Tetrahedron Letters 50 (2009) 4058–4062

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Silica-bonded *S*-sulfonic acid as a recyclable catalyst for chemoselective synthesis of 1,1-diacetates

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ARTICLE INFO

Article history:
Received 16 December 2008
Revised 6 April 2009
Accepted 24 April 2009
Available online 3 May 2009

Keywords:
Silica-bonded *S*-sulfonic acid
1,1-Diacetates
Aldehydes
Solvent-free

ABSTRACT

A simple and efficient procedure for the preparation of silica-bonded *S*-sulfonic acid (**SBSSA**) by reaction of 3-mercaptopropylsilica (MPS) and chlorosulfonic acid in chloroform is described. This solid acid is employed as a recyclable catalyst for the synthesis of 1,1-diacetates from aromatic aldehydes and acetic anhydride under mild and solvent-free conditions at room temperature.

1. Introduction

The development of heterogeneous catalysts for organic synthesis has become a major area of research. The potential advantages of these materials over homogeneous systems (simplified recovery, reusability and the potential for incorporation in continuous reactors and microreactors) could lead to novel, environmentally benign chemical procedures for academia and industry.[1] Application of solid acids in organic transformations is important because they have many advantages including ease of handling, decreased reactor and plant corrosion problems and more environmentally safe disposal.[2–7]

Selective protection and deprotection of carbonyl groups are essential steps in modern organic chemistry.[8] The protection of aldehydes as acetals, acylals, oxathioacetals or dithioacetals is common practice for manipulation of other functional groups during multi-step syntheses. Protection of aldehydes as acylals is often preferred due to their ease of preparation and their stability towards basic and neutral conditions.[8,9] In addition, the preparation of 1,1-diacetates from the corresponding aldehydes can be achieved very easily in the presence of ketones. Moreover, they also serve as valuable precursors for asymmetric allylic alkylation[10] and natural product synthesis[11] as well as for the synthesis of 1-acetoxydienes and 2,2-dichlorovinylacetates for Diels–Alder reactions.[12,13] Acylals have also been used as cross-linking agents for cellulose in cotton[14] and are useful intermediates in industry.[12] Moreover, the acylal functionality can be converted into other functional groups by reaction with appropriate nucleophiles.[15,16] Numerous methods for the preparation of 1,1-diacetates from aldehydes and acetic anhydride have been reported.[17–39] Although some of these methods afford good to high yields of the corresponding diacetates, the majority suffer from one or more of the following disadvantages: reactions under oxidizing conditions, use of strong acids, high temperatures, long reaction times, moisture sensitivity as well as high cost and high toxicity of the reagents. In continuation of our studies on the design and application of solid acid catalysts in organic transformations,[40–43] herein, we describe the preparation of silica-bonded *S*-sulfonic acid (**SBSSA**) and its application as a catalyst for the synthesis of aromatic 1,1-diacetates.

We prepared **SBSSA** by the reaction of 3-mercaptopropylsilica **1** with chlorosulfonic acid as illustrated in Scheme 1.

To study the effect of catalyst loading on the protection of aromatic aldehydes as the corresponding 1,1-diacetates the reaction of 4-methylbenzaldehyde with acetic anhydride was chosen as a model reaction (Table 1). The results show clearly that **SBSSA** is an effective catalyst for this transformation and in the absence of **2** the reaction did not take place, even after 12 h. Although a lower catalyst loading (1 mg of **SBSSA**) could be used to accomplish this protection, 5 mg of **SBSSA** per 1 mmol of aldehyde was optimum in terms of reaction time and isolated yield.

The model reaction was also examined in various solvents as well as under solvent-free conditions in the presence of 5 mg $mmol^{-1}$ of **SBSSA** (Table 2). The yield of the reaction under solvent-free conditions was the highest and the reaction time was the shortest. In protic solvents such as water and ethanol this protection reaction proceeded in longer reaction times and with

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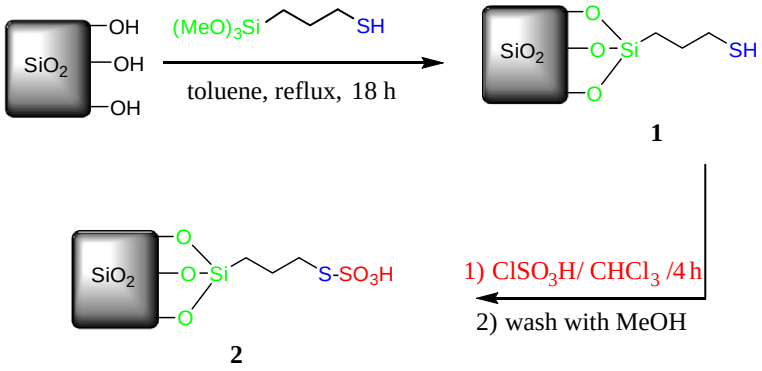
doi:10.1016/j.tetlet.2009.04.096



Scheme 1. Preparation of silica-bonded *S*-sulfonic acid (**SBSSA**).

