [$(M+1)^+$, 8]; 330 (M^+, 16); 314 [$(M-O)^+$, 9); 245 [$(M-CF_3O)^+$, 12]; 169 ($C_3F_7^+$, 8); 101 ($C_2F_4H^+$, 100). ^{19}F NMR (−9 °C) δ: *p*-$NC_5F_4\overline{N-O-C}(CF_3^A)CF_3^B$: A −70.25 (3F, d–q); B −75.37 (3F, q); F_o, F_o' −150.3 (d–d), −150.05 (m 2F); F_m −88.48 (1F, d–d–d); F_m' −86.28

Table 4
Oxidation of arylimines with MCPBA

Imine [a]	MCPBA [b]	Sulfolane (ml)	Time [c] (min)	Product (%)
4 (3.5)	6	4	30	**12** (60)
5 (4.2)	13.8	5	30	**13** (63)
8 (3)	9.9	5	15	**14** (89)
9 (3.7)	7.1	10	30	**15** (70)

[a] In mmol.
[b] Based on 95% MCPBA.
[c] At 22 °C.

(1F, d–d–d) ppm; $J_{A-B}=7$ Hz, $J_{A-F_o}=10$ Hz, $J_{F_m-F_o}=J_{F_{m'}-F_{o'}}=20$ Hz, $J_{F_m-F_{m'}}=15$ Hz, $J_{F_m-F_{o'}}=26$ Hz, $J_{F_o-F_{o'}}=0$ Hz, $J_{F_o-F_{m'}}=28$ Hz, $J_{F_m-F_{o'}}=28$ Hz.

p-CF_3–$C_6F_4\overline{N–O–C}(CF_3)_2$ (**13**): IR (cm^{-1}): 1658 (m); 1505 (s); 1420 (m); 1400 (m); 1336 (s); 1258 (vs); 1232 (vs); 155 (vs); 1008 (m); 978 (m); 895 (m); 877 (m); 727 (m); 716 (m). MS (CI) *m/z*: 398 [$(M+1)^+$, 64]; 397 (M^+, 43); 381 [$(M-O)^+$, 17]; 378 [$(M-F)^+$, 100]; 362 [$(M-OF)^+$, 50]; 233 ($C_7F_7NH_3^+$, 55); 232 ($C_7F_7NH^+$, 89); 214 ($C_7F_6NH^+$, 57). ^{19}F NMR (−10 °C, $CDCl_3$) δ: *p*-CF_3^C–$C_6F_4\overline{N–O–C}(CF_3^A)CF_3^B$: A −69.87 (3F, oct.); B −75.09 (3F, q); F_o, F_o −147.26 (2F, m); F_m −139.81 (1F, d–d–d); F'_m −137.51 (1F, d–d–d); C −56.65 (3F, t) ppm; $J_{A-B}=7$ Hz, $J_{C-F_o,F_{o'}}=22$ Hz, $J_{A-F_o}=11$ Hz, $J_{F_o-F_{m'}}=20$ Hz, $J_{F_{o'}-F_{m'}}=10$ Hz.

p-$CF_3C_6F_4\overline{N–O–C}(CF_2Cl)CF_3$ (**14**) (1:1 mixture of *cis* and *trans* isomers): IR (cm^{-1}): 1657 (m); 1511 (s); 1427 (w); 1342 (vs); 1299 (vs); 1161 (s); 1041 (m); 1001 (s); 901 (m); 877 (m); 717 (s). MS (CI, ^{35}Cl) *m/z*: 414 [$(M+1)^+$, 60); 413 (M^+, 85); 410 [$(M-OF)^+$, 10]; 397 [$(M-O)^+$, 100]; 362 [$(M-OCl)^+$, 16]. ^{19}F NMR (22 °C, $CDCl_3$) δ: *p*-$CF_3^DC_6F_4\overline{N–O–C}(CF_3^C)CF^AF^BCl$: ($Ar_f$ and CF_3 are *cis*): A −62.70 (d–q); B −64.80 (d–q, 2F, AB pattern); F_o,F'_o −148.80 (2F, br t); F_m −140.14 (1F, br s); F'_m −138.12 (1F, br s); C −68.31 (3F, m); D −56.93 (3F, t) ppm; $J_{A-B}=180$ Hz, $J_{C-F_o}=11$ Hz, $J_{A-C}=9$ Hz, $J_{B-C}=8.5$ Hz, $J_{D-F_m,F_{m'}}=22$ Hz (Ar_f and CF_2Cl are *cis*): A −59.75 (d–m); B −61.85 (d–pent., 2F, AB pattern); F_o,F'_o −148.80 (2F, br t); F_m −140.14 (1F, br s); F'_m −138.12 (1F, br s); C −56.87 (3F, t); D −73.20 (3F, d–d) ppm; $J_{A-B}=181$ Hz, $J_{B-F_o}=16$ Hz, $J_{A-F_o}=6$ Hz, $J_{A-C}=8$ Hz, $J_{B-C}=5$ Hz, $J_{D-F_m,F_{m'}}=22$ Hz.

