Oxidation by Singlet Oxygen of Arylazonaphthols exhibiting Azo–Hydrazone Tautomerism

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Self-sensitised and Methylene Blue-sensitised photo-oxidation of 4-arylazo-1- and 1-arylazo-2-naphthols gives 1,4- and 1,2-naphthoquinone, respectively, *via* the reaction of singlet oxygen with the hydrazone tautomeric forms. The reactivity in both cases decreases with increasing electron-withdrawing strength of substituents in the aryl ring.

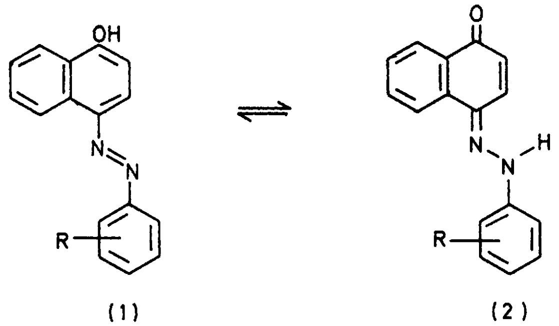
THE azo dyes are the most important single group of dyestuffs at the present time, yet little is known about the mechanisms of their photofading reactions. Many hydroxy-azo-dyes exist in azo–hydrazone tautomeric equilibrium, provided that the hydroxy-group is situated *ortho* or *para* to the arylazo-residue. The known sensitivity of simple hydrazones towards photo-oxidation[1] suggested that the photodegradation of these dyes might involve the hydrazone form, and that singlet oxygen might be a reactive intermediate in these processes.

In a preliminary study,[2] the 4-arylazo-1-naphthols (1) were found to undergo sensitised photo-oxidation, quenching experiments suggesting a singlet oxygen mechanism. We now report additional evidence for the mechanism of these reactions, and have shown that the 1-arylazo-2-naphthols undergo photodegradation in solution by a similar route.

RESULTS AND DISCUSSION

Photo-oxidation of 4-*Arylazo*-1-*naphthols*.—The dye chosen for detailed study was 4-(*p*-tolylazo)-1-naphthol (1a), which exists in solution in equilibrium with the hydrazone form (2a).[3] In methanol the ratio of hydrazone to azo-compound concentration is *ca*. 1 : 3. Solutions of (1a) in methanol containing Methylene Blue as sensitiser were irradiated under oxygen with filtered visible radiation ($\lambda > 570$ nm); smooth decomposition of the azo-compound occurred. 1,4-Naphthoquinone was isolated in 21% yield, together with a mixture of several red compounds. Separation of the latter by preparative t.l.c. afforded the predominant component, shown to be 2,4-bis-(*p*-tolylazo)-1-naphthol by comparison with a sample prepared from (1a) and toluene-*p*-diazonium chloride in strongly alkaline solution.

The most probable mechanism for the photo-oxidation of (1a) is shown in Scheme 1, and involves attack by photochemically generated singlet oxygen (presumably $^1\Delta_g$) on the hydrazone form (2a) in a concerted 'ene' reaction (or possibly to give an epidioxide intermediate).[4] This would lead to the hydroperoxide (3), which could decompose homolytically or heterolytically to 1,4-naphthoquinone and the toluene-*p*-diazonium ion. The lowest excited singlet and triplet states of Methylene Blue should lie well below those of (1a), and thus energy transfer to (1a) can be neglected. The formation of the bisazo-compound can be accounted for by the coupling of the diazonium ion to (1a).

