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Chemoselective synthesis of geminal diacetates (acylals) using eco-friendly reusable propylsulfonic acid based nanosilica (SBA-15-Ph-$PrSO_3H$) under solvent-free conditions

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ABSTRACT

An expeditious method for the acetylation of aldehydes by mesoporous solid sulfonic acid (SBA-15-Ph-$PrSO_3H$) under solvent-free reaction conditions was described. The route furnished selectively and in excellent yields the corresponding 1,1-diacetates starting from aldehydes and acetic anhydride using the environmentally friendly catalyst. The catalyst was found to be highly active and selective and could be recycled several times.

1. Introduction

Acylal formation plays a pivotal role in selective protection of carbonyl groups because of their stability in neutral and basic media as well as toward aqueous acids [1]. Hence, protection of aldehydes as acylals plays an important role in multi-step organic synthesis. Accordingly, methods for their synthesis have received considerable attentions. Usually the formation of 1,1-diacetates is catalyzed by strong protic acids, such as H_2SO_4 [2,3], CH_3SO_3H [4], NH_2SO_3H [5], $KHSO_4$ [6] and Lewis acids such as PCl_3 [7], NBS [8], $Bi(OTf)_3$ [9], $In(OTf)_3$ [10], $AlCl_3$ [11], CAN [12] and $ZrCl_4$ [13]. From the environmental and economical standpoints, various inorganic heterogeneous catalysts, such as Nafion-H [14], K-10 [15], $AlPW_{12}O_{40}$ [16], $HClO_4.SiO_2$ [17], silica sulfuric acid [18], $H_3PMo_{12}O_{40}$ supported MCM-41 [19], BEA-SO_3H [20], and *N*-sulfonic acid poly(4-vinylpyridinum) chloride [21] were also reported. However, except a few, many of these methods have not been entirely satisfactory, because the use of conventional Bronsted or Lewis acid catalysts as well as excess organic solvents usually entails the problems of corrosiveness, tedious work-up and effluent pollution. Moreover, some of these methods are not chemoselective in terms of aldehydes and keto carbonyl functional groups. Therefore, a great deal of research focused on development of efficient, recyclable and environmentally benign catalytic methods for this transformation by using inexpensive and nonpolluting reagents and solvents. We have recently initiated studies into new catalytic properties of solid sulfonic acid SBA-15-Ph-$PrSO_3H$ as a reusable, heterogeneous and easily recyclable catalyst for the von Pechmann synthesis of coumarin [22], Strecker syntheses of α-amino nitriles [23] and silylation of hydroxyl groups using HMDS [24]. In further extension to our interest on solvent-free catalytic method and our ongoing green organic chemistry program, herein we describe a simple, convenient and chemoselective method for the synthesis of acylals from aldehydes using recoverable solid sulfonic acid SBA-15-Ph-$PrSO_3H$ (Scheme 1).

2. Results and discussion

In the beginning, efforts were made toward the catalytic evaluation of SBA-15-Ph-$PrSO_3H$ for the synthesis of acylal from benzaldehyde. In the initial catalytic activity experiment, a reaction was carried out using 1 mmol benzazldehyde, 1.2 mmol Ac_2O and 0.5 mol% catalyst. These were stirred at ambient temperature in solvent-free reaction conditions and 55% of the corresponding geminal diacetate was obtained after 2 h. Considerable improvement was observed in the yield of the related product when amount of catalyst increased to 1 mol%. As shown in Table 1 (entry 1), the corresponding product was obtained in quantitative yield after 5 min.

