

Heteropoly acids: a green and efficient heterogeneous Brønsted acidic catalyst for the intermolecular hydroamination of olefins

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Abstract

Intermolecular hydroamination of non-activated olefins with amides and benzyl carbamate proceeds efficiently in the presence of environmentally benign silicotungstic acid (HSiW) catalyst under mild conditions in air to afford addition products in good to excellent yields.

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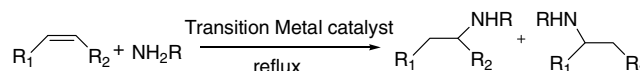
In recent years, Keggin type heteropoly acids (HPAs) catalysts have received much attentions in both academic and industrial applications due to their unique properties, which offers several advantages in terms of catalytic performance, strong acidic, and redox site and selectivity to particular reaction product by selective stabilization of reaction intermediate.¹ HPAs are non-corrosive, environmentally benign, and economically feasible solid acid catalysts compared to conventional homogeneous acids, such as H₂SO₄ or TfOH. Furthermore, they can be reused and recycled easily in most cases after the reaction and hence they are regarded as green catalysts. As a consequence, a variety of synthetically useful transformations have been developed using HPAs as catalysts, such as oxidation of alcohols,² esterification,³ Friedel–Crafts reactions,⁴ Mannich reactions,⁵ cyanosilylation,⁶ ring-opening of epoxides,⁷ and dehydration.⁸

Hydroamination, the simple addition of an N–H bond across C–C unsaturated organic fragment, has attracted much attention in the past decades. Intermolecular hydroamination of olefins is one of the most important and challenging topics in this area.⁹ Despite significant efforts that have been devoted into the intermolecular hydroamination of olefins with alkylamines and arylamines, only a few reports of the intermolecular hydroamination of non-activated alkenes with weakly basic amine nucleophiles such as sulfonamides, carbamates, and carboxamides are known (Scheme 1).

Recently, efficient platinum(II),¹⁰ gold(I),¹¹ Cu(II),¹² Fe(III),¹³ and other metal salts¹⁴ catalyzed hydroaminations of amides and carbamates were reported. Along with the metal catalysts, there also have been examples using metal-free catalysts for the hydroaminations of olefins and amides.¹⁵ Although some notable progress has been made on the hydroamination reactions of alkenes with

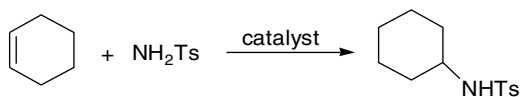
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Scheme 1. Hydroamination reaction.

Table 1
Hydroamination between toluenesulfonamide and cyclohexene under different reaction conditions



Entry ^a	Catalyst	Solvent	Yield ^b (%)
1	H ₃ PW ₁₂ O ₄₀ ·nH ₂ O	DCE	63
2	H ₃ PMo ₁₂ O ₄₀ ·nH ₂ O	DCE	82
3	H ₃ SiW ₁₂ O ₄₀ ·nH ₂ O	DCE	95
4	Na ₃ PMo ₁₂ O ₄₀	DCE	NR
5	(NH ₄) ₃ PW ₁₂ O ₄₀	DCE	Trace
6	Ag ₃ PW ₁₂ O ₄₀	DCE	Trace
7	H ₂ MoO ₄	DCE	NR ^c
8	NH ₂ SO ₃ H	DCE	NR ^c
9	H ₃ SiW ₁₂ O ₄₀ ·nH ₂ O	CH ₃ CN	Trace
10	H ₃ SiW ₁₂ O ₄₀ ·nH ₂ O	<i>n</i> -Heptane	86
11	H ₃ SiW ₁₂ O ₄₀ ·nH ₂ O	CH ₃ Ph	92
12	H ₃ SiW ₁₂ O ₄₀ ·nH ₂ O	1,2-Dioxane	75

^a Reaction conditions: cyclohexene (2 mmol), NH₂Ts (1 mmol), catalyst (100 mg), solvent (2 ml), 85 °C, 18 h, sealed tube, in air.

^b GC yield.

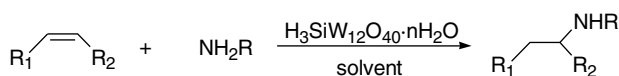
^c Using 0.1 mmol of solid acid as catalyst.

amides in the past two years, there are also some drawbacks on the reported methods, such as using expensive and toxic metals, higher reaction temperature, large excess amounts of olefins, and tedious reaction procedures. *Additionally, most of the reported methods must be carried out under inert atmosphere.* Therefore, the development of a novel, green, and simple catalyst for addition reactions of non-activated alkenes with sulfonamides, carboxamides and carbamates remains an intriguing challenge.

Although silver-exchanged tungstophosphoric acid¹⁶ or using HPAs as acid additive¹⁷ have been examined for intermolecular hydroamination of alkynes with aromatic amines, to the best of our knowledge, there are no studies and reports of HPAs-catalyzed intermolecular hydroamination of olefins with amides. In the present letter, we report an efficiently, easy operational, and reusable heteropoly acids catalyst for the intermolecular hydroamination of various olefins with both amides and carbamates.

In order to study the feasibility of HPAs-catalyzed hydroamination of amides, hydroamination of cyclohexene with *p*-toluenesulfonamide (TsNH₂) was selected as a model reaction (Table 1). Under our reaction conditions,

Table 2
Hydroamination of unactivated olefins with nitrogen nucleophiles¹⁸



Entry ^a	Olefin	Nucleophile	Time (h)/Temp (°C)	Solvent	Product	Yield ^b (%)
1		NH ₂ Ts	23/85	DCE		78
2		NH ₂ Ts	18/85	DCE		91
3		PhSO ₂ NH ₂	18/85	DCE		54
4		NH ₂ Ts	24/45	DCE		78
5		NH ₂ Ts	24/rt	DCE		64
6		NH ₂ Ts	24/45	DCE		68
7		NH ₂ Ts	24/85	DCE		88

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