



Acetylation of Phenols, Alcohols and Amines Catalyzed by Mono Ammonium Salt of 12-Tungstophosphoric acid under Ambient Conditions

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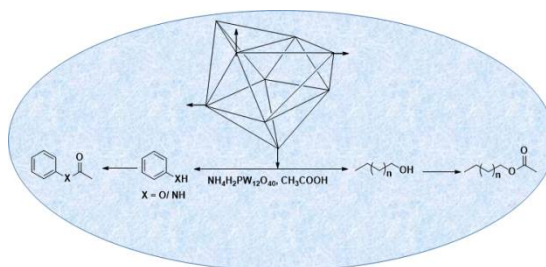
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ABSTRACT

A simple, highly rapid and efficient method is developed for the acetylation of phenols, alcohols and amines with excellent yield using monoammonium salt of 12-Tungstophosphoric acid $[(NH_4)_2H_2PW_{12}O_{40}]$ as a solid phase catalyst under ambient conditions. The salient features of this hetero polyacid catalyst are simple workup procedure, short reaction time, insoluble both in protic and aprotic solvents, high yield and reusable nature.

Graphical Abstract



Hilights

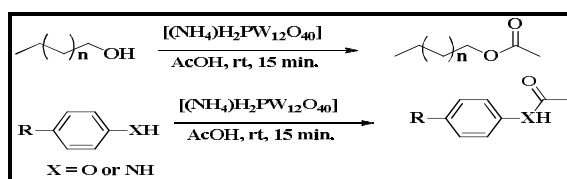
- Acetylation of alcohols, phenols and anilines in the presence of monoammonium salt of tungstophosphoric acid $[(NH_4)_2H_2PW_{12}O_{40}]$.
- Very easy to separate catalyst and products
- Obtained pure products with high yields.
- Catalyst is recycled for five times and yield of the products marginally varied from the first to fifth cyclic process.

Keywords: Acetylation, Monoammonium Salt of 12-Tungstophosphoric Acidcatalyst, Ambient conditions.

INTRODUCTION

Acetylation of alcohols, phenols and amines is the most important step in the synthesis of organic and poly functional molecules such as nucleoside, natural products, steroids and carbohydrates. The protection of alcohols, phenols and amines is an important and widely used transformation in the synthetic organic chemistry [1, 2]. Among different protecting methods used for the hydroxyl and amine groups, Acetylation is one of the most significant route, due to its high stability in the acid reaction conditions and also easy removal using mild alkaline hydrolysis [3]. Usually, acetic anhydride or acetyl chloride is the most commonly used catalysts in the presence of Et₃N and pyridine [4-6]. 4-(Dimethylamino) pyridine (DMAP) is known to basis for notable rate acceleration in the reaction [7]. Various catalysts are used such as silica gel supported sulphuric acid [8, 9], ammonium acetate in acetic acid [10], Zinc dust [11], ZnCl₂ [12], CoCl₂ [13], Sc(OTf)₃ [14], TaCl₅ [15] Montmorillonit-K10 [16], HY Zeolite [17], In(OTf)₃ [18], Cu(OTf)₂ [19], Yittria-Zirconia based Lewis acid [20], InCl₃/Montomorillonit-K10 [21], Manganese (III) bis(2-hydroxyanil) acetyl acetonato complex [22], Silica sulfate [23], p-MeC₆H₄SO₂NBr₂ [24], DBDMH or TCCA [25], H₆P₂W₁₈O₆₂·24H₂O [26], La(NO₃)₃·6H₂O [27], Ionic liquid based on morpholine [28], Borated zirconia [29], 2,4,6-Triacyloxy-1,3,5-triazine (TAT) [30], Sodium dodecyl sulfate (SDS) [31] and DMAP saccharin [32] to catalyze the acetylation of alcohols, phenols and amines. In the past years, the search for environmentally benign chemical processes has received much attention [33-36]. However, some of these methods suffer from any one or more of the following disadvantages like vigorous reaction conditions, prolonged reaction time, toxicity and expensive reagents, tedious workup procedures, low yields, instability nature of the reagents. Even after remarkable efforts, the development of an efficient method for the acetylation of alcohols, phenols, and amines is still a significant challenge.

