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Study on the Reactions of Fluoroalkanesulfonyl Azides with Pyridine and its Derivatives

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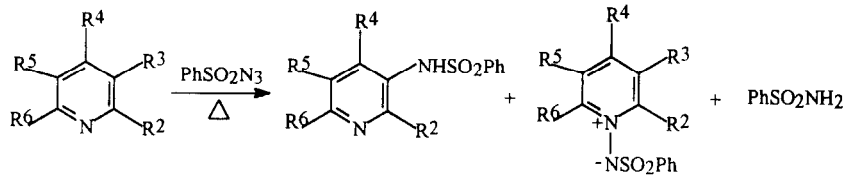
Abstract: The thermal reactions of fluoroalkanesulfonyl azides $R_fSO_2N_3$ **1** with pyridine and its derivatives have been investigated in detail. In many cases, *N*-fluoroalkanesulfonyl pyridinium imides Y^+-$N^-SO_2R_f$ (Y: pyridine, 3-picoline, 3,5-lutidine and quinoline) and the hydrogen abstraction products $R_fSO_2NH_2$ were obtained. 2-Picoline and 4-picoline reacted with **1** to give $R_fSO_2NH_2$ exclusively. Interestingly, in the reaction of azides **1c** $IC_2F_4OC_2F_4SO_2N_3$ with 4-picoline or quinoline, the ω-iodine of the azide was substituted to form $ArC_2F_4OC_2F_4SO_2NH_2$. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *fluoroalkanesulfonyl azides, pyridinium imides, pyridines, quinolinium imides, nitrenes, thermolysis.*

INTRODUCTION

Many azides (*e.g.*, phenyl azide, alkane or arene sulfonyl azide and azidoformate etc,), on heating or irradiating give a nitrene intermediate R-N (R=aryl, R`OCO, R`OSO_2, $ArSO_2$, etc.).[1-4] The reaction of pyridines with sulfonyl azides was first studied by Curtius sixty years ago and the reaction product was incorrectly formulated as 2-, 3- or 4-aminopyridine derivatives RSO_2NH-Ar.[5] This reaction was reinvestigated by Abramovitch and coworkers, it was found that, the reaction products of pyridine with benzenesulfonyl azide is actually *N*-benzenesulfonyl pyridinium imide, hydrogen abstraction product benzenesulfonamide and the insertion product $PhSO_2NHAr$.[6] On the other hand, the thermal decomposition of $PhSO_2N_3$ in 2- or 4- picoline gave the C-amination products in addition to the pyridinium imide and benzenesulfonamide.



The reactions of perfluoroalkanesulfonyl azide, which was first synthesized from the reaction of trifluoromethanesulfonic acid anhydride with sodium azide in 1965,[7] has not been studied as extensively as its hydrocarbon analogues. One paper reported the reaction of $CF_3SO_2N_3$ as a trifluoromethanesulfonyl nitrene precursor with benzene.[8] Recently we have investigated the photolysis and thermolysis of per- or polyfluoroalkanesulfonyl azides and found the formed per- or polyfluoroalkanesulfonyl nitrene reacted readily with alkenes, cyclohexane, dimethyl sulfide, triphenylphosphine, nitrosobenzene etc. to afford the insertion or addition products.[9,10] As an extension of the exploration of fluoroalkanesulfonyl nitrenes, we have studied the thermal reaction of $R_fSO_2N_3$ with pyridine and its derivatives. Herein we wish to report these results.

RESULTS AND DISCUSSION

Fluoroalkanesulfonyl azides **1** were conveniently prepared in good yield by treatment of fluoroalkanesulfonyl fluoride or chloride with sodium azide in methanol or acetonitrile at 0°C or room temperature.[9,11,12]

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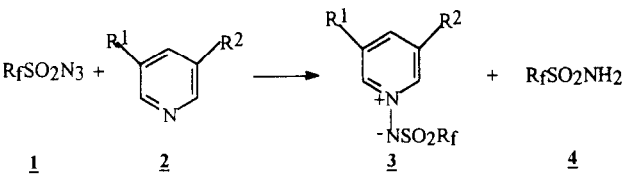
$$R_fSO_2X + NaN_3 \xrightarrow[CH_3OH \text{ or } CH_3CN]{0^oC \text{ or rt, } 12hr} R_fSO_2N_3 + NaX$$

X: F,Cl

1

Thermolysis of fluoroalkanesulfonyl azides **1** in excess pyridine gave pyridinium *N*-fluoroalkanesulfonyl imide **3** as the major products and the corresponding fluoroalkansulfonamide **4**. The decomposition temperature of **2** in pyridine is around 110°C, and the reaction of azide **1** (1mmol) in pyridine (3ml) was complete in 12h as indicated by TLC. At 120 °C, the reaction time was shortened to 8h. The two products **3** and **4** were separated by chromatography using CH_2Cl_2/CH_3OH (20:1) as eluant. Other pyridine derivatives such as 3-picoline and 3,5-lutidine reacted similarly with the azides **1** and all gave the corresponding pyridinium imides and sulfonamides. **(Scheme 1)**



1 **2** **3** **4**

R^1,R^2=H,H(a); CH_3,H(b); CH_3,CH_3(c).
R_f=CF_3 (a), C_6F_{13} (b); $IC_2F_4OC_2F_4$ (c); $ClC_2F_4OC_2F_4$ (d); $HC_2F_4OC_2F_4$ (e).

Scheme 1

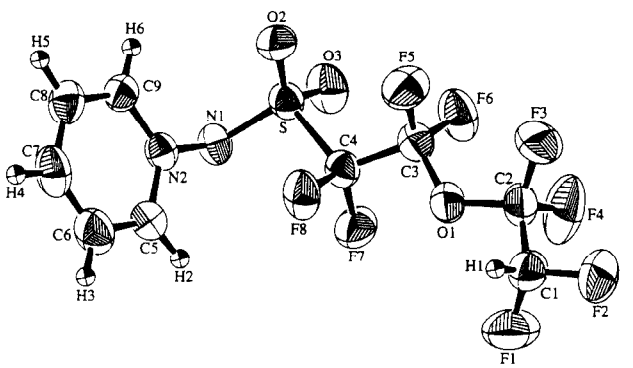
Table 1 Reaction of fluoroalkanesulfonyl azides with pyridine, picoline and lutidine.

