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$H_3PW_{12}O_{40}/SiO_2$: an efficient, reusable and eco-friendly catalyst for the synthesis of 1,1-diacetates at room temperature

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Abstract: Silica supported 12-tungstophosphoric acid as an effective, heterogeneous, readily available, low cost and reusable catalyst has been used for the synthesis of acylals at ambient temperature under solvent free conditions.

Keywords: Silica supported heteropolyacid, 12-Tungstophosphoricacid, Acylal, Aldehydes, Protecting group.

Introduction

12-Tungstophosphoric acid (TPA), is known to be very active catalyst for both homogeneous and heterogeneous acid catalyzed reactions. This allows it to be used as catalyst for various reactions such as esterification of palmitic acid [1], alkylation of *p*-cresol [2], synthesis of thiochromans [3], Friedel-Crafts benzoylation [4], oxathiacetalization of carbonyl compounds [5], and etc.

Acylals or 1,1-diacetates, as alternative to acetals, are synthetically useful as aldehyde protecting groups, due to their stability towards aqueous acids and mild bases. In addition, they can be used as building blocks for the synthesis of 1-acetoxy dienes in Diels-Alder reactions [6]. Some reagents and catalysts such as $Zn(OTf)_2.6H_2O$ [7], $InBr_3$ [8], Indium triflate [9], 12-molybdophosphoric acid [10], P_2O_5/SiO_2 [11], bronsted acidic ionic liquid [12], SO_4^{-2}/SnO_2 [13] and Ru(III)chloride [14] have been used for acylal formation by acetic anhydride. At present, considerable efforts are being made to find suitable, recyclable and eco-friendly solid acid catalysts which can successfully carry out for acylal formation from aldehydes.

Results and discussion

It is common that TPA is supported on a carrier, in order to ensure high dispersion since bulk TPA has low specific surface. In case of supported TPA catalyst recovery and reutilization is easier and the production of harmful effluents to the environment could be avoided. According to previous reports, silica is a support with useful properties for acidic catalysts. The use of silica supported 12-tungstophosphoric acid has received considerable attention in different areas of organic synthesis, due to its environmental compatibility, high selectivity, experimental simpilicity and ease of isolation of product. Herein we wish to disclose a mild, efficient and eco-friendly silica supported 12-tungstophosphoric acid promoted acylal formation in good to excellent yields at ambient temperature under solvent free condition.

1 mmol of 2,6-Dichlorobenzaldehyde was reacted with 2 mmol of acetic anhydride in the presence of variety mmoles of catalysts as a model reaction. The obtained results are summarized in Table **1**. The best ratio of aldehyde (mol): Ac_2O (mol): 60% $H_3PW_{12}O_{40}/SiO_2$ (g) was 1: 2: 0.01. It was observed that when 60% $H_3PW_{12}O_{40}/SiO_2$ was carried out as catalyst, the efficiency of it was twice in comparison with TPA.

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We have checked the various reaction conditions for preparation of acylal of 2,6-dichlorobenzaldehyde. The obtained results were recorded in Table **2**. According to this data, we have found that the solvent free condition was the best. Thus, various aldehydes and ketones were applied for acylal formation under solvent free condition at room temperature (Scheme **1**)

$$\text{R-CHO} \xrightarrow[\substack{Ac_2O,\ \text{r.t.} \\ \text{solvent free}}]{60\%\ H_3PW_{12}O_{40}/SiO_2} \text{R-CH(OAc)}_2$$

Scheme 1: Acylal formation from aldehydes in the presence of silica supported TPA.

The mild reaction conditions, short reaction times, occasional enhanced selectivity and clean products are salutary features of this approach. Representative examples are given in Table **3**. The results revealed that aldehydes with electron withdrawing groups are more efficient than others, due to the high electrophilic activity of carbonyl group in former.

Table 1: The reaction of 1 mmol of 2,6-dichlorobenzaldehyde and 2 mmol of Ac_2O in the presence of various mmol of catalysts at room temperature under solvent free condition.

