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Research Article

Acetylation of Phenols, Anilines, and Thiols Using Silica Sulfuric Acid under Solvent-Free Conditions

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Silica sulfuric acid was employed as a heterogeneous catalyst for the acetylation of a variety of phenols, amines, and thiols under solvent-free conditions at room temperature. Deactivated substrates also acetylated rapidly, and the method showed the preferential selectivity for acetylation of amino group in the presence of hydroxyl groupin which no C-acylation was observed.

1. Introduction

The protection of hydroxyl groups of alcohols and phenols is often necessary during the course of various transformations in a synthetic sequence, especially in the construction of polyfunctional molecules such as nucleosides, carbohydrates, steroids, and natural products. A variety of procedures are routinely performed for the preparation of acetyl derivatives, including homogeneous or heterogeneous catalysts. Protection reactions have to proceed rapidly, readily, quantitatively, and keeping costs to a minimum. Typically, the acetylation of hydroxyl groups is performed with an excess of Ac_2O under basic or acidic catalysis; in some cases, acetyl halides have been used [1, 2].

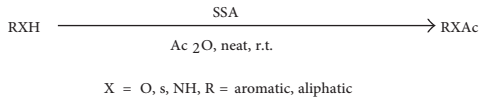
Several methods have been developed for preparation of acetate from the corresponding phenol or thiol using various metal salts, such as $CoCl_2$ [3], $ZnCl_2$ [4], $RuCl_3$ [5], $TiCl_4$-$AgClO_4$ [6], $LiClO_4$ [7], $Mg(ClO_4)_2$ [8], $Zn(ClO_4)_2{\cdot}6H_2O$ [9], and some triflates such as $Sc(OTf)_3$ [10], Me_3SiOTf [11], $In(OTf)_3$ [12], $Cu(OTf)_2$ [13, 14], $Ce(OTf)_3$ [15], and $Bi(OTf)_3$ [16]. The $Cp_2Sm(thf)_2$ [17], tetrabutyl ammonium salt [18], and vinyl carboxylate [19] have proved to be the best catalysts for the acylation of amines with esters.

However, quite a few of the reported methods have limitations mainly in respect of stability, cost, availability, load, and reusability of the catalyst or in terms of yields and flammability or risk of explosion of the reagents. Thus, there is still a demand to develop new and mild methods for the acetylation in the presence of inexpensive and bench top reagents.

In continuation to our environmentally benign synthesis and synthesis of nitrogen-containing compounds [20–27], we intend to report a mild, clean, simple, and efficient method for the acetylation of phenols, amines, and thiols with Ac_2O in the presence of silica sulfuric acid (SSA) [28] as a heterogeneous catalyst under solvent-free conditions [29–33] at room temperature (Scheme 1).

2. Experimental

2.1. General Procedures. All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Products were characterized by FT-IR, ^{1}H NMR, and melting points. The NMR spectra were recorded on a Bruker Avance DRX 300 and 500 MHz instruments in DMSO and $CDCl_3$. The chemical shifts (δ) are reported in ppm relative to the TMS as internal standard, and J values are given in Hz. FT-IR (KBr) spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting



Scheme 1: General acylation method.

Table 1: Solvent effect on acetylation of 4-chloroaniline by SSA at room temperature.

Entry	Solvent	Time (min)	Conversion (%)
1	n-Hexane	7	98
2	CH_3CN	10	98
3	CH_2Cl_2	7	98
4	$CHCl_3$	5	90
5	MeOH	30	85
6	Neat	3	98

point apparatus and were uncorrected. TLC was performed on silica gel Polygram SIL G/UV 254 plates.

2.2. General Experimental Procedure. A mixture of substrate (phenol, amine, thiol, or thiophenol) (1.0 mM), Ac_2O (2.0 mM), and SSA (0.1 g) was stirred at room temperature in solvent-free condition. The progress of the reaction was monitored by TLC or GC.

After completion of the reaction, CH_2Cl_2 was added, the mixture was filtered, and water (10 mL) was added. The mixture was extracted with CH_2Cl_2 (2 × 12 mL), and the organic layers were separated, washed with saturated $NaHCO_3$ (2 × 15 mL) and water (10 mL), and dried over anhydrous $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel afforded the pure product.

3. Results and Discussion

Several experiments were carried out to optimize the amount of SSA and found that 0.1 g is the best condition. Reactions do not take place with less than 0.1 g, and with more SSA, rates will remain steady.

The reaction condition was standardized after conducting the acetylation of 4-chloroaniline (1.0 mM) with Ac_2O (2.0 mM) in the presence of SSA (0.1 g) using various solvents at room temperature (Table 1). Since the 98% yield of 4-chloroacetanilide was obtained under neat conditions, the reactions continued under solvent-free condition.

