

The silver salt of 12-tungstophosphoric acid: an efficient catalyst for the three-component coupling of an aldehyde, an amine and an alkyne[☆]

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Abstract—A three-component coupling of an aldehyde, an alkyne and an amine to prepare propargylamines was performed using the silver salt of 12-tungstophosphoric acid ($\text{Ag}_3\text{PW}_{12}\text{O}_{40}$) as a heterogeneous catalyst under mild reaction conditions in the absence of any co-catalyst. A variety of aldehydes and amines were converted to the corresponding propargylamines demonstrating the versatility of the reaction. The $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ (AgTPA) catalyst was recovered quantitatively by a simple filtration and reused several times.

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Multicomponent reactions play an important role in modern synthetic organic chemistry since they generally occur in a single pot and exhibit a higher atom economy and selectivity. They also deliver less by-products compared to classical stepwise synthetic routes. Furthermore, in many cases, multicomponent reactions are easy to perform leading to simpler experimental procedures as well as lower costs, time and energy. Metal mediated C–C bond formations are among the most important reactions in organic synthesis.¹ Among the transition elements, silver salts have been less explored as catalysts for coupling reactions. Very recently, silver salts have proved to be potential catalysts for many organic transformations.^{2–6} Propargylamines are important synthetic intermediates in the preparation of potential therapeutic agents and polyfunctional amino derivatives.⁷ However, such reactions are conventionally carried out by amination of propargylic halides, propargylic phosphates or propargylic triflates.⁸ Recently, a number of efficient and mild metal-catalyzed reactions based on the nucleophilic addition of in situ generated metal acetylides to imines and enamines have been reported for the synthesis of propargylamines.⁹ Tu and

co-workers have reported microwave-assisted three-component coupling reactions using CuI as a catalyst, a reaction which otherwise requires five days under thermal conditions.¹⁰ Li and co-workers reported a highly efficient three-component coupling reaction through C–H activation in water using salts of gold, silver and silver in ionic liquids without using any noble metal co-catalyst.¹¹ Lo et al. reported an Au(III) salen complex catalyzed three-component coupling reaction in water.¹² However, the success so far achieved in such three-component couplings has been largely limited to aromatic aldehydes, whereas aliphatic aldehydes have led to both low yields and poor conversion. Despite the advantages of homogeneous metal catalysts, difficulties in recovering the catalyst from the reaction mixture severely obstructs its wide use in the industry. Thus, the development of improved synthetic methods for the preparation of propargylamines remains an active research area.

Heterogeneous catalysts are particularly attractive as they often lead to the formation of large quantities of products with the use of only small amounts of catalysts, which can be easily separated by simple filtration. Heteropoly acids (HPAs), such as 12-tungstophosphoric acid, have been extensively studied as super acid catalysts for many organic reactions and they have found industrial application in several processes.¹³ The Keggin-type HPAs typically represented by the formula $\text{H}_{8-x}[\text{XM}_{12}\text{O}_{40}]$, where X is the heteroatom (e.g., P^{5+}

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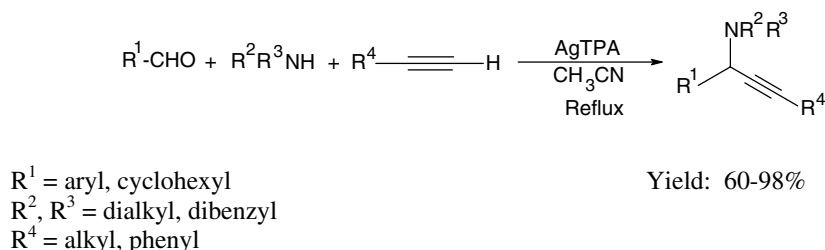
or Si^{4+}), x is its oxidation state and M is the addenda atom (usually Mo^{6+} or W^{6+}), form an important class of catalysts, and among them $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ¹⁴ are the most common. These HPAs have been reported as efficient catalysts for three-component coupling reactions.¹⁵ However, they are readily soluble in polar solvents. The solubility problem can be overcome by changing these HPAs into their corresponding salts, which are generally insoluble in polar solvents. The silver salts of heteropoly acids have been studied in different organic transformations under heterogeneous conditions.¹⁶

We have designed and developed a method involving the silver salt of tungstophosphoric acid (AgTPA) for the three-component coupling of aldehydes, amines and alkynes to generate propargylamines without using any co-catalyst or additive (Scheme 1).

In an effort to obtain improved yields, various solvents were screened in the three-component reaction of benzaldehyde, piperidine and phenylacetylene under reflux and the results are summarized in Table 1. Acetonitrile provided excellent yields and proved to be the solvent of choice, whereas toluene and 1,4-dioxane afforded lower yields. The reaction in DCE afforded very poor yields whilst the use of THF and water did not yield any product. The optimum ratio of aldehyde, amine and alkyne was found to be 1:1.2:1.3. The controlled three-component reaction conducted under identical

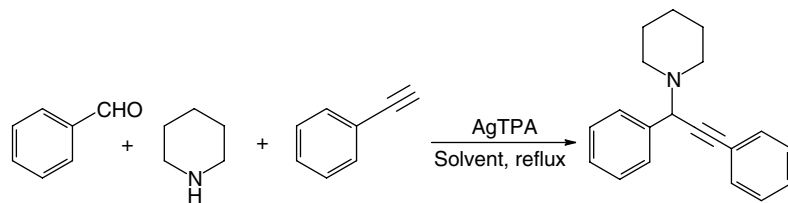
conditions and devoid of AgTPA gave no coupled product, despite prolonged reaction times. AgTPA was recovered quantitatively by a simple filtration and reused. It is noteworthy that the catalyst exhibited comparable activity even after the fourth cycle (Table 1, entry 1). The absence of silver in the filtrate was confirmed by atomic absorption spectroscopy (AAS), which confirmed that no leaching of silver occurred during the reaction, thereby providing a strong evidence for heterogeneity throughout the reaction.

We chose a variety of aldehydes and amines to investigate the scope and generality of the AgTPA-promoted reactions and the results are summarized in Table 2. The amines used for this study included aliphatic, alicyclic and aromatic compounds. Among the various amines tested, aliphatic amines such as piperidine (Table 2, entry 1), morpholine (entry 2) and dibutylamine (entry 5) gave very good yields, whereas the dibenzylamine (entry 4) afforded a poor yield of the coupling product. When cyclohexylcarboxaldehyde was coupled with phenylacetylene and various amines, the reaction time was dramatically reduced with excellent yields of corresponding propargylamines. However, a slight decrease in the yield was observed in the case of dibenzylamine. Aryl aldehydes possessing an electron-withdrawing group afforded better yields (entries 11 and 12) than that with an electron-donating group (entry 13). It is worth noting that 4-nitrobenzaldehyde gave only traces of the coupled product despite a long reaction times



Scheme 1.

Table 1. AgTPA catalyzed three-component coupling of benzaldehyde, piperidine and phenylacetylene in different solvents^a



Entry	Solvent	Yield ^b (%)
1	Acetonitrile	98, 96 ^c
2	Toluene	85
3	1,4-Dioxane	70
4	DCE	5
5	THF	0
6	Water	0

^a Benzaldehyde (1 mmol), piperidine (1.2 mmol), phenylacetylene (1.3 mmol), catalyst (30 mg), acetonitrile, 80 °C, 6 h.

^b Based on isolated yields.

^c Yield after fourth cycle.

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