# TiO<sub>2</sub>-photocatalyzed reactions of some benzylic donors

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Abstract: TiO<sub>2</sub>-photocatalyzed oxidation of toluene (1a), benzyltrimethylsilane (1b), and 4-

methoxybenzyltrimethylsilane (**1c**) has been carried out in acetonitrile under oxygen, under nitrogen, and in the presence of electrophilic alkenes under various conditions (using  $Ag_2SO_4$  as electron acceptor, adding 2.5% H<sub>2</sub>O, changing solvent to CH<sub>2</sub>Cl<sub>2</sub>). Benzyl radicals, formed via electron transfer and fragmentation, are trapped. A good material balance is often obtained. The overall efficiency of the process depends on the donor  $E_{ox}$ , on the rate of fragmentation of the radical cation, and on the acceptor present (Ag<sup>+</sup> is an efficient oxidant, an electrophilic alkene a poor one, O<sub>2</sub> is intermediate). With ring-unsubstituted benzyl derivatives **1a** and **1b**, oxidative fragmentation occurs mainly close to the catalyst surface. The benzyl radicals form at a high local concentration and give benzaldehyde under O<sub>2</sub>, bibenzyl under N<sub>2</sub> and dibenzylated derivatives by attack on the alkenes (acrylonitrile, fumaronitrile, maleic acid). In this case, using CH<sub>2</sub>Cl<sub>2</sub>-O<sub>2</sub> enhances the yield of benzaldehyde. With methoxylated **1c**, however, the radical cation migrates into the solution before fragmentation and, therefore, the free benzyl radical is formed. This radical in part is oxidized to the cation, giving a considerable amount of benzylacetamide (or of the alcohol with water), and in part is trapped by the alkenes. The last reaction is less efficient in this case and yields monobenzyl derivatives.

Key words: photocatalysis, oxidation, alkylation.

**Résumé :** On a effectué l'oxydation photocatalysée du toluène (**1a**), du benzyltriméthylsilane (**1b**) et du 4-méthoxybenzyltriméthylsilane (**1c**) par le TiO<sub>2</sub> dans l'acétonitrile, sous atmosphère d'azote ou d'oxygène, et en présence d'alcènes électrophiles et sous diverses conditions (faisant appel au Ag<sub>2</sub>SO<sub>4</sub> comme accepteur d'électron, avec addition de 2,5% d'eau et en changeant le solvant pour le CH<sub>2</sub>Cl<sub>2</sub>). On a piégé les radicaux benzyles qui se forment par transfert d'électron et fragmentation. On a souvent obtenu une bonne balance pour les produits ayant réagi. L'efficacité globale du processus dépend du  $E_{ox}$  du donneur, de la vitesse de fragmentation du cation radical et de la présence d'un accepteur (Ag<sup>+</sup> est un oxydant efficace, un alcène électrophile est mauvais alors que O<sub>2</sub> est intermédiaire). Avec les dérivés **1a** et **1b** comportant un noyau benzyle non substitué, la fragmentation oxydante se produit relativement près de la surface du catalyseur. Les radicaux benzyles se forment à une concentration locale élevée et conduisent à la formation de benzaldéhyde en présence de O<sub>2</sub>, en bibenzyle sous N<sub>2</sub> et en dérivés dibenzylés par attaque sur les alcènes (acrylonitrile, fumaronitrile, acide maléique). Dans ce cas, l'utilisation de CH<sub>2</sub>Cl<sub>2</sub>–O<sub>2</sub> conduit à une augmentation du rendement en benzaldéhyde. Toutefois, avec le dérivé méthoxy **1c**, le cation radical migre en solution avant la fragmentation et on observe la formation d'un radical libre. Ce radical est partiellement oxydé en cation conduisant à la formation de benzaldéhyde et à une quantité considérable de benzylacétamide (ou d'alcool avec l'eau); il est aussi piégé par les alcènes. La dernière réaction est moins efficace dans ce cas et elle conduit aux dérivés monobenzyliques.

Mots clés : photocatalyse, oxydation, alkylation.

