

Silica Gel-Supported Tungstosilicic Acid: An Efficient Catalyst for Synthesis of Diacetals

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An efficient and convenient method for synthesis of diacetals from aldehydes and ketones with pentaerythritol in refluxing benzene or toluene using silica gel-supported tungstosilicic acid as catalyst is described. This method provides several advantages such as neutral condition, high yields and environment friendly.

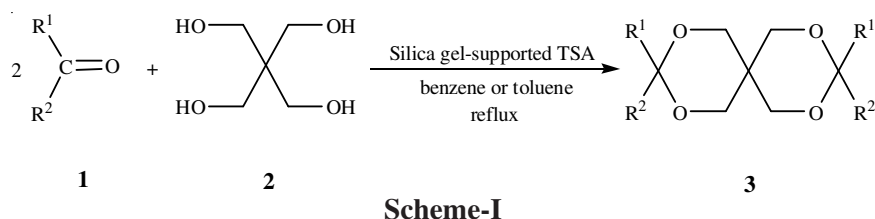
Key Words: Synthesis, Diacetals, Pentaerythritol, Aldehydes, Ketones, Tungstosilicic acid.

INTRODUCTION

Pentaerythritol diacetals are crystalline substances and have sharp melting points. They can be extensively used as plasticizers and vulcanizers of various polymeric materials, as raw materials for production of valuable resins and lacquers, as physiologically active substances and as defoamers for washing solution containing anionic surfactants¹. On the other hand, they can also be changed into originally maternal aldehydes and ketones. In general, the preparation of pentaerythritol diacetals catalyzed by acid has been reported. There are protic acids, such as hydrochloric acid², sulfonic acid³, *p*-toluenesulfonic acid⁴, polyphosphoric acid⁵ and Lewis acids, such as zinc chloride⁶. However, each of the above methods has its own merit, while some of these methods have not been satisfactory owing to such drawbacks as secondary reaction (oxidation, dehydration and etherification), corrosion of equipment, contaminant of environment, long reaction time, non-reprocessing, *etc.* Consequently, the catalyst of the environment friendly for synthesis of pentaerythritol diacetals under mild condition are demanded. More recently, montmorillonite⁷, expansive graphite⁸ and silica sulfate⁹ have been used as catalysts to accelerate the condensation of pentaerythritol with aldehydes and ketones to obtain improved results.

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Tungstosilicic acid (TSA) is a kind of type of heteropoly acids (HPA). In recent years, heteropoly acids have been proven to be a practical and useful catalyst in a variety of organic reactions¹⁰⁻¹⁹. Heteropoly acids is superior to common inorganic acids for its high reactivity, ease of handling, low cost, inodorous, non-volatile and excellent stability. This prompted us to investigate their use in the synthesis of pentaerythritol diacetals from aldehydes and ketones with pentaerythritol. The work-up of the reactions is very simple, usually only removal of the catalyst by filtration and evaporation of the solvent are involved. Herein, a general and practical route for the condensation of pentaerythritol with aldehydes and ketones in the presence of silica gel-supported TSA is reported (**Scheme-I**).



EXPERIMENTAL

Melting points are determined in open capillaries and uncorrected. IR spectra were recorded on a Bio-Rad FTS-40 spectrometer (KBr). ¹H NMR spectra were measured on a Bruker Avance 400 (400 MHz) spectrometer using TMS as internal reference and CDCl₃ as solvent. Elemental analyses were determined using Heraeus (CHN, Rapid) elemental analyzer. The products were also characterized by comparison of their melting points with literature values.

Preparation of catalyst: 10 g of Tungstosilicic acid (TSA) is dissolved in 50 mL of diethyl ether and 10 g of silica gel is added to the solution. After the mixture is stirred for 1 h, then evaporate the solvent under reduced pressure. The mixture is dried at 105 °C for 2 h and finally stored in a desiccator until use.

