

Glycerol-based SO₃H-Carbon Catalyst: A green recyclable catalyst for the chemoselective synthesis of pentaerythritol diacetals

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ABSTRACT

Glycerol-based SO₃H-functionalized carbon catalyst was demonstrated as an efficient and recyclable green catalyst for the chemoselective synthesis of pentaerythritol diacetals with aromatic aldehydes in the presence of ketones in excellent yields in toluene at 80 °C. In addition, the catalyst also has the capability for the deprotection of pentaerythritol diacetals in methanol at reflux temperature. The recovered catalyst without any pre-treatment was reused for 5 cycles without any deactivation and leaching into the reaction medium under optimum conditions.

1. Introduction

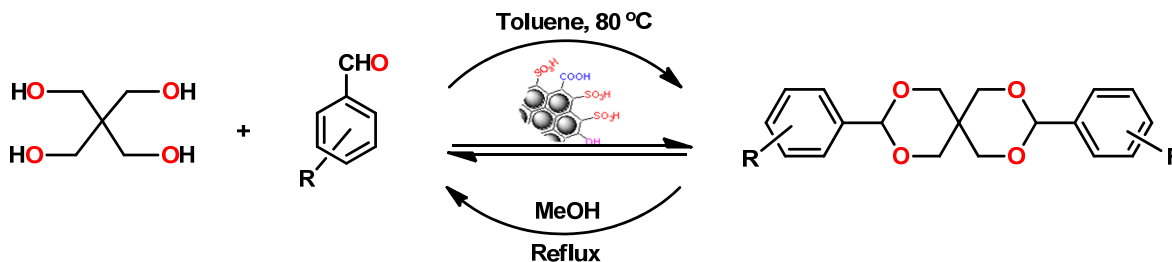
The protection of aldehydes and ketones as acetals or ketals plays an important role for the preparation of different molecules in the presence of variety of different functional groups in drug design chemistry, medicinal chemistry and in multi-step organic synthesis [1,2]. Acetals as a functional group, 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 [3]. Acetals are used in the pharmaceutical and fragrance industries [4] as intermediates or as end products. Pentaerythritol diacetals in general are used as plasticisers and vulcanisers of several polymeric materials, as raw materials for the production of valuable resins, as physiologically active substances [5], and as defoamers in washing solutions containing anionic surfactants [6,7].

Several publications have described the preparation of pentaerythritol (PE) diacetals by using different acidic catalyst like Montmorillonite clay [6,7], ZrO₂/S₂O₈²⁻ solid superacid [8], heteropoly acid H₃PW₁₂O₄₀ [9], InCl₃·4H₂O [10], expansive graphite [11], anhydrous FeSO₄ [12], NH₂SO₃H [13], SO₃H-functionalized ionic liquids [14], Al-MCM-41 [15], cellulose sulfuric acid [16], and P₂O₅/SiO₂ [17]. However, many of these methods suffer from several drawbacks in terms of corrosion,

long reaction times, tedious workup, unsatisfactory yields, large excess of aldehyde, non reusability and environmental polluting of catalysts and no selectivity towards particular carbonyl compound (aldehyde/ketone). Hence, there is a lot of scope and need to develop a mild and environmentally eco-friendly, most suitable catalyst for the preparation of pentaerythritol diacetals under mild conditions by the protection of carbonyl groups in multistep organic synthesis with selectivity towards particular carbonyl compounds.

In recent years, carbon-based solid acid catalysts have gained significant attraction over homogeneous catalysts as they are highly efficient, sustainable, and eco-friendly [18-21]. We have reported a sustainable method for the preparation of -SO₃H functionalized carbon-based solid acid catalyst having 1.6 mmol/g acid density with surface area of 0.21 m²/g from bioglycerol (biodiesel by-product) and also from the glycerol-pitch (waste from fat splitting industry) by the *in situ* partial carbonization in a single step [22,23]. This catalyst exhibited excellent catalytic properties by demonstrating its effectiveness for various transformations [24-30] due to its high thermal stability, reusability and strong acid sites of sulfonic acid functional groups.

