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Montmorillonite KSF clay as novel and recyclable heterogeneous solid acid for the conversion of D-glycals into furan diol

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Abstract

A simple, efficient and environmentally benign protocol has been developed for the conversion of glycals into 2-(D-glycero-1,2-dihydroxy ethyl) furan derivatives using montmorillonite KSF as inexpensive and environmentally benign solid acid to afford excellent yields with high selectivity.

Keywords: Glucal; Montmorillonite KSF; Furan diol

Furan diol is an important chiral building block for the synthesis of biologically active Proxy authorization required natural products [1]. Among various methods for the synthesis of these compounds, the acid catalyzed transformation of D-glucal to furan diol is versatile [2] due to its simplicity, milder reaction conditions and easy availability of glucals. The conversion of D-glucal to furan diols was first reported by Gonzalez et al. using a catalyst made of toxic mercuric salt ($HgSO_4$) and concentrated sulfuric acid [3]. Later on less toxic $Pd(OAc)_2$ or $RuCl_2(PPh_3)_3$ have been used for the same transformation [4]. Recently, $InCl_3{\cdot}H_2O$ is also found to effect this transformation [5]. However, most of these procedures involve the use of strongly acidic and toxic reagents in stoichiometric amounts and the yields and selectivities reported are far from satisfactory. Therefore, the use of inexpensive and environmentally safe solid acids would extend the scope of this transformation. Recently, the use of solid acidic catalysts like clays, zeolites and ion-exchange resins has received much research interest in different areas of organic synthesis because of their environmental compatibility, reusability, greater selectivity, non-corrosiveness, low cost and ease of handling [6]. Particularly, the clay catalysts make the reaction process more convenient, economic and environmentally benign and act as both Bronsted and Lewis acids in their natural and ion-exchanged forms enabling them to function as efficient catalysts for various transformations [7].

In continuation of our interest on the use of solid acids as catalysts [8], we report herein a simple and efficient protocol for the synthesis of optically active furan diol from D-glucal using montmorillonite KSF clay as promoter (Scheme 1).

Thus, treatment of D-glucal **1** with montmorillonite KSF clay in acetonitrile afforded 2-(D-glycero-1,2-dihydroxy ethyl) furan **2** in 85% yield. The reaction proceeded smoothly at ambient temperature with high selectivity. Similarly, D-galactal also reacted well to give the same furan diol **2** in 78% yield in a short reaction time. Among the solvents, acetonitrile appears to give the best results. We have examined the catalytic activity of various Lewis acids, such as $CeCl_3{\cdot}7H_2O$, $Mn(OAc)_3{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ and the results are presented in the Table 1. Among these catalysts, $FeCl_3{\cdot}6H_2O$ was found to be more effective in terms of yields and reaction times, but it could not be recovered and reused. The mechanism is envisaged to proceed through the addition of water on glucal followed by opening of pyranose ring, subsequent cyclization and dehydration results in the formation of furan diol. The catalyst was recovered by simple filteration and the recovered catalyst was reused for three times without

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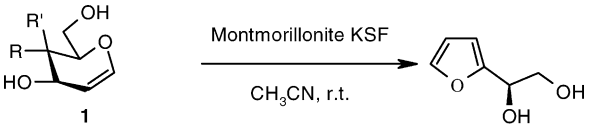
Table 1
Conversion of D-glucal into furan diol[a]

Entry	D-Glycal	Catalyst	Reaction conditions			Yield[b] (%)
			Solvent	Temperature (°C)	Time (h)	
a	D-Glucal	(stoichiometric) $CeCl_3 \cdot 7H_2O$	CH_3CN	80	5.0	65
b	D-Glucal	20% $Mn(OAc)_3 \cdot 4H_2O$	AcOH	27	8.0	80
c	D-Glucal	10% $FeCl_3 \cdot 6H_2O$	CH_3CN	27	1.0	87
d	D-Glucal	15% $Yb(OTf)_3 \cdot H_2O$	CH_3CN	80	3.5	68
e	D-Glucal	KSF clay	CH_3CN	27	5.0	85
f	D-Galactal	KSF clay	CH_3CN	27	7.5	78
g	D-Galactal	10% $FeCl_3 \cdot 6H_2O$	CH_3CN	27	1.5	81

[a] The reactions were carried out with 2 mmol scale.
[b] Yield refers to pure products after column chromatography.



1
R = OH, R' = H, glucal
R = H, R' = OH, galactal

2

Scheme 1.

any significant decrease in activity after being washed with methanol and activated at 120 °C. Thus, the use of reusable solid acid makes this method quite simple, more convenient and economically viable.

In summary, we have developed a mild and efficient protocol for the synthesis of furan diol from glucal using montmorillonite clay as inexpensive and environmentally friendly solid acid. The method offers several advantages, such as high conversions, operational simplicity, great selectivity, low cost and recyclability of the catalyst which makes it useful and attractive strategy for the conversion of glycals into furan diols.

1. Experimental procedure

A mixture of D-glucal or D-galactal (2 mmol) and montmorillonite KSF (1.0 g) in acetonitrile (10 mL) was stirred at room temperature for the appropriate time (Table 1). After completion of the reaction as indicated by the TLC, the catalyst was recovered by filtration. The resulting filtrate was concentrated in vacuo, and purified by column chromatography on silica gel (Merck, 100–200 mesh; ethyl acetate–hexane, 2:8) to afford pure furan diol as colourless oil. $[\alpha]_D^{27} = +36.45$ ($C = 1.2$, $CHCl_3$) Lit[3], +38.0 ($C = 3.3$, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.50 (brs, OH), 3.05 (brs, OH), 3.80 (d, 2H, $J = 5.7$ Hz), 4.78 (t, 1H, $J = 5.5$ Hz), 6.38 (m, 2H), 7.40 (m, 1H). IR (KBr): ν 3550, 3421, 2934, 1593, 1487, 1370, 1140, 1071, 930. EIMS: m/z: 128 M^+, 110, 97, 81, 69, 53, 40.

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