Typical experimental procedure: A mixture of carbonyl compound **1** (2.00 mmol), pentaerythritol (**2**) (1.20 mmol) and silica gel-supported TSA (300 mg) in benzene or toluene (10 mL) was stirred at refluxing temperature for 0.6-5.0 h. The progress of the reaction was monitored with TLC. After completion of the reaction, the mixture was cooled, the catalyst was filtered off and washed by CH₂Cl₂ (2 × 5 mL). Evaporation of the solvent under reduced pressure afforded the crude product. The crude product was purified by column chromatography on silica gel light petroleum-diethyl ether as eluent or recrystallized to give diacetals **3** yield. Spectral data of some of the products are given below:

3a: IR (KBr, ν_{\max} , cm^{-1}): 2958, 2930, 2870, 1162, 1078, 992, 726. ^1H NMR (CDCl_3): δ = 0.91 [t, 6 H, J = 6.4 Hz, $2 \times (\text{CH}_3)$], 1.20-1.70 [m, 8H, $2 \times (\text{CH}_2)_2$], 3.25-3.70 (m, 6H, H_{eq} , H_{ax}), 4.42 [t, 2H, $2 \times (\text{CH})$], 4.64 (d, 2H, J = 11.4 Hz, H_{eq}) ppm. Anal. (%) calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_4$: C 68.55, H 8.63; found: C 68.61, H 8.58.

3b: IR (KBr, ν_{\max} , cm^{-1}): 2954, 2930, 2854, 1471, 1384, 1160, 1114, 1031, 940. ^1H NMR (CDCl_3): δ = 0.88 [t, 6H, $2 \times (\text{CH}_3)$], 1.28-1.62 [m, 20H, $2 \times (\text{CH}_2)_5$], 3.20-4.54 [m, 10H, $(\text{OCH}_2)_4$, $2 \times (\text{CH})$] ppm. Anal. (%) calcd. for $\text{C}_{19}\text{H}_{36}\text{O}_4$: C 69.47, H 11.05; found C 69.51, H 11.01.

3c: IR (KBr, ν_{\max} , cm^{-1}): 3036, 2922, 2856, 1608, 1498, 1204, 1164, 1118, 1086, 1024, 750. ^1H NMR (CDCl_3): δ = 3.50-3.96 (m, 6H, H_{eq} , H_{ax}), 4.81 (d, 2H, J = 11.4 Hz, H_{eq}), 5.42 [s, 2H, $2 \times (\text{ArCH})$], 7.20-7.58 [m, 10H, $2 \times (\text{ArH}_5)$] ppm. Anal. (%) calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_4$: C 73.06, H 6.45; found: C 73.01, H 6.54.

3d: IR (KBr, ν_{\max} , cm^{-1}): 3012, 2860, 1602, 1462, 1391, 1048, 804. ^1H NMR (CDCl_3): δ = 2.34 [s, 6H, $2 \times (\text{CH}_3)$], 3.66 (d, 2H, J = 11.4 Hz, H_{ax}), 3.80-3.86 (m, 4H, H_{eq}), 4.58 (d, 2H, J = 11.4 Hz, H_{ax}), 5.41 [s, 2H, $2 \times (\text{ArCH})$], 7.19 [d, 4H, J = 8.0 Hz, $2 \times (3',5'\text{-ArH}_2)$], 7.37 [d, 4H, J = 8.0 Hz, $2 \times (2',6'\text{-ArH}_2)$] ppm. Anal. (%) calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_4$: C 74.09, H 7.11; found: C 74.04, H 7.14.

3g: IR (KBr, ν_{\max} , cm^{-1}): 3032, 2984, 2906, 1620, 1532, 1470, 1354, 1202, 1080, 1024, 714, 680. ^1H NMR (CDCl_3): δ = 3.72 (d, 2H, J = 11.4 Hz, H_{ax}), 3.86-3.92 (m, 4H, H_{eq}), 4.84 (d, 2H, J = 11.4 Hz, H_{ax}), 5.54 [s, 2H, $2 \times (\text{ArCH})$], 7.50-8.38 (m, 8H, ArH) ppm. Anal. (%) calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_8$: C 56.72, H 4.51, N 6.96; found: C 56.77, H 4.42, N 7.02.

