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Reaction of Triarylphosphine Radical Cations Generated from Photoinduced Electron Transfer in the Presence of Oxygen

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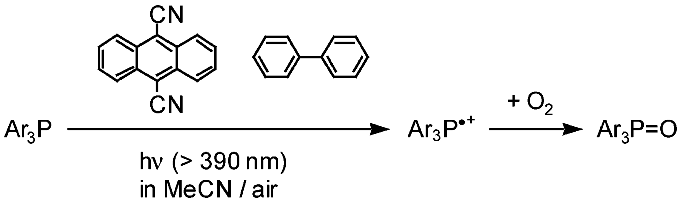
Received June 9, 2004



The 9,10-dicyanoanthracene (DCA)-sensitized photoreaction of triarylphosphines (**1**) was carried out in acetonitrile under aerobic conditions. Phosphine **1** was oxidized to the corresponding phosphine oxide with no appreciable side reactions. Product analysis and laser flash photolysis experiments suggest that the radical cation of **1** formed by the electron transfer from **1** to DCA in the singlet excited state (^{1}DCA*) reacts with O_2 to eventually afford the phosphine oxide.

Introduction

Trivalent phosphorus compound is known to be a nucleophile, whereas it behaves as an electron donor toward good electron acceptors either in the ground[1−5] or excited state,[1,6−9] producing the corresponding trivalent phosphorus radical cations. It is of great importance to elucidate the reactivity of the radical cations not only from a mechanistic point of view but also for potential application in organic syntheses.[10] Our previous work showed that radical cations generated from phenylphosphonite $PhP(OR)_2$, diphenylphosphinite Ph_2POR, and triphenylphosphine Ph_3P during the reaction with diazonium salts in the dark undergo an ionic reaction with methanol or ethanol in the solvent.[3] Meanwhile, the radical cation resulting from phosphite $(RO)_3P$ in this reaction undergoes, besides the ionic reaction, radical coupling with the aryl radical simultaneously generated in the system. The predominance of the ionic reaction for aromatic trivalent phosphorus radical cations was interpreted in terms of the delocalization of the spin into the phenyl substituent(s), which makes the central phosphorus atom less radical-like. However, since the reaction was carried out in an alcoholic solvent, the rapid ionic reaction with the alcohol could have obscured the radical reaction. A question then remained unsolved as to whether the aromatic trivalent phosphorus radical cations can also react with radical species under certain circumstances.

Photoexcitation of 9,10-dicyanoanthracene (DCA) to DCA in the singlet excited state (^{1}DCA*) in polar solvents provides a powerful method to examine the reactivity of the radical cations of various compounds[11,12] because of

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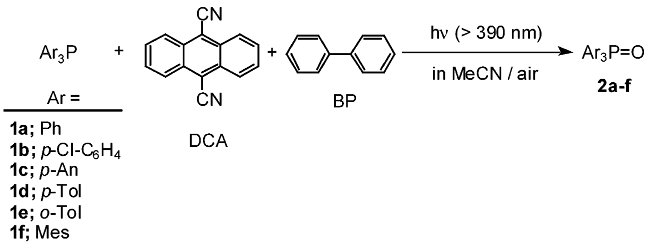
SCHEME 1



the excellent ability of ^{1}DCA* as an one-electron oxidant ($E_{1/2}$ = 1.69 V vs Ag/Ag$^+$).[6,13] Recently, we examined the photoreaction of triarylphosphines (**1**) with DCA and found that the radical cation of **1** ($\mathbf{1}^{\bullet+}$) exhibits a cationic character.[6] Thus, when the reaction is carried out in aqueous acetonitrile under an argon atmosphere, the resulting $\mathbf{1}^{\bullet+}$ undergoes an ionic reaction with water to give the corresponding phosphine oxides. In this reaction, water plays an important role acting as a nucleophile.

