

$\text{SO}_4^{2-}/\text{SnO}_2$ as an efficient, chemoselective and reusable catalyst for the synthesis and deprotection of 1,1-diacetates

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Abstract

An efficient method for the synthesis of 1,1-diacetates (acylals) from different aldehydes in the presence of $\text{SO}_4^{2-}/\text{SnO}_2$ and acetic anhydride under solvent-free conditions at ambient temperature is achieved. Selective conversion of aldehydes was observed in the presence of ketones. The deprotection of acylals has also been achieved using $\text{SO}_4^{2-}/\text{SnO}_2$ in methanol. $\text{SO}_4^{2-}/\text{SnO}_2$ catalyst was characterized by XRD, SEM, IR and BET surface area techniques. The catalyst was found to possess good activity and considerable level of reusability.

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1. Introduction

Selective protection and deprotection of carbonyl groups are essential steps in synthetic organic chemistry [1]. 1,1-Diacetates are one of the most useful carbonyl protecting groups due to their stability under both neutral and basic media as well as under mild conditions [2]. The diacetates of α,β -unsaturated aldehydes are important starting materials for Diels–Alder reactions and they are also useful intermediates [3,4]. Moreover, acylal functionality can be converted into other functional groups by reaction with appropriate nucleophiles [5,6]. Some of the reported reagents for the preparation of 1,1-diacetates from aldehydes and acetic anhydride include sulphuric acid [7], triflic acid [8], PCl_3 [9], iodine [10], FeCl_3 [11], *N*-bromosuccinimide [12], $\text{Sc}(\text{OTf})$ [13], $\text{Cu}(\text{OTf})_3$ [14], $\text{Bi}(\text{OTf})_3$ [15], CAN [16], $\text{AlPW}_{12}\text{O}_{40}$ [17], β -Zeolite [18], LiBF_4 [19], ZrCl_4 [20], $\text{In}(\text{OTf})_3$ [21], $\text{H}_2\text{NSO}_3\text{H}$ [22], Zn-Montmorillonite [23], bismuth nitrate [24], $(\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O})$ [25] and silica sulphuric acid [26]. Very few reports are applicable to both the

synthesis as well as deprotection of acylals [13,20,26,27]. Although some of these methods have convenient protocols with good to high yields, majority of these methods suffer at least from one of the following disadvantages: reactions under oxidizing conditions, use of halogenated solvents, high temperature, long reaction times and moisture sensitivity of the catalyst, high cost and high toxicity.

We recently have reported several transition metal based mesoporous silicates, mixed metal oxides and sulfated metal oxides, as catalysts for a variety of industrially important organic transformations [28]. In continuation of our studies on sulfated metal oxides we have found that $\text{SO}_4^{2-}/\text{SnO}_2$ is an excellent catalyst. Catalytic activity of $\text{SO}_4^{2-}/\text{SnO}_2$ is already explored for various organic reactions such as benzylation, benzoylation and esterification [29]. Moreover this catalyst is safe, easy to handle, reusable and environmentally benign.

2. Experimental

2.1. Catalyst preparation

The catalyst is being prepared as per reported procedure [30]. Tin (IV) hydroxide samples were prepared by adding

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28 wt.% aqueous ammonia solution to an aqueous solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.3 M), until pH 8.4 was achieved with constant stirring. The precipitate was aged at 373 K over a waterbath for 1 h, washed with deionised water, until the chloride free filtrate was obtained, and finally was dried at 393 K for 24 h.

For sulfation, $x\text{g}$ of dry gel was introduced, at room temperature, into $15x\text{ cm}^3$ of a 0.1 M H_2SO_4 solution for 20 min under vigorous stirring and then filtered without washing, dried at 393 K and calcinated at 773 K for 4 h. The solid obtained after sulfation and calcinations is designated as $\text{SO}_4^{2-}/\text{SnO}_2$.

