Structural Effects in the TiO$_2$-Photocatalyzed Oxidation of Alkylaromatic Compounds in Acetonitrile in the Presence of Ag$_2$SO$_4$

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The TiO$_2$-sensitized photochemical reactions of some alkylbenzenes (ArCH$_2$R; R = H, Me), 1-aryl-2-propanols, and corresponding methyl ethers (ArCH$_2$C(OR″)R′CH$_3$; R′, R″ = H, Me) have been investigated in MeCN, in the presence of Ag$_2$SO$_4$, which traps the photogenerated electrons. With ArCH$_2$R, the corresponding radical cations are generated by the photoexcited TiO$_2$ and are then deprotonated to form benzyl radicals; from the latter 1,2-diarylethanes, 3-arylpropanonitriles, and benzylacetamides are obtained as major products. With ArCH$_2$C(OR″)R′CH$_3$, the formed radical cations undergo C—C bond cleavage as the only observed route, when Ar = Ph. However, when Ar = 4-MeOPh and R′ = H, the radical cation undergoes C—H bond cleavage as the major or exclusive reaction path. These results are compared with those obtained in the corresponding homogeneous photochemical reactions, and their implications with respect to the role of the structure on the side-chain reactivity of aromatic radical cations are discussed.

Introduction

The homogeneous photochemical oxidation of alkylaromatics in the presence of suitable sensitizers (generally a cyanoaromatic compound) has been intensively investigated in the last decade.[1] The crucial step of this process is the transfer of one electron from the substrate to the sensitizer with formation of an alkylaromatic radical cation. This species can undergo a variety of reaction pathways, and important information in this respect, particularly on the competition between different fragmentation modes involving the cleavage of a side-chain bond β to the aromatic ring, has been provided by careful products studies. Together with that of the radical cation structure, the role of the sensitizer, the solvent and the reaction conditions have been established in a very satisfactory way.

Comparable studies concerning the heterogeneous counterpart of the above reactions, i.e., photochemical oxidations with TiO$_2$ as the sensitizer, are not, however, available, whereas they would certainly be of interest since in these oxidations no reaction of the alkylaromatic radical cation and/or the benzyl radical generated therefrom is possible with either the sensitizer or its reduced form.[2] Moreover, since the electron transfer occurs from the *adsorbed* aromatic substrate to the hole (h$^+$) generated in the photoexcited TiO$_2$, the radical cation forms at the semiconductor surface and may exhibit different behaviors than when formed in the solution bulk. A different products pattern, with respect to that observed under homogeneous conditions, is therefore anticipated for the TiO$_2$-induced photochemical oxidations of alkylaromatics, which may provide additional information on the scope of these reactions as well as on the chemistry of alkylaromatic radical cations.

Generally, the TiO$_2$-induced photochemical oxidations of alkylaromatics are carried out in the presence of dioxygen, which traps the photogenerated electron, being reduced to O$_2$$^{•-}$,[3] and allows the reaction to proceed. Under these conditions, however, a really informative product study is of limited significance since the benzyl radicals formed by the β bond cleavage reactions of the radical cation are trapped by dioxygen to give peroxidic products. From the latter, by decomposition and further oxidation, carbonyl compounds, mainly benzaldehydes and benzoic acids, are obtained. Moreover, reactions of the radical cation as well as of the benzyl radicals with O$_2$$^{•-}$ cannot be excluded. These problems, however, can be overcome by replacing dioxygen with Ag$^+$ as the photogenerated electron trap, a procedure already used by us in our recent study of the TiO$_2$-induced photochemical oxidations of benzyltrimethylsilanes.[4] In the absence of dioxygen, the structures of the products can easily be correlated to those of the benzyl radicals formed in the β bond cleavage reactions, and meaningful information on the reaction pathways followed by the radical cations can be obtained.

In this paper we report on the photochemical oxidation, sensitized by TiO$_2$ in MeCN, in the presence of Ag$_2$SO$_4$, of toluene (**1**), *p*-xylene (**2**), durene (**3**), ethylbenzene (**4**), 4-methoxytoluene (**5**), and the 1-aryl-2-propanols and corresponding methyl ethers **6-11**.

