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

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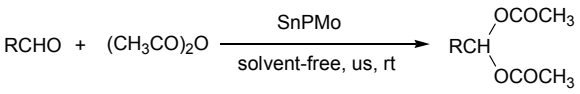
Summary: An efficient method for the synthesis of acylals from different aldehydes and acetic anhydride in the presence of Keggin-type stannum (IV) phosphomolybdate under ultrasound irradiation at room temperature was achieved. This method provides a new and efficient protocol in terms of cost effective 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 H_2SO_4, H_3PO_4, CH_3SO_3H [4], aminosulfonic acid [5], indium(III) chloride [6], ruthenium(III) chloride [7], bismuth triflate [8], iodine [9] and other types of catalysts such as sulfurated silica gel [10], $[Hmim]HSO_4^-$ [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 $H_3PMo_{12}O_{40}$ 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 $H_3PMo_{12}O_{40}$ and $SnCl_4$ 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).



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 Ac_2O in the presence of SnPMo at room temperature under different conditions (Table-1). The reaction was best carried out using 2 equiv of Ac_2O 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 Ac_2O afforded 87% yield, we preferred to use 2 equiv of Ac_2O 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.

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

[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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Table-2: Preparation of acylals in the presence of SnPMo under ultrasound irradiation.

Entry	Aldehyde	Product	Time (h)	Yield (%)[a]
1	C_6H_5CHO	$C_6H_5CH(OAc)_2$	0.5	96, 93, 89, 85[c]
2	2-ClC_6H_4CHO	2-$ClC_6H_4CH(OAc)_2$	0.5	90
3	4-ClC_6H_4CHO	4-$ClC_6H_4CH(OAc)_2$	0.5	98
4	2, 4-$Cl_2C_6H_3CHO$	2, 4-$Cl_2C_6H_3CH(OAc)_2$	1.0	88
5	3-$NO_2C_6H_4CHO$	3-$NO_2C_6H_4CH(OAc)_2$	2.0	75
6	Furfural	2-Furyl$CH(OAc)_2$	0.2	90
7	(E)-PhCH=CHCHO	(E)-PhCH=CHCH$(OAc)_2$	2.0	85
8	(E)-CH_3CH=CHCHO	(E)-CH_3CH=CHCH$(OAc)_2$	1.0	94
9	4-$CH_3OC_6H_4CHO$	4-$CH_3OC_6H_4CH(OAc)_2$	1.0	95
10[b]	2-HOC_6H_4CHO	2-$AcOC_6H_4CH(OAc)_2$	2.0	85
11[b]	4-HOC_6H_4CHO	4-$AcOC_6H_4CH(OAc)_2$	2.5	91
12[b]	4-HO-3-$CH_3OC_6H_3CHO$	4-AcO-3-$CH_3OC_6H_3CH(OAc)_2$	2.0	90

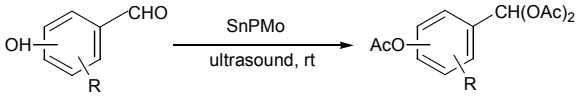
[a] Isolated yield.

[b] 4 equiv. of Ac_2O was used.

[c] Reuse of SnPMo.

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 Ac_2O, when 4 equiv of Ac_2O 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 Ac_2O. 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 Ac_2O was sufficient (Scheme 2).



Scheme-2: The hydroxyl was acylated with the same condition.

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 CH_2Cl_2, then dried at 120 ^oC, 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.

