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Heteropolyacid encapsulated into mesoporous silica framework for an efficient preparation of 1,1-diacetates from aldehydes under a solvent-free condition

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Abstract—Acylals were prepared from aliphatic and aromatic aldehydes using heteropolyacid (SiPW-8) encapsulated into the framework of mesoporous silica as catalysts in a solvent-free procedure. The catalyst was very effective and reusable for the production of 1,1-diacetates from aldehydes under a mild reaction condition.

The use of protecting groups is greatly significant in organic synthesis,[1] and acylal preparation is one of the most useful methods to protect carbonyl groups due to the stability of the 1,1-diacetates in neutral and basic media.[1c] 1,1-Diacetates are usually prepared from carbonyl compounds with acetic anhydride in the presence of Brønsted, Lewis acid catalysts (such as $KHSO_4$,[2] H_2SO_4, CH_3SO_3H, H_3PO_4,[3] NH_2SO_3H,[4] Nafion-7,[5] $ZnCl_2$,[6] PCl_3,[7] $FeCl_3/SiO_2$,[8] I_2,[9] WCl_6,[10] LiOTf,[11] $LiBF_4$,[12] $Sc(OTf)_3$,[13] $ZrCl_4$[14]) under neutral conditions (such as NBS).[15] Several other catalysts have also been employed for acylal preparation, for example, expansive graphite,[16] zeolites,[1b,2] tungstosilicic acid, HZSM-5, Fe^{3+} on montmorillonite, PVC–$FeCl_3$ complex and zirconium sulfophenyl phosphonate.[17] However, these cases were a high cost, rigorous reaction condition, and not environmentally benign because of the use of mineral acids, requirement of organic solvents. Recently, searching for a greener chemical process has become one of the most important tasks of today's chemical researchers.[18] There are lots of methods to achieve this goal such as green solvents, catalysts, and economic feedbacks.

Heteropolyacids are useful solid catalysts because of their super acidic properties.[19] As a part of a research project to develop environmentally friendly organic reactions, heteropolyacid catalysts have recently applied to different reactions. Heteropolyacid catalysts ($H_6P_2W_{18}O_{62}{\cdot}24H_2O$) have been also recently applied to protect aldehydes as acylals.[20] Although the substrates could be completely consumed, the separation of products with catalysts is very difficult. Herein, we report a simple, convenient and efficient process for the preparation of 1,1-diacetates from aliphatic and aromatic aldehydes using heteropolyacids encapsulated into mesoporous silica frameworks (SiPW-8)[21,22] as solid catalysts under a solvent-free condition.

The results of the solvent-free preparation of acylal from aliphatic and aromatic aldehydes in the presence of 0.1 g SiPW-8 at room temperature are shown in Table 1. 1,1-Diacetates were produced in a nearly 98% yield by the reaction of benzaldehyde with acetic anhydride in less than 10 min. Benzaldehyde with electron-donating groups, that is, 4-methyl-benzaldehyde, were converted into their corresponding acylal with high yields after a short reaction time. Compared to that with electron-donating groups, the one with electron-withdrawing groups, that is, 3-nitro-benzaldehyde needed a longer reaction time to form the corresponding acylal. Aliphatic aldehydes were similarly converted into the corresponding acylal with good to excellent yields. The acid sensitive substrate (furfural) also led to the formation of acylal with a 98% yield without any by-products. Some aliphatic and aromatic ketones (acetone, butanone,

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Table 1. Catalytic conversion of aldehydes to acylals using SiPW-8

Entry	Substrate	Products	Yield (%)
1	Benzaldehyde	A	95
2	4-Methyl-benzaldehyde	B	98
3	4-Methoxy-benzaldehyde	C	98
4	4-Chloro-benzaldehyde	D	96
5	2-Nitro-benzaldehyde	E	93
6	3-Nitro-benzaldehyde	F	93
7	4-Nitro-benzaldehyde	G	92
8	Butyl aldehyde	H	89
9	Heptyl aldehyde	I	94
10	Cinnamaldehyde	J	92
11	Furfural	K	98
12	Acetophenone	L	—
13	Bezophenone	M	—
14	Ethyl *n*-butyl ketone	N	—
15	Butanone	O	—
16	Acetone	P	—
17	Heptanone	Q	—

Reactions condition: reaction temperature 20 °C, reaction time 30 min, catalyst amount 0.1 g, yields are expressed from crystallized products (see text).

