The Role of Aromatic Radical Cations and Benzylic Cations in the 2,4,6-Triphenylpyrylium Tetrafluoroborate Photosensitized Oxidation of Ring-Methoxylated Benzyl Alcohols in CH_2Cl_2 Solution

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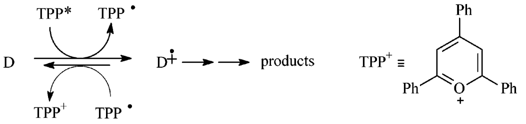
A steady-state and laser flash photolysis (LFP) study of the $TPPBF_4$-photosensitized oxidation of ring-methoxylated benzyl alcohols has been carried out. Direct evidence on the involvement of intermediate benzyl alcohol radical cations and benzylic cations in these reactions has been provided through LFP experiments. The reactions lead to the formation of products (benzaldehydes, dibenzyl ethers, and diphenylmethanes) whose amounts and distributions are influenced by the number and relative position of the methoxy substituents. This behavior has been rationalized in terms of the interplay between the stabilities of benzyl alcohol radical cations and benzyl cations involved in these processes. A general mechanism for the $TPPBF_4$-photosensitized reactions of ring-methoxylated benzyl alcohols has been proposed, where the α-OH group of the parent substrate acts as the deprotonating base promoting α-C−H deprotonation of the benzyl alcohol radical cation (formed after electron transfer from the benzyl alcohol to TPP*) to give a benzyl radical and a protonated benzyl alcohol, precursor of the benzylic cation. This hypothesis is in contrast with previous studies, where formation of the benzyl cation was suggested to occur from the neutral benzyl alcohol through the Lewis acid action of excited TPP^+ (TPP*).

2,4,6-Triarylpyrylium salts are easily photoexcited by visible light, and the photosensitizing ability of these species has been widely applied in photoinduced electron transfer (PET) processes. Among these salts, 2,4,6-triphenylpyrylium tetrafluoroborate ($TPPBF_4$) has received most attention.[2] $TPPBF_4$ is a very strong oxidant in both the singlet and triplet excited state, able to oxidize several organic donors (D) to the corresponding radical cations ($D^{•+}$) with concomitant formation of the triphenylpyranyl radical, $TPP^•$ (Scheme 1). The neutral character of $TPP^•$ reduces the importance of the competing back-electron-transfer (BET) process, thus favoring the followup reactions of $D^{•+}$.

Very importantly, since TPP^+ may be regenerated through the reaction of $TPP^•$ with O_2, photooxidation processes can be usually carried out in air or O_2-saturated solution using catalytic amounts of TPP^+.

SCHEME 1



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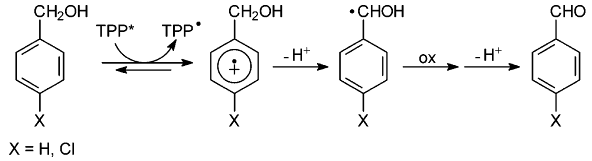

It has been shown that in acetonitrile or dichloromethane solution the $TPPBF_4$-photosensitized reaction of ring-substituted benzyl alcohols proceeds through two different pathways depending on the nature of the ring substituent.[3] With benzyl and 4-chlorobenzyl alcohol, formation of the corresponding benzaldehyde has been observed. This result has been explained in terms of the formation of an intermediate aromatic radical cation followed by deprotonation (Scheme 2), a typical reaction of benzyl alcohol radical cations.[4,5]

No oxidation products have been instead observed when 4-methoxybenzyl alcohol (**1**) has been reacted under

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(2) See, for example: (a) Miranda, M. A.; Garcia, H. *Chem. Rev.* **1994**, *94*, 1063−1089. (b) Sanjuan, A.; Pillai, M. N.; Alvaro, M.; Garcia, H. *Chem. Phys. Lett.* **2001**, *341*, 153−160. (c) Akaba, R.; Iwasaki, M.; Matsumura, T.; Kamata, M.; Itoh, H. *J. Phys. Org. Chem.* **1996**, *9*, 187−190. (d) Akaba, R.; Kamata, M.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1992**, *33*, 8105−8108. (e) Akaba, R.; Sakuragi, H.; Tokumaru, K. *J. Chem. Soc., Perkin Trans. 2* **1991**, 291−297.

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10.1021/jo048546h CCC: $27.50

SCHEME 3

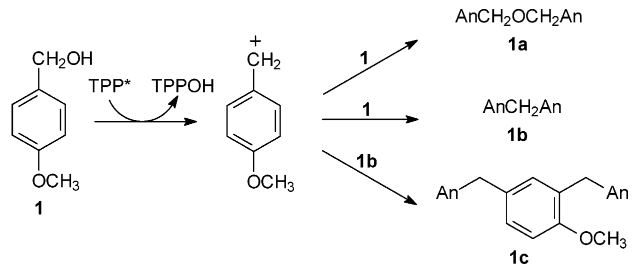
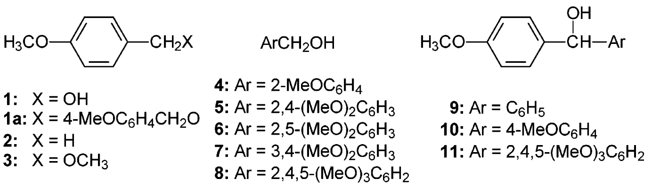


CHART 1



1: X = OH
1a: X = 4-MeOC$_6$H$_4$CH$_2$O
2: X = H
3: X = OCH$_3$

4: Ar = 2-MeOC$_6$H$_4$
5: Ar = 2,4-(MeO)$_2$C$_6$H$_3$
6: Ar = 2,5-(MeO)$_2$C$_6$H$_3$
7: Ar = 3,4-(MeO)$_2$C$_6$H$_3$
8: Ar = 2,4,5-(MeO)$_3$C$_6$H$_2$

9: Ar = C$_6$H$_5$
10: Ar = 4-MeOC$_6$H$_4$
11: Ar = 2,4,5-(MeO)$_3$C$_6$H$_2$

the same experimental conditions, the reaction leading to bis(4-methoxybenzyl) ether (**1a**), 4,4′-dimethoxydiphenylmethane (**1b**), and [4-methoxy-3-(4-methoxybenzyl)-phenyl](4-methoxyphenyl)methane (**1c**). This behavior has been explained in terms of excited TPP$^+$ (TPP*) acting as a Lewis acid catalyst promoting the formation of an intermediate 4-methoxybenzyl cation from which, following different pathways, products **1a**−**c** can be formed (Scheme 3; An = 4-MeOC$_6$H$_4$).[3]

The change in mechanism observed on going from benzyl and 4-chlorobenzyl alcohol to 4-methoxybenzyl alcohol (**1**) has been thus attributed to the greater stability of the 4-methoxybenzyl cation as compared to the benzyl and 4-chlorobenzyl ones: no radical cation intermediate is formed in the reaction of **1** even though $\mathbf{1}^{\bullet+}$ is expected to be significantly more stable than both benzyl alcohol and 4-chlorobenzyl alcohol radical cations.[6,7]

Along this line, in view of our continuing interest on the one-electron oxidation of ring methoxylated arylalkanols, and in order to gain additional information on the mechanism of the TPPBF$_4$-photosensitized oxidation of benzyl alcohols, and in particular on the eventual role of aromatic radical cations and benzylic cations in this process, we have carried out a detailed steady-state and laser flash photolysis (LFP) study of the TPPBF$_4$-photosensitized reaction of 4-methoxybenzyl alcohol (**1**) and of some structurally related substrates (**1a**, **2**−**11**) whose structures are shown in Chart 1.

Additional information comes from the results of DFT calculations for the determination of the relative stabilities of ring-methoxylated benzyl cations, carried out at the B3LYP/6-31G(d) level of theory.

Results

Steady-State Photolysis. In a typical experiment, air- or O$_2$-saturated CH$_2$Cl$_2$ solutions (10 mL) at $T = 25$ °C, containing TPPBF$_4$ (5×10^{-4} M) and the substrate (**1**, **1a**, **2**−**8**, **10**: $2.5-5 \times 10^{-3}$ M), were irradiated at $\lambda = 365$ nm (10 × 15 W lamps) for times varying between 1 and 60 min. After workup, the reaction products were identified by ^{1}H NMR and GC−MS (comparison with authentic samples). Unreacted substrate and reaction products were quantitatively determined by GC in the presence of an internal standard (1,2-diphenylethane). Good to excellent mass balances (≥85%) were obtained in all experiments.

The product distributions obtained in the TPPBF$_4$-photosensitized reactions of **1** are collected in Table 1. Some experiments were also carried out in the presence of a cosensitizer such as biphenyl (BP) (entry 3) or of a base such as pyridine (entries 4, 7, and 10−12) or 1,2-epoxybutane (entries 5, 8, 13, and 14). In the absence of added base, fast consumption of **1** is observed in both air- and O$_2$-saturated solution, accompanied by formation of **1a** as the main reaction product. At longer irradiation times consumption of **1a** is observed accompanied by an increase in the amount of 4-methoxybenzaldehyde. In O$_2$-saturated solution, in line with the greater efficiency of the TPP$^+$ regeneration process, consumption of **1a** occurs significantly faster than in air, and after 10 min of irradiation a decrease in the amount of 4-methoxybenzaldehyde is observed, accompanied by the formation of 4-methoxybenzoic acid. Comparison between entries 2 and 3 shows that both product distribution and substrate consumption are not influenced to a significant extent by the presence of the cosensitizer BP.

