

Efficient Protection of Alcohols with Carboxylic Acids Using a Variety of Heteropolyoxometallates as Catalysts, Studying Effective Reaction Parameters

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Esterification is an important class of reactions in the preparation of perfumery and flavor chemicals, wherein homogeneous, solid acidic, and superacidic catalysts are normally used. Now, an efficient and selective protocol for protection of various functionalized alcohols employing carboxylic acids as protecting agents is realized through the catalytic mediation of simple heteropolyoxometallates. In this methodology, water is the only by-product and notably the aspect of effluent treatments does not arise. The advantages include the operational simplicity, recycle ability of the catalyst and mild reaction conditions. The present catalytic system may be a potential candidate not only for laboratory practice but also for commercial applications and offers an environmentally safer alternative to the existing processes.

Key Words: Acetylation, Heteropolyoxometallate, Catalytic, Alcohol, Formylation

Introduction

The protection of hydroxyl functional groups is an important and widely used transformation and is often necessary during the course of various organic synthesis sequences, in particular in the construction of polyfunctional molecules such as nucleosides, carbohydrates, steroids, natural products, and drugs. A number of reagents coupled with different catalysts have been put forth for the protection of alcohols. Protection of alcohols is usually performed employing acid anhydrides or acyl chlorides in the presence of stoichiometric amounts of protonic and Lewis acids, such as *p*-toluenesulfonic acid,¹ scandium trifluoromethanesulfonate,² trimethylsilyl trifluoromethanesulfonate,³ zinc chloride,⁴ and cobalt chloride.⁵ The above options employing acetic anhydride as acetylating agent and soluble acids as reagents or catalysts presents achieve less than 50% atom economy in the consumption of acetic anhydride by utilizing only the acetyl group. Moreover, acid halides and acid anhydrides are usually employed as the acetylating agents in the presence of an acid or base catalyst such as H₂SO₄,⁶ PTSA,⁷ Shvo's catalyst,⁸ distannoxane catalyst⁹ and lipase.¹⁰ Most of the above procedures can be applied for the protection of various acid/base sensitive substrates. However, limitations in terms of reagent availability, prolonged reaction times, formation of unwanted side products, and need for halogenated solvents are of drawbacks of these common methods. Considering the importance of environmental awareness in chemical technology, it is important to minimize the prevalence of undesirable hazardous chemical substances that are dangerous to human health and the environment.

Heteropolyoxometallates of the *Keggin* series have been proven to be good catalysts in many homogenous organic transformations and for the synthesis of fine and specialty chemicals.¹¹⁻¹⁴ Due to their acidic nature, redox properties, catalytic activity, selectivity, thermal resistance, and reusability, heteropoly compounds are useful and versatile catalysts in a number of transformations.¹⁵⁻¹⁶ These interesting compounds generally exhibit higher catalytic activities than con-

ventional catalysts, such as mineral acids, ion-exchange resins, zeolites, *etc.* in both heterogeneous and homogeneous systems.¹¹ Furthermore, heteropoly catalysis lacks side reactions, such as sulfonation, chlorination, *etc.* that frequently occur with mineral acids. Most of usual *Keggin*-type heteropolyoxometallates are soluble in water and polar organic solvents, such as lower alcohols and carboxylic acids, but insoluble in hydrocarbons. This provides an opportunity for the easy recovery of catalysts from liquid-phase reaction systems without neutralization, simply by precipitating with a hydrocarbon solvent.¹¹

In continuation of our ongoing research program on using heteropolypolyoxometallates in organic synthesis,¹⁷⁻²⁷ herein, we wish to report a simple, efficient, selective, and general method for the protection of some alcohols by the mediation of some heteropoly compounds at room temperature or under reflux conditions. The reactions were carried out in good yields within quite short reaction times.

Results and Discussion

Functional group protection is the heart and soul of multi-functional and multi step syntheses of target molecules. The protection of alcohol moieties represents one of the most ubiquitous steps in chemistry. Organic esters are a very important class of chemicals having applications in pharmaceuticals. Since, acetyl is the most common group in view of easy introduction, being stable under acidic conditions, and being easily removable by mild alkaline hydrolysis, the protection of alcohol functional groups is usually achieved through acetylation and obviously different approaches have been employed on both laboratory and commercial scales to prepare esters.

