S. Afr. J. Chem., 2012, **65**, 10–13,
<http://journals.sabinet.co.za/sajchem/>.

A Highly Efficient Solvent-Free Acetalization of Aldehydes to 1,1-Diacetates Catalyzed by SiO_2-Pr-SO_3H

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Received 11 August 2011, revised 12 September 2011, accepted 2 December 2011.

ABSTRACT

1,1-Diacetates are prepared in excellent yields from aldehydes and acetic anhydride under solvent-free conditions at room temperature in short reaction times using catalytic amount of sulfonic acid functionalized silica (SiO_2-Pr-SO_3H) which could be easily handled and removed from the mixture of reaction.

KEYWORDS

1,1-Diacetates, sulfonic acid functionalized silica, acetalization, solvent-free reaction, SiO_2-Pr-SO_3H.

1. Introduction

Protection of aldehydes is a frequently used and important method in organic chemistry. Many procedures have been developed for this aim. For the acetalization of carbonyl groups, acetic anhydride can be used in the presence of different catalysts such as sulphuric acid,[1] NBS,[2] $ZrCl_4$,[3] zinc(II) perchlorate,[4] copper *p*-toluenesulfonate/HOAc,[5] ionic liquids,[6] $(NH_4)_3PW_{12}O_{40}$,[7] Bronsted acidic ionic liquid,[8a] indium tribromide,[8b] $RuCl_3.xH_2O$,[9] P_2O_5/Al_2O_3,[10] ruthenium(III) chloride,[11] SO_4^{-2}/SnO_2,[12] H_2NSO_3H,[13] alum,[14] SBSSA,[15] $Fe(NO_3)_3.9H_2O$,[16] silica chloride,[17] silica phosphoric acid,[18] ferrous methanesulfonate,[19] iodine,[20] and morpholinium bisulfate.[21] Development of novel catalysts for the protection of aldehydes is still in great demand.

Heterogeneous catalysts have found considerable interest in organic reactions, since these catalysts can be recovered and reused several times after the reaction without noticeable loss of reactivity. Reactions with these catalysts are generally clean and selective and give high yields of products. Therefore, for the development of more effective methods and in continuation of our studies on the application of heterogeneous solid acid catalyst in organic synthesis,[22–24] we have decided to use sulfonic acid functionalized silica (SiO_2-Pr-SO_3H) as highly efficient heterogeneous acid catalyst in the acetalization of aldehydes to 1,1-diacetates. This catalyst was used in a few organic transformation methods.[24–27]

2. Experimental

IR spectra were recorded from KBr disk using a FT-IR Bruker Tensor 27 instrument. Melting points were measured by using the capillary tube method with an electro thermal 9200 apparatus. The ^{1}H-NMR (250 MHz) was run on a Bruker DPX, 250 MHz. SiO_2 was purchased from Merck and its particle size, surface area, and average pore diameter are respectively 2–5 mm, 499 m^2 g^{-1}, and 6.4 nm.

2.1. Preparation of Catalyst

2.1.1. *Synthesis of 3-Mercaptopropylsilica (MPS) and its Oxidation*

To 20 g SiO_2 in dry toluene, 25 mL of (3-mercaptopropyl) trimethoxysilane was added, and the reaction mixture was refluxed for 24 h. After this period, the mixture was filtered to obtain 3-mercaptopropylsilica (MPS) which was washed with acetone and dried. Then, 3-mercaptopropylsilica (MPS) (20 g) was oxidized with H_2O_2 (50 mL) and one drop of H_2SO_4 in methanol (20 mL) for 24 h at rt. and then the mixture was filtered and washed respectively with H_2O, and acetone to obtain SiO_2-Pr-SO_3H catalyst. The modified SiO_2-Pr-SO_3H was dried and used as solid acid catalyst in the acetalization of aldehydes to 1,1-diacetates.