For the radical cations of **1-5**, only cleavage of a β C—H bond is possible, whereas, for the radical cations of **6-11**, β C—C bond cleavage should be the most likely possibility, in light of a recent work by Arnold and his associates concerning the homogeneous photochemical oxidation of **7** sensitized by 1,4-dicyanobenzene.[5]

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(3) (a) Takagi, K.; Fujioka, T.; Sawaki, Y.; Iwamura, H. *Chem. Lett.* **1985,** 913. (b) Fujihira, M.; Satoh, Y.; Osa, T. *J. Electroanal. Chem.* **1981,** *126,* 277. (c) Fujihira, M.; Satoh, Y.; Osa, T. *Bull. Chem. Soc. Jpn.* **1982,** *55,* 666. (d) Pichat, P.; Disdier, J.; Herrmann, J.-M. *Nouv. J. Chim.* **1986,** *10,* 545. (e) Mozzanega, M.-N.; Herrmann, J.-M.; Pichat, P. *Tetrahedron Lett.* **1977,** 2965. (f) Blatt, E.; Furlog, D. N.; Mau, A. W.-H.; Sasse, W. H. F.; Wells, D. *Aust. J. Chem.* **1989,** *42,* 1351. (g) Pincock, J. A.; Pincock, A. L.; Fox M. A. *Tetrahedron* **1985,** *41,* 4107. (h) Fox, M. A.; Chen, C.-C.; Younathan J. N. N. *J. Org. Chem.* **1984,** *49,* 1969.
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Table 1. Product Yields in TiO2-Photosensitized Oxidation of Alkylbenzenes 1–5, in CH3CN, in the Presence of Ag2SO4

ArCH2R[a]	time,[b] h	ArC(R)=O 15	ArC(R)HC(R)HAr 12	ArC(R)HCH2CN 13	ArC(R)HNHCOCH3 14
		products,[c] %			
1	6	3	13	20	<2
2	6	3	23	23	2
3	6	3	16	23	7
4	5	3	14[d]	13	14
5	2	3	5	7	19 (16)[e]

[a] R = H, except for **4** where R = Me. [b] At room temperature, in deaerated solvent. [c] With respect to the starting material. [d] An equimolar mixture dl:meso. [e] The formation of **16** was observed only if product analysis was directly carried in the crude after solvent evaporation from the reaction mixture. However, when this mixture was worked up as usual, **16** was not detected and material balance was unsatisfactory. If the reaction time is lenghtened to 5 h, the dimer **16** is not present and 4-methoxybenzylacetamide is one of the products, but the material recovery is again incomplete.
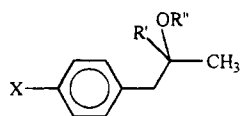
	X	R'	R''
6	H	H	H
7	H	H	CH3
8	H	CH3	H
9	H	CH3	CH3
10	OCH3	H	H
11	OCH3	H	CH3

Results

A deareated solution of 0.30 mmol of substrate in 25 mL of MeCN was subjected to external irradiation by a 500-W high-pressure mercury lamp, with a Pyrex filter, in the presence of 130 mg of TiO2 and 0.30 mmol of Ag2SO4, under gentle bubbling of N2. During the irradiation Ag was formed (presumably deposited on TiO2)[6] but without any consequence on the efficiency of the photochemical process.[7] At the end of the irradiation, the reaction mixture was worked up as usual (see Experimental) and the isolated products characterized by spectroscopic methods and/or comparison with authentic specimens.
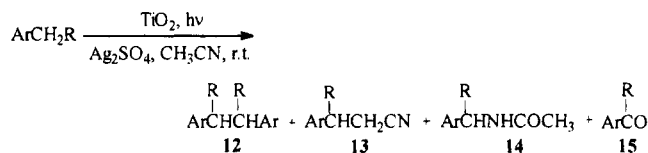
The quantitative analysis of the reaction products and unreacted substrate was performed by ¹H-NMR in the presence of an internal standard. In some cases the amount of the substrate was determined by VPC vs an internal standard. Material balance was generally satisfactory (in the range 85–95%).

The products formed in the reactions of **1-4** are described in Scheme 1 (R = H, Me).

In the reaction of **5**, **14** is not observed, whereas the diarylmethane **16** is also formed.