Now, our interest is to determine what reaction takes place if the photoreaction is carried out in "dry" acetonitrile under aerobic conditions. This system does not contain a nucleophile, whereas molecular oxygen O_2 as a radical is available. Thus, there is the possibility that $\mathbf{1}^{\bullet+}$ undergoes radical coupling with O_2. We examined the photoreaction of **1** in the presence of DCA and biphenyl (BP) in acetonitrile (MeCN) under aerobic conditions, and found the almost quantitative conversion of **1** into the corresponding phosphine oxides (**2**) (Scheme 1). The results from the product analysis as well as in the laser flash photolysis demonstrate the occurrence of the reaction of $\mathbf{1}^{\bullet+}$ with O_2 under aerobic conditions. To the best of our knowledge, only a few reports have been presented by one group on the reactions of $\mathbf{1}^{\bullet+}$ with O_2.[14]

Results

Laser Flash Photolysis. During the irradiation of a solution of **1**, BP, and DCA in MeCN with a 355-nm laser, a transient absorption spectrum with absorption maxima at 370 and 525 nm was observed and assigned to $\mathbf{1}^{\bullet+}$ by comparison with our previous observation.[6] In the absence of BP, the absorbance of $\mathbf{1}^{\bullet+}$ was too small to be monitored. The absorbance at 525 nm decreased according to first-order kinetics with the rate constant as summarized in Table 1. The decay rate was accelerated under aerobic conditions. The pseudo-first-order decay rate of $\mathbf{1c}^{\bullet+}$ was found to be roughly proportional to the concentration of O_2 as shown in Figure 1. No appreciable acceleration in the decay was observed with the addition of methanol (up to 0.48 mol dm^{-3}).

TABLE 1. Decay Rate Constant of $\mathbf{1}^{\bullet+}$ Determined by Transient Absorption Measurement[a]

radical cation	atmosphere	k_{decay} (10^5 s^{-1})[b]
$\mathbf{1a}^{\bullet+}$	air	4.3
	Ar	1.4
$\mathbf{1c}^{\bullet+}$	O_2	52
	air	7.2
	Ar	2.2
$\mathbf{1d}^{\bullet+}$	air	2.2
	Ar	1.8
$\mathbf{1e}^{\bullet+}$	air	6.9
	Ar	3.1

[a] Laser flash photolysis of **1** with a 4-ns and 355-nm laser under aerobic conditions: [**1**] = 1.00×10^{-2} M, [BP] = 1.00×10^{-1} M, [DCA] = 5.00×10^{-5} M in MeCN. [b] Pseudo-first-order rate constant.

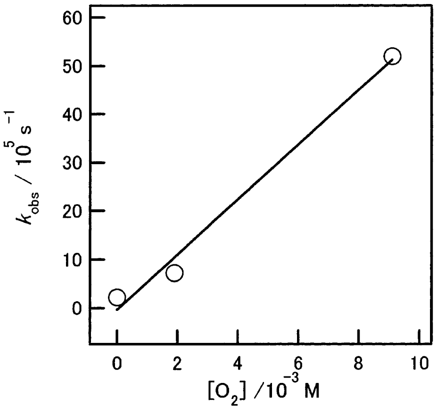


FIGURE 1. Relationship between the pseudo-first-order rate constant of the decay $\mathbf{1c}^{\bullet+}$ (k_{obs}) and concentration of O_2.

TABLE 2. Time-Course of the Photooxidation of 1a[a]

time (s)	yield[b] (%) **1a**	**2a**	material balance[c] (%)
0	100.0	0.0	100.0
20	86.0	13.9	99.9
40	74.0	26.5	100.5
60	61.9	37.5	99.4
90	48.0	54.0	102.0

[a] [**1a**] = 1.00×10^{-2} M, [BP] = 1.00×10^{-1} M, [DCA] = 5.00×10^{-5} M; under aerobic conditions in MeCN; irradiated with visible light (>390 nm) from a Xe lamp. [b] Determined by GC using benzyl ether as the external standard. [c] Sum of the yields of **1a** and **2a**.

