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Excited state intramolecular redox reaction of 2-(hydroxymethyl)anthraquinone in aqueous solution

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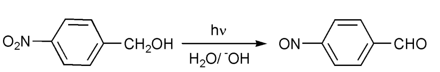
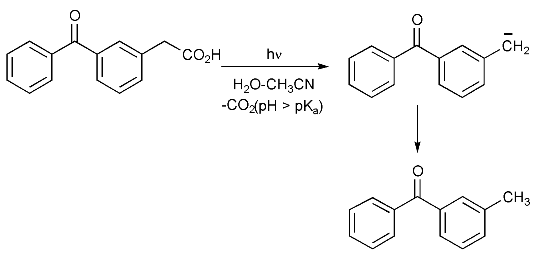
The title compound undergoes a novel excited state intramolecular redox reaction in which the 'distal' side chain benzylic alcohol is oxidized to the aldehyde and the carbonyl moieties of anthraquinone reduced, with evidence suggesting that the primary photochemical process is a deprotonation of the benzylic C–H proton (by water) mediated by the solvent.

The electron donating or withdrawing ability of functional groups attached to benzene and other aromatic rings are known to be considerably enhanced on electronic excitation.[1] A number of nucleophilic and electrophilic aromatic photosubstitution reactions and other types of reactions have been attributed to these enhanced effects.[1] We discovered that the enhanced electron-withdrawing effect of both *m* and *p*-nitro groups in the excited triplet state can induce intramolecular redox chemistry for *m* and *p*-nitrobenzyl alcohols (*e.g.* eqn. (1)).[2] Evidence suggests that the primary photochemical step is benzylic C–H bond deprotonation mediated by solvent water, to generate the corresponding nitrobenzyl carbanion intermediate. The utility of this type of reaction has not been explored fully due to the perceived enigmatic character of the nitro group in organic photochemistry.[3] It would be desirable if a more readily available functional group could be found that would induce an equivalent intramolecular photoredox chemistry as in eqn. (1). A lead came from a recent study[4] by our group of the efficient photodecarboxylation of a variety of phenacyl and acetyl-substituted phenylacetic acids (eqn. (2)), where we showed that phenyl or methyl ketones act as highly electron withdrawing groups on the benzene ring on electronic excitation (for the photodecarboxylation reactions reported), although it was not clear whether this characteristic is best attributed to its S_1 or T_1 state or both.† Although ketones classically react *via* their triplet excited states, typically *via* Type I and Type II photochemistry,[1c,d] they have strong structural resemblance to the nitro group and hence could potentially act simply as an enhanced electron withdrawing group, as it was apparently the case in the above photodecarboxylations.[4] This led us to explore the potential photoredox chemistry of several simple aromatic ketones chosen with a readily oxidizable benzylic alcohol substituent along with several model compounds.

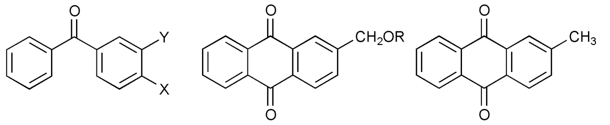


(1)



(2)

The study involved readily available aromatic ketones **1–5** related to the substrates used in the photodecarboxylation work.[4] With the exception of **5**, each of these compounds have an oxidizable benzyl alcohol moiety that is also 'distal' (*i.e. meta* or *para*) to the ketone, to avoid intramolecular hydrogen abstraction, which is well-known for *ortho*-substituted benzophenones and anthraquinones.[1c,d,5]‡ Photolysis ($\approx 10^{-3}$ M, 1 : 1 H_2O–CH_3CN, neat CH_3CN, or neat propan-2-ol; Rayonet RPR 100 photochemical reactor, 300 or 350 nm lamps, argon purged continuously; ≈ 12 °C; photolysis times 5–60 min; NMR or 100 mL quartz tubes) of **1** and **2** gave benzhydrol-type photoreduction products that are readily rationalized by initial hydrogen abstraction of the solvent by the benzophenone ketone. No chemistry was observed at the benzyl alcohol moiety. This is expected photobehavior for these compounds.



1 X = CH_2OH; Y = H
2 X = H; Y = CH_2OH

3 R = H
4 R = CH_3

5

The photochemical behavior of **3** and **4** is quite different. Whereas photolysis of the simple methyl analog **5** gave essentially no reaction (not even simple photoreduction), even on prolonged irradiation times, even brief exposure of either **3** or **4** (but not **1**, **2** or **5**) to 300 or 350 nm light in 1 : 1 H_2O–CH_3CN (deaerated by purging with argon) produced a deep yellow–orange colored solution that slowly faded (within about an hour). Introduction of oxygen accelerated the bleaching. Analysis of the solution after aeration gave a positive test for peroxides indicating that oxygen was mostly likely reduced to hydrogen peroxide in the course of bleaching the transient. UV-Vis traces (Fig. 1) showed formation of intense UV and visible bands on photolysis suggestive of efficient photoreaction. These new transient absorption bands for **3** and **4** were also

