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Convenient Synthetic Method of Functional Phosphines under Photochemical Conditions

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Keywords

Functional phosphine; triarylphosphine; steady-state photolysis

Abstract

Steady-state photolysis of triarylphosphines, Ar_3P , under an argon atmosphere in a solvent with the structure CH_3X (X = CN, $COOC_2H_5$, $COCH_3$) afforded an adduct with the solvent molecule, Ar_2PCH_2X , in significant amount. This photoreaction is acknowledged as a convenient method to prepare functional phosphines.

Graphical Abstract

 $\begin{array}{c} \text{Ar}_{3}\text{P} & \xrightarrow{\text{hv} (> 310 \text{ nm})} \\ \hline \text{in CH}_{3}\text{X under argon} \\ \hline \text{Ar} \\ \hline \hline \text{o-Tolyl} \\ p\text{-Tolyl} \\ \text{Mesityl} \end{array} \qquad \begin{array}{c} \text{Ar}_{2}\text{PCH}_{2}\text{X} \\ X = \text{CN, COOEt, COMe} \\ \end{array}$

Introduction

Functional phosphines, which have substituent(s) involving heteroatom(s), not only act as monodentate ligands through either the phosphine atom or another heteroatom, but also act as bidentate or multidentate ligands.¹ In addition, these phosphines can connect two transition metals to form a binuclear complex. Recently, we found that the steady-state photolysis of triarylphosphine, Ar_3P , under an argon atmosphere in acetonitrile (MeCN), ethyl acetate (MeCOOEt), or acetone (MeCOMe) affords an adduct with the solvent molecule, Ar_2PCH_2X (X = CN, COOC₂H₅, and COCH₃, respectively), in significant amounts (Scheme 1).² Thus, this photoreaction gives functional phosphines swiftly, cleanly, and safely, without using expensive reagents. This is much more advantageous than previously reported routes, which are tedious and require the use of toxic reagents.^{3,4}



Scheme 1 Steady-state photolysis of triarylphosphines under an argon atmosphere.

Results and Discussion

The solution of triarylphosphine, Ar₃P (**1**), was photolyzed by an Ushio xenon short arc UXL-500D-0 lamp (> 310 nm with a glass filter) under an argon atmosphere. The reaction mixture was analyzed by gas-chromatography mass-spectroscopy (GCMS) using a JEOL JMS-GC mate II spectrometer, which showed the formation of an adduct, Ar₂PCH₂X (X = CN (**2**), C(=O)OC₂H₅ (**3**), and C(=O)CH₃ (**4**) from the photolysis in MeCN, MeCOOEt, and MeCOMe, respectively), and arene, ArH (**5**), along with a trace amount of diarylphosphine, Ar₂PH (**6**).⁵ The photolysis of the MeCN-d₃ solution of trimesitylphosphine, Mes₃P (**1c**), was followed by ³¹P NMR spectroscopy using a Bruker BioSpin AVANCE-III instrument. The formation of tetramesityldiphosphine, Mes₂P-PMes₂ (**7c**), was observed in the spectrum, along with **2c** and **6c**. Table 1 lists the yields of the products from the photolysis of **1a-c** in MeCN. The reactivity of **1a-c** depends on the efficiency in absorbing the irradiating light. Difference in the extinction coefficients ε of **1a-c** at 310 nm (see Table 1) explains well the observed order of the reaction rate, **1b** < **1a** < **1c**.

 Table 1. Steady-state photolysis of triarylphosphines, Ar₃P (1), in MeCN under argon atmosphere^{a)}

	Ar ₃ P			Time		Yield /	Yield / % ^{b)}		
entry	(1)	Ar	$\log \varepsilon (310)^{c)}$	/ min	1 ^{d)}	2	5	7	
1	1a	<i>o</i> -tolyl	3.20	45	0	>29 (2a)	e)	f)	
2	1b	<i>p</i> -tolyl	2.80	180	10 (1b)	>26 (2b)	e)	f)	
3	1c ^{g)}	mesityl	4.16	7	0	53 [46] ^{h)} (2c)	92 (5c)	$[22]^{h}$ (7c)	

^{a)} Data from Ref. 5. Light with wavelengths of > 310 nm was irradiated. At room temperature. [**1**] = 1.0×10^{-3} M. ^{b)} Determined by GC based on the initial amount of **1** unless otherwise indicated. ^{c)} Logarithm of the extinction coefficient ε at 310 nm. ^{d)} Recovered. ^{e)} Not determined. ^{f)} Not detected on GC. ^{g)} A trace amount of **6c** was observed. ^{h)} The values in brackets indicate the isolated yield after a 20-min irradiation.

The photolysis of **1** in MeCN, MeCOOEt, or MeCOMe was also performed on a larger scale to isolate the products. A solution of **1** (10 mL) in a quartz test tube was irradiated by light from a xenon lamp under an argon atmosphere. The experiments were repeated 5 times to obtain a sufficient amount of the material for the subsequent workups and analyses. When the photolysis of **1** was performed in MeCN, the combined reaction mixture was concentrated *in vacuo*, and the residue was subjected to column chromatography using a mixture of dichloromethane and hexane (1:1 (v/v)) as the eluent. The photolysis of **1c** (53.5 mg 0.134 mmol) gave **2c** (20 mg, 46 %) as a white powder and **7c** (8 mg, 22 %) as a white solid. The isolation of **3c** failed due to its high volatility. Full characterization of the isolated **2c** and **7c** by ¹H, ¹³C, and ³¹P NMR spectroscopy, elemental analysis, and IR spectroscopy has been reported in a previous

paper.² The photolysis of **1a** (55.6 mg, 0.183 mmol) in MeCN resulted in the isolation of only 6 % of **2a**, probably due to the facile oxidation of **2a** to the corresponding phosphine oxide during the isolation procedure.