Product Analysis. A solution of **1**, BP, and DCA in MeCN was irradiated using a xenon lamp (>390 nm with a glass filter) under aerobic conditions. At appropriate intervals, the reaction mixture was analyzed by GC, showing that **1** was gradually oxidized to the corresponding **2**. For each reaction, the sum of the amounts of **1** and **2** accounted for more than 80% of the material balance. No other product was detected by the GC. Table 2 gives the time-course of the photooxidation of **1a** as a typical example.

The amount of **1** consumed (in moles when normalized to 1dm^3 solution) was plotted versus the irradiation time in Figure 2, which gave a linear line up to 30−90% consumption of **1** for each reaction. Table 3 summarizes the slopes of the linear lines obtained from the reactions under the various conditions. Our previous work has shown the intensity of the incident light from our xenon lamp to be 1.76×10^{-6} einstein s^{-1}cm^{-2} at 450 nm.[8] The lamp intensity at this wavelength was almost the same as that at 420 nm where DCA was excited. Using this intensity together with the values of the slopes in Figure 2, the apparent quantum yields for the conversion of **1** to **2** (Φ_{cons}) were calculated as shown in Table 3 (see the Experimental Section).

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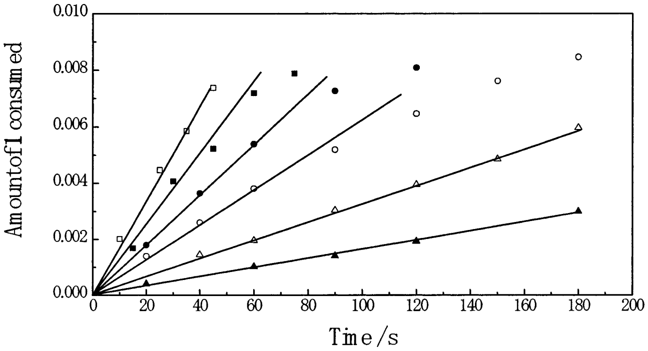


FIGURE 2. Time-course of the amount of **1** consumed in the DCA-sensitized photoreaction of **1** under the conditions given in footnote a of Table 2, except for the concentration of **1f**; [**1f**] = 3.88 × 10^{-3} M. For simplicity, only selected plots are indicated in this figure: **1a**, ○; **1b**, ●; **1c**, □; **1d**, ■; **1e**, △; **1f**, ▲. The solid lines show the linear relationships between the amount of **1** consumed and irradiation time.

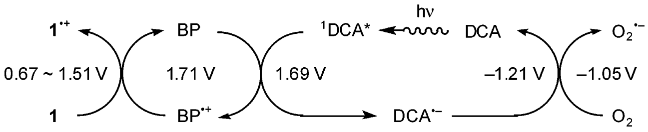
TABLE 3. Photoreaction of 1 in the Presence of DCA and BP in MeCN[a]

run	phosphine **1**	[**1**] (10^2 M)	atmosphere	slope[b] (10^5 mol in 1 L s^{-1})	quantum yield (Φ_{cons})[c]
1	**1a**	2.00	air	5.96	0.034
2	**1a**	1.00	air	5.78	0.033
3	**1a**	0.341	air	5.45	0.031
4	**1a**[d]	1.00	air	4.90	0.028
5	**1a**[e]	1.00	air	5.92	0.034
6	**1a**[f]	1.00	air	7.35	0.042
7	**1a**	1.00	O_2	16.2	0.092
8	**1a**[g]	1.00	air	0.466	0.0026
9	**1a**[h]	1.00	air	no reaction	
10	**1a**	1.00	Ar	no reaction	
11	**1b**	1.00	air	9.02	0.051
12	**1c**	1.00	air	16.2	0.092
13	**1d**	1.00	air	12.0	0.068
14	**1e**	1.00	air	3.26	0.019
15	**1f**[i]	0.388	air	1.67	0.0095

[a] Carried out under the conditions given in footnote a of Table 2, unless otherwise indicated. [b] Slope of the plot of the amount of **1** consumed versus time; see the text. [c] Estimated by assuming that the intensity of the incident light is 1.76 × 10^{-6} einstein s^{-1} cm^{-2} at 420 nm. [d] [DCA] = 2.50 × 10^{-5} M. [e] [DCA] = 1.00 × 10^{-4} M. [f] [BP] = 5.10 × 10^{-2} M. [g] In the absence of BP. [h] In the absence of DCA. [i] Poor solubility of **1f** in MeCN did not allow the reaction under standard conditions.

