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Some fluorine-containing nitrogen acids and their derivatives

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Contents

Abstract

Fluorine-containing nitrogen acids and their derivatives are highly useful compounds in a variety of applications. For example, the acids find practical use as electrolytes or additives for electrolytes in fuel cells, the lithium salt of $(CF_3SO_2)_2NH$ is being developed for use in batteries, polymeric nitrogen acid electrolytes have been prepared, and the *N*-fluoro derivatives of some of the nitrogen acids are the most useful electrophilic fluorinating agents available. The first Xe–N bond was prepared using $(FSO_2)_2NH$. Interest in these materials has been increasing rapidly over the last 10 years because of the large number of applications in which their physical and chemical properties make them suitable candidates for study. © 1997 Elsevier Science S.A.

Keywords: Fluorine-containing nitrogen acids; Fuel cells

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1. Introduction

Nitrogen acids are a class of compounds in which the proton(s) bonded to nitrogen are highly acidic. A number of fluorine-containing nitrogen acids have been prepared, including $HN(SO_2F)_2$, $HN(SO_2CF_3)_2$, $CF_3SO_2N(H)SO_2C_4F_9$ and $HNSO_2(C_nF_{2n+1})SO_2$. These compounds have found application as fuel cell electrolytes [1,2], and their derivatives are useful synthetic reagents. The *N*-fluoro derivatives, for example, are highly selective fluorinating agents for many organic substrates [3]. The chemistry of these materials is diverse, and continues to attract attention from chemists around the world. Jacquelain was the first to report the synthesis of imidobis(sulfuric acid) ($HN(SO_2OH)_2$) [4] which is the foundation for the chemistry of nitrogen acids.

2. Bis(fluorosulfonyl)imide, $HN(SO_2F)_2$

2.1. *Syntheses of* $HN(SO_2F)_2$

Bis(chlorosulfuryl)imide was first prepared in low yield by the reaction of urea with chlorosulfonic acid [5].

$$(NH_2)_2C{=}O + 3HSO_3Cl \rightarrow HN(SO_2Cl)_2 + NH_4HSO_4 + HCl + CO_2$$

An effective route to $HN(SO_2Cl)_2$ involves the reaction of PCl_5 with sulfamic acid, followed by reaction of that product with chlorosulfonic acid [5,6].

$$2PCl_5 + H_2NSO_3H \rightarrow Cl_3P{=}NSO_2Cl + POCl_3 + 3HCl$$

$$Cl_3P{=}NSO_2Cl + HSO_3Cl \rightarrow HN(SO_2Cl)_2 + POCl_3$$

$HN(SO_2Cl)_2$ is a highly moisture sensitive, colorless crystalline solid (m.p. 37 °C, b.p. 115 °C/4 Torr) [6]. Its important physical properties and acid strength in acetic acid are reported [7]. The S–Cl bond in $HN(SO_2Cl)_2$ is very susceptible to alkaline hydrolysis, which leads to the formation of salts such as $HN(SO_3K)_2$.

Fluorination of $HN(SO_2Cl)_2$ with AsF_3 results in the formation of bis(fluorosulfuryl)imide, $HN(SO_2F)_2$ [8,9]. Improved yields of $HN(SO_2F)_2$ can be obtained as a result of better separation of $HN(SO_2Cl)_2$ and HSO_3Cl, and removal of HSO_3F via stoichiometric addition of KCl [10].

$$3HN(SO_2Cl)_2 + 2AsF_3 \rightarrow 3HN(SO_2F)_2 + 2AsCl_3$$

Other preparative routes to $HN(SO_2F)_2$ are summarized below ([11]; [12,13]; [13]; and [14] respectively).

$$(H_2N)_2C{=}O + 3HOSO_2F \rightarrow HN(SO_2F)_2 + CO_2$$

$$FSO_2NCO + HOSO_2F \rightarrow HN(SO_2F)_2 + CO_2$$

$$SO_2(NCO)_2 + 2HOSO_2F \rightarrow HN(SO_2F)_2 + 2CO_2$$

$$2POF_2N{=}PCl_3 + 2HOSO_2F \rightarrow HN(SO_2F)_2 + HN(POF_2)_2$$

When $FSO_2N{=}PCl_3$ is cleaved with fluorosulfonic acid, an azeotrope with $POCl_3$ is formed, thereby precluding the isolation of pure $HN(SO_2F)_2$ [15]. Basic hydrolysis of FSO_2NSOF_2 yields $HN(SO_2F)_2$ [16].

Bis(fluorosulfonyl)imide, $HN(SO_2F)_2$, is representative of fluorinated nitrogen acids containing N–S–F bonds. Summaries of work on compounds containing N–S–F bonds are published [17,18]. $HN(SO_2F)_2$ is a strong monobasic acid, $pK_a = 1.28$ [19]. It is a colorless, crystalline solid (m.p. 17 °C, b.p. 170 °C) and is soluble in organic solvents, as well as SO_2Cl_2 and $POCl_3$. Acetic acid has been used as a differentiating medium for the study of the relative acid strengths of protonic acids [20]. The acidity of $HN(SO_2F)_2$ in acetic acid is comparable with that of fluorosulfonic acid in that medium [21]. Molar conductance measurements in nitrobenzene and nitromethane suggest that it is a 1 : 1 electrolyte [21]. The high value of specific conductance of $HN(SO_2F)_2$ ($23.3 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$) suggests that it autoionizes according to

$$2HN(SO_2F)_2 \rightleftharpoons [H_2N(SO_2F)_2]^+ + [N(SO_2F)_2]^-$$

2.2. Derivatives of $HN(SO_2F)_2$

$HN(SO_2F)_2$ behaves as a strong acid in aqueous medium and several alkali metal salts of the type $MN(SO_2F)_2$ (M = K, Rb, Cs) are obtained by neutralization with metal carbonates [19].

$$2HN(SO_2F)_2 + M_2CO_3 \rightarrow 2MN(SO_2F)_2 + CO_2 + H_2O$$

These salts are soluble in polar organic solvents and behave as 1 : 1 electrolytes in $MeNO_2$. Their IR spectra are reported [19]. Upon reaction with ammonia, a stable ammonium salt of $HN(SO_2F)_2$, $NH_4N(SO_2F)_2$, is formed. This reflects the stability of the S–F bond vis-à-vis the S–Cl bond in $HN(SO_2Cl)_2$ that undergoes cleavage on ammonolysis. These observations suggest that some aqueous chemistry of $HN(SO_2F)_2$ is possible, and that compounds containing the $N(SO_2F)_2$ ligand should be stable in aqueous medium. In behavior analogous to that of strong oxy-acids [18], $HN(SO_2F)_2$ cleaves the tin–carbon bond in $(CH_3)_4Sn$.

$$(CH_3)_4Sn + HN(SO_2F)_2 \rightarrow (CH_3)_3SnN(SO_2F)_2 + CH_4$$

$CsN(SO_2F)_2$ reacts with $S_2O_6F_2$ to give tris(fluorosulfonyl)hydroxylamine, $(FSO_2)_2NOSO_2F$ [22].

$$CsN(SO_2F)_2 + S_2O_6F_2 \rightarrow (FSO_2)_2NOSO_2F + CsOSO_2F$$

An interesting aspect of the chemistry of $HN(SO_2F)_2$ is the pseudohalide character of the $N(SO_2F)_2$ group. As with interhalogens, compounds of the type $XN(SO_2F)_2$ (X = F, Cl, Br) are prepared as follows ([9,23]; [24]; and

