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PHOTOLYSIS OF SOME 1-HYDROXYBENZIMIDAZOLE-3-OXIDES

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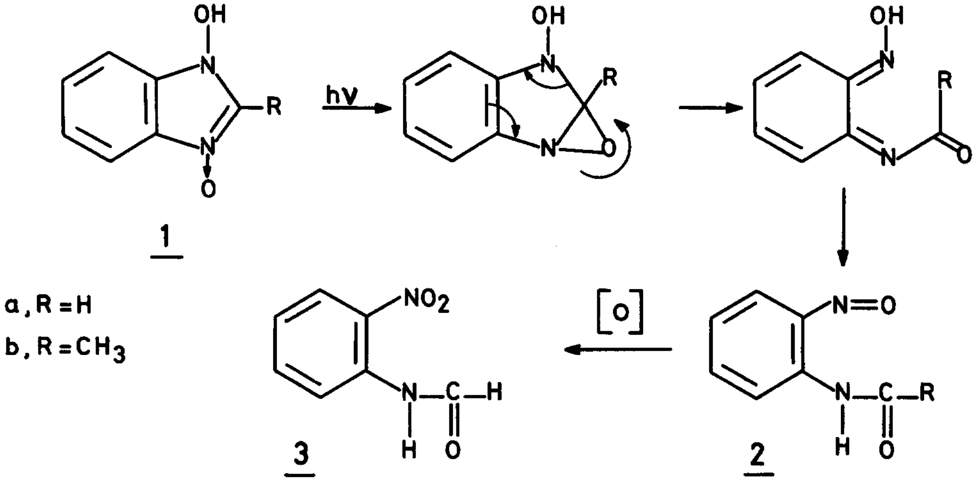
Although the photochemistry of some aromatic N-oxides has been thoroughly investigated[1], the photochemical reactions of benzimidazole N-oxides have received little attention. Ogata and coworkers[2] reported the formation of 1,3-benzylethylbenzimidazolone (71%) as the major product from the irradiation of 1-benzyl-2-ethylbenzimidazole-3-oxide. Similarly, Suschitzky and coworkers[3] found that 1-(n-propyl)-2-ethyl-5-chlorobenzimidazole-3-oxide yielded 1,3-(n-propyl)ethyl-5-chlorobenzimidazolone on photolysis. Recently, the formation of acetone-O-(2-nitrophenyl)oxime from the irradiation of 2,2-dimethyl-2H-benzimidazole-1,3-dioxide was briefly described[4].

In this communication, 1-hydroxybenzimidazole-3-oxide (1a) and 1-hydroxy-2-methylbenzimidazole-3-oxide (1b) were prepared by the method of Abu el-Haj[5]. Methanolic solutions (90%, 400 ml) of 1a (0.5 g) and 1b (0.5 g) were separately irradiated, in pyrex flasks, by sunlight for one day. The progress of the reaction was accompanied by the development of a yellow color that eventually became dark brown. The solution was evaporated to dryness and the residue extracted with hot petroleum ether (200 ml), the remainder of the residue was recrystallized from methanol to give 10-20% of the starting material. The greenish petroleum ether extract was evaporated and the products were separated by preparative TLC. Benzimidazole-3-oxide 1a gave N-formyl-o-nitroaniline (3, 2%, m.p. 117-8^{o}, IR 3280, 1675 cm^{-1}) which was identified by comparison with an authentic sample[6]. The isolation of 3 rather than the expected N-formyl-o-nitrosoaniline (2a) might be due to the oxidation of the latter on prolonged exposure. On the other hand, benzimidazole-3-oxide (1b) gave N-acetyl-o-nitrosoaniline (2b, 12%, m.p. 96-8°, IR 3300, 1675 cm^{-1}, NMR δ 2.25 (s, 3H), 7.15 (m, 3H), 8.44 (d, 1H), 9.9 (broad s, 1H)). 2b was obtained in 22% yield by irradiation with light from a Hanovia 679A36 high pressure mercury lamp with pyrex filter for two hours. 2b was also prepared by the acetylation of o-nitrosoaniline[7] with acetic anhydride.



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