Catalysis Communications 9 (2008) 2365–2370

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Acetylation of alcohols, phenols and amines using ammonium salt of 12-tungstophosphoric acid: Environmentally benign method

Jitendra R. Satam [1], Radha V. Jayaram *

Department of Chemistry, University Institute of Chemical Technology, Nathalal Parekh Road, Matunga, Mumbai 400 019, India

ARTICLE INFO

Article history:
Received 29 December 2007
Received in revised form 24 May 2008
Accepted 26 May 2008
Available online 7 July 2008

Keywords:
Acetylation
Chemoselective
Room temperature
Solvent-free

ABSTRACT

The ammonium salt of 12-tungstophosphoric acid was employed for the acetylation of a variety of alcohols, phenols and amines under solvent-free conditions at 30 °C. This method showed preferential selectivity for the acetylation of the amino group in the presence of hydroxyl group. No, *C*-acylation was observed under the present conditions. The method is simple, mild and environmentally viable as it involves stoichiometric use of acetylating agent. The catalyst was found to be reusable for five cycles, without appreciable loss in activity.

1. Introduction

The acetylation of alcohols and phenols is a fundamental process in organic chemistry. It also provides an efficient route for protecting –OH groups during oxidation, peptide coupling and glycosidation reactions [1,2]. This –OH group protection is commonly achieved through acylation with acetic anhydride due to the ease of deprotection [3]. The various catalysts developed for acylation include nucleophilic agents [4,5] such as DMAP and Bu_3P, Lewis acids such as metal halides [6–8], metal triflates [9–13], metal perchlorates [14–19], ionic liquids [20] and several solid acids such as Naffion-H [21], zeolites [22], clays [23] HBF_4–SiO_2 [24] and $HClO_4$–SiO_2 [25]. Some of these above mentioned catalytic systems are homogeneous, nonrecoverable and suffers from the limitations like longer reaction times, stringent conditions, use of halogenated solvents and hazardous materials, e.g., DMAP is highly toxic (LD_{50} in the rat intravenous: 56 mg/kg) [26], Bu_3P is inflammable (flash point: 37 °C) and air sensitive, perchloric acid and its salts are potentially explosive and triflates are not cost effective. In recent years there has been a tremendous upsurge of interest in various chemical transformations performed under heterogeneous catalysis [27–29]. However, the practice of expensive and toxic metal precursors limits the use of these methods and they become unsuitable in the context of green chemistry. Furthermore, many of these methods are applicable for the acetylation of alcohols only. Lack of chemoselectivity and reusability of some of these reported catalysts made us think about the development of a mild and efficient methodology.

Keggin type heteropolyacids and there salts are a class of highly acidic solid acid catalysts made up of heteropolyanion having metal-oxygen octahedral as the basic structural unit [30]. Catalytic activity of various salts of 12-tungstophosphoric acid has been reported for several organic conversions such as hydrocarbon cracking [31], methanol to hydrocarbons, cracking of alkenes [32], esterification [33], benzylation and benzoylation [34]. In the present work we have tested the catalytic activity of various salts for the transesterification of soybean oil. The salts of 12-tungstophosphoric acid were prepared by standard procedure and the catalytic activity was studied at the reflux temperature of methanol-oil mixture.

2. Experimental

2.1. Catalyst preparation

The ammonium salt of 12-tungstophosphoric acid was prepared using known procedure [34]. By adding, drop wise, quantitative amount of aqueous ammonium carbonate solution to $H_3PW_{12}O_{40}$ in deionised water. The excess water was evaporated to dryness and the sample was kept overnight for drying in an air oven at 393 K, the salt obtained was $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40} \cdot 8H_2O$. Later it was calcined in air at 623 K for 4 h, which looses water of crystallization and becomes $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$. The molecular formulae were confirmed by elemental analysis technique (Table 1).

* Corresponding author. Tel.: +91 22 24145614; fax: +91 22 24145616.
E-mail addresses: jiten_uict@yahoo.co.in (J.R. Satam), rvjayaram@udct.org (R.V. Jayaram).
[1] Tel./fax: +91 22 24145616.

