Photolysis of Pyridazine 1,2-Dioxides; Formation of the Novel 1,4,6,7-Dioxadiazocin Ring System

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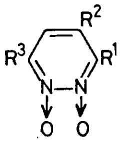
Summary Irradiation of pyridazine 1,2-dioxides in dichloromethane afforded 1,4,6,7-dioxadiazocins as major products, together with the deoxygenated pyridazines.

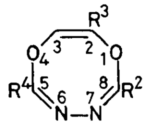
PHOTOCHEMICAL reactions of heterocyclic amine *N*-oxides, *e.g.*, pyridine,[1] pyridazine[2a,b,c] and pyrimidine *N*-oxides,[3] have been widely investigated. Photochemical reactions of *NN'*-dioxides of heteroaromatic compounds such as quinoxaline[4] and naphthiridine[5] have also been reported.

We now report that photo-isomerization of pyridazine 1,2-dioxides (**1**)[6] affords 1,4,6,7-dioxadiazocins (**2**), a novel ring system.

A 1—2% solution of the dioxide in dichloromethane was irradiated (200 W high-pressure Hg lamp; Pyrex) for 4—9 h under N_2 atmosphere and the product was chromatographed on silica gel.† In each case, (**2**) was isolated as the major product in the following yields together with 10—20% of the deoxygenated pyridazine:‡ (**2a**) 37%, m.p. 50—52 °C; (**2b**) 10%, b.p. 83—85 °C at 0·8 mmHg (bath temp.); (**2c**) 3%, b.p. 87—88 °C at 0·7 mmHg (bath temp.); and (**2d**) 10%, m.p. 95—96 °C.



(1)



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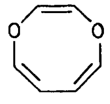


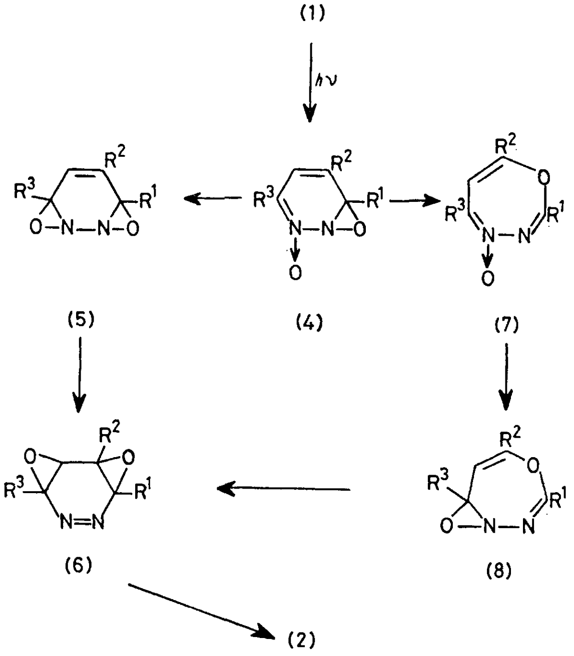
(3)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = Me; R^2 = R^3 = H$
c; $R^1 = R^3 = H; R^2 = Me$
d; $R^1 = R^3 = Me; R^2 = H$

The structures of (**2**) were confirmed by spectral data; *e.g.* the mass spectrum of (**2d**) showed peaks at *m/e* 112 (M^+) and 82 (base peak, $C_4H_6N_2$) which indicated that (**2d**) contained the -(Me)C=N-N=C(Me)- group. The i.r. spectrum of (**2d**) showed no hydroxy or amido-carbonyl absorptions, while an absorption was observed at 1610 cm^{-1} (KBr) which was assigned to C=C and/or C=N vibrations. The ^{1}H n.m.r. spectrum showed two singlets at δ 2·10 (5- and 8-Me) and 5·75 [2- and 3-H; *cf.* n.m.r. spectrum of 1,4-dioxocin (**3**)[7]] having an intensity ratio of 3 : 1 ($CDCl_3$).§

The structure of (**2d**) was also supported by its ^{13}C n.m.r. spectrum: δ ($CDCl_3$; Me_4Si) 10·56 (*sp*^{3}; Me), 89·98 (*sp*^{2}; C-2 and C-3), and 153·74 (*sp*^{2}; C-5 and C-8). It showed no u.v. absorption at >220 nm (EtOH). Spectra of the other analogues (**2a**—**c**) were consistent with data expected for the structures assigned.

The formation of the dioxadiazocins (**2**) is interesting in connection with the mechanism of the formation of cyclopropenyl ketones and pyrazoles by photolysis of pyridazine monoxides.[2a] By analogy with the photo-rearrangement of other heterocyclic amine *N*-oxides,[1,2a,b,c,3] the



oxaziridine (**4**) may be formed initially, followed by the formation of the intermediate (**6**) *via* the bis-oxaziridine (**5**). An alternative mechanism, in which (**4**) gives the oxadiazepine-*N*-oxide (**7**), followed by isomerization to (**6**) *via* the oxaziridine (**8**), is also possible.

The authors thank Dr. I. Suzuki of the National Institute of Hygienic Sciences for advice on the syntheses of pyridazine dioxides.

(*Received, 5th November* 1976; *Com.* 1226.)

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† A considerable amount of insoluble black residue was deposited after irradiation of each dioxide (**2a**—**d**).

‡ In the case of (**1d**), 3-acetyl-5-methylpyrazole (m.p. 92—94 °C) was obtained in 10% yield.

§ The ^{1}H n.m.r. spectrum of (**2a**) showed two singlets at δ 6·05 (2- and 3-H) and 7·38 (5- and 8-H) with equal intensities ($CDCl_3$).

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