As mentioned in the introduction, research has been directed to overcome the drawbacks of conventional methods and insurmountable problems in the recovery of the catalysts and by-products and there is a need to develop a reusable and economic solid acid catalyst for acetylation using carboxylic acids as acetylating agents to achieve high atom economy.

Table 1. Protection of some Alcohols with Acetic Acid Catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$.^a

R = H, alkyl, benzyl, phenyl

Entry	Alcohol	Short time Conv. % (min.)	Long time Conv. % (min.)	Selectivity (%)	TON ^b short time (long time)	TOF ^c short time (long time)
1		45(5)	90(15)	100	132(264)	1594(1058)
2		25(5)	90(25)	100	73.5(264)	885(635)
3		5(5)	75(50)	100	14.7(220)	177(264)
4		75(5)	86(15)	> 98	220(252)	2657(1011)
5 ^d		24(120)	70(300)	100	73.5(205)	35(41)
6		7(5)	35(60)	100	20.5(103)	248(103)
7		7(15)	26(60)	> 97	20.5(76.4)	82(76)
8		20(5)	90(35)	100	58.8(264)	708(453)
9		50(5)	90(20)	98	147(264)	1771(794)
10		---	3(180)	100	---(8.82)	---(3)

^aCatalyst (0.034 mmol) was dissolved in a solution of acetic acid (50 mmol) and alcohol (10 mmol) followed by heating the reaction mixture to 70 °C under vigorous stirring. All acetylated products were known compounds and were identified by means of IR and ¹H-NMR spectroscopy and/or comparison of their b.p. or m.p. with authentic samples.⁴³ ^bTurnover number (TON) is the number of moles of product per mole of catalyst. ^cTurnover frequency (TOF) was calculated by the expression [product]/[catalyst] × time (h⁻¹). ^dBenzoic acid was used instead of acetic acid.

Considering this demand, heteropolyacids have emerged as green catalysts for chemical technology owing to their high catalytic activity in low concentration and being environmentally friendly. Heteropolyacids are yet non-corrosive and work in low concentration, thus avoiding disposal problems.

Initially, 1-phenyl ethanol was chosen for the acetylation reactions (Table 1). The protection reactions were carried out in a glass reactor equipped with a magnetic stirrer. The homogeneous reactions were performed by adding the above alcohol (10 mmol) as a model substrate to a solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.034 mmol) in acetic acid (50 mmol). At appropriate time intervals, aliquots were taken, diluted ~ten-fold with dichloromethane and analyzed by GLC. In the presence of 0.34 mol% of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as the dissolved heteropoly acid, acetic acid was added to 1-phenyl ethanol and progressed up to 90% with almost complete selectivity at 70 °C after 15 min. In the absence of catalyst, acetic acid was much less efficient for the conversion of 1-phenyl ethanol and led to < 5% of product after 60 min. (Table 2, entry 16).

To evaluate the efficiency of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as catalyst, the general applicability and scope of the method was studied by use of various alcohols. As shown in Table 1, a series of structurally diverse aliphatic and aromatic primary, secondary, tertiary, and benzylic alcohols underwent smooth acetylation in good yields with acetic acid in the presence of 0.34 mol% of $\text{H}_3\text{PW}_{12}\text{O}_{40}$. A sterically hindered $t\text{BuOH}$ yields 86% of the corresponding acetate after 15 min. (Table 1, entry 4); whereas, cyclohexanol and menthol as secondary cyclic alcohols showed lower reactivity than other examined alcohols and produced 35% and 26% of the corresponding products, respectively, after 60 min. Phenolic hydroxyl group could not be acetylated under the reported condition. Phenol underwent the acetylation slowly in the presence of catalyst and led to 3% of product after 3 h (Table 1, entry 10). This inertness has been exploited to selective acetylation of alcoholic hydroxyl groups in phenols. Primary and secondary linear alcohols were also acetylated with good yields in this system. 1-Butanol produced 90% of conversion after 25 min; whereas, 2-propanol led to 75% of the acetylated product after 50 min (Table 1, entries 2 and 3). This means that secondary alcohol, 2-pro-

panol, was less reactive than the primary one in the protection protocol. Benzyl alcohol and 4-methoxy-benzyl alcohol were also acetylated in a reasonable time and produced 90% of conversion after 35 and 20 min, respectively (Table 1, entries 8 and 9).

