Photolysis of Pyridazine *N*-Oxides; Formation of Cyclopropenyl Ketones

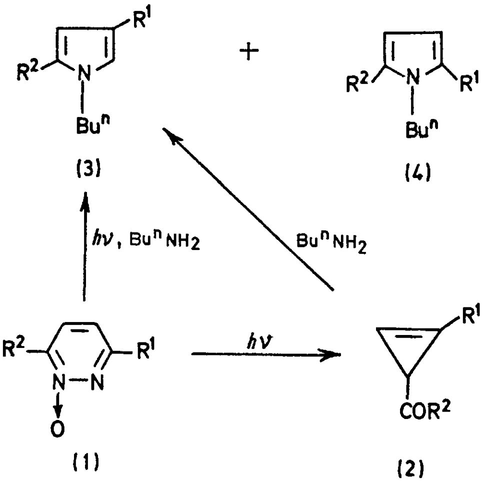
By Takashi Tsuchiya, Heihachiro Arai, and Hiroshi Igeta*

(*School of Pharmaceutical Sciences, Showa University, Shinagawa, Tokyo*)

Summary Irradiation of pyridazine *N*-oxides with primary amines in dichloromethane gives *N*-substituted pyrroles, suggesting that cyclopropenyl ketones are intermediates.

The photolysis of the pyridazine 1-oxides (**1a**—**c**) has already been reported by Ogata *et al.*,[1]† but the product yields were low compared with the photolyses[2–4] of phenyl substituted pyridazine *N*-oxides. We have re-examined the photolyses of the *N*-oxides and have found that cyclopropenyl ketones were formed.

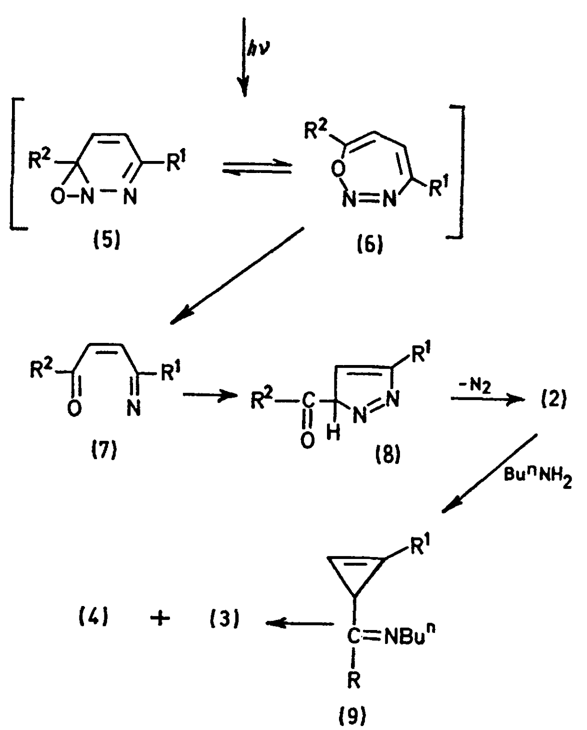
The 1-oxide (**1a**) was irradiated (200 W high-pressure Hg lamp) in dichloromethane for 2—3 h and the mixture was then distilled *in vacuo* at low temperature, to give an oil (7%), b.p. 40°/4 mmHg, whose spectral properties [m/e 96 (M^+); ν_{max} (liquid) 1690 (Ac) and 1795 (C=C) cm^{-1}; δ (CCl_4) 1·84 (3H, s, Ac), 2·18 (1H, d, 3-H), 2·20 (3H, s, 1-Me), and 6·40br (1H, 2-H) p.p.m.] were in accord with its formulation as the cyclopropene (**2a**).[5]



a; R^1 = R^2 = Me
b; R^1 = H, R^2 = Me
c; R^1 = R^2 = H

When a mixture of (**2a**) and n-butylamine was heated under reflux for 1 h or stirred for 3—4 h at room temperature a mixture (1:2) of the pyrroles[6] (**3a**) and (**4a**) [*ca.* 80% based on (**2a**)]. Irradiation of the *N*-oxide (**1a**) in dichloromethane, without isolation of (**2a**), followed by addition of the amine also gave (**3a**) and (**4a**) in about the same yields (6 and 3%) as were obtained by irradiation of the *N*-oxide in the presence of 3—5 mol. equiv. of the amine.