[25] and [26] respectively):

$$HN(SO_2F)_2 + F_2 \rightarrow FN(SO_2F)_2 + HF$$

$$AgN(SO_2F)_2 + Cl_2 \rightarrow ClN(SO_2F)_2 + AgCl$$

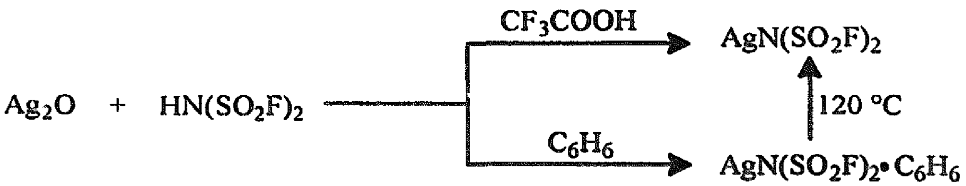
$$HN(SO_2F)_2 + ClF \rightarrow ClN(SO_2F)_2 + HF$$

$$Hg[N(SO_2F)_2]_2 + BrOSO_2F \rightarrow BrN(SO_2F)_2 + Hg(SO_3F)_2$$

The *N*-halobis(fluorosulfonyl)imides undergo a variety of reactions. Although no reactions of *N*-fluorobis(fluorosulfonyl)imide are reported, the corresponding *N*-fluorobis(perfluoroalkylsulfonyl)imides behave as selective fluorinating reagents for organic compounds [27–32]. *N*-chloro-bis(fluorosulfonyl)imide undergoes addition reactions with CO and XCN (X=Cl, Br) to give $ClC(O)N(SO_2F)_2$ and $XCN \cdot ClN(SO_2F)_2$ respectively, and with various unsaturated substrates to form compounds that contain the $N(SO_2F)_2$ moiety [24,33]. In the case of hexafluoropropene, $CF_3CFClCF_2N(SO_2F)_2$ is formed exclusively, probably by a radical mechanism. Additions of $ClN(SO_2F)_2$ to *cis*- and *trans*-2-butene are stereospecific, whereas with *cis*-CHF=CHF the addition takes place in a non-stereospecific manner. Analogous reactions of these alkenes, as well as $CH_2{=}CF_2$ with $HN(SO_2F)_2$, follow Markovnikov's rule.

Metathesis reactions of $ClN(SO_2F)_2$ with some metallic, non-metallic and organometallic chlorides with the concomitant formation of chlorine support the partial positive nature of chlorine in $ClN(SO_2F)_2$. NOCl and $(CH_3)_3SnCl$ react with $ClN(SO_2F)_2$ to form $NON(SO_2F)_2$ and $(CH_3)_3SnN(SO_2F)_2$ respectively. The stability of the $N(SO_2F)_2$ radical is demonstrated by the fact that photolysis of $ClN(SO_2F)_2$ gives a fluorosulfonyl hydrazine derivative, $[N(SO_2F)_2]_2$, in good yield [24].

$AgN(SO_2F)_2$ is prepared by reacting Ag_2O with $HN(SO_2F)_2$ either in trifluoroacetic acid or benzene. In the latter, a benzene adduct is formed that can be desolvated at 120 °C [19].



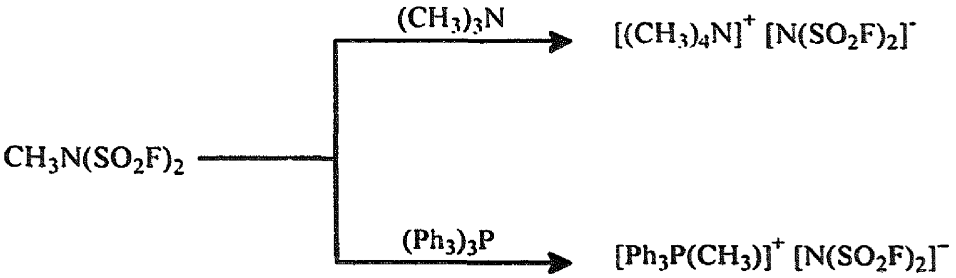
Crystals of $AgN(SO_2F)_2 \cdot C_6H_6$ belong to the space group *Cmcm*, and its molecular structure reveals that the asymmetric unit contains one quarter of the formula unit with silver and nitrogen atoms lying at the intersection of two mirror planes with an Ag–N bond distance of 2.26(1) Å. The sulfur atom and one oxygen atom also lie on the same mirror plane [34]. The bonding between silver and benzene is of a rare type, in which each benzene is symmetrically η^2-coordinated (Ag–C bond distance 2.490(7) Å) to each of the two silver atoms to give infinite chains parallel to the *c*-axis.

Alkyl halides react directly with the silver salt to form *N*-alkylbis(fluorosulfonyl)-

imides [19].

$$AgN(SO_2F)_2 + RI \rightarrow RN(SO_2F)_2 + AgI \quad R = CH_3, C_2H_5$$

These *N*-alkylbis(fluorosulfonyl)imides alkylate amines and phosphines [19], in contrast to the behavior of organic amides.



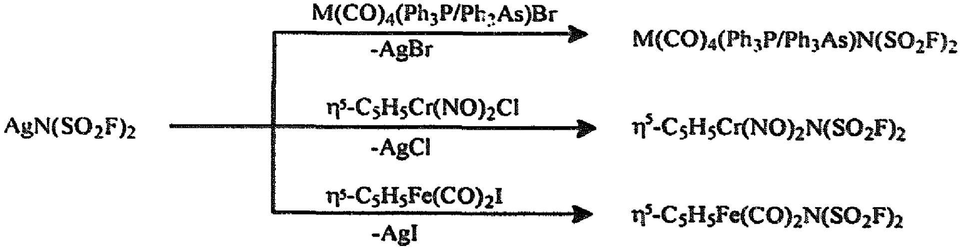
Tetraphenylphosphonium/arsonium derivatives of bis(fluorosulfonyl)imide, $Ph_4MN(SO_2F)_2$ (M = P, As) are prepared by the hydrolysis of fluorosulfonyliminosulfuroxy difluoride in the presence of the corresponding tetraphenylelement chloride [16]. The tetraphenylphosphonium derivative is also prepared by the reaction of tetraphenylphosphonium chloride and $NH_4N(SO_2F)_2$ in water [35]. Its crystal structure reveals that the anion adopts a staggered conformation with C_2 symmetry at 112 K, while at room temperature the anion has an unfavorable eclipsed conformation. The mean S–N bond distance in $Ph_4As^+[N(SO_2F)_2]^-$ is found to be 156.8 pm [36].

The reaction of $AgN(SO_2F)_2$ with CH_2Cl_2 in a sealed ampoule at 100 °C results in the formation of $CH_2[N(SO_2F)_2]_2$ (m.p. of 90–91 °C) that can be sublimed in vacuo. $CH_2[N(SO_2F)_2]_2$ is monoclinic, space group $P2_1/c$ and the asymmetric unit contains two crystallographically independent molecules [37].

$AgN(SO_2F)_2$ is an effective reagent for introducing the $N(SO_2F)_2$ group into transition metal compounds. $M(CO)_5N(SO_2F)_2$ (M = Mn [38], Re [39]) are prepared by the reaction of the corresponding bromides with $AgN(SO_2F)_2$ in CH_2Cl_2.

$$M(CO)_5Br + AgN(SO_2F)_2 \rightarrow M(CO)_5N(SO_2F)_2 + AgBr$$

Other organotransition metal derivatives are isolated via metathesis reactions with silver salts [18].



