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Photochemistry of Tris(2,4-dibromophenyl)amine and its Application to Co-oxidation on Sulfides and Phosphines†

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ABSTRACT

The photochemistry of tris(2,4-dibromophenyl)amine was investigated *via* time-resolved nanosecond spectroscopy. The tris(2,4-dibromophenyl)amine radical cation ("Magic Green") was immediately detected after the laser pulse; this intermediate then cyclizes to *N*-aryl-4a,4b-dihydrocarbazole radical cation. The latter transient reacted with molecular oxygen to provide the corresponding hydroperoxyl radical, which smoothly co-oxidize sulfides into sulfoxides. On the other hand, the photogenerated "Magic Green" was exploited to promote the co-oxidation of nucleophilic triarylphosphines to triarylphosphine oxides through an electron transfer process preventing the amine cyclization. In this case, the intermediate $Ar_3POO^{\bullet+}$ was found to play a key role in phosphine oxide formation.

INTRODUCTION

Stable nitrogen-centered radical cations can be smoothly electrogenerated *in situ* from triarylamines bearing substituents in the *para* position (1,2), as early testified by the formation of trianisylamine radical cation, that was in turn employed as the redox catalyst in the oxidation of cyanide anions (3). Throughout the years, tris(2,4-dibromophenyl)amine radical cation (also known as Magic Green, MG, today commercially available) has been widely employed as an oxidizing reagent and tris(2,4-dibromophenyl)amine can be considered as the precursor of the corresponding radical cation.

Apart from the use in mechanistic studies (see below), some technological applications of MG have been recently developed, including, among the others, its use in measuring the overcharge protection in lithium-ion batteries (LIBs) (4). The species was also used as a co-reactant in producing an intense blue light emission of corannulene derivatives (5).

Recently, electrochemistry has emerged as sustainable approach to access chemical intermediates (including radical ions and radicals) under mild conditions and to perform reactions that it is not possible to be accomplished by other synthetic approaches (6,7).

In this context, radical cations deriving from triarylamines such as tris(4-bromophenyl)amine and tris(2,4-dibromophenyl) amine have been employed as efficient redox mediators for the *gem*-difluorodesulfurization reaction of dithioacetals (8) for the monodesulfurization of phenylthio-β-lactams (9) and S-aryl thiobenzoates (10) and as redox mediator in the efficient conversion of substituted S-phenyl thiobenzoate into phenyl benzoates (11).

On the other hand, the electrochemical generation of tris(2,4-dibromophenyl)amine radical cation was exploited in the spectroscopic detection of short-lived aromatic intermediates deriving from anthracene derivatives and *N*-methyldiphenyl- and diphenylamine by means of electron transfer stopped-flow (ETSF) methods (12). Likewise, the same authors described in details the kinetic of the electron transfer process between a series of 9-substituted anthracene and tris(2,4-dibromophenyl)amine radical cation electrogenerated *in situ* and the reactivity of the anthracene derivative radical cations against nucleophiles like water and methanol applying electron transfer stopped-flow (ETSF) methodology (13).

This method was also extended to the evaluation of the reactivity of a series of mono- and dicationic states of meta-connected oligoarylamines and characterization of the species through their absorption spectra (14).

When stabilized as the hexachloroantimonate salt (15), MG is often employed oxygenation reactions in apolar solvents. As an example, the reaction of 4,4-dimethyladamantylidene with molecular oxygen in the presence of catalytic amounts of MG (5 mol %) in dichloromethane at −78°C provided 4,4-dimethylspiro [adamantane-2,3'-[1,2]-dioxetane] as the primary photoproduct that in turn is converted at room temperature to 2-methyladamantyl-methyl ketone (16). Likewise, the monoelectronic oxidation of hindered olefins by the aminium salts have been investigated at both low and room temperature in dichloromethane and a series of dioxetanes, epoxides, ketones or allylic derivatives were formed in good to excellent yields (17).

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The cyclopropanation reaction of a series of *m*- and *p*-substituted *trans*-3-methylstyrenes with diazoacetate has been carried out with commercially available MG aminium salt. The thermal reaction provided the cyclopropyl styrenes in good yields as a mixture of *anti:syn* diastereomers (18,19). Another synthetic example involves the use of tris(2,4-dibromophenyl)aminium hexachloroantimonate in the preparation of 1-(2-pyridyl)-1,2,4-triazoles from 2-pyridyl hydrazones (20).

An alternative approach to triarylaminium radical cations is the photoionization of triarylamines, and in this case, depending on the substitution pattern of the aryl moiety, cyclization to the corresponding carbazoles has been also observed (21,22,23). In this context, direct irradiation of tris(4-bromophenyl)amine led to the formation *in situ* of the corresponding radical cation known as the Magic Blue that was described to cyclize providing carbazole derivatives (23). Further, direct irradiation of structurally related di- and triaryl amines was reported to give smoothly the corresponding carbazole derivatives through an intramolecular cyclization reaction of the radical cation (21,22,23). Surprisingly, the photochemistry of tris(2,4-dibromophenyl)amine, which is the precursor of tris(2,4-dibromophenyl)aminium radical cation, has not been reported in the literature yet. Therefore, we embarked to study systematically the photochemical behavior of tris(2,4-dibromophenyl)amine in different polar and nonpolar solvents, under nitrogen and oxygen atmospheres, and in the presence of nucleophilic additives such as aryl and alkyl sulfides and triarylphosphines. Furthermore, the direct irradiation of tris(2,4-dibromophenyl)amine in the presence of the additives under oxygen-saturated solvents led to the preparation of the corresponding sulfoxides and phosphine oxides.

MATERIALS AND METHODS

Materials. Tris(2,4-bromophenyl)amine (**1**), thioanisole, *p*-methoxythioanisole, diphenyl sulfide, triphenylphosphine, triphenylphosphine oxide, tris(2-methylphenyl)phosphine, diphenyl sulfoxide, methyl phenyl sulfoxide, *p*-methoxyphenyl methyl sulfoxide and benzaldehyde were commercially available. Sulfoxides and triarylphosphine oxides used as reference compounds were prepared by reported procedures (25,26). The benzyl ethyl sulfide and the corresponding sulfoxide were prepared by reported procedures (27,28).

Co-Oxidation reactions. The co-oxidation experiments were performed by using **1** (5.0×10^{-3} M) 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. The laser pulse photolysis apparatus consisted of a Flash lamp-pumped Q-switched SpitLight-100 Nd:YAG laser from InnoLas used at the fourth harmonic of its fundamental wavelength. The LP920-K monitor system (supplied by Edinburgh Instruments), arranged in a cross-beam configuration, consisted of a high-intensity 450 W ozone free Xe arc lamp (operating in pulsed wave), a Czerny-Turner with triple grating turret monochromator and a five-stage dynode photomultiplier. The signals were captured by means of a Tektronix TDS 3012C digital phosphor oscilloscope, and the data were processed with the L900 software supplied by Edinburgh Instruments. The solutions to be analyzed were placed in a fluorescence cuvette (d = 10 mm).

Nuclear magnetic resonance spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 300 MHz spectrometer; chemical shifts (δ) are reported in parts per million (ppm), relative to the signal of tetramethylsilane, used as an internal standard. 2D NMR spectra (heteronuclear single quantum correlation (HSQC) and heteronuclear multiple quantum correlation (HMQC) sequences) were recorded in $CDCl_3$ on 300 MHz and 500 MHz spectrometers. Coupling constant (J) values are given in hertz (Hz). The measurements were carried out using standard pulse sequences.

Ion chromatography analysis. Ion chromatography analyses have been performed by means of a Dionex GP40 instrument equipped with a conductimetric detector (Dionex 20 CD20) and an electrochemical suppressor (ASRS Ultra II, 4 mm) by using the following conditions: chromatographic column IONPAC AS23 (4 × 250 mm), guard column IONOPAC AG12 (4 × 50 mm), eluent $NaHCO_3$ 0.8 mM + Na_2CO_3 4.5 mM, flux: 1 mL min^{-1}; current imposed at detector: 50 mA.

RESULTS

Photochemistry of tris(2,4-dibromophenyl)amine in solution

The photolysis of **1** was carried out in both nitrogen- and oxygen-saturated acetonitrile; analysis of the photolyzed mixture pointed out the presence of bromocarbazole derivatives as main photoproducts, along with HBr (see Scheme 1 and Figures S1–-S10). The formation of bromocarbazoles points out that a photoinduced cyclization reaction is involved and the main photoproduct is compound **1a** when compound **1** is consumed in *ca* 50%. Furthermore, compound **1a** was detected by GC-MS in the photolyzed reaction mixture.

The course of the photoreaction of compound **1** in O_2-saturated acetonitrile solution monitored by UV-visible spectroscopy is detailed in Fig. 1, where it is apparent that cyclization reaction to provide carbazole moiety (that is responsible for the absorption bands located in the 340–360 nm region) is the main process. The consumption profiles of **1** measured in N_2- and O_2-saturated acetonitrile solutions are overlapped, indicating that there is no effect of the atmosphere chosen for carrying out the photoreaction (see Fig. 1b). Furthermore, comparing the consumption profile of **1** in O_2-saturated acetonitrile with the consumption profiles of tris(p-bromophenyl)amine and triphenylamine, respectively, measured in the same experimental conditions (Fig. 1b) led to conclude that the cyclization reaction of **1** under oxygen atmosphere is slower than that of the two other amines. This behavior can be ascribed to the quenching of the triplet excited state of compound **1** by molecular oxygen, which is the photoreactive excited state inhibiting in part the photoreaction due to singlet oxygen production (23). The population of the triplet excited state of **1** is favored because of the known heavy atom effect (HAE) of the bromine atoms attached on the phenyl moieties (29). A similar oxygen effect was observed for the photochemical reaction of tris(*p*-bromophenyl) amine and triphenylamine in different solvents. In the case of triphenylamine, the quenching of the triplet excited state by molecular oxygen produced singlet oxygen with a quantum yield (ϕ_Δ) value of 0.63, which is a competitive pathway of the electrocyclization reaction (24). Therefore, the photoreaction of triphenylamine is faster than that of tris(*p*-bromophenyl)amine and the photoreaction of this latter substrate is faster than that of **1** (see Fig. 1b). This is because the efficiency of singlet oxygen production is expected to increase as the number of bromine atoms attached to the phenyl moiety increases.

