An Atom-Economical Route to Substituted β-Arylethyl Ketones: Phosphomolybdic Acid-Catalyzed Carbohydroxylation of Terminal Alkynes in Organic Carbonate

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Abstract: A highly efficient and atom-economical route for the synthesis of substituted β-arylethyl ketones was developed by using cheap phosphomolybdic acid $(H_3PMo_{12}O_{40})$ as catalyst and non-volatile propylene carbonate (PC) as green solvent via the carbohydroxylation of terminal alkynes with benzylic alcohols under mild conditions. Various functional groups on the benzylic alcohols and terminal alkynes were tolerated, giving the corresponding substituted β -arylethyl ketones as products in good to excellent yields (up to 95%). It is worth noting that a turnover number (TON) of up to 520 was achieved in the protocol. The mechanism investigation showed that PC might stabilize the heteropoly anion and the carbocation intermediate thus facilitating the carbohydroxylation reaction.

Keywords: alcohols; alkynes; carbohydroxylation; organic carbonates; polyoxometalates

The construction of C–C bonds has emerged as one of the most intriguing areas of organic chemistry as proved by the award of the 2010 Nobel Prize in chemistry.^[1–3] Apart from the traditional coupling reactions of organometallic reagents and corresponding coupling partners, reactions such as the Sonogashira coupling which directly uses C–H type substrates as reactant have drawn much attention in the recent decades.^[4–6] However, organic halides were required and waste was produced by using stoichiometric amounts of base in these methods. Particularly, the direct application of C–OH type substrates like aryl alcohols and phenols as proelectrophiles is receiving broad at-

tention because these abundant, low toxic building blocks can be regarded as an economical alternative for organic halides and analogues.^[7,8] In 2009, the Jiao group reported the first example of $C(sp^3)$ –C(sp)bond formation *via* dehydrative coupling of benzylic alcohols with terminal alkynes catalyzed by inexpensive Fe(OTf)₃/TfOH in the absence of a base.^[9] Subsequently, Cu(OTf)₂,^[10] In(OTf)₃,^[11] and Brønsted acidic ionic liquids^[12] were demonstrated as efficient systems for this dehydrative coupling reaction (Scheme 1a).

Carbonyl groups are of great importance in natural products, bioactive compounds and pharmaceutical compounds, etc. Unlike many other syntheses of carbonyl compounds, the hydration of alkynes is an atom-economical alternative for ketone synthesis.^[13,14] Consequently, various approaches have been developed for the hydration of alkynes. However, in these protocols toxic or expensive catalysts such as mercury(II), gold(I), gold(III), platinum(II), and palladium(II) were generally required for highly efficient transformations.^[15-20]

Recently, the construction of β -arylethyl ketones via a Friedel–Crafts-type reaction of benzylic alcohols and aryl methyl ketones was disclosed using Fe(OTf)₃/PhCl at 130°C,^[21] AgSbF₆/CH(OMe)₃,^[22] and Amberlyst-15/ [Bmim][PF₆]/CH(OMe)₃^[23] (Scheme 1b). Notably, these dehydrative coupling procedures suffer from certain limitations with respect to the use of elevated temperature or a stoichiometric amount of triethyl orthoformate as an activating reagent. Alternatively, Hashmi et al. developed the Au(III)-catalyzed addition reactions of electronrich arenes to methyl vinyl ketone for the synthesis of β -arylethyl ketones.^[24,25] However, in these approaches, precious Au catalysts were needed.

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(a) Dehydrative coupling of benzylic alcohols with terminal alkynes



(b) Dehydrative coupling of benzylic alcohols with aryl methyl ketone



(c) This work: carbohydroxylation of terminal alkynes with benzylic alcohols



Scheme 1. C–C bond formation from benzylic alcohol.

Ideally, β -arylethyl ketones can be directly achieved from benzylic alcohols and terminal alkynes with 100% atom economy (Scheme 1c). Although this carbohydroxylation strategy was recently realized by using FeCl₃·6H₂O/MeNO₂,^[26] FeCl₃/AgSbF₆,^[27] Amberlyst-15/[Bmim][PF₆],^[28] a large amount of catalyst or promoter (10–300 mol%) was required to obtain moderate yields. In this context, it is highly desirable to exploit an efficient and practical catalytic system for this reaction from readily available starting materials in an atom- and step-economical manner.

On the other hand, the inexpensive polyoxometalates (POMs) have exhibited broad activities in organic synthesis by avoiding conventional organic and inorganic acids.^[29-32] Particularly, a Keggin-type POM, such as phosphotungstic acid ($H_3PW_{12}O_{40}$), exhibited potential for dehydrative reactions of benzylic alcohols and different nucleophiles for the construction of C–C bonds^[33] and C–N bonds.^[34] In these protocols, it is believed that the benzylic alcohol is protonated by POM to generate a stable benzyl cation for further transformation. Therefore, we envisioned that the coupling reaction between benzylic alcohol and terminal alkynes catalyzed by a POM-based system would be feasible.

