

Photo-oxidative dealkylation of α -alkylbenzyl methyl ethers induced by titanium dioxide in acetonitrile

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ABSTRACT: TiO₂-sensitised photo-oxidation of α -alkylbenzyl methyl ethers in deaerated CH₃CN gives the expected corresponding ketone, whereas in an aerated medium a dealkylation compound (methyl benzoate) is obtained as the principal product, with respect to the ketone, or the exclusive product (when the alkyl group is *tert*-butyl). The product analysis and distribution, together with a qualitative estimate of the relative reactivity, suggest that the mechanism in deaerated CH₃CN is the same as that previously hypothesized for non- α -alkylated benzyl ethers; in particular, the carbonyl compound should be formed through oxidation of the benzylic radical (obtained by deprotonation of the cation radical) to the corresponding cation. To justify the formation of methyl benzoate in an aerated medium, a reasonable hypothesis is that the α -alkyl- α -methoxybenzylperoxy radical (obtained from the competitive attack of oxygen on the benzylic radical) undergoes a dealkylation process; in particular, this intermediate, as a tertiary peroxy radical, could form a dimer that evolves into the corresponding oxy radical, giving the ester through a β -scission process. The general mechanism suggested in aerated medium was confirmed by evaluating the relationship between the ester/carbonyl (E/C) molar ratio and the adiabatic ionization potential of the benzylic radical intermediate. To evaluate the influence of medium heterogeneity, the E/C ratio data were compared with those obtained from an electron-transfer photosensitised [by 9,10-dicyanoanthracene (DCA)] oxidation in a homogeneous phase. A significant confirmation of the mechanism, in both deaerated and aerated media, was obtained by the reaction performed from 4-methoxy- α -ethylbenzyl methyl ether (as a model) in the presence of H₂¹⁸O, sensitised by either TiO₂ or DCA. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: titanium dioxide; photo-oxidation; benzyl ethers; ionization potential

INTRODUCTION

The heterogeneous photo-oxidation of organic compounds sensitised by semiconductors such as TiO₂, a process used to decontaminate waste water,¹ can also be used to generate radical cations (electron-transfer process from the substrate) and radicals (derived from these intermediates) and to study their decomposition pathways.²

This mechanistic investigation also provides interesting information about the photodegradation pathway of the investigated organic substrates as pollutants or pollutant models. In this context, we have pointed out³ that the intermediates generated from benzylic derivatives have different fates depending on the reaction conditions, the

substrate structure and the preferential adsorption site of the molecule at the semiconductor surface. It should be noted that the mechanistic approach preferentially involves CH₃CN as a solvent because, in contrast to water, it is inert under the experimental conditions used and the primary oxidation products can usually be detected. This approach is reasonable because, with the above substrates, the same primary steps are involved in both solvents.⁴

In this context, we have become interested in the photo-oxidation of alkyl benzyl ethers (4-X-PhCH₂OR') sensitised by TiO₂ as powder in CH₃CN.^{5–7} These are interesting substrates because they can be simplified model compounds for lignin, a biopolymer whose degradative oxidation has been widely studied.⁸

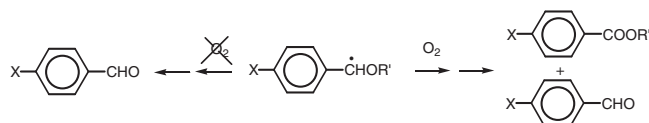
In particular, the mechanistic study concerning these ethers showed that an α -OR' benzyl radical, obtained by the deprotonation of the cation radical, gives the corresponding carbonyl compound (aldehyde) in deaerated CH₃CN, accompanied by alkyl benzoate when the mixture is bubbled with oxygen (Scheme 1).⁶

In this paper we extend the mechanistic study to the TiO₂-sensitised photo-oxidation of α -alkylbenzyl methyl ethers **1a–d**.