In continuation of our ongoing research on the applications of the glycerol-based catalyst, we herein report a simple and highly efficient chemoselective method for the preparation of



Scheme 1

pentaerythritol diacetals by condensation of pentaerythritol with aromatic aldehydes (1:2 mmol) in toluene at 80 °C in quantitative yields. Deprotection of the prepared pentaerythritol diacetals was also obtained by changing the solvent medium to MeOH in the presence of the same catalyst at moderate temperature (Scheme 1).

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Sd. Fine or Merck Chemical companies and were used without further purification. All other reagents and solvents used were of analytical grade. All yields refer to isolated products after purification. Products were characterized by comparison with physical data with authentic samples and spectroscopic data (IR, NMR and EI-MS). IR Spectra were recorded on a Perkin Elmer (Model: Spectrum BX) FT-IR spectrophotometer by KBr pellet method. The NMR spectra were recorded on a Varian 300, Palo Alto, USA spectrometer at 300 MHz in CDCl₃ at 25 °C; using Me₄Si (TMS) as an internal standard. EI-Mass spectra were recorded on a Waters (Micromass-Quatromicro electron spray ionization) LC-MS system. Melting points were uncorrected.

2.2. Glycerol-based sulfonic acid functionalized carbon catalyst [22,30]

A mixture of glycerol (10 g) and concentrated sulphuric acid (30 g) was heated from ambient temperature to 220 °C for 20 min, to facilitate *in situ* partial carbonization and sulfonation. The reaction mixture was allowed to remain at that temperature for about 20 min (until foaming ceased) to obtain solid carbon material and was cooled to ambient temperature and washed with hot water until the wash water becomes neutral to pH. The partially crystalline product was filtered and dried in an oven at 120 °C for 2 h until it was moisture free to obtain the carbon acid catalyst in ~56% yield (5.40 g).

2.3. General procedure for the synthesis of pentaerythritol diacetal derivatives

A mixture of aldehyde (2 eq), 2,2-bis (hydroxymethyl) propane-1,3-diol (PE, 1 eq.) and carbon acid catalyst (5 wt% of PE) in toluene (10 mL) was stirred at 80 °C. The progress of the reaction was monitored by TLC (hexane:ethyl acetate, 7:3, v:v). After completion of the reaction, the catalyst was filtered and crude product was isolated by distillation of toluene and was purified by recrystallization with EtOH. The recovered catalyst was washed with MeOH and acetone and dried for reuse. All the products were characterized by FT-IR, ¹H NMR, EI-MS and comparison of their melting point with literature values [6,9,11,14].

3,9-Diphenyl-2,4,8,10-tetraoxaspiro[5.5]undecane (Table 1, entry 1): FT-IR (KBr, v, cm⁻¹): 2940, 2853, 1451, 1384, 1334, 1203, 1160, 1075, 1016, 970, 928, 745. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.66 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 3.82-3.87 (m, 4H, OCH₂-H_{ax}, H_{eq}), 4.87 (d, 2H, J = 11.5 Hz, OCH₂-H_{eq}), 5.46 (s, 2H, ArCH), 7.34-7.40 (m, 6H, ArH), 7.47-7.50 (m, 4H, ArH). EI-MS: *m/z* 312.

3,9-Bis(2-methoxyphenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Table 1, entry 2): FT-IR (KBr, v, cm⁻¹): 2948, 2851, 1610, 1514, 1452, 1382, 1248, 1155, 1035, 817. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.63 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 3.80-3.85 (m, 4H, OCH₂-H_{eq}), 3.81 (s, 6H, OCH₃), 4.84 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 5.42 (s, 2H, ArCH), 6.80-6.96 (m, 4H, ArH), 7.40-7.60 (m, 4H, ArH). MS (EI, *m/z*): 372.

3,9-Bis(4-methoxyphenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Table 1, entry 3): FT-IR (KBr, v, cm⁻¹): 2959, 2850, 1611, 1514, 1459, 1393, 1383, 1312, 1301, 1253, 1157, 1064, 1033, 823. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.63 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 3.80-3.85 (m, 4H, OCH₂-H_{eq}), 3.81 (s, 6H, OCH₃), 4.84 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 5.42 (s, 2H, ArCH), 6.90 (d, 4H, J = 8.5 Hz, ArH), 7.41 (d, 4H, J = 8.5 Hz, ArH). MS (EI, *m/z*): 372.