Entry	Pyridines	Azides	Reaction conditions Temp(°C) Time(h)	Products and yield (%)	
1	**2a**	**1a**	80 ; 8 [a]	**3aa** (47)	**4a** (33)
2	**2a**	**1b**	120 ; 12	**3ab** (43)	**4b** (32)
3	**2a**	**1c**	120 ; 12	**3ac** (46)	**4c** (22)
4	**2a**	**1d**	120 ; 12	**3ad** (43)	**4d** (21)
5	**2a**	**1e**	120 ; 12	**3ae** (49)	**4e** (22)
6	**2b**	**1b**	120 ; 12	**3bb** (48)	**4b** (39)
7	**2b**	**1c**	120 ; 12	**3bc** (57)	**4c** (23)
8	**2b**	**1d**	120; 12	**3bd** (41)	**4d** (21)
9	**2b**	**1e**	120 ; 12	**3be** (46)	**4e** (32)
10	**2c**	**1b**	120 ; 12	**3cb** (53)	**4b** (22)
11	**2c**	**1c**	120 ; 12	**3cc** (47)	**4c** (26)
12	**2c**	**1d**	120 ; 12	**3cd** (47)	**4d** (28)
13	**2c**	**1e**	120 ; 12	**3ce** (44)	**4e** (24)
14	**2a**	**1c**	110 ; 12[b]	**3cc** (36)	**4c** (34)
15	**2a**	**1c**	110 ; 12[c]	**3cd** (45)	**4d** (22)
16	**2a**	**1c**	110 ; 12[d]	**3ce** (46)	**4e** (22)

All reactions were carried out in a ration of azides/pyridines(quinoline) =1mmol/3-5ml, unless otherwise indica -ted. (a) 0.1 eq CuCl as catalyst and acetonitrile as solvent. (b) azides/pyridine = 1mmol /1mmol. (c) azides /pyridine =1mmol/10mmol. (d) azides/pyridine =1mmol/50ml.

Pyridinium *N*-fluoroalkanesulfonylimides **3** are stable colorless solids. They are not decompose at their melting point and are readily recrystallized from many organic solvents (hexane/ethyl acetate, ether, CH_3Cl, CH_2Cl_2, CH_3CN etc.). Their structures are fully supported by spectra data, elemental analysis and further confirmed by X-ray diffraction analysis. The molecular structure of compound **3ae** is show in **Fig.1**. The N-N bond length is (1.425A) indicating its single bond character. In our previous work, we have prepared the

triphenylphosphonium imide $R_fSO_2N^-P^+Ph_3$ and triphenylarsenium imide $R_fSO_2N^-As^+Ph_3$. According to their X-ray crystal analysis, both N-P bond (1.609A) and N-As bond (1.725A) have double bond character.[12] This difference between N-ylide and P-ylide or As-ylide should be attributed to the absence of an empty d-orbital in the nitrogen atom. The average value of S-O bond length (1.430A) is close to the S-O bond length in $(CF_3SO_2)_2CHK$ (1.428A), in which the electron is delocalized on two oxygen atoms.[13] The S-N-N bond angle is 114.4°, which is smaller than that theoretically expected (120°), an effect arising from the localized lone pair of the nitrogen atom. From this data, it is possible to conclude that the S-N-O group of compound **3** contains a delocalized d-π bond system.



Molecular structure of $HCF_2CF_2OCF_2CF_2SO_2\dot{N}-\overset{+}{N}$

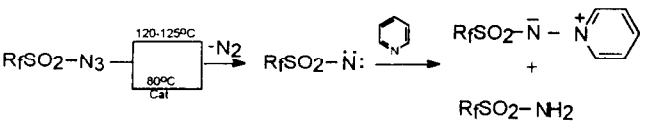
Fig. 1 Molecule structure of compound **3ae**

Two possible reaction pathways have been proposed for the reaction of $ArSO_2N_3$ with pyridine *i.e.* a concerted attack of the pyridine nitrogen lone pair on the azides function with the elimination of N_2 or a direct trapping of the electrophilic sulfonyl nitrene intermediate.[6] Thus:

$$C_5H_5N: + N_2{-}NSO_2Ar \xrightarrow{-N_2} C_5H_5\overset{+}{N}{-}\overset{-}{N}SO_2Ar$$

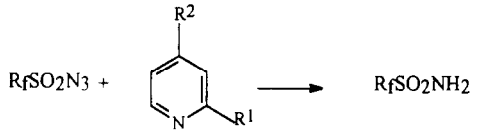
$$ArSO_2N_3 \xrightarrow{-N_2} ArSO_2N: \xrightarrow{C_5H_5N:}$$

In our case, it was found that the thermal reaction rate of **1** is independent of the concentration of pyridine. For example, the mole ratio of the azide **1** : pyridine was varied from 1:1, to 1:10 and 1:50 and the reaction rate is nearly unchanged (see **Table 1**). Also, it was well known that copper atoms or copper ions could catalyze the nitrene formation.[14,15] In the thermal reactions of **1** with pyridine, the decomposition temperature is around 120°C, however in the presence of a catalytic amount of CuCl or $Cu(OAc)_2$ the N_2 was evolved at 80°C. To sum up we concluded that in the thermal reaction of **1** with pyridine and its derivatives, the R_fSO_2N intermediate should be involved.