In the presence of pyridine, formation of ether **1a** is strongly depressed as compared to the experiment carried out in the absence of base (compare entries 2 and 4), while a significantly higher amount of substrate **1** is recovered. By increasing irradiation time (entries 7 and 10), an increase in substrate consumption is observed accompanied by an increase in the amount of 4-methoxybenzaldehyde.

By increasing pyridine concentration (from 5×10^{-4} to 2.5×10^{-3} M, entries 10−12) the amount of recovered substrate increases while the amount of 4-methoxybenzaldehyde and of ether **1a** decreases. Since it is known that sensitizer regeneration requires the presence of H$^+$,[8] it may be suggested that at relatively high concentrations, pyridine, due to its basic character, prevents sensitizer regeneration, resulting in a lower substrate conversion.

An analogous behavior is observed after addition of 1,2-epoxybutane. However, to observe a quantitatively similar effect on substrate consumption and product formation a concentration of 1,2-epoxybutane 200 times higher than that of pyridine is needed.

The results of the TPPBF$_4$-photosensitized reaction of bis(4-methoxybenzyl) ether (**1a**) in air- or O$_2$-saturated CH$_2$Cl$_2$ solution at different irradiation times are collected in Table 2.

Under all conditions, consumption of **1a** is observed, accompanied by the formation of 4-methoxybenzyl alcohol (**1**) and 4-methoxybenzaldehyde as main reaction products. At longer irradiation times an increase in the amount of 4-methoxybenzaldehyde is observed while the

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TABLE 1. Product Distributions Observed after $TPPBF_4$-Photosensitized Reaction of 4-Methoxybenzyl Alcohol (1) in CH_2Cl_2 Solution at Different Irradiation Times, under a Variety of Conditions[a]

entry	irradiation time (min)	conditions[b]	yield (%) 1	AnCHO[c]	1a	1b
air saturated						
1	2		40	13	46	1
2	5		27	19	52	2
3	5	[BP] = 5 × 10^{-2} M	24	29	45	2
4	5	[pyr] = 5 × 10^{-4} M	72	26	2	
5	5	[1,2-eb] = 0.1 M	79	22	1	
6	15		18	35	46	1
7	15	[pyr] = 5 × 10^{-4} M	59	37	4	
8	15	[1,2-eb] = 0.1 M	60	38	2	
9	30		15	52	31	2
10	30	[pyr] = 5 × 10^{-4} M	33	61	6	
11	30	[pyr] = 1 × 10^{-3} M	58	41	1	
12	30	[pyr] = 2.5 × 10^{-3} M	69	31		
13	30	[1,2-eb] = 5 × 10^{-2} M	39	50	11	
14	30	[1,2-eb] = 0.1 M	47	52	1	
15	60		5	89	6	

entry	irradiation time (min)	yield (%) 1	AnCHO[c]	1a	1b	$AnCO_2H$[c]
O_2 saturated						
16	1	48	15	36	1	
17	2	14	28	57	1	
18	5	12	48	38	2	
19	10		96			4
20	15		78			22
21	30		54			46

[a] [**1**] = 5 × 10^{-3} M; [$TPPBF_4$] = 5 × 10^{-4} M; λ_{irr} = 365 nm; T = 25 °C. [b] BP = biphenyl; pyr = pyridine; 1,2-eb = 1,2-epoxybutane. [c] An = $4\text{-}MeOC_6H_4$.

TABLE 2. Product Distributions Observed after $TPPBF_4$-Photosensitized Reaction of Bis(4-methoxybenzyl) Ether (1a) in CH_2Cl_2 Solution at Different Irradiation Times[a]

conditions	irradiation time (min)	yield (%) 1a	AnCHO[b]	1	1b
O_2	2	72	11	14	3
O_2	5	43	44	10	3
air	5	66	20	13	1
air	15	37	51	11	1
air	30	20	71	8	1

[a] [**1a**] = 2.5 × 10^{-3} M; [$TPPBF_4$] = 5 × 10^{-4} M; λ_{irr} = 365 nm; T = 25 °C. [b] An = $4\text{-}MeOC_6H_4$.

TABLE 3. Product Distributions Observed after $TPPBF_4$-Photosensitized Reaction of 4-Methoxytoluene (2) and 4-Methoxybenzyl Methyl Ether (3) in CH_2Cl_2 Solution at Different Irradiation Times

substrate	conditions	irrad time (min)	yield (%) recovered substrate	AnCHO[b]	1	$AnCO_2Me$[b]
2	air	30	96	4		
2	air	60	90	9	1	
2	air	30[c]	76	19	5	
3	O_2	1	94	3	1	2
3	O_2	2	78	13	1	8

[a] [**2**] = 5 × 10^{-3} M; [$TPPBF_4$] = 5 × 10^{-4} M; λ_{irr} = 365 nm; T = 25 °C. [b] An = $4\text{-}MeOC_6H_4$. [c] In the presence of 5 × 10^{-4} M pyridine.

amount of **1** decreases. In O_2-saturated solution, the reaction occurs significantly faster than in air saturated solution.

To obtain information on the role of the α-OH group in the $TPPBF_4$-photosensitized reactions of **1**, the $TPPBF_4$-photosensitized reactions of 4-methoxytoluene (**2**) and 4-methoxybenzyl methyl ether (**3**), substrates structurally related to **1** but lacking the presence of the α-OH group, were also studied. The results of the $TPPBF_4$-photosensitized reactions of **2** and **3** in air- or O_2-saturated CH_2Cl_2 solution at different irradiation times are collected in Table 3.

After 30 min of irradiation the $TPPBF_4$-photosensitized reaction of **2** leads to the formation of 4-methoxybenzaldehyde as the exclusive product. By increasing irradiation time an increase in the amount of 4-methoxybenzaldehyde is observed, accompanied by the formation of a small amount of 4-methoxybenzyl alcohol (**1**). In the presence of pyridine a significant increase in the amounts of both 4-methoxybenzaldehyde and **1** is observed.

The $TPPBF_4$-photosensitized reaction of **3** leads instead to the formation of comparable amounts of 4-methoxybenzaldehyde and methyl 4-methoxybenzoate as main reaction products. By increasing irradiation time an increase in the amount of both products is observed.

To obtain information on the role of the aromatic ring structure on the $TPPBF_4$-photosensitized reactions of benzyl alcohols, the reactions of 2-methoxybenzyl alcohol (**4**), 2,4-dimethoxybenzyl alcohol (**5**), 2,5-dimethoxybenzyl alcohol (**6**), 3,4-dimethoxybenzyl alcohol (**7**), and 2,4,5-trimethoxybenzyl alcohol (**8**) were also studied. The results of the $TPPBF_4$-photosensitized reactions of alcohols **4**−**8** in O_2-saturated CH_2Cl_2 solution are collected in Table 4 where, as a matter of comparison, also the corresponding data obtained for **1** are included.

The results collected in Table 4 show that in the $TPPBF_4$-photosensitized reaction of ring-methoxylated benzyl alcohols **1** and **4**−**8** the product amounts and distributions are strongly influenced by the number and

TABLE 4. Product Distributions Observed after $TPPBF_4$-Photosensitized Reaction of Ring-Methoxylated Benzyl Alcohols $ArCH_2OH$ (1, 4−8) in O_2-Saturated CH_2Cl_2 Solution[a]

	yield (%)			
substrate	$ArCH_2OH$	ArCHO	$ArCH_2OCH_2Ar$	$ArCH_2Ar$
1	48	15	36	1
4	92	8		
5[b,c]	88	<1	6	6
6	99	<1		
7	88	<1	11	
8	92	<1		7

[a] $[ArCH_2OH] = 5 \times 10^{-3}$ M; $[TPPBF_4] = 5 \times 10^{-4}$ M; $\lambda_{irr} = 365$ nm; irradiation time = 1 min; $T = 25$ °C. [b] Irradiation carried out under air. [c] A significant material loss was observed (mass balance = 63%).

relative position of the methoxy substituents. Thus, with **4** and **6** the corresponding benzaldehyde was the only observed product (in 8% and <1% yields, respectively). With **5** the reaction leads instead to the formation of comparable amounts of the corresponding dibenzyl ether and diphenylmethane accompanied by traces of 2,4-dimethoxybenzaldehyde. With **1** and **7**, formation of the corresponding dibenzyl ether as major product (accompanied in the former substrate by the formation of a significant amount of 4-methoxybenzaldehyde) was observed. Finally, with **8** no dibenzyl ether was detected, the reaction leading instead to the formation of the corresponding diphenylmethane as major product.

No quantitative product studies were carried out for the $TPPBF_4$-photosensitized reaction of **10** but only qualitative ones, which showed the formation of 4,4′-dimethoxybenzophenone and bis(4,4′-dimethoxydiphenylmethyl)ether ($An_2CHOCHAn_2$; An = 4-$MeOC_6H_4$) as the exclusive reaction products.

Laser Flash Photolysis. 355 nm laser flash photolysis (LFP) experiments (third armonic of a Nd:YAG laser; laser energy ≈ 10 mJ/pulse) were carried out in air-saturated CH_2Cl_2 solution ($T = 25$ °C) containing $TPPBF_4$ (2.5×10^{-5} M) and the substrate (**1**, **5**, **6**, **8**−**11**; between 5×10^{-3} and 0.1 M).

LFP of an air-saturated CH_2Cl_2 solution containing $TPPBF_4$ (2.5×10^{-5} M) gave the transient absorption spectra shown in Figure 1.

