Metal-catalyzed transformation of D-glucal to optically active furan diol

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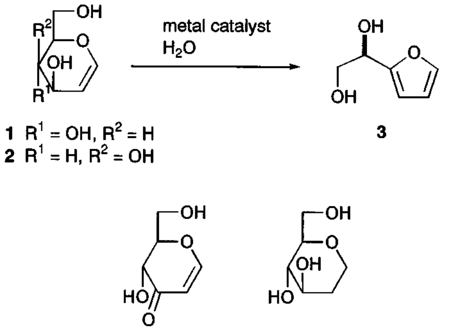
The treatment of D-glucal with a catalytic amount of $Sm(OTf)_3$ or $RuCl_2(PPh_3)_3$ in the presence of 1 equiv. of H_2O afforded optically active furan diol in good yield under mild conditions.

In 1975, Gonzales and co-workers reported the conversion of 3,4,6-tri-*O*-acetyl-D-glucal into 4,6-di-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-erythro-*trans*-hex-2-enose in the presence of mercuric sulfate in 1,4-dioxane–sulfuric acid solution.[1,2] This mercuric ion-assisted acid glycal opening reacton has been applied to hexose and pentose derivatives to obtain acyclic α,β-unsaturated aldehydes. They also reported that the reaction of unprotected D-glucal under the same mercuric ion-assisted acidic conditions afforded optically active furan diol, 2-(D-*glycero*-1,2-dihydroxyethyl)furan. These transformations are very useful to obtain chiral building blocks, however, these reactions require acidic conditions. Therefore, the use of mild and neutral conditions to accomplish these transformations would be desirable, Here we report metal ion-catalyzed furan diol synthesis from D-glucal under mild conditions.

We recently reported the oxidation of the allylic alcohol moiety in D-glucal **1** by the aid of a catalytic amount of palladium complexes, which leads to the efficient synthesis of 1,5-anhydrohex-1-en-3-uloses.[3] During this study, we found that when the reactions were carried out in water, the formation of optically active furan diol **3** was observed (44% yield). The reaction in MeCN in the presence of water resulted in the formation of a mixture of furan diol **3**, oxidation product **4** and hydrogenated product **5**. These results promoted us to examine this transformation in detail. After examining several systems for the efficient conversion of **1** to furan diol **3**, we found that $RuCl_2(PPh_3)_3$ and $Sm(OTf)_3$ worked effectively to convert D-glucal to furan diol (Scheme 1). Some of the results obtained are summarized in Table 1. The treatment of D-glucal with 5–10 mol% of $RuCl_2(PPh_3)_3$ in the presence of 1 equiv. of H_2O afforded optically active furan diol in 64–70% yield. In the case of the reaction without H_2O, very slow dehydrogenation–hydrogenation to form **4** and **5** occured. Some rare-earth metal triflates also proved to be effective. Among the rare-earth metal triflates we examined, $Sm(OTf)_3$ exhibited the highest activity. The treatment of D-galactal **2** with 5 mol% of $Sm(OTf)_3$ afforded furan diol **3** with the same configuration. The reaction probably proceeds *via* nucleophilic attack of H_2O on glucal. Then opening of pyranose ring followed by cyclization to a five-membered ring and dehydration furnished the furan ring.



Scheme 1

A typical procedure is as follows: D-Glucal (204 mg, 0.356 mmol), MeCN (1.5 ml) and H_2O (0.03 ml) were placed under argon in an ampoule equipped with a magnetic stirring bar and a Young valve. After addition of $Sm(OTf)_3$ (44.8 mg, 0.07 mmol), the mixture was stirred for 40 min at 80 °C. The completion of the reaction was confirmed by TLC, then the mixture was poured into brine. Extracton with EtOAc (15 ml × 5) and concentration afforded the crude product, which was chromatographed on silica gel to give 2-(D-*glycerol*-1,2-dihydroxyethyl)furan **3** (131 mg, 70%) as a colorless oil {$[\alpha]_D$ +36.4 (*c* 1.2, $CHCl_3$) [lit.,[1] +38.0 (*c* 3.3, $CHCl_3$)]}.

The present method has the following advantages: (1) The reaction proceeds under neutral conditions, unlike the conventional mercuric ion-assisted acidic reaction; (2) highly toxic mercury can be replaced by less toxic metals; (3) operational simplicity—the direct derivatization of glycol to a protected species is possible.

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Table 1 The conversion of D-glycals to furan glycol[a]

Entry	Glycal	Catalyst (mol%)	Solvent	H_2O/equiv.	Conditions T/°C	t/min	Yield[b] (%)
1	**1**	$Pd(OAc)_2$ (5)	H_2O	—	80	30	44
2	**1**	$RuCl_2(PPh_3)_3$ (5)	C_6H_6	1	100	165	64
3	**1**	$RuCl_2(PPh_3)_3$ (10)	CH_2=CHOAc	1	100	45	70
4	**1**	$Sm(OTf)_3$ (5)	MeCN	1	80	40	70
5	**2**	$Sm(OTf)_3$ (5)	MeCN	1	80	50	60
6	**1**	$Yb(OTf)_3$, (5)	MeCN	1	80	50	51

[a] All reactions were carried out under argon atmosphere. [b] Isolated yield after silica gel column chromatography.

Notes and references

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