DOI: 10.1002/hc.21468

### SPECIAL ISSUE: A TRIBUTE TO PROFESSOR NAOMICHI FURUKAWA ON THE OCCASION OF HIS 82ND BIRTHDAY - BY INVITATION ONLY

# A new method to prepare functional phosphines through steadystate photolysis of triarylphosphines\*

## Shinro Yasui<sup>1</sup>

| Taro Ando<sup>2</sup> | Masashi Ozaki<sup>2</sup> | Yuya Ogawa<sup>2</sup> | Kosei Shioji<sup>2</sup>

<sup>1</sup>Institute of Human and Environmental Sciences, Tezukayama University, Nara, Japan

<sup>2</sup>Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka, Japan

#### Correspondence

Shinro Yasui, Institute of Human and Environmental Sciences, Tezukayama University, Nara, Japan. Email: yasui@tezukayama-u.ac.jp

#### Abstract

The steady-state photolysis of triarylphosphine, Ar<sub>3</sub>P, was carried out using a xenon lamp or a high-pressure mercury lamp under an argon atmosphere in a solvent containing a functional group, CH<sub>2</sub>X. Gas chromatograph-mass spectroscopic analysis on the photolysis showed that a phosphine to which the functional group from the solvent is incorporated, Ar<sub>2</sub>PCH<sub>2</sub>X, was formed in a moderate yield, along with tetraaryldiphosphine, Ar<sub>2</sub>PPAr<sub>2</sub>. The product, Ar<sub>2</sub>PCH<sub>2</sub>CN, from the photolysis in acetonitrile (X=CN) was isolated by column chromatography. In the photolysis in solvents other tried here (ethyl acetate, acetone, 2-butanone, and 3,3-dimethyl-2-butanone), Ar<sub>2</sub>PCH<sub>2</sub>X formed in the reaction mixture was so labile on a silica-gel column that it was treated with S<sub>8</sub> powder to convert to the corresponding phosphine sulfide,  $Ar_2P(=S)CH_2X$ . The resulting phosphine sulfide was isolated by column chromatography. The isolated products in these reactions, Ar<sub>2</sub>PCH<sub>2</sub>CN and Ar<sub>2</sub>P(=S)CH<sub>2</sub>X, were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy, IR spectroscopy, and elemental analysis or high-resolution mass spectroscopy. The formation of Ar<sub>2</sub>PCH<sub>2</sub>X as well as Ar<sub>2</sub>PPAr<sub>2</sub> is explained by homolytic cleavage of a P-C bond of Ar<sub>3</sub>P in the photoexcited state. This reactivity of Ar<sub>3</sub>P in the photoexcited state is in sharp contrast to that exerted under aerobic conditions, where Ar<sub>3</sub>P in the photoexcited state donates readily an electron to oxygen producing the radical cation,  $Ar_3P^+$ . This photoreaction, which affords a functional phosphine, Ar<sub>2</sub>PCH<sub>2</sub>X, in one-pot with generating very small amounts of unidentified side products, has potential for use in preparing functional phosphines.

#### 1 INTRODUCTION

In the chemistry of organic synthesis, photolysis is a powerful option, which could bring about reactions that cannot occur in the dark. We have been studying nonsensitized photolysis of phosphines expecting that phosphines, when photoexcited, may exert novel reactivity.<sup>[1-2]</sup> Through steady-state photolysis and laser flash photolysis, we found that phosphine-bearing chromophores, such as triarylphosphine, Ar<sub>3</sub>P, are directly photoexcited to its singlet excited state, <sup>1</sup>Ar<sub>3</sub>P\*, which undergoes various reactions depending on the conditions. Under aerobic conditions, <sup>1</sup>Ar<sub>3</sub>P\* undergoes electron transfer to oxygen in the ground state, generating the phosphine radical cation, Ar<sub>3</sub>P<sup>+</sup>. The resulting radical cation, Ar<sub>3</sub>P<sup>+</sup>, undergoes an ionic reaction and a radical reaction competitively.<sup>[1c]</sup> Another interesting finding is that homolytic cleavage of a P-C bond in <sup>1</sup>Ar<sub>3</sub>P\*

Dedicated to 82nd birthday of Professor Naomichi Furukawa.

<sup>\*</sup>Steady-state photolysis of triarylphosphine under anaerobic conditions results in homolytic cleavage of a P-C bond, the resulting radicals affording a phosphine to which a functional group from a solvent is incorporated.