The time-resolved spectrum recorded 0.2 μs after the laser flash (filled circles) is characterized by two absorption maxima around 340 and 470 nm and a strong bleaching in the region between 360 and 440 nm. In agreement with literature data the absorption bands are assigned to the triplet excited state of TPP^+ [2a,9,10] and the bleaching to the depletion of ground-state TPP^+.[2] Both the 340 and 470 nm bands decay following first-order kinetics, with an observed rate constant $k_{obs} \approx 6 \times 10^5$ s^{-1} which, in agreement with literature data, is assigned to the reaction of triplet TPP^+ with oxygen.[10]

LFP of an air saturated CH_2Cl_2 solution containing $TPPBF_4$ (2.5×10^{-5} M) and 4-methoxybenzyl alcohol (**1**) (10^{-2} M) gave the transient absorption spectra shown in Figure 2. The time-resolved absorption spectrum recorded in the 300−600 nm range 0.5 μs after the laser flash (filled circles) shows, in addition to the features described above (Figure 1), two new absorption bands around 310 and 550 nm. In agreement with literature data, these absorption bands are assigned to the triphenylpyranyl radical $TPP^•$.[2a,11]

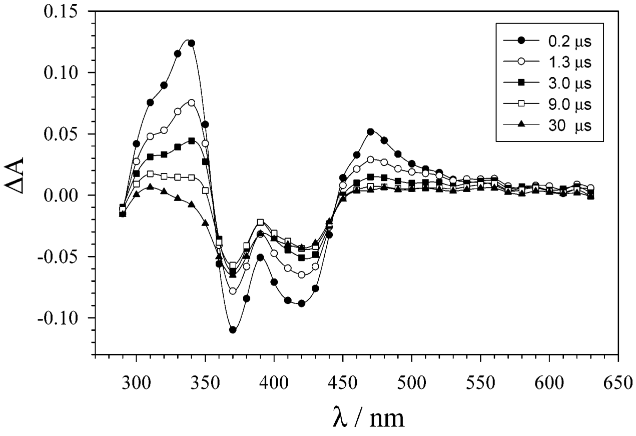

FIGURE 1. Time-resolved absorption spectra recorded after 355 nm LFP of an air-saturated CH_2Cl_2 solution ($T = 25$ °C) containing 2.5×10^{-5} M $TPPBF_4$ at 0.2 (filled circles), 1.3 (empty circles), 3.0 (filled squares), 9.0 (empty squares), and 30 μs (triangles) after the 8 ns, 10 mJ laser flash.

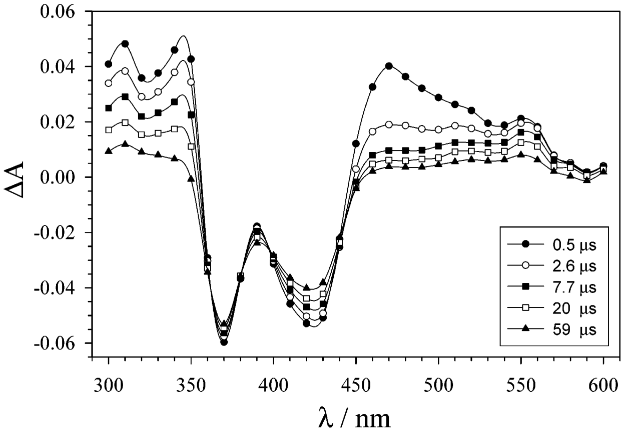

FIGURE 2. Time-resolved absorption spectra recorded after 355 nm LFP of an air-saturated CH_2Cl_2 solution ($T = 25$ °C) containing 2.5×10^{-5} M $TPPBF_4$ and 10^{-2} M 4-methoxybenzyl alcohol (**1**) at 0.5 (filled circles), 2.6 (empty circles), 7.7 (filled squares), 20 (empty squares), and 59 μs (triangles) after the 8 ns, 10 mJ laser flash.

The decay of the 470 nm band follows first-order kinetics and is not influenced by the presence of **1** (up to 0.1 M), occurring again with $k_{obs} \approx 6 \times 10^5$ s^{-1}. The decay of the 550 nm band is instead slower than that of the 470 nm band and follows second-order kinetics.

LFP of an air-saturated CH_2Cl_2 solution containing $TPPBF_4$ (2.5×10^{-5} M) and 2,5-dimethoxybenzyl alcohol (**6**) (10^{-2} M) gave the transient absorption spectra shown in Figure 3. The time-resolved spectrum recorded in the 430−600 nm range 0.5 μs after the laser flash (filled circles) shows two absorption bands around 470 and 550 nm which, in analogy with the experiments reported in

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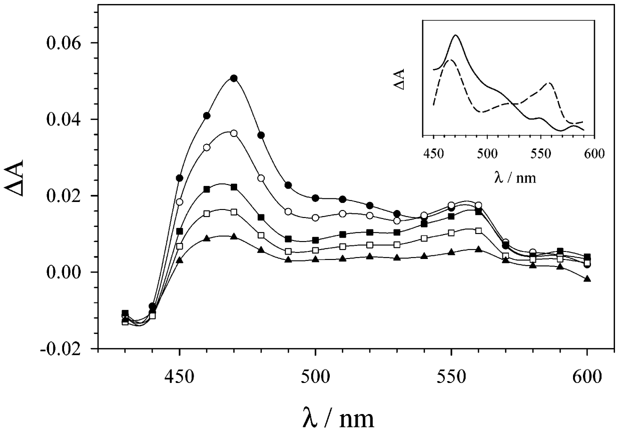

FIGURE 3. Time-resolved absorption spectra recorded after 355 nm LFP of an air-saturated CH_2Cl_2 solution ($T = 25$ °C) containing 2.5×10^{-5} M $TPPBF_4$ and 10^{-2} M 2,5-dimethoxybenzyl alcohol (**6**) at 0.5 (filled circles), 1.5 (empty circles), 4.5 (filled squares), 14 (empty squares), and 47 μs (triangles) after the 8 ns, 10 mJ laser flash. Inset: Deconvoluted spectra resulting from the global analysis of the kinetic data, corresponding to 0.5 μs after the laser flash.

Figure 2, are assigned to triplet TPP^+ and $TPP^\bullet$, respectively. Decay of the 470 nm band is not influenced by the presence of **6** (up to 0.1 M), occurring again with $k_{obs} \approx 6 \times 10^5$ s^{-1}.

This decay shows a residual absorption centered around 460 nm which was not present in the experiments carried out in the absence of substrate (Figure 1) and in the presence of **1** (Figure 2) and which decays following second-order kinetics (see below). Decay of the 550 nm band also follows second-order kinetics (see below).

A global analysis of the kinetic data (for details see the Experimental Section) allowed the deconvolution of the time-resolved spectra of transients, leading to the two new spectra shown in the inset and corresponding to the situation observed 0.5 μs after the laser flash. The solid line spectrum, which decays with $k = 6.4 \times 10^5$ s^{-1}, is characterized by a band centered at 470 nm and corresponds to the spectrum of triplet TPP^+ (see above). The dashed line spectrum is instead characterized by two bands around 460 and 550 nm: the latter band corresponds to $TPP^\bullet$ (see above) while the former one can be reasonably assigned to $\mathbf{6}^{\bullet+}$, based on the comparison with the absorption spectrum of this radical cation, generated by pulse radiolysis in aqueous solution, characterized by a relatively intense absorption band in the visible region of the spectrum around 455 nm.[13,14] As mentioned above, decay of the 460 and 550 nm bands follows second-order kinetics and from the second-order fits of the experimental data, values k/ϵ of 2.75×10^6 and 3.54×10^6 cm s^{-1}, respectively, have been obtained. On the basis of the extinction coefficients available for $\mathbf{6}^{\bullet+}$ ($\epsilon_{455} \approx 4500$ M^{-1} cm^{-1}, in water)[14] and $TPP^\bullet$ ($\epsilon_{550} = 2790$ M^{-1} cm^{-1}, in MeCN),[15] the following second-order rate constants have been obtained: $k_{460} = 1.2 \times 10^{10}$ M^{-1} s^{-1} and $k_{550} = 9.9 \times 10^9$ M^{-1} s^{-1}.[16] The similarity of these values suggests that the main reactive pathway of $\mathbf{6}^{\bullet+}$ and $TPP^\bullet$ is represented by the back electron transfer (BET) reaction.

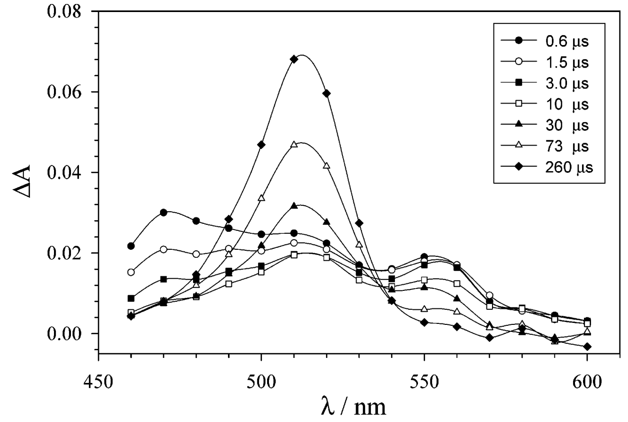

FIGURE 4. Time-resolved absorption spectra recorded after 355 nm LFP of an air-saturated CH_2Cl_2 solution ($T = 25$ °C) containing 2.5×10^{-5} M $TPPBF_4$ and 10^{-2} M 4,4′-dimethoxydiphenylmethanol (**10**) at 0.6 (filled circles), 1.5 (empty circles), 3.0 (filled squares), 10 (empty squares), 30 (filled triangles), 73 (empty triangles), and 260 μs (diamonds) after the 8 ns, 10 mJ laser flash.

