PERKIN 2

Some evidence in favour of an electron transfer mechanism in the TiO_2 photosensitized oxidation of benzyl derivatives in aqueous media

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The structure and/or distribution of products from the TiO_2-sensitized photooxidation of some benzyl derivatives in aerated and/or deaerated aqueous media and in the presence of Ag_2SO_4 are reported. The results suggest that the single electron transfer process from the substrate to the photogenerated hole, previously proposed in CH_3CN, should also be operative on gradually going from aqueous CH_3CN to pure water.

Introduction

There is considerable interest in TiO_2 suspensions principally because of their ability, under irradiation, to mineralize organic pollutants in waste water. In this context, mechanistic investigations on primary oxidation reactions could provide useful information about the degradation pathways.[1,2]

It is recognized that the heterogeneous photooxidation of organic compounds sensitized by TiO_2 as powder in CH_3CN, an inert solvent under oxidative reaction conditions, involves a single electron transfer (SET) from the adsorbed substrate to the photogenerated hole (h^+) in the valence band, while the electron (e^-) in the conduction band is captured by a suitable acceptor (O_2,[3] Ag^+,[4] *etc.*). In all cases the intermediate radical cations are responsible for the primary oxidation products.

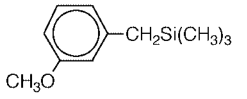
Unlike CH_3CN, water is easily photooxidized by TiO_2 and, therefore, the primary chemical events subsequent to the photoinduced production of h^+ remain a controversial issue.[5] In fact it has been proposed that the holes can: *i*) directly oxidize previously adsorbed compounds *via* a SET process and/or *ii*) react either with surface-bound HO^- derived from dissociative chemisorption of water on TiO_2, eqn. (1), or physisorbed H_2O, eqn. (2), to produce $HO^\bullet$, responsible for the non-SET reaction paths (indirect oxidation).

$$Ti^{IV}–OH^- + h^+ \longrightarrow Ti^{IV}OH^\bullet \qquad (1)$$

$$Ti^{IV}\cdots OH_2 + h^+ \longrightarrow Ti^{IV}OH^\bullet + H^+ \qquad (2)$$

Much evidence has been collected in favour of both the direct and the indirect processes and, in some cases, it has been suggested that both processes could be operative in different ratios depending on the substrate.[5] Generally, the mechanistic analysis is based on a comparison between the structure and/or distribution of the products obtained from TiO_2-photosensitized reaction in water and those derived from test reactions that involve $HO^\bullet$ radicals (as γ-radiolysis,[5b] pulse-radiolysis,[5h,i] Fenton reaction,[5d,e] *etc.*) or a SET mechanism (as the reaction with $SO_4^{-\bullet}$ [5b]). Otherwise some substrates that have been considered are phenols,[5j,k] also substituted with alkyl groups,[5e,l] which yield nuclear hydroxylated or side chain substituted products which, as previously suggested,[5h] do not always represent an unequivocal test in favour of direct or indirect oxidation.

In this work we consider some alkylaromatic compounds with a structure that is suitable for distinguishing between a SET mechanism and $HO^\bullet$-induced non-SET reaction process. In particular, the substrates **1**–**4** have been subjected to TiO_2-sensitized photooxidation in the presence of Ag_2SO_4 (Ag^+ is a more efficient electron acceptor than oxygen) [4a] in deaerated and/or aerated CH_3CN, $CH_3CN–H_2O$ (different ratios) and H_2O. In this way it was possible to evaluate the gradual changes in product selectivity on going from CH_3CN (SET process) to aqueous CH_3CN, to pure water.



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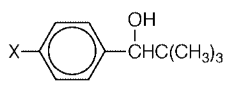
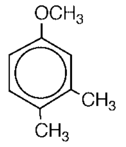


2: X=OCH$_3$; **3**: X=H



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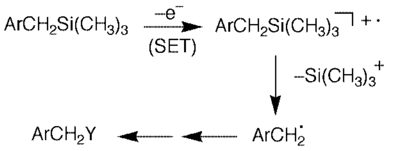
Results and discussion

3-Methoxybenzyltrimethylsilane (1)

It is known that benzyltrimethylsilane radical cations, produced by a SET process, rapidly desilylate to give products that maintain the $ArCH_2$-moiety[6] (Scheme 1).