**SCHEME 1** Steady-state photolysis of **1** in MeCN under an argon atmosphere

takes place under anaerobic conditions to afford diarylphosphanyl radical,  $Ar_2P_2$ , and aryl radical,  $Ar_2$ .<sup>[2]</sup> In fact, when we carried out the steady-photolysis of Ar<sub>3</sub>P in acetonitrile (MeCN) under an argon atmosphere, we found the formation of the products resulting from Ar<sub>2</sub>P, namely, diaryl(cyanomethyl)phosphine, Ar<sub>2</sub>PCH<sub>2</sub>CN, and tetraaryldiphosphine, Ar<sub>2</sub>PPAr<sub>2</sub>. In this reaction, Ar picks up an α-hydrogen in the MeCN molecule to give cyanomethyl radical, ·CH<sub>2</sub>CN, and arene, ArH. The former radical couples with Ar<sub>2</sub>P· to afford Ar<sub>2</sub>PCH<sub>2</sub>CN. Anticipating that a similar photoreaction would take place in other solvents as well, we photolyzed Ar<sub>3</sub>P in a solvent containing a functional group, CH<sub>3</sub>X, namely, ethyl acetate, acetone, 2-butanone, and 3,3-dimethyl-2-butanone. As expected, we found the formation of Ar<sub>2</sub>PCH<sub>2</sub>X in the photolysis of Ar<sub>3</sub>P under an argon atmosphere in these solvents.<sup>[3]</sup>

Phosphines we obtained here,  $Ar_2PCH_2X$  (X=CN, (C=O) R, (C=O)OR), belong to a family of functional phosphines. These phosphines are important in coordination chemistry because they can tune reactivity of a transition metal complex by coordinating to a transition metal in several ways.<sup>[4]</sup> In this paper, we present the results from the photolysis of  $Ar_3P$  under an argon atmosphere in several solvents. We discuss possibility in using this photoreaction for preparation of functional phosphines.

#### YASUI ET AL.

#### 2 | RESULTS AND DISCUSSION

# **2.1** | Steady-state photolysis of triarylphosphine (1) in acetonitrile

We studied previously the photolysis of triarylphosphine, Ar<sub>2</sub>P (1a; Ar = 2-tolyl, 1b; Ar = 4-tolyl, 1c; Ar = mesityl), using a xenon lamp under an argon atmosphere at room temperature in acetonitrile (MeCN) (Scheme 1).<sup>[2]</sup> Analysis by gas chromatography (GC) and gas chromatograph-mass spectroscopy (GCMS) showed the formation of diaryl(cyanomethyl)phosphine (2a-c). The formation of mesitylene (MesH; 3c; 92%) was also shown by GCMS in the photolysis of 1c. An involatile product, tetraaryldiphosphine, Ar<sub>2</sub>PPAr<sub>2</sub> (4a (-37.7 ppm)) or 4c (-29.4 ppm)),<sup>[5,6]</sup> was detected by <sup>31</sup>P NMR spectroscopy in the photolysis of **1a** or **1c** in MeCN- $d_3$ , along with **2a**- $d_2$  (-35.1 ppm) or **2c**- $d_2$  (-24.7 ppm). The products **2** and 4 were isolated and characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy as well as IR spectroscopy. Table 1 summarizes the yields of 2 determined by GC in the photolysis under various reaction conditions. The yield of 2 depends on the wavelengths of the irradiating light. The more the light absorbed by 1, the higher the yield of 2.

The photolysis of **1c** was also performed using a xenon lamp under an argon atmosphere in ethyl acetate (AcOEt) and acetone (MeCOMe). The GCMS analysis of the reaction mixture strongly suggested the formation of dimesityl(carboethoxymethyl)phosphine,  $Mes_2PCH_2C(=O)OEt$  (**5c**), and dimesityl(acetylmethyl)phosphine,  $Mes_2PCH_2C(=O)$ Me (**6c**), respectively. However, an attempt to isolate these products by column chromatography failed. Probably, **5c** and **6c** were too sensitive to oxidation to remain intact on the silica-gel column. We then converted the product to the stable phosphine sulfide before isolation by treating with S<sub>8</sub> powder (see Section 4). The resulting phosphine sulfide,  $Mes_2P(=S)CH_2C(=O)OEt$  (**5cS**) or  $Mes_2P(=S)CH_2C(=O)$ 

					Yield (%	6)5	
Entry	$Ar_{3}P(1)$	Ar	Irradiated at (nm)	Time (min)	1 <sup>c</sup>	2	Ar <sub>3</sub> P=O <sup>d</sup>
1	1a	2-Tolyl	$>310(3.20)^{\rm e}$	45	0	>29 [6] <sup>f</sup>	7
2	1b	4-Tolyl	$>310 (2.80)^{\rm e}$	180	10	>26	16
3			$>350 (1.69)^{\rm e}$	60	77	0	5
4	1c	Mesityl	>310 (4.16) <sup>e</sup>	7	0	53 [46] <sup>g</sup>	5
5			>420 (—) <sup>h</sup>	60	88	0	5

**TABLE 1** GC analysis of photolysis of  $Ar_3P(1)$  by a xenon lamp<sup>a</sup>

<sup>a</sup>At room temperature. [1] =  $1.0 \times 10^{-3}$  mol/L. Data from Ref.<sup>[2b]</sup>

<sup>b</sup>Determined by GC based on the initial amount of **1** unless otherwise indicated. <sup>c</sup>Recovered.

