Interaction of NH-Azoles with *O*-Fluorosulfonyl-*N,N*-difluorohydroxylamine

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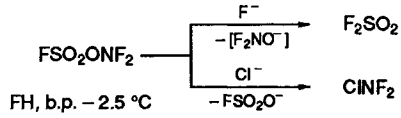
O-Fluorosulfonyl-*N,N*-difluorohydroxylamine interacts with NH-azoles in an alkaline medium, affording the corresponding *N*-fluorosulfonylazoles and in certain cases also the products of their further reactions, *N,N'*-sulfonylbisazoles.

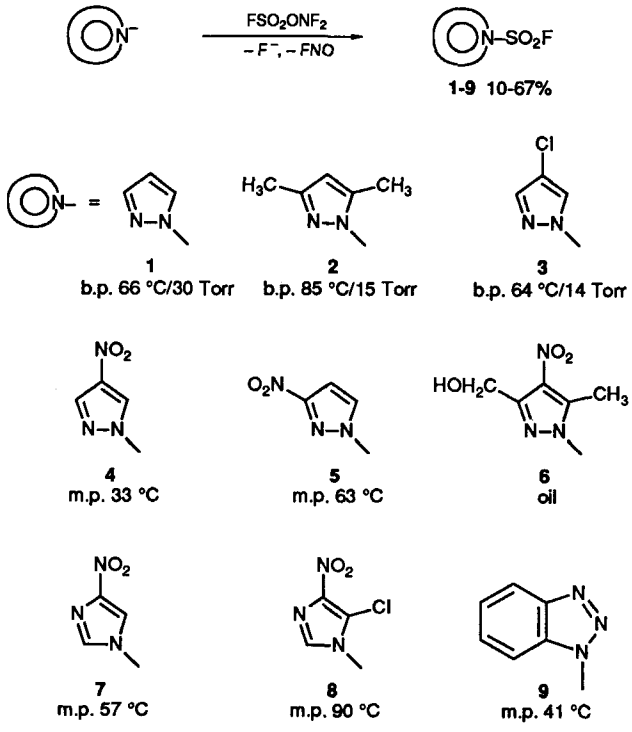
Judging from the available limited data,† *O*-fluorosulfonyl-*N,N*-difluorohydroxylamine (FH)[1] is a rare type of ambident electrophile: when acted upon by a nucleophile such as fluoride ion, it is substituted at the sulphur atom of the sulfonyl group, and when acted upon by the chloride ion, it is substituted at the nitrogen atom of the NF_2 group[2] (Scheme 1).



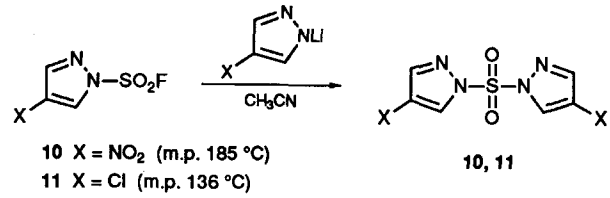
Scheme 1

On the other hand, the behaviour of FH in relation to organic anions has not been investigated. This communication describes a study of the interaction of FH with NH-azoles as possible nucleophiles in relation to FH. The NH-azoles employed were imidazoles and pyrazoles with electron-donating and electron-accepting substituents as well as certain triazoles.

It was found that NH-azoles do not react with FH. On the other hand, the anions of the azoles obtained by treating NH-azoles with base react rapidly with FH at temperatures ≤ 0°C, whereupon the azoles are *N*-fluorosulfonylated with formation of an hitherto unknown type of compound, *N*-fluorosulfonylazoles **1–9**. Their formation can be regarded as a result of the nucleophilic attack of the azolate anions on the sulphur atom of FH. The reaction can be carried out both under phase-transfer catalysis (PTC) in a liquid–liquid system and under homogeneous conditions.



The lithium salts of the azoles were used for the homogeneous version of the reaction. A solution of the lithium salt in CH_3CN was added at −20°C to twice the molar amount of FH dissolved in CH_3CN and the resulting mixture was maintained for 1 h at this temperature. When the reactants were mixed in the opposite order, the yield of *N*-fluorosulfonylazoles was lower and in addition, in the case of the 4-nitro- and 4-chloropyrazoles, *N,N'*-sulfonylbispyrazoles **10** and **11** are formed (in 5–7% yield), together with the corresponding *N*-fluorosulfonylpyrazoles, as a result of the reaction of the initial lithium salt with the *N*-fluorosulfonyl compound (Scheme 2).



