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RESEARCH ARTICLE

Protection of Carbonyl Compounds as Diacetals Using P_2O_5/SiO_2 and P_2O_5/Al_2O_3 as Catalysts

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Abstract: A new, efficient and environmentally benign protocol for the acetalization of carbonyl compounds as pentaerythritol diacetal and diketal derivatives catalyzed by P_2O_5/SiO_2 or P_2O_5/Al_2O_3 as an eco-friendly catalyst with high catalytic activity and reusability at 100 °C under solvent-free conditions in excellent yields and short reaction times is reported.

Keywords: Heterogeneous catalyst, P_2O_5/SiO_2, P_2O_5/Al_2O_3, Pentaerythritol, Diacetals, Diketals.

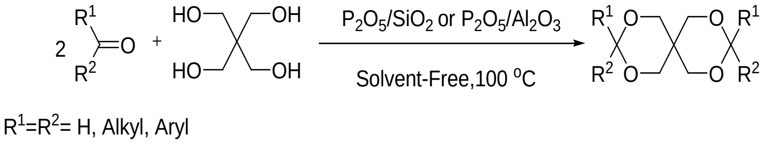
Introduction

When a chemical reaction is to be carried out selectively at one in a reactive site in a multifunctional compound, other reactive sites must be temporarily blocked. Diacetals can be used as a potential protective group for aldehydes and ketones and are important derivatives of carbonyl compounds since most of them are crystalline substances and have sharp melting points[1]. The role of acetals in the chemistry of carbohydrates makes them biologically important[2]. Acetals are used both as intermediates and as end products in the fragrance and pharmaceutical industries[3,4]. Pentaerythritol diacetals can be applied as plasticisers and vulcanisers of several of polymeric materials, as raw materials for production of valuable resins and lacquers, as physiologically active substances[5] and as defoamers in washing solutions containing anionic surfactants[6].

Several publications have described the preparation of diacetals pentaerythritol[7-14] that some of them use acidic catalyst like ZrO_2/S_2O_{82}- solid superacid[7], heteropoly acid $H_3PW_{12}O_{40}$[14], $InCl_3 \cdot 4H_2O$[10], SO_3H-functionalized ionic liquids[11] and Al-MCM-41[12] however; these methods have not been entirely satisfactory, owing to the problems of corrosion, long reaction time, tedious workup, use of toxic solvent such as toluene and benzene, non reusability and environmental polluting of catalysts.

Phosphorus pentoxide is a white, flammable, dangerous, corrosive to metal and extremely deliquescent compound[15a]. It reacts vigorously with water and water- containing substances, liberates much heat and may even cause fire[15]. P_2O_5 is difficult to handle due to moisture sensitivity. To escape from these disadvantages, the preparation of P_2O_5 on silica (P_2O_5/SiO_2) or alumina (P_2O_5/Al_2O_3) is straightforward. This supported compound could be removed from the reaction mixture by simple filtration[16].

In continuation of our ongoing interest in using heterogeneous catalysts in organic synthesis[17], we herein report application of P_2O_5/SiO_2 and P_2O_5/Al_2O_3 as a heterogeneous recoverable catalyst in acetalystion of carbonyl compounds as pentaerythritol diacetal and diketal derivatives (scheme 1).



Scheme 1

Experimental

All reagents were purchased from Merck and Sigma-Aldrich and used without further purification. P_2O_5/SiO_2 (w/w 7%)[16b] and P_2O_5/Al_2O_3 (w/w 50 %)[18] was prepared according to the reported procedure. All yields refer to isolated products after purification. Products were characterized by comparison physical data with authentic samples and spectroscopic data (IR and NMR). The NMR spectra were recorded on a Bruker Avance DPX 300 MHz instrument. The spectra were measured in DMSO relative to TMS (0.00 ppm). IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on Silica–gel polygram SILG/UV 254 plates.