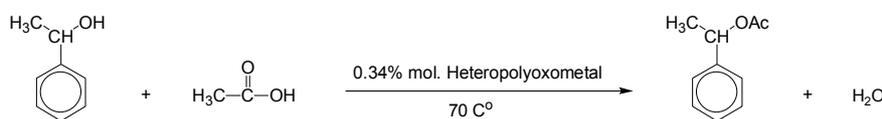
Our findings showed that $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ is capable of catalyzing acetylation of 1-phenyl ethanol with acetic acid. It led to 86% of 1-phenyl ethyl acetate with almost complete selectivity after 15 min. (Table 2, entry 15). The reactivity of other heteropolyanions such as $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{K}_4\text{SiW}_9\text{Mo}_2\text{O}_{39}$, and $\text{Na}_3\text{PW}_9\text{Mo}_3\text{O}_{40}$ were also examined (Table 2). Within the examined catalysts, the reactivity pattern $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{H}_3\text{PMo}_{12}\text{O}_{40} > \text{Na}_3\text{PW}_9\text{Mo}_3\text{O}_{40} > \text{K}_4\text{SiW}_9\text{Mo}_2\text{O}_{39}$ was observed.

We extended the scope of this procedure by performing the protection reaction of 1-phenyl ethanol in other carboxylic acids (Table 3). The results proved that formic acid is distinctly more reactive than acetic acid, and led to 85% of conversion after 5 min. (Table 3, entry 19). Acetic acid behaved as well as glacial acetic acid; while propionic acid revealed less reactivity and produced 90% of the corresponding product after 25 min. (Table 3, entry 20). Dichloroacetic acid was more effective than other analogues and produced 96% of acetate after 5 min. (Table 3, entry 22). Obviously, benzoic acid showed little activity and produced 24% of the acetylated product after 120 min. (Table 3, entry 21).

Formylation is also a very important process and several catalysts have been used for this transformation.²⁸ Because of the instability of the anhydride and the acid chloride of formic acid, formylation of alcohols has been achieved using ethyl formate. As previously described, ethyl formate is capable of protecting alcohols, such as 1-butanol, and led to 85% of 1-butyl acetate after 10 min. (Table 3, entry 23).

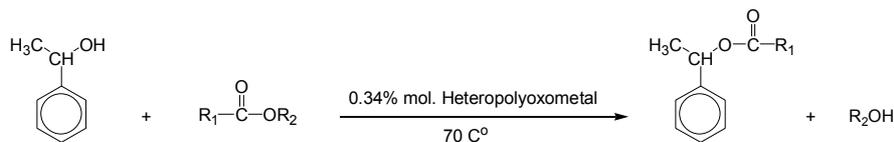
Industrially a variety of applied esterification procedures are commonly catalyzed using mineral liquid acids. Although, the catalytic activity of these homogeneous catalysts is high, they suffer from several drawbacks, such as their corrosive nature, the existence of side reactions, and the fact that the catalyst cannot be easily separated from the reaction mixture.²⁹⁻³² The use of reusable acid catalysts, offer an alterna-

Table 2. Protection of 1-Phenyl Ethanol with Acetic Acid Catalyzed by Various Heteropolyoxometals.^a



Entry	Catalyst	Short time Conv.% (min.)	Long time Conv.% (min.)	Selectivity (%)	TON short time (long time)	TOF short time (long ime)
11	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	45 (5)	90 (15)	> 98	132 (264)	1594 (1058)
12	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	30 (5)	90 (40)	> 98	88 (264)	1059 (397)
13	$\text{Na}_3\text{PW}_9\text{Mo}_3\text{O}_{40}$	15 (5)	80 (45)	97	44 (228)	531 (314)
14	$\text{K}_4\text{SiW}_9\text{Mo}_2\text{O}_{39}$	1 (35)	4 (150)	100	3 (11.7)	50 (5)
15	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	60 (5)	86 (15)	> 98	176 (252)	2126 (1011)
16	Without	5 (60)	20 (180)	> 98	14.7 (58)	14.7 (19.6)

^aThe reactions were carried out as described below Table 1.

