

Intermolecular hydroamination of vinyl arenes using tungstophosphoric acid as a simple and efficient catalyst

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Abstract—The intermolecular hydroamination of vinyl arene derivatives has been efficiently carried out using a tungstophosphoric acid (TPA) catalyst under solvent free and mild reaction conditions. The present protocol provides an environmentally benign, easy to handle and highly active solid acid catalyst for hydroamination of vinyl arenes. The catalyst yields both hydroamination and hydroarylation products and the selectivity mostly depends on the reaction conditions.

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1. Introduction

The reaction between an alkene and an amine for the synthesis of substituted amines involves multiple steps.¹ The addition of amines to unsaturated carbon–carbon multiple bonds, a process termed hydroamination, has proved to be the best method for preparing highly substituted amines. This methodology has attained considerable interest from both industry and academia. It is well known that acid catalyzed addition of amines to alkenes is generally unsuccessful due to the buffering effect of the amine substrate.² Also Friedel–Crafts alkylations of aryl amines are hindered by coordination of the amine to the Lewis acid catalyst.^{3a} Therefore the development of these reactions remains an intriguing challenge for chemists. In previous studies, hydroamination of alkenes with amine derivatives has been carried using various ligand mediated acid catalysts.^{3b–d} Hartwig and Schlummer⁴ reported that several common Brønsted acids catalyze the intermolecular hydroamination of tosyl-protected amino olefins. Beller et al.⁵ reported alkylation of electron rich anilines with styrene promoted by $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. Furthermore, Anderson et al. described the proton catalyzed hydroamination and hydroarylation of an alkene with an amine,⁶ whereas Kaspar et al. reported TiCl_4 catalyzed hydroamination and hydroarylation reactions.⁷ A number of significant

contributions have been made on the use of late-transition metal complexes for the hydroamination of olefins using iridium,⁸ rhodium,⁹ nickel,¹⁰ palladium,¹¹ platinum¹² and ruthenium.¹³ The high cost of these complexes and their stabilizing ligands or the additives constitute limitations of these protocols. Indeed, the hydroamination mainly proceeds over long reaction times and at high reaction temperatures. Recently, several Brønsted acids such as triflic acid and H-montmorillonite have been reported for the hydroamination of activated and unactivated alkenes with numerous reactive amide derivatives.¹⁴ However, the hydroamination of styrene and aniline derivatives is limited due to rapid oligomerization of the styrene. Thus, it remains an intriguing challenge for researchers to develop improved catalytic systems for the hydroamination of vinyl arenes with substituted aniline derivatives.

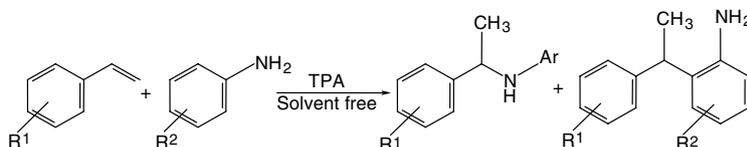
In the present Letter, we disclose an environmentally benign, efficient, reusable tungstophosphoric acid (TPA) catalyst for intermolecular hydroamination of alkenes under mild and solvent-free conditions (Scheme 1). The present catalyst promotes the complete reaction within reasonable reaction times and affords high product yields.

2. Results and discussion

Experimental results showed that 1 mmol of the styrene derivative reacts with 2 mmol of the aromatic amine in the presence of TPA under solvent-free conditions.

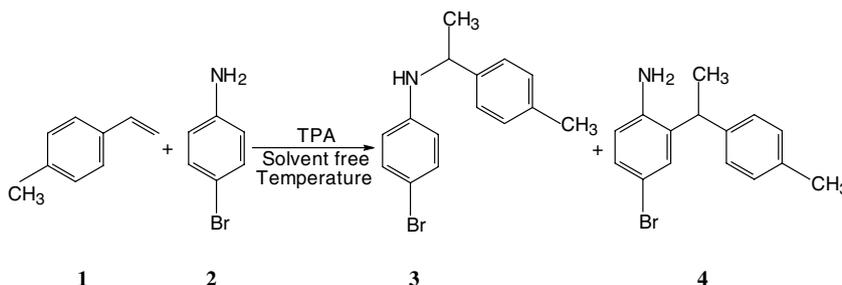
Keywords: Hydroamination; Vinyl arene; Solvent free; TPA.