Scheme 2

Using the reaction of an authentic *N*-fluorosulfonyl derivative with the lithium salt of the same azole in CH_3CN at 20°C, the symmetrical *N,N'*-sulfonylbispyrazoles **10** and **11** were obtained in preparative yields (50–70%).

When the process was carried out under phase-transfer catalysis, a solution of FH (3 mol) in dichloroethane was treated at −20°C with a solution of the NH-azole (1 mol), NaOH (3 mol) and 0.1 mol of the phase-transfer catalyst [poly(ethylene glycol), PEG-400] in a 1:1 (by volume) mixture of water and ethylene glycol and was then stirred vigorously for 1 h at −20°C.

It is essential to note that in the case of very strong NH-acids (3,4-dinitropyrazole and 3-nitro-1,2,4-triazole), the formation of the products of the interaction of the azoles with FH in both the homogeneous version and under phase-transfer catalysis is not observed, probably owing to the low nucleophilicity of the azolate anion.

The reaction of FH with 4-nitro-1,2,3-triazole takes place in an unusual manner. The hitherto undescribed formylnitrodiazomethane‡ **12** is formed in this case under phase-transfer catalysis. Compound **12** was most probably formed as a result of the opening of the *N*-fluorosulfonylazole ring and subsequent hydrolysis of the intermediate (Scheme 3). A similar ring opening in certain *N*-sulfonyl derivatives of 1,2,3-triazoles without a nitro-group in the ring was detected previously by an NMR method.[3,4]

All new compounds obtained in the present study were characterised by a set of spectroscopic methods (^1H, ^{19}F, ^{13}C, ^{14}N, ^{15}N and ^{17}O NMR spectroscopy, IR spectroscopy and

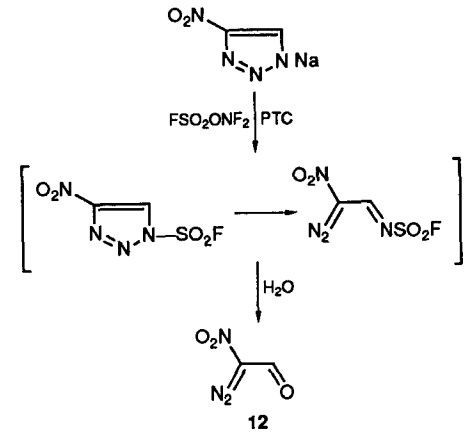
† Addition reactions of F_2NOSO_2F with tetrafluoroethene (M. Lustig and J. K. Ruff, *Inorg. Chem.*, 1965, **4**, 1441) and with hexafluorocyclobutadiene (M. Takashima and J. M. Shreeve, *Inorg. Chem.*, 1979, **18**, 3281) are known.

‡ Spectroscopic data for compound **12**: (IR, ν/cm^{-1}): 2168, 1672, 1516 and 1332; ^1H NMR ($CDCl_3$): δ_{TMS} 10.0 (s, 1 H, COH); ^{13}C NMR ($CDCl_3$): δ_{TMS} 109.1 (d, C=N=N, ^2J 35.6 Hz) and 175.6 (d, C=O, ^1J 203.7 Hz); ^{14}N NMR ($CDCl_3$): $\delta_{CH_3NO_2} = -15.4$ (NO_2), −135.0 (C=*N*=N) and +13.0 (C=N=*N*); mass spectrum: $m/z = 125$ (M^+), 97 ($M^+ - N_2$) and 79 ($M^+ - NO_2$).

mass spectrometry).§ Their structures were confirmed by elemental analysis. The IR spectra of all the *N*-fluorosulfonylazoles contain the characteristic absorption bands of the SO_2F group (1460–1480, 1230–1340 and 810–820 cm^{-1}), while the mass spectra revealed the presence of the molecular ion.

It must be emphasised that fluorosulfonylation takes place regiospecifically at the nitrogen atom remote from the most electron-accepting substituent, while in the case of benzotriazole at the 1-position (only one isomer is formed in all cases).

The position of the SO_2F group is indicated by the ^{15}N NMR spectra recorded in the INEPT regime with decoupling from protons. The signal for the substituted nitrogen atom has the form of a doublet under these conditions with $^2J_{N-F} = 5.8$–10 Hz. Combination of ^{13}C and ^{15}N NMR data makes it possible to determine unambiguously the position of the SO_2F group at a particular ring nitrogen atom.