<sup>d</sup>The system may be contaminated by a trace amount of O<sub>2</sub>.

<sup>c</sup>The values in parentheses denote loge, where  $\varepsilon$  is the extinction coefficient (mol L<sup>-1</sup> cm<sup>-1</sup>) of the shortest wavelength of the irradiating light.

<sup>f</sup>The values in brackets denote isolated yield after 180 min irradiation.

<sup>g</sup>The values in brackets denote isolated yield after 20 min irradiation.

<sup>h</sup>No absorption observed.

**FIGURE 1** IR spectra of Mes<sub>2</sub>P(=S)CH<sub>2</sub>C(=O)OEt (**5cS**). Lower (in black); Observed by FT-IR spectrometer in carbon tetrachloride (0.04 mmol/L). Upper (in gray); Simulated based on DFT B3LYP/6-31G(d) with the scaling factor of 0.9613. Ref.<sup>[7]</sup>



**FIGURE 2** IR spectra of Mes<sub>2</sub>P(=S)CH<sub>2</sub>C(=O)Me (**6cS**). Lower (in black); Observed by FT-IR spectrometer in carbon tetrachloride (0.04 mmol/L). Upper (in gray); Simulated based on DFT B3LYP/6-31G(d) with the scaling factor of 0.9613. Ref.<sup>[7]</sup>

Me (**6cS**), from the photolysis in AcOEt or in MeCOMe, respectively, was isolated by column chromatography. A small amount of **4c** was also isolated from each reaction mixture. The products **5cS** and **6cS** as well as **4c** were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy and high-resolution mass spectrometry. IR spectroscopy on **5cS** and **6cS** gave the spectra consistent with the spectra simulated based on DFT B3LYP/6-31G(d), as shown in Figures 1 and 2, respectively. Clearly, **5c** and **6c** are the precursors of **5cS** and **6cS** formed during the photolysis in AcOEt and in MeCOMe, respectively (Scheme 2).

The isolated yields of **5cS** and **6cS** are given in Table 2, which also reports the yield of **2c** from the photolysis in MeCN for the sake of comparison. During the photolysis, a small amount of **4c** precipitated due to its poor solubility into these solvents. The precipitates were mixed with  $S_8$  powder during the work-up and were removed through the filtration with  $S_8$  powder. Therefore, the isolated yield reported in the last column of Table 2 is lower than the yield of **4c** formed in situ.

# 2.2 | Photolysis by a high-pressure mercury lamp

The steady-state photolysis of **1c** under an argon atmosphere was carried out using a high-pressure mercury lamp (Hg lamp). The photolysis with an Hg lamp in MeCN, AcOEt, and Me(C=O)Me gave the same products as the photolysis with a xenon lamp. There were no big differences in their yields.

The photolysis under an argon atmosphere was performed in 2-butanone (methyl ethyl ketone; MEK), or 3,3-dimethyl-2-butanone (*tert*-butyl methyl ketone (pinacolone); BMK) by an Hg lamp (Entries 4 and 5 in Table 3, respectively). The products, dimesityl(but-2-one-3-yl)phosphine, Mes<sub>2</sub>PCH(CH<sub>3</sub>)C(=O)CH<sub>3</sub> (7c), and dimesityl(2,2dimethylbut-3-one-4-yl)phosphine, Mes<sub>2</sub>PCH<sub>2</sub>C(=O)Bu<sup>t</sup> (8c), respectively, were labile on the silica-gel column. Therefore, the corresponding phosphine sulfides, 7cS and 8cS, obtained by treatment with S<sub>8</sub>, were isolated, along with 4c, from the reactions in MEK and BMK, respectively



#### **TABLE 2** Photolysis of $Mes_3P(1c)$ by a xenon lamp<sup>a</sup>

Entry	Solvent; CH <sub>3</sub> X (mL) <sup>b</sup>	CH <sub>2</sub> X	1c ( <b>mg</b> ) <sup>c</sup>	Y	Mes <sub>2</sub> P(=Y)CH <sub>2</sub> X	Isolated yield (%)
$1^d$	MeCN [60] <sup>b</sup>	CH <sub>2</sub> CN	53.51	Lone pair	2c	46
2 <sup>e</sup>	AcOEt [50] <sup>b</sup>	CH <sub>2</sub> C(=O)OEt	52.86	S	5cS	17
3 <sup>e</sup>	MeCOMe [52] <sup>b</sup>	CH <sub>2</sub> C(=O)Me	54.40	S	6cS	46

<sup>a</sup>At room temperature under an argon atmosphere for 60 min.  $[1c] = (2.3 \sim 2.8) \times 10^{-3} \text{ mol/L}.$ 

<sup>b</sup>Numbers in brackets denote sum of the solvent in five experiments in mL.