Scheme 1

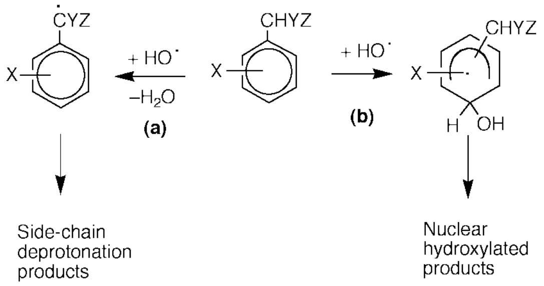
The efficient C–Si fragmentation process yields the benzylic radical that quickly gives the corresponding side chain derivative.[6] In contrast, it is expected that an $HO^\bullet$-promoted non-SET oxidative process should give either side chain deprotonation products, where the $ArCH_2$-moiety is not maintained (Scheme 2, path **a**, Y = H, Z = $Si(CH_3)_3$), or nuclear hydroxylated derivatives (path **b**).[7]

Recently a SET mechanism was also hypothesized in TiO_2-sensitized photooxidation of benzyltrimethylsilanes in CH_3CN.[4a,8] In particular, in deaerated medium and in the presence

Table 1 TiO_2-photosensitized oxidation of 3-methoxybenzyltrimethylsilane (**1**) in deaerated CH_3CN, CH_3CN–H_2O and H_2O, in the presence of Ag_2SO_4

Entry	H_2O (%)	t/min	Unreacted substrate (%)[a]	Products (%)[a] 5	6
1	—	30	58	41	—
2	20	30	50	34	7
3	50	10	70	21	8
4	50	30	—	68	27
5	80	30	52	15	19
6	100	30	71	4	10

[a] With respect to the starting material, considering the reaction stoichiometry.



Scheme 2

of Ag^+, the exclusive reaction product was the corresponding 1,2-diarylethane, formed by the coupling of the surface-adsorbed benzylic radicals derived from the intermediate radical cations.[4a]

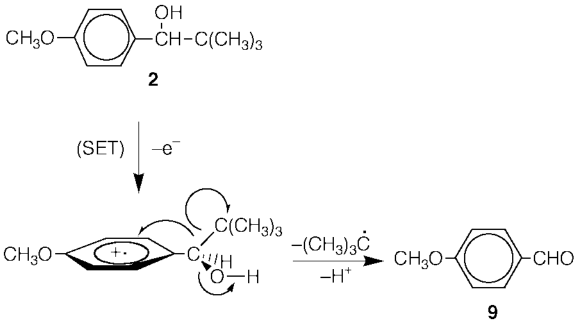
In this work we report (Table 1) the percentage distribution of the products in the TiO_2-photosensitized oxidation of 3-methoxybenzyltrimethylsilane (**1**) in the different media. In CH_3CN, 1,2-bis(3-methoxyphenyl)ethane (**5**) is the exclusive reaction product (entry 1), whereas in aqueous medium the dimer **5** is accompanied by 3-methoxybenzyl alcohol (**6**). The **6**:**5** molar ratio increased from 0.21 to 2.5 as the water content increased from 20 to 100% (entries 2–6). The presence of the dimer **5** and of the alcohol **6**, that maintain the $ArCH_2$-moiety, suggests a SET mechanism also in the presence of water.

Other products derived from HO•-induced non-SET processes, such as nuclear hydroxylation (phenolic products) or side chain hydrogen atom abstraction (probably 3-methoxybenzaldehyde, **7** [9,10]), were not present.

The dimer **5** should be derived from **1** through the previously suggested mechanism[4a] (Scheme 3, path **a**). The alcohol **6** cannot be derived from the oxidation of the final product **5** since the **6**:**5** ratio remained practically unchanged with time (compare entries 3 and 4). A possible explanation is that **6** comes from the competitive coupling between the benzylic radical and the HO• (Scheme 3, path **b**), both adsorbed on the semiconductor surface. Accordingly, the **6**:**5** molar ratio increases as the amount of water increases, probably as the HO• concentration gradually increases on the semiconductor. In line with this suggestion, water should be competitively oxidized (eqns. (1) and (2)) but the HO• formed should only participate in the steps following the primary oxidative step.[11]