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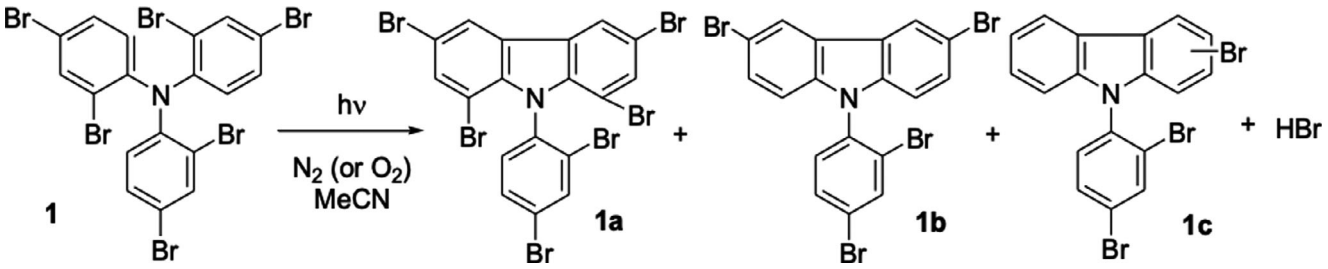

Scheme 1. Irradiation of **1** in acetonitrile solution and product distribution.

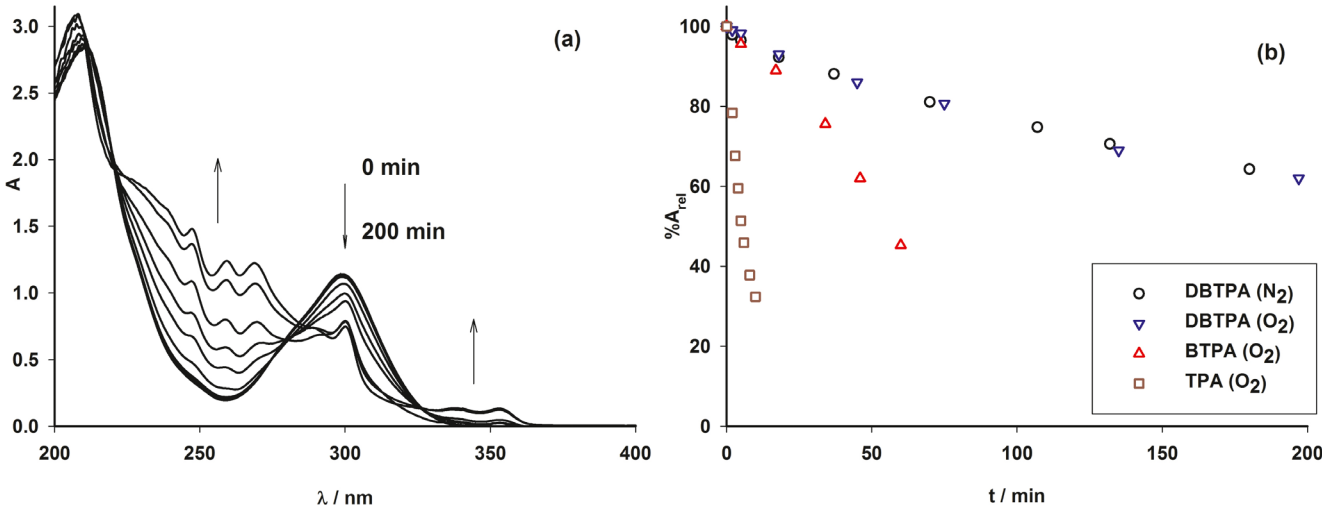

Figure 1. (a) Variation of the UV-visible spectra of **1** (λ_{exc} = 310 nm) in oxygen-saturated acetonitrile. (b) Kinetic profiles of consumption of: (○) **1** (N_2); (▼) **1** (O_2); (Δ) tris(p-bromophenyl)amine (O_2) and (□) triphenylamine (O_2) in acetonitrile (λ_{exc} = 310 nm).

When the photochemical reaction of **1** was carried out in oxygen-saturated acetonitrile and dichloromethane solutions, bromocarbazole derivatives such as **1b** and **1c** were also formed and bromide ion was detected in the reaction mixture at long period of irradiation time (t > 60 min) as can be seen in Fig. 2. Bromocarbazole **1b** was isolated from the photolyzed reaction mixture through column chromatography and fully characterized by NMR spectroscopy, whereas bromocarbazole **1c** was detected by GC-MS in the photoreaction mixture. The formation of bromide ion in the reaction mixture was ascribed to secondary processes that are involved during the photoreaction of **1**. Indeed, compound **1b** and the regioisomers **1c** are clearly formed because of a photoinduced C-Br fragmentation of bromocarbazole **1a** and consequently bromide ion is released to the solution. A similar behavior was also observed under nitrogen atmosphere. Photoinduced homolytic fragmentation of the C(sp^2)-Br bond in aromatic compounds is a known photochemical pathway that is also observed in heteroaryl bromide derivatives (30). Generally, in the case of chloroarenes (benzene, biphenyl, and naphthalene moieties) the excited singlet state possesses sufficient energy to produce C-Cl homolytic fragmentation, whereas the triplet state does not display sufficient energy to promote the homolytic fragmentation (31). Photoinduced heterolytic fragmentation of C (sp^2)-X of polyhaloarenes can also occur from the triplet excited state in the presence of a one-electron donor, that is triethylamine, involving a photoinduced electron transfer process and producing the radical anion of the polyhaloarene (31).

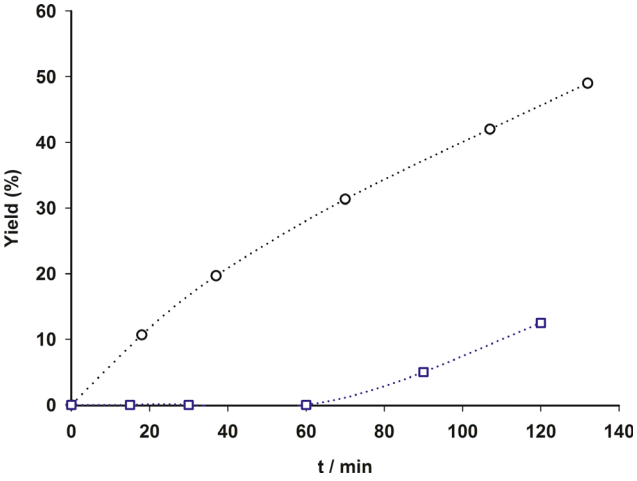

Figure 2. Conversion of amine **1** (○) and yield of bromide ion (□) profiles measured under oxygen-saturated acetonitrile solution (λ_{exc} = 366 nm).

Time-resolved absorption spectroscopy of amine **1** in acetonitrile and dichloromethane, respectively, was carried out under N_2 and O_2 atmospheres. A broad band centered at 400 nm was detected in N_2-saturated acetonitrile solution, whereas two absorption bands, the former centered at 410 nm and the latter as a shoulder starting at 700 nm, were detected in dichloromethane

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(see Fig. 3). These bands were assigned to the UV-visible absorption spectra of two transient species, viz. radical cation $\mathbf{1}^{\cdot+}$ and radical cation polybromosubstituted dihydrocarbazole ($\mathbf{2}^{\cdot+}$) (see Scheme 2) (23,24). A similar behavior was observed when the experiments were performed under O_2 atmosphere.

The decay traces and the grow-in trace were measured under N_2- and O_2-saturated acetonitrile and dichloromethane solutions of **1** at $\lambda_{abs} = 400$ nm showing mono-exponential decay and grow-in curves (see Fig. 4). Applying a nonlinear regression fitting, the lifetime (τ) values were easily obtained and are collected in Table 1. The lifetime values were assigned to the intramolecular cyclization process (τ_{cyc}) of the radical cation $\mathbf{1}^{\cdot+}$ leading to the radical cation bromodihydrocarbazole ($\mathbf{2}^{\cdot+}$) in acetonitrile and dichloromethane, which show very long lifetime values ($\tau > 1000$ μs, see Scheme 2). Another bromodihydrocarbazole radical cation intermediate ($\mathbf{2'}^{\cdot+}$) can be formed involving a cyclization pathway since the radical cation $\mathbf{1}^{\cdot+}$ is an unsymmetrical intermediate (see Scheme 3). However, the sequential pathways followed by intermediate $\mathbf{2'}^{\cdot+}$ involve the elimination of bromonium cation (Br^+), which is unlikely in comparison with the sequential pathways involved for intermediate $\mathbf{2}^{\cdot+}$.

The cyclization rate constants k_{cyc} of the radical cation $\mathbf{1}^{\cdot+}$ to the bromodihydrocarbazole intermediate ($\mathbf{2}^{\cdot+}$) were easily calculated as the reciprocal of the lifetime values because the cyclization reaction is a unimolecular reaction. The cyclization rate constants k_{cyc} are also collected in Table 1.

