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A mild, efficient and α-selective glycosidation by using potassium dodecatungstocobaltate trihydrate as catalyst

Ezzat Rafiee, Shahram Tangestaninejad,* Mohammad H. Habibi and Valiollah Mirkhani

Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran

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Abstract—Treatment of tri-*O*-acetyl-D-glucal† **1** with several alcohols in the presence of catalytic amount of POM ($K_5CoW_{12}O_{40}\cdot 3H_2O$) as a heterogeneous, reusable, efficient and environmentally benign catalyst under neutral conditions and ambient temperature gave the corresponding 2,3-unsaturated glycopyranosides in excellent yields, with good anomeric selectivity. This catalyst proved to be not efficient for phenols.

1. Introduction

The stereoselective O-glycosidation of glycals is one of the most important and straight-forward methods for the preparation of glycosides, which are utilized for the biologically active substances and the substrates for synthesis of medicines such as antibiotics.[1] Among glycosides the 2,3-unsaturated glycosides[2] has a unique place and importance in carbohydrate chemistry since this unsaturation can be further functionalized. Significantly, as well as participation in simple addition reaction across the glucal double bond, the presence of a good leaving group at C-3 facilitate S_N2' reactions allowing for the introduction of a wide variety of nucleophiles at C-1 of the sugar nucleus with concomitant migration of the double bond.[3] Lewis acid-catalyzed allylic rearrangement of glycols is well known as the Ferrier reaction[4] and widely employed to obtain the 2,3-unsaturated glycosides. Different reagents such as, boron trifluride-ether,[4a,b,5] tin(IV) chloride,[6] clay catalyst montmorillonite K-10,[7] DDQ,[8] $BiCl_3$[9] and *N*-iodosuccinimide[10] have been introduced for the Ferrier rearrangement under mild conditions. Fraser-Reid et al. announced an oxidative alternative to this rearrangement by using 3-*O*-pentenoyl glycols and iodonium dicollidinium perchlorate under mild conditions.[11] Recently, the ability of several Lewis acid catalysts; $LiClO_4$, $LiBF_4$, $BF_3\cdot Et_2O$, $SnCl_4$, $InCl_3$, $TaCl_5$ and $LnCl_3$ was also examined for the Ferrier rearrangement of 3,4,6-tri-*O*-acetyl D-glucal with selected alcohols; the best result was achieved using $InCl_3$.[12] Therefore, the introduction of new effective and environmentally friendly glycosidation method have attracted considerable attention in current synthetic organic chemistry related to both biomolecules and functional materials.[13,4f]

The successful applications of $K_5CoW_{12}O_{40}\cdot 3H_2O$ as electron transfer[14] catalyst for a wide variety of organic transformations[15] prompted us to explore the potential of this polyoxometale as catalyst for glycosidation reaction.

2. Results and discussion

Since, $K_5CoW_{12}O_{40}\cdot 3H_2O$, behaved just like an electron transfer catalyst in the later cases,[14,15] we pursued the utilization of such POM's properties in glycosidation reaction. We first examined the glycosidation of **1** with benzyl alcohol in several solvents (Table 1, entries 1–4). Tri-*O*-acetyl-D-glucal (1.0 mmol) was treated with

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* Corresponding author. Tel.: +98-311-7932705; fax: +98-311-66897-32; e-mail: e.rafiee@sci.ui.ac.ir
† 3,4,6-Tri-*O*-acetyl-1,5-anhyro-2-deoxy-D-arabinahex-1-enitol.