1566-7367/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2008.05.033

Table 1
N, P and W content in the ammonium salt of 12-tungstophosphoric acid catalyst calcined at various temperatures

Temperature (K)	N (%)	P (%)	W (%)	Surface area (m^2/g)	Molecular formula of the ammonium salt
Uncalcined	1.14	1.02	71.78	124	$(NH_4)_{2.5}H_{0.5}PW_{12}O_{40} \cdot 8H_2O$
623 (Fresh)	1.21	1.06	75.50	110	$(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$
623 (Spent)	1.20	1.05	75.47	110	$(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$
673	0.72	1.08	76.02	102	$(NH_4)_{1.5}H_{1.5}PW_{12}O_{40}$
723	0.24	1.09	76.56	96	$(NH_4)_{0.5}H_{2.5}PW_{12}O_{40}$

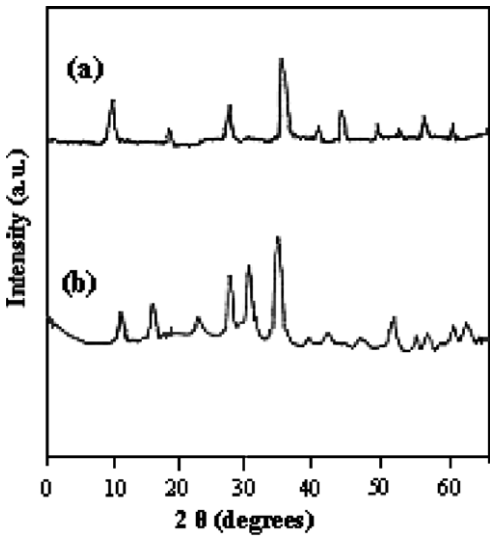


Fig. 1. XRD patterns of (a) $H_3PW_{12}O_{40} \cdot 16H_2O$ and (b) $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$.

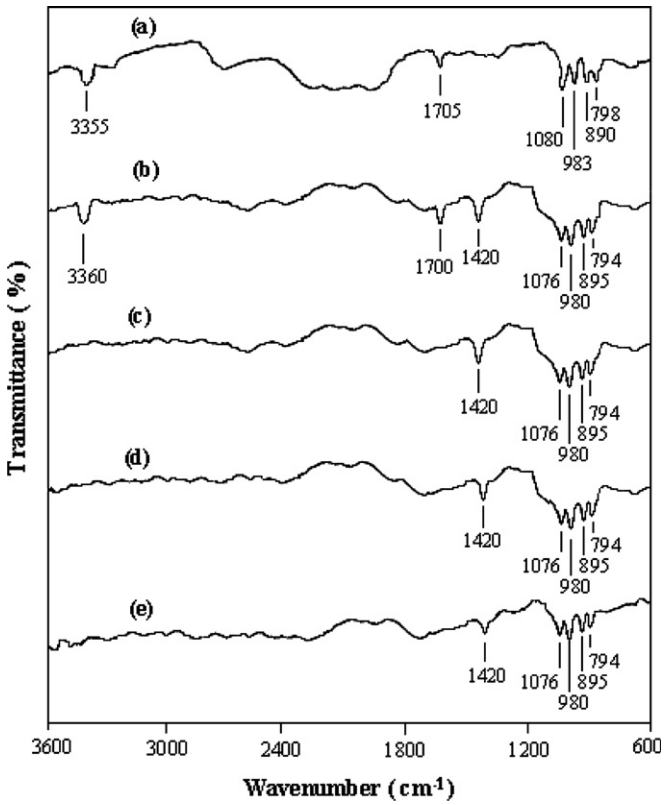


Fig. 2. FTIR spectra of (a) $H_3PW_{12}O_{40} \cdot 16H_2O$, (b) $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40} \cdot 8H_2O$, (c) $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40} \cdot 8H_2O$, 623 K, (d) $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40} \cdot 8H_2O$, 673 K and (e) $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40} \cdot 8H_2O$ (723 K).

