Synthesis of polyfluoro-2-alkanesulfonyl-3,3-dialkyloxaziridines

Viacheslav A. Petrov†, Todd E. Mlsna and Darryl D. DesMarteau*
Howard L. Hunter Chemistry Laboratory, Box 341905, Clemson University, Clemson, SC 29634-1905 (USA)

Abstract

Polyfluoro-*N*-alkanesulfonamides of the type $FSO_2N(H)CF(CF_2X)CF_2Y$ and $R_fSO_2N(H)CF(CF_2X)CF_2Y$ (X, Y = F, Cl) have been prepared by the reaction of the imines of polyfluoroketones with perfluoroalkanesulfonyl fluorides or SO_2ClF in the presence of CsF, followed by reaction with sulfuric acid. Reaction of these sulfonamides with *m*-chloroperoxybenzoic acid in a polar solvent leads to the formation of the novel title compounds in 30%–80% yields. The sulfonamides do not undergo dehydrofluorination with cesium fluoride, but react to form the stable cesium salts. Several imines of the type $R_fSO_2N{=}C(CF_2X)CF_2Y$ were isolated by reduction of the respective oxaziridines.

Introduction

The reactivity of the imine anion from the imine of hexafluoroacetone has been studied with a wide range of organic and inorganic substrates [1], including sulfur(II) and sulfur(IV) derivatives [2]. However, reactions of this anion with sulfonyl fluorides have not been reported. Recently, we have found that imines of polyfluoroketones with CsF in a polar solvent are effective for nucleophilic substitution by imine anions on activated fluoroaromatics [3]. In an extension of this reaction, reaction with perfluoroalkylsulfonyl fluorides or SO_2ClF can be used for the preparation of the amide derivatives $R_fSO_2N(Cs)CF(CF_2X)CF_2Y$ which are readily converted by H_2SO_4 to the respective amine.

Only two representative compounds of this class, $FSO_2N(H)CF_3$ and $FSO_2N(H)C_2F_5$ [4], were known. In contrast to fluorinated secondary amines $(R_f)_2NH$ [5] or secondary amides $R_fC(O)N(H)R_f'$ [6], which rapidly eliminate HF in the presence of bases such as alkali metal fluorides, these new amines behave as strong acids. Similar to $(CF_3SO_2)_2NH$ [7], these compounds react with cesium fluoride producing stable cesium salts. Surprisingly the amines react with *m*-chloroperoxybenzoic acid in polar solvents to give the new oxaziridines, $R_fSO_2N{-}C(CF_2X)CF_2Y$ (O). This is in contrast with hydrocarbon amines, which yield hydroxylamines with peroxy acids [8].

†Permanent address: INEOS AN USSR, Vavilova 28, Moscow, 117813, Russian Federation.

*Author to whom correspondence should be addressed.

Results and discussion

The imine of hexafluoroacetone (**1**) reacts readily with alkylsulfonyl fluorides **2–4** in the presence of excess CsF in MeCN.

$$(CF_3)_2C{=}NH + R_fSO_2F \xrightarrow[MeCN,\ CsF]{80\text{–}90\ ^\circ C,\ 16\text{–}24\ h} R_fSO_2{-}N(Cs)CF(CF_3)_2$$

$$\xrightarrow{H_2SO_4} R_fSO_2{-}N(H)CF(CF_3)_2\ (75\%\text{–}87\%)$$

(**1**) (**2–4**) (**5–7**)

(**2**, **5**) $R_f = CF_3$
(**3**, **6**) $R_f = C_4F_9$
(**4**, **7**) $R_f = C_6F_{13}$

By following the reaction with ^{19}F NMR spectroscopy, we were able to determine that the first step involves the formation of the stable cesium salts of **5–7**. The pure polyfluoro-*N*-alkylsulfonyl amines or sulfonamides were then isolated in 75%–87% yield after evaporation of the solvent and distillation from concentrated H_2SO_4.

The imines of chloropentafluoroacetone (**8**) and 1,3-dichlorotetrafluoroacetone (**9**) react with sulfonyl fluorides **2–4** under similar conditions, and after acidification also yield the corresponding sulfonamides **10–12** and **13–15**.

$$CF_2X(CF_2Cl)C{=}NH + \mathbf{2\text{–}4} \xrightarrow[MeCN,\ CsF]{80\text{–}90\ ^\circ C,\ 16\text{–}24\ h} CF_2X(CF_2Cl)CFN(Cs)SO_2R_f$$

(**8**, **9**)

SSDI 0022-1139(93)05007-N

$\xrightarrow{H_2SO_4}$ $CF_2X(CF_2Cl)CFN(H)SO_2R_f$

(10–12, X = F)	(13–15, X = Cl)
(10) $R_f = CF_3$ (86%)	(13) $R_f = CF_3$ (85%)
(11) $R_f = C_4F_9$ (84%)	(14) $R_f = C_4F_9$ (74%)
(12) $R_f = C_6F_{13}$ (83%)	(15) $R_f = C_6F_{13}$ (66%)

Imines **1**, **8** and **9** also react in an analogous manner with SO_2ClF.

$$\mathbf{1, 8, 9} + SO_2ClF \xrightarrow[MeCN,\ CsF]{80\text{–}90\ ^\circ C,\ 16\text{–}24\ h} CF_2X(CF_2Y)CFN(Cs)SO_2F \xrightarrow{H_2SO_4} CF_2X(CF_2Y)CFN(H)SO_2F$$

(**16**) X = Y = F (73%)
(**17**) X = F, Y = Cl (83%)
(**18**) X = Y = Cl (77%)

According to ^{19}F NMR spectroscopy, the first step in this reaction is the conversion of SO_2ClF into SO_2F_2 by CsF, followed by the reaction of the imine anion of **1**, **8** or **9**.

Perfluoroalkylsulfonyl chlorides can also be used in place of the alkylsulfonyl fluorides in this reaction. Reaction of sulfonyl chloride **22** with imine **1** under identical conditions to those used for sulfonyl fluorides **2–4**, gives amine **23** in 82% yield.

$$C_2F_5SO_2Cl + \mathbf{1} \xrightarrow[MeCN,\ CsF]{70\ ^\circ C,\ 18\ h} \underset{(22)}{} \xrightarrow{H_2SO_4} C_2F_5SO_2N(H)CF(CF_3)_2 \quad (23)$$

In this case, **22** is probably converted to $C_2F_5SO_2F$ before reaction but this was not checked. The new compounds (**5**, **10**, **13**, **16–18**, **23**) are liquids at room temperature with boiling points > 100 °C. These values are consistent with literature data for $FSO_2N(H)R_f$ ($R_f = CF_3$, b.p. 100 °C; $R_f = C_2F_5$, b.p. 25 °C/12 mmHg [4]). Compounds with larger fluoroalkyl groups are white solids at 22 °C. Compound **6** sublimed slowly at 22 °C under reduced pressure to form large crystals [9]. All of these compounds are very hygroscopic and were hydrolyzed by moisture in air within 1 h. Compounds **16–18** are less stable than $FSO_2N(H)CF_3$, which can be distilled without decomposition in glass at 100 °C [4a]. Heating **16–18** in glass (100–110 °C) led to decomposition within a few minutes, probably due to loss of HF.

The IR spectra of the amides with R_fSO_2 groups exhibited strong absorptions at 3260–3270 cm^{-1} (NH) and at 1460, 1410 cm^{-1} (SO_2, NH). For compounds **16–18**, these bands were shifted to higher wavenumbers (3280, 1480, 1430 cm^{-1}). In the cesium salt of **5**, the band corresponding to the SO_2 group was shifted to lower wavenumber (1371 cm^{-1}) similar to $(CF_3SO_2)_2NCs$ [7]. In the cesium salts of **16–18**, this shift was not as large (1460 cm^{-1}).