3h: IR (KBr, ν_{\max} , cm^{-1}): 3030, 2982, 2904, 1620, 1532, 1472, 1356, 1200, 1078, 1004, 710, 678. ^1H NMR (CDCl_3): δ = 3.68 (d, 2H, J = 11.4 Hz, H_{ax}), 3.82-3.92 (m, 4H, H_{eq}), 4.82 (d, 2H, J = 11.4 Hz, H_{ax}), 5.56 [s, 2H, $2 \times (\text{ArCH})$], 7.52-8.38 (m, 8H, ArH) ppm. Anal. (%) calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_8$: C 56.72, H 4.51, N 6.96; found: C 56.79, H 4.43, N 7.05.

3j: IR (KBr, ν_{\max} , cm^{-1}): 3028, 2858, 1576, 1480, 1382, 1076, 964, 704. ^1H NMR (CDCl_3): δ = 3.65 (d, 2H, J = 11.4 Hz, H_{ax}), 3.83 (d, 4H, J = 11.4 Hz, H_{eq}), 4.84 (d, 2H, J = 11.4 Hz, H_{ax}), 5.42 [s, 2H, $2 \times (\text{ArCH})$], 7.30-7.38 [m, 6H, $2 \times (4',5',6'\text{-ArH}_3)$], 7.50 [s, 2H, $2 \times (2'\text{-ArH})$] ppm. Anal. (%) calcd. for $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{O}_4$: C 59.86, H 4.76; found: C 59.91, H 4.72.

3k: IR (KBr, ν_{\max} , cm^{-1}): 3028, 2940, 1614, 1534, 1349, 1204, 1072, 1014, 752, 700. ^1H NMR (CDCl_3): δ = 3.70 (d, 2H, J = 11.4 Hz, H_{ax}), 3.86-3.94 (m, 4H, H_{eq}), 4.80 (d, 2H, J = 11.4 Hz, H_{ax}), 5.52 [s, 2H, $2 \times (\text{ArCH})$], 8.06-8.42 (m, 8H, ArH) ppm. Anal. (%) calcd. for $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{O}_4$: C 59.86, H 4.76; found: C 59.93, H 4.68.

3l: IR (KBr, ν_{\max} , cm^{-1}): 2977, 2934, 2867, 1600, 1472, 1387, 1211, 1083, 955, 822, 759. ^1H NMR (CDCl_3): δ = 3.71 (d, 2H, J = 11.6 Hz, H_{ax}),

3.84-3.92 (m, 4H, H_{eq}), 4.88 (d, 2H, $J = 11.2$ Hz, H_{ax}), 5.78 [s, 2H, 2 × (ArCH)], 7.31 [d, 2H, $J = 8.4$ Hz, 2 × (6'-ArH)], 7.41 [d, 2H, $J = 8.4$ Hz, 2 × (5'-ArH)], 7.65 [d, 2H, $J = 8.4$ Hz, 2 × (3'-ArH)] ppm. Anal. (%) calcd. for C₁₉H₁₆Cl₄O₄: C 50.70, H 3.58; found: C 50.73, H 3.62.

3p: IR (KBr, ν_{\max} , cm⁻¹): 2972, 2864, 1470, 1382, 1162, 1074. ¹H NMR (CDCl₃): $\delta = 0.88$ [t, 6H, 2 × (CH₂)₅CH₃], 1.28 [m, 16H, 2 × (CH₂)₄], 1.36 [s, 6H, 2 × (CH₃)], 1.68 [t, 4H, $J = 8.0$ Hz, 2 × (CH₂)], 3.71-3.88 [m, 8H, (CH₂O)₄] ppm. Anal. (%) calcd. for C₂₁H₄₀O₄: C 70.74, H 11.31; found: C 70.78, H 11.27.