General procedure for the synthesis of pentaerithrotol diacetal and diketal derivatives

A stirred mixture of pentaerythritol (1 mmol), aldehydes and ketones (2 mmol) and P_2O_5/SiO_2 (0.08 g, 7 w/w %) or P_2O_5/Al_2O_3 (0.12 g, 50 w/w %) was added and the reaction mixture was stirred for the indicated time (Table 3) at 100 °C under solvent free conditions. After completion of the reaction (monitored by TLC) the reaction mixture was cooled and dissolved in 5 mL of ethylacetate. Then, the mixture was filtered to remove P_2O_5/SiO_2 or P_2O_5/Al_2O_3. The catalyst was washed four times with ethylacetate (4×5 mL), and then recovered catalyst was dried in oven at 100 °C for 3 h. Finally the filtrate solution containing crude product was evaporated and recrystallised in ethanol. Some selected spectroscopic data for known products are given below:

Product 1: (Table 3, entry 10): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.35 (d, J = 8.0 Hz, 4H),7.20 (d, J = 8.0 Hz 4H), 5.38 (s, 2H), 4.40 (d, J = 11.0 Hz, 2H), 3.81-3.85 (m, 4H), 3.58 (d, J = 11.5 Hz, 2H), 2.40 (s, 6H) ppm; IR(KBr) ν: 2915, 2850, 1610, 1450, 1388, 1400, 1065, 810 cm^{-1}

Product 2: (Table 3, entry 18): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.59 (d, J =8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.5, 2H), 5.74 (s, 2H), 4.75 (d, J =11.4 Hz , 2H), 3.78-3.90 (m, 4H), 3.68 (d, J = 11.5, 2H) ppm; IR(KBr) ν: 2973, 2930, 2863, 1610, 1470, 1390, 1210, 1070, 960, 821, 757 cm^{-1}

Product 3: (Table 3, entry 5): ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.55–7.60 (m, 2H),7.24–7.30 (2H, m), 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) ppm; IR(KBr) ν: 2980, 2900, 2850, 1610, 1470, 1400, 1250, 1070, 1030, 760 cm^{-1}

Product 4: (Table 3, entry 19): ^{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) ppm; IR(KBr) ν: 2970, 2920, 2850, 1610, 1460, 1400, 250, 1070, 1040, 708 cm^1

Results and Discussion

In order to be able to carry out acetalization of carbonyl compounds derivatives in a more efficient way minimizing the time, temperature and amount of catalyst, the reaction of benzaldehyde (2 mmol), and pentaerythritol (1 mmol) was selected as model system to study the reaction at different reaction temperatures (60, 80, 90, 100, 110 and 120 ^oC) and the different amount of catalyst (0.05, 0.06, 0.08, 0.1, 0.12 g). The best result was obtained by carrying out the reaction with 2.0:1.0 molar ratios of benzaldehyde, and pentaerythritol, in the presence of 0.08 g of P_2O_5/SiO_2 and 0.12 g of P_2O_5/Al_2O_3 as catalysts at 100 ^oC under solvent-free conditions (Table 1, 2).

Table 1. Optimization temperature in the reaction of pentaerithritol and benzaldehyde in the presence of P_2O_5/SiO_2 (100 mg) or P_2O_5/Al_2O_3 (100 mg) as catalyst under solvent-free conditions at different temperatures

Entry	Temperature, ^oC	P_2O_5/SiO_2	P_2O_5/Al_2O_3
		Time, min/ Yield, %[a]	Time, min/ Yield, %[a]
1	60	45/55	55/78
2	80	30/74	43/84
3	90	20/89	38/85
4	100	14/91	35/90
5	110	12/88	34/87
6	120	13/87	34/86

[a] *Yields refer to the isolated pure products*

Table 2. Optimization the amount of P_2O_5/SiO_2 and P_2O_5/Al_2O_3 as the catalyst in the reaction of pentaerithrotol and benzaldehyde under solvent-free conditions at 100 ^oC

Entry	Temperature, ^oC	P_2O_5/SiO_2	P_2O_5/Al_2O_3
		Time, min/ Yield, %[a]	Time, min/ Yield, %[a]
1	60	25/87	65/78
2	80	8/95	50/79
3	90	8/90	40/89
4	100	7/91	35/90
5	120	7/89	20/93
6	130	8/88	19/91