The mass spectra (CI) of sulfonamides **5–7** and **10–18** did not exhibit parent ions, but in most cases high intensity ions were found corresponding to the protonated form of $R_fSO_2NH_2$ formed by loss of an *N*-alkyl group. ^{19}F NMR spectra were in good agreement with the proposed structures of all compounds. The spectrum of **5** ($CDCl_3$) for example, contained three resonances at δ −77.67, −79.91 and −159.55 ppm with the relative areas 3:6:1, which may be assigned to CF_3SO_2, $(CF_3)_2C$ and CF groups. Replacement of the proton in **5** by cesium resulted in a significant downfield shift of the single C–F fluorine (~16 ppm). The same shift has been found for **16**, and **17** and their cesium salts ($\Delta\delta$ 11 and 17.6 ppm). The ^1H NMR spectra of all sulfonamides exhibited a broad resonance for NH in the δ 6.4–6.8 ppm range in $CDCl_3$. Sulfonamides **5–7** and **10–18** are strong acids and reaction of **5** with CsF in MeCN at 22 °C produced only the cesium salt (according to ^{19}F NMR spectroscopy).

$$\mathbf{5} + CsF \xrightarrow[MeCN]{22\ ^\circ C,\ 1\ h} (CF_3)_2CFN(Cs)SO_2CF_3 \quad (100\%)$$
$$\not\longrightarrow (CF_3)_2C{=}N{-}SO_2CF_3 \quad (\mathbf{24})$$

No evidence for the formation of the *N*-sulfonyl imine **24** was found in this experiment. The formation of stable salts in the reaction of $FSO_2N(H)CF_3$ with tetraphenylphosphonium and tetraphenylarsonium chlorides has been reported [4a].

The cesium salts of the amides are the intermediate products of the reaction of imines **1**, **8** and **9** with sulfonyl fluorides, and they are extremely stable. Samples may be kept for 2 h at 100–120 °C without visible decomposition (^{19}F NMR spectroscopy) but the pure salts could not be isolated. Removal of the solvent after filtration of the reaction mixture resulted in an oily yellow to orange residue and even prolonged (24 h) pumping of the sample in high vacuum did not remove the solvent, and/or products of condensation of MeCN under action of fluoride anion [10] from the salts. Attempts to isolate the cesium salt of **6** by adding absolute ethanol to the salt solution in dry MeCN resulted in the formation of ether **25**, isolated in 87% yield after purification with sulfuric acid.

$$(CF_3)_2CFN(Cs)SO_2C_4F_9 + C_2H_5OH \xrightarrow[MeCN]{22\ ^\circ C,\ 2\ h} (CF_3)_2C(OC_2H_5)NHSO_2C_4F_9 \quad (\mathbf{25})$$

This result may indicate the presence of an equilibrium between the salt and free sulfonyl imine **26** in a polar solvent (Scheme 1).

$$(CF_3)_2CFN(Cs)SO_2C_4F_9 \rightleftharpoons (CF_3)_2C{=}NSO_2C_4F_9 + CsF$$
(26)

$$\mathbf{26} + C_2H_5OH \xrightarrow{CsF} (CF_3)_2C(OC_2H_5)N(X)SO_2C_4F_9 \xrightarrow{H_2SO_4}$$
(X = H or Cs)

$$(CF_3)_2C(OC_2H_5)N(H)SO_2C_4F_9$$
(25)

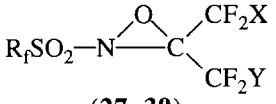
Scheme 1.

The results recorded below on the reaction of sulfonamides **5–7** and **10–18** with *m*-chloroperoxybenzoic acid (MCPBA) in polar solvents are also supportive of this mechanism.

Preparation and reactions of perhalo-1-alkylsulfonyl- and -1-fluorosulfonyl-3,3-dialkyloxaziridines

The reaction of compounds **5–7** and **10–18** with *m*-chloroperoxybenzoic acid (MCPBA) in a polar solvent provides a facile route for the preparation of this new class of polyfluorooxaziridines (Table 1).

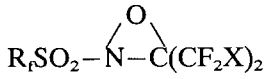
5–7, 10–18, 23 + MCPBA $\xrightarrow[CH_3CN \text{ or sulfolane}]{22\ ^\circ C,\ 1\text{–}3\ h}$



(27–39)

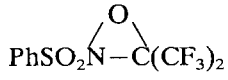
In contrast to the starting amide, the oxaziridines are virtually insoluble in MeCN and separate out as a lower layer during the course of the reaction. Sulfolane was used as a solvent for the preparation of oxaziridines **29**, **31**, **34**, **37** and **39** since the products were somewhat soluble in MeCN, and for good yields it was necessary to distil the oxaziridine from the solvent. We propose that the oxidation of the sulfonimides proceeds via the sulfonyl imine which is in equilibrium with the amide. The equilibrium is shifted to the right by the irreversible formation of the oxaziridine. The oxidation of the imine by MCPBA is similar to that proposed for perfluoroazaalkenes [11].

$$R_fSO_2N(H)CF(CF_2X)_2 \rightleftharpoons R_fSO_2N{=}C(CF_2X)_2 + HF \xrightarrow{MCPBA}$$



Despite the fact that hydrocarbon *N*-sulfonyloxaziridines are well known and widely employed in organic synthesis [12], only a few partially fluorinated oxaziridines are known to date [13, 14]. *N*-Sulfonyl imines of polyfluoroketones are readily available through condensation of RSO_2NH_2 with polyfluoroketones and are known to be extremely reactive towards nucleophiles [15]. The *N*-phenylsulfonyl imine of hexafluoroacetone **40** was used for the preparation of the corresponding oxaziridine **41** by oxidation with MCPBA.

$$\underset{\mathbf{(40)}}{PhSO_2N{=}C(CF_3)_2} + MCPBA \xrightarrow[CH_2Cl_2]{2\ h,\ 22\ ^\circ C}$$



(41)

According to ^{19}F NMR spectroscopy, oxaziridine **41** was the only product of this reaction. It is interesting that, in contrast to internal perfluoroazaalkenes [11], **40** reacts with MCPBA in CH_2Cl_2 solvent. Compound **41** has a lower stability compared to the perhalogenated analogs and decomposes completely at 22 °C within 24 h.

Oxaziridines **27–39** and **41** are strong oxidizers; thus, they readily produce iodine from aqueous KI. Compounds **27–39** are colorless liquids which are stable at 22 °C, but they readily decompose to the imine and other unidentified products at temperatures higher than 100 °C. Their IR spectra exhibited strong absorptions at 1440 cm^{-1} (SO_2) and a weak absorption in the 1390–1410 cm^{-1} region characteristic of the oxaziridine ring [11, 16]. With oxaziridines **37–39**, the SO_2 absorption was shifted to higher wavenumbers (1480–1485 cm^{-1}). The mass spectra (CI) of the oxaziridines exhibited parent ions of high intensity. Some interesting information about the structure of oxaziridines obtained from the ^{19}F NMR spectra is discussed in the next section.

TABLE 1. New oxaziridines

Compound	R_f	X	Y
27	CF_3	F	F
28	C_4F_9	F	F
29	C_2F_5	F	F
30	C_6F_{13}	F	F
31	CF_3	Cl	F
32	C_4F_9	Cl	F
33	C_6F_{13}	Cl	F
34	CF_3	Cl	Cl
35	C_4F_9	Cl	Cl
36	C_6F_{13}	Cl	Cl
37	F	F	F
38	F	Cl	F
39	F	Cl	Cl

Compounds **27–39** demonstrate unique chemical properties. Compound **28** reacted readily with trifluorochloroethene at 22 °C, producing the corresponding ethene oxide and imine **26**.

$$\mathbf{28} + CF_2{=}CFCl \xrightarrow[2\ d]{22\ °C}$$

$$(CF_3)_2C{=}NSO_2C_4F_9 + F_2C{-}CFCl$$
$$\mathbf{(26)}$$

In contrast, a similar reaction of $C_4F_9N{-}CFC_3F_7$ proceeded only after prolonged heating (100–120 °C, 16–18 h) [17]. In a similar fashion to hydrocarbon *N*-sulfonyloxaziridines [12] or perfluoro-2,3-dialkyloxaziridine [17], these polyfluoro-*N*-sulfonyloxaziridines readily transfer oxygen to organosulfur substrates. The reaction of **27** and **32** with methylphenylsulfoxide was used for the isolation of the *N*-sulfonyl imines **24** and **42**.

$$\mathbf{27} + CH_3S(O)Ph \xrightarrow[\text{sulfolane}]{0\text{–}22\ °C,\ 30\ min}$$

$$(CF_3)_2C{=}NSO_2CF_3 + CH_3SO_2Ph$$
$$\mathbf{(24)}\ (80\%)$$

$$\mathbf{32} + CH_3S(O)Ph \xrightarrow[\text{sulfolane}]{22\ °C,\ 30\ min}$$

$$CF_3(CF_2Cl)C{=}NSO_2C_4F_9 + CF_3(CF_2Cl)C{=}O$$
$$\mathbf{(42)}\ (60\%)$$
$$+ CH_3SO_2Ph$$

These new sulfonyl imines are colorless liquids and are extremely moisture sensitive. Their IR spectra exhibited strong absorptions at 1700 (C=N) and 1420 (SO_2) cm^{-1}. The mass spectra (CI) exhibited M+1 ions of high intensity. A discussion of the ^{19}F NMR spectra is given in next section.

