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), AIPW12O40 (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-bromosuccinimide (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 methansulfonate (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 acid.
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 pH ≈ 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 (SiO₂) 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 SO₂ 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-silicapropyl)sulfanyl]propyl)ester 4.35 m²g⁻¹ and a total pore volume 0.456 cm³g⁻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) | Ac₂O (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.
4-chlorobenzaldehyde, as a model compound was used to compare recently reported catalysts for acylation of aromatic aldehydes in the presence of ketones under solvent-free conditions (Table 3, entry p).

The chemoselective acylations of benzaldehyde and 4-chlorobenzaldehyde in the presence of acetophenone were acylated (Table 3, entry k). Several aliphatic and aromatic ketones including cyclohexanone, acetophenone, and 4-chloroacetophenone were not reactive (Table 3, entry n). Benzaldehydes with electron-donating or electron-withdrawing groups, i.e. 4-methylbenzaldehyde, 2-hydroxybenzaldehyde, and 2-methoxybenzaldehyde, were acylated (Table 3, entry e). Several aliphatic and aromatic ketones including cyclohexanone, acetophenone, and 4-chloroacetophenone were not reactive (Table 3, entry n).

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 the recovered catalysts I and II was run and confirmed the same as before the reaction (see supporting information).

The acid sensitive substrate thiophene-2-carbaldehyde was treated with acetic anhydride and gave the expected acylal, which 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 and 2-methoxybenzaldehyde, were converted into the corresponding acylals from aromatic aldehydes (Scheme 1).

We also investigated the reactions of 2-hydroxybenzaldehyde 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).

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, $^1$H NMR, and $^{13}$C 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-mercaptopropylsilica (10 g) in toluene (30 mL), then some drops of triethyl amine was added and the resulting mixture was heated until chloroform was evolved. The reaction mixture was filtered and the resulting mixture was washed with dichloromethane, dried in air, and the catalyst was reused in the next reaction.
Table 3. Preparation of various acylals in the presence of \textbf{I} and \textbf{II} under solvent-free conditions at room temperature.\textsuperscript{a,b}

| Entry | Ar (I) | Product 2 | Time (min) | Yield (%)\textsuperscript{c} | Melting point (°C) | Lit. melting point (°C) |
|-------|--------|-----------|------------|-----------------------------|-------------------|--------------------------|
| a     | C\textsubscript{6}H\textsubscript{5} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 5 (5) | 83 (86) | 44–45 | 45\textsuperscript{34} |
| b     | 4-Me–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 7 (7) | 96 (92) | 79–81 | 80–81\textsuperscript{35} |
| c     | 4-O\textsubscript{2}N–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 3 (3) | 90 (85) | 123–125 | 125\textsuperscript{32} |
| d     | 4-Cl–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 3 (3) | 89 (87) | 81–83 | 82\textsuperscript{32} |
| e     | 2-MeO–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 3 (3) | 89 (89) | 75–77 | 76\textsuperscript{32} |
| f     | 4-Br–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 3 (4) | 85 (92) | 90–93 | 92–95\textsuperscript{22} |
| g     | 4-F–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 2 (3) | 86 (87) | 51–53 | 51\textsuperscript{32} |
| h     | 4-NC–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 4 (3) | 82 (83) | 99–101 | 100–102\textsuperscript{31} |
| i     | 2,4-(Cl)\textsubscript{2}–C\textsubscript{6}H\textsubscript{3} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 3 (3) | 84 (87) | 99–101 | 100–102\textsuperscript{34} |
| j     | 2,6-(Cl)\textsubscript{2}–C\textsubscript{6}H\textsubscript{3} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 3 (3) | 80 (80) | 87–89 | 88–89\textsuperscript{31} |
| k     | 2-HO–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 3 (3) | 83 (80) | 99–101 | 100–102\textsuperscript{31} |
| l     | 2-O\textsubscript{2}N–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 3 (3) | 87 (82) | 84–86 | 85\textsuperscript{32} |
| m     | 3-OHC–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 3 (3) | 81 (80) | 108–110 | 108–110\textsuperscript{7} |
| n     | 4-OHC–C\textsubscript{6}H\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 4 (4) | 85 (86) | 172–174 | 174–175\textsuperscript{34} |
| o     | 2-thienyl– | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 4 (4) | 76 (75) | 67–68 | 66–67\textsuperscript{21} |
| p     | Me(CH\textsubscript{2})\textsubscript{4} – | \begin{tikzpicture} \draw[thick] (0,0) -- (0.5,0.5) -- (0.5,1) -- (1,1) -- (1,0) -- cycle; \end{tikzpicture} | 3 (3) | 70 (69) | Boiling point 127–129 (2 mm) | Boiling point 128–129 (2 mm)\textsuperscript{12a} |

\textsuperscript{a}Reaction conditions: aromatic aldehyde (1 mmol), acetic anhydride (15 mmol), catalyst \textbf{I} or \textbf{II} (0.03 g), room temperature, solvent-free.

\textsuperscript{b}The time and yield in parenthesis are related to catalyst \textbf{II}.

\textsuperscript{c}Isolated yield.
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, CH$_2$Cl$_2$ (5 mL) was added and the reaction mixture was filtered and the remaining solid was washed with CH$_2$Cl$_2$ (3 × 5 mL) in order to separate the catalyst. The CH$_2$Cl$_2$ 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.

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

| Entry | Substrates | Product (selectivity%)$^b$ |
|-------|------------|-----------------------------|
| 1     | ![Image](https://example.com/image1.png) | ![Image](https://example.com/image2.png) (100%) (0%) |
| 2     | ![Image](https://example.com/image3.png) | ![Image](https://example.com/image4.png) (100%) (0%) |

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

$b$Conversion.

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

| Catalyst                  | Catalyst load (mmol) | Time (min) | Yield (%)$^a$ | Reference |
|---------------------------|----------------------|------------|---------------|-----------|
| H$_2$NSO$_3$H             | 0.4                  | 10         | 92 (14–17)    | (38)      |
| 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)       | (46–50)   |
| Fe(CH$_3$SO$_3$)$_2$·4H$_2$O | 0.45                | 360        | 92 (51–55)    |           |
| CoBr$_2$                  | 0.1                  | 25         | 93 (51–55)    |           |
| I (II)                    | 0.009                | 3 (3)      | 89 (87)       | Present work |

$a$Isolated yield.

$b$0.045 mmol of CPTS and 12 mmol of HOAC were used.
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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, CDCl₃): 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). 13C NMR (125 MHz, CDCl₃): δ (ppm) 21.27, 89.66, 125.44, 128.59, 129.42, 136.49, 169.13. Analysis Calculated for C₁₆H₁₈O₈: C, 56.80%; H, 5.36%; found: C, 56.51%; H, 5.14.

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.
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