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Photochemical Co-Oxidation of Sulfides and Phosphines with Tris(*p*-bromophenyl)amine. A Mechanistic Study

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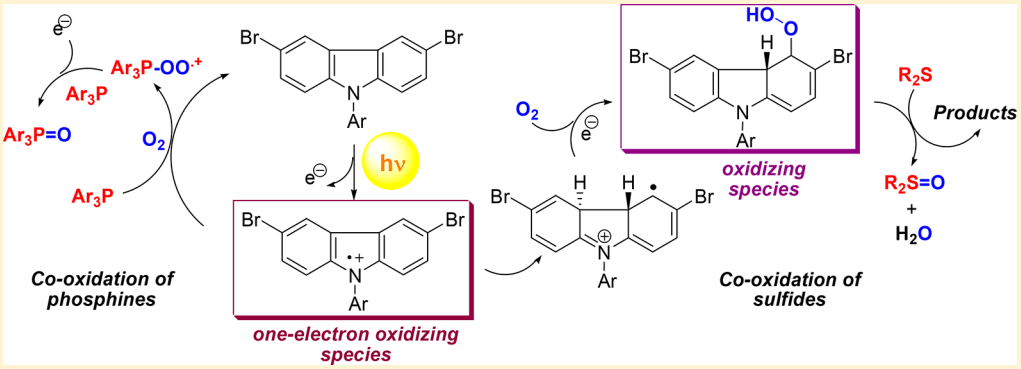
Supporting Information



ABSTRACT: The photochemistry of tris(*p*-bromophenyl)amine was investigated in a nitrogen- and oxygen-flushed solution under laser flash photolysis conditions. The detected intermediates were the corresponding amine radical cation ("Magic Blue") and the *N*-phenyl-4a,4b-dihydrocarbazole radical cation that, under an oxygen atmosphere, is converted to the corresponding hydroperoxyl radical. The role of the last species was supported by the smooth co-oxidation of sulfides to sulfoxides. On the other hand, co-oxidation of nucleophilic triarylphosphines to triarylphosphine oxides arose from an electron transfer between the photogenerated "Magic Blue" and phosphine that prevented the amine cyclization. In this case, intermediate $Ar_3POO^{\bullet+}$ was found to play a key role in phosphine oxide formation.

INTRODUCTION

Single-electron-transfer processes [SETs (Scheme 1a)] play a key role in fields ranging from synthetic chemistry[1] to material chemistry.[2] However, because the key intermediate contains an unpaired electron, it is much more reactive than the starting compound, and therefore multielectron processes, interference with oxygen, and chain reactions often followed spontaneously SET.

In the case of SET-based oxidation processes, organic oxidants, such as the popular "Magic Blue",[3] are often preferred over metal ions for mechanistic investigations because these reagents allow better control of the kinetics of the reaction. In this context, the case of tris(4-bromophenyl)amine [**1** (Chart 1)], the precursor of Magic Blue would be of high interest, because in the past, structurally related but less oxidizing reagents such as di- and triaryl amines were reported to undergo smooth cyclization to the corresponding carbazoles upon irradiation. The reactions of such compounds in the presence of nucleophiles under photochemical conditions have also been investigated in detail,[3] and the competition between different processes may be more informative. Furthermore, the photoinduced electrocyclization of stable triarylamine radical cations has been thoroughly described by Fox and co-workers.[4]

Scheme 1. (a) Single-Electron-Transfer (SET) Processes and (b) SET Occurring on Triarylamines and Following the Observed Pathways

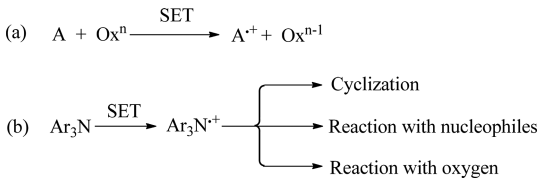
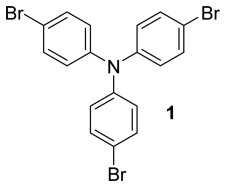


Chart 1. Structure of Tris(4-bromophenyl)amine



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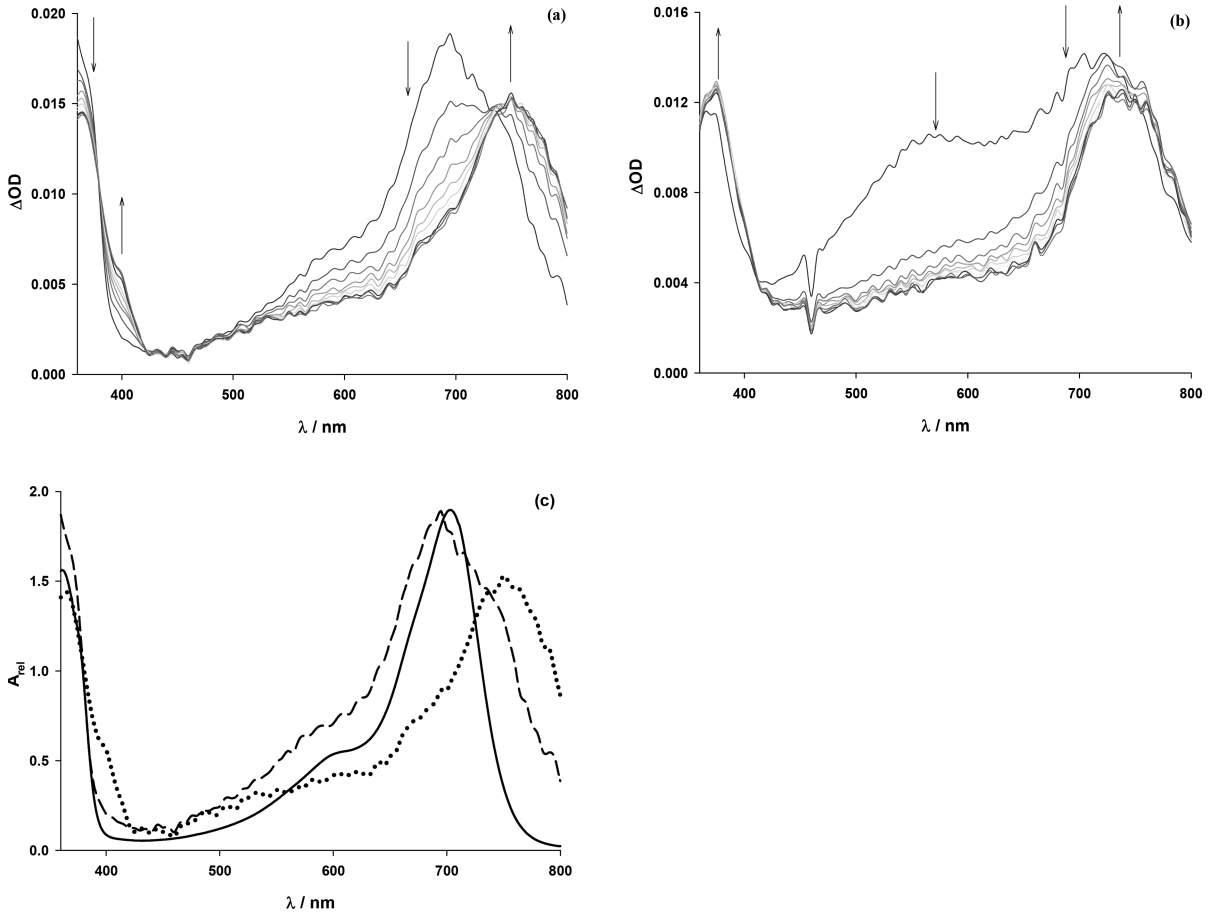

Figure 1. Time-resolved absorption spectra of transients of tris(*p*-bromophenyl)amine (**1**, 0.3 mM) recorded 200 μs after the laser pulse (355 nm) in MeCN under (a) nitrogen and (b) oxygen atmospheres. (c) Absorption spectra of commercial Magic Blue (—), photogenerated $\mathbf{1}^{\bullet+}$ recorded 10 μs after the pulse (– – –), and transient **2** recorded 90 μs after the pulse (···).