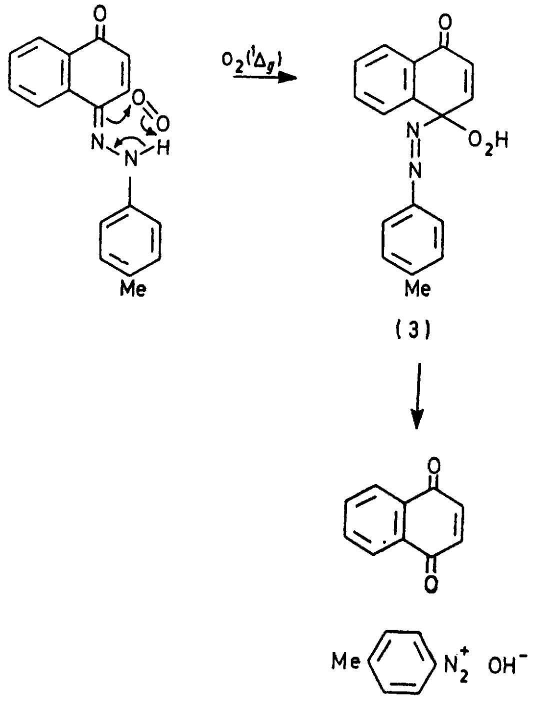


(1) (2)

a ; R = *p*-Me b ; R = *p*-MeO

c ; R = H d ; R = *p*-Cl

e ; R = *m*-Cl f ; R = *p*-Ac



SCHEME 1

The intermediacy of singlet oxygen was suggested by the efficient quenching of the reaction with 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.4M),[5] whereas 2,6-di-t-butylphenol, an efficient peroxide-radical scavenger,[6] had no effect on the rate of formation of 1,4-naphthoquinone. However, quenching by DABCO cannot be regarded as conclusive evidence for the involvement of singlet oxygen, as quenching of the sensitiser itself could occur. Additional evidence was obtained by examining the effect of chemical sources of singlet oxygen on (1a). Thus the *endo*-peroxide of 9,10-diphenylanthracene[7] was heated with the azo-dye in benzene under nitrogen; the formation of 1,4-naphthoquinone was observed. Similarly, the azo-compound was oxidised to 1,4-naphthoquinone by singlet oxygen formed from hydrogen peroxide and sodium hypochlorite,[8] and the reaction was suppressed by DABCO.

The involvement of singlet oxygen in the reaction is thus established, but it is not possible to differentiate between a concerted 'ene' (or possibly epidioxide) reaction and a two-step process involving hydrogen abstraction from the NH group by singlet oxygen. (The triplet excited state of the sensitiser could also take part

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[1] G. O. Schenck and H. Wirth, *Naturwiss.*, 1953, **40**, 141.

[2] J. Griffiths and C. Hawkins, *J.C.S. Chem. Comm.*, 1972, 463.

[3] A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 1953, 1443.

[4] W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, 1969, **91**, 7771.

[5] C. Ouannès and T. Wilson, *J. Amer. Chem. Soc.*, 1968, **90**, 6527.

[6] C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Letters*, 1965, 4111.

[7] H. H. Wasserman and J. R. Scheffer, *J. Amer. Chem. Soc.*, 1967, **89**, 3073.

[8] C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Amer. Chem. Soc.*, 1968, **90**, 975; E. McKeown and W. A. Waters, *J. Chem. Soc.* (*B*), 1966, 1040.

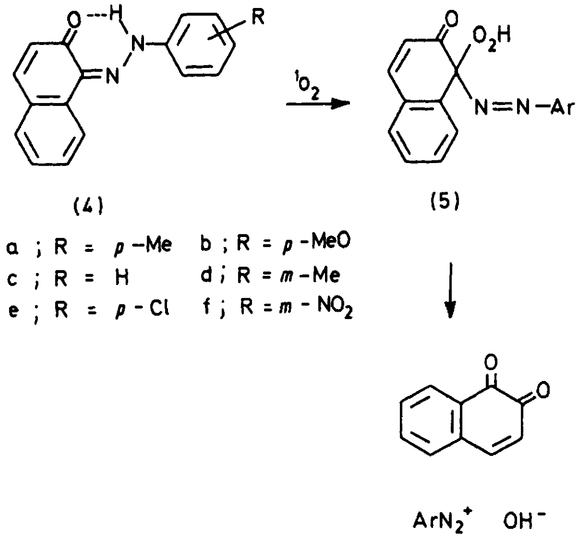
in hydrogen abstraction, but the DABCO quenching experiments suggest that this is not significant.) In the absence of Methylene Blue, self-sensitised photo-oxidation of (1a) occurred, at a significantly lower rate. The formation of singlet oxygen by energy transfer from an azo-compound is unusual, but was confirmed by the observation that (1a) sensitised the photo-oxidation of tetraphenylcyclopentadienone to *cis*-dibenzoylstilbene.[9] Obviously one cannot distinguish between the azo and hydrazone forms as the sensitising species.

