

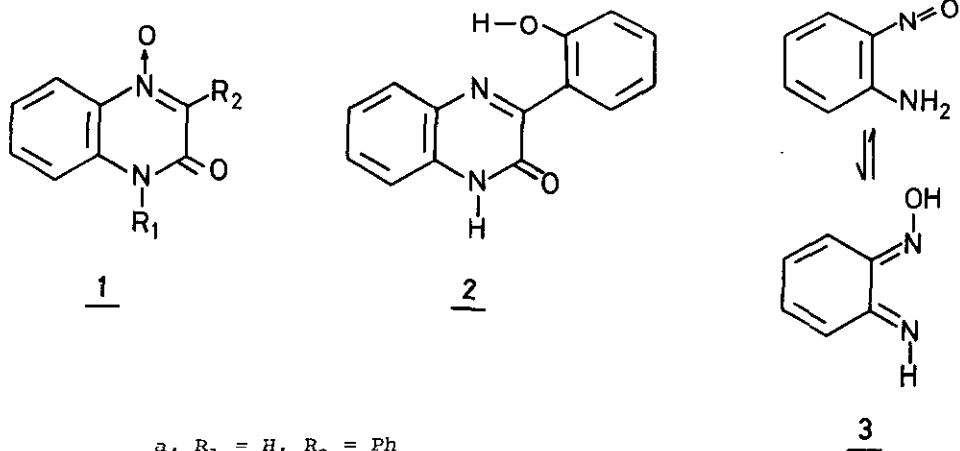
PHOTOLYSIS OF SOME QUINOXALIN-2-ONE 4-OXIDES

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Abstract - Upon photolysis, 3-phenylquinoxalin-2-one 4-oxides rearranged to 3-(o-hydroxyphenyl)-quinoxalin-2(1H)-one whereas 1-hydroxyquinoxalin-2-one 4-oxides yielded o-nitrosoaniline and o-nitroaniline.

Photolysis of quinoxaline 1,4-dioxides and quinoxaline 1-oxides has been investigated¹. Little is known about the photolysis of quinoxalin-2-one 4-oxides². This communication describes the photolysis of a number of quinoxalin-2-one 4-oxides (1a-d).

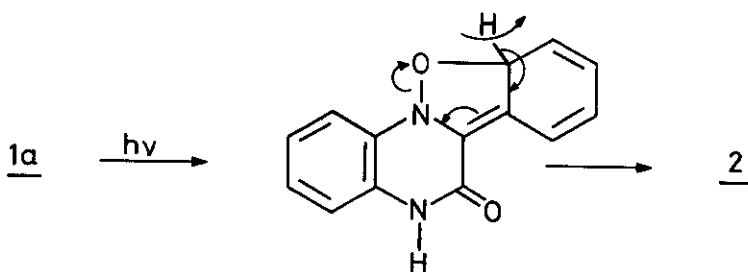


- a, $R_1 = H, R_2 = Ph$
- b, $R_1 = OH, R_2 = H$
- c, $R_1 = OH, R_2 = CH_3$
- d, $R_1 = OH, R_2 = Ph$

Quinoxalin-2-one 4-oxides 1a-c were prepared according to literature methods^{3,4}. We extended the Abushanab⁴ method to the preparation of quinoxalin-2-one 4-oxide 1d (32%, m.p. 193-5°, lit.⁵ 196°) via the condensation of o-benzoquinone dioxime with phenylglyoxal.