^{19}F NMR spectra of N-*sulfonyloxaziridines and* N-*sulfonyl imines*

The ^{19}F NMR spectra of oxaziridines **27–39** and **41** provide the most definitive proof of their structures. The spectrum of **37** contained three resonances at δ −66.98, −75.10 and 60.48 ppm, with relative areas of 3:3:1. The downfield signal had a chemical shift typical for an SO_2F group. The chemical shifts of the CF_3 groups in **37** and the coupling constants between them (7.5 Hz) were both in excellent agreement with those reported for 2,3,3-trifluoromethyloxaziridine (δ −66.18, −75.70 ppm, J = 8.5 Hz) [16]. The downfield CF_3 group showed a small coupling with the SO_2F group (J = 3.5 Hz) and could be assigned as being *cis* to the SO_2F group. Compound **38** exists as a mixture of two isomers (60:40) in which the isomer with the CF_3 *cis* to the SO_2F dominated the mixture. The CF_2Cl group in both isomers appeared as an AB pattern (J_{AB} = 174 and 180 Hz, respectively) due to the presence of chiral centers in the molecule.

The ^{19}F NMR spectra of perfluoroalkylsulfonyloxaziridines were temperature dependent. At 22 °C, compound **27** exhibited three resonances (δ −68.07, −74.83 and −74.72 ppm) with relative areas of 1:1:1, the CF_3 resonances at C-3 being broad. At −10 °C, these signals became sharp and the two CF_3 groups at C-3 showed a coupling of 8 Hz. This behavior is typical for all oxaziridines containing R_fSO_2 groups at a nitrogen atom. In the low-temperature ^{19}F NMR spectrum of **29**, the only CF_2 group appeared as an AB pattern. Decoupling experiments at low temperature on **28** demonstrated that the CF_2 group at SO_2 and the next alternate CF_2 group exhibited AB patterns with only small differences in the chemical shifts of the fluorine atoms ($\Delta\delta$ 0.3, $\Delta\delta$ 0.8 ppm). Similar observations were made for all oxaziridines containing the $C_4F_9SO_2$ group. These experimental results can be explained in terms of the chirality of the nitrogen giving rise to the magnetic nonequivalence of fluorines in the indicated CF_2 groups.

Heating a solution of **27**, **29** or **28** in *sym*-tetrachloroethane-d_2 led to broadening and coalescence of the CF_3 groups at C-3, and reversion to the original spectrum on cooling. This behavior can be explained by an inversion process at the nitrogen. This process has not been observed for the polyfluorinated oxaziridines of perfluoroazaalkenes, but is well documented for hydrocarbon *N*-sulfonyloxaziridines [18]. The free energies of activation for the nitrogen inversion of **27–29** were estimated from the differences of the chemical shifts for the CF_3 groups at C-3 ($\Delta\nu$) and the coalescence temperatures (T_c) of these signals, which were calculated using a coalescence approximation [19]. Table 2 provides these data as well as the calculated values. The fact that the process of nitrogen inversion at 22 °C was not observed for fluorooxaziridines with an SO_2F group or compound **41** implies that the barrier to nitrogen inversion for these oxaziridines is considerably higher.

Oxaziridines **31–33**, which contain both a CF_3 and a CF_2Cl group at C-3, exist as a mixture of two isomers as in compound **38**. The assignment of isomers was more complicated in this case because of the absence

TABLE 2. Free energies for nitrogen inversion in $R_fSO_2N{-}C(CF_3)_2$ (O)

Compound	R_f	T_c (K)	$\Delta\nu$ (Hz)	ΔG^* (kcal mol^{-1})
27	CF_3	347	1475	14.9
29	C_2F_5	345	1430	14.8
28	C_4F_9	336	1375	14.4

of coupling between CF_2X (X=F or Cl) and the R_f group connected to the SO_2 group. The change in the ratio of isomers from 60:40 for **38** to 80:20 for compounds **31–33** may be interpreted as due to the dominance of the less sterically hindered isomer with CF_3 and SO_2R_f groups in a *cis* position.

Interestingly, a temperature dependence for the ^{19}F NMR spectrum was found for imine **24**. At −62 °C in $CDCl_3$, the spectrum exhibited three resonances at δ −65.73, −69.68 and −77.03 ppm (1:1:1), but at 22 °C the spectrum contained only two resonances at δ −68.12 and −77.40 ppm with relative areas of 2:1. The coalescence temperature was −20±1 °C and the calculated [19] activation energy of the observed dynamic process 10.9 kcal mol^{-1}, in very good agreement with literature results for the acyl and sulfonyl imines of hexafluoroacetone. However, it is difficult to predict which process, nitrogen inversion or rotation around C=N, is responsible for the observed dynamic process in sulfonyl imine **24**.

Experimental

General methods

Volatile compounds were handled in a Pyrex vacuum system equipped with glass–Teflon valves. Pressures were measured on a Wallace and Tiernan series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing and by PVT measurements. Temperatures were measured with a digital indicating iron–constantan thermocouple. Molecular weights were obtained by gas density measurements. IR spectra were recorded on a Perkin-Elmer 1430 spectrometer with a 7500 data station using a 10-cm glass cell fitted with either KCl windows for gases or KCl plates for liquids. NMR spectra were recorded on an IBM NR-200 AF instrument using $CDCl_3$ as sample solvent and $CFCl_3$ (^{19}F, 188 MHz) and TMS (^1H, 200 MHz) as internal references. Coalescence points were obtained on 10% solutions of **27–29** in *sym*-$C_2Cl_4D_2$ or $CDCl_3$ (**24**). Temperature measurements were accurate to ±1 °C. Mass spectra were recorded at 70 eV for electron-impact (EI) and chemical ionization (CI, CH_4). For chlorine-containing compounds, the expected isotope ratios were observed and only the ^{35}Cl masses are listed. Sample melting points were measured directly while boiling points were determined by Swiloboff's method [20] and are uncorrected.

The purity of new compounds was established by ^{19}F NMR spectroscopy with the spectra indicating >99.0% purity.

All starting materials were obtained from commercial sources and were purified by standard methods as required. Cesium fluoride was dried in a porcelain dish with a Bunsen burner flame for 1–2 h and was used directly after drying. The imines of hexafluoro-, chloropentafluoro- and 1,3-dichlorotetrafluoro-acetone were prepared by a literature method [21]. Trifluorochloroethene oxide and CH_3SO_2Ph were identified by comparison of their IR and ^{19}F NMR data with those of authentic samples.

General procedure for the reaction of the imines of fluoroketones with sulfonyl fluorides

To a mixture (see Table 3) of dry CsF and MeCN, placed in a 250 ml Pyrex flask fitted with a glass–Teflon valve, the imine and sulfonyl fluoride were added by vacuum-transfer at −196 °C or added directly at 22 °C. The reaction mixture was kept at 80–90 °C for 16–24 h (in the case of SO_2ClF the flask was first held at 22 °C for 1 h to convert SO_2ClF into SO_2F_2). The solvent was then removed *in vacuo* followed by the addition of 20–50 ml of 96% H_2SO_4 to the yellow–orange residue. The product was then distilled or sublimed. To avoid hydrolysis, the sulfonyl amides were stored at room temperature in evacuated flasks. The reaction conditions, ratio of reactants, and yields of products are summarized in Table 3.

$(CF_3)_2CFSO_2N(H)CF_3$ (**5**): b.p. 28–30 °C/1 mmHg. IR (liq.) (cm^{-1}): 3261 (m); 1466 (m); 1415 (s); 1213 (m); 1250 (s); 1140 (m); 1103 (m); 984 (s); 893 (m). MS (CI, major) *m/z*: 317 [$(M)^+$, 1, 6]; 298 [$(M-F)^+$, 24]; 234 [$(M-FSO_2)^+$, 8); 167 [$(M-C_3F_6)^+$, 100]; 150 ($CF_3SO_2NH_3^+$, 24); 133 ($CF_3SO_2^+$, 11). ^{19}F NMR $(CF_3)_2{}^A CF^C N(H)SO_2CF_3{}^B$ δ: A −79.91 (6F, d); B −77.66 (3F, d); C −159.55 (1F, m) [J_{BC}=11, J_{AC}=5 Hz ppm. ^1H NMR δ: 6.81 (br s) ppm. ^{19}F NMR Cs salt δ: A −81.42 (6F, d); B −80.49 (3F, d); C −143.34 (1F, d) [J_{AC}=5, J_{BC}=11 Hz] ppm.

