

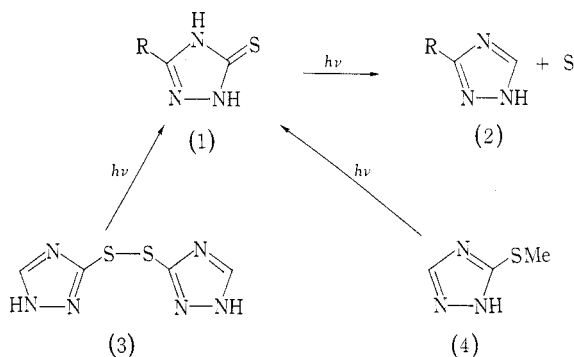
PREPARATION OF *N*-UNSUBSTITUTED 1,2,4-TRIAZOLES BY PHOTOLYSIS OF 1,2,4-TRIAZOLINE-3-THIONES

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The photochemistry of heterocyclic thiones has been little investigated¹⁻³ and no reference to the photolysis of 1,2,4-triazoline-3-thiones could be found. In this communication the behaviour of 1,2,4-triazoline-3-thione and several *C*- and *S*-substituted derivatives upon irradiation with ultraviolet light is reported.

Irradiation of methanolic solutions of 1,2,4-triazoline-3-thione (1; R = H) by either low- or medium-pressure mercury vapour lamps gave near quantitative yields of 1,2,4-triazole (2; R = H) and sulphur. As 1,2,4-triazoline-3-thione has an intense characteristic absorption at 251 m μ and the reaction products do not have significant absorption⁴ above 210 m μ the progress of the photolysis could readily be followed by u.v. spectroscopy. In this way the irradiation was continued until the reaction had gone to completion. The photolysis occurred only in a quartz container and was not dependent on the presence or absence of oxygen.



Irradiation of either 3,3'-di(1,2,4-triazolyl) disulphide (3) or 3-methylthio-1,2,4-triazole (4) also gave only 1,2,4-triazole and sulphur as final products. Before irradiation both these compounds showed no absorption at 251 m μ . However, on

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¹ Schönberg, A., "Preparative Organic Photochemistry." (Springer-Verlag: New York 1968.)

² Mustafa, A., *Adv. Photochem.*, 1964, **2**, 63.

³ Wolf, H. P., and Weiss, K., in "Mechanisms of Reactions of Sulphur Compounds." (Eds. N. Kharasch, B. S. Thyagarajan, and A. I. Khodair.) Vol. 2, p. 19. (Intra-science Research Foundation: Los Angeles 1968.)

⁴ Atkinson, M. R., Parkes, E. A., and Polya, J. B., *J. chem. Soc.*, 1954, 4256.

irradiation, an absorption band at this wavelength developed and then decreased until eventually only end absorption occurred, indicating that both reactions proceeded via 1,2,4-triazoline-3-thione.

Photolysis of several 3-alkyl or aralkyl-1,2,4-triazoline-5-thiones⁵⁻⁸ also gave the corresponding 3-substituted 1,2,4-triazoles^{5,7,9-11} and sulphur in excellent yields (see Table 1).

TABLE 1
DETAILS OF PHOTOLYSIS REACTIONS (1) → (2)
(Ultraviolet spectra in methanol)

R	1,2,4-Triazoline-3-thione (1)			Photolysis Product (2)	
	Ref.	λ_{\max} (m μ)	log ϵ	Ref.	Yield (%)
H	5	251	4.25	5	97
Me	6	252	4.41	9	82
Et	6	253	4.46	10	84
C ₆ H ₁₁	7	253	4.37	7	86
PhCH ₂	8	253	4.27	11	96

1,2,4-Triazole and 3-substituted 1,2,4-triazoles are usually prepared by oxidative removal of the sulphur.¹² Photochemical desulphuration however appears to be a superior method of preparation of *N*-unsubstituted 1,2,4-triazoles which are stable to ultraviolet light.

3-Phenyl-1,2,4-triazole is not stable to ultraviolet light, as shown by change in its ultraviolet spectrum on irradiation, so that this method is not applicable to the preparation of 3-aryl-1,2,4-triazoles. Photolysis of *N*-substituted 1,2,4-triazoline-3-thiones is currently being investigated.