To find out the efficiency of acylating agents, 4-chloroaniline was chosen as a representative electron-deficient aniline and treated with various acylating agents such as ethyl acetate, acetic acid, vinyl acetate, acetyl chloride, and Ac_2O in the presence of SSA (0.1 g) at room temperature under solvent-free conditions (Table 2). The best result was obtained in 98% yield with Ac_2O, so the acetylation continued with Ac_2O as a best acylating agent.

The reaction of 2-naphthol, 4-chloroaniline, and 4-bromobenzenethiol (1.0 mM) with different mole ratios of Ac_2O (1.0, 1.2, 1.5, 1.7, and 2.0) was carried out in the presence of SSA (0.1 g) at room temperature in solvent-free condition, and the results were only reported for 2-naphthol as a representative compound (Table 3). The best condition was achieved with 1.0 equivalent of the substrate (2-naphthol 90%, Table 4, entry 12; 4-chloroaniline 98%, Table 4, entry 16; 4-bromobenzenethiol 70%, Table 4, entry 25) and 2.0 equivalent of Ac_2O, so the ratio of 1 : 2 of substrate to Ac_2O was used in all acylation reactions.

Table 2: Acylation of 4-chloroaniline (A) by different acylating reagents (B) with SSA under solvent-free conditions at room temperature.

Entry	Reagent	A : B (mole ratio)	Time (min)	Yield %
1	CH_3CO_2Et	1.0 : 2.0	10	0
2	CH_3CO_2H	1.0 : 2.0	10	0
3	Vinyl acetate	1.0 : 2.0	10	20
4	CH_3COCl	1.0 : 2.0	10	95
5	$(CH_3CO)_2O$	1.0 : 2.0	3	98

Table 3: Acylation of 2-naphthol with Ac_2O by SSA in solvent-free condition at room temperature.

Entry	2-Naphthol : Ac_2O (mole ratio)	Yield %
1	1.0 : 1.0	40
2	1.0 : 1.2	50
3	1.0 : 1.5	70
4	1.0 : 1.7	83
5	1.0 : 2.0	90

Then, the acylation of different types of phenols, amines, and sulfur-containing compounds was carried out with Ac_2O (1 : 2, the mole ratio of substrate to Ac_2O) in the presence of SSA (0.1 g) at room temperature in solvent-free condition (Table 4). All the products

The present procedure is chemoselective for the acetylation of bifunctional are known and were characterized by spectroscopic methods. compounds containing $–NH_2$ and –OH groups. So, the selective acetylation of $–NH_2$ group of ortho- or para-aminophenol was observed even with two equivalents of Ac_2O to give the corresponding *o*- or *p*-hydroxyacetanilide. This might be due to the more nucleophilicity of $–NH_2$ group rather than –OH group.

Deactivated substrates could also be acetylated rapidly. For example, strongly deactivated 2-nitroaniline and 3-nitroaniline (Table 4, entries 13 and 14) quantitatively afforded the corresponding acetates within 5–10 min. Again, we observed that 4-nitrophenol (Table 4, entry 9) was converted to the acetate derivatives much faster compared to the earlier reported procedure [5].

The exclusive formation of acylated products in quantitative yields is a significant achievement indicating the capability of the applied procedure.

Table 5 shows the efficiency of SSA compared with those catalysts which were used before. Most of the other catalysts either had lesser yields or needed longer reaction time for completion.

Table 4: Acylation of phenols, amines, and thiols using Ac_2O in the presence of SSA under solvent-free conditions at room temperature.