Entry	TPA (g)/yield(%)[a]	$60\%H_3PW_{12}O_{40}/SiO_2$ (g)/yield(%)[b]
1	0.005/15	0.005/20
2	0.007/45	0.007/55
3	0.008/80	0.008/85
4	0.009/90	0.009/90
5	0.01/90	0.01/95
6	0.02/90	0.02/95

[a]The time of reaction is 30 minutes.
[b]The time of reaction is 5 minutes.

Table 2: preparation of acylal of 2,6-dichlorobenzaldehyde in various conditions in the presence of 60% $H_3PW_{12}O_{40}/SiO_2$

Entry	Solvent	Condition	Time(min)	Yield(%)[a]
1	n-hexane	reflux	45	50
2	n-hexane	r.t	45	65
3	dichloromethane	reflux	45	20
4	dichloromethane	r.t	45	90
5	acetonitrile	reflux	45	30
6	acetonitrile	r.t	45	80
7	diethyl ether	reflux	45	60
8	diethyl ether	r.t	45	75
9	ethyl acetate	reflux	45	35
10	ethyl acetate	r.t	45	35
11	-	r.t	5	94
12	- (2nd run)	r.t.	5	88
13	- (3rd run)	r.t.	5	80

[a] The ratio of aldehyde: Ac_2O: 60% $H_3PW_{12}O_{40}/SiO_2$ is 1 (mol): 2 (mol): 0.01 g

4-nitroacetophenone, 4-acetyl benzaldehyde and an acetal were also checked for acylal formation in this method. The keto or acetal groups of these compounds have not reacted (Scheme **2**). It is suggested that the chemo-selective protection of aldehydes in the presence of ketones or acetals can be achieved by this method.

Likewise, 4-*N,N*-dimethyl amino benzaldehyde failed to give the expected acylal under grinding condition in room temperature. The explanation for this result may be due to the strong electron donating dimethyl amino group which will reduce the reactivity. Mention must be made here that phenolic group was also protected as acetate in hydroxyl containing aromatic aldehyde (Table **3**, entries 19 and 20). Some products which have not been reported previously (Table **3**, entries 2, 4, 9 and 11), are introduced by spectroscopic data.

To examine the reusability of 60% $H_3PW_{12}O_{40}/SiO_2$ in solvent free condition, after each run, the product was dissolved to $CHCl_3$ and filtered. The catalyst residue was washed with acetone and reused. Treatment with acetone removes the tar from the catalyst surface more efficiently (Table **2**, entries 12 and 13). The catalyst was reusable although a gradual decline was observed in its activity.

Conclusion

The present simple method is carried out at ambient temperature under solvent free conditions using silica supported 12-tungstophosphoric acid as an effective, heterogeneous, readily available, low cost and reusable catalyst. This procedure is a green protocol for the synthesis of acylals.