Table 2. Comparison of the effect of catalysts for *gem*-diacetate synthesis from 4-methylbenzaldehyde

Entry	Catalyst	Yield	Time	Ref.
1[a]	SiPW-8	96	6 min	
2[a]	$H_3PW_{12}O_{40}\cdot 12.5H_2O$	99	10 min	
3[a]	$H_6P_2W_{18}O_{62}\cdot 24H_2O$	97	10 min	
4[a]	$AlPW_{12}O_{40}$	96	5 min	
6	Sc(OTf)3	95	10 min	16
8	$LiBF_4$	92	24 h	15
9	NBS	93	9 h	18
10	$Zr(CH_3PO_3)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}$	75	12 min	20

[a] Reaction condition: catalyst 0.1 g, alcohol 5 mmol, acetic anhydride 15 mmol, room temperature.

acetophenone, and ethyl *n*-butyl ketone) studied for the reaction were not reactive under the described experimental conditions.

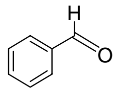
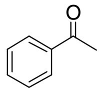
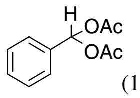
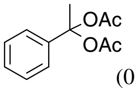
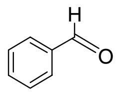
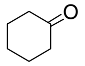
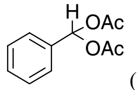
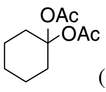
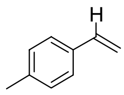
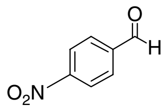
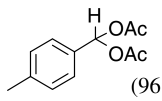
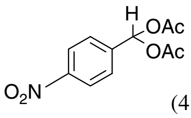
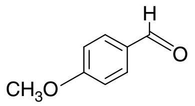
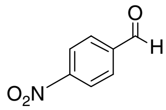
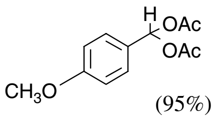
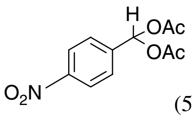
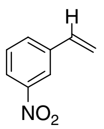
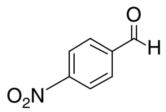
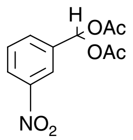
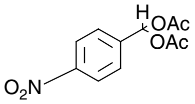
The results of the *gem*-diacetate synthesized from 4-methylbenzaldehyde in the presence of $H_3PW_{12}O_{40}\cdot 12.5H_2O$, $AlPW_{12}O_{40}$, $H_6P_2W_{18}O_{62}\cdot 24H_2O$, $Sc(OTf)_3$, $LiBF_4$, NBS and Zr $(CH_3PO_3)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}$ are listed in Table 2. It showed that SiPW-8 catalyzed the reactions more effectively than did NBS, metal triflates and zirconium sulfophenyl phosphonate at the same reaction conditions. Reaction with $LiBF_4$ as the catalyst required a higher temperature and longer reaction time. The preparation of acylals with zirconium sulfophenyl phosphonate and metal triflates as catalysts was performed in solvents such as CH_3CN and at room temperature with longer reaction times and lower yields. It is interesting that the catalytic activity of the silica-included $H_3PW_{12}O_{40}$ (SiPW-8) was higher than that of $H_3PW_{12}O_{40}\cdot 12.5H_2O$, $AlPW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}\cdot 24H_2O$ for the preparation of acylals, which suggested that $H_3PW_{12}O_{40}$ formed a highly concentrated aqueous solution in the matrix.

