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Unexpected formation of the novel fluorinated diazenes

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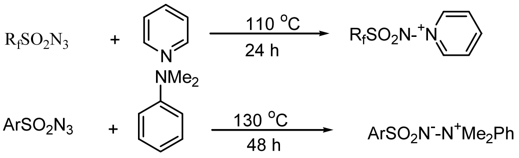
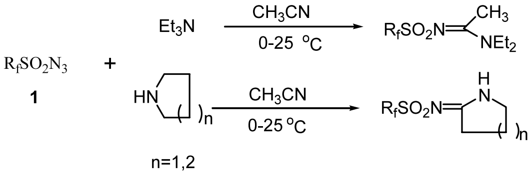
Abstract—Fluoroalkanesulfonyl azides reacted with morpholine giving unexpectedly *N*-fluoroalkanesulfonyl-*N*-morpholino diazenes, which were fully characterized by using spectral methods and X-ray diffraction analysis.

Nitrenes generated thermally or photochemically from arenesulfonyl azides and alkoxylcarbonyl azides have been found to add to the nitrogen atom of heteroaromatic bases to give the corresponding *N*-ylide compounds.[1] The mechanisms for the decomposition of the azides are well established,[2] which may explain how the products form from the reaction with pyridine[3] or *N*,*N*-dimethylaniline[4] (Scheme 1).

Recently, we have investigated the reactions of fluoroalkanesulfonyl azides **1** with tertiary or secondary amines, such as piperidine and pyrrolidine. In these reactions, *N*-fluoroalkanesulfonyl amidines were formed through a single electron transfer process and the nitrene intermediate was not involved[5] (Scheme 2).



Scheme 1.



Scheme 2.

However, to our surprise we observed that under the same conditions, the reaction of azides **1** with morpholine did not give the corresponding amidines. Instead, *N*-morpholino-*N*-fluoroalkanesulfonyl diazenes were produced.

A solution of the perfluoroalkanesulfonyl azide **1a** in dry acetonitrile was treated with an equal molar amount of freshly distilled morpholine at room temperature. After stirring for 5 h at 80°C, the starting reagents had disappeared (monitored by TLC). General work-up and purification gave two products. One was readily identified as $R_fSO_2NH_2$. The second product **3a** (obtained in 15% yield) was a white solid, which was identified by spectral data and single-crystal X-ray diffraction analysis.†

The molecular structure of **3a** is shown in Figure 1. The bond length between the morpholine nitrogen atom and diazene nitrogen (N_{23}–N_{22}) is lightly shorter than the diazene double bond (N_{22}–N_{21}) and both are shorter than normal N–N single bonds. The fluoroalkanesulfonyl group and the morpholino group are *trans* to each other in the molecular conformation, with the morpholino group adopting the stable chair conformation (see Fig. 1). Other fluoroalkanesulfonyl azides **1**(**b**–**e**) also reacted with the morpholine, giving the corresponding diazenes in similar yields (Scheme 3).

When tosylazide was used instead of **1** to react with the morpholine in CH_3CN, the product was *N*-morpholino tosylamide **4** (Scheme 4).

We noticed that Koga and Anselme[6] reported in 1970 a similar compound *N*-dibenzylamino-*N*-tosyl diazene Ts-N=N-N(CH_2Ph)$_2$ which was obtained as a by-product (13% yield) from the reaction of TsN_3 with

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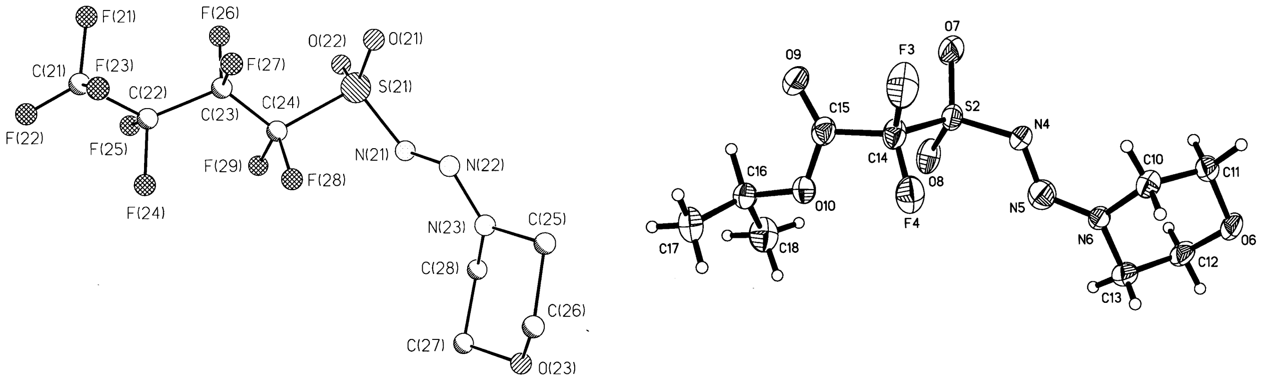
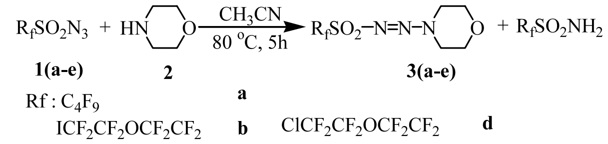


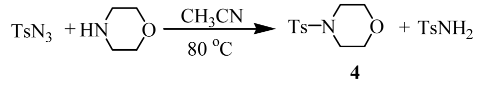
3a

3e

Figure 1. The ORTEP structure of **3a** and **3e**.



