Ultrasound-Assisted Synthesis of Acylals Catalyzed by Stannum (IV) Phosphomolybdate under Solvent-Free Condition

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Summary: An efficient method for the synthesis of acylals from different aldehydes and acetic anhydride in the presence of Keggin-type stannum (IV) phosphomolybdate under ultrasound irradiation at room temperature was achieved. This method provides a new and efficient protocol in terms of cost effective of catalyst, a wide scope of substrates, and simple work-up procedure.

Introduction

Ultrasound has increasingly been used in organic synthesis in the last three decades. Ultrasound irradiation has been demonstrated as an alternative energy source for organic reactions ordinarily accomplished by heating. A large number of organic reactions can be carried out in higher yields, shorter reaction time or milder conditions under ultrasound irradiation. Many homogeneous and heterogeneous reactions can be conducted smoothly by sonication to provide improved yields and increased selectivities [1-3].

Acylals are conventionally prepared from aldehydes with acetic anhydride under an acidic catalyst. Some of these reagents and catalysts that have been employed include H₂SO₄, H₃PO₄, CH₃SO₃H [4], aminosulfonic acid [5], indium(III) chloride [6], ruthenium(III) chloride [7], bismuth triflate [8], iodine [9] and other types of catalysts such as sulfated silica gel [10], [Hmim]HSO₄ [11]. Although some improvements have been observed in above methods, there still some limitations existed, such as the long reaction time, the highly corrosive and expensive catalysts. Hence, a practical and more efficient alternative is still of interest.

Heteropoly acids (HPAs) are strong Bronsted acids, which have been used widely as homogeneous and heterogeneous acid. Among heteropolyacids, the Keggin-type H₃PMO₁₂O₴₀ is a widely used catalyst owing to its excellent solubility in water, high catalytic activities, ease of handing, cleaner reactions in comparison to conventional catalysts, non-toxicity and experimental simplicity [12]. Stannum (IV) phosphomolybdate (noted SnPMo) was prepared easily from commercially available H₃PMO₁₂O₴₀ and SnCl₄ in ethanol [13]. This salt is nonhygroscopic which has not been reported as a catalyst. Following our previous work on the synthesis of acylals [14], we describe the use of stannum (IV) phosphomolybdate as an effective catalyst for the synthesis of acylals under ultrasound irradiation (Scheme 1).

\[
\begin{align*}
\text{RCHO} + (\text{CH₃CO})₂O & \xrightarrow{\text{solvent-free, us, rt}} \text{RCHOCOCH₃}
\end{align*}
\]

Scheme-1: Synthesis of acylals in the presence of SnPMo under ultrasound irradiation.

Results and discussion

To find the standard experimental procedure, we took benzaldehyde as model substrate and treated with Ac₂O in the presence of SnPMo at room temperature under different conditions (Table-1). The reaction was best carried out using 2 equiv of Ac₂O under solvent-free conditions for 0.5 h at room temperature in presence of 0.5 g SnPMo (Table-1, entry 4). Although the use of 1.5 equiv of Ac₂O afforded 87% yield, we preferred to use 2 equiv of Ac₂O otherwise in some cases the reaction remained incomplete due to precipitation of the acylals.

Table-1: Effect of stannum (IV) phosphomolybdate on the reaction of benzaldehyde with acetic anhydride.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Mole ratio (aldehyde/anhydride)</th>
<th>Catalyst amount (g)</th>
<th>Time (h)</th>
<th>Yield (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:2</td>
<td>0</td>
<td>4.0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1:2</td>
<td>0.1</td>
<td>0.5</td>
<td>77</td>
</tr>
<tr>
<td>3</td>
<td>1:2</td>
<td>0.3</td>
<td>0.5</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>1:2</td>
<td>0.5</td>
<td>0.5</td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td>1:2</td>
<td>0.7</td>
<td>0.5</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>1:2</td>
<td>1.0</td>
<td>0.5</td>
<td>95</td>
</tr>
<tr>
<td>7</td>
<td>1:2</td>
<td>0.5</td>
<td>0.25</td>
<td>82</td>
</tr>
<tr>
<td>8</td>
<td>1:1</td>
<td>0.5</td>
<td>0.5</td>
<td>75</td>
</tr>
<tr>
<td>9</td>
<td>1:1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>87</td>
</tr>
</tbody>
</table>

a Isolated yield.