Scheme 2

It was surprising that thermal decomposition of azides 1 in 2- or 4- picoline which was considered a better electron donor than pyridine gave fluoroalkansulfonamide 4 as the sole product. This reaction showed the large difference between the fluoroalkanesulfonyl azide and the arenesulfonyl azide. Abromovitch has reported that benzenesulfonyl azides reacted with 2- or 4- picoline to give three products *i.e.* *N*-sulfonyliminopyridinium imide, phenyl sulfonamide and the insertion product $PhSO_2NHAr$ (Ar: 2- or 4-picoline). In the reaction of azides 1 with 2- or 4-picoline, the picoline acted as a hydrogen-donor and not as an electron-donor and afforded only the sulfonamide.[6]



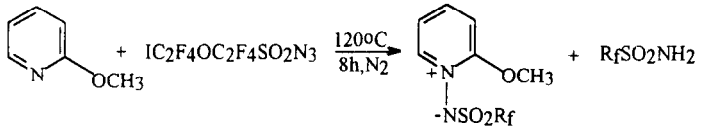
1 5 4

R_1,R_2=CH_3,H(a); H,CH_3(b).

Scheme 3

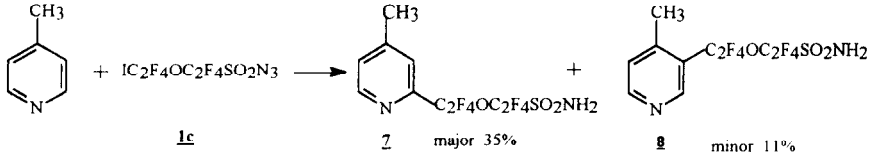
In our previous work on the bis(fluoroalkanesulfonyl)carbene $(R_fSO_2)_2C$:, formed by thermolysis or photolysis of $(R_fSO_2)_2C^-$-I^+Ph, it was found that this very electron deficient carbene is easily combined with many electron-donors such as R_2S, C_6H_5N, C_6H_5I.[16] The chemical behavior of R_fSO_2N is similar to that of $(R_fSO_2)_2C$:. Due to the powerful electron-withdrawing effect of the R_fSO_2 group, R_fSO_2N is more electrophilic than its hydrocarbon analogues RSO_2N or $ArSO_2N$ and is readily captured by an electron donor rather than carrying out the insertion reaction. That is why the reaction of 1 with pyridine or 3-picoline or 3,5-lutidine gave only imide and sulfonamide and no insertion product R_fSO_2NHAr.

Because the methyl of the 2- or 4-picoline was activated by the nitrogen atom, the activity of C-H in 2-picoline's methyl is stronger than the benzyl C-H.[17] As expected, when azides 1 were decomposed in 2-methoxy pyridine, which has an oxygen atom in the methyl group and the hydrogen of the methyl is not as reactive as that of 2-picoline, the corresponding imide 6 was obtained in addition to the fluoroalkane sulfonamide **4c**.



1c 6 4c

It was interesting to find that thermolysis of azide $IC_2F_4OC_2F_4SO_2N_3$ 1c in 4-picoline afforded two deiodinated products 7 , 8 and fluoroalkansulfonamide 4c, in 35%, 11% and 30% yields respectively. Compounds 7 and 8 could be conveniently separated by column chromatography and they have different melting points. The structures of compounds 7 and 8 are fully characterized from their IR, NMR and MS spectra and microanalysis and compound 7 was further confirmed by X-ray crystal diffraction analysis. Its molecular structure is shown in **Fig. 2**.



1c 7 major 35% 8 minor 11%

Scheme 4

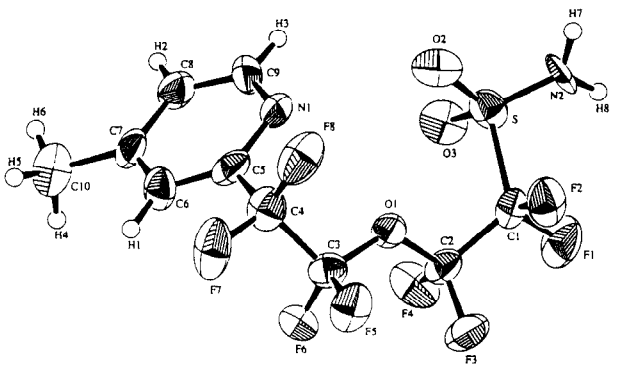
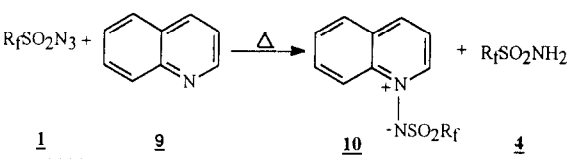


Fig.2 The molecular structure of compound 7.

In general, the nucleophilicity of 4-picoline was not strong enough to substitute the iodine of perfluoroalkyl iodides. Under the same reaction conditions per- or polyfluoroalkyl iodides such as C_4F_9I, $IC_2F_4C_2F_4Cl$ and fluoroalkansulfonamide $IC_2F_4OC_2F_4SO_2NH_2$ were also tried to react with 4-picoline, but no reaction occurred at all. The SET reaction mechanism was also ruled out by ESR techniques. This reaction process was followed by ESR analysis, however, no corresponding radical could be detected. It is apparent that deiodination is related with the presence of the azido-group. We also examined the reaction of azide $I(C_2F_4)_3OC_2F_4SO_2N_3$ with 4-picoline, but the only product is sulfonamide $I(C_2F_4)_3OC_2F_4SO_2NH_2$. According to all these reaction results, it could be concluded that the deiodination process in reaction of azide **1c** with 4-picoline is not only related to the azide group $-N_3$ but also with the length of fluoro-carbon chain.

Corresponding thermal reactions of **1** with quinoline, which has many common properties with pyridine, have also been studied. Under the similar reaction conditions, quinolinium *N*-fluoroalkanesulfonylimides **9** and fluoroalkansulfonamides **4** were obtained, however the yields of the product **10** are lower than the reaction of **1** with pyridine. The reason should be attributed to the lower nucleophilicity of quinoline.

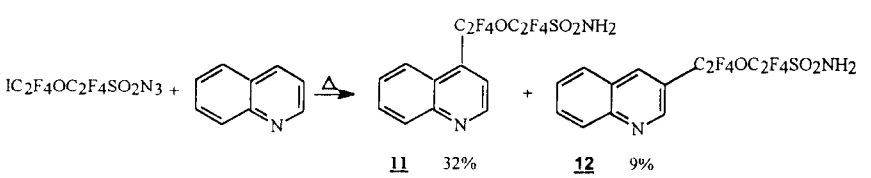


1 **9** **10** **4**

R_f: C_6F_{13} (b); $HC_2F_4OC_2F_4$ (e); $Cl(C_2F_4)_4OC_2F_4$ (f).