The Φ_{cons} value was nearly constant irrespective of the initial concentration of **1** (runs 1–3). Differences in the concentrations of BP and DCA exerted only a small effect on Φ_{cons} (runs 4–6). No reaction took place in the absence of DCA (run 9). Meanwhile, the conversion of **1** to **2** was observed even in the absence of BP, although the reaction was much slower than the reaction in the presence of BP (run 8). The reaction under O_2 atmosphere was faster than the reaction in air (run 7). Practically, no reaction took place under the argon atmosphere (run 10). With either an electron-withdrawing substituent (*p*-Cl) or electron-releasing substituents (*p*-Me and *p*-MeO) on the phenyl rings of **1**, Φ_{cons} increased (runs 11–13). Meanwhile, in the reactions of tris(*o*-tolyl)phosphine (**1e**) and trimesitylphosphine (**1f**), the Φ_{cons} values were smaller than those predicted from the electronic effect of the methyl substituents (runs 14 and 15).

SCHEME 2



Discussion

Photocatalytic Cycle. The photoreaction is certainly initiated by the excitation of DCA to ^{1}DCA*. The electron transfer from BP to ^{1}DCA* takes place to give the radical cation of BP ($BP^{•+}$) and the radical anion of DCA ($DCA^{•-}$). This process is followed by an electron transfer (ET) from **1** to $BP^{•+}$ (i.e., hole transfer from $BP^{•+}$ to **1**), giving $\mathbf{1}^{•+}$ and BP. Only a catalytic amount of DCA is necessary for the conversion of **1** to **2** to be completed. That is, DCA acts as a catalyst in the photooxidation reaction. Most likely, O_2 regenerates DCA by oxidizing $DCA^{•-}$ to drive the catalytic cycle as shown in Scheme 2. Comparing the potentials of the pertinent compounds, each process is found to be feasible.[15]

Reaction of $\mathbf{1}^{•+}$ with O_2. Taking into account the fact that the MeCN solvent used in this study cannot be absolutely “dry”,[17] $\mathbf{1}^{•+}$ could react with water. The ionic reaction of $\mathbf{1}^{•+}$ with water is a major process for the decay of $\mathbf{1}^{•+}$ in aqueous MeCN under an argon atmosphere.[6] The reaction would initially afford the phosphoranyl radical $Ar_3P^{•}$-OH which would easily react with O_2 to give a peroxy radical $Ar_3P(OH)$-O-$O^{•}$ under the aerobic conditions.[18] This type of peroxy radical, namely, a radical bearing a hydroxyl group on the phosphorus atom, undergoes a chain reaction, where the hydroxyl radical is the chain carrier.[7] This is not the case in the present photoreaction because no reaction occurred when the reaction mixture was kept in the dark after irradiation.

As seen in Table 1, results of the laser flash photolysis experiments show that the decay rate of $\mathbf{1}^{•+}$ was faster in air than in argon. Figure 1 indeed shows a linear relationship of the decay rate constant of $\mathbf{1c}^{•+}$ with the concentration of O_2, although only three data points are available. This observation suggests that $\mathbf{1}^{•+}$ bimolecularly reacts with O_2. This mechanism predicts a pseudo-first-order kinetics for the decay of $\mathbf{1}^{•+}$ under our conditions, and this is indeed the case. Alternatively, $\mathbf{1}^{•+}$ could undergo radical coupling with the superoxide radical anion $O_2^{•-}$ generated by the electron transfer from $DCA^{•-}$ to O_2 (Scheme 2).[19,20] However, if $\mathbf{1}^{•+}$ decays according to this mechanism, the decay would follow the second-order

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(15) The oxidation or reduction potentials of DCA, ^{1}DCA*, and BP were taken from ref 6. The reduction potential of O_2 was reported in ref 16. All values were adjusted to half-wave potentials vs Ag/Ag^+ in V.