2.2. Catalyst characterization

The catalyst is characterised by XRD, SEM, IR and BET surface area techniques. XRD studies were performed with a conventional powder diffractometer (Philips 1050) using graphite monochromatised Cu $K\alpha$ radiation. Surface area measurements were performed after degassing the sample under high vacuum at 300 °C for 4 h, by nitrogen adsorption on micromeritics ASAP 2010 instrument at an adsorption temperature of 77 K. IR spectra were recorded on Buck scientific (Model 500). Sulfate promoted SnO_2 exhibits strong IR bands at 982, 1040, 1150, 1210 cm^{-1} which shows bidentate sulphate ion coordinated to the metal Fig. 1. These bands were not observed in unsulfated SnO_2 . The morphology of the catalyst was evaluated by scanning electron micrograph (SEM).

2.3. X-ray diffraction technique

XRD studies were performed with a conventional powder diffractometer (Philips 1050) using graphite monochromatised Cu $K\alpha$ radiation. Spectras were recorded in Fig. 2 for unsulfated and sulfated samples of SnO_2 calcined at 773 K. The degree of crystallization of $\text{SO}_4^{2-}/\text{SnO}_2$ (773 K) was much lower than that of SnO_2 (773 K) [29,30].

2.4. Scanning electron micrograph

In order to study the morphology changes after sulfation of SnO_2 SEM analysis was done. There is certain change in the morphology observed; this might be due to cracking down of the particles to smaller size after sulfation [31]. SEM were recorded at 1 μm Figs. 3a and 3b.

2.5. BET Surface area measurements

The N_2 adsorption–desorption isotherms were measured at 78 K on a Quantachrome Autosorb-I porosimeter. Specific surface area S_{BET} were determined with Brunauer–Emmett–Teller (BET) method using adsorption data points in the relative pressure P/P_0 . Surface areas of SnO_2 and $\text{SO}_4^{2-}/\text{SnO}_2$ were found to be 15 and 70 m^2/g , respectively.

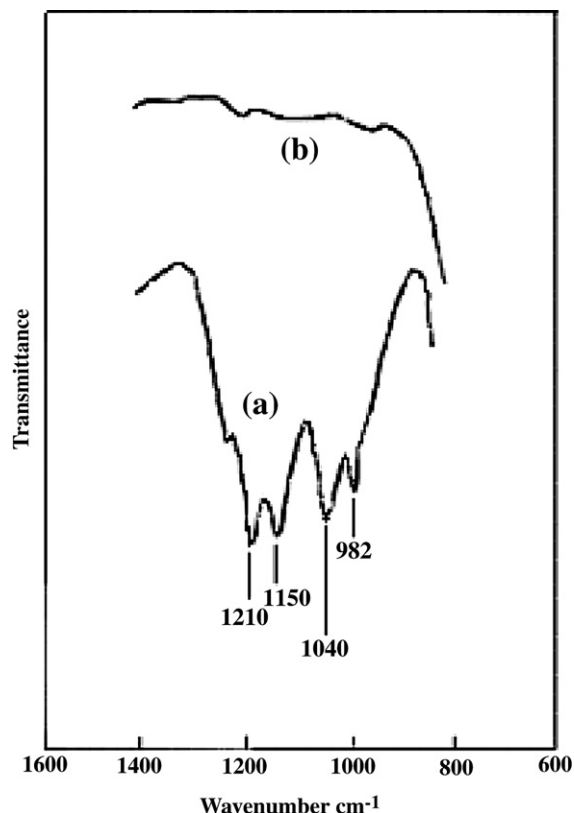


Fig. 1. IR spectra of (a) $\text{SO}_4^{2-}/\text{SnO}_2$ and (b) SnO_2 .

