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### Reactions of Various Nucleophiles with d-Glucal over Keggin-Type Heteropoly Compounds: A Simple, Rapid, and Expedient Method for the Synthesis of Pseudoglycals

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# Reactions of Various Nucleophiles with D-Glucal over Keggin-Type Heteropoly Compounds: A Simple, Rapid, and Expedient Method for the Synthesis of Pseudoglycals

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The reaction of benzyl alcohol with 3,4,6-tri-*O*-acetyl-D-glucal has been investigated with several heteropoly compounds, and the optimal catalyst is 12-tungstophosphoric acid supported on carbon. In the presence of this catalyst, various alcohols gave the corresponding alkyl and aryl 2,3-unsaturated glycopyranosides in excellent yields and good anomeric selectivity under solvent-free condition. 4,6-Di-*O*-acetyl-2,3-dideoxy- $\alpha$ -D-erythro-hex-2-enopyranosyl cyanide and ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-1-thio- $\alpha$ -D-erythro-hex-2-enopyranoside have also been prepared with trimethylsilyl cyanide and ethanethiol as nucleophiles, respectively. The catalyst could be easily recovered and reused several times with slight loss of activity. The selectivity to give  $\alpha$ -anomers predominantly did not show any change in all runs.

**Keywords** Ferrier rearrangement; Pseudoglycals; *C*-Glycosylations; Glycosides; Thio-glycosides

## INTRODUCTION

There are only a limited number of reports on the synthesis of pseudoglycals (hex-2-enoglycopyranosides), but it has an important place in the field of carbohydrate chemistry. These compounds can be further functionalized

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and serve as chiral intermediate<sup>[1,2]</sup> in the synthesis of glycopeptide building blocks,<sup>[3]</sup> uronic acids,<sup>[4]</sup> and modified carbohydrates and oligosaccharides.<sup>[5]</sup> 2,3-Dideoxy sugars, which are easily derived from hex-2-enoglycopyranosides, are common structural units in many medicinally significant molecules such as antibiotics.<sup>[6,7]</sup> For these reasons, preparation of 2,3-unsaturated glycosides is an interesting goal.

The acid-catalyzed allylic rearrangement of glycals in the presence of alcohols, known as Ferrier rearrangement,<sup>[8–11]</sup> is widely used to obtain 2,3-unsaturated glycosides. Besides, the synthetic utility of the Ferrier rearrangement is not limited to the preparation of unsaturated *O*-glycosides, since the variation of nucleophiles can result in *S*- and *C*-glycosides. The catalysts commonly employed to form 2,3-unsaturated glycosides are either Lewis acids or oxidizing agents.<sup>[12–21]</sup> In addition, the use of protic acid catalysts such as  $\text{HClO}_4/\text{SiO}_2$ <sup>[22]</sup> has also been reported for the preparation of these compounds. With a few exceptions, many of these procedures have limitations in terms of yields, selectivities, reaction temperatures, high amounts of reagent or catalyst, expensive reagent, and equipment. In addition, some catalysts are toxic, which restrict their applications. As a result, most of these methods do not satisfy the rule of green chemistry. The establishment of “Green Carbohydrate Chemistry” is of significant importance as a major branch of “Green Chemistry.” Therefore, progressive efforts have been done to introduce new environmentally benign catalysts or safe reaction media. This can be achieved by the development of strong solid acid catalysts that are stable, regenerable, and active at moderate temperatures.

Heteropoly acids (HPAs) are promising solid acid catalysts for various organic reactions.<sup>[23]</sup> Among them, the catalytic function of the Keggin family has attracted much attention. Keggin-type HPAs have the general formula  $\text{L}_{8-x}\text{XM}_{12}\text{O}_{40}$ , where L is a countercation (proton, group I and II metals, and transition metals); X is the heteroatom, also called the central atom ( $\text{P}^{5+}$ ,  $\text{Si}^{4+}$ , etc.); x is its oxidation state; and M is the addenda atom (most commonly  $\text{Mo}^{6+}$ ,  $\text{W}^{6+}$ , or  $\text{V}^{5+}$ ).<sup>[24]</sup> These compounds provide a good basis for the molecular design of mixed oxide catalysts and possess special characteristics that make them very useful in catalysis; for instance, their highly acidic nature is very interesting in industrial reactions.<sup>[25]</sup> In this context, we investigated glycosylation reaction using environmentally benign HPA-based catalysts.

