



Tetrahedron Letters 44 (2003) 6247-6251

TETRAHEDRON LETTERS

## 9,10-Dicyanoanthracene photosensitized oxidation of aryl alkanols: evidence for an electron transfer mechanism

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Abstract—9,10-Dicyanoanthracene (DCA) photosensitizes the oxidation of a series of *para* substituted aryl alkanols in oxygen-saturated acetonitrile. Product analysis and Hammett correlations support an electron transfer mechanism for the title reaction. © 2003 Elsevier Ltd. All rights reserved.

Dicyanoanthracene (DCA) is a fluorescent molecule with reduction potential DCA<sup>•-</sup>/DCA=-0.97 V versus SCE in CH<sub>3</sub>CN.<sup>1</sup> The oxidation of various organic compounds photosensitized by 9,10-dicyanoanthracene (DCA) in the presence of molecular oxygen has been extensively studied over the past thirty years. Two competing mechanisms have been reported: (a) an electron transfer (ET) to the excited singlet DCA and (b) the formation of singlet oxygen (<sup>1</sup>O<sub>2</sub>) by energy transfer.<sup>2</sup> The relative contribution of these two pathways depends on the solvent polarity and the nature of the substrate. For example in the presence of singlet oxygen acceptors, the singlet oxygen adducts may be the only observable product (Scheme 1).<sup>1,2</sup>

Most of the work has focused on Type I reactions. In non-polar solvents an exciplex emission is observed (Scheme 2).<sup>3</sup> However, in acetonitrile and other polar solvents no emission is observed because the ion pairs diffuse apart to give solvent-separated radical ions, which can react further. This useful photochemical property of DCA has been applied extensively in photosensitized oxidations of alkenes,<sup>2,4–6</sup> aromatic alkanes,<sup>7</sup> cyclopropanes,<sup>8</sup> 1,2-diaryl oxirane,<sup>9</sup> aryl disilane,<sup>10</sup> and anisyl ether.<sup>11,12</sup>

Our previous long-standing mechanistic studies<sup>13</sup> on Type II sensitized photooxygenation reactions prompted us to investigate for the first time the DCA sensitized photooxidation of a series of aryl alkanols to aryl ketones. Photooxidation of aryl alkanols is chemoselective and produces mainly the corresponding aryl ketones. Apart from the mechanistic interest, this reaction is of synthetic use. In light of these results we also discuss mechanistic possibilities for the title reaction.

In this study we have used a number of properly designed 1-aryl-1-alkanols, compounds 1–10 (Table 1), and 2-aryl-1-alkanols 11 and 12 (Table 2). These substrates are totally inert to singlet oxygen (Type II mechanism), however they provide competition





Keywords: 9,10-dicyanoanthracene; photooxidation sensitizer; aryl alkanols.

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<sup>0040-4039/\$ -</sup> see front matter @ 2003 Elsevier Ltd. All rights reserved. doi:10.1016/S0040-4039(03)01549-1

 ${}^{1}\text{DCA} + \text{S} \longrightarrow \begin{bmatrix} \text{DCA}^{\overline{5}} - \text{S}^{\overline{5}^{+}} \end{bmatrix} \longrightarrow \text{DCA}^{-\bullet} + \text{S}^{+\bullet}$   $\downarrow \text{non-polar} \qquad \downarrow \text{polar}$   $\downarrow \text{solvents} \qquad \downarrow \text{solvents}$   $\text{exciplex emission} \qquad \text{reactions}$ 

Scheme 2. A radical cation intermediate by an electron transfer mechanism from excited DCA.

between  $C_{\alpha}$ -H and  $C_{\alpha}$ -C<sub> $\beta$ </sub> oxidative bond cleavage in the side-chain (Scheme 3).<sup>14,15</sup>

In a 4-mL Pyrex cell, a 0.05 M solution of aryl alkanol and DCA,  $5.5 \times 10^{-5}$  M, as the sensitizer in oxygen saturated acetonitrile was irradiated (>300 nm) with a 300 Watt Xenon lamp as the light source. The results of the photooxidation of 1-aryl-1-alkanols 1–10 are shown in Table 1.

After 20 min irradiation of the aryl alkanols 1, 3, 4, 8, 9 and 10 the corresponding aryl ketones 1a, 3a, 4a, 8a, 9a and 10a, were produced as the only oxidation prod-

ucts. It is interesting to note that the conversions in these photooxidations (based on the remaining starting materials), increase proportionally with increasing electron-donating ability of the corresponding *para* substituent. For example, the conversion of **3**,  $(X = CH_3O)$  is three times higher than that of **8**  $(X = CH_3)$ . In the case of an electron-withdrawing substituent such as *para* trifluoromethyl  $(X = CF_3)$ , substrate **2**, no reaction product was detected after 20 min of irradiation (Table 1).