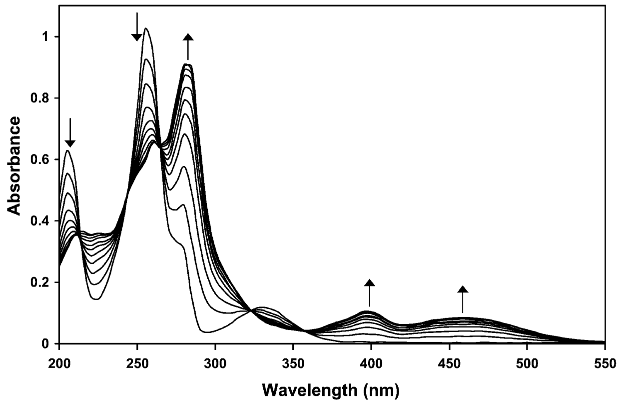


Fig. 1 UV-Vis traces of photolysis of **3** in 1 : 1 H_2O–CH_3CN (λ_{ex} = 350 nm; deaerated). Each trace represents 5 s of photolysis. The highly absorbing species (yellow–orange) that is formed on photolysis decays within 60 min under a deaerated solution, to give a spectrum identical to that of anthraquinone-2-aldehyde (**6**); no visible transient was observed under aerated conditions, although the same photochemistry occurs (as determined by product studies, see text).

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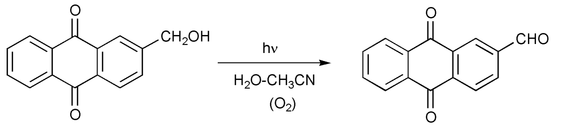
observable on photolysis in MeOH (but formed less efficiently) but *not* in neat CH_3CN. Preparative photolysis of **3** in 1 : 1 H_2O–CH_3CN under argon purge followed by work-up in air gave up to quantitative yield of anthraquinone-2-aldehyde (**6**) (eqn. (3)),



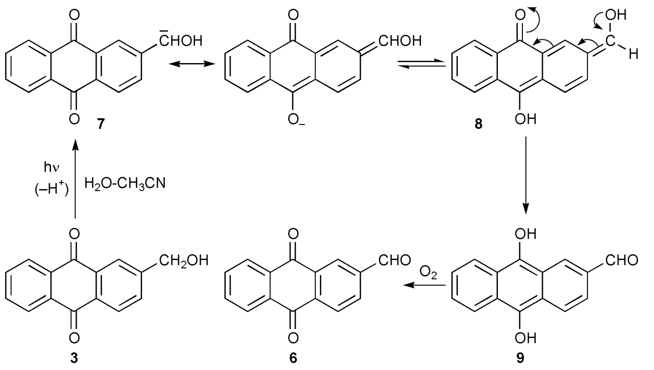
(3)

3 **6**

with $\Phi \approx 0.8$.§ Work-up in the absence of air gave a product with an intense color and aromatic NMR peaks (in DMSO-d_6) including an aldehyde peak at δ 10.2. Introduction of oxygen to the NMR sample converted these peaks to those of **6**, with a characteristic sharp aldehyde peak at δ 10.1. Photolysis under oxygen purge also cleanly produced **6** but in reduced yield ($\approx 25\%$ less) under otherwise identical conditions. Preparatory photolyses in neat MeOH and neat CH_3CN confirmed the observations made above by UV-Vis spectra; that is, the yield of **6** is considerably lower in neat MeOH ($\approx$ 50% less) and not observed at all in neat CH_3CN. These observations are consistent with a mechanism of reaction that requires a protic solvent, suggestive of excited state acid–base chemistry. In addition, the sensitivity of the transient towards oxygen and its general resemblance of its UV-Vis spectrum to that of the known 9,10-dihydroxyanthracene (which is known to be oxygen sensitive)[6] strongly suggests that the photogenerated colored intermediate is the intramolecular redox product **9**.

Photolysis of **4** in 1 : 1 H_2O–CH_3CN also cleanly gave **6** (after aeration) but with a reactivity that is about 30% less than that observed for **3**. In addition, an equimolar amount of MeOH was also formed, in photolysis experiments carried out in an NMR tube (in 1 : 1 D_2O–CD_3CN). This makes the reaction potentially useful for the photorelease of alcohols and other substrates.¶

The photochemistry observed for **3** and **4** resembles the intramolecular photoredox chemistry reported[2] for *m* and *p*-nitrobenzyl alcohols. For example, runs carried out for **3** employing varying initial substrate concentrations (100 fold change, from 10^{-6} to 10^{-4} M) showed no difference in quantum yield of reaction (as monitored by UV-Vis). The necessity of a protic solvent for the reaction also draws parallels to the nitrobenzyl alcohol systems, suggesting that the primary photochemical step is benzylic C–H bond deprotonation by water (in aqueous solution), as proposed for *m*-nitrobenzyl alcohol (hydroxide in the case of *p*-nitrobenzyl alcohol), to give a highly resonance stabilized carbanion **7** (Scheme 1). In order to satisfy the unimolecular nature of the reaction, we propose that the next step involves protonation of the oxygen to give bis-enol intermediate **8**, which can readily transform to dihydroxyanthracene **9** by a ketonization–enolization step. Although this is a preliminary mechanism that requires additional verification, the observations presented clearly point to a new type of redox photochemistry available for suitably designed anthraquinones and possibly other ketones.



