Copper-catalyzed direct oxyphosphorylation of alkynes with H-phosphine oxides and dioxygen: A convenient approach to β-ketophosphine oxides

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ABSTRACT
A simple and facile copper-catalyzed synthesis of β-ketophosphine oxides via direct oxyphosphorylation of alkynes with H-phosphine oxides and dioxygen has been developed under mild conditions without any base or cocatalyst. A radical reaction pathway for the formation of β-ketophosphine oxides is proposed. An 18O labeling experiment suggested that the carbonyl oxygen atom of β-ketophosphine oxides originated from dioxygen.

GRAPHICAL ABSTRACT

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Introduction
Phosphorus-containing molecules exhibit a wide range of applications in organic synthesis,[1] medicinal chemistry,[2] and materials science.[3] In particular, β-ketophosphine oxides are extremely versatile intermediates that can be used for various organic transformations toward many useful compounds such as olefins,[4] cyclopropanes,[5] and α,β-unsaturated ketones.[6] Furthermore, they can also serve as potential bidentate ligands and metal-extracting agents.[7] As a result, the synthesis of β-ketophosphine oxides has gained much attention.[8–12] The conventional synthetic methods usually rely on acylation of alkyl phosphine oxides with carboxylic acid derivatives by employing stoichiometric amounts of the hazardous organometallic reagents.[8] Alternative methods including the hydrolysis of enamine phosphate oxides,[9] base-promoted substitution reaction of hydrophosphoryl
compounds with chloroacetophenone,[10] palladium-catalyzed hydration of alkynylphosphine oxides,[11] and copper-catalyzed C(sp3)-H/P-H cross-coupling reaction of aryl ketone O-acetyl oximes with phosphine oxides have also been developed.[12] However, most of these methods suffered from limitations such as relatively harsh or complex reaction conditions, multistep reactions, preformed starting materials, toxic wastes, or excess amounts of organometallic reagents.

Recently, methods for the synthesis of β-ketophosphine oxides through the oxyphosphorylation of terminal alkynes and alkynylcarboxylic acids have been reported by several groups.[13–18] Zhao reported a AgNO₃/CuSO₄-cocatalyzed direct oxyphosphorylation of terminal alkynes for the construction of β-ketophosphine oxides in the presence of K₂S₂O₈ (4.0 equiv) (Scheme 1, Eq. 1).[13] Song and He developed copper/iron-cocatalyzed aerobic oxyphosphorylation of terminal alkynes and alkynyl carboxylic acids to access β-ketophosphine oxides in the presence of Et₃N (Scheme 1, Eqs. 2 and 3).[14,15] Tang reported a CuSO₄·5H₂O-catalyzed coupling of alkynyl acids with H-phosphine oxides leading to β-ketophosphine oxides by using tert-butylhydroperoxide (TBHP) as the oxidant and NH₃·H₂O as the base.[16] Wang described a novel method for the synthesis of β-ketophosphine oxides through the silver-catalyzed oxidative decarboxylative coupling of arylpropionic acids with H-phosphine oxides.[17] Nevertheless, bimetallic catalysts, base, or stoichiometric amounts of oxidants such as K₂S₂O₈ and TBHP were inevitably used in these well-developed reaction systems. Herein, we report a simple approach for the synthesis of β-ketophosphine oxides via copper-catalyzed direct oxyphosphorylation of alkynes with H-phosphine oxides and dioxygen (Scheme 1, Eq. 4). The present reaction provides a convenient and efficient approach to various β-ketophosphine oxides in moderate to good yields with excellent functional group tolerance, which make it unnecessary for any metal cocatalyst or additives.