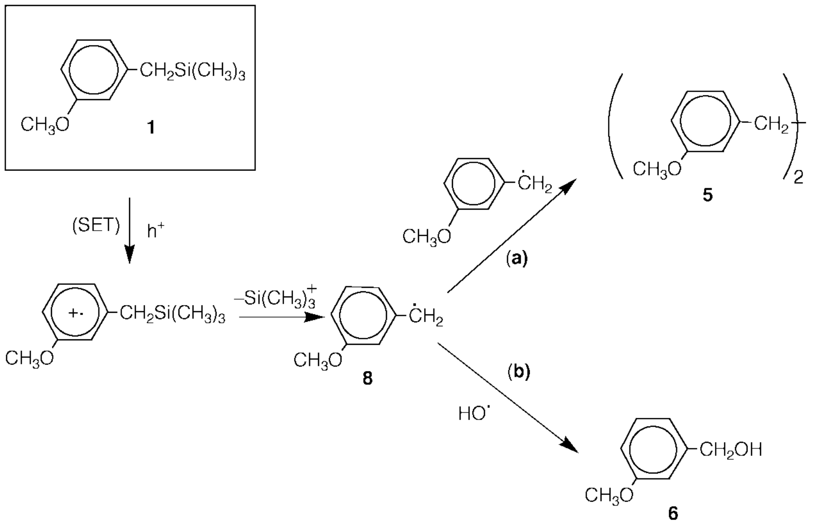
2,2-Dimethyl-1-arylpropan-1-ols (2 and 3)

It was recently reported that 4-methoxybenzaldehyde (**9**) can only be derived from **2** by a SET process (concerted homolytic and base-catalyzed C–C fragmentation of the corresponding radical cation, Scheme 4).[12]



Scheme 4

Alternatively, through benzylic hydrogen abstraction, the HO•-induced non-SET reaction should yield either *tert*-butyl 4-methoxyphenyl ketone (**10**)[13] as a side chain deprotonation product (Scheme 2, path **a**, X = 4-OCH_3, Y = OH, Z = $C(CH_3)_3$) or nuclear hydroxylated derivatives, by aromatic ring attack (path **b**). Previously[4e] we showed that, in the TiO_2-photosensitized oxidation of **2** in deaerated and aerated CH_3CN, in the presence of Ag^+ as the electron acceptor, **9** is the principal product accompanied by a minor amount of ketone **10** (Table 2, entries 1 and 3); moreover it has been suggested that both products should come from the same intermediate, the radical cation **11**, *via* a SET process (paths **a** and **b** in Scheme 5, X = OCH_3). This hypothesis is also confirmed by the fact that

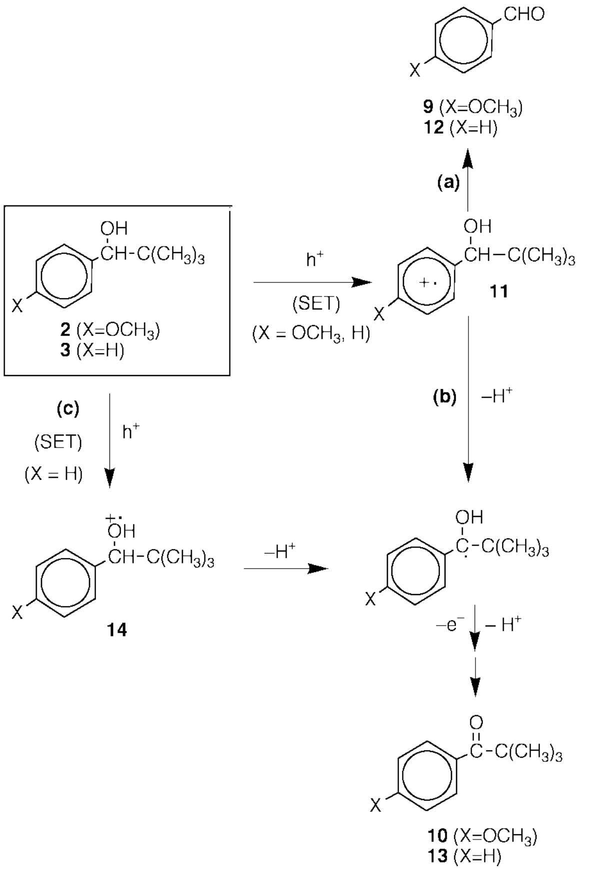


Scheme 3

Table 2 TiO_2-photosensitized oxidation of 2,2-dimethyl-1-(4-methoxyphenyl)propan-1-ol (**2**) in deaerated and aerated CH_3CN, CH_3CN–H_2O and H_2O, in the presence of Ag_2SO_4