However, besides electronic effects, steric factors play an important role in the transition state of these photooxidation reactions. For example, in the case of substrate **8** where the *para* substituent is a methyl group, the conversion of the photoreaction is three times higher (15%), compared to that of substrate **10** (5%), with an isopropyl group as the *para* substituent. This result may indicate that formation of an exciplex between the excited DCA and the substrate **8** is of lower energy than that with substrate **10** due to steric reasons.

Table 1. DCA sensitized photooxidation of secondary 1-aryl-1-alkanols 1-10

R Х н  $CH_3$ 1  $CH_3$  $CF_3$ 2 CH<sub>3</sub>O CH<sub>3</sub> 3 1a - 10a 1b - 10b CH<sub>3</sub>O Et 4 5 CH<sub>3</sub>O *i*-Pr CH<sub>3</sub>O PhCH<sub>2</sub> 6 CH<sub>3</sub>O C(CH<sub>3</sub>)<sub>3</sub> 7  $CH_3$  $CH_3$ 8 Et 9  $CH_3$ *i*-Pr  $CH_3$ 10

Substrate	Irrad. time (min)	% Conversion <sup>a,b</sup>	Relative product yield <sup>b</sup> (%)	
			ArCOR	ArCHO
1	20	2	100	Nd <sup>c</sup>
2	20	_	_	_
3	20	47	100	Nd
3	60	67	>99	<1
3	90	97	>98	<2
4	20	60	94	6
4	90	98	95	5
5	20	25	78	22
5	60	63	80	20
6	10	74	30 <sup>d</sup>	31 <sup>d</sup>
7	20	30	25°	65°
8	20	15	100	Nd
8	60	41	100	Nd
9	20	10	100	Nd
9	60	35	>99	<1
10	20	5	100	Nd
10	60	20	>99	<1

<sup>a</sup> Aryl alkanols 0.05 M, DCA 5.5×10<sup>-4</sup> M, in oxygen saturated CH<sub>3</sub>CN, 5–10°C, irradiation with Xenon Lamp, 300 W (>300 nm).

<sup>d</sup> In the case of substrate 6, benzaldehyde 1b 34% and 4-methoxybenzoic acid 3c 5%, were determined by <sup>1</sup>H NMR.

 $^{\rm e}$  An additional 10% of 4-methoxybenzoic acid was determined by  $^1{\rm H}$  NMR.

<sup>&</sup>lt;sup>b</sup> Determined by gas chromatography. The error was  $\pm 1\%$ .

<sup>°</sup> Not detected.





<sup>a</sup> Aryl alkanol 0.05M, DCA  $5.5 \times 10^{-4}$  M, in oxygen saturated CH<sub>3</sub>CN in a 4 mL Pyrex cell was irradiated (>300 nm), 5–10°C, irradiation with Xenon Lamp, 300 W.

<sup>b</sup> Determined by gas chromatography. The error was ±1%.



Scheme 3. Two possible side-chain oxidative cleavages.

It is interesting to emphasize here that in the transition state the  $C_{\alpha}-C_{\beta}$  bond cleavage leading to the aryl aldehyde, may be facilitated by increasing the stability of the newly forming radical fragment R<sup>•</sup>. For example, the ratio of aryl ketone : aryl aldehyde decreases from 94:6 to 78:22 to 30:31 to 25:65 with the increase in radical stability in going from ethyl to isopropyl, to benzyl and *t*-butyl radicals in substrates **4**, **5**, **6** and **7**, respectively (Table 1). We point out here that in the case of substrate **7** where R is a *t*-butyl group (forming a stable leaving *t*-butyl radical), the oxidative cleavage of  $C_{\alpha}-C_{\beta}$  leading to the corresponding 4-methoxybenzaldehyde **3b**, is the predominant pathway.

In addition to these results a Hammett correlation in the competition of *para* (X) substituted 1-aryl-1ethanols (X=CH<sub>3</sub>O, CH<sub>3</sub>, Et, *i*-Pr and CF<sub>3</sub>) versus 1-phenyl-1-ethanol, for the photooxidation reaction, gave a negative slope of  $\rho = -1.12$ ,  $R^2 = 0.9932$ , for example  $k_{\rm CH_3O}/k_{\rm H} = 15.84 \pm 0.30$  and  $k_{\rm CF_3}/k_{\rm H} = 0.50 \pm 0.02$ (Scheme 4). This result indicates the development of positive charge (e.g. a radical cation) in the transition state, which is better stabilized by electron-donating substituents. All these results indicate the formation of a radical cation intermediate of aryl alkanols whose  $C_{\alpha}$ -H and/ or  $C_{\alpha}$ - $C_{\beta}$  side-chain cleavage leads to the corresponding aryl ketones and/or aryl aldehydes (Scheme 3).<sup>16</sup> In similar studies, Baciocchi and co-workers have shown previously that the side-chain oxidation of aromatic alcohols proceeds via a radical cation intermediate.<sup>14,15</sup>