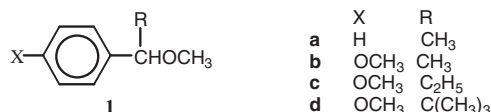
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Scheme 1

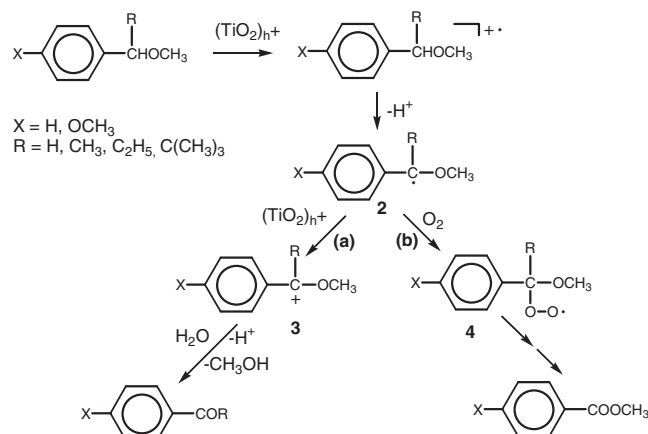
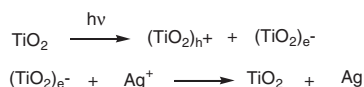


Whereas in deaerated CH₃CN the expected carbonyl derivative (in this case the corresponding ketone) is the exclusive reaction product, in the aerated medium the principal or exclusive product is methyl benzoate. The formation of this ester from any one of the α -R-substituted ethers is interesting as it derives from a dealkylation process, through a C α —C bond breaking pathway, which is a crucial process in the mineralization of a pollutant containing a moiety structurally similar to **1**.

The mechanistic study was carried out (i) through product analysis, (ii) considering the benzoate/ketone ratio in the aerated medium and (iii) by comparing the ratio obtained in this heterogeneous process with that observed in the homogeneous electron-transfer (ET) photo-oxidation sensitised by 9,10-dicyanoanthracene (DCA).

RESULTS AND DISCUSSION

In the TiO₂-sensitised photo-oxidation of a series of α -alkylbenzyl methyl ethers (**1a–d**), in deaerated CH₃CN and in the presence of Ag₂SO₄ (as an electron acceptor), the only observed product was the corresponding ketone (Table 1). As shown, the previously investigated benzyl methyl ethers **1e** (R = H, X = H) and **1f** (R = H, X = OCH₃) gave the corresponding aldehyde as product.⁶ Based on these results, it seems reasonable to suppose that the mechanism for the photo-oxidation of α -alkylbenzyl methyl ethers is the same as that suggested for **1e**

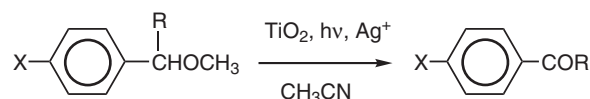


Scheme 2

and **1f**.⁶ Therefore, the mechanistic pattern reported in Scheme 2 (path **a**), involves, in the first step, the oxidation of the substrate by the photogenerated hole, (TiO₂)_h⁺, to give the corresponding radical cation that, by deprotonation, gives benzylic radical **2**; the last intermediate should then be oxidized to cation **3** by a second hole (as previously shown from photoelectrochemical experiments with benzyl alcohols⁹) giving the corresponding carbonyl products.

In an attempt to confirm this mechanistic hypothesis, the product yields and the reaction times in Table 1 provide qualitative information on the relative reactivity of the substrates, taking in account that the material recovery (substrate + product) was nearly quantitative. In line with the suggested mechanism that involves a kinetically significant electron-transfer step, the introduction of a 4-methoxy group into the ring increased the reaction rate, as can be noted by comparing the data for

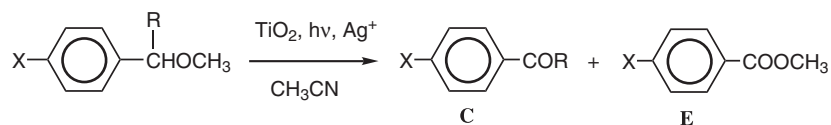
Table 1. Product yield in the TiO₂-sensitised photo-oxidation of benzyl methyl ethers in deaerated CH₃CN and in the presence of Ag₂SO₄



Substrate	X	R	Time (h)	Unreacted substrate (%) ^a	Product yield (%) ^a	E _p (V vs SCE)
1a	H	CH ₃	2.0	75	22	2.30
1b	OCH ₃	CH ₃	1.0	10	85	1.50
1c	OCH ₃	C ₂ H ₅	1.0	26	64	1.53
1d	OCH ₃	C(CH ₃) ₃	1.0	81	10	1.57
1e^b	H	H	2.0	77	18	2.22 ^b
1f^b	OCH ₃	H	1.0	30	62	1.55 ^b

^a With respect to the starting material.

