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Keggin structure heteropolyacid-catalyzed phosphinylation of secondary propargyl alcohols with phosphine oxides to γ -ketophosphine oxides†

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Phosphotungstic acid with a Keggin structure as an efficient, simple and green catalyst for the phosphinylation of secondary propargyl alcohols with phosphine oxides to afford γ -ketophosphine oxides with up to 88% isolated yield was developed using dimethyl carbonate as a green solvent. Diaryl- or alkylaryl-substituted propargyl alcohols, and diaryl or arylalkylphosphine oxides could tolerate the system, which reduced the catalyst dosage, and avoided the use of multi-components and toxic solvents. More interestingly, phosphotungstic acid exhibited the best activity when 0.58 moles of water were added per mole of HPWA, elevating the yield from 55% to 85%. An ^{18}O labelled product was afforded using trace H_2^{18}O instead of H_2O , indicating the participation of water in the reaction. Besides, our work underscores the importance and effect of a small amount of water, acting to promote the transformation of secondary propargyl alcohols into enones, which should be the real intermediates of the reaction. A mechanism involving a carbocation, Meyer–Schuster rearrangement and Michael addition of enones was proposed.

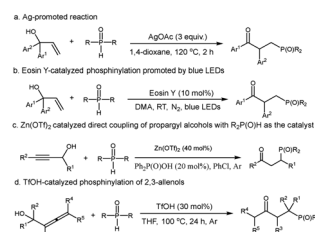
Alcohols are very common and versatile synthons in organic chemistry, and can be used in a variety of chemical transformations due to the high activity of the hydroxyl, which has been proposed as one of the ten key green chemistry research areas since 2018.¹ Recently, a nickel radical sorting-mediated alcohol–alcohol cross-coupling achieved a significant breakthrough.² Propargyl alcohols, exhibiting excellent flexibility and availability for the presence of both alkyne and hydroxyl,³ are widely used for nucleophilic substitutions,⁴ rearrangement reactions,⁵ cyclization⁶

and multicomponent reactions⁷ *etc.* to constitute C–C bonds and C–hetero bonds.⁸

Since Hidai's seminal report on the phosphinylation of propargyl alcohol,⁹ significant progress has been made in the phosphorylation of alcohols (C–OH) with P(O)–H species over the last few decades.¹⁰ γ -Ketophosphine oxides have drawn considerable attention due to their unusual structural characteristics, and unique properties.¹¹ However, there are only several reports on the synthesis of γ -ketophosphine oxides from alcohols and phosphine oxides. Ji and colleagues unveiled the radical phosphonation reaction of α,α -diaryl allyl alcohols with aryl phosphine oxides promoted by 3 equiv. of AgOAc (Scheme 1a). This reaction facilitates the preparation of γ -ketophosphine oxides; however, it is often hindered by the necessity for large amounts of noble silver salts.¹² Zhang's team recently developed a blue LED-assisted process using eosin Y to catalyze the phosphinylation of allyl alcohols to generate γ -ketophosphine oxides in moderate to good yields (Scheme 1b).¹³ Gao and Xu reported Zn(OTf)₂-catalyzed phosphinylation of secondary propargyl alcohols with arylphosphine oxides to give γ -ketophosphine oxides, which needed the assistance of Ph₂P(O)OH as the co-catalyst (Scheme 1c).¹⁴ And their group also first achieved phosphinylation of 2,3-allenols to create γ -ketophosphine oxides catalyzed by TfOH (Scheme 1d).¹⁵ Although significant progress has been made,

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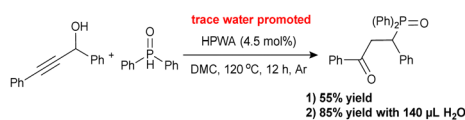


Scheme 1 Reported (a) Ag-promoted; (b) Eosin Y; (c) Zn(OTf)₂; or (d) TfOH-catalyzed system to obtain γ -ketophosphine oxides from alcohols and phosphine oxide.

challenges to develop a simple, efficient, green, and one-component catalytic system with low dosage of catalyst still remain.

Heteropolyacids, including phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$, HPWA), phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 11\text{H}_2\text{O}$, HPMA), *etc.*, as solid Brønsted acids, are a type of stable, non-toxic, highly effective and green catalysts in both homogeneous and heterogeneous phases.¹⁶ DMC (dimethyl carbonate) is designated as one of the greenest solvents for low toxicity, good miscibility and biodegradability.¹⁷ According to previous reports,^{14,15} the carbocation may be the important intermediate and can be formed from the corresponding alcohol under the influence of Brønsted acids. Continuing our research on Brønsted acid-catalyzed alcohol conversion,¹⁸ we speculate that propargyl alcohol can be transformed into a propargyl carbocation, balancing with the diene carbocation, which reacts with enone to provide γ -ketophosphine oxide. Fortunately, a simple and green system was developed using HPWA as the exclusive catalyst for phosphinylation of 1,3-diphenylprop-2-yn-1-ol with phosphine oxides in dimethyl carbonate (DMC) that acts as a low toxicity and green solvent (Scheme 2). Interestingly, the addition of trace water could promote the reaction, affording a yield of 85% of the desired product. Control experiments indicated that water would participate in and promote the transformation of secondary propargyl alcohols into enones.