4,4'-(2,4,8,10-Tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2-methoxyphenol) (Table 1, entry 4): FT-IR (KBr, v, cm⁻¹): 2950, 2851, 1603, 1521, 1455, 1427, 1383, 1273, 1176, 1163, 1119, 1072, 1027, 963, 863, 816. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.64 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 3.80-3.85 (m, 4H, OCH₂-H_{eq}), 3.91 (s, 6H, OCH₃), 4.86 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 5.40 (s, 2H, ArCH), 5.70 (s, 2H, OH), 6.89-6.98 (m, 4H, ArH), 7.03 (s, 2H, ArH). MS (EI, *m/z*): 404.

3,9-Bis(2-chlorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Table 1, entry 5): FT-IR (KBr, v, cm⁻¹): 2989, 2900, 2848, 1599, 1576, 1442, 1397, 1286, 1243, 1202, 1160, 1073, 1049, 946, 754. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.7 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 3.81-3.88 (m, 4H, OCH₂-H_{eq}), 4.92 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 5.79 (s, 2H, ArCH), 7.28-7.71 (m, 8H, ArH). MS (EI, *m/z*): 380.

3,9-Bis(4-chlorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Table 1, entry 6): FT-IR (KBr, v, cm⁻¹): 2952, 2864, 1492, 1382, 1334, 1204, 1163, 1075, 1014, 819, 715, 683. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.64 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 3.80-3.85 (m, 4H, OCH₂-H_{eq}), 4.81 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 5.43 (s, 2H, ArCH), 7.34-7.43 (dd, 8H, J = 8.5 Hz, ArH). MS (EI, *m/z*): 380.

3,9-Bis(2,6-dichlorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Table 1, entry 7): FT-IR (KBr, v, cm⁻¹): 2908, 2832, 2849, 1565, 1584, 1438, 1402, 1272, 1247, 1203, 1163, 1099, 1067, 769, 728. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.63 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 3.80-3.85 (m, 4H, OCH₂-H_{eq}), 4.83 (d, 2H, J = 11.5 Hz, OCH₂-H_{ax}), 5.42 (s, 2H, ArCH), 6.90-7.50 (m, 6H, ArH). MS (EI, *m/z*): 449.

4,4'-(2,4,8,10-Tetraoxaspiro[5.5]undecane-3,9-diyl)diphenol (Table 1, entry 8): FT-IR (KBr, v, cm⁻¹): 3395, 2948, 2851, 1610, 1515, 1452, 1382, 1311, 1248, 1155, 1035, 817. ¹H NMR (300

Table 1. Preparation of pentaerythritol diacetals with aromatic aldehydes employing SO₃H-carbon catalyst at 80 °C

Entry	Aldehyde	Product ^a	Time (h)	Yield (%) ^b	M.p. [Lit. M. p.] (°C)
1			3.0	98	156-157 [158-159, 14]
2			6.0	95	154-155 [155, 9]
3			4.0	96	180-182 [182-183, 9]
4			4.0	95	170-172 [170-171, 6]
5			5.0	94	140-142 [141-142, 14]
6			1.5	95	198-200 [198-199, 9]
7			4.5	94	176-179
8			4.5	95	169-170 [170-171, 11]
9			2.5	94	162-164 [164-165, 14]
10			2.0	96	185-186 [185, 9,14]
11			8.5	95	189-190 [188-189, 6]

^a All the compounds were characterized by their melting points, IR and ¹H NMR spectra by comparing their data reported in the literature.

^b Isolated yield.

MHz, CDCl₃, δ, ppm): 3.61 (d, 2H, *J* = 11.5 Hz, OCH₂-H_{ax}), 3.81-3.85 (m, 4H, OCH₂-H_{eq}), 4.83 (d, 2H, *J* = 11.5 Hz, OCH₂-H_{ax}), 5.42 (s, 2H, ArCH), 6.90-7.60 (m, 8H, ArH). MS (EI, *m/z*): 344.