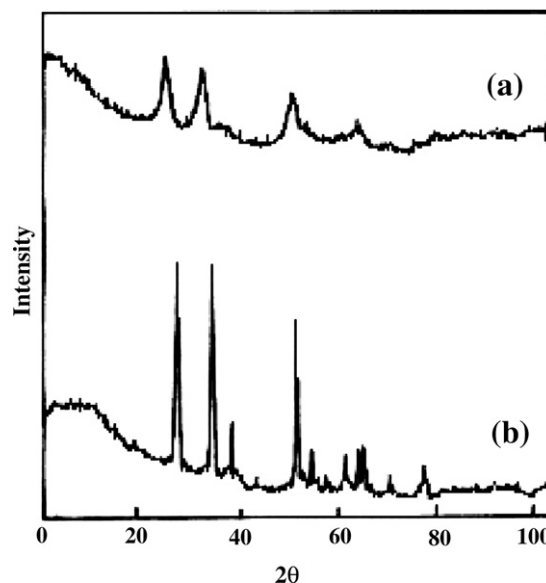
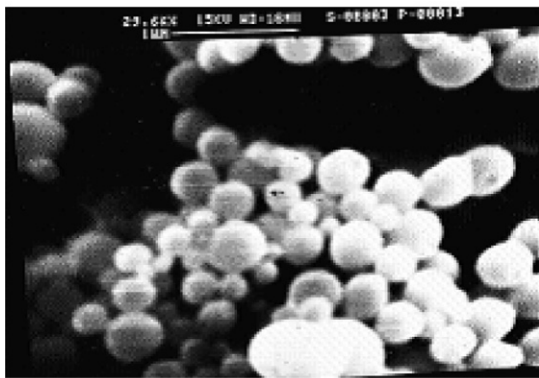
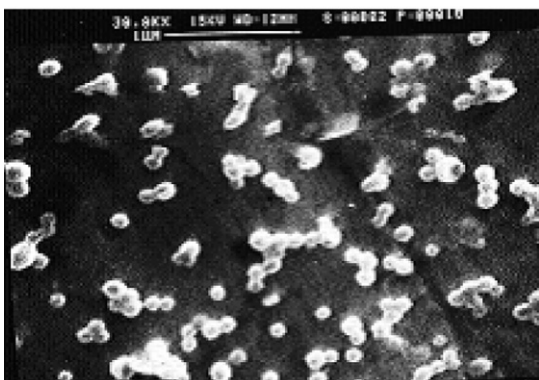


Fig. 2. XRD profiles of (a) $\text{SO}_4^{2-}/\text{SnO}_2$ (b) SnO_2 calcined at 773 K.

2.6. General procedure for the synthesis of 1,1-diacetates

To a solution of respective aldehyde (2 mmol) in freshly distilled Ac_2O (4 mmol) was added $\text{SO}_4^{2-}/\text{SnO}_2$ (1 mol%, 0.015 g) and the mixture was stirred magnetically for specified time at room temperature (Table 2).

Fig. 3a. SEM of SnO₂ at 1 μm.Fig. 3b. SEM of SO₄²⁻/SnO₂ 1 μm.

Course of the reaction was monitored by TLC (*n*-hexane-EtOAc, 9:1) and GC. The reaction mixture was diluted with Et₂O (20 mL) and filtered to separate the catalyst. The filtrate was washed successively with 10% aq. NaHCO₃ to remove excess of Ac₂O and then with aq. sat. NaHSO₃ to remove unreacted aldehyde, dried over Na₂SO₄. The solvent was evaporated under reduced pressure to give the corresponding pure 1,1-diacetates which was in full agreement with the mp and spectral data (IR, ¹H NMR) of the authentic samples. The catalyst was found to be reusable for five cycles without significantly affecting the yield.

2.7. General procedure for the deprotection of 1,1-diacetates

A mixture of 1,1-diacetates (2 mmol), SO₄²⁻/SnO₂ (1 mol%, 0.015 g) in methanol (2 mL) was stirred vigorously for specified time (Table 2). The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted by Et₂O (20 mL) and filtered to separate the catalyst. The filtrate was washed successively with 10% aq. NaHCO₃ to remove excess of Ac₂O and dried over Na₂SO₄. The solvent was evaporated under reduced pressure. The resultant product was passed through short column of silica gel (*n*-hexane-EtOAc, 9:1) to afford pure aldehyde.

3. Results and discussion

For optimization of the reaction conditions, we have tried the conversion of 4-methylbenzaldehyde (2 mmol) to the corresponding acylal with acetic anhydride (4 mmol) in the presence of various solvents and also under solvent-free conditions. In comparison to conventional methods the yield of the product under solvent-free conditions is higher and reaction time is less (Table 1). Therefore, we have employed the solvent-free conditions for the conversion of various aldehydes to the corresponding acylals (Table 2). For optimization of the quantity of acetic anhydride required for the reaction, we have altered the stoichiometry of the reaction. When 1:1 ratio of 4-methylbenzaldehyde to acetic anhydride was tried, no complete conversion was found. But on further increase in the acetic anhydride from one equivalent to two equivalents, reaction attains completion and no further increase in the yield was observed even after changing the equivalents of acetic anhydride to three or four equivalents. Hence we have maintained 1:2 stoichiometry throughout the reaction. Amount of catalyst was also optimized to 1 mol% (0.015 g).