(16) Fukuzumi, S.; Patz, M.; Suenobu, T.; Kuwahara, Y.; Itoh, S. *J. Am. Chem. Soc.* **1999**, *121*, 1605–1606.

(17) Acetonitrile was refluxed over calcium hydride for at least 10 h and distilled. The solvent purified in this way still contains about 0.1% water. See, Yasui, S.; Shioji, K.; Ohno, A.; Yoshihara, M. *Chem. Lett.* **1993**, 1393–1396.

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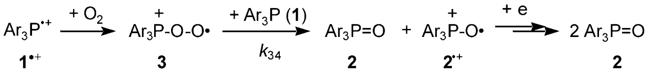
(20) Somasundaram, N.; Srinvasan, C. *J. Org. Chem.* **1996**, *61*, 2895–2896.

kinetics,[19c] which is opposite the observation. The mechanism is incompatible with the first-order kinetics even by assuming that a much higher concentration of $O_2^{\bullet-}$ than that of **1**$^{\bullet+}$ provides pseudo-first-order conditions. Thus, taking into account the fact that the concentration of $O_2^{\bullet-}$ is lower than the initial concentration of DCA (5×10^{-5} M), the pseudo-first-order rate constant is predicted to be $<10^5$ s^{-1} when the second-order rate constant is diffusion-limited. This value is not consistent with the observed pseudo-first-order rate constants, 10^5-10^6 s^{-1} (Table 1). The discussion here eliminates the possibility of radical coupling between **1**$^{\bullet+}$ and $O_2^{\bullet-}$.

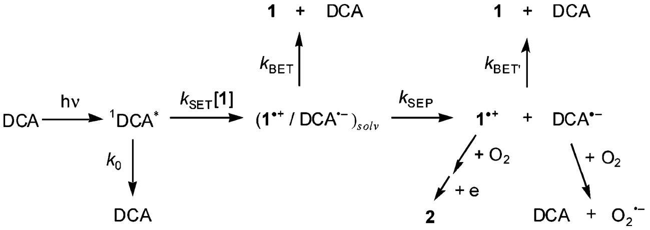
There is a possibility that the reaction of **1** with singlet oxygen $^1O_2$ affords **2**, since it has been reported that $^1O_2$ is generated in the DCA-sensitized photoreaction.[21] Phosphine reacts with $^1O_2$, when it is available, to give the corresponding phosphine oxide.[22-24] The pseudo-first-order rate constant of the formation of $^1O_2$ in oxygen-saturated MeCN in the presence of DCA has been reported to be 5.45×10^7 s^{-1}.[21b] Apparently, the rate constant for the reaction in air is about one-fifth, i.e., about 1×10^7 s^{-1}. This value is significantly smaller than the pseudo-first-order rate constant for the electron-transfer quenching of ^{1}DCA* by BP; this value is estimated to be 6.1×10^7 s^{-1} under the aerobic conditions where $[O_2] = 8.1 \times 10^{-3}$ M.[25] This means that the DCA-mediated formation of $^1O_2$ cannot compete with the electron-transfer quenching of ^{1}DCA* by BP. In fact, we have observed DCA$^{\bullet-}$ during the laser flash photolysis. In addition, crowded triarylphosphine, such as tris(*o*-methoxy)phosphine, gives a considerable amount of aryl triarylphosphinate (ArO−P(=O)Ar$_2$) upon the reaction with $^1O_2$ in an aprotic solvent,[24] whereas in the reactions of the crowded arylphosphines, **1e** and **1f**, phosphinate was not detected in the present study. Therefore, the participation of $^1O_2$ into the present reactions is very unlikely.

