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RESEARCH LETTER

Silica immobilized sulfuric acid ([3-(propyl)sulfanyl]propyl]ester and *N*-propylsulfamic acid as recyclable catalysts for chemoselective synthesis of 1,1-diacetates

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Silica immobilized sulfuric acid ([3-(propyl)sulfanyl]propyl]ester and *N*-propylsulfamic acid are employed as recyclable catalysts for the synthesis of 1,1-diacetates from the reaction between an aromatic aldehyde and acetic anhydride under mild- and solvent-free conditions at room temperature. These solid acids could be recycled several times without losing any catalytic activity.

Keywords: silica immobilized sulfuric acid ([3-(propyl)sulfanyl]propyl]ester; silica-bonded *N*-propylsulfamic acid; 1,1-diacetates; aldehydes; solvent-free

Introduction

Selective protection and deprotection of carbonyl groups plays an important role in many multi-step organic syntheses (1). Ease of preparation and stability of 1,1-diacetates toward basic and neutral conditions make them as a preferred method of protection of aldehydes (1, 2). In addition, protection of aldehydes as the corresponding acylals can be achieved very easily in the presence of ketones. Moreover, acylals are used as good precursors for asymmetric allylic alkylation (3) and natural product synthesis (4) as well as the synthesis of 1-acetoxydienes and 2,2-dichlorovinylacetates for Diels–Alder reactions (5, 6). Also, they have been used as cross-linking agents for cellulose in cotton (7) and are useful intermediates in industry (5). Appropriate nucleophiles can convert the acylal functionality into other functional groups (8, 9). Generally, they are synthesized from acetic anhydride and aldehydes using strong protonic acids as catalysts, such as sulfuric (10), phosphoric (11), methanesulfuric (12), or perchloric acid (13), Lewis acids, such as FeCl₃ (2), PCl₃ (14), InCl₃ (15), ZrCl₄ (16), WCl₆ (17), LiBF₄ (18), Cu(BF₄)₂·xH₂O (19), ceric ammonium nitrate (CAN) (20), Zn(BF₄)₂ (21), H₆P₂W₁₈O₆₂·24H₂O (22), AlPW₁₂O₄₀ (23), Cu(OTf)₂ (24), Sc(OTf)₃ (25), LiOTf (26), and heterogeneous catalysts such as Nafion-H (27), expansive graphite (28), zeolites (29), montmorillonite clay (30, 31), and supported reagents (32–35). Other catalysts, such as iodine (36), *N*-bromosuccini-

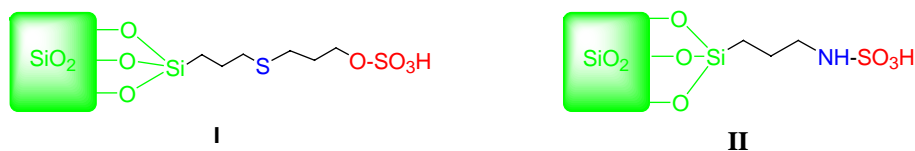
imide (37), and trimethylchlorosilane/sodium iodide (38), have also been used for this transformation, but these procedures are often accompanied by longer reaction times, poor product yields, stringent conditions, good catalyst loading; require the use of toxic solvents; and so on. More recently, cobalt (II) bromide (39), SO₃H-functionalized ionic liquids (40), ferrous methanesulfonate (41), poly(*N,N'*-dibromo-*N*-ethylbenzene-1,3-disulfonamide) (42), NbCl₅ (43), SbCl₃ (44), silica-bonded S-sulfonic acid (45), and supported catalysts (46–50) were reported for the synthesis of 1,1-diacetates.

In recent years, heterogeneous catalysts have been prepared and applied as an alternative to traditional acids and homogeneous acids in catalyzing various organic transformations. The advantages of heterogeneous catalysts are environmentally friendly, easy catalyst separation, high-yielding, and recyclability. We recently applied several heterogeneous catalysts to discover different novel useful synthetic methodologies (51–55). In continuation of the work, we have observed that sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl]ester (I), and silica-bonded *N*-propylsulfamic acid (II) (Figure 1) are efficient heterogeneous catalysts for the synthesis of aromatic 1,1-diacetates (Scheme 1).