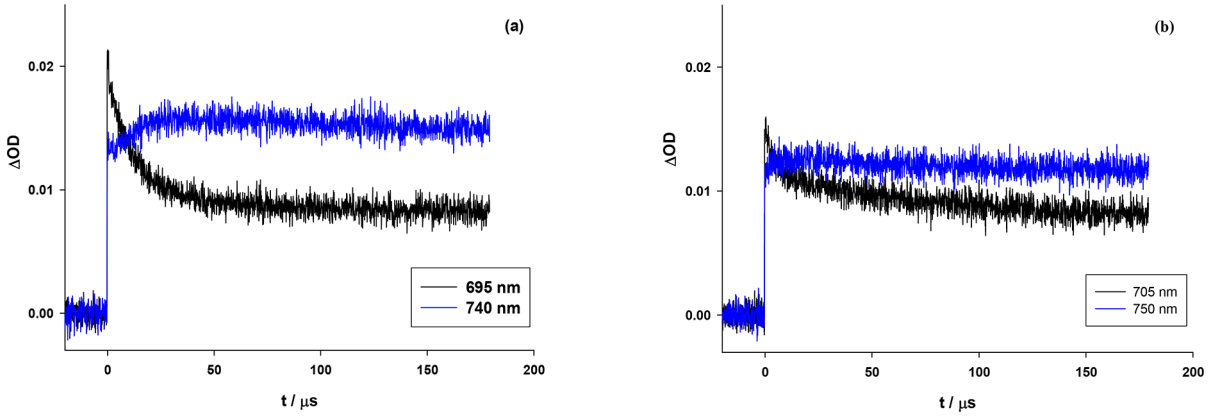

Figure 2. Decay traces of transients from tris(*p*-bromophenyl)amine (0.3 mM) recorded after the laser pulse (355 nm) in MeCN under (a) nitrogen and (b) oxygen atmospheres.

For this purpose, we thought that examining in detail the photochemical behavior of the Magic Blue precursor, viz., tris(*p*-bromophenyl)amine (**1**), in the presence of nucleophilic additives such as sulfides and triarylphosphines, oxygen, and solvents of different nature would be worthwhile.

RESULTS

Time-Resolved Spectroscopic Measurements of Tris(*p*-bromophenyl)amine (1) in Solution. To obtain mechanistic information about the photochemistry of amine **1** in MeCN at room temperature, laser flash photolysis studies were performed. Under a nitrogen atmosphere, the initial formation of a transient with three bands centered at 370, 590, and 695 nm was evidenced (see Figure 1). This absorption pattern was identical to that of Magic Blue ($\mathbf{1}^{\bullet+}$)[5] and evolved in 38 μs into a further transient (λ_{max} = 750 nm; τ > 200 μs) that has been assigned, on the basis of previous studies, to dihydrocarbazole **2** (Figure 1).[4a,6] A comparison between the absorption spectra of transients $\mathbf{1}^{\bullet+}$, **2**, and commercial Magic Blue (Figure 2) pointed out that $\mathbf{1}^{\bullet+}$ is formed after the laser pulse. In Figure 2a, the decay of the intermediate

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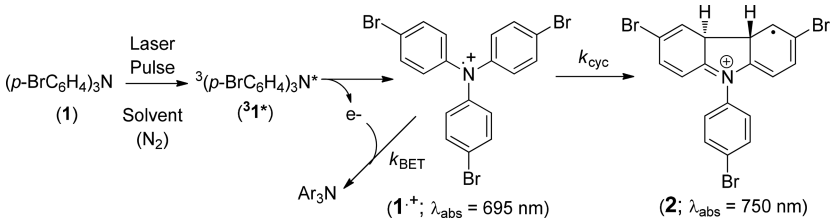
Scheme 2. Formation of Transients $1^{\bullet+}$ and 2 in Nitrogen-Equilibrated Media



and its corresponding conversion to **2** are clearly shown, and Scheme 2 depicts the observed stepwise process.

On the other hand, in an oxygen-equilibrated solution, the end-of-pulse spectrum showed an additional feature at 550 nm, then evolving to give the same end spectrum as under nitrogen, where the absorption spectra of transients $\mathbf{1}^{\bullet+}$ and **2** were detected (Figure 1b). Figure 2b shows the decay trace of $\mathbf{1}^{\bullet+}$ and the formation trace of transient **2** recorded after the laser pulse under an oxygen atmosphere. The quantum yield values for formation of the two intermediates along with their lifetime were measured under both atmospheres, by using benzophenone in benzene as a reference (Table 1).

Table 1. Measured Quantum Yields (Φ) for the Formation of Intermediates $1^{\bullet+}$ and 2 under the Examined Conditions[a]

transient	λ_{abs} (nm)	atmosphere	concentration (M)	ϕ	τ (μs)
$\mathbf{1}^{\bullet+}$	695	N_2	1.24×10^{-6}	0.158	39
		O_2	8.29×10^{-7}	0.077	
5	750	N_2	3.53×10^{-7}	0.066	>200
		O_2	2.17×10^{-7}	0.030	

[a]Measured in MeCN after the laser pulse (355 nm); $\varepsilon(\mathbf{1}^{\bullet+})$ = 19000 M^{-1} s^{-1}, and $\varepsilon(\mathbf{2})$ = 30000 M^{-1} s^{-1}. The initial absorbance of **1** was fixed at 0.40. Actinometer: solution of benzophenone in benzene under a N_2 atmosphere [A(355 nm) = 0.37]; ε(ketyl radical) = 7220 M^{-1} cm^{-1}.

The fleeting band located at 550 nm in the time-resolved absorption spectrum of tris(*p*-bromophenyl)amine **1** (see Figure 1b) was assigned to the charge-separated complex between **1** and molecular oxygen that is an energetically favorable process in polar solvents as it was proposed by Wilkinson[7] and in a recently reported study.[8] Scheme 3 shows the formation of the charge-transfer complex that is converted to the tris(*p*-bromophenyl)-amine radical cation ($\mathbf{1}^{\bullet+}$) and superoxide ion, and Figure 3 depicts the decay trace of the charge-transfer complex in MeCN under an O_2 atmosphere.