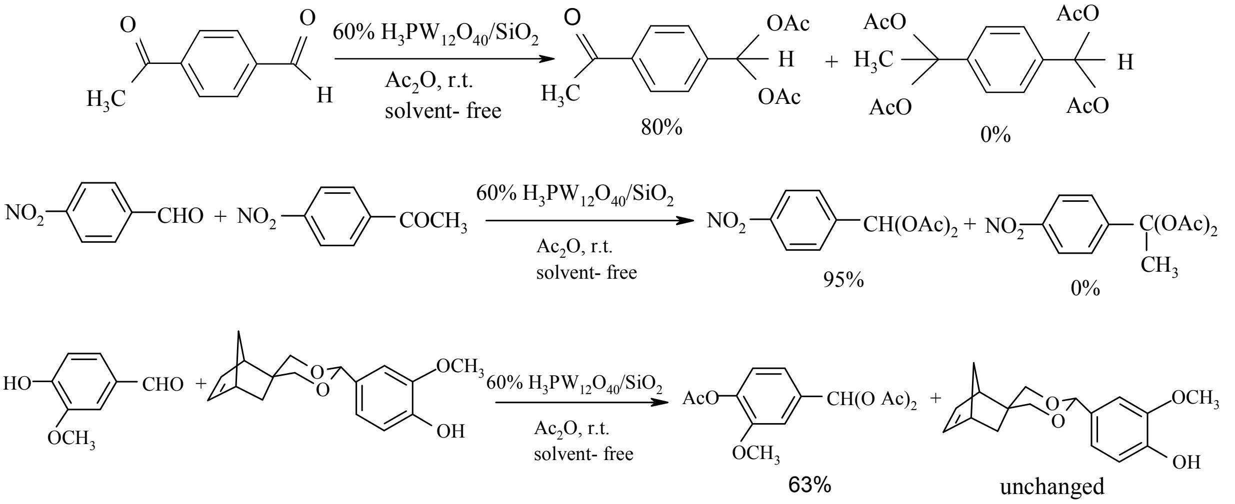
Experimental

Preparation of silica supported 12-tungstophosphoric acid (60% $H_3PW_{12}O_{40}/SiO_2$)

A mixture of 0.6 g (0.2 mmol) of 12-tungstophosphoric acid and 0.4 g of silicagel was ground to fine particles. A suspension of this mixture, 0.2 mL of HCl 0.5 M and 1 mL of methanol was stirred for 20 min at room temperature. The solvent of the suspension was evaporated at about 80-90 ºC until dryness. The obtained solid was dried in a domestic microwave oven for 20 min in power 100.

General procedure for the preparation of acylals using 60%$H_3PW_{12}O_{40}/SiO_2$ at room temperature under solvent free condition

In a mortar, a mixture of substrate (2 mmol), acetic anhydride (4 mmol), and catalyst (0.01 g) was pulverized for 5 minutes. The reaction progress was followed by TLC. After completion of the reaction, diethyl ether was added and the heterogeneous mixture was filtered. In some cases, after evaporation of solvent, the product was crystallized by ethanol and water mixture. In another cases, by washing the reaction mixture with sodium bisulphite aqueous solution (40%), the acylal as a pure oily liquid or solid was obtained.



Scheme 2: Chemo-selectivity in acylal formation in the presence of 60% $H_3PW_{12}O_{40}/SiO_2$.

Table 3: Conversion of aldehydes to corresponding acylals by silica supported 12-tungstophosphoric acid as catalyst under solvent free condition at room temperature.

Entry	Substrate	Yield[a](%)		Mp (Bp) °C[ref]
		Subs(2mmol)/Ac_2O (4mmol)/TPA(0.018gr)[d]	Subs(2mmol)/ Ac_2O(4mmol)/ TPA-SiO_2(60%w/w)(0.018gr)[e]	
1	3-Nitrobenzaldehyde	86	91	65-66[23,22]
2	4-Chlorobenzaldehyde	81	87	79-80[23]
3	Methyl-4-formylbenzoate	68	72	68-69
4	4-Bromobenzaldehyde	87	91	92-93[23]
5	3-Methoxybenzaldehyde	75	79	(191-193)[22]
6	2,6-Dichlorobenzaldehyde	81	89	86-88[23]
7	2-chloro-6-Fluorobenzaldehyde	85	90	99-101
8	4-Cyanobenzaldehyde	86	92	93-95[23]
9	2-Chloro-5-nitrobenzaldehyde	87	90	106-107
10	Furfural[b]	55	59	45-47[23]
11	4-Methylbenzaldehyde	71	76	80-81[23]
12	3-Phenylpropionaldehyde	70	76	(186-187)[24]
13	1sobutyraldehyde	69	73	(182-184)[24]
14	Salicylaldehyde[c]	71	74	88-90[22]
15	4-Acetylbenzaldehyde	73	80	55-57[24]
16	4-Nitrobenzaldehyde	89	95	124-125[23,22]
17	2-Chlorobenzaldehyde	76	82	51-53[22]

[a] Yields refer to isolated pure products.

