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Tin(IV) hydrogen phosphate nanodisks: A mild and efficient catalyst for the protection of carbonyl compounds as 1,3-oxathiolanes

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ABSTRACT

A mild and efficient heterogeneous catalyst, Tin(IV) hydrogen phosphate $[Sn(HPO_4)_2 \cdot H_2O]$ nanodisks is investigated for the protection of carbonyl compounds as 1,3-oxathiolanes. The yields of 1,3-oxathiolanes are very good to excellent.

1. Introduction

Nano-materials research has witnessed tremendous growth in recent years due to their intriguing chemical and physical properties different from those of their corresponding bulk materials [1]. Therefore, research and development works on various fields like drug delivery, gene therapy, electronics, green chemistry, material science [2–4] etc. are getting tremendous attentions both in academia and industries. Nano-materials with their large surface area and high density active sites, for example Ni, Cu, Ag nanoparticle [5–7], polysilane-supported Pd and Pt nanoparticles [8], RuO_2-FAU nanoclusters [9] are used as heterogeneous catalysts in organic synthesis and the research on this line still continues [10].

The development of mild and efficient method for the protection and deprotection of functional groups is a very important strategy in organic synthesis [11]. On the other hand, the protection of carbonyl group plays an important role in multi-steps synthesis of complex natural products and heterocyclic compounds [12]. 1,3-Oxathiolanes are important carbonyl protecting group and acyl anion equivalent for the formation of carbon–carbon bond in organic synthesis [13,14]. Also, they are considerably stable in acidic media in comparison to S/S and O/O acetals protecting groups, and can be easily synthesized and deprotected to generate parent carbonyl compounds in a reaction. Besides, they are valuable starting materials for the enantioselective synthesis of tertiary α-hydroxy acids and glycols [15]. A plethora of reagents for the synthesis of 1,3-oxathiolanes are reported, such as, Lewis acids-$BF_3 \cdot OEt_2$ [16], $ZrCl_4$ [17], Brønsted acids – $HClO_4$ [18], *p*-TsOH [19]; solid acid catalysts – $TaCl_5/SiO_2$ [20], montnorillonite K10 [21], PPA/SiO_2 [22], $H_3PW_{12}O_{40}/SiO_2$ [23], Amberlyst 15 [24]; metal triflates – $In(OTf)_3$ [25], $Y(OTf)_3$ [26], $MoO_2(acac)_2$ [27], $[bmim]BF_4$ [28] etc. However, despite the potential utility of these catalysts, many of these methodologies for the protection of carbonyl groups suffer from several drawbacks such as harsh reaction conditions, long reaction time, use of expensive and moisture sensitive catalysts, refluxing temperature and tedious work-up procedure. On the other hand, the use of high catalytic activity, high stability, eco-friendly, cost effective and reusable catalyst have found great demand from industrial and academic point of view, and particularly in relation to today's environmental concern. In continuation of our effort to develop acid catalyzed synthetic methodologies [29–33], we disclose herein for the first time, the use of Tin (IV) hydrogen phosphate $[Sn(HPO_4)_2 \cdot H_2O]$ nanodisks [34] as a novel and efficient Lewis acid catalyst for the protection of carbonyl compounds by employing mercaptoethanol as the protecting group (Scheme 1).

2. Experimental

^1H NMR spectra were recorded on Advance DPX 300 MHz FT-NMR spectrometer. Chemical shifts are expressed in δ units relative to tetramethylsilane (TMS) signal as internal reference. IR spectra were recorded on FT-IR-system-2000 Perkin Elmer spectrometer. SEM was recorded by Scanning Electron Microscope Model: LEO 1430 VP, Make: M/S Carl Zeiss, UK. Physical and spectroscopic data

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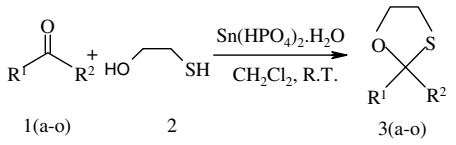


1(a-o) 2 3(a-o)

R^1 = aryl, alkyl, heterocyclic

R^2 = alkyl, aryl, H

Scheme 1. Protection of carbonyl groups by mercaptoethanol.

of all the known compounds are in well agreement with those of authentic samples [16–28].