<sup>c</sup>Sum of **1c** in five experiments in mg.

<sup>d</sup>Data from Entry 4 in Table 1.

<sup>e</sup>S<sub>8</sub> powder was added immediately after the photolysis.

(Scheme 2). Due to the precipitation of **4c** during the reaction, Table 3 reports a lower yield of **4c** than that in situ.

#### 2.3 | Regioselectivity of the photoreaction

In the photolysis in MEK, **7cS** was obtained exclusively (Table 3; Scheme 3), strongly suggesting that **7c** is an exclusive product during the photolysis in MEK. DFT calculations were done on energy of carbon-centered radicals resulting from hydrogen abstraction from MEK. As shown in Table 4, 2-butanon-3-yl radical (**13**) is the most stable among the possible radicals (**12~14**). The radical **13** is the most likely candidate to produce **7c**, where the 3-position carbon in MEK is attached to the phosphorus atom.

From the photolysis in BMK, **8cS** was isolated exclusively (Table 3; Scheme 3). The precursor, **8c**, is the product that would result from more stable radical  $\cdot$ CH<sub>2</sub>COC(CH<sub>3</sub>)<sub>3</sub> (Table 5). Interestingly, preference based on stability of the radical overcomes statistical factor in this case. The photolysis was carried out also in MeOH, where **9cS** was isolated upon the treatment with S<sub>8</sub> powder even though its yield is quite low (Entry 6 in Table 3; Scheme 3). Interestingly, the precursor **9c** is the product expected from the reaction with more stable hydroxymethyl radical  $\cdot$ CH<sub>2</sub>OH (Table 6). Mes<sub>2</sub>PH (**15c**) was a major product in the photolysis in MeOH. Ar<sub>2</sub>P· would pick up the hydrogen atom in the hydroxy group much more facilely than an  $\alpha$ -hydrogen, making only a small amount of  $\cdot$ CH<sub>2</sub>OH available for the radical coupling with Ar<sub>2</sub>P·.

In conclusion, the stability of the radicals resulting from a solvent molecule explains regioselectivity of the reaction, which supports the radical mechanism for the present photoreaction.

#### 2.4 | Mechanistic aspects

As shown in Table 1, the larger the light absorbed by 1, the higher the vield. Therefore, there is no doubt that the initial step of the present photoreaction is the photoexcitation of 1 to its singlet state, <sup>1</sup>1\*. This, directly or after intersystem crossing to its triplet state, <sup>3</sup>1\*, undergoes homolytic cleavage to produce diarylphosphanyl radical, Ar<sub>2</sub>P<sub>2</sub>, and aryl radical, Ar<sub>2</sub> (Equation 1).<sup>[2b]</sup> Homolytic cleavage of a P-C bond in a triarylphosphine has been reported to occur either from the singlet or the triplet state of the phosphine.<sup>[8]</sup> The aryl radical,  $Ar_{\cdot}$ , thus generated abstracts a hydrogen from the solvent CH<sub>3</sub>X to produce a radical  $\cdot$ CH<sub>2</sub>X as well as arene, ArH (3) (Equation 2). The radical ·CH<sub>2</sub>X would couple with Ar<sub>2</sub>P· to give Ar<sub>2</sub>PCH<sub>2</sub>X (Equation 3). Summarizing Equations 1-3, the mechanism is depicted as in Scheme 4.<sup>\*</sup> In support of this mechanism, the photolysis of trimesitylphosphine, 1c, in MeCN- $d_3$  gave mesitylene- $d_1$ , MesD, in a considerable amount, as revealed by GCMS analysis. In addition, this mechanism well explains the formation of **4** and diarylphosphine (Ar<sub>2</sub>PH, **15**).

$${}^{1}\mathrm{Ar}_{3}\mathrm{P}^{*} \longrightarrow \mathrm{Ar}_{2}\mathrm{P} \cdot + \mathrm{Ar} \cdot \tag{1}$$