Scheme 5

Similar to 4-picoline, reaction of quinoline with azide $IC_2F_4OC_2F_4SO_2N_3$ **1c** did not afford the quinolinium imide, but gave two deiodinated products, ω-quinoline substituted polyfluoroalkane sulfonamides **11**, **12** and sulfonamide **4c**, in 32%, 9% and 23% yields respectively .



11 32% **12** 9%

Scheme 6

Table 2 Reactions of fluoroalkanesulfonyl azides with 2, 4- picoline and quinoline

Entry	Reactants	Azides	Temp (°C)	Time (h)	Product and yield (%)
1	**5a**	**1b**	120	6	**4b** (90)
2	**5a**	**1c**	120	8	**4c** (60)
3	**5a**	**1e**	120	6	**4e** (70)
4	**5b**	**1c**	100	6	**4c** (64)
5	**5b**	**1e**	90	2	**4e** (72)
6	**5b**	**1f**	120	4	**4f** (74)
7	**9**	**1b**	120	6	**10b** (31); **4b** (44)
8	**9**	**1e**	120	6	**10e** (25); **4e** (42)
9	**9**	**1f**	120	6	**10f** (25); **4f** (47)
10	**9**	**1c**	120	8	**11** (32), **12** (9); **4c** (23)

In conclusion, the thermolysis reaction of fluoroalkanesulfonyl azides in pyridines and quinoline afford a new kind of fluorine-containing imides such as pyridinium *N*-fluoroalkanesulfonylimide and quinolinium imide via the fluoroalkanesulfonyl nitrene intermediate. It is notable that the chemical behavior of fluoroalkanesulfonyl azides is different to arenesulfonyl azides. Also in all thermolysis reaction of **1** in pyridine or its derivatives, no insertion products R_fSO_2NHAr are formed. This difference should be attributed to the electron-withdrawing abilities of per- or polyfluoroalkane sulfonyl group.

EXPERMENTIAL

M.p.s were measured in a melting point apparatus and are uncorrected. Solvents and reagents were purified before use. ^{1}H-NMR and ^{19}F-NMR spectra were recorded on a Varian-360L or Bruker AM-300 spectometer instrument with Me_4Si and $CFCl_3$ (with upfield negative) as an internal and external standard, respectively. Elemental analyses were performed by this Institute. IR spectra were obtained with an Perkin Elmer 983G spectrophotometer and using KBr disks of the compounds. X-ray structure analysis was performed with Rigaku /AFC 7R Diffractometer. All the pyridines and quinoline were dried over calcium hydride and distilled. All reactions were carried out under a positive atmosphere of dry N_2, unless otherwise indicated.

General procedure for the reactions of azides with pyridines.

A stirred solution of fluoroalkanesulfonyl azides **1c** (0.532g, 1.185mmol) in freshly distilled pyridine 9.5ml was heated in an oil bath at 120°C until no more nitrogen evolved (about 8h) and TLC indicated that the azides had disappeared completely. The excess pyridine was distilled under vacuum and the residue was chromatographed on a silica gel column. Elution with light petroleum ether (b.p. 60-90°C)-ethyl acetate (3:1) gave fluoroalkanesulfonyl amide **4c** (0.110g, 0.261mmol, 22%), and elution with CH_2Cl_2 -CH_3OH (20:1) gave pyridinium *N*-fluoroalkanesulfonylimide **3ac** (0.273g, 0.535mmol, 46%). Compound **4** are known products and they are identical with the author's sample.[9]

Pyridinium trifluoromethanesulfonylimide 3aa colorless solid; m.p. 103-4°C ($CHCl_3$); ν_{max} (KBr)/cm^{-1} 3120m, 1619m, 1480 s, 1340vs, 1254 -1134vs, 967s, 800s. δ_H($CDCl_3$): 8.68 (2H, d, J 6), 8.22 (1H, t, J 8), 7.85 (2H, t, J 8). δ_F($CDCl_3$): -73.5 (CF_3, s). m/z 226 (M^+, 6.62), 157 (M^+-CF_3, 100), 158 (M^+H-CF_3, 9.41), 93 (M^+-SO_2CF_3, 25.79), 79 ($C_5H_5N^+$, 9.29). (Found: C, 31.60; H, 1.81; N, 12.72%. Calcd. For $C_6H_5F_3N_2O_2S$ C, 31.86; H, 2.21; N,12.39%.)

Pyridinium perfluorohexanesulfonylimide 3ab colorless solid; m.p. 127-8°C ($CHCl_3$); ν_{max}(KBr)/cm^{-1} 3120 (m), 1619 (m), 1476 (m), 1341 (s), 1239 -1151 (vs), 970 (m), 890 (m). δ_H($CDCl_3$): 8.65 (2H, d, J 7), 8.20 (1H, t, J 8), 7.83 (2H, t, J 8). δ_F($CDCl_3$): -79.9 (CF_3, s), -109.7 (CF_2, t, J 17), -119.1 (CF_2, s), -120.7 (CF_2, s), -121.3 (CF_2, s), -125.8 (CF_2, s). m/z 477 (M^++1, 10.20), 393 (M^+-C_5H_5N, 4.96), 158 (M^+H-C_6F_{13}, 12.88), 157 (M^+-

C_6F_{13}, 100.00), 93 (M^+-$SO_2C_6F_{13}$, 41.03), 69 (CF_3^+, 13.98). (Found: C, 27.35; H, 0.62; N, 5.78%. Calcd. for $C_{11}H_5F_{13}N_2O_2S$ C, 27.35; H, 0.62; N,5.78%.)

Pyridinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)-ethanesulfonylimide 3ac colorless solid; m.p. 99-100°C ($CHCl_3$); ν_{max} (KBr)/cm^{-1} 3121m, 1615w, 1476m, 1344s, 1295m, 1205 -1033vs, 938m, 919s, 882m. δ_H($CDCl_3$): 8.58 (2H, d, J 7), 8.18 (1H, t, J 8), 7.58 (2H, t, J 8). δ_F($CDCl_3$): -63.8 (CF_2, s), -80.8 (CF_2, t, J 17), -84.1 (CF_2, t, J 17), -113.0 (CF_2, s). m/z 501 (M^+H, 0.69), 227 (C_2F_4I, 3.47), 157 (M^+-R_f, 100.00), 93 (M^+-SO_2R_f, 34.83), 79 ($C_5H_5N^+$, 7.14). (Found: C, 21.73; H, 1.02; N, 5.51%. Calcd. for $C_9H_5F_8IN_2O_3S$ C, 21.60; H, 1.00; N, 5.60%.)

Pyridinium 1,1,2,2-tetrafluoro-2-(2-chloro-1,1,2,2-tetrafluoroethoxy)-ethanesulfonylimide 3ad colorless solid; m.p. 97-8°C ($CHCl_3$); ν_{max} (KBr)/cm^{-1} 3143m, 3120m, 1610m, 1470s, 1340vs, 1300m, 1220 -1100vs, 1000m, 960s, 790m. δ_H($CDCl_3$): 8.71 (2H, d, J 6), 8.19 (1H, t, J 7), 6.79 (2H, t, J 7). δ_F($CDCl_3$): -72.6 (CF_2, s), -80.9 (CF_2, t, J 17), -85.8 (CF_2, t, J 17), -113.8 (CF_2, s). m/z 410/408 (M^++2/M^+, 0.13/2.01), 372 (M^+-Cl, 0.85), 158 (M^+H-R_f, 8.22), 157 (M^+-R_f, 100.00), 100 ($C_2F_4^+$, 8.43), 93 (M^+-SO_2R_f, 32.43). (Found: C, 26.44; H, 1.09; N, 6.65%. Calcd. for $C_9H_5F_8ClN_2O_3S$ C, 26.44; H, 1.22; N, 6.85%.)

Pyridinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)-ethanesulfonylimide 3ae colorless solid; m.p. 99-100°C ($CHCl_3$); ν_{max} (KBr)/cm^{-1} 3120m, 3090w, 1615m, 1480s, 1470s, 1340-1310vs, 1310s, 1210 -1100vs, 960m, 940m, 800s. δ_H($CDCl_3$): 8.69 (2H, d, J 6), 8.15 (1H, t, J 8), 7.80 (2H, t, J 7), 5.86 (1H, t-t, J 53, 5). δ_F($CDCl_3$): -80.8 (CF_2, t, J 17), -88.0 (CF_2, t, J 17), -113.5 (CF_2, s), -136.8 (CF_2, d, J 53). m/z 374 (M^+, 3.25), 157 (M^+-R_f, 100.00), 101 ($C_2F_4H^+$, 5.63), 93 (M^+-SO_2R_f, 23.47), 79 ($C_5H_5N^+$, 5.15). (Found: C, 28.88; H, 1.60; N, 7.49%. Calcd. for $C_9H_6F_8N_2O_3S$ C, 28.98; H, 1.47; N, 7.33%.)

Crystal data of compound **3ae**

$C_9H_6O_3N_2F_8S$: MW=74.21, monoclinic; space group $P2_1/n$ (#14), a=13.143(3), b=7.244(3), c=15.045(2)Å, β=108.06(1)°, V=1361.9(6)Å^3, Z=4, Dc=1.825g/cm^3, F(000)=744.00. Radition, MoKα(λ=0.71069Å). Crystal dimension, 0.2x0.2x0.3mm.

Intensity data were collected at 20°C with a Rigaku AFC 7R diffractometer using graphite-monochromated Mo-Kα radition (λ=0.71069Å). A total of 2731 independent reflection were measured in range 18.41<2θ<21.63°, The structure was solved by directed methods and explained using Fourier techniques. The nonhydrogen atoms were refined anisotropically, hydrogen atoms were refined anisotropically. The finical cycle of fullmatrix least-square refinement was based on 1437 observed reflections (I>3.00 (I)) and 233 variable parameters. The final R and R_w value were 0.036 and 0.039 respectively. All calculations were performed using the texson crystallographic software package of molecular structure corporation.

3-Methylpyridinium perfluorohexanesulfonylimide 3bb colorless solid; m.p. 114-5°C (ether); ν_{max} (KBr)/cm^{-1} 3112m, 1616w, 1466m, 1365 s, 1243 -1025vs, 983w, 856w, 690m. δ_H($CDCl_3$): 8.49 (2H, m), 7.95 (1H, d, J 9), 7.75 (1H, t, J 9), 2.55 (3H, s). δ_F($CDCl_3$): -79.9 (CF_3, s), -109.7 (CF_2, t, J 17), -119.1 (CF_3, s), -120.7 (CF_2, s), -121.3 (CF_2, s), -125.8 (CF_2, s). m/z 491 (M^+H, 18.81), 172 (M^+H-C_6F_{13}, 11.76), 171 (M^+-C_6F_{13}, 100.00), 107 (M^+-$SO_2C_6F_{13}$, 29.36), 80 (M^+-$N_2SO_2C_6F_{13}$, 21.65), 69 (CF_3^+, 14.40). (Found: C, 28.99; H, 1.07; N, 5.56%. Calcd. for $C_{12}H_7F_{13}N_2O_2S$ C, 29.39; H, 1.43; N, 5.72%.)