The transition-metal–nitrogen bond in these derivatives is highly polar, and as a result the $N(SO_2F)_2$ group is displaced by Lewis bases, such as CH_3CN and Ph_3P, to give ionic complexes [38].

$$M(CO)_5N(SO_2F)_2 + L \rightarrow [M(CO)_5L]^+[N(SO_2F)_2]^-$$
$$(M = Mn, Re; L = MeCN, Ph_3P)$$

$$\eta^5\text{-}C_5H_5Fe(CO)_2N(SO_2F)_2 + L \rightarrow [\eta^5\text{-}C_5H_5Fe(CO)_2L]^+[N(SO_2F)_2]^-$$

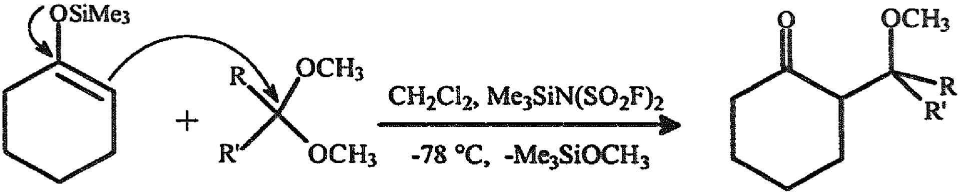
Trialkyltin(IV) bis(fluorosulfonyl)imides, $R_3SnN(SO_2F)_2$ ($R = Me$, Et, ^nPr, ^nBu), are obtained in almost quantitative yield by metathesis reactions of the corresponding organotin(IV) chloride with $AgN(SO_2F)_2 \cdot C_6H_6$ in dichloromethane at room temperature [40].

$$R_3SnCl + AgN(SO_2F)_2 \cdot C_6H_6 \rightarrow R_3SnN(SO_2F)_2 + AgCl + C_6H_6$$

Tributyltin(IV) bis(fluorosulfonyl)imide is prepared by the low temperature reaction of $^nBu_3SnH$ with $HN(SO_2F)_2$ in $CFCl_3$. These compounds are viscous oily liquids that are characterized by their IR, ^1H, ^{13}C, ^{19}F and ^{119}Sn NMR and mass spectral data [40]. The ^{119}Sn NMR chemical shifts for these compounds are ca. 250 ppm downfield from the reference tetramethyltin (0 ppm). This shift suggests appreciable cationic character of the organotin(IV) moiety in these compounds. The $N(SO_2F)_2$ group in $R_3SnN(SO_2F)_2$ is very labile and is easily displaced by nucleophiles, such as pyridine (Py) and dimethylsulfoxide (DMSO), to form ionic complexes of the type $[R_3SnL_2]^+[N(SO_2F)_2]^-$. The ^{119}Sn Mössbauer spectrum of the Py complex suggests a trans trigonal bipyramidal (TBP) geometry at tin in $[Me_3SnPy_2]^+[N(SO_2F)_2]^-$.

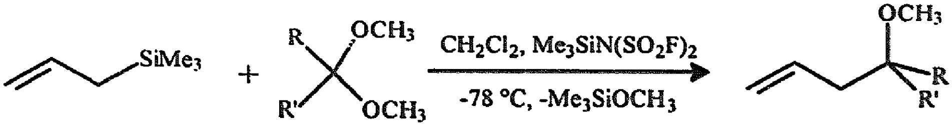
Dimethyltin(IV) bis(fluorosulfonyl)imide, $Me_2Sn[N(SO_2F)_2]_2$, is isolated as a thermally stable white hygroscopic solid (m.p. > 270 °C) by the solvolysis of $Me_3SnCl/Me_2SnCl_2/Me_2Sn(OOCCF_3)_2$ in $HN(SO_2F)_2$ [41]. The solvation studies of Me_3SnCl in $HN(SO_2F)_2$ show initial formation of the Me_3Sn^+ cation that undergoes further solvolysis to give the Me_2Sn^{2+} cation with concomitant elimination of CH_4. This is in agreement with similar observations made earlier during analogous solvolysis reactions in strong oxyacids [42]. A large splitting of the SO_2 stretching vibrations in the IR spectrum of $Me_2Sn[N(SO_2F)_2]_2$ and a strong Mössbauer effect at room temperature suggest that the material is polymeric.

Trimethysilyl(IV) bis(fluorosulfonyl)imide, $Me_3SiN(SO_2F)_2$, has been prepared and characterized [43]. This compound contains a highly electron deficient silicon atom ($\delta\ ^{29}Si = 44.92$ ppm) and is found to be more effective as a synthetic reagent than $Me_3SiOSO_2CF_3$. The reaction of trimethylsilylenol ethers with various acetals in the presence of 5 mol% $Me_3SiN(SO_2F)_2$ goes to completion within 30 min with isolated yields of 82–90%.



R, R' = CH_3; H, OCH_3; H, Ph; H, p-$MeOC_6H_4$; H, $C_6H_5CH{=}CH$; H, C_6H_{13}

Similar reactions of acetals with allyltrimethylsilane [43] yield the corresponding allylated products in ca. 90% yield within 30 min.



R, R' = H, Ph; H, p-$MeOC_6H_4$; H, -$C{=}CHCHC_6H_5$; H, C_6H_{13}; -$CH_2(CH_2)_3CH_2$-, etc.

The enhanced catalytic activity of $Me_3SiN(SO_2F)_2$ vis-à-vis $Me_3SiOSO_2CF_3$ in aldol-type reactions is demonstrated by the reaction (5 mol%) with heptaldehyde where, after a reaction time of 1 min, the condensation products are obtained in 73% and 27% respectively [43].

Metal bis(fluorosulfonyl)imides (metal = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Zr(IV) and Th(IV)) are prepared in over 90% yield by reacting the corresponding anhydrous metal trifluoroacetates with $HN(SO_2F)_2$ in CF_3COOH medium [44–46]. These compounds behave as strong Lewis acids and form complexes with donor molecules such as triphenylphosphine oxide, 2,2′-bipyridyl, Py, acetonitrile, etc. Thiotrithiazyl bis(fluorosulfonyl)imide, $S_4N_3N(SO_2F)_2$, is prepared by the reaction of S_4N_3Cl with $HN(SO_2F)_2$ [47]. Complexes of some anhydrous metal chlorides (metal = Fe(III), Sb(V), Ti(IV), V(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)) with $XN(SO_2F)_2$ ($X = S_4N_3$ and NH_4^+) are reported [48,49]. Molar conductance studies of these complexes in nitromethane suggest that they behave as 1 : 1 (M = Sb(V), Fe(III) and V(III)) or 1 : 2 electrolytes (M = Ti(IV), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)).

Cavanaugh and Bailey [50] and Thrasher et al. [51] have used ^1H NMR spectroscopy to determine the relative electronegativities of some fluorinated nitrogen–sulfur and sulfur–oxygen ligands. The group electronegativity value of $N(SO_2F)_2$ (3.6) is larger than the electronegativity of nitrogen (3.1) or the SO_2F group (3.1). A significant consequence of the high electronegativity of the $N(SO_2F)_2$ group is its ability to form compounds with xenon [52,53]. The reactions of XeF_2 with strong oxy-acids HX ($X = OTeF_5$, $OSeF_5$, OSO_2F, OSO_2CF_3, $OClO_3$, $OPOF_2$, ONO_2 and $OC(O)CF_3$) give compounds of the type F–Xe–X and XeX_2 [54]. In all of these derivatives, the oxy-acid anion has high group electronegativity. These factors suggested the synthesis of new compounds containing an Xe–N bond.

$$XeF_2 + HN(SO_2F)_2 \xrightarrow[0\,^{\circ}C,\,4\,d]{CF_2Cl_2} F\text{–}Xe\text{–}N(SO_2F)_2 \rightarrow Xe[N(SO_2F)_2]_2$$