Table 3. Protection of 1-Phenyl Ethanol with some Carboxylic Acids and Ethyl Formate Catalyzed by $H_3PW_{12}O_{40}$.^a

Entry	Protecting agent	Short time Conv.% (min.)	Long time Conv.% (min.)	Selectivity (%)	TON short time (long time)	TOF short time (long time)
17	Glacial 	47 (5)	90 (15)	100	138 (264)	1665 (1058)
18		52 (5)	90 (15)	100	153 (264)	1842 (1058)
19		85 (5)	90 (10)	95	237 (251)	3012 (1588)
20		44 (5)	90 (25)	100	129 (264)	1559 (635)
21		24 (120)	70 (300)	97	68 (200)	35 (41)
22		96 (5)	99 (10)	95	268 (276)	3401 (1747)
23		70 (5)	85 (10)	100	206 (250)	2500 (1500)

^aThe reactions were carried out as described below Table 1.

tive and have received a lot of attention in the past few years.³³⁻³⁶ It is worth mentioning that heteropolyoxometallate catalysts could be used as recyclable catalysts. The acetylation of 1-phenyl ethanol with acetic acid was chosen as a model substrate for studying of catalyst's reuse and stability. After the reaction was worked up, $H_3PW_{12}O_{40}$ has been recovered and subsequently used as catalyst in a second esterification reaction to investigate the reusability of catalyst. In the second esterification experiment, the activity of the catalyst was nearly similar to the activity of the fresh compound and no important loss of catalytic activity was observed. After the use of catalyst for five consecutive cycles, the yield of acetylated product produced from the reaction of 1-phenyl ethanol with acetic acid was 85% and after ten times was 80%. Thus, it can be concluded that the used heteropolyoxometallates can be regenerated and reused after a simple work up.

The selectivity towards the competitive acetylation of benzylic and secondary alcohols with acetic acid was also investigated. A mixture of equal amounts of benzyl alcohol (5 mmol) and cyclohexanol (5 mmol) was conducted to the protection reaction with acetic acid (50 mmol). Findings revealed that benzyl alcohol was more reactive than cyclohexanol, and

produced 90% of product after 45 min; whereas, the same conversion was achieved for cyclohexanol after 120 min.

Fig. 1 describes effect of increasing concentration of $H_3PW_{12}O_{40}$ on the efficiency of 1-phenyl ethanol protection with acetic acid. According to our findings, this protection system was unsuccessful to acetylate alcohols in the absence of catalyst under the reaction conditions reported here. Enhancing the catalyst concentration to 0.07 mol% caused a distinct increase in the conversion of alcohol. Increasing the catalyst concentration from 0.07 to 1 mol%, led to higher amounts of products in short and long reaction times. Increasing catalyst concentration more than 1 mol%, had only a little effect on the conversion%.

The mole ratio of acetic acid : 1-phenyl ethanol was varied from 1 : 1 to 10 : 1 to assess its effect on the reaction progress (Fig. 2). It was found that conversion of alcohol was increased with enhancing concentration of the carboxylic acid. A large increase in the yield% was observed for 10 : 1 mole ratio in comparison with 5 : 1 mole ratio after 5 min. However, the corresponding conversions were close to each other after 15 min.

Effect of temperature on the reaction progress was studied by performing the acetylation of 1-phenyl ethanol in acetic

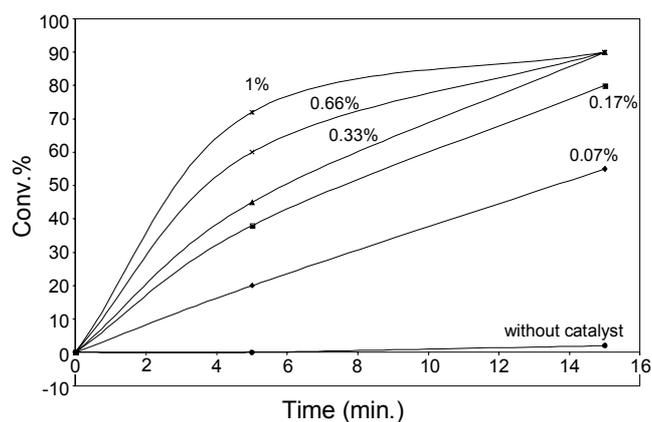


Figure 1. Effect of Catalyst Concentration (mol% of $\text{H}_3\text{PW}_{12}\text{O}_{40}$) on the Protection of 1-Phenyl Ethanol with Acetic Acid.

