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Transition Metal-free Phosphorylation of Vinyl Azides: A Convenient Synthesis of β-Ketophosphine Oxides

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In recent years, organophosphorus compounds have attracted considerable attention in medicinal chemistry and material science due to their chemical and biological properties.[1] They can be also used as synthetic intermediates in organic chemistry.[2] Among the various organophosphorus compounds available, β-ketophosphine oxides are highly valuable organic compounds that serve as versatile building blocks in organic synthesis[3] as well as potential ligands in various complexes due to their coordination property.[4] Therefore, the development of practical and efficient methods for their synthesis has been a subject of intensive research. In general, β-ketophosphine oxides are synthesized by the Arbuzov-type reactions of α-halogenated ketones[5] and the α-acylation of alkylphosphine oxides.[6] Various studies have reported on a number of methods based on the transition metal-catalyzed phosphorylation of alkenes[7] and their derivatives, such as cinnamic acids,[8] allyl alcohols,[9] cinnamyl/alkynylcarboxylates,[10] carbonyl compounds,[11] and alkynes.[12] Recently, Yu *et al.* reported on the Mn-catalyzed phosphonylation of vinyl azide with phosphine oxides to afford β-ketophosphine oxides (Scheme 1 (a)).[13] Despite the advancements described above, more mild and environmentally benign approaches for the synthesis of β-ketophosphine oxides are still highly desired. To the best of our knowledge, no study has investigated the transition metal-free oxidative coupling of vinyl azides with phosphine oxides. We thus envisioned the transformation of vinyl azides into β-ketophosphine oxides by the $K_2S_2O_8$-mediated phosphorylation with diphenylphosphine oxides as the phosphorus radical precursor (Scheme 1(b)).

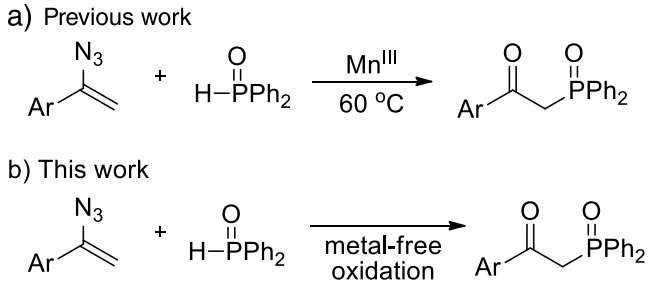
As part of our ongoing research program on the C–H bond activation,[14] we recently presented the radical-mediated functionalization of alkenes and aromatics.[15] Herein, we report on the transition metal-free oxidative phosphorylation of vinyl azides with phosphine oxides.

We began by investigating the transition metal-free phosphorylation of (1-azidovinyl)benzene (**1a**) and diphenylphosphine oxide (**2**) in the presence of $K_2S_2O_8$ in acetonitrile at 60 °C. Fortunately, the desired β-ketophosphine oxide **3a** was obtained in 82% yield (Table 1, entry 1). The results showed that several other oxidants could also be used, albeit with relatively low yields compared to $K_2S_2O_8$, such as $Na_2S_2O_8$, $(NH_4)_2S_2O_8$, *tert*-butyl hydrogen peroxide (TBHP), and $PhI(OAc)_2$. The reaction was further investigated in various solvents (Table 1, entries 1 and 6–11). Of these, acetonitrile was found to be the optimal solvent in this reaction (Table 1, entry 1). Next, we lowered the amount of oxidant to 1.5 equiv, and this led to an increased yield of β-ketophosphine oxide **3a** (Table 1, entry 13). However, a further decrease in the amount of oxidant to 1.0 equiv led to a decreased yield (Table 1, entry 14). No conversion was observed in the absence of $K_2S_2O_8$ as the oxidant (Table 1, entry 15). Finally, the reduction of the amount of **2** to 2.0 equiv resulted in a decrease in yield even at the extended reaction time (Table 1, entry 16).

After determining the optimized reaction conditions, we examined the substrate scope of vinyl azides **1** with diphenylphosphine oxide (**2**) (Table 2). The reactions of the (1-azidovinyl)benzene derivatives **1a–1g** with various substituents in the aryl group furnished the corresponding β-ketophosphine oxides **3a–3g** with 61–91% yields (Table 2). The heteroaryl-substituted vinyl azide **1h** provided the products with moderate yields (70%, Table 2, for **3h**). Alkyl-substituted vinyl azide was also examined. When 2-azidohex-1-ene was used as the substrate, corresponding β-ketophosphine oxide **3i** was obtained in 61% yield.

