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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Synthesis Of Diacetals By Condensation Of Carbonyl Compounds With Bis(Hydrox Ymethyl)-1,3-Propanediol Catalysed By Expansive Graphite

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To cite this article: Tong-Shou Jin, Tong-Shuang Li, Zhan-Hui Zhang & Yan-Jun Yuan (1999) Synthesis Of Diacetals By Condensation Of Carbonyl Compounds With Bis(Hydrox Ymethyl)-1,3-Propanediol Catalysed By Expansive Graphite, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 29:9, 1601-1606, DOI: <u>10.1080/00397919908086141</u>

To link to this article: http://dx.doi.org/10.1080/00397919908086141

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SYNTHESIS OF DIACETALS BY CONDENSATION OF CARBONYL COMPOUNDS WITH BIS(HYDROXYMETHYL)-1,3-PROPANEDIOL CATALYSED BY EXPANSIVE GRAPHITE

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Abstract: Synthesis of diacetals from 2,2-bis(hydroxymethyl)-1,3-propanediol with aldehydes and ketones under catalysis of expansive graphite in refluxing benzene or toluene in good to excellent yield has been described.

2,2-Bis(hydroxymethyl)-1,3-propanediol acetals (3) can be used as potential protective groups for aldehydes and ketones as well as important derivatives of carbonyl compounds since most of them are crystalline substances and have sharp melting points.¹ Several publications have described the synthesis of 3 under acidic conditions.¹⁻¹³

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Expansive graphite has been used as efficient catalysts for a number of organic reactions.¹⁴⁻¹⁷ Herein we wish to report a mild and efficient procedure for synthesis of diacetals by condensation of aldehydes and ketones with 2,2-bis(hydroxymethyl)-1,3-propanediol under catalysis of expansive graphite.

As shown in Table 1, several aldehydes or ketones in the presence of expansive graphite were heated with 2,2-bis(hydroxymethyl)-1,3-propanediol in refluxing benzene or toluene, resulting in the corresponding diacetals in good to excellent yields except for benzophenone (1r, no reaction).

The reaction rate is markedly dependent on temperature. We found that the reaction proceeded much slower in refluxing benzene than in toluene. For example, complete conversion 3-chlorobenzalyde (1f) to the corresponding diacetal (3f) needed 0.8 h in refluxing toluene whereas needed 1.5 h in refluxing benzene under catalysis of expansive graphite. Ketones show less reactivity than aldehydes for this reaction, for example, dibenzalpentaerythritol (3b) was obtained in refluxing benzene for 1.5 h in quantitative yield (99%) whereas conversion rate of acetophenone (1q) was only 79% even in refluxing toluene for 8 h in the presence of expansive graphite. Benzophenone (1r) failed to give the corresponding diacetal and the starting materials were quantitatively recovered. It is worth noting that when 4-hydroxybenzaldehyde (1k) and 4-(dimethylamino)-benzaldehyde (1m) were treated with 2,2-bis(hydroxymethyl)-1,3-propanediol in the presence of expansive graphite, the reactions needed longer time even the reaction mixtures were refluxed in toluene. The explanation for this result, we