We studied the competitive reaction for the acylation of aldehydes in the presence of ketones using SiPW-8 as the catalyst at room temperature. In the presence of

Table 3. Competitive acylal formation of aldehydes using Ac_2O in the presence of SiPW-8 at room temperature

$$\text{RCHO} + \text{R'CHO} + \text{Ac}_2\text{O} \xrightarrow[\text{room temp. 5 min}]{\text{SiPW-8, 0.1 g}} \text{RCH(OAc)}_2 + \text{R'CH(OAc)}_2$$

R, R' = alkyl, aryl

Entry	Substrate		Product (selectivity %)	
1			 (100%)	 (0%)
2			 (100%)	 (0%)
3			 (96%)	 (4%)
4			 (95%)	 (5%)
5				

Reaction condition: Each substrate 2 mmol, acetic anhydride 2 mmol, catalyst amount 0.1 g, room temperature, time 5 min.

ketones, the highly selective conversion of aldehydes was observed. The acylation of 4-methylbenzaldehyde versus 4-nitro-benzaldehyde and 3-nitro-benzaldehyde also showed a high selectivity in the presence of this catalyst, which indicated the importance of electronic effects upon these reactions (Table 3).

One of the main aims of using SiPW-8 as the catalyst was to study the possibility of catalyst separation and recycle. We found that the catalyst SiPW-8 could be easily separated from the reaction system by a simple procedure. Recycling experiments results of benzyl aldehydes to acylals are listed in Table 4. It showed that the catalyst was easily separated from the reaction mixture and was reusable without a significant loss of activity and selectivity for the preparation of 1,1-diacetates.

General procedure for the protection of aldehydes: A mixture of aldehyde (10 mmol), acetic anhydride (20 mmol) and SiPW-8 catalyst (0.1 g) in a flask was stirred at room temperature for 30 min and filtered, and then diethyl ether (10 mL) was added to the filtrate. The resulting solution was successively washed with 1 M NaOH and water, solvent evaporated to get the crude product, which was then dried over anhydrous Na_2SO_4. Further purification was performed by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford the pure product in good to excellent yields. All products are known compounds, which were satisfactorily characterized by spectral data.[2,3,8,14,23]

Recycling of the catalyst: A mixture of aldehyde (10 mmol), acetic anhydride (20 mmol) and SiPW-8 catalyst (0.1 g) in a flask was stirred at room temperature for 30 min and filtered. The solid was successively washed with water and dried for recycling. The next run was performed by adding fresh benzyl aldehyde (10 mmol), and acetic anhydride (20 mmol) and the washed SiPW-8 catalyst into the flask under the same experimental conditions.

In conclusion, a very simple and convenient catalytic method was developed for the preparation of acylal from a variety of aldehydes under solvent-free conditions. The method has advantages of low environmental impact, high yields, high selectivity, short reaction time, and the catalyst can be recycled. It is believed that this protocol would be a useful synthetic methodology.

Spectra data of selected compounds:

A: White solid, melting point: 44 °C, ^{1}H NMR δ 2.14 (s, 6H, 2COCH$_3$), 7.38–7.55 (m, 5H, Ar–H), 7.71 (s, 1H, CH); IR (KBr, v/cm^{-1}): 3063, 3032, 2930, 1760, 1512, 1446, 1253, 1225, 1011.

Table 4. Catalytic conversion of benzyl aldehydes to acylals using SiPW-8 as catalyst

Run	1	2	3	4
Yield (%)	95	96	95	94

Reactions condition: Reaction temperature 20 °C, reaction time 30 min, catalyst amount 0.1 g, yields are expressed from crystallized products.