The yields for the photochemical oxidations of the substrates **1–5** are displayed in Table 1. With **1** and **2** the major products are the 1,2-diarylethanes **12** and the 3-arylpropanonitriles **13** accompanied by very small amounts of the corresponding benzylacetamides **14** and benzaldehydes **15**. With **3**, the products pattern is quite similar, the only difference being a substantial increase in the amount of the benzylacetamide. This increase is still more marked in the reaction of **4**, where the yield of **14** is comparable to those of **12** and **13** . In the reaction

(5) Arnold, D. R.; Lamont L. *J. Can. J. Chem.* **1989**, *67*, 2119.

(6) (a) Pichat, P.; Fox, M. A. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier : Amsterdam, 1988; Vol. D, p 272. (b) Ohtani, B.; Okugawa, Y; Nishimoto, S.; Kagiya, T. *J. Phys. Chem.* **1987**, *91*, 3550. (c) Wang, C. M.; Mallouk, T. E. *J. Am. Chem. Soc.* **1990**, *112*, 2016.
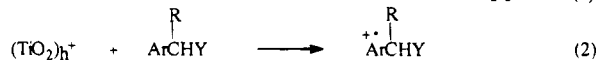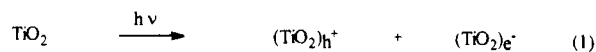
(7) During our previous work on the photooxidation of benzyltrimethylsilanes[4] we have found that TiO2 can be reused without any significant decrease in the efficiency of the reaction.

Scheme 1

$$ArCH_2R \xrightarrow[Ag_2SO_4, CH_3CN, r.t.]{TiO_2, h\nu}$$

$$ArCHCHAr + ArCHCH_2CN + ArCHNHCOCH_3 + ArCO$$

12   13   14   15

of **5**, the major product is the diarylmethane **16**, together with minor amounts of **12**, **13**, and **15**.

16
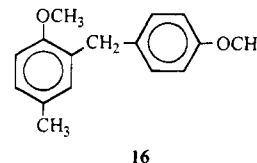
From the phenylpropanols **6** and **8** and the corresponding ethers **7** and **9**, the same products form, found in the oxidation of toluene and with a similar distribution (see Table 2). In addition, with **6** and **7** substantial amounts of benzyl methyl ketone are also observed. A different situation holds with the 4-methoxy derivative **10**, which affords 4-methoxybenzaldehyde as the major product, accompanied by minor amounts of 4-methoxybenzylacetamide. 4-Methoxybenzaldehyde is the only product observed in the reaction of **11**. Finally, it must be noted that, in all reactions leading to the nitriles **13**, small amounts of succinonitrile are also formed.

Discussion

There is clear evidence[2,8] that the photooxidation of aromatic compounds sensitized by TiO2 in the presence of Ag2SO4 takes place as described in Scheme 2, for the particular case of an alkylaromatic compound, ArCHRY, as the substrate, where the fundamental role of Ag⁺ is that of the electron-trapping species. However, when radicals of suitable oxidation potential are formed, Ag⁺ may convert them into the corresponding carbocations (vide infra).

With compounds **1-5**, where R = H, CH3 and Y = H, the only route available to the radical cation is the cleavage of a β C—H bond (eq 3). A benzyl radical forms for which, on the basis of the nature of the observed products (Table 1), the reaction pathways illustrated in Scheme 3 can be suggested: (a) dimerization to give **12**; (b) H-abstraction from the solvent (MeCN) to form the radical •CH2CN which then can couple with the benzyl

(8) Baciocchi, E.; Rosato, G. C.; Rol, C.; Sebastiani G. V. *Tetrahedron Lett.* **1992**, *33*, 5437.

Table 2. Product Yields in TiO₂-Photosensitized Oxidation of Some 1-Aryl-2-propanols and Corresponding Methyl Ethers, in CH₃CN, in the Presence of Ag₂SO₄

substrate ArCH₂C(R″)(OR′)CH₃	products,[a,b] %				
	ArCHO	ArCH₂CH₂Ar	ArCH₂CH₂CN	ArCH₂NHCOCH₃	ArCH₂COCH₃
6	<2	22	16	3	14
7		13	9		6
8	3	20	15	2	
9	3	14	14	<2	
10	18	<2	<2	9	
11	8				

[a] After 5 h, at room temperature, and in deaerated solvent. [b] With respect to the starting material.