Keggin type of heteropoly acids (HPAs) have gained much attention due to their economical and environmental importance for both academic and industrial applications. They are suitable as acid and oxidation catalysts for numerous reactions since their catalytic features can varied at the molecular level [37, 38]. The most commonly used heteropoly acid is the dodeca tungstophosphoric acid (12-TPA, H₃PW₁₂O₄₀) [39]. Nevertheless, the main disadvantage to put into practice of acid form of heteropoly mixtures is their solubility in polar solvents as well as water. This problem can be solved by converting it into its salt. Salt of HPA was prepared by partial replacing of the protons from paternal HPA with bulky cations, such as Cs⁺, K⁺, Rb⁺ and NH₄⁺, which are not soluble in water and are with a rather high surface area (> 100 m²/g) [40, 41]. Using HPA, with tunable catalytic functionality, less in toxicity, stable at high temperature, water-insoluble, environmentally approachable have originated more responsiveness in freshcycles. In this framework, a heterogeneous TPA catalyst was synthesised by partial proton-replacement with ammonium carbonate to result in water insoluble catalyst namely mono-ammonium salt of 12-tungstophosphoric acid (ATPA) [(NH₄)H₂PW₁₂O₄₀] [42] and employed for different applications [43-47]. In continuation of our efforts towards exploring the applications of the mono ammonium salt of 12-tungstophosphoric acid catalyst we report, a modest and an efficient methodology for the acetylation of alcohols, phenols and amines with acetic acid under ambient conditions in excellent yields (Scheme 1). The improvement of the present catalyst is that it does not involve any additives or promoters. Furthermore, the preparation of the catalyst is very simple, inexpensive and reusable without any loss of activity. Monoammoniumsalt of 12-TPA has excellent catalytic properties with good selectivity and reusability [42].



Scheme 1. Acetylation of Alcohols, phenols, and amines employing [(NH₄)H₂PW₁₂O₄₀] catalyst.

MATERIALS AND METHODS

All chemicals and reagents were procured from suppliers and used without further purification. The $[(\text{NH}_4)_2\text{H}_2\text{PW}_{12}\text{O}_{40}]$ catalyst was prepared according to our previously published works [42-47]. We monitored the progress of the reactions on observing TLC. The products were characterized by chromatographic and spectral studies (GC, GC-MS, FT-IR and ^1H NMR). The spectra are compared with those of standard esters. The ^1H NMR spectra of the products were obtained using Bruker AC-300 MHz spectrometer with TMS as the internal standard.

Overall procedure for the preparation of the catalyst: Mono ammonium salt of 12-tungstophosphoric acid (ATPA) was prepared by simple ion exchange of 12-tungstophosphoric acid (TPA) with a required amount of ammonium carbonate in an aqueous medium. Ammonium carbonate solution (0.167 g, 0.17 mmol, dissolved in 10 mL of distilled water) was added dropwise to an aqueous solution of 12-tungstophosphoric acid (10 g, 0.35 mmol, dissolved in 50 mL of distilled water) at 80°C under continuous stirring. The reaction mixture was stirred at 80°C for 3 h, evaporated, dried and kept at 120°C overnight. The catalyst was calcined in air at 350°C for 4 h to obtain mono-ammonium salt of 12-tungstophosphoric acid (yield. 9.25 g, 92%).

General procedure for the catalytic Acetylation of Alcohols, Phenols, and Amines: A mixture of the alcohol/amine (1 mmol) and acetic acid (2 mL), mono-ammonium salt of 12-tungstophosphoric acid catalyst (5 wt% of substrate) was added and stirring at room temperature for 15 to 30 min. The progress of the reaction was monitored by observing TLC. After completion of the reaction, the reaction mixture was filtered to separate the catalyst. The reaction mixture was evaporated, and final compound was purified by silica gel column chromatography using hexane/ethyl acetate as eluting solvent. The yield was calculated as mmol of purified product with respect to mmol of initial alcohol/amine. The reaction times and yields of the products are presented in tables 1 and 2. All the purified products were characterized by GC, IR and ^1H NMR studies and the data is in comparison with authentic samples.

Table 1. Effect of $(\text{NH}_4)_2\text{H}_2\text{PW}_{12}\text{O}_{40}$ catalyst loading on the acetylation of 1-decanol^a

S.No.	Catalyst loading (wt.% of alcohol)	Time (min)	Yields (%) ^b
1	2	30	60
2	3	25	75
3	4	20	89
4	5	15	94
5	10	10	95

^aReaction conditions: 1-Decanol (1 mmol), Ac_2O (2 mmol), RT, ^bGC yield)

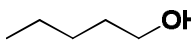
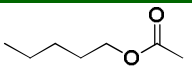
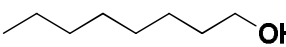
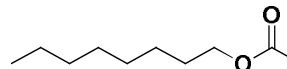
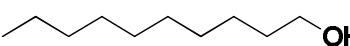
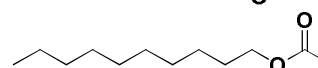
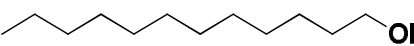
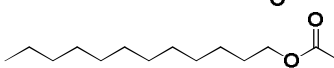
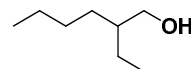
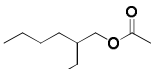