In order to study further the  $C_{\alpha}$ -H versus  $C_{\alpha}$ - $C_{\beta}$  bond cleavage of this reaction, we examined the photooxidation of aryl alkanols **11** and **12**. Both of these substrates have the hydroxyl group on the carbon next to benzylic  $(C_{\beta})$ . The results of the photooxidations are summarized in Table 2. Oxidation of both aryl alkanols leads to  $C_{\alpha}$ - $C_{\beta}$  bond scission, producing mainly 4-methoxy benzaldehyde. These results suggest also that the OH group on  $C_{\beta}$  increases the stability of the newly forming cation or radical fragment. Subsequent heterolytic or homolytic  $C_{\alpha}$ - $C_{\beta}$  bond cleavage produces almost exclusively the arylaldehyde in more than 97% relative yield. These results also suggest that DCA photosensitized oxidations of 2-aryl-1-alkanols proceed via an electron transfer mechanism.

A reasonable mechanistic rationalization for the sensitized photooxidation of aryl alkanols is presented in Scheme 5. An electron is transferred from the aryl substrate to the photoexcited sensitizer to form the radical ions. In the case of a stable cation or radical  $\mathbf{R}^{+/\bullet}$  fragment, a  $\mathbf{C}_{\alpha}$ - $\mathbf{C}_{\beta}$  scission is the exclusive or the predominant path, followed by oxygen capture of the intermediate radical which consequently decomposes to the observed aryl aldehyde (ArCHO). However, when the R fragment is relatively unstable (Me or Et) a  $C_a$ -H scission is greatly preferred to  $C_{\alpha}$ - $C_{\beta}$  bond cleavage, leading to the aryl ketone (substrates 1-4 and 8-10). The photoselective oxidation of these substrates to the aryl ketone makes this reaction, at least for these examples, preparatively useful. The two pathways are always in competition. The  $C_{\alpha}-C_{\beta}$  bond cleavage is dictated by the stability of the newly forming  $R^{+/\bullet}$ . The more stable R fragment leads to more extensive  $C_{\alpha}-C_{\beta}$ bond scission. The subsequent oxidation of DCA<sup>-</sup> by electron transfer to molecular oxygen producing the



**Scheme 4.** Hammett plot of the DCA sensitized photooxidation of 1-aryl-1-alkanols. The values for  $\sigma^+$  were taken from the textbook *Mechanism and Theory in Organic Chemistry*; Lowry, T. H.; Richardson, K. S.; 3rd Edition, 1987.

superoxide anion  $O_2^{\bullet-}$ , is a well established pathway by Foote and co-workers in previous studies of DCA sensitized photooxidation of alkenes.<sup>2</sup>

In conclusion, the sensitized photooxidation of aromatic alcohols with DCA proceeds via an electron transfer mechanism (ET). In the photooxidation of

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1-aryl-1-alkanols the nature of the R substituent on the  $\beta$ -carbon  $C_{\beta}$ , dictates the ratio of  $C_{\alpha}$ -H to  $C_{\alpha}$ - $C_{\beta}$  bond cleavage and consequently the corresponding ratio of aryl ketone versus aryl aldehyde. However, the photooxidation of 2-aryl-1-alkanols, gave the corresponding aryl aldehydes, as the only products. The results support the view that electron transfer to DCA from the substrate takes place to form the radical cation intermediate, which undergoes heterolytic  $C_{\alpha}$ - $C_{\beta}$  bond cleavage.

## Acknowledgements

We thank the Ministry of Education (B-EPEAEK graduate program) and the Greek Secretariat of Research and Technology (Greek-French collaborative research program Platon 2001) for financial support and graduate fellowships to I. Lykakis.

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$$DCA \longrightarrow DCA^{*}$$

$$rCH(OH)R + DCA^{*} \longrightarrow ArCH(OH)R + DCA^{-\bullet}$$

$$\overrightarrow{ArCH}(OH)R \longrightarrow (ArCH(OH) + R^{+}) \xrightarrow{O_{2}}_{-HOO\bullet} ArCHO$$

$$\overrightarrow{ArCH}(OH)R \longrightarrow (ArC(OH)R + H^{+}) \xrightarrow{O_{2}}_{-HOO\bullet} ArCOR$$

$$\overrightarrow{ArCH}(OH)R \longrightarrow (ArCHO) + R^{\bullet} + H^{+}$$

$$DCA^{-\bullet} + O_{2} \longrightarrow DCA + O_{2}^{-\bullet}$$

$$\overrightarrow{ArCH}(OH)R + O_{2}^{-\bullet} \longrightarrow ArCH(OH)R + \bullet OOH \longrightarrow ArCHO$$

$$\begin{pmatrix}OOH\\ArCH(OH)R \end{pmatrix}$$

hv

Scheme 5. Proposed mechanism of the photooxidation of aryl alkanols with DCA as a sensitizer, in the presence of  $O_2$ .

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