Atmosphere-controlled Dual Reactivity of Triarylphosphine in the Photoexcited State: P-C Bond Cleavage vs. Electron Transfer

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(Received August 12, 2013; CL-130748; E-mail: yasui@tezukayama-u.ac.jp)

Steady-state photolysis of an acetonitrile solution of triarylphosphine (Ar₃P) was carried out using a xenon lamp. The major products resulting from photolysis under deoxy-genated conditions and under air were diaryl(cyanomethyl)-phosphine Ar₂PCH₂CN and triarylphosphine oxide Ar₃P=O, respectively. Intrinsically, Ar₃P in the excited state undergoes homolytic cleavage of a P–C bond; however, electron transfer to O₂ is predominant under air. Reactivity of Ar₃P in the excited state is readily controlled by the choice of atmosphere used in the reaction.

Triarylphosphines (Ar₃P) are a class of conventional organic reagents, which exhibit absorption bands around 250-350 nm due to an $n \to \pi^*$ transition. This suggests that the activation of Ar₃P by photoexcitation may be a useful strategy in the field of organic synthesis. In order to be able to use Ar₃P as an organic reagent under irradiation, it is essential to understand its photochemical behavior. In our previous work on laser flash photolysis time-resolved infrared spectroscopy (LFP-TRIR) of Ar₃P, we found that Ar₃P, when photoexcited under air, undergoes electron transfer (ET) to oxygen O₂, generating the radical cation $Ar_2P^{+,1}$ On the other hand, it has been reported that UV laser flash of Ar₃P under completely oxygen-free conditions results in homolytic cleavage of a P-C bond to form the diarylphosphinyl radical Ar₂P[•] and aryl radical Ar[•].² We now know through these studies that, depending on the atmosphere, different transient intermediates are formed initially upon irradiation. In the present study, we carried out steady-state photolysis on tris(2-methylphenyl)phosphine (1a), tris(4-methylphenyl)phosphine (1b), and tris(2,4,6-trimethylphenyl)phosphine (1c) with varying wavelengths of irradiating light and under different atmospheres, and the products were analyzed by gas-chromatography (GC) and ³¹P NMR spectroscopy (Scheme 1). A unique compound, diaryl(cyanomethyl)phosphine, was obtained in substantial yield under "deoxygenated" conditions, without a rigorous degassing process.

An Ushio xenon short arc lamp (UXL-500D-0) was used as the source of light. Wavelength of the irradiating light was controlled by a Toshiba sharp-cut glass filter that was put between the lamp and reaction vessel. The progress of the reaction was followed by GC with a Shimadzu GC14A. In some cases, ³¹P NMR spectra were recorded on a Varian INOVA400 operating at 161.9 MHz (85% phosphoric acid as the reference standard (0.0 ppm)) to follow the reaction.

When an acetonitrile solution of 1 (1.0 mM) was photolyzed under air, the corresponding phosphine oxide 2 was detected along with 1 in GC experiments. The yields of 2 as well as recovered 1 with varying wavelengths of irradiating light are

	c in the absence of O ₂				
Ar ₃ P Xe lamp 1 in CH ₃ CN	Ar ₂ PCH ₂ C 3 (major)	CN + Ar ₂ P-PAr ₂ + ot 6 (minor)	hers		
1a; Ar = 2-methylphenyl	in the presence of O ₂				
1b ; Ar = 4-methylphenyl	Ar ₃ P=O	+ Ar ₂ P-PAr ₂			
1c; Ar = 2,4,6-trimethylphen	yl 2	6			
	(major)	(small amount)			

Scheme 1. Photolysis of triarylphosphines under deoxygenated conditons and under air.