Herein we report an efficient solvent-free method for the preparation of acylals from different aldehydes in the presence of SO₄²⁻/SnO₂ and acetic anhydride (Scheme 1). Various aldehydes were converted to their corresponding diacetates in good yields and in short reaction times (Table 2). Aliphatic and α,β-unsaturated aldehydes produced acylals in good yields (Table 2, entries, 13 and 14). Mixture of products was observed under the given conditions in case of 2-hydroxybenzaldehyde and vanillin. We have found that both carbonyl and phenolic –OH groups were acylated (Table 2, entries, 12, 16). But when excess acetic anhydride was used, formation of triacetate was observed due to the acylation of phenolic –OH group.

To explore the selectivity of this method, we have investigated competitive reactions for acylal formation in the mixtures of aldehydes (Table 3, entries 1, 2, 3) and in the mixture of aldehyde and ketone (Table 3, entries 4, 5). These reactions proceeded with high selectivity in the

Table 1

Conversion of 4-methylbenzaldehyde to its corresponding diacetate in different solvents and under solvent-free conditions in the presence of SO₄²⁻/SnO₂ at 30 °C^a

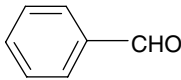
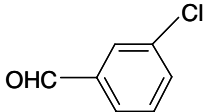
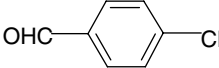
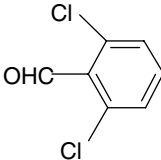
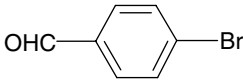
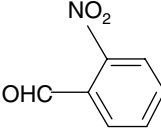
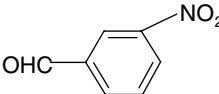
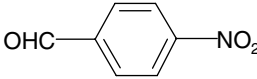
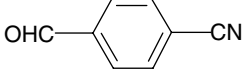


Entry	Solvent	Yield (%) ^b	Time (min)
1	Cyclohexane	70	60
2	Et ₂ O	62	60
3	EtOAc	52	30
4	CH ₂ Cl ₂	84	30
5	Acetone	78	30
6	Solvent-free ^c	97	15

^a Reaction conditions: 4-methylbenzaldehyde (2 mmol), Ac₂O (4 mmol) and catalyst (1 mol%, 0.015 g) at room temperature for specified time.

^b The yields refer to isolated pure product.

^c The reaction was conducted by stirring with 4 mmol of Ac₂O.

Table 2
 $\text{SO}_4^{2-}/\text{SnO}_2$ catalyzed protection of aldehydes under solvent-free conditions and their deprotection in methanol

Entry	Substrate	Protection		Deprotection	
		Time (min)	Yield (%) ^{a,b,c}	Time (min)	Yield (%) ^{a,b,c}
1		25	90	40	90
2		30	84	45	86
3		30	84	45	85
4		35	80	60	83
5		30	82	45	86
6		30	81	45	87
7		30	83	45	88
8		30	84	45	89
9		30	86	50	84
10		15	95	30	93
11		15	97	30	96

(continued on next page)

Table 2 (continued)

Entry	Substrate	Protection		Deprotection	
		Time (min)	Yield (%) ^{a,b,c}	Time (min)	Yield (%) ^{a,b,c}
12		20	94	50	92
13		15	86	30	88
14		25	90	45	87
15		25	79	45	85
16	Vanillin	25	84	40	88
17		20	90	40	90
18		6 ^d	NR	–	–
19		6 ^d	NR	–	–

^a Reaction conditions: substrate (2 mmol), Ac₂O (4 mmol) and catalyst (1 mol%, 0.015 g) at room temperature for specified time NR-no reaction.

^b The yields refer to isolated pure product.

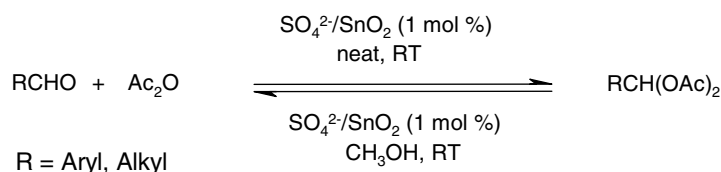
^c The products are characterised from their spectra (IR, ¹H NMR) and comparison with authentic samples.