TABLE 3. Reaction of imines **1**, **8** and **9** with perfluorosulfonyl fluorides and SO_2ClF

Imine[a]	Sulfonyl fluoride[a]	CsF (g)	MeCN (ml)	Time (h) (80–90 °C)	Product (yield %)
1 (21)	**2** (21)	9.3	25	16	**5** (87)
1 (20)	**3** (20)	6.1	15	16	**6** (75)
1 (20)	**4** (20)	6.4	20	20	**7** (85)
8 (30)	**2** (30)	10.5	15	18	**10** (86)
8 (20)	**3** (20)	6.4	20	16	**11** (84)
8 (20)	**4** (20)	6.5	15	18	**12** (83)
9 (30)	**2** (30)	9.9	35	20	**13** (85)
9 (20)	**3** (20)	8.5	40	38	**14** (74)
9 (20)	**4** (20)	6.5	27	40	**15** (66)
1 (30)	SO_2ClF (30)	19.4	30	20	**16** (73)
8 (32)	SO_2ClF (35)	19	50	18	**17** (83)
9 (20)	SO_2ClF (20)	12.3	30	25	**18** (77)

[a]Concentrations in mmol shown in parentheses.

$(CF_3)_2CFN(H)SO_2F$ (**16**): b.p. 25 °C/1 mmHg. IR (liq.) (cm^{-1}): 3289 (s); 1489 (s); 1435 (s); 1242 (vs); 1108 (s); 1002 (s); 824 (s); 743 (m); 720 (m); 592 (s); 536 (s). IR Cs salt (Nujol) (cm^{-1}): 1457 (s); 1374 (s); 1313 (vs); 1232 (s); 1156 (m); 1026 (m); 988 (s); 766 (m); 732 (m); 697 (m). MS (CI, major) *m/z*: 248 [$(M-F)^+$, 2]; 198 [$(M-CF_3)^+$, 3]; 163 [$(M-SO_2F_2)^+$, 63]; 147 ($CF_3SO_2N^+$, 100). ^{19}F NMR $(CF_3)_2{}^ACF^B$-$N(H)SO_2F^C$ δ: A −78.63 (6F, dd); B −153.28 (1F, m); C 60.25 (1F, m) [$J_{AB}=J_{AC}=4$ Hz] ppm. ^1H NMR δ: 6.44 (br s) ppm. ^{19}F NMR ($CDCl_3$/MeCN, 1:1) Cs salt δ: A −80.17 (6F, t); B −142.13 (1F, m); C 56.97 (1F, d hept.) [$J_{AB}=J_{AC}=5$, $J_{BC}=7.5$ Hz] ppm.

$(CF_3)_2CFN(H)SO_2C_4F_9$ (**6**): m.p. 61–62 °C. IR (Nujol) (cm^{-1}): 3350 (s); 1462 (s); 1377 (vs); 1218 (s); 1200 (m); 1140 (m); 952 (m); 722 (m). MS (CI, major) *m/z*: 448 [$(M-F)^+$, 2]; 384 [$(M-SO_2F)^+$, 1]; 300 ($C_4F_9SO_2NH_3{}^+$, 100); 219 ($C_4F_9{}^+$, 30); 167 [$(M-C_6F_{12})^+$, 5]. ^{19}F NMR $(CF_3{}^A)_2CF^EN(H)SO_2CF_2{}^CCF_2{}^D$-$CF_2{}^ECF_3{}^B$ δ: A −79.82 (6F, d); B −81.43 (3F, t); C −111.26, (2F, q); D −121.50 (2F, m); E −126.67 (2F, t); F −158.96 (1F, m) [$J_{AF}=5$, $J_{CF}=11$, $J_{BC}=10$ Hz] ppm. ^1H NMR δ: 6.83 (br s) ppm.

$(CF_3)_2CFN(H)SO_2C_6F_{13}$ (**7**): m.p. 95–96° C. IR (Nujol) (cm^{-1}): 3267 (m); 1461 (s); 1412 (m); 1377 (m); 1248 (m); 1213 (s); 1151 (m); 986 (w); 955 (w); 718 (m). MS (CI, major) *m/z*: 548 [$(M-F)^+$, 2]; 498 [$(M-CF_3)^+$, 10]; 484 [$(M-SO_2F)^+$, 7]; 400 ($C_6F_{13}SO_2NH_3{}^+$, 100). ^{19}F NMR $(CF_3{}^A)_2CF^IN(H)SO_2$-$CF_2{}^CCF_2{}^DCF_2{}^ECF_2{}^FCF_2{}^GCF_3{}^B$ δ: A −79.50 (6F, d); B −81.35 (3F, t); C −110.70 (2F, q); D −120.29 (2F, m); E −122.20 (2F, m); F −123.15 (2F, m); G −126.63 (2F, m); I −158.14 (1F, m) [$J_{AI}=4$, $J_{CI}=15$, $J_{BF}=10$ Hz] ppm. ^1H NMR δ: 6.40 (br s) ppm.

$(CF_3)_2CFN(H)SO_2C_2F_5$ (**23**): b.p. 35–36 °C/1 mmHg. IR (gas) (cm^{-1}): 3252 (w); 1468 (m); 1421 (m); 1247 (vs); 1146 (s); 988 (m); 877 (m); 615 (m); 513 (m). ^{19}F NMR $(CF_3{}^A)_2CF^DN(H)SO_2CF_2{}^CCF_3{}^B$ δ: A −79.50 (6F, br s); B −79.20 (3F, s); C −115.72 (2F, d); D −157.72 (1F, m) [$J_{CH}=15$ Hz] ppm. ^1H NMR δ: 6.42 (br s) ppm. ^{19}F NMR Cs salt δ: A −82.31 (6F, br s); B −80.99 (3F, s); C −119.91 (2F, br s); D −143.21 (1F, m) ppm.

$CF_3(CF_2Cl)CFN(H)SO_2CF_3$ (**10**): b.p. 30 °C/0.1 mmHg. IR (liq.) (cm^{-1}): 3256 (m); 1461 (m); 1412 (m); 1294 (m); 1255 (vs); 1214 (vs); 1136 (s); 1199 (s); 1034 (m); 929 (w); 859 (m); 612 (m). ^{19}F NMR $CF_3{}^C(CF^AF^BCl)CF^EN(H)SO_2CF_3{}^D$ δ: A −66.93 (1F, dqd); B −68.25 (1F, dqd) (typical AB pattern); C −77.90 (3F, t); D −77.34 (3F, d); E −156.50 (1F, m) [$J_{AB}=184$, $J_{AC}=7$, $J_{AE}=J_{DE}=10$, $J_{BC}=J_{BE}=11$ Hz] ppm. ^1H NMR δ: 6.44 (br s) ppm.

$CF_3(CF_2Cl)CFN(H)SO_2F$ (**17**): b.p. 28 °C/0.8 mmHg. IR (liq.) (cm^{-1}): 3284 (s); 1481 (s); 1429 (s); 1297 (m); 1236 (vs); 1163 (m); 1107 (s); 1036 (s); 931 (m); 861 (s); 814 (s); 712 (w); 645 (w); 584 (m); 538 (m). IR Cs salt (Nujol) (cm^{-1}); 1461 (s); 1377 (m); 1315 (vs); 1212 (s); 1182 (s); 1145 (m); 1049 (m); 1000 (m); 978 (m); 909 (s); 870 (m); 709 (s); 590 (m). MS (CI, major) *m/z*: 284 [$(M+1)^+$, 6)]; 282 [$(M-H)^+$]; 248 [$(M-Cl)^+$, 100]; 228 [$(M+1-ClF)^+$, 41]; 200 [$(M-SO_2F$, 18]; 198 [$(M-CF_2Cl)^+$, 14]; 166 ($CF_2ClSO_3H^+$, 16). ^{19}F NMR $CF_3{}^C(CF^AF^BCl)CF^DN(H)SO_2F^E$ δ: A −63.45 (1F, d pent.); B −64.15 (1F, d pent.) (typical AB pattern); C −73.47 (3F, m); D −148.83 (1F, m); E 60.47 (1F, m) [$J_{AB}=180$ Hz] ppm. ^1H NMR δ: 6.52 (br s) ppm. ^{19}F NMR ($CDCl_3$/MeCN, 1:1) Cs salt δ: A −66.34 (1F, d pent.); B −67.64 (1F, d pent.) (typical AB pattern); C −77.95 (3F, m); D −138.81 (1F, oct.); E 58.06 (1F, m) [$J_{AB}=168$. $J_{AC}=12$, $J_{AD}=4$, $J_{BC}=8$ Hz] ppm.