Table 1. Photoreaction of triarylphosphines Ar₃P 1^a

Dun 1		Irradiated at	Atmograhara	Time	Yield/% ^b		
Kull I	1	/nm	Aunosphere	/min	1 ^c	2	3
1	1a	>310 (3.20) ^d	air	10	4	68	0
2		$>350 (1.48)^{d}$	air	60	76	15	0
3		$>310 (3.20)^d$	argon ^e	45	0	7	$> 29^{f}$
4		$>350 (1.48)^d$	argon ^e	180	81	15	0
5	1b	$>310 (2.80)^{d}$	air	20	6	69	0
6		$>350 (1.69)^d$	air	60	80	20	0
7		$>310 (2.80)^{d}$	argon ^e	180	10	16	$>26^{f}$
8	1c	$>310 (4.16)^{d}$	air	2	0	46	0
9		$>350 (3.37)^d$	air	10	2	58	0
10		$>390 (1.26)^d$	air	60	19	67	0
11		>420 (—) ^g	air	90	89	6	0
12 ^h		$>310 (4.16)^d$	argon ^e	7	0	5	53 (50) ⁱ
13		>420 (—) ^g	argon ^e	60	88	5	0

^aIn acetonitrile. At room temperature. $[1] = 1.0 \times 10^{-3} \text{ M}$. ^bDetermined on GC based on the initial amount of 1. ^cRecovered. ^dThe values in parentheses denote the logarithm of the extinction coefficient (M⁻¹ cm⁻¹) of the shortest wavelength of the irradiating light. ^eThe system may contain a trace amount of O₂; see the text. ^fBased on an assumption that the factor of GC analysis for **3** is larger than that for **1**. The assumption holds for **3c**. ^gNo absorption observed. ^hMesitylene **5c** (92%) was detected. ⁱIsolate yield after 20 min irradiation.

summarized in Table 1. To eliminate the effects of O_2 , the photolysis of 1 (1.0 mM in acetonitrile) was carried out under deoxygenated conditions, where air was replaced with as much argon as possible. GC analysis of the reaction mixture showed a major peak at a retention time slightly less than that of 1, along with a small peak corresponding to 2.³ To identify this product, GCMS analysis was performed with a JEOL JMS-GC mate II for each photolyzed solution. The fragments obtained are listed

Table 2. Fragments resulting from the major product formed in the photolysis of 1a-1c in acetonitrile under deoxygenated conditions^a

	m/z				
	1a	1b	1c		
Fragment 1	253 [255]	253 [255]	309 [311]		
Fragment 2	238 [240]		294 ^b [296]		
Fragment 3	213 ^b [213]	213 ^b [213]	269 [269]		

^aValues in brackets denote m/z values of the fragments obtained in the photolysis in acetonitrile- d_3 , ^bBase peak.

in Table 2, where fragments 1, 2, and 3 are assignable to Ar₂PCH₂CN, Ar₂PCH₂CN-15, and Ar₂P, respectively, for each derivative. For photolysis carried out in acetonitrile- d_3 under otherwise identical conditions, GCMS gave fragments that are expected to result from Ar₂PCD₂CN (shown in brackets in Table 2). With these results from GCMS analyses, the product was assigned to diaryl(cyanomethyl)phosphine Ar₂PCH₂CN 3. This assignment is further supported by spectroscopic characterization of the material isolated from the photolysis of 1c.⁴ Thus, the ¹H and ¹³CNMR spectra of the isolated material are compatible with the structure of 3c,⁵ and the ³¹P NMR chemical shift (-23.1 ppm) also supports the structure of **3c**, a compound containing a trivalent phosphorus.⁶ The IR spectra (recorded on a JASCO FT/IR-4200) of a carbon tetrachloride solution of the material (0.06 mM) exhibit a characteristic absorption band of C-N stretching at 2243 cm⁻¹. The IR spectrum over the entire measured range is in excellent agreement with the spectrum theoretically simulated for 3c based on DFT B3LYP/6-31G(d) (Figure 1).⁷ To summarize these results, the photolysis of 1 in acetonitrile under deoxygenated conditions affords 3 as a major product. The yields of 3 as well as 2 are given in Table 1. Besides 3 and 2, GCMS analysis of 1c, photolysed under deoxygenated conditions, showed a tiny peak with a shorter retention time. Its mass spectrum $(m/z \ 105, \ 135, \ 150 \ (base))$. 255, and 270) was in accordance with the structure of bis(2,4,6trimethylphenyl)phosphine Mes₂PH (4c). Mesitylene MesH (5c) was also detected in GC experiments in 92% yield. The photolysis of 1c in hexane under deoxygenated conditions did not form 3c; however, a tiny peak corresponding to 4c was observed in GC experiments.