<sup>\*</sup>We have determined the intensity of the incident light from our xenon lamp apparatus based on chemical actinometry. Taking into account this value, the quantum yield for production of **2c** from **1c** is roughly estimated to be  $10^{-3} \sim 10^{-2}$ . For details, see Ref.<sup>[2b]</sup>

**TABLE 3** Steady-state photolysis of 1c using a high-pressure Hg lamp<sup>a</sup>

				Yield (%) <sup>b</sup>	
Entry	Solvent	CH <sub>2</sub> X	Y	Mes <sub>2</sub> P(=Y)CH <sub>2</sub> X	$Mes_2PPMes_2 (4c)^c$
1	MeCN	CH <sub>2</sub> CN	Lone pair	27 ( <b>2c</b> )	20
2 <sup>d</sup>	AcOEt	$CH_2C(=O)OEt$	S	28 ( <b>5cS</b> )	31
3 <sup>d</sup>	MeCOMe	CH <sub>2</sub> C(=O)Me	S	47 ( <b>6cS</b> )	16
4 <sup>d</sup>	MeCOEt (MEK)	MeCHC(=O)Me	S	22 ( <b>7cS</b> )	20
5 <sup>d</sup>	MeCOBu <sup>t</sup> (BMK)	$CH_2C(=O)Bu^t$	S	15 ( <b>8cS</b> )	8
6 <sup>d</sup>	MeOH	CH <sub>2</sub> OH	S	5 <sup>e</sup> ( <b>9cS</b> )	13

<sup>a</sup>At room temperature. Irradiated by light from a high-pressure mercury lamp under an argon atmosphere for 120 min. [1c] =  $6.0 \times 10^{-3}$  mol/L. <sup>b</sup>Isolated vield.

<sup>c</sup>Some part of this material was lost with S<sub>8</sub> powder before the column chromatography. See the text.

<sup>d</sup>S<sub>8</sub> powder was added immediately after the photolysis.

<sup>e</sup>Mes<sub>2</sub>PH (15c) is obtained as a major product.



**SCHEME 3** Isolated products from the photolysis in MEK, BMK, and MeOH

$$Ar \cdot + CH_3 X \longrightarrow ArH(3) + \cdot CH_2 X$$
 (2)

$$\cdot CH_2 X + Ar_2 P \cdot \longrightarrow Ar_2 P CH_2 X \tag{3}$$

Concentrations of  $Ar_2P \cdot and \cdot CH_2X$  may be too low for these radicals to encounter each other to combine efficiently. It seems more plausible that  $\cdot CH_2X$  attacks predominantly upon the parent phosphine  $Ar_3P$  (Equation 4). According to this mechanism, phosphoranyl radical,  $Ar_3P \cdot CH_2X$ , is generated, which collapses to  $Ar_2PCH_2X$ , regenerating aryl radical  $Ar \cdot$  (Equation 4). The radical  $Ar \cdot acts$  to regenerate  $\cdot CH_2X$ according to Equation 2. In other words, this mechanism predicts a catalytic feature taking place in the dark, as depicted in Scheme 5. However, a control experiment showed that this is not the case. The reaction ceased upon the shutdown of the irradiation. Therefore, this mechanism is less likely.

$$\cdot CH_2X + Ar_3P \longrightarrow Ar_3P CH_2X \longrightarrow Ar_2P CH_2X + Ar \cdot (4)$$

#### 2.5 | The previously reported methods

(Cyanomethyl)phosphines,  $R_2CH_2CN$  (R = alkyl, aryl), have been prepared by several methods. One method uses the reaction of chlorophosphines with LiCH<sub>2</sub>CN.<sup>[9]</sup> This method is not applicable to preparation of a functional phosphine having an ester or a carbonyl group by using an ester or a ketone as a solvent, because butyl lithium, which is necessary for



**TABLE 4** Energy of radicals

 generated from MEK calculated based on
 DFT B3LYP/6-31+G(d,p)

**TABLE 5** Energy of radicals generated from CH<sub>3</sub>COC(CH<sub>3</sub>)<sub>3</sub> (BMK) calculated based on DFT B3LYP/6-31+G(d,p)

·CH <sub>2</sub> X	$\Delta G (kJ mol^{-1})$
$CH_3(C=O)C(CH_3)_2CH_2$	0
$\cdot CH_2(C=O)C(CH_3)_3$	-26.19543371

**TABLE 6** Energy of radicals generated from MeOH calculated based on DFT B3LYP/6-31+G(d,p)

·CH <sub>2</sub> X	$\Delta G (kJ mol^{-1})$
CH <sub>3</sub> O·	0
·CH <sub>2</sub> OH	-23.48137766

this method, promotes Claisen condensation of the former or Aldol reaction of the latter. The other papers have reported that  $R_2CH_2CN$  is prepared through reduction of (cyanomethyl)phosphine oxides obtained by the Arbuzov attack of phosphinites upon ClCH<sub>2</sub>CN.<sup>[10]</sup> For this method, use of an irritant reductant, diphenylsilane, may be disadvantageous.