2.1. Preparation of the catalyst

$Sn(HPO_4)_2 \cdot H_2O$ nanodisks were prepared by following the published procedure [34]. H_3PO_4 (85%) (0.3 ml) was added to a solution of 0.35 g of $SnCl_4 \cdot 5H_2O$ (AR) in anhydrous ethanol (12 ml). The resulting reaction mixture was transferred to a 22 ml teflon-sealed autoclave and stored at 180 °C for 24 h, then air-cooled to room temperature. The product was washed several times with anhydrous ethanol and finally dried at 60 °C in a vacuum oven. The structure of the catalyst was characterized by SEM (Fig. 1) and FT-IR (Fig. 2).

2.2. Typical experimental procedure for the synthesis of 1,3-oxathiolane

Benzaldehyde (106 mg; 1.0 mmol) mercaptoethanol (94 mg; 1.2 mmol) and $Sn(HPO_4)_2 \cdot H_2O$ nanodisks (5 mol%) were stirred in CH_2Cl_2 (5 ml) at room temperature for 30 min. The progress of the reaction was monitored by TLC. The catalyst was filtered off; the filtrate was diluted with ethyl acetate (20 ml), washed with water (2 × 10 ml), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was separated and purified by column chromatography on silica gel (60–120 mesh) using an ethyl acetate/petroleum ether mixture as the eluent to afford a pure 2-phenyl-1,3-oxathiolane (96%).

2.2.1. Spectroscopic data for selected compounds

2.2.1.1. 2-phenyl-1,3-oxathiolane (3a). Liquid; FT-IR ($CHCl_3$, cm^{-1}): 1065, 680; ^1H NMR (300 MHz, $CDCl_3$): δ 3.0–3.24 (m, 2H, S-CH_2), 3.78–3.91 (m, 1H, OCH_2), 4.52–4.58 (m, 1H), 6.04 (s, 1H, –O–CH–S), 7.30–7.42 (m, 3H), 7.45–7.50 (m, 2H).

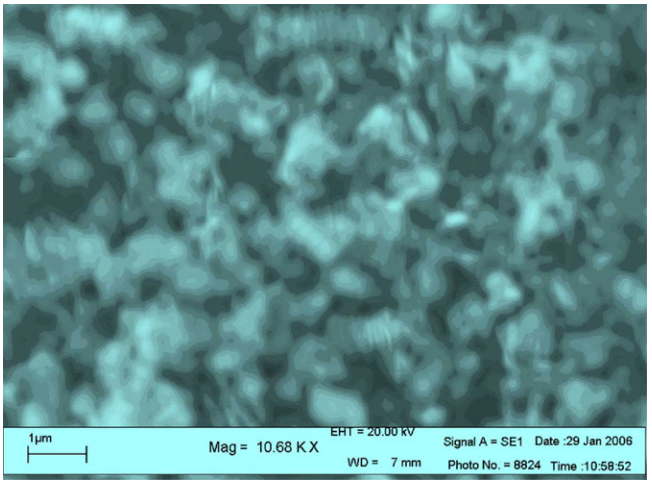


Fig. 1. SEM image of Tin(IV)hydrogen phosphate [$Sn(HPO_4)_2 \cdot H_2O$] nanodisks.

