Photochemical Oxidation of Nitrobenzyl Alcohols in Aqueous Solution

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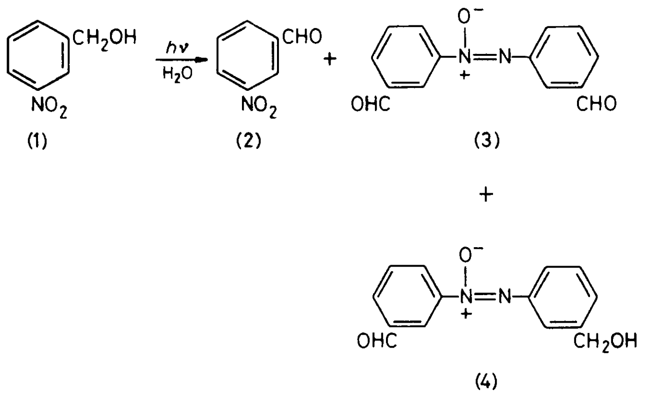
Summary When irradiated with u.v. light in deoxygenated aqueous solutions, *m*-nitrobenzyl alcohol (**1**) is found to give *m*-nitrobenzaldehyde (**2**), and the azoxy-compounds (**3**) and (**4**).

Nitro-aromatic compounds are known to undergo photochemical reduction in hydroxylic solvents,[1] during which the solvent is oxidised. In cases where either (i) a side chain *ortho* to a nitro-group is available for oxidation[1] or (ii) a second, different molecule, with an available site for oxidation, is present in solution,[2,3] an alternative pathway for the photoreduction of the nitro-group is available. We report herein a novel variation in which the photo-oxidation of the side chain of a nitro-aromatic molecule by another member of the same substrate occurs, which offers additional insight into the photo-oxidation–reduction process of nitro-aromatic compounds.

Irradiation of *m*-nitrobenzyl alcohol (**1**) (0·02 M) in deoxygenated distilled water (Rayonet RPR-100 reactor, 254 or 350 nm lamps) afforded *m*-nitrobenzaldehyde (**2**) (*ca.* 60% of the product mixture) and *m*-azoxybenzaldehyde (**3**) and *m*-(3-hydroxymethylphenyl-*NNO*-azoxybenzaldehyde (**4**) (remaining 40%) (Scheme 1). These compounds, the only isolable products, were isolated by preparative t.l.c. on silica gel (CH_2Cl_2–EtOAc, 1 : 1), and were characterised by ^1H n.m.r., i.r., and mass spectroscopy, and by comparison with authentic samples, where available. The ratio of compound (**2**) to the azoxy-compounds (**3**) and (**4**) remained essentially constant over 5–30% conversion, which suggests that any photoreduction product formed [possibly compound (**6**)] reacted in a subsequent fast step to give the coupled products. Irradiation in deoxygenated organic solvents (*e.g.* MeOH, MeCN, or cyclohexane) failed to effect this reaction. In aqueous MeCN, the efficiency of the reac tion depended strongly on the proportion of water in the mixture.

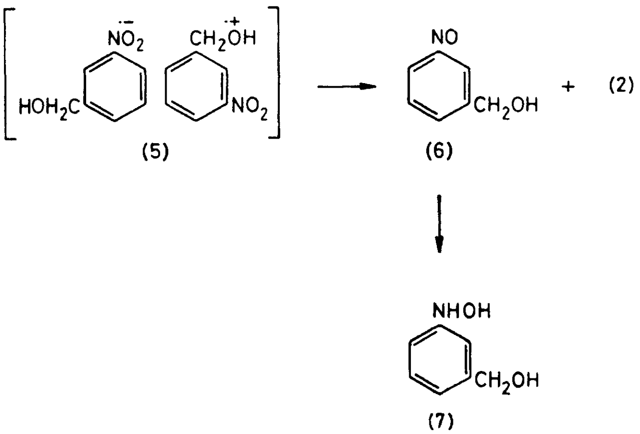


Scheme 1

The reaction can be sensitised by both acetone and sodium benzophenone-4-carboxylate, which suggests a triplet reactive state, consistent with other reports[1–5] of nitro-group photoreduction.

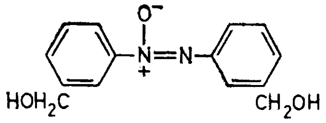
The photoreaction was monitored by u.v. spectroscopy and, upon irradiation, an intense band at λ 233 nm, due to compound (**2**), appeared at the expense of the λ 270 nm absorption associated with compound (**1**). A weak band at λ 325 nm due to the azoxy-chromophore was also observed after further irradiation.

p-Nitrobenzyl alcohol was found to be inert to photo-oxidation† under similar conditions as for the alcohol (**1**), with $> 95\%$ recovery of the starting material. However, both *m*-cyano- and 3,5-dinitro-benzyl alcohols have been found to give the corresponding aldehydes as major products when irradiated in aqueous solution. A detailed study of these products is under investigation.



Scheme 2

The postulated intermediacy of the radical-ion pair (**5**) in this photo-oxidation–reduction is based on previous reports of the photoreduction of nitro-groups,[2,4,5] and on the strong solvent dependence of the present reaction. Thus, in solvents less polar than water, the radical-ion pair (**5**) is insufficiently stablised, and the reaction does not proceed. One possible mechanistic scheme is shown in Scheme 2. Collapse of the radical-ion pair (**5**) gives the oxidation product (**2**) and the initial reduction product, *m*-nitrosobenzyl alcohol (**6**). In a similar process, compound (**6**) is converted into the alcohol (**7**), and coupling of these compounds *via* a known ground-state reaction gives initially the azoxybenzyl alcohol (**8**). Since this compound was not detected in the product mixture, its rapid photo-oxidation to compounds (**3**) and (**4**) by (**1**) is postulated. Compounds (**3**) and (**4**) are not secondary photoproducts of the aldehyde (**2**) since (**2**) was found to be photostable under similar irradiation conditions. Other mechanistic schemes, for example the photo-oxidation of the alcohol (**6**) to give *m*-$OHCC_6H_4NO$ and then coupling with compound (**7**) to give (**4**), cannot, as yet, be eliminated.



(8)

The results presented here suggest that aqueous solvents in photochemical reactions may give previously unexpected results; especially if the intermediate requires large solvation energies for its formation.

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† Differences in photochemical reactivity between the *meta*- and *para*-isomers of nitro-compounds are well known and have been attributed to both a lifetime effect and a difference in intrinsic reactivity (E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, 1968, **16**, 137; H. E. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, 1963, **85**, 922).

[1] (a) D. Döpp, *Top. Curr. Chem.*, 1975, **55**, 49; (b) H. A. Morrison, in 'The Chemistry of the Nitro and Nitroso Groups,' Part I, ed. H. Feuer, Interscience, New York, 1969, p. 167.

[2] J. Libman, *J. Chem. Soc., Chem. Commun.*, 1977, 868.

[3] J. W. Weller and G. A. Hamilton, *Chem. Commun.*, 1970, 1390.

[4] G. G. Wubbels, J. W. Jordan, and N. S. Mills, *J. Am. Chem. Soc.*, 1973, **95**, 1281.

[5] D. Döpp, D. Müller, and K.-H. Sailer, *Tetrahedron Lett.*, 1974, 2137.