^b Ref. 6.

Table 2. Product yield and distribution in the TiO₂-sensitised photo-oxidation of benzyl methyl ethers in aerated^a CH₃CN and in the presence of Ag₂SO₄

Substrate	X	R	Time (h)	Unreacted substrate (%) ^b	Product yield (%) ^b		E/C molar ratio	IP (eV) ^c
					C	E		
1a	H	CH ₃	2.0	80	2	11	6	6.28
1b	OCH ₃	CH ₃	1.0	20	26	45	1.8	6.06
1c	OCH ₃	C ₂ H ₅	1.5	31	22	35	1.6	6.01
1d	OCH ₃	C(CH ₃) ₃	1.5	80	—	10	>200	6.39
1e	H	H	2.0	63	2	27	14	6.45
1f	OCH ₃	H	1.0	2	30	66	2.2	6.18

^a Equilibrated with atmosphere before and during irradiation.^b With respect to the starting material.^c Adiabatic ionization potential for the radical **2**, calculated at semiempirical levels by using the AM1, PM3 and PM5 Hamiltonians and corrected for the solvent effect (see Experimental).

1a and **1b**. The rate increase in the presence of an electron-donating group was expected because this structural modification significantly lowers the substrate reduction potential ($E_{1^+/1}$, determined as E_p by voltammetric measurements; see Table 1), according to the Rehm–Weller equation for a photochemical electron transfer process.¹⁰ By comparing the data relative to ethers with the same substituent (4-CH₃O) in the ring, it can be noted that the introduction of an α -CH₃ or an α -C₂H₅ group does not significantly change the reactivity as shown by the similar E_p values (compare **1f** with **1b** or **1c**). As an exception, the reactivity of ether **1d** is much lower than that of **1f**, **1b** and **1c**, despite a similar E_p ; this behaviour can be principally ascribed to the very limited adsorption of **1d** at the semiconductor surface, because this substrate is highly hindered owing to the presence of the *tert*-butyl group.

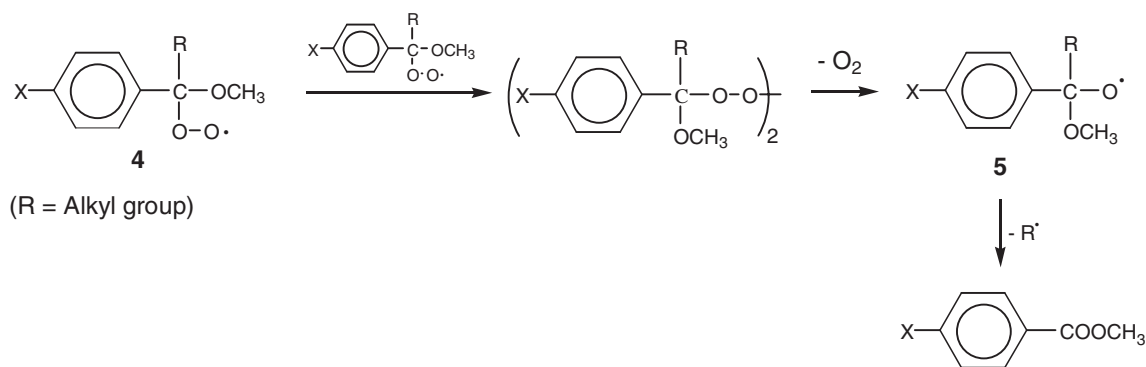
When the reaction is carried out in aerated CH₃CN (equilibrated with atmosphere before and during irradiation), the principal product from **1a–c** is the corresponding methyl benzoate with smaller amounts of the ketone, whereas this ester is the exclusive reaction product for **1d** (Table 2). For the sake of comparison, the reaction of benzyl methyl ethers **1e** and **1f** was again performed under the experimental conditions of this work, to yield the methyl benzoate accompanied by minor amounts of aldehyde (Table 2). The relative reactivities of the substrates considered are qualitatively similar to those in deaerated medium. The results (product analysis and reactivity data in aerated medium) are in line with the mechanistic hypothesis in Scheme 2, where radical **2** can either be oxidized to cation **3** (path **a**) or, competitively, it can be trapped by oxygen to yield the ester through the peroxy radical intermediate **4** (path **b**), as suggested previously for **1e** and **1f**.⁶