$FXeN(SO_2F)_2$ is a thermally unstable white crystalline solid at 22 °C. At 70–75 °C, decomposition is quantitative according to

$$2FXeN(SO_2F)_2 \rightarrow Xe + XeF_2 + [N(SO_2F)_2]_2$$

Solution ^{15}N, ^{129}Xe and ^{19}F NMR studies of ^{15}N-enriched $FXeN(SO_2F)_2$ show the presence of an Xe–N bond. The first example of a directly bonded ^1J coupling between ^{129}Xe–^{15}N (305 Hz) is reported [55]. The existence of an Xe–N bond in $F\text{–}Xe\text{–}N(SO_2F)_2$ is confirmed from its crystal structure at −55 °C. The F–Xe–N bond is nearly linear [55,56]. The S–N bond distances in $FXeN(SO_2F)_2$ (162.8 and 162.3 pm) are shorter than those found in H_2NSO_3H ($H_3N^+SO_3^-$) (177.2 pm) [57]. This suggests that the S–N bond in the former has some π-bond character resulting from overlap of the nitrogen lone pair and empty 3d-orbitals on sulfur. Since no lone pair is available for such pπ–dπ bonding in sulfamic acid, the S–N bond distance of 177.2 pm is assumed to correspond to an S–N single bond. However, compared with the S–N bond distance in $Ph_4AsN(SO_2F)_2$ (156.8 pm) [36], $FXeN(SO_2F)_2$ shows a lower extent of charge delocalization over the S–N–S π-framework as it has a lower S–N bond order. Similar arguments can be extended to the S–O bond distances. An average S–O bond length of 140.4 pm for $FXeN(SO_2F)_2$ is significantly shorter than that found in $S_6N_4(SO_3F)_2$ (141.5 and 141.9 pm) [58], $NH_2(SO_3)^-$ (145.7 pm) [59,60], $NH(SO_3)_2^{2-}$ (144.9 pm) [61,62], $N(SO_3)_3^{3-}$ (146.8 pm) [63] and $Ph_4AsN(SO_2F)_2$ (av. 141.5 pm) [36] but similar to that found in SO_2F_2 (140.5 pm) where an S–O bond order of 2.0 has been assigned by Gillespie and Robinson [64]. An increase in bond order in going from an ionic to a covalent $-N(SO_2F)_2$ group may be visualized as the dispersal of charge from nitrogen indicative of S–O pπ–dπ bonding. Bond angles of 119.7° (av.) and 121.4° in $FXeN(SO_2F)_2$ and $Ph_4AsN(SO_2F)_2$ respectively are indicative of an sp^2-hybridized nitrogen atom with a planar S–N–S framework.

The Raman spectral data and band assignments are given for $FXeN(SO_2F)_2$ [55]. The highest frequency observed in $N(SO_2F)_2$ derivatives lies in the region 1500–1350 cm^{-1} and is assigned to the $\nu_{as}SO_2$ frequency. This band is diagnostic for differentiation between ionic and covalent bis(fluorosulfonyl)imide derivatives. As inferred from the X-ray structure analyses of ionic and covalent $N(SO_2F)_2$ compounds, e.g. $Ph_4As^+[N(SO_2F)_2]^-$ and $FXeN(SO_2F)_2$, the S–O bond order in ionic derivatives is lower than the bond order observed in covalent compounds. Maximum S–O bond order can, therefore, be expected for the dimer $[N(SO_2F)_2]_2$ where the bonding of the $N(SO_2F)_2$ group is purely covalent and the $\nu_{as}SO_2$ frequency is at 1506 cm^{-1} [24]. In $FXeN(SO_2F)_2$, this band is found at 1451 cm^{-1} and the $N(SO_2F)_2$ group has partial ionic character [55]. Ionic $N(SO_2F)_2$ derivatives such as $CsN(SO_2F)_2$, show the $\nu_{as}SO_2$ frequency at 1376 cm^{-1} [19], which is about 100 cm^{-1} lower than for covalent compounds. The order of the $\nu_{as}SO_2$ stretching frequency decreases in the following order:

$$[N(SO_2F)_2]_2 > ClN(SO_2F)_2 > HN(SO_2CF_3)_2 \sim Xe[N(SO_2F)_2]_2 >$$
$$FXeN(SO_2F)_2 > N(SO_2F)_2^-$$

The synthesis of ^{15}N-enriched $Xe[N(SO_2F)_2]_2$ via the reaction of $[^{15}N]$-$FXeN(SO_2F)_2$ with $[^{15}N]$-$HN(SO_2F)_2$ is described. ^{15}N and ^{129}Xe NMR evidence for the proposed structure is based on the observed $^1J(^{15}N-^{129}Xe)$ couplings [65]. These couplings demonstrate conclusively that the compound contains two equivalent Xe–N bonds. The bands at 420 cm^{-1} in $FXeN(SO_2F)_2$ and at 413 and 406 cm^{-1} in $Xe[N(SO_2F)_2]_2$ are assigned to the Xe–N bond. The Raman spectrum of $[^{15}N]FXeN(SO_2F)_2$ shows a low frequency isotopic shift of the band at 420 cm^{-1} by 5.2 cm^{-1}, which provides definitive proof for the existence of an Xe–N bond [65].

In addition to the neutral Xe(II) derivatives, some novel cationic xenon–nitrogen bonded adducts, i.e. $[XeN(SO_2F)_2]^+[Sb_3F_{16}]^-$, are reported [54,66]. Reaction of $FXeN(SO_2F)_2$ with AsF_5 yields a bright yellow unstable 1 : 1 complex, $FXeN(SO_2F)_2 \cdot AsF_5$. Upon warming this complex to room temperature under dynamic vacuum, 0.5 mol of AsF_5 is lost to form a pale yellow adduct of the composition $[FXeN(SO_2F)_2]_2 \cdot AsF_5$. This adduct can be reacted with SbF_5 to give $[XeN(SO_2F)_2]^+[Sb_3F_{16}]^-$. Spectroscopic studies [54,66] support the ionic nature of these adducts.

$$FXeN(SO_2F)_2 + AsF_5 \xrightarrow{-78\,^\circ C} [XeN(SO_2F)_2]^+[AsF_6]^-$$

$$2[XeN(SO_2F)_2]^+[AsF_6]^- \xrightarrow[\text{vacuum}]{22\,^\circ C} [F[XeN(SO_2F)_2]_2]^+[AsF_6]^- + AsF_5$$

$$[F[XeN(SO_2F)_2]_2]^+[AsF_6]^- + 6SbF_5 \xrightarrow{SbF_5}$$
$$2[XeN(SO_2F)_2]^+[Sb_3F_{16}]^- + AsF_5$$

Crystal structure analysis [66] has established the existence of discrete $[XeN(SO_2F)_2]^+[Sb_3F_{16}]^-$ species. The Xe–N bond (202 pm) in the cation is significantly shorter than the Xe–N bond in $FXeN(SO_2F)_2$ (220 pm). Similar changes in bond length have been reported for XeF_2 (Xe–F = 201.6 pm) [67] and the fluorine-bridged cation $[XeF]^+[Sb_2F_{11}]^-$ that has a terminal Xe–F bond length of 184 pm [68].

The EPR spectrum of $^{\cdot}N(SO_2F)_2$ [54] shows a five-line spectrum at 250 K with $a_{iso} = 8.3$ G and $g = 2.063$ with peak intensities in the ratio 1 : 3 : 4 : 3 : 1. This is interpreted as the interaction of an unpaired electron with a nucleus with $I = 1$ and two nuclei with $I = 1/2$. At 280 K, additional splitting is observed yielding a nine-line spectrum. The spectrum is explained on the basis of an interaction of an unpaired electron with one nitrogen and two equivalent fluorine nuclei. The isotropic hyperfine coupling constants A_N and A_F also suggest delocalization of the unpaired electron over the S–N–S π-framework.