$CF_3(CF_2Cl)CFN(H)SO_2C_4F_9$ (**11**): b.p. 48–49 °C/0.2 mmHg. IR (Nujol) (cm^{-1}): 3262 (s); 1460 (m); 1414 (m); 1292 (s); 1205 (vs); 1145 (s); 1110 (s); 1033 (s); 930 (m); 860 (m); 801 (w); 748 (m); 585 (m). MS (CI, major) *m/z*: 483 (M^+, 0.1); 464 [$(M-F)^+$, 3]; 448 [$(M-Cl)^+$, 0.2]; 300 ($C_4F_9SO_2NH_3{}^+$, 100); 219 ($C_4F_9{}^+$, 4). ^{19}F NMR $CF_3{}^C(CF^AF^BCl)CF^IN(H)SO_2CF_2{}^ECF_2{}^F$-$CF_2{}^GCF_3{}^D$ δ: A −66.70 (1F, dq); B −67.70 (1F, d hept.) (AB pattern); C −77.62 (3F, t); D −81.20 (3F, t); E −111.15 (2F, q); F −121.31 (2F, m); G −126.49 (2F, m); I −155.50 (1F, m) [$J_{AB}=178$, $J_{DF}=9$, $J_{EF}=J_{EG}=13$ Hz] ppm. ^1H NMR δ: 6.88 (br s) ppm.

$CF_3(CF_2Cl)CFN(H)SO_2C_6F_{13}$ (**12**): b.p. 57–58 °C/1 mmHg. IR (Nujol) (cm^{-1}): 3252 (s); 1457 (m); 1376 (s); 1205 (vs); 1146 (s); 1045 (m); 842 (m). ^{19}F NMR $CF_3{}^C(CF^AF^BCl)CF^LN(H)SO_2CF_2{}^ECF_2{}^FCF_2{}^GCF_2{}^ICF_2{}^K$-$CF_3{}^D$ δ: A −66.50 (1F, dq); B −67.72 (1F, dq) (AB pattern); C −78.95 (3F, m); D −81.48 (3F, t); E −112.04 (2F, q); F −120.62 (2F, m); I −123.35 (2F, m); G −122.41 (2F, m); K −126.85 (2F, m); L −155.54 (1F, m) [$J_{AB}=172$, $J_{AC}=J_{DI}=10$, $J_{BC}=12$, $J_{EL}=J_{EG}=14$ Hz] ppm. ^1H NMR δ: 6.52 (br s) ppm.

$(CF_2Cl)_2CFN(H)SO_2CF_3$ (**13**): b.p. 26 °C/1 mmHg. IR (liq.) (cm^{-1}): 3252 (s); 1456 (s); 1410 (s); 1227 (vs); 1097 (s); 986 (s); 886 (w); 839 (s); 745 (m); 635 (m); 604 (s); 574 (w). ^{19}F NMR $(CF^AF^BCl)_2CF^CN(H)SO_2$-$CF_3{}^D$ δ: A −64.48 (2F, m); B −65.10 (2F, m) (typical AB pattern); C −152.81 (1F, m); D −77.08 (3F, d) [$J_{AB}=186$, $J_{CD}=10$ Hz] ppm. ^1H NMR δ: 6.60 (br s) ppm.

$(CF_2Cl)_2CFN(H)SO_2F$ (**18**): b.p. 28 °C/0.1 mmHg. IR (liq.) (cm^{-1}): 3274 (m); 1478 (s); 1426 (s); 1233 (vs); 1177 (vs); 1103 (s); 992 (m); 843 (m); 810 (m); 747 (m); 633 (m); 544 (s). MS (CI, major) *m/z*: 280 [$(M-F)^+$, 0.5]; 217 [$(M-SO_2F)^+$, 4]; 163 ($CF_2ClSO_2H^+$, 100); 151 ($CF_2ClSO_2H^+$, 22). ^{19}F NMR $(CF^AF^BCl)_2CF^CN(H)SO_2F^D$ δ: A −64.50 (2F, dm); B −65.53 (2F, dm) (AB pattern); C −151.37 (1F, hept.);

D 60.35 (1F, m) [J_{AB} = 190 Hz] ppm. ^{1}H NMR δ: 6.54 (br s) ppm.

$(CF_2Cl)_2CFN(H)SO_2C_4F_9$ (**14**): 45 °C/0.01 mmHg, m.p. 65 °C. IR (Nujol) (cm^{-1}): 3252 (s); 1405 (m); 1408 (s); 1349 (m); 1226 (vs); 1141 (s); 1093 (m); 981 (w); 837 (w); 735 (w); 580 (w). ^{19}F NMR $(CF^AF^BCl)_2CF^GN(H)SO_2CF_2{}^CCF_2{}^DCF_2{}^ECF_3{}^F$ δ: A −63.96 (2F, dm); B −64.91 (2F, dm) (AB pattern); C −111.24 (2F, pent.); D −121.03 (2F, m); E −126.34 (2F, dm); F −81.24 (3F, t); G −151.84 (1F, m) [J_{AB} = 180, J_{FE} = 13 Hz] ppm. ^{1}H NMR δ: 6.34 (br s) ppm.

$(CF_2Cl)_2CFN(H)SO_2C_6F_{13}$ (**15**): b.p. 65 °C/0.01 mmHg. IR (Nujol) (cm^{-1}): 3253 (s); 1455 (s); 1406 (s); 1260 (vs); 1097 (s); 1053 (s); 987 (s); 874 (m); 841 (s); 746 (s); 698 (m). ^{19}F NMR $(CF^AF^BCl)_2$-$CF^CN(H)SO_2CF_2{}^DCF_2{}^FCF_2{}^GCF_2{}^HCF_3{}^I$ δ: A −64.07 (2F, dm); B −65.01 (2F, dm) (typical AB pattern); C −151.50 (1F, m); D −110.82 (2F, m); F −122.18 (2F, m); G −123.15 (2F, m); H −126.60 (2F, m); I −81.25 (3F, m) [J_{AB} = 176, J_{FG} = 11 Hz] ppm. ^{1}H NMR δ: 6.62 (br s) ppm.

General procedure for the preparation of N-*sulfonyloxaziridines*

The sulfonyl amide was added, with stirring, to a solution of *m*-chloroperoxybenzoic acid in acetonitrile at 22 °C and allowed to react for 0.5– 3 h (see Table 4). The product separated during the course of the reaction as a lower layer. This was separated out, washed with water and dried over P_2O_5.

Oxidation of **10**, **13** and **16–18** was carried out with sulfolane as the solvent. The product of the reaction was pumped out of the reaction mixture under high vacuum. The experimental conditions for the reactions are given in Table 4.

TABLE 4. Oxaziridines obtained by reaction with MCPBA

Substrate[a]	MCPBA (g)	Solvent (ml)	Time (h) (22 °C)	Product (yield %)
5 (15)	3.5	10[b]	1	**27** (44)
6 (8.5)	5	20[b]	2	**28** (48)
7 (2.8)	1.6	15[b]	2	**30** (82)
10 (3.3)	1.5	5[c]	1	**31** (73)
11 (4.7)	2	15[b]	1	**32** (57)
12 (6.7)	3	7[b]	1	**33** (72)
13 (4.1)	1.2	12[c]	1	**34** (26)
14 (3.8)	1.9	20[b]	0.5	**35** (35)
15 (1.5)	0.4	15[b]	2.5	**36** (41)
16 (6)	2	10[c]	0.5	**37** (44)
17 (14)	3	20[c]	2.5	**38** (50)
18 (4.7)	1.4	10[c]	2	**39** (43)
40 (11)	2	20[d]	3	**41** (50)

[a]Concentrations in mmol shown in parentheses.
[b]MeCN.
[c]Sulfolane.
[d]CH_2Cl_2.

$(CF_3)_2\overline{CONSO_2CF_3}$ (**27**): IR (liq.) (cm^{-1}): 1437 (s); 1405 (w); 1324 (s); 1273 (s); 1220 (vs); 1201 (vs); 1125 (s); 999 (m); 976 (m); 822 (w); 720 (m); 701 (m); 610 (s). MS (CI, major) *m/z*: 314 [$(M+1)^+$, 78]; 298 [$(M-O)^+$, 100]; 250 [$(M+1-SO_2)^+$, 43], 230 [$(M-SO_2F)^+$, 45]; 228 [$(M-CF_3O)^+$, 50]; 167 [$(M-C_3F_6O)^+$, 75]; 150 ($C_3F_6{}^+$, 69); 133 ($CF_3SO_2{}^+$, 73) ^{19}F NMR (22 °C, $CDCl_3$) $CF_3{}^A(CF_3{}^B)\overline{CONSO_2CF_3}{}^C$ δ: A −68.07 (3F, br s); B −74.83 (3F, br s); C −74.72 (3F, s) ppm. ^{19}F NMR (−10 °C) δ: A −68.09 (3F, q); B −74.83 (3F, q); C −74.76 (3F, s) [J_{AB} = 8 Hz] ppm.