It must be observed that, in contrast to ethers **1e** and **1f** (both with R = H), the methyl benzoate from **1a–d** is a

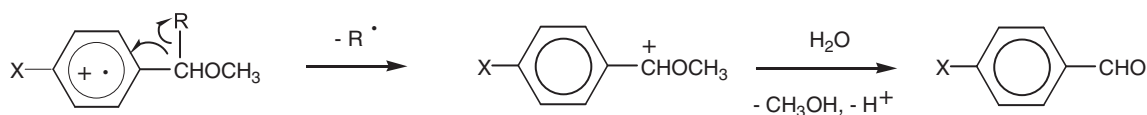
dealkylation product derived from the breaking of the C $_{\alpha}$ —C bond. Therefore, for all the considered α -alkylbenzyl ethers, we propose the hypothesis that was previously suggested for **1d** only on the basis of the product analysis,⁵ where the methyl benzoate is derived from the C $_{\alpha}$ —C fragmentation process that occurs in path **b** in Scheme 2. In particular, the peroxy radical intermediate **4**, as reported for tertiary peroxy radicals,¹¹ could undergo dimerisation and subsequent fragmentation to the corresponding oxy radical **5** and, in turn, this intermediate should yield the ester through a β -scission process (Scheme 3).¹²

An alternative hypothesis for this C $_{\alpha}$ —C bond breaking could be the direct fragmentation of the radical cation,¹³ but this can be excluded because the corresponding benzaldehyde should be formed through the homolytic step shown in Scheme 4 (the most probable C $_{\alpha}$ —C bond breaking of this intermediate, based on the high stability of the α -methoxybenzyl cation¹³).

The values of the ester/carbonyl compound molar ratio, E/C (Table 2), can be used to confirm the reaction mechanism in aerated medium. It should be noted that these values are reproducible and independent of the reaction time when the medium is equilibrated with atmosphere before and during irradiation. In particular, the distribution of the two products should be associated with the competition between paths **a** and **b** in Scheme 2. More precisely, path **a** should depend on the reduction potential of the cation **3**, whereas path **b** should not be influenced by this parameter. In previous studies,^{5,14} the reduction potentials of these intermediates were used to evaluate the oxidisability of benzylic radicals. They were estimated as the electrochemical oxidation half-wave potentials ($E_{1/2}$), measured by Wayner *et al.* using photo-modulation voltammetry.¹⁵ These authors also showed a good correlation between the values of the experimental $E_{1/2}$ in CH₃CN and those of the calculated adiabatic



Scheme 3



Scheme 4

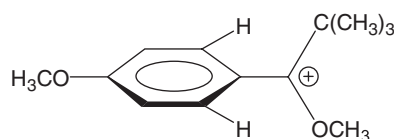
ionization potentials (IP) of an extended series of substituted benzyl radicals.¹⁵ Therefore, in this paper, we used the IP values as a valid alternative, calculating them by a similar method (AM1, PM3 and PM5 Hamiltonians, corrected for the CH₃CN solvation effect; see Experimental).

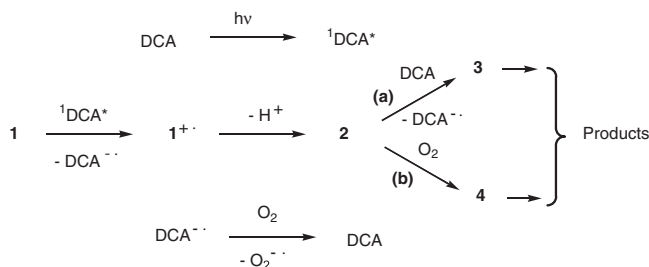
Relative to the ethers without the α -alkyl group, the E/C ratio for **1e** (Table 2) is very high (14), whereas for the 4-OCH₃ ring-substituted ether, **1f**, the ratio is much lower (2.2). In fact, the insertion of an electron donor into the ring (such as a 4-OCH₃ group) lowers the ionization potential of the benzylic radical **2** because it stabilizes the corresponding carbocation **3**, which causes the rate of path **a** to increase with respect to that of path **b** (Scheme 2).