3q: IR (KBr, ν_{\max} , cm⁻¹): 2933, 2855, 1450, 1255, 1162, 1100, 1044, 922, 844. ¹H NMR (CDCl₃): $\delta = 1.53$ -1.58 [m, 8H, 2 × (3,4-C₅H₄)], 1.73-1.75 [m, 8H, 2 × (2,5-C₅H₄)], 3.75-3.87 [s, 8H, (CH₂O)₄] ppm. Anal. (%) calcd. for C₁₅H₂₄O₄: C 67.14, H 9.01; found: C 67.21, H 9.07.

3s: IR (KBr, ν_{\max} , cm⁻¹): 3030, 2900, 1470, 1380, 1250, 1175, 890, 704. ¹H NMR (CDCl₃): $\delta = 1.50$ [s, 6H, 2 × (CH₃)₂], 3.15 (dd, 2H, $J = 11.4$ Hz, $J = 2.4$ Hz, 2 × H_{eq}), 3.25 (d, 2H, $J = 11.4$ Hz, 2 × H_{ax}), 3.63 (d, 2H, $J = 11.4$ Hz, 2 × H_{ax}), 4.47 (dd, 2H, $J = 11.4$ Hz, $J = 2.4$ Hz, 2 × H_{eq}), 7.31-7.42 [10H, m, 2 × (ArH₅)] ppm. Anal. (%) calcd. for C₂₁H₂₄O₄: C 74.09, H 7.11; found: C 74.14, H 7.06.

3t: IR (KBr, ν_{\max} , cm⁻¹): 3030, 2854, 1600, 1482, 1074, 750, 704. ¹H NMR (CDCl₃): $\delta = 2.88$ [s, 8H, 2 × (ArCH₂)₂], 3.58 [s, 8H, (CH₂O)₄], 7.14-7.34 [m, 20H, 2 × (ArH₅)₂]. Anal. (%) calcd. for C₃₅H₃₆O₄: C 80.74, H 6.97; found: C 80.68, H 7.04.

The diacetals have two rigid hexatomic rings, on which there are five kinds of hydrogen that have different magnetic dipole moments, we take H_{eq} to represent the equatorial hydrogen, H_{ax} to axial hydrogen.

RESULTS AND DISCUSSION

When several aldehydes or ketones **1** and pentaerythritol (**2**) were heated in refluxing benzene or toluene in the present of silica gel-supported tungstosilicic acid (TSA) to give the corresponding diacetals **3** in good to excellent yields. The results are summarized in Table-1.

From Table-1, it is observed that the reaction rate is markedly dependent on temperature. The reaction proceeded in refluxing toluene gives better results and needs shorter reaction time than benzene. For instance, complete conversion of 2,4-dichlorobenzaldehyde (**11**) with pentaerythritol (**2**) into the corresponding diacetal needed 0.6 h in refluxing toluene in 96 % yield, but 1 h in refluxing benzene in 94 % yield under catalysis of silica gel-supported TSA.

It is also observed that ketones show less reactivity than aldehydes for this reaction, for example, pentaerythritol diacetal (**3i**) was obtained with quantitative yield 97 % in refluxing toluene for 0.8 h whereas acetophenone

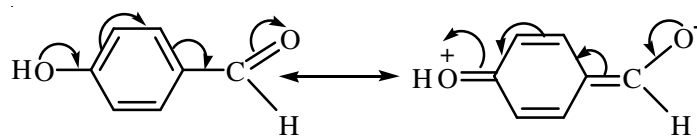
TABLE-1
SYNTHESIS OF PENTAERYTHRITOL DIACETALS
CATALYZED BY SILICA GEL-SUPPORTED TSA

