Preparation and Pyrolysis of Phenyldiazonium Bis(trifluoromethylsulfonyl)amide

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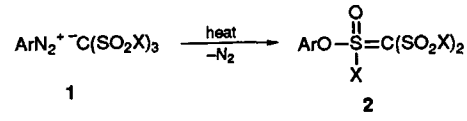
The stable phenyldiazonium bis(trifluoromethylsulfonyl)amide has been made by reacting $PhN_2^+Cl^-$ with $HN(SO_2CF_3)_2$ in water, which on heating led to *N*-(trifluoromethylsulfonyl)phenoxytrifluoromethylsulfoximine (62%) and $PhN(SO_2CF_3)_2$ (5%) as the products of O- and N-attack by the phenyl cation.

In previous publications we reported some unusual examples of the formation of the fluoro-containing oxosulfonium ylides **2** by the pyrolysis of arenediazonium salts **1**, stabilized by fluorinated tris(sulfonyl)methanide anions (Scheme 1).[1–4]



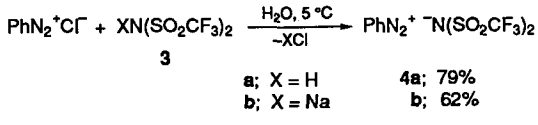
1 **2**

a; X = F
b; X = CF_3
c; X = F, OPh

Scheme 1

The reaction occurs because the phenyl cation, produced by the decomposition of the arenediazonium salt, attacks one of the oxygen atoms of the sulfonyl groups and not the central C-atom of the methanide anion. Ylides **2** can be considered as the phenyl esters of the corresponding alkanesulfonyl fluoride or trifluoromethylalkylsulfone aci-forms. Arenediazo compounds **1** are remarkably stable owing to the planar, large anion (the conjugated base of the superstrong CH-acid).

We now report the synthesis and the results of thermal decomposition of phenyldiazonium bis(trifluoromethylsulfonyl)amide **4**, the salt of the strong NH-acid $HN(SO_2CF_3)_2$ **3a**.



3

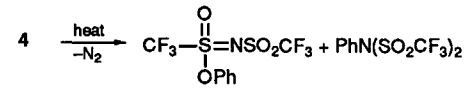
a; X = H **4a**; 79%
b; X = Na **b**; 62%

Scheme 2

The expected salt **4** is readily prepared in high yield by simple addition to an aqueous solution of benzenediazonium chloride of an equimolar quantity of aqueous bis(trifluoromethylsulfonyl)amine **3a**[5] or the corresponding sodium salt **3b** (Scheme 2).[5] Compound **4** is precipitated immediately as a white solid upon mixing the reagents. It can be stored in a refrigerator for a long time without decomposition. The structure of **4** has been confirmed by satisfactory C, H, N-analyses and IR and NMR spectroscopic data: IR (KBr) ν_{max}/cm^{-1} 2280 (N_2^+); F^{19} NMR (80 MHz, $CDCl_3$) δ −79.5(s).

To our knowledge, salt **4** is the first example of a stable arenediazonium compound containing an N-anion. This may be due to the steric overcrowding of the central N-atom of the anion and to the powerful electron-withdrawing properties of the two $—SO_2CF_3$ groups, both of which lead to high stability of the anion.

Salt **4** is stable up to 77–79 °C, when it rapidly decomposes with N_2 evolution. From investigations of the reaction mixture it can be concluded that two compounds are formed, in contrast with the results obtained from thermal decomposition of $PhN_2^+ \ ^-C(SO_2CF_3)_3$.[3] The products were separated by



5 (62%) **6** (5%)

Scheme 3

medium pressure column chromatography (toluene) and the main product is *N*-(trifluoromethylsulfonyl)phenoxytrifluoromethylsulfoximine **5** (62%) with *N*,*N*-bis(trifluoromethylsulfonyl)aniline **6** (5%) as the minor product (Scheme 3).

Sulfimine **5** is a colourless, oily liquid and was identified by mass and ^{19}F NMR spectroscopy and elemental analyses. The ^{19}F NMR spectrum (80 MHz) of compound **5** in $CDCl_3$ shows two peaks of equal intensity at δ −73.4 [$PhO(O)S(CF_3)$=] and −78.3 (=NSO_2CF_3). In the mass spectrum a peak at 357 (M^+) was observed.

According to the principle developed by Professor L. M. Yagupolskii,[6] the acceptor strength of a whole substituent can be greatly increased by the replacement of an oxygen atom bonded to the central atom by a strongly electron-withdrawing group, such as =NSO_2CF_3. Thus, sulfimine **5** can be considered as a phenyl ester of the superstrong acid trifluoromethanesulfonic acid in which one oxygen atom is replaced by a =NSO_2CF_3 group.

The aniline derivative **6** was identified by comparison with an authentic product (Fluka).† During our studies on the decomposition of arenediazonium salts, the formation of **6** is the first observed attack of the phenyl cation on the central atom of the anion.

Support of this research by the Deutsche Forschungsgemeinschaft is gratefully acknowledged by one of the authors (Y.L.Y.).

Received: Cambridge, 27th November 1991; Com. 1/06020A
Moscow, 7th January 1992

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† Compound **6**: m.p. 104 °C, ^{19}F NMR (80 MHz, $CDCl_3$) δ −71.07.