Entry	H_2O (%)	*t*/min	Unreacted substrate (%)[a]	Products (%)[a] **9**	**10**
1[b]	—	15	58	27	2
2	—	120	—	85	9
3[b,c]	—	15	44	38	4
4	20	15	90	7	—
5[c]	20	15	83	14	2
6	50	15	82	16	—
7[c]	50	15	72	23	—
8	80	15	55	28	—
9[c]	80	15	62	37	—
10	100	15	69	28	—
11[c]	100	15	69	27	—

[a] With respect to the starting material. [b] Ref. 4*e*. [c] In the presence of oxygen.



Scheme 5

the **9**:**10** molar ratio (*ca.* 10) is practically constant with time (compare entries 1 and 2).

Either in deaerated or in aerated aqueous media (Table 2, entries 4–11) the selectivity changes in favour of aldehyde **9**, a product in line with the operation of a SET mechanism. This change in selectivity is reasonable since the medium basicity should decrease on going from CH_3CN to H_2O (the basic sites on the semiconductor surface[14] are probably occupied by water) slowing the rate of the cation radical deprotonation path (Scheme 5, path **b**, $X = OCH_3$).

To evaluate the incidence of substrate reduction potential on the competition between direct and indirect oxidation, the ring unsubstituted propanol **3** was submitted to photooxidation. In fact, **3** ($E_p = 2.18$ V *vs.* SCE) has a higher reduction potential than **2** ($E_p = 1.52$ V) and, therefore, the TiO_2-induced SET process should be less efficient with alcohol **2**.

Table 3 TiO_2-photosensitized oxidation of 2,2-dimethyl-1-phenylpropan-1-ol (**3**) in deaerated CH_3CN, CH_3CN–H_2O and H_2O, in the presence of Ag_2SO_4

Entry	H_2O (%)	*t*/h	Unreacted substrate (%)[a]	Products (%)[a] **12**	**13**
1	—	3	39	24	23
2	20	5	91	7	—
3	50	5	76	11	2
4	80	5	75	14	2
5	100	5	82	14	—

[a] With respect to the starting material.

Table 4 TiO_2-photosensitized oxidation of 3,4-dimethylanisole (**4**) in aerated CH_3CN, CH_3CN–H_2O and H_2O, in the presence of Ag_2SO_4

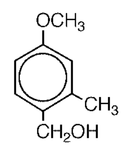
Entry	H_2O (%)	*t*/h	Unreacted substrate (%)[a]	Products (%)[a] **15**	**17**
1	—	1	76	19	—
2	10	2	75	22	—
3	20	2	68	20	4
4	50	2	65	16	5
5	80	2	75	16	7
6	100	1	69	7	5

[a] With respect to the starting material.

The product distributions (benzaldehyde, **12**, and *tert*-butyl phenyl ketone, **13**) from the photooxidation of **3** are reported in Table 3. As expected, **3** is less reactive than **2** in all the considered media (by comparing Tables 2 and 3, it can be seen that similar product conversions were obtained but over longer times). The reaction in CH_3CN gave **12** and **13** in nearly equimolar amounts (*ca.* 1, see Table 3, entry 1); in this medium, where a SET mechanism is operative, the lower molar ratio **12**:**13** from the reaction of **3**, with respect to the ratio **9**:**10** (*ca.* 10) from the reaction of **2**, could be attributed to the involvement of another SET process from **3** (Scheme 5, path **c**) that gives the ketone **13** from the radical cation **14**. In fact it has been reported that, within a series of benzylic alcohols, those with higher reduction potential can also lose the electron from the OH moiety, more easily oxidizable than expected, as preferentially adsorbed at the semiconductor surface.[4f,15] As observed for **2**, in aqueous media (Table 3, entries 2–5) the reaction product was almost exclusively the aldehyde **12**, a species unequivocally derived from a SET process (Scheme 5, path **a**, X = H).