Although attack on the hydrazone form (2a) by singlet oxygen seems most likely, the possibility of direct attack on the azo-form (1a) must also be considered. Addition of singlet oxygen across the substituted ring of the naphthalene system of (1a) could lead to the hydroperoxide (3); this type of reaction has been observed for simple 1-naphthols.[10] However, two observations preclude this possibility. Thus the methyl ether of (1a) is extremely resistant to photo-oxidation, whereas 1-methoxynaphthalene reacts readily.[10] Secondly, (1a) and 1-(*p*-tolylazo)-2-naphthol are photo-oxidised at roughly similar rates, presumably by the same mechanism, whereas 2-naphthol is markedly more resistant to photo-oxidation than 1-naphthol.[10] The evidence thus favours the involvement of the hydrazone form in the photo-oxidation.

The generality of the photosensitised oxidation was demonstrated with compounds (1a—f), which were converted into 1,4-naphthoquinone at different rates. The change in hydrazone concentration with time was measured spectrophotometrically for solutions in benzene–methanol (4 : 1) containing equal amounts of Methylene Blue, with light of $\lambda > 570$ nm. The reactions were first-order with respect to hydrazone, which is to be expected if singlet oxygen is generated at a constant rate and if the rate-determining step is the ' ene ' addition process. The relative rate constants at 15 °C, corrected for the position of azo–hydrazone equilibrium, were: *p*-MeO, 3.9; *p*-Me, 1.9; H, 1.0; *p*-Cl, 1.0; *m*-Cl, 0.56; *p*-Ac, 0.13. Thus substituents diminishing the electron density at the hydrazone grouping reduce the reactivity towards singlet oxygen. A similar observation has been made in the ' ene ' reaction of singlet oxygen with ring-substituted αββ-trimethylstyrenes.[11]

Photo-oxidation of 1-*Arylazo*-2-*naphthols*.—The 1-arylazo-2-naphthols exist to a significant extent in the hydrazone form (4) in solution;[12] thus it was of interest to examine their reactions with singlet oxygen. By analogy with the *para*-isomers (2), 1,2-naphthoquinone should be formed *via* the intermediate peroxide (5) (Scheme 2). Steric factors would render a concerted ' ene ' reaction less likely, although the relief of *peri*-interactions on forming (5) would favour the reaction. It is more likely that a two-step reaction would be involved, where singlet oxygen abstracts hydrogen from the NH group, and the hydroperoxide radical combines with the resultant hydrazyl radical to give (5).

The orange compound (4a) exists about 50% in the hydrazone form in methanol, and its photo-oxidation was examined for comparison with the isomer (1a). Thus under the conditions described for (1a), with Methylene Blue as sensitiser, photo-oxidation occurred roughly ten times more slowly, and 1,2-naphthoquinone was formed in about 35% yield. Because of the instability of the quinone this yield represents a lower limit, and was estimated spectrophotometrically after separating 1,2-naphthoquinone from the reaction mixture by preparative t.l.c. No bisazo-compounds were detected, which is to be expected in view of the very low coupling efficiency of (4a).