Scheme 1. Synthesis of β-ketophosphine oxides via oxyphosphorylation of alkynes.
**Result and discussion**

In an initial experiment, under an oxygen atmosphere, phenylacetylene (1a) and diphenylphosphine oxide (2a) were chosen as model substrates to examine the catalytic activity of various transition-metal complexes such as Cu, Ag, Au, Fe, Ni, and Co salts in CH$_3$CN at 55 °C (Table 1, entries 1–11). Among the various metals screened (5 mol%), copper salts (especially CuCN) were found to catalyze the formation of the desired product 3aa, albeit in low yield (Table 1, entry 5). The screening of a range of solvents showed that the reaction performed in dimethylsulfoxide (DMSO) was better than those in MeCN, tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), dimethylformamide (DMF), toluene, and 1,4-dioxane (Table 1, entries 5 and 12–17). A low yield (33%) was obtained when the reaction was carried out at room temperature, and the best yield was obtained at 55 °C (Table 1, entries 17, 21, and 22). In addition, the proportion of the substrates also exerted influence on the efficiencies. The optimal proportion of phenylacetylene (1a) to diphenylphosphine oxide (2a) was 1:2, and the decrease of the amount of 2a (Table 1, entry 23) or increase of 1a (Table 1, entry 24) would inhibit this transformation. Moreover, no desired product was observed

### Table 1. Optimization of the reaction conditions.

| Entry | Catalyst (mol%) | Solvent | Temp. (°C) | Yield (%)$^a$ |
|-------|-----------------|---------|------------|---------------|
| 1     | CuBr$_2$ (5)    | CH$_3$CN| 55         | Trace         |
| 2     | CuBr (5)        | CH$_3$CN| 55         | 23            |
| 3     | CuF (5)         | CH$_3$CN| 55         | 24            |
| 4     | CuI (5)         | CH$_3$CN| 55         | 17            |
| 5     | CuCN (5)        | CH$_3$CN| 55         | 33            |
| 6     | Cu(AcO)$_2$ (5)| CH$_3$CN| 55         | 26            |
| 7     | AuI (5)         | CH$_3$CN| 55         | Trace         |
| 8     | AgNO$_3$ (5)    | CH$_3$CN| 55         | 26            |
| 9     | FeBr$_3$ (5)    | CH$_3$CN| 55         | Trace         |
| 10    | NiCl$_2$ (5)    | CH$_3$CN| 55         | 19            |
| 11    | Co(OAc)$_2$ - 4H$_2$O (5)| CH$_3$CN| 55         | 28            |
| 12    | CuCN (5)        | THF     | 55         | 30            |
| 13    | CuCN (5)        | DMF     | 55         | 33            |
| 14    | CuCN (5)        | DME     | 55         | 19            |
| 15    | CuCN (5)        | Toluene | 55         | 32            |
| 16    | CuCN (5)        | 1,4-Dioxane| 55      | 29            |
| 17    | CuCN (5)        | DMSO    | 55         | 65            |
| 18    | CuCN (2.5)      | DMSO    | 55         | 58            |
| 19    | CuCN (10)       | DMSO    | 55         | 62            |
| 20    | CuCN (20)       | DMSO    | 55         | 56            |
| 21    | CuCN (5)        | DMSO    | 25         | 33            |
| 22    | CuCN (5)        | DMSO    | 80         | 53            |
| 23    | CuCN (5)        | DMSO    | 55         | 34$^c$        |
| 24    | CuCN (5)        | DMSO    | 55         | 39$^d$        |
| 25    |—                | DMSO    | 55         | 0             |
| 26    | CuCN (5)        | DMSO    | 55         | 0$^e$         |

$^a$Reaction conditions: 1a (0.5 mmol), 2a (1.0 mmol), catalyst (2.5–20 mol%), solvent (1.0 ml), O$_2$ (balloon), 24 h.

$^b$Isolated yields based on 1a.

$^c$1a (0.5 mmol), 2a (0.5 mmol).

$^d$1a (1.0 mmol), 2a (0.5 mmol), isolated yields based on 2a.

$^e$Under N$_2$. 
in the absence of catalyst or dioxygen (Table 1, entries 25 and 26). After an extensive screening of the reaction parameters, the best yield of 3aa (65%) was obtained by employing 5 mol% CuCN in DMSO at 55 °C under an oxygen atmosphere (Table 1, entry 17).