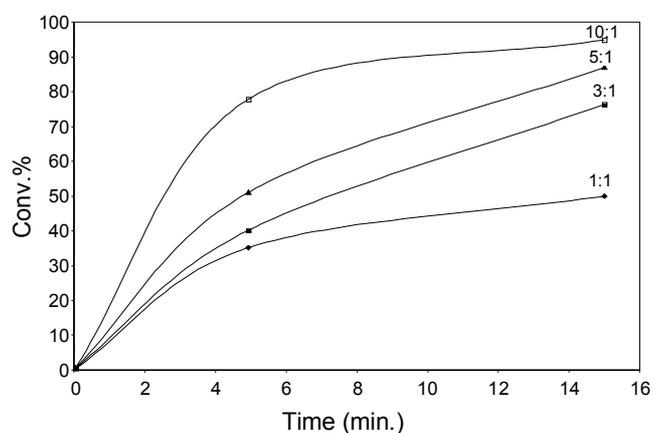


Figure 2. Effect of Acetic Acid : 1-Phenyl Ethanol Mole Ratio on the Efficiency of the Protection Procedure in the presence of 0.34 mol% $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

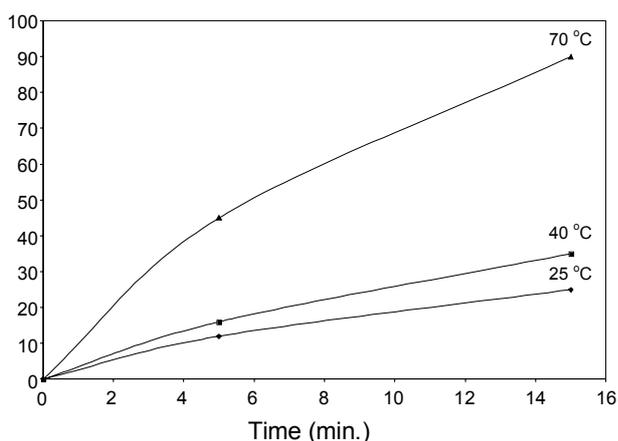


Figure 3. Effect of Raising Temperature on the Extent of 1-Phenyl Ethanol Protection with Acetic Acid Catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

acid catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$ at 25, 40 and 70 °C (Fig. 3). The ester yield% was increased sharply with enhancing temperature from 25 to 70 °C. It was also interesting that even at elevated temperatures no olefin, ether or polymeric products were found in the acetylation of alcohols coaxed with carboxylic acids.

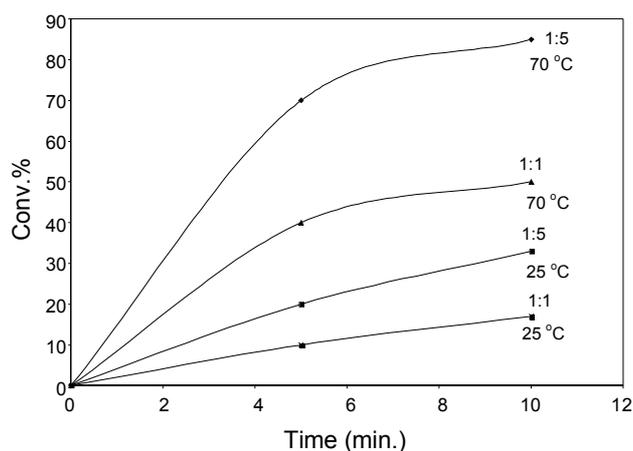


Figure 4. Protection of 1-Buthanol with Ethyl Formate (1:1 and 1:5 mole ratio of alcohol : ethyl formate) Catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$ at 25 and 70 °C.

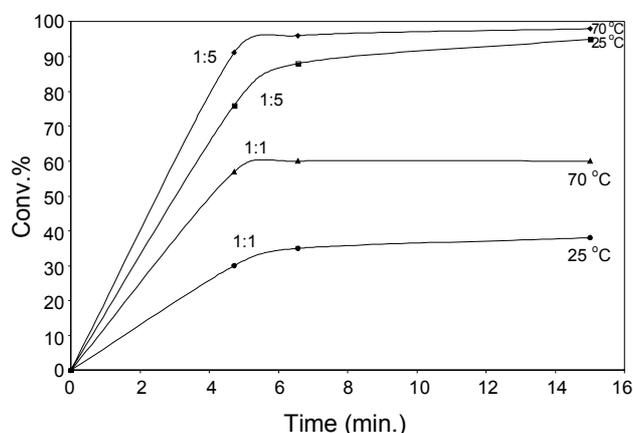


Figure 5. Protection of 1-Buthanol with Formic Acid (1:1 and 1:5 mole ratio of alcohol : formic acid) Catalyzed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$ at 25 and 70 °C.

