PHOTOLYSIS OF SOME QUINOXALIN-2-ONE 4-OXIDES

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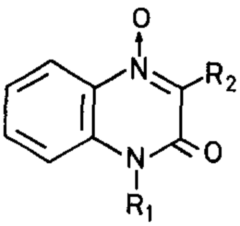
Abstract - Upon photolysis, 3-phenylquinoxalin-2-one 4-oxides rearranged to 3-(o-hydroxyphenyl)-quinoxalin-2(1H)-one whereas 1-hydroxyquinoxalin-2-one 4-oxides yielded o-nitrosoaniline and o-nitroaniline.

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



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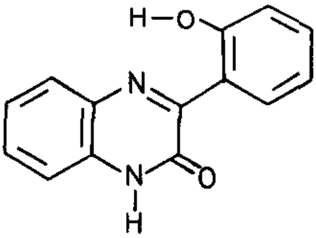

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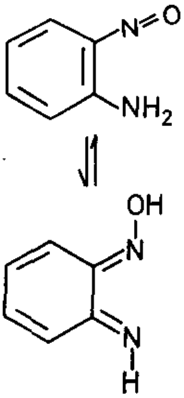

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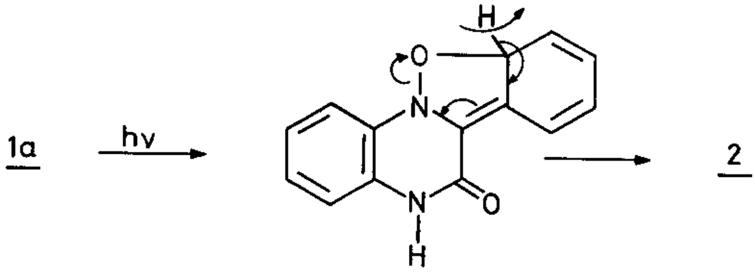
a, R_1 = H, R_2 = Ph
b, R_1 = OH, R_2 = H
c, R_1 = OH, R_2 = CH_3
d, R_1 = OH, R_2 = Ph

Quinoxalin-2-one 4-oxides 1a-c were prepared according to literature methods[3,4]. We extended the Abushanab[4] 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.

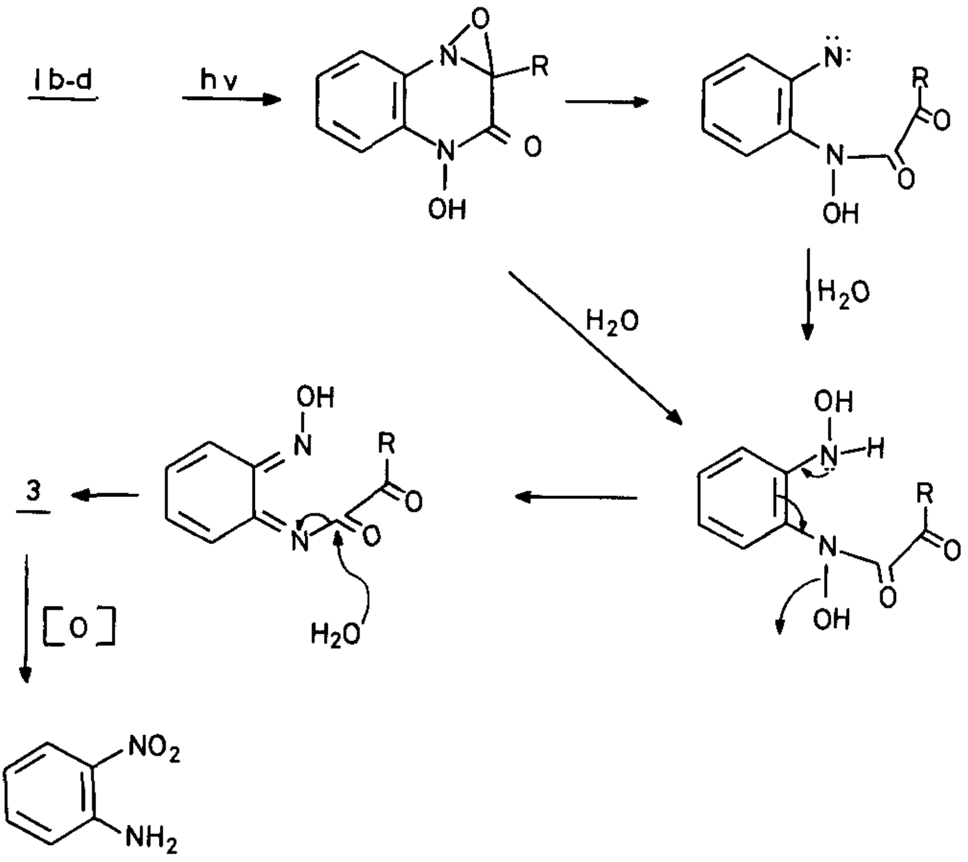
Sunlight irradiation of 1a (200 mg) in 90% methanol (350 ml) in a Pyrex flask for nine days resulted in changing the yellowish color of the solution to orange. Evaporation of the solvent to dryness and treatment of the residue with chloroform gave 3-(o-hydroxyphenyl)-quinoxalin-2(1H)-one (2) in 20% yield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

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 Buttery[7].



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 samples[8]. 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.

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REFERENCES

1. a) G.G. Spence, E.C. Taylor, and O. Buchardt, Chem. Rev., 1970, 70, 236.
   b) F. Bellamy and J. Streith, Heterocycles, 1976, 4, 1391.
   c) A.A. Jarrar, S.S. Halawi, and M.J. Haddadin, ibid., 1976, 4, 1077.
2. A.A. Jarrar and Z.A. Fataftah, Tetrahedron, 1977, 33, 2127
3. G. Tennant, J. Chem. Soc., 1964, 2666.
4. E. Abushanab, J. Org. Chem., 1970, 35, 4279.

5. J.C. Mason and G. Tennant, J.C.S. Chem. Comm., 1971, 586.

6. J.J. Zamet, M.J. Haddadin, and C.H. Issidorides, J. Chem. Soc. Perkin 1, 1974, 1687.

7. G.M. Badger and R.G. Buttery, J. Chem. Soc., 1954, 2243. We thank one of the referees for pointing to us this analogy.

8. M.Z. Nazer, M.J. Haddadin, J.P. Petridou, and C.H. Issidorides, Heterocycles, 1977, **6**, 541.

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