

Meso-ionic 1,3,4-Thiadiazoles: Photochemical Oxidative Cyclization

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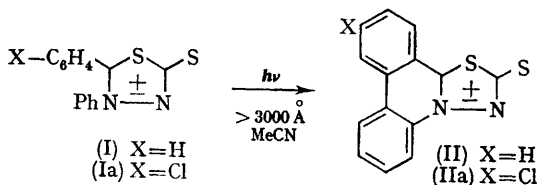
THE photochemically-induced cyclisation of stilbene and its derivatives has been studied in detail.¹ Analogous cyclisations have been demonstrated for related compounds in which a nitrogen atom

replaces one of the carbon atoms of the ethylene part of the system. Among such examples are Schiff bases,² stilbazoles,³ and 1-styrylpyridinium salts.⁴

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We now report the analogous cyclisation of meso-ionic anhydro-4,5-diaryl-2-mercapto-1,3,4-thiadiazolium hydroxides.⁵ Transformation (I → II) produces a new meso-ionic system.

Irradiation[†] of a 0.3% solution in acetonitrile of 4,5-diphenyl-2-mercapto-1,3,4-thiadiazolium hydroxide (I), λ_{\max} 403 m μ (log ϵ 3.48), with a medium pressure lamp equipped with a Pyrex filter, yielded 30% of (II) which had m.p. 250–251°, λ_{\max} (EtOH), 257 (log ϵ 3.77), 275 (3.69), 400 (3.01).



Both analytical data corresponding to the composition and molecular weight of (II), and the i.r. and n.m.r. spectra were in agreement with expectation. The mass spectrum of (II) was compared with that of (I). Both compounds displayed parent molecular ions at m/e 270 for the (I) and m/e 268 for (II) respectively. Characteristic fragmentation of the thiadiazolium portion of the molecules occurred; however, the photo-product showed peaks differing by two mass units from comparable ones in the starting material. Compound (II) formed a methiodide of m.p. 118–120°, which was not desulphurised upon treatment with mercuric oxide. These properties are likewise shown by (I). Anhydro-4-phenyl-5-*p*-chlorophenyl-2-mercapto-1,3,4-thiadiazolium hydroxide (Ia) upon irradiation under the conditions described above behaved in an analogous fashion yielding

photoisomer (IIa), m.p. 284–286°, λ_{\max} (MeCN) 252 m μ (log ϵ 4.6); 258 (4.7); 282 (4.4); 293 (4.4); 431 (3.75). The mass and n.m.r. spectra of (IIa) also corroborated the proposed structure.

Decomposition of (IIa) with aqueous base gave 5-amino-9-chlorophenanthridin-6-one, m.p. 310–311° decomp., m/e 244 (100%). This transformation is in agreement with the suggested structure and also argues against structures in which the ring atoms of the heterocyclic portion have exchanged positions.⁶

The results obtained here are somewhat unexpected. Photochemically induced loss of carbon disulphide from carboxylic dithiocarbonyl anhydrides has been reported.⁷ Irradiation of *N*-phenylsyndnone proceeds with loss of carbon dioxide.⁸

As a step towards elucidating the mechanism of the photoisomerisation, an effort was made to identify the nature of the longer-wavelength electronic transition shown by meso-ionic 1,3,4-thiadiazoles. A consistent shift to shorter wavelengths was observed when the spectrum was determined in various solvents of increasing polarity. § Typically for (I) the λ_{\max} values are:

$$\lambda(\text{CS}_2) 466 \text{ m}\mu, \lambda(\text{C}_6\text{H}_6) 433 \text{ m}\mu, \lambda(\text{MeOH}) 388 \text{ m}\mu.$$

This kind of variation, which was observed for over twenty different solvents, is characteristic of an $n \rightarrow \pi^*$ transition. Furthermore, the longer-wavelength absorption disappears when (I) is dissolved in trifluoroacetic acid. The transition may involve transfer of a lone-pair electron on the C=S sulphur atom as an initial step in the cyclisation.

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[†] Some of the photochemical experiments reported here were carried out by Mr. F. Triem, National Institutes of Health, Bethesda, Md.

§ Unpublished results with J. Hynes, N.S.F. undergraduate research participant.

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⁵ For references to the preparation and reaction of these compounds with dimethyl azodicarboxylate, see R. M. Moriarty, J. M. Kliegman, and R. B. Desai, *Chem. Comm.*, 1967, 1045. In this Communication these compounds were incorrectly named as anhydrothiothiadiazolium thiols.

⁶ For example, in the case of isoxazoles: E. F. Ullman, B. Singh, *J. Amer. Chem. Soc.*, 1966, **88**, 1844; thiophens: H. Wynberg and H. von Driel, *J. Amer. Chem. Soc.*, 1965, **87**, 3998; *Chem. Comm.*, 1966, 203.

⁷ E. H. Hoffmeister and D. S. Tarbell, *Tetrahedron Letters*, 1965, 35.

⁸ C. H. Krauch, J. Kuhls, and H. J. Pick, *Tetrahedron Letters*, 1966, 4043.