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Scheme 1. Catalytic intermolecular hydroamination of vinyl arenes.

Table 1. Acid catalyzed hydroamination of 4-methyl styrene^a



Entry	Catalyst	Time (h)	(%) Yield 3 ^c	(%) Yield 4 ^c
1	TPA	3 ^b	82	Trace
2	TPA	1.5	75	Trace
3	TPA	6	25	70
4	H ₂ SO ₄	18	—	—
5	TFA	12	—	—
6	CH ₃ COOH	18	—	—
7	Cp ₂ TiCl ₄	18	—	—

^a Reaction conditions: 4-methylstyrene (1.0 mmol); 4-bromoaniline, (2 mmol); catalyst wt: 30 mg; reaction temperature, 80 °C.

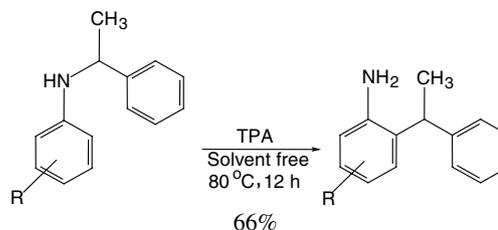
^b Reaction temperature, 60 °C.

^c Yields were determined by ¹H NMR spectroscopy.

Initially, the hydroamination of 4-methylstyrene with 4-bromoaniline (Table 1) was carried out using TPA and its activity was compared with other acid reagents such as H₂SO₄, triflic acid (TFA) and CH₃COOH. TPA catalyzed the reaction within a reasonable time, whereas simple Brønsted acids did not catalyze this reaction (Table 1, entries 4–6). These results are in agreement with observations made by Hartwig and Schlummer.⁴

Under the present reaction conditions, a mixture of hydroamination and *ortho*-hydroarylation products was obtained. In order to study the ratio of these products, the reaction conditions were varied with respect to reaction time and temperature. Experiments showed that the yield of the *ortho*-alkylated hydroarylation product increased with an increase in reaction time and temperature. Prolonged reaction times resulted in rearrangement of the hydroamination product to give the *ortho*-alkylated hydroarylation product.

In order to confirm the rearrangement of the hydroamination product over time, we prepared the secondary amine independently¹⁵ and subjected it to the present reaction conditions (Scheme 2). Indeed, the secondary amine was converted quantitatively into the hydroarylation product by a Hofmann–Martius rearrangement.¹⁶ Marcsekova and Doye¹⁷ reported that the hydroamination reaction is favourable for aliphatic alkenes and the hydroarylation becomes more favourable for styrene derivatives. In the present studies, it was also found that



Scheme 2. TPA catalyzed rearrangement of the hydroamination product.

the product selectivity varied with reaction time (Table 1, entries 2, 3 and Table 2, entry 11) and our results are in good agreement with those reported.¹⁷

Catalytic intermolecular hydroaminations of styrene derivatives were carried out using TPA to study the scope of this catalyst (Table 2). A number of vinyl arenes **1** and aniline derivatives **2** were converted to hydroaminated **3** and hydroarylated **4** products in high yields. It is interesting to note that anilines with electron withdrawing groups present on the aromatic ring reacted smoothly. In marked contrast, vinyl arenes with an electron donating substituent (4-methyl) present on the aromatic ring reacted at a faster rate compared to those with electron withdrawing groups such as 4-chloro or 4-bromo. Additionally, α -methylstyrene (Table 2, entry 14) was converted into **3** and **4** (70:30). TPA also catalyzed the reaction of a sterically demanding aniline

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