## RESULTS AND DISCUSSION

As a part of our endeavor to develop a mild, rapid, and eco-friendly method for glycosylation reaction, the we explored the use of heteropoly compounds (HPCs) for Ferrier rearrangement. Successful uses of  $\text{K}_5\text{CoW}_{12}\text{O}_{40}\cdot 3\text{H}_2\text{O}$  as an electron transfer catalyst in the reaction of 3,4,6-tri-*O*-acetyl-D-glucal (**1**)

**Table 1:** Effect of different catalysts in the reaction of **1** with benzyl alcohol<sup>a</sup>

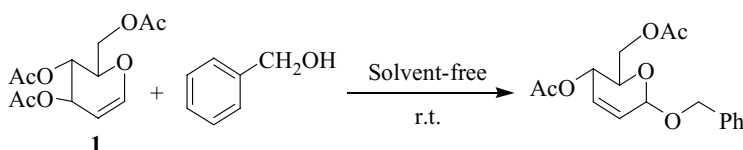
Entry	Catalyst	Time (min)	Yield (%) <sup>b</sup>
1	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	4	90
2	H <sub>5</sub> PMO <sub>10</sub> V <sub>2</sub> O <sub>40</sub>	20	41
3	H <sub>6</sub> PMO <sub>9</sub> V <sub>3</sub> O <sub>40</sub>	20	54
4	H <sub>7</sub> PMO <sub>8</sub> V <sub>4</sub> O <sub>40</sub>	20	32
5	K <sub>7</sub> (PTi <sub>2</sub> W <sub>10</sub> O <sub>40</sub> )	30	5
6	((n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N) <sub>5</sub> PMO <sub>2</sub> W <sub>9</sub> O <sub>39</sub> (Sn <sup>2+</sup> .H <sub>2</sub> O)	30	0
7	((n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N) <sub>3</sub> PMO <sub>2</sub> W <sub>9</sub> O <sub>39</sub> (Sn <sup>4+</sup> .H <sub>2</sub> O)	30	13
8	((n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N) <sub>3</sub> PMO <sub>2</sub> W <sub>9</sub> O <sub>39</sub> (Ti <sup>4+</sup> .H <sub>2</sub> O)	30	0
9	((t-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N) <sub>4</sub> PW <sub>11</sub> CoO <sub>39</sub>	30	0
10	CS <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	30	6

<sup>a</sup>Only  $\alpha$ -anomer was observed.

<sup>b</sup>Isolated yield after purification by column chromatography and characterized by <sup>1</sup>H NMR.

with various alcohols and aryl amines were previously studied in our laboratory.<sup>[26,27]</sup> However, these reactions were performed in CH<sub>3</sub>CN as solvent and have not been extended either with *S*- or *C*-nucleophiles. In this report, we describe our results on the interesting use of other HPCs as a catalyst for  $\alpha$ -selective synthesis of pseudoglycals in a solventless system.

Initially, catalytic performance of different HPAs, their salts, and transition metal-substituted heteropoly anions was investigated in model reaction (Sch. 1). The results are summarized in Table 1. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (PW) gave superior results in terms of yield and reaction time (Table 1, entry 1) while mixed-addenda HPAs had low activities (Table 1, entries 2–4). HPA salts and metal-substituted heteropoly anions showed poor or no catalytic activity in the reaction of **1** with benzyl alcohol (Table 1, entries 5–10).

**Scheme 1:** Reaction of **1** with benzyl alcohol.

From environmental and economic considerations, it is desirable to use HPAs as heterogeneous catalysts. This encouraged us to investigate the efficiency of PW/support as a catalyst in the reaction of **1** with benzyl alcohol (Sch. 2). The results are summarized in Table 2. It is assumed that resonance of the double bond increases the electron density of C3 and exerts its influence in the selective departure of the OAc group in this position. This resonance makes the allylic oxonium intermediate more stable.<sup>[19,21]</sup> In all cases,

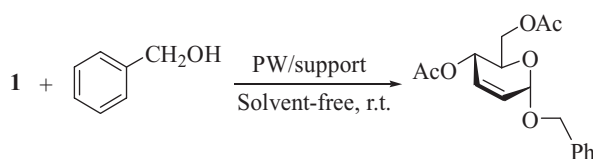
**Table 2:** Effect of different supported  $H_3PW_{12}O_{40}$  (PW) catalysts in glycosylation of benzyl alcohol<sup>a</sup>

Entry	Catalyst	Time (min)	Yield (%) <sup>b</sup>
1	PW/ $\gamma$ - $Al_2O_3$ (0.05 g)	60	11
2	PW/K10 (0.05 g)	30	32
3	PW/KSF (0.05 g)	30	41
4	PW/ $TiO_2$ (0.05 g)	15	43
5	PW/ $SiO_2$ (0.05 g)	10	91
6	PW/C (0.05 g)	5	96
7	PW/C (0.1 g)	3	96
8	PW/C (0.2 g)	2	96

<sup>a</sup>Only  $\alpha$ -anomer was observed.

<sup>b</sup>Isolated yield after purification by column chromatography and characterized by  $^1H$  NMR.

