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# Aluminium dodecatungstophosphate ($AlPW_{12}O_{40}$) as a highly efficient catalyst for the selective acetylation of –OH, –SH and –$NH_2$ functional groups in the absence of solvent at room temperature

**Habib Firouzabadi,* Nasser Iranpoor,* Farhad Nowrouzi and Kamal Amani**

*Department of chemistry, Shiraz University, Shiraz 71454, Iran. E-mail: Firouzabadi@ chem.susc.ac.ir Iranpoor@ chem.susc.ac.ir; Fax: +98-711-2280926; Tel: +98-711-2284822*

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**$AlPW_{12}O_{40}$ was found to be an effective catalyst for the selective acetylation of alcohols, thiols, and amines in the absence of solvent at room temperature.**

Heteropoly acids (HPAs) have been extensively studied as acid and oxidation catalysts for many reactions and found industrial application in several processes.[1] HPAs are promising solid acids to replace environmentally harmful liquid acid catalysts such as $H_2SO_4$.[1c–f] The Keggin type $H_3PW_{12}O_{40}$ is more active than conventional solid acids such as $SiO_2$–$Al_2O_3$, $H_3PO_4$–$SiO_2$, and zeolites.[1c,f] Solid acid catalysts are harmless to the environment with respect to corrosiveness, safety, quantity of waste, and separability.

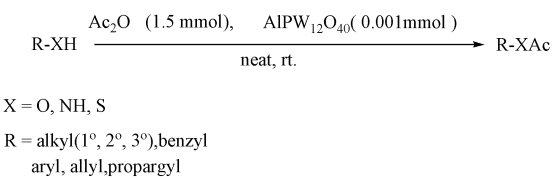
Protection of alcohols, amines, and thiols by acetyl chloride or acetic anhydride is an important transformation reaction in organic synthesis.[2] For this purpose, acetic anhydride or acetyl chloride in the presence of stoichiometric amounts of amine bases, such as tertiary amines, 4-(dimethylamino)pyridine (DMAP) and tributylphosphine have been used.[3] Protic or Lewis acids have also been used to catalyze acetylation of alcohols.[4]

Preparation of aluminium dodecatungstophosphate ($AlPW_{12}O_{40}$) was reported in 1982 by Ono by the reaction of aluminium nitrate and dodecatungstophosphoric acid in a quantitative yield. We have also prepared this compound by the addition of aluminium nitrate or by aluminium carbonate to the aqueous solution of tungstophosphoric acid which on complete evaporation of water gave the desired compound as a white powder in a quantitative yield. $AlPW_{12}O_{40}$ prepared by both protocols gave satisfactory analytical results within the range of the experimental errors. This salt is a water stable and a non-hygroscopic compound. To the best of our knowledge there is a report available in the literature, which deals with the conversion of methanol into hydrocarbons using this compound as a catalyst.[5] In continuation of our interest to study the catalytic activities of heteropolyacids,[6] now in this communication, we describe the use of a catalytic amount (0.1 mol%) of $AlPW_{12}O_{40}$ as an effective catalyst for the acetylation of alcohols, thiols and amines in the presence of acetic anhydride at room temperature (Scheme 1).

Acetylation of benzylic, primary, secondary, hindered tertiary alcohols and phenols were proceeded efficiently in high isolated yields using 1.5 mmol of acetic anhydride (Table 1, entries 1–20). Sensitive alcohols towards acidic conditions were also acetylated under similar reaction conditions in high yields in short reaction times without giving by-products (Table 1, entries 21–23). Hydroquinone, glycerol, and pentaerithrotriol were also converted to their corresponding acetates in excellent yields in short reaction times by 3, 4.5, and 6 mmol of acetic anhydride for acetylation of all hydroxy groups present in the molecules respectively (Table 1, entries 24–26). We observed that L-(+)-ascorbic acid requires a higher molar ratio of acetic anhydride (8 mmol) in order to acetylate all four hydroxy groups of the molecule (Table 1, entry 27). We found that this method was also suitable for the acetylation of amines and thiols and they were converted to their corresponding acetamides and thioacetates respectively in short reaction times in excellent yields (Table 1, entries 28–35).

In order to show the scope and limitation of this catalytic system, we have studied several competitive reactions under similar reaction conditions. The results of this study are shown in Table 2.

In a typical procedure, a mixture of benzyl alcohol (5 mmol, 0.54 g), acetic anhydride (7.5 mmol, 0.7 ml) and $AlPW_{12}O_{40}$ (0.005 mmol, 0.015 g) was stirred at room temperature for 4 min (monitored by TLC and GC). The reaction mixture was diluted




**Scheme 1**

**Table 1** Acetylation of alcohols, amines and thiols using $Ac_2O$ in the presence of $AlPW_{12}O_{40}$ as a catalyst[a]

