Photosensitised Oxidation of 1-Naphthols

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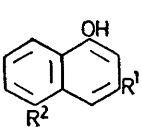
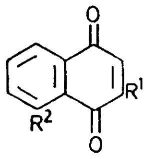
Summary Whereas oxidation of 1-naphthols with Fremy's salt often affords significant amounts of the corresponding 1,2-naphthoquinone, dye-sensitised photo-oxidation gives exclusively the 1,4-naphthoquinone *via* the addition of singlet oxygen to the naphthalene ring.

The photosensitised oxidation of phenols has received considerable attention in recent years,[1–4] but the generally more reactive naphthols have not been investigated. We now report the efficient dye-sensitised photo-oxidation of 1-naphthols to 1,4-naphthoquinones, and provide evidence for the reaction mechanism.

Solutions of the naphthols (**1a**—**d**) (10^{-2} M) in methylene chloride–methanol (9:1) containing Methylene Blue were irradiated with visible light (tungsten lamp) under oxygen. Oxygen uptake was rapid at 15 °C, and ceased abruptly after the absorption of 1 mol. equiv. T.l.c. revealed only the corresponding 1,4-naphthoquinones, and none of the 1,2-isomers. Except for (**2b**), which was isolated by extraction with boiling light petroleum, the 1,4-quinones were isolated by chromatography, and were identified by comparison of i.r. spectra and m.p. with those of authentic samples. Yields of pure material were: (**2a**), 64%; (**2b**), 70%; (**2c**), 43%; and (**2d**), 50%.



(1)



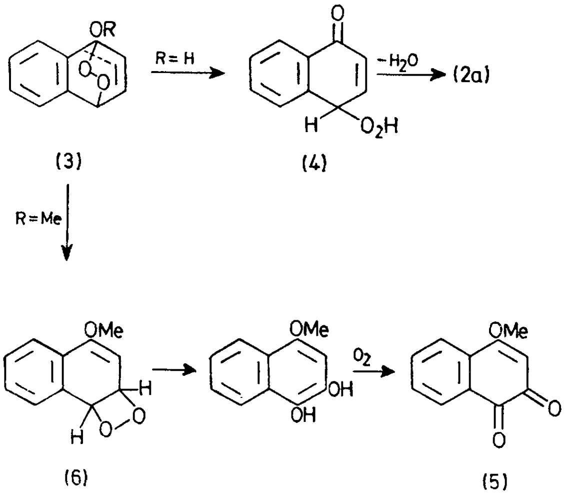
(2)

a, $R^1 = R^2 = H$
b, $R^1 = H$, $R^2 = OH$
c, $R^1 = H$, $R^2 = OMe$
d, $R^1 = OH$, $R^2 = H$

These reactions are of general synthetic value, as chemical oxidation of 1-naphthols often gives significant amounts of the 1,2-quinone isomers, particularly when 5-substituents are present.[5] For example, only the 1,2 naphthoquinone is formed by oxidation of (**1c**) with Fremy's salt. The above procedure provides the most convenient route to juglone (**2b**).

The photosensitised oxidations appear to involve singlet oxygen (presumably ${}^1\Delta_g$), since in the presence of 1,4-diazabicyclo[2.2.2]octane[6] (0·2 M) the reaction of (**1a**) was completely suppressed. Free radical processes can be discounted, since oxidation of (**1a**) was unaffected by 2,6-di-t-butylphenol[7] (10^{-2} M). Moreover, heating (**1c**) with the *endo*-peroxide of 9,10-diphenylanthracene[8] in benzene gave (**2c**), and none of the 1,2-naphthoquinone.

These reactions appear to be much more efficient than the corresponding reactions of phenols [*cf.* the negligible competitive effect of 2,6-di-t-butylphenol in the photo-oxidation of (**1a**)], and thus they probably follow a different reaction pathway. Phenols apparently suffer hydrogen abstraction from the hydroxy group by both singlet oxygen and the triplet excited state of the sensitiser.[1] The phenoxyl radical adds triplet oxygen at the *para*-position, and ultimately forms the 1,4-benzoquinone. The low rate of oxidation and low product yields can be attributed to the difficult hydrogen abstraction step and to other reaction pathways available to the phenoxyl radical.[2] Since free radical oxidation of 1-naphthols, presumably involving naphthoxyl radicals, often gives 1,2-quinones, the absence of the latter from the photo-oxidation reactions suggests that hydrogen abstraction is not the principal reaction pathway. This is demonstrated most clearly with (**1c**), which gives only the 1,4-quinone photochemically, and only the 1,2-quinone on heating with benzoyl peroxide in benzene under oxygen (unpublished observation.)



Scheme

An alternative mechanism, which has been suggested for some phenol oxidations,[3] would involve addition of singlet oxygen to the naphthol, thus giving the *endo*-peroxide (**3**, R = H). The peroxide can rearrange to (**4**) by intramolecular hydrogen abstraction, and thence to the 1,4-naphthoquinone by elimination of water (Scheme). Although cycloaddition of singlet oxygen occurs with 1,4-dimethoxynaphthalene,[9] similar addition has not been observed for monosubstituted naphthalenes. To test the feasibility of such a reaction, the photosensitised oxidation of 1-methoxynaphthalene was examined. This compound underwent photo-oxidation at a rate comparable to the naphthols (**1a**—**d**), absorbing 2 mol. equiv. of oxygen. The sole tractable product was 4-methoxy-1,2-naphthoquinone (**5**), isolated in 20% yield. It is reasonable to assume that the *endo*-peroxide (**3**, R = Me) is formed, and as this cannot form a hydroperoxide analogous to (**4**), it rearranges to the dioxetan (**6**). Rearrangement of (**6**) to 1,2-dihydroxy-4-methoxynaphthalene, and oxidation of the latter by a second oxygen molecule would give the observed product

(Scheme). The evidence is thus in favour of a cycloaddition mechanism for the photo-oxidation of 1-naphthols, rather than a pathway involving hydrogen abstraction.

It is interesting that 2-naphthol, which is readily oxidised to 1,2-naphthoquinone by chemical methods, is photo-oxidised only with difficulty, presumably because of its reluctance to undergo cycloaddition with singlet oxygen.

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