$\alpha$ -glycosides was exclusively produced. It was found that PW/C is the best catalyst in comparison with others (Table 2, entries 1–6). Different amounts of 40 wt.% of PW/C were used in the model reaction (Table 2, entries 6–8). It was observed that by using 0.2 g of the catalyst, reaction time decreased only 3 min in comparison with 0.05 g of PW/C. Hence, from an economical point of view, 0.05 g of 40 wt.% PW/C was selected as the best case for more investigations.

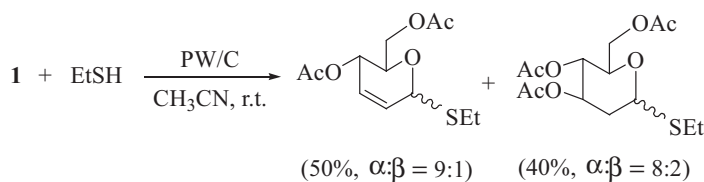
**Scheme 2:** Reaction of **1** with benzyl alcohol in the presence of supported PW.

To examine the universality of PW/C in glycosylation reaction, this catalyst was applied to the reaction of various nucleophiles with **1** in solvent-free condition (Table 3). With alcohols as nucleophile, the reactions were completed within less than 10 min, except for cyclohexanol (Table 3, entries 1–4). In the case of *p*-methoxyphenol (Table 3, entry 5), the reaction proceeded smoothly to afford *p*-methoxyphenyl-4,6-di-*O*-acetyl-2,3-dideoxy- $\alpha$ -D-erythro-hex-2-enopyranoside, whereas in our previous work,<sup>[26]</sup>  $K_5CoW_{12}O_{40} \cdot 3H_2O$  was not efficient for phenols with different substitutions.  $Me_3SiCN$  was rapidly reacted with **1** to obtain 4,6-di-*O*-acetyl-2,3-dideoxy- $\alpha$ -D-erythro-hex-2-enopyranosyl cyanide in excellent yield (Table 3, entry 6). When EtSH was used as nucleophile (Table 3, entry 7), in addition to Ferrier product (4,6-di-*O*-acetyl-2,3-dideoxy-1-thio-D-erythro-hex-2-enopyranoside), an anomeric mixture of ethyl 2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-D-hexopyranoside was also

**Table 3:** PW/C catalyzed the reaction **1** with various nucleophiles

Entry	Nucleophile	Product	Time (min)	Yield (%) <sup>a</sup>	$\alpha:\beta$ <sup>b</sup>	Ref.
1	C <sub>4</sub> H <sub>9</sub> OH		6	96	8:2	(28)
2			5	95	8:2	(28)
3			25	94	5:5	(28)
4			5	97	10:0	(29)
5			30	91	9:1	(14)
6	Me <sub>3</sub> SiCN		10	95	7:3	(30,31)
7 <sup>c</sup>	EtSH		30	50	9:1	(32)

<sup>a</sup>Isolated yield after purification by column chromatography and characterized by <sup>1</sup>H NMR.<sup>b</sup> $\alpha:\beta$  Ratios were determined by <sup>1</sup>H NMR spectroscopy.<sup>c</sup>This reaction was performed in CH<sub>3</sub>CN as solvent.



**Scheme 3:** Reaction of **1** with ethanethiol.

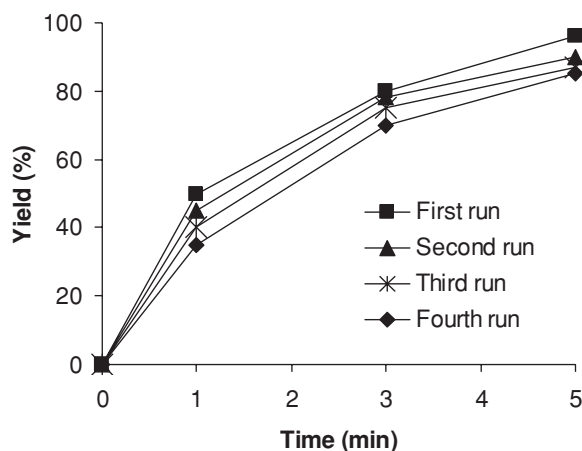
formed with 40% yield (Sch. 3). Due to the volatility of EtSH (bp. = 35°C), this reaction was performed in CH<sub>3</sub>CN as solvent.

The reusability of the PW/C was studied in the reaction of **1** with benzyl alcohol. After each run, the reaction mixture was diluted with CH<sub>3</sub>CN; the catalyst was removed by filtration, washed with CH<sub>3</sub>CN, and calcinated at 150°C for 1 h before reusing. We have found that 40 wt.% of PW/C can be reused several times with slightly loss of activity. The yield of the product for model reaction decreased to 85% after the fourth run (Fig. 1). The selectivity to  $\alpha$ -anomer did not show any change and  $\alpha$ -glycosides was exclusively produced in all runs.