The k_{cyc} rate constants were also measured under oxygen-saturated acetonitrile and dichloromethane solutions, and it was found that the values were similar to those obtained under nitrogen atmosphere. However, the rate constants measured in dichloromethane show values that are halved in comparison with those measured in acetonitrile (see Table 1). On the other hand, the concentration of the radical cation $\mathbf{1}^{\cdot+}$ at zero time after the laser pulse has been measured in both solvents (Table 1) showing a rather dependence on the atmosphere used. Indeed, the concentration of the radical cation measured under oxygen atmosphere is lower than in nitrogen, which was ascribed to the quenching of the triplet excited state of amine **1** by molecular oxygen.

Co-oxidation of sulfides and phosphines by tris(2,4-dibromophenyl)amine (1) in O_2-saturated solution

The oxidative properties of transient $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ have been tested by irradiating oxygen-saturated solutions of **1** in the presence of sulfides and phosphines that can be easily oxidized by the photogenerated transients (see Scheme 4). In the first case, **1** is consumed during irradiation, while the sulfides were co-oxidized selectively to the corresponding sulfoxides (see Table 2) with rates ranging from 0.004 to 0.332 μmol min^{-1}. Notably, diphenyl sulfide (Ph_2S), that is inert toward singlet oxygen (32), was oxidized. When using benzyl ethyl sulfide, significant amounts of benzaldehyde were also detected in dichloromethane and acetonitrile.

The results summarized in Table 3 describe the selective co-oxidation of triphenylphosphine and tris (o-tolyl)phosphine to the corresponding phosphine oxides (see Scheme 4) that occurs in up to 8.53 μmol min^{-1}, while no consumption of **1** was detected in all the solvents studied. Irradiation of both substrates in the presence of oxygen but without **1** did not provide any sulfoxides or phosphine oxides. Likewise, irradiations under a nitrogen atmosphere but in the presence of **1** did not give any oxidation products.

Time-resolved spectroscopy analysis of tris(2,4-dibromophenyl)amine (1) in the presence of sulfides and phosphines

Time-resolved spectroscopy of **1** in the presence of selected phosphines and sulfides was carried in N_2- and O_2-saturated acetonitrile and dichloromethane solutions, respectively. Thus, triphenylphosphine and tris(o-tolyl)phosphine were found to quench efficiently radical cation $\mathbf{1}^{\cdot+}$ and consequently inhibition of the formation of radical cation $\mathbf{2}^{\cdot+}$ was observed as shown in Fig. 5 a. Furthermore, triethylamine (TEA) was also employed as the electron donor to quench the radical cation $\mathbf{1}^{\cdot+}$ (magenta line in Fig. 5a) and subsequently inhibiting the formation of intermediate $\mathbf{2}^{\cdot+}$. On the other hand, no quenching of the radical cation $\mathbf{1}^{\cdot+}$ was observed when sulfides such as diphenyl sulfide, thioanisole, *p*-methoxy thioanisole and benzyl ethyl sulfide were used

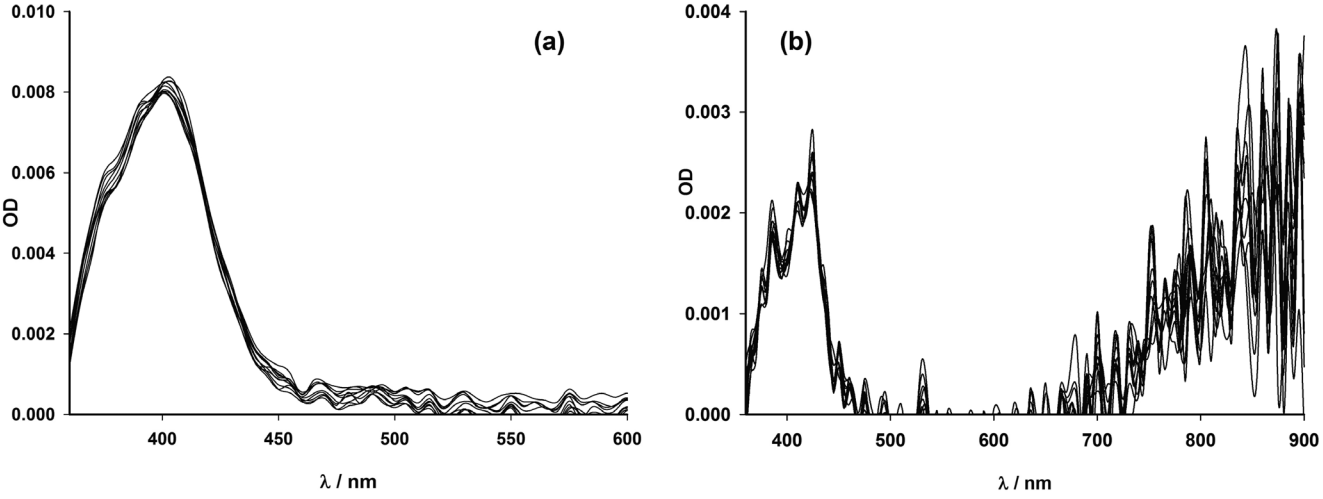

Figure 3. Time-resolved absorption spectra recorded after a laser pulse of 355 nm of amine **1** (3.0×10^{-3} M) transients in: (a) acetonitrile and (b) dichloromethane in nitrogen atmosphere.

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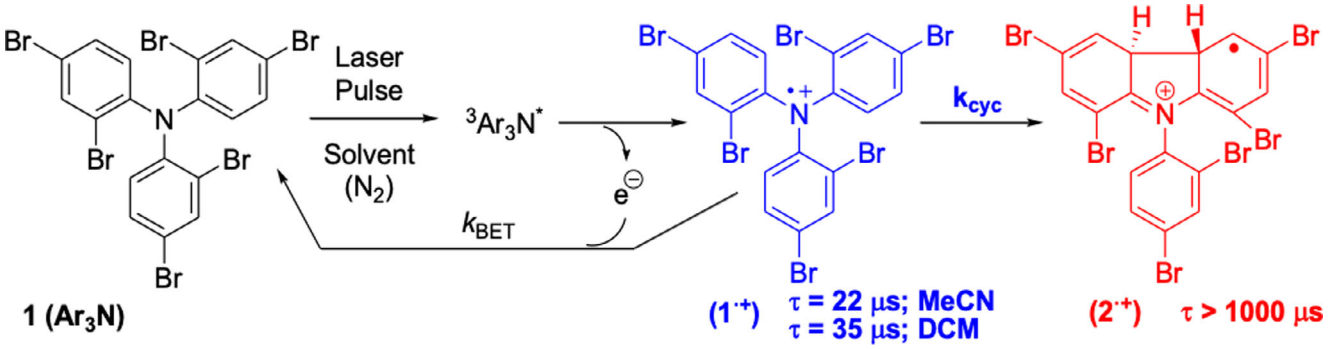

Scheme 2. Formation of transients $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\cdot+}$ in nitrogen-equilibrated media.

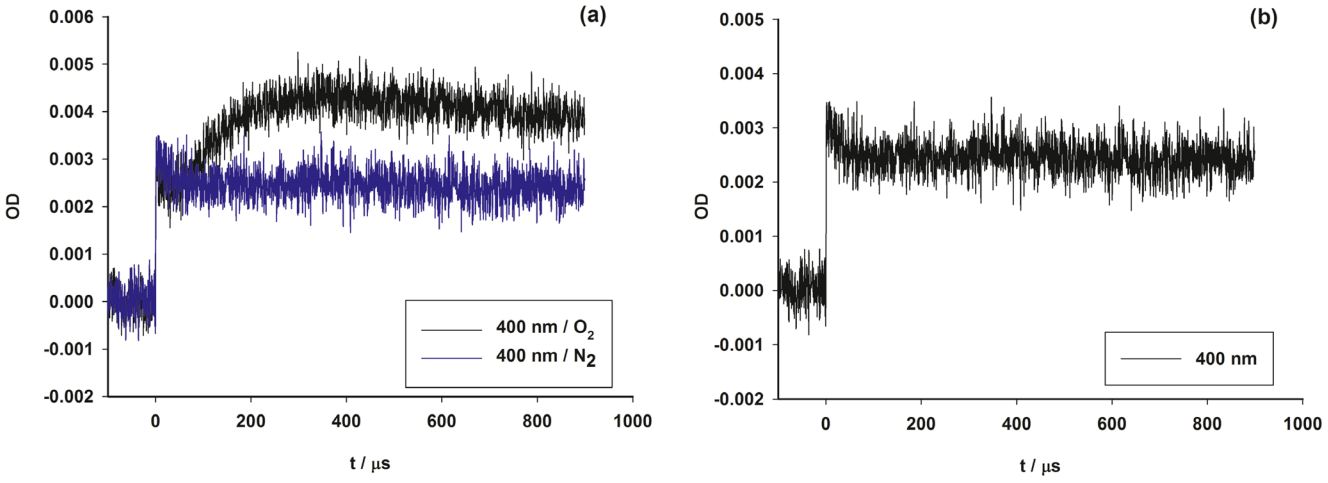

Figure 4. Decay traces and grow-in trace of transient spectra arising from **1**, recorded at λ_{abs} = 400 nm in (a) N_2- and O_2-saturated acetonitrile and (b) in N_2-saturated dichloromethane after a laser pulse of 355 nm.