In the photolysis in MeCOOEt or MeCOMe, the products were so air-sensitive that they were readily oxidized to the corresponding phosphine oxide during the isolation procedure. We then added S_8 powder immediately after the completion of the photolysis to convert the phosphine moieties in the products to stable phosphine. sulfides. The excess of S_8 was filtered off, and the combined solution was concentrated and subjected to column chromatography. The isolated products were identified by ¹H, ¹³C, and ³¹P NMR spectroscopy, as well as by high-resolution mass spectrometry (HRMS) to be the phosphine sulfides $Mes_2P(-S)CH_2C(=O)OEt$ (3cS) and $Mes_2P(=S)CH_2C(=O)Me$ (4cS) from the photolysis of 1c in MeCOOEt and in MeCOMe, respectively. The IR spectra of these products recorded with a JASCO FT/IR-4200 instrument using a KRS-5 cell (0.01 cm) were consistent with the spectra simulated for 3cS and 4cS, based on DFT B3LYP/6-31G(d) calculations, respectively. Figure 1 shows the observed and simulated IR spectra of 3cS and 4cS. The isolated yields are listed in Table 2. The results demonstrate the existence of $Mes_2PCH_2C(=O)OEt$ (3c) and $Mes_2PCH_2C(=O)Me$ (4c) in the reaction mixture from the photolysis in MeCOOEt and in MeCOMe, respectively.



Figure 1a IR spectra of **3cS**. Lower (in black); Observed by FT-IR spectrometer in CCl₄ (0.04 mM). Upper (in grey); Simulated based on DFT B3LYP/6-31G(d) calculations with the scaling factor of 0.9613. See Ref. 6.



Figure 1b IR spectra of **4cS**. Lower (in black); Observed by FT-IR spectrometer in CCl₄ (0.04 mM). Upper (in grey); Simulated based on DFT B3LYP/6-31G(d) calculations with the scaling factor of 0.9613. See Ref. 6.

entry	Solvent; CH ₃ X	Starting 1c	Time	Mes ₂ P(=Y)CH ₂ X	H ₂ X Isolated					
	[/ mL] ^{b)}	x	/ mg ^{c)}	/ min ^{d)}		Yield / %				
1 ^{e)}	MeCN [60]	CN	53.5	7	2c ^{g)}	46				
20	MeCOOEt [50]	C(=O)OEt	52.9	60	$3cS^{h)}$	17				
30	MeCOMe [52]	C(=O)Me	54.4	60	4cS ^{h)}	46				

Table 2Steady-state photolysis of 1c under argon atmosphere^{a)}

^{a)} At room temperature. $[1] = (2.3 \sim 2.8) \times 10^{-3}$ M. ^{b)} Numbers in brackets denote the total amount of the solvent of five experiments in mL. ^{c)} Total amount of **1c** of five experiments in mg. The amount of the starting **1c** and the solvent in each experiment are listed below. See also footnote b). for **2c**; 11.47 mg (13 mL), 10.35 (11), 10.66 (12), 10.47 (12), 10.56 (12). For **3cS**; 10.51 (10), 10.41 (10), 10.54 (10), 10.99 (10), 10.41 (10). For **4cS**; 11.67 (12), 10.45 (10), 10.70 (10), 10.58 (10), 11.00 (10). ^{d)} Reaction

time for five experiments. ^{e)} Data from Table 1. ^{f)} S_8 powder was added after the photolysis. ^{g)} Y = lone pair. ^{h)} Y = S.

Regarding the mechanism of the reaction, the triarylphosphine **1** is excited under the present photochemical conditions to its singlet excited state, ${}^{1}\mathbf{1}^{*}$, which (or its triplet state ${}^{3}\mathbf{1}^{*}$ after intersystem crossing) would undergo homolytic cleavage of the P-C bond in Ar₃P to afford the aryl radical, Ar•, and the diarylphosphinyl radical, Ar₂P•. The former abstracts a hydrogen atom in the solvent molecule, CH₃X, to give the radical, •CH₂X, as well the arene, ArH (**5**). The radical coupling of Ar₂P• with •CH₂X yields Ar₂PCH₂X (**2-4**) (Scheme 2). This mechanism is supported by the results from the photolysis of **1c** in acetonitrile-*d*₃, in which mesitylene-*d* (ArD, Ar = mesityl) was formed in place of ArH. Generation of **6** and **7** also supports this mechanism.



Scheme 2 Photoreaction of 1 under oxygen free conditions.

Conclusions

We report in this study that the steady-state photolysis of triarylphosphine under anaerobic conditions is a convenient method to prepare functional phosphines. By varying the solvent, we can obtain a variety of functional phosphines with nitrogen and oxygen atoms in the substituents. Attempts are now underway to prepare functional phosphines with multi-functional groups using acetylacetone and diethyl malonate as the solvent and phosphines with halogen functional groups using chloroform as the solvent.

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