Tetrahedron Letters No. 21 pp 1739-1740, 1975. Pergamon Press. Printed in Great Britain.

NOVEL GENERATION OF BENZONITRILE-N-SULFIDE

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(Received in USA 4 November 1974; received in UK for publication 12 April 1975)

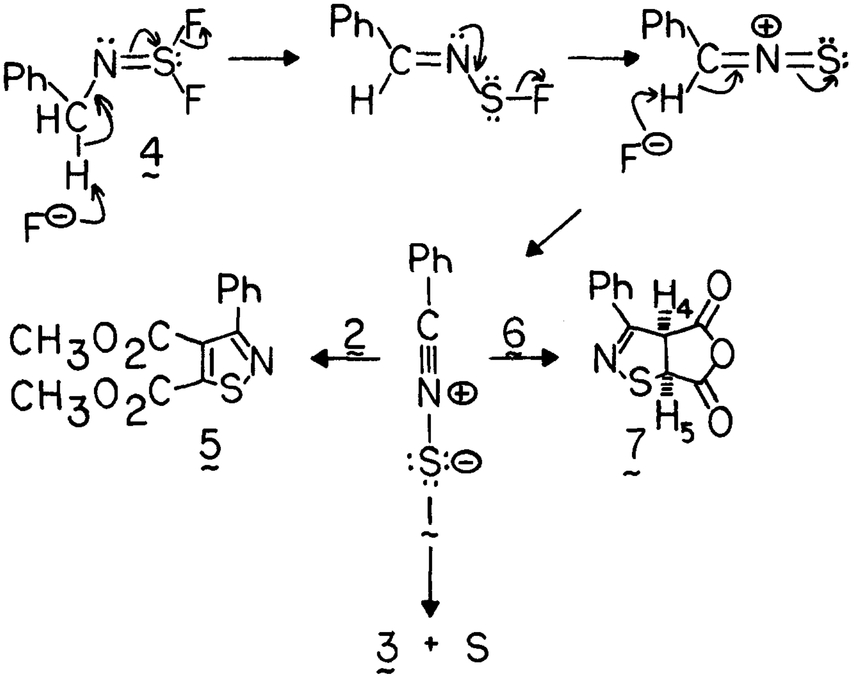
The generation of benzonitrile-N-sulfide **1** is significant because not only is **1** a useful synthetic intermediate but also it is the first example of a molecule containing a coordinate covalent bond between elements of the fifth and sixth groups in which the element bearing formal negative charge is <u>less</u> electronegative than the element bearing formal positive charge. Recently Franz, Black, and Howe reported the formation of **1** from the thermolysis of 5-phenyl-1,3,4-oxathiazol-2-one.[1,2] Gotthardt and later Holm *et al*. observed **1** as a transient in the photolysis of 4-phenyl-1,3,2-oxathiazolylio-5-oxide.[3,4,5] Each group found **1** to cycloadd to dimethylacetylene dicarboxylate **2** and to decompose to benzonitrile **3** and sulfur.

We wish to report the novel generation of **1** by the rare 1,3-elimination of two moles of hydrogen fluoride from N-benzyliminosulfurdifluoride **4** which was prepared in 50-60% yield by reacting benzylamine with sulfur tetrafluoride in trimethylamine and sodium fluoride at -45° for 8-12 hrs. The nmr of **4** is: $\delta_{TMS}^{CCl_4}$ 7.07 (5H, s) and 4.33 (2H, t, $J_{H,F}$ = 10Hz). Introduction of **4** into the inlet system of a mass spectrometer at 250° gives rise to peaks deriving from the thermal decomposition of **4** as well as those due to fragmentation of the radical cation of **4**. The thermolysis of **4** in a sealed tube for 5.5 hrs at 130° gave sulfur, **3**, and 2,4,6-triphenyl-1,3,5-triazine which probably arises from the acid-catalyzed trimerization of **3**.

In order to obtain evidence for the intermediacy of **1**, a chlorobenzene solution of **4** and **2** was heated for 12 hrs at 132° with two equivalents of sodium fluoride powder on the bottom of the flask to sponge the hydrogen fluoride formed from the solution. The reaction gave an isolated yield of 22% dimethyl-3-phenylisothiazole-4,5-dicarboxylate **5**[7] which is the 1,3-dipolar adduct of **1** and **2**. The yield of **5** can be improved to 42% by refluxing for 24 hrs in chlorobenzene (132°), or for 12 hrs in bromobenzene (156°), or by refluxing for 12 hrs in chlorobenzene with four equivalents of sodium fluoride.

The iminosulfurdifluoride **4** and **2** were reacted in chlorobenzene for 12 hrs at 132° in the presence of 2 equivalents of sodium fluoride and 0.1 equivalents of 18-crown-6 ether to give a 65% yield of **5**. Crown ether partially solubilizes sodium fluoride allowing fluoride ion to catalyze the elimination of hydrogen fluoride from **4**.[6]

A previous attempt to isolate an adduct from **1** and an olefin was unsuccessful.[1] We now report that refluxing **4** and maleic anhydride **6** for 12 hrs in benzene with 2 equivalents of sodium fluoride gave 20% of <u>cis</u>-3-phenyl-4,5-isothiazoline-4,5-dicarboxylic acid anhydride **7** m.p. 163-164°; ir (KBr) 1780 and 1820 cm^{-1}; nmr $\delta_{TMS}^{(CD_3)_2CO}$ 5.58 (1H, d, J = 11 Hz), 5.98 (1H, d, J = 11 Hz), 7.48 (3H, m), and 7.98 (2H, m); ms, m/e 233, 231, 162, 135, 103, and 77. *Anal.* Calcd for $C_{11}H_7NO_3S$: C, 56.62; H, 3.03; N, 6.01; S, 13.75. Found: C, 56.77; H, 2.82; N, 6.20; S, 13.68. Running the reaction at higher temperature and/or with crown ether gave no isolable adduct. The assignment of *cis*-stereochemistry to 7 is made based on the large coupling constant between the 4 and 5 protons and a model which shows the dihedral angle of the 4 and 5 protons to be nearly 0°.



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7. Spectral properties and m.p. of 5 were identical with those reported in the literature.[1]