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Highly efficient conversion of aldehydes to geminal diacetates (solvent-free) and their deprotection using facile and reusable molybdenum and tungsten polyoxometalates

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Abstract

Keggin-type supported polyoxometalates (supported-$H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$) were found to be efficient catalysts for preparation of 1,1-diacetates under solvent-free conditions. Deprotection of the resulting 1,1-diacetates were achieved using the same catalysts in acetonitrile solvent. This new method consistently has the advantage of excellent yields and short reaction times. Further, the catalysts can be reused for several times but they will be less active.

Keywords: 1,1-Diacetates (acylals); Supported catalysts; Polyoxometalates (POMs); Heteropolyacids (HPAs); Keggin-type polyoxometalates; Solvent-free reaction

1. Introduction

1,1-Diacetates (acylals) are efficient protecting groups for aldehyde because they are stable in neutral and basic media [1]. In addition, acylals are important precursors for the preparation of 1-acetoxydienes [2] and vinyl acetates [3a], in Diels–Alder reactions. Compounds bearing the acylal functionality are used as cross-linking reagents for cellulose in cotton [3b]. Usually, the preparation of 1,1-diacetates from aldehydes includes the use of protic acids such as sulfuric, phosphoric or methanesulfonic acids [4,5], solid acidic materials [6], Lewis acids such as iodine [7], trimethylchlorosilane and sodium iodide [8], zinc chloride [9], $FeCl_3$ [10], $FeSO_4$ [11], phosphorus trichloride [12], indium trichloride [13], $Sc(OTf)_3$ [14], $Cu(OTf)_2$ [15], $Bi(OTf)_3$ [16], LiOTf [17] and $In(OTf)_3$ [18]. The use of montmorillonite clay [19], expansive graphite [20], zeolites [21], *N*-bromosuccinimide [22], ceric ammonium nitrate [23], NH_2SO_3H [24], WCl_6 [25], $AlPW_{12}O_{40}$ [26], $H_6P_2W_{18}O_{62}{\cdot}24H_2O$ [27], zirconium sulfophenyl phosphonate [28], $ZrCl_4$ [29], $LiBF_4$ [30], LiBr [31], $Zn(BF_4)_2$ [32], $Cu(BF_4)_2{\cdot}xH_2O$ [33] and $Bi(NO_3)_3{\cdot}5H_2O$ [34], $LiClO_4$ [35] and (ZrO_2/SO_4^{2-}) [36] as catalysts have also been reported. A few of the above mentioned catalysts are claimed to give protection as well as deprotection. Deprotection of 1,1-diacetates to their parent aldehydes is also of practical importance and several methods have been reported in the literature for this purpose [37]. Many of these methods have certain drawbacks such as low yields of products, expensive and hazardous reagents, long reaction times, corrosivity, tedious work up and pollution problems. Furthermore, very few methods are known for the chemoselective protection of aldehydes in the presence of ketones. Consequently, the development of novel and mild catalytic methods for the preparation of 1,1-diacetates and their deprotection is still desirable.

In this regard, polyoxometalates (POMs) are in the center of focus to inorganic chemists. In view of this, we have utilized POMs as efficient Bronsted acid catalysts for the efficient conversion of aldehydes to geminal diacetates. The majority of POMs have structures composed of molybdenum and tungsten polyhedrons. Other elements occur in small amounts in these structures [38].

Usually, tungsten heteropolyacids are the catalysts of choice because of their stronger acidity, higher thermal stability and

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lower oxidation potential compared to molybdenum acids. Generally, if the reaction rate is controlled by the catalyst acid strength, $H_3PW_{12}O_{40}$ shows the highest catalytic activity in the Keggin series. The $H_3PW_{12}O_{40}$ (HTP) and $H_3PMo_{12}O_{40}$ (HMP) acids are readily available and most frequently used as catalysts [39].

The development of green chemistry is a challenging goal in recent organic chemistry. In this regard, as Anastas and Warner have proposed, it is important to realize reaction systems in water instead of organic solvents, to use safe reagents, to decrease hazardous inorganic and organic wastes, and to use a minimal amount of reusable catalysts [40–41].

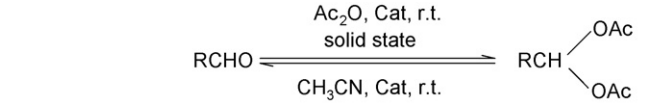
We believe that a promising reaction system for achieving these goals, is the use of heterogeneous catalysis. By using heterogeneous catalysis, the procedure can be simplified, providing an easier work up and isolation of products and quantitative recovery of the catalyst.