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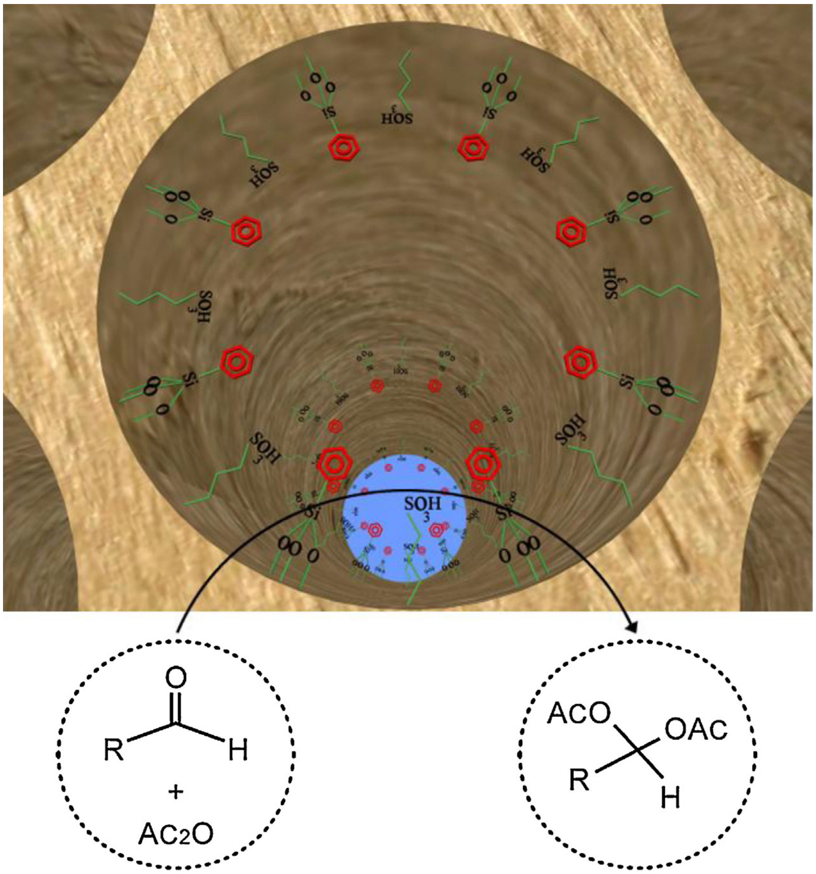
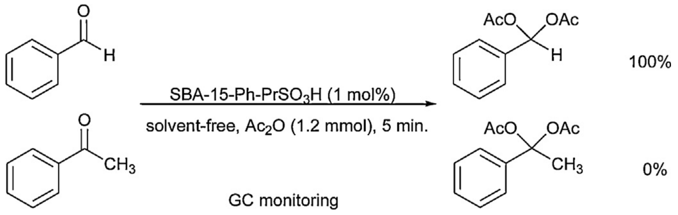


Scheme 1. Schematic synthesis of *gem*-diacetate using catalyst SBA-15-Ph-PrSO$_3$H (1 mol%) under solvent-free reaction conditions.

Having established the preferred reaction conditions, we varied aldehydes while retaining other reactants (Ac$_2$O and SBA-15-Ph-PrSO$_3$H). The reactions took place efficiently in good to excellent yields for all studied aldehydes. The electronic effects and the nature of substituents on the aromatic ring did not show strongly obvious effects in terms of yields under the present reaction conditions (Table 1, entries 1–14). Noteworthy, this catalyst was not able to prepare acylal from *p*-(*N*,*N*-dimethylamino)benzaldehyde (Table 1, entry 15). It should be noted that furfural as an acid sensitive substrate gave the related 1,1-diacetate in excellent yield (Table 1, entry 16). The tolerance of various functional groups under the present reaction conditions is also worthy of mention in that acid sensitive groups, such as chloro, bromo, methoxy and nitro do survive under such conditions. Aliphatic aldehydes also underwent the reaction producing the corresponding geminal diacetate in excellent yields (Table 1, entries 17–20). The generality of this reaction was tested by subjecting 2-hydroxy benzaldehyde which both the hydroxyl and carbonyl groups were acetylated (Table 1, entry 21).

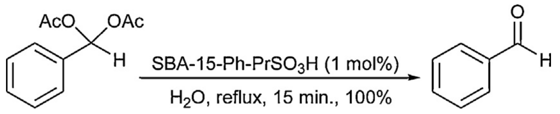
As shown in Table 1, Ketone could not be converted into the corresponding *gem*-diacetate even when the reaction mixture was stirred for 24 h (Table 1, entry 22). Encouraged by this result, we studied competitive reactions for acylation of benzaldehyde in the presence of acetophenone under the same reaction conditions. We found that benzaldehyde was converted to the related *gem*-diacetate while the acetophenone remained unaffected (Scheme 2). This observation suggested that chemoselective acylal formation from aldehydes in the presence of ketones could be achieved with this catalytic system.



Scheme 2. Competitive acylal formation from benzaldehyde in the presence of acetophenone.

In addition to these results, we further studied the possibility of deprotection of resulting acylals in this catalytic system by addition of water as a green solvent. Indeed, when the formation of 1,1-diacetate from benzaldehyde was completed, water was added and the reaction temperature increased to 100 °C. By this procedure, related acylal has been completely transformed into benzaldehyde in short reaction time (Scheme 3).

Our attention next turned to the recycling performance of the catalyst in the synthesis of 1,1-diacetate from benzaldehyde. After the completion of the first run, ethyl acetate was added and then catalyst was isolated from the reaction mixture by filtration. As shown in Fig. 1, the recovered SBA-15-Ph-PrSO$_3$H could be directly reused in nine successive runs without significant loss of activity. Additionally, for better investigation of catalyst recyclability,



Scheme 3. Cleavage of acylal to benzaldehyde in water catalyzed by SBA-15-Ph-PrSO$_3$H.