3,9-Bis(2-nitrophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Table 1, entry 9): FT-IR (KBr, *v*, cm⁻¹): 2955, 2887, 1580, 1456, 1396, 1256, 1208, 1166, 1080, 1016, 837, 783. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.62 (d, 2H, *J* = 11.5 Hz, OCH₂-H_{ax}), 3.79-3.84 (m, 4H, OCH₂-H_{eq}), 4.80 (d, 2H, *J* = 11.5 Hz, OCH₂-H_{ax}), 5.41 (s, 2H, ArCH), 7.10-7.80 (m, 8H, ArH). MS (EI, *m/z*): 402.

3,9-Bis(3-nitrophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Table 1, entry 10): FT-IR (KBr, *v*, cm⁻¹): 2955, 2887, 1609, 1581, 1456, 1396, 1208, 1080, 1016, 913, 783, 670. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.62 (d, 2H, *J* = 11.5 Hz, OCH₂-H_{ax}), 3.79-3.84 (m, 4H, OCH₂-H_{eq}), 4.80 (d, 2H, *J* = 11.5 Hz, OCH₂-H_{ax}), 5.41 (s, 2H, ArCH), 7.03-7.80 (m, 8H, ArH). MS (EI, *m/z*): 402.

3,9-Distyryl-2,4,8,10-tetraoxaspiro[5.5]undecane (Table 1, entry 11): FT-IR (KBr, *v*, cm⁻¹): 3013, 2936, 2961, 2860, 1614, 1587, 1518, 1460, 1382, 1251, 1172, 1039, 991, 970, 831, 732, 690. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.63 (d, 2H, *J* = 11.5 Hz, OCH₂-H_{ax}), 3.80-3.84 (m, 4H, OCH₂-H_{eq}), 4.82 (d, 2H, *J* = 11.5 Hz,


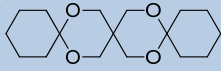
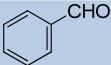
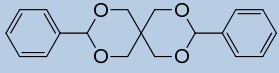
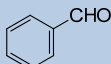
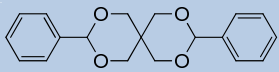
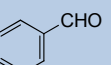
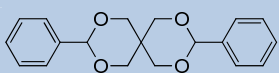
OCH₂-H_{ax}), 5.48 (s, 2H, ArCH), 6.34 (m, 2H, C-CH=), 7.30-7.80 (m, 12H, ArH and ArCH=). MS (EI, *m/z*): 364.

7,11,18,21-Tetraoxatrispiro[5.2.2.5.2.2]heneicosane (Table 2, entry 4): FT-IR (KBr, *v*, cm⁻¹): 2911, 2852, 1452, 1380, 1332, 1247, 1201, 1161, 1066, 1012, 931, 740, 718. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 1.39-1.75 (m, 20H, CH₂), 3.20-3.73 (s, 8H, OCH₂). MS (EI, *m/z*): 296.

3. Results and discussion

Acetalization of pentaerythritol (1 mmol) with benzaldehyde (2 mmol) was selected as model reaction to optimize the reaction parameters namely, reaction temperatures (60, 80, 90 and 100 °C) and the amount of catalyst (1, 2, 3, 4 and 5 wt% of PE). The best result was obtained by carrying out the reaction with 2:1 molar ratios of benzaldehyde and pentaerythritol, in the presence of 5 wt% g of SO₃H-carbon catalyst in toluene at 80 °C for 3 h. After the reaction, the mixture was cooled and the catalyst was separated by filtration.

Table 2. Chemoselective diacetalization of pentaerythritol with aromatic aldehydes in presence of aliphatic aldehydes and ketones using SO₃H-carbon catalyst at 80 °C.

Entry	R = Carbonyl (Aldehyde/Ketone)	Product ^a	M.p. [Lit. M.p.] (°C)
1	CH ₃ CHO	No reaction	-
2	C ₇ H ₁₅ CHO	No reaction	-
3	C ₉ H ₁₉ CHO	No reaction	-
4		 (98%) ^b	115-116 [114-115, 14]
5	C ₂ H ₅ COCH ₃	No reaction	-
6	C ₆ H ₅ COCH ₃	No reaction	-
7	C ₆ H ₅ CO C ₆ H ₅	No reaction	-
8	CH ₃ CO C ₆ H ₄ (OCH ₃)	No reaction	-
9	(CH ₃) ₂ CHCOCH ₃	No reaction	-
10	(CH ₃) ₂ CHCOCH(CH ₃) ₂	No reaction	-
11	CH ₃ CHO + 		156-157 [158-159, 14]
12	C ₂ H ₅ COCH ₃ + 		156-157 [158-159, 14]
13	CH ₃ COC ₆ H ₅ + 		156-157 [158-159, 14]

^a Compound was characterized by their melting point, IR and ¹H NMR spectra by comparing their data reported in the literature.