Concerning the α -alkylbenzyl ethers, the E/C ratio (6.0) for **1a** is lower than that for **1e** (14) because the IP value of radical **2** decreases when an electron donor (methyl group) is inserted into the α -position. In addition, the introduction of a further electron donor (4-OCH₃ group) in the ring of **1a** (substrate **1b**) further reduces the E/C ratio (to 1.8), in line with the lower IP of radical **2b** with respect to that of **2a**. Moreover, on going from **1f** to **1b** (both 4-methoxy derivatives), it can be noted that the E/C ratio decreases slightly in line with a slightly higher IP value of the benzylic radical **2f** with respect to **2b**; this small E/C ratio decrease is probably due to the slight stabilizing effect of an α -methyl group when two strong electron-donor groups, α - and 4-methoxy, are already present in intermediate **2**. Moreover, the E/C ratios for **1b** and **1c** and the ionization potentials of radicals **2b** and **2c** show similar values, in line with the similar electronic effect of the methyl and the ethyl group in the α -position of the benzylic cation **3**.

In contrast to **1c** and **1b**, the only product observed for the α -*tert*-butyl-substituted ether **1d** is the methyl benzoate (the E/C ratio is >200, considering the experimental error of the gas chromatographic method). A significant contribution to the absence of the corresponding ketone can be given by the presence of a bulky α -*tert*-butyl group that should destabilize the cation **3d** owing to the steric hindrance to resonance (Fig. 1). This phenomenon is consistent with a higher IP value for **2d** than for **2b** or **2c** (see Table 1), even if the observed E/C ratio for **1d** is too high in relation to the IP (6.39 eV) of the corresponding radical **2d**. A possible explanation could be as follows. The IPs of the radicals **2a–d** corrected for the CH₃CN solvation, as expected, are significantly different (0.3–0.4 eV lower) to the values in the gas phase. Actually, the radical **2d** should present a significantly higher IP (similar to the value in the gas phase) owing to steric inhibition of the *tert*-butyl group to the **3d** cation solvation, but this effect is not evaluated in the IP calculation.

To determine if the results (E/C ratio) obtained with α -alkyl ethers in aerated CH₃CN depend on the medium heterogeneity, an electron-transfer photosensitised [by 9,10-dicyanoanthracene (DCA)] reaction in the homogeneous phase was carried out on 4-methoxy derivatives **1b–d**. Following the previously suggested mechanism for this process,¹⁶ as reported in Scheme 5 the first electron should be removed from the substrate **1** by the excited

Figure 1. Cation **3d** (preferred conformation)



Scheme 5

sensitiser ($^1\text{DCA}^*$), whereas the benzylic radical **2** should be oxidized to the cation or captured by oxygen; the sensitiser should then be regenerated by the reaction of $\text{DCA}^{\cdot-}$ with O_2 (DCA is used in a catalytic amount).

It has been observed that in this homogeneous medium, aerated as described for the heterogeneous medium, the E/C ratio, reproducible and independent of time, for **1b** is similar to that for **1c** (6–7; see entries 1 and 3 in Table 3), but is much lower than that for **1d** (entry 5). This similar trend allowed us to hypothesize that radical **2** undergoes the same fate in either homogeneous or heterogeneous phase.

In addition, the results that are different in the two media could be consistent with a common mechanism:

1. The E/C ratios with DCA for **1b** and **1c** are higher than those (1.8 and 1.6 in Table 2) observed for the same substrates in the presence of TiO_2 . This can be explained by considering that in the homogeneous phase the oxidant of intermediate **2** (probably the sensitiser in the ground state or oxygen) should be less powerful than that in heterogeneous medium, $(\text{TiO}_2)_h^+$ ($E^\circ = 2.4 \text{ V}^{17}$) and therefore path **a** is disfavoured.