The charge-transfer complex trace shown in Figure 3 fitted with a biexponential decay and two half-lifetime decays were

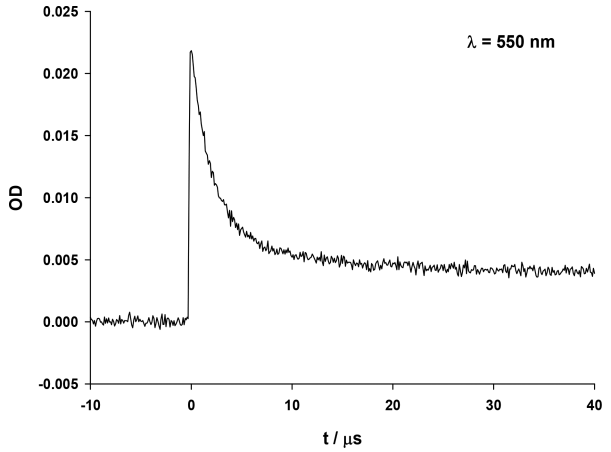
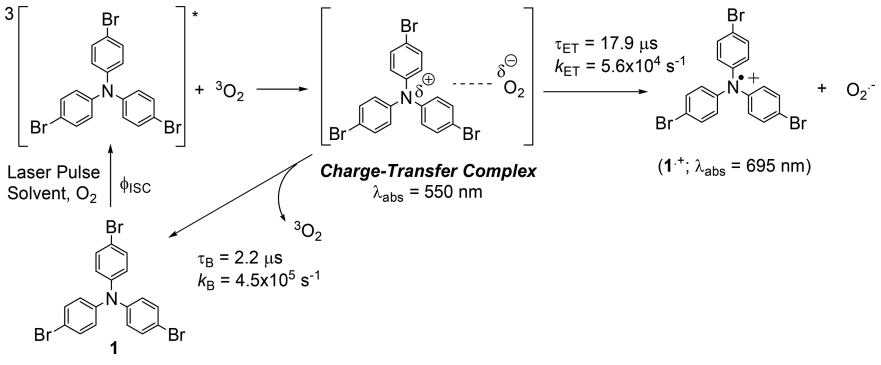


Figure 3. Decay trace of the charge-transfer complex recorded at 550 nm after excitation with a laser pulse (355 nm) of a solution of tris(*p*-bromophenyl)amine (0.3 mM) in MeCN under an oxygen atmosphere.

obtained, viz., 2.2 and 17.9 μs, respectively. The evolution of the charge-transfer complex involved the reversion pathway to tris(*p*-bromophenyl)amine (**1**) and molecular oxygen with a rate constant k_B of 4.5×10^5 s^{-1} and an electron-transfer pathway with a rate constant k_{ET} of 5.6×10^4 s^{-1} to provide tris(*p*-bromophenyl)-amine radical cation ($\mathbf{1}^{\bullet+}$) and superoxide ion (see Scheme 3).

It is noteworthy that under an O_2 atmosphere the quantum yield values for the formation of $\mathbf{1}^{\bullet+}$ and **2** were halved, highlighting the interaction between molecular oxygen and **1** in its triplet excited state to produce singlet oxygen. Therefore, this competitive pathway diminishes the level of formation of both of the ensuing intermediates, $\mathbf{1}^{\bullet+}$ and **2**. A similar oxygen effect was observed during the irradiation of triphenylamine in different solvents and was attributed to the quenching of the triplet excited state of triphenylamine by molecular oxygen producing singlet oxygen with a ϕ_Δ of 0.63.[6] In this case, the corresponding intermediate dihydrocarbazole, which is equivalent to intermediate **2**, is formed to a lesser extent under an oxygen atmosphere than under a nitrogen atmosphere.

Scheme 3. Formation of a Charge-Transfer Complex and Transient $1^{\bullet+}$ in Oxygen-Equilibrated Media



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In addition, the decay traces of transient $\mathbf{1}^{\bullet+}$ at 695 nm were also measured in MeCN after a laser pulse (355 nm) under different conditions (Figure 4) with the aim of determining both

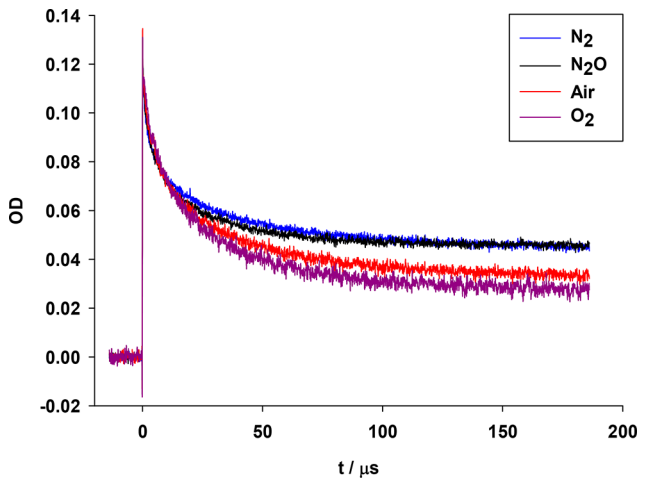

Figure 4. Normalized decay traces of transients from tris(*p*-bromophenyl)amine (**1**, 0.3 mM) recorded after the laser pulse (355 nm) in MeCN under N_2 (blue), N_2O (black), Air (red), and O_2 (violet) atmospheres.

the rate constants of cyclization (k_{cyc}) and back-electron transfer [k_{BET} (see Scheme 2)]. The obtained results are listed in Table 2.

Table 2. Rate Constants, Lifetimes, and Concentrations of Tris(*p*-bromophenyl)amine Radical Cation ($\mathbf{1}^{\bullet+}$) at the End of the Pulse[a]

atmosphere	τ_{cyc} (μs)	k_{cyc} (s^{-1})	τ_{BET} (μs)	k_{BET} (M^{-1} s^{-1})	concentration (M)
N_2	40.0	2.5×10^4	3.7	2.2×10^{10}	5.93×10^{-6}
N_2O	40.0	2.5×10^4	3.7	2.1×10^{10}	5.93×10^{-6}
air	39.2	2.6×10^4	5.4	1.9×10^{10}	4.39×10^{-6}
O_2	37.0	2.7×10^4	6.4	1.4×10^{10}	3.29×10^{-6}

[a]Measured in MeCN after the laser pulse (266 nm); $\varepsilon(\mathbf{1}^{\bullet+})$ = 19000 M^{-1} s^{-1}. The initial absorbance of the solutions was fixed at 0.64. The error in τ_1 is ±0.2 and in τ_2 is ±0.1.

It is noteworthy that the traces of $\mathbf{1}^{\bullet+}$ show a nicely biexponential decay fitting with r^2 values of >0.998 independent of the atmosphere used. As shown in Table 2, τ_{cyc} and k_{cyc} remain almost constant for all the atmospheres used and also in an air-equilibrated solution while a noticeable dependence on the atmosphere was seen for the back-electron-transfer process (τ_{BET} and k_{BET}), particularly in the cases of air-equilibrated and oxygen atmospheres. Likewise, a similar behavior was observed for the concentration of $\mathbf{1}^{\bullet+}$ at zero time after the laser pulse, which was attributed to the quenching of the triplet excited state of **1** by molecular oxygen.