Results and discussion

Solid sulfuric acid I was prepared by the reaction of 3-(3-silicapropylthio)-1-propanol with chlorosulfonic

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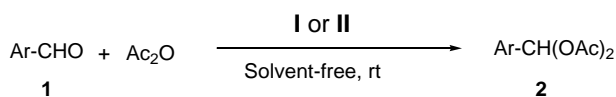
Figure 1. The structure of catalysts **I** and **II**.

acid in chloroform. Elemental analysis showed the S content to be 15.51%. Typically a loading at approximately 0.35 mmol/g is obtained. On the other hand, when the washed sulfonated product **I** was placed in an aqueous NaCl solution, the solution pH dropped virtually instantaneously to $\text{pH} \approx 1.93$, as ion exchange occurred between protons and sodium ions proton exchange capacity: 0.33 mmol/g of sulfuric acid **I** which is in good agreement with the result obtained from TGA.

The thermo gravimetric curve (TGA) seems to indicate two-stage decomposition which is considered to be due to removal of physically absorbed water (100–130°C) or basic silica sulfonic acid (150–230°C), respectively, and is involved with a total overall weight loss of catalyst 43.1% (Figure 6 supporting information). The TGA of silica-bonded *N*-propylsulfamic acid (**II**) was shown a total overall weight loss of catalyst 50% (Figure 18 supporting information).

In the FT-IR spectrum of catalyst, the major peaks for silica (SiO_2) are broad antisymmetric Si–O–Si stretching from 1300 to 1010.6 cm^{-1} and symmetric Si–O–Si stretching near 880–852.5 cm^{-1} . For sulfuric acid functional group, the FT-IR absorption range of the O=S=O asymmetric and symmetric stretching modes lie in 1170 and 1060 cm^{-1} , respectively, the S–O stretching mode lies around 574.7 cm^{-1} . FT-IR spectrum shows the overlap asymmetric and symmetric stretching bands of SO_2 with Si–O–Si stretching bands in the silica functionalized alkyl-sulfuric acid. The spectrum also shows a broad OH stretching absorption around 3600 to 2520 cm^{-1} (Figure 1 supporting information).

The BET surface area of sulfuric acid ([3-(3-silicapropryl)sulfanyl]propyl)ester 4.35 m^2g^{-1} and a total pore volume 0.63 cm^3g^{-1} were measured (figures 3–5 supporting information) and also, for silica-bonded *N*-propylsulfamic acid the BET

Scheme 1. Synthesis of 1,1-diacetate derivatives catalyzed by **I** or **II**.

2.91 m^2g^{-1} and a total pore volume 0.456 cm^3g^{-1} were obtained (figures 15–17 supporting information).

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 **I** and **II** are effective catalysts for this transformation and in the absence of **I** or **II** the reaction did not take place, even after 12 h. Although lower catalyst loading 0.01 g of **I** or **II** accomplished this protection, however, 0.03 g of **I** or **II** per 1 mmol of aldehyde was optimum in terms of reaction time and isolated yield. Also, as shown in Table 1, the best result in the case of time and isolated yield was obtained by using 15 mmol of acetic anhydride.

The model reaction was also examined in various solvents as well as under solvent-free conditions in the presence of 0.03 g mmol^{-1} of **I** or **II** (Table 2).

The yield of the reaction under solvent-free conditions was the highest and the reaction time was shorter. In protic solvents such as water and ethanol this protection reaction proceeded in longer reaction times and with very poor yields, which maybe related to the instability of acetic anhydride in protic solvents. Therefore, we employed the optimized conditions (0.03 g mmol^{-1} of **I** or **II** and solvent-free conditions) for the conversion of

Table 1. Conversion of *p*-methylbenzaldehyde to the corresponding diacetate with acetic anhydride in the presence of different amounts of catalysts **I** and **II** under solvent-free conditions and at room temperature.^a

Entry	Catalyst loading (g)	Ac_2O (mmol)	Time (min)	Yield % ^b
1	No catalyst	15	12 h	0
2	0.01	15	10 (10)	80 (79)
3	0.03	15	7 (7)	96 (92)
4	0.03	1	7 (7)	70 (67)
5	0.03	3	7 (7)	70 (68)
6	0.03	6	7 (7)	76 (73)
7	0.03	10	7 (7)	83 (80)
8	0.03	12	7 (7)	88 (85)
9	0.05	15	5 (5)	95 (93)

^aThe time and yield in parenthesis are related to catalyst **II**.