$(CF_3)_2\overline{CONSO_2F}$ (**37**): IR (gas) (cm^{-1}): 1484 (vs); 1462 (w); 1404 (w); 1325 (s); 1279 (vs); 1246 (vs); 1029 (w); 982 (s); 861 (s); 815 (w); 719 (s); 628 (m); 529 (m). MS (CI, major) *m/z*: 264 [$(M+1)^+$, 5]; 244 [$(M-F)^+$, 2]; 200 [$(M+1-SO_2)^+$, 2]; 180 [$(M-SO_2F)^+$, 100]; 167 ($C_3F_6OH^+$, 5); 166 ($C_3F_6O^+$, 2). ^{19}F NMR $CF_3{}^ACF_3{}^B\overline{CONSO_2F}{}^C$ δ: A −66.98 (3F, dq); B −75.10 (3F, q); C 60.48 (1F, q) [J_{AC} = 3.5, J_{AB} = 7.5 Hz] ppm.

$(CF_3)_2\overline{CONSO_2C_4F_9}$ (**28**): IR (liq.) (cm^{-1}): 1439 (s); 1406 (w); 1354 (m); 1324 (s); 1232 (vs); 1144 (vs); 1121 (m); 999 (m); 975 (vs); 799 (m); 720 (s); 698 (m); 590 (m). MS (CI, major) *m/z*: 464 [$(M+1)^+$, 9); 448 [$(M+1-O)^+$, 42); 400 [$(M+1-SO_2)^+$, 12]; 219 ($C_4F_9{}^+$, 100). ^{19}F NMR ($CDCl_3$, −5 °C) $CF_3{}^A(CF_3{}^B)\overline{CONSO_2CF^CF^DCF_2{}^ECF^FF^GCF_3{}^H}$ δ: A −68.09 (3F, q); B −74.87 (3F, q); C −108.40 (1F, d); D −108.72 (1F, d); E −121.06 (2F, m); F,G −126.68 (2F, dt); H −81.10 (3F, t) [homodecoupling experiment data {−126.68 ppm}] AB pattern; F −126.32 (1F, d); H −127.10 (1F, d) [decoupling experiment {−108.63 ppm}] AB pattern [J_{AB} = 8, J_{CD} = 258, J_{FH} = 295, J_{HE} = 9 Hz] ppm. $T_{coalescence}$ = 336 K (*sym*-$C_2Cl_4D_2$).

$(CF_3)_2\overline{CONSO_2C_2F_5}$ (**29**): IR (gas) (cm^{-1}): 1445 (vs); 1408 (w); 1332 (s); 1277 (s); 1237 (vs); 1199 (s); 1142 (m); 1028 (w); 975 (s); 826 (w); 719 (m); 650 (m); 612 (s). ^{19}F NMR $CF_3{}^A(CF_3{}^B)\overline{CONSO_2CF^CCF^DCF_3{}^E}$ ($CDCl_3$, −13 °C) δ: A −68.01 (3F, q); B −74.75 (3F, q); C −113.32 (1F, d); D −114.01 (1F, d) (typical AB pattern); E −78.47 (3F, s) [J_{AB} = 8, J_{CD} = 250 Hz] ppm.

$(CF_3)_2\overline{CONSO_2C_6F_{13}}$ (**30**): IR (liq.) (cm^{-1}): 1438 (s); 1402 (w); 1364 (w); 1252 (s); 1152 (s); 991 (w); 975 (w); 889 (w); 720 (m); 703 (w). MS (CI, major) *m/z*: 548 [$(M+1-O)^+$, 26]; 400 ($C_6F_{13}SO_2NH_3{}^+$, 100); 319 ($C_6F_{13}{}^+$, 43). ^{19}F NMR ($CDCl_3$, 4 °C) $CF_3{}^A(CF_3{}^B)\overline{CONSO_2CF_2{}^CCF_2{}^ECF_2{}^FCF_2{}^GCF_2{}^ICF_3{}^D}$ δ: A −68.16 (3F, q); B −74.90 (3F, q); C −108.38 (2F, q); D −81.40 (3F, t); E −120.10 (2F, m); F −122.19 (2F, m); G −123.65 (2F, m); I −126.83 (2F, m) [J_{AB} = 7.5, J_{CF} = 10 Hz, other coupling constants not readily determined] ppm.

$CF_3(CF_2Cl)\overline{CONSO_2CF_3}$ (**31**): IR (gas) (cm^{-1}): 1435 (m); 1279 (m); 1242 (vs); 1146 (m); 1039 (m); 909 (m); 739 (m); 696 (m). MS (CI, major) *m/z*: 330 $[(M+1)^+$, 6]; 314 $[(M+1-O)^+$, 3]; 310 $[(M-F)^+$, 2]; 246 $[(M-SO_2F)^+$, 8]; 202 ($C_2F_6SO_2^+$, 100); 182 ($C_3F_5ClO^+$, 3); 166 ($C_3F_4Cl^+$, 9). ^{19}F NMR ($CDCl_3$, −18 °C) $CF_3^C(CF^AF^BCl)\overline{CONSO_2CF_3^D}$ (mixture of two isomers, ratio 78:22) δ: Major isomer: A −63.58 (1F, dq); B −65.18 (1F, dq); C −66.16 (3F, t); D −74.74 (3F, s) [$J_{AB}=176$, $J_{AC}=J_{BC}=10$ Hz] ppm. Minor isomer: A −57.42 (1F, dq); B −61.64 (1F, dq); C −72.66 (3F, t); D −71.87 (3F, s) [$J_{AB}=182$, $J_{AC}=J_{BC}=8$ Hz] ppm.

$CF_3(CF_2Cl)\overline{CONSO_2F}$ (**38**): IR (gas) (cm^{-1}): 1480 (vs); 1460 (w); 1393 (w); 1285 (s); 1238 (vs); 1219 (vs); 1186 (m); 1035 (s); 915 (m); 852 (vs); 744 (m); 709 (m); 584 (m). MS (CI, major) *m/z*: 280 $[(M+1)^+$, 100]; 279 (M^+, 20); 264 $[(M-O)^+$, 40]; 260 $[(M-F)^+$, 69]; 244 $[(M-Cl)^+$, 55]; 196 $[(M-SO_2F)^+$, 97]; 166 ($C_3F_5Cl^+$, 74); 161 $[(M-C_2F_3Cl)^+$, 97]. ^{19}F NMR ($CDCl_3$, 22 °C) $CF_3^C(CF^AF^BCl)\overline{CONSO_2F^D}$ (mixture of two isomers, ratio 60:40) δ: Major isomer: A −63.90 (1F, dq); B −64.91 (1F, dq); C −65.73 (3F, m); D 60.34 (1F, q) [$J_{AB}=174$, $J_{AC}=J_{BC}=10$, $J_{CD}=4$ Hz ppm. Minor isomer: A −56.37 (1F, dqd); B −60.50 (1F, dqd); C −72.92 (3F, t); D 61.95 (1F, t) [$J_{AB}=180$, $J_{AD}=J_{BD}=5$, $J_{AC}=J_{BC}=10$ Hz] ppm.

$CF_3(CF_2Cl)\overline{CONSO_2C_4F_9}$ (**32**): IR (liq.) (cm^{-1}): 1437 (s); 1404 (w); 1360 (m); 1237 (vs); 1210 (vs); 1146 (s); 1121 (m); 1039 (m); 989 (m); 860 (w); 741 (w); 697 (w); 590 (m); 576 (m). ^{19}F NMR (−20 °C, $CDCl_3$) $CF_3^C(CF^AF^BCl)\overline{CONSO_2CF^EF^FCF_2^GCF^HF^ICF_3^D}$ (two isomers, ratio 85:15) δ: Major isomer: A −63.40 (1F, dq); B −65.70 (1F, dq) (AB pattern); C −66.22 (3F, dd); D −80.78 (3F, t); E,F −108.43 (2F, t); G −120.74 (2F, m); H,I −126.31 (2F, m) [$J_{AB}=168$, $J_{AC}=10$, $J_{BC}=8$ Hz] ppm. Minor isomer: A −57.00 (1F, dm); B −61.40 (1F, dm); C −72.73 (3F, m); D −80.78 (3F, t); E,F −108.43 (2F, m); G −120.74 (2F, m); H,I −126.31 (2F, m) [$J_{AB}=174$, $J_{AC}=J_{BC}=8$ Hz] ppm decoupling {−126.31 ppm}] E −108.50 (1F, d); F −108.0 [$J_{EE'}=260$ Hz] ppm [decoupling {−108.43 ppm}] H −126 (1F, d); I −126 (1F, d) [$J_{HI}=296$ Hz] ppm.