B: White solid, melting point: 81 °C, ^{1}H NMR δ 2.13 (s, 6H, 2COCH$_3$), 2.40 (s, 3H, CH$_3$), 7.28 (d, 2H, $J = 8.2$ Hz, Ar–H), 7.65 (d, 2H, $J = 7.9$ Hz, Ar–H), 7.80 (s, 1H, CH); IR (KBr, v/cm^{-1}): 2950, 1778, 1719, 1520, 1400, 1250, 1220, 1015, 956, 910.

D: White solid, melting point: 81 °C, ^{1}H NMR, δ 2.14 (s, 6H, 2COCH$_3$), 7.30–7.41 (m, 2H, Ar–H), 7.45–7.50 (m, 2H, Ar–H), 7.60 (s, 1H, CH); IR (KBr, v/cm^{-1}): 1772, 1590, 1348, 1235, 986.

F: White solid, melt point: 64 °C, ^{1}H NMR, δ 2.12 (s, 6H, 2COCH$_3$), 7.60–7.70 (m, 1H), 7.71 (s, 1H, Ar–H), 7.75–7.84 (m, 1H, Ar–H), 8.22–8.23 (m, 1H, Ar–H), 8.35 (m, 1H, CH); IR (KBr, v/cm^{-1}): 1774, 1540, 1439, 1351, 1012.

I: Colorless liquid; ^{1}H NMR δ 0.98 (t, 3H, $J = 6.8$ Hz, CH$_3$), 1.22–1.40 (m, 8H, 4CH$_2$), 1.60–1.80 (m, 2H, CH$_2$O), 2.07 (s, 6H, 2COCH$_3$), 6.77 (t, 1H, CH); IR (KBr, v/cm^{-1}): 3030, 2963, 1762, 1465, 1378, 1250, 1214, 1112, 1015, 968.

References and notes

1. (a) Greene, T. W.; Wuts, P. G. M. *Protection for the Carbonyl Group. Protective Groups in Organic Synthesis*; 2nd ed.; John Wiley: New York, 1991; p 184; (b) Pereira, C.; Gigante, B.; Marcelo-Curto, M. J.; Carreyre, H.; Pe'rot, G.; Guisnet, M. *Synthesis* **1995**, 1077; (c) Kochhar, K. S.; Bal, B. S.; Deshpande, R. P.; Rajadhyaksha, S. N.; Pinnick, H. W. *J. Org. Chem.* **1983**, *48*, 1765.
2. Heravi, M. M.; Bakhtiari, K.; Taheri, S.; Oskooie, H. A. *Green Chem.* **2005**, *7*, 867.
3. Freeman, I.; Karcherski, E. M. *J. Chem. Eng. Data* **1977**, *22*, 355.
4. Jin, T. S.; Sun, G.; Li, Y. W.; Li, T. S. *Green Chem.* **2002**, *4*, 255.
5. Olah, G. A.; Mehrotra, A. K. *Synthesis* **1982**, 962.
6. Scriabine, I. *Bull. Soc. Chim. Fr.* **1961**, 1194.
7. Kumar, P.; Hedge, V. R.; Kumar, T. P. *Tetrahedron Lett.* **1995**, *36*, 601.
8. Wang, C.; Li, M. *Synth. Commun.* **2002**, *32*, 3469.
9. Deck, N.; Kalita, D. J.; Borah, R.; Sarma, J. C. *J. Org. Chem.* **1977**, *62*, 1563.
10. Karimi, B.; Ebrehimian, G. R.; Seradj, H. *Synth. commun.* **2002**, *32*, 669.
11. Karimi, B.; Maleki, J. *J. Org. Chem.* **2003**, *68*, 4951.
12. Sumida, N.; Nishioka, K.; Sato, T. *Synth. Lett.* **2001**, 1921.
13. Aggarwal, V. K.; Fonquerna, S.; Vennall, G. P. *Synth. Lett.* **1998**, 849.
14. Smitha, G.; Reddy, Ch. S. *Tetrahedron* **2003**, *59*, 9571.
15. Karimi, B.; Seradj, H.; Ebrahimian, G. R. *Synth. Lett.* **2000**, *5*, 623.
16. Jin, T.-S.; Ma, Y.-R.; Zhang, Z.-H.; Li, T.-S. *Synth. Commun.* **1997**, *27*, 3379.
17. (a) Li, Y.-Q. *Synth. Commun.* **2000**, *30*, 3913; (b) Joshi, M. V.; Narasimhan, C. S. *J. Catal.* **1993**, *141*, 308; (c) Li, T.-S.; Zhang, Z.-H.; Gao, Y.-J. *Synth. Commun.* **1998**, *28*, 4665; (d) Curini, M.; Epifano, F.; Marcotullio, M. C.;