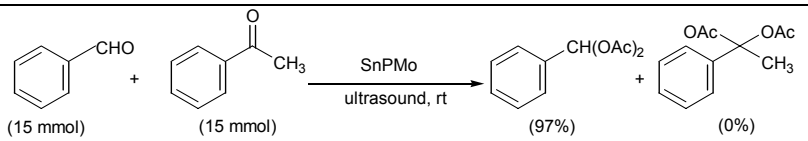
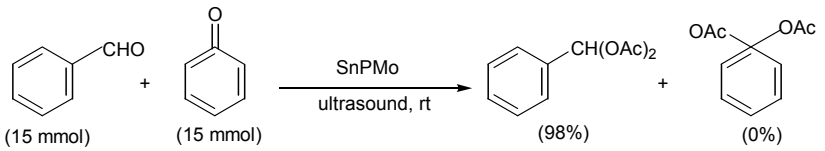
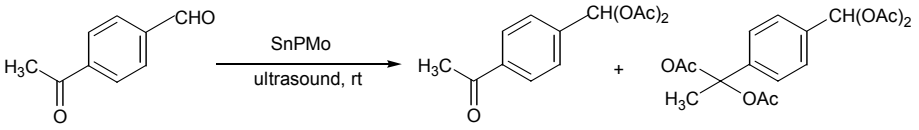
Experimental

All reagents were purchased and used without further purification. GC analysis was carried out on a Shanghai GC-7890α gas chromatograph. Ultrasonication 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), Ac_2O (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 CH_2Cl_2 was added to dissolve the solid product. The organic layer was washed twice with saturated Na_2CO_3 solution (20 mL), dried (Na_2SO_4) 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 Ac_2O in the presence of SnPMo[a]

Entry	Substrate	Yield (%)[b]
1	 (15 mmol) (15 mmol) (97%) (0%)	
2	 (15 mmol) (15 mmol) (98%) (0%)	
3	 (30 mmol) (100%) (0%)	

[a] 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

1. J. Hofmann, U. Freier and M. Wecks. *Ultrasonics Sonochemistry*, **10**, 271 (2003).
2. H. J Zang,. M. L Wang, B. Cheng and J. Song. *Ultrasonics Sonochemistry*, **16**, 301 (2009).
3. V. Calvino, M. Picallo, A. J. López-Peinado, R. M. Martín-Aranda and C.J. Durán-Valle. *Applied Surface Science*, **252**, 6071 (2006).
4. F. Freeman and E. M. Karchefski. *Journal of Chemical and Engineering Data*, **22**, 355 (1977).
5. T. S. Jin, G. Sun, Y. W. Li and T. S. Li. *Green Chemistry*, **4**, 255 (2002).
6. J. S. Yadav, B. V. S. Reddy and C. Srinivas. *Synthetic Communications*, **32**, 2169 (2002).
7. N. Sheikhan, B. F. Mirjalili, A. Hajipour and Bamoniri A. *Acta Chimica Slovenica*, **55**, 209 (2008).
8. M. D. Carrigan, K. J. Eash, M. C. Oswald and R. S. Mohan. *Tetrahedron Letters*, **42**, 8133 (2001).
9. N. Deka, D. J. Kalita, R. Borah and J. C. Sarma. *Journal of Organic Chemistry*, **62**, 1563 (1997).
10. A. Barua and P. J. Das. *Indian Journal of Chemistry-Section* B, **47**, 938 (2008).
11. A. R. Hajipour, L. Khazdooz and A. E. Ruoho. *Catalysis Communications*, **9**, 89 (2008).
12. T. K. Huang, L. Shi, R. Wang, X. Z. Guo and X. X. Lu. *Chinese Chemical Letters*, **20**, 161 (2009).
13. V. M. Fuchs, L. R. Pizzio and M. N. Blanco. *Catalysis Today*, **133**, 181 (2008).
14. H. Gong, Q. Liu and H. Jiang. *Chinese Journal of Synthetic Chemistry*, **16**, 176 (2008).
15. M. R. Sohrabi, A. Marjani, S. Moradi M. Dawallo and S. Shirazian, *Journal of the Chemical Society of Pakistan,* **33**, 464 (2011).
16. Y. Khan, A. Khan, S. S. Sakhawa, G. Hamid, G. Fatima and M. Siddiq, *Journal of the Chemical Society of Pakistan,* **33**, 474 (2011).
17. H. Masood, M. Khan, A. Ishaq and S. Taj, *Journal of the Chemical Society of Pakistan,* **33**, 503 (2011).