Similar results were obtained after LFP of air-saturated CH_2Cl_2 solutions containing $TPPBF_4$ and 2,4-dimethoxybenzyl alcohol (**5**) or 2,4,5-trimethoxybenzyl alcohol (**8**) (see the Supporting Information, Figures S1 and S2, respectively), showing in both cases formation of the corresponding radical cation, $\mathbf{5}^{\bullet+}$ or $\mathbf{8}^{\bullet+}$, and of $TPP^\bullet$.

LFP of an air-saturated CH_2Cl_2 solution containing $TPPBF_4$ (2.5×10^{-5} M) and 4,4′-dimethoxydiphenylmethanol (**10**) (10^{-2} M) gave the transient absorption spectra shown in Figure 4.

The time-resolved spectrum recorded in the 460−600 nm range 0.6 μs after the laser flash (filled circles) is characterized by absorption maxima around 470 and 550 nm which are assigned to triplet TPP^+ and $TPP^\bullet$, respectively. Decay of the 470 nm band occurs again with $k_{obs} \approx 6 \times 10^5$ s^{-1}. The decay of the 550 nm band is instead slower than that of the 470 nm band following second-order kinetics and is accompanied by the delayed formation of a species characterized by an intense absorption band at 510 nm, which on the basis of literature data can be assigned to the 4,4′-dimethoxydiphenylmethyl cation $(4\text{-}MeOC_6H_4)_2CH^+$.[17]

Quite interestingly, the rate of formation of the 4,4′-dimethoxydiphenylmethyl cation was found to be influenced by the concentration of **10**, and by plotting the observed rate constant measured at 510 nm against the concentration of **10** (between 5×10^{-3} and 2×10^{-2} M),

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(12) In THF solution the UV band maximum is observed at 330 nm.

(13) Baciocchi, E.; Bietti, M.; Gerini, M. F.; Manduchi, L.; Salamone, M.; Steenken, S. *Chem. Eur. J.* **2001**, *7*, 1408−1416.

(14) $\mathbf{6}^{\bullet+}$ was generated by pulse radiolysis (3 MeV van de Graaf accelerator, 300 ns electron pulse, 5 Gy/pulse) of an argon-saturated aqueous solution (pH = 4.2) containing **6** (0.2 mM), $K_2S_2O_8$ (5 mM), and 2-methyl-2-propanol (0.1 M). The time-resolved spectrum recorded 8 μs after the pulse shows two absorption bands at 310 nm ($\epsilon_{310} \approx 8000$ M^{-1} cm^{-1}) and 455 nm ($\epsilon_{455} \approx 4500$ M^{-1} cm^{-1}).

(15) Jayanthi, S. S.; Ramamurthy, P. *J. Phys. Chem. A* **1997**, *101*, 2016−2022.

(16) Quite importantly, even though the available extinction coefficient values refer to water (for $\mathbf{6}^{\bullet+}$) and MeCN (for $TPP^\bullet$), the observation that the ratio of the initial absorbances (A_{460}/A_{550}) parallels the extinction coefficient ratio ($\epsilon_{460}/\epsilon_{550}$), justifies their use in CH_2Cl_2 solution.

(17) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918−6928.

TABLE 5. Stern−Volmer Constants (K_{SV}) and Singlet Quenching Rate Constants (k_q) for Substrates 1, 6, and 10, Measured in Air-Saturated CH_2Cl_2 Solution at $T = 25$ °C[a]

quencher	K_{SV} (M^{-1})	$k_q \times 10^9$ ($M^{-1}\ s^{-1}$)
1	58	19
6	95	32
10	86	27

[a] [Q] = 2.5×10^{-3} to 2.5×10^{-2} M; [$TPPBF_4$] = 2.5×10^{-6} M; $\lambda_{exc} = 370$ nm.

a linear dependence was observed.[18] From the slope of this plot, a second-order rate constants $k = 1.04 \times 10^6$ $M^{-1}\ s^{-1}$ was determined. In contrast with this finding, the decay of both the 470 and 550 nm bands was found to be unaffected by the concentration of **10** (in the same concentration range).

An analogous behavior was observed after LFP of an air-saturated CH_2Cl_2 solution containing $TPPBF_4$ and 4-methoxydiphenylmethanol (**9**) (see the Supporting Information, Figure S4), where the slow formation of a species absorbing around 465 nm was attributed in this case to the formation of the 4-methoxydiphenylmethyl cation $4\text{-}MeOC_6H_4CH^+C_6H_5$.[17]

The details of the LFP experiments carried out with 2,4,4′,5-tetramethoxydiphenylmethanol (**11**) are given in the Supporting Information. With this substrate formation of the corresponding radical cation $\mathbf{11}^{\bullet+}$ and of $TPP^{\bullet}$ was observed (Figure S5), and the kinetic data suggest that, again, the BET reaction is the main reactive pathway of these species. Interestingly, in contrast with the results of the experiments carried out with substrates **9** and **10**, with **11** no evidence for the formation of an intermediate diarylmethyl cation was obtained up to 5 ms after the laser flash.

Fluorescence Quenching. To obtain information on the photophysical behavior of the TPP^+ singlet excited state, fluorescence quenching experiments were carried out employing 4-methoxybenzyl alcohol (**1**), 2,5-dimethoxybenzyl alcohol (**6**), and 4,4′-dimethoxydiphenylmethanol (**10**) as quenchers. The experiments were performed by recording the fluorescence emission intensity of TPP^+ solutions (I_0) and of TPP^+ solutions containing different quencher (Q) concentrations (I). Fluorescence lifetime measurements of a 2.5×10^{-6} M TPP^+ solution in air-saturated CH_2Cl_2 gave single-exponential decay profiles (see the Supporting Information, Figure S6) from which a singlet lifetime $\tau_s = 2.97$ ns was obtained, in agreement with literature data.[10] For all substrates efficient quenching of singlet TPP^+ was observed, as clearly shown by the plots of the fluorescence intensity against quencher concentration (see the Supporting Information, Figure S7) which gave excellent fits of the Stern−Volmer equation (eq 1; where $K_{SV} = k_q\tau_s$ is the Stern−Volmer constant).

$$(I_0/I) - 1 = K_{SV}[Q] \tag{1}$$

The Stern−Volmer constants (K_{SV}) and the singlet quenching rate constants (k_q) determined for substrates **1**, **6**, and **10** are collected in Table 5, showing that with all substrates TPP^+ fluorescence quenching occurs at diffusion controlled rates.

TABLE 6. Relative Hydride Affinity of the Ring-Methoxylated Benzyl Cations 1ct, 4ct−8ct in the Gas Phase and in CH_2Cl_2 Solution Calculated by the B3LYP/6-31G(d) Method[a]

cation	$-\Delta E_{gas}$ (kcal/mol)	$-\Delta E_{sol}{}^b$ (kcal/mol)
1ct	15.3	9.7
4ct	18.7	13.0
5ct	4.7	2.3
6ct	14.6	11.8
7ct	10.8	8.1
8ct	0.0	0.0

[a] The reference hydride affinity is that of **8ct** in the gas phase and in CH_2Cl_2 solution, respectively. [b] Calculated by integral equation formalism of polarized continuum model (IEFPCM).

DFT Calculations. To obtain information about the relative stabilities of the ring-methoxylated benzyl cations **1ct** and **4ct**−**8ct**, hybrid density functional theory (DFT) calculations were carried out at the B3LYP/6-31G(d) level of theory.

The structures corresponding to the global energy minimum, depicted in Chart 2, have the methyl groups on the same plane with the aromatic ring. The relative stability of the various benzyl cations was established by calculating their relative hydride affinity. Since the hydride affinity is defined as the negative of the energy change ($-\Delta E$) accompanying the process $R^+ + H^- \rightarrow RH$, calculation of the energy of the corresponding neutral H-adducts of the cations in Chart 2 was also required. The global energy minimum conformation of the neutral H-adducts was found in general analogous to that of the corresponding cation with the notable exceptions of the H-adducts relative to cations **5ct** and **6ct**. In the former case, the 4-methoxy group changes from syn to anti in relation to the 2-methoxy group going from the corresponding cation to the neutral H-adduct whereas in the latter case the 5-methoxy group changes from anti to syn. The relative hydride affinity of the various benzyl cations is shown in the second column of Table 6. Note that the higher the hydride affinity, the lesser the stability of the cation.

The same calculations were also performed taking into account the effect of CH_2Cl_2 as the solvent by using the integral equation formalism of polarized continuum model (IEFPCM) of Tomasi.[19] The obtained results are shown in the third column of Table 6.

The relative stabilizing effect of the solvent on the various benzyl cations appears to depend on the number of methoxy groups substituting the benzene ring. Indeed, taking as reference the trisubstituted benzyl cation **8ct**, the monosubstituted cations **1ct** and **4ct** are more stabilized by about 6 kcal/mol, whereas the disubstituted cations **5ct**−**7ct** are more stabilized by about 3 kcal/mol.

