

## THE REACTION BETWEEN THIOBENZOYL CHLORIDE $\underline{S}$ -OXIDE AND AZIDE IONS

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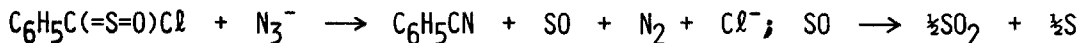
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As part of a study on the thermal and photochemical properties of the thia-triazole ring system we have investigated the reaction between thiobenzoyl chloride  $\underline{S}$ -oxide and azide ions in an attempt to obtain the unknown 5-phenyl-1,2,3,4-thiatriazole  $\underline{S}$ -oxide.

When ethanolic solutions (0.1 M) of either cis- or trans-thiobenzoyl chloride  $\underline{S}$ -oxide (I) (1) and ammonium azide are mixed, a yellow color is rapidly developed followed by the brisk evolution of gas. After a few minutes at room temperature gas evolution ceases and a pale yellow solution is obtained. Combined quantitative gas chromatography-mass spectrometry identifies benzonitrile as a reaction product in 88% yield (based on thiobenzoyl chloride  $\underline{S}$ -oxide and using calibration curves for the quantitative measurements). Besides nitrogen, both sulfur and sulfur dioxide are observed, the latter corresponding to ca. 0.5 equivalents of the benzonitrile formed. The amount of sulfur dioxide was determined by iodine titration of the gas evolved in an experiment carried out in the absence of oxygen. Thus the reaction scheme can be formulated as:



The reaction between (I) and ammonium azide takes place even at  $-80^\circ\text{C}$  and the formation of a yellow precipitate is observed. When the solid is heated a strong exothermic reaction sets in with the usual evolution of gas.

An infrared spectrum of a 1% methylene chloride solution of the yellow product at  $-80^\circ\text{C}$  (from  $\emptyset$  and tetrabutylammonium azide) strongly indicates that the aromatic thiatriazole ring system has not been formed but that the compound has an open structure, i.e., is a thiobenzoyl azide  $\underline{S}$ -oxide. Thus an intense absorption band is found at  $2120\text{ cm}^{-1}$  ( $\pm 5\text{ cm}^{-1}$ ), well within the region where organic azides are generally observed to absorb. The C=S=O group is reported to give rise

to intense absorptions ascribed to the symmetric and asymmetric stretching vibrations. Thus cis-(I) possesses absorptions at 1145 and 1025  $\text{cm}^{-1}$ ; the trans isomer, at 1120 and 1005  $\text{cm}^{-1}$  (1). In the spectrum of the yellow compound a strong absorption is observed at 1110  $\text{cm}^{-1}$ . When the compound is heated both this and the absorption at 2120  $\text{cm}^{-1}$  begin to disappear around -40 to -30°C. At room temperature both bands have disappeared, confirming their assignment to the yellow unstable compound. It cannot be known whether only one of the possible cis- and trans-thiobenzoyl azide S-oxides will be formed. The absorption at 1110  $\text{cm}^{-1}$  lies within a region in which the solvent itself exhibits strong absorptions and may thus screen the absorption of the other isomer. This question will have to await further experiments.

Although thiobenzoyl azide S-oxide most probably is the main reaction product between azide ions and thiobenzoyl chloride S-oxide, the presence of a small amount of 5-phenyl-1,2,3,4-thiatriazole S-oxide cannot be excluded. Addition of triphenylphosphine or hexachlorodisilane, which would be expected to act as deoxygenating agents, to solutions of the reaction product between (I) and azide, after evolution of gas has taken place, did, however, not result in traceable amounts of 5-phenyl-1,2,3,4-thiatriazole.

From decomposition experiments in ethanol and in methylene chloride with added benzene some information as to the decomposition mechanism of thiobenzoyl azide S-oxide has been obtained. It can be concluded that a nitrene is an unlikely intermediate. Some of the reaction products expected from a nitrene in the solvents employed are thiobenzamide S-oxide and thiobenzanilide S-oxide. However, chromatographic analysis with authentic samples as standards has revealed that these compounds have not been formed. This is not inconsistent with either a concerted mechanism in which SO and N<sub>2</sub> are lost simultaneously or a stepwise mechanism for example via unstable cyclic intermediates.

#### REFERENCES

1. J. F. King and T. Durst, J. Amer. Chem. Soc., 85, 2676 (1963); Can. J. Chem., 44, 819 (1966).