| Entry | Substrate | Time/min | Yield (%)[b] |
|---|---|---|---|
| 1 | $PhCH_2OH$ | 4 | 94 |
| 2 | $4\text{-}OMeC_6H_4CH_2OH$ | 1 | 93 |
| 3 | $PhCH(OH)CH_3$ | 5 | 94 |
| 4 | PhCH(OH)Ph | 8 | 88 |
| 5 | Octan-1-ol | 8 | 94 |
| 6 | 1,4-Butandiol | 5 | 91 |
| 7 | Norborneol | 12 | 96 |
| 8 | (−)-Menthol | 11 | 95 |
| 9 | Octan-2-ol | 18 | 96 |
| 10 | Benzoin | 95 | 89 |
| 11 | Cholesterol | 22 | 87 |
| 12 | Adamantanol | 100 | 92 |
| 13 | *tert*-Butyl alcohol | 120 | 94 |
| 14 | Terpineol | 140 | 92 |
| 15 | $(Ph)_2C(OH)CH_3$ | 200 | 91 |
| 16 | PhOH | 3 | 90 |
| 17 | $4\text{-}NO_2C_6H_4OH$ | 12 | 88 |
| 18 | $4\text{-}ClC_6H_4OH$ | 4 | 92 |
| 19 | 2,6-Dicholorophenol | 3 | 95 |
| 20 | 2-Naphthol | 15 | 92 |
| 21 | 3-Methyl-2-buten-1-ol | 12 | 91 |
| 22 | 1-Octen-3-ol | 5 | 93 |
| 23 | 3-Hexyne- 2,5-diol | 15 | 92 |
| 24 | Hydroquinone | 12 | 88 |
| 25 | Glycerol | 37 | 89 |
| 26 | Pentaerithrotriol | 35 | 94 |
| 27 | L-(+)-Ascorbic acid | 120 | 93 |
| 28 | $PhNH_2$ | 1 | 96 |
| 29 | $2\text{-}Me\text{-}C_6H_4NH_2$ | 1 | 98 |
| 30 | $4\text{-}NO_2\text{-}C_6H_4NH_2$ | 12 | 89 |
| 31 | PhNH(Me) | 10 | 91 |
| 32 | Cyclohexylamine | 3 | 92 |
| 33 | $NH(CH_2Ph)_2$ | 10 | 96 |
| 34 | PhSH | 2 | 91 |
| 35 | $PhCH_2SH$ | 3 | 89 |

[a] All products were identified by their $^1H$ NMR spectra. [b] Isolated yield.

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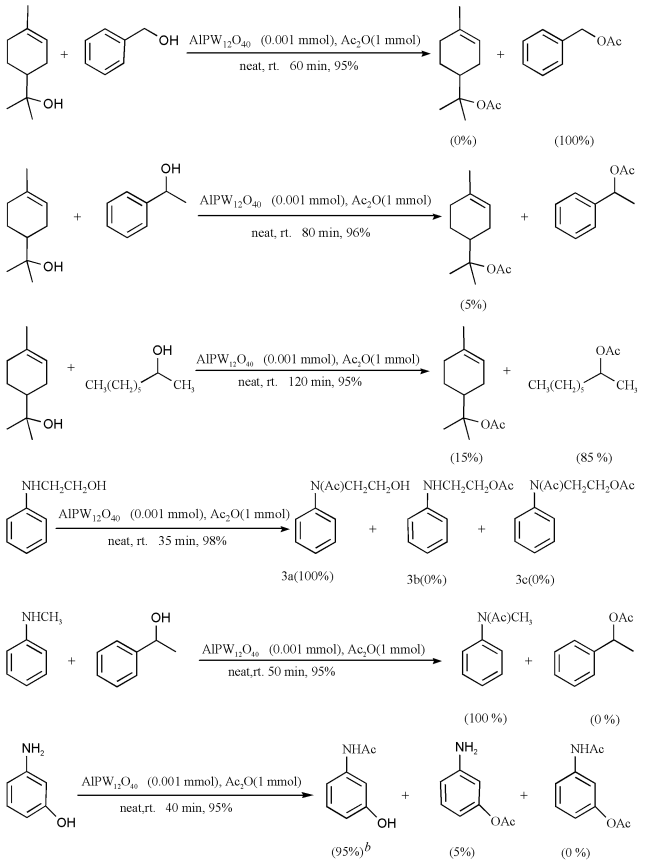
**Table 2** Competitive acetylation reactions of alcohols and amines using $Ac_2O$ in the presence of $AlPW_{12}O_{40}$ at room temperature under solvent-free conditions[a]




[a] The percentage of the products in the reaction mixture was determined by GC analysis. [b] Products were separated by plate in ethylacetate–n-hexane(9 : 1).

with n-hexane (10 ml) and filtered. The filter cake was also washed with another portion of n-hexane (10 ml). The filtrates were combined together and the resulting organic phase was washed with an aqueous solution of $NaHCO_3$ (20%, 2× 10 ml). The organic layer was separated, dried over anhydrous $Na_2SO_4$ and filtered. Evaporation of the solvent gave the desired pure product without further purification.[7]

In conclusion, in this study, we have introduced aluminium dodecatungstophosphate ($AlPW_{12}O_{40}$) as a new highly effective non-hygroscopic, heterogeneous, non-corrosive and environmentally benign catalyst for the efficient conversion of a variety of alcohols, phenols, amines, and thiols to their acetic esters, acetamides, and thioacetates in the absence of solvent.

Extensive studies upon applications of this catalyst in organic reactions such as Friedel–Crafts, Fries and Beckmann rearrangements, Diels–Alder, Michael and aldol condensation reactions are underway in our laboratories.

## Notes and references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7 Spectral data for protected ascorbic acid: $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 6.82(d,1H), 5.6(d, 1H), 3.84–4.16(m,2H), 2(s,3H),1.83(s,3H), 1.79(s,3H), 1.78(s,3H). $^{13}$CNMR (250 MHz, $CDCl_3$): $\delta$ = 175.4, 172.2, 171.3, 170.6, 145, 75, 69, 64, 21, 20.8, 20.2, 18. IR (KBr): 1800, 1751, 1741, 1373, 1226, 1161, 1056. **3a(Table 2):** $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 7–7.4(m,5H), 5.3(s,1H), 3.65(m,2H), 3.75(m,2H), 1.95(s,3H). $^{13}$CNMR (250 MHz, $CDCl_3$): $\delta$ = 20.84, 55, 60, 125, 127, 129, 143, 172. IR (KBr): 3430, 1650. 1595, 1496, 1409, 1330, 1074.