

Montmorillonite Clays Catalysis. Part 12.¹ An Efficient and Practical Procedure for Synthesis of Diacetals from 2,2-Bis(hydroxymethyl)propane- 1,3-diol with Carbonyl Compounds†

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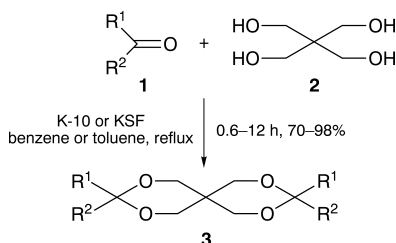
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Preparation of diacetals from 2,2-bis(hydroxymethyl)propane-1,3-diol with aldehydes and ketones is catalysed by montmorillonite clays in refluxing benzene or toluene in good to excellent yield.

Pentaerythritol acetals are applied as plasticizers and vulcanizers of various polymeric materials, as raw materials for production of valuable resins and lacquers, as physiologically active substances² and as defoamers for washing solution containing anionic surfactants.³ They can be used as potential protective groups for aldehydes and ketones as well as important derivatives of carbonyl compounds since most are crystalline substances and have sharp melting points. Several publications have described the preparation of pentaerythritol diacetals under acidic conditions.⁴ Protic acids (hydrochloric acid,⁵ sulfuric acid,^{3,6,7} and *p*-toluenesulfonic acid^{5,8,9}) and Lewis acids (zinc chloride,¹⁰ anhydrous copper sulfate¹¹) have been employed as catalysts. However, these methods have not been entirely satisfactory, owing to problems of corrosion, tedious work-up, environmental pollution and non-recoverable catalysts. Consequently, there is a demand for environmentally friendly acid catalysts to synthesize pentaerythritol diacetals under mild conditions. Cation exchanger KU-2² and 12-tungstophosphoric acid¹² have been used as catalysts for the condensation of 2,2-bis(hydroxymethyl)propane-1,3-diol with aldehydes and ketones. More recently, microwave irradiation was applied to accelerate this reaction.¹³

Clay minerals are known to catalyse a variety of organic reactions in which the catalyst acts as a solid Lewis acid or Brønsted acid.¹⁴ Recently, we have developed efficient and convenient procedures for preparation¹⁵ and cleavage¹⁶ of 1,3-dioxolanes catalysed by montmorillonite K-10. As a part of ongoing work on montmorillonite clay catalysis,¹⁷ we now describe a direct condensation of aldehydes and ketones with 2,2-bis(hydroxymethyl)propane-1,3-diol catalysed by montmorillonites K-10 and KSF.



Scheme 1

As summarized in Table 1, several aldehydes and ketones in the presence of montmorillonites K-10 or KSF were heated with 2,2-bis(hydroxymethyl)propane-1,3-diol in refluxing benzene or toluene, resulting in the corresponding

diacetals in good to excellent yields. K-10 worked better than KSF in terms of reaction time and yield. This may be due to it having a greater surface area (220–270 m² g^{−1}) than that of KSF (20–40 m² g^{−1}). The reaction proceeds cleanly and the work-up is simple, involving only filtration of the catalyst and removal of solvent to obtain the product in high purity.

The reaction rate is markedly dependent on temperature. The reaction proceeded much more slowly in refluxing benzene than in toluene. For example, complete conversion of 3-chlorobenzaldehyde (**1i**) into the corresponding diacetal (**3i**) needed 0.8 h in refluxing toluene, but 1.5 h in refluxing benzene under catalysis by montmorillonite K-10. Ketones show less reactivity than aldehydes for this reaction, for example dibenzal pentaerythritol (**3f**) was obtained in quantitative yield (98%) from refluxing benzene for 1 h whereas acetophenone (**1s**) provided 89% yield of product from refluxing toluene for 8 h in the presence of montmorillonite K-10. It is worth noting that when 4-hydroxybenzaldehyde (**1l**) and 4-(dimethylamino)benzaldehyde (**1n**) were treated with 2,2-bis(hydroxymethyl)propane-1,3-diol in the presence of K-10 the reactions took longer (> 8 h) even under refluxing in toluene. The explanation, we propose, is that the strong donor groups hydroxy and dimethylamino reduce the reactivity.