2.2. Catalyst characterization

The catalyst was characterized by XRD, FTIR, BET surface area, TG–DTA and elemental analysis techniques. XRD studies were performed with a conventional powder diffractometer (Philips 1050) using graphite monochromatised Cu Kα radiation. FTIR spectra were recorded on Perkin–Elmer (Spectra 100). Surface area measurements were performed by nitrogen adsorption on a micromeritics (ASAP 2010) instrument at an adsorption temperature of 77 K. Thermal gravimetry (TG) and differential thermal analysis (DTA) studies were carried out between 273 and 1073 K, on a SETARAM TG-DTA A92 equipment with 32.5 mg of solid and a heating rate of 10 K min^{-1} and an air flow of 20 cm^3 min^{-1}.

Table 2
Effect of solvent during the $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$ catalyzed acetylation of phenol with Ac_2O using different solvents

Entry	Catalyst (mol %)	Solvent	Time (h)	Yield (%)[a,b,c]
1	0.5	CH_3CN	2	40
2	0.5	THF	2	60
3	0.5	$PhCH_3$	2	73
4	0.5	CH_2Cl_2	2	80
5	0.5	Neat	1.5	96

[a] Phenol (5 mmol) was treated with Ac_2O (5 mmol).
[b] Isolated yield of the corresponding acetylated product.
[c] Room temperature.

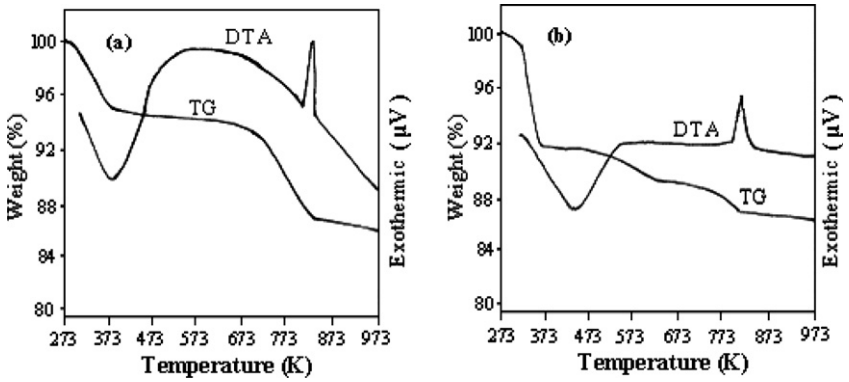
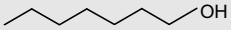
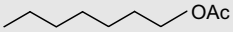
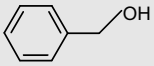
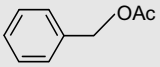
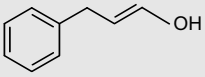
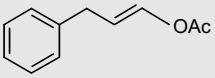
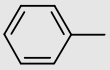
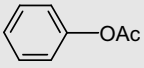
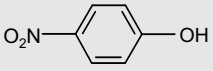
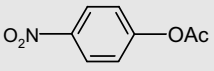
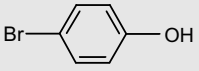
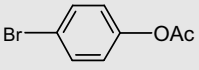
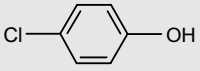
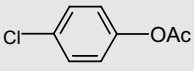
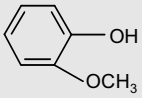
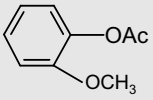
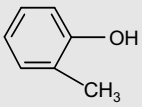
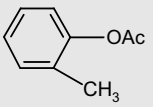
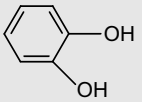
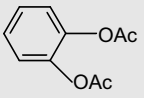
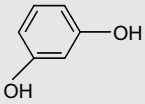
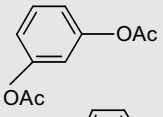
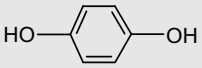
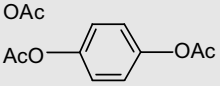
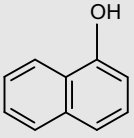
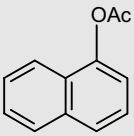
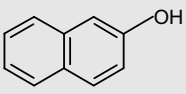
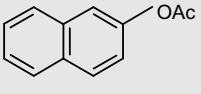
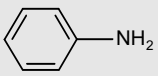
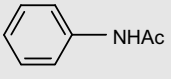


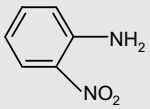
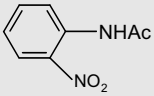
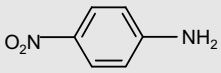
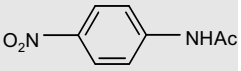
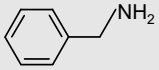
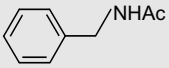
Fig. 3. TG-DTA profiles of (a) $H_3PW_{12}O_{40} \cdot 16H_2O$ and (b) $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40} \cdot 8H_2O$.

