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PRELIMINARY NOTE

The Reactions of NN-Bistrifluoromethylaminotrifluoromethanesulphonate with Nucleophiles

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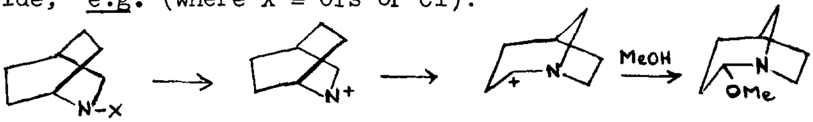
Nitrenium ions have been postulated as intermediates in the rearrangements resulting from treatment of N-chloroamines with silver compounds and of hydroxylamines with tosyl chloride,[1] e.g. (where X = OTs or Cl):



The intermediacy of such species in the former reaction has recently been questioned.[2] Attempts to prepare nitrenium ions from amide sulphonates by pyrolysis or photolysis failed because the compounds underwent radical reactions;[3] nucleophiles attacked the amide sulphonates at sulphur or carbon and not at nitrogen.[4]

In the present work NN-bistrifluoromethylaminotrifluoromethanesulphonate (I), a liquid b.p. 66° , was prepared (82%) as follows:

$$\underset{\text{(IIa)}}{(CF_3)_2N.ONa} + CF_3.SO_2F \xrightarrow{CFCl_3} \underset{\text{(I)}}{(CF_3)_2N.O.SO_2.CF_3} + NaF$$

The ester (I) did not react with toluene, stilbene, ethanol, phenol, pyridine, or diazabicyclo-octane at ca. 70°

establishing that heterolytic or homolytic cleavage, or the alternative pathway of electrophilic delivery of fluorine [i.e. $B: + (I) \longrightarrow \overset{+}{B}F + CF_3.N{:}CF_2 + CF_3.SO_3^-$], are not facile reactions. The reactions of (I) with various nucleophiles were then investigated to determine if nucleophilic attack occurred at nitrogen.

Sodium phenolate, sodium thiophenolate, or ammonia reacted with (I) to give the corresponding trifluoromethanesulphonyl derivatives (III, Nu = PhO, PhS, or NH_2; 50-100%) and the hydroxylamine (IV) [isolated as a complex with the solvent (MeOH or THF) or excess of the nucleophile[5]] via nucleophilic attack at sulphur.

$$(I) + Nu: \longrightarrow \underset{(III)}{CF_3.SO_2Nu} + (CF_3)_2N.O^- \longrightarrow \underset{(IV)}{(CF_3)_2N.OH}$$

The following equilibrium is established on treatment of (I) with caesium fluoride in the absence of solvent or in a solvent such as toluene.

$$(I) + CsF \rightleftharpoons \underset{(IIb)}{(CF_3)_2N.OCs} + CF_3.SO_2F$$

However, in an ethereal solvent (Et_2O, glyme, or diglyme), in which the salt (IIb) is soluble, the products are trifluoromethanesulphonyl fluoride (50%), caesium trifluoromethanesulphonate, and an ethereal solution of perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) (V); the last two compounds are best explained by nucleophilic attack on (I) by the salt (IIb) at nitrogen.

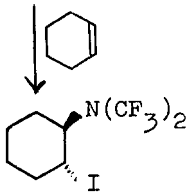
$$(I) + (IIb) \xrightarrow[\text{solvent}]{\text{ethereal}} \underset{(V)}{(CF_3)_2N.O.N(CF_3)_2} + CF_3.SO_3Cs$$

A comparable but slower reaction occurs when (I) is treated with the sodium salt (IIa) in diglyme, i.e.

$$\text{(I)} + \text{(IIa)} \longrightarrow \text{(V)} + CF_3.SO_3Na$$

Treatment of (I) with lithium iodide in the absence of solvent affords perfluoro-2-azapropene (100%), iodine (100%), lithium trifluoromethanesulphonate, and lithium fluoride presumably via N-iodobistrifluoromethylamine (VI)[6], since reaction in the presence of cyclohexene gave the adduct (VII), albeit in low yield (15%).

$$\text{(I)} + LiI \longrightarrow CF_3.SO_3Li + \underset{\text{(VI)}}{(CF_3)_2NI} \xrightarrow{LiI} LiF + I_2 + CF_3.N{:}CF_2$$



(VII)

The reactions of (I) with amines are more complex. Thus treatment with diethylamine (1:2 molar ratio) gives the diethylammonium salt (VIII) (30%) together with an unstable volatile mixture from which the sulphonamide (IX) (25%) was isolated with difficulty. The ^{19}F n.m.r. spectrum of the volatile material shows that it contains a mixture of (IX), (IV), and the hydrazine (X) in the ratio 7:7:3; the last compound is presumably the unstable component. The products can be explained by two competing processes involving major nucleophilic attack at sulphur and minor attack at nitrogen, i.e.

$$\text{(I)} + Et_2NH \xrightarrow[\text{at S}]{\text{70\% attack}} \text{(IV)} + \underset{\text{(IX)}}{CF_3.SO_2.NEt_2}$$

$$\text{(I)} + Et_2NH \xrightarrow[\text{at N}]{\text{30\% attack}} \underset{\text{(VIII)}}{Et_2\overset{+}{N}H_2\ CF_3.SO_3^-} + \underset{\text{(X)}}{(CF_3)_2N.NEt_2}$$

The reaction of (I) with aniline (solvent PhMe or CH_2Cl_2) or trimethylamine (neat or solvent PhMe or Et_2O) (various molar ratios) affords trifluoromethanesulphonyl fluoride in a yield (83-100%) higher than would be obtained had amine attack occurred on nitrogen in (I) followed by decomposition of, for example, $(CF_3)_2N.NHPh$ to fluoride, the source of CF_3SO_2F by attack on (I). Direct displacement of fluoride from carbon by amine attack on (I) thus seems probable; concurrent amine attack on sulphur in (I) would have given the sulphonamide and bistrifluoromethylhydroxylamine known to be stable to the amines used, but not detected.

The above reactions indicate that the ester (I) is susceptible to nucleophilic attack at three sites, i.e. C in $(CF_3)_2N$, N, and S. The softer nucleophiles tend to attack nitrogen[7] (cf. the related reactions of the fluorosulphonate $FSO_2.O.NF_2$ with F^- to give SO_2F_2 and with Cl^- to give NF_2Cl[8]).

1 P.G. Gassman, Acc. Chem. Res., 3 (1970) 26.

2 O.E. Edwards, G. Bernath, J. Dixon, J.M. Paton, and D. Vocelle, Can. J. Chem., 52 (1974) 2132.

3 J.I.G. Cadogan and A.G. Rowley, J.C.S. Perkin I, (1975) 1069.

4 T.M. Chapman and E.A. Freedman, J. Org. Chem., 38 (1973) 3908.

5 G. Flaskerud and J.M. Shreeve, Inorg., Chem., 8 (1969) 2065.

6 E.S. Alexander, R.N. Haszeldine, M.J. Newlands, and A.E. Tipping, J. Chem. Soc. (C), (1968) 796.

7 J.O. Edwards and R.G. Pearson, J. Amer. Chem. Soc., 84 (1962) 16.

8 J.K. Ruff, Inorg. Chem., 4 (1965) 1788.