

PHOTOINDUCED RING OPENING AND COS ELIMINATION OF MESOIONIC THIADIAZOLES

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(Received in UK 13 April 1976; accepted for publication 23 April 1976)

A variety of photochemical reactions of five membered mesoionic compounds have been reported. Among these a majority describes fragmentation into a heterocumulene and a 1,3-dipole.<sup>1</sup>

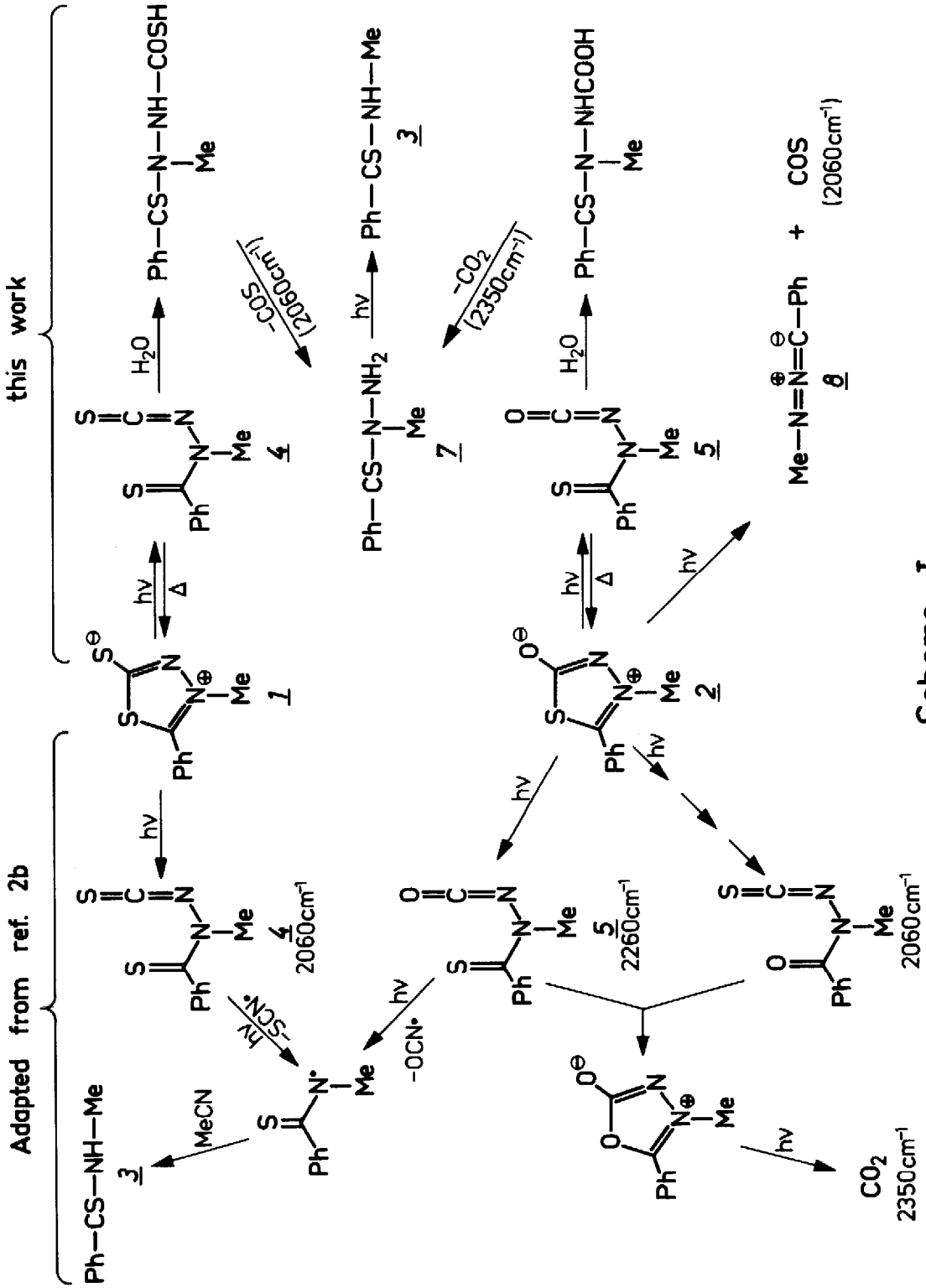
Moriarty, Chapman and co-workers<sup>2</sup> have suggested ring opening to be another primary photochemical process from mesoionic thiadiazoles, exemplified by 4-methyl-5-phenyl-1,3,4-thiadiazolylio-2-sulfide (1) and 4-methyl-5-phenyl-1,3,4-thiadiazolylio-2-oxide (2). The main photolysis product from both compounds is N-methyl thiobenzamide (3).<sup>2a</sup> They monitored the reactions in acetonitrile<sup>3</sup> and nujol by means of infrared spectroscopy.<sup>2b</sup> The absorptions produced, their assignments and the mechanism suggested are summed in the left hand part of Scheme I.