$CF_3(CF_2Cl)\overline{CONSO_2C_6F_{13}}$ (**33**): IR (liq.) (cm^{-1}): 1435 (s); 1364 (w); 1280 (m); 1243 (vs); 1211 (vs); 1146 (s); 1040 (m); 986 (m); 909 (m); 740 (m); 696 (m); 640 (m). ^{19}F NMR ($CDCl_3$, −7 °C) $CF_3^C(CF^AF^BCl)\overline{CONSO_2CF_2^DCF_2^ECF_2^FCF_2^GCF_2^ICF_3^K}$ (two isomers, ratio 83:17) δ: Major isomer: A −63.32 (1F, dq); B −65.00 (1F, dq) (AB pattern); C −66.18 (3F, t); D −108.01 (2F, t); E −119.71 (2F, m); F −122.07 (2F, m); G −123.01 (2F, m); I −126.56 (2F, m); K −81.03 (3F, t) [$J_{AB}=178$, $J_{AC}=J_{BC}=9$ Hz] ppm. Minor isomer: A −57.38 (1F, dq); B −61.58 (1F, dq); C −72.57 (3F, m); D −108.01 (2F, t); E −119.71 (2F, m); F −122.07 (2F, m); G −123.01 (2F, m); I −126.56 (2F, m); K −81.03 (3F, t) [$J_{AB}=180$, $J_{AC}=J_{BC}=7$ Hz] ppm.

$(CF_2Cl)_2\overline{CONSO_2CF_3}$ (**34**): IR (liq.) (cm^{-1}): 1435 (s); 1370 (w); 1234 (vs); 1197 (s); 1152 (s); 1124 (s); 1063 (m); 1014 (m); 962 (m); 866 (m); 830 (m); 629 (m); 604 (s). ^{19}F NMR ($CDCl_3$, −20 °C) $Cl\text{-}CF^AF^B(CF^CF^DCl)\overline{CONSO_2CF_3^E}$ δ: A −54.76 (1F, dt); B −59.49 (1F, dt) (AB pattern); C −60.49 (1F, dt); D −62.62 (1F, dt) (AB pattern); E −74.83 (3F, s) [$J_{AB}=180$, $J_{CD}=175$, $J_{A(B)\text{-}C(D)}=J_{B(A)\text{-}D(C)}=8$ Hz] ppm.

$(CF_2Cl)_2\overline{CONSO_2F}$ (**39**): IR (gas) (cm^{-1}): 1480 (vs); 1460 (w); 1237 (vs); 1203 (m); 1162 (s); 1070 (m); 1029 (vs); 970 (m); 848 (vs); 698 (m); 586 (s). MS (CI, major) *m/z*: 276 $[(M-F)^+$, 9]; 260, $[(M-Cl)^+$, 14]; 212 $[(M-SO_2F)^+$, 9]; 194 $[(M-C_2F_4)^+$, 49]; 177 $[(M-C_2F_5)^+$, 6]; 147 ($CF_3SO_2N^+$, 100). ^{19}F NMR $ClCF^AF^B(CF^CF^DCl)\overline{CONSO_2F^E}$ δ: A −53.52 (1F, dt); B −57.63 (1F, dtd) (AB pattern); C −60.93 (1F, dt); D −62.60 (1F, dt) (AB pattern); E 61.74 (1F, m) [$J_{AB}=184$, $J_{CD}=176$, $J_{AE}=9$, $J_{BE}=6$ Hz] ppm.

$(CF_2Cl)_2\overline{CONSO_2C_4F_9}$ (**35**): IR (liq.) (cm^{-1}): 1436 (s); 1353 (m); 1244 (vs); 1146 (s); 1064 (w); 1000 (w); 960 (w); 878 (w); 830 (m); 588 (m). ^{19}F NMR ($CDCl_3$, −10 °C) $ClCF^AF^B(CF^CF^DCl)\overline{CONSO_2CF^EF^FCF_2^G\text{-}CF^HF^ICF_3^J}$ δ: A −54.78 (1F, dt); B −59.57 (1F, dt) (AB pattern); C −60.24 (1F, dt); D −62.49 (1F, dt) (AB pattern); E,F −108.90 (2F, t); G −121.00 (2F, m); H,I −126.20 (2F, dt); J −80.82 (3F, t) [decoupling {−126.69 ppm}] E −108.84 (1F, d); F −108.92 (1F, d) AB pattern [decoupling {−108.90 ppm}] H −126.20 (1F, d); I −127.10 (1F, d) AB pattern [$J_{AB}=180$, $J_{CD}=176$, J_{AC} or $J_{AD}=J_{BD}$ or $J_{BC}=8$, $J_{EF}=260$, $J_{HI}=295$, $J_{GJ}=9$ Hz] ppm.

$(CF_2Cl)_2\overline{CONSO_2C_6F_{13}}$ (**36**): IR (liq.) (cm^{-1}): 1430 (s); 1360 (m); 1237 (vs); 1061 (m); 960 (s); 876 (s); 740 (m); 698 (m); 596 (m). ^{19}F NMR ($CDCl_3$, −20 °C) $ClCF^AF^B(CF^CF^DCl)\overline{CONSO_2CF_2^ECF_2^FCF_2^GCF_2^H\text{-}CF_2^ICF_3^J}$ δ: A −54.78 (1F, dt); B −59.84 (1F, dt) (AB pattern); C −60.25 (1F, dt); D −62.82 (1F, dt) (AB pattern); E −108.72 (2F, m); F −120.10 (2F, m); G −122.43 (2F, m); H −123.35 (2F, m); I −126.85 (2F, m); J −81.06 (3F, t) [$J_{AB}=180$, $J_{CD}=176$, J_{AC} or $J_{AD}=J_{BD}$ or $J_{BC}=8$ Hz] ppm.

Preparation of compound 41

A solution consisting of 3.05 g (10 mmol) of **40** and 2 g of MCPBA in 7 ml of CH_2Cl_2 was stirred at 22 °C for 2 h. The precipitated *m*-chlorobenzoic acid was filtered out (1.2 g) and the solution was washed three times with an aqueous 10% solution of Na_2CO_3 and dried over sodium sulfate. The solvent was then removed *in vacuo*. The oily residue crystallized after washing with a small amount of pentane giving **41** (1.6 g, 50%).

$(CF_3)_2\overline{CONSO_2C_6H_5}$ (**41**): m.p. 77–78 °C (decomp.). IR (Nujol) (cm^{-1}): 3068 (w); 1583 (m); 1450 (s); 1389

(vs); 1324 (vs); 1270 (s); 1216 (s); 1088 (m); 971 (s); 753 (m); 718 (vs); 689 (m); 585 (m). ^{19}F NMR $CF_3{}^ACF_3{}^B\overline{CONSO_2C_6H_5}$ δ: A −63.93 (3F, q); B −74.72 (3F, q) [J_{AB} = 8.5 Hz] ppm. ^{1}H NMR δ: 8.9 (2H, dm); 7.9 (1H, t); 7.48 (2H, t) ppm.

General procedure for the preparation of polyfluoro-N-sulfonylimines

Method a

Compound **28** (1 mmol) and 1.3 mmol of CF_2=CFCl were stored in a 100 ml Pyrex flask fitted with a Teflon–glass valve for 5 d at 22 °C. Trap-to-trap vacuum distillation gave 1.2 mmol of a mixture (25:75, ^{19}F NMR spectroscopy) of trifluoroethene and its oxide in the −196 °C trap and 0.9 mmol of imine **26** in the −40 °C trap.

Method b

The oxaziridine (0.5 g) was added to a solution consisting of 0.4 g $PhS(O)CH_3$ in 5 ml of sulfolane at 0 °C (**25**) or at 22 °C (**32**). After 20 min, the reaction products **24** and **42** were isolated by pumping on the reaction mixture through a trap at −196 °C. Compound **42** was then separated from $CF_3(CF_2Cl)CO$ by vacuum pumping on the mixture collected at −196 °C for 5 min at −10 °C.

