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THE PHOTOCHEMISTRY OF AN AMINATED 1,4-BENZOQUINONE

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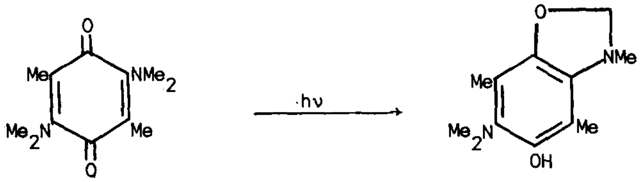
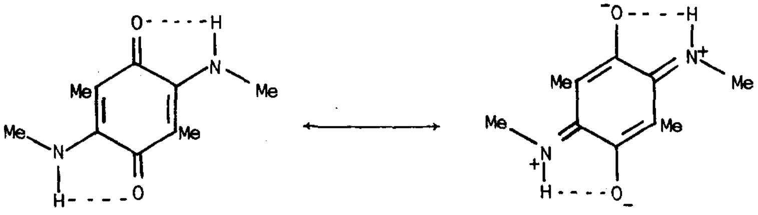
2,5- Dimethyl -1,4- benzoquinones bearing certain secondary amino substituents have been shown to photoisomerise readily in sunlight (e.g.1 → 2).[1]



1 2

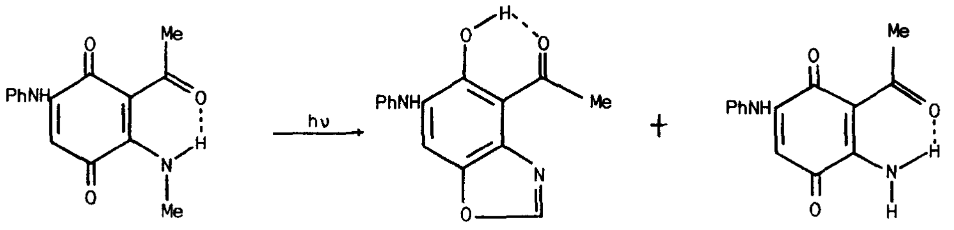
No reaction took place when the bismonomethylamino quinone 3 ↔ 4 was similarly irradiated,[1] probably because in the latter molecule hydrogen bonding (indicated in structures 3 and 4)[2] causes the N-methyls to be held away from the quinone carbonyls.



3 4

This communication describes the photochemistry of a quinone 5 bearing a primary methylamino substituent in which the N-methyl group is held proximate to the quinone carbonyl by means of an alternative hydrogen bond between the methylamino hydrogen and an acetyl group (see structure 5). Confirmation of strong hydrogen bonding by the methylamino proton is afforded by the p.m.r. spectrum [$CDCl_3$, δ ppm: 13.4 (br m, 1H, methylamino NH), 8.4 (br s, 1H, anilino NH), 7.8 - 6.9 (5H, m, ArH), 6.16 (s, 1H, quinonoid H), 3.56 (d, J = 6Hz, 3H, N methyl), 2.70 (s, 3H, acetyl methyl); double resonance irradiation at 13.4δ collapsed the doublet at 3.56δ to a singlet, showing that the very low field proton is that of the methylamino group]. That this hydrogen bond is with the acetyl rather than with the quinone carbonyl is supported by the course of the photoreaction.

When irradiated in sunlight in benzene solution under nitrogen, the quinone 5 was quantitatively converted into two new compounds. The major product (73%), a yellow crystalline material, has been assigned structure 6[3] [infrared spectrum (nujol): 3410 (N-H), 3115 (oxazole C-H), 1630 cm^{-1} (chelated aromatic carbonyl) and p.m.r. spectrum, CDCl$_3$, δ ppm: 13.67 (s, 1H, exchanged in D$_2$O, hydrogen bonded OH), 7.94 (s, 1H, oxazole H), 7.58 (s, 1H, ArH), 7.5 - 6.9 (m, 5H, Ar'H), 6.5 (br s, 1H, exchanged in D$_2$O, NH), 3.02 (s, 3H, methyl)]. A second product (27%), highly insoluble and maroon in colour, was shown to be the N-demethylated quinone 7 by an independent synthetic route.



5 6 7

Preparation of quinones 5 and 7 was achieved by ready nucleophilic displacement of aniline from 2-acetyl-3,6-bisanilino-1,4-benzoquinone by aqueous methylamine and aqueous ammonia respectively. These reactions have since been reported.[4]

The structure of the benzoxazole 6 was further confirmed by an alternative synthesis which involved the hydrogenation of the quinone 7 followed by the *in situ* treatment of the intermediate quinol with aqueous formaldehyde.

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2.(a) S. Dähne, J. Ranft, and H. Paul, Tetrahedror Letters, 1964, 3355.

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3. Satisfactory analytical data have been obtained for this compound.

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