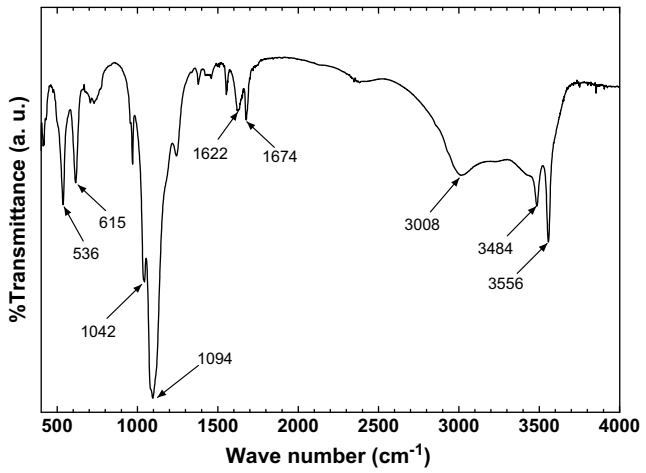
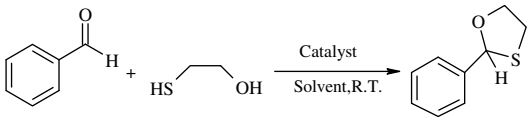


Fig. 2. FT-IR Spectra of Tin(IV)hydrogen phosphate [$Sn(HPO_4)_2 \cdot H_2O$] nanodisks.

2.2.1.2. 2-[4′-methoxyphenyl]-1,3-oxathiolane (3b). Colorless liquid; FT-IR ($CHCl_3$, cm^{-1}): 1610, 1514, 1258, 1180, 1020, 825; ^1H NMR (300 MHz, $CDCl_3$): δ 3.16–3.29 (m, 2H, S–CH_2), 3.84 (s, 3H, CH_3), 3.86–4.49 (m, 2H, OCH_2), 6.01 (s, 1H, –O–CH–S), 6.89 (d, 2H, J = 8.5 Hz, ArH), 7.42 (d, 2H, J = 8.5 Hz).

Table 1
Protection of benzaldehyde with mercaptoethanol catalyzed by $Sn(HPO_4)_2 \cdot H_2O$ nanodisks under different catalyst loadings, solvent systems and their TOF



Entry	Solvents	Amount of catalyst (mol%)	Time (h)	Conversion[b]	Yield[a](%)	Selectivity[c](%)	TOF[d]
1	Neat	–	48	–	–	–	–
2	Neat	5	24	12	10	99.5	2
3	CH_3CN	5	4	52	50	99.5	82
4	THF	5	4.5	46	45	100	65
5	CH_2Cl_2	3	1	82	80	99.5	877
6	CH_2Cl_2	5	0.5	97	96	100	1200
7	CH_2Cl_2	10	1	97	96	100	315

[a] Isolated yield.
[b] Determined by ^{1}GC.
[c] Determined by GC.
[d] TOF = Amount of the product(mol)/[Amount of the catalyst (Sn mol) × time(h)].

Table 2
Synthesis of 1,3-oxathiolanes by $Sn(HPO_4)_2 \cdot H_2O$ nanodisks from carbonyl compounds