Discussion

The results collected in Table 1 show that in the $TPPBF_4$-photosensitized reaction of 4-methoxybenzyl alcohol (**1**) in air- or O_2-saturated CH_2Cl_2 solution rapid

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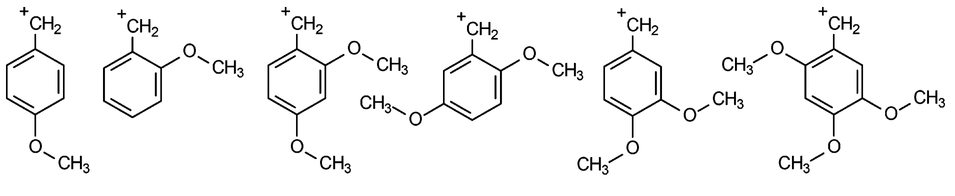
[18] From the regression analysis: intercept = $5.10 \times 10^3\ s^{-1}$; slope = $1.04 \times 10^6\ M^{-1}\ s^{-1}$; $r^2 = 0.9973$.

[19] (a) Cancès, M. T.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032. (b) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1998**, *286*, 253. (c) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151.

CHART 2



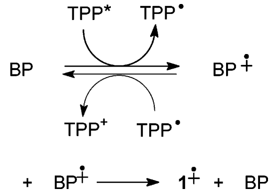
1ct **4ct** **5ct** **6ct** **7ct** **8ct**

substrate consumption is observed, accompanied by initial formation of bis(4-methoxybenzyl) ether (**1a**) as the main reaction product, together with 4-methoxybenzaldehyde and small amounts of 4,4′-dimethoxydiphenylmethane (**1b**). At longer irradiation times in both air- and O_2-saturated solution, consumption of **1a** is observed accompanied by an increase in the amount of 4-methoxybenzaldehyde. This result is in line with the observation that in air- or O_2-saturated CH_2Cl_2 solution the $TPPBF_4$-photosensitized reaction of **1a** leads to the formation of 4-methoxybenzaldehyde as the main reaction product (Table 2). In O_2-saturated solution (Table 1, entries 16−21), formation and consumption of **1a** occur significantly faster than in air, and after 10 min of irradiation a decrease in the amount of 4-methoxybenzaldehyde is observed, accompanied by the formation of 4-methoxybenzoic acid, a behavior which can be rationalized in terms of the oxidation of the first formed aldehyde.

Quite importantly, no substrate consumption was observed when a CH_2Cl_2 solution containing **1** and $TPPBF_4$ was kept in the dark, whereas formation of products **1a** and **1b** was also observed when an *equimolar* amount of a Brønsted (H_2SO_4) or Lewis ($AgBF_4$) acid was added to a CH_2Cl_2 solution of **1**, in the absence of $TPPBF_4$. These observations clearly indicate that in order to observe the formation of products **1a** and **1b** in acid-free CH_2Cl_2 solution and in the presence of $TPPBF_4$ irradiation is required.

Formation of products **1a** and **1b** in the $TPPBF_4$-photosensitized reaction of **1** is in agreement with the results obtained by Steckhan,[3] even though in this study no evidence for the formation of 4-methoxybenzaldehyde was obtained. Steckhan proposed that products **1a**, **1b**, and **1c** are formed via an intermediate 4-methoxybenzyl cation ($4\text{-MeOC}_6H_4CH_2^+$ (**1ct**): Scheme 3),[20] which in turn was suggested to be formed from **1** through excited TPP^+ (TPP*) which acts as a Lewis acid. The hypothesis of the intermediacy of **1ct** in the formation of products **1a** and **1b** is well supported by the results of the experiments carried out with **1** in the presence of *equimolar* amounts of acid. Under these conditions, interaction between the α-OH group of the alcohol and the acid occurs, leading to the formation of **1ct**, from which products **1a** and **1b** can be formed as described in Scheme 3. However, it is well-known that by addition of an appropriate concentration of a cosensitizer such as biphenyl (BP) singlet TPP* is quantitatively and selectively scavenged by BP to give $BP^{\bullet+}$ (with $k_q \approx 2 \times 10^{10}$ M^{-1} s^{-1}, in CH_2Cl_2 or MeCN solution),[9,10] which in turn can act as a one-electron oxidant toward **1** eventually leading to the formation of $\mathbf{1}^{\bullet+}$ (Scheme 4), thus preventing the reaction between TPP* and **1**.

SCHEME 4



Accordingly, the observation that in the $TPPBF_4$-photosensitized reactions of **1** substrate consumption and product distribution are not influenced to a significant extent by the presence of 0.05 M BP (Table 1, entries 2 and 3) rules out the hypothesis that **1ct** is formed through the action of TPP*, indicating that formation of **1ct** must occur through a different pathway.

The results collected in Table 1 also show that in the $TPPBF_4$-photosensitized reaction of **1**, negligible amounts of products **1a** and **1b** are formed in the presence of added base (pyridine or 1,2-epoxybutane, respectively), the exclusive or predominant reaction product being 4-methoxybenzaldehyde. Moreover, substrate consumption is significantly reduced as compared to the corresponding experiments carried out in the absence of base. This behavior suggests that in the presence of a base formation of **1ct** does not occur or is strongly depressed. Quite interestingly, base strength seems to be an important factor as shown by the fact that similar effects are observed in the presence of 5×10^{-4} M pyridine or 0.1 M of the weaker base 1,2-epoxybutane. In particular, with the latter base a concentration which is 20 times higher than that of **1** is needed in order to suppress the formation of products **1a** and **1b**.

The product distributions observed in the $TPPBF_4$-photosensitized reactions of **1** in the presence of added base are in agreement with a mechanism that proceeds through the formation and base-induced deprotonation of $\mathbf{1}^{\bullet+}$, formed after electron transfer from **1** to TPP*. The α-hydroxy 4-methoxybenzyl radical thus formed reacts with O_2 to give a peroxyl radical which is then converted into 4-methoxybenzaldehyde (Scheme 5).[21] This observation indicates that 4-methoxybenzaldehyde may derive from the deprotonation of an intermediate radical cation and from the oxidative decomposition of the first formed dibenzyl ether **1a**.

Indirect evidence on the role of an intermediate cation in the reaction of **1** is also provided by the results of the $TPPBF_4$-photosensitized reactions of substrates **2** and **3**, substrates structurally related to **1** lacking, however, the presence of the α-OH group.

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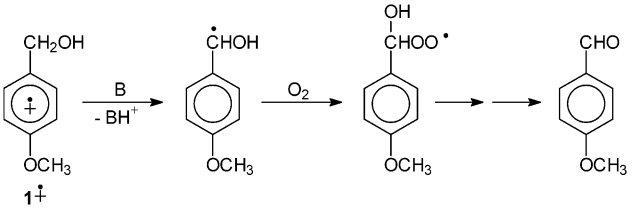
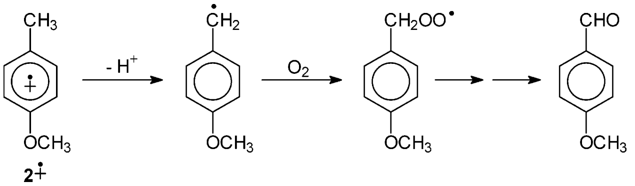
[20] In the present study, no effort was made to detect the eventual formation of product **1c**.

[21] See, for example: (a) *The Chemistry of Free Radicals: Peroxyl Radicals*; Alfassi, Z. V., Ed.; John Wiley & Sons: New York, 1997. (b) von Sonntag, C. *The Chemical Basis of Radiation Biology*; Taylor & Francis: London, 1987.

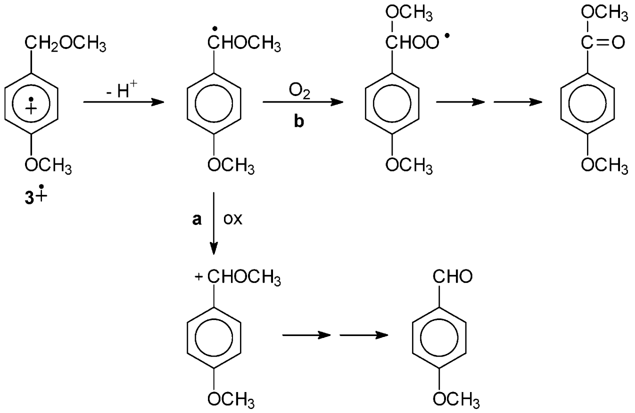
SCHEME 5



SCHEME 6



SCHEME 7



The results of the $TPPBF_4$-photosensitized reactions of **2** are collected in Table 3, showing the formation of 4-methoxybenzaldehyde as the exclusive or predominant product. This result can be explained in terms of the α-C−H deprotonation of $\mathbf{2}^{\bullet +}$, formed after electron transfer from **2** to TPP*, to give a 4-methoxybenzyl radical which then reacts with O_2 finally leading to 4-methoxybenzaldehyde (Scheme 6). The significant increase in the amount of 4-methoxybenzaldehyde observed in the presence of pyridine (from 3% to 17%) is in line with its action as a base which accordingly promotes the deprotonation of $\mathbf{2}^{\bullet +}$.[22–24]

The results of the $TPPBF_4$-photosensitized reactions of **3** in O_2-saturated CH_2Cl_2 solution are collected in Table 3, showing the formation of 4-methoxybenzaldehyde and methyl 4-methoxybenzoate (in a ~3:2 ratio) as main reaction products. Formation of the same products in a 2:1 ratio has been recently observed in the $TPPBF_4$-photosensitized reaction of **3** in O_2-saturated MeCN solution.[26] This result has been explained as described in Scheme 7, in terms of the α-C−H deprotonation of $\mathbf{3}^{\bullet +}$, formed after electron transfer from **3** to TPP*, to give an α-methoxy 4-methoxybenzyl radical which then can follow two pathways: (a) oxidation by ground-state TPP^+ to give 4-methoxybenzaldehyde and (b) reaction with O_2 to give a peroxyl radical which is then converted into methyl 4-methoxybenzoate. A similar explanation can in principle be extended also to the reaction carried out in CH_2Cl_2 solution even though, at this stage, it cannot be excluded that both products derive from the decomposition of the intermediate peroxyl radical, as described above (Schemes 5 and 6) for the formation of 4-methoxybenzaldehyde.