^bIsolated yield.

Table 2. Conversion of *p*-methylbenzaldehyde to the corresponding diacetate in different solvents and under solvent-free conditions in the presence of **I** and **II** (0.03 g).

Entry	Solvent ^{a,b}	Time (min)	Yield ^c
1	H ₂ O	30 (30)	10 (10)
2	EtOH	30 (30)	25 (25)
3	CH ₂ Cl ₂	7 (7)	90 (87)
4	<i>n</i> -hexane	40 (40)	82 (80)
5	MeCN	10 (10)	85 (83)
6	Solvent-free ^d	7 (7)	96 (92)

^aThe reaction was carried out in 5 mL of solvent at room temperature.

^bThe time and yield in parenthesis are related to catalyst **II**.

^cIsolated yield.

^dThe reaction was carried out with 15 mmol of Ac₂O at room temperature.

various aryl aldehydes into the corresponding acylals (Scheme 1).

The results of the solvent-free preparation of acylals from aromatic aldehydes **I** in the presence of **I** and **II** at room temperature are shown in Table 3. 1,1-Diacetate **2a** was obtained in high yield in 5 minutes by the reaction of benzaldehyde with acetic anhydride. Benzaldehydes with electron-donating or electron-withdrawing groups, i.e. 4-methylbenzaldehyde **1b** and 2-methoxybenzaldehyde **1e**, or 4-nitrobenzaldehyde **1c** and 2-nitrobenzaldehyde **1f**, were converted into the corresponding acylals **2b**, **2e**, **2c**, and **2f** in high yields after very short reaction times. The acid sensitive substrate thiophene-2-carbaldehyde **1g** gave the expected acylal **2g** in 75–76% yield without any by-products (Table 3, entry o). Aliphatic aldehyde such as hexanal was treated with acetic anhydride and gave the corresponding product **1p** in 69–70% yield (Table 3, entry p).

We also investigated the reactions of 2-hydroxybenzaldehyde **1k** under the above conditions and observed that both the carbonyl and phenolic groups were acylated (Table 3, entry k). 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 **I** or **II**. In the presence of ketones, 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.

Finally, a comparative study of **I** and **II** with other recently reported catalysts for acylation of 4-chlorobenzaldehyde, as a model compound was

made which revealed that **I** or **II** is an equally efficient but much cheaper and reusable catalyst (Table 5).

The possibility of recycling the catalyst was examined using the reaction of *p*-methylbenzaldehyde and acetic anhydride under the optimized conditions. Upon completion, 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 could be reused 10 times in the presence of **I** and **II** without any additional treatment. No observation of any appreciable loss in the catalytic activity of **I** and **II** was observed (Figures 2 and 3). Also, the characterization (TGA, IR, XRD, and BET) of after recovered catalysts **I** and **II** was run and confirmed the same as before the reaction (see supporting information). TGA of recycled catalysts confirmed the same thermal stability until 250°C. The XRD confirmed that there is no change in the pattern of catalysts. The IR of recycled catalysts slightly changed and in most cases shown broader peaks. In addition, the BET of recycled catalysts slightly changed as for catalyst **I** the BET before the reaction was 4.35 m²g⁻¹ while after recycling 5.67 m²g⁻¹ and for catalyst **II** the BET was 2.91 m²g⁻¹ and after recycling 1.89 m²g⁻¹.

In conclusion, we have shown that silica-bonded functionalized sulfonic acids **I** and **II**, which can be prepared from commercially available and cheap starting materials, catalyzed efficiently the synthesis of aromatic 1,1-diacetates from aryl aldehydes. The mild reaction conditions and simplicity of the procedure and reusability of catalysts offer improvements over many existing methods.

Experimental section

General

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. All the products are known compounds and were characterized by comparison of their IR, ¹H NMR, and ¹³C NMR spectroscopic data and their melting points with reported values (10–25). Silica immobilized sulfuric acid ([3-(propyl)sulfanyl]propyl]ester (**I**) and silica-bonded *N*-propylsulfamic acid (**II**) were prepared according to our previously reported procedures (51, 52).