The sum of the yields of 2 and 3 is smaller than the conversion of 1 either under air or under deoxygenated conditions (Table 1). To detect product(s) that were undetectable in GC experiments, ³¹P NMR spectroscopy was used to analyze the photolysis of 1c in acetonitrile- d_3 . The spectrum obtained after a 2-min irradiation with light of wavelengths over 310 nm under deoxygenated conditions, displayed signals resonating at -24.7 and -29.5 ppm, along with a small signal from 1c at -35.6 ppm. The signal at -24.7 ppm, which resonates at slightly upper field than that from the isolated 3c, i.e., a hydrogen analogue (-23.1 ppm), most likely results from $3c-d_2$ (Mes_2PCD_2CN) ⁸ The signal at -29.5 ppm is assignable to 1,1,2,2-tetrakis(2,4,6-trimethylphenyl)diphosphine Mes₂PPMes₂ (6c) based on the value of the chemical shift reported in literature.9-11 The spectrum obtained on photolysis for 1 min under air displayed a weak signal corresponding to 6c besides an intense signal from 2c. Product 6c, which is undetectable on our



Figure 1. IR spectra of Mes_2PCH_2CN (3c). Lower (in black); Observed on a FT-IR spectrometer measured in carbon tetrachloride (0.04 mM). Upper (in gray); Simulated based on DFT B3LYP/6-31G(d) with a scaling factor 0.9892. See ref 7.

GC apparatus, accounts for the discrepancy between the sum of the yields of 2 and 3 and the conversion yields of 1.

Table 1 lists the extinction coefficient ε at the shortest wavelength of the irradiating light. Clearly, the stronger the absorption of 1, the higher the conversion of 1, which clearly indicates that reactions leading to the observed products are initiated by the photoexcitation of 1 to its singlet excited state ¹1^{*}.¹² Intersystem crossing to the triplet state could take place under some circumstances. It is more likely that ${}^{1}1^{*}$ directly undergoes subsequent reactions, because the system under consideration in the present study does not have a triplet sensitizer. Under deoxygenated conditions, 11^* can undergo homolytic P-C bond cleavage, as has been reported,² to form the radical pair, Ar₂P' and Ar'. Nearly quantitative formation of mesitylene 5c in the reaction of 1c (Run 12 in Table 1) strongly suggests generation of Ar, which would readily abstract a hydrogen atom from the solvent CH₃CN to give 5c as well as the cyanomethyl radical 'CH₂CN (eq 1).

$$Ar^{\bullet} + CH_3CN \longrightarrow ArH + {}^{\bullet}CH_2CN$$
 (1)

An almost theoretical amount of MesD (mesitylene- d_1) was obtained when photolysis was carried out in CD₃CN. Radicals 'CH₂CN and Ar₂P', if formed, explain the observed products. Thus, they couple with each other to afford 3, while dimerization of Ar₂P' forms 6. A small amount of 4 results from hydrogen abstraction from the solvent molecule by Ar₂P[•] (Scheme 2). An alternate possibility is that 'CH₂CN and Ar₂P' attack the parent Ar₃P 1, which exists in large amounts, resulting in the formation of phosphoranyl radicals 7 and 8, respectively. These radicals would afford 3 (eq 2) and 6 (eq 3), respectively, by ejecting Ar. However, theoretical calculations based on DFT B3LYP/6-31G(d) predict extremely congested and unstable structures of 7 and 8, especially when Ar = mesityl. In addition, while the reactions in eqs 2 and 3 predict a catalytic character in producing 3 and 6, this is not the case. When the irradiation was switched off, the progress of the reaction was found to be halted.

$$CH_2CN + Ar_3P$$
 $H = \begin{bmatrix} Ar_3PCH_2CN \end{bmatrix} \xrightarrow{-Ar^*} 3 (2)$

$$Ar_2P^{\bullet} + Ar_3P \not // [Ar_2P \cdot PAr_3] \xrightarrow{} 6 \quad (3)$$



Scheme 2. Reaction of ${}^{1}1^{*}$ under deoxygenated conditions.