Scheme 3

References

1 M. Lustig and G. H. Cady, *Inorg. Chem.*, 1963, **2**, 388.
2 J. K. Ruff, *Inorg. Chem.*, 1965, **4**, 1788.
3 M. Regitz and G. Himbert, *Tetrahedron Lett.*, 1970, 2823.
4 R. E. Harmon, F. Stanley, S. K. Gupta and J. Jonson, *J. Org. Chem.*, 1970, **35**, 3444.

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§ Certain spectroscopic data for compounds **1–11**.

1 ^1H NMR ($CDCl_3$): δ_{TMS} 7.96 (dd, 3-H, $^3J_{3,4}$ 1.7 Hz, $^4J_{3,5}$ 0.6 Hz), 6.62 (ddd, 4-H, $^3J_{4,5}$ 3.0 Hz, $^4J_{4,3}$ 1.7 Hz, $^5J_{4\text{-H,F}}$ 0.4 Hz) and 8.11 (dd, 5-H, $^3J_{5,4}$ 3.0 Hz, $^4J_{5,3}$ 0.6 Hz); ^{19}F NMR ($CDCl_3$): δ_{CFCl_3} 53.82 (s).

2 ^1H NMR ($CDCl_3$): δ_{TMS} 2.21 (d, 3H, 3-CH_3, $^6J_{CH_3,F}$ 0.6 Hz), 2.43 (d, 3H, 5-CH_3, $^4J_{CH_3,4\text{-H}}$ 1.0 Hz) and 6.08 (q, 1H, 4-H, $^4J_{H,5\text{-}CH_3}$ 1.0 Hz); ^{19}F NMR ($CDCl_3$): δ_{CFCl_3} 54.94 (s).

3 ^1H NMR ($CDCl_3$): δ_{TMS} 7.87 (d, 3-H, $^4J_{3,5}$ 0.6 Hz) and 8.08 (d, 5-H, $^4J_{5,3}$ 0.6 Hz); ^{19}F NMR ($CDCl_3$): δ_{CFCl_3} 54.13 (s).

4 ^1H NMR ($CDCl_3$): δ_{TMS} 8.47 (d, 3-H, $^4J_{3,5}$ 0.5 Hz) and 8.94 (d, 5-H, $^4J_{5,3}$ 0.5 Hz); ^{19}F NMR ($CDCl_3$): δ_{CFCl_3} 55.12 (s).

5 ^1H NMR ($CDCl_3$): δ_{TMS} 7.19 (dd, 4-H, $^3J_{4,5}$ 3.0 Hz, $^5J_{4H,F}$ 0.7 Hz) and 8.25 (dd, 5-H, $^3J_{5,4}$ 3.0 Hz, $^4J_{5\text{-H,F}}$ 0.4 Hz); ^{19}F NMR ($CDCl_3$): δ_{CFCl_3} 55.55 (s).

6 ^1H NMR ($CDCl_3$): δ_{TMS} 2.99 (s, 3H, CH_3) and 4.97 (s, 2H, CH_2OH); ^{19}F NMR ($CDCl_3$): δ_{CFCl_3} 58.10 (s).

7 ^1H NMR ($CDCl_3$): δ_{TMS} 8.12 (dd, 2-H, $^4J_{2,5}$ 1.7 Hz, $^4J_{2\text{-H,F}}$ 0.5 Hz) and 8.27 (d, 5-H, $^4J_{5,2}$ 1.7 Hz); ^{19}F NMR ($CDCl_3$): δ_{CFCl_3} 61.26 (s).

8 ^1H NMR ($CDCl_3$): δ_{TMS} 8.11 (d, 2-H, $^4J_{2\text{-H,F}}$ 0.7 Hz); ^{19}F NMR ($CDCl_3$): δ_{CFCl_3} 59.00 (s).

9 ^1H NMR ($CDCl_3$): δ_{TMS} 8.26 (m, 4-H), 7.77 (m, 5-H), 7.95 (m, 6-H) and 7.97 (m, 7-H); ^{19}F NMR ($CDCl_3$): δ_{CFCl_3} 58.10 (s).

10 ^1H NMR [$(CD_3)_2CO$]: δ_{TMS} 8.59 (d, 3-H, $^4J_{3,5}$ 0.6 Hz) and 9.59 (d, 5-H, $^4J_{5,3}$ 0.6 Hz).

11 ^1H NMR ($CDCl_3$): δ_{TMS} 7.71 (d, 3-H, $^4J_{3,5}$ 0.6 Hz) and 8.16 (d, 5-H, $^4J_{5,3}$ 0.6 Hz).