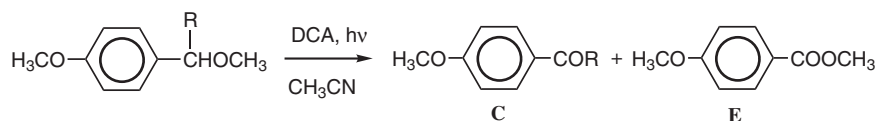
2. With DCA, anisaldehyde is obtained from **1d** (entry 5 in Table 3) in addition to the corresponding ester. The formation of this product can be explained by supposing that, when $\text{R} = \text{C}(\text{CH}_3)_3$, the homolytic $\text{C}_\alpha\text{—C}$ fragmentation of $\text{1d}^{\cdot+}$ (Scheme 4) competes with the thermodynamically favoured deprotonation of this intermediate (Scheme 5) because of stereoelectronic requirements (collinearity of the scissible $\text{C}_\alpha\text{—X}$ bond and the π -system). In fact, the steric hindrance of the bulky $\text{C}(\text{CH}_3)_3$ group in the radical cation makes the conformation suitable for the $\text{C}_\alpha\text{—C}$ fragmentation much more stable (Fig. 2).¹³

This competition was excluded for the reaction of **1d** with TiO_2 (see above) owing to the absence of aldehyde as product (Table 2). This result agrees with the known basicity of the semiconductor surface,¹⁸ which is high enough to favour the radical cation deprotonation also with this substrate. As a confirmation, in the DCA-sensitised photo-oxidation in the presence of lutidine (as base), the aldehyde is not present as product from **1d** (Table 3, entry 6).

It can be observed that the introduction of a base did not change the E/C ratio in any of the substrates considered in DCA-sensitised photo-oxidation; this observation therefore confirms that deprotonation is not involved in the steps responsible for the ester/ketone distribution.

3. A final difference observed between the two oxidizing systems is that with DCA/lutidine (the homogeneous medium that can be compared with the heterogeneous one, see previous point) the reactivity of **1d** is qualitatively similar to that of **1b** and **1c** (compare, for example, entries 2, 4 and 6 in Table 3), while with TiO_2 **1d** is much less reactive than **1b** and **1c** (Table 2). This confirms the above suggested hypothesis that the lower reactivity of **1d** in TiO_2 -sensitised

Table 3. Product yield and distribution in the photo-oxidation of 4-methoxybenzyl methyl ethers (**1b–d**) sensitised by 9, 10-dicyanoanthracene (DCA) in aerated^a CH_3CN



Entry	Substrate	R	Time (h)	Unreacted substrate (%) ^b	Product yield (%) ^b		
					C	E	E/C molar ratio
1	1b	CH_3	4	62	4	24	6
2 ^c			0.5	74	3	17	6
3	1c	C_2H_5	3	27	8	56	7
4 ^c			0.6	79	2	14	7
5	1d	$\text{C}(\text{CH}_3)_3$	0.3	76	—	7 ^d	>200
6 ^c			1	61	—	30	>200

^a Equilibrated with atmosphere before and during irradiation.

^b With respect to the starting material.

^c In the presence of lutidine ($1.1 \times 10^{-5} \text{ M}$).

^d Anisaldehyde is also present as reaction product (13%).

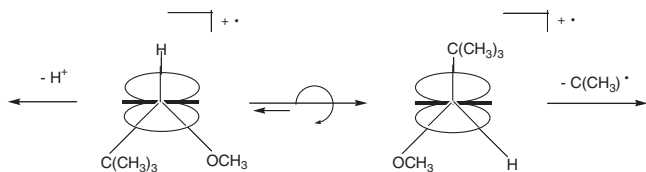


Figure 2. The conformations of **1d**⁺ suitable for C—H and C_α—C fragmentation

heterogeneous photo-oxidation is principally due to a reduced substrate adsorption at the semiconductor surface.

A significant confirmation of the mechanism, both for the TiO₂- and DCA-sensitised photo-oxidation, was obtained by labelling experiments in the presence of H₂¹⁸O. In particular, we considered substrate **1c** as a model and we observed that the corresponding ketone (path **a** in Scheme 2) shows the complete incorporation of ¹⁸O (after correction of the ¹⁸O content of the labelled water), whereas the methyl benzoate (via **b** in Scheme 2) did not show any ¹⁸O incorporation. This fact also allows us to exclude (within the experimental error) the possibility that the ketone should also be formed through a β -scission process from the oxy radical **5c** (path **b**) with the loss of a methoxy radical.