[Traduit par la Rédaction]

# Introduction

Titanium dioxide is extensively used for the photoinduced mineralization of organic contaminants in polluted water (1). Under these conditions, photoinduced charge separation is followed by hole and electron transfer to water and oxygen, respectively, and the reaction of the organic molecule mainly involves hydrogen abstraction by the thus formed hydroxyl radicals; the organic radicals then react with oxygen or the superoxide anion. The alternative possibility that the organic substrate is directly oxidized at the semiconductor surface is of interest in two respects. First, because it has been shown that, at least with reasonable donors, this mechanism participates in the  $TiO_2$  photocatalytic oxidation in water (2) and second, because, particularly in nonaqueous solvents, such a path may lead to the controlled oxidation of the substrate, rather than to the complete oxidation to  $CO_2$  that is the target when photocatalysis is used for the recovery of polluted

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Dedicated to Professor Don R. Arnold, the pioneer of electron transfer photochemistry.

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water. With reference to the second aspect, a number of positive results have been obtained. As an example,  $TiO_2$ photocatalyzed oxygenation of cyclohexane neat or mixed with organic solvents gives useful yields of products from the intermediate oxidation, e.g., of cyclohexanone (3, 4). Substituting a different electron acceptor for oxygen, e.g., the silver cation, adds flexibility (5). In this case different radical reactions, e.g., radical dimerization, occur in nitrogen-flushed solution while controlled oxygenation takes place in the presence of oxygen. Furthermore, the acceptor can be an organic molecule, e.g., an electrophilic alkene, which functions also as a radical trap and is alkylated (6). More generally, photocatalysis in organic solvents may have some synthetic interest (7), as opposed to the destructive mineralization occurring in water.

Both controlled oxygenation and alkylation reactions have been carried out successfully with benzylic derivatives. This is not surprising because the pioneering work by Arnold has shown that these compounds are both susceptible to photoinduced single electron oxidation and prone to fragmentation at the radical cation stage (8). In particular, benzylic oxygenation and benzylic coupling in acetonitrile and in aqueous media by  $TiO_2$ -Ag<sup>+</sup> have been described by Baciocchi and Sebastiani and co-workers (5, 9) in several reports. We were curious to compare such a reaction with the TiO<sub>2</sub>-photocatalyzed alkylation of alkenes (6, 10) through a systematic examination. We surmised that this comparison may give information about the mode of reaction, in particular with regard to the formation of the radicals either as solvated species or close to the semiconductor surface, a difference that is important for synthetic applications.

Therefore, we chose a small group of benzyl derivatives and compared the effect of some key experimental parameters as well as the effect of trapping by electrophilic alkenes. As described in the following, this examination indeed revealed new facets and demonstrated the versatility of the system.

# **Results and discussion**

#### Photocatalysis of benzylic derivatives

Three benzylic derivatives were examined under standard conditions (0.02 M solutions in, 3.5 mg mL<sup>-1</sup> Degussa TiO<sub>2</sub>, 3 h irradiation) in tightly stoppered vessels, after flushing either with oxygen or with nitrogen. Scheme 1 shows the products formed and Table 1 reports the % conversion of starting material and the % yield (calculated on the converted substrate) of products formed.

The effects of adding silver sulfate and of a small percentage of water on the reaction in acetonitrile as well as of changing the solvent to dichloromethane are compared. For each condition, the results with the three substrates are listed in sequence. No significant reaction took place over this time when  $TiO_2$  was omitted.

Toluene (1a) reacted sluggishly in oxygen-flushed acetonitrile and gave only traces of benzaldehyde 2a. Both conversion and yield of the aldehyde increased in the presence of 2.5% water, and further some benzyl alcohol (3a) and phenylpropionitrile (6a) were formed. Adding 0.01 M Ag<sub>2</sub>SO<sub>4</sub> or having both this salt and water present at the same time did not increase the rate of conversion, but enhanced the yield of the aldehyde (35–45%), accompanied, in the latter case, by some benzyl alcohol. Carrying out the photoreaction in oxygen-flushed dichloromethane rather than in MeCN caused more extensive oxidation leading to the aldehyde (59% at a 42% conversion of **1a**), but also to a large amount of benzoic acid (**4a**, 29%).