SCHEME 2

The photosensitised oxidation could be suppressed effectively by DABCO (0.4M), but was unaffected by 2,6-di-t-butylphenol. Direct chemical evidence for the involvement of singlet oxygen was difficult to obtain, since the low reactivity of (4a) necessitated longer reaction times, and under these conditions 1,2-naphthoquinone was unstable. However, convincing physical evidence for the role of singlet oxygen was obtained by the deuterium isotope method described by Kearns *et al.*[13] These authors noted that in D_2O–CD_3OD (1 : 1) the lifetime of singlet oxygen ($^1\Delta_g$) was increased ten-fold as compared with H_2O–CH_3OH, and the resultant increase in photo-oxidation rate could be used diagnostically for singlet oxygen. When oxygenated solutions of (4a) (10^{-4}M) in 1 : 1 D_2O–CD_3OD and in 1 : 1 H_2O–CH_3OH containing equivalent amounts of Methylene Blue were irradiated ($\lambda > 570$ nm) under identical conditions, it was found that after 5 min the deuteriated solutions showed

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[9] J. Griffiths and C. Hawkins, *J. Soc. Dyers and Colourists*, 1973, **89**, 173; R. W. Murray, W. C. Lumma, and J. W. P. Lin, *J. Amer. Chem. Soc.*, 1970, **92**, 3205.

[10] J. Griffiths, K. Y. Chu, and C. Hawkins, *J.C.S. Chem. Comm.*, 1976, 676.

[11] C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, 1971, **93**, 5162.

[12] A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, 1952, 4793.

[13] P. B. Merkel, R. Nilsson, and D. R. Kearns, *J. Amer. Chem. Soc.*, 1972, **94**, 1030.

64% conversion, whereas the undeuteriated solutions showed only 14% conversion. Thus the photo-oxidation of (4a) proceeds predominantly by a singlet oxygen mechanism.*

Self-sensitised oxidation of (4a) was also observed, although this was less efficient than with Methylene Blue. The azo-compound sensitised the photo-oxidation of tetraphenylcyclopentadienone more rapidly than did (1a).

As for the *para*-isomers (1), the photosensitised oxidation of the 1-arylazo-2-naphthols proved to be a general reaction. Thus the derivatives (4a—f) were photo-oxidised to 1,2-naphthoquinone in the presence of Methylene Blue, the rate decreasing with the increasing electron-withdrawing strength of the aryl substituents. The reactions followed first-order kinetics with respect to hydrazone, and the relative rate constants (corrected for the azo–hydrazone equilibrium) at 15 °C were: *p*-MeO, 4.0; *p*-Me, 1.4; H, 1.0; *m*-MeO, 0.82; *p*-Cl, 0.45; *m*-NO$_2$, 0.16.

Relevance to Photofading of Azo-dyes in Commercial Usage.—Few *para*-derivatives (1) are used commercially, whereas the *ortho*-compounds based on (4) are used extensively as textile dyes and pigments. The ability of these dyes to sensitise singlet oxygen, which can then cause degradation of the dye, suggests that photochemical fading in commercial usage might proceed by this mechanism. In the adsorbed state on silica gel, which is more relevant to the conditions involved in the practical application of these dyes, the derivatives (1a—f) and (4a—f) were found to undergo photo-oxidation to 1,4- and 1,2-naphthoquinone respectively, on prolonged exposure to visible light and air, and the fading processes could be inhibited by DABCO. Similar results were obtained for (4a) adsorbed on polypropylene film. It is noteworthy that there is a commercial preference for dyes (4) bearing strongly electron-withdrawing groups in the aryl ring, as it has been established empirically that these have better photochemical stability. This can now be explained theoretically in terms of the singlet oxygen mechanism.

Many *ortho*-hydroxy-azo-dyes show greatly improved photostability when complexed with transition metals (*e.g.* Cr^{III}, Ni^{II}),[14] and in addition to general protection of the hydrazone ligand by the metal ion, the chelates might themselves act as quenchers of singlet oxygen.[15] To examine this further, the derivative (4a) was chelated with nickel(II) acetate in aqueous ethanol and irradiated under oxygen with visible light in the presence of Methylene Blue. Control solutions of (4a) containing no added nickel salt showed 25% degradation after 45 min, whereas the metal complex showed no decomposition. The chelate does not quench singlet oxygen, however: it had no effect on the Methylene Blue-sensitised oxidation of tetraphenylcyclopentadienone. Metal complexation thus improves photochemical stability solely by modification of the hydrazone function.