#### 3 | CONCLUSION

We have shown that the steady-state photolysis of triaryphosphines in a proper solvent under an argon atmosphere affords functional phosphines. This is a one-pot reaction with giving very small amounts of unidentified side products. At this stage of the study, we are not in success in using this method for synthetic purpose mainly because the conditions have not been optimized to maximize the yields of the products. Deprotect of the sulfur atom in the phosphine sulfide is another problem to be overcome. Nevertheless, the finding that a conventional irradiation apparatus such as a xenon lamp or

$${}^{1}\operatorname{Ar}_{3}\operatorname{P}^{*} \longrightarrow \operatorname{Ar}_{2}\operatorname{P}_{\bullet} + \operatorname{Ar}_{\bullet}$$
(1)

$$Ar \bullet + CH_3 X \longrightarrow ArH(3) + \bullet CH_2 X (2)$$

•CH<sub>2</sub>X + Ar<sub>2</sub>P• 
$$\longrightarrow$$
 Ar<sub>2</sub>PCH<sub>2</sub>X (3)

Supposed mechanism of the photoreaction of 1



**SCHEME 4** 

under anaerobic

**SCHEME 5** Alternative mechanism of the photoreaction of **1** under anaerobic conditions

a high-pressure mercury lamp readily gives rise to homolytic cleavage of a P-C bond may provide a new protocol to obtain functional phosphines.

#### 4 | EXPERIMENTAL

#### 4.1 | General

Photolysis was performed by an Ushio xenon short arc UXL-500D-0 lamp and a 100 W high-pressure mercury lamp with a RIKO UVL-100P photochemical reactor.

Analysis by a GCMS was performed using a JEOL JMS-GC mate II spectrometer. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded by a Bruker BioSpin AVANCE-III against TMS (<sup>1</sup>H and <sup>13</sup>C) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). IR spectra were recorded on a JASCO FT/IR-4200 with a KRS-5 cell (0.01 cm).

NMR spectroscopy was performed on the acetonitrile- $d_3$  solution of **1a** or **1c** ( $2.0 \times 10^{-3}$  mol/L) prepared in a quartz NMR tube under an argon atmosphere. After the irradiation for 30 (**1a**) or 2 minutes (**1c**), <sup>1</sup>H and <sup>31</sup>P NMR spectra were measured.

DFT calculations were performed using the Gaussian 09, Revision A.02 program.<sup>[11]</sup> The IR spectra of **2c**, **5cS**, and **5cS** were simulated based on DFT B3LYP/6-31(G) level of theory. The total energy of the alkyl radicals was calculated based on DFT B3LYP/6-31+G(d,p) level of theory.

#### 4.2 | Photolysis in a large scale

A MeCN solution of **1c** in a quartz test tube was irradiated by light from a xenon lamp under an argon atmosphere. The experiments were repeated 5 times (**1c**; 11.47 mg (MeCN; 13 mL), 10.35 (11), 10.66 (12), 10.47 (12), 10.56 (12), 53.51 mg (0.134 mmol) in 60 mL in total). The combined

YASUI ET AL.



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 to give 2c (20 mg (46%)) as a white powder and 7c (8 mg (22%)) as a white solid. An AcOEt or MeCOMe solution of 1c was likewise irradiated under the same conditions for 60 minutes. Immediately after the completion of the photolysis,  $S_8$ powder (ca. 100 mg) was added into the reaction mixture, and the solution was stirred vigorously for several minutes. Residual S<sub>8</sub> powder was removed by filtration. The experiments were repeated 5 times for the photolysis in each solvent (In AcOEt; 1c; 10.51 mg (AcOEt; 10 mL), 10.41 (10), 10.54 (10), 10.99 (10), 10.41 (10), 52.86 mg (0.136 mmol) in 50 mL in total. In MeCOMe; 1c; 11.67 mg (MeCOMe; 12 mL), 10.45 (10), 10.70 (10), 10.58 (10), 11.00 (10), 54.40 mg (0.140 mmol) in 52 mL in total). For the photolysis in each solvent, the combined solution was concentrated in vacuo, and the residue was subjected to column chromatography using the same eluent as mentioned above to give 5cS (9 mg (17%)) as a while crystal from the photolysis in AcOEt and 6cS (23 mg (46%)) as a while crystal from the photolysis in MeCOMe.