No appreciable reaction took place in nitrogen-flushed acetonitrile (not reported), but it did in the presence of silver sulfate, where the main product was bibenzyl (**5a**, 65% for a 16% conversion) accompanied by minor amounts of aldehyde **2a** and nitrile **6a**, as well as traces of **3a** and of benzylacetamide (**7a**). No significant reaction occurred in the presence of 2.5% water in MeCN nor upon irradiation in nitrogen-flushed  $CH_2Cl_2$  (not reported; the other substrates examined likewise did no react under these conditions).

Compared with **1a**, benzyltrimethylsilane (**1b**) was more easily photooxidized in MeCN–O<sub>2</sub> (25% conversion, 66% aldehyde, compare entries 2 and 1). Adding water had little effect (except for the formation of a small amount of propionitrile), while adding  $Ag_2SO_4$  did not increase the rate of oxidation but improved selectivity for the formation of benzaldehyde (92%, entry 8). In dichloromethane the reaction was faster than in MeCN, with a similar product distribution.

Again, no reaction took place under nitrogen in MeCN, MeCN – 2.5%  $H_2O$  or  $CH_2Cl_2$ . However, **1b** was quite reactive in deoxygenated MeCN in the presence of  $Ag^+$ . The conversion was larger than under oxygen (64 rather than 25%, entry 17) and bibenzyl was the main product (70%). Also formed were small amounts of alcohol, aldehyde, and propionitrile, as well as compounds resulting, as indicated by mass spectrometry, from the benzylation of bibenzyl and the starting benzylsilane. The experiment with both water and  $Ag^+$  gave somewhat less of bibenzyl and more of benzyl alcohol.

With 4-methoxybenzylsilane (1c) the rate of photooxidation in MeCN further increased (85% conversion) and the aldehyde (2c, 77%) was accompanied by a significant amount of the alcohol (3c, 6%), which increased in the presence of water (12%, entry 6). The presence of the silver salt made the reaction more selective for the aldehyde (83%, entry 9). This time, in dichloromethane the oxidation was slower than in MeCN (55% rather than 85%, entry 15) and led to both aldehyde and alcohol. Compound 1c was reactive under nitrogen, though somewhat slower than under oxygen, provided, as with the previous donors, that Ag<sup>+</sup> was present; the main product was the bibenzyl derivative (5c, 55%), but 4-methoxybenzylacetamide (7c, 25%) was also important (entry 18). In the presence of both water and Ag<sup>+</sup>, 4-methoxybenzyl alcohol (3c) was the main product (36%, entry 21). The solution became acidic during the irradiation and was neutralized with triethylamine before work-up. If this precaution was omitted, further benzylation reactions via the benzylic cation formed from the alcohol led to the formation of small amount of diphenylmethanes, a fact that has been previously noted (9a), but is an artifact due to the acidity developed (compare to 11). Small amounts (0.5 to 1%) of 4methoxytoluene were detected in all the photocatalytic experiments with 1c. The photooxidation of 1c was tested at a somewhat large scale (0.78 g) in an immersion well appara-

#### Scheme 1.

$$\begin{array}{c} 4-YC_{6}H_{4}CH_{2}X & \xrightarrow{h\nu, \ TiO_{2}} & 2 & 3 & 4 \\ 1 & & & & \\ 1 & & & \\ a, X, Y = H & & & \\ b, X = SiMe_{3}, Y = H & & \\ c, X = SiMe_{3}, Y = OMe \end{array}$$