Similarly, the 1-oxides (**1b**) and (**1c**) were irradiated; the i.r. and n.m.r. spectra of the mixtures indicated that the corresponding cyclopropenyl ketones had been formed. Because of difficulty in isolation of these products, they were allowed to react with n-butylamine without isolation, affording the corresponding pyrroles (**3b**)[6] (8—10%) and (**3c**)[7] (8—9%).



In each of these reactions, deoxygenated starting material[8] was obtained (25—35%), but products such as pyrazoles and furans were not detected by t.l.c. or g.l.c.

Besides the work of Ogata *et al.*[1] on the photolysis of pyridazine *N*-oxides, Buchardt *et al.*[2] reported the formation of 3-benzoyl-5-phenylpyrazole (75%) from 2,6-diphenylpyridazine 1-oxide and we have also reported[3,4] the formation of tetraphenylfuran (30—35%) and 1-(1,2,3-triphenylcyclopropenyl)bicyclo[3,2,0]hepta-3,6-dien-2-one from the 3,4,5,6-tetraphenyl 1-oxide.

By analogy with the photolyses of other aromatic amine *N*-oxides[9] and with the formation of pyrazoles and furans from pyridazine *N*-oxides, oxaziridine (**5**) may be formed initially, followed by ring fission of the intermediate (**5**) or (**6**) to form the diazo-compound[2] (**7**). Ring closure of (**7**) may then give (**8**), followed by elimination[10] of N_2 to give cyclopropenyl ketone (**2**).

---

† In photolyses of (**1a**—**c**), (**1d**; R^1 = Cl, R^2 = Me), and (**1e**; R^1 = OMe, R^3 = Me) deoxygenated starting material was obtained mainly, except for (**1d**) and (**1e**), when traces (0·2%) of acetylpyrazoles were obtained. Other products included solvent adducts, *i.e.*, hydroxymethylpyridazines (<0·5%).

The formation of (**2**) *via* furans[11] or pyrazoles was excluded since photolysis of either with primary amines under similar conditions did not afford pyrroles. The effect of substituents and solvent is now being investigated.

With other primary amines, the corresponding *N*-substituted pyrroles were also obtained; these results will be reported elsewhere.

(*Received*, 12*th January* 1972; *Com.* 042.)

---

[1] M. Ogata and H. Klano, *Chem. Comm.*, 1967, 1176.

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

[3] T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Letters*, 1971, 2579.

[4] T. Tsuchiya, H. Arai, T. Tonami, and H. Igeta, *Chem. Pharm. Bull.* (*Japan*), 1972, **20**, 300.

[5] M. Vidal, B. Chollet, and P. Arnaud, *Tetrahedron Letters*, 1967, 1073; P. Arnaud, J. Pierre, and M. Vidal, *Bull. Soc. chim. France*, 1967, 3810; M. Vidal, J. Pierre, and P. Arnaud, *ibid.*, 1969, 2864.

[6] A. Couture and A. Lablache-Combier, *Tetrahedron*, 1971, **27**, 1059.

[7] H. Gross, *Chem. Ber.*, 1962, **95**, 2270; M. F. Fegley, N. M. Bortnick, and C. H. McKeever, *J. Amer. Chem. Soc.*, 1957, **79**, 4144

[8] There are many reports on the deoxygenation of the *N*-oxides, including those of pyridazine *N*-oxides. *Cf.* ref. 1, 3, and H Iegta, T. Tsuchiya, and H. Arai, *Chem. Pharm. Bull.* (*Japan*), 1968, **16**, 767; T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Letters* 1969, 2479; 1970, 2213.

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

[10] G. L. Closs and W. Boell, *Angew. Chem.*, 1963, **75**, 640.

[11] A. Couture and A. Lablache-Combier, *Chem. Comm.*, 1971, 891.