With the optimized conditions in hand, the scope and limitations of this oxyphosphorylation reaction were investigated, with the results shown in Table 2. Generally, aromatic alkynes bearing both electron-rich and electron-poor groups on the aryl rings were all suitable for this process, producing the corresponding products in moderate to good yields (3aa–3na). It was found that this oxyphosphorylation was not significantly affected by the steric effect. The sterically congested ortho- or meta-methyl substituted aromatic alkynes could also be suitable for the reactions to deliver products (3ea and 3fa) in good yields. Notably, various functional groups such as fluoro, chloro, bromo, ester, acetyl, cyano, and nitro groups were also found to be tolerated in this reaction to give the corresponding products (3ga–3na), which could be employed in further transformations. Naphthyl alkyne such as 1-ethynylnaphthalene and heteroaryl alkyne such as 3-ethynylthiophene were also compatible with this reaction, providing the desired products in 60% and 54% yields, respectively (3oa and 3pa). In addition, when internal alkyne such as 1-phenyl-1-propyne was employed in the present reaction system, the desired product 3qa was obtained in 17% yield. Nevertheless, when aliphatic alkynes such as 3-cyclohexyl-1-propyne and 4-phenyl-1-butyn e were used as the substrates, none of the corresponding products were obtained. The scope of this reaction was further expanded to other H-phosphine oxides, and in addition to diphenylphosphine oxide (2a), other diarylphosphine oxides bearing electron-donating and electron-withdrawing groups could also be used in the reaction to give the expected products (3ab–3ae) in moderate yields.

A number of control experiments were performed to gain some insights into the reaction mechanism. Initially, the 18O isotope-labeled product was obtained in 61% yield when an isotope-labeling experiment using 18O2 was performed in the reaction of phenylacetylene (1a) and diphenylphosphine oxide (2a), indicating that the carbonyl oxygen atom of the β-ketophosphine oxide originated from dioxygen (Scheme 2).

Subsequently, the addition of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) to model reaction completely inhibited the reactivity (Scheme 3). Furthermore, when the reaction of 2a and TEMPO was performed in the absence of phenylacetylene (1a), a TEMPO-trapped compound (4a') was obtained in 13% yield (Scheme 3). These results suggested that the present reaction should proceed through a radical pathway.

On the basis of these experiments and previous reports,[13–19] a tentative mechanism was proposed in Scheme 4. First, the reaction of CuI and O2 would form CuII-(O2·), which interacted with diphenylphosphine oxide 2a, leading to phosphonyl radical 4a and CuII-(OOH).[19] Subsequently, the selective addition of the resulting phosphonyl radical 4a to alkyne 1a gave vinyll radical 5a.[13–15] Then, the reaction of vinyll radical 5a with CuII-(OOH) led to the formation of vinyllperoxyl intermediate 6a.[14] Next, the O-O bond of vinyllperoxyl intermediate 6a produced vinyloxy radical 7a and hydroxyl radical ·OH. The coupling of hydroxyl radical ·OH with 4a gave diphenylphosphonic acid 9a.[13] Finally, vinyloxy radical 7a would abstract the hydrogen of diphenylphosphine oxide 2a to afford enolated phosphonate 8a, which underwent tautomerization to yield the desired product 3aa.[13–15]
Table 2. Copper-catalyzed oxyphosphorylation of alkynes to form β-ketophosphine oxides.\textsuperscript{a,b}

\[ \text{R}^1\equiv + \text{H}_2\text{P-}\text{R}^2 + \text{O}_2 \xrightarrow{\text{CuCN (5 mol\%), DMSO, 55 °C, 24 h}} \text{R}^1\text{C}=\text{O}P=\text{O}\text{R}^2 \]

| 3aa (65%) | 3bb (63%) | 3ca (61%) |
|------------|------------|------------|
| \[
\begin{array}{c}
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{Et} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |

| 3da (57%) | 3ea (62%) | 3fa (65%) |
|------------|------------|------------|
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{CH}_3\text{O} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |

| 3ga (61%) | 3ha (55%) | 3ia (50%) |
|------------|------------|------------|
| \[
\begin{array}{c}
\text{F} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{Br} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |