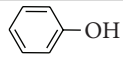
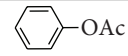
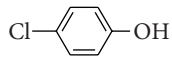
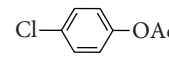
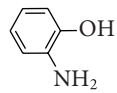
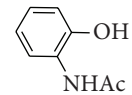
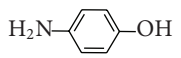
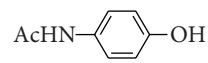
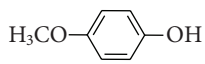
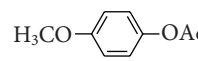
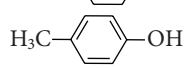
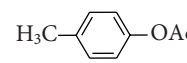
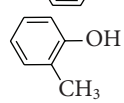
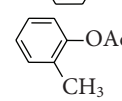
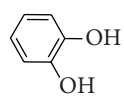
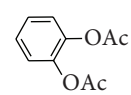
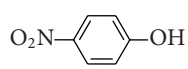
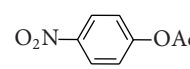
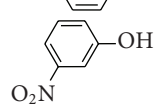
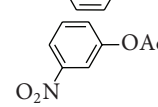
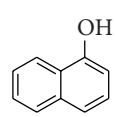
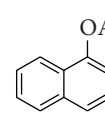
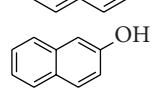
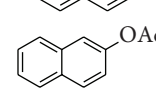
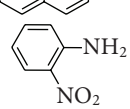
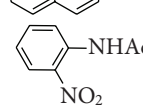
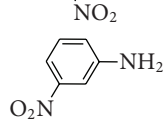
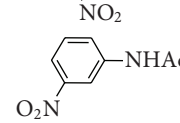
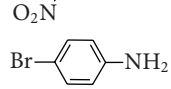
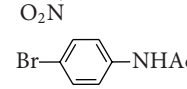
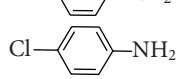
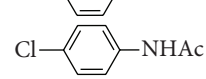
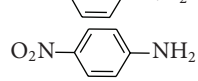
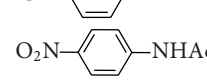
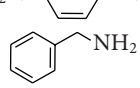
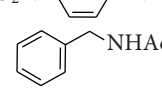
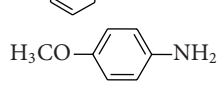
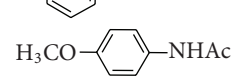
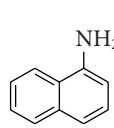
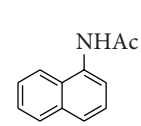
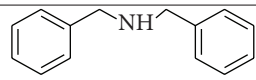
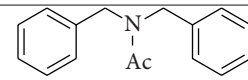
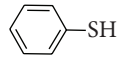
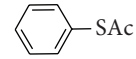
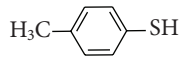
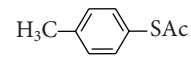
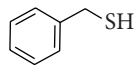
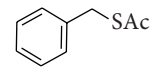
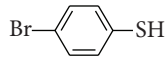
Entry	Substrate	Product[a]	Time (min)	Yield (%)
1			2	90
2			2	99
3			10	90
4			10	80
5			3	98
6			2	95
7			4	95
8			6	80
9			12	90
10			10	95
11			2	95
12			2	90
13			5	80
14			10	95
15			1	98
16			3	98
17			12	90
18			1	96
19			6	98
20			15	90

Table 4: Continued.

Entry	Substrate	Product[a]	Time (min)	Yield (%)
21			0.5	95
22			2	95
23			10	80
24			2	95
25			7	70

[a]All products were known [34–37].

Table 5: Comparison of different acylation methods under solvent-free conditions.

Entry	Substrate	Reaction conditions	Ratio (substrate : acylating agent)	Time (min)	Yield %	The literature reference
1	1-Naphtol	$TiCl_3(OTf)$ (1.0 mol%), Ac_2O, r.t.	1.0 : 2.0	10	84	[35]
		$(NH_4)_{2.5}H_{O.5}PW_{12}O_{40}$, Ac_2O, r.t.	1.0 : 1.0	2.0	92	[34]
		$Zn(ClO_4)_2{\cdot}6H_2O$, (1.0 mol%), Ac_2O, r.t.	1.0 : 1.0	15	90	[36]
		SSA, Ac_2O, r.t.	1.0 : 2.0	2.0	95	Present work
2	Benzylamine	Sulphated zirconia, Ac_2O, r.t.	1.0 : 1.0	10	85	[38]
		Bromodimethylsulfonium bromide, Ac_2O, r.t.	1.0 : 2.0	20	87	[39]
		SSA, Ac_2O, r.t.	1.0 : 2.0	1.0	96	Present work
3	4-Nitrophenol	$TiCl_3(OTf)$ (1.0 mol %), Ac_2O, r.t.	1.0 : 1.0	60	85	[35]
		$Zn(ClO_4)_2{\cdot}6H_2O$, (1.0 mol %), Ac_2O, r.t.	1.0 : 1.0	30	93	[36]
		Bromodimethylsulfonium bromide, Ac_2O, r.t.	1.0 : 2.0	90	87	[39]
		SSA, Ac_2O, r.t.	1.0 : 2.0	12	90	Present work

3.1. Reusability of the Catalyst. We also investigated the reusability of the catalyst. For this purpose after completion of the reaction (4-chloroaniline + ethyl acetate + SSA), CH_2Cl_2 was added to the reaction mixture. The catalyst was separated by a simple filtration, washed with CH_2Cl_2, and used for four successive reactions without significant loss of activity. The results of the first experiment and subsequent reactions were almost consistent in the yields.

4. Conclusions

We used SSA as an active and capable heterogeneous catalyst for the acylation of phenols, amines, and thiols. Moreover, this catalyst offers a mild reaction condition with short reaction times under the neat condition. Also, the present procedure is chemoselective for the *N*-acetylation of bifunctional compounds containing $-NH_2$ and –OH groups. In addition, deactivated substrates could also be acetylated rapidly (Table 3, entries 13 and 14).

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