The catalysts are easily regenerated by washing with ethanol followed by drying at 120 °C for 4 h. The catalyst could be reused three times for the synthesis of pentaerythritol diacetal **3f** without significant loss of activity.

In conclusion, the present procedure appears to be efficient for aldehydes and ketones. The operational simplicity, use of inexpensive, non-corrosive and reusable catalysts and high yields can make it a useful and attractive alternative to the currently available methods.

Experimental

Melting points are uncorrected. ¹H NMR spectra were determined on a Varian VXR-300 S (300 MHz) spectrometer using CDCl₃ as solvent and tetramethylsilane (TMS) as internal reference, IR spectra on a FTS-40 spectrometer. Montmorillonite K-10 and KSF were purchased from Aldrich and dried at 120 °C for 2 h prior to use.

General Procedure for Preparation of Diacetals.—A mixture of carbonyl compound (**1**, 3.00 mmol), 2,2-bis(hydroxymethyl)propane-1,3-diol (**2**, 1.80 mmol) and montmorillonite K-10 or KSF (300 mg) in benzene or toluene (20 ml) was stirred at refluxing temperature for 0.6–12 h (Table 1) using a Dean–Stark apparatus for water removal. The progress of the reaction was monitored by TLC. After cooling, the catalyst was filtered off and washed with CH₂Cl₂ (5 ml × 2). Evaporation of the solvent under reduced pressure afforded the crude product. This was purified by column chromatography on silica gel [light petroleum (bp 60–90 °C)–dichloromethane as eluent] or recrystallised to give diacetals **3**, yield 70–98% (Table 1).

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Table 1 Preparation of diacetals catalysed by montmorillonite clays

Substrate	Catalyst	Solvent	<i>t</i> /h	Yield (%) ^a	mp(°C)	
					Found	Reported
<i>n</i> -C ₆ H ₁₃ CHO (1a)	K-10	Benzene	1	93	62–63	63 ⁶
<i>n</i> -C ₉ H ₁₉ CHO (1b)	K-10	Benzene	1	95	75–76	77–78 ¹³
4-MeC ₆ H ₄ CHO (1c)	KSF	Benzene	3	93		
	K-10	Benzene	1	92	211–213	
4-MeOC ₆ H ₄ CHO (1d)	KSF	Benzene	5	88		
	K-10	Benzene	1.5	90	182–184	177 ⁶
3,4-(OCH ₂ O)C ₆ H ₃ CHO (1e)	KSF	Benzene	6	85		
	K-10	Benzene	1.5	92	192–193	188 ⁶
C ₆ H ₅ CHO (1f)	K-10	Benzene	0.6	98	155–156	155–156 ¹³
	KSF	Benzene	2.5	93		
2-O ₂ NC ₆ H ₄ CHO (1g)	K-10	Benzene	2.5	93	164–165	163–164 ¹³
3-O ₂ NC ₆ H ₄ CHO (1h)	K-10	Toluene	1	92	185–186	185 ⁶
3-ClC ₆ H ₄ CHO (1i)	K-10	Benzene	1.5	95	121–122	
	K-10	Toluene	0.8	94		
4-ClC ₆ H ₄ CHO (1j)	K-10	Benzene	2	92	200–201	197–198 ¹³
2-HOC ₆ H ₄ CHO (1k)	K-10	Benzene	3	90	160–161	
	K-10	Toluene	1.5	91		
4-HOC ₆ H ₄ CHO (1l)	K-10	Toluene	10	70 ^b	110–112	109–110 ¹³
3-MeO-4-HOC ₆ H ₃ CHO (1m)	K-10	Benzene	2.5	95	170–171	
4-Me ₂ NC ₆ H ₄ CHO (1n)	K-10	Benzene	6	89 ^b	222–224	223 ¹⁸
	K-10	Toluene	8	94		
<i>E</i> -C ₆ H ₅ CH=CHCHO (1o)	K-10	Benzene	3	93	188–189	195 ⁶
2-Furaldehyde (1p)	K-10	Benzene	3	89	159–160	158–159 ¹³
	KSF	Benzene	7	87		
Cyclohexanone (1q)	K-10	Toluene	3	90	113–114	112–113 ⁷
	KSF	Toluene	6	89		
CH ₃ (CH ₂) ₅ COCH ₃ (1r)	K-10	Toluene	4	90	44–45	
C ₆ H ₅ COCH ₃ (1s)	K-10	Toluene	8	89	147–148	
(C ₆ H ₅ CH ₂) ₂ CO (1t)	K-10	Toluene	8	91	166–167	
(C ₆ H ₅) ₂ CO (1u)	K-10	Toluene	12	97 ^b	163–164	

^aYield refers to isolated pure products. ^bNet yield, conversion rate of **1l** = 33%; conversion rate of **1n** = 43%; conversion rate of **1u** = 79%.

