

Short communication

H₁₄[NaP₅W₃₀O₁₁₀]: A heteropoly acid catalyzed acetylation of alcohols and phenols in acetic anhydride

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Abstract

A trace amount of H₁₄[NaP₅W₃₀O₁₁₀] (0.1 mol%) has been effectively used as heteropoly acid catalyst for acetylation of alcohols and phenols with acetic anhydride at room temperature.

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Keywords: H₁₄[NaP₅W₃₀O₁₁₀]; Acetylation; Acetic anhydride; Alcohols; Phenols

1. Introduction

Acetylation of hydroxyl groups is one of the most frequently used transformations in organic synthesis. Among the various protecting groups used for the hydroxyl function, acetyl is the most common group in view of its easy introduction, being stable to the acidic reaction conditions, and also easily removable by mild alkaline hydrolysis [1]. The most commonly used reagent combination for this reaction uses acid anhydride in the presence of acid or base catalysts [2]. Various metal salts such as CoCl₂ [3], TiCl₄–AgClO₄ [4], Me₃SiCl [5], LiClO₄ [6], Mg(ClO₄)₂ [7] and some metal triflates such as Se(OTf)₃ [8] MeSiOTf [9], In(OTf)₃ [10], Cu(OTf)₂ [11] and Bi(OTf)₃ [12] have been investigated to meet the demand for more efficient and selective methods. In spite of these waves of interest due to the importance of acetylation, introduction of inexpensive and green catalyst for this purpose is still in much demand.

Development of methods using heteropoly acids (HPAs) as catalysts for fine organic synthetic processes related to fine chemicals, such as flavors, pharmaceuticals and food industries [13] have been under attention in the last decade. Heteropoly acids are more active catalysts than conventional inorganic and organic acids for various reactions in solution [14]. They are used as industrial catalysts for several liquid-phase reactions [15–18],

such as alcohol dehydration [19], alkylation [20], or esterification [21] reactions. Among heteropoly acids, polytungstic acids are the most widely used catalysts owing to their high acid strengths, thermal stabilities and low reducibilities. The catalysts based on heteropoly acids have many advantages over liquid acid catalysts. They are not corrosive and environmentally benign, presenting fewer disposal problems. Solid heteropoly acids have attracted much attention in organic synthesis owing to easy workup procedures, easy filtration, and minimization of cost and waste generation due to reuse and recycling of the catalysts [22].

2. Results and discussion

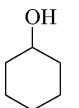
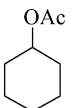
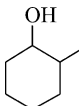
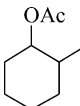
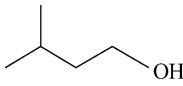
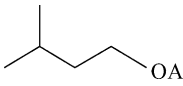
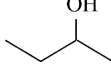
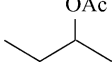
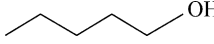
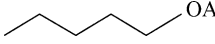


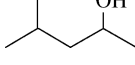
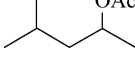
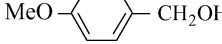
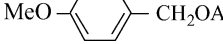
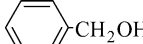
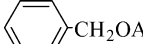
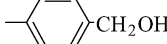
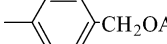
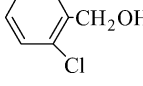
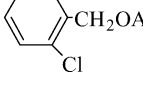
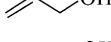
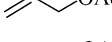
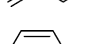
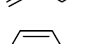
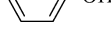
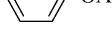
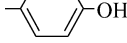
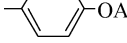
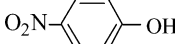
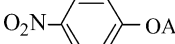
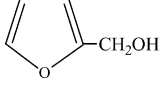
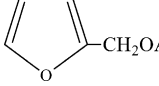
Recently, we described acetylation of alcohols and phenols [23] and direct acetylation of tetrahydropyranyl ethers [24] by ferric perchlorate and acetylation of THP ethers by bismuth nitrate [25]. In continuation with our work using heteropoly acids [26] which are low in toxicity, highly stable towards humidity, being recyclable and air stable, we found that a trace of H₁₄[NaP₅W₃₀O₁₁₀] (0.1 mol%) is able to promote quantitative acetylation of alcohols and phenols using acetic anhydride as acetylating agent, at room temperature, in high yields and short reaction time in solvent free conditions with a simple method and easy workup procedure (Scheme 1; Table 1).