As part of our interest in the field of POM catalysis and green chemistry,^[35,36] we herein disclose an atomeconomical and operationally simple Ritter-type addition of benzylic alcohols and terminal alkynes towards substituted β -arylethyl ketones by using the unique system of H₃PMo₁₂O₄₀/propylene carbonate (Scheme 1c). It was found that the combination of H₃PMo₁₂O₄₀/propylene carbonate is critical for this carbohydroxylation reaction.

Initially, diphenylmethanol 1a and phenylacetylene 2a were chosen as model compounds for the reaction using Keggin-type POMs, e.g., $H_4SiW_{12}O_{40}$, H₃PW₁₂O₄₀, and H₃PMo₁₂O₄₀, as catalysts in dichloroethane at 80°C for 3 h. The desired product 3a was obtained in yields of 18%, 26% and 57%, respectively (Table 1, entries 1–3). Among those Keggin-type POMs, $H_3PMo_{12}O_{40}$ possesses the weakest acidity but is the softest heteropoly anion.^[37] It was assumed that a soft heteropoly anion may stabilize the reaction intermediate and thus facilitate the carbohydroxylation reaction.^[38] Subsequently, H₃PMo₁₂O₄₀ was applied as catalyst for solvent screening. Poor yields were detect-

Table 1. Effects of various solvents on the carbohydroxylation reaction.^[a]



Entry	Solvent	Conv. of 1a [%]	Yield ^[b] [%]	
1 ^[c]	ClCH ₂ CH ₂ Cl	>99	18	
2 ^[d]	ClCH ₂ CH ₂ Cl	>99	26	
3	ClCH ₂ CH ₂ Cl	>99	57	
4	EtOH	96	<1	
5	<i>i</i> -PrOH	2	<1	
6	H_2O	85	2	
7	DMF	56	1	
8	<i>n</i> -octane	98	21	
9	PhCl	>99	46	
10	toluene	>99	53	
11	EtOAc	>99	62	
12	BrCH ₂ CH ₂ Br	95	64	
13	DMC	>99	59	
14	EC	>99	76	
15	PC	>99	99	

^[a] Reaction conditions: diphenylmethanol (0.2 mmol), phenylacetylene (0.22 mmol), H₃PMo₁₂O₄₀ (3 mol%), solvent (1 mL). 80°C, 3 h. DMC=dimethyl carbonate, PC=propylene carbonate, EC=ethylene carbonate.

^[b] The yields were determined by GC with biphenyl as the internal standard. The main by-product is benzhydrol ether.

^[c] $H_4SiW_{12}O_{40}$ (3 mol%) as catalyst.

^[d] $H_3PW_{12}O_{40}$ (3 mol%) as catalyst.

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ed when the reactions were conducted in solvents like EtOH, *i*-PrOH, H₂O, DMF and *n*-octane (entries 4– 8). Reactions in other solvents, including PhCl, toluene, EtOAc, BrCH₂CH₂Br gave the product 3a in higher yields, but the selectivities were not satisfactory (entries 9-12). Based on these results, it seems that the presence of aprotic polar solvents is beneficial to give a better yield of **3a**. Considering the high polarity of the aprotic organic carbonates, commercially available organic carbonates like DMC, EC and PC were surveyed in the further investigation (entries 13–15). To our delight, the reaction selectivity was significantly increased providing 3a in a yield of 99% when PC was applied as solvent.

These results encouraged us to evaluate different catalysts based on $[PMo_{12}O_{40}]^{3-}$ using PC as a unique solvent. As shown in Table 2, the control experiment without catalyst in PC did not lead to any 3a but a trace amount of benzhydrol ether was detected, demonstrating the importance of the catalyst (entry 1). Cs_{0.5}H_{2.5}PMo₁₂O₄₀ showed a good catalytic activity but lower selectivity (entry 3). However, other salts of $[PMo_{12}O_{40}]^{3-}$ such as $Cs_{1.5}H_{1.5}PMo_{12}O_{40}$, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, $[DBUH]_{3}PMo_{12}O_{40},$ and $[NMPH]_{3}PMo_{12}O_{40}$ gave inferior results (entries 4–7). These results revealed that the protons of H₃PMo₁₂O₄₀ are significantly essential for the reaction, which might promote protonation of the alcohol and further generation of the carbocation intermediate after dehydration.^[33,34]

Table 2. Examination of various catalysts.^[a]



- [a] Reaction conditions: diphenylmethanol (0.2 mmol), phenylacetylene (0.22 mmol), catalyst (3 mol%), PC (1 mL), 80°C, 3 h. DBU=1, 8-diazabicyclo[5.4.0]undec-7-ene, NMP = N-methyl-2-pyrrolidinone.
- [b] The yields were determined by GC with biphenyl as the internal standard. The main by-product is benzhydrol ether.