In the initial study, we focused on the phosphinylation of 1,3-diphenylprop-2-yn-1-ol (**1a**) with diphenylphosphine oxide (**2a**), as shown in Table 1. The desired product, 3-(diphenylphosphoryl)-1,3-diphenylpropan-1-one (**3a**), was afforded in 72% yield at 120 °C with HPWA as the catalyst in DMC under an Ar atmosphere (Table 1, entry 1). And the materials were recovered when there was no catalyst (Table 1, entry 2). Other catalysts, such as H_3PO_4 , $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 11\text{H}_2\text{O}$, or $\text{Bu}_4\text{NH}_2\text{PO}_4$, were explored (Table 1, entries 3–5), and HPWA was the most suitable catalyst, despite the close acidity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$.¹⁹ And the valence change of Mo in the $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 11\text{H}_2\text{O}$ -catalyzed system would result in a colour change from orange to blue, which led to the low activity. Meanwhile, the influences of different solvents, catalyst amount, and temperature were exploited and the best result was obtained in DMC using 4.5 mol% HPWA (Table 1, entries 1, and 6–13; and Table S1, ESI†, entries 1–4). Moderate yields were obtained in most polar or non-polar solvents and the reaction did not occur in H_2O . The substrate was nearly recovered at room temperature (rt) or 40 °C (Table S1, ESI†, entries 5 and 6). When the reaction temperature increased to 120 °C, the yield was raised to 72% (Table S1 (ESI†), entry 1). Further raising the temperature to 140 °C led to a slight reduction in yield (Table S1, ESI†, entry 10). Therefore,



Scheme 2 Water-promoted phosphotungstic acid-catalyzed phosphinylation of 1,3-diphenylprop-2-yn-1-ol.

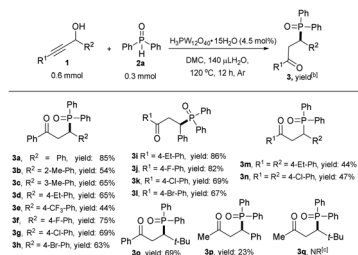
Table 1 Optimization of the reaction conditions^a

Entry	Catalyst ^b	Solvent	<i>t</i> (h)	H_2O (μL)	Yield ^c /%	Sel. ^c /%
1	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	18	—	72	99
2	—	DMC	18	—	NR	—
3	H_3PO_4	DMC	18	—	43	98
4	$\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 11\text{H}_2\text{O}$	DMC	18	—	NR ^d	—
5	$\text{Bu}_4\text{NH}_2\text{PO}_4$	DMC	18	—	NR ^d	—
6	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	H_2O	18	—	NR ^d	—
7	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	EtOAc	18	—	56	98
8	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	MeOH	18	—	68	98
9	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	CH_3Ph	18	—	56	98
10	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	CF_3Ph	18	—	38	98
11	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	1,4-Dioxane	18	—	60	98
12	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	THF	18	—	41	98
13	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	<i>n</i> -Hexane	18	—	48	98
14	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	18	150	75	98
15	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	12	150	84	99
16	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	8	150	76	98
17	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	4	150	64	98
18	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	12	50	65	98
19	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	12	100	81	99
20	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	12	120	83	99
21	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	12	140	85	99
22	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	12	160	81	99
23	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	12	180	78	99
24	$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$	DMC	12	—	55	99

^a Reaction conditions: **1a** (0.6 mmol), **2a** (0.3 mmol) and catalyst (4.5 mol%) in a solvent (2 mL) were stirred at 120 °C for 18 h under argon. ^b The number of water molecular was tested according to the method in the ESI. ^c Isolated yield. ^d NR: No reaction.

120 °C was chosen as the best reaction temperature. Initially, we speculated that the hydration of alkyne was considered as the first step for the reaction, and water may be significant for the reaction. Therefore, we tried to add a small amount of water to the reaction. Fortunately, the yield increased to 75% when 150 μL water was added (Table 1, entry 14). Surprisingly, 84% yield of the desired product was acquired through shortening the reaction time to 12 h (Table 1, entry 15). Continuing to reduce the reaction time led to lower yields (Table 1, entries 16 and 17). The amount of water was screened. The results showed that the addition of 140 μL H_2O was the most beneficial amount for the reaction and the yield could reach 85%, while only 55% yield could be provided in the absence of water (Table 1, entry 21 vs. 24). That's to say, phosphotungstic acid exhibited the best activity when 0.58 moles of water were added per mole of HPWA. Moreover, there was nearly no by-product for the catalytic system and the selectivities were good. The addition of water just affected the reaction activity.

