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SO_4^{2-}/SnO_2: Efficient, Chemoselective, and Reusable Catalyst for Acylation of Alcohols, Phenols, and Amines at Room Temperature

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SO_4^{2-}/SnO_2: Efficient, Chemoselective, and Reusable Catalyst for Acylation of Alcohols, Phenols, and Amines at Room Temperature

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Abstract: SO_4^{2-}/SnO_2 was employed for the acylation of a variety of alcohols, phenols, and amines under solvent-free conditions at room temperature. This method showed preferential selectivity for acetylation of the amino group in the presence of a hydroxyl group. The reported method is simple, mild, and environmentally viable, using several other acid anhydrides at room temperature.

Keywords: acetylation, acylation, chemoselective, room temperature

INTRODUCTION

The acylation of alcohols and phenols is a fundamental process in organic chemistry. It also provides an efficient route for protecting -OH groups during oxidation, peptide coupling, and glycosidation reactions.[1] This -OH group protection is commonly achieved through acylation with acetic anhydride because of the ease of deprotection.[2] The various catalysts developed for acylation include nucleophilic agents[3] such as 4-dimethyl-aminopyridine (DMAP) and Bu_3P; Lewis acids such as metal halides,[4] metal triflates,[5] and metal perchlorates;[6] ionic liquids;[7] and several solid acids such as clays, zeolite, yttria-zirconia and Naffion-H.[8] Some of these

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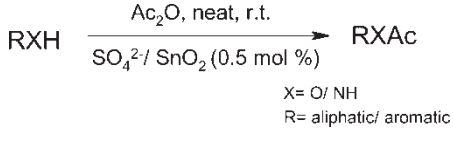
catalytic systems are homogeneous and nonrecoverable and suffer from limitations such as longer reaction times, stringent conditions, use of halogenated solvents, and hazardous materials (e.g., DMAP is highly toxic [LD_{50} in the rat intravenous: 56 mg/kg],[9] Bu_3P is inflammable [flash point: 37°C] and air sensitive; perchloric acid and its salts are potentially explosive; and triflates are not cost effective). In recent years, there has been a tremendous upsurge of interest in various chemical transformations performed under heterogeneous catalysis.[10]

SO_4^{2-}/SnO_2 have been used for various organic transformations because of its ease in preparation and higher activity.[11] SO_4^{2-}/SnO_2 was prepared by standard procedures.[12] The reaction conditions were standardized after conducting the acetylation of 2-naphthol with Ac_2O using various solvents at room temperature (Table 1). Excellent yield was obtained under neat conditions with 0.5 mol% of the catalyst with an equivalent amount of Ac_2O, so we have continued the reactions under solvent-free conditions. To explore the scope and activity of the catalyst, various alcohols, phenols, and amines with electron-donating and electron-withdrawing groups were studied. We have observed that acetylation of phenols was slightly slower than that of alcohols and amines. No competitive Fries rearrangement was observed in the case of phenolic substrates. The efficacy of the catalyst can be clearly visualized in the acetylation of polyhydroxy compounds under similar conditions (Table 2, entries 3–5). Another noteworthy feature of this methodology is that polyols such as D-mannitol underwent exhaustive acetylation, demonstrating the practical utility of this method (Table 2, entry 3).

The present procedure is excellent for the acetylation of alcohols (primary and secondary), phenols, amines, and bifunctional compounds containing -NH_2 and -OH groups. To examine the chemoselectivity of the

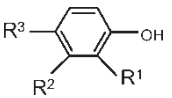
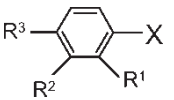
Table 1. Effect of solvent during the SO_4^{2-}/SnO_2-catalyzed acetylation of 2-naphthol with Ac_2O using different solvents



Entry	Mol (%)	Solvent	Time	Yield (%)[a,b]
1	0.5	CH_3CN	2 h	82
2	0.5	THF	2 h	50
3	0.5	$PhCH_3$	2 h	80
4	0.5	CH_2Cl_2	2 h	84
5	0.5	Neat	30 min	95

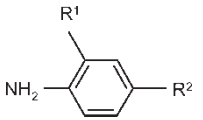
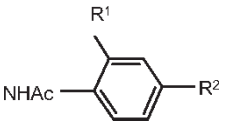
[a]The substrate was treated with Ac_2O (1 equiv.).
[b]Isolated yield of the corresponding acetylated product.