In conclusion, **1**$^{\bullet+}$ undergoes a radical coupling with O_2 under aerobic conditions, showing the reactivity as a radical. In support of this mechanism, the yield of **2f** from **1f** was much smaller compared with the other cases (Table 3). That is, the reactivity of **1f**$^{\bullet+}$ with two *o*-methyl groups at each aryl group is much lower than those of the other **1**$^{\bullet+}$. It has been shown that aryl groups with bulky ortho substituents flatten the tetrahedral geometry to a pyramidal geometry of **1**$^{\bullet+}$, making the spin on the central phosphorus atom more delocalized into the aryl groups.[26] Such flattening may occur in **1f**$^{\bullet+}$ and make **1f**$^{\bullet+}$ less reactive toward O_2 than the other **1**$^{\bullet+}$. Interestingly, such a steric effect is seen even with only one *o*-methyl group at each aryl group, since the yield of **2e** from **1e** was slightly smaller than those from **1a**−**d** (Table 3). On the other hand, the decay rate of **1e**$^{\bullet+}$ determined from the laser flash photolysis is comparable to those of the other **1**$^{\bullet+}$ (Table 1). The steric effect by *o*-methyl groups in **1e** may be operative in a step other than the reaction of **1e**$^{\bullet+}$ with O_2 to lower the yield of **2e**.[27]

SCHEME 3



SCHEME 4



Most likely, the reaction of **1**$^{\bullet+}$ with O_2 affords **3**, which well explains the formation of **2**, although no specific absorption was observed for the intermediacy of **3**. Another molecule of **1** may attack **3** to give **2** and **2**$^{\bullet+}$. The radical cation **2**$^{\bullet+}$ eventually reacts with DCA$^{\bullet-}$ and/or $O_2^{\bullet-}$ to give **2** (Scheme 3). A similar mechanism has been presented for the γ-radiolysis of **1** in air-saturated CH_2Cl_2, where the initially generated **1**$^{\bullet+}$ eventually gives **2** via an intermediate **3**.[14] In that study, the sequential hole transfer from **2**$^{\bullet+}$ to **1** that produces **1**$^{\bullet+}$, which results in a chain mechanism, has been proposed to explain the efficient formation of **2**. On the other hand, under the present experimental condition, the concentration of BP is much higher than **1**, and therefore **2**$^{\bullet+}$ is quenched by BP and the positive charge developed on BP disappears through a charge recombination with DCA$^{\bullet-}$ and/or $O_2^{\bullet-}$. The reaction mechanism is summarized as in Schemes 3 and 4.

Interestingly, Φ_{cons} was not dependent on the concentrations of DCA and BP in the range of the present experimental conditions, indicating the rapid operation of the catalytic cycle shown in Scheme 2. Thus, ^{1}DCA* and BP$^{\bullet+}$ are at the photostationary concentrations and determined by the number of photons in the incident light, at least during the early stage of the reaction.

Comparison of the Reactivity of 1$^{\bullet+}$ with Those of Other Radical Cations. We have shown that the *cis*-stilbene radical cation generated during pulse radiolysis in 1,2-dichloroethane undergoes either isomerization to the trans isomer or radical coupling with O_2.[28] Dichotomy in the reactivity of this radical cation has been interpreted in the term of its distonic structure; thus, the charge-spin separation is responsible for the radical character of the radical cation. It is usually accepted that trivalent phosphorus radical cations are not distonic but

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(25) In the absence of BP, ^{1}DCA* is quenched by **1** with the first-order rate constant of $(1.2-1.7) \times 10^8$ s^{-1}, which was independently determined by the Stern−Volmer analysis.

(26) Culcasi, M.; Berchadsky, Y.; Gronchi, G.; Tordo, P. *J. Org. Chem.* **1991**, *56*, 3537−3542.

(27) Although no experimental data are available, we are tempted to speculate that the peroxy radical **3** attacks the phosphine **1** to give the phosphoranyl radical with TBP geometry. This step would be subjected to a steric effect by the ortho substituent since the C−P−C angle becomes smaller.