^d Time in hours.

presence of this catalyst showing the electronic effects upon these reactions. Ketones are not affected under similar conditions.

A comparative study was done for the use of SO₄²⁻/SnO₂ with some of the reported catalysts for the synthesis of acylal from 4-nitrobenzaldehyde as a model substrate (Table 4). From this study it can be concluded that

SO₄²⁻/SnO₂ has comparable activity with other catalysts, but it has added advantage that it is reusable for five cycles and could be used for synthesis and deprotection of acylals. Moreover, amount of catalyst used in the reaction is low 1 mol% (0.015 g). In some of the reported procedure even protection of aldehydes involves use of MeNO₂ [13], CH₂Cl₂ [14] solvents.



Scheme 1.

Table 3
Competitive acylal formation reactions using $\text{SO}_4^{2-}/\text{SnO}_2$ under solvent-free conditions

Entry	Substrate	Yield (%) ^{a,b}
1		
2		
3		
4		
5		

The products are characterised from their spectra (IR, ^1H NMR) and comparison with authentic samples.

^a Reaction conditions: Ac_2O (4 mmol) and catalyst (1 mol%, 0.015 g) at room temperature for 1 h.

^b The yields refer to isolated pure product. The isolation was done by column chromatography using (*n*-hexane-EtOAc, 9:1).

Table 4
Comparison of the efficiency of $\text{SO}_4^{2-}/\text{SnO}_2$ with other catalysts in the synthesis of acylals from 4-nitrobenzaldehyde^b

Catalyst	Catalyst loading (mol%)	Time (min)	Yield (%)	Ref.
None	–	4 ^a	2	–
SnO_2	1	4 ^a	40	–
$\text{SO}_4^{2-}/\text{SnO}_2$	1	30	84	–
$\text{Sc}(\text{OTf})_3$	2.0	10	99 ^c	13
$\text{Cu}(\text{OTf})_3$	2.5	4 ^a	94 ^d	14
$\text{AlPW}_{12}\text{O}_{40}$	0.1	45	89	17
ZrCl_4	5	30	92	20
SSA	0.52	25	86	26

^a Time in hours.

^b Reaction conditions: 4-nitrobenzaldehyde (2 mmol), Ac_2O (4 mmol) and catalyst (1 mol%, 0.015 g) at room temperature for specified time.

^c The reaction is performed in MeNO_2 solvent.

^d The reaction is performed in CH_2Cl_2 solvent.

4. Reusability study

It is well known that $\text{SO}_4^{2-}/\text{SnO}_2$ is reusable catalyst [32,33]. Reusability of the catalyst is tested by carrying out repeated runs of the reaction on the same batch of the catalyst. After each cycle the catalyst was filtered off,

Table 5
Reusability study of the catalyst for the synthesis of benzylidene diacetate^a

Cycle	1	2	3	4	5
Yield (%) ^b	90	90	88	85	82

^a Reaction conditions: benzaldehyde (2 mmol), Ac_2O (4 mmol) and catalyst (1 mol%, 0.015 g) at room temperature for specified time.

^b Yields were analyzed by GC.

washed with acetone, dried and activated at 120 °C and then reused for successive cycles. It was observed that the activity of $\text{SO}_4^{2-}/\text{SnO}_2$ did not decrease appreciably even after five cycles (Table 5). Reusability of $\text{SO}_4^{2-}/\text{SnO}_2$ is comparable with other catalytic systems [26] and some of the catalysts are not reusable [13,14].

5. Conclusion

In conclusion, herein we report a mild and efficient catalyst for the preparation of 1,1-diacetates from aldehydes in the presence of acetic anhydride under solvent-free conditions at room temperature. This method is selective for the preparation of 1,1-diacetates from aldehydes in presence of ketones. 1,1-Diacetates can be conveniently deprotected by using $\text{SO}_4^{2-}/\text{SnO}_2$ in methanol. Good yields were obtained within short reaction times, reusability of the catalyst, non-toxic nature and mild conditions are some of the notable features of this protocol.

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