To demonstrate the practicality of the transition metal-free phosphorylation of vinyl azides, the gram-scale reaction was conducted under optimized reaction conditions. As shown in Scheme 2, the reaction of (1-azidovinyl)benzene (**1a**) with diphenylphosphine oxide under the optimized reaction conditions (**2**) afforded the desired β-ketophosphine oxide **3a** with 82% yield.

To further elucidate the reaction mechanism, some controlled experiments were conducted. The results showed that the absence of $K_2S_2O_8$ completely shut down the reactivity (Table 1, entry 15). A trace of the product was detected in the presence of 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) as a radical scavenger (Table 1, entry 17). This indicates that radical intermediates may be involved in this pathway. Based on our preliminary results as well as previous literature, we propose the plausible reaction pathway shown in Figure 1.[16] Initially, phosphinous acid **A** reacted with $K_2S_2O_8$ to generate radical cation **B** via a single-electron transfer process. Following deprotonation, phosphinoyl radical **C** is formed, which



Scheme 1. Strategy for phosphorylation of vinyl azides.

undergoes an addition with vinyl azides **1** to furnish iminyl radical intermediate **D**. Radical **D** is reduced to afford anions **E**. Protonation and hydrolysis leads to the yield of the β-ketophosphine oxides **3**.

In conclusion, we have developed a practical synthetic method for the preparation of β-ketophosphine oxide derivatives from the reaction between vinyl azide derivatives and diphenylphosphine oxides under transition metal-free conditions. The results presented here show that this protocol is a practical and convenient method for the preparation of β-ketophosphine oxide derivatives using $K_2S_2O_8$ as the sole oxidant.

Experimental

General Procedure for the Synthesis of β-Ketophosphine Oxide Derivatives. An oven-dried flask was equipped with a magnetic stir bar, (1-azidovinyl)arene **1**[17] (0.1 mmol) diphenylphosphine oxide **2** (0.3 mmol), $K_2S_2O_8$ (1.9 mg, 0.15 mmol), and acetonitrile (1 mL). The reaction mixture was then stirred for 8–20 h at 60 °C. Upon completion of the reaction, the mixture was concentrated in vacuum and purified by chromatography on silica gel (ethyl acetate: *n*-hexane = 2:1) to afford the β-ketophosphine oxides **3**.[10–13]

2-(Diphenylphosphoryl)-1-phenylethanone (3a)**.** Yield: 85%; white solid; m.p. 136–138 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.83–7.78 (m, 4H), 7.54–7.42 (m, 9H), 4.15 (d, *J* = 15.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.8 (d, *J* = 5.7 Hz), 137.0, 133.6, 132.2 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 103 Hz), 131.1 (d, *J* = 9.5 Hz), 129.3, 128.6 (d, *J* = 12.4 Hz), 128.5, 43.4 (d, *J* = 57.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): *δ* 27.5; EI-MS: *m/z* = 320.1 [M^+].

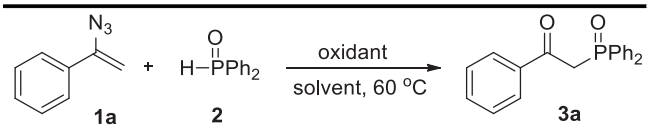
2-(Diphenylphosphoryl)-1-(*p*-tolyl)ethenone (3b)**.** Yield: 91%; white solid; m.p. 140–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.83–7.78 (m, 4H), 7.56–7.44 (m, 6H), 7.21 (d, *J* = 7.6 Hz, 2H), 4.13 (d, *J* = 14.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3 (d, *J* = 5.8 Hz), 144.6134.5, 132.1 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 103 Hz), 131.1 (d, *J* = 9.6 Hz), 129.4, 129.2, 128.6 (d, *J* = 11.4 Hz), 43.2 (d, *J* = 58.2 Hz), 21.7; ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 28.0; EI-MS: *m/z* = 334.1 [M^+].

2-(Diphenylphosphoryl)-1-(4-fluorophenyl)ethenone (3c)**.** Yield: 82%; white solid; m.p. 156–158 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07–8.02 (m, 2H), 7.82–7.77 (m, 4H), 7.56–7.45 (m, 6H), 7.11–7.07 (m, 2H), 4.11 (d, *J* = 15.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.2 (d, *J* = 5.7 Hz), 166.1 (d, *J* = 254.5 Hz), 133.4, 132.3 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 10.5 Hz), 131.7 (d, *J* = 102.1 Hz), 131.1 (d, *J* = 9.6 Hz), 128.7 (d, *J* = 12.4 Hz), 115.7 (d, *J* = 21.9 Hz), 43.6 (d, *J* = 56.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.3; ^{19}F NMR (376 MHz, CDCl): δ −104.0; EI-MS: *m/z* = 338.1 [M^+].