Table 1
Conversion of *p*-methylbenzaldehyde to the corresponding diacetate with acetic anhydride in the presence of different amounts of **SBSSA**[a]

Entry	Catalyst loading (g)	Time (min)	Yield[b]
1	No catalyst	12 h	0
2	0.1	3	35
3	0.05	3	45
4	0.01	3	65
5	0.005	3	91
6	0.004	10	91
7	0.003	25	90
8	0.002	60	90
9	0.001	180	88

[a] Reaction conditions: *p*-methylbenzaldehyde (1 mmol), acetic anhydride (15 mmol), room temperature, solvent-free.
[b] Isolated yield.

Table 2
Conversion of *p*-methylbenzaldehyde to the corresponding diacetate in different solvents and under solvent-free conditions in the presence of **SBSSA** (0.005 g)

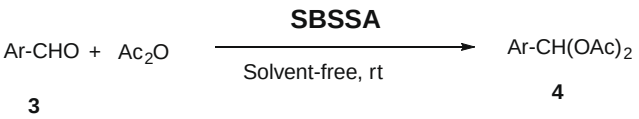
Entry	Solvent[a]	Time (min)	Yield[c]
1	EtOH	30	10
2	H_2O	30	25
3	CH_2Cl_2	3	85
4	*n*-Hexane	20	80
5	MeCN	3	80
6	Solvent-free[b]	3	91

[a] The reaction was carried out in 5 mL of solvent at rt.
[b] The reaction was carried out with 15 mmol of Ac_2O at rt.
[c] Isolated yield.

very poor yields, which maybe related to the instability of acetic anhydride in protic solvents.

Therefore, we employed the optimized conditions (5 mg $mmol^{-1}$ of **SBSSA** and solvent-free conditions) for the conversion of various aryl aldehydes into the corresponding acylals (Scheme 2).

The results of the solvent-free preparation of acylals from aromatic aldehydes **3** in the presence of **SBSSA** at room temperature are shown in Table 3. 1,1-Diacetate **4a** was obtained in high yield in 4 min by the reaction of benzaldehyde with acetic anhydride.



Scheme 2. Synthesis of 1,1-diacetate derivatives catalyzed by **SBSSA**.

Benzaldehydes with electron-donating or electron-withdrawing groups, for example, 4-methylbenzaldehyde **3b** or 3-nitrobenzaldehyde **3c**, were converted into the corresponding acylals **4b** and **4c** in high yields after very short reaction times. The acid-sensitive substrate thiophene-2-carbaldehyde **3o** gave the expected acylal **4o** in 75% yield without any by-product formation (Table 3, entry o).

We also investigated the reactions of 4-hydroxybenzaldehyde **3h**, 3-hydroxybenzaldehyde **3i**, 3,4-dihydroxybenzaldehyde **3j**, 2-hydroxy-5-nitrobenzaldehyde **3k** and 2-hydroxy-5-methoxyisophthalaldehyde **3l** under the above-mentioned conditions and observed that both the carbonyl and phenolic groups were acylated (Table 3, entries h–l). Several aliphatic and aromatic ketones including cyclohexanone, acetophenone and 4-chloroacetophenone were not reactive under the described experimental conditions, even after 2 h.

Next, we studied the competitive acylation reactions of aromatic aldehydes in the presence of ketones using **SBSSA**. Under these conditions exclusive acylation of the aldehyde functions was observed. The chemoselective acylations of benzaldehyde and 4-chlorobenzaldehyde in the presence of acetophenone and 4-chloroacetophenone are shown in Table 4.

The possibility of recycling the catalyst was examined using the reaction of *p*-methylbenzaldehyde and acetic anhydride under the optimized conditions. Upon completion of acylation, the reaction mixture was filtered and the remaining solid was washed with dichloromethane, dried in air and the catalyst reused in the next reaction. The recycled catalyst was reused twenty times without any additional treatment. No observation of any appreciable loss in the catalytic activity of **SBSSA** was observed (Fig. 1).