Because of the biexponential decay fitting of $\mathbf{1}^{\bullet+}$, the consumption of transient $\mathbf{1}^{\bullet+}$ can be written as eq 1 highlighting the unimolecular electrocyclization step and the bimolecular back-electron-transfer process, where the one ejected electron after the laser pulse is the solvated electron and is designated e^-.

$$\frac{d[\mathbf{1}^{\bullet+}]}{dt} = k_{cyc}[\mathbf{1}^{\bullet+}] + k_{BET}[\mathbf{1}^{\bullet+}][e^-] \quad (1)$$

The conversion of $\mathbf{1}^{\bullet+}$ to **2** (see Scheme 2) involves a first-order decay, and the k_{cyc} can be calculated in a straightforward manner from the reciprocal of the half-lifetime (τ_{cyc}^{-1}) under all the conditions examined, and the data thus obtained are listed in Table 2. On the other hand, back electron transfer (BET) of $\mathbf{1}^{\bullet+}$ to tris(*p*-bromophenyl)amine (see Scheme 2 and eq 1) can be represented by k_{BET}. From the slopes of the linear regression of the reciprocal of the concentration of transient $\mathbf{1}^{\bullet+}$ versus time plots, bimolecular rate constants, k_{BET}, of 10^{10} M^{-1} s^{-1} were obtained under all the conditions examined (see Table 2).

Co-Oxidation of Sulfides and Phosphines. The oxidation activity of the photogenerated intermediates, namely, $\mathbf{1}^{\bullet+}$ and **2**, was tested by irradiating solutions of **1** in the presence of some substrates acting as electron donors such as sulfides and phosphines (see Scheme 4). Under such conditions, **1** was consumed while the additives were co-oxidized selectively to the corresponding sulfoxides and phosphine oxides. In the case of benzyl ethyl sulfide, however, significant amounts of benzaldehyde were also formed. The results are summarized in Tables 3 and 4.

Sulfides (including Ph_2S that is inert toward singlet oxygen[9]) were co-oxidized with a rate ranging from 0.003 and 0.244 μmol min^{-1}, while the sulfoxidation/electrocyclic cyclization ratio was lower than unity (0.06−0.80) in all of the solvents investigated, the only exception being benzyl ethyl sulfide in a 9/1 MeCN/H_2O mixture. Nucleophilic triarylphosphines were also co-oxidized with a phosphine oxidation/electrocyclic cyclization ratio ranging from ~26/1 to 5/1 under irradiation of amine **1** in acetonitrile.

Blank experiments were also performed. Thus, irradiation of oxygenated solutions of sulfides and phosphines in all the solvents used in the absence of tris(*p*-bromophenyl)amine (**1**) did not provide any sulfoxides or phosphine oxides. Likewise, experiments performed under a N_2 atmosphere but in the presence of tris(*p*-bromophenyl)amine (**1**) did not give any oxide.

Scheme 4. Co-Oxidation of Sulfides (top path) and Triarylphosphines (bottom path) in the Presence of 1

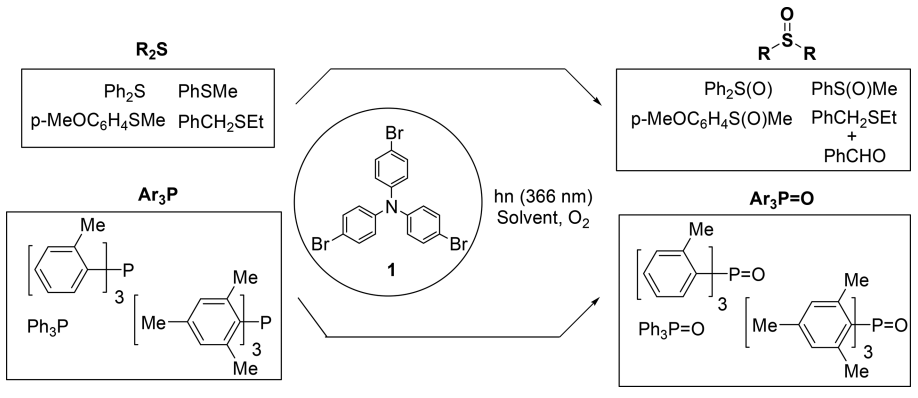

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Table 3. Rate of Co-Oxidation of Sulfides upon Irradiation in the Presence of 1[a]

substrate	solvent	rate of reaction (μmol min^{-1})		
		sulfoxide	1[b]	other products
Ph_2S	MeCN	0.003	0.051	
	9/1 MeCN/H_2O	0.005	0.041	
	TFE	0.033	0.049	
	DCM	0.008	0.026	
PhSMe	MeCN	0.024	0.20	
	9/1 MeCN/H_2O	0.091	0.31	
	TFE	0.193	0.24	
	DCM	0.012	0.05	
p-$MeOC_6H_4SMe$	MeCN	0.026	0.085	
	9/1 MeCN/H_2O	0.118	0.239	
	TFE	0.240	0.234	
	DCM	0.005	0.030	
$PhCH_2SEt$	MeCN	0.088	0.065	PhCHO, 0.010
	9/1 MeCN/H_2O	0.184	0.150	PhCHO, 0.024
	TFE	0.244	0.320	PhCHO, 0.030
	DCM	0.093	0.024	PhCHO, 0.013

[a]A 5×10^{-3} M solution of **1** irradiated in the presence of the chosen sulfide (10^{-2} M) at 310 nm (10 × 15 W lamps). [b]Rate of consumption of **1**.

Table 4. Rate of Co-Oxidation of Triarylphosphines upon Irradiation in the Presence of 1 in MeCN[a]

substrate	rate of co-oxidation (μmol min^{-1})	
	phosphine oxide	1[b]
Ph_3P	2.91	0.11
$(o\text{-}MeC_6H_4)_3P$	2.75	0.31
$(2,4,6\text{-}Me_3C_6H_2)_3P$	4.13	0.91

[a]A 5×10^{-3} M solution of **1** irradiated in the presence of the chosen phosphine (1.1×10^{-2} M) at 366 nm (high-pressure Hg lamp provided with a 366 nm interference Schott filter). [b]Rate of consumption of **1**.

Interaction of Sulfides and Triphenylphosphine with Photogenerated Transients. Time-resolved spectroscopy was applied to solutions of **1** in the presence of selected sulfides and triphenylphosphine. Diphenyl sulfide, thioanisole, and benzyl ethyl sulfide caused no change in the previously observed transients. On the other hand, *p*-methoxythioanisole and triphenylphosphine quenched radical cation $\mathbf{1}^{\bullet+}$ as shown in Figure 5.

In the case of *p*-methoxythioanisole and triphenylphosphine, the observed first-order decay constant (k_{obs}) of $\mathbf{1}^{\bullet+}$ depends linearly on the quencher concentration as shown in eq 2.

$$k_{obs} = k_{cyc} + k_Q[Q] \quad (2)$$

Plotting k_{obs} versus quencher concentration [Q] resulted in a linear correlation (see Figure 5). The corresponding bimolecular rate constants were obtained from the slope of the linear regressions, viz., $k_{pMeO} = 9.7 \times 10^5$ M^{-1} s^{-1} for *p*-methoxythioanisole and $k_{Ph_3P} = 2.1 \times 10^6$ M^{-1} s^{-1} for triphenylphosphine.