Scheme 3.

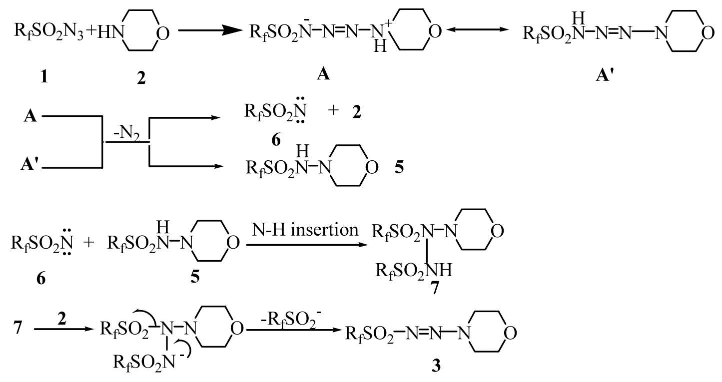


Scheme 4.

$(PhCH_2)_2NHNH_2$ in the presence of BuLi. However, to the best of our knowledge, the reaction of *N*-fluoroalkanesulfonyl azides with a secondary amine to give *N*-fluoroalkanesulfonyldiazene compound has never been reported before.

A possible mechanism for the formation of this product is tentatively proposed as shown in Scheme 5.

In summary, we reported the first examples in which the fluoroalkanesulfonyl azides reacted with morpholine through a zwitterionic tetraazene intermediate. The reaction product *N*-fluorosulfonylalkane-*N*-morpholino



Scheme 5.

[†] General procedure for the reaction of azide **1** with morpholine.

A mixture of **1a** (4 g, 10 mmol), **2** (1.3 g, 15 mmol) in acetonitrile was stirred at 80°C for 5 h, when TLC analysis showed completion of the reaction, solvent was removed and the residue was purified by column chromatography (pentane/EtOAc, 5:1) to give $R_fSO_2NH_2$ (1.3 g, 42%), and (pentane/EtOAc, 2:1) to give **3a** (0.6 g, 15%).

3a IR (KBr): $\nu=1628$ (vs), 1446 (m), 1336 (s) cm^{-1}; ^1H NMR (300 Hz, $CDCl_3$): δ_H 3.84–3.78 (m, 4H, 2×O-CH_2), 3.64–3.61 (m, 4H, 2×N-CH_2); ^{19}F NMR (300 Hz, $CDCl_3$): δ_F −79.8 (s, 2F), −113.0 (t, 2F, $^4J_{FF}=17.0$ Hz), −120.0 (s, 2F), −125.2 (t, 2F, $^4J_{FF}=17.0$ Hz); *m/z*: 397 (M^+, 35.86), 177 ($M^+H-C_4F_9$, 100.00), 86 ($C_4H_8NO^+$, 33.46); HRMS for $C_8H_8F_9O_3N_3S$: calcd 397.0143, found: 397.0124.

Crystal data for **3a** $C_8H_8N_3O_3F_9S$: CCDC: 219647, MW=397.22, 0.3×0.2×0.1 mm, monoclinic, space group $P2_1$, $D_{calcd}=1.772$ Mg/m^3, $a=10.542$ (1), $b=25.525$ (3), $c=11.069$ (1) Å, $\beta=91.51°$, $V=2977.6$ (6) Å^3, $Z=8$, asymmetry unit contains four molecules, $F(000)=1584.0$, λ(Cu-Ka)= 1.54178 Å, cell parameters determined from 25 reflections with $2\theta_{max}=55.0°$, intensity data were collected at 293 K with a Rigaku AFC-5R diffractometer, and employing $\omega/2\theta$ scanning technique, in the range of $0\leq h\leq 11$, $0\leq k\leq 28$, $-12\leq l\leq 12$. The structure was solved by a direct method. All non-hydrogen atoms were positioned and anisotropic thermal parameters refined from 2416 observed reflections with $F>4\sigma(F)$ by a block-matrix least-squares technique converged to $R=0.072$ and $R_w=0.066$ [$w=1/\sigma^2$ (F^2)].

Crystal data for **3e** $C_9H_{15}N_3O_5F_2S$: CCDC: 219646, MW=315.30, 0.2×0.2×0.1 mm, monoclinic, space group *P*2 (1), $D_{calcd}=1.497$ Mg/m^3, $a=9.4249$ (7), $b=15.0840$ (12), $c=10.0185$ (8) Å, $\beta=100.841$ (2)°, $V=1398.86$ (19) Å^3, $Z=4$, $F(000)=656.00$, radiation, Mo Ka ($\lambda=0.71073$ Å), $4.14\leq 2\theta\leq 56.58$, intensity data were collected at 293 K with a Bruker axs D8 diffractometer, and employing $\omega/2\theta$ scanning technique, in the range of $-12\leq h\leq 11$, $-19\leq k\leq 17$, $-11\leq l\leq 13$. The structure was solved by a direct method, all non-hydrogen atoms were positioned and anisotropic thermal parameters refined from 5375 observed reflections with R(int)=0.0404 by a full-matrix least-squares technique converged to $R=0.0463$ and $Rw=0.0862$.

diazene was formed by the insertion of fluoroalkanesulfonyl nitrene into *N*-morpholino fluoroalkanesulfonylamine, both were generated in situ, followed by elimination of a fluoroalkanesulfinic acid from the insertion product **7**.

The chemical property of the *N*-fluoroalkanesulfonyl-*N*-morpholino diazene compound is under investigation in our laboratory.

Acknowledgements

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