Table 2. Acetylation of heteroatom using SO_4^{2-}/SnO_2 and Ac_2O at room temperature[a]

Entry	Substrate (RXH)	Time (min)	Yield (%)[b,c]	Product (RXAc)[d]	Bp (Torr) or mp (°C) Found	Bp (Torr) or mp (°C) Reported
1	R = $CH_3(CH_2)_7$, X = O	10	95	R = $CH_3(CH_2)_7$, X = O	100–101	98–99[13]
2	R = Ph CH_2, X = O	10	94	R = Ph CH_2, X = O	212–213	214–215[14]
3	Ethylene glycol	45	94[g]	Hexa-O-acetyl-D-Mannitol	120–121	123–124[14]
4	D-Mannitol	15	90[e]	Ethane-1,2-diyl diacetate	186–188	186[15]
5	Glycerol	30	90[f]	Propane-1,2,3-triyl triacetate	259–260	258[16]
						
6	$R^1 = R^2 = R^3 = H$	30	88	$R^1 = R^2 = R^3 = H$, X = OAc	194	196[14]
7	$R^1 = R^2 = H$, $R^3 = NO_2$	60	90	$R^1 = R^2 = H$, $R^3 = NO_2$, X = OAc	79–81	81–82[14]
8	$R^1 = R^2 = H$, R^3 = Br	45	88	$R^1 = R^2 = H$, R^3 = Br, X = OAc	235–237	237–240[14]
9	$R^1 = R^2 = H$, R^3 = Cl	30	88	$R^1 = R^2 = H$, R^3 = Cl, X = OAc	226–228	226–228[14]
10	$R^3 = R^2 = H$, R^1 = Me	20	94	$R^3 = R^2 = H$, R^1 = Me, X = OAc	210–211	208[14]
11	$R^3 = R^2 = H$, R^1 = OMe	30	90	$R^3 = R^2 = H$, R^1 = OMe, X = OAc	105–107	107[14]
12	1-Naphthol	60	90	1-Naphthyl acetate	45–47	48–49[14]

(*continued*)

Table 2. Continued

Entry	Substrate (RXH)	Time (min)	Yield (%)[b,c]	Product (RXAc)[d]	Bp (Torr) or mp (°C) Found	Bp (Torr) or mp (°C) Reported
13	2-Naphthol	30	95	2-Naphthyl acetate	68–69	70[14]
						
14	$R^1 = R^2 = H$	5	95	$R^1 = R^2 = H$	163–165	164–165[14]
15	$R^1 = NO_2$, $R^2 = H$	20	90	$R^1 = NO_2$, $R^2 = H$	92–93	94[14]
16	R^1, $R^2 = NO_2$	30	88	R^1, $R^1 = NO_2$	119	121[14]
17	$PhCH_2NH$	20	94	$PhCH_2NHAc$	61	61[14]

[a]The substrate was treated with Ac_2O (1 equiv. per OH/NH_2 group except for entries 3, 4, and 5) in the presence of SO_4^{2-}/SnO_2 (0.5 mol%) under neat conditions at room temperature.

[b]Isolated yield of the corresponding acetylated product.

[c]The unreacted substrate was recovered.

[d]All compounds have been satisfactorily characterized (IR, ^1H NMR).

[e]Isolated yield of the di-acetate.

[f]Isolated yield of the tri-acetate.

[g]Isolated yield of the hexa-acetate.

present method, bifunctional substrates containing -NH_2 and -OH groups were studied (Table 3). Selective acetylation of the -NH_2 group in the presence of the -OH group was observed at room temperature with 1 equivalent of acetic anhydride to give corresponding N-acetate product, and no O-acetate product was found under this conditions. This might be due to more nucleophilicity of amines than phenols. The scope of this methodology was further extended by acylation of alcohols, phenols, and amines with variety of other acid anhydrides. Thus, acylation of octanol, phenol, and aniline can be achieved with different anhydrides such as $(PhCO)_2O$, succinic anhydride, and phthalic anhydride (Table 4, entries 1–5). The reactions were performed in MeCN at room temperature. It should be noted that the catalyst is reusable for five cycles without significant loss of its efficacy. Unreacted substrate can be recovered. The product obtained does not need much purification.

In conclusion, SO_4^{2-}/SnO_2 is found to be a new, highly efficient, chemoselective, and reusable catalyst for acylation of primary and secondary alcohols, phenols, and amines. With the increasing tight legislation on the release of waste and use of toxic substances as a measure to control environmental pollution,[21] the use of a stoichiometric amount of acetylating agent and the solvent-free conditions employed in the present method make it environmentally friendly and suitable for industrial applications.

EXPERIMENTAL

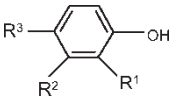
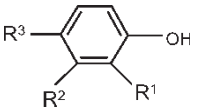
Typical Procedure for the Acetylation

2-Naphthol (0.720 g, 5 mmol) was treated with Ac_2O (0.48 mL, 5 mmol) under neat conditions at rt for 30 min under magnetic stirring in the presence of SO_4^{2-}/SnO_2 (0.5 mol%) with respect to substrate. The course of the reaction was monitored by thin-layer chromatography (TLC) and gas chromatography (GC). The reaction mixture was diluted with Et_2O (20 mL), and the solution was filtered to separate the catalyst. The filtrate was washed successively with 1% aqueous NaOH (15 mL) and brine (15 mL), dried (Na_2SO_4), and concentrated to afford the product, which was in full agreement with the mp and spectral data (IR, ^1H NMR) of an authentic sample of 2-acetoxynaphthalene (0.883 g, 95% with SO_4^{2-}/SnO_2). The catalyst was recovered and reused for a fresh lot of 2-hydroxynaphthalene.