Entry	Substrate	Solvent	Time (h)	Yield (%) [†]	m.p. (°C)	
					Found [‡]	Reported [Ref. 4,7,8]
1	CH ₃ CH ₂ CH ₂ CHO 1a	Benzene	1.5	90	42-44	43-44
2	CH ₃ (CH ₂) ₅ CHO 1b	Benzene	1.5	88	62-64	62-63
3	C ₆ H ₅ CHO 1c	Toluene	0.8	90	154-156	155-156
		Benzene	1.0	88		
4	4-MeC ₆ H ₄ CHO 1d	Toluene	1.5	87	210-212	211-213
		Benzene	2.0	84		
5	4-MeOC ₆ H ₄ CHO 1e	Toluene	1.5	85	182-183	182-184
		Benzene	2.0	83		
6	3,4-(OCH ₂ O)C ₆ H ₃ CHO 1f	Toluene	1.5	85	187-189	188
		Benzene	2.5	83		
7	2-NO ₂ C ₆ H ₄ CHO 1g	Toluene	0.8	95	163-165	163-164
		Benzene	1.2	92		
8	3-NO ₂ C ₆ H ₄ CHO 1h	Toluene	0.8	96	185-187	185
		Benzene	1.0	93		
9	4-NO ₂ C ₆ H ₄ CHO 1i	Toluene	0.8	97	225-227	227-228
		Benzene	1.0	94		
10	3-ClC ₆ H ₄ CHO 1j	Toluene	0.8	94	121-123	121-122
		Benzene	1.0	91		
11	4-ClC ₆ H ₄ CHO 1k	Toluene	0.8	95	198-200	197-198
		Benzene	1.0	93		
12	2,4-Cl ₂ C ₆ H ₃ CHO 1l	Toluene	0.6	96	186-188	186-187
		Benzene	1.0	94		
13	C ₆ H ₅ CH=CHCHO 1m	Toluene	1.5	90	188-190	188-189
		Benzene	2.0	86		
14	4-HOC ₆ H ₄ CHO 1n	Toluene	4.0	74	168-170	170-171
15	4-Me ₂ NC ₆ H ₄ CHO 1o	Toluene	4.0	78	222-225	222-224
16	CH ₃ CO(CH ₂) ₅ CH ₃ 1p	Toluene	3.0	82	43-45	44-45
17	Cyclopentanone 1q	Toluene	4.0	84	116-118	115-117
18	Cyclohexanone 1r	Toluene	4.0	83	112-113	113-114
19	C ₆ H ₅ COCH ₃ 1s	Toluene	5.0	78	147-148	147-148
20	(C ₆ H ₅ CH ₂) ₂ CO 1t	Toluene	5.0	80	166-168	166-167

[†]Yield refer to isolated products; [‡]After recrystallization.

diacetal (**3s**) in 78 % yield in refluxing toluene for 5 h in presence of silica gel-supported TSA.

It is worth noting that when 4-hydroxybenzaldehyde or 4-dimethylaminobenzaldehyde was treated with pentaerythritol to give in moderate yield (74 and 78 %) under the same conditions. The explanation for this result may be due to the strong electron donating hydroxy group and dimethylamino group in (**1n** and **1o**) which will reduce the reactivity. A degree of tautomerization may occur in (**1n** and **1o**) with formation of quinoid structure and thus decreased reactivity of the aldehyde group (**Scheme-II**).



Scheme-II

The catalyst were easily regenerated washing with dichloromethane and diethyl ether, followed in adessiccator drying at room temperature for 4 h. The catalyst could be reused five times for the synthesis of pentaerythritol diacetal **3i** without significant loss of activity.

In conclusion, an efficient and convenient method for the preparation of pentaerythritol diacetals catalyzed by silica gel-supported TSA in refluxing benzene or toluene is described. For this method have operational simplicity, higher yield, shorter reaction time, non-corrosive, non-polluting and employing a reusable catalyst.

ACKNOWLEDGEMENTS

This project was supported by the National Natural Science Foundation of China, Educational Ministry of China, Educational Department of Hebei Province, Science and Technology Commission of Hebei Province (2006000969).

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(Received: 19 March 2007; Accepted: 5 April 2008) AJC-6501