Polyoxoanions can be used directly (bulk material) or deposited on different supports (supported material). Unfortunately, the useful HPAs are found to be thermally unstable, decomposing at temperatures higher than 723 K, and easily soluble in both water and alcohol, which makes difficult the separation of HPAs, reactants and products. These drawbacks may subsequently limit the practical application of HPAs. Hydrogen forms (or free acids) of HPAs usually have low surface areas (the drawback to the HTP and HMP is their low surface area, 1–5 $m^2\ g^{-1}$, and low porosity, $<0.1\ cm^3\ g^{-1}$). Supported heteropoly acid catalysts have much greater surface areas. Many attempts have been made to disperse and fix HPA catalysts on various supports. Support materials such as silica, carbon and organic resins have been applied with varying levels of success, with new supporting materials and methods being actively pursued. Although the structure and composition of the supported HPAs are sometimes uncertain, high catalytic activities are often observed and separation made easier. For various reasons, such as efficiency, better accessibility to the active sites, cost, *etc.*, depositing on a support is currently favoured [42–45].

In continuation of our work on the catalytic properties of heteropoly acids [46–48], herein, we wish to report a mild and efficient method for the preparation and deprotection of 1,1-diacetates in the presence of catalytic amount of Keggin-type, bulk and supported-, polyoxometalate (HTP and HMP) (Scheme 1).

2. Results and discussion

The reaction of aldehyde and acetic anhydride under solvent free conditions using a catalytic amount of Keggin-type polyoxometalate (bulk or supported) resulted in formation of 1,1-diacetates. Results show the effect of HTP and HMP heteropolyacids as bulk catalysts on the yield of conversion of aldehydes to geminal diacetates (Table 1).



Cat = POM or supported-POM
POM = $H_3PW_{12}O_{40}$(HTP), $H_3PMo_{12}O_{40}$ (HMP)
Support = PMP, KSF-mont, SiO_2(cabosil), Al_2O_3, TiO_2(degussa), ZrO_2.

Scheme 1.

Table 1
Bulk POM ($H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$) catalyzed conversion of aldehyde to corresponding 1,1-diacetate (solvent-free) and their deprotection in CH_3CN[a]

Entry	R	POM	Protection[a]		Deprotection[b]	
			Yield[c,d] (%)	Time (min)	Yield[c,d] (%)	Time (min)
1	4-(NO_2)-C_6H_4	HTP	70	25	75	20
		HMP	75	30	75	35
2	4-(Cl)-C_6H_4	HTP	75	35	78	45
		HMP	61	80	66	35
3	2-(OH)-C_6H_4	HTP	63	48	71	60
		HMP	65	60	60	60
4	4-(OH)-C_6H_4	HTP	78	35	73	60
		HMP	78	40	78	110
5	4-(OMe)-C_6H_4	HTP	78	35	83	45
		HMP	80	60	65	55
6	4-(Me)-C_6H_4	HTP	76	60	75	60
		HMP	70	60	54	75

[a] Reaction conditions: aldehydes (1 mmol), acetic anhydride (3 mmol), POM (0.02 mmol), room temperature, solvent-free.
[b] Reaction conditions: 1,1-diacetates (1 mmol), POM (0.02 mmol), CH_3CN (3 mL), room temperature.
[c] All of the products were characterized by comparison of their spectral and physical data with those of authentic samples.
[d] Isolated yields.

Following the above reaction condition, as shown in Tables 2 and 3, a variety of aromatic aldehydes are converted to the corresponding 1,1-diacetates under solvent free conditions using acetic anhydride in the presence of Keggin-type supported polyoxometalates at room temperature in excellent yields and short reaction times.

The best results were obtained using 2 mol% bulk POM (HTP as model catalyst) or 0.4 g supported POM (*ca.* 0.009 mol% for HTP-KSF as model catalyst). Lower amounts of catalyst resulted in lower yields, while higher amounts did not affect the reaction times and yields.

More importantly, all aromatic aldehydes carrying either electron-withdrawing (Tables 1 and 2: entries 1 and 2) or electron-donating (Tables 1 and 2: entries 3–6) substituents reacted very well, giving moderate to excellent yields.

The 1,1-diacetates were deprotected to the corresponding aldehydes using a catalytic amount of Keggin-type polyoxometalate (bulk or supported) in CH_3CN at room temperature (Tables 1–3). Two types of POMs (HTP and HMP) were used for these reactions. The reactivity of HTP and HMP proved to be almost the same.

Even for other aldehydes (such as PhCHO, furfural, cinnamaldehyde and also aliphatic aldehydes), which normally show extremely poor yields for conversion of aldehydes to geminal diacetates, better yields of the corresponding 1,1-diacetates could be obtained. Additionally, it is worth noting