EXPERIMENTAL

Photosensitised Oxidation of 4-(p-*Tolylazo*)-1-*naphthol* (1a).—An oxygen-saturated solution of (1a) (0.15 g) and Methylene Blue (0.015 g) in methanol (200 ml) was exposed to a 250 W tungsten lamp with dyed cellophane films to filter the radiation ($\lambda > 570$ nm). After 24 h the solvent was removed under reduced pressure, and the resulting solid was dissolved in a little methylene chloride and separated by preparative t.l.c. (silica; benzene). Three major bands were isolated, and after extraction with methanol afforded starting material (0.033 g), 1,4-naphthoquinone (0.017 g), and 2,4-bis-(*p*-tolylazo)-1-naphthol (0.5 mg). The quinone and bis-azo-dye were identified by comparison (i.r. and m.p.) with authentic samples.

Self-sensitised Photo-oxidation of the Naphthol (1a).—The previous experiment was repeated using two solutions, one with Methylene Blue and one with no added sensitiser. Irradiation was carried out for 20 min with unfiltered light ($\lambda >$ *ca.* 350 nm); the solution with Methylene Blue showed 80% conversion and the solution without this dye showed 1% conversion. T.l.c. analysis of both solutions showed the same distribution of products. In the presence of 0.4M-DABCO, the self-sensitised reaction showed no degradation after 1 h irradiation.

Quenching of the Photosensitised Oxidation of the Naphthol (1a) *with DABCO.*—Solutions of (1a) (2 mg) and Methylene Blue (5 mg) in benzene (40 ml) and methanol (10 ml) were prepared, and half were made 0.4M in DABCO. The solutions were flushed with oxygen, sealed in identical Pyrex tubes, and exposed to the filtered radiation ($\lambda > 570$ nm) from a 650 W tungsten lamp. The tubes were contained in a rotating apparatus with the lamp mounted centrally to ensure uniform irradiation, and were cooled to *ca.* 15 °C. After 20 min the solutions were analysed spectrophotometrically. Those containing DABCO showed *ca.* 1% conversion, whereas those containing no quencher showed *ca.* 70% conversion. Similar results were observed when the reactions were monitored for the amount of 1,4-naphthoquinone formed, by g.l.c. analysis.

Attempted Quenching of the Photosensitised Oxidation of the Naphthols (1a) *and* (4a) *with* 2,6-*Di-t-butylphenol.*—Solutions of (1a) (10 mg) and Methylene Blue (1 mg) in methanol (20 ml) were prepared, and in each of these was dissolved 2,6-di-t-butylphenol (8 mg). A similar set of solutions was prepared without added phenol, and all were sealed under oxygen in identical Pyrex tubes. After irradiation with a 250 W tungsten lamp for 6 h as already described, the solutions were analysed by g.l.c. (4% silicone OV-17 on 80—100 mesh Supasorb AW at 200 °C). The average yield of 1,4-naphthoquinone in the presence of the phenol was 21.6%, and without the phenol, 21.0%.

A similar experiment with (4a) revealed no inhibition of the reaction by the phenol. In this case the reactions were monitored spectrophotometrically.

Reaction of the Naphthol (1a) *with the* endo-*Peroxide of* 9,10-*Diphenylanthracene.*—A solution of (1a) (0.05 g) and the *endo*-peroxide of 9,10-diphenylanthracene [7] (0.5 g) in benzene (50 ml) was flushed with oxygen-free nitrogen and heated under reflux, with complete exclusion of air and light. After 24 h the solvent was removed under reduced pressure and the residue separated by preparative t.l.c. (silica;

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* The visible spectra showed that the position of azo–hydrazone equilibrium was not affected by deuterium exchange.

[14] K. Venkataraman, 'Synthetic Dyes,' vol. 1, Academic Press, New York, 1952, pp. 523—569.

[15] D. J. Carlsson, G. D. Mendenhall, T. Suprunchuk, and D. M. Wiles, *J. Amer. Chem. Soc.*, 1972, **94**, 8960.

benzene). This gave (1a) (0.023 g) and 1,4-naphthoquinone (6 mg) after extraction of the silica with methanol.