These results indicate that the process of acetylation affords excellent possible atom economy when accounted with respect to substrate, product, acetylating reagent and the catalyst.

Finally, to obtain a deeper insight on the role of kind and concentration of the protecting agent on the efficacy of the protocol, formylations of 1-buthanol with ethyl formate and formic acid in the presence of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ were compared at 25 and 70 °C (Figs. 4 and 5). Results revealed that formic acid was more effective protecting agent than ethyl formate in short reaction time (< 5 min.). Aside from temperature, the first led to > 75% of conversion with 1 : 5 mole ratio of alcohol : ethyl formate after 5 min. Moreover, the conversion of alcohol was strongly depended on the mol% of the protecting agent in both temperatures. Effect of increasing mol% of the protecting agent was more pronounced for formic acid than for ethyl formate. It seems that in the case of formic acid, enhancing mol% of acid was more effective than elevation of temperature on the reaction progress.

Experimental Section

General. All products were characterized by comparison of

their spectral and physical data with those of authentic samples. Silica gel 60 (70 - 230 mesh) was used for column chromatography. Progress of the reactions was monitored by gas chromatography on a *Shimadzu* GC-17A instrument equipped with a flame ionization detector using 25 m × 0.25 mm CPB 5 - 20 capillary columns. ¹H NMR spectra was recorded in CHCl₃ as solvent on a spectrometer using TMS as an internal standard. UV-Vis spectra were recorded on a UV-2550 (*Shimadzu*) spectrophotometer. Infrared spectra were run on a 8700 *Shimadzu* Fourier Transform spectrophotometer. The catalysts were prepared and characterized according to literature procedures.³⁷⁻⁴²

Typical Experimental Procedure for Acetylation of Alcohols with Acetic Acid Catalyzed by Heteropolyoxometallates. In a round-bottom flask (10 mL) equipped with a magnetic stirrer, the catalyst (0.034 mmol) was dissolved in acetic acid (50 mmol). Then, the corresponding alcohol (10 mmol) was added to the stirred solution and the reaction mixture was heated to 70 °C for the required time. The reaction progress was monitored by GLC. After completion of the reaction, acetic acid was removed under reduced pressure and 20 mL of ether were added. The reaction mixture was washed with 5% NaHCO₃ solution, then with H₂O, and dried with MgSO₄. Evaporation of the solvent followed by silica-gel chromatography provided the pure acetate.

Conclusion

In conclusion, we have demonstrated an efficient and selective protection procedure for various alcohols using some carboxylic acids and esters as protecting agents in the presence of catalytic amounts of heteropolyoxometallates to achieve optimum yields. In this methodology, notably the aspect of effluent treatments does not arise, as water is the only by-product. The advantages include the operational simplicity, recycle ability of the catalyst, and mild reaction conditions. The present catalytic system may be a potential candidate not only for laboratory practice but also for commercial applications and offers an environmentally safer alternative to the existing processes.