Experimental

Light sources used were (1) the Oliphant ultraviolet lamp which consisted of a bank of 16 low-pressure mercury vapour lamps with Vycor tubes, and (2) a Hanovia L water-cooled quartz immersion medium-pressure mercury vapour lamp (450 W) fitted with a Vycor filter sleeve. Ultraviolet spectra were determined on a Hitachi Perkin-Elmer 124 spectrophotometer and infrared spectra on a Hilger & Watts Infracord H1200. Extinction coefficients were measured on a Hilger & Watts H700 spectrophotometer.

1,2,4-Triazoline-3-thiones were prepared by methods described in the literature (see Table 1). 1,2,4-Triazoline-3-thione was converted into 3,3'-di(1,2,4-triazolyl) disulphide by oxidation¹³ and into 3-methylthio-1,2,4-triazole by *S*-methylation.¹⁴ The 1,2,4-triazoline-3-thiones

⁵ Ainsworth, C., *Org. Synth.*, 1960, **40**, 99.

⁶ Willems, J. F., and Vandenberghe, A., *Bull. Soc. chim. Belg.*, 1966, **75**, 358.

⁷ Blackman, A. J., B.Sc. Honours Thesis, University of Tasmania, 1964.

⁸ Takagi, S., and Sugii, A., *Yakugaku Zasshi*, 1958, **78**, 280 (*Chem. Abstr.*, 1958, **52**, 11822).

⁹ Jones, R. G., and Ainsworth, C., *J. Am. chem. Soc.*, 1955, **77**, 1538.

¹⁰ Bachman, G. B., and Heisey, L. V., *J. Am. chem. Soc.*, 1949, **71**, 1985.

¹¹ Postovskii, I. Ya., and Vereshchagina, N. N., *Zh. obshch. Khim.*, 1959, **29**, 2139 (*Chem. Abstr.*, 1960, **54**, 9898).

¹² Potts, K. T., *Chem. Rev.*, 1961, **61**, 87.

¹³ Freund, M., and Meineke, C., *Ber. dt. chem. Ges.*, 1896, **29**, 2485.

¹⁴ Kröger, C.-F., Sattler, W., and Beyer, H., *Liebigs Ann.*, 1961, **643**, 121.

were oxidized by nitric acid to provide authentic samples of 1,2,4-triazole and 3-substituted 1,2,4-triazoles (see Table 1). Photolysis products were identified by their melting points and mixed melting points with authentic samples, and by comparison of their ultraviolet and infrared spectra.

Typical experiments are given.

Photolysis of 1,2,4-Triazoline-3-thione

A solution of 1,2,4-triazoline-3-thione (5.00 g) in methanol (250 ml) was irradiated with the medium-pressure mercury immersion lamp until the ultraviolet spectra of the reaction solution indicated that the reaction was complete (approximately 18 hr). During the course of the photolysis sulphur separated out of solution, and any which precipitated on the lamp housing was periodically removed by scraping. After the reaction was complete the sulphur (1.49 g) was removed by filtration and the filtrate evaporated to dryness under reduced pressure. The residue was extracted with hot ethyl acetate leaving insoluble sulphur (0.05 g, i.e. a total of 1.54 g; 97%). Concentration of the extract followed by addition of benzene yielded 1,2,4-triazole (3.32 g; 97%).

Similar irradiation of the disulphide (3) or the methylthio compound (4) in methanol also gave 1,2,4-triazole in 67% and 81% yields respectively.

Photolysis of 3-Methyl-1,2,4-triazoline-5-thione

A solution of 3-methyl-1,2,4-triazoline-5-thione (1.0 g) in methanol (45 ml) in a quartz vessel was irradiated with the low-pressure mercury lamps until the reaction was complete (3–4 days). The sulphur which separated out on the sides of the container was removed by periodic scraping. The reaction mixture was evaporated to dryness under reduced pressure and extracted with water leaving a residue of sulphur (0.25 g; 89%). The aqueous extract was concentrated under reduced pressure to yield an oil which was dissolved in hot benzene. On cooling crystalline 3-methyl-1,2,4-triazole (0.59 g; 82%) separated.

Photolysis of 3-Benzyl-1,2,4-triazoline-5-thione

A solution of 3-benzyl-1,2,4-triazoline-5-thione (1.0 g) in methanol was photolysed as described for the 3-methyl isomer. The insoluble sulphur (0.10 g) was removed by filtration and the filtrate evaporated under reduced pressure to yield an oil. The oil was chromatographed on alumina in chloroform. Sulphur (0.05 g, i.e. a total of 0.15 g; 89%) and then 3-benzyl-1,2,4-triazole (0.80 g; 96%) were recovered from the column.