1-(4-Chlorophenyl)-2-(diphenylphosphoryl)ethenone (3d)**.** Yield: 83%; white solid; m.p. 160–163 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.82–7.77 (m, 4H), 7.56–7.47 (m, 6H), 7.40 (d, *J* = 8.8 Hz, 2H), 4.11 (d, *J* = 14.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.7 (d, *J* = 5.7 Hz), 140.3, 135.2, 132.3 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 103 Hz), 131.0 (d, *J* = 9.6 Hz), 130.8, 128.9, 128.7 (d, *J* = 11.4 Hz), 43.6 (d, *J* = 56.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.3; EI-MS: *m/z* = 354.1 [M^+].

1-(4-Bromophenyl)-2-(diphenylphosphoryl)ethenone (3e)**.** Yield: 80%; white solid; m.p. 149–152 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.82–7.77 (m, 4H), 7.58–7.42 (m, 8H), 4.11 (d, *J* = 15.2 Hz, 2H); ^{13}C

Table 1. Optimization of the reaction conditions.[a]

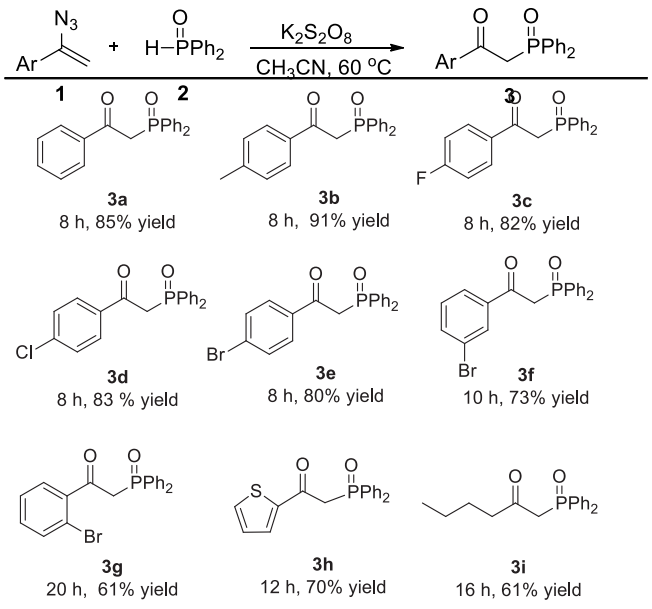


1a 2 3a

Entry	Oxidant	Solvent	Time (h)	Yield (%)[b]
1	$K_2S_2O_8$	CH_3CN	8	82
2	$Na_2S_2O_8$	CH_3CN	8	74
3	$(NH_4)_2S_2O_8$	CH_3CN	8	78
4	TBHP	CH_3CN	8	5
5	$PhI(OAc)_2$	CH_3CN	8	8
6	$K_2S_2O_8$	DMSO	12	73
7	$K_2S_2O_8$	DMF	12	73
8	$K_2S_2O_8$	EtOH	12	68
9[c]	$K_2S_2O_8$	CH_2Cl_2	12	35
10	$K_2S_2O_8$	DCE	12	61
11	$K_2S_2O_8$	PhMe	12	49
12[d]	$K_2S_2O_8$	CH_3CN	8	83
13[e]	$K_2S_2O_8$	CH_3CN	8	85
14[f]	$K_2S_2O_8$	CH_3CN	8	71
15	—	CH_3CN	8	0
16[g]	$K_2S_2O_8$	CH_3CN	15	70
17[h]	$K_2S_2O_8$	CH_3CN	8	trace

[a] Reaction conditions: (1-azidovinyl)benzene (**1a**, 0.1 mmol), diphenylphosphine oxide **2** (0.3 mmol), oxidant (0.3 mmol), solvent (1 mL), room temperature.
[b] Isolated yield.
[c] At 40 °C.
[d] 2.0 equiv of $K_2S_2O_8$ was added.
[e] 1.5 equiv of $K_2S_2O_8$ was added.
[f] 1.0 equiv of $K_2S_2O_8$ was added.
[g] 2.0 equiv of **2** was loaded.
[h] Reaction performed in the presence of TEMPO (5 equiv).

Table 2. Substrate scope.[a,b]

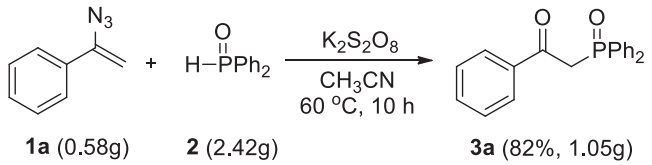


[a] Reaction conditions: vinyl azides **1** (0.1 mmol), diphenylphosphine oxide **2** (0.3 mmol), $K_2S_2O_8$ (0.15 mmol), acetonitrile (1 mL) at 60 °C.
[b] Isolated yield.