Table 1.	TiO <sub>2</sub>	photocatalytic	oxidation	of	benzylic	donors."
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			Conversion (%)	Products (%) <sup>b</sup>					
	Donor	Conditions	1	2	3	4	5	6	7
1	1a	MeCN, O <sub>2</sub>	8	12					
2	1b		25	66	3	16			
3	$\mathbf{1c}^{c}$		85	77	6	3			
4	<b>1</b> a	$O_2, H_2O^d$	20	35	5			4	
5	1b		31	66	9	11		1	
6	1c		76	72	12	4			
7	1a	$O_2$ , $Ag^{+e}$	10	35					
8	1b		25	92	4	3			
9	1c		90	83	2	3			
10	1a	$O_2$ , $H_2O$ , $Ag^+$	11	45	11				
11	1b		32	86	8	6			
12	1c		75	80	2	3			
13	1a	$CH_2Cl_2, O_2$	42	59	2	36			
14	1b		57	63	5	1			
15	1c		55	55	29	1			
16	1a	MeCN, N <sub>2</sub> , Ag <sup>+</sup>	16	8	1		65	12	2
17	1b		64	6	1		70		
18	<b>1c</b> <sup><i>f</i></sup>		66		tr		53	tr	25
19	1a	$N_2$ , $H_2O$ , $Ag^+$	_						
20	1b <sup>f</sup>		59	2	8		58	6	
21	1c		56	1	36	1	7		6

<sup>a</sup>Upon irradiation of 0.02 M suspensions of the benzylic derivatives 1 (140 mg TiO<sub>2</sub>, 40 mL acetonitrile) for 3 h.

<sup>*b*</sup>% Yields on converted **1**.

<sup>c</sup>Small amounts (0.5–1%) of 4-methoxytoluene formed in all experiments with 1c.

 ${}^{d}\text{H}_{2}\text{O}$  (2.5%).

 ${}^{e}Ag_{2}SO_{4} (0.01 \text{ M}).$ 

<sup>f</sup>Small amounts (up to 3%) of (4-methoxybenzylbenzyl)trimethylsilane and 4-methoxybenzyltoluenes revealed by GC-MS.

tus and it gave 90% conversion (of which 91% was the aldehyde) after 8 h irradiation.

These results clearly support the role of radical cations formed by hole transfer at the surface of the semiconductor in the photooxidation of benzylic substrates (see Scheme 2), adding to previous evidence by Baciocchi and Sebastiani and co-workers (5, 9), showing that Ag<sup>+</sup> can be a substitute for oxygen in the role of electron acceptor. Favorable conditions for the process are that the reagent is reasonably easily oxidized and bears a good electrofugal group that makes fragmentation of the radical cation competitive with back electron transfer to the semiconductor. Thus, a moderate donor such as toluene ( $E_{ox}$  2.2 V vs. SCE) with a poor leaving group is slowly oxidized; in MeCN, cleavage of a proton from the toluene radical cation  $(1a^{+})$  is more than 100 times slower than cleavage of a trimethylsilyl cation from  $1b^{+}$ (12). Introduction of a silvl group in  $\alpha$  and of a methoxy group on the ring both make the reagents better donors such as **1b** ( $E_{\text{ox}}$  1.78 V) and **1c** ( $E_{\text{ox}}$  1.31V) (13) and offer a good electrofugal cation  $Me_3Si^+$  from the radical cation. These compounds react much faster than **1a** and give consistently a good material balance. Fragmentation is no longer the ratelimiting step. With these highly reactive radical cations, it can be appreciated that  $Ag^+$  is a superior oxidant to  $O_2$  (with **1b**, an increase in the rate of reaction by a factor of 2.5 in MeCN/Ag<sup>+</sup> in comparison with the experiments under oxygen).

Fragmentation leads to benzyl radicals (Scheme 2). In nitrogen-flushed solution, these mainly dimerize to bibenzyls **5a**, **5c**. A minor process is hydrogen abstraction from the solvent, which generates  $\cdot$ CH<sub>2</sub>CN radicals revealed by the presence of arylpropionitriles **6a**, **6c** and is consistent with the formation of a small amount of methylanisole from **1c**. The ratio of nitrile (**6**) – bibenzyl (**5**) is larger with toluene (0.2) than with silane **1b** (<0.02 in neat MeCN, though it grows to 0.1 with 2.5% H<sub>2</sub>O), consistently with the fast desilylation and thus the higher local concentration of radicals in the latter case. Scheme 2.



Scheme 3.