2.1.2. *General Procedure for the Acetalization of Aldehydes to 1,1-Diacetates*

At first the catalyst (0.02 g) in a round-bottomed flask (25 mL) must be activated by heating for 10 min in water bath (90 °C) under vacuum. After cooling to room temperature, aldehyde (3 mmol) was added to catalyst. After stirring for 2 min, acetic anhydride (0.6 mL) was added. The reaction mixture was stirred at the room temperature for an appropriate time as mentioned in Table 1. The progress of reaction was monitored by TLC. The obtained mixture was dissolved in dichloromethane and filtered for removing of the catalyst. The filtrate was washed with saturated $NaHCO_3$ solution and then dried with Na_2SO_4. The crystals of 1,1-diacetate of aldehydes were appeared after gradual evaporation of solvent at room temperature (30 °C). The catalyst could be washed subsequently with diluted acid solution, water and then acetone. After drying, it can be reused several times without noticeable loss of reactivity.

1,1-Diacetoxy-1-(4-chlorophenyl)methane 2h:[8a] IR (KBr, cm^{-1}): ν_{max} = 3092, 2984, 1759, 1599, 1495, 1379, 1245, 1201, 978, 913, 542. ^{1}H NMR ($CDCl_3$): δ = 7.55 (s, 1H), 7.32 (d, 2H), 7.20 (d, 2H), 2.09 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.8, 89.1, 128.2, 128.9, 134.1, 135.7, 168 ppm. Mass (*m/z*): 242[M$^+$], 199, 180, 139, 111, 75, 43.

1,1-Diacetoxy-1-(4-nitrophenyl)methane 2j:[8a] IR (KBr, cm^{-1}): ν_{max} = 3105, 2926, 1762, 1604, 1530, 1349, 1234, 1198, 1061, 1008, 976, 942, 852, 816, 736 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.07 (d, 2H), 7.54 (s, 1H), 7.51 (d, 2H), 1.96 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.7, 88.4, 123.9, 127.9, 142.0, 148.7, 168.6 ppm. Mass (*m/z*): 253[M$^+$], 207, 180, 151, 122, 105, 77, 51.

1,1-Diacetoxy-1-(3-nitrophenyl)methane 2k:[8a] IR (KBr, cm^{-1}):

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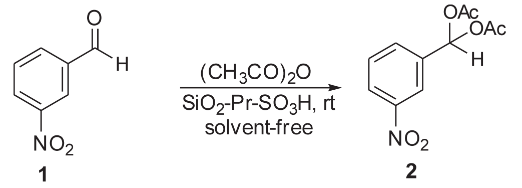
Table 1 Protection of aldehydes using of SiO_2-Pr-SO_3H under solvent-free conditions at room temperature

Entry	Aldehyde (3 mmol)	Product	Time/min	Yield/%	Mp /°C	Lit.
1	Benzaldehyde	**2a**	5	98	44–45	44–46 [8a]
2	2-OH-benzaldehyde	**2b**	5	90	101–103	101–102 [8a]
3	Cinnamaldehyde	**2c**	5	98	80–83	84–86 [7]
4	2-OCH_3-benzaldehyde	**2d**	10	85	67–69	68–80 [8a]
5	3,4-$(OCH_3)_2$-benzaldehyde	**2f**	10	85	72–74	70–72 [8a]
6	2,4-Cl_2-benzaldehyde	**2g**	15	98	105–106	102–104 [13]
7	4-Cl-benzaldehyde	**2h**	10	92	82–84	81–82 [8a]
8	2,6-Cl_2-benzaldehyde	**2i**	20	95	86–90	88–90 [8a]
9	4-NO_2-benzaldehyde	**2j**	5	98	125–127	124–126 [8a]
10	3-NO_2-benzaldehyde	**2k**	5	98	63–65	65–67 [8a]
11	5-Methylfuran-2-carbaldehyde	**2l**	30	80	89–91	90–92 [8a]
12	2-CH_3-benzaldehyde	**2m**	15	85	58–60	59–61 [8b]



Scheme 1
The acetalization of 3-nitro-benzaldehyde with acetic anhydride using SiO_2-Pr-SO_3H.