Table 3
Acetylation of heteroatom using $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$ and Ac_2O at room temperature[a]

Entry	Substrate (R × H)	Time (min)	Yield (%)[b,c]	Product (RXAc)[d]
1		1	90	
2		1	92	
3	D-Mannitol	3	94[g]	Hexa-*O*-acetyl-D-Mannitol
4		1.5	92[e]	
5		2	90[f]	
6	Geraniol	1	88	Geranyl acetate
7		2	90	
8		2	96	
9		2.5	92	
10		2.5	90	
11		2.5	90	
12		1.5	98	
13		1.5	97	
14		2.5	90[e]	
15		2.5	92[e]	
16		2.5	94[e]	
17		2	92	
18		1.5	96	
19		0.5	97	

(*continued on next page*)

Table 3 (*continued*)

Entry	Substrate (R × H)	Time (min)	Yield (%)[b,c]	Product (RXAc)[d]
20		0.5	90	
21		0.5	92	
22		0.5	94	

[a] The substrate (5 mmol) was treated with Ac_2O ((5 mmol) except for entries 3, 4, 5, 14, 15, 16) in the presence of $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$ (0.5 mol%) under neat conditions at room temperature.
[b] Isolated yield of the corresponding acetylated product.
[c] The unreacted substrate was recovered.
[d] All compounds have been satisfactorily characterized (IR, ^1H NMR).
[e] Isolated yield of the di-acetate.
[f] Isolated yield of the tri-acetate.
[g] Isolated yield of the hexa-acetate.

2.3. Typical procedure for the acetylation

Phenol (5 mmol) was treated with Ac_2O (5 mmol) under neat conditions at 303 K for 1.5 h under magnetic stirring in the presence of $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$ (0.5 mol%) with respect to substrate. Course of the reaction was monitored by TLC and GC. The reaction mixture was diluted with Et_2O (20 mL) and the solution was filtered to separate the catalyst. The filtrate was washed successively with 1% aqueous NaOH (15 mL), saturated solution of NaCl (15 mL), dried (Na_2SO_4) and concentrated to afford the product which was in full agreement with the mp and spectral data (IR, ^1H NMR) of an authentic sample of phenyl acetate. The catalyst was recovered and reused for fresh lot of phenol.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. BET surface area and elemental analysis study

Surface area of ammonium salt was found to be much higher than parent heteropolyacid. This could be attributed to the microporosity of the salt (Table 1). From the elemental composition of the salts calcined at various temperatures, corresponding molecular formulae were determined (Table 1).

3.1.2. X-ray diffraction studies

XRD patterns of $H_3PW_{12}O_{40}\cdot 16H_2O$ and $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$ samples are as shown in Fig. 1. XRD spectrum of $H_3PW_{12}O_{40}\cdot 16H_2O$ exhibits characteristic peaks ($2\theta = 10^\circ$ and 28°).

3.1.3. IR spectral analysis

$H_3PW_{12}O_{40}\cdot 16H_2O$ exhibits typically three major bands at 1080, 983, 890 and 798 cm^{-1} which are assigned to stretching absorption modes of oxygen atom bonded to tungsten and phosphorous (P–O), (W = O), (W–O_c–W) and (W–O_e–W) respectively of the Keggin ion $[PW_{12}O_{40}]^{3-}$. These bands are slightly shifted in the ammonium salt (Fig. 2). The ammonium salts show a band at ca. 1420 cm^{-1} characteristic of the NH_4^+ ion. FTIR spectra of salts calcined at various temperatures are shown in Fig. 2. It was observed that as the NH_4^+ content decreases, the intensity of the band at 1420 cm^{-1} also decreases.