Data

Hexa-O-acetyl-D-mannitol (Table 2, entry 3).[15] Found: $[\alpha]_D^{25} = +34.4$ (c 1.2 $CHCl_3$); $[\alpha]_D^{25} = +27$ (c 1.0 $CHCl_3$). ^1H NMR ($CDCl_3$): δ 2.06 (s, 6H), 2.10 (s, 6H), 4.10 (m, 4H), 5.05 (m, 2H), and 5.44 (m, 2H).

Table 3. Chemoselective N-acetylation of bifunctional substrates using SO_4^{2-}/SnO_2 under solvent-free conditions at room temperature[a]

Entry	Substrate	Time (min)	Yield (%)[b,c]	Product[d]	Bp (Torr) or mp (°C)	
					Found	Reported
						
1	$R^1 = NH_2$, $R^2 = R^3 = H$	15	90	$R^1 = NHAc$, $R^2 = R^3 = H$	126–127	129–130[14]
2	$R^1 = R^2 = H$; $R^3 = NH_2$	20	90	$R^1 = R^2 = H$; $R^3 = NHAc$	167–169	169–170.5[14]
3	2-Amino ethanol	10	90	N-(2-Hydroxyethyl acetamide)	62–64	63–65[14]
4	2-Amino-1-propanol	15	88	N-(2-Hydroxypropyl acetamide)	95–98	96–99[14]

[a]The substrate was treated with Ac_2O (1 equiv. per OH/NH_2 group) in the presence of SO_4^{2-}/SnO_2 (0.5 mol%) under neat conditions at room temperature.

[b]Isolated yield of the corresponding acetylated product.

[c]The unreacted substrate was recovered.

[d]All compounds have been satisfactorily characterized (IR, ^1H NMR).

Table 4. Acylation of alcohols, phenols, and amines with acid anhydrides in the presence of SO_4^{2-}/SnO_2 (0.5 mol%) in MeCN at room temperature[a]

Entry	Substrate (RXH)	Acid anhydride	Time (h)	Yield (%)[b,c]	Product ($ROCOR^1$)	Bp (Torr) or mp (°C)	
						Found	Reported
1	$R = CH_3(CH_2)_7$, X = O	$(PhCO)_2O$	3	90	$R = CH_3(CH_2)_7$, $R^1 = Ph$	302–303	304[17]
2	$R = CH_3(CH_2)_7$, X = O	Phthalic anhydride[d]	12	90[d]	Dioctyl phthalate	380	380[18]
3	R = Ph, X = O	$(PhCO)_2O$	6	94	Phenyl benzoate	68–69	71[14]
4	R = Ph, X = O	Succinic anhydride[d]	6	93[d]	Diphenyl succinate	120–121	120–121[19]
5	$PhNH_2$	$(PhCO)_2O$	1	95	Benzanilide	163–165	164–165[20]

[a] The substrate was treated with Ac_2O (1 equiv. per OH/NH_2 group) in the presence of SO_4^{2-}/SnO_2 (0.5 mol%) at room temperature.
[b] Isolated yield of the corresponding acylated product.
[c] The unreacted substrate was recovered.
[d] Acid anhydride–substrate (1:2).

Ethane-1,2-diyl diacetate (Table 2, entry 4).[22] IR (neat): 2934, 1730, 1380, 1245 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.03 (s, 6H) and 4.21 (s, 4H).

Propane-1,2,3-triyl triacetate (Table 2, entry 5).[22] IR (neat): 2935, 1730, 1370, 1240 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.05 (s, 3H), 2.07 (s, 6H), 4.30 (m, 4H), and 5.23 (m, 1H).

N-(2-Hydroxyphenyl acetamide) (Table 3, entry 1).[22] IR (neat): 3447, 2980, 1740 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.08 (s, 3H), 6.86 (m, 3H), 7.65 (1H, d) 9.27 (br, 1H), and 9.67 (s, 1H).

N-(4-Hydroxyphenyl acetamide) (Table 3, entry 2).[22] IR (neat): 3380, 3070, 2850, 1697, 1570, 1280 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.08 (s, 3H), 6.55–6.67 (m, 3H), 7.22 (d, 1H), 8.95 (br, 1H), and 9.55 (s, 1H).

N-(2-Hydroxethyl acetamide) (Table 3, entry 3).[22] IR (neat): 3303, 3097, 2935, 1705, 1250, 1066 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.93–2.03 (d, 3H), 3.35 (m, 2H), 3.7 (m, 2H), 5.18 (bs, 1H), 6.67 (s, 1H).

Dioctyl phthalate (Table 4, entry 2).[22] IR (neat): 2990, 2953, 1760, 1120 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.88 (t, 6H), 1.25–1.32 (m, 16H), δ 1.40 (quintet, $J = 7.0$, 4H), 1.73 (quintet, $J = 7.0$, 4H), 4.30 (t, $J = 7.0$, 4H), 7.50–7.54 (m, 2H).

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