Table 1. Lifetime (τ) of radical cation $\mathbf{1}^{\bullet+}$, cyclization rate constants (k_{cyc}) and concentration of radical cation $\mathbf{1}^{\bullet+}$ at zero time after the laser pulse.[a]

Solvent	Atmosphere	τ/μs	$k_{cyc} \times 10^4$/s^{-1}	$[\mathbf{1}^{\cdot+}]$/M
MeCN	N_2	22 ± 3	4.5 ± 0.2	1.8×10^{-7}
	O_2	25 ± 4	4.0 ± 0.6	1.3×10^{-7}
DCM	N_2	35 ± 5	2.9 ± 0.4	1.9×10^{-7}
	O_2	41 ± 6	2.4 ± 0.4	1.5×10^{-7}

[a]Concentration of **1**: 3.0×10^{-3} M; λ_{exc} = 355 nm; Errors: 15%; ϵ ($\mathbf{1}^{\cdot+}$) = 14000 M^{-1} cm^{-1} (19).

as quenchers and no inhibition of the formation of transient $\mathbf{2}^{\cdot+}$ occurred for the case of *p*-methoxythioanisole (see Fig. 5b: compare black curve with blue curve in the figure). This spectroscopic behavior led to conclude that radical cation $\mathbf{1}^{\cdot+}$ is not able to oxidize the sulfides to the corresponding sulfoxides but cyclizes competitively to radical cation $\mathbf{2}^{\cdot+}$. However, there is another oxidizing intermediate formed by the reaction of radical cation $\mathbf{2}^{\cdot+}$ and molecular oxygen that displays a long lifetime undetectable by laser flash photolysis but is able to oxidize efficiently sulfides to the corresponding sulfoxides as it was observed under preparative conditions.

The quenching of radical cation $\mathbf{1}^{\cdot+}$ by triphenylphosphine is depicted in Fig. 6, showing that the observed first-order decay constant (k_{obs}) of $\mathbf{1}^{\cdot+}$ depends linearly on the quencher concentration according to Eq. (1).

$$k_{obs} = k_{cyc} + k_{ET}[Q] \quad (1)$$

Plotting k_{obs} versus triphenylphosphine concentration resulted in a linear correlation (see Fig. 6), and the bimolecular rate constant k_{ET} of 1.4×10^5 M^{-1} s^{-1} was obtained from the slope of the linear regression. The k_{ET} values measured for triphenylphosphine, tris(o-tolyl)phosphine and triethylamine in different experimental conditions are collected in Table 4. As it is apparent from the table, the rate constants k_{ET} range from 10^4 to 10^6 M^{-1} s^{-1} including the data measured for triethylamine, and do not depend on the nature of the solvent. However, the rate constants measured under O_2 atmosphere show values rather lower than those obtained under nitrogen flushed solutions.

DISCUSSION

Photochemistry of tris(2,4-dibromophenyl)amine (1) under N_2- and O_2-saturated solutions

Direct irradiation of amine **1** with a laser pulse (355 nm) generates two key intermediates in both N_2- and O_2-saturated solutions, viz. radical cations $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$, and it was found that radical cation $\mathbf{2}^{\cdot+}$ reacts efficiently with molecular oxygen as

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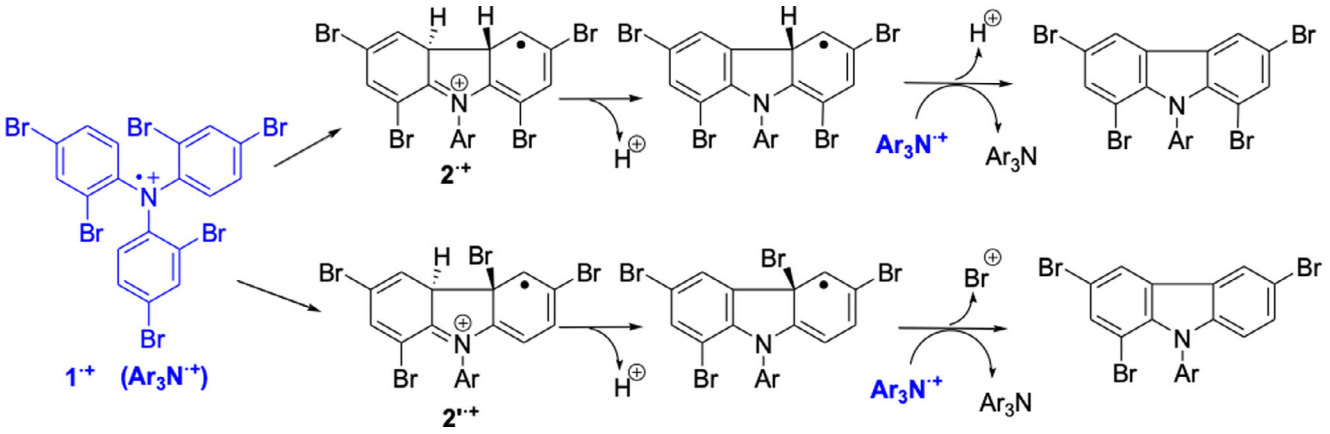
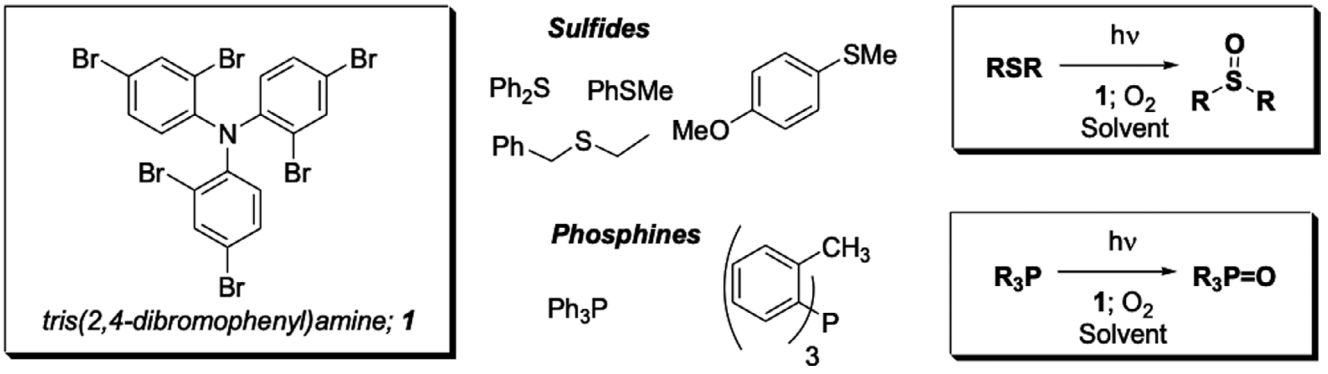


Scheme 3. Proposed electrocyclization of $\mathbf{1}^{\cdot+}$ and sequential pathways of intermediates $\mathbf{2}^{\cdot+}$ and $\mathbf{2'}^{\cdot+}$.



Scheme 4. Co-oxidation of sulfides and triarylphosphines in the presence of **1**.

depicted in Scheme 5. Ionization of photo-excited triplet state of amine **1** under nitrogen atmosphere forms the radical cation ($\mathbf{1}^{\cdot+}$) (***path (a)***). Two competitive pathways consumed $\mathbf{1}^{\cdot+}$. One involves the back-electron transfer process (***path (c)***) giving back the amine **1** with an estimated diffusional rate constant of 10^{10} M^{-1} s^{-1}. The other pathway involves the intramolecular cyclization reaction (***path (b)***) giving brominated dihydrocarbazole radical cation $\mathbf{2}^{\cdot+}$ with a rate constant of 4.5×10^4 s^{-1} and 2.9×10^4 s^{-1} in acetonitrile and dichloromethane, respectively. Next, intermediate $\mathbf{2}^{\cdot+}$ loses two protons and oxidizes amine **1** to radical cation $\mathbf{1}^{\cdot+}$ (***path (d)***) to give polybromocarbazole **1a** as the primary photoproduct. Finally, direct irradiation of compound **1a** under preparative conditions produces debromination photoproducts (**1b** and **1c**) because bromide ion was detected at long period of irradiation time (see Fig. 2). The photocyclization of di- and triarylamines is a known pathway to convert these substrates into carbazoles (23,29,33). The visible irradiation of triarylamines in the presence of a copper-based sensitizer provided a family of substituted carbazoles, and the proposed mechanism involved the formation of a triarylamine radical cation that in turn cyclized to the corresponding dihydrocarbazole. This intermediate then collapsed to bromo carbazole through oxidation and re-aromatization of the intermediate (34). Further photoinduced debromination of the primary photoproduct provides the bromocarbazole observed in the reaction mixture.

Based on these results, a reaction mechanism was proposed for the direct irradiation of amine **1** under O_2 atmosphere in acetonitrile and dichloromethane solutions (see Scheme 5). Molecular oxygen reacts efficiently with the triplet excited state $^3\mathbf{1}$ and converted to singlet oxygen, reducing slightly the formation of radical cations $\mathbf{1}^{\cdot+}$ and, as a consequence, the formation of $\mathbf{2}^{\cdot+}$ as can be judged from the values of the concentration of $\mathbf{1}^{\cdot+}$ in both solvents (see Table 1). The photoionization of **1** under oxygen atmosphere provided $\mathbf{1}^{\cdot+}$ and the ejected electron, which was trapped by molecular oxygen with a bimolecular rate constant of 2×10^{10} M^{-1} s^{-1} giving superoxide ion (35).