3.1.4. TG-DTA analysis

TG–DTA studies of $H_3PW_{12}O_{40}\cdot 16H_2O$ and $(NH_4)_{2.5}H_{0.5}$-$PW_{12}O_{40}\cdot 16H_2O$ are shown in Fig. 3. In case of $(NH_4)_{2.5}H_{0.5}$-$PW_{12}O_{40}\cdot 16H_2O$ the first weight loss occurred at 373 K accompanied by an endothermal peak due to the loss of physically adsorbed water. The latter occurred continuously between 373 K and 623 K corresponding to the loss of chemical adsorbed water. The weight loss observed at 623–723 K can be attributed to the decomposition of salt with the liberation of ammonia. Above 800 K strong exotherm was observed, which can be attributed to the decomposition of Keggin anion.

3.2. Catalytic activity

3.2.1. Optimization of the reaction parameters

The reaction conditions were standardised after conducting the acetylation of phenol with Ac_2O using various solvents at room temperature (Table 2). 96% yield of phenyl acetate was obtained under neat conditions with 0.5 mol% of the catalyst with equivalent amount of Ac_2O. So we have continued the reactions under solvent-free conditions. In order to explore the scope and activity of the catalyst various alcohols, phenols and amines with electron donating and electron withdrawing groups were studied. We have observed that acetylation of phenols was slightly slower than that of alcohols and amines. No competitive Fries rearrangement was observed in case of phenolic substrates. The efficacy of the catalyst can be clearly visualized in the acetylation of di- and tri-hydroxy compounds under similar conditions (Table 3, entries 4 and 5). Another noteworthy feature of this methodology is that polyols such as D-mannitol underwent exhaustive acetylation demonstrating the practical utility of this method (Table 3, entry 3) (see Fig. 4).

The present procedure is excellent for the acetylation of alcohols (primary and secondary), phenols, amines and bifunctional compounds containing –NH_2 and –OH groups. In order to examine the chemoselectivity of the present method, bifunctional substrates containing –NH_2 and –OH groups were studied (Table 4). Selective acetylation of –NH_2 group in the presence of –OH group

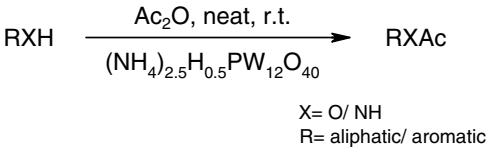
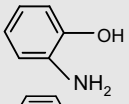
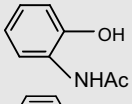
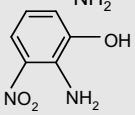
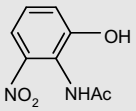
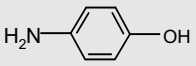
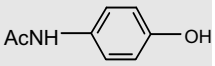
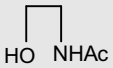
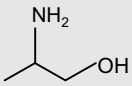
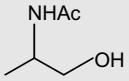


Fig. 4. Scheme.

Table 4
Chemoselective *N*-acetylation of bifunctional substrates using $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$ under solvent-free conditions at room temperature[a]

Entry	Substrate	Time (min)	Yield (%)[b,c]	Product[d]
1		1	92	
2		2	90	
3		1	92	
4		1	90	
5		1	94	

[a] The substrate (5 mmol) was treated with Ac_2O ((5 mmol) in the presence of $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$ (0.5 mol %) under neat conditions at room temperature.
[b] Isolated yield of the corresponding acetylated product.
[c] The unreacted substrate was recovered.
[d] All compounds have been satisfactorily characterized (IR, ^{1}H NMR).

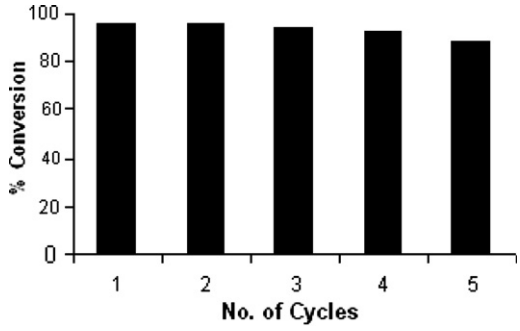


Fig. 5. Reusability study of $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$ for acetylation of phenol.

was observed at room temperature with one equivalent of acetic anhydride to give corresponding *N*-acetate product and no *O*-acetate product was found under these conditions. This might be due to more nucleophilicity of $-NH_2$ group than –OH group. It should be noted that the catalyst is reusable for five cycles without significant loss of its efficacy. Unreacted substrate can be recovered. The product obtained did not require much purification.