EXPERIMENTAL

¹H-NMR spectra were run on a Bruker AC 200 (200 MHz) spectrometer, with solutions in CDCl₃ with TMS as an internal standard. GC–MS analyses were performed on a Hewlett-Packard (HP) 6890A gas chromatograph (HP-Innovax capillary column, 15 m) coupled with an MSD-HP 5973 mass-selective detector (70 eV). GC analyses were carried out on an HP 5890 gas chromatograph using an HP-Innovax capillary column (15 m).

Materials. TiO₂ (anatase) (Aldrich, 99.9%, dried at 110 °C), CH₃CN (HPLC grade, water content 0.02% by Karl Fischer coulometry), Ag₂SO₄, H₂¹⁸O (Aldrich, 97 atom%), benzaldehyde, 4-methoxybenzaldehyde, 4-methoxyacetophenone, 4-methoxypropiofenone, methyl benzoate and methyl 4-methoxybenzoate were commercial samples. α -Methylbenzyl methyl ether (**1a**),¹⁹ 4-methoxy- α -methylbenzyl methyl ether (**1b**),²⁰ 4-methoxy- α -ethylbenzyl methyl ether (**1c**),²⁰ α -*tert*-butyl-4-methoxybenzyl methyl ether (**1d**),⁵ benzyl methyl ether (**1e**)⁶ and 4-methoxybenzyl methyl ether (**1f**)⁶ were prepared and characterized as described in the literature.

Photochemical oxidation sensitised by TiO₂. The reactions with benzyl methyl ethers were carried out by external irradiation (Helios Italquartz 500 W high-pressure mercury lamp, Pyrex filter) of a TiO₂ (70 mg) suspension in 10 ml of CH₃CN either deaerated (N₂

purged) or aerated (equilibrated with the atmosphere before and during irradiation), containing the substrate (0.05–0.10 mmol) and Ag₂SO₄ (0.10–0.20 mmol) in a cylindrical flask provided with a water cooling jacket. After irradiation with stirring at room temperature, the reaction mixture was filtered through double paper and analysed by GC (in the presence of durene as an internal standard). Quantitative analysis of the crude product was performed by ¹H NMR and/or GC with a suitable internal standard (durene).

Photochemical oxidation sensitised by DCA. The substrate (0.10 mmol) was dissolved in 10 ml of a solution containing DCA in aerated CH₃CN (4×10^{-4} M), in either the absence or presence of lutidine (0.10 mmol). The resulting solution was irradiated with an Applied Photophysics Multilamp Photochemical reactor (12 lamps at $\lambda = 355 \pm 20$ nm).

Reaction products. The products were identified directly from the crude by comparison of ¹H NMR and GC–MS data with those for commercial samples (aldehydes, ketones and esters).

Cyclic voltammetry. *E*_p values were obtained from cyclic voltammetry experiments, conducted with an AMEL 552 potentiostat controlled by a programmable AMEL 568 function generator (at 100 mV s⁻¹, 1 mm diameter platinum disc anode and SCE as reference) in CH₃CN–LiClO₄ (0.1 M).

Adiabatic ionization potentials. The ionization potentials of the substrates were calculated at semiempirical levels by using the AM1, PM3 and PM5 Hamiltonians (MOPAC2002, CAChe 6.1, Fujitsu).²¹ The Conductor-like Screening Model (COSMO) was also included in the calculations to model the effect of the polar solvent on the molecular properties.²²

Photochemical oxidation of **1c** in the presence of H₂¹⁸O. The photo-oxidation of **1c**, sensitised by either TiO₂ or DCA, was also carried out in CH₃CN–H₂¹⁸O (99.5:0.5, v/v). The reaction mixture was analysed by GC–MS. The percentage of ¹⁸O incorporated in the two reaction products (ketone and methyl benzoate) was determined by the relative abundances of the peaks at *m/z* 166 and 164 [*M*⁺] and at 137 and 135 (for the corresponding ketone); at *m/z* 168 and 166 [*M*⁺] and at 137 and 135 (for the methyl benzoate). In the ester, in both cases, ¹⁸O is absent, whereas in the ketone the amount of incorporated ¹⁸O (corrected considering the ¹⁸O content of the labelled water) is 100 ± 8%.

Acknowledgements

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