We have reexamined these experiments as part of our current investigations of the photochemistry of mesoionic compounds<sup>4</sup> and suggest new assignments for all the infrared absorptions observed by Moriarty and Chapman according to the following Table:

	Ref. 2b <sup>5</sup>	This work	
	2350 cm <sup>-1</sup> CO <sub>2</sub> ?	CO <sub>2</sub>	In addition, we have identified a new intermediate <u>7</u> and a new product <u>6</u> . Our results confirm, that <u>4</u> and <u>5</u> are indeed primary products of <u>1</u> and <u>2</u> , respectively. A revised and simplified mechanism is displayed in the right hand part of Scheme I.
ca.	2300 cm <sup>-1</sup> ?	solvent (MeCN)	
	2260 cm <sup>-1</sup> -N=C=O	solvent (MeCN)	
	2060 cm <sup>-1</sup> -N=C=S	COS	

Scheme I is established as a consequence of the following experiments. Photolysis<sup>6</sup> of 1 in moist acetonitrile in an infrared cell was accompanied by appearance of an absorption at 2060 cm<sup>-1</sup> as observed previously.<sup>2b</sup> However, this band disappeared when argon was bubbled slowly through the solution for three minutes after photolysis. The rest of the spectrum was unchanged.

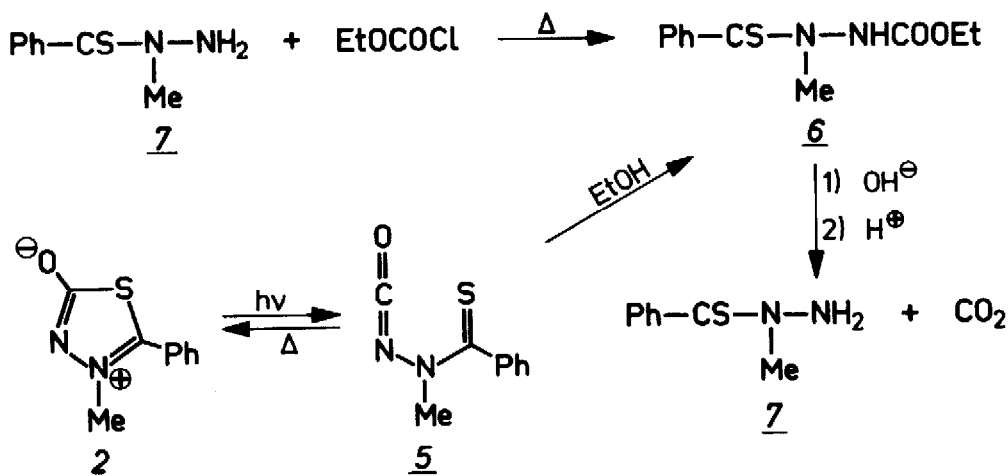
The photolysis of 2 was likewise monitored by means of infrared spectroscopy in moist acetonitrile, in methylene chloride, in nujol and as a solid solution in poly(vinyl chloride)



(PVC). We have not been able to reproduce the two bands which were seen<sup>2b</sup> at 2260  $\text{cm}^{-1}$  and 2300  $\text{cm}^{-1}$ . It is striking, that the solvent acetonitrile show two strong absorptions at the same wave numbers with the same relative intensities.<sup>7</sup> In all media except PVC bands were produced at 2060  $\text{cm}^{-1}$  and 2350  $\text{cm}^{-1}$  ( $\text{CO}_2$ ). The  $\text{CO}_2$ -absorption was absent in the PVC-film. Both bands disappeared from the fluid solutions when they were purged cautiously with argon. The 2060  $\text{cm}^{-1}$  absorption could be removed from the PVC-film by evacuation. In case of the methylene chloride solution, drying was attempted by passing the solvent through neutral alumina before the experiment. This precaution led to a greatly reduced photosensitivity of 2, but both bands (2060  $\text{cm}^{-1}$  and 2350  $\text{cm}^{-1}$ ) were observable after prolonged irradiation.