3. Fluorosulfonyl trifluoromethylsulfonylimide

The synthesis of a nitrogen acid that contains both fluorosulfonyl and trifluoromethylsulfonyl functionalities has also been reported by the reaction of $CF_3SO_2NPCl_3$ and fluorosulfonic acid [69].

$$CF_3SO_2NPCl_3 + FSO_3H \rightarrow FSO_2N(H)SO_2CF_3 + POCl_3$$

This acid cannot be obtained if FSO_2NPCl_3 and trifluoromethanesulfonic acid are used as starting material.

$$FSO_2NPCl_3 + 2CF_3SO_3H \rightarrow FSO_2N(H)POCl_2 + (CF_3SO_2)_2O + HCl$$

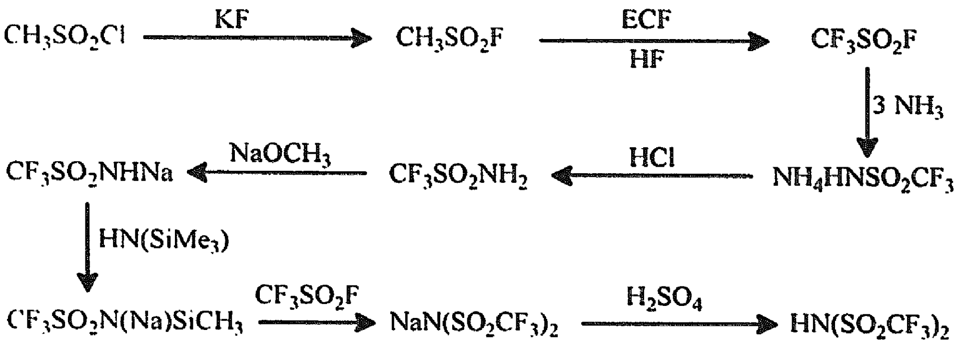
The preparation of the silver salt, $AgN(SO_2F)(SO_2CF_3)$, is also described by the reaction of the acid with Ag_2O in aqueous medium [69].

$$Ag_2O + FSO_2N(H)SO_2CF_3 \rightarrow FSO_2N(Ag)SO_2CF_3$$

4. Bis(perfluoroalkylsulfonyl)imides

4.1. *Bis(trifluoromethysulfonyl)imide, $HN(SO_2CF_3)_2$*

Bis(trifluoromethysulfonyl)imide, $HN(SO_2CF_3)_2$, was initially synthesized in ca. 48% yield [70], but with modifications in the synthetic procedure the yield improved to 80% [71]. The steps involved in synthesis of $HN(SO_2CF_3)_2$ are shown below:



Several other $R_fSO_2N(H)SO_2R_f'$ derivatives ($R_f = CF_3$, C_4F_9, C_8F_{17}; $R_f' = C_4F_9$, C_8F_{17}] were obtained earlier using the same methodology [72].

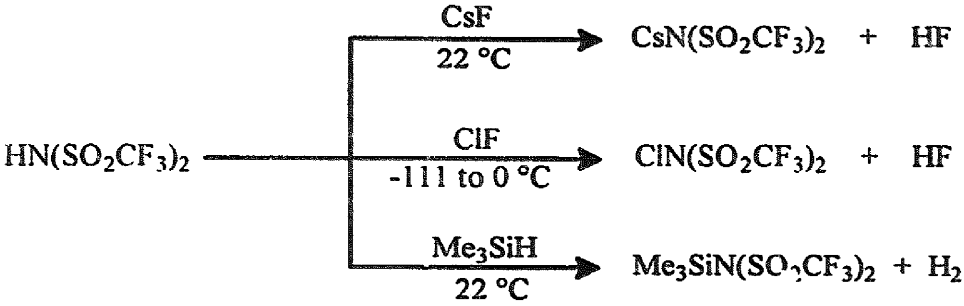
Recently, Hu and DesMarteau found a convenient route to the synthesis of some perfluoroalkanesulfonyl halides via sodium sulfinates as intermediates [73]. Some of the sulfonyl fluorides thus obtained are converted to the corresponding sulfonylimides in high yields according to the synthetic methodology adopted for the preparation of $HN(SO_2CF_3)_2$ [70,71]. The new bis(fluoroalkylsulfonyl)imides of the type HNR_fR_f' are very acidic, hygroscopic, low melting solids (R_f, $R_f' = C_2F_5$, C_2F_5; CF_3, C_2F_5; C_3F_7, C_3F_7; CF_3, C_3F_7) or liquids (R_f, $R_f' = CF_3$,

$ClCF_2CFClCF_2CF_2$; CF_3, $CF_2{=}CFCF_2CF_2$). These solid acids exhibit unique acidity values for superacids in the gas phase [74].

$HN(SO_2CF_3)_2$ is a white crystalline solid (m.p. 49–50 °C). It fumes in air and dissolves exothermically in water. Its aqueous solution is stable towards hydrolysis. The pK_a in water (1.7) is similar to that of $HN(SO_2F)_2$ (1.2) [19]. The pK_a values for $HN(SO_2CF_3)_2$ and $HN(SO_2F)_2$ determined by ^1H NMR in acetic acid [75] are 7.8 and 8.7 respectively, compared with CF_3COOH (11.4), HNO_3 (10.1), $HOTeF_5$ (8.8), H_2SO_4 (7.0), $HOSO_2F$ (6.1), $HClO_4$ (4.1) and CF_3COOH (4.2). $HN(SO_2CF_3)_2$ is characterized by vibrational spectra and NMR studies [70].

4.2. Derivatives of $HN(SO_2CF_3)_2$

Taking advantage of the acidic proton, $HN(SO_2CF_3)_2$ readily undergoes metathesis reactions with some ionic or polar compounds.



The alkali metal salts of bis(trifluoromethylsulfonyl)imide are known to have graphite-like layered structures in the solid state [76].

Lithium bis(trifluoromethylsulfonyl)imide is found to be quite inert towards active halogen-containing compounds, such as $R_fN{=}CF_2$, CF_3COCl, CH_3COF, etc. However, it reacts readily with strong electrophiles. With $S_2O_6F_2$ and H_2SO_4, $LiN(SO_2CF_3)_2$ forms $FSO_2ON(SO_2CF_3)_2$ and $HN(SO_2CF_3)_2$ respectively, in good yield. The S–N bond in $LiN(SO_2CF_3)_2$ is susceptible to cleavage. This is observed when the lithium salt is reacted with KF or ClF to form CF_3SO_2F or CF_3SO_2Cl respectively. In the latter reaction, $ClN(SO_2CF_3)_2$ is the major product [77].

In an important application, $LiN(SO_2CF_3)_2$ (available commercially from 3M) has been shown to be one of the highest conducting 1 : 1 lithium electrolytes and is presently undergoing long-term testing in proprietary lithium ion batteries [78,79].

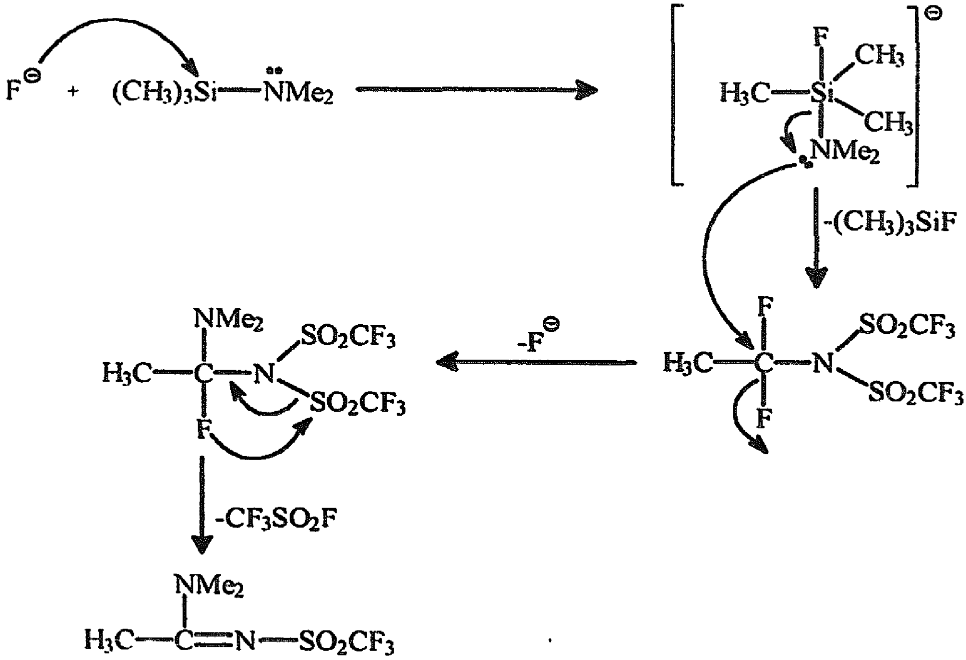
Trialkyltin(IV) derivatives of bis(trifluoromethylsulfonyl)imide can be conveniently prepared in almost quantitative yields by reacting $AgN(SO_2CF_3)_2$ with the corresponding R_3SnCl (R = Me, ^{n}Bu or Ph) [77]. These derivatives contain a highly deshielded tin(IV) nucleus, as suggested by the ^{119}Sn NMR chemical shift of about 250 ppm downfield from tetramethyltin. Compounds of this type have been postulated as tricoordinated tin cations under neutral conditions. In the trimethyltin(IV) derivative, the average Me–Sn–Me angle is found to be ca. 115° based on solution