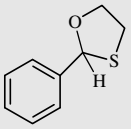
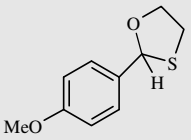
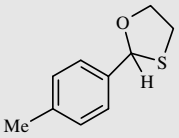
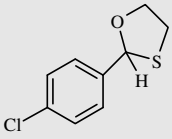
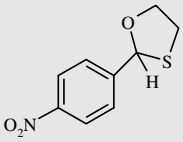
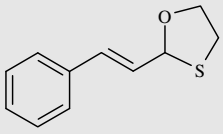
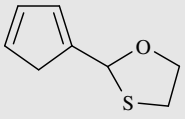
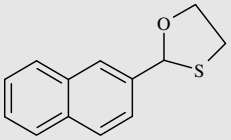
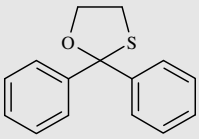
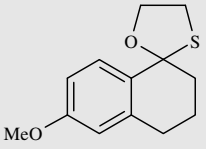
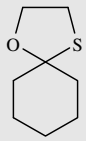
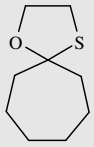
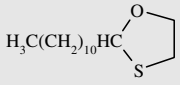
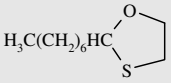
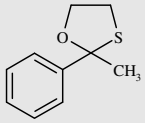
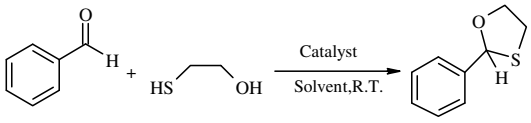
Entry	Substrates 1(a–o)	Products 3 (a–o)	Time (min)	Conversion[b] (%)	Selectivity[c] (%)	Yield[a] (%)
a	Benzaldehyde		30	97	100	96
b	*p*-Methoxy-benzaldehyde		35	97	100	96
c	*p*-Methyl-benzaldehyde		45	96	100	95
d	*p*-Chloro-benzaldehyde		45	92	99.5	90
e	*p*-Nitro-benzaldehyde		50	90	99.5	88
f	Cinnamaldehyde		55	91	99	88
g	Furfuraldehyde		55	88	99	85
h	2-Napthaldehyde		55	87	99	84
i	Benzophenone		60	72	99.5	70
j	6-Methoxy-tetralone		55	81	99	78

Table 2 (*continued*)

Entry	Substrates 1(a- o)	Products 3 (a –o)	Time (min)	Conversion[b] (%)	Selectivity[c] (%)	Yield[a] (%)
k	Cyclohexanone		50	85	99	82
l	Cycloheptanone		55	84	99	81
m	Dodecanal-		50	82	99.5	80
n	Octanal		50	82	100	81
o	Acetophenone		110	12	99.5	10
p	Benzaldehyde + acetophenone	3a + 3o	120	92:8	92:8	90: 7
q	*p*-Nitrobenzaldehyde + cychexanone	3e + 3k	120	77:23	77:23	76:20

[a] Isolated yield by column chromatography.
[b] Determined by GC.
[c] Determined by GC.

Table 3
Recycling of $Sn(HPO_4)_2 \cdot H_2O$ nanodisks catalyst



Entry	No. of run	Time (min)	Conversion[b] (%)	Yield[a] (%)
1	First run	30	97	96
2	Second run	30	97	95
3	Third run	30	96	95
4	Fourth run	30	96	94
5	Fifth run	30	96	93
6	Sixth run	30	95	94

[a] Isolated yield.
[b] Determined by GC.

2.2.1.3. 2-[4′-nitroyphenyl]-1,3-oxathiolane (3e). Solid; FT-IR ($CHCl_3$, cm^{-1}): 1600, 1522, 1344, 1072, 858, 719; ^1H NMR (300 MHz, $CDCl_3$): 3.20–3.33 (m, 2H, S–CH_2), 4.00–4.55 (m, 2H, O–CH_2), 6.15 (s, H, –O–CH–S), 7.58 (d, 2H, J = 8.6 Hz), 8.24 (d, 2H, J = 8.6 Hz).

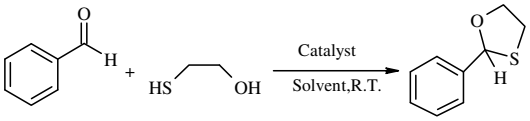
3. Results and discussion

In order to study the catalytic effectiveness of $Sn(HPO_4)_2 \cdot H_2O$ nanodisks, we carried out the protection of carbonyl groups by employing mercaptoethanol as the protecting group at room temperature. Initially, the catalytic activity and the influence of solvents for oxathioacetalization of benzaldehyde were carried out under various reaction conditions (Table 1). The optimum load of the catalyst was found to be 5 mol% in CH_2Cl_2 at room temperature (Table 1, entry 6). In a typical procedure, benzaldehyde (1 mmol), mercaptoethanol (1.2 mmol) were stirred in presence of $Sn(HPO_4)_2 \cdot H_2O$ nanodisks (5 mol%) in dichloromethane (5 ml) at room temperature for 30 min. After work-up, 2-phenyl-1,3-oxathiolane was isolated in 96% yield. The catalyst was filtered off, washed with CH_2Cl_2 (2 × 5 ml), dried and reused for fresh reactions.