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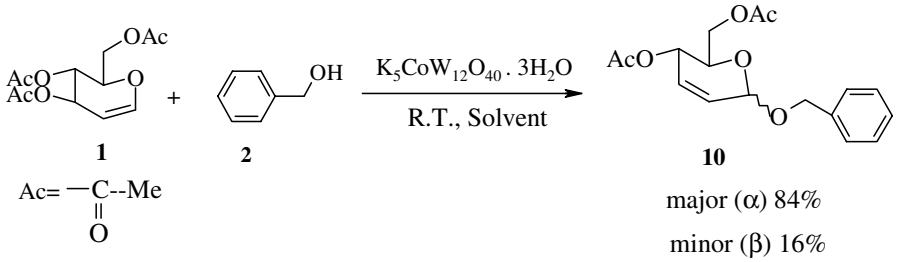
Table 1. Glycosidation of **1** with benzyl alcohol by $K_5CoW_{12}O_{40}{\cdot}3H_2O$

Entry	Solvent	POM (mol%)	*T* (min)	Yield (%)[a]
1	CH_2Cl_2	10	10	60
2	PhH	10	30	10
3	Et_2O	10	60	20
4	CH_3CN	10	10	95
5	CH_3CN	20	10	96
6	CH_3CN	5	30	80

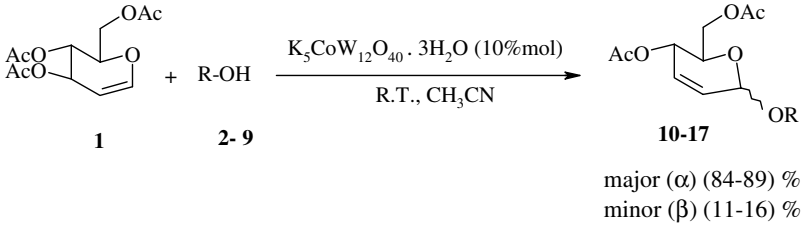
[a] Isolated yield after purification by column chromatography.

benzyl alcohol (1.5 mmol) and $K_5CoW_{12}O_{40}{\cdot}3H_2O$ (0.1 mmol) in CH_3CN, CH_2Cl_2, benzene or Et_2O at ambient temperature to give the benzyl 2,3-unsaturated glycopyranoside **10**. Acetonitrile was shown to be superior to the other solvents examined (Scheme 1). Next, we optimized the quantity of catalyst used in this reaction (Table 1, entries 4–6). The reaction was extended to other alcohols (**3**–**7**) under such conditions (Scheme 2).

As shown in Table 2, entries 1–6, these glycosidation reactions performed to afford the corresponding 2,3-unsaturated glycosides in excellent yields with the α-anomer as the major products. The orientation of the glycoside bond is α or β depends on some combination

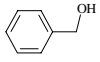
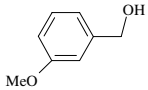
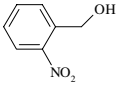
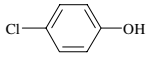
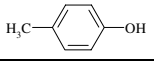


Scheme 1.

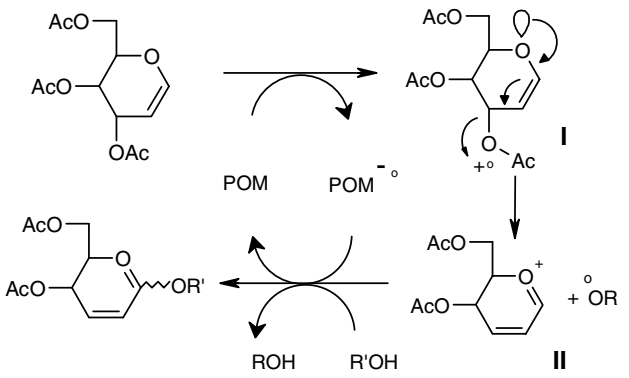


Scheme 2.

Table 2. Glycosidation of **1** with several alcohols and phenols by $K_5CoW_{12}O_{40}{\cdot}3H_2O$

Entry	R–OH (R =)		Product	Time	Yield (%)[a]	α:β[b]
1		**2**	10	10 (min)	95	6:1
2		**3**	11	48 (h)	93	9:1
3		**4**	12	1 (h)	95	7:1
4		**5**	13	12 (h)	90	9:1
5	CH_3–	**6**	14	10 (min)	95	6:1
6	C_2H_5–	**7**	15	15 (min)	95	6:1
7		**8**	—	24 (h)	0	—
8		**9**	—	24 (h)	0	—

[a] Isolated yield after purification by column chromatography and characterized by ^1H NMR.[2a,8,12,18]
[b] α:β Ratios were determined by ^1H NMR (200 MHz) spectroscopy.