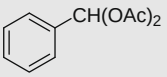
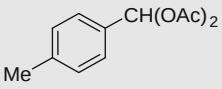
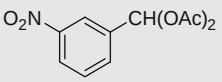
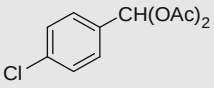
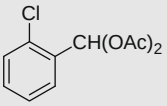
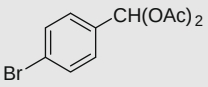
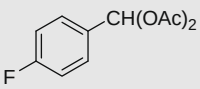
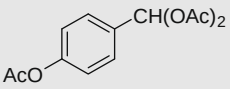
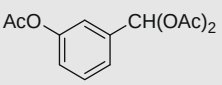
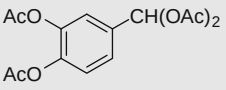
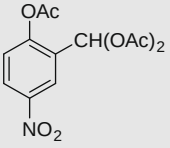
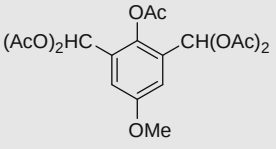
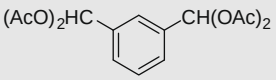
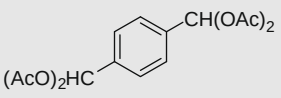
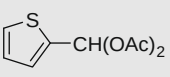
In conclusion, we have shown that silica-bonded *S*-sulfonic acid, which can be prepared from commercially available and cheap starting materials, catalyzed efficiently the synthesis of aromatic 1,1-diacetates from aryl aldehydes. The catalyst shows high thermal stability and was recovered and reused without any noticeable loss of activity. The mild reaction conditions and simplicity of the procedure offer improvements over many existing methods. Studies on the use of the catalyst **2** for other functional group transformations are ongoing in our laboratories.

All the products are known compounds (except **4k, 4l** and **4m**) and were characterized by comparison of their IR, ^1H NMR and ^{13}C NMR spectroscopic data and their melting points with reported values.[21–39] Mercaptopropylsilica **1** (MPS) was prepared according to the procedure reported by Karimi et al.[4]

1.1. Synthesis of silica-bonded S-sulfonic acid 2

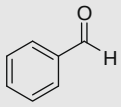
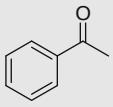
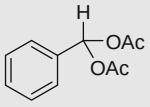
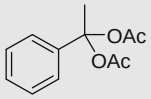
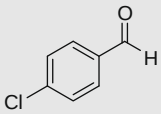
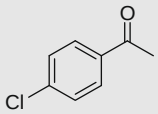
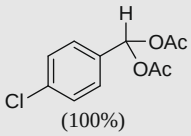
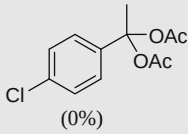
To a magnetically stirred mixture of 3-mercaptopropylsilica **1** (5 g) in $CHCl_3$ (20 mL), chlorosulfonic acid (1.00 g, 9 mmol) was

Table 3
Preparation of various acylals in the presence of **SBSSA** under solvent-free conditions at room temperature[a]

Entry	Ar (**3**)	Product **4**	Time (min)	Yield[b] (%)	Mp (°C)	Lit. mp (°C)
a	C_6H_5–		4	84	44–45	45[34]
b	4-Me–C_6H_4–		3	91	79–81	80–81[35]
c	3-O_2N–C_6H_4–		2	87	64–65	65[34]
d	4-Cl–C_6H_4–		3	85	81–83	82[32]
e	2-Cl–C_6H_4–		3	89	58–60	59[39]
f	4-Br–C_6H_4–		2	90	90–93	92–95[22]
g	4-F–C_6H_4–		2	87	51–53	51[32]
h	4-HO–C_6H_4–		2	83	94–96	95[33]
i	3-HO–C_6H_4–		2	82	76–77	76[33]
j	3,4-$(HO)_2$–C_6H_3–		2	78	130–132	128–130[22]
k	2-HO,5-O_2N–C_6H_3–		2	84	121–122	—
l	2-HO-3-OHC-5-MeO–C_6H_2–		2	72	151–152	—
m	3-OHC–C_6H_4–		3	80	108–110	—
n	4-OHC–C_6H_4–		4	86	172–174	174–175[34]
o	2-Thienyl–		4	75	67–68	66–67[21]

[a] Reaction conditions: aromatic aldehyde (1 mmol), acetic anhydride (15 mmol), **SBSSA** (5 mg), room temperature, solvent-free.
[b] Isolated yield.