When various aldehydes were treated with acetic anhydride in the presence of SnPMo under ultrasound irradiation, the corresponding acylals were obtained. All of the results are shown in Table-2.

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As shown in Table-2, aromatic aldehydes with an electron-withdrawing group were converted to their corresponding acylals under these conditions in high yields after a short time (Table-2, entries 2-4). On the other hand, 3-nitrobenzaldehyde proceeded with difficulty (Table-2, entry 5). Furthermore, the sensitive heteroaromatic furfural, crotonaldehyde, and cinnamaldehyde were converted to the corresponding 1,1-diacetates successfully (Table-2, entries 6-8). The aromatic aldehydes with electron-donating group afforded the corresponding acylal in high yield and purity (Table-2, entry 9).

It should be stressed that the targeted acylals were not obtained using 2 equiv of Ac₂O, when 4 equiv of Ac₂O was used, both carbonyl and phenolic hydroxyl were acylated (Table-2, entries 10-12). The hydroxyl is strong electron-donating group, which decreases the activity of aldehyde and is also protected as acetate with Ac₂O. On the other hand, the electron-donation of acetyl oxide was weaker than that of hydroxyl, which increased the activity of aldehyde. So the corresponding acylals were received when the amount of Ac₂O was sufficient (Scheme 2).

Catalyst reusability was assessed in the reaction of benzaldehyde with acetic anhydride. Table-2, entry 1 showed the results obtained after three reuse cycles. SnPMo was filtered when the solid product was dissolved by CH₂Cl₂, then dried at 120 °C, and reused for its next run. It could be recycled three times without distinct loss of activity.

To evaluate the chemoselectivity of this method, we also investigated competitive reactions for acylation of aldehydes in the presence of ketones using SnPMo as catalyst under ultrasound irradiation at room temperature. Employing this catalytic system, the highly selective conversion of aldehydes rather than ketones was observed although both were present as a mixture (Table-3). Smooth conversion of the aldehyde to the acylal was observed while the ketone functionality remained unaffected. This observation indicates that aldehydes are more reactive than ketones and this may be due to higher electrophilicity and lower steric hindrance of aldehyde in comparison to ketones.

**Experimental**

All reagents were purchased and used without further purification. GC analysis was carried out on a Shanghai GC-7890α gas chromatograph. Ultrasound was performed in a KQ-300VDE ultrasound cleaner with a frequency of 45 kHz and an output power 300W.

**General Procedure for the Preparation of Acylals**

A mixture of aldehyde (30 mmol), Ac₂O (60 mmol), 0.50 g SnPMo were put in a flask. The flask was located at the maximum energy area in the cleaner at room temperature. After completion of the reaction (monitored by GC), most of the mixture solidified gradually, 20 mL CH₂Cl₂ was added to dissolve the solid product. The organic layer was washed twice with saturated Na₂CO₃ solution (20 mL), dried (Na₂SO₄) and evaporated to yield the almost pure product. The product was purified further by crystallization from cyclohexane or by column chromatography on silica gel (ethyl acetate/hexane, 1:9 as the eluent). The products were identified by comparing the M.P., IR, ¹H NMR with those observed for the authentic samples [14].
Table-3: Competitive acylal formation of aldehydes using Ac₂O in the presence of SnPMo

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHO + CH₃(CH(OAc)₂ + OAcOAc) SnPMo ultrasound, rt (15 mmol) (15 mmol) (97%) (0%)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CHO + SnPMo ultrasound, rt (15 mmol) (15 mmol) (98%) (0%)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>H₃C-OCHO + SnPMo ultrasound, rt H₃C-OCHO (30 mmol) (100%) (0%)</td>
<td></td>
</tr>
</tbody>
</table>

* Isolated yield.

Conclusion

We have developed an ultrasound-assisted, efficient and chemoselective method for the preparation of acylals from aldehydes under solvent-free conditions using a catalytic amount of Keggin-type SnPMo. The reaction proceeded smoothly under mild conditions at room temperature and the products were obtained in good to high yields within short time. The catalyst remained active and exhibits no substantial loss of activity over up to three reaction cycles [15-17].

References