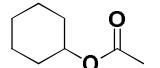

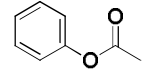
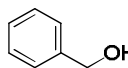
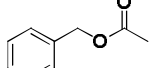
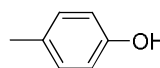
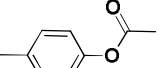
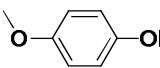
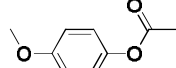
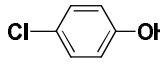
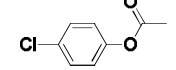

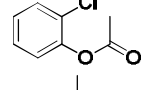


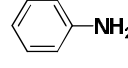
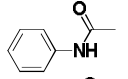
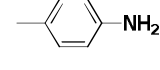
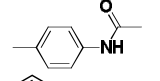
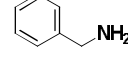
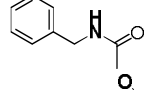
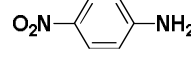
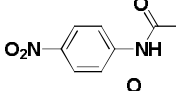
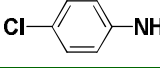
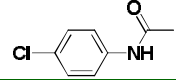
N-phenylacetamide (Entry 1, Table 2), ^1H NMR (300 MHz, CDCl_3) δ 2.15 (s, 3H), 7.16-7.11 (m, 1H), 7.25 (broad s, 1H), 7.36-7.30 (m, 2H), 7.55-7.52 (m, 2H). IR (cm^{-1}): 3290, 1660, 1595, 1550, 1500, 1430, 1368, 1327, 1262, 1040, 1012, 962, 906, 750. GC-MS m/z: 135 $[\text{M}]^+$.

N-benzylacetamide (Entry 2, Table 2), ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.29 (m, 5H), 6.05 (bs, 1H), 4.43 (d, 2H), 2.03 (s, 3H). IR (cm^{-1}): 3292, 1644, 1546, 1503, 1280. GC-MS m/z: 149 $[\text{M}]^+$.

1-Decyl acetate (Entry 3, Table 2), ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, 3H), 1.15 -1.45 (m, 30H), 2.0 (m, 2H), 2.04 (s, 3H), 4.05 (t, 2H). IR (cm^{-1}): 2927, 2855, 1731, 1239. GC-MS m/z: 200 $[\text{M}]^+$.

2-Ethyl-1-hexyl acetate (Entry 6, Table 2), ^1H NMR (300 MHz, CDCl_3) δ 0.9 (t, 6H), 1.15-1.4 (m, 7H), 2.10 (s, 3H); 3.92 (t, 2H). IR (cm^{-1}): 3020, 2962, 1726, 1215, 763. GC-MS m/z 172 $[\text{M}]^+$.

Table 2. Acetylation of Alcohols, phenols by employing (NH₄)H₂PW₁₂O₄₀ catalyst^c

Entry	Substrate	Product	Time (min)	Yield (%) ^d
1			15	94
2			15	92
3			15	90
4			15	86
5			15	89
6			15	95
7			20	85
8			15	91
9			20	86
10			20	88
11			20	89
12			45	78
13			25	84
14			30	90
15			30	88
16			30	90
17			45	76
18			30	85

Cyclohexyl acetate (Entry 7, Table 2), ¹H NMR (300 MHz, CDCl₃) δ 1.20-1.90 (m, 10H), 2.05 (s, 3H), 4.55 (m, 2H). IR (cm⁻¹): 3022, 2935, 1720, 1255, 1225, 760. GC-MS m/z: 142 [M]⁺.

Phenyl acetate (Entry 8, Table 2), ¹H NMR (300 MHz, CDCl₃) δ 2.26 (s, 3H), 7.0-7.36 (m, 5H). IR (cm⁻¹): 1755, 1185, 750. GC-MS m/z: 136 [M]⁺.

Benzyl acetate (Entry 9, Table 2), ¹H NMR (300 MHz, CDCl₃) δ 2.10 (s, 3H), 5.10 (s, 2H), 7.16-7.30 (m, 5H). IR (cm⁻¹): 3025, 1725, 1221, 766. GC-MS m/z: 150 [M]⁺.