Figure 1. (A) Effect of temperature for the reaction at 3 h and (B) effect of reaction time at 80 °C.

Based on these results, the reaction temperature was further optimized by using the system of H₃PMo₁₂O₄₀/propylene carbonate. As shown in Figure 1A, poor yields were observed when the reactions were performed at lower temperature (<80°C) for 3 h. Therefore, 80°C was chosen for subsequent studies. We further optimized the reaction time (Figure 1B) and found that an almost quantitative yield of **3a** could be obtained after reaction at 80 °C for 2 h.

Having established the optimal conditions, we surveyed the scope of this carbohydroxylation reaction by using the system of H₃PMo₁₂O₄₀/propylene carbonate. As can be seen in Table 3, aromatic alkynes with electron-withdrawing group or electron-donating groups (2a-d) could be converted into the corresponding products (3a-d) in excellent yields (84-95%) via the reaction with **1a** for 2–3 h (entries 1–4). However, an aliphatic alkyne, such as 1-octyne 2e exhibited diminished activity even at elevated temperature and extended time (100°C, 5 h). Unfortunately, attempts to isolate the corresponding product 3e failed, possibly due to its chemical lability (entry 5). On the other hand, diphenylmethanols 1b-e substituted with electron-withdrawing or electron-donating

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H₃PMo₁₂O₄₀ (3 mol%)



		$R^{1} \xrightarrow{I_{1}} R^{2} \xrightarrow{+} R^{3} \xrightarrow{=} X$ propylene carbonate $80-100 \ ^{\circ}C, 2-5 \text{ h}$ $R^{1} \xrightarrow{I_{1}} H$ $X = CH, N$					
Entry	Alcohol	Alkyne	Conditions	Product	Yield ^[b] [%]		
1	OH Ph Ph 1a	Ph 2a	80°C, 2 h	3 a	91		
2	OH Ph Ph 1a	F	80°C, 2.5 h	3b	95		
3	OH Ph Ph 1a	Me 2c	80°C, 3 h	3c	86		
4	Ph Ph 1a	MeO 2d	80°C, 3 h	3d	84		
5	Ph 1a OH	<i>n</i> -C ₆ H ₁₂ 2e	100°C, 5 h	Зе	35°		
6		Ph— — 2a	80°C, 2 h	3f	93		
7	MeO 1c Me OH	Ph-== 2a	80°C, 3 h	3g	87		
8		Ph-== 2a	80°C, 3 h	3h	94		
9		Ph— 2a	80°C, 2.5 h	3i	91		
10	Ph 1f	Ph-== 2a	80°C, 3 h	3ј	56		
11	Ph Ph 1g	Ph 2a	80°C, 3 h	3k	14, ^[c] 77 ^[d]		
12		PhC≡N 2f	100°C, 4 h	31	88		
13	Ph 1a	PhCH ₂ C≡N 2g	100°C, 4 h	3m	77		
14		CH ₃ C≡N 2h	100 °C, 4 h	3n	64		

Table 3. Substrate scope of H₃PMo₁₂O₄₀-catalyzed carbohydroxylation reaction in propylene carbonate.^[a]

[a] *Reaction conditions*: alcohol (0.6 mmol), alkyne (1.1 equiv) or nitrile (2.0 equiv), H₃PMo₁₂O₄₀ (3 mol%), and PC (3 mL) as solvent.

^[b] Isolated yield.

^[c] Yield was estimated by GC-MS.

^[d] Direct dehydrative coupling product detected by GC-MS.

groups (Cl, Me, OMe) can smoothly react with alkyne 2a to give the desired products 3f-i in 87-94% yield (entries 6-9). When 2-methylbenzyl alcohol 1f was employed as substrate to react with 2a, only a 56% yield of product 3j was observed (entry 10). In the case of tertiary alcohol 1g, the dehydrative coupling product 1,3,3,3-tetraphenylpropyne was observed by GC-MS as the main product in a yield of 77% (entry 11). Unfortunately, only a trace amount of the corresponding products were detected by GC-MS when benzylic alcohol and cyclohexanol were employed as substrates even at 100 °C for 5 h (results not

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shown). These results indicate that primary alcohols and aliphatic alcohols are probably not suitable for this protocol.

The Ritter reaction is widely used for the preparation of acyclic amides as well as heterocycles.^[39-41] A Brønsted acid was found to be critical for the goldcatalyzed system used in this reaction.^[42-45] In this $H_3PMo_{12}O_{40}/PC$ system, reactions of diphenylmethanol **1a** with nitriles **2f-h**, i.e., Ritter reactions, gave the corresponding amide products in good yields (entries 12–14).