3-Methylpyridinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)-ethanesulfonylimide 3bc colorless solid; m.p. 87-8°C (ether); ν_{max} (KBr)/cm^{-1} 3121m, 1615w, 1489w, 1344 vs, 1290s, 1196 -1029vs, 976s, 917s, 897m. δ_H($CDCl_3$): 8.49 (2H, m), 7.95 (1H, d, J 9), 7.75 (1H, t, J 9), 2.50 (3H, s). δ_F($CDCl_3$): -63.8 (CF_2, s), -80.8 (CF_2, t, J 17), -84.1 (CF_2, t, J 17), -113.0 (CF_2, s). m/z 515 (M^+H, 11.14), 172 (M^+H-R_f, 15.31), 171 (M^+-R_f, 100.00), 107 (M^+-SO_2R_f, 26.14). (Found: C, 23.42; H, 1.28; N, 5.33%. Calcd. for $C_{10}H_7F_8IN_2O_3S$ C, 23.35; H, 1.36; N, 5.45%.)

3-Metylpyridinium 1,1,2,2-tetrafluoro-2-(2-chloro-1,1,2,2-tetrafluoroethoxy)-ethanesulfonylimide 3bd colorless solid; m.p. 96-7°C (ether); ν_{max} (KBr)/cm^{-1} 3085w, 1610w, 1485m, 1458 w, 1340vs, 1300s, 1210 - 1100vs, 1020w, 967m, 958m, 859m, 800m. δ_H($CDCl_3$): 8.49 (2H, m), 7.95 (1H, d, J 9), 7.75 (1H, t, J 9), 2.55 (3H, s). δ_F($CDCl_3$): -72.6 (CF_2, s), -79.6 (CF_2, t, J 17), -86.0 (CF_2, t, J 17), -113.7 (CF_2, s). m/z 425/423 (M^++3/M^++1, 0.47/1.13), 422 (M^+, 0.22), 387 (M^+-Cl, 0.90), 172 (M^+H-R_f, 13.31), 171 (M^+-R_f, 100.00), 107 (M^+-SO_2R_f, 19.13). (Found: C, 28.27; H, 1.54; N, 6.24%. Calcd. for $C_{10}H_7F_8ClN_2O_3S$ C, 28.44; H, 1.66; N, 6.64%.)

3-Methylpyridinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)-ethanesulfonylimide 3be colorless solid; m.p. 81-2°C (ether); ν_{max} (KBr)/cm^{-1} 3095m, 1617w, 1491m, 1406 m, 1341vs, 1208 -1105vs, 989m, 881m. δ_H($CDCl_3$): 8.49 (2H, m), 7.95 (1H, d, J 9), 7.75 (1H, t, J 9), 5.86 (1H, t-t, J 53, 5), 2.55 (3H, s). δ_F($CDCl_3$): -80.8 (CF_2, t, J 17), -88.0 (CF_2, t, J 17), -113.2 (CF_2, s), -126.3 (CF_2, d, J 53). m/z 389 (M^++1, 5.51), 388 (M^+, 39.41), 172 (M^+H-R_f, 12.35), 171 (M^+-R_f, 100.00), 107 (M^+-SO_2R_f, 30.11). (Found: C, 31.06; H, 1.95; N, 7.18%. Calcd. for $C_{10}H_8F_8N_2O_3S$ C, 30.93; H, 2.06; N, 7.22%.)

3,5-Dimethylpyridinium perfluorohexanesulfonylimide 3cb colorless solid; m.p. 158-9°C (ether); ν_{max} (KBr)/cm^{-1} 3112m, 1600w, 1476m, 1348 s, 1245 -1127vs, 1051m, 989w, 980m. δ_H($CDCl_3$): 8.32 (2H, s), 7.64 (1H, s), 2.42 (6H, s). δ_F($CDCl_3$): -79.9 (CF_3, s), -109.7 (CF_2, t, J 17), -119.1 (CF_3, s), -120.7 (CF_2, s), -121.3 (CF_2, s), -125.8 (CF_2, s). m/z 505 (M^+H, 12.60), 186 (M^+H-C_6F_{13}, 13.52), 185 (M^+-C_6F_{13}, 100.00), 121 (M^+-$SO_2C_6F_{13}$, 37.98), 107 (M^+-$NSO_2C_6F_{13}$, 21.65), 69 (CF_3^+, 10.90). (Found: C, 31.02; H, 1.69; N, 5.44%. Calcd. for $C_{13}H_9F_{13}N_2O_2S$ C, 30.95; H, 1.79; N, 5.56%.)

3,5-Dimethylpyridinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)-ethanesulfonylimide 3cc colorless solid; m.p. 103-4°C (ether); ν_{max} (KBr)/cm^{-1} 3106m, 1596w, 1475w, 1392 w,1350s, 1334s, 1289 - 1058vs, 910m, 894m. δ_H($CDCl_3$): 8.30 (2H, s), 7.74 (1H, s), 2.45 (6H, s). δ_F($CDCl_3$): -63.8 (CF_2, s), -80.8 (CF_2, t, J 17), -84.1 (CF_2, t, J 17), -113 (CF_2, s). m/z 530 (M^+H, 4.89), 529 (M^+, 31.09), 186 (M^+H-R_f, 15.38), 185 (M^+-R_f, 100.00), 121 (M^+-SO_2R_f, 30.19). (Found: C, 24.72; H, 1.34; N, 5.02%. Calcd. for $C_{11}H_9F_8IN_2O_3S$ C, 24.95; H, 1.70; N, 5.29%.)

3,5-Dimethylpyridinium 1,1,2,2-tetrafluoro-2-(2-chloro-1,1,2,2-tetrafluoroethoxy)-ethanesulfonylimide 3cd colorless solid; m.p. 125-6°C (ether); ν_{max} (KBr)/cm^{-1} 3050w, 1596m, 1470m, 1338vs, 1210 -1095vs, 1055m, 864s. δ_H($CDCl_3$): 8.30 (2H, s), 7.75 (1H, s), 2.45 (6H, s). δ_F($CDCl_3$): -72.6 (CF_2, s), -79.6 (CF_2, t, J 17), -86.0 (CF_2, t, J 17), -113.7 (CF_2, s).m/z 439/437 (M^++3/M^++1, 3.67/9.94), 186 (M^+H-R_f, 11.87), 185 (M^+-R_f, 100.00), 135 (C_2F_4Cl, 4.23), 121 (M^+-SO_2R_f, 32.96), 107 (M^+-NSO_2R_f, 7.16). (Found: C, 29.95; H, 1.71; N, 6.34%. Calcd. for $C_{11}H_9F_8ClN_2O_3S$ C, 30.28; H, 2.06; N, 6.42%.)