3,4-Dimethylanisole (4)

It is reported that, in the side-chain oxidative functionalization of 1-X-3,4,5-trimethylbenzenes, the relative reactivity of the 4- and 3-methyl groups (k_4/k_3 ratio) is much higher in a SET than in a non-SET (hydrogen atom transfer) process.[16] Recently we considered 3,4-dimethylanisole as a test substrate for the SET process in the TiO_2-sensitized photooxygenation of methylaromatic compounds in CH_3CN and in the presence of Ag_2SO_4.[4b] In Table 4 (entry 1) we report that, in this medium, 4-methoxy-2-methylbenzaldehyde (**15**), a product derived from the functionalization of 4-CH_3, is exclusively formed ($k_4/k_3 >$ 100 as 5-methoxy-2-methylbenzaldehyde (**16**) is undetectable by ^1H-NMR and GC analysis). To verify the validity of the mechanistic test, **4** was anodically oxidized in AcOH–AcOK (SET process) and brominated with *N*-bromosuccinimide (hydrogen atom abstraction process). The k_4/k_3 ratio was determined from the molar ratio of 4-methoxy-2-methylbenzyl alcohol (**17**) and 5-methoxy-2-methylbenzyl alcohol (**18**) obtained by $LiAlH_4$ reduction of the corresponding benzylic acetates (anodic oxidation, $k_4/k_3 > 100$) or by hydrolysis of the corresponding benzylic bromides (reaction with *N*-bromosuccinimide, $k_4/k_3 = 11$). The results confirmed that, in CH_3CN, the k_4/k_3 ratio observed in the TiO_2 photooxidation is in line with a SET process (Scheme 6, path **a**).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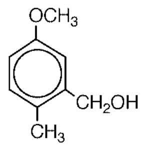
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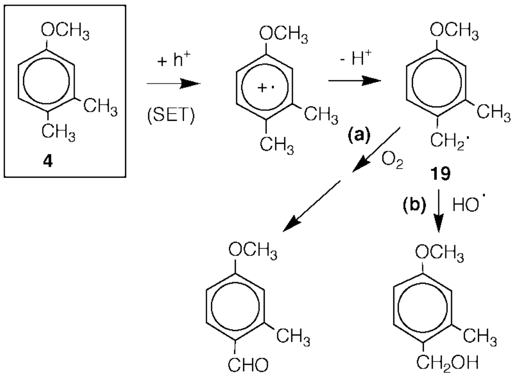

Scheme 6

The photooxidation products obtained in the presence of water are also reported in Table 4 (entries 2–6). Besides the benzaldehyde **15**, a small amount of alcohol **17** was also present and then, as both products were functionalized at 4-CH_3, the exclusive operation of a SET mechanism was also confirmed in the presence of water. In particular, in line with the hypothesis relative to the formation of alcohol **6** from silane **1**, **17** should be derived from the coupling between $HO^•$ and the benzylic radical **19**, both adsorbed on the TiO_2 surface (Scheme 6, path **b**).

Experimental

^1H-NMR spectra were obtained on a Bruker AC 200 (200 MHz) spectrometer, from solutions in $CDCl_3$ with TMS as internal standard. GCMS analyses were performed on a Hewlett Packard 5890A gas-chromatograph (HP-1 capillary columns, 30 m) coupled with a mass selective detector 5970 (70 eV). VPC analyses were carried out on a HP 5890 gas-chromatograph using a SPB-20 and HP-Innovax capillary column. E_p values were obtained from an AMEL 552 potentiostat (cyclic voltammetry at 100 mV s^{-1}, 1 mm diameter platinum disc anode) in CH_3CN–$LiClO_4$ (0.1 M).

Starting materials

TiO_2 (anatase, dried at 110 °C), Ag_2SO_4, CH_3CN (HPLC grade), 2,2-dimethyl-1-phenylpropan-1-ol (**3**) and 3,4-dimethylanisole (**4**) were commercial samples.