To further understand the reaction, we investigated the reaction mechanism by a series of control experiments. As shown in Scheme 2, the dehydrative coupling of diphenylmethanol **1a** with acetophenone (Scheme 2a) and hydration of 1,3,3-triphenylpropyne **3a'** (Scheme 2b) under standard conditions did not generate the desired products, therefore ruling out of the tandem "alkyne hydration/dehydration coupling" pathway and the tandem "dehydration coupling/

(a)



Scheme 2. Control experiments for exploring the reaction mechanism.

alkyne hydration" pathway. More importantly, the experiment using deuterium labelled phenylacetylene [D]-**2a** as reactant afforded the corresponding product [D]-**3a** in 90% yield, demonstrating that cleavage of the terminal C–D bond was impossible under the reaction conditions (Scheme 2c). On the other hand, benzhydrol ether was detected during the time-course investigation. Then the gradual formation of the desired products accompanied by the decrease of ether was observed, suggesting that benzhydrol ether probably is one of the intermediates in this reaction.

Further studies showed that the $H_3PMo_{12}O_{40}$ catalyst does not completely dissolve in propylene carbonate under the reaction conditions. However, the reaction also proceeded well when we removed the insoluble portion; the insoluble solid did not show any activity under identical conditions. These results indicated that this reaction runs via homogeneous catalysis. To explore the unique effect of propylene carbonate in this reaction, the model reaction of 1a and 2a catalyzed by $H_3PMo_{12}O_{40}$ in PC was monitored with ESI-MS. Interestingly, a species of m/z = 1034 was observed when PC and H₃PMo₁₂O₄₀ were mixed for 5 min in MeOH, which is probably attributed to $[(HPMo_{12}O_{40}) + 2PC + H_2O]^{2-}$ (Figure 2). However, the interaction between PC and other reactants was not observed. Based on these results and previous reports,^[48,49] we can presume that (i) PC might enhance the catalytic activity of POM by stabilizing the corresponding heteropoly anion and (ii) PC as polar solvent could stabilize the carbocation intermediate and increase the nucleophilicity of terminal alkyne.

On the basis of our observations and the relevant reports,^[23,28,49] a possible mechanism of the carbohydroxylation reaction was proposed as shown in Scheme 3. Under the promotion of heteropoly acid $H_3PMo_{12}O_{40}$ and PC, carbocation species **A** would generate *via* the ether **4** or directly by protonation/dehydration of the alcohol **1**. Then nucleophilic addition



Figure 2. Observation of the interaction between POM catalyst and PC by ESI-MS: (a) $H_3PMo_{12}O_{40}$ in MeOH, (b) $H_3PMo_{12}O_{40}$ and PC mixture in MeOH.

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Scheme 3. Plausible mechanism for addition of alcohol and alkyne.

of A and alkyne 2 delivered the intermediate B. The addition of water onto B gave the corresponding intermediate C, followed by tautomerization which provides the desired product 3.

To further validate the efficaciousness of this methodology, an experiment with a lower catalyst amount was performed as depicted in Scheme 4. To our delight, over 88.3% yield of **3a** was obtained with a turnover number (TON) of 520.



Scheme 4. Evaluation of the catalytic activity.

In conclusion, we have developed a methodology for the synthesis of substituted β -arylethyl ketones (or amides) from the carbohydroxylation reaction of terminal alkynes (or nitriles) with secondary aromatic alcohols by using the H₃PMo₁₂O₄₀/propylene carbonate catalytic system. This green protocol provides a range of β -arylethyl ketones and amides in good yields with high atom-economy. The present system has notable advantages, such as operational simplicity, mild reaction conditions, inexpensive and non-toxic catalyst and solvent system. Further studies on applications of this interesting combined system are being carried out in our laboratory.

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Experimental Section

Typical Procedure for the POM-Catalyzed Carbohydroxylation Reaction

To a 4-mL reaction vial, diphenylmethanol (0.2 mmol), phenylacetylene (0.22 mmol), $H_3PMo_{12}O_{40}$ (3 mol%) and propylene carbonate (1 mL) were added. Then the reaction was carried out in screw cap vials with a Teflon seal at 80 °C for the desired time. After cooling to room temperature, the mixture was diluted with H_2O and extracted with ethyl ether. The combined organic layers were washed with saturated NaCl solution, then dried with anhydrous Na₂SO₄. The residue was further purified by column chromatography (petroleum ether/EtOAc) to afford the desired products.

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 8 An Atom-Economical Route to Substituted β-Arylethyl Ketones: Phosphomolybdic Acid-Catalyzed Carbohydroxylation of Terminal Alkynes in Organic Carbonate

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