3,5-Dimethylpyridinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)-ethanesulfonylimide 3ce colorless solid; m.p 78-9°C (ether); ν_{max} (KBr)/cm^{-1} 3040m, 1601w, 1481m, 1343 vs, 1345vs, 1285 -1012vs, 884m. δ_H($CDCl_3$): 8.25 (2H, s), 7.73 (1H, s), 5.83 (1H, t-t, J 53, 5), 2.45 (6H, s). δ_F($CDCl_3$): -80.5 (CF_2, t, J 17), -87.5 (CF_2, t, J 17), -113.3 (CF_2, s), -126.3 (CF_2, d, J 53). m/z 403 (M^+H, 23.13), 186 (M^+H-R_f, 16.50), 185 (M^+-R_f, 100.00), 121 (M^+-SO_2R_f, 40.07). (Found: C, 32.93; H, 2.45; N, 6.87%. Calcd. for $C_{11}H_{10}F_8N_2O_3S$ C, 32.84; H, 2.49; N, 6.97%.)

2-Methoxylpyridinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)-ethanesulfonylimide 6 colorless solid; m.p. 113-4°C; ν_{max} (KBr)/cm^{-1} 3096w, 2960w,1668vs, 1592s, 1534s, 1404s, 1296m, 1210-1100vs, 921s, 812m. δ_H($CDCl_3$): 7.40 (2H, m), 6.70 (1H, d, J 9.1), 6.23 (1H, m), 3.55 (3H, s). δ_F($CDCl_3$): -63.1 (CF_2, s), -80.5 (CF_2, t, J 17), -84.6 (CF_2, t, J 17), -114.6 (CF_2, s). m/z 531 (M^+H, 4.26), 530 (M^+, 0.73), 187 (M^+-R_f, 0.75), 124 (M^+H-SO_2R_f, 8.56), 123 (M^+-SO_2R_f, 100.00). (Found: C, 22.41; H, 1.02; N, 5.55%. Calcd. for $C_{10}H_7F_8IN_2O_3S$ C, 22.64; H, 1.32; N, 5.28%.)

1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-(4-methyl-2-pyridyl)ethoxy) ethanesulfonylamide 7 colorless solid; m.p. 120-2 °C ($CHCl_3$); ν_{max} (KBr)/cm^{-1} 3341vs, 3060w, 2934m, 1614 m, 1517m, 1370s, 1282 -1009vs, 939m, 860m. δ_H($CDCl_3$): 8.52 (1H, d, J 5.6), 7.57 (1H, s), 7.38 (2H, s) 7.23 (1H,d, J 5.6), 2.50 (3H, s). δ_F($CDCl_3$): -81.8 (CF_2O, t, J 17), -86.3 (OCF_2, t, J 17), -117.3 (CF_2S, s), -118.6 (CF_2, s). m/z 390 (M^++2, 10.22), 389 (M^+H, 66.63), 388 (M^+, 9.95), 309 (M^+H-SO_2NH_2, 64.94), 308 (M^+-SO_2NH_2, 7.02), 143 (M^+H-$CF_2OC_2F_4SO_2NH_2$, 36.81), 142 (M^+-$CF_2OC_2F_4SO_2NH_2$,, 100.00), 92 (M^+-$NH_2SO_2R_f$, 25.47). (Found: C, 31.47; H, 2.22; N, 7.25%. Calcd. for $C_{10}H_8F_8N_2O_3S$ C, 30.93; H, 2.06; N, 7.22%.)
crystal data of compound 7

$C_{10}H_8O_3N_2F_8S$: MW=388.23, monoclinic; space group $P2_1/c$ (#14), a=5.829(1), b=10.746(3), c=25.66(1)Å, β=93.01(3)°, V=1456.6(8)Å^3, Z=4, Dc=1.770g/cm^3, F(000)=776.00. Radition, MoKα(λ=0.71069Å). Crystal dimension, 0.2x0.2x0.3mm.

Intensity data were collected at 20°C with a Rigaku AFC 7R diffractometer using graphite-monochromated Mo-Kα radition (λ=0.71069Å). A total of 3552 independent reflection were measured in range 14.83<2θ<20.88°, The structure was solved by directed methods and explained using Fourier techniques. The nonhydrogen atoms were refined anisotropically, hydrogen atoms were included but not refined. The finical cycle of fullmatrix least-square refinement was based on 1451 observed reflections (I>3.006(I)) and 218 variable parameters. The final R and R_w value were 0.090 and 0.106 respectively. All calculations were performed using the texson crystallographic software package of molecular structure corporation.

1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-(4-methyl-3-pyridyl)ethoxy) ethanesulfonylamide 8 colorless solid; m.p 90-2°C ($CHCl_3$); ν_{max} (KBr)/cm^{-1} 3317vs, 3065w, 3000m, 1699m, 1607s, 1562m, 1378 -1280vs, 770s.δ_H(CD_3COCD_3): 8.42 (2H, m), 7.40 (1H, s), 3.72 (2H, s), 2.55 (3H,s). δ_F(CD_3COCD_3): -81.8 (CF_2O, t, J 17), -86.9 (OCF_2, t, J 17), -110.0 (CF_2S, s), -116.5 (CF_2, s). m/z 390 (M^++2, 20.99), 389 (M^+H, 41.87), 388 (M^+, 42.44), 309 (M^+H-SO_2NH_2, 28.82), 308 (M^+-SO_2NH_2, 18.67), 143 (M^+H-$CF_2OC_2F_4SO_2NH_2$, 25.24), 142 (M^+-$CF_2OC_2F_4SO_2NH_2$,, 100.00). (Found: C, 31.58; H, 1.67; N, 7.20%. Calcd. for $C_{10}H_8F_8N_2O_3S$ C, 30.93; H, 2.06; N, 7.22%.)