The results presented above for the $TPPBF_4$-photosensitized reactions of substrates **2** and **3** clearly show that the formation of products deriving from an intermediate 4-methoxybenzyl cation is observed only in the presence of an α-OH group as in **1**. On the other hand, the product distributions observed in the $TPPBF_4$ photosensitized reactions of substrates **2** and **3** are in full agreement with the formation of intermediate aromatic radical cations.

Additional information on the role of an intermediate benzyl cation is provided by the results of the $TPPBF_4$-photosensitized reactions of ring-methoxylated benzyl alcohols **4**−**8**, collected in Table 4, and by DFT calculations carried out on the corresponding ring-methoxylated benzyl cations. The results collected in Table 4 show that in the $TPPBF_4$-photosensitized reaction of substrates **1** and **4**−**8** the product amounts and distributions are strongly influenced by the number and relative position of the methoxy substituents. Along this line, in the reactions of **4** and **6** exclusive formation of the corresponding benzaldehyde is observed. In the reaction of **1**, dibenzyl ether **1a** is formed as the major reaction product accompanied by significant amounts of 4-methoxybenzaldehyde. With **7** the corresponding dibenzyl ether is formed as the major reaction product, and only traces of 3,4-dimethoxybenzaldehyde have been observed. With **5** comparable amounts of the corresponding dibenzyl ether and diphenylmethane are formed and a significant substrate loss is observed. In the reaction of **8**, the corresponding diphenylmethane is formed as the major reaction product accompanied by traces of 2,4,5-trimethoxybenzaldehyde. As discussed above, dibenzyl ethers and diphenylmethanes are likely to be formed from an intermediate benzyl cation; whereas benzaldehydes may derive from the deprotonation of an intermediate radical cation and from the oxidative decomposition of the first formed dibenzyl ether, as described above for the reactions of **1**. It is thus very important to obtain information on the relative stabilities of the radical cations formed from ring-methoxylated benzyl alcohols **1**, **4**−**8** and of the corresponding benzyl cations **1ct** and **4ct**−**8ct**.

The following one-electron oxidation potentials have been determined in aqueous solution for anisole, 1,2-, 1,3-, 1,4-dimethoxybenzene, and 1,2,4-trimethoxybenzene, respectively, 1.62, 1.44, 1.58, 1.30, and 1.13 V/NHE,[27,28] substrates which can be reasonably taken as models for **1** (and **4**), **7**, **5**, **6**, and **8**, respectively. Thus,

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[22] Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290−12295.

[23] Schlesener, C. J.; Kochi, J. K.; *J. Org. Chem.* **1984**, *49*, 3142−3150.

[24] Excluding the presence of adventitious water in CH_2Cl_2 solution, the formation of **1** in small amounts in the $TPPBF_4$-photosensitized reactions of **2** may be explained in terms of the "Russel mechanism" via decomposition of an intermediate tetroxide (see refs 21 and 25).

[25] Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 3871−3877.

[26] Del Giacco, T.; Lipparoni, L.; Ranchella, M.; Rol, C.; Sebastiani, G. V. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1802−1807.

[27] Jonsson, M.; Lind, J.; Reitberger, T.; Eriksen, T. E.; Merényi, G. *J. Phys. Chem.* **1993**, *97*, 11278−11282.

[28] The same order was also observed in MeCN solution (see ref 29).

the following radical cation stability order is to be expected: $\mathbf{1}^{\bullet+} \cong \mathbf{4}^{\bullet+} < \mathbf{5}^{\bullet+} < \mathbf{7}^{\bullet+} < \mathbf{6}^{\bullet+} < \mathbf{8}^{\bullet+}$. Along this line, it is well-known that the rate constant for α-C−H deprotonation of benzyl alcohol (and more generally alkylaromatic) radical cations decreases by increasing radical cation stability.[4,22,30,31] Accordingly, also the amount of ring-methoxylated benzaldehyde formed is likely to depend on the deprotonation rate constant (and thus stability) of the radical cation precursor.

For what concerns instead the ring-methoxylated benzyl cations (**1ct** and **4ct**−**8ct**), the results of DFT calculations collected in Table 6, where also the contribution of the solvent is taken into account, lead to the following stability order: **4ct** < **6ct** < **1ct** < **7ct** < **5ct** < **8ct**. The most stable cations are **8ct** and **5ct** both characterized by the presence of methoxy substituents in positions 2 and 4 which contribute significantly to the stabilization of the positive charge. Comparable energies have been found for **1ct** and **7ct**, while the lowest stabilities were found for **4ct** and **6ct**.

Very interestingly the relative stabilities of the radical cations and benzyl cations discussed above are in line with the product distributions given in Table 4 for the TPPBF$_4$-photosensitized reactions of substrates **1** and **4**−**8**. Along this line, by comparing the results shown in Table 4 for substrates **4** and **6**, it appears that the amount of ring-methoxylated benzaldehyde formed reflects the stability (and the deprotonation rate constants) of the corresponding radical cations, whereas no products deriving from an intermediate cation are observed, in full agreement with the relatively low stability of the corresponding cations **4ct** and **6ct**. Comparison between **1** and **4** is more difficult because, as mentioned above, in the TPPBF$_4$-photosensitized reaction of **1**, 4-methoxybenzaldehyde also derives from the oxidative decomposition of dibenzyl ether **1a**, which in turn is formed via **1ct**, in line with the greater stability of **1ct** as compared to **4ct**. However, based on the similar rate constants measured for the deprotonation of $\mathbf{1}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ in acidic aqueous solution (1.5×10^4 and 5.7×10^3 s^{-1}, respectively),[33] comparable amounts of products (4-methoxy- and 2-methoxybenzaldehyde, respectively) deriving from this pathway should be observed. The results obtained with **5**, **7**, and **8** clearly reflect the high stability of the corresponding cations **5ct**, **7ct**, and **8ct**; accordingly in the TPPBF$_4$-photosensitized reactions of these substrates very small amounts of products deriving from the corresponding radical cations have been observed.

As described in Scheme 3 for the TPPBF$_4$-photosensitized reaction of **1**, products **1a**, **1b**, and **1c** are formed through the intermediacy of a 4-methoxybenzyl cation (**1ct**). While **1a** can be formed by nucleophilic attack of the α-OH group of **1** on the positively charged benzylic carbon of **1ct**, formation of **1b** and **1c** requires instead an electrophilic attack of **1ct** on the aromatic nucleus of **1** (or **1b**). Such an explanation is in line with the product distributions observed in the TPPBF$_4$-photosensitized reactions of **1** and **4**−**8**. Accordingly, significant amounts of diphenylmethane products are formed only in the reactions of **5** and **8**, substrates which, due to the relative positions of the methoxy substituents, are strongly activated toward an electrophilic attack in position 1. Along this line, also the observation that in the reaction of **5** significant substrate loss occurred, may reflect the formation of product **5c** (corresponding to **1c** in Scheme 3) via electrophilic attack of **5ct** on the aromatic nucleus of **5b**.[34]

Direct evidence on the involvement of intermediate radical cations and benzylic cations in the TPPBF$_4$ photosensitized reactions of ring-methoxylated benzyl alcohols are provided by the results of laser flash photolysis (LFP) experiments, carried out in air saturated CH$_2$Cl$_2$ solution for substrates **1**, **5**, **6**, and **8**−**11**.

LFP of an air-saturated CH$_2$Cl$_2$ solution containing TPPBF$_4$ gave, 0.2 μs after the laser flash, a transient absorption spectrum characterized by two absorption maxima around 340 and 470 nm and a strong bleaching in the region between 360 and 440 nm (Figure 1). In agreement with literature data, the absorption bands are assigned to the triplet excited state of TPP$^+$ [2a,9,10] and the bleaching to the depletion of ground-state TPP$^+$.[2] Both the 340 and 470 nm bands decay with an observed rate constant $k_{\text{obs}} \approx 6 \times 10^5$ s^{-1}, attributed to the reaction of triplet TPP$^+$ with oxygen.[10] Very interestingly, the transient assigned to triplet TPP$^+$ was always present in the LFP experiments carried out in the presence of substrates **1**, **5**, **6**, and **8**−**11**, and in all cases the decay of the 470 nm band was not affected by the presence of the substrate (up to 0.1 M) occurring always with $k_{\text{obs}} \approx 6 \times 10^5$ s^{-1}. This observation indicates that under the experimental conditions employed no substrate induced quenching of triplet TPP$^+$ occurs.[35]

LFP of air-saturated CH$_2$Cl$_2$ solutions containing TPPBF$_4$ and the substrate (**1**, **5**, **6**, **8**−**11**) showed in all cases the formation of an absorption band around 550 nm which, in agreement with literature data, is assigned to the triphenylpyranyl radical TPP$^\bullet$.[2a,11] The direct observation of TPP$^\bullet$ confirms the occurrence of photoinduced electron transfer (PET) from the substrate to the singlet excited state of TPP$^+$, in line with the results of the fluorescence quenching experiments carried out with **1**, **6**, and **10** (Table 5), showing that with these substrates TPP$^+$ fluorescence quenching always occurs at diffusion controlled rates.