The ejected electron was also trapped, at least in part, by the solvent, and then, a back-electron transfer between intermediate $\mathbf{1}^{\cdot+}$ and the solvated electron occurred with a diffusion rate constant (***path (c)*** in Scheme 5. Competitive cyclization of intermediate $\mathbf{1}^{\cdot+}$ afforded radical cation $\mathbf{2}^{\cdot+}$ with rate constants k_{cyc} of 4.0 x 10^4 s^{-1} (in MeCN) and 2.4 x 10^4 s^{-1} (in dichloromethane) that, in turn, reacted efficiently with molecular oxygen to give 4-peroxyl radical (**I**) according to ***path (e)***. Intramolecular hydrogen transfer and reduction of intermediate **I** gave intermediate **II** (***path (f)***) that then released H_2O_2 to the solution and re-aromatized to give the primary photoproduct **1a** (***path (g)***). It is worth mentioning that intermediates **I** and **II** are potential oxidizing agents in the presence of donor substrates that are formed during the irradiation of amine **1** under oxygen atmosphere. Besides, superoxide ion was converted to ROS (Reactive Oxygen Species) such as $^{\cdot}$OH, HOO$^{\cdot}$ and H_2O_2 because of adventitious water in the reaction solvent.

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Table 2. 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	0.004	0.022	
	MeCN – H_2O (9:1)	0.019	0.033	
	TFE	0.073	0.056	
	CH_2Cl_2	0.038	0.030	
PhSMe	MeCN	0.015	0.019	
	MeCN – H_2O (9:1)	0.076	0.047	
	TFE	0.042	0.046	
	CH_2Cl_2	0.026	0.043	
p-$MeOC_6H_4SMe$	MeCN	0.025	0.012	
	MeCN – H_2O (9:1)	0.179	0.039	
	TFE	0.332	0.075	
	CH_2Cl_2	0.034	0.020	
$PhCH_2SEt$	MeCN	0.086	0.025	PhCHO; 0.032
	MeCN – H_2O (9:1)	0.164	0.035	
	TFE	0.101	0.101	
	CH_2Cl_2	0.109	0.093	PhCHO; 0.035

[a]A 5×10^{-3} M solution of amine **1** irradiated in the presence of the chosen sulfide (10^{-2} M) at 366 nm (10 × 15 W lamps). [b]Rate of consumption of **1**.

Table 3. Rate of co-oxidation of phosphines upon irradiation in the presence of amine **1**.[a]

Substrate	Solvent	Rate of reaction (μmol.min^{-1})	
		Phosphine oxide	**1**[b]
Ph_3P	MeCN	1.34	0
	MeCN – H_2O (9:1)	1.12	0
	TFE	3.30	0
	CH_2Cl_2	3.25	0
$(o\text{-}MeC_6H_4)_3P$	MeCN	2.77	0
	MeCN – H_2O (9:1)	3.30	0
	TFE	3.53	0
	CH_2Cl_2	3.44	0

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

Photoinduced co-oxidation of aryl and alkyl sulfides in tris (2,4-dibromophenyl)amine (1) / O_2 system

As hinted above, the irradiation of amine **1** in the presence of a variety of aryl and alkyl sulfides under O_2-saturated solutions promoted the co-oxidation of the sulfides to the corresponding sulfoxides depending on the structure and the solvent employed (see Table 2). Furthermore, during the co-oxidation of sulfides, amine **1** was consumed with noticeable efficiency and this photochemical behavior was attributed to the presence of one (or more) common oxidant intermediate that oxidizes the sulfides to the sulfoxides and furnishes the bromo carbazole derivatives. Singlet oxygen and superoxide ion were formed during the irradiation of **1** under O_2 atmosphere (see Scheme 5), but these species do not intervene the oxidation of sulfides because sulfones were not observed in the present experiments (23,24). Likewise, in the case of benzyl sulfides, S-oxidation to sulfoxides and sulfones and oxidative cleavage to benzaldehyde in polar solvents is commonly observed under singlet oxygen photosensitization. Furthermore, diphenyl sulfide was oxidized efficiently with amine **1** but is unreactive against to singlet oxygen. On the other hand, superoxide ion is not involved in the oxidation of sulfides but reduces $\mathbf{1}^{\cdot+}$ to **1** efficiently through a back-electron transfer process. Therefore, we proposed that intermediate 4-hydroperoxydihydrocarbazole (**II**) is the actual oxidant reagent that is responsible of the oxidation of sulfides to the corresponding sulfoxides as is depicted in Scheme 6.

Thus, triplet excited state of amine **1** underwent ionization to give the radical cation $\mathbf{1}^{\cdot+}$ that cyclizes efficiently to generate radical cation $\mathbf{2}^{\cdot+}$. This intermediate reacts with molecular oxygen providing 4-peroxyl intermediate (**I**) (***path (a)*** in Scheme 6). Intramolecular hydrogen atom transfer followed by a reduction process (***path (b)***) affords intermediate **II**. This key intermediate oxidizes the sulfides to sulfoxides (***path (c)***) releasing intermediate **III**, a 4-hydroxy-dihydrocarbazole derivative, that in turn loses water and affords compound **1a** (***path (d)***). Competitively, intermediate **II** releases H_2O_2 and generates photoproduct **1a** without direct oxidation of sulfides (***path (e)***).

Photo-co-oxidation of triarylphosphines in tris(2,4-dibromophenyl)amine (1) / O_2 system

Triarylphosphines are easily and efficiently oxidized upon irradiation of amine **1** under oxygen atmosphere because phosphines are stronger oxygen acceptors. The phosphine co-oxidation occurs in rather high rates, but no consumption of amine **1** was detected in all the solvent used (see Table 3). This photochemical behavior indicates that there is only one oxidant intermediate responsible for the oxidation of phosphines inhibiting the consumption of amine **1**. Based on the preparative and time-resolved spectroscopic measurements, the reaction mechanism regarding the co-oxidation of triarylphosphines is depicted in Scheme 7.

Direct irradiation of **1** generates radical cation $\mathbf{1}^{\cdot+}$ (***path (a)*** in Scheme 7). Then, intermediate $\mathbf{1}^{\cdot+}$ was efficiently quenched by triarylphosphine giving the triarylphosphine radical cation ($Ar_3P^{\cdot+}$) (***path (b)***) as it was apparent from the linear relationship between k_{obs} and the concentration of the triphenyl phosphine (see Fig. 6). Furthermore, tris(o-tolyl)phosphine was found to quench efficiently radical cation $\mathbf{1}^{\cdot+}$ as can be seen in Fig. 5(a). Indeed, quenching of intermediate $\mathbf{1}^{\cdot+}$ with the triarylphosphine proceeded with electron transfer rate constants (k_{ET}) between 2.4×10^4 M^{-1} s^{-1} and 2.8×10^6 M^{-1} s^{-1} in acetonitrile and dichloromethane, respectively, under O_2 atmosphere (see Table 4). Competitively, the solvated electron reduces, in part, the radical cation $\mathbf{1}^{\cdot+}$ to amine **1** through a back-electron transfer process. Additionally, it is worthy to mention that no cyclization pathway from $\mathbf{1}^{\cdot+}$ occurred because no consumption of **1** was observed (see Table 3). The electron transfer pathway (***path (b)*** in Scheme 7) is thermodynamically feasible process because the one-electron oxidation potential of **1** is + 1.49 V versus SCE (36) and is capable to oxidize both triphenylphosphine and tris (*o*-tolyl)phosphine + 1.16 V and + 1.11 V (versus SCE), respectively (37). Therefore, the ΔG^0 value is − 0.33 V for the case of triphenylphosphine and − 0.30 V for tris(o-tolyl)phosphine. The

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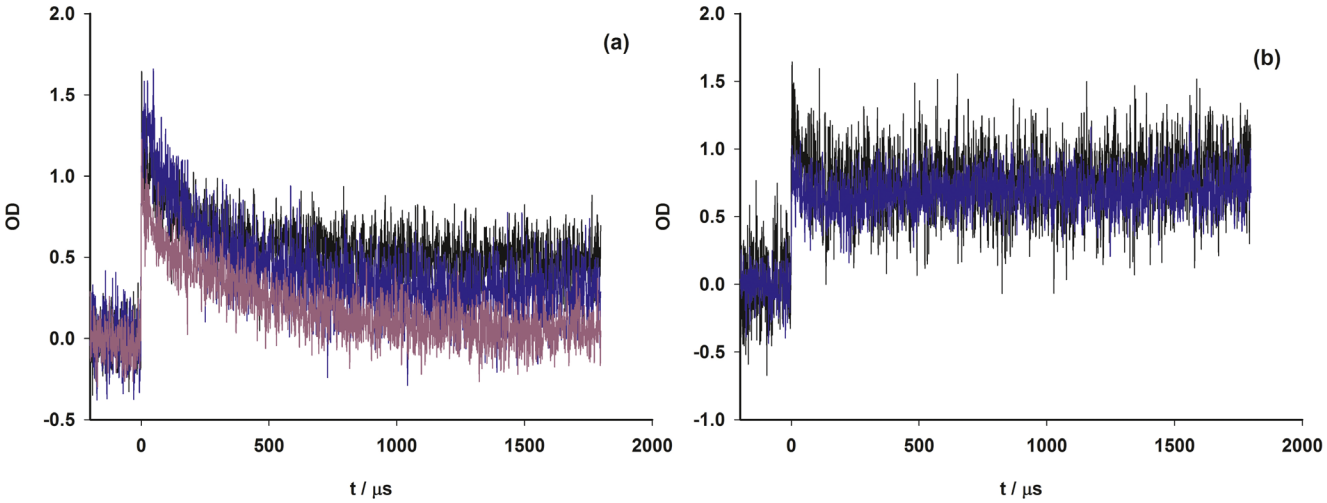

Figure 5. (a) Decay traces of radical cation $\mathbf{1}^{\cdot+}$ transient (1.0×10^{-3} M) recorded at λ_{abs} = 380 nm under O_2-saturated dichloromethane after a laser pulse of 355 nm in the presence of PPh_3 (1.2×10^{-3} M) (black line); $(o\text{-Tol})_3P$ (1.2×10^{-3} M) (blue line); and triethylamine (3.4×10^{-3} M) (magenta line). (b) Decay traces of radical cation $\mathbf{1}^{\cdot+}$ transient (1.0×10^{-3} M) recorded at λ_{abs} = 380 nm under O_2-saturated dichloromethane after a laser pulse of 355 nm in the absence of quencher (black line) and in the presence of p-MeOPhSMe (1.2×10^{-3} M) (blue line).