Selected spectral data.—For **3c**: $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2910, 2862, 1600, 1460, 1390, 1050, 805; δ_{H} 2.346 (6 H, s, 2 × CH₃), 3.638 (2 H, d, *J* 11.7, 2 × H_{ax}), 3.789–3.848 (4 H, m, 4 × H_{eq}), 4.583 (2 H, d, *J* 11.7, 2 × H_{ax}), 5.424 (2 H, s, 2 × Ar CH), 7.181 (4 H, d, *J* 8.0, 2 × 3',5' Ar H), 7.370 (4 H, d, *J* 8.0 Hz, 2 × 2',6' Ar H). For **3i**: $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2986, 2856, 1577, 1479, 1381, 1074, 966, 702; δ_{H} 3.656 (2 H, d, *J* 11.4, 2 × H_{ax}), 3.840 (4 H, d, *J* 11.4, 4 × H_{eq}), 4.829 (2 H, d, *J* 11.4 Hz, 2 × H_{ax}), 5.432 (2 H, s, 2 × Ar CH), 7.307–7.381 (6 H, m, Ar H), 7.503 (2 H, s, 2 × 2' Ar H). For **3k**: $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3400, 2860, 2362, 1600, 1500, 1080, 780; δ_{H} 3.703 (2 H, d, *J* 11.8, 2 × H_{ax}), 3.879–3.927 (4 H, m, 4 × H_{eq}), 4.847 (2 H, d, *J* 11.8 Hz, 2 × H_{ax}), 5.655 (2 H, s, 2 × Ar CH), 6.872–7.284 (8 H, m, Ar H), 7.565 (2 H, br s, 2 × OH). For **3m**: $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3407, 2858, 1604, 1522, 1383, 1163, 1075, 1027, 864, 780; δ_{H} 3.650 (2 H, d, *J* 11.5, 2 × H_{ax}), 3.795–3.863 (4 H, m, 4 × H_{eq}), 3.916 (6 H, s, 2 × OCH₃), 4.868 (2 H, d, *J* 11.5, 2 × H_{ax}), 5.402 (2 H, s, 2 × Ar CH), 5.667 (2 H, br s, 2 × OH), 6.910 (2 H, d, *J* 8.2, 2 × 5' Ar H), 6.970 (2 H, dd, *J* 8.2, 1.5, 2 × 6' Ar H), 7.033 (2 H, s, 2 × 2' Ar H). For **3r**: $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2970, 2865, 1470, 1380, 1160, 1075; δ_{H} 0.880 [6 H, t, *J* 6.5, 2 × (CH₂)₅CH₃], 1.28 (16 H, m, 8 × CH₂), 1.353 (6 H, s, 2 × CH₃), 1.662 (4 H, t, *J* 7.9 Hz, 2 × CH₂), 3.712–3.881 (8 H, m, 4 × CH₂O). For **3s**: $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2980, 2900, 1470, 1380, 1250, 1175, 890, 704; δ_{H} 1.502 (6 H, s, 2 × CH₃), 3.150 (2 H, dd, *J* 11.1, 2.4, 2 × H_{eq}), 3.248 (2 H, d, *J* 11.1, 2 × H_{ax}), 3.631 (2 H, d, *J* 11.7, 2 × H_{ax}), 4.474 (2 H, dd, *J* 11.7, 2.4 Hz, 2 × H_{eq}), 7.313–7.425 (10 H, m, Ph H). For **3t**: $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2990, 2855, 1600, 1480, 1075, 750, 702; δ_{H} 2.878 (8 H, s, 4 × PhCH₂), 3.589 (8 H, s, 4 × CH₂O), 7.142–7.322 (20 H, m, Ph H). For **3u**: $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 2960, 2860, 1610, 1500, 1450, 1100, 780; δ_{H} 3.879 (8 H, s, 4 × CH₂O), 7.256–7.503 (20 H, m, Ph H).

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