4-Methylphenyl acetate (Entry 10, Table 2), ^1H NMR (300 MHz, CDCl_3) δ 2.05 (s, 3H), 2.20 (s, 3H), 6.95 (d, 2H), 7.05 (d, 2H). IR (cm^{-1}): 3017, 2956, 1730, 1150, 751. GC-MS m/z : 150 $[\text{M}]^+$.

4-Methoxyphenyl acetate (Entry 11, Table 2), ^1H NMR (300 MHz, CDCl_3) δ 2.10 (s, 3H), 3.70 (s, 3H), 6.80-7.10 (m, 4H). IR (cm^{-1}): 3010, 2965, 1750, 1516, 1227, 1183, 755. GC-MS m/z : 166 $[\text{M}]^+$.

4-Chlorophenyl acetate (Entry 12, Table 2), ^1H NMR (300 MHz, CDCl_3) δ 1.95 (s, 3H), 7.05 (d, 2H), 7.25 (d, 2H); IR (cm^{-1}): 1760, 1210, 1195, 755; GC-MS m/z : 170 $[\text{M}]^+$.

2-Chlorophenyl acetate (Entry 13, Table 2), ^1H NMR (300 MHz, CDCl_3) δ 2.15 (s, 3H), 7.05 (d, 2H), 7.45 (d, 2H). IR (cm^{-1}): 1761, 1212, 756. GC-MS m/z : 170 $[\text{M}]^+$.

1-Naphthyl acetate (Entry 14, Table 2), ^1H NMR (300 MHz, CDCl_3) δ 2.35 (s, 3H), 7.15-7.85 (m, 7H). IR (cm^{-1}): 3065, 2920, 1755, 1360, 1205, 775. GC-MS m/z : 186 $[\text{M}]^+$.

RESULTS AND DISCUSSION

Characterization of mono-ammonium salt of tungstophosphoric acid: The atomic ratio of the three samples is evaluated from energy dispersive spectra (Figure 1a). The thermal stability of the compound was examined by thermogravimetric analysis. The thermogram gives information about the lattice held by water molecules as 2.5 %, in the $[(\text{NH}_4)_2\text{H}_2\text{PW}_{12}\text{O}_{40}]$ (ATPA) which is shown in figure 1b. ATPA phases are observed as a similar pattern with respect to TPA. However, ATPA particles can be found in the SEM image quite different than TPA particles as shown figure 1c. Figure 1d displays the UV-Vis absorption spectra of ATPA and TPA. The absorption band edge of TPA is at about 396 nm, corresponding to the band gap energy of 3.13 eV. In the case of ATPA bandgap energy fell around 0.6 eV which indicates that the absorption bands are moved towards red shift i.e, higher wavelength region.