NMR studies. When the ^{119}Sn NMR of $R_3SnN(SO_2CF_3)_2$ ($R=Me$, ^nBu) is recorded in donor solvents such as CH_3CN, DMSO-d_6, Py and HMPA, there is a marked upfield shift of the ^{119}Sn signal. The donor strength of the solvent can be correlated with the chemical shift (^{119}Sn shift with respect to Me_4Sn in brackets) that follows the order:

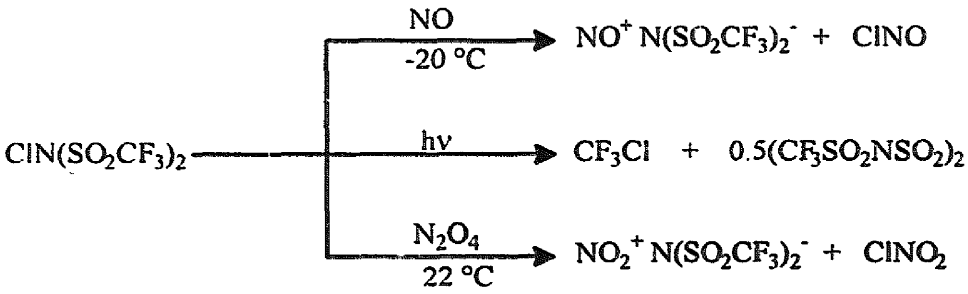
$$\text{HMPA}(-30.8) > \text{Py}(-12.3) > \text{DMSO}(37.4) > CH_3CN(44.6) \gg CH_2Cl_2(251)$$

The computed Me–Sn–Me angles (ca. 120°) suggest a trans-TBP geometry with donor molecules occupying the axial positions [77]. This behavior is similar to that observed for $R_3SnN(SO_2F)_2$ derivatives that also behave as strong Lewis acids. The electron deficient nature of these compounds makes them attractive reagents for organic syntheses.

Similar to the reaction chemistry of $HN(SO_2F)_2$, electrophilic addition reactions of $HN(SO_2CF_3)_2$ with polyfluoroolefins such as $CHF{=}CH_2$, $CH_2{=}CF_2$ and $CHF{=}CF_2$ obey Markovnikov's rule [77]. As the fluorine content of the olefin increases, it is found that more drastic conditions are required to carry out the addition reactions. Attempts to cleave the CF_2–N bond in $CH_3CF_2N(SO_2CF_3)_2$ by using CsF results in the formation of CH_3CF_3 as a minor product (ca. 12%), with CF_3SO_2F as the major product. When Me_3SiNMe_2 is used as a reagent, $CH_3CF_2N(SO_2CF_3)_2$ forms $CH_3C(NMe_2){=}NSO_2CF_3$ in good yield accompanied by Me_3SiF and CF_3SO_2F. The mechanism for this reaction is reported as:



Based on a low melting point of 115 °C, $CsN(SO_2CF_3)_2$ appears to be covalent. However, the Raman spectrum of the solid supports the ionic nature of this compound [70]. The trimethylsilyl derivative is a potentially useful transfer reagent, and has been used to prepare $Xe[N(SO_2CF_3)_2]_2$ by reaction with XeF_2 [80]. Relative to $Xe[N(SO_2F)_2]_2$, $Xe[N(SO_2CF_3)_2]_2$ is more stable with no appreciable decomposition at 22 °C under nitrogen or vacuum for several days. However, when this xenon derivative is exposed to air, decomposition is complete within 1 h. Upon heating at 72 °C in a glass vessel, $Xe[N(SO_2CF_3)_2]_2$ decomposes readily to form Xe, C_2F_6, $CF_3N(SO_2CF_3)_2$ and a volatile dimeric solid of $[CF_3SO_2NSO_2]_2$. No evidence is found for the formation of the postulated product $[N(SO_2CF_3)_2]_2$. This reflects the instability of the $^{\cdot}N(SO_2CF_3)_2$ radical vis-á-vis that of the $^{\cdot}N(SO_2F)_2$ radical. This is also confirmed by the photolysis of $ClN(SO_2CF_3)_2$ that results in the quantitative formation of CF_3Cl and $[CF_3SO_2NSO_2]_2$ [70]. The *N*-chloro derivative reacts readily to form additional derivatives:



Reactions of $ClN(SO_2CF_3)_2$ with a variety of per/polyfluoroolefins, such as $CF_2{=}CFX$ ($X{=}H$, F, $\overline{CF_2CF_2CF_2CF_2N}$–, $\overline{CF_2CF_2OCF_2CF_2N}$–; and $CH_2{=}CXY$ ($X{=}H$, $Y{=}F$, CF_3; $X{=}Y{=}F$) result in uni- as well as bidirectional addition. Insertion of ClCN into the nitrogen–chlorine bond in $ClN(SO_2CF_3)_2$ results in the formation of an azaalkene, $CCl_2{=}NN(SO_2CF_3)_2$. The partial positive character of chlorine in $ClN(SO_2CF_3)_2$ is demonstrated by its reaction with R_3SnCl ($R{=}Me$, ^{n}Bu) and $CFCl_2S(O)Cl$ to form the corresponding $N(SO_2CF_3)_2$ derivative with concomitant evolution of chlorine gas. Attempts to add $ClN(SO_2CF_3)_2$ to the fluorovinyl group in $CF_2{=}CFSnMe_3$ result in the formation of $CF_2{=}CFCl$ and $Me_3SnN(SO_2CF_3)_2$ [77].

The reaction of $BrOSO_2F$ with $Hg[N(SO_2CF_3)_2]_2$ gives $BrN(SO_2CF_3)_2$ (92% yield) in a manner analogous to the formation of $BrN(SO_2F)_2$ [26]. This compound is thermally stable in the dark and is characterized by IR, Raman, NMR and mass spectroscopy. It reacts with AgCl forming $AgN(SO_2CF_3)_2$ and BrCl.

4.3. *Perfluoromethylsulfonyl perfluorobutylsulfonylimide, $CF_3SO_2N(H)SO_2C_4F_9$*

Perfluoromethylsulfonyl perfluorobutylsulfonylimide, $CF_3SO_2N(H)SO_2C_4F_9$, is obtained [81] by modification of an earlier method [70]. Its physical and chemical properties are reported. The imide dissolves in water to give stable acidic solutions with $pK_a \approx 1$.