Table 4
Competitive acylal formation from aldehydes in the presence of ketones using **SBSSA** under solvent-free conditions[a]

Entry	Substrates		Product (selectivity%)[b]	
1			 (100%)	 (0%)
2			 (100%)	 (0%)

[a] Reaction conditions: Substrate (1 mmol each), acetic anhydride (15 mmol), catalyst (0.005 g), 5 min at rt.
[b] Conversion.

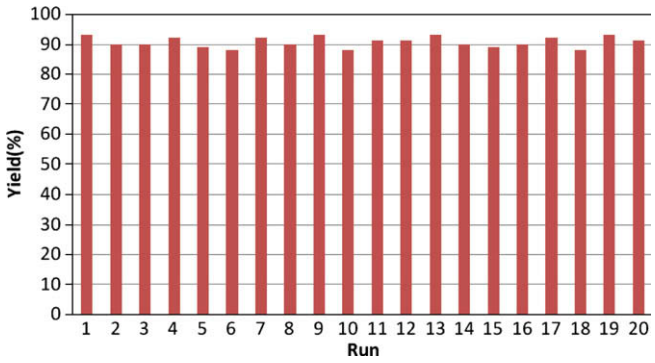


Figure 1. Recyclability of **SBSSA** (0.005 g) in the reaction of *p*-methylbenzaldehyde (1 mmol) and acetic anhydride (15 mmol) at room temperature. Reaction time = 4 min.

added dropwise at 0 °C over 2 h. After the addition was complete, the mixture was stirred for another 2 h and then filtered, the solid washed with methanol (30 mL) and dried at room temperature to afford silica-bonded *S*-sulfonic acid as a cream powder (5.22 g). Elemental analysis showed the S content to be 16.12%. Typically a loading of 0.35 mmol/g was obtained. When **SBSSA** was placed in aqueous NaCl solution, the pH of the solution dropped almost instantaneously to pH ≈1.85, as ion exchange occurred between the protons and sodium ions (proton exchange capacity: 0.34 mmol/g of **SBSSA**.

1.2. General procedure for acylation

To a mixture of aldehyde (1 mmol) and acetic anhydride (15 mmol) was added **SBSSA** catalyst (5 mg) and the mixture was stirred at room temperature. When the reaction was complete as judged by TLC, CH_2Cl_2 (5 mL) was added and the reaction mixture was filtered and the remaining solid was washed with CH_2Cl_2 (3×5 mL) in order to separate the catalyst. The CH_2Cl_2 layer was washed with water (2×10 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the obtained residue was recrystallized from ethanol.

2. Spectral data

Compound **4k**: IR (KBr): 3010, 2800, 1610, 1565, 1515, 1430, 1340, 1258, 1235, 1160, 1060, 902, 821, 728 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.13 (s, 6H), 2.37 (s, 3H), 7.34 (d, 1H, J = 8.9 Hz), 7.93 (s, 1H), 8.29 (dd, 1H, J_1 = 8.9 Hz, J_2 = 2.7 Hz), 8.53 (d, 1H, J = 2.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 21.09, 21.77, 84.34, 124.21, 124.79, 126.26, 130.05, 145.98, 153.14, 168.64, 168.74. Anal. Calcd for $C_{13}H_{13}NO_8$: C, 50.17; H, 4.21; N, 4.50. Found: C, 49.87; H, 4.11; N, 4.27.

Compound **4l**: IR (KBr): 3480, 3002, 2805, 1750, 1601, 1476, 1437, 1365, 1240, 1200, 1168, 1090, 1040, 970, 942, 880, 759, 723 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.07 (s, 12H), 2.32 (s, 3H), 3.84 (s, 3H), 7.18 (s, 2H), 7.76 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 20.96, 21.09, 56.25, 85.22, 115.06, 130.53, 139.82, 158.04, 168.66, 170.44. Anal. Calcd for $C_{19}H_{22}O_{11}$: C, 53.52; H, 5.20. Found: C, 53.20; H, 5.00.

Compound **4m**: IR (KBr): 3005, 2820, 1756, 1580, 1430, 1367, 1240, 1200, 1158, 1060, 998, 942, 903, 802, 705 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.12 (s, 12H), 7.44 (t, 1H, J = 7.5 Hz), 7.55 (d, 2H, J = 7.5 Hz), 7.65 (s, 1H), 7.68 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 21.27, 89.66, 125.44, 128.59, 129.42, 136.49, 169.13. Anal. Calcd for $C_{16}H_{18}O_8$: C, 56.80; H, 5.36. Found: C, 56.51; H, 5.14.

Acknowledgement

We are thankful to Persian Gulf University Research Council for partial support of this work.

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