Scheme 2

$$TiO_2 \xrightarrow{h\nu} (TiO_2)h^+ + (TiO_2)e^- \quad (1)$$

$$(TiO_2)h^+ + \underset{ArCHY}{\overset{R}{|}} \longrightarrow \overset{R}{\underset{ArCHY}{|}}{}^{+\cdot} \quad (2)$$

$$\overset{R}{\underset{ArCHY}{|}}{}^{+\cdot} \longrightarrow \overset{R}{\underset{ArCH}{|}}{}^{\cdot} + Y^+ \quad (3)$$

$$\overset{R}{\underset{ArCH}{|}}{}^{\cdot} \longrightarrow Products \quad (4)$$

$$(TiO_2)e^- + Ag^+ \longrightarrow Ag \quad (5)$$

Scheme 3

Table 3. Yields of Products Deriving from Benzylic Radicals and Carbocations Intermediates in the Photooxidation of Alkylbenzenes and Oxidation Potentials of the Benzylic Radicals

ArCH₂R	products from (%)		E°(ArC⁺HR/ArĊHR),[c]
	ArĊHR[a]	ArC⁺HR[b]	V vs SCE
1	36	<2	0.73
2	49	2	0.51
4	30	14	0.37[d]
5	15	19	0.26

[a] Sum of 12, 13, and 15. Data from Table 1. [b] Benzylacetamide 14 for 1, 2, and 4; diarylmethane 16 for 5. Data from Table 1. [c] Reference 11. [d] Reference 12.

radical itself to afford 13;[9] (c) oxidation to a benzyl cation (presumably by Ag⁺) which then reacts either with the solvent to form a benzylnitrilium cation, immediately hydrolyzed (by adventitious water) to the corresponding benzylacetamide 14, or with the neutral substrate to form a diarylmethane.[10] The latter possibility requires an electron-rich substrate and, accordingly, is observed exclusively with compound 5 (formation of 16). Besides these main reaction paths, some trapping of the benzyl radicals by residual oxygen is also possible, as indicated by the minor amounts of carbonyl compounds 15 detected in the reaction products of all reactions. It is worthy of note that, as expected, the relative importance of pathway c, the carbocation route, with respect to pathways a and b, increases by decreasing the oxidation potential of the intermediate benzyl radical, as clearly shown in Table 3.

An interesting notation is that in our previous study of TiO₂-promoted photochemical oxidations of benzyltri-

methylsilanes, in the presence of Ag₂SO₄, exclusive formation of 1,2-diarylethanes was observed.[4] In these reactions, a benzyltrimethylsilane radical cation forms, undergoing C—Si bond cleavage. Dimerization of the produced benzyl radical is the only observed reaction. This discrepancy with respect to the present results is probably due to the heterogeneous nature of these oxidations as well as to the much faster rate of the C—Si bond cleavage in a benzyltrimethylsilane radical cation with respect to the rate of C—H bond cleavage in an alkylaromatic radical cation.[13] Thus, the former once formed at the semiconductor surface should rapidly desilylate, providing a high local concentration of benzyl radical, which makes dimerization the most favored process. An alkylaromatic radical cation, instead, might have a lifetime long enough to diffuse into the medium since deprotonation is a relatively slow process, especially under conditions where no base is present. The benzyl radical may therefore be formed in the bulk of the solution, and pathways b and c can efficiently compete with dimerization.

Coming to the results for the reactions of 6–11, the data in Table 2 show that the photooxidations of the phenylpropanols 6 and 8 and their methyl ethers 7 and 9 lead to the same products, and with similar distribution, found in the photooxidation of toluene (Table 1). In addition, the formation of benzyl methyl ketone is observed with 6 and 7.

Clearly, a benzyl radical is also formed in the photooxidation of 6-9, which now derives from the cleavage of the C—C β bond in the intermediate radical cation. Such a cleavage should take place in a heterolytic way, as indicated in eq 3 where R = H and Y = C(OR′)R″CH₃, due to the much larger stability of an α-oxy carbocation with respect to a benzyl carbocation.[5] No significant competition by the cleavage of a β C—H bond has been observed in all cases since the yields of benzaldehyde,

(9) In favor of this suggestion is the presence of succinonitrile as the side product derived from coupling of the ·CH₂CN radical.