Scheme 1

In summary, we have discovered a new type of photochemistry available for simple anthraquinone derivatives that is mechanistically related to the photoredox chemistry of *m* and *p*-nitrobenzyl alcohols. All of these reactions are best explained by a highly polarized excited state. The results further support the notion that aromatic ketones can act as enhanced electron withdrawing groups in the excited state, inducing photochemistry not normally associated with carbonyl excited states.

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Notes and references

† Cosa, Martinez and Scaiano (G. Cosa, L. J. Martinez and J. C. Scaiano, *Phys. Chem. Chem. Phys.*, 1999, **1**, 3533) have shown that for one such phenylacetic acid (ketoprofen), the photodecarboxylation is from S_1.

‡ Electronically excited anthraquinones are also known to be excellent electron acceptors, a behavior that has often been exploited in many photochemical systems. See for example: (*a*) S. M. Gaspar and G. B. Schuster, *J. Am. Chem. Soc.*, 1997, **119**, 12762; (*b*) D. T. Breslin and G. B. Schuster, *J. Am. Chem. Soc.*, 1997, **119**, 10463; (*c*) H. Gan, X. Zhao and D. G. Whitten, *J. Am. Chem. Soc.*, 1991, **113**, 10463; (*d*) I. Loeff, A. Treinin and H. Linschitz, *J. Phys. Chem.*, 1983, **87**, 2536. A viable electron donor is not available for the anthraquinones studied in this work; their reactivity is best explained by other means.

§ Quantum yield of reaction was estimated by comparison with the photoredox chemistry of *m*-nitrobenzyl alcohol (Φ = 0.055).[2]

¶ We are aware of two reports (T. Furuta, H. Torigai, M. Sugimoto and M. Iwamura, *J. Org. Chem.*, 1995, **60**, 3953; T. Furuta, Y. Hirayama and M. Iwamura, *Org. Lett.*, 2001, **3**, 1809) where 2-anthraquinonemethyl derivatives have been employed for photodeprotection, where the functionality attached to the methyl moiety is released on photolysis. However, the authors do not comment on the mechanisms of these reactions, which may or may not be related to the photoredox chemistry reported in this work for our anthraquinone derivatives.

1 (*a*) E. Havinga and J. Cornelisse, *Chem. Rev.*, 1975, **75**, 353; (*b*) J. Cornelisse, in *CRC Handbook of Organic Photochemistry and Photobiology*, ed. W. M. Horspool and P.-S. Song, CRC Press, Boca Raton, Florida, 1995, chapter 20; (*c*) N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings Publishing Co., Menlo Park, California, 1978; (*d*) A. Gilbert and J. Baggott, *Essentials of Molecular Photochemistry*, CRC Press, Boca Raton, Florida, 1991; (*e*) H. Shizuka, *Acc. Chem. Res.*, 1985, **18**, 141; (*f*) P. Wan and G. Zhang, *Res. Chem. Intermed.*, 1993, **19**, 119; (*g*) P. Wan and S. Muralidharan, *J. Am. Chem. Soc.*, 1988, **110**, 4336.

2 P. Wan and K. Yates, *Can. J. Chem.*, 1986, **64**, 2076.

3 D. Döpp, in *CRC Handbook of Organic Photochemistry and Photobiology*, ed. W. M. Horspool and P.-S. Song, CRC Press, Boca Raton, Florida, 1995, chapter 81.

4 M. Xu and P. Wan, *Chem. Commun.*, 2000, 2147.

5 (*a*) R. L. Blankespoor, R. L. De Jong, R. Dykstra, D. A. Hamstra, D. B. Rozema, D. P. VanMeurs and P. Vink, *J. Am. Chem. Soc.*, 1991, **113**, 3507; (*b*) N. P. Gritsan, I. V. Khmelinski and O. M. Usov, *J. Am. Chem. Soc.*, 1991, **113**, 9615; (*c*) K. Maruyama and Y. Kubo, in *CRC Handbook of Organic Photochemistry and Photobiology*, ed. W. M. Horspool and P.-S. Song, CRC Press, Boca Raton, Florida, 1995, chapter 60.

6 (*a*) S. A. Carlson and D. M. Hercules, *Photochem. Photobiol.*, 1973, **17**, 123; (*b*) P. Suppan, *Chemistry and Light*, The Royal Society of Chemistry, 1994, p. 254.