#### 4.2.1 | Dimesityl(cyanomethyl)phosphine, Mes<sub>2</sub>PCH<sub>2</sub>CN (2c)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 6.86$  (d, 4H, J = 4.4 Hz, **ArH**),  $\delta = 3.80$  (d, 2H, J = 12.4 Hz, P-**CH<sub>2</sub>-**),  $\delta = 2.40$ (s, 12H, Ar-**CH**<sub>3</sub>),  $\delta = 2.27$  (s, 6H, Ar-**CH**<sub>3</sub>), <sup>31</sup>P NMR (161 MHz, CDCl<sub>3</sub>)  $\delta = -24.13$ , MS (EI<sup>+</sup>) *m/z*, Calcd for C<sub>20</sub>H<sub>24</sub>NP: 309.16; Found; 309.0957. Anal. Calcd. for C<sub>20</sub>H<sub>24</sub>NP: C, 77.64%, 7.82%, N, 4.53%, Found: C, 77.78%, H, 7.54%, N, 4.41%. mp. 124.3~126.0°C.

#### 4.2.2 | Dimesityl(carboethoxymethyl) phosphine sulfide, $Mes_2P(=S)CH_2C(=O)$ $OC_2H_5$ (5cS)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 6.80$  (d, 4H, J = 4.0 Hz, **ArH**),  $\delta = 3.91$  (d, 2H, J = 14.0 Hz, P-CH<sub>2</sub>-),  $\delta = 3.83$ (q, 2H, J = 7.2 Hz, O-CH<sub>2</sub>-),  $\delta = 2.39$  (s, 12H, Ar-CH<sub>3</sub>),  $\delta = 2.24$  (s, 6H, Ar-CH<sub>3</sub>),  $\delta = 1.03$  (t, 3H, J = 7.2 Hz, CH<sub>2</sub>-CH<sub>3</sub>), <sup>31</sup>P NMR (161 MHz, CDCl<sub>3</sub>)  $\delta = 35.39$ , MS (EI<sup>+</sup>) m/z, Calcd for C<sub>22</sub>H<sub>29</sub>O<sub>2</sub>PS: 388.16; Found; 388.

### 4.2.3 | Dimesityl(acetylmethyl)phosphine sulfide, Mes<sub>2</sub>P(=S)CH<sub>2</sub>C(=O)CH<sub>3</sub> (6cS)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 6.81$  (d, 4H, J = 4.0 Hz, **ArH**),  $\delta = 4.01$  (d, 2H, J = 14.8 Hz, P-**CH<sub>2</sub>-**),  $\delta = 2.39$  (s, 12H, Ar-**CH<sub>3</sub>**),  $\delta = 2.33$  (s, 3H, CO-**CH<sub>3</sub>**),  $\delta = 2.25$  (s, 6H, Ar-**CH<sub>3</sub>**), <sup>31</sup>P NMR (161 MHz, CDCl<sub>3</sub>)  $\delta = 32.31$ , MS (EI<sup>+</sup>) *m*/*z*, Calcd for C<sub>21</sub>H<sub>27</sub>OPS: 358.15; Found; 358.04.

### 4.2.4 | Dimesityl(but-2-one-3-yl)phosphine sulfide, Mes<sub>2</sub>P(=S)CH(CH<sub>3</sub>)C(=O)CH<sub>3</sub> (7cS)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 6.80$  (d, 2H, J = 4.4 Hz, **ArH**),  $\delta = 6.76$  (d, 2H, J = 4.0 Hz, **ArH**),  $\delta = 4.17$  (qui, 1H, J = 6.8 Hz, **CH**),  $\delta = 2.45$  (s, 6H, **ArCH**<sub>3</sub>),  $\delta = 2.33$  (s, 6H, **ArCH**<sub>3</sub>),  $\delta = 2.23$  (d, 6H, J = 4.8 Hz, **ArCH**<sub>3</sub>),  $\delta = 1.92$  (s, 3H, CO-**CH**<sub>3</sub>),  $\delta = 6.80$  (d, 2H, J = 4.4 Hz, **ArH**),  $\delta = 1.77$ (dd, 3H, J = 6.8, 12.8 Hz, CH-**CH**<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 204.92$ , 142.15, 142.05, 141.19, 141.16, 139.95, 139.92, 138.82, 138.72, 132.22, 132.11, 131.74, 52.75, 52.38, 28.33, 23.68, 23.27, 20.81, 20.69, 14.97, <sup>31</sup>P NMR (161 MHz, CDCl<sub>3</sub>)  $\delta = 43.14$ , MS (GC) *m/z*, Calcd for 372.17, found 372.