$(CF_3)_2C$=NSO_2CF_3 (**24**): Yield, 80%; b.p. 76–77 °C. IR (gas) (cm^{-1}): 1714 (m) (C=N); 1434 (vs); 1425 (w); 1323 (vs); 1272 (vs); 1228 (vs); 1138 (vs); 982 (m); 824 (m); 621 (s); 499 (m). MS (CI, major) *m/z*: 298 [$(M+1)^+$, 47]; 280 [$(M+1-F)^+$, 100]; 214 [$(M-SO_2F)^+$, 58]; 167 ($C_3F_6OH^+$, 35); 166 ($C_3F_6O^+$, 19); 150 ($C_3F_6{}^+$, 80). ^{19}F NMR (22 °C, $CDCl_3$) $CF_3{}^A(CF_3{}^B)C$=$NSO_2CF_3{}^C$ δ: A,B −68.13 (6F, br s); C −77.40 (3F, s) ppm. ^{19}F NMR (−62 °C, CD_3CN) δ: A −65.73 (3F, q); B −69.68 (3F, q); C −77.03 (3F, s) [J_{AB} = 5 Hz] ppm. T_c = 253 K.

$(CF_3)_2C$=$NSO_2C_4F_9$ (**26**): Yield, 90%; b.p. 120 °C. IR (liq.) (cm^{-1}): 1712 (m) (C=N); 1424 (vs); 1355 (m); 1323 (s); 1210 (vs); 1141 (m); 1119 (m); 1029 (m); 1012 (m); 975 (s); 799 (m); 725 (m). ^{19}F NMR (22 °C, $CDCl_3$) $CF_3{}^A(CF_3{}^B)C$=$NSO_2CF_2{}^CCF_2{}^DCF_2{}^ECF_3{}^F$ δ: A,B −68.15 (6F, br s); C −110.76 (2F, tm); D −121.22 (2F, m); E −126.46 (2F, tm); F −81.14 (3F, t) [J_{CE} = 11, J_{DF} = 8 Hz] ppm.

$CF_3(CF_2Cl)C$=$NSO_2C_4F_9$ (**42**): Yield, 60%; b.p. 156–157 °C. IR (liq.) (cm^{-1}): 1703 (m) (C=N); 1418 (s); 1290 (m); 1240 (vs); 1144 (vs); 1025 (m); 904 (m); 789 (m); 727 (m); 589 (m). ^{19}F NMR ($CDCl_3$) $CF_3{}^B(CF_2Cl^A)C$=$NSO_2CF_2{}^CCF_2{}^DCF_2{}^ECF_3{}^F$ δ: A −60.05 (2F, q); B −66.57 (3F, br t); C −110.95 (2F, t hex.); D −120.98 (2F, m); E −126.38 (2F, m); F −81.03 (3F, tt) [J_{CE} = 13, J_{DF} = 10, J_{AB} = 9 Hz] ppm.

Reaction of $(CF_3)_2CFN(Cs)SO_2C_4F_9$ with ethanol

A solution consisting of 3 g of the Cs salt of **6** in 7 ml of MeCN was mixed with excess (5 ml) of absolute ethanol at 22 °C. After 2 h, the solvent and excess ethanol were removed *in vacuo* and the residue distilled out of concentrated sulfuric acid giving 2.0 g (83%) of **25**.

$(CF_3)_2C(OC_2H_5)N(H)SO_2C_4F_9$ (**25**): b.p. 83–84 °C/1 mmHg. IR (liq.) (cm^{-1}): 3263 (m) (NH); 2998 (m); 2929 (m); 1455 (m); 1399 (s); 1354 (m); 1256 (m); 1147 (s); 1089 (m); 1024 (m); 982 (m); 801 (m); 736 (m); 585 (m). MS (CI, major) *m/z*: 494 [$(M+1)^+$, 4]; 474 [$(M-F)^+$, 24]; 300 ($C_4F_9SO_2NH_3{}^+$, 96); 121 ($C_4F_2H_5NO^+$, 100). ^{19}F NMR $(CF_3{}^A)_2C(OC_2H_5)N(H)$-$SO_2CF_2{}^CCF_2{}^DCF_2{}^ECF_3{}^B$ δ: A −75.99 (6F, t); B −81.33 (3F, t); C −110.49 (2F, t); D −121.58 (2F, m); E −125.37 (2F, m) [J_{BD} = 10, J_{CE} = 13 Hz] ppm. ^{1}H NMR δ: 1.33 (3H, t); 4.05 (2H, q); 6.4 (1H, br) ppm.

Reaction of 5 with CsF

The mixture consisting of 1.0 g of **5** and 1.0 g of dry CsF in 3 ml of MeCN was stirred at 22 °C. After 1 h, only the Cs salt of **5** was found by ^{19}F NMR ($CDCl_3$/MeCN, 1:1) spectroscopy.

Acknowledgment

Financial support for this research by Ausimont SpA (Italy) is gratefully acknowledged.

References

1 A.V. Fokin, A.F. Kolomiets and N.V. Vasil'ev, *Russ. Chem. Rev., 53* (1984) 238.
2 (a) R.E. Swindell, D.P. Bobb, T.J. Ouellette and J.M. Shreeve, *Inorg. Chem., 11* (1972) 242; (b) S.P. Halasz and O. Glemser, *Chem. Ber., 102* (1969) 3333.
3 D.D. DesMarteau and V.A. Petrov, *Abst. 13th Int. Symp. Fluorine Chem., J. Fluorine Chem., 54* (1991) 35; V.A. Petrov and D.D. DesMarteau, to be published.
4 (a) H.W. Roesky, *Angew. Chem., Int. Ed. Engl., 7* (1968) 63; (b) H.W. Roesky and H.H. Giere, *Z. Anorg. Allg. Chem., 378* (1970) 177.
5 A.F. Gontar, E.N. Glotov, A.A. Rybachev and I.L. Knunyants, *Bull. Acad. Sci. USSR, Div. Chem. Sci.,* (1984) 1711.
6 M.I. Cook and D.D. DesMarteau, *J. Org. Chem., 56* (1991) 5256.
7 J. Foropoulos, Jr. and D.D. DesMarteau, *Inorg. Chem., 23* (1984) 3720.
8 M. Hudlicky, *Oxidation in Organic Chemistry, ACS Monograph No. 186,* Am. Chem. Soc., Washington, DC, 1990, p. 236.
9 T.E. Mlsna, D.A. Mlsna, W.T. Pennington, V.A. Petrov and D.D. DesMarteau, *Acta Crystallogr.,* submitted for publication.
10 K.O. Christe, W.W. Wilson, R. Ban and J. Feng, *J. Am. Chem. Soc., 112* (1990) 7619.
11 V.A. Petrov and D.D. DesMarteau, *J. Org. Chem., 58* (1993).
12 F.A. Davis and A.C. Sheppard, *Tetrahedron, 45* (1989) 5703.

13 F.A. Davis, J.P. McColly, S. Chattoopadhyay, M.E. Harakal, J.C. Towson, W.H. Watson and T. Tawanaka, *J. Am. Chem. Soc., 109* (1987) 3370.
14 A.F. Davis, R.T. Reddy, W. Han and P.J. Carrol, *J. Am. Chem. Soc., 114* (1992) 1428.
15 Yu.V. Zeifman and I.L. Knunyants, *Proc. Acad. Sci. USSR, Chem., 173* (1967) 249.
16 L. Bragante and D.D. DesMarteau, *J. Fluorine Chem., 53* (1991) 181.
17 V.A. Petrov, V. Montanari, G. Resnati and D.D. DesMarteau, *Abs. 13th Int. Symp. Fluorine Chem., J. Fluorine Chem., 54* (1991) 399; D.D. DesMarteau, V.A. Petrov, V. Montanari, M. Pregnoloto and G. Resnati, *Tetrahedron Lett., 33* (1992) 7245.
18 (a) W.B. Jennings, S.P. Watson and U.S. Tolley, *J. Am. Chem. Soc., 109* (1987) 8099; (b) W.G. Jennings, S.P. Watson and D.R. Boyd, *J. Chem. Soc., Chem. Commun.*, (1988) 931.
19 J. Sandstrom, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982, p. 84; (b) *ibid.*, pp. 65–71.
20 D.L. Pavia, *Introduction to Organic Laboratory Techniques*, W.B. Sanders, Philadelphia, 1976, p. 527.
21 W.J. Middleton and C.G. Krespan, *J. Org. Chem., 30* (1965) 1398.