| 3ja (55%) | 3ka (52%) | 3la (57%) |
|------------|------------|------------|
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{MeOC} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{NC} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |

| 3ma (82%) | 3na (51%) | 3oa (60%) |
|------------|------------|------------|
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{O}_2\text{N} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{O}_2\text{N} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |

| 3pa (54%) | 3qa (17%) | 3ab (53%) |
|------------|------------|------------|
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |

| 3ac (50%) | 3ad (47%) | 3ae (51%) |
|------------|------------|------------|
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |
| \[
\begin{array}{c}
\text{Me} \\
\text{O} \\
\text{P} \\
\text{C}_{\text{Ph}} \\
\text{C}_{\text{Ph}} \\
\end{array}
\] |

\textsuperscript{a} Reaction conditions: 1 (0.5 mmol), 2 (1.0 mmol), CuCN (5 mol\%), DMSO (1.0 ml), 55 °C, 24 h, O\textsubscript{2} (balloon).

\textsuperscript{b} Isolated yields based on 1.
Fortunately, the proposed vinylperoxyl intermediate $6a$, diphenylphosphinic acid $9a$, and TEMPO-trapped radicals $4a$, $5a$, and $7a$ were all detected by liquid chromatography–mass spectrometry (LC-MS) when TEMPO was added to the model reaction system after 2 h [CuCN (5 mol%), DMSO (1 mL), 55 °C, O$_2$ (balloon); Fig. 1]. These results indicated that the proposed vinylperoxyl intermediate $6a$ and radicals $4a$, $5a$, and $7a$ should be involved in the present reaction system.

**Experimental**

All the reagents were bought from Alfa Aesar, TCI, and J&K chemical companies. The products were purified by column chromatography using silica gel (200–300 mesh) and
aluminum oxide (neutral). $^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR were recorded on a Bruker Avance 400 spectrometer. $^1$H NMR spectra were recorded on 400 MHz in CDCl$_3$ with tetramethylsilane (TMS) as internal standard, $^{13}$C NMR spectra were recorded on 100 MHz in CDCl$_3$ with TMS as internal standard, and $^{31}$P NMR spectra were recorded on 162 MHz in CDCl$_3$ with H$_3$PO$_4$ (phosphoric acid) as internal standard. HR-MS was performed on a Brucker Daltonics Bio-TOF-Q mass spectrometer by the electrospray ionization (ESI) method and LC-MS data were obtained on a Waters Acquity HPLC (PDA Detector) Quattor Premier XE triquadrupole mass spectrometer. IR spectra were obtained with a Perkin-Elmer Spectrum One FTIR spectrometer. Melting points were obtained with a WRS-100 melting-point apparatus.

**General procedure for construction of $\beta$-ketophosphine oxides**

An oven-dried flask with the mixture of CuCN (0.025 mmol), alkynes 1 (0.5 mmol), H-phosphine oxides 2 (1.0 mmol), and DMSO (1.0 ml) was charged with O$_2$. The reaction mixture was stirred at 55 °C for 24 h. After completion of the reaction, water (10 ml) was added and extracted with EtOAc (5.0 ml $\times$ 3). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The resulting mixture purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products 3.

**Spectral data for 2-(diphenylphosphoryl)-1-phenylethanone (3aa)$^{[16,17]}$**

White solid; mp 139.5–140.4 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.99–7.97 (m, 2H), 7.83–7.78 (m, 4H), 7.55–7.50 (m, 3H), 7.48–7.39 (m, 6H), 4.14 (d, $J$ = 15.4 Hz, 2H);
Conclusion

In conclusion, a simple and convenient method for the synthesis of β-ketophosphine oxides has been developed via copper-catalyzed direct oxyphosphorylation of alkynes with H-phosphine oxides and dioxygen. Preliminary mechanistic studies suggested that the present reaction might involve a radical process and the carbonyl oxygen atom of β-ketophosphine oxides came from the dioxygen. This simple reaction system is expected to expand the potential applications of β-ketophosphine oxides in synthetic and pharmaceutical chemistry. Further studies of the detailed mechanism of this process and its application are under way in our laboratory.

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