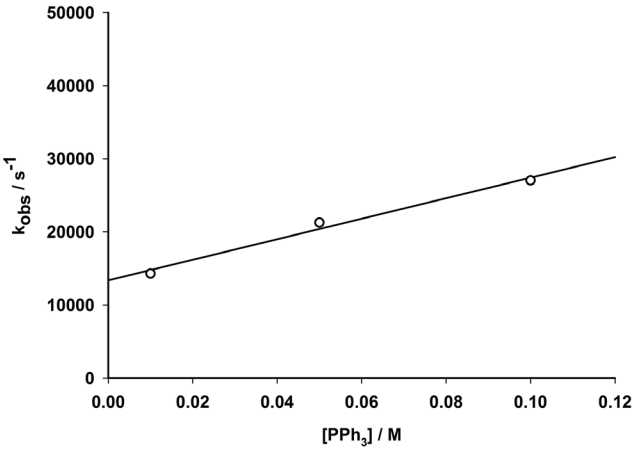

Figure 6. Quenching of radical cation $\mathbf{1}^{\bullet+}$ with increasing concentrations of triphenylphosphine (○). Straight line is the best linear regression fit ($r^2 > 0.98$).

Table 4. Quenching rate constants (k_{ET}) of radical cation $\mathbf{1}^{\cdot+}$ in different conditions.[a]

Quencher	Solvent	Atmosphere	k_{ET}/M^{-1} s^{-1}
Ph_3P	MeCN	N_2	2.3×10^6
		Air	1.4×10^5
		O_2	2.8×10^6
Ph_3P	DCM	N_2	3.2×10^5
		O_2	2.4×10^5
$(o\text{-}CH_3C_6H_4)_3P$	MeCN	N_2	4.9×10^5
$(o\text{-}CH_3C_6H_4)_3P$	DCM	N_2	3.4×10^5
		O_2	3.3×10^5
Et_3N	DCM	N_2	7.5×10^4

[a]Measured in MeCN after the laser pulse (355 nm). The initial absorbance of the solutions was fixed at 0.70. Error: ± 10%.

triarylphosphine radical cations ($Ar_3P^{\cdot+}$) generated in ***path (b)*** then reacted with molecular oxygen producing the corresponding peroxyl intermediate $Ar_3PO_2^{\cdot+}$ (***path (c)***). This latter pathway has been observed during laser flash photolysis and pulse radiolysis experiments (23,38). $Ar_3PO_2^{\cdot+}$ thus reacted with another molecule of triarylphosphine-producing triarylphosphine oxide, and a new $Ar_3PO^{\cdot+}$ species is formed through a mesolytic cleavage reaction (***path (d)*** in Scheme 7). Finally, the radical cation $Ar_3PO^{\cdot+}$ reacted with superoxide ion to provide another equivalent of triarylphosphine oxide and molecular oxygen according to ***path (e)***.

On the other hand, oxidation of triarylphosphines with singlet oxygen has been excluded as a competitive reaction pathway (***path (c)***, Scheme 7), because it was found that the reaction between $Ar_3P^{\cdot+}$ and molecular oxygen displays a bimolecular rate constant k of 1.6×10^{10} M^{-1} s^{-1} (38), which is higher than the rate constant between Ar_3P and singlet oxygen (1.6×10^7 M^{-1} s^{-1}) (39). Superoxide ion was also excluded as a possible oxidizing agent of the $Ar_3P^{\cdot+}$ since is involved as an electron carrier in the reduction of $Ar_3PO^{\cdot+}$ to triarylphosphine oxide (***path (e)***) as well as in the reduction of radical cation $\mathbf{1}^{\cdot+}$ the amine **1** through a back-electron transfer process. Therefore, we excluded from the proposed reaction mechanism (Scheme 7) both competitive oxidative pathways, viz. oxidation of triarylphosphine with singlet oxygen as well as with superoxide ion. Finally, we can conclude that during the co-oxidation of triarylphosphine molecular oxygen is the only species capable to oxidize efficiently the radical cation $Ar_3P^{\cdot+}$, which is generated through a one-electron transfer process between Ar_3P and $Ar_3N^{\cdot+}$.

Finally, it is noteworthy to mention that the triphenylamine (TPA), tris(4-bromophenyl)amine (BTPA) and compound **1** are photooxidizing reagents capable to co-oxidize sulfides and phosphines. However, these photosensitizers oxidize the nucleophilic substrates involving different oxidizing intermediates. In fact, no photoionization of TPA occurs and no radical cation ($TPA^{\cdot+}$) is formed during the direct irradiation with a laser pulse.(24) 6π-Electrocyclization process from the triplet state of TPA provides, in the presence of molecular oxygen, two consecutive

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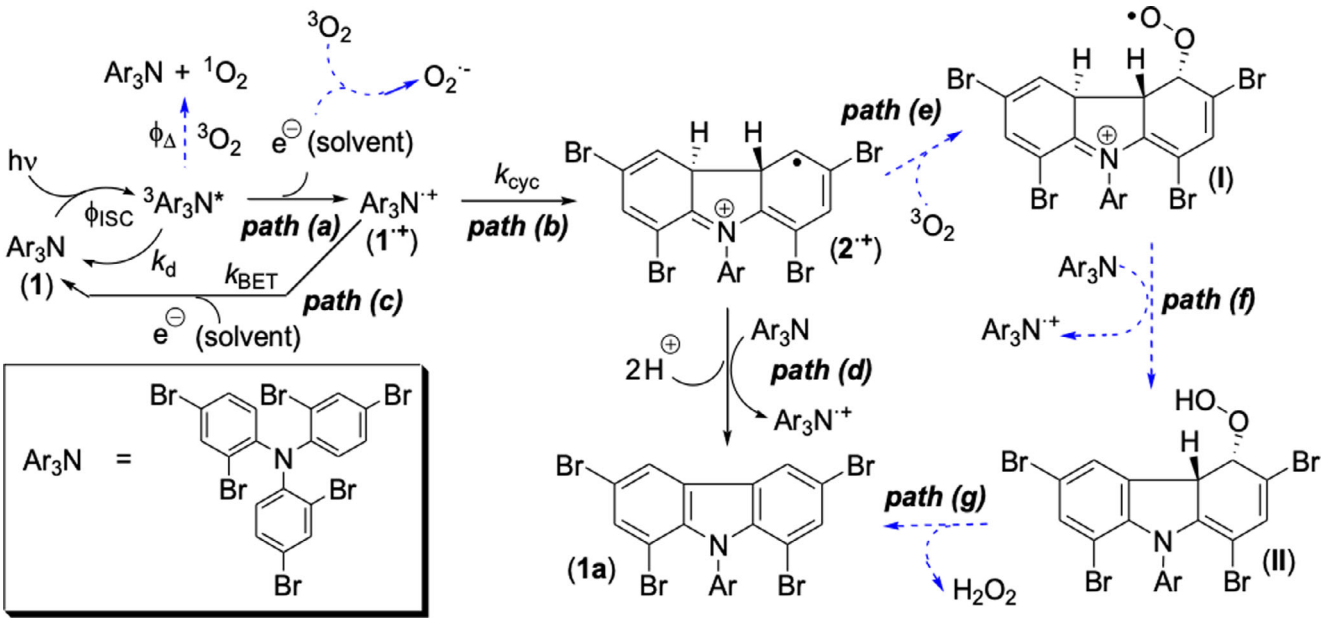
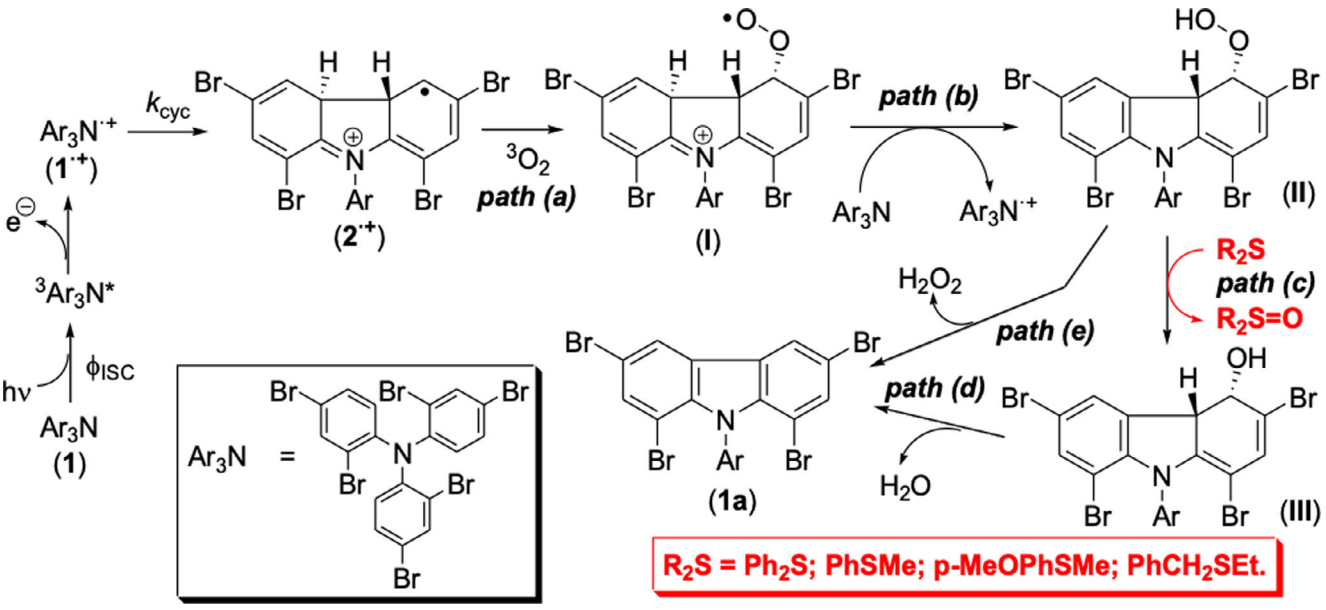


Scheme 5. Proposed reaction mechanism of the photocyclization of amine **1** under N_2 atmosphere (filled black arrows) and O_2 atmosphere (dashed blue arrows).