(10) (a) Kaborè, L.; Laurent, E.; Marquet, B. *J. Chem. Res., Synop.* **1993**, 12. (b) Eberson, L.; Olofsson, B. *Acta Chem. Scand.* **1969**, *23*, 2355.
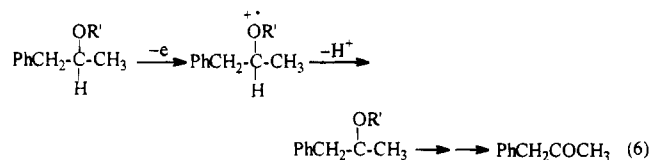
(11) Wayner, D. D. M.; Sim, B. A.; Dannemberg, J. J. *J. Org. Chem.* **1991**, *56*, 4853.

(12) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(13) (a) Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290. (b) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973.

which should be the final product of this type of cleavage (*via* further oxidation, with the breaking of the C—C bond of a first formed α-substituted derivative[14]), are very low and moreover are again similar to those observed in the photooxidation of toluene. It is therefore very likely that also in this case benzaldehyde derives from the reaction of benzyl radical with adventitious dioxygen, as suggested before.

The formation of benzyl methyl ketone from **6** and **7** might indicate an electron abstraction from the OR′ group, followed by deprotonation at C_β (eq 6). This route,

$$PhCH_2\underset{H}{\overset{OR'}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow{-e} PhCH_2\underset{H}{\overset{\overset{+\cdot}{OR'}}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow{-H^+}$$

$$PhCH_2\underset{\cdot}{\overset{OR'}{\underset{|}{\overset{|}{C}}}}-CH_3 \longrightarrow \longrightarrow PhCH_2COCH_3 \quad (6)$$

which is thermodynamically unfavored with respect to the one involving an electron abstraction from the π system, since aliphatic alcohols and ethers are less oxidizable than aromatic compounds,[15] might take advantage from a preferential adsorption of **6** and **7** at the TiO₂ surface through the OR′ group.[2,16] On the other hand the capacity of photoexcited TiO₂ to oxidize aliphatic alcohols has been demonstrated.[18]

The behavior of **7** in the TiO₂-induced photochemical oxidation is quite close to that observed by Arnold and his associates for the same compound in the photooxidation sensitized by 1,4-dicyanobenzene.[5] Also in that case, as mentioned before, the radical cation underwent C—C bond cleavage exclusively. However, the reaction products were significantly different than those observed here, since the benzyl radical reacted with the reduced form of the sensitizer rather than to dimerize or to abstract a hydrogen atom from the solvent. Moreover, benzyl methyl ketone was not found among the reaction products.

The occurrence of C—C bond cleavage in **7·⁺** has been attributed by Arnold[5] to the fact that, due to the already-mentioned stability of the α-alkoxy carbocation formed in the cleavage, the C—C bond dissociation energy (BDE) is quite low (8.6 kcal mol⁻¹)[19] and under the threshold (15 kcal mol⁻¹)[20] above which he was unable to observe any C—C bond cleavage. Of course, this also holds for **6·⁺** (with similar C—C BDE than **7·⁺**) and, to a greater degree, for **8·⁺** and **9·⁺**. Accordingly, C—C bond scission in the latter two radical cations leads to a tertiary α-oxy

carbocation, and therefore, the C—C BDEs are expected to be much lower than in **7·⁺**.