Also with **1c** only traces of nitrile are formed, but there another reaction competes. This is oxidation of the benzyl radical to the cation (Scheme 2). This process is revealed both by addition to acetonitrile, resulting after reaction with adventitious water, in the formation of amide **7c**, and, in the presence of 2.5% water, in the formation of alcohol **3c**. As previously proposed (9), the radical is oxidized by silver cations (0.4 V in MeCN) (14). Accordingly, from **1c** the yield of amide is 25%, and with the better nucleophile H<sub>2</sub>O the sum of the alcohol + amide is 42%, because oxidation of the 4-methoxybenzyl radical, with  $E_{ox}$  0.23 V (15), is fast. In contrast, no amide is formed from **1b** and only traces from **1a**, since oxidation of the unsubstituted benzyl radical ( $E_{ox}$ 0.73 V) (15) is slow.

In the presence of oxygen, benzyl radicals are trapped by oxygen or the superoxide anion formed in the initial electron transfer (Scheme 2). Decomposition of the hydroperoxides or of the peroxyl radicals leads to the aldehydes (Ag<sup>+</sup> when present makes the decomposition faster). In the case of 1c, the presence of the hydroperoxide was revealed by an enhancement of the yield of alcohol 3c (by a factor of 2) upon treatment of the irradiated solution by triphenylphosphine. When this process is efficient, secondary oxidation to benzoic acids is less important. Thus the aldehyde:acid ratio grows when the SET path is favored by the electron donating characteristics of the reagent (the ratio is 4 with 1b, 25 with 1c) or by the use of a better acceptor, such as  $Ag^+$ , which allows better transient charge separation at the semiconductor surface (the ratio is ca. 30 for both 1b and 1c). Water is oxidized competitively with the aromatic substrate in the case of poorly reacting toluene and the increased yield of aldehyde and the formation of some propionitrile (entry 4) are indicative of the participation of OH radicals. However, competitive oxidation of water does not occur in the case of silanes **1b** and **1c**. With these compounds, the result is not affected by the presence of 2.5% water, except for the formation of more alcohol with the latter one, another indication of the increased role of the benzyl cation in this case.

Using dichloromethane in the place of acetonitrile obliterates the difference in the rate of oxidation in the series 1a-**1c**, enhancing the rate of the first two substrates and slightly lowering the rate for the last one. This remarkable effect can again be rationalized on the basis of the electron transfer mechanism for the fragmentation. A less polar solvent increases absorption of the substrate on the surface, thus facilitating oxidation. Furthermore, superoxide anion is expected to be a stronger base in less polar CH<sub>2</sub>Cl<sub>2</sub> than in MeCN (compare to 16), and assists deprotonation of the radical cation (and apparently also desilylation, since some alcohol is formed from the silanes), adding to the action of basic centres on TiO<sub>2</sub>. This offers an alternative mechanism of reaction (path b in Scheme 3) for substrates for which fragmentation of the *free* radical cation is unimportant (see below).

# Photocatalysis of benzylic derivatives in the presence of electrophilic alkenes

Previous work had shown that  $TiO_2$  photocatalysis in the presence of electrophilic alkenes leads to efficient alkylation (6, 10). In that case, the alkene functions both as electron ac-

#### Scheme 4.



Table 2. TiO<sub>2</sub> photocatalytic reactions of benzylic donors in the presence of alkenes 8 and 0.01 M silver sulfate.<sup>*a*</sup>

			$\frac{\text{Conversion (\%)}}{1}$	Products (%) <sup>b</sup>					
	Donor Alkene	Alkene		2	5	7	9	10	
1	1b	8x (0.02 M)	30	3	60			5	
2	1a	8x (0.1 M)	9	7	33	2		5	
3	1b		65	4	39			15	
4	1a	<b>8y</b> (0.02 M)	20	4	30	3		28	
5	1b	• • •	67	6	43			33	
6	1c		66		13	32	8	3	
7	1b	8z (0.02 M)	60	3	34		2	34	
8	1c		60		10	33	8		

"Upon irradiation of 0.02 M suspensions of the benzylic derivatives 1 (140 mg TiO2, 40 mL acetonitrile) for 3 h.