To examine the scope of the reaction, a wide variety of carbonyl compounds [aryl/heteroaryl/aliphatic] were protected as 1,3-oxathiolanes using mercaptoethanol as the protecting group. The results are summarized in Table 2. Both aromatic (Table 2, entries a-e) and aliphatic aldehydes (Table 2, entries m–n) produced corresponding1,3-oxathiolanes in very good to excellent yields. It may be mentioned that acid and heat sensitive furfural afforded the desired product in excellent yield (Table 2, entry g). It was observed that the electron donating groups in the aromatic ring produced high yield of products with faster reaction rate in comparison to the electron withdrawing groups. Aliphatic ketones also reacted efficiently to produce oxathiolanes in good yields (Table 2, entries k–l).

Interestingly, the aromatic ketones produced the corresponding 1,3-oxathiolanes in trace amounts under the same reaction conditions (Table 2, entry o). This indicates that the present reaction condition is applicable for the chemoselective protection

Table 4
Comparison of catalyst efficiency of $Sn(HPO_4)_2 \cdot H_2O$ nanodisks with other reported catalysts



Entry	Catalyst	Catalyst load	Time (min/h)	Yield (%)[a]	Ref.
1	Montmorillonite K10	200 mg	30 min	86	[23]
2	$MoO_2(acac)_2$	22 mg	4 h	86	[27]
3	$Y(OTf)_3$	5 mol%	1.75 h	79	[26]
4	$In(OTf)_3$	5 mol%	1 h	82	[25]
5	$HClO_4$	10 mol%	20 min	68	[18]
6	$[bmim]BF_4$	2 ml	2.5 h	92	[28]
7	Amberlyst 15	220 mg	1 h	84	[24]
8	PPA/SiO_2	0.5 g	30 min	99	[22]
9	$H_3PW_{12}O_{40}/SiO_2$	1 mol%	15 min	95	[23]
10	Tin(IV)hydrogen phosphate nanodisks	5 mol%	30 min	96	Present method

[a] Isolated yield.

of aldehydes in presence of ketones. To examine this, an equimolar mixture of benzaldehyde and acetophenone were subjected to the same reaction conditions. The resulting 2-phenyl-1,3-oxathiolane (Table 2, entry p) was obtained in excellent yield (90%) whereas, acetophenone oxathiolanes was obtained in very low yield (10%).

The catalyst could be easily recovered quantitatively from the reaction mixture by simple filtration. After washed with CH_2Cl_2 (2×5 ml) it was dried and reused for fresh reactions. The catalyst was tested for six consecutive times for the fresh reactions without any loss of its activity (Table 3).

In order to study the superiority of the $Sn(HPO_4)_2 \cdot H_2O$ nanodisks as a catalyst for the protection of carbonyl compounds, it was compared to some of the best known catalysts (Table 4) which showed that the present protocol is well compatible to the others in terms of yield, reaction time and catalyst loading.

4. Conclusion

The salient features of the reaction are: $Sn(HPO_4)_2 \cdot H_2O$ nanodisks was found to be a mild and efficient catalyst for the protection of carbonyl groups using mercaptoethanol as the protecting group at room temperature. Both aromatic and aliphatic carbonyl compounds can be efficiently protected by this protocol. The yields of 1,3-oxathiolanes are very good to excellent. Further studies on the application of this nano catalyst in organic synthesis are in progress.

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