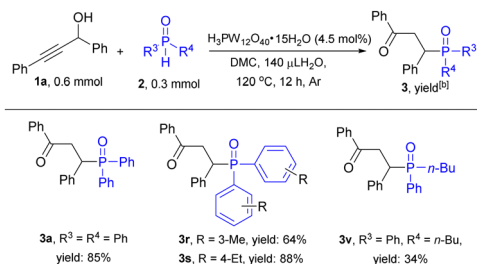
After establishing the optimized reaction conditions, the substrate scope of propargyl alcohols was investigated. As shown in Scheme 3, a set of propargyl alcohols reacted successfully with **2a** to give the corresponding γ -ketophosphine oxides **3a–3p** in moderate to good yields. Aryl propargyl alcohols with aryl groups on both the hydroxyl and triple bond could tolerate the system well. The substituent of an aryl group on the hydroxyl or triple bond side led to a similar influence, generating yields lower than that of **3a**, except for **3i**. There was no obvious



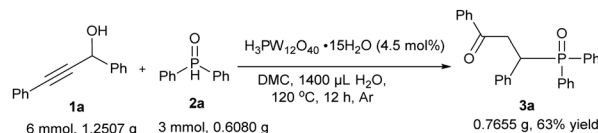
Scheme 3 Reaction scope of propargyl alcohols with **2a**.^a [a]Reaction condition: **1** (0.6 mmol) and **2a** (0.3 mmol) were catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 15\text{H}_2\text{O}$ (4.5 mol%) in 2 mL DMC with 140 μL H_2O as additive at 120 °C for 12 h. [b]Isolated yield. [c]NR: No reaction.

relationship between the yields and electronic properties of the substituted groups on the aryl. And only 44% yield of **3e** could be provided using a 4- CF_3 -substituted phenyl group at the hydroxyl side (**1e**) as the substrate. Besides, steric hindrance of the substituents on the aryl group had a slight effect on the reaction (**3b** vs. **3c**). Furthermore, the disubstituted 1,3-diphenylprop-2-yn-1-ols would result in a further decrease in the yields to 44% of **3m** and 47% of **3n**. Besides, **1o** with *tert*-butyl on the hydroxyl side still gave 69% of **3o**. The yield of **3p** would decrease to 23% when the group on the triple bond side is a methyl. And there was no reaction when the groups on the two sides of the propargyl alcohols are both alkyls, such as **1q**.

To further explore the substrate scope of this reaction, phosphinylation of **1a** with various phosphine oxides was also investigated (Scheme 4). Arylphosphine oxides with two aromatic groups exhibited moderate to good activities, giving 64–88% yields (**3a**, **3r–3v**). Phosphine oxide with a *meta*-substituent (**3r**) furnished a poor yield for steric hindrance. Butyl(phenyl)-phosphine oxide having an aliphatic group would result in a reduction in yield and only 34% of the desired product (**3v**) was obtained. The reaction did not occur when dimethylphosphine oxide was used as the substrate and no desired product was generated under different reaction conditions (Table S2, ESI[†]). Aryl groups are electron-donating groups in diarylphosphine oxides because there is π - π conjugation between the aryl group and $\text{P}=\text{O}$, and an inductive effect. And the electron-donating ability of the aryl group is stronger than that of the methyl group.



Scheme 4 Phosphinylation of **1a** with phosphine oxides.^a [a]Reaction condition: **1a** (0.6 mmol) and **2** (0.3 mmol) were catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 15\text{H}_2\text{O}$ (4.5 mol%) in 2 mL DMC with 140 μL H_2O as additive at 120 °C for 12 h. [b]Isolated yield.



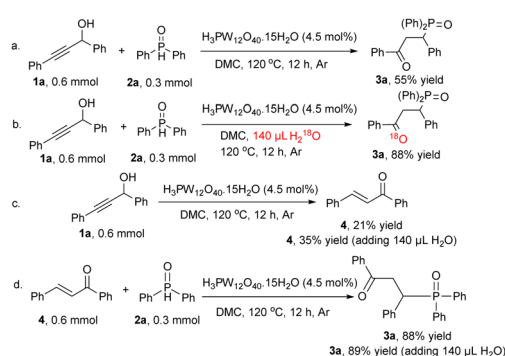
Scheme 5 Gram-scale reaction of **1a** and **2a** catalyzed by HPWA in the presence of trace water.