3.3. Reusability of the catalyst

In order to find the reusability of $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$, it was separated from the reaction mixture, washed with ethyl acetate and acetone. The catalyst was dried in vacuum and reused for fresh lot of phenol. The catalyst was found to be reusable for five cycles without significant loss in activity. The reusability results revealed that the activity of the spent and fresh catalyst was almost the same clearly demonstrating the efficiency of the catalyst (Fig. 5). In the sixth cycle the yield was decreased to 80%. After the seventh cycle appreciable loss in catalytic activity was observed.

3.4. Spectral data for selected products

3.4.1. Hexa-O-acetyl-D-mannitol (Table 2, entry 3)

Found: $[\alpha]_D^{25}$ = +34.4 (c 1.2 $CHCl_3$); $[\alpha]_D^{25}$ = +27 (c 1.0 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 2.06 (s, 6H), 2.10 (s, 6H), 4.10 (m, 4H), 5.05 (m, 2H) and 5.44 (m, 2H).

3.4.2. Ethane-1,2-diyl di-acetate (Table 2, entry 4)

IR (Neat): 2934, 1730, 1380, 1245 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 6H) and 4.21 (s, 4H).

3.4.3. Propane-1,2,3- triyl tri-acetate (Table 2, entry 5)

IR (Neat): 2935, 1730, 1370, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 3H), 2.07 (s, 6H), 4.30 (m, 4H) and 5.23 (m, 1H).

3.4.4. N-(2-hydroxyphenyl acetamide) (Table 3, entry 1)

IR (Neat): 3447, 2980, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.08 (s, 3H), 6.86 (m, 3H), 7.65 (1H, d) 9.27 (br 1H) and 9.67 (s, 1H).

3.4.5. N-(4-hydroxyphenyl acetamide) (Table 3, entry 2)

IR (Neat): 3380, 3070, 2850, 1697, 1570, 1280 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.08 (s, 3H), 6.55–6.67 (m, 3H), 7.22 (d, 1H), 8.95 (br, 1H) and 9.55 (s, 1H).

3.4.6. N-(2-hydroxethyl acetamide) (Table 3, entry 3)

IR (Neat): 3303, 3097, 2935, 1705, 1250, 1066 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.93–2.03 (d, 3H), 3.35 (m, 2H), 3.7 (m, 2H), 5.18 (bs, 1H), 6.67 (s, 1H).

4. Conclusion

$(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$ is found to be highly efficient, chemoselective and reusable catalyst for acetylation of primary and secondary alcohols, phenols and amines. With the increasing tight legislations on the release of waste and use of toxic substances as a measure to control environmental pollution [35], the use of stoichiometric amount of acetylating agent and solvent-free conditions employed in the present method make it 'environmentally friendly' and suitable for industrial applications.

Acknowledgments

The authors are thankful to RSIC, Indian Institute of Technology Mumbai, for providing the ^{1}H NMR facility.

References

[1] T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, third ed., John Wiley & Sons Inc., New York, 1999.
[2] J.R. Hanson, Protective Groups in Organic Synthesis, Blackwell Science, Malden, MA, 1999.
[3] A.K. Chakraborti, M.K. Nayak, L. Sharma, J. Org. Chem. 67 (2002) 1776.
[4] DMAP W. Steglich, G. Hofle, Angew. Chem. Int. Ed. Engl. 8 (1969) 981.
[5] Bu_3P E. Vedejs, S.T. Diver, J. Am. Chem. Soc. 115 (1993) 3358.
[6] $CoCl_2$ S. Ahmad, J. Iqbal, Tetrahedron Lett. 27 (1986) 3791.
[7] $TaCl_5$ S. Chandrashekhar, T. Ramchander, M. Takhi, Tetrahedron Lett. 39 (1998) 3263.
[8] $InCl_3$ A.K. Chakraborti, R. Gulhane, Tetrahedron Lett. 44 (2003) 6749.
[9] $Sc(OTf)_3$ K. Ishihara, M. Kubota, H. Kurihara, H. Yamamoto, J. Org. Chem. 61 (1996) 4560.
[10] TMSOTf P.A. Procopiou, S.P.D. Baugh, S.S. Flack, G.G.A. Inglis, J. Org. Chem. 63 (1998) 2342.
[11] $Bi(OTf)_3$ A. Orita, C. Tanahashi, A. Kakuda, J. Otera, J. Org. Chem. 66 (2001) 8926.
[12] $Cu(OTf)_2$ K.K. Chauhan, C.G. Frost, I. Love, D. Waite, Synlett (1999) 1743.
[13] $Ce(OTf)_3$ Dalpozzo, R. De Nino, A. Maiuolo, L. Procopio, A. Nardi, M. Bartoli, G. Romeo, R. Tetrahedron Lett. 44 (2003) 5621.
[14] $LiClO_4$ Y. Nakae, I. Kusaki, T. Sato, Synlett (2001) 1584.
[15] $Mg(ClO_4)_2$ A.K. Chakraborti, L. Sharma, R. Gulhane, Shivani. Tetrahedron 59 (2003) 7661.