ν_{max} = 3049, 3015, 1760, 1533, 1354, 1240, 1202, 1011, 819, 739, 685, 626 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.3 (s, 1H), 8.2 (d, 1H), 7.8–7.5 (m, 2H), 2.0 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.8, 88.4, 121.9, 124.6, 129.9, 133.0, 137.6, 148.4, 168.6 ppm. Mass (*m/z*): 253, 210 (M^+ – 43), 194, 150, 134, 105, 77, 51, 43.

3. Results and Discussion

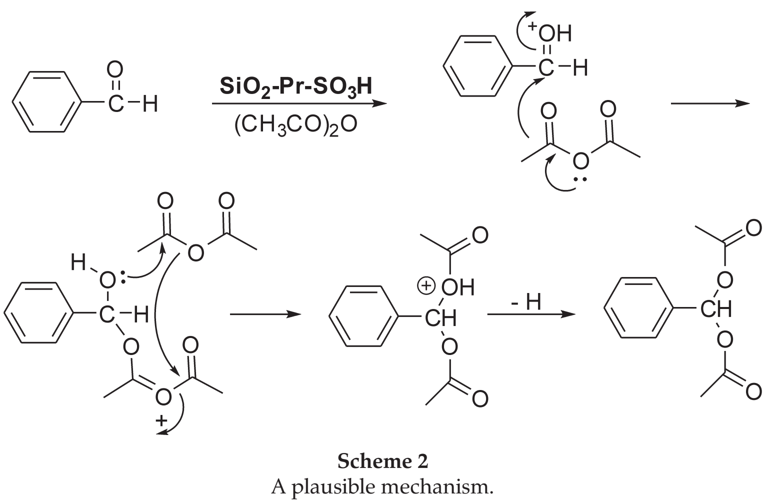
In this work, a mild and efficient method for the conversion of aldehydes to 1,1-diacetates using sulfonic acid functionalized silica with solvent-free conditions is reported. For optimization of the reaction conditions, the acetalization of 3-nitro-benzaldehyde with acetic anhydride in the presence of SiO_2-Pr-SO_3H was used as a model reaction (Scheme 1). The catalyst was activated in vacuum at 100 °C and then after cooling to room temperature, aldehyde (3 mmol) and then acetic anhydride (0.6 mL, 6 mmol) were added to catalyst to produce 1,1-diacetates derivatives under solvent-free conditions. The reaction time was just 5 min at room temperature and the yield of reaction was more than 96 %. The results for other aldehydes are summarized in Table 1. A plausible mechanism of reaction is demonstrated in Scheme 2.

The high yields of products and short reaction time are attributed to the power of heterogeneous catalyst which has the pore size of about 5.9 nm. It is proposed that the reaction takes place in the pores of catalyst.

The acetalization of benzaldehyde has been studied with several catalysts in literature in Table 2. As shown results, the present methodology, using SiO_2-Pr-SO_3H (entry 9) as catalyst in solvent-free condition, offers several advantages such as excellent yields, a simple procedure, short reaction times, easy synthesis, simple work-up and greener conditions in contrast with other existing methods. The scalability of the reaction was verified using 9 mmol of aldehyde and 1.8 mL of acetic anhydride in the presence of 0.05 g of catalyst. The yield of reaction was more than 95 % and the reaction time was 10 min as shown in Table 3. These results demonstrate that SiO_2-Pr-SO_3H can be used on a larger scale.