4.4. Derivatives of $CF_3SO_2N(H)SO_2C_4F_9$

Neutralization of aqueous solutions with metal carbonates leads to the formation of the corresponding salts:

$$2CF_3SO_2N(H)SO_2C_4F_9 + M_2CO_3 \rightarrow CF_3SO_2N(M)SO_2C_4F_9 + H_2O + CO_2$$

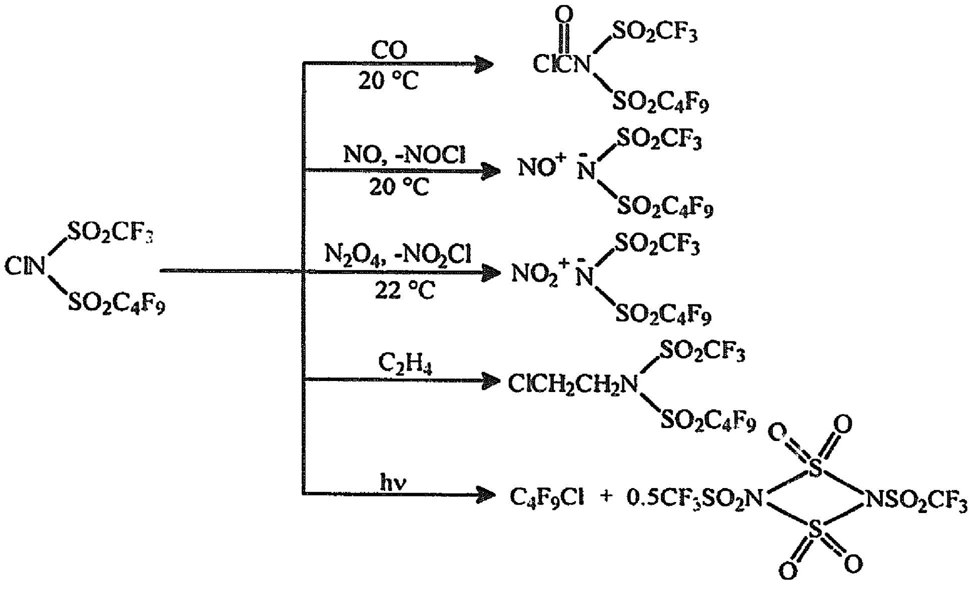
$$(M = K, Cs, Ag)$$

The IR spectra of these metal salts are similar and suggest the presence of the $[CF_3SO_2NSO_2C_4F_9]^-$ anion [81]. The silver salt is soluble in various organic solvents and is a useful ligand-transfer reagent, as evidenced by its reaction with alkyl iodides.

$$CF_3SO_2N(Ag)SO_2C_4F_9 + RI \rightarrow CF_3SO_2N(R)SO_2C_4F_9 + AgI$$

$$(R = CH_3, C_2H_5)$$

Chlorine reacts with the silver salt in the dark at room temperature to give the *N*-chloro derivative, $CF_3SO_2N(Cl)SO_2C_4F_9$, which is a useful synthetic reagent as shown below [81]:



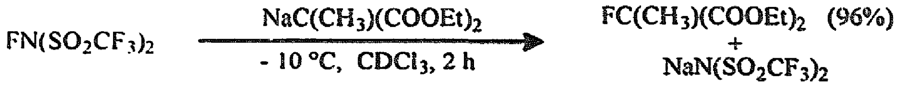
5. Applications

5.1. N-Fluorobis(perfluoromethylsulfonyl) imides as selective fluorinating reagents

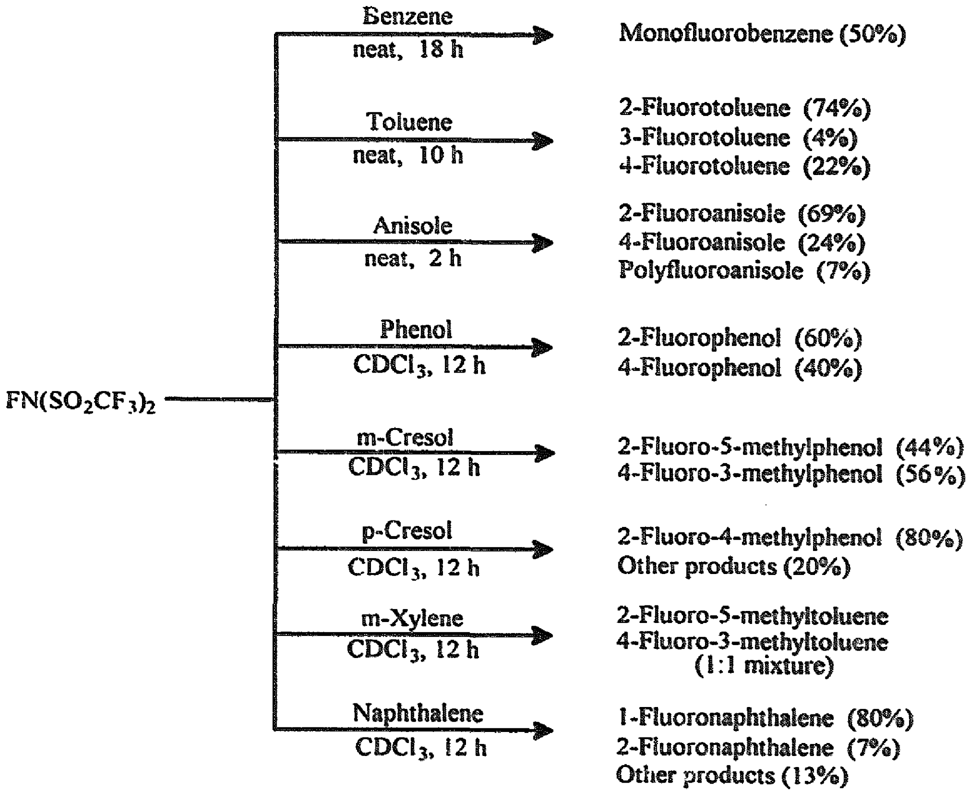
Fluorination of organic compounds to give biologically active molecules [82] by using a variety of electrophilic fluorinating reagents including F_2, CF_3OF, $FClO_3$, CH_3CO_2F, CF_3CO_2F, XeF_2 and $CsSO_4F$ is reported [83]. However, the reagents that have gained considerable attention contain the N–F functionality. Some of these

N-fluoro compounds are 1-fluoro-2-pyridone, *N*-fluoro lactams, *N*-fluoropyridinium salts, *N*-fluorosulfonamide, optically active *N*-fluorosulfonamide, *N*-fluorosultams, *N*-fluoroquinuclidinium fluorides, *N*-fluoroperfluoro(*N*-pyridylmethanesulfonamides) [84]. Among the *N*-fluoro compounds used as electrophilic fluorinating agents, the most important are the *N*-fluoro-bis(perfluoroalkylsulfonyl)imides [29,30]. These reagents complement nucleophilic fluorination reagents such as diethylaminosulfur trifluoride (DAST) and tris(dialkylamino)sulfonium difluorotrimethyl siliconate (TASF) [85].

The most versatile reagent in the *N*-fluoro bis(perfluoroalkylsulfonyl)imide class, $FN(SO_2CF_3)_2$ (m.p. −69.8 °C), is prepared in nearly quantitative yield by the direct fluorination of $HN(SO_2CF_3)_2$ with F_2. It has long term stability, favorable physical properties (b.p. 90–91 °C) and high reactivity. Numerous other *N*-fluorosulfonimides have been prepared and similarly characterized [29]. Selected fluorination reactions are described below.

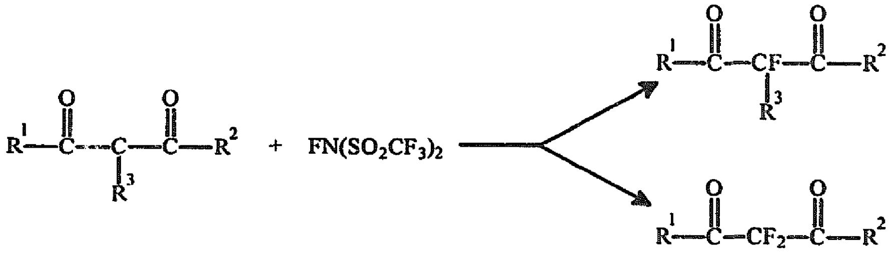


$$FN(SO_2CF_3)_2 \xrightarrow[-10\,^\circ C,\ CDCl_3,\ 2\ h]{NaC(CH_3)(COOEt)_2} FC(CH_3)(COOEt)_2\ (96\%) + NaN(SO_2CF_3)_2$$



The reaction involving the formation of diethyl-1-fluoro-1-methylmalonate is an excellent method for the preparation of this compound in high yield [27,28]. Fluorination of nitrobenzene, acetophenone and chlorobenzene with $FN(SO_2CF_3)_2$ is not successful.