The absence of any competion by C—H bond breaking in **6·⁺** and **7·⁺** is, however, intriguing since thermochemical calculations show that this cleavage is strongly favored with respect to that of the C—C bond from a thermodynamic point of view, being exoergonic by as much as 13.4 kcal mol⁻¹.[23] A tentative explanation is that the cleavage of the C—H bond is kinetically disfavored by stereoelectronic effects,[25] since the preferential conformation of **6** and **7** is that with the C—C bond (and not the C—H bond) collinear with the π system. Another possible suggestion is that the C—C bond cleavage is not an unimolecular process, as depicted in eq 3, but it requires nucleophilic assistance by the solvent.[26]

That our understanding of the factors influencing the side-chain reactivity of a radical cation is still far from being satisfactory is also shown by the observation that the introduction of a *p*-methoxy group in **6** and **7** leads to a quite different situation than that illustrated before for the unsubstituted substrates. In the photooxidation of **10** the major product is 4-methoxybenzaldehyde, accompanied by minor amounts of 4-methoxybenzylacetamide; with **11**, 4-methoxybenzaldehyde is practically the only observed product. This indicates that in **10·⁺** and in **11·⁺** C—H bond cleavage is the major and exclusive reaction path, respectively, an outcome which sharply contrasts with the behaviors of **6·⁺** and **7·⁺**. Thus, the presence of a *p*-methoxy group has profoundly influenced the C—H *vs* C—C bond cleavage competion in the radical cation, strongly favoring the former dissociation path. More exactly, since a ring methoxy group stabilizes the radical cation and decreases its reactivity, the observed results indicate that this negative effect concerns more the cleavage of the C—C bond than that of the C—H bond.

For the cleavage of a β bond in an alkylaromatic radical cation it is necessary that one electron is transferred from the σ orbital of the β bond itself to the aromatic π system. Thus, in the transition state of the process, significant buildup of positive charge on the bond to be cleaved is expected. Now, such a buildup should be opposed by the presence of a *p*-methoxy group due to the great capacity of this group to delocalize a positive charge, and the effect should be felt more effectively the larger the extent of positive charge transfer to the scissible bond required to reach the transition state of the cleavage reaction.

If the above reasonings are correct, the observation that a *p*-methoxy group disfavors more C—C than C—H bond cleavage in alkylaromatic radical cations might be taken to indicate that the former process requires, in the transition state, more accumulation of positive charge on the bond to be cleaved than the second. Interestingly, this conclusion seems supported by the information available at the present. Accordingly, the work by Maslak and Chapman, Jr.[27] has clearly shown that a substantial amount of positive charge is present on the β C—C bond, in the transition state of the C—C bond cleavage reaction of bicumyls radical cations. In contrast,

(14) Baciocchi, E.; Bartoli, D.; Rol, C.; Ruzziconi, R.; Sebastiani G. V. *J. Org. Chem.* **1986**, *51*, 3587.

(15) (a) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962. (b) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(16) Another possible way to the ketone could be a 1,2 H shift during the oxidation (presumably by Ag⁺) of the benzylic radical formed by deprotonation of **6·⁺** (or **7·⁺**).[17]

(17) Walling, C.; El-Taliawi, G. M.; Zhao, C. *J. Org. Chem.* **1983**, *48*, 4914.

(18) Mu, W.; Hermann, J.-M.; Pichat, P. *Catal. Lett.* **1989**, *3*, 73.

(19) The values used in the thermochemical cycle[20] were as follows: the C—C BDEs in **6** and **7** were taken to be equal to that of the PhCH₂—CH(CH₃)₂ bond (71.3 kcal mol⁻¹);[21] the oxidation potentials of **6** and **7** were considered to be equal to that of ethylbenzene (2.27 V *vs* SCE);[22] for the *E°* of MeO(Me)ĊH· we have used that of EtO(Me)-ĊH· (−0.45 V *vs* SCE).[12]

(20) Popielarz, R; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068.

(21) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

(22) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(23) The values used in the thermochemical cycle[20] were as follows: C—H BDEs in **6** and **7** were taken to be equal to the C—H BDE in ethylbenzene (85.2 kcal mol⁻¹);[24] *E°* of H⁺/H· is 2.01 V *vs* SCE;[24] for the *E°* of **6** and **7** see ref 19.

(24) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287.

(25) Baciocchi, E.; Mattioli, M.; Romano, R.; Ruzziconi, R. *J. Org. Chem.* **1991**, *56*, 7154.

(26) Dinnocenzo, J. P.; Todd, W. P.; Simpsons, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462.

(27) Maslak, P.; Chapman, W. H., Jr. *Tetrahedron* **1990**, *46*, 2715.

small buildup of positive charge on the C—H bond has been observed in the transition state for the deprotonation of α-substituted 4-methoxytoluene radical cations.[13a] Of course, in spite of this agreement, more systematic investigations appear necessary to reach a satisfactory understanding of the phenomenon.