NMR ($CDCl_3$, 100 MHz): δ 191.9 (d, *J* = 5.7 Hz), 135.6, 132.3 (d, *J* = 1.9 Hz), 131.8, 131.6 (d, *J* = 105.9 Hz), 131.1 (d, *J* = 9.5 Hz), 130.8, 129.1, 128.7 (d, *J* = 12.4 Hz), 43.6 (d, *J* = 56.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.4; EI-MS: *m/z* = 398.0 [M^+].

1-(3-Bromophenyl)-2-(diphenylphosphoryl)ethenone (3f)**.** Yield: 73%; white solid; m.p. 144–147 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (t, *J* = 1.6 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.82–7.77 (m, 4H), 7.67–7.64 (m, 1H), 7.57–7.45 (m, 6H), 7.30 (t, *J* = 8.0 Hz, 1H), 4.12 (d, *J* = 15.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.6 (d, *J* = 5.8 Hz), 138.6, 136.4, 132.3 (d, *J* = 1.9 Hz), 131.9, 131.7 (d, *J* = 103.9 Hz), 131.1 (d, *J* = 10.5 Hz), 130.1, 128.7 (d, *J* = 12.4 Hz), 128.1, 122.9, 43.5 (d, *J* = 57.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.2; EI-MS: *m/z* = 398.0 [M^+].

1-(2-Bromophenyl)-2-(diphenylphosphoryl)ethenone (3g)**.** Yield: 61%; white solid; m.p. 149–151 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81–7.75 (m, 4H), 7.56–7.44 (m, 8H), 7.31–7.21 (m, 2H), 4.24 (d, *J* = 14.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.6 (d, *J* = 5.7 Hz), 141.0,



Scheme 2. Gram scale synthesis of **3a**.

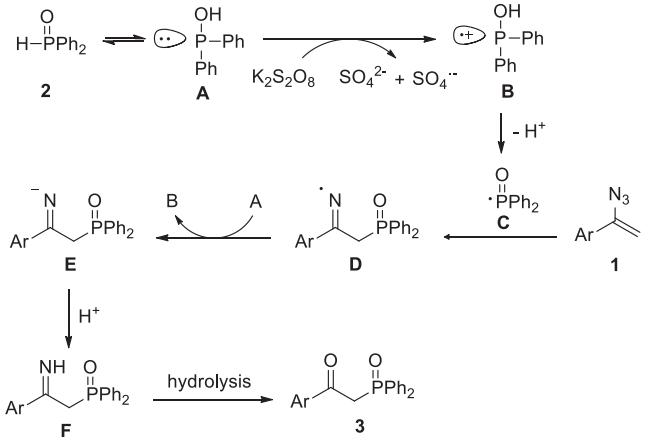


Figure 1. Plausible reaction mechanism.

133.4, 132.2 (d, *J* = 2.9 Hz), 132.1, 131.8 (d, *J* = 103 Hz), 131.1 (d, *J* = 9.5 Hz), 129.9, 128.7 (d, *J* = 12.4 Hz), 127.5, 118.9, 46.5 (d, *J* = 57.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.7; EI-MS: *m/z* = 398.0 [M^+].

2-(Diphenylphosphoryl)-1-(thiophen-2-yl)ethenone (3h)**.** Yield: 70%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 4.2, 1.0 Hz, 1H), 7.83–7.78 (m, 4H), 7.63 (d, *J* = 4.2 Hz, 1H), 7.60–7.44 (m, 6H), 7.09 (dd, *J* = 4.8, 4 Hz, 1H), 4.07 (d, *J* = 15.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.1 (d, *J* = 4.8 Hz), 144.6, 135.4, 135.2, 132.4 (d, *J* = 1.9 Hz), 131.8 (d, *J* = 103.9 Hz), 128.8 (d, *J* = 12.4 Hz), 128.6, 44.5 (d, *J* = 57.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.5; EI-MS: *m/z* = 326.1 [M^+].

1-(Diphenylphosphoryl)hexan-2-one (3i)**.** Yield: 61%; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.74 (m, 4H), 7.55–7.48 (m, 6H), 3.59 (d, *J* = 15.2 Hz, 2H), 2.64 (t, *J* = 7.6 Hz 2H), 1.50–1.44 (m, 2H), 1.22–1.18 (m, 2H), 0.83 (t, *J* = 7.6 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.2 (d, *J* = 5.7 Hz), 132.3, 131.7 (d, *J* = 105.9 Hz), 130.9 (d, *J* = 9.6 Hz), 128.8 (d, *J* = 12.4 Hz), 47.0 (d, *J* = 56.2 Hz), 45.1, 25.4, 21.9, 13.8; ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 27.2; EI-MS: *m/z* = 300.1 [M^+].

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