### 4.2.5 | Dimesityl(2,2-dimethylbut-3-one-4yl)phosphine sulfide, Mes<sub>2</sub>P(=S)CH<sub>2</sub>C(=O)Bu<sup>t</sup> (8cS)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 6.80$  (d, 4H, J = 4.0 Hz, **ArH**),  $\delta = 4.10$  (d, 2H, J = 12.8 Hz, **CH**<sub>2</sub>),  $\delta = 2.41$  (s, 12H, Ar-**CH**<sub>3</sub>),  $\delta = 2.24$  (s, 6H, Ar-**CH**<sub>3</sub>),  $\delta = 1.11$  (s, 9H, C-**CH**<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 207.42$ , 140.05, 139.95, 131.73, 131.29, 130.49, 47.11, 46.60, 45.54, 26.31, 23.53, 20.79, <sup>31</sup>P NMR (161 MHz, CDCl<sub>3</sub>)  $\delta = 34.61$ , MS (GC) *m/z*, Calcd for 400.20, found 400.

### 4.2.6 | Dimesityl(hydroxymethyl)phosphine sulfide, Mes<sub>2</sub>P(=S)CH<sub>2</sub>OH (9cS)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 6.82$  (d, 4H, J = 4.4 Hz, **ArH**),  $\delta = 3.60$  (d, 2H, J = 14.4 Hz, **CH**<sub>2</sub>),  $\delta = 2.40$  (s, 12H, Ar-**CH**<sub>3</sub>),  $\delta = 2.25$  (s, 6H, Ar-**CH**<sub>3</sub>), <sup>31</sup>P NMR (161 MHz, CDCl<sub>3</sub>)  $\delta = 83.96$ , MS (GC) *m/z*, Calcd for 332.13, found 332.

### **4.2.7** | Tetramesityldiphosphine, Mes<sub>2</sub>PPMes<sub>2</sub> (4c)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.18~2.39 (m, 36H, CH<sub>3</sub>), 6.63 (s, 4H, CH), 6.72~6.86 (m, 4H, CH), <sup>31</sup>P NMR (161 MHz, CDCl<sub>3</sub>):  $\delta$  -30.0.

#### ORCID

Shinro Yasui D https://orcid.org/0000-0002-8752-9227

#### REFERENCES

a) S. Yasui, S. Tojo, T. Majima, J. Org. Chem. 2005, 70, 1276; b)
 S. Yasui, S. Tojo, T. Majima, Org. Biomol. Chem. 2006, 4, 2969.
 c) S. Yasui, S. Kobayashi, M. Mishima, J. Phys. Org. Chem. 2016, 29, 443.
 d) S. Yasui, S. Kobayashi, M. Mishima, Phosphorus Sulfur Silicon 2016, 191, 1.

# WILEY-Heteroatom

- [2] a) S. Yasui, Y. Ogawa, K. Shioji, S. Yamazaki, *Chem. Lett.* 2013, 42, 1478. b) S. Yasui, Y. Ogawa, K. Shioji, M. Mishima, S. Yamazaki, *Bull. Chem. Soc. Jpn.* 2014, 87, 988.
- [3] S. Yasui, T. Ando, M. Ozaki, Y. Ogawa, K. Shioji, *Phosphorus Sulfur Silicon* 2018, 193, 481.
- [4] P. Braunstein, Chem. Rev. 2006, 106, 134.
- [5] H. H. Karsch, G. Hanika, B. Huber, J. Riede, G. Müller, J. Organometal Chem. 1989, 361, C25.
- [6] W. MacFarlane, N. H. Rees, L. Constanza, M. Patel, I. J. Colquhoun, J. Chem. Soc., Dalton Trans. 2000, 4453.
- [7] To adjust the calculated wavenumbers with the observed ones, the scaling factor 0.9613 was taken here. This value is reported to be valid for gas phase at this level of theory. J. B. Foresman, Æ. Frisch, in Exploring Chemistry with Electronic Structure Methods, 2nd ed. Gaussian, Inc., Pittsburgh, PA 1996, Chapter 4.
- [8] a) Y. Sakaguchi, H. Hayashi, *Chem. Phys. Lett.* **1995**, *245*, 591; b)
   Y. Sakaguchi, H. Hayashi, *J. Phys. Chem. A* **2004**, *108*, 3421.
- [9] R. Zhang, Y. Zhou, Synthesis 1987, 10, 938.
- [10] O. Dahl, F. K. Jensen, Acta Chem. Scand. B 1975, 29, 863.
- [11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F.

Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT **2009**.

#### SUPPORTING INFORMATION

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

How to cite this article: Yasui S, Ando T, Ozaki M, Ogawa Y, Shioji K. A new method to prepare functional phosphines through steady-state photolysis of triarylphosphines. *Heteroatom Chem.* 2018;e21468. https://doi.org/10.1002/hc.21468