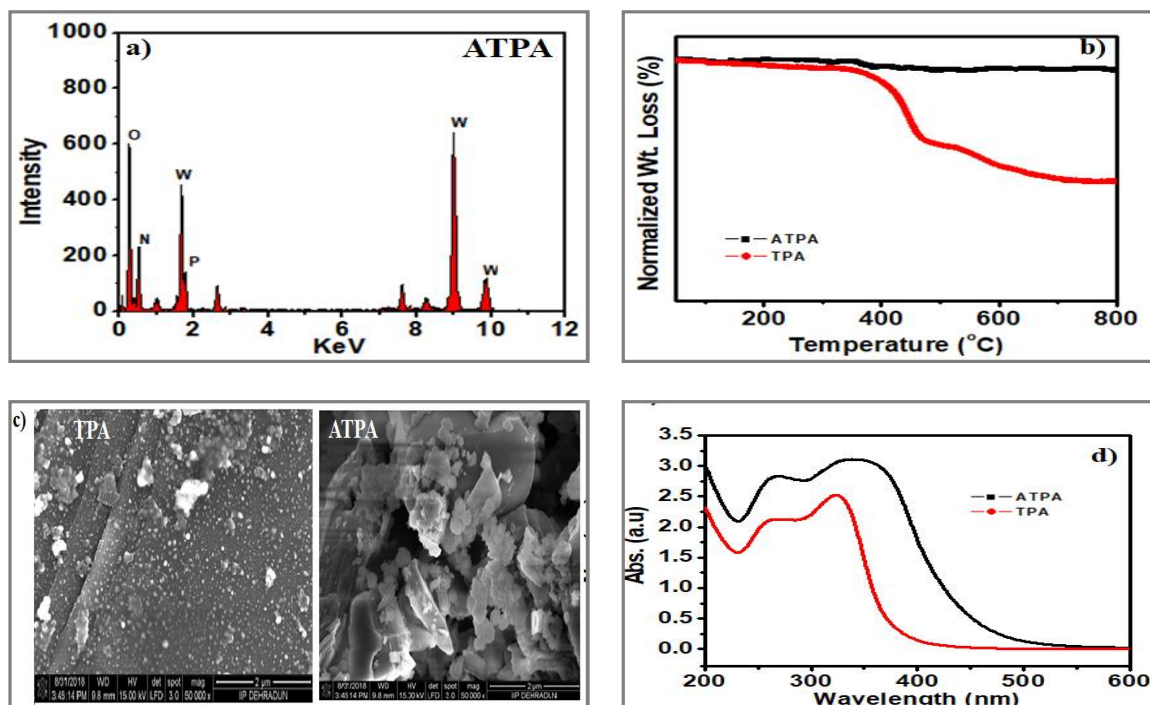


Figure 1. a) EDS image of ATPA, b) thermogram of ATPA and TPA, c) SEM images of ATPA and TPA, d) UV-Vis-DRS spectra of ATPA and TPA.

APPLICATION

Applications of mono-ammonium salt of tungstophosphoric acid: The initial acetylation of 1-decanol (1 mmol) with acetic acid in presence of 5 wt% of the $[(\text{NH}_4)\text{H}_2\text{PW}_{12}\text{O}_{40}]$ catalyst with stirring at ambient condition afford 1-decyl acetate with 97% yield in 15 min. However, the acetylation of 1-decanol with acetic anhydride at room temperature resulted in 98% acetylated product only after 1 h. After the successful acetylation of 1-decanol to decyl acetate with excellent yield, the effect of catalyst for the acetylation of 1-decanol with acetic acid(1:2 mmol) to decyl acetate was considered by varying the catalyst dosage from 2 to 10 wt% of alcohol (Table 2). The rate of the reaction was found to increase slowly at room temperature with the rise of the catalyst loading from 2 to 10 wt% of alcohol. The reaction time substantially decreased from 30 min to 10 min with conversions ranging from 60% to 96% (entries 1-4, Table 2). However, with increase of the catalyst loading to 10 wt% decreased the reaction time marginally from 15 min to 10 min with 98% conversion. The reactions are monitored by GC using HP-1 capillary column. Based on this study, 5 wt% of the $[(\text{NH}_4)\text{H}_2\text{PW}_{12}\text{O}_{40}]$ catalyst was found to be optimum for the acetylation of 1-decanol with 96% conversion at RT in 15min.

In order to improve the efficiency and the adequacy of the technique in a extensive perspective of synthetic organic chemistry, Acetylation of various alcohols and phenols with electron donating and electron withdrawing groups were studied in presence of acetic acid under optimum conditions and the results are given in table 1. Acetylation of phenols was found to be slow when compared to aliphatic alcohols. Phenols with electron donating and electron withdrawing groups (entries 9, 11 -13 and15, Table 2) acetylated in 91-94% yields within 15-30 min. Similar results are observed in case of benzyl alcohol also (entry 10, Table 2). However, acetylation of 2-chlorophenol resulted in 2-chlorophenyl acetate (81%, entry 14, Table 2) in less yields when compared to 4-chlorophenyl acetate (93% yields, entry 13, Table 2) due to steric effect. In a similar fashion acetylation of aromatic amines also executed and obtained the corresponding acylated products in good yields (92% - 96%, entries 1-5, Table 2) in 15-25 min.

The reusability studies of the $[(\text{NH}_4)\text{H}_2\text{PW}_{12}\text{O}_{40}]$ catalyst were done by the acetylation of benzyl alcohol employed for three cycles under the optimum conditions. After the completion of the reaction, the catalyst was recovered by simple filtration and washed several times with ethyl acetate. Later the catalyst was dried in the oven at 120°C for 1h and reused. The reusability of the catalyst was found to be effective up to three cycles without any loss in the activity. All the products were characterized by FT-IR, $^1\text{H-NMR}$ and GC-MS analysis.

CONCLUSION

In conclusion, the use of a simple, efficient and eco-friendly procedure for the solvent-free acetylation of alcohols, phenols, and amines with acetic acid using mono-ammonium salt of 12-tungstophosphoric acid catalyst as a solid acid catalyst is studied. The advantages of the present procedure are i) mild reaction conditions; ii) heterogeneous reaction conditions; iii) shorter reaction time; iv) low cost and v) simple method of synthesis of the catalyst. The very simple, straight forward procedure and workup process makes the catalyst very efficient and attractive for this type of reactions. The yields are exquisite, and, in addition, the mono-ammonium salt of 12-tungstophosphoric acid catalyst based solid acid catalyst can be recovered by simple filtration for reuse without any pre treatment.

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