Therefore, the electron of P in diarylphosphine oxide or arylalkylphosphine oxide is richer than that of dimethylphosphine oxide. Then the nucleophilic ability of diarylphosphine oxide or arylalkylphosphine oxide was stronger than that of dimethylphosphine oxide.

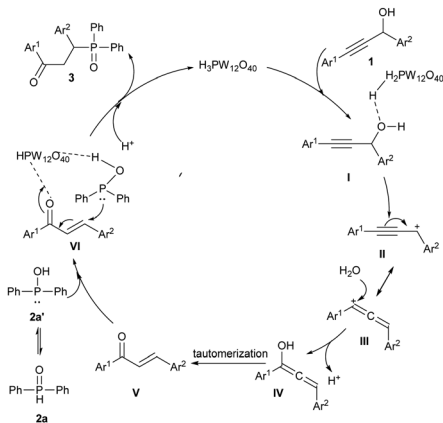
A gram-scale experiment was one important aspect for proving the potential application of the developed system. A gram-scale reaction was performed with 1,3-diphenylprop-2-yn-1-ol (**1a**) and diphenylphosphine oxide (**2a**) as the substrates under the optimal reaction conditions, and still 63% yield was observed with high selectivity (Scheme 5).

To demonstrate the reaction mechanism, some control experiments were designed and performed (Scheme 6). The yield was 55% under standard conditions, but increased to 88% by adding a small amount of water (140 μL H_2^{18}O). The isotopic labelling of ^{18}O was detected in the product, indicating that water participated and facilitated the reaction (Scheme 6a and b and Fig. S1, ESI[†]). Subsequently, 21% of chalcone was obtained with **1a** as the substrate catalyzed by 4.5 mol% HPWA. However, adding 140 μL H_2O into the above system promoted the transformation and up to 35% yield of chalcone was formed (Scheme 6c). The phenomenon demonstrated that water had a beneficial effect on the reaction. Additionally, chalcone **4** was employed as the substitute of **1a** to react with **2a** catalyzed by 4.5 mol% HPWA in DMC, affording an 88% yield of **3a**. And there was nearly no increase in yield through addition of water (Scheme 6d). The results showed that chalcone may be the key intermediate for the phosphinylation of 1,3-diphenylprop-2-yn-1-ol (**1a**) with diphenylphosphine oxide **2a** and water would not affect the transformation of **4** and **2a** to **3a**.

Based on our experimental investigation and relevant reports,²⁰ a possible mechanism has been proposed in Scheme 7. The transformation of a propargyl alcohol (**1**) to an α,β -unsaturated



Scheme 6 Control experiments (a) without H_2O ; (b) with H_2^{18}O as the additive; (c) without **2a**; (d) chalcone as the substrate.



Scheme 7 Plausible mechanism for HPWA-catalyzed phosphinylation of propargyl alcohols with phosphine oxide promoted by trace water.

carbonyl compound (V) belongs to the Meyer-Schuster rearrangement process.²⁰ Initially, there should be a hydrogen bonding interaction between the hydroxyl of the propargyl alcohol and phosphotungstic acid, which removes the hydroxyl group to form the propargyl carbocation II. The hydrogen bonding effect and formation of a carbocation have a certain relationship with the solvent according to the experimental results. DMC as a polar aprotic solvent is beneficial for stabilization of the carbocation,^{18b,21} and advantageous to obtain high yield. The strong hydrogen-bonding effect between propargyl alcohol and water may inhibit the formation of a carbocation and result in no reaction. Moreover, allenyl cation III and propargyl carbocation II are resonance structures.²⁰ Intermediate IV can be furnished by the attack of water on the cation site of III, which has been proven by the promoted effect of water on the reaction. A more stable chalcone V can be obtained by the tautomerization of enol IV.²⁰ Meanwhile, diphenylphosphine oxide 2a and diphenylphosphinous acid 2a' are tautomers.²² Then, diphenylphosphinous acid 2a' undergoes a Michael addition reaction to an α,β -unsaturated carbonyl compound under the effect of HPWA, giving the desired product 3 accompanied by recovery of the catalyst into the next cycle.

In conclusion, HPWA-catalyzed phosphinylation of various unprotected secondary propargyl alcohols with phosphine oxides with DMC as a green solvent has been developed, providing a novel, efficient and rapid route for the simultaneous generation of structurally diverse γ -ketophosphine oxides. Interestingly, the system was promoted by adding a trace amount of water, increasing the yield from 55% to 85%. Control experiments indicated that water would participate and promote the transformation of secondary propargyl alcohols to enones. A possible mechanism involving carbocation and Michael addition to enones is proposed for this reaction. The approach avoids the use of large amounts of complex ligands, metals, and Lewis acids, making it a safer and more environmentally friendly strategy.

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Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Notes and references

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