Unfortunately, the strong bleaching in the region between 360 and 440 nm did not allow detection of the radical cations of substrates **1**, **9**, and **10**, which are characterized by a relatively weak absorption band around 430−440 nm ($\epsilon \leq 3500$ M^{-1} cm^{-1}).[5,22,33,36] With **5**, **6**, **8**, and **11**, clear evidence for the formation of the corresponding radical cations, characterized by an ab-

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(29) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4124−4129.

(30) Amatore, C.; Kochi, J. K. *Adv. Electron-Transfer Chem.* **1991**, *1*, 55−148.

(31) As an example, the following rate constants have been measured for the deprotonation of $\mathbf{1}^{\bullet+}$ and $\mathbf{7}^{\bullet+}$ in acidic aqueous solution: 1.5×10^4 and 17 s^{-1}, respectively (see refs 5 and 32).

(32) Bietti, M.; Baciocchi, E.; Steenken, S. *J. Phys. Chem. A* **1998**, *102*, 7337−7342.

(33) Baciocchi, E.; Bietti, M.; Ercolani, G.; Steenken, S. *Tetrahedron* **2003**, *59*, 613−618.

(34) No attempt was made to detect the eventual formation of **5c**.

(35) This observation is quite surprising as triplet TPP$^+$ should be characterized by a significantly higher oxidation potential ($E_{\text{TPP}^*(\text{T1})/\text{TPP}^\bullet}$ = 2.00 V/SCE.; see ref 2a) than the ring-methoxylated benzyl alcohols **1** and **4**−**8** (see refs 27, 29, and 32).

(36) O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1975**, *79*, 2773−2779.

sorption band around 450−460 nm ($\epsilon \approx 5000$ M^{-1} cm^{-1}),[13,36] was instead obtained. Moreover, in the deconvoluted spectra shown in the inset of Figure 3 for substrate **6**, the difference in absorbance between $\mathbf{6}^{\bullet+}$ and TPP$^\bullet$ parallels the differences in extinction coefficents between these species.[14,15]

In all cases, decay of the radical cation and TPP$^\bullet$ band at 550 nm followed second-order kinetics. Based on the fact that in the LFP experiments carried out in the presence of **6**, **8**, and **11** similar values of the second-order rate constants for decay of the radical cation and of TPP$^\bullet$ were measured, it is reasonable to conclude that the main reactive pathway of the substrate radical cations (D$^{\bullet+}$) and TPP$^\bullet$ is represented by the back-electron transfer (BET) reaction which regenerates the neutral substrate (D) and TPP$^+$ (Scheme 1).

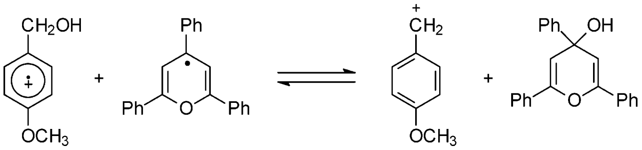
Benzyl cations are characterized by absorptions in the UV region of the spectrum at $\lambda < 350$ nm.[37] On the other hand, it is well-known that in MeCN solution diarylmethyl cations display very intense absorption bands in the visible region of the spectrum.[17] For this purpose, to obtain direct evidence on the involvement of diarylmethyl cations in these processes, LFP experiments of air saturated CH_2Cl_2 solutions containing TPPBF$_4$ and diarylmethanols **9**−**11** have also been carried out.

With **9**, slow formation of a species which shows a weak absorption around 465 nm is observed (see the Supporting Information, Figure S4). A similar behavior is observed with **10**, where a species characterized by an intense absorption band at 510 nm is formed (Figure 4). On the basis of literature data the former species can be assigned to the 4-methoxydiphenylmethyl cation (4-MeOC$_6$H$_4$CH$^+$C$_6$H$_5$: **9ct**) and the latter one to the 4,4′-dimethoxydiphenylmethyl cation ((4-MeOC$_6$H$_4$)$_2$-CH$^+$: **10ct**).[17] Based on the literature values of the extinction coefficients of **9ct** ($\epsilon_{466} = 3.3 \times 10^4$ M^{-1} cm^{-1}, in MeCN)[17] and TPP$^\bullet$ ($\epsilon_{550} = 2790$ M^{-1} cm^{-1}, in MeCN),[15] a very small amount of **9ct**, as compared to TPP$^\bullet$, is formed 1 ms after the laser flash. Figure 4 shows that 260 μs after the laser flash a significantly greater amount of **10ct** ($\epsilon_{507} = 1.1 \times 10^5$ M^{-1} cm^{-1}, in MeCN)[17] is instead formed, an amount which, however, is still lower than that of TPP$^\bullet$. The different behavior observed in the experiments carried out with **9** and **10** is likely to reflect the greater stability of **10ct** as compared to **9ct**. With **11** no evidence for the formation of the corresponding diarylmethyl cation but only of the corresponding radical cation $\mathbf{11}^{\bullet+}$ was instead obtained (see below).

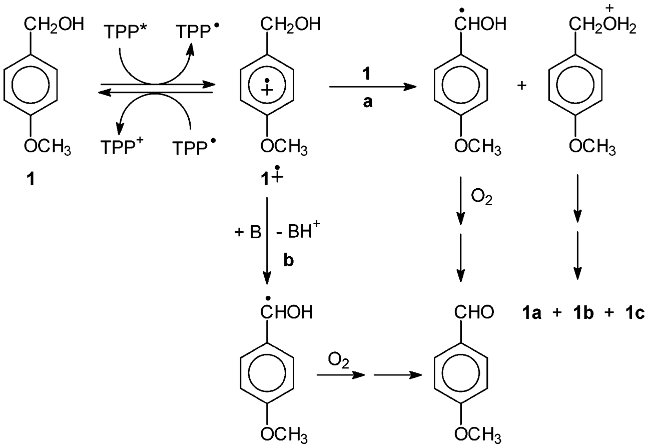
Taken together, the results presented above indicate that in the TPPBF$_4$-photosensitized reactions of ring-methoxylated substrates **1**−**11** products formation is governed by the interplay between radical cation and benzyl cation stability. The results of the LFP experiments clearly show that radical cations are intermediates in these processes and thus, formation of the benzyl cations may be suggested to occur as described in Scheme 8, via $^\bullet$OH transfer from the benzyl alcohol radical cation to TPP$^\bullet$.

However, the results obtained after LFP of **9** and **10** (see Figure S4 of the Supporting Information and Figure 4, respectively) show that in both cases TPP$^\bullet$ decay occurs significantly faster that the buildup of **9ct** and **10ct**. Moreover, **9ct** and **10ct** are formed in amounts that are significantly smaller than that of TPP$^\bullet$. Finally, if an OH radical transfer mechanism operates, cation formation should not be influenced by substrate concentration. The rate of formation of **10ct** was instead found to be influenced by the concentration of **10**, and a second-order rate constant $k = 1.04 \times 10^6$ M^{-1} s^{-1} was determined, an observation which suggests that cation formation proceeds through the reaction between the radical cation $\mathbf{10}^{\bullet+}$ and the parent substrate **10**.

SCHEME 8



SCHEME 9



On the basis of these considerations, it is thus possible to rule out cation formation via $^\bullet$OH transfer from the benzyl alcohol radical cation to TPP$^\bullet$ as described in Scheme 8 and to propose a general mechanism for the TPPBF$_4$-photosensitized reactions of ring methoxylated benzyl alcohols, able to account for all the experimental evidence presented above (Scheme 9, where **1** is chosen as representative substrate). The substrate (**1**) reacts with the singlet excited state of TPP$^+$ to give $\mathbf{1}^{\bullet+}$ and TPP$^\bullet$ (which may undergo competing BET reaction). In a nonbasic solvent such as CH_2Cl_2, **1** can act as a base, undergoing α-C−H deprotonation from $\mathbf{1}^{\bullet+}$ to give an α-hydroxy 4-methoxybenzyl radical and a cation (path a). The former reacts with O_2 to give 4-methoxybenzaldehyde while the latter can form products **1a**−**c** as described in Scheme 3.

In the presence of pyridine or 1,2-epoxybutane, which may act as the deprotonating base, competition with **1** occurs and, depending on base strength and concentration, the relative importance of path a decreases and the path b takes over, leading again to the formation of an α-hydroxy 4-methoxybenzyl radical, precursor of 4-methoxybenzaldehyde. Along this line, in the presence of 1,2-epoxybutane, whose basic strength should be comparable to that of **1**, a 0.1 M concentration is needed in order to completely suppress pathway a.

With substrates lacking the α-OH group such as **2** and **3**, no cationic intermediate can be formed and the

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(37) Cozens, F. L.; Kanagasabapathy, V. M.; McClelland, R. A.; Steenken, S. *Can. J. Chem.* **1999**, *77*, 2069−2082.

reaction proceeds through path b. In this context, it is important to point out that even though **1** and **3** should be characterized by comparable base strengths, with the latter substrate α-C−H deprotonation from $\mathbf{3}^{\bullet+}$ leads, via methanol loss, to **1ct** from which, however, formation of products **1a**−**c** is expected to be an unfavorable process since it would require cleavage of an $O-CH_3$ bond with formation of a very unstable methyl cation. Accordingly, in the $TPPBF_4$-photosensitized reaction of **3** no products deriving from an intermediate cation have been observed but only 4-methoxybenzaldehyde and methyl 4-methoxybenzoate suggested to be formed after α-C−H deprotonation from $\mathbf{3}^{\bullet+}$ as described in Scheme 7.

