

Photochemistry of α -Aryl Carbonyl Compounds in Aqueous Solution

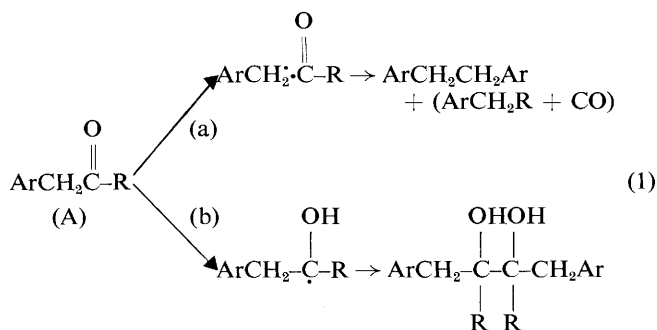
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Irradiation of the α -aryl carbonyl compounds (1)—(4) with u.v. light in aqueous solution gave different results from those observed in organic solvents.

The photochemistry of α -aryl carbonyl compounds (A) has been extensively studied in organic solvents.¹ As far as we are aware, the aqueous photochemistry of these compounds

consists of a number of studies in detergent (or soap) solutions.² The photochemistry of these compounds in the above solvent systems [equation (1)] can be rationalized in terms of



either (a) α -cleavage (Type I reaction) or (b) hydrogen abstraction (Type II reaction). We report that when the α -aryl carbonyl compounds (1)–(4) are irradiated in aqueous media, photoredox chemistry is observed. For compounds (1) and (2), this was in addition to the products shown by equation (1).

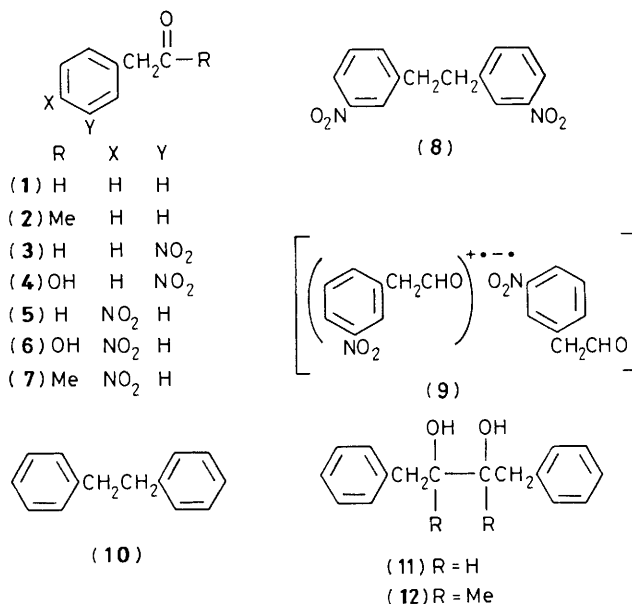
Irradiation of the α -aryl acetaldehyde (3) in deoxygenated aqueous acetonitrile (200 mg; 20% MeCN–H₂O; Rayonet RPR-100 photochemical reactor; 254 nm lamps; 48 h) afforded *m*-nitrotoluene (60%), *m*-nitrobenzaldehyde (40%), and a trace of 1,2-bis-(*m*-nitrophenyl)ethane (8). These products were separated by preparative t.l.c. and characterized by ¹H n.m.r., i.r., and mass spectroscopy, and by comparison with authentic samples, where available. No reduction products were isolated but highly coloured dyes were observed by t.l.c., all of which were uncharacterisable. Irradiation in deoxygenated organic solvents (*e.g.* methanol, acetonitrile, or cyclohexane) failed to effect this reaction. Under similar irradiation times, 90–95% of the substrate was recovered in these solvents. Similar results were observed for *m*-nitrophenylacetic acid (4).

The reaction was sensitized by both acetone and sodium 2-benzoylbenzoate, and suggests a triplet reactive state, in agreement with findings reported elsewhere on nitro group photochemistry.³

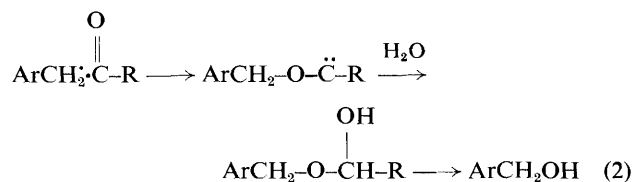
p-Nitrophenylacetone (7) was found to be inert in both aqueous and organic solvents. Irradiation of this compound in a quartz vessel for >72 h (Hanovia 450 W lamp) resulted in >95% recovery of the substrate. Irradiation of the α -aryl carbonyl compounds (5) and (6) in aqueous solution resulted only in the formation of *p*-nitrotoluene. Thus it seems clear that the photoredox chemistry of these compounds depends not only on the solvent, but also on subtle changes in molecular structure.

The efficiency of the photoredox reaction was observed to depend strongly on the proportion of water and added LiCl (in 30% MeCN–H₂O) in the aqueous acetonitrile mixture. In addition, the quantum yield for *m*-nitrobenzaldehyde formation relative to that in pure water (Φ/Φ_0), for substrates (3) and (4), was found to depend on the acidity of the medium. Φ/Φ_0 increased by a factor of 5 on going from pH = 1 to $H_0 = -3$. No effect on Φ/Φ_0 was observed on going from pH 7 to 1. The possibility that these observations were due to a salt effect was eliminated since addition of up to 3 M NaCl (in pure H₂O) failed to enhance the photoreaction. Thus it would appear that hydronium ions can catalyse the photoredox reaction. These observations suggest that a radical ion pair is on the reaction pathway.^{3c,4} The exact nature of this ion pair is unknown but we presume it might resemble (9). Charge-transfer mechanisms of this sort have been previously proposed to explain the photoredox chemistry of other nitroaromatics.⁴

Irradiation of the α -aryl carbonyl compounds (1) or (2) in methanol afforded compounds (10) and (11) [or (12) in the case of substrate (2)] as the only products. However, in deoxygenated aqueous acetonitrile, in addition to the above



products, benzyl alcohol and benzaldehyde were isolated as *ca.* 15% of the total product mixture. The observation of benzaldehyde in the product mixture is evidence for a photoredox pathway in aqueous solution. Although benzyl alcohol can also be formed *via* such a process, an alternate route to this compound *via* initial oxacarbene formation [equation (2)] has not been ruled out.



The employment of aqueous solvents for photoreactions resulting in previously unobserved photobehaviour has been clearly demonstrated in this work.

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