Quinolinium perfluorohexanesulfonylimide 10b colorless solid; m.p. 162-3°C (CH_3COCH_3); ν_{max} (KBr)/cm^{-1} 3070w, 3020w, 1691m, 1580m, 1519m, 1336vs, 1240 -1152vs, 958m, 834m. δ_H(CD_3COCD_3): 9.31 (1H,d, J 7), 9.05 (1H, d, J 9), 8.86 (1H, d, J 9), 8.41-7.87 (4H, m). δ_F(CD_3COCD_3): -81.8 (CF_3, s), -112.0 (CF_2, t, J 17), -120.9 (CF_2, s), -122.6 (CF_2, s), -123.4 (CF_2, s), -125.8 (CF_2, s). m/z 527 (M^+H, 0.85), 526 (M^+, 0.72), 208 (M^+H-C_6F_{13}, 17.98), 207 (M^+-C_6F_{13}, 100.00), 143 (M^+-$SO_2C_6F_{13}$, 62.63). (Found: C, 33.99; H, 0.94; N, 5.21%. Calcd. for $C_{15}H_7F_{13}N_2O_2S$ C, 34.22; H, 1.33; N, 5.32%.)

Quinolinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)-ethanesulfonylimide 10e colorless solid; m.p. 115-6°C (CH_3COCH_3); ν_{max} (KBr)/cm^{-1} 3100m, 3050w, 1615m, 1582m, 1512s, 1325s, 1316s, 1220 -1080vs, 920s, 840s. δ_H(CD_3COCD_3): 9.27 (1H, d, J 6), 9.02 (1H, d, J 8), 8.85 (1H, d, J 9), 8.42-7.82(4H, m), 6.52 (1H, t-t, J 53, 5). δ_F(CD_3COCD_3): -82.1 (CF_2, t, J 17), -89.4 (CF_2, t, J 17), -116.6 (CF_2, s), -139.7 (CF_2, t, J 53). m/z 425 (M^+H, 6.25), 424 (M^+, 0.94), 208 (M^+H-R_f, 15.45), 207 (M^+-R_f, 100.00), 143 (M^+-SO_2R_f, 51.95). (Found: C, 36.81; H, 1.55; N, 6.52%. Calcd. for $C_{13}H_8F_{13}N_2O_3S$ C, 36.79; H, 1.89; N, 6.60%.)

Quinolinium 2-(8-Chloro-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hexadecafluorooctoxy)- 1,1,2,2-tetrafluoroethanesulfonylimide 10f colorless solid; m.p. 159-160°C (ether); ν_{max} (KBr)/cm^{-1} 3050w, 2998w, 1632m, 1588m, 1330s, 1298s, 1240 -990vs, 985s, 938s, 822s. δ_H(DMSO-d_6): 9.31 (1H, d, J 6), 8.99 (1H, d, J 9), 8.70 (1H, d, J 9), 8.41-7.80 (4H, m). δ_F(DMSO-d_6): -80.5 (CF_2, s), -82.0 (CF_2, s), -115.0 (CF_2, s), -119.5 (C_6F_{12}, m), -124.6 (CF_2, s). m/z 761/759 (M^++3/M^++1, 0.77/1.72.), 209 (M^++2-R_f, 11.92), 208(M^+H-R_f, 23.22), 207 (M^+-R_f, 100.00), 143 (M^+-SO_2R_f, 24.25). (Found: C, 29.90; H, 0.58; N, 3.58%. Calcd. for $C_{19}H_7F_{20}ClN_2O_3S$ C, 30.06; H, 0.92; N, 3.69%.)

1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-(4-methyl-4-quinolinyl)ethoxy) ethanesulfonylamide, 11 colorless solid; m.p. 174-5°C ($CHCl_3$); ν_{max} (KBr)/cm^{-1} 3329vs, 3059m, 2499m, 1683 m, 1582m, 1423m, 1341s, 1285 -1046vs, 953s, 838m. $\delta_H(CD_3COCD_3)$: 8.40 (1H, d, J 5), 7.97 (1H, d, J 9), 7.72 (1H, d, J 9), 7.19 (2H, m), 6.97 (1H, m), 2.75 (2H, s). $\delta_F(CD_3COCD_3)$: -82.0 (CF_2, t, J 17), -84.8 (CF_2, t, J 17), -107.9 (CF_2, s), -118.4 (CF_2, s). m/z 425 (M^+H, 4.00), 424 (M^+, 16.65), 345 (M^+H-SO_2NH_2, 18.63), 179 (M^+H-$CF_2OC_2F_4SO_2NH_2$, 27.22), 178 (M^+-$CF_2OC_2F_4SO_2NH_2$, 100.00), 128 (M^+-$R_fSO_2NH_2$-1, 6.28). (Found: C, 36.81; H, 1.51; N, 6.52%. Calcd. for $C_{13}H_8F_8N_2O_3S$ C, 36.79; H, 1.89; N, 6.60%.)

1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-(4-methyl-3-quinolinyl)ethoxy) ethanesulfonylamide 12 colorless solid; m.p. 161-2 °C ($CHCl_3$); ν_{max} (KBr)/cm^{-1} 3318vs, 3060m, 1581m, 1513m, 1386s, 1288 -1060vs, 958m, 830s. $\delta_H(CD_3COCD_3)$: 8.42 (1H, d, J 3), 7.25-6.97 (2H, m), 8.04-7.51 (3H, m), 2.75 (2H, s). $\delta_F(CD_3COCD_3)$: -81.8 (CF_2, t, J 17), -86.1 (CF_2, t, J 17), -107.5 (CF_2, s), -117.6 (CF_2, s). m/z 426 (M^++2, 8.62), 425 (M^+H, 14.55), 424 (M^+, 8.78), 344 (M^+-SO_2NH_2, 2.98), 179 (M^+H-$CF_2OC_2F_4SO_2NH_2$, 21.88), 178 (M^+-$CF_2OC_2F_4SO_2NH_2$, 100.00). (Found: C, 36.52; H, 1.55; N, 6.49%. Calcd. for $C_{13}H_8F_8N_2O_3S$ C, 36.79; H, 1.89; N, 6.60%.)

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