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 3). Ketones show less reactivity than aldehydes for this reaction, for example dibenzalpentaerythritol (Table 3, entry1) was obtained in 95% and 93% yield in 10 and 20 min, whereas acetophenone (Table 3, entry 16) provided 85% and 82% yield of product in 14 and 22 min in the presence of P_2O_5/SiO_2 and P_2O_5/Al_2O_3 respectively. Aromatic aldehydes with stronger electron-donor groups such as methoxy and methyl (Table 3, 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 3, entries 2, 3, 11-14) reacted faster than the other aldehydes. Alkyl aldehydes are converted to their desired acetals such as aryl aldehydes in excellent yield. (Table 3, entries 6-9).

Table 3. Preparation of pentaerithritol diacetal and dicetal deravatives from the reaction of pentaerithritol and aldehyde or ketone (molar ratio: 1/2) catalyzed by A: P_2O_5/SiO_2 (80 mg), B: P_2O_5/Al_2O_3 (120 mg) under solvent free condition at 100 °C

Entry	Substrate	Time, min		Yield, % [a]		m.p.°C (Lit. M.p.)[Ref]
		A	B	A	B	
1	Benzaldehyde	8	20	95	93	155-158 (158-159) [11]
2	4-Chlorobenzaldehyde	5	10	95	91	198-200 (198-199)[8]
3	4-Nitrobenzaldehyde	4	8	91	89	225-227 (227-228)[8]
4	4-Methoxybenzaldehyde	10	20	90	88	180-182(182-183)[8]
5	2-Methoxybenzaldehyde	8	15	82	84	154-158 (155)[14]
6	Cyclohexanone	20	30	93	90	113-115 (114-115)[11]
7	Cycloheptanone	17	25	86	89	116-118(115-117)[7]
8	Butyraldehyde	5	10	89	92	45-47 (43-45)[11]
9	Heptanaldehyde	5	8	85	83	64-65(63-64)[8]
10	4-Methylbenzaldehyde	12	15	90	91	212-214 (212-213)[11]
11	3-Nitrobenzaldehyde	4	8	91	90	186-188(185-186)[8,14]
12	3-Chlorobenzaldehyde	5	11	90	89	122-124(121-122)[8]
13	2-Nitrobenzaldehyde	5	10	89	90	162-165(164-165)[8]
14	2-Chlorobenzaldehyde	6	8	90	89	140-143(141-142)[11]
15	4-Bromoacetophenones	10	21	95	88	160-163(161)[14]
16	Acetophenone	14	22	85	82	145-146(147-148)[9]
17	Benzophenone	15	25	87	89	160-161(162)[14]
18	2,4- Dichlorobenzaldehyde	4	8	97	90	185-188(186-187)[7]
19	4-Chloroacetophenone	10	20	90	88	171-173(172)[14]
20	4-Nitroacetophenone	15	25	87	89	72-74(70-71)[14]

[a] *Yields refer to the isolated pure products. The desired pure products were characterized by comparison of their physical data (melting points, IR, ^1H and ^{13}C NMR) with those of known compounds[7-14]. The reaction was carried out under thermal solvent-free conditions in an oil bath at 100 °C*

In order to show the accessibility of the present work in comparison with the reported results in the literature[7,8,11,14], we summarized some of the results for acetalizaton of carbonyl compounds in Table 4. As shown in Table 4, P_2O_5/SiO_2 or P_2O_5/Al_2O_3 can act as effective catalyst with respect to reaction times, amount of the catalyst, and yields of the obtained products. Thus, the present protocol with P_2O_5/SiO_2 and P_2O_5/Al_2O_3 catalysts is convincingly superior to the some reported catalytic methods (Table 4).