Reaction of the Naphthol (1a) *with Hydrogen Peroxide–Sodium Hypochlorite.*—A solution of (1a) (0.05 g) in methanol (100 ml) was cooled to 0 °C, and aqueous hydrogen peroxide (3 molar proportions) was added. A solution of sodium hypochlorite (0.2 ml of a 30% solution in 20 ml water) was added over 90 min with vigorous stirring. The solution was extracted with methylene chloride and the residue from the extracts separated by preparative t.l.c. (silica; benzene). The product distribution closely resembled that from the photosensitised oxidation, and no starting material remained. 1,4-Naphthoquinone was isolated (9 mg) and was identified by i.r. and m.p. comparison with an authentic sample.

When the reaction was repeated in the presence of DABCO (0.4M) the extent of oxidation of (1a) was greatly reduced, and starting material was recovered (0.02 g, 40%).

Photo-oxidation of Tetraphenylcyclopentadienone sensitised by the Naphthols (1a) *and* (4a).—Solutions of (1a) (3 mg) and tetraphenylcyclopentadienone (8 mg) in methylene chloride (10 ml) were sealed in Pyrex tubes under oxygen. After 4 h irradiation with a 250 W tungsten lamp the solutions were analysed by g.l.c. The solutions showed an average of 8% conversion into *cis*-dibenzoylstilbene. Similar solutions containing (4a) in place of (1a) were irradiated for the same time, and showed an average conversion of 40%. In both cases, control solutions containing only tetraphenylcyclopentadienone were irradiated simultaneously and contained no detectable amounts of *cis*-dibenzoylstilbene after irradiation.

Photosensitised and Self-sensitised Oxidation of 1-(p-*Tolylazo*)-2-*naphthol* (4a).—An oxygen-saturated solution of (4a) (0.15 g) and Methylene Blue (15 mg) in methanol (200 ml) was irradiated for 48 h as described for (1a). The solvent was removed under reduced pressure and the residue chromatographed over silica gel in benzene, to give a yellow solution, from which 1,2-naphthoquinone was isolated; the quinone was identified by i.r. and m.p. comparison with an authentic sample. As the quinone decomposed extensively during isolation, giving a black insoluble residue, the experiment was repeated, and 1,2-naphthoquinone was purified by preparative t.l.c. (silica; benzene). Extraction of the yellow band with methanol gave a clear yellow solution, which was analysed spectrophotometrically; yield of 1,2-naphthoquinone, 35%. In the absence of Methylene Blue, *ca.* 1% conversion of (4a) occurred under the same conditions. 1,2-Naphthoquinone was detected as the only product.

Quenching of the Photosensitised Oxidation of the Naphthol (4a) *with DABCO.*—Solutions of (4a) (2 mg) and Methylene Blue (5 mg) in benzene (40 ml) and methanol (10 ml) were prepared, and half were made 0.4M in DABCO. The solutions were sealed under oxygen in identical tubes and were irradiated as described for the quenching experiments with (1a). After 20 min spectrophotometric comparison of the solutions showed that DABCO had inhibited the degradation of (4a) by an average of 95%.

Comparison of the Rates of Photo-oxidation of the Naphthol (4a) *in Methanol–Water and in Tetradeuteriomethanol–Deuterium Oxide.*—A solution of (4a) (40 mg) and Methylene Blue (60 mg) in methanol was prepared. Samples (100 μl) were added to oxygenated mixtures of CH_3OH (1.0 ml) and H_2O (1.0 ml) or CD_3OD (1.0 ml) and D_2O (1.0 ml) in sealed Pyrex cuvettes. The absorbances of the solutions were recorded directly at the $\lambda_{max.}$ of (4a) (495 nm), and the solutions were then immersed in a water bath at 15 °C and irradiated with filtered radiation ($\lambda > 570$ nm) from a 250 W tungsten lamp, with uniform exposure of the samples. After 3 min the absorbance values were recorded. The deuteriated solutions showed an average decrease in absorbance from 1.6 to 0.58 (64% conversion), whereas the non-deuteriated solutions showed a decrease from 1.6 to 1.38 (14% conversion).