<sup>b</sup>% Yield on converted **1**.

ceptor and as radical trap, and we were curious to compare the present system with  $Ag^+$  as the oxidant.

As shown in Table 2 and Scheme 4, with  $TiO_2-Ag^+$  the percentage conversion of donors 1a-1c was similar to that observed in the absence of the alkene, but even a poor trap such as acrylonitrile (8x, 0.1 M) led to the formation of a certain amount of adduct. As an example, from 1b 15% of the bibenzylated propionitrile 10ax was formed at the expense of bibenzyl (dropping from 70% to 39%, entry 3). A lower amount of 10ax (5%) was formed from 1b with a lower trap concentration (0.02 M 8x, entry 1) as well as from a poorer radical precursor such as toluene and 0.1 M 8x (entry 2). However, a better trap such as fumaronitrile (8y) was effective at the 0.02 M concentration with both 1a and 1b, making the yield of bibenzylated 10ay (28-33%, mixture of the two diastereoisomers) comparable to that of bibenzyl (30-43%, entries 4, 5). Bibenzylation was obtained in a similar yield (34%) also from 1b and maleic acid (8z, entry 7).

The result was different with the methoxybenzylsilane **1c**. In this case, the yield of bibenzyl was much reduced when the alkenes **8** were present (while the yield of amide **7c**, if anything, slightly increased), but trapping by the alkene was inefficient, giving a small amount of the mono derivatives **9cy**, **9cz**, and with **8y** only traces of bisadduct **10cy** (entries 6, 8).

As compared with our previous data on the benzylation reaction in the absence of the silver salt (6), a large difference in rate and product distribution is now observed. In the absence of  $Ag^+$ , the reaction of **1b** with e.g., **8z** required 20 h for a 15% conversion and gave 7% bibenzyl, 80% monoadduct, and 5% bisadduct, rather than 60% conversion in 3 h and 34, 2, and 34%, respectively, of the products in the present experiment. In the presence of the alkene alone, the conversion of **1b** reached 35% after 60 h and that of **1c** 100% after 30 h; it was 10–50 times slower than in the presence of  $Ag^+$  and the monoadducts were by far the major products (50–80%). No useful result was obtained from **1a**.

The difference is due to the double role of 1,2-electronwithdrawing substituted alkenes such as **8y** and **8z**. These act both as electron acceptors (**8y**,  $E_{red}$  –1.63 V vs. Ag/Ag<sup>+</sup>) (17) and as radical traps. In the absence of other acceptors, the alkene radical anions build up and either directly trap the radicals or reduce the radical adducts, thus leading to the monobenzylated alkenes (path *a*, *d'*, Scheme 4).

With the silver cation the two functions are separated, the inorganic cation being the main oxidant and the alkene functioning as radical trap because  $Ag^+$  is a better acceptor. Under these conditions photoinduced fragmentation of the donors is much faster with **1b** and **1c**, and even with **1a** some reaction occurs, while none was observed in the absence of  $Ag^+$ . Furthermore, the radical anion **8**<sup>-</sup> does not

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build up in this case, and the relatively stable ( $\alpha$ -cyano or carboxyl) adduct radicals have no easy path for reduction. Thus, these couple with a benzyl radical to give the bisadduct (path *b*, Scheme 4, see below). This path requires a high concentration of benzyl radicals, a situation that applies in the vicinity of the photocatalyst surface with donors **1a**, **1b**. The nonstabilized radical cations of these substrates do not migrate and fragment (with different efficiency) close to the surface (path *a* in Scheme 3), generating a high local concentration of the radicals.

On the contrary, migration of the longer lived stabilized radical cation from 1c precedes fragmentation; thus, the free benzyl radical is formed from the solvated radical cation (path *c* in Scheme 3). The solvated radical is in part oxidized by  $Ag^+$  (soluble in MeCN), and thus, is not available for trapping. A part is trapped, as revealed by the strong decrease of bibenzyl in the presence of alkenes, but the radical adduct has little opportunity both for coupling with benzyl radicals (because of the low concentration in solution) and for reduction (since no reducing  $8^-$  builds up). Presumably higher molecular weight products are formed and the yield of isolated products (monoadducts 9 and traces of bisadducts 10) is far from balancing the amount of radicals trapped.