^b Isolated yield.

The crude product obtained was further recrystallized in hot EtOH to obtain pure product in 98% yield (Table 1, entry 1).

Using these optimized reaction conditions, the scope of the SO₃H-carbon catalyzed methodology was extended for a wide variety of substituted aromatic aldehydes (Table 1). Aromatic aldehydes with stronger electron-donor groups such as MeO and OH (Table 1, entries 2, 3, 4 and 8) showed to be less reactive and required longer reaction period to obtain the product in 95-96% yield. Electron-withdrawing substituents such as mono NO₂ and Cl derivatives of benzaldehyde (Table 1, entries 6, 9 and 10) enhanced the rate of acetal formation and gave the corresponding PE diacetals in 94-96% yields in 1.5, 2.5 and 2 h, respectively. In case of cinnamaldehyde, corresponding PE diacetal was obtained in 95% yield after 8.5 h (Table 1, entry 11). All these PE diacetal compounds have sharp melting points, since they are crystalline.

Aliphatic aldehydes did not show any reactivity for this reaction (Table 2, entries 1, 2 and 3) and among aliphatic and aromatic ketones (Table 2, entries 4-10) only cyclohexanone (Table 2, entry 4) was found to be reactive to obtain corresponding PE-diketetal in 96% yield in 6 h. To demonstrate the chemoselectivity of the SO₃H-carbon catalyst towards aromatic aldehydes, the PE condensation reaction was conducted with benzaldehyde in the presence of aliphatic aldehydes or aliphatic and aromatic ketones (Table 2, entries 11, 12 and 13). In all these cases, only the PE diacetal of benzaldehyde was obtained even after 48 h of reaction in toluene at 80 °C, thus demonstrating the catalyst selectivity towards aromatic aldehydes. This methodology here in pays a greener alternative route for the direct transformation of aromatic aldehydes into their respective PE diacetals in shorter reaction time with high selectivity and yield in contrast to conventional method.

The SO₃H-carbon catalyst was also found to be active for the deprotection of all the prepared PE diacetals in MeOH at reflux temperature (65 °C) with in 30 min. The catalyst is easily recoverable and recyclable. The recyclability experiments of the SO₃H-carbon catalyst were conducted by the acetalization of pentaerythritol (1 mmol) with benzaldehyde (2 mmol) in toluene at 80 °C as a test reaction. After completion of the reaction, the reaction mixture was allowed to cool and the

catalyst was recovered by simple filtration. The recovered catalyst was washed with MeOH and acetone, then dried and reused for the next cycle of reaction. The catalyst was used for five runs without significant loss of catalytic activity (Figure 1).

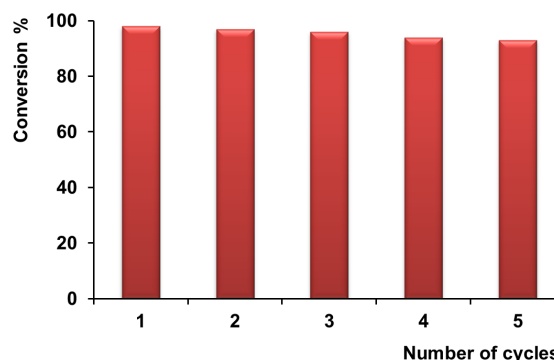


Figure 1. Recyclability of SO₃H-carbon catalyst.

4. Conclusion

In conclusion a simple and efficient chemoselective methodology was developed for the preparation of pentaerythritol diacetals with aromatic aldehydes in excellent yields by employing glycerol-based SO₃H-carbon solid acid catalyst. These reactions can be conveniently performed in atmospheric conditions in excellent yields. The salient features of the present methodology are: catalyst ability for deprotection of PE diacetals in methanol at moderate temperatures apart from its recyclability and easy recovery of product. Further investigations to expand the usage of this catalyst to more catalytic reactions are underway in our lab.

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