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Acetalization of Carbonyl Compounds as Pentaerythritol Diacetals and Diketals in the Presence of Cellulose Sulfuric Acid as an Efficient, Biodegradable and Reusable Catalyst

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This paper reports a practical and green method for the acetalization of carbonyl compounds as pentaerythritol diacetals and diketals derivatives using cellulose sulfuric acid as a biodegradable and reusable solid acid catalyst under thermal solvent-free conditions.

Keyword synthetic method, aldehyde, cellulose sulfuric acid; pentaerythritol, solvent-free, acetalization

Introduction

Protective groups are introduced into a molecule by chemical modification of a functional group in order to obtain chemo selectivity in a subsequent chemical reaction.[1] The carbonyl group is one of the most versatile functional groups in organic chemistry and a great deal of synthetic work has been done on the protection and masking of the carbonyl compounds so that the protection of them plays an important role in multistep organic synthesis, medicinal, carbohydrate, and drug design chemistry.[2] Tremendous effort has been made to search for a suitable protective group for carbonyl compounds.[3]

The protection of aldehydes and ketones by the formation of acetals or ketals is important in the preparation of a variety of multi functional organic molecules.[4] Acetals as a functional group which is stable under neutral and basic conditions are not only the most widely used protective groups but also efficient chiral auxiliary groups for enantioselective synthesis.[1] In general, pentaerythritol acetals are also applied as plasticizers and vulcanizers,[5,6] as physiologically active substance and potential protective groups for aldehydes and ketones. Several publications have described the protection of carbonyl compounds with pentaerythritol.[7-18] However, these methods have not been entirely satisfactory, owing to the problems of corrosion, tedious workup, use of toxic solvent such as toluene and benzene, non reusability and environmental polluting of catalysts.

Cellulose is one of the most abundant natural materials in the world and it has been widely studied in organic transformations.[19] Cellulose constitutes the most abundant renewable polymer resource available today. As a chemical raw material, it is generally well-known that it has been used in the form of fibers or derivatives for nearly 150 years for a wide spectrum of products and materials in daily life.[20] Cellulose is potential as a biodegradable material, and can be used for several applications and also as support for bonding several functional groups which act as catalysts to yield clean, efficient and fast chemical reactions.[21] Cellulose sulfuric acid (CellSA) can be easily prepared by the reaction of inexpensive cellulose with chlorosulfonic acid.[22] The number of acidic (H^+) sites in the cellulose sulfuric acid is 0.50 meq/g in the basis of acid-base titration.[22] Cellulose sulfuric acid (CellSA) has excellent catalytic properties, which are attributed to the high thermal stability and strong acid sites of sulfonic acid functional groups. CellSA as a non-hygroscopic solid acid catalyst acts as an efficient and environmentally benign catalyst for the synthesis of several organic compounds such as 3,3'-indolyloxindole derivatives,[23] 2,4,5-triarylimidazoles,[24] β-acetamido carbonyl derivatives,[25] Knoevenagel condensation,[26] oxazolines, imidazolines and thiazolines.[27]

In continuation of our ongoing interest in using heterogeneous catalysts in organic synthesis,[28] we report an efficient and green method for the acetalization of carbonyl compounds under solvent-free conditions with simple work-up and excellent yields in the presence of cellulose sulfuric acid as a reusable, biodegradable catalyst in the reaction of pentaerythritol with aldehydes and ketones (Scheme 1).

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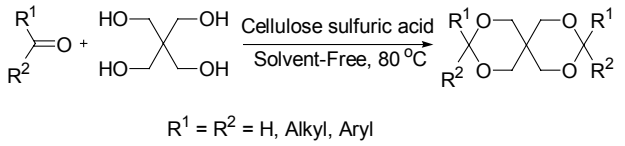
Scheme 1



Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. CellSA was preapared according to the literature.[22] The NMR spectra were recorded on a Bruker Avance DPX 300 MHz instrument. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. Mass spectra were recorded on an Agilent technologies 5973 network mass selective detector (MSD) operating at an ionization potential of 70 eV. TLC was performed on silica-gel Poly Gram SIL G/UV 254 plates.