[b] An unidentified polymer was produced in low yield.

[c] Salicylaldehyde gave the corresponding triacetates.

[d] The time of reaction is 30 minutes.

[e] The time of reaction is 5 minutes.

Table 4: Selected spectroscopic data.

Entry	Product name	IR, υ(Cm^{-1})	MS, m/z	^{1}H-NMR, δ(ppm)
1	1,1-diacetoxy-1-(2-chlorophenyl) methane	2880-3100, 1750, 1600, 1500,1220	242(M^+), 183, 139, 111, 105, 104	2.2(s, 6H), 7.3(m, 4H), 7.8(s, 1H)
2	1,1-diacetoxy-1-(4-chlorophenyl) methane	2880-3100, 1750, 1600, 1500,1250, 1200	-	2.2(s,6H), 7.4(sbr, 4H), 7.6(s, 1H)
3	1,1-diacetoxy-1-(4-cyanophenyl) methane	2880-3100, 2250, 1750,1600, 1500, 1375, 1250, 1200	233(M^+), 174, 190, 130, 103, 102	2.14(s, 6H), 7.68(br s, 5H).
4	1,1-diacetoxy-2-methyl propane	2870-3000, 1750, 1440, 1380, 1200	-	0.65(d, 3H), 0.7(m, 1H), 1.72(s, 6H), 6.24(d,1H)
5	1,1-Diacetoxy-1-(4-acetylphenyl)methan	3100-2976, 1767, 1678, 1609, 1373, 1200, 1011	-	2.1(6H, s), 2.6(3H, s), 7.5(2H, d, J=8.5 Hz), 7.7(1H, s), 8.3(2H, d, J=8.5 Hz)

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References

[1] Giri, B. Y.; Rao, K. N.; Devi, B. L. A. P.; Lingaiah, N.; Suryanarayana, I.; Prasad, R. B. N.; Prasad, P. S. S. *Catal. Commun.* **2005**, *6*, 788.

[2] Devassy, B. M.; Shanbhag, G. V.; Lefebvre, F.; Halligudi, S. B. *J. Mol. Catal. A*. **2004**, *210*, 125.

[3] Jafarzadeh, M.; Amini, K.; Nikpour, F. *Tetrahedron Lett*. **2005**, *46*, 7567-7569.

[4] Sawant, D. P.; Devassy, B. M.; Halligudi, S. B. *J. Mol. Catal. A,* **2004**, *217*, 211-217.

[5] Firouzabadi, H. Iranpoor, N. Jafari, A.A. Jafari, M. R. *J. Mol. Catal. A*, **2006**, *247*, 14.

[6] Banks, R. E. Miller, J. A. Nunn, M. J. Stanley, P. Weakley, T. J. Ullah, R. Z. *J. Chem. Soc., Perkin Trans.1* **1981**, 1096.

[7] Weike, S.; Jin, C. *J. Chem. Res*. **2005**, 88.

[8] Yin, L.; Zhang, Z-H.; Wang, Y-M.; Pang, M-L. *Synlett* **2004**, 1727.

[9] Ghosh, R.; Maiti, S.; Chakraborty, A.; Halder, R. *J. Mol. Catal. A*, **2004**, *215*, 49.

[10] Heravi, M. M.; Bakhtiari, K.; Bamoharram, F. F. *Catal. Commmun*. **2006**, *7*, 499.

[11] Mirjalili, B. F.; Zolfigol, M. A.; Bamoniri, A. H. *Phosphorus, Sulfur and Silicon* **2004**, *179*, 19.

[12] Hajipour, A. R.; Leila Khazdooz, L.; Ruoho, A. E. *Catal. Commun*. **2008**, *9*, 89.

[13] Satam, J.R.; Jayaram, R.V. *Catal. Commun*. **2007**, *8*, 1414.

[14] Sheikhan, N.; Mirjalili, B. F.; Hajipour, A. R.; Bamoniri, A. *Acta Chim. Slov*. **2008**, *55*, 209.