Aldehyde or ketones	Solvent	T/h	Yield(%) ^a	Mp(°C)	
				Found	Reported
n-C ₆ H ₁₃ CHO (1a)	Benzene	0.7	97	62-63	63 ⁶
C ₆ H ₅ CHO (1b)	Benzene	1.5	99	155-156	155-156 ¹³
$4-\text{MeC}_{6}\text{H}_{4}\text{CHO}(1c)$	Benzene	1.5	97	212-213	211-213 ¹
$4-MeOC_6H_4$ CHO(1d)	Benzene	1.8	96	182-183	1776
3,4-(OCH ₂ O)-	Benzene	2	95	192-193	1886
C ₆ H ₃ CHO(1e)					
3-ClC ₆ H ₄ CHO(1f)	Benzene	1.5	97	121-122	121-122 ¹
	Toluene	0.8	97		
$4\text{-}\mathrm{ClC}_{6}\mathrm{H}_{4}\mathrm{CHO}\left(\mathbf{1g}\right)$	Benzene	2	95	196-197	197-198 ¹³
$2-O_2NC_6H_4CHO(1h)$	Benzene	2.5	97	165-166	163-164 ¹³
3-O ₂ NC ₆ H ₄ CHO (1i)	Benzene	2.5	90	185-186	1856
2-HOC ₆ H ₄ CHO(1 j)	Benzene	3	91	160-161	160-161 ¹
$4-\text{HOC}_6\text{H}_4(1\text{k})$	Toluene	5	72*	109-110	109-110 ¹³
3-MeO-4-HOC ₆ H ₃ CHO(11)	Benzene	2.5	95	170-171.5	170-171 ¹
$4-Me_2NC_6H_4CHO(1m)$	Benzene	8	87*	223-224	223 ¹⁸
	Toluene	8	93		
2-Furaldehyde(1n)	Benzene	2	93	158-159	158-159 ¹³
Cyclohexanone(10)	Toluene	8	94 ^{<i>b</i>}	113-114	112-1137
(C ₆ H ₅ CH ₂)CO(1p)	Toluene	10	92	166-167	166-167 ¹
C ₆ H ₅ COCH ₃ (1q)	Toluene	8	92 ^{<i>b</i>}	145-146	147-148 ¹
$(C_{6}H_{5})_{2}CO(1r)$	Toluene	8	0°		

 Table 1
 Synthesis of diacetals catalysed by expansive graphite

^aIsolated yield. ^bNet yield, conversation rate of 1k = 48%, 1m = 64%, 10 = 89%, 1q = 79%. ^c100% of 1r was recovered.

proposed, should be that strong donor groups of hydroxy and dimethylamino reduce the reactivity.

The catalysts are easily regenerated by washing with dichloromethane and followed by drying at 100 °C for 1 h. The catalyst could be reused three times for the synthesis pentaerythritol diacetal **3b** without significant loss of activity.

In conclusion, we have provided a convenient method for the preparation of 2,2-Bis(hydroxymethyl)-1,3-propanediol diacetals catalysed by expansive graphite. This procedure appears to be efficient for aldehydes, aliphatic ketones and monoaryl ketones but not for diaryl ketones.

Experimental

The expansive graphite catalyst was prepared according to the literature.^{14,19} Melting points are uncorrected. ¹H NMR spectra were determined on a Varian VXR-300S spectrometer using CDCl₃ as solvent and tetramethylsilane (TMS) as internal reference. IR spectra were obtained on a Perkin-Elmer 983G spectrometer. The products were also characterised by comparison of their melting with literature values.

Representative experimental procedure for the preparation of diacetals 3:

A mixture of *p*-tolualdehyde (1c, 2.00 mmol), 2,2-bis(hydroxymethyl)-3propanediol, (2, 1.25 mmol) and expansive graphite (30 mg) in benzene (10 ml) was stirred at refluxing temperature for 1.5 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 removed by filtration and washed with CH₂Cl₂ (5 ml × 2). Evaporation of the solvent under reduced pressure to provide crude product. The crude product was purified by silica gel column chromatography (petroleum-dichloromethane as eluent) to afford 3c in 97% yield. mp 212-213 °C (colourless needles from ethanol-dichloromethane); v_{max} : 2910, 2862, 1600, 1460, 1390, 1050, 805; $\delta_{\rm H}$: 2.346 (6H, s, 2 x CH₃), 3.638 (2H, d, J 11.7 Hz, 2 x H_{ax}), 3.789-3.848 (4H, m, 4 x H_{eq}), 4.853 (2H, d, J 11.7 Hz, 2 x H_{ax}), 5.424 (2H, s, 2 x ArCH), 7.181 (4H, d, J 8.0 Hz, 2 x 3',5'-Ar-H), 7.370 (4H, d, J 8.0 Hz, 2 x 2',6'-Ar-H).

Acknowledgements: The project was supported by NSFC, Natural Science Foundation of Hebei Province(297065) and Science and Technology Commission of Hebei Province.

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Accepted 19 September 1998