General procedure for the preparation of pentaerythritol diacetals and diketals

Pentaerythritol (1 mmol), aldehydes or ketones (2 mmol), and CellSA (0.07 g, 3.5 mol %) were added at 80 ℃ under solvent-free conditions. The completion of reaction is monitored by TLC. After completion, the reaction mass was cooled to 25 ℃, then the solid residue was dissolved in hot EtOH and the catalyst was filtered off. The filtrate solution was concentrated and the solid product was purified by recrystallization in aqueous EtOH (25%). Some selected spectroscopic data for known products are given below.

1: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.55—7.60 (m, 2H), 7.24—7.30 (m, 2H), 6.91—6.96 (m, 2H), 6.83 (d, J=8.2 Hz, 2H), 5.79 (s, 2H), 4.87 (d, J=11.5 Hz, 2H), 3.27—3.87 (m, 10H), 3.61 (d, J=11.5 Hz, 2H); IR (KBr) v: 2980, 2900, 2850, 1610, 1470, 1400, 1250, 1070, 1030, 760 cm^{-1}.

2: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.50 (d, J=8.4 Hz, 4H), 7.26 (d, J=8.4 Hz, 4H), 4.40 (d, J=11.5, 2H), 3.54 (d, J=11.5 Hz, 2H), 3.17 (s, 4H), 1.46 (s, 6H); IR (KBr) v: 2970, 2920, 2850, 1610, 1460, 1400, 250, 1070, 1040, 708 cm^{-1}.

Results and Discussion

To choose optimum conditions, first we tried to perform acetatalization of carbonyl compound from the reaction of benzaldehyde (2 mmol) and pentaerythritol (1 mmol) as a model under solvent-free conditions at different temperatures (60, 70, 80, 100 ℃) in the presence of CellSA (0.05 g, 0.5 mol%). The best result was obtained at 80 ℃. Next, the model was examined at different amount of CellSA (0.05, 0.06, 0.07, 0.08 g) at 80 ℃. The highest yield and short reaction time was obtained at 80 ℃ and 0.07 g (3.5 mol%) of the catalyst.

Using these optimized reaction conditions, the scope and efficiency of these procedures were explored for a wide variety of substituted aldehydes and ketones derivatives (Table 1). Ketones show less reactivity than aldehydes for this reaction, for example dibenzalpentaerythritol (Table 1, Entry1) was obtained in 96% yield in 15 min, whereas acetophenone (Table 1, Entry 16) provided 85% yield of product in 22 min. Aromatic aldehydes with stronger electron-donor groups such as methoxy and methyl (Table 1, Entries 4, 10) showed less reactivity and give lower yields, whereas electron-withdrawing substituents enhanced the rate of acetal formation. So, nitro and chloro derivatives of benzaldehyde (Table 1, Entries 2, 3, 11—14) reacted faster than the other aldehydes. Alkyl aldehydes are converted to their respective acetals such as aryl aldehydes in excellent yield. (Table 1, Entries 6—9).

In order to show the accessibility of the present work in comparison with the reported results in the literature,[7,8,12,13] we summarized some of the results for acetalizaton of carbonyl compounds in Table 2, which shows that CellSA is the most efficient catalyst with respect to the reaction time and temperature and exhibits broad applicability in terms of yield.

We also studied the reusability of the catalysts in the reaction of benzaldehyde and pentaerythritol under solvent-free conditions at 80 ℃. In this procedure, after completion of the reaction, the reaction mixture was cooled to room temperature, and the crude solid was dissolved in hot ethanol. The mixture was filtered for separation of the catalyst. The catalyst was washed with hot ethanol (5 mL×2). The recovered catalyst was dried in 60 ℃ and used for the subsequent catalytic runs. The recovered catalyst was reused four times without any loss of its activities (Figure 1).