Catalyst preparation

3-(3-Silicapropylthio)-1-propanol

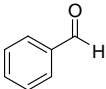
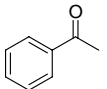
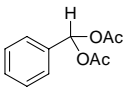
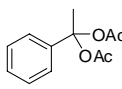
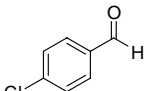
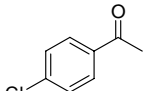
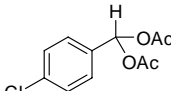
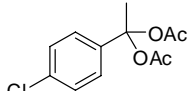
3-Chloro-1-propanol (5 mmol, 0.473 g) was added to a magnetically stirred mixture of 3-mercaptopropyl-silica (10 g) in toluene (30 mL), then some drops of triethyl amine was added and the resulting mixture

Table 3. Preparation of various acylals in the presence of **I** and **II** under solvent-free conditions at room temperature.^{a,b}

Entry	Ar (I)	Product 2	Time (min)	Yield (%) ^c	Melting point (°C)	Lit. melting point (°C)
a	C ₆ H ₅ –		5 (5)	83 (86)	44–45	45 ³⁴
b	4-Me–C ₆ H ₄ –		7 (7)	96 (92)	79–81	80–81 ³⁵
c	4-O ₂ N–C ₆ H ₄ –		3 (3)	90 (85)	123–125	125 ³²
d	4-Cl–C ₆ H ₄ –		3 (3)	89 (87)	81–83	82 ³²
e	2-MeO–C ₆ H ₄ –		3 (3)	89 (89)	75–77	76 ³²
f	4-Br–C ₆ H ₄ –		3 (4)	85 (92)	90–93	92–95 ²²
g	4-F–C ₆ H ₄ –		2 (3)	86 (87)	51–53	51 ³²
h	4-NC–C ₆ H ₄ –		4 (3)	82 (83)	99–101	100–102 ³¹
i	2,4-(Cl) ₂ –C ₆ H ₃ –		3 (3)	84 (87)	99–101	100–102 ³⁴
j	2,6-(Cl) ₂ –C ₆ H ₃ –		3 (3)	80 (80)	87–89	88–89 ³¹
k	2-HO–C ₆ H ₄ –		3 (3)	83 (80)	99–101	100–102 ³¹
l	2-O ₂ N–C ₆ H ₄ –		3 (3)	87 (82)	84–86	85 ³²
m	3-OHC–C ₆ H ₄ –		3 (3)	81 (80)	108–110	108–110 ⁷
n	4-OHC–C ₆ H ₄ –		4 (4)	85 (86)	172–174	174–175 ³⁴
o	2-thienyl-		4 (4)	76 (75)	67–68	66–67 ²¹
p	Me(CH ₂) ₄ –		3 (3)	70 (69)	Boiling point 127–129 (2 mm)	Boiling point 128–129 (2 mm) ^{12a}

^aReaction conditions: aromatic aldehyde (1 mmol), acetic anhydride (15 mmol), catalyst **I** or **II** (0.03 g), room temperature, solvent-free.^bThe time and yield in parenthesis are related to catalyst **II**.^cIsolated yield.

Table 4. Competitive acylal formation from aldehydes in the presence of ketones using **I** or **II** under solvent-free conditions.^a

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

^aReaction conditions: Substrate (1 mmol each), acetic anhydride (15 mmol), catalyst (0.03 g), 5 min at room temperature.

^bConversion.

refluxed for 24 h. The mixture was filtered and the solid was washed with ethanol (3 × 20 mL), and then dried in an oven. 3-(3-Silicapropylthio)-1-propanol was obtained as a cream powder (10.3 g).

Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl) ester (**I**)

To a mixture of 3-(3-silicapropylthio)-1-propanol (5 g) in chloroform (20 mL), chlorosulfonic acid (0.19 g, 1.65 mL) was added dropwise at 0°C during 2 h. After addition was complete, the mixture was stirred for 2 h until HCl gas evolution was stopped. Then, the mixture was filtered and washed with ethanol (30 mL) and dried at room temperature to obtain sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester as a cream powder (5.13 g). Sulfur content of the samples by conventional elemental analysis was 15.51% (51).