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References

- Cope, A. C.; Herrick, E. C. *Org. Synth.* **1963**, *4*, 304.
- Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 4560.
- Procopiou, P. A.; Baugh, S. P. D.; Flank, S. S.; Inglis, G. A. *Chem. Commun.* **1996**, 2625.
- Baker, R. H.; Bordwell, F. G. *Org. Synth. Coll.* **1955**, *3*, 141.
- Iqbal, J.; Srivastva, R. R. *J. Org. Chem.* **1992**, *57*, 2001.
- Sarel, S.; Newman, M. S. *J. Am. Chem. Soc.* **1956**, *78*, 5416.
- Hossain, N.; Magnussan, G. *Tetrahedron Lett.* **1999**, *40*, 2217.
- Matute, B. M.; Backvall, J.-E. *J. Org. Chem.* **2004**, *69*, 9191.
- Orita, A.; Ito, T.; Yasui, Y.; Otera, J. *Syn. Lett.* **1999**, 1927.
- Adam, W.; Moller, C. R. S.; Schmid, K. S. *J. Org. Chem.* **2001**, *66*, 7365, and references therein.
- Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171.
- Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113.
- Jansen, R. J. J.; van Veldhuizen, H. M.; Schwegler, M. A.; van Bekkum, H. *Recl. Trav. Chim. Pays-Bas.* **1994**, *113*, 115.
- Misono, M.; Nojiri, N. *Appl. Catal.* **1990**, *64*, 1.
- Tiofeeva, M. N.; Dimidov, A. V.; Kozhevnikov, I. V. *J. Mol. Catal.* **1979**, *179*, 21.
- Drago, R. S.; Dias, J. A.; Maier, T. *J. Am. Chem. Soc.* **1997**, *119*, 7702.
- Alizadeh, M. H.; Tayebee, R. *J. Braz. Chem. Soc.* **2005**, *16*, 108.
- Alizadeh, M. H.; Razavi, H.; Bamoharram, F. F. *J. Mol. Catal. A: Chem.* **2003**, *200*, 105.
- Tayebee, R. *J. Korean Chem. Soc.* **2008**, *52*(1), 23.
- Alizadeh, M. H.; Harmalkar, S. P.; Jeanin, Y.; Pope, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2662.
- Alizadeh, M. H.; Kermani, T.; Tayebee, R. *Monatsh. Chem.* **2007**, *138*, 165.
- Alizadeh, M. H.; Tayebee, R. *Monatsh. Chem.* **2006**, *137*, 1063.
- Tayebee, R.; Rafiee, E. *Bull. Chem. Soc. Ethiop.* **2006**, *20*(2), 1.
- Tayebee, R.; Mahdavi, B. *Asian Journal of Chemistry* **2009**, *21*, 1565.
- Tayebee, R.; Alizadeh, M. H. *Cur. Sci.* **2007**, *93*, 133.
- Tayebee, R.; Alizadeh, M. H. *Chin. J. Chem.* **2007**, *25*, 1031.
- Tayebee, R.; Alizadeh, M. H. *Monatsh. Chem.* **2007**, *138*, 763.
- Green, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley-Interscience, New York: 1999.
- Altiokka, M. R.; Citak, A. *Appl. Catal. A: Gen.* **2003**, *239*, 141.
- Chen, X.; Xu, Z.; Okuhara, T. *Appl. Catal. A: Gen.* **1999**, *180*, 261.
- Liu, W. T.; Tan, C. S. *Liquid-Phase Ind. Eng. Chem. Res.* **2001**, *40*, 3281.
- Yadav, G. D.; Thathagar, M. B.; *React. Funct. Polym.* **2002**, *52*, 99.
- Hoek, I.; Nijhuis, T. A.; Stankiewicz, A. I.; Moulijn, J. A. *Appl. Catal. A: Gen.* **2004**, *266*, 109.
- Kirumakki, S. R.; Nagaraju, N.; Narayanan, S. *Appl. Catal. A: Gen.* **2004**, *273*, 1.
- Hiyoshi, M.; Lee, B.; Lu, D.; Hara, M.; Kondo, J. N.; Domen, K. *Catal. Lett.* **2004**, *98*, 181.
- Iizuka, T.; Fujie, S.; Ushikubo, T.; Chen, Z. H.; Tanabe, K. *Appl. Catal.* **1986**, *28*, 1.
- Okun, N. M.; Anderson, T. M.; Hill, C. L. *J. Am. Chem. Soc.* **2003**, *125*, 3194.
- ten Brink, G. J.; Arends, I. W. C. E.; Sheldon, R. A. *Science* **2000**, *258*, 1636.
- ten Brink, G. J.; Arends, I. W. C. E.; Sheldon, R. A. *Adv. Synth. Catal.* **2002**, *344*, 355.
- North, E. O. *Inorg. Synth.* **1993**, *1*, 129.
- Wu, H. *J. Biol. Chem.* **1920**, *43*, 189.
- Brevard, C.; Schimpf, R.; Tourne, G.; Tourne, C. M. *J. Am. Chem. Soc.* **1983**, *105*, 7059.
- CRC, *Handbook of Tables for Organic Compound Identification*, 3rd and 54th ed.