Sulfonic acid functionalized silica as an efficient heterogeneous solid acid catalyst that can be prepared by simple operation from commercially available cheap starting materials such as silica. Acid sites were incorporated into silica surface by existing methods.[31–32] At first, the surface of silica was functionalized and treated with (3-mercaptopropyl)trimethoxysilane (MPTS) and then the thiol functionalities were oxidized into sulfonic acid groups by hydrogen peroxide to obtain sulfonic acid functionalized silica (SiO_2-Pr-SO_3H) (Scheme 3). The surface of catalyst was analyzed by different method such as TGA, BET and CHN methods which were demonstrated that the organic goups (propyl sulfonic acid) were immobilized into the pores.[23]

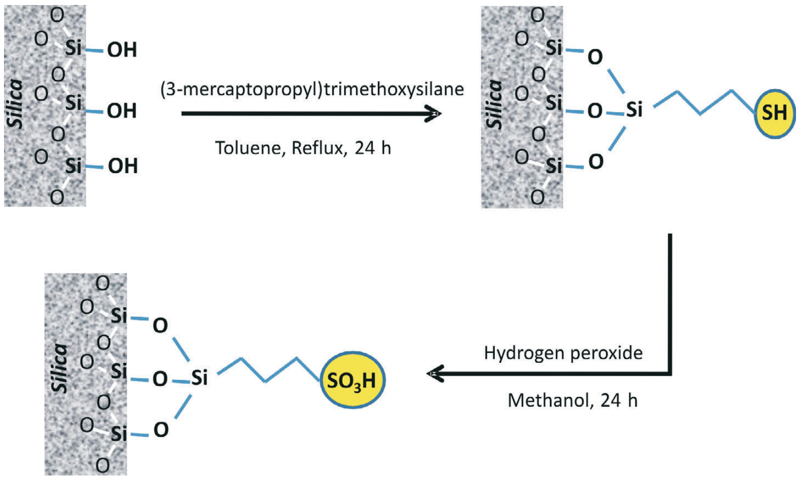
The catalyst can be reused several times without noticeable loss of reactivity



Scheme 2
A plausible mechanism.

Table 2 Comparison of different conditions in the acetalization of benzaldehyde (3 mmol).

No.	Catalyst	Solvent	Time	Yield/%	Year	Ref.
1	Brønsted acidic ionic liquid	–	25 min	90	2008	8a
2	P_2O_5/montmorillonite K10	–	10 min	90	2004	21
3	PEG-supported sulfonic acid	–	35 min	92	2007	29
4	SO_4^{-2}/SnO_2	–	25 min	90	2007	12
5	$RuCl_3.xH_2O$	CH_2Cl_2	10 min	97	2008	9
6	Copper *p*-toluenesulfonate/HOAc	HOAc	42 min	92	2007	5
7	[bmim]BF_4 ionic liquid	–	4.5 h	96	2008	6
8	Silica sulphuric acid	–	30 min	84	2006	30
9	SiO_2-Pr-SO_3H	–	5 min	98	This work	



Scheme 3
Synthesis of sulfonic acid functionalized silica.

Table 3 Comparison of the scalability of this reaction in the presence of SiO_2-Pr-SO_3H

No.	Aldehyde	Catalyst /g	Time /min	Yield/%
1	Benzaldehyde (3 mmol)	0.02	5	98
2	Benzaldehyde (9 mmol)	0.05	10	96
3	3-NO_2-benzaldehyde (3 mmol)	0.02	5	98
4	3-NO_2-benzaldehyde (9 mmol)	0.05	10	95

4. Conclusion

We have developed a convenient and facile protocol for the acetalization of aldehyde to 1,1-diacetates using sulfonic acid functionalized silica (SiO_2-Pr-SO_3H), in short reaction times (5–30 min) and excellent yields (80–98 %). Moreover, the mild reaction conditions, high yields of products, ease of workup, and the ecologically clean procedure make this reaction an attractive and useful method in the protection of aldehydes to 1,1-diacetates.

Acknowledgements

We gratefully acknowledge the financial support from the Research Council of Alzahra University and the University of Tehran.

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