Experimental Section

¹H-NMR spectra were obtained from a Bruker AC 200 (at 200 MHz) spectrometer, for solutions in CDCl₃. GCMS analyses were performed on a Hewlett-Packard gas chromatograph 5890A (SPB-1 and SPB-5 capillary columns, 30 m, at 45—300 °C) connected with a mass selective detector 5970 (at 70 eV). VPC analyses were carried out on a HP 5890 gas chromatograph using a SPB-5 capillary column at 45—300 °C.

Materials. TiO₂ (anatase, dried at 110 °C), Ag₂SO₄, CH₃-CN (HPLC grade), toluene (**1**), *p*-xylene (**2**), durene (**3**), ethylbenzene (**4**), 4-methoxytoluene (**5**), 1-phenyl-2-propanol (**6**), and 1-phenyl-2-methyl-2-propanol (**8**) were commercial samples. 1-(4-Methoxyphenyl)-2-propanol (**10**)[28] was obtained by NaBH₄ reduction of 4-(methoxyphenyl)propanone. 1-Phenyl-2-methoxypropane (**7**),[29] 1-phenyl-2-methoxy-2-methylpropane (**9**),[30] and 1-(4-methoxyphenyl)-2-methoxypropane (**11**)[31] were prepared by Williamson reaction from the corresponding alcohols.

Photochemical Oxidation. Reactions have been carried out by external irradiation (500-W high-pressure mercury lamp, Pyrex filter), under magnetic stirring and gentle N₂ bubbling, of an acetonitrile solution (25 mL) of substrate (0.30 mmol), in the presence of TiO₂ (130 mg) and Ag₂SO₄ (0.30 mmol); the reactor was a cylindrical flask (i.d. = 1.6 cm, *h* = 16 cm) equipped with a water cooling jacket and intensive condenser. After paper filtration of TiO₂, the reaction mixture was poured into water and extracted with ether. The reaction product analysis was performed by ¹H-NMR in the presence of an internal standard (1,4-dimethoxybenzene or bibenzyl). The amount of unreacted substrate was determined, when possible, by ¹H-NMR of the crude product or by VPC analysis

of reaction mixture before work up, in the presence of an internal standard (durene or bibenzyl). Material balance was always *ca.* 85—95% *vs* the amount of starting substrate.

Reaction Products. The crude reaction product was chromatographed on silica gel eluting with light petroleum, light petroleum:ethyl ether (from 9:1 to 1:1 v/v), and chloroform. The structure of isolated products was attributed by comparison with authentic specimens or literature data. The details are as follows: bibenzyl, 1,2-bis(4-methylphenyl)-ethane, 1,2-bis(4-methoxyphenyl)etane, 1-phenyl-2-propanone, 4-methoxybenzaldehyde, N-benzylacetamide, and N-(4-methoxybenzyl)acetamide were commercial products or avilable from previous works.[4,8,14,32] The structures of 3-phenylpropanonitrile,[33] 3-(4-methylphenyl)propanonitrile,[33] 1,2-bis-(2,4,5-trimethylphenyl)ethane,[34,35] N-(2,4,5-trimethylbenzyl)-acetamide,[36] 3-(4-methoxyphenyl)propanonitrile,[37] 2,3-diphenylbutane (dl/meso = 1),[38] 3-phenylbutanonitrile,[39] N-(α-methylbenzyl)acetamide,[40] 5-methyl-2,4'-dimethoxydiphenylmethane,[41] and N-(4-methylbenzyl)acetamide[42] were confirmed by comparison with literature data. 3-(2,4,5-Trimethylphenyl)-propanonitrile was identified by spectroscopic analysis [¹H-NMR δ 6.96 (s, 1H, ArH), 6.95 (s, 1H, ArH), 2.90 (t, 2H, CH₂), 2.55 (t, 2H, CH₂), 2.29 (s, 3H, CH₃), 2.24 (s, 6H, CH₃); MS *m/z* (rel intensity) 173 M⁺, 133 (100), 117, 115, 105, 91, 77, 51].

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