Tetrahedron Letters No.5, pp. 397-400, 1971. Pergamon Press. Printed in Great Britain.

INTERMEDIATES IN THE PHOTOLYSES OF MESOIONIC THIADIAZOLES: DETECTION OF HETEROCUMULENES BY INFRARED

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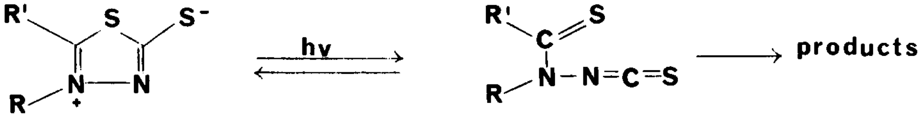
(Received in USA 23 December 1970; received in UK for publication 30 December 1970)

We reported previously that photolyses of mesoionic thiadiazoles in solution yielded thioamides and elemental sulfur possibly <u>via</u> initial photochemically induced valence tautomerization to an open-chain intermediate which then cleaves in a second photon process.[1]

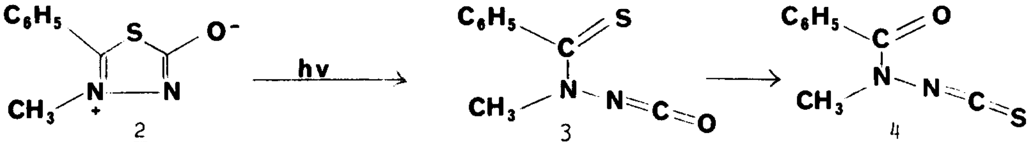
<u>Equation 1</u>



1a: R' = C_6H_5, R = CH_3

1b: R' = CH_3, R = C_6H_5

<u>Equation 2</u>



2 3 4

We now have demonstrated the intermediacy of the N-isothiocyanato thioamide by timed interval infrared recording during the course of photolysis at variable temperatures.[2] Photolyses were carried out in nujol mull, neat melt and in acetonitrile solution and the development of absorption in the heterocumulene region of the spectrum was observed.

Figure 1a shows the appearance of the -N=C=S absorption at 2060 cm^{-1} for anhydro-5-mercapto-3-methyl-2-phenylthiadiazolium hydroxide (1a) at 25° after photolysis for 3 hr in acetonitrile solution.[3,4] Similarly, absorption at 2060 cm^{-1} developed upon irradiation of 1a in nujol mull or neat melt. Analogous behavior was found for anhydro-5-mercapto-3-phenyl-2-methylthiadiazolium hydroxide (1b).

That there is both a thermal component in the photochemical ring opening and a dark thermal pathway is indicated by two observations: a) Irradiation of 1a at -190° for 4 hr caused no development of -N=C=S absorption; b) Heating of 1b to 160° with simultaneous recording of the infrared spectrum leads to strong absorption at 2060 cm^{-1}.

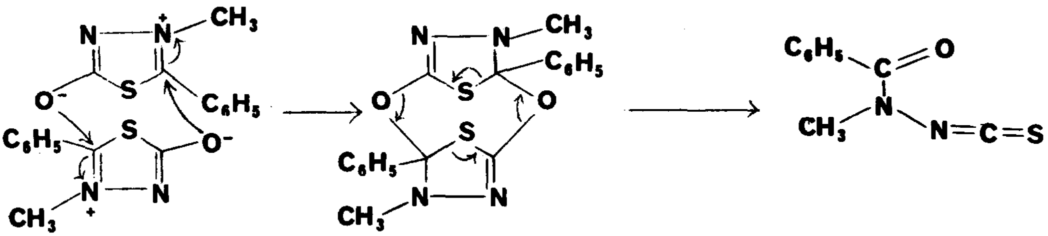
Photolysis of anhydro-5-hydroxy-3-methyl-2-phenylthiadiazolium hydroxide (2) at 25° in acetonitrile solution or as a nujol mull caused development of absorption at 2260 cm^{-1} (-N=C=O)[5], in agreement with Equation 2, namely, 2 → 3. Figure 1b illustrates this behavior.

The unexpected reaction 3 → 4 was observed in the photolysis of 2 in both nujol mull and acetonitrile solution by the gradual appearance of absorption at 2060 cm^{-1} (-N=C=S). In the solution photolysis the initial -N=C=O band increases in intensity. This conversion may be due to either a bimolecular reaction or a unimolecular isomerization. Erner[6] has shown that isocyanates and isothiocyanates undergo an exchange reaction when simply heated together. Bond switching to yield a three membered ring which ring expands in the reverse sense to its formation is well known.

The absorption which appears at 2350 cm^{-1} may be due to CO_2 formed by photofragmentation as depicted in Equation 4.[7]

The quantum yields for the disappearance of 1a and 2 are shown in the Table 1. The Φ_{dis} of 1a and 2 were measured by reduction of the 385 mμ and 320 mμ peaks, respectively. The absence of a reaction (Φ_{dis} = 0.00) for 2 at 10^{-2} M concentration suggests self-quenching and implies that the initial ring-opening reaction is unimolecular.