$FN(SO_2CF_3)_2$ fluorinates 1,3-dicarbonyl derivatives to afford, depending on the reaction conditions, either 2-fluoro or 2,2-difluoro products in high yield [31].

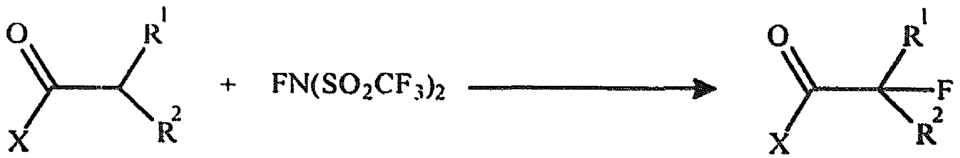


$R^1 = R^2 = R^3 = Me$; $R^1 = R^3 = Me$, $R^2 = OEt$; $R^1 = R^3 = (CH_2)_3$, $R^2 = OEt$; $R^1 = R^2 = Me$, $R^3 = H$;

$R^1 = Me$, $R^2 = OEt$, $R^3 = H$; $R^1 = C_6H_5$, $R^2 = Me$, $R^3 = H$; $R^1 = p\text{-}NO_2C_6H_4$, $R^2 = OEt$, $R^3 = H$;

$R^1 = (Me)_2CH$, $R^2 = OEt$, $R^3 = H$; $R^1 = R^2 = OMe$, $R^3 = H$; $R^1 = R^2 = OEt$, $R^3 = C_6H_5$.

N-fluorobis(trifluoromethylsulfonyl)imide is an efficient reagent for the α-fluorination of functionalized carbonyl compounds [32]. The lithium enolates of esters, amides and ketones (generated by the standard procedure by using lithium isopropylamide in tetrahydrofuran in situ) are selectively monofluorinated when treated with $(CF_3SO_2)_2NF$ in yields generally higher than those reported in the literature for similar reactions. The direct fluorination of neutral compounds can be readily performed.

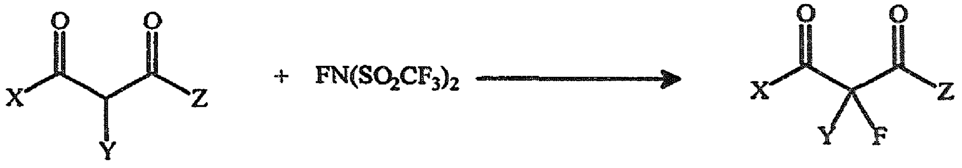


$R^1 = H, CH_3, C_2H_5, C_6H_5$; $X = OC_2H_5, OCH_2C_6H_5, N(i\text{-}C_3H_7)_2, CH_3C_6H$

$R^2 = H, C_2H_5, C_6H_5$

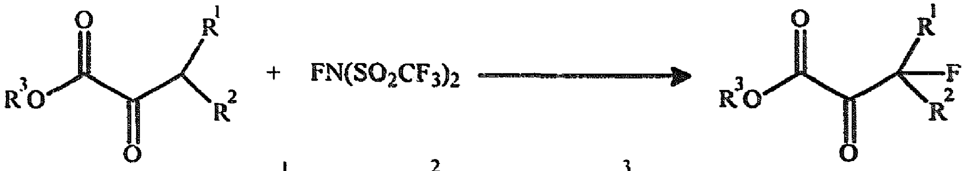
The corresponding α-fluorocarbonyl compounds are obtained in good yields [32].

The α-fluorination of β-diesters, β-diamides, β-keto-esters and β-diketones is performed either on the neutral compounds or the metal enolates [32].



$X = CH_3, OC_2H_5, -N(CH_3)CH_2N(CH_3)-,$
$Y = Cl, NO_2, OCOCH_3$
$Z = CH_3, OC_2H_5$

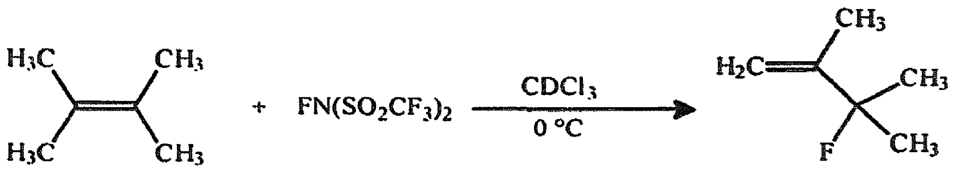
If Y = H, the difluorinated compound is formed. In this way, some geminal azafluoro, chlorofluoro and fluoroxy compounds are prepared in high yield. Some keto-esters and acids are selectively monofluorinated in the *β*-position by simple treatment of the neutral compound with $(CF_3SO_2)_2NF$ [32].



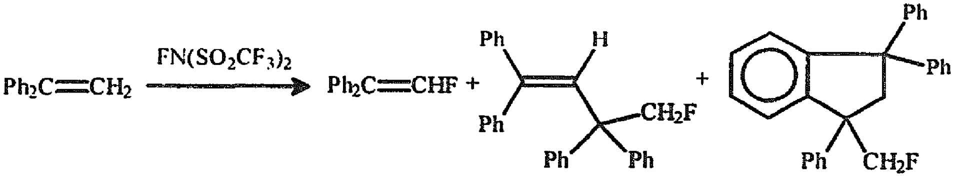
$R^1 = CH_3, H; R^2 = CH_3, C_2H_5; R^3 = H, C_2H_5$

$(CF_3SO_2)_2NF$ reacts with many types of alkenes in solvents of varying nucleophilicity to yield products resulting from the formation of fluoro carbocation intermediates [86]. These cationic intermediates are postulated to arise through an electron transfer mechanism. In solvents of higher nucleophilicity, such as water, acetic acid, aqueous HCl and $(HF)_nPy$, *α*-fluorohydrins or their acetates, *α*-, *β*-chlorofluoro- and *α*,*β*-difluoroalkenes are obtained.

N-fluorobis(trifluoromethylsulfonyl)imide undergoes rapid reaction with electron-rich olefins in various solvents of low nucleophilicity, such as $CHCl_3$, CH_2Cl_2, Freon-113, THF, Et_2O, etc., to give complicated product mixtures. The following reaction occurs between tetramethylethylene and $(CF_3SO_2)_2NF$ in a 10 : 1 molar ratio [86]:



With 1,1-diphenylethylene, the following products are obtained [77]:



Introduction of fluorine to steroids at specific positions reduces their tumorigenicity. $(CF_3SO_2)_2NF$ reacts with 1,3,5(10)-estratrien-3-ols in chloroform solution to give ortho and para fluorinated products. Similar regio- and stereoselectivities are observed when dioxane and acetonitrile are employed as solvents. In contrast, when acetic acid is used as a solvent, fluorination in the para position occurs selectively and 10-β-fluoro-3-oxo-1,4-estradiene derivatives are formed in high yields [78]. The structures assigned to the fluorinated products are based on ^1H, ^{19}F and ^{13}C NMR studies.

5.2. *Perfluorinated ionomers*

Perfluorinated ionomers such as Nafion (E.I. du Pont) exhibit marked thermal and chemical stabilities and, as a result, have found uses in a variety of special applications. Most frequently the substituents on the side chain termini were sulfonate, carboxylate and sulfonamide. Recently DesMarteau and his coworkers [87–89] have copolymerized bis(perfluoroalkylsulfonyl)imide monomers with tetrafluoroethylene to give rise to new ionomer materials. This new type of perfluorinated ionomer has the bis(perfluoroalkylsulfonyl)imide functionality on the side chain. The number of sulfonimide groups in the latter can be greater than one, depending on the monomer reacted. The presence of the non-terminal sulfonimide functionality in the side chain and the existence of more than one such group per side chain promise to significantly alter the ion cluster characteristics of these ionomers relative to existing materials.

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