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Heteropoly acids as useful recyclable heterogeneous catalysts for the facile and highly efficient aza-cope rearrangement of *N*-allylanilines

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ABSTRACT

Heteropoly acid phosphomolybdic acid ($H_3Mo_{12}O_{40}P$) has been found to be an excellent catalyst for aza-cope rearrangement of *N*-allylanilines. Various organic solvents and ionic liquids were tested as reaction media. Better results were obtained in ionic liquid reaction media in terms of reaction time and yield of the product. Catalyst could be efficiently recovered from the reaction and reused with negligible loss of catalyst activity even after two cycles. Short reaction time, ambient conditions, simple workup and high yield are some of the striking features of the present protocol.

1. Introduction

The Claisen rearrangement involving [3,3] sigmatropic shift in vinyl and aryl allyl ethers is one of the important C–C bond formation reactions, and thus has been studied extensively [1–4]. However, the nitrogen analogue of this reaction (aza-cope rearrangement) has many limitations, such as slow rates, requirement of high temperature, and low yield [5–8]. The thermal, uncatalysed aromatic amino claisen rearrangement (aza-cope rearrangement) requires a temperature of 250–280 °C; under such a high temperature, aromatic *N*-allylamines are not stable; e.g., *N*-allylaniline heated at 275 °C gave aniline, propane and tar instead of the expected *ortho*-allylaniline [9]. The rearrangement is promoted in the presence of transition metals, Lewis or protic acids as catalysts [10–17]. Protic acids such as HCl, H_2SO_4 and H_3PO_4 [18–19] have been used in certain aromatic aza-cope rearrangements. But the use of strong protic acids with *N*-allylanilines may form indole and indoline products, thereby reducing the effectiveness of this reaction [20].

Another approach for this reaction is the generation of quaternary intermediates by using electrophilic reagents. The electrophile sources such as Bronsted acids have been used to promote this rearrangement at the temperature of 140–150 °C; e.g., polyphosphoric acid has been used to promote charge accelerated 3 aza-cope rearrangement, but effective use of this reagent is limited. To overcome the limitations of the present catalysts, we decided to explore the HPAs as catalyst for this reaction. This was a successful attempt to utilize it for aza-cope rearrangement.

In recent decades, the use of heteropoly acids (HPAs) as catalysts has become important in industries related with fine chemicals [21]. HPAs are more active catalyst than conventional inorganic and organic acids for various reactions in solution [22,23]. Solid HPAs have gained importance due to easy work-up procedures and minimization of waste generation. They are non-corrosive and are environmentally benign, as they can be reused and recycled [24].

We have attempted the aza-cope rearrangement of *N*-allylaniline using heteropoly acid $H_3Mo_{12}O_{40}P$ (Scheme 1) in an ionic liquid.

2. Experimental

All commercial reagents were used as received without purification and all solvents were reagent grade. The reaction was monitored by TLC using on 0.25 mm E-Merck silica gel 60 F_{254} precoated plates, which were visualized with UV light. Melting points were taken in open capillaries. The IR spectra were recorded

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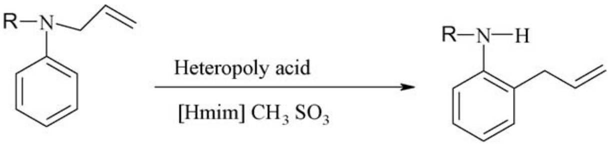


Scheme 1.

Table 1
Catalyst effect on aza-cope rearrangement of *N*-allylaniline.[a].

Entry	Catalyst	Time (h)	Yield (%)[b]
1	$H_3Mo_{12}O_{40}P$	4.5	80
2	$BiCl_3$	6	65
3	$CdCl_2$	6.5	50
4	$InCl_3$	6	65
5	$CeCl_3$	6	60
6	$FeCl_3$	6.5	47
7	$ZrCl_3$	5.5	62
8	$AlCl_3$	6	65

[a] Reaction conditions: *N*-allylaniline (0.01 mol), catalyst (0.002 mol), ionic liquid (2 ml) as solvent, stirred.
[b] Isolated yield.

Table 2
Solvent effect on the aza-cope rearrangement of *N*-allylaniline.[a].

Entry	Solvent	Time (h)	Yield (%)[b]
1	CH_3CN	6	70
2	CH_2Cl_2	5	70
3	$CHCl_3$	5.5	68
4	CCl_4	5.5	65
5	THF	6	60
6	CH_3COCH_3	6	65
7	$ClCH_2CH_2Cl$	5	70
8	CH_3OH	5.5	55
9	Ionic liquid	4.5	80

[a] Reaction conditions: *N*-allylaniline (0.01 mol), phosphomolybdic acid (0.002 mol), solvent (2 ml), stirred.
[b] Isolated yield.

on a PerkinElmer 257 spectrometer using KBr discs. ^1H NMR and ^{13}C NMR spectra were recorded on a VXR-300 MHz instrument using TMS as an internal standard.

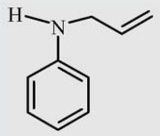
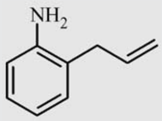
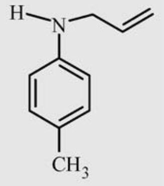
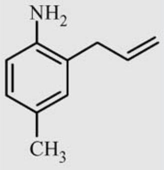
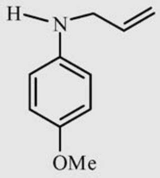
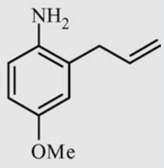
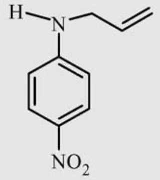
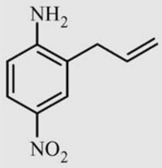
2.1. General experimental procedure

A mixture of 4-chloro *N*-allyl aniline (0.01 mol), ionic liquid 3-methylimidazolinium methane sulfonate (2 ml) and phosphomolybdic acid (0.0002 mol) was stirred at ambient temperature for the appropriate time, as indicated in Table 3. After completion of reaction, as monitored by TLC, the reaction mixture was extracted with diethyl ether and washed with water. Diethyl ether extract was dried on anhydrous sodium sulphate and concentrated under reduced pressure. The product obtained was purified by column chromatography.

2.1.1. Representative spectral data for product 2-allyl-4-chloroaniline (5)

IR (KBr): 3460, 3350, 2958, 1620, 1578, 1510, 1305, 1280, 1045 cm^{-1}.

Table 3
Aza-cope rearrangement of various *N*-allylanilines.[a].

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			4.5	80
2			4.5	80
3			4	78
4			5	60