(28) Tojo, S.; Morishima, K.; Ishida, A.; Majima, T.; Takamuku, S. *J. Org. Chem.* **1995**, *60*, 4684−4685.

conventional.[29] It is suggested that the unpaired spin is highly localized on the central phosphorus atom.

The reactivity of $\mathbf{1}^{\bullet+}$ is compared with that of the amine counterpart. Although many reports have been presented on aliphatic and aromatic amine radical cations, there is no report that amine radical cations undergo radical coupling.[30–32] One reason is that the amine radical cations have a structure much more flattened than the phosphine radical cations.[30] That is, the spin in the amine radical cations is more delocalized into the aryl rings. An ab initio calculation for the triphenylamine radical cation predicts that the unpaired electron is 59% localized on the amine nitrogen atom,[31] which can be compared with the observation that about 85% of the unpaired electron is localized on the phosphorus atom in $\mathbf{1}^{\bullet+}$ of the single crystals.[33]

Conclusions

The photooxidation of **1** was studied in the presence of DCA as a sensitizer and BP as a co-sensitizer in “dry” acetonitrile under aerobic conditions. Phosphine **1** converted to the corresponding **2** without any appreciable side reactions. Examining the substituent effects on the total efficiency of the reaction and on the decay rate of $\mathbf{1}^{\bullet+}$, based on the product analysis and laser flash photolysis, respectively, we showed that $\mathbf{1}^{\bullet+}$ undergoes radical coupling with O_2.

Experimental Section

Instruments. Laser flash photolysis measurements were performed using the third harmonic generation (355 nm, 5 ns full width at half-maximum, 6 mJ/pulse) from a Q-switched Nd^{3+}:YAG laser for the excitation operated with temporal control by a delay generator. The reflected analyzing light from a pulsed 450-W Xe-arc lamp was collected by a focusing lens and directed through a grating monochromator to a photomultiplier tube. The transient signals were observed upon the pulse excitation of DCA (ca. 5×10^{-5} M) in the presence of 0.1 M biphenyl in MeCN and recorded with a digitizer.

Materials. Phosphines **1a**–**e** and biphenyl (BP) were commercially available and purified by recrystallization from ethanol. Trimesitylphosphine (**1f**) was prepared by a conventional Grignard method based on a literature procedure.[26] 9,10-Dicyanoanthracene (DCA) was purchased and purified by recrystallization from benzene.

General Procedure. The solution of **1** (1.00×10^{-2} M), BP (1.00×10^{-1} M), and DCA (5.00×10^{-5} M) in 2 mL of MeCN was prepared in a square quartz cell (1 cm × 1 cm) in air and irradiated with light from a xenon arc short lamp through a sharp-cut filter (irradiation at $\lambda > 390$ nm). At intervals, a 50-μL aliquot was taken and diluted with 25 μL of MeCN involving benzyl ether (for **1a**,**d**,**e**) or hydroquinone dibenzyl ether (for **1b**,**c**,**f**) as an external standard, and the resulting mixture was analyzed by GC.

Laser Flash Photolysis. The solution of **1** (1.00×10^{-2} M), BP (1.00×10^{-1} M), and DCA (5.00×10^{-5} M) in MeCN was photolyzed in air. The decay of the resulting absorption was monitored at 525 nm.

Quantum yield $\Phi_{\mathbf{cons}}$. The intensity of the incident light at 420 nm was assumed to be 1.76×10^{-6} einstein s^{-1} cm^{-2} on the basis of the measurement at 450 nm in a previous study.[8] Meanwhile, the area where the light was applied to the reaction vessel (a square cell) was 2 cm^2. The number of photons being received by the reaction mixture was then 3.52 $\times 10^{-6}$ einstein s^{-1}. Comparing this number with the amount of **1** consumed per second (mol s^{-1}) upon irradiation, Φ_{cons} was then calculated.

JO049032L

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