Relative Rates of Photo-oxidation of the Naphthols (1a—f) *and* (4a—f).—Solutions of the dyes were prepared (7.2×10^{-5}M) in benzene–methanol (4 : 1) containing Methylene Blue (50 mg l^{-1}). Samples (10 ml) were sealed in identical Pyrex tubes and were thoroughly oxygenated. A volume of at least 5 ml of oxygen above each solution was obtained, ensuring a large excess relative to the amount of azo-compound. The tubes were arranged about a centrally mounted 150 W tungsten filament lamp, and were rotated about the lamp to ensure uniform irradiation. The radiation was filtered through suitably dyed films, ensuring $\lambda > 570$ nm, and the tubes were maintained at 15 °C by a constant flow of water. Samples were removed during irradiation and were monitored spectrophotometrically at the $\lambda_{max.}$ of the hydrazone tautomer, noting the change in absorbance, ΔA. Plots of log $\Delta A/A_0$ (where A_0 is the absorbance at zero time) gave a straight-line relationship for (1a—f) and (4a—f). To determine the first-order rate constant from the slope of these lines it was necessary to multiply by the factor ($1 + K_E$), where K_E is the equilibrium constant for the hydrazone $\rightleftharpoons$ azo process. The equilibrium constants were estimated from the spectra of the dyes in benzene–methanol (4 : 1) at 15 °C, assuming averaged extinction coefficients of 23 000 and 18 000 for the hydrazone and azo-forms respectively of (1),[3] and values of 22 000 and 16 000 for the corresponding forms of (4).[12] The resultant equilibrium constants were: (1a), 6.3; (1b), 3.1; (1c), 1.7; (1d), 1.5; (1e), 1.3; (1f), *ca.* 0; (4a), 2.5; (4b), 1.1; (4c), 0.93; (4d), 0.85; (4e), 0.98; (4f), 0.90. The corrected first-order rate constants, measured relative to the unsubstituted derivatives, are given in the Discussion section.

Photo-oxidative Fading of the Naphthols (1a—f) *and* (4a—f) *on Silica Gel.*—Solutions of the dyes were spotted on silica gel t.l.c. plates and dried. The plates were exposed to daylight and air for several days, and then eluted with benzene. The photodegradation products were identified as 1,4-naphthoquinone in the case of (1), and 1,2-naphthoquinone in the case of (4), by t.l.c. comparison with authentic samples. Small t.l.c. plates were similarly treated with solutions of the dyes, and were sealed under oxygen in Pyrex tubes, half containing added DABCO as quencher. The tubes were maintained at 45 °C to ensure evaporation of the quencher, and were irradiated with a medium-pressure mercury lamp for 2 days. Qualitative examination of the plates after elution with benzene showed that DABCO has a pronounced inhibiting effect on photo-oxidation.

Effect of Nickel(II) *Complexation on the Photo-oxidation of the Naphthol* (4a).—Nickel(II) acetate (0.10 g) in ethanol (1.5 ml) and water (1.5 ml) was added to a solution of (4a) (2 mg) in ethanol (5 ml) and water (5 ml). Methylene Blue (2 mg) was then added. A similar solution was prepared containing no nickel(II) acetate. The two solutions were sealed under oxygen and irradiated ($\lambda > 570$ nm) for 45 min. Spectrophotometric analysis revealed 25% degradation for the nickel-free solution and no degradation for the nickel-containing solution.

Attempted Quenching of Singlet Oxygen by the Nickel(II) *Complex of the Naphthol* (4a).—The previous experiment was repeated but with tetraphenylcyclopentadienone (7.7 mg) added to each solution. The solutions were sealed under oxygen and irradiated ($\lambda > 570$ nm) for 30 min. The photo-oxidation of the dienone to *cis*-dibenzoylstilbene was monitored by g.l.c. Both solutions showed 92% conversion into the latter compound.

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