[16] $Mg(ClO_4)_2$ G. Bartoli, M. Bosco, R. Dalpozzo, E. Marcantony, M. Massaccesi, S. Rinaldi, L. Sambri, Synlett (2003) 39.
[17] $BiO(ClO_4)_2$ A.K. Chakraborti, R. Gulhane, Shivani, Synlett (2003) 1805.
[18] $Zn(ClO_4)_2 \cdot 6H_2O$ Shivani, R. Gulhane, A. Chakraborti, J. Mol. Catal. A: Chem. 264 (2007) 208.
[19] $Cu(ClO_4)_2 \cdot 6H_2O$ K. Jeyakumar, D.K. Chand, J. Mol. Catal. A: Chem. 255 (2006) 275.
[20] S.A. Forsyth, D.R. MacFarlane, R.J. Thomson, M. von Itzestein, Chem. Commun. (2002) 714.
[21] Naffion-H R. Kumareswaran, K. Pachmuthu, Y.D. Vankar, Synlett (2000) 652.
[22] Zeolites R. Ballini, G. Bosica, S. Carloni, L. Ciarralli, R. Maggi, G. Sartory, Tetrahedron Lett. 39 (1998) 6049.
[23] Clays A.-X. Li, T.-S. Li, T.-H. Ding, Chem. Commun. (1997) 1389.
[24] HBF_4-SiO_2 A.K. Chakraborti, R. Gulhane, Tetrahedron Lett. 44 (2003) 3521.
[25] $HClO_4$-SiO_2 A.K. Chakraborti, R. Gulhane, Chem. Commun. (2003) 1896.
[26] D.V. Sweet, Registry of Toxic Effects of Chemical Substances 1985–86, vol. 3336, US Government Printing Office, Washington, DC, 1988, p. 4049.
[27] P. Laszlo, Acc. Chem. Res. 19 (1986) 121.
[28] A. Arienti, F. Bigi, R. Maggi, E. Marzi, P. Moggi, M. Rastelli, G. Sartori, F. Tarantola, Tetrahedron 53 (1997) 3795.
[29] A. Arienti, F. Bigi, R. Maggi, E. Marzi, P. Moggi, M. Rastelli, G. Sartori, A. Trere, J. Chem. Soc. Perkin Trans. 1 (1997) 1391.
[30] B.M. Devassy, S.B. Halligudi, J. Catal. 236 (2005) 313.
[31] H. Hayashi, J.B. Moffat, J. Catal. 83 (1983) 192.
[32] S.V. Nayak, J.B. Moffat, Appl. Catal. 77 (1991) 251.
[33] B.Y. Giri, K.N. Rao, B.L.A. Prabhavati Devi, N. Lingaiah, I. Suryanarayana, R.B.N. Prasad, P.S. Sai Prasad, Catal. Commun. 6 (2005) 788.
[34] Y. Izumi, M. Ogawa, U. Kazuo, Appl. Catal. A: Gen. 132 (1995) 127.
[35] R.L. Garrett, in: R.L. Garrett, S.C. De Vito (Eds.), Designing Safer Chemicals, American Chemical Society Symposium Series 640, Washington, DC, 1996. Chapter 1.