Tetrahedron Letters No.53, pp. 4627-4630, 1969. Pergamon Press. Printed in Great Britain

MESO-IONIC 1,3,4-THIADIAZOLES: PHOTOCHEMICAL FRAGMENTATION

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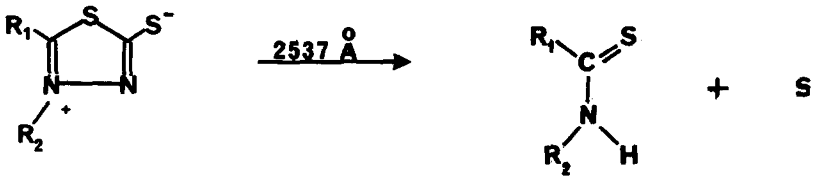
(Received in USA 4th September 1969; redeived in UK for publication 11th October 1969)

IN an earlier communication we reported the photochemical oxidative cyclization of meso-ionic anhydro-5-mercapto-2,3 diaryl-1,3,4-thiadiazolium hydroxides (eg. III →VI)[1]. In continuation of the study of the photochemistry of meso-ionic system we have found a new mode of photofragmentation as well as an interesting wavelength dependence for the course of the reaction.

For C-2 or N-3 alkyl substituted 1,3,4-meso-ionic thiadiazoles of type Ia or Ib photochemically induced oxidative cyclization is clearly unlikely. Accordingly, the photolysis of anhydro-5-mercapto-3-methyl-2-phenylthiadiazolium hydroxide (Ia)[2] was investigated. Irradiation of Ia in 0.01$\underline{M}$ CH_3CN at 2537Å for 72 hr. yielded 21% N-methylthiobenzamide (IIa)[3], m.p. 78-79° and 40% elemental sulfur. Photolysis under the same conditions in CH_3CN: CH_3OH,1:4, yielded 33% IIa and 26% sulfur.

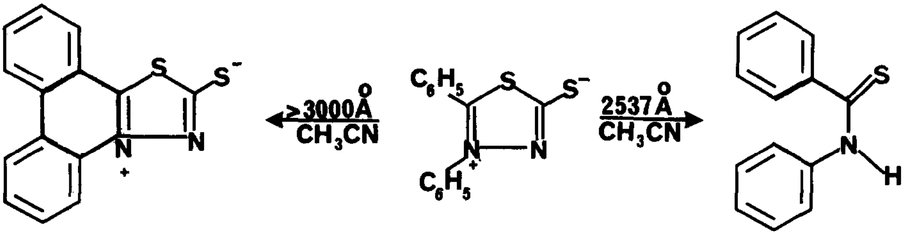
Similarly photolysis of the isomeric meso-ionic anhydro-5-mercapto-3-phenyl-2-methylthiadiazolium hydroxide (Ib)[2] in CH_3CN yielded 20% N-phenylthioacetamide (IIb)[3] m.p. 76° and sulfur 35%.



(Ia) $R_1 = C_6H_5$; $R_2 = CH_3$
(Ib) $R_1 = CH_3$; $R_2 = C_6H_5$

(IIa) $R_1 = C_6H_5$; $R_2 = CH_3$
(IIb) $R_1 = CH_3$; $R_2 = C_6H_5$

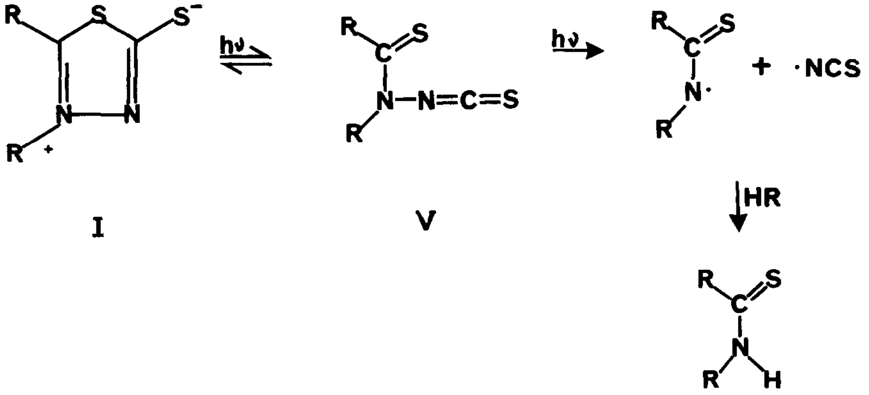
Since no fragmentative photodecomposition of anhydro-5-mercapto-2,3-diphenylthiadiazolium hydroxide (III) was observed in our earlier study of the photolysis of this compound in CH_3CN with radiation of wavelength greater than 3000Å, it was decided to investigate the photolysis of this compound at 2537Å. Indeed fragmentation was found to occur yielding 27% of N-phenylthiobenzamide (IV)[3] m.p. 101°.