Table 4. Comparison results of P_2O_5/SiO_2 and P_2O_5/Al_2O_3 with $ZrO_2/S_2O_8^{-2}$[7], Tungstophosphoric acids in liquid phase[14], SO_3H-functionalized ionic liquids[11] and silica sulfate[8] for the preparation of pentaerythritol diacetals from the reaction of benzaldehyde with pentaerythritol

Entry	Catalyst	Conditions	Time, h	Yield, %[a]
1	$ZrO_2/S_2O_8^{-2}$(100 mg)	Toluene or benzene reflux	0.5	96
2	Tungstophosphoric acids in liquid phase (400 mg)	Toluene reflux	2	92
3	SO_3H-functionalized ionic liquids(IL [PSPy][OTf] 20 mmol)	100 °C	1.5	93
4	Silica Sulfate (100 mg)	Benzene microwave irradiation	0.5	96
5	P_2O_5/SiO_2(0.08 g, 7 w/w %)	Solvent-free100 °C	8 min	95
6	P_2O_5/Al_2O_3(0.12 g, 50 w/w %)	Solvent-free100 °C	20 min	93

[a] *Yields refer to the isolated pure products. Based on the reaction of benzaldehyde with pentaerythritol*

We also studied the reusability of the catalysts in the reaction of benzaldehyde, and pentaerythritol under solvent-free conditions at 100 ^{o}C. In this procedure, after completion of the reaction, the reaction mixture was cooled to room temperature and the crude solid was dissolved in ethylacetate. The mixture was filtered for separation of the catalysts. The catalyst was washed four times with (4×5 mL) ethylacetate. The recovered catalyst was dried in vacuum and was used as such for the subsequent catalytic runs. The recovered catalysts were reused five times without any loss of their activities (Figure I for catalyst A: P_2O_5/SiO_2, and figure II for catalyst B: P_2O_5/Al_2O_3).

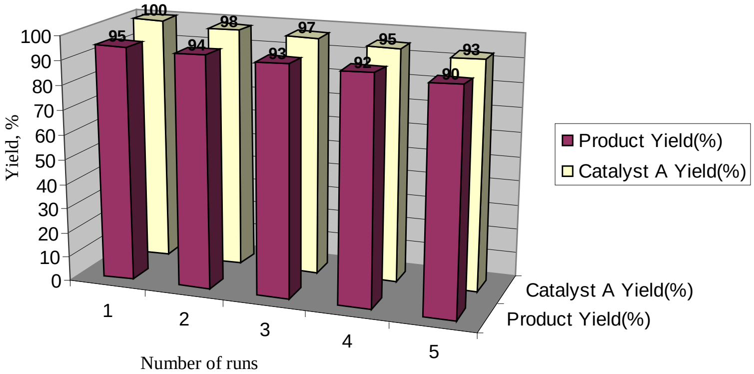


Figure 1

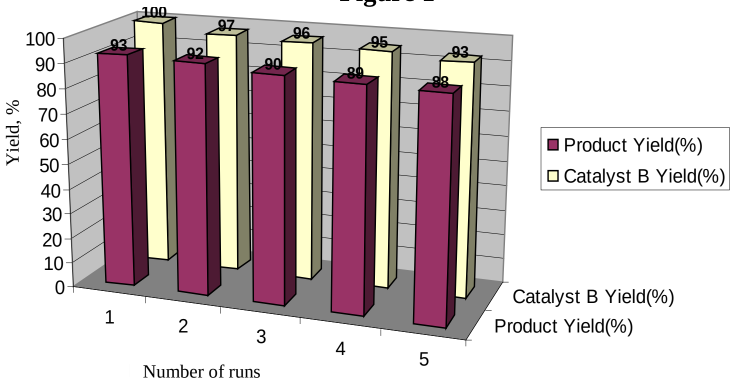


Figure 2

Conclusion

A new, efficient and environmentally benign protocol for the acetalization of carbonyl compounds as pentaerythritol diacetal and diketal derivatives catalyzed by P_2O_5/SiO_2 or P_2O_5/Al_2O_3 as an eco-friendly catalyst with high catalytic activity and reusability at 100 ^{o}C under solvent-free conditions in excellent yields and short reaction times is reported. This method offers significant advantages such as high conversion, clean work-up, short reaction times and simplicity in operation.

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