Silica-bonded *N*-propylsulfamic acid (**II**)

To a mixture of 3-aminopropylsilica (5 g) in chloroform (20 mL) chlorosulfonic acid (0.2 g, 1.75 mL) was

added dropwise at 0°C during 2 h. After addition was complete, the mixture was stirred for 2 h until HCl gas evolution was stopped. Then, the mixture was filtered and washed with ethanol (30 mL) and dried at room temperature to obtain silica-bonded *N*-propylsulfamic acid (**2**) as cream powder (5.13 g). Sulfur content of the samples by conventional elemental analysis was 9.29% (52).

General procedure for acylation

To a mixture of aldehyde (1 mmol) and acetic anhydride (15 mmol) was added catalyst (**I** or **II**) 0.03 g and the mixture was stirred at room temperature. When the reaction was complete as judged by TLC, CH₂Cl₂ (5 mL) was added and the reaction mixture was filtered and the remaining solid was washed with CH₂Cl₂ (3 × 5 mL) in order to separate the catalyst. The CH₂Cl₂ layer was washed with water (2 × 10 mL) and dried over anhydrous MgSO₄. After removal of the solvent in vacuo, the obtained residue was recrystallized from ethanol.

Table 5. Comparison of the efficiency of **I** and **II** with some of the reported procedure on the reaction of 4-chlorobenzaldehyde with acetic anhydride.

Catalyst	Catalyst load (mmol)	Time (min)	Yield (%) ^a	Reference
H ₂ NSO ₃ H	0.4	10	92	(14–17)
HClO ₄ /SiO ₂	0.005	2	98	(38)
CPTS-HOAc	– ^b	150	92	(40)
H ₃ PW ₁₂ O ₄₀ -supported MCM-41	0.3 g (20 wt%)	240	91	(42)
PEG-SO ₃ H	0.1	30	94	(43)
SBSSA	0.0017	3	85	(45)
Fe(CH ₃ SO ₃) ₂ ·4H ₂ O	0.45	360	92	(46–50)
CoBr ₂	0.1	25	93	(51–55)
I (II)	0.009	3 (3)	89 (87)	Present work

^aIsolated yield.

^b0.045 mmol of CPTS and 12 mmol of HOAc were used.

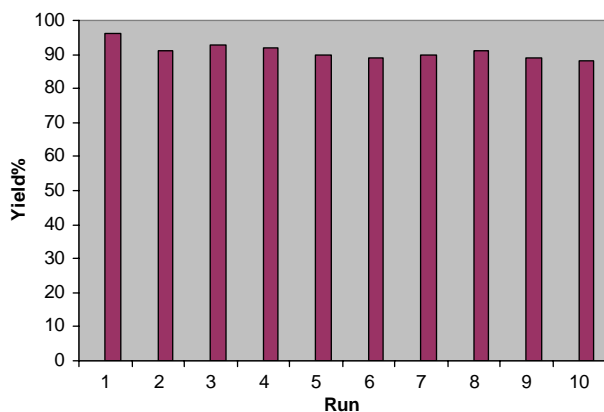


Figure 2. Recyclability of **I** (0.03 g) in the reaction of *p*-methylbenzaldehyde (1 mmol) and acetic anhydride (15 mmol) at room temperature. Reaction time = 7 min.

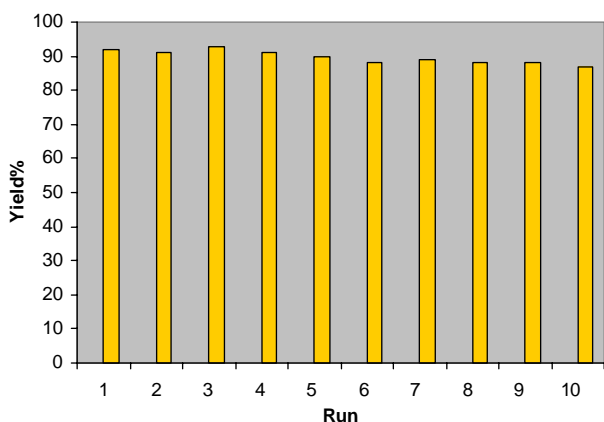


Figure 3. Recyclability of **II** (0.03 g) in the reaction of *p*-methylbenzaldehyde (1 mmol) and acetic anhydride (15 mmol) at room temperature. Reaction time = 7 min.

Spectral data

2m: 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. Analysis Calculated for $\text{C}_{16}\text{H}_{18}\text{O}_8$: C, 56.80; H, 5.36; found: C, 56.51; H, 5.14.

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