Equation 3



Equation 4

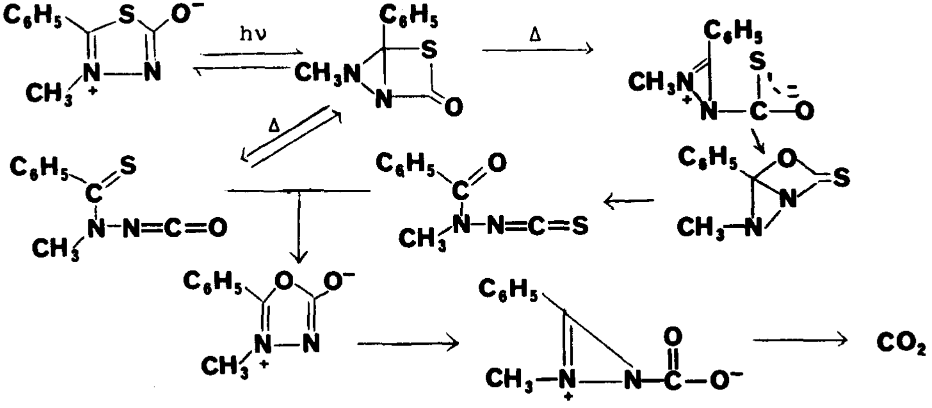


Table 1

Quantum Yields for the Disappearance of the Mesoionic Thiadiazoles

compound	conc.^{a}	Φ_{dis}
1a	10^{-3} M	0.04
2	10^{-3} M	0.002
2	10^{-2} M	0.00

a) in acetonitrile solution

References

1) R. M. Moriarty and R. Mukherjee, Tetrahedron Letters, 4627 (1969).

2) O. L. Chapman and J. D. Lassila, J. Am. Chem. Soc., 90, 2449 (1968); L. L. Barber, O. L. Chapman, and J. D. Lassila, Ibid., 90, 5933 (1968); 91, 531 (1969); O. L. Chapman and C. L. McIntosh, Ibid., 91, 4309 (1969).

3) Details of the apparatus have been described earlier.^{2} In the present case an 800 watt source with maximum emission at 3660 A was used.

4) E. Liebler, C. N. R. Roa, and J. Ramachandran, Spectrochimica Acta, 13, 296 (1959).

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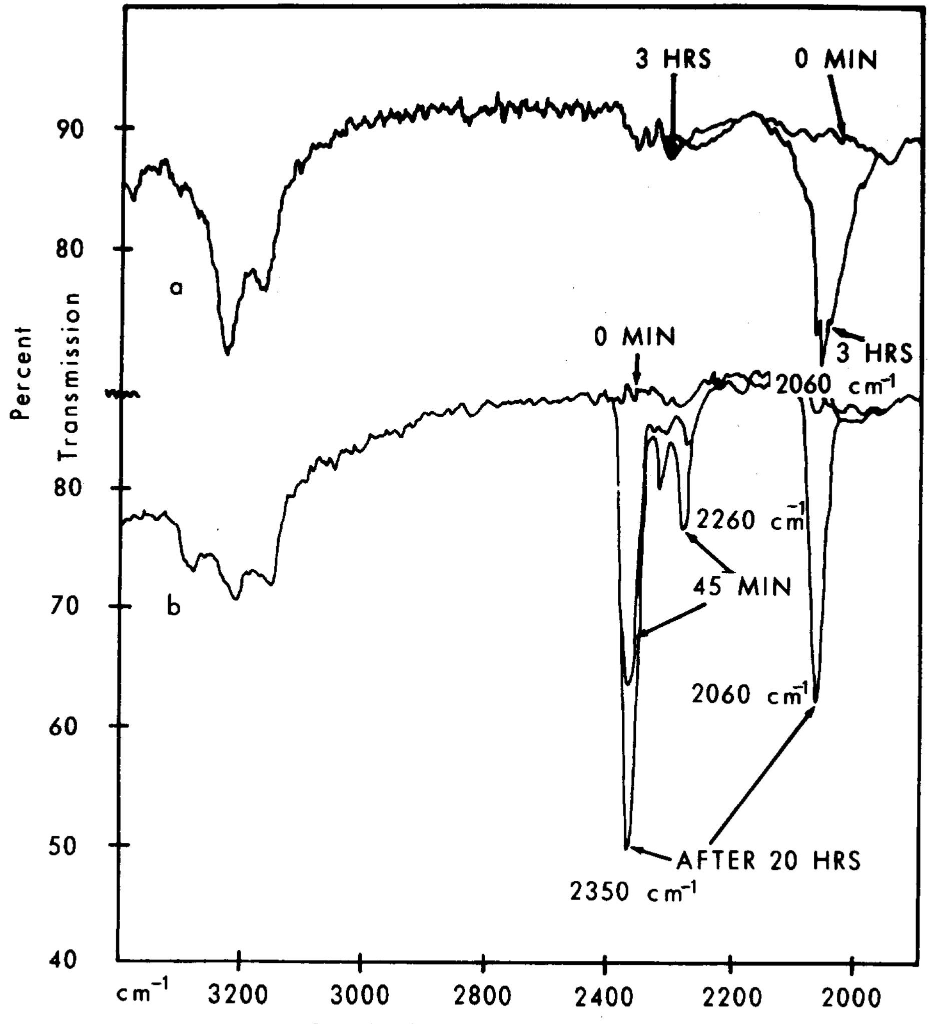

Figure 1 (a) Photolysis of anhydro-5-mercapto-3-methyl-2-phenylthiadiazolium hydroxide (1a) in acetonitrile solution
(b) Photolysis of anhydro-5-hydroxy-3-methyl-2-phenylthiadiazolium hydroxide (2) in acetonitrile solution