The observation that in the LFP of **11** no evidence for the formation of the corresponding diarylmethyl cation (up to 5 ms after the laser flash) but only of the corresponding radical cation $\mathbf{11}^{\bullet+}$ was obtained is likely to reflect the high stability of $\mathbf{11}^{\bullet+}$,[13,27] which accordingly is expected to undergo a very slow deprotonation reaction. The relatively less stabilized radical cations $\mathbf{9}^{\bullet+}$ and $\mathbf{10}^{\bullet+}$ may instead undergo significantly faster deprotonation reactions,[38] and formation of the corresponding cations **9ct** and **10ct** (according to the mechanism described in Scheme 9) has been observed in both cases (see Figure S4 of the Supporting Information and Figure 4, respectively).

In conclusion, on the basis of the results of steady-state and laser flash photolysis experiments on the $TPPBF_4$-photosensitized oxidation of ring-methoxylated benzyl alcohols in organic solution, clear evidence in favor of the involvement of benzyl alcohol radical cations and benzyl cations in these processes is provided, leading to a general mechanism for these reactions. The product distributions observed in the steady-state irradiation experiments are interpreted in terms of the interplay between radical cation and benzyl cation stability. Quite importantly, in contrast with previous studies where formation of the 4-methoxybenzyl cation was suggested to occur from the neutral 4-methoxybenzyl alcohol through excited TPP^+ (TPP^*) acting as a Lewis acid,[3] the experimental data presented above allow to rule out such hypothesis and benzyl cation formation is now rationalized in terms of α-C−H deprotonation of the radical cation (formed after electron transfer from the substrate to TPP^*) by the α-OH group of the parent substrate which acts as the deprotonating base.

Experimental Section

Materials. Commercial samples of 4-methoxybenzyl alcohol (**1**), 4-methoxytoluene (**2**), 2-methoxybenzyl alcohol (**4**), 2,4-dimethoxybenzyl alcohol (**5**), 2,5-dimethoxybenzyl alcohol (**6**), 3,4-dimethoxybenzyl alcohol (**7**), 2,4,5-trimethoxybenzyl alcohol (**8**), 4,4′-dimethoxydiphenylmethanol (**10**), pyridine, 1,2-epoxybutane, and biphenyl of the highest quality available were used as received. CH_2Cl_2 was purified on a basic alumina column prior to use. 2,4,6-Triphenylpyrylium tetrafluoroborate was recrystallized twice from ethanol before use.[39] 4,4′-Dimethoxydiphenylmethane (**1b**) was available from previous work.[38]

4-Methoxybenzyl methyl ether (**3**) was prepared by reaction of 4-methoxybenzyl alcohol with methyl iodide and sodium hydride in anhydrous tetrahydrofuran; purified by column chromatography (silica gel, eluent hexane/ethyl acetate 4:1) and identified by ^1H NMR and GC−MS.[5]

Bis(4-methoxybenzyl) ether (**1a**) was prepared carrying out the $TPPBF_4$-photosensitized reaction of 4-methoxybenzyl alcohol (**1**) on a preparative scale. After workup, the residue was purified by column chromatography (basic alumina, eluent petroleum ether/ethyl acetate 5:1) and identified by GC−MS. GC−MS *m/e* (relative abundance): 258 [M^+], 151, 137, 136, 122, 121 (100), 107, 77.

4-Methoxydiphenylmethanol (**10**) was prepared by reduction of 4-methoxybenzophenone with $NaBH_4$ in 2-propanol, purified by column chromatography (basic alumina, eluent petroleum ether/ethyl acetate 10:1), and identified by ^1H NMR and GC−MS.[38]

2,4,4′,5-Tetramethoxydiphenylmethanol (**11**) was prepared by reaction of 4-methoxyphenylmagnesium bromide with 2,4,5-trimethoxybenzaldehyde in anhydrous tetrahydrofuran, purified by column chromatography (basic alumina, eluent petroleum ether/ethyl acetate 3:1) and identified by ^1H NMR and GC−MS.

^1H NMR ($CDCl_3$): δ 3.77 (s, 3H), 3.79 (s, 6H), 3.88 (s, 3H), 5.98 (s, 1H), 6.52 (s, 1H), 6.84 (s, 1H), 6.83−6.87 (m, 2H), 7.26−7.31 (m, 2H).

GC−MS *m/e* (relative abundance): 304 [M^+] (100), 287, 271, 257, 195, 169, 135, 121, 109.

Product Studies. Air- or oxygen-saturated CH_2Cl_2 solutions containing $TPPBF_4$ (5×10^{-4} M) and the substrate (**1**, **1a**, **2**−**8**, **10**; between 2.5 and 5×10^{-3} M) were irradiated for times varying between 1 and 60 min employing a Photochemical Multirays Reactor equipped with 10 × 15 W 365 nm lamps. The reactor was a cylindrical flask equipped with a water cooling jacket thermostated at $T = 25$ °C. After irradiation, the reaction mixture was washed with a saturated NaCl solution and then with a 10% $NaHCO_3$ solution, and the solvent was evaporated under vacuum. Addition of diethyl ether to the residue allowed removal of the insoluble $TPPBF_4$ through filtration. The quantitative analysis of the ethereal filtrate was performed by GC in the presence of an internal standard (bibenzyl). Unreacted substrate and reaction products were generally identified by ^1H NMR, GC−MS, and GC by comparison with authentic samples. Good to excellent mass balances (≥85%) were obtained in all experiments.

Blank experiments carried out in the absence of irradiation or irradiating solutions without $TPPBF_4$ showed no substrate consumption.

Laser Flash Photolysis Studies. Laser flash photolysis experiments were carried out with a laser kinetic spectrometer using the third armonic (355 nm) of a Q-switched Nd:YAG laser. The laser energy was adjusted to ~10 mJ at 355 nm by the use of the appropriate filter. A 3 mL Suprasil quartz cell (10 mm × 10 mm) was used for all experiments. Air-saturated CH_2Cl_2 solutions containing $TPPBF_4$ (2.5×10^{-5} M, $A_{355nm} \approx 1$) and the substrate (**1**, **5**, **6**, **8**−**11**; between 5×10^{-3} M and 0.1 M) were used. All the experiments were carried out at $T = 25 \pm 0.5$ °C under magnetic stirring. Rate constants were obtained by averaging three or four values. The stability of the solution to the experimental conditions was checked spectrophotometrically comparing the spectrum of the solution before irradiation with that obtained after irradiation.

With substrates **6**, **8**, and **11**, the decay kinetics were monitored at 460, 470 and 550 nm. At 460 and 470 nm, the best fit to the experimental data was obtained using consecutive first-order second order kinetics, assigned, respectively to the decay of triplet TPP^+ and of the substrate radical cation ($\mathbf{6}^{\bullet+}$, $\mathbf{8}^{\bullet+}$, and $\mathbf{11}^{\bullet+}$). At 550 nm, the experimental data were fitted according to second-order kinetics, assigned to the decay of $TPP^\bullet$.

In the global kinetic analysis[40] (for LFP experiments of substrates **6** and **8**) the deconvolution of the time-resolved spectra of transients was carried out employing the Pro-K 4.0 program, according to the following model: a first-order

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(38) Bietti, M.; Lanzalunga, O. *J. Org. Chem.* **2002**, *67*, 2632−2638.

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reaction (T → S) and a second-order one (2A → P) corresponding, respectively, to the pseudofirst-order decay of triplet TPP^+ (by reaction with O_2) and to the BET reaction between $TPP^\bullet$ and substrate radical cation, (assuming $[TPP^\bullet] = [\text{substrate}^{\bullet+}]$).

Fluorescence Quenching Studies. Fluorescence quenching experiments were performed with a spectrofluorimeter employing 4-methoxybenzyl alcohol (**1**), 2,5-dimethoxybenzyl alcohol (**6**), or 4,4′-dimethoxydiphenylmethanol (**10**) as quenchers. A 3 mL Suprasil quartz cell (10 mm × 10 mm) was used for all experiments. Air-saturated CH_2Cl_2 solutions ($T = 25$ °C) containing $TPPBF_4$ (2.5×10^{-6} M) and different quencher concentrations (between 2.5×10^{-3} and 2.5×10^{-2} M) were irradiated at $\lambda = 370$ nm, and the emission due to excited TPP^+ was monitored from 400 to 600 nm. The absorbance of the solutions at the excitation wavelength was adjusted at ~0.1.

DFT Calculations. Hybrid DFT calculations were carried out with the Gaussian 98 series of programs.[41] Search of the global minima and geometry optimizations in the gas phase were carried out at the B3LYP/6-31G(d) level of theory. The effect of methylene chloride as solvent was evaluated by single point calculations on the optimized gas-phase molecular geometries at the same level of theory by using the integral equation formalism of polarized continuum model (IEFPCM) of Tomasi[19] as implemented in Gaussian 98.

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Supporting Information Available: Time-resolved absorption spectra recorded after 355 nm LFP of CH_2Cl_2 solutions containing $TPPBF_4$ and substrates **5**, **8**, **9**, or **11**. Fluorescence lifetime measurement of excited TPP^+ in CH_2Cl_2. Plots of the fluorescence intensity against quencher concentration for the reactions between excited TPP^+ and quenchers **1**, **6**, or **10**. DFT-optimized geometries and energies, in the gas phase and in CH_2Cl_2 solution, of the cations **1ct**, **4ct**−**8ct** and the corresponding neutral H-adducts, **1ct-H**, **4ct-H**−**8ct-H**. This material is available free of charge via the Internet at http://pubs.acs.org.

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