DISCUSSION

Analysis of the Intermediates Formed during Irradiation of Tris(*p*-bromophenyl)amine (1). The data presented above show that excitation of **1** with a laser pulse (355 nm) generates two key intermediates in both N_2- and O_2-saturated solutions. However, one of these species reacts efficiently with molecular oxygen, as shown in Scheme 5. Photoionization of **1** forms radical cation $\mathbf{1}^{\bullet+}$ (path a). Under a nitrogen atmosphere, electrocyclization to radical cation **2** occurs [$k_{cyc} = 2.5 \times 10^4$ s^{-1} in acetonitrile (path b)] in competition with electron recombination [$k_{BET} = 2.2 \times 10^{10}$ M^{-1} s^{-1} in acetonitrile (path b′)]. Via an ensuing an electron-transfer pathway (path c) intermediate, **2** reverts to amine **1** in competition with formation of products (path d). Irradiation of di(tri)arylamines can be counted among the many mild conversions into carbazoles.[6,10,11] Indeed, the photochemical preparation of carbazoles under visible light in the presence of a copper-based sensitizer has been reported,[7] and formation of the triarylamine radical cation followed by cyclization to the dihydrocarbazole intermediate that in turn provides a substituted carbazole was also proposed.[11f] However, when amine **1** was irradiated under visible light photoredox catalysis conditions, no tribromocarbazole was observed, and only *N*-phenylcarbazole was obtained in a low yield (>16%).[11f]

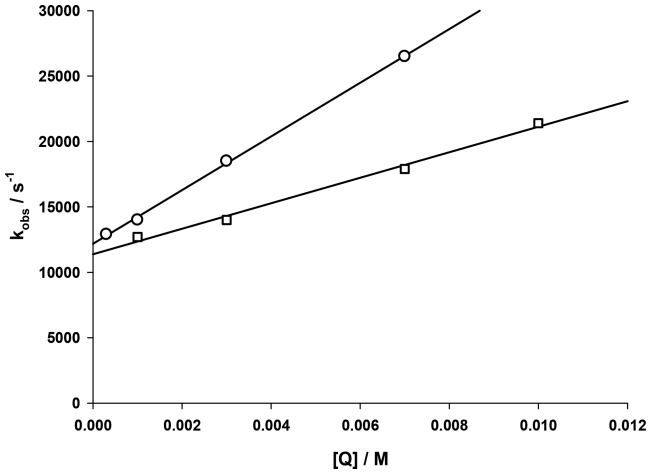

Figure 5. Quenching of $\mathbf{1}^{\bullet+}$ with increasing concentrations of *p*-methoxythioanisole (□) and triphenylphosphine (○). Straight lines are the best linear regression fits.

On the other hand, under aerobic conditions, amine **1** in its triplet excited state sensitizes singlet oxygen, thus halving the formation of intermediates $\mathbf{1}^{\bullet+}$ and, as a consequence, **2**, as can be judged from the quantum yields obtained under an oxygen atmosphere (see Table 1 and compare these values with those obtained under a nitrogen atmosphere). Photoionization of triplet amine (**1**) formed $\mathbf{1}^{\bullet+}$, and the ejected electron was trapped, at least in part, by molecular oxygen giving superoxide ion with a bimolecular rate constant of 2×10^{10} M^{-1} s^{-1}.[12] Additionally, a back-electron-transfer process (path b′ in Scheme 5) can occur between $\mathbf{1}^{\bullet+}$ and the ejected electron with a bimolecular rate constant (k_{BET}) of 1.4×10^{10} M^{-1} s^{-1}. Cyclization (path b) afforded **2** that reacted with molecular oxygen and provided 4-peroxyl radical (**I**) (path e). Ensuing intramolecular hydrogen atom transfer led to intermediate **II** (path f), and both intermediates are, at least in part, potential oxidizing agents that are formed during irradiation of amine **1** under an oxygen atmosphere. Superoxide ion then further reacted with adventitious water present in the organic media and led to ROS species, including OH$^{\bullet}$, HOO$^{\bullet}$, and H_2O_2.

Under air-equilibrated conditions, a similar photochemical behavior was observed for **1** in MeCN, where both $\mathbf{1}^{\bullet+}$ and **2** were detected. Transient $\mathbf{1}^{\bullet+}$ decays competitively by two pathways, back-electron transfer to amine **1** (path b′ in Scheme 4; $k_{BET} = 1.9 \times 10^{10}$ M^{-1} s^{-1}) and electrocyclization to **2** (path b in Scheme 4; $k_{cyc} = 2.6 \times 10^4$ s^{-1}).

Nitrous oxide is a good quencher of solvated electron and has often been used under pulse radiolysis and laser flash photolysis.[13]

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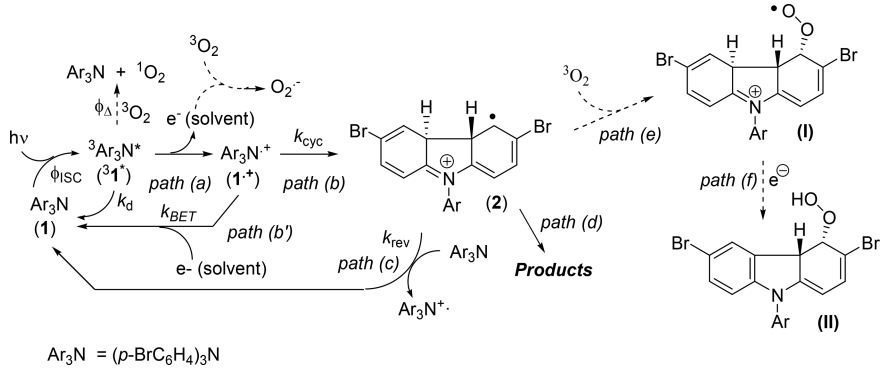
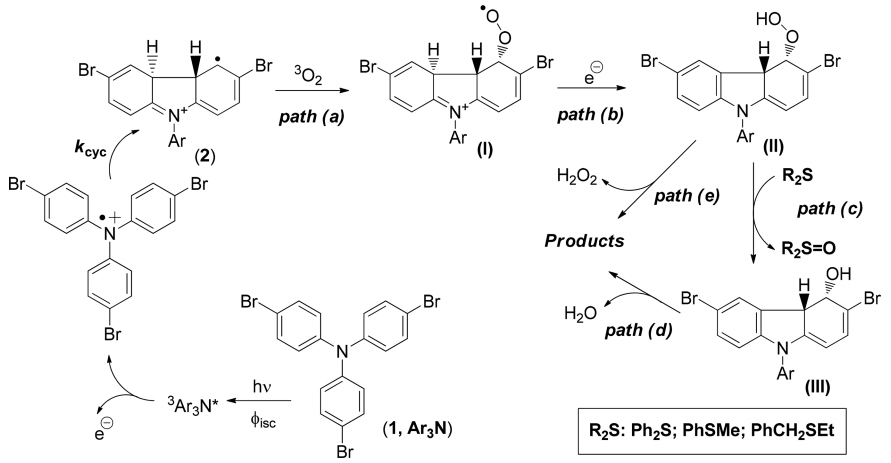
Scheme 5. Proposed Reaction Mechanism of the Photocyclization of 1 (filled arrows, nitrogen atmosphere; dashed arrows, oxygen atmosphere)



Scheme 6. Proposed Mechanism for the Co-Oxidation of Sulfides during the Photocyclization of 1



However, bubbling N_2O into a solution of **1** in MeCN had no effect on the transient intermediates, the competitive rate constants k_{cyc} and k_{BET} exhibiting the same values under N_2O and N_2 atmospheres (see Table 3). This is due to the fact that chemical reaction occurs at the geminate pair level ($\mathbf{1}^{\bullet+}\cdots e^-$) and no solvated electron (e^-_{solv}) is formed. Furthermore, comparison of the rate constant for the reaction of N_2O with the electron ($9 \times 10^9\ M^{-1}\ s^{-1}$)[13e] and the BET reaction of $\mathbf{1}^{\bullet+}$ ($2.1 \times 10^{10}\ M^{-1}\ s^{-1}$) accounts for the observed spectroscopic behavior.

