

Photolysis of Pyridazinium Dicyanomethylides

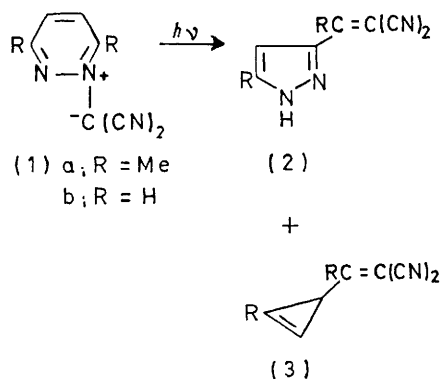
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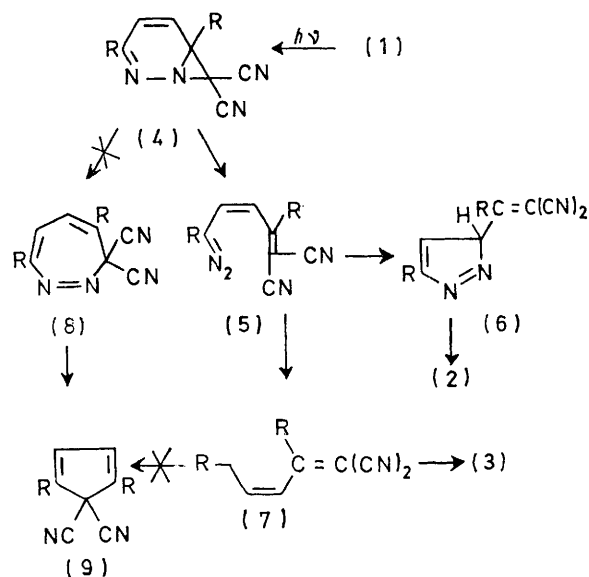
Summary Irradiation of pyridazinium dicyanomethylide gave 3-(2,2-dicyanovinyl)pyrazoles (2) and 3-(2,2-dicyanovinyl)cyclopropenes (3) formed it is believed *via* a mechanism similar to that operating in the photolysis of pyridazine *N*-oxides.

MANY reports have been published on the photolyses of *N*-oxides¹ and *N*-imino-ylides² of aza-aromatic compounds, including those³⁻⁵ of pyridazine *N*-oxides. For *N*-methyl-

ides, only one report,⁶ the photolysis of pyridinium dicyanomethylide, was known. Thus, we have examined



SCHEME 1



SCHEME 2

the photolysis of pyridazinium dicyanomethylide (**1**).

The methylide⁷ (**1a,b**) was irradiated in benzene for ca. 40 h (400 W, high-pressure Hg lamp) and the following products were isolated by chromatography on alumina: (**2a**): † m.p. 128–130° (15%); (**2b**) m.p. 118–119° (20%); (**3a**) oil, b.p. 96–98/1 mmHg (bath temp.), (20–25%); (**3b**) an oil, b.p. 80°/1 mmHg (bath temp.) (3–5%). Pyridazine and 7,7-dicyanonorcaradiene, formed by addition of the solvent benzene to dicyanomethylcarbene, derived from (**1**), were also obtained (1–2%).

Irradiation of (**1**) in methylene chloride resulted in an

increased yield of pyrazole (**2**) and a decreased yield of cyclopropene (**3**).

It is likely that compounds (**2**) and (**3**) are formed *via* a mechanism similar to that which operates in the photolyses^{3,5} of pyridazine *N*-oxides (see Scheme 2).

Since 1*H*-1,2-diazepines are formed in high yield upon photolysis of *N*-iminopyridinium ylides,² the formation of 3*H*-1,2-diazepine (**8**) or cyclopentadiene (**9**), derived from (**8**) by elimination of molecular nitrogen, was possible. This proved not to be so.

(Received, 21st May 1972; Com. 729.)

† Satisfactory elemental analyses, i.r. (CN: 2210 cm⁻¹) and mass spectral data were obtained for all compounds reported.

¹ C. Kaneko, *J. Syn. Org. Chem. (Japan)*, 1968 **26**, 758; G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 1970, **231**, and references cited therein.

² J. Streith and J.-M. Cassal, *Bull. Soc. chim. France*, 1969, 2175; T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, 1970, **35**, 426; A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *ibid.*, p. 433.

³ P. L. Kumler and O. Buchardt, *J. Amer. Chem. Soc.*, 1968, **90**, 5640.

⁴ T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Letters*, 1971, 2579; T. Tsuchiya, H. Arai, T. Tonami, and H. Igeta, *Chem. Pharm. Bull. (Japan)*, 1972, **20**, 300.

⁵ T. Tsuchiya, H. Arai, and H. Igeta, *J.C.S. Chem. Comm.*, 1972, 550; *Tetrahedron*, in the press.

⁶ J. Streith, A. Blind, J.-M. Cassal, and C. Cigwalt, *Bull. Soc. chim. France*, 1969, 948.

⁷ T. Sasaki, K. Kanematsu, Y. Yukimoto, and S. Ochiai, *J. Org. Chem.*, 1971, **36**, 813.