

Photochemical Oxidation of a Quinophthalone Dye

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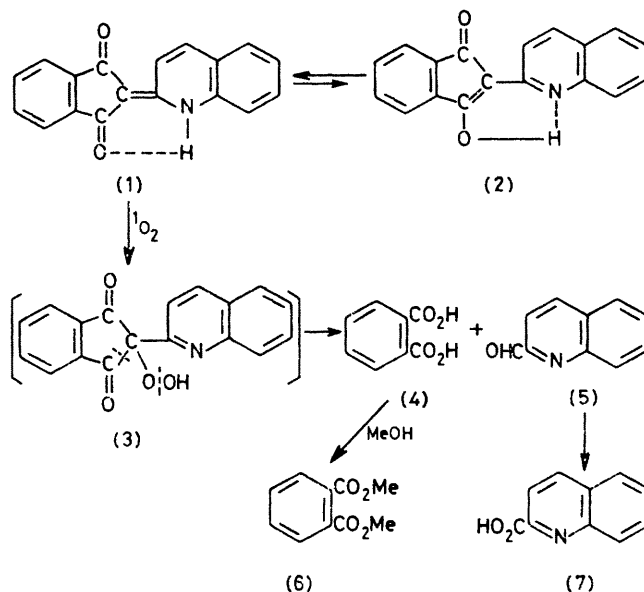
Summary Self-sensitised and Methylene Blue- or Rose Bengal-sensitised photo-oxidation of 2-(2-quinolyl)-indane-1,3-dione (**1**) in solution gives phthalic acid, quinoline-2-carbaldehyde, and quinoline-2-carboxylic acid, *via* the reaction of singlet oxygen with (**1**).

THE contribution of singlet oxygen to the photofading of some dyes has been examined recently. For example, Griffiths and Hawkins have reported on the photochemical oxidation of 4-arylaazo-1-naphthols and analogous dyes,¹ and we have also showed that 1-arylaazo-2-naphthols² and indigo³ undergo self-sensitised or dye-sensitised photo-oxidation in solution. We have investigated the photofading behaviour of 2-(2-quinolyl)indane-1,3-dione [(**1**), λ_{\max} 418 and 442 nm] in solution, and now report this photochemical oxidation together with evidence for the mechanism of the reaction.

Solutions of (**1**) in methanol, acetone, or dichloromethane-methanol (9:1, v/v) faded under oxygen on irradiation with filtered ($\lambda > 390$ nm) or unfiltered radiation from a 500 W high-pressure mercury lamp (Ushio Electric Inc., UI-501 type). The effect of singlet oxygen sensitisers was examined; Methylene Blue (λ_{\max} 656 nm) and Rose Bengal (λ_{\max} 566 nm) accelerated the reaction. The photo-oxidation proceeded smoothly with filtered radiation ($\lambda > 520$ nm) which was absorbed by the sensitizer only, and analysis of the products showed that the reaction was identical to the slower self-sensitised process. When (**1**) was irradiated with filtered radiation ($\lambda > 520$ nm) in dichloromethane-methanol containing Rose Bengal, the products were phthalic acid (**4**) (38%), dimethyl phthalate (**6**) (9%), quinoline-2-carboxylic acid (**7**) (5%), and quinoline-2-carbaldehyde (**5**) (trace), which were identified by comparison with authentic samples (m.p., u.v. spectra, and R_f values). In addition, the formation of unidentified material which seems to be identical to the compound

derived from irradiation of quinoline-2-carbaldehyde alone under these conditions was observed by t.l.c.

The catalytic effect of Methylene Blue or Rose Bengal suggested the involvement of singlet oxygen (presumably $^1\Delta_g$) in the photo-oxidation of (**1**), and the most probable mechanism for the reaction is shown in the Scheme.



SCHEME

The quinophthalone derivative (**1**) exists in equilibrium with the tautomeric form (**2**), and it is known that form (**1**) is more sensitive than (**2**) towards photo-decomposition.⁴ Attack on form (**1**) by singlet oxygen should lead to the

unstable peroxide (3), presumably by the 'ene' reaction or possibly *via* a 'peroxide' type intermediate.^{1,2} It seems that (3) is thermally or photochemically decomposed to give (4) and (5).

Further evidence for the involvement of singlet oxygen was obtained by quenching experiments. In the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) or nickel dimethyldithiocarbamate (NMC)⁵ the rate of the photo-oxidation was retarded. The possibility of a free-radical reaction was also examined using 2,6-di-*t*-butyl-*p*-cresol as a radical scavenger. The rate of photo-oxidation of (1) was only slightly altered in the presence of 2,6-di-*t*-butyl-*p*-cresol. The effect of chemical sources of singlet oxygen on (1) was examined. Thus, (1) was oxidised to the same products as those produced by photo-oxidation by singlet oxygen formed from hydrogen peroxide and sodium hypochlorite,⁶ and the reaction was also suppressed by DABCO.

Additional evidence for the intermediacy of singlet oxygen was obtained by carrying out competitive photo-

oxygenation experiments as described by Wilson.⁷ Compound (1) (4.0×10^{-5} M) and NMC were used as acceptors in acetone [NMC acts as a quencher only, while (1) undergoes oxidation and also acts as its own sensitiser]. Assuming steady states for (1)* and $^1\text{O}_2$ concentrations, the reciprocal of the rate of decomposition of (1) and the concentration of NMC were found to have a linear relationship, which leads to a value of $k(\text{NMC})/k(1)$ of *ca.* 15 at all times for the self-sensitised photo-oxidation ($\lambda > 390$ nm), and for the Methylene Blue- and Rose Bengal-sensitised photo-oxidation ($\lambda > 520$ nm). NMC reacts with singlet oxygen about 15 times as fast as (1), and so it is reasonable to assume that the photochemical oxidation of (1) in solution proceeds entirely *via* singlet oxygen by a self-sensitised process.

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