Photolysis of Mesoionic 1,4-Diaryl-1,2,4-triazol-3-ones

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Summary The photolysis of mesoionic 1-phenyl-4-aryl-1,2,4-triazol-3-ones gives benzimidazole, aryl isocyanate, and arylazobenzene.

IT has been suggested that the photochemical behaviour of many mesoionic ring systems may be rationalized in terms of their initial electrocyclic ring closure to bicyclic systems followed by their valence isomerization or fragmentation depending on the nature of components comprising the ring.[1,2]

It was reported[2] that the photolysis of mesoionic 1,4-diphenyl-1,2,4-triazol-3-one (Ia) gave mainly phenyl isocyanate and the cycloadduct (V). A closer investigation shows that the irradiation through Pyrex of a solution of (Ia) in methylene chloride containing 5% methanol afforded methyl phenyl carbamate (25%), benzimidazole (VIII) (18%), and a third product which was identified as azobenzene (IVa, 7%);† compound (V) was not one of the photoproducts but an impurity in the sample of (Ia) used. The reaction of 3-phenylsydnone (IXa) and phenyl isocyanate at 140° gave (Ia),[3] while the reaction of phenyl isocyanate and (IXa) or (Ia) at 160—180° resulted in almost exclusive formation of (V).

The formation of azobenzene is probably an intramolecular process because the photolysis of (Ib) under the same conditions gave methyl *p*-tolylcarbamate (44%), benzimidazole (18%), and *p*-tolylazobenzene (IVb) (23%).†

The photochemistry of sydnone derivatives (IX) has frequently been explained by conversion of (IX) into the bicyclic ring (X), fragmentation to diazirine (VI), and rearrangement to nitrile imine (XII).[4] The photoproducts of (I) described above and the absence of benzimidazole

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† Yields are based on products after separation and purification. Products were identified by elemental analyses and by comparison with authentic samples.

among the photolysates of 3-phenylsydnone (IXa)[5] show that the photolyses of these two mesoionic ring systems (I) and (IX) cannot involve a common intermediate (VI), and suggest a more deep-seated rearrangement.

An attractive rationalization of the behaviour of (I) is the initial electrocyclic ring closure of (I) to (II), valence isomerization to (III), and finally, fragmentation of (III) to aryl isocyanate, phenylazomethine nitrene (to give benzimidazole),[6] and arylazobenzene. A similar isomerization of a mesoionic 1,3-dithiol-4-imine to a 1,2-dithiol-3-imine has been observed.[3]

The photolysis of sydnones (IX) may also be explainable by consideration of photo-isomerization of the intermediate (X) to (XI), followed by fragmentation to the nitrile imine, thus by-passing the energy barrier to the diazirine intermediate (VI).[7] The results presented here also cast doubt on the possible interconversion of an azomethine nitrene and a nitrile imine through a diazirine intermediate.[8]

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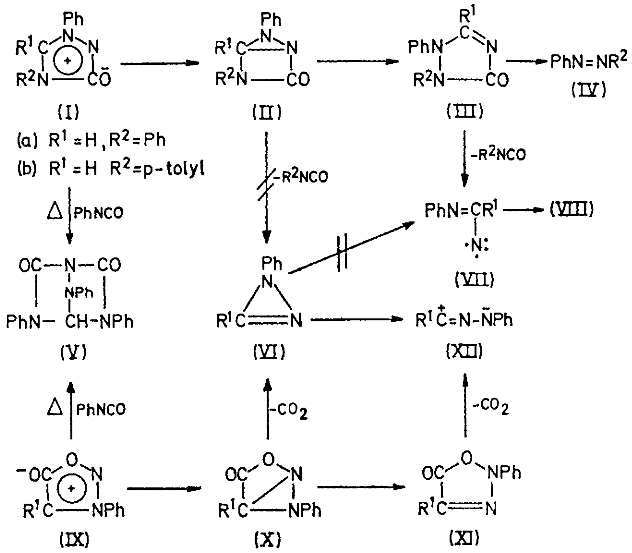

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[1] H. Kato, M. Kawamura, T. Shiba, and M. Ohta, *Chem. Comm.*, 1970, 959.

[2] H. Kato, T. Shiba, H. Yoshida, and S. Fujimori, *Chem. Comm.*, 1970, 1591.

[3] H. Kato, S. Sato, and M. Ohta, *Tetrahedron Letters*, 1967, 4261.

[4] C. H. Krauch, J. Kuhls, and H.-J. Piek, *Tetrahedron Letters*, 1966, 4043; Y. Huseya, A. Chinone, and M. Ohta, *Bull. Chem. Soc. Japan*, 1971, **44**, 1667; C. S. Angadiyavar and M. V. George, *J. Org. Chem.*, 1971, **36**, 1589; M. Märkyl, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1971, **54**, 1275; H. Gotthardt and F. Reiter, *Tetrahedron Letters*, 1971, 2749.

[5] H. Kato, T. Shiba, and Y. Miki, unpublished results.

[6] T. Bacchetti and A. Alemagna, *Gazzetta*, 1961, **91**, 1475; J. Sauer and K. K. Mayer, *Tetrahedron Letters*, 1968, 325; F. L. Bach, J. Karliner, and G. E. von Lear, *Chem. Comm.*, 1969, 1110; J. H. Boyer and P. J. A. Frints, *J. Heterocyclic Chem.*, 1970, **7**, 59.

[7] For a review on this system, see H. Kato, *Yuki Gosei Kagaku Kyokai-Shi J. Synthetic Org. Chem. Japan*, 1971, **29**, 146.

[8] J. H. Boyer, "Mechanisms of Molecular Migrations," ed. B. S. Thyagarajan, Interscience Publishers, New York, vol. 2, 1969, p. 267.