In order to extend the scope of this acetylation reaction, it was carried out on a variety of substrates using a typ-

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Table 1
Acetylation of alcohols and phenols with acetic anhydride catalyzed by $H_{14}[NaP_5W_{30}O_{110}]$

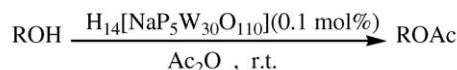
Entry	Substrate	Product	Time (h)	Yield% ^a
1			0.5	95
2			0.75	92
3			1.5	93
4			2.0	90
5			0.5	88
6			2.0	90
7			1.5	92.5
8			0.5	98
9			1.2	95
10			0.5	93
11			3.0	97
12			2.0	91
13			2.0	87
14			1.0	95
15			0.75	91
16			1.5	89
17	$Ph-CH=CH-CH_2-OH$	$Ph-CH=CH-CH_2-OAc$	2.0	96
18			0.5	95

^a Yields are based on GC analysis.

ical procedure where 0.1 mol% of $H_{14}[NaP_5W_{30}O_{110}]$ and 1–1.5 equivalent of substrate to acetic anhydride was added, at room temperature. We carried out the reaction in the absence of catalyst for cyclohexanol (entry 1, Table 1). No acety-

lation was observed over the same or prolonged reaction time.

The general efficiency of this reaction is evident from the variety of hydroxyl compounds including primary, secondary,



R: benzy-, allyl-, n-Pentyl-, propargyl-, cyclohexyl-, 2-methyl cyclohexyl-, tert-butyl-, cinnamyl-, p-methyl phenyl-, phenyl-, 4-nitro phenyl-, 2-butyl-, 2-chloro benzyl-, 4-methoxy benzyl-, 4-methyl benzyl-, isoamyl-, 2-furyl-, 4-methyl 2-pentyl-

Scheme 1.

tertiary, benzylic alcohols and phenols, which react in excellent yields within a short reaction time.

Primary alcohols being acetylated within less time than secondary and tertiary alcohols. It is very interesting to note that tertiary and secondary alcohols such as *t*-butanol and 4-methyl-2-pentyl alcohol (entries 6 and 7, Table 1) can also be acetylated with satisfactory yields and there was no elimination product in the mixture.

This method tolerates other functionalities on the substrate such as double and triple bonds. It was, in fact, possible to obtain easily, the quantitative acetylation of propargyl, allyl and cinnamyl alcohols (entries 12, 13 and 17, Table 1). We also used phenols with withdrawing, and releasing electron groups, which are converted to the corresponding phenyl acetates in excellent yields and short reaction time (entries 14–16, Table 1).

3. Experimental

All products were known and their physical and spectroscopic data were compared with those of authentic samples. IR spectra were recorded on Bruker 4000–400 cm^{-1} . Yields are based on GC/mass analysis using Agilent 6890 GC system Hp-5 capillary 30 m \times 530 μm \times 1.5 μm nominal. All chemicals were purchased from commercial suppliers and were used as received.

3.1. Acetylation of alcohols and phenols catalyzed by $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$: typical procedure

Benzyl alcohol (1 mmol, 0.12 g), acetic anhydride (1.5 mmol, 0.18 ml) and $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ (0.001 mmol, 0.074 g) were mixed. The mixture was stirred at room temperature 75 min (Table 1). Upon completion of the reaction monitored by (TLC) the reaction mixture was diluted with sodium bicarbonate 10% (15 ml) and extracted with CH_2Cl_2 (3 \times 20). Combined organic layers were dried over Na_2SO_4 , the solvent was removed by evaporation to afford the acetylated compound (Table 1).

3.2. Recycling of the catalyst

At the end of the reaction, the catalyst was filtered, washed with dichloromethane, dried at 130 $^\circ\text{C}$ for 1 h, and re-used in another reaction. The recycled catalyst was used for five reactions without observation of appreciable loss in its catalytic activities.

4. Conclusions

We have reported a catalytic method for acetylation of alcohols and phenols using $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ as an efficient,

reusable and eco friendly heterogeneous inorganic catalyst. The salient features of these reactions are, use of 1–1.5 equivalent of substrate to acetic anhydride and catalytic amounts of $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ which is concomitant to solvent less and catalytic nature of the reaction. High yields, working at room temperature and short reaction time with an easy workup procedure are other features of this reaction. The catalyst is also reusable after filtration and can be used at least five times without loss of appreciable catalytic activities.

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