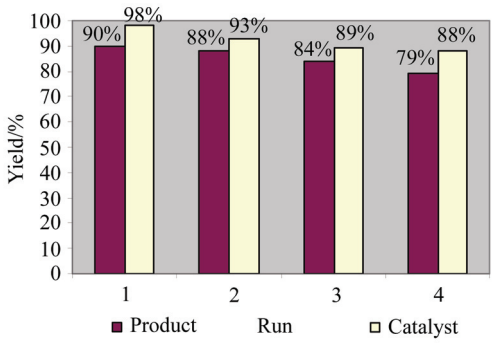


Figure 1 Reusability of the catalyst.

Conclusions

We have developed a green and straightforward protocol for acetalization of carbonyl compounds as biscyclic acetals derivatives via the reaction of aldehydes and pentaerythritol using CellSA as a bio-

Table 1 Preparation of pentaerythritol diacetals and diketals from various aldehydes or ketones (2 mmol) with pentaerythritol (1 mmol) catalyzed by CellSA (0.07 g, 3.5 mol%) at 80 ℃ under solvent-free conditions

Entry	Substrate	Time/min	Yield[a]/%	m.p. (Lit.)/℃
1	Benzaldehyde	15	96	155—158 (158—159)[12]
2	4-Chlorobenzaldehyde	6	95	198—200 (198—199)[8]
3	4-Nitrobenzaldehyde	5	91	225—227 (227—228)[8]
4	4-Methoxybenzaldehyde	20	80	180—182 (182—183)[8]
5	2-Methoxybenzaldehyde	10	82	154—158 (155)[13]
6	Cyclohexanone	11	93	113—115 (114—115)[12]
7	Cycloheptanone	15	86	116—118 (115—117)[7]
8	*n*-Butyraldehyde	5	89	45—47 (43—45)[12]
9	*n*-Heptanaldehyde	5	85	64—65 (63—64)[8]
10	4-Methylbenzaldehyde	17	82	212—214 (212—213)[12]
11	3-Nitrobenzaldehyde	8	91	186—188 (185—186)[8,13]
12	3-Chlorobenzaldehyde	6	90	122—124 (121—122)[8]
13	2-Nitrobenzaldehyde	5	89	162—165 (164—165)[8]
14	2-Chlorobenzaldehyde	6	90	140—143 (141—142)[12]
15	4-Bromoacetophenones	15	95	160—163 (161)[13]
16	Acetophenone	22	85	145—146 (147—148)[10]
17	Benzophenone	18	94	160—161 (162)[13]
18	2,4-Dichlorobenzaldehyde	6	97	185—188 (186—187)[7]
19	4-Chloroacetophenone	15	90	171—173 (172)[13]
20	4-Nitroacetophenone	18	95	72—74 (70—71)[13]
21	*α*-Furaldehyde	20	85	159—160 (156—158)[7]

[a] Yields refer to the isolated pure products. The desired pure products were characterized by comparison of their physical data (melting points, IR, ^{1}H and ^{13}C NMR) with those of known compounds.[7-18]

Table 2 Comparison results of CellSA with $ZrO_2/S_2O_8^{-2}$ [7] Tungstophosphoric acids in liquid phase,[13] SO_3H-functionalized ionic liquids[12] and silica sulfate[8] for the preparation of pentaerythritol diacetals and diketals

Entry	Catalyst	Condition	Time/h	Yield[a]/%
1	$ZrO_2/S_2O_8^{-2}$ (100 mg)	Toluene or benzene (solvent), reflux	0.5	96
2	Tungstophosphoric acids in liquid phase (400 mg)	Toluene (solvent)	2	92
3	SO_3H-functionalized ionic liquids (IL, [PSPy][OTf], 20 mmol)	Solvent-free, 100 ℃	1.5	93
4	Silica sulfate (100 mg)	Benzene (solvent), microwave irradiation	0.5	96
5	CellSA 3.5 mol% (present work)	Solvent-free, 80 ℃	0.25	96

[a] Yields refer to the isolated pure products. Based on the reaction of benzaldehyde (2 mmol) with pentaerythritol (1 mmol).

supported catalyst under solvent-free conditions. This procedure provides several advantages such as cleaner reactions, easier workup, and reduced reaction times, reusable catalyst and eco-friendly promising strategy.

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