In a semipreparative run, the gaseous photoproducts from 2 were collected in a  $\text{CdCl}_2/\text{NH}_3$  solution. This caused precipitation of CdS which indicates the presence of hydrogen sulfide or another gaseous product capable of hydrolyzing to ionic sulfide. On the basis of these experiments we reassign the 2060  $\text{cm}^{-1}$  band observed during photolysis of 1 and 2 to COS.<sup>8</sup> Independent experiments proved the hydrolysis of COS whether irradiated or not to be far too slow in moist acetonitrile in order to account for the  $\text{CO}_2$  formed during irradiation of 2.

Though not observable in the infrared spectra, powerful evidence for the formation of 5 as a primary photoproduct has been obtained. Photolysis of 2 in absolute ethanol (proceeding ca. 16 times faster than in acetonitrile) led to a single product 6, shown to be identical (tlc, uv, ir) with the product of the thermal reaction between ethyl chloroformate and 1-N-methyl thiobenzhydrazide (7) (Scheme II). Authentic 6 was transformed into 7 by consecutive



Scheme II

treatments with aqueous base and acid. The acidification was accompanied by immediate evolution of carbon dioxide. Compound 7 could be detected (prep. tlc, uv) among the photoproducts from a preparative photolysis of 2 in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (20:1). Photolysis of authentic 7 in acetonitrile led to a single product identified as N-methyl thiobenzamide (3) (Scheme I).

The detection of COS among the photoproducts of 2 in  $\text{CH}_3\text{CN}$  shows that this mesoionic compound does follow the other members of the class yet investigated in its response to irradiation.<sup>1</sup> The literature, to the best of our knowledge, appears to be devoid of photoeliminations of COS.<sup>9</sup> Attempts to trap the nitrilimine 8 presumably formed along with COS (Scheme I) with dipolarophiles have failed due to an extreme complexity of the reaction mixtures. Neither have we been able to detect  $\text{CS}_2$  (glc) after photolysis of 1 in  $\text{CH}_3\text{CN}$ .

#### REFERENCES AND NOTES

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- 2) a) R. M. Moriarty and R. Mukherjee, Tet. Lett., 1969, 4627; b) R. M. Moriarty, R. Mukherjee, O. L. Chapman and D. R. Eckroth, ibid., 1971, 397.<sup>10</sup>
- 3) The communication does not indicate whether drying of the solvent was attempted or not.
- 4) a) A. Holm, N. Harrit, K. Bechgaard, O. Buchardt and S.E. Harnung, Chem. Comm., 1972, 1125; b) A. Holm, N. Harrit and N. H. Toubro, J. Am. Chem. Soc., 97 (1975) 6197.
- 5) Compound 5 was reportedly observed at  $2260\text{ cm}^{-1}$ , but the spectrum reproduced in the communication features an additional band at ca.  $2300\text{ cm}^{-1}$ . Isocyanates, unlike isothiocyanates, do not give rise to clearly resolved doublet infrared absorptions: L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1969, p. 62.
- 6) Osram HBO-200 high pressure Hg point source. When not specified, photolysis was performed through pyrex as well as quartz without significant differences in the course of the reactions. Neither were any results influenced by purging the solutions with argon before photolysis.
- 7) C. J. Pouchert, "The Aldrich Library of Infrared Spectra," 1970.
- 8) Infrared spectrum of COS: F. D. Verderame and E. R. Nixon, J. Chem. Phys., 44 (1966) 43.
- 9) O. Buchardt (ed.), "Photochemistry of Heterocyclic Compounds," John Wiley Inc., New York, 1976, in press. See, however, ref. 1h.
- 10) After the submission of this manuscript further studies on the photochemistry of mesoionic thiadiazoles have been reported: R. Mukherjee and R.M. Moriarty, Tetrahedron, 32 (1976), 661