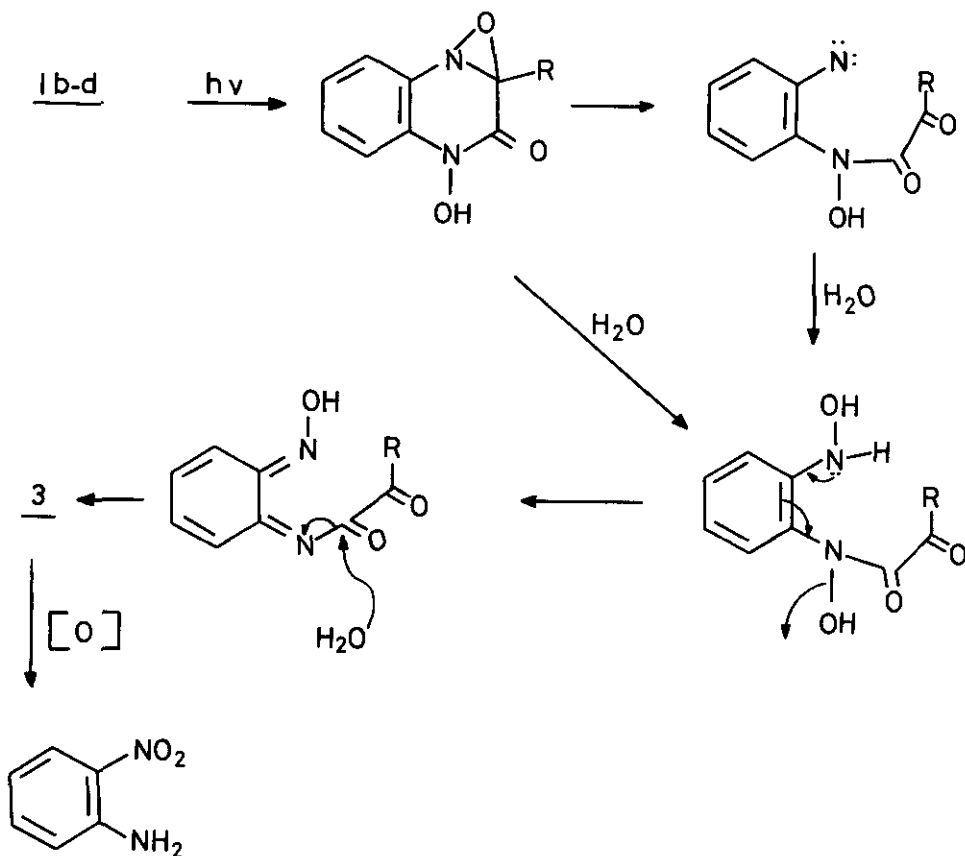
Sunlight irradiation of 1a (200 mg) in 90% methanol (350 ml) in a Pyrex flask for nine days resulted in changing the yellowish color of the solution to orange. Evaporation of the solvent to dryness and treatment of the residue with chloroform gave 3-(o-hydroxyphenyl)-quinoxalin-2(1H)-one (2) in 20% yield (m.p. 300°, MeOH, lit.⁶ 294-5°). The structure of 2 was established by comparison with an authentic sample⁶.

The formation of quinoxaline 2 appears to result from an intramolecular photochemical rearrangement of 1. This reaction is analogous to the photochemical rearrangement of 4-bromoazoxybenzene to 2-hydroxy-4-bromoazobenzene reported by Badger and Buttery⁷.



Quinoxaline 1a was recovered unchanged after heating it in a methanol solution for five days.

Photolysis of 1-hydroxyquinoxalin-2-one 4-oxides 1b-d took a different course than that of 1a. Sunlight irradiation of each of 1b-d in methanol for two days gave nitrosoaniline (3) and nitroaniline in low yields (1%) respectively. The yields were improved slightly (6%) when the irradiation was carried out in chloroform as a solvent. The identity of the products were established by comparison with authentic samples⁸. It is believed that nitroaniline resulted from oxidation of 3 by either 1b-d and/or air. No product analogous to 2 was detected from the photolysis of 1d. The formation of nitrosoaniline could be rationalized by the following mechanism.



All the above reactions (**1b-d**) are accompanied by darkening in the original coloration which probably slows down the rate of the primary reaction and introduces side reactions that account for the observed low yields.

Acknowledgment: The authors wish to thank Professor M.Z. Nazer for helpful discussions.

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Received, 20th November, 1979