Rosati, O.; Nocchetti, M. *Tetrahedron Lett.* **2002**, *43*, 2709.

18. (a) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press, New York, 1998; (b) Anastas, P. T.; Williamson, T. C. *Green Chemistry-Frontiers in Benign Chemical Syntheses and Processes*; Oxford University Press, New York, 1998.
19. Kozhevnikov, I. *Chem. Rev.* **1998**, *98*, 171.
20. Romanelli, G. P.; Baronetti, G.; Thomas, H. J.; Autino, J. C. *Tetrahedron Lett.* **2003**, *44*, 1301.
21. The catalyst was synthesized according to the literature[22] as follows: (1) Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) (4.0 g) was dissolved in a solution of deionized water (100 mL) containing hydrochloric acid (20 mL, 36 wt %), followed by the addition of TEOS (10 mL). The mixture was stirred at 40 °C for 3 h. (2) A requisite amount of Na_2WO_4 and Na_2HPO_4 was added simultaneously to the above mixture to form a white precipitate. (3) The mixture was further stirred at 40 °C for 20 h and then transferred to a stainless steel autoclave for crystallization at 100 °C for 48 h. The obtained products were collected and dried in vacuo ($<10^{-2}$ Pa) at 150 °C for 6 h and washed with an ethanol solution containing HCl and distilled water three times, and finally dried in vacuo ($<10^{-2}$ Pa) at 300 °C for 5 h. The final products were designated as SiPW-8, where 8 stands for the Si/W molar ratio in the initial gel. The final products have been intensively characterized by various techniques, such as XRD, TEM, N_2 adsorption isotherm analysis, and by IR, UV/visible, and ^{31}P magic angle spinning (MAS) NMR spectroscopy. Characterization results suggest that the sample shows very ordered hexagonal meso-structures.
22. Shi, Ch. F.; Wang, R. W.; Zhu, G. Sh.; Qiu, Sh. L.; Long, J. *Eur. J. Inorg. Chem.* **2005**, 4801.
23. (a) Negron, G. E.; Palacios, L. N.; Angeles, D.; Lomas, L.; Gavino, R. *J. Braz. Chem. Soc.* **2005**, *16*, 490; (b) Carrigan, M. C.; Eash, K. J.; Oswald, M. C.; Mohan, R. S. *Tetrahedron Lett.* **2001**, *42*, 8133; (c) Bhatia, B.; Punniyamurthy, T.; Iqbal, J. *J. Org. Chem.* **1993**, *58*, 5518; (d) Jin, T. S.; Du, G. Y.; Li, T. S. *India J. Chem., Sect. B* **1998**, 939; (e) Jin, T. S.; Ma, Y. R.; Sun, X.; Liang, D.; Li, T. S. *J. Chem. Res. (S)* **2000**, 96; (f) Zhang, Z. H.; Li, T. S.; Fu, C. G. *J. Chem. Res. (S)* **1997**, 174; (g) Kumar, P.; Hegda, V. R.; Kumar, T. P. *Tetrahedron Lett.* **1995**, *36*, 601; (h) *Dictionary of Organic Compounds*, 5th ed., Chapman and Hall, New York, 1982, Vol. 4, p 4224.