VI III IV

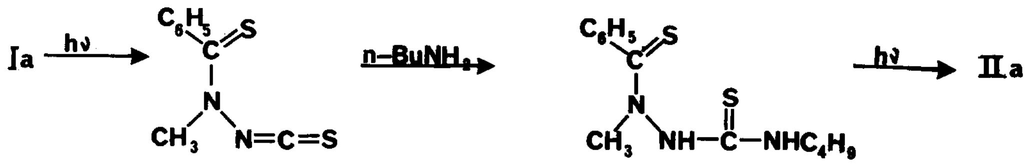
As a working hypothesis for the explanation of the photofragmentation reactions of meso-ionic 1,3,4 thiadiazoles we propose an initial valence tautomerization to yield an N-isothiocyanatothioamide (V)[4] which undergoes cleavage of the N-N bonds to yield the radical precursor of the thioamide and the isothiocyanate radical. The thioamide is formed by hydrogen abstraction from solvent (either CH_3CN or CH_3OH): thus the yield of thioamide increases in Ia → IIa with the better hydrogen donor solvent CH_3OH.

The photochemical decomposition of the isothiocyanate group is known to proceed with loss of elemental sulfur.[5]



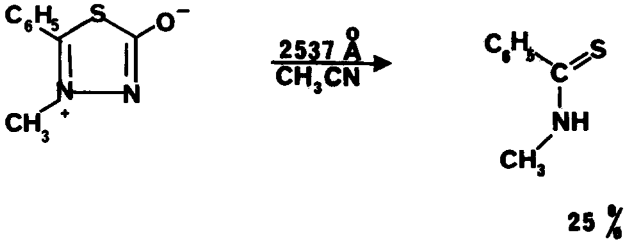
I V

In order to substantiate this mechanistic pathway a trapping experiment was carried out to intercept the postulated intermediate (V). To this end the photolysis of Ia was carried out in CH_3CN:n-$BuNH_2$, 1:1 at 2537Å. A 52% yield of N-methyl-thiobenzamide (IIa) was obtained, and significantly, no elemental sulfur was produced. We interpret this to mean that nucleophilic addition of the n-butylamine has occurred at the open-chain stage and subsequent decomposition proceeds as indicated.[6,7]



VII

Finally the photofragmentation described here is not restricted to the 5-mercapto-thiadiazolium compounds for the 5-hydroxy-thiadiazolium analogs behave similarly:



The technical assistance of Mr. Jerry T. Hewitt was appreciated.

References

(1) R. M. Moriarty, J. M. Kliegman, and R. B. Desai, *Chem. Comm.*, 1255(1967).

(2) For recent synthetic methods for this type of compound see:

  (a) K. T. Potts and C. Sapino, Jun., *Chem. Comm.*, 672(1968).

  (b) R. Grashey, M. Baumann, and W. D. Lubos, *Tetrahedron Letters*, **56**, 5881(1968).

(3) The identity of the thioamides formed in these photolyses was established by comparison with authentic samples.

(4) Such a valence tautomerization occurs in the case of the analogous 1,3,4-thiadiazol-2-one system. Reaction of N-methyl-N-thiobenzoylhydrazine with phosgene yields initially the open chain N-isocyanatothioamide which cyclizes thermally to the meso-ionic derivative. A. Y. Lazaris, *Zh. Org. Khim.*, **3**, 1902(1967); *Chem. Abs.*, **68**, 12910p(1968). The occurrence of a carbonyl band at 1630-1650 cm^{-1} indicates the semicyclic nature of these compounds (R. Grashey, M. Baumann, and W. D. Lubos, *Tetrahedron Letters*, **56**, 5877(1968).

(5) U. Schmidt, Kabitzke, I. Boie, C. Osterroht, *Chem. Ber.*, **98**, 3819(1965). The behavior of the isothiocyanate radical under photolytic conditions has been investigated (R. G. R. Bacon and R. S. Irwin, *J. Chem. Soc.*, 2447(1961) who reported the reaction ($NCS_2 \xrightarrow{h\nu} 2NCS$).

(6) In a dark experiment the stability of Ia towards n-butylamine under the reaction conditions was established.

(7) Compound VII, m.p. 67-68^{o}, was prepared from N-methyl-N-thiobenzoylhydrazine and N-butylisothiocyanate.