Scheme 3.

of control elements, one presumed control element is commonly known as the 'kinetic anomeric effect'. There is a well-known thermodynamic effect ('the anomeric effect') in tetrahydropyrans, which favours axial linkage of electronegative functional groups to C-1. It is thus assumed that this thermodynamic 'anomeric effect' exerts its influence in the transition state for bond forming to the electrophilic C-1, hence axial (or α) bond formation. In fact, the axial preference for the incoming nucleophile may be better viewed as the general stereoelectronic effect that favours axial attack in any six-membered ring.[16]

The experimental results show that secondary alcohol (Table 2, entry 2) and benzylic alcohol with electron withdrawing substitution (Table 2, entry 4) a long reaction time was required to get a high yields. This catalyst is not efficient for phenols with different substitutions (Table 2, entries 7 and 8).

Mechanistically, since potassium dodecatungstocobaltate, $K_5CoW_{12}O_{40}{\cdot}3H_2O$, is apparently a perfect outer sphere one-electron oxidant due to the presence of a sheet of chemically inert oxygen atoms, which protect the central ion from undesired inner-sphere substitution reactions,[14] this glycosidation reaction probably proceeds via a one-electron transfer with the initial formation of the radical cation **I**[8a,17] and the allylic oxonium intermediate **II**[6a] as shown in Scheme 3. The possibility of a concerted electron transfer mechanism was strongly supported by a large decrease of the reaction rate upon addition of a small amount of acrilonitrile or 2,6-di-*tert*-butylphenol as a radical scavenger.

In addition, we have found that $K_5CoW_{12}O_{40}{\cdot}3H_2O$ can be reused several times without loss of activity by filtering the catalyst, washing with acetone, drying and immediately reusing. The yield of **10** promoted by recovered catalyst for four times reminded 90%.

3. Conclusion

To the best of our knowledge, this is the first report on POM mediated Ferrier rearrangements. The present methodology offers an efficient glycosidation of glucal by a cheap, recyclable with very easy work-up, relatively nontoxic and easily prepared catalyst, which performed the corresponding 2,3-unsaturated glycosides under neutral and catalytic conditions.

4. Experimental

4.1. Preparation of the catalyst

The synthesis of potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}{\cdot}3H_2O$) starts with the preparation of sodium tungstodicobalt(II)ate from cobaltous acetate (2.5 g, 0.01 mol) and sodium tungstate (19.8 g, 0.06 mol) in acetic acid and water at pH 6.5–7.5. The sodium salt is then converted to the potassium salt by treatment with potassium chloride (13 g).

Finally the cobalt(II) complex is oxidized to the cobalt(III) complex by potassium persulfate (10 g) in 40 mL of 2 M H_2SO_4. The crystals of $K_5CoW_{12}O_{40}{\cdot}20H_2O$ were dried at 200 °C, after recrystallization with methanol, potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}{\cdot}3H_2O$) was obtained.

4.2. Typical procedure for glycosidation of tri-*O*-acetyl-D-glucal with $K_5CoW_{12}O_{40}{\cdot}3H_2O$

To a solution of tri-*O*-acetyl-D-glucal **1** (1.0 mmol) and the alcohol (1.5 mmol) in acetonitrile (5 mL) was added $K_5CoW_{12}O_{40}{\cdot}3H_2O$ (0.1 mmol). The mixture was stirred for the appropriate time according to Table 1 at ambient temperature. The progress of the reaction was monitored by TLC. The reaction mixture was filtered and the filtrate was quenched with saturated $NaHCO_3$ (10%, 25 mL) and then extracted with dichloromethane (3 × 25 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated. The residue was purified by plate silica gel chromatography to afford the pure products. Products were characterized from their NMR spectral data.[2a,8,12,18]

Acknowledgements

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