The Photochemical Oxidation of 4-Arylazo-1-naphthols

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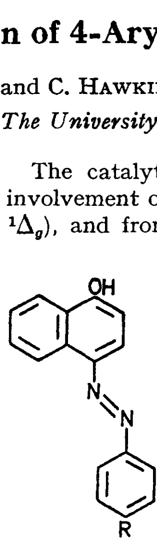
Summary The 4-arylazo-1-naphthols (**1**) undergo self-sensitised or dye-sensitised photo-oxidation in solution, giving 1,4-naphthaquinone and the aryl-diazonium ion.

THE photochemistry of aromatic azo-compounds is of importance particularly in connection with the fading of azo-dyes. The favoured mechanism for the photochemical degradation of azo-dyes involves reductive cleavage of the azo-group,[1] and although oxidative mechanisms have been suggested, no firm chemical evidence has been obtained for such processes. We have investigated the 4-arylazo-1-naphthols (**1**), members of an important class of azo-dyes, and now report their photochemical oxidation together with evidence for the mechanism of the reaction.

Solutions of (**1**; R = Me) in methanol were stable to visible light (200 W tungsten source) under anaerobic conditions, but decomposed in the presence of oxygen. The effect of singlet oxygen sensitisers was examined, and it was found that methylene blue (λ_{max} 656 nm) accelerated the reaction, without itself being affected. The photo-oxidation proceeded smoothly with filtered light ($\lambda > 600$ nm) which was absorbed by the sensitiser only, and analysis of the products showed that the reaction was identical to the slower self-sensitised process. The major monomeric product (21%) was isolated and identified as 1,4-naphthaquinone by comparison with an authentic sample (mixed m.p. and i.r.). In addition to polymer, the residual material contained a small quantity of highly coloured products, the principal component of which was isolated (0·3%) by preparative t.l.c. and shown to be identical to the bisazo-compound (**3**) prepared from (**1**; R = Me) and *p*-toluenediazonium chloride.

The catalytic effect of methylene blue suggested the involvement of singlet oxygen in the reaction (presumably $^1\Delta_g$), and from a consideration of the photo-oxidation of simple hydrazones[2] a mechanism can be postulated to account for the observed products. The azo-compounds (**1**) exist in equilibrium with their hydrazone tautomeric



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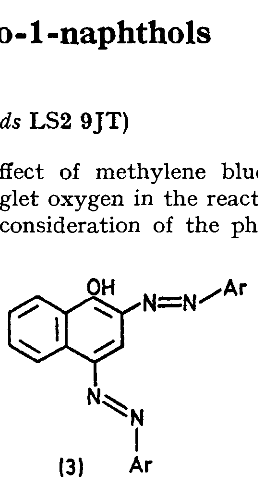

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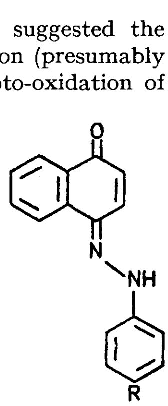

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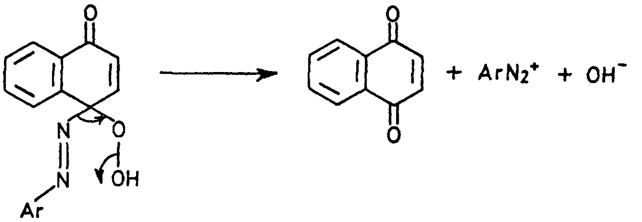

(4)

Ar = *p* - tolyl

forms (**2**) in solution. In methanol at room temperature the ratio of azo to hydrazone forms for (**1**; R = Me) is *ca.* 3:1. Attack at the hydrazone function by singlet oxygen should lead to the unstable peroxide (**4**),[2] presumably by the 'ene' reaction,[3] or possibly *via* a 'perepoxide' type intermediate.[4] One of the thermal decomposition pathways available to (**4**) is indicated, and leads to 1,4-naphthaquinone and the *p*-toluenediazonium ion. The latter species would be trapped by (**1**; R = Me) to give the bisazo-compound (**3**). The low yield from this step is to be expected from the inherent instability of the diazonium ion and the low coupling efficiency of (**1**; R = Me) in neutral solution. The involvement of the hydrazone form in the reaction is assumed by analogy with the known reactions of simple hydrazones with singlet oxygen, although oxidation of the hydroxyazo-form to give the same intermediate peroxide (**4**) cannot be discounted. However, it is of interest that the *O*-methyl ether of (**1**; R = Me) is completely insensitive to photo-oxidation under the conditions employed.

Further evidence for the intermediacy of singlet oxygen was sought by quenching experiments. 1,4-Diazabicyclo-[2,2,2]octane has been shown to quench singlet oxygen without affecting free radical reactions.[5] In 2×10^{-3}M methanolic solutions of this amine the rate of formation of 1,4-naphthaquinone from (**1**; R = Me) was reduced by *ca.* 25%. The possibility of free radical reactions was also examined using 2,6-di-t-butylphenol as a radical scavenger. Although an efficient inhibitor of radical oxidations, this compound appears to have no effect on singlet oxygen reactions,[6] and in the presence of a one molar proportion of the phenol, the rate of formation of 1,4-naphthaquinone from (**1**; R = Me) was unaltered. Thus it appears that singlet oxygen is involved in the reaction.

The generality of the sensitised photo-oxidation was shown with the derivatives (**1**; R = MeO, H, Cl, and NO_2), and in each case 1,4-naphthaquinone was formed. The relative rates of quinone formation were in the order Me $\sim$ MeO $>$ H $>$ Cl $>$ NO_2, which is to be expected[7] for an initial electrophilic attack by singlet oxygen at the hydrazone function. The relevance of these solution phase reactions to the fading of dyes on solid substrates was shown by irradiating (**1**; R = Me) adsorbed on silica gel with visible light in the presence of air. Identical products to those formed in the solution reactions were obtained.

We thank the S.R.C. for a research studentship (to C.H.).

(*Received*, 9*th February* 1972; *Com.* 215.)

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