3-Methoxybenzyltrimethylsilane (**1**) was prepared by reacting trimethylsilylmagnesium chloride with 3-methoxybenzyl chloride, distilled under vacuum and chromatographed on alumina (eluent petroleum ether) [δ_H (200 MHz) 6.94 (2H, d, $J = 10$, ArH), 6.79 (2H, d, $J = 10$, ArH), 3.78 (3H, s, OCH_3), 2.02 (2H, s, CH_2) and 0.00 (9H, s, $Si(CH_3)_3$); *m*/*z* 194 (M^+), 179 (100%), 164, 149, 121, 73, 45]. 1-(4-Methoxyphenyl)-2,2-dimethylpropan-1-ol (**2**) was prepared, as previously described,[12] by reacting *tert*-butylmagnesium bromide with 4-methoxybenzaldehyde in anhydrous diethyl ether and purified by chromatography on a silica gel column (eluent *n*-hexane–diethyl ether 9 : 1) [δ_H 7.16 (2H, d, $J = 8$, ArH), 6.78 (2H, d, $J = 8$, ArH), 4.24 (1H, s, CH), 3.72 (3H, s, OCH_3) and 0.86 (9H, s, CH_3);[17] *m*/*z* 137 ($M^+ - 57$, 100%), 121, 109, 66, 43].

5-Methoxy-2-methylbenzyl alcohol (18)

The alcohol was prepared as follows. 3-Bromo-4-methylphenol [δ_H 7.07 (1H, d, $J = 8$, ArH), 6.69 (1H, dd, $J = 8$, $J = 3$, ArH), 7.05 (1H, d, $J = 3$, ArH), 5.21 (1H, s, OH) and 2.31 (3H, s, CH_3);[18] *m*/*z* 186 (M^+), 157, 131, 117, 107 (100%), 94, 85, 77, 63, 51, 43] was obtained by hydrolysis of diazonium salt of 3-bromo-4-methylaniline.[19] The phenol was methylated with dimethyl sulfate to give 3-bromo-4-methylanisole [δ_H 7.00 (1H, d, $J = 9$, ArH), 6.90 (1H, d, $J = 3$, ArH), 6.75 (1H, dd, $J = 9$, $J = 3$, ArH), 3.76 (3H, s, OCH_3) and 2.31 (3H, s, CH_3);[18] *m*/*z* 202 (M^+, 100%), 185, 169, 157, 121, 105, 91, 77, 63, 51] and carboxylated *via* Grignard reaction to 5-methoxy-2-methylbenzoic acid [mp: 145–147 (lit.[20] 146–147 °C); δ_H 7.59 (1H, d, $J = 3$, ArH), 7.18 (1H, d, $J = 9$, ArH), 7.02 (1H, dd, $J = 9$, $J = 3$, ArH), 3.84 (3H, s, OCH_3) and 2.58 (3H, s, CH_3); *m*/*z* 166 (M^+, 100%), 148, 133, 120, 105, 91, 77, 63, 51, 45] and the acid was reduced by $LiAlH_4$ in anhydrous ether to 5-methoxy-2-methylbenzyl alcohol (**18**) [δ_H 7.05 (1H, d, $J = 8$, ArH), 6.93 (1H, d, $J = 3$, ArH), 6.72 (1H, dd, $J = 8$, $J = 3$, ArH), 4.66 (2H, s, CH_2), 3.79 (3H, s, OCH_3), 2.26 (3H, s, CH_3) and 2.18 (1H, br s, OH); *m*/*z* 152 (M^+), 134 (100%), 121, 109, 104, 91, 77, 65, 51, 45].

5-Methoxy-2-methylbenzaldehyde (16)

The aldehyde was obtained by TiO_2-photosensitized oxidation of the corresponding benzyl alcohol (**18**)[4f] [δ_H 10.28 (1H, s, CHO), 7.33 (1H, d, $J = 3$, ArH), 7.17 (1H, d, $J = 8$, ArH), 7.05 (1H, dd, $J = 8$, $J = 3$, ArH), 3.84 (3H, s, OCH_3) and 2.60 (3H, s, CH_3);[21] *m*/*z* 150 (M^+, 100%), 135, 121, 107, 91, 65, 63, 51, 43].