The singlet excited state, ¹1*, if formed under air, may undergo ET to molecular oxygen O2, generating the radical cation Ar₃P^{•+} 1^{•+} and superoxide radical anion O₂^{•-}. Taking oxidation potentials of 1 in the ground state¹³ together with the excitation energy of 1 into consideration, oxidation potentials of ${}^{1}\mathbf{1}^{*}$ are predicted to be between -4 and -3 V vs. Ag/Ag⁺. These values are much more negative than the reduction potential of O_2 (-1.05 V vs. Ag/Ag⁺),¹⁴ indicating that ET from ${}^{1}\mathbf{1}^{*}$ to O₂ is exothermic. The resulting radical cation $\mathbf{1}^{+}$ is trapped by O_2 to give the peroxidic radical cation $Ar_3P^+OO^{\bullet}$ as a transient intermediate, which eventually affords phosphine oxide 2 (eq 4).¹ That is, the formation of 2 is explained by the radical cation intermediate 1'+. This mechanism predicts the production of O2'-, which was indeed suggested by an experiment using the spin trap agent, 2-diphenylphosphinoyl-2methyl-3,4-dihydro-2H-pyrrole N-oxide (DPhPMPO). When a solution of 1c in dimethyl sulfoxide (DMSO) was photolyzed at 365 nm with bubbling O2 in the presence of DPhPMPO for 3 min, the DPhPMPO- O_2^{-} adduct was detected by ESR spectroscopy on a JEOL RE ESR spectrometer.¹⁵ ³¹P NMR spectroscopy has confirmed the formation of a small amount of 6c from the photolysis of 1c under air as well, which suggests that ¹1* undergoes P-C bond cleavage in competition with ET to O₂ under air. Interestingly, it has been reported that nitrogen counterparts, aromatic amines such as N,N-dimethylanilines, also undergo ET to O2 under photochemical conditions to give the radical pair, aniline radical cation and $O_2^{-.16}$

$$0_2 \quad 0_2^{\bullet}$$

 $1^{\bullet} \quad 1^{\bullet+} \quad + \quad 0_2 \quad + \quad 0_2^{\bullet} \quad 2 \quad (4)$

In summary, this study disclosed the dual reactivity of Ar₃P 1 in the excited state, most likely the singlet state 1^{1} , exerted depending on the atmosphere. Intrinsically, ¹1* cleaves at a P-C bond homolytically into Ar₂P' and Ar', which afford products **3–6.** Meanwhile, ${}^{1}\mathbf{1}^{*}$ undergoes ET to O₂ in the ground state when O_2 is present. The ET results in formation of the radical cation 1^{+} , which eventually leads to phosphine oxide 2. This study also showed that the number and the position of methyl substituents on the aryl ligands exert only little effect on the reactivity of ${}^{1}1^{*}$. It is worth pointing out that the photolysis of 1 in acetonitrile under deoxygenated conditions affords the unique compound 3. This class of phosphines may be useful in coordination chemistry, where there is a demand for electronically and sterically tuned ligands. Cyanomethylphosphines have been previously prepared through the reduction of cyanomethylphosphine oxides, which were obtained by the Arbuzov attack

of phosphinites on ClCH₂CN,¹⁷ or through the reaction of chlorophosphines with LiCH₂CN.¹⁸ Compared with these methods, the method of photolysis is quite simple. It is a one-pot and apparently one-step reaction without any additives. No rigorous degassing process is required to obtain **3** in practical yields even though some phosphine is wasted by its oxidation to phosphine oxide.

Further studies on using laser flash photolysis to reveal a whole scheme of photoreactions of Ar_3P , with an attempt to specify multiplicity of the active species, is underway.

This study was financially supported by a Tezukayama research grant 2012.

References and Notes

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- 3 For photolysis under deoxygenated conditions, solvent was bubbled with argon for several hours to degas oxygen from the solvent, and air in each vessel was carefully replaced by argon. Nevertheless, formation of a small amount of **2** in the photolysis under these conditions indicates that the system was more or less contaminated by O_2 . Argon gas used in this work may contain a trace amount of O_2 . Or, we may have failed to get rid of O_2 from the system completely.
- 4 Trimesitylphosphine (1c) was photolyzed for 20 min under deoxygenated conditions in several repeated experiments (54 mg in total), and the combined reaction mixture was subjected to column chromatography using a mixture of dichloromethane-hexane (1:1 (v/v)) as eluent, which gave 20 mg of white powder (50% as 3c).
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