Scheme 6. Proposed mechanism for the co-oxidation of sulfides during the photocyclization of **1**.

intermediates, viz. a peroxyl radical and a hydroperoxide intermediate. The first one is capable to oxidize triarylphosphines efficiently without production of *N*-phenylcarbazole, whereas the second intermediate oxidizes sulfides to sulfoxides and N-phenylcarbazole is formed. Conversely, tris(4-bromophenyl)amine and compound **1** give the corresponding radical cations known as "Magic Blue" (23) and "Magic Green," respectively. In these cases, the radical cations are capable to oxidize through an electron transfer process the triarylphosphines into the corresponding radical cations that in the presence of molecular oxygen finally provide the triarylphosphine oxides. Again, the inhibition of the formation of *N*-phenylpolybromocarbazoles was observed. On the other hand, N-phenyl-4a,4b-polybromocarbazole peroxides are the oxidizing species responsible to convert sulfides into sulfoxides providing simultaneously the formation of the corresponding N-phenylpolybromocarbazole derivatives. It is apparent from the above comparison that there is a remarkable difference between the oxidation pathways and the oxidizing species involved in the photoreaction when TPA, BTPA and compound **1** are employed as the photosensitizers. The quantum yield of co-oxidation (ϕ) of diphenylsulfide in acetonitrile in the presence of molecular oxygen has been measured for each photosensitizer, and the ϕ values are 0.20 for TPA, 0.08 for BTPA and 0.03 for compound **1**. The results also highlight that TPA is a good

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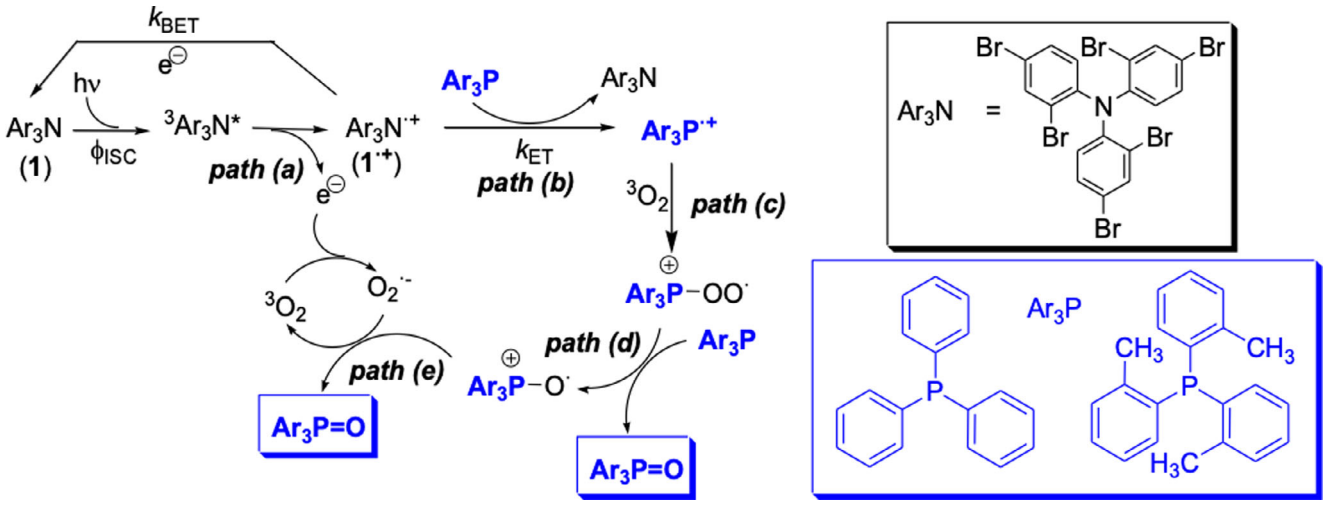

Scheme 7. Proposed mechanism for the co-oxidation of triarylphosphines during the photocyclization of **1**.

oxidizing photosensitizer and we can suggest that the oxidant power decreases as the number of bromo atoms increases. However, BTPA and **1** are also oxidizing reagents and similar trends were observed for other sulfide derivatives.

CONCLUSIONS

The photoinduced co-oxidation of phosphines and sulfides with tris-(2,4-dibromophenyl)amine (**1**) under oxygen atmosphere gave the corresponding sulfoxides and phosphine oxides in polar and apolar solvents. However, amine **1** was consumed efficiently during the co-oxidation of sulfides, whereas no consumption of amine **1** was observed when phosphines are co-oxidized. This photochemical behavior was demonstrated proposing the formation of two distinctly oxidizing intermediates, *viz*. radical cation $\mathbf{1}^{\cdot+}$ and radical cation $\mathbf{2}^{\cdot+}$. An intramolecular cyclization reaction converted $\mathbf{1}^{\cdot+}$ into $\mathbf{2}^{\cdot+}$ with rate constants from 2.4×10^4 s^{-1} to 4.5×10^4 s^{-1} in acetonitrile and dichloromethane measured by laser flash photolysis. Under preparative conditions, radical cation $\mathbf{2}^{\cdot+}$ evolves to carbazole derivative **1a** as the primary photoproduct (see Scheme 5).

During the photoinduced co-oxidation of sulfides to sulfoxides, amine **1** was efficiently consumed providing carbazole **1a**. This concomitant photochemical behavior was allowed by the reaction of radical cation $\mathbf{2}^{\cdot+}$ with molecular oxygen, giving two successively intermediates, peroxyl radical cation **I** and hydroperoxy intermediate **II**, that are both potential oxidants. Thus, sulfides are oxidized by intermediate **II** transferring an oxygen atom to the nucleophilic sulfur atom and generating intermediate **III**.

In the case of co-oxidation of phosphines (Ar_3P), radical cation $\mathbf{1}^{\cdot+}$ oxidized the phosphines to the corresponding radical cation $Ar_3P^{\cdot+}$ through a thermodynamically feasible one-electron transfer process (ΔG^0 of ca. −0.30 V) with rate constants up to 2.8 x 10^6 s^{-1} depending on the reaction solvent employed. Then, intermediate $Ar_3P^{\cdot+}$ reacted with molecular oxygen to give a peroxyl radical cation $Ar_3P\text{-}OO^{\cdot+}$ that was converted into the triarylphosphine oxide (see Scheme 7). Competitively, the radical cation $\mathbf{1}^{\cdot+}$ was reduced in part to amine **1** with the solvated electron through a back-electron transfer process and no cyclization pathway from $\mathbf{1}^{\cdot+}$ to $\mathbf{2}^{\cdot+}$.

In conclusion, direct irradiation of tris-(2,4-bromophenyl) amine (**1**) that is the precursor of radical cation $\mathbf{1}^{\cdot+}$ has been stated a versatile photochemical tool that led to the oxidation of organic substrates.

Acknowledgements—Sergio M. Bonesi is a research member of CONICET.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article:

Scheme S1. Irradiation of **1** in acetonitrile solution and product distribution.

Figure S1. GC-MS mass spectrum (up) and calculated fragmentation for compound **1**.

Figure S2. GC-MS mass spectrum (up) and calculated fragmentation for compound **1a**.

Figure S3. GC-MS mass spectrum (up) and calculated fragmentation for compound of formula $C_{18}H_{10}Br_5N$.

Figure S4. GC-MS mass spectrum (up) and calculated fragmentation for compound of formula $C_{18}H_{10}Br_3N$.

Figure S5. GC-MS mass spectrum (up) and calculated fragmentation for compound of formula $C_{18}H_{11}Br_2N$.

Figure S6. GC-MS mass spectrum (up) and calculated fragmentation for compound **1b**.

Figure S7. ^{1}HNMR (500 MHz) spectra of a mixture of **1** and **1b** isolated by the irradiation of **1** at 355 nm in MeCN

Figure S8. ^{13}CNMR (500 MHz) spectra of a mixture of **1** and **1b** isolated by the irradiation of **1** at 355 nm in MeCN

Figure S9. H/H COSY (500 MHz) spectrum of a mixture of **1** and **1b** isolated by the irradiation of **1** at 355 nm in MeCN

Figure S10. HSQC (700 MHz) spectrum of a mixture of **1** and **1b** isolated by the irradiation of **1** at 355 nm in MeCN

REFERENCES

1. Seo, E. T., R. F. Nelson, J. M. Fritsch, L. S. Macoux, D. T. Leedy and R. N. Adams (1966) Anodic oxidation pathways of aromatic amines. Electrochemical and electron paramagnetic resonance studies. *J. Am. Chem. Soc.* **88**, 3498–3503.