## EXPERIMENTAL

### Materials

PW was purchased from Aldrich and H<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub> hydrate from Merck. Activated carbon, KSF, and K10 montmorillonite were purchased from Fluka. Aerosil silica and titania were used from Degussa.  $\gamma$ -Alumina was obtained



**Figure 1:** Reusability of 40 wt.% of PW/C; only  $\alpha$ -anomer was observed in all runs.

from Aldrich.  $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$ ,  $[(t\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$ ,  $\text{Cs}_2\text{CO}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ , sodium molybdate, and disodium hydrogen phosphate were obtained from Merck; sodium metavanadate and  $\text{SnCl}_2$  were used from Aldrich and Fluka, respectively.

### Catalyst Preparation

$\text{H}_{3+x}\text{PMo}_{12-x}\text{V}_x\text{O}_{40}$  ( $x = 2\text{--}4$ ),  $\text{K}_7\text{PTi}_2\text{W}_{10}\text{O}_{40}$ , and  $[(t\text{-C}_4\text{H}_9)_4\text{N}]_4\text{PW}_{11}\text{CoO}_{39}$  catalysts were prepared and purified by literature procedures.<sup>[33–35]</sup> The acidic salt  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  was prepared from the  $\text{Cs}_2\text{CO}_3$  and PW solution according to the literature method.<sup>[36]</sup> The syntheses of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5\text{PMo}_2\text{W}_9\text{O}_{39}$  ( $\text{Sn}^{2+}\cdot\text{H}_2\text{O}$ ),  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{PMo}_2\text{W}_9\text{O}_{39}$  ( $\text{Sn}^{4+}\cdot\text{H}_2\text{O}$ ), and  $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{PMo}_2\text{W}_9\text{O}_{39}$  ( $\text{Ti}^{4+}\cdot\text{H}_2\text{O}$ ) were started with the preparation of  $\alpha\text{-K}_7\text{PMo}_2\text{W}_9\text{O}_{39}\cdot 19\text{H}_2\text{O}$  from  $\beta\text{-Na}_8\text{HPW}_9\text{O}_{34}\cdot 24\text{H}_2\text{O}$  and sodium molybdate according to the procedures that were described in our previously published papers.<sup>[37]</sup>

All supported catalysts were prepared by the impregnation method. The solution of PW was used to impregnate activated carbon, silica, alumina, titania, KSF, and K10 montmorillonite as supports, followed by drying as described in our previously published papers.<sup>[38,39]</sup>

### Glycosylation Using Alcohols and Phenol

The D-glucal (**1**) (1 mmol), an alcohol or phenol (1.5 mmol), and 0.05 g of catalyst were added to a Pyrex tube fitted with a ground glass joint. These compounds were ground together using a glass rod at rt (ca. 25°C). Progress of the reaction was followed by TLC. The mixture was diluted with  $\text{CH}_3\text{CN}$  ( $2 \times 5$  mL) and filtered. The filtrate was quenched with saturated  $\text{NaHCO}_3$  (10%, 25 mL) and then extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 25$  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 product. Products were characterized from their NMR spectral data.

### Glycosidation Using $\text{Me}_3\text{SiCN}$

A mixture of **1** (1 mmol),  $\text{Me}_3\text{SiCN}$  (1 mmol), and 0.05 g of 40 wt.% PW/C was added to a Pyrex tube fitted with a ground glass joint and crushed using a glass rod at rt (ca. 25°C). Progress of the reaction was followed by TLC. The reaction mixture was diluted by diethyl ether ( $2 \times 5$  mL) and poured into mixture of 1 M HCl (10 mL) and diethyl ether (5 mL). Extractive workup with EtOAc ( $3 \times 15$  mL) followed by column chromatography afforded pure glycoside, which was characterized from its NMR spectral data.



## Glycosidation Using EtSH

A solution of **1** (1 mmol) and EtSH (5 mmol) in CH<sub>3</sub>CN (2 mL) was treated with 0.05 g of 40 wt.% PW/C and stirred at rt (ca. 25°C). Progress of the reaction was followed by TLC. The reaction mixture was extracted with EtOAc, dried, and concentrated. The resulting crude product was subjected to column chromatography to afford the pure product, which was characterized from its NMR spectral data.

## CONCLUSIONS

In summary, various nucleophiles reacted with 3,4,6-tri-*O*-acetyl-D-glucal to yield the corresponding 2,3-unsaturated glycosides in good to excellent yield and short reaction times with high to excellent  $\alpha$ -selectivity. The catalytic activity of PW/C is remarkable and the use of inexpensive and reusable catalyst under solvent-free conditions makes this method a quite simple, environmentally benign, and eco-friendly procedure to prepare various 2,3-unsaturated glycosides.

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