Photochemical oxidation sensitized by TiO_2

The reactions were carried out by external irradiation (500 W high-pressure mercury lamp, Pyrex filter) of acetonitrile, aqueous acetonitrile or water solutions (25 ml) of the substrate (0.30 mmol), in the presence of TiO_2 (130 mg) and Ag_2SO_4 (0.30 mmol); N_2 or O_2 were gently bubbled in the magnetically stirred heterogeneous mixture; the reactor was a cylindrical flask ($\emptyset = 1.6$ cm, $h = 16$ cm) equipped with a water cooling jacket and intensive condenser. After double paper filtration of TiO_2, the reaction mixture was poured into water and extracted with ether. The analysis of the reaction products and of the unreacted substrate was performed by ^1H-NMR and/or by VPC of the reaction mixture in the presence of an internal standard (1,4-dimethoxybenzene or bibenzyl). Material balance was always ≥85% *vs.* the amount of starting substrate.

Reaction products from photooxidation reactions

The crude reaction product was chromatographed on silica gel eluting with light petroleum, light petroleum–diethyl ether (from 9 : 1 to 1 : 1 w/w) and diethyl ether. The structure of isolated products was attributed by comparison with authentic specimens or literature data. The details are as follows: 3-methoxybenzyl alcohol (**6**), 4-methoxybenzaldehyde (**9**), benzaldehyde (**12**) and *tert*-butyl phenyl ketone (**13**) were commercial samples; *tert*-butyl 4-methoxyphenyl ketone (**10**) was available from a previous work;[4e] 5-methoxy-2-methylbenzaldehyde (**16**) and 5-methoxy-2-methylbenzyl alcohol (**18**) were prepared as described above; 1,2-bis(3-methoxyphenyl)ethane (**5**) [δ_H 7.1–6.7 (8H, m, ArH), 3.70 (6H, s, OCH_3) and 2.84 (4H, s, CH_2);[22] *m*/*z* 242 (M^+), 122, 121 (100%), 91, 65], 4-methoxy-2-methylbenzaldehyde (**15**) ([δ_H 10.11 (1H, s, CHO), 7.76 (1H, d, $J = 9$, ArH), 6.85 (1H, dd, $J = 9$, $J = 3$, ArH), 6.75 (1H, d, $J = 3$, ArH), 3.86 (3H, s, OCH_3) and 2.65 (3H, s, CH_3);[23] *m*/*z* 150 (M^+), 149 (100%), 121, 106, 91, 77, 65, 63, 51] and 4-methoxy-

2-methylbenzyl alcohol (**17**) [δ_H 7.24 (1H, d, $J = 8$, ArH), 6.74 (1H, d, $J = 3$, ArH), 6.71 (1H, dd, $J = 8$, $J = 3$, ArH), 4.62 (2H, s, CH_2), 3.79 (3H, s, OCH_3), 2.35 (3H, s, CH_3) and 1.71 (1H, br s, OH); *m/z* 152 (M^+), 137, 123, 108, 91(100%), 77, 65, 51][24] were identified by comparison with literature data.

Bromination of 3,4-dimethylanisole (4) with *N*-bromosuccinimide (NBS)

The substrate (18 mmol), NBS (5.5 mmol) and azobis(isobutyronitrile) (1.2 mmol) in CCl_4 (40 ml, from P_2O_5) were refluxed under nitrogen for 2 h. The mixture was worked up as previously reported.[25]

Anodic oxidation of 3,4-dimethylanisole (4)

The electrochemical experiments were performed in a jacketed microcell with Pt as anode and cathode. The magnetically stirred solutions were electrolysed (1.6 V *vs.* SCE constant potential, and 5–20 mA cm^{-2}) under nitrogen until 1 F mol^{-1} of charge was passed. To avoid drastic current decreases during electrolysis, the principal circuit was opened periodically (*ca.* 10 s). The substrate (2.3 mmol) was dissolved in 40 ml AcOH–AcOK (3×10^{-2} M). The reaction mixture was worked up as previously described.[26]

Determination of isomeric distributions in the reactions from 3,4-dimethylanisole (4)

The products isomeric distributions in the bromination and anodic oxidation of **4** were determined, respectively, by hydrolysis (NaOH, 2.5% in aqueous acetone) and by reduction ($LiAlH_4$ in anhydrous ether) of the reaction (side chain) products to the corresponding benzylic alcohols.[27] The crude was analysed by VPC and ^{1}H-NMR (on the basis of the relative intensity of CH_2 peaks).

Acknowledgements

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