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2. Ambrose, J. F., L. L. Carpenter and R. F. Nelson (1975) Electrochemical and spectroscopic properties of cation radicals. III. Reaction pathways of carbazolium radical ions. *J. Electrochem. Soc.* **122**, 876–894.
3. Papouchado, L., R. N. Adams and S. W. Feldberg (1969) Anodic catalytic currents involving cyanide ion. *J. Electroanal. Chem. Interfacial Electrochem.* **21**, 408–410.
4. Odon, S. A., S. Ergun, P. P. Poudel and S. R. Parkin (2014) A fast, inexpensive method for predicting overcharge performance in lithium-ion batteries. *Energy Environ. Sci.* **7**, 760–767.
5. Valenti, G., C. Bruno, S. Rapino, A. Fiorani, E. A. Jackson, L. T. Scott, R. Paolucci and M. Marcaccio (2010) Intense and tunable electrochemiluminescence of corannulene. *J. Phys. Chem. C.* **114**, 19467–19472.
6. Horn, E. J., B. R. Rosen and P. S. Baran (2016) Synthetic organic electrochemistry: an enabling and innately sustainable method. *ACS Cent. Sci.* **2**, 302–308.
7. Schotten, C., T. P. Nicholls, R. A. Bourne, N. Kapur, B. N. Nguyen and C. E. Willans (2020) Making electrochemistry easily accessible to the synthetic chemist. *Green Chem.* **22**, 3358–3375.
8. Fuchigami, T., K. Mitomo and H. Ishii (2001) Electrolytic partial fluorination of organic compounds Part 44. Anodic *gem*-difluorodesulfuration using triarylamine mediators. *J. Electroanal. Chem.* **507**, 30–33.
9. Fuchigami, T., M. Tetsu, T. Tajima and H. Ishii (2001) Indirect anodic monofluorodesulfurization of β-phenylsulfenyl β-lactams using a triarylamine mediator. *Synlett* **8**, 1269–1271.
10. Shen, Y., K. Suzuki, M. Atobe and T. Fuchigami (2003) Indirect anodic fluorodesulfurization of S-aryl thiobenzoates using a triarylamine mediator. *J. Electroanal. Chem.* **540**, 189–194.
11. Shen, Y., H. Hattori, K. Ding, M. Atobe and T. Fuchigami (2006) Triarylamine mediated desulfurization of S-arylthiobenzoates and a tosylhydrazone derivative. *Electrochim. Acta* **51**, 2819–2824.
12. Oyama, M., J. Matsui and H. Park (2002) Spectroscopic detection of short-lived anthracene derivative cation radicals using an electron transfer stopped-flow method wit tris-(2,4-dibromophenyl)amine cation-radical. *Chem. Commun.* **6**, 604–605.
13. Matsui, J., H. Park, K. Otsuka and M. Oyama (2003) Kinetics and mechanisms of the reactions of 9-substituted anthracene cation radicals with water or methanol in acetonitrile. *J. Electroanal. Chem.* **558**, 49–57.
14. Yano, M., Y. Isida, M. Tatsumi, K. Sato, D. Shiomi, M. Oyama and T. Takui (2004) Organic high-spin systems: synthesis, electrochemical and ETSF studies of a series of tetraaryl-meta-phenylenediamines. *J. Phys. Chem. Solids* **65**, 733–736.
15. Schmidt, W. and E. Steckham (1980) Elektrochemische und spektroskopische Untersuchung bromsubstituierter Triarylamin-Redoxsysteme. *Chem. Ber.* **113**, 577–585.
16. Lopez, L., G. M. Farinola, N. Naci and S. Sportelli (1998) Monodeoxygenation of spiro adamantine-1,2-dioxetanes induced by aminium salt. *Tetrahedron* **54**, 6939–6946.
17. Lopez, L., L. Troisi and G. Melel (1991) Electron-transfer reactions on hindered olefins induced by aminium salts. *Tetrahedron Lett.* **32**, 117–120.
18. Yueh, W. and N. L. Bauld (1997) Mechanistic aspects of the substrate ionization step in aminium salt catalyzed cyclopropanation. *Res. Chem. Intermed.* **23**, 1–16.
19. Yueh, W. and N. L. Bauld (1995) Mechanistic criteria for cation radical reactions: aminium salt-catalyzed cyclopropanation. *J. Am. Chem. Soc.* **117**, 5671–5676.
20. Park, K. H., K. Jun, S. R. Sim and S. W. Oh (1997) Cation radicals with 2-pyridylhydrazones in nitrile solvents s-triazolo[4,3-a]pyridines by thianthrane cation radical perchlorate and 1-(2-pyridyl)-1,2,4-triazoles by tris(2,4-dibromophenyl)aminium hexachloroantimonate. *Bull. Korean Chem. Soc.* **18**, 604–608.
21. Breslin, D. T. and M. A. Fox (1994) Photochemical electrocyclization of thermally stable triarylamine radical cations. *J. Org. Chem.* **59**, 7557–7561.
22. Breslin, D. T. and M. A. Fox (1994) Excited-state behavior of thermally stable radical ions. *J. Phys. Chem.* **98**, 408–411.
23. Bonesi, S. M., S. Protti and A. Albini (2018) Photochemical Co-oxidation of sulfides and phosphines with tris(p-Bromophenyl)amine. A Mechanistic Study. *J. Org. Chem.* **83**, 8104–8113.
24. Bonesi, S. M., D. Dondi, S. Protti, M. Fagnoni and A. Albini (2014) (Co)oxidation/cyclization processes upon irradiation of triphenylamine. *Tetrahedron Lett.* **55**, 2932–2935.
25. Bordwell, F. G. and P. Boutan (1957) Synthesis of aryl methyl sulfoxides and determination of the conjugative effect of the methylsulfinyl group. *J. Am. Chem. Soc.* **79**, 717–722.
26. Senear, A. E., W. Valient and J. Wirth (1960) Derivatives of triphenylphosphine and triphenylphosphine oxide. *J. Org. Chem.* **25**, 2001–2006.
27. Modena, G., F. Taddei and P. E. Todesco (1960) Nucleophilic substitutions in ethylene derivatives: 1-arylsulfonyl-1-methyl-2-haloethylenes. *Gazz. Chim. Ital.* **89**, 894.
28. Cerniani, A., G. Modena and P. E. Todesco (1960) Oxidation of organic sulfides. IV. Oxidation of benzyl and phenyl alkyl sulfoxides to sulfones. *Gazz. Chim. Ital.* **90**, 3.
29. Turro, N. J., V. Ramamurthy and J. C. Scaiano (2010) *In Modern Molecular Photochemistry of Organic Molecules*. University Science Books, Sausalito, CA.
30. Davidson, R. S., J. W. Goodin and K. Graham. (1984) The photochemistry of aryl halides and related compounds. In *Advances in Physical Organic Chemistry*, Vol. **20** (Edited by V. Gold and D. Bethell), pp 191–233.Academic Press, London. https://doi.org/10.1016/S0065-3160(08)60149-5
31. Freeman, P. K., R. Srinivasa, J.-A. Campbell and M. L. Deinzer (1986) The photochemistry of polyhaloarenes. 5. Fragmentation pathways in polychlorobenzene radical anions. *J. Am. Chem. Soc.* **108**, 5531–5536.
32. Liang, J. J., C. L. Gu, M. L. Kacher and C. S. Foote (1983) Chemistry of singlet oxygen. 45. Mechanism of the photooxidation of sulfides. *J. Am. Chem. Soc.* **105**, 4717–4721.
33. Parisien-Collette, S., A. C. Hernández-Pérez and S. K. Collins (2016) Photochemical synthesis of carbazoles using an $[Fe(phen)_3](NTf_2)_2/O_2$ catalyst system: catalysis toward sustainability. *Org. Lett.* **18**, 4994–4997.
34. Hernández-Pérez, A. C. and S. K. Collins (2013) A visible-light-mediated synthesis of carbazoles. *Angew. Chem. Int. Ed.* **52**, 12696–12700.
35. Buxton, G. V., C. L. Greenstock, W. P. Helman and A. B. Ross (1988) Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O− in Aqueous solution. *J. Phys. Chem. Ref. Data* **17**, 513–885.
36. Dapperheld, S., E. Steckhan, K.-H.-G. Brinkshaus and T. Esch (1991) Substituted triarylamine cation-radical redox systems. Synthesis, electrochemical and spectroscopic properties, Hammett behavior, and suitability as redox catalysts. *Chem. Ber.* **124**, 2557–2567.
37. Lee, Y.-M., M. Yoo, H. Yoon, X.-X. Li, W. Nam and S. Fukuzumi (2017) Direct oxygen atom transfer versus electron transfer mechanism in the phosphine oxidation by nonheme Mn (IV)-oxo complexes. *Chem. Commun.* **53**, 9352–9355.
38. Bonesi, S. M., S. Protti and A. Albini (2016) A reactive oxygen species (ROS) vs peroxyl-mediated photosensitized oxidation of triphenylphosphine: a comparative study. *J. Org. Chem.* **81**, 11678–11685.
39. Zhang, D., B. Ye, D. G. Ho, R. Gao and M. Selke (2006) Chemistry of singlet oxygen with arylphosphines. *Tetrahedron* **62**, 10729–10733.

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