p-$NC_5F_4\overline{N–O–C}(CF_2Cl)_2$ (**15**): IR (cm^{-1}): 1639 (s); 1486 (vs); 1423 (m); 1250 (m); 1148 (vs); 1059 (s); 976 (m); 857 (m); 828 (m); 750 (m). MS (CI, ^{35}Cl) *m/z*: 363 [$(M+1)^+$, 100]; 362 (M^+, 41); 347 [$(M+1-O)^+$, 56); 346 [$(M-O)^+$, 18]. ^{19}F NMR (−30 °C, $CDCl_3$) δ: *p*-$NC_5F_4\overline{N–O–C}(CF^AF^BCl)CF^{A'}F^{B'}Cl$: A −58.10 (d–q); B −62.70 (d–t, 2F, typical AB pattern); A′ −60.20 (d–q); B′ −60.10 (d–d, 2F, AB pattern); F_o −148.00 (1F, d, d); F'_o −150.28 (1F, d–d); F_m −88.83 (1F, d–d–d); F'_m −86.60 (1F, d–d–d) ppm; $J_{A-B}=180$ Hz, $J_{A'-B'}=176$ Hz, $J_{F_m-F_{o'}}=28$ Hz, $J_{F_m-F_o}=21$ Hz, $J_{F_o-F_{o'}}=0$ Hz, $J_{F_{m'}-F_{o'}}=20$ Hz, $J_{F_o-F_m}=29$ Hz, $J_{F_{m'}-F_m}=13$ Hz, $J_{A(B)-C}=5$ Hz, $J_{B(A)-C}=9$ Hz.

3.5. Thermal isomerization of N-aryloxaziridines

The oxaziridines (0.3–0.5 g) were kept at 80–100 °C in a 5 ml glass sample tube for 0.5–2 h. ^{19}F NMR spectroscopy indicated that the main product of each reaction was the corresponding amide, containing a very small amount of the starting imine.

p-$NC_5F_4N(CF_3)C(O)CF_3$ (**16**): b.p. 149–150 °C. IR (cm^{-1}): 1788 (C=O, m); 1767 (m); 1641 (m); 1499 (s); 1358 (m); 1259 (m); 1220 (m); 1159 (m); 974 (s); 887 (m); 834 (m); 699 (m). MS (CI) *m/z*: 331 [$(M+1)^+$, 100]; 314 [$(M-O)^+$, 4]; 311 [$(M-F)^+$, 6]. ^{19}F NMR δ: *p*-$NC_5F_4N(CF_3^A)C(O)CF_3^B$: A −57.28 (3F, br s); B −72.10 (3F, hex.); F_o −142.73 (2F, m); F_m −85.05 (2F, m) ppm.

p-$CF_3C_6F_4N(CF_3)C(O)CF_3$ (**17**): b.p. 170–171 °C. IR (cm^{-1}): 1787 (C=O, s); 1766 (m); 1654 (m); 1504 (s); 1430 (m); 1349 (s); 1157 (vs); 1114 (m); 997 (s); 890 (m); 713 (m). MS (CI) *m/z*: 398 [$(M+1)^+$, 100]; 397 (M^+, 27); 382 [$(M-O)^+$, 10]; 378 [$(M-F)^+$, 36]; 328 [$(M-CF_3)^+$, 4]. ^{19}F NMR δ: *p*-$CF_3^CC_6F_4N(CF_3^B)CF_3^A$: A −57.91 (3F, br s); B −72.53 (3F, s); F_o −140.25 (2F, m); F_m −137.75 (2F, m); C −57.20 (3F, t) ppm; $J_{C-F_o}=22$ Hz.

p-$CF_3C_6F_4N(CF_2Cl)CF_3$ (**18**): b.p. 180 °C (decomp.). IR (cm^{-1}): 1776 (C=O, m); 1658 (w); 1513 (vs); 1431 (w); 1347 (s); 1244 (s); 1162 (vs); 1115 (m); 999 (s); 848 (m); 716 (m). ^{19}F NMR δ: *p*-$CF_3^CC_6F_4N(CF_2Cl^A)C(O)CF_3^B$: A −37.03 (2F, br s); B −72.45 (3F, t); F_o −139.18 (2F, m); F_m −137.90 (2F, m); C −57.23 (3F, t) ppm; $J_{C-F_o}=22$ Hz, $J_{A-B}=4$ Hz.

p-$NC_5F_4N(CF_2Cl)C(O)CF_2Cl$ (**19**): b.p. 200 °C (decomp.). IR (cm^{-1}): 1766 (C=O, s); 1638 (m); 1485 (s); 1420 (w); 1294 (m); 1143 (s); 972 (s); 826 (s). ^{19}F NMR δ: *p*-$NC_5F_4N(CF_2Cl^A)C(O)CF_2Cl^B$: A −36.86 (2F, s); B −61.20 (2F, t); F_o −140.76 (2F, m); F_m −85.70 (2F, m) ppm; $J_{A-B}=4$ Hz.

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