With regard to oxygen trapping by **2**, it was surmised that some intermediates generated during the irradiation may similarly oxidize other compounds under mild conditions.

Photo-Co-Oxidation of Sulfides (Ph_2S, PhSMe, and $PhCH_2SEt$) in the Tris(*p*-bromophenyl)amine/O_2 System. In steady-state experiments in which amine **1** was irradiated in the presence of a range of sulfides, the latter are co-oxidized to sulfoxides at a rate dependent on their structure and the solvent used (rate values ranging from 0.003 to 0.244 μmol s^{-1}) while amine **1** is consumed efficiently. In addition, the rate ratio of sulfoxide versus consumption of **1** was <1 (see Table 3), a fact that we attributed to the intermediacy of one (or more) common intermediate that is responsible for both cyclization and co-oxidation of sulfides. It was pointed out that oxidant species such as singlet oxygen and superoxide ion are formed during the irradiation of amine **1** under an oxygen atmosphere (see Scheme 6). However, we can state that the co-oxidation reaction is not a result of a singlet oxygen reaction as shown by the following evidence: (1) Sulfones are known to always accompany the sulfoxides in the singlet oxygen oxidation of sulfides (not observed in that case). (2) Benzyl sulfides undergo both sulfoxidation and oxidative cleavage to benzaldehyde in protic media,[14] and oxidation also takes place on diphenyl sulfides, which are usually nonreactive toward singlet oxygen. With regard to superoxide ion, under these conditions it is not involved in the co-oxidation of sulfides but reduces the radical cation $\mathbf{1}^{\bullet+}$ to **1** through a back-electron-transfer process. Therefore, according to our results and to the literature data, we assigned to hydroperoxide intermediate **II** the role of the oxidant species that can transfer an oxygen atom to the sulfides to afford the corresponding sulfoxides and a new intermediate **III**. The latter underwent dehydration to furnish products (see Scheme 6). Intermediate **II** also underwent aromatization by losing hydrogen peroxide, a process that has been previously observed to occur at room temperature with a rather slow radical chain mechanism.[15] It is worth mentioning that dihydrocarbazole aromatization (path e) and donor oxidation (path c) were coupled, and the result depended on the nature of the sulfide. Thus, diphenyl sulfide was co-oxidized with an efficiency lower than that of thioanisole or benzyl ethyl sulfide as can be observed in Table 3.

Photo-Co-Oxidation of *p*-Methoxythioanisole in the Tris(*p*-bromophenyl)amine/O_2 System. The photo-co-oxidation of *p*-methoxythioanisole with tris(*p*-bromophenyl)-amine in the presence of O_2 deserves some comment and additional analysis. *p*-Methoxythioanisole sulfoxide could arise from two alternative sequences of pathways: (1) an electron-transfer process followed by oxidation with molecular oxygen involving

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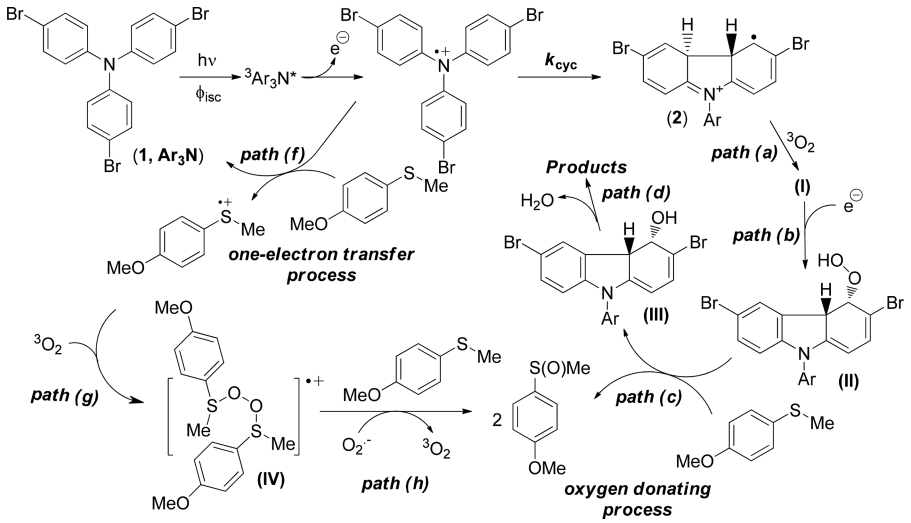
Scheme 7. Proposed Mechanism for the Co-Oxidation of *p*-Methoxythioanisole during the Photocyclization of 1



the sequence from path f to path h (see Scheme 7) and (2) oxygen donation from intermediate **II** to *p*-methoxythioanisole (path c in Scheme 7).

The electron-transfer process (path f in Scheme 7) occurs efficiently because tris(*p*-bromophenyl)amine radical cation ($\mathbf{1}^{\bullet+}$) has an oxidation potential of 1.16 V versus SCE[16] and can thus oxidize *p*-methoxythioanisole (E_{ox} = 1.13 V vs SCE),[17] providing the corresponding radical cation (see Scheme 7). Also, this process is a thermodynamically feasible process by −0.03 V. On the other hand, laser flash spectroscopy showed that *p*-methoxythioanisole quenches $\mathbf{1}^{\bullet+}$ with a bimolecular rate constants k_{pMeO} of 9.7×10^5 M^{-1} s^{-1} (see Figure 4), giving the *p*-methoxythioanisole radical cation. Once the *p*-methoxythioanisole radical cation was formed, reaction with molecular oxygen in the presence of a further molecule of sulfide gave electrophilic radical cation intermediate **IV** (path g). Then, this last intermediate reacted with the sulfide and superoxide ion to give finally two molecules of the sulfoxides (path h) completing the sequence from path f to path h.

On the other hand, we pointed out above that in the photoreaction of tris(*p*-bromophenyl)amine under an O_2 atmosphere, superoxide ion was also formed (see Scheme 5). A possible reaction between superoxide ion and sulfide radical cation could provide a thiodioxirane, an electrophilic intermediate, as proposed by Baciocchi.[18] However, we have earlier demonstrated[19] that dialkyl and diaryl sulfide radical cations react efficiently with molecular oxygen to give a loose dipolar complex ($R_2S{-}O{-}O^{\bullet+}$) that further reacts with another molecule of sulfide and gives a strongly bound electrophilic intermediate ($R_2S{-}O{-}O{-}SR_2^{\bullet+}$) rather than a thiadioxirane intermediate. The strongly bound electrophilic intermediate was assigned to intermediate **IV**, which is shown in Scheme 7. Then, we can conclude that $O_2^{\bullet-}$ has a role but does not add to the sulfide radical cation. A reasonable alternative is that superoxide ion operates as an electron carrier in the reduction of intermediate IV (ArMeS−O−O−$SArMe^{\bullet+}$) as shown in path h (Scheme 7).