Thus, trapping by alkenes gives an indication about the mode of  $\alpha$ -cleavage, in solution or close to the surface. On the other hand, the photoinduced reaction becomes mush faster with Ag<sup>+</sup>, but the yield of the useful process, alkylation of the electron-withrawing substituted alkene is decreased by the competing oxidation of the radical, and from the synthetic point of view the reaction in the absence of silver salts (6) is preferable.

# Conclusions

The TiO<sub>2</sub> photocatalytic oxidation of benzylic donors gives products resulting from the trapping of benzyl radicals (benzaldehydes, bibenzyl or alkylated derivatives), sometimes with satisfactory material balance. The efficiency of the electron transfer oxidation of these substrates depends on the oxidation potential of the donor, on the presence of an electrofugal group in the  $\alpha$  position, and on the presence of a good electron acceptor that allows exploitation of the transient charge separation on the semiconductor surface. Among these,  $Ag^+$  is more efficient than  $O_2$ , and both of these are much better than an electrophilic alkene. On the other hand, the presence of a strong oxidant such as silver sulfate causes partial further oxidation of the radical to the cation and limits the benzylation of electrophilic alkenes since it hinders a required step, reduction of the adduct radical.

Comparing photocatalysis for the substrates 1a-1c suggests that the reaction occurs via two main mechanisms. The stabilized radical cation  $1c^+$  is solvated and fragments in solution (path *c*, Scheme 3). The free radical formed can be trapped. Further oxidation of the radical to the cation also has an important role. The shorter lived, less stable analogues  $1a^+$ ,  $1b^+$  do not migrate and mainly fragment close to the surface of the catalyst (path *a*), e.g., yielding bibenzyl or bibenzylation of added electrophilic alkenes. Deprotonation of  $1a^+$  is slow, so that with 2.5% water the

cosolvent is competitively oxidized. This process is faster in  $CH_2Cl_2$ , probably via a  $O_2^{-}$  assisted reaction (path *b*).

# Experimental

#### Reagents

Degussa P25 titanium dioxide was dried in a oven at 110°C for 24 h and acetonitrile was distilled over calcium hydride and stored over molecular sieves. The chemicals were commercially available or prepared through conventional procedures for the case of **1c**.

#### Irradiations

Irradiations were carried out on magnetically stirred solutions contained in 4.5 cm diameter serum-capped Pyrex cylindrical reactors. Suspensions (40 mL) containing the benzylic derivatives (0.02 M), the appropriate additives (see Tables 1 and 2) and 140 mg TiO<sub>2</sub> were used. These were sonnicated for 1 min and then stirred and flushed with either oxygen or purified nitrogen (through needles) in the dark for 20 min. The tubes were put in the centre of four 15 W phosphor-coated lamps (centre of emission, 360 nm) and irradiated for 3 h while maintaining slow gas flow and stirring. The suspension was then filtered over a 0.2  $\mu$ m porosity filter under vacuum and either directly analyzed or rotary evaporated and taken up to a fixed volume.

The products were identified by comparison of their GC– MS spectra with authentic samples (compounds **9cy**, **9az**, **9cz** and diastereoisomeric **10ax**, **10ay**, **10cy**, **10az** were previously reported) (6) and quantified by GC on the basis of calibration curves using dodecane or cyclododecane as the internal standard. Gas chromatography analyses were carried out by using an HP 5890 apparatus with a 0.3 mm  $\times$  30 m capillary column with a flame ionization detector. Gas chromatography – mass spectrometry determination was performed using an HP 5970B instrument operating at a ionizing voltage of 70 eV, connected to an HP 5890 instrument equipped with the same column as above.

A larger scale irradiation was carried out with 1c (0.78 g, 0.02 M) in a suspension of TiO<sub>2</sub> (0.7 g) in MeCN (200 mL) in an immersion well apparatus fitted with a Pyrex-filtered, water-cooled medium pressure mercury arc (150 W). The suspension was magnetically stirred and flushed with argon during irradiation (8*h*).

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