It is worth mentioning that the oxygen-donating sequence pathways illustrated from path a to path d in Scheme 7 providing *p*-methoxythioanisole sulfoxide cannot be ruled out. In fact, the cyclization process of tris(*p*-bromophenyl)amine radical cation ($\mathbf{1}^{\bullet+}$) competes to a lesser extent with the one-electron-transfer process between $\mathbf{1}^{\bullet+}$ and *p*-methoxythioanisole (path f in Scheme 7). Via comparison of the rate constant values of both competitive processes ($k_{cyc} = 2.5 \times 10^4$ s^{-1}, and $k_{pMeO} = 9.7 \times 10^5$ M^{-1} s^{-1}), it is clear that the main reaction pathway in the formation of *p*-methoxythioanisole sulfoxide is the one-electron-transfer oxidation process (path f) over the cyclization process of the tris(*p*-bromophenyl)amine radical cation ($\mathbf{1}^{\bullet+}$).

Photo-Co-Oxidation of Phosphines. Phosphines were stronger oxygen acceptors and, as demonstrated in Table 4 were co-oxidized efficiently upon irradiation of amine **1** in the presence of molecular oxygen with a rate ranging from 2.75 to 4.13 μmol s^{-1}, while **1** is consumed smoothly. In addition, the rate ratio of phosphine oxidation versus consumption of **1** increases from ∼5/1 to 26/1, indicating that at least two common oxidant intermediates are responsible for the co-oxidation of phosphines that inhibit significantly the consumption of amine **1**. On the basis of steady-state and laser flash photolysis measurements, the proposed reaction mechanism is shown in Scheme 8.

As one can see in Scheme 8, irradiation of **1** gave amine radical cation $\mathbf{1}^{\bullet+}$ and superoxide ion. Two competitive pathways exist: (1) electrocyclization to provide intermediate **2** and (2) one-electron oxidation of triarylphosphine to furnish the corresponding radical cation. The first path exhibits a rate constant of 2.5×10^4 s^{-1}, while the second pathway (path f in Scheme 8) exhibits a rate constant of 2.1×10^6 M^{-1} s^{-1}. Following the electrocyclization pathway, intermediate **2** reacted with molecular oxygen to form **I** and, after intramolecular hydrogen abstraction, **II**. Both species are potential oxygen-donating species that are able to transfer oxygen to the phosphines. It appears to be reasonable that phosphines, which are strong nucleophiles, were able to trap intermediate **I** efficiently in competition with intramolecular hydrogen abstraction (path b vs path d). Indeed, the reactivity of peroxy radicals with phosphines has been previously demonstrated.[21] Thus, **I** oxidized the phosphine to the corresponding phosphine oxides (path b), P−O bond formation being the driving force for the process. Finally, intermediate **III** transferred a second oxygen atom to phosphines (path c), and radical cation **2** was formed. Thus, two oxygen atoms were sequentially transferred to the phosphine and led back to **2** completing the oxidation cycle. This reaction pathway was previously proposed when triphenylamine was used instead of tris(*p*-bromophenyl)amine.[6] The oxidation of phosphines inhibits the conversion of intermediate **II** to products, in agreement with the experimental evidence

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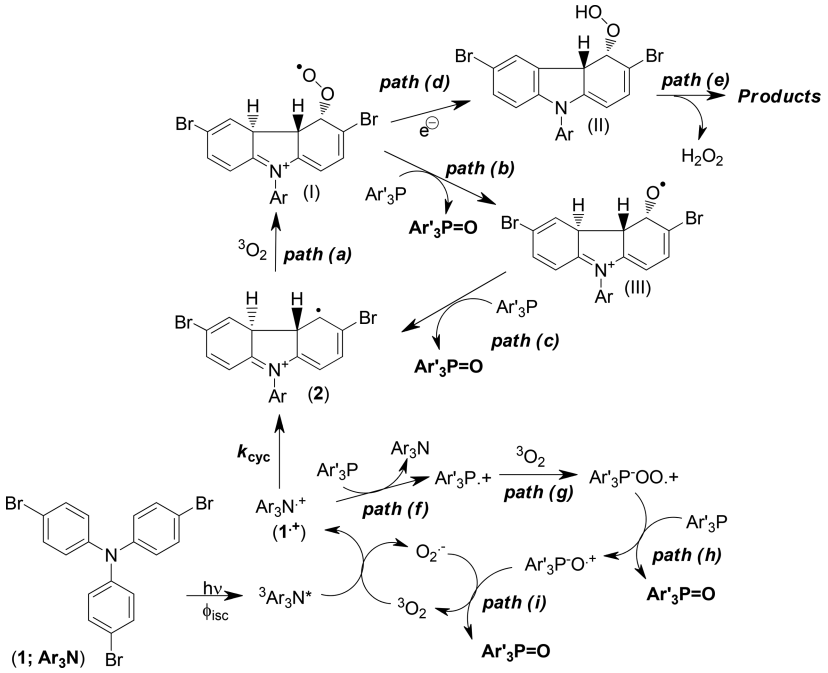
Scheme 8. Proposed Mechanism for the Co-Oxidation of Triarylphosphines during the Photocyclization of 1



indicating that path b is an efficient process that competes with path d.

On the other hand, an alternative oxidation pathway of phosphine may involve the direct one-electron transfer between $\mathbf{1}^{\bullet+}$ and Ar_3P (path f in Scheme 8) to give triarylphosphine radical cation ($Ar_3P^{\bullet+}$) as it was clearly confirmed by laser flash photolysis experiments and thermodynamic calculations. In fact, triphenylphosphine quenched $\mathbf{1}^{\bullet+}$ with a bimolecular rate constant (k_{Ph_3P}) of $2.1 \times 10^6\ M^{-1}\ s^{-1}$ (see Figure 5), and the one-electron-transfer process is thermodynamically feasible ($\Delta G = -0.13$ V), because $\mathbf{1}^{\bullet+}$ has an oxidation potential of 1.16 V (vs SCE) whereas the oxidation potential of triphenylphosphine is 1.00 V (vs SCE).[20] Trapping of generated $Ar_3P^{\bullet+}$ with molecular oxygen occurred, producing peroxyl radical cation $Ar_3PO_2^{\bullet+}$ (path g), a reaction pathway that has been previously observed during pulse radiolysis and laser flash photolysis experiments.[22] Reaction of this intermediate with another molecule of Ar_3P and the ensuing mesolytic cleavage yield triarylphosphine oxide and radical cation $Ar_3PO^{\bullet+}$ (path h). Finally, the last intermediate reacted with superoxide ion, giving another molecule of Ar_3PO and molecular oxygen (path i).

An active role of singlet oxygen that is formed during the oxidative photoreaction was excluded because the reaction between $Ar_3P^{\bullet+}$ and molecular oxygen is faster than expected. In fact, comparison of the bimolecular rate constant between Ph_3P and singlet oxygen ($k_r = 1.6 \times 10^7\ M^{-1}\ s^{-1}$)[23] and the bimolecular rate constant between $Ph_3P^{\bullet+}$ and molecular oxygen ($k_2 = 1.6 \times 10^{10}\ M^{-1}\ s^{-1}$ for DCA/biphenyl, and $k_2 = 3.4 \times 10^{10}\ M^{-1}\ s^{-1}$ for NMQ^+ in MeCN)[22e] makes it clear that singlet oxygen sensitization cannot compete efficiently with path g (see Scheme 8). Furthermore, formation of intermediate $Ar_3PO_2^{\bullet+}$ was proposed for path g instead of a phosphodioxirane intermediate (Ph_3PO_2),[23] as recently demonstrated in the photosensitized electron-transfer oxidation of triphenylphosphine with DCA and NMQ^+ in different organic solvents.[22e] Therefore, we excluded the reaction of singlet oxygen with arylphosphines from the reaction mechanism as a competitive oxidative pathway.

As mentioned for the co-oxidation of sulfides, superoxide ion is not involved in the oxidation pathway and coupling of $Ph_3P^{\bullet+}$ with superoxide ion has been excluded. Therefore, the role of $O_2^{\bullet-}$ is to operate as an electron carrier in the reduction of intermediate $Ph_3PO^{\bullet+}$, as depicted in path i (see Scheme 8).

We can conclude that two competitive oxidation pathways exist, oxygen transfer from intermediates **I** and **III** to Ar_3P (paths b and c, respectively) and subsequent oxidation of triarylphosphine radical cation (paths h and i). However, intermediates **I** and **III** arise from the electrocyclization of $\mathbf{1}^{\bullet+}$ with a rate constant that is lower than the rate constant of the electron-transfer process between $\mathbf{1}^{\bullet+}$ and Ar_3P. Therefore, the last competitive pathway prevails significantly over the first oxidation pathway because inhibition of the consumption of amine **1** in the presence of Ar_3P was clearly described.

CONCLUSIONS

The photochemical co-oxidation of sulfides and phosphines examined in this paper takes place through at least two distinct reaction mechanisms, depending on the nucleophilicity of the substrates used. In any case, irradiation of tris(*p*-bromophenyl)-amine (**1**) gives the corresponding radical cation $\mathbf{1}^{\bullet+}$. The intermediate can undergo electrocyclization to **2** that in turn reacts with molecular oxygen to provide peroxyl **I** and hydroperoxyl **II** radicals, successively. These last two intermediates are potential oxidants and react with a mechanism that depends on the substrate used. Thus, sulfides are oxidized by hydroperoxyl **II**, while phosphines are oxidized by peroxyl **I** because of the strong nucleophilicity of these substrates in comparison with that of sulfides. In addition, consumption of amine **1** is observed in the presence of sulfides but in the presence of phosphines is significantly inhibited. On the other hand, for the case of *p*-methoxythioanisole and triarylphosphines, a one-electron-transfer process between $\mathbf{1}^{\bullet+}$ and these substrates operates efficiently (path f in both Schemes 7 and 8), which is supported by laser flash photolysis experiments. Then, reaction of *p*-methoxythioanisole and triarylphosphine radical cations with molecular oxygen gave

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intermediates $R_2SOO^{\bullet+}$ and $Ar_3POO^{\bullet+}$, respectively, that finally were converted into the corresponding oxides (path h in Scheme 5 for sulfides and paths h and i in Scheme 8 for phosphines). Singlet oxygen sensitization of sulfides and phosphines was excluded from the reaction mechanism as a competitive oxidation pathway because reaction of triarylphosphine radical cation with molecular oxygen is faster than singlet oxygen sensitization (compare the rate constant of singlet oxygen, $k = 1.6 \times 10^7$ M^{-1} s^{-1}, with the rate constant of $Ph_3P^{\bullet+}$ with molecular oxygen, $k = 1.6 \times 10^{10}$ M^{-1} s^{-1}) and the product distributions obtained for sulfides under our experimental conditions are not those expected for a singlet oxygen sensitization. In fact, under singlet oxygen sensitization, Ph_2S is unreactive with respect to singlet oxygen while benzyl ethyl sulfide gives benzaldehyde and the corresponding sulfoxide and sulfone.[14a,b] Furthermore, thioanisole and *p*-methoxythioanisole give the corresponding sulfoxides and sulfones as the main products under singlet oxygen sensitization.[14c] Finally, the role of superoxide ion that is formed during irradiation of **1** under an oxygen atmosphere operates as an electron carrier that is involved for sulfides in path h (see Schemes 6 and 7) and for phosphines in path i (see Scheme 8) and does not react directly with sulfides and phosphine radical cations, respectively.[19,22e] In conclusion, the photoionization of the Magic Blue precursor (amine **1**) is a versatile tool for promoting oxidation of organic substrates.

EXPERIMENTAL DETAILS

Materials. Tris(*p*-bromophenyl)amine, thioanisole, *p*-methoxythioanisole, diphenyl sulfide, triphenylphosphine, triphenylphosphine oxide, tris(2-methylphenyl)phosphine, tris(2,4,6-trimethylphenyl)-phosphine, diphenyl sulfoxide, methyl phenyl sulfoxide, *p*-methoxyphenyl methyl sulfoxide, benzaldehyde, and benzophenone were commercial products. Sulfoxides and triarylphosphine oxides used as reference compounds were prepared by reported procedures.[24] The benzyl ethyl sulfide[25] and the corresponding sulfoxide[26] were prepared by reported procedures.

Co-Oxidation Reactions. The co-oxidation experiments were performed by using 5.0×10^{-3} M **1** in the presence of 0.01 M solutions of the chosen sulfide or triarylphosphine in different solvents (2,2,2-trifluoroethanol, acetonitrile, acetonitrile/water mixture, and dichloromethane). The solutions were contained in rubber-stoppered, 1 cm diameter quartz tubes, and a stream of dry oxygen saturated with the appropriate solvent was passed into the solution through a needle for 10 min in the dark. The quartz tubes were exposed to 10 phosphor-coated 15 W lamps (Rayonet) emitting at 366 nm. The products were assessed by GC on the basis of calibration curves in the presence of cyclododecane as the internal standard.

Time-Resolved Laser Flash Spectroscopy. Nanosecond-to-microsecond transient absorption experiments were performed using a nanosecond laser flash photolysis apparatus equipped with a 20 Hz Nd:YAG laser (20 ns, 1 mJ at 355 and 266 nm) and a 150 W Xe flash lamp as the probe light. Samples were placed in a quartz cell (10 mm × 10 mm section) at a concentration adjusted to obtain an OD value of 1.0 at 355 nm. Nonlinear fitting procedures by the least-squares method and χ^2 and the distribution of residuals were used to judge the goodness of fit. Quantum yields of formation [ϕ (see Table 1)] for $\mathbf{1}^{\bullet+}$ and **2** were measured by comparison of the zero time intensity of the signal of the transients with that of the ketyl radical formed after flash excitation (355 nm) of a solution (in benzene) of benzophenone.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b00913.

Determination of the kinetic data of transient decay traces, determination of the rate data of product formation, ^{1}H NMR and ^{13}C NMR spectra of compound **1**, and ^{1}H spectra of compound **1** irradiated in MeCN (reaction mixture) (PDF)

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Notes

The authors declare no competing financial interest.

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