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Ferric Sulphate Hydrate-Catalyzed, Microwave-Assisted Synthesis of 2,3-Unsaturated O-Glycosides via the Ferrier Reaction

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Ferric Sulphate Hydrate–Catalyzed, Microwave-Assisted Synthesis of 2,3-Unsaturated *O*-Glycosides via the Ferrier Reaction

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Abstract: $Fe_2(SO_4)_3 \cdot xH_2O$ catalyzes the Ferrier reaction of per-*O*-acetylated/benzylated glycals with alcohols to give 2,3-unsaturated α-glycosides in a few minutes under microwave irradiation.

Keywords: Ferrier rearrangement, ferric sulphate hydrate, 2,3-unsaturated *O*-glycosides

Ferrier rearrangement has gained great significance since 1969 in the area of carbohydrate chemistry because it can give access to 2,3-unsaturated-*O*-glycosides[1]. 2,3-Unsaturated glycosides, which can be obtained from the reaction of glycal with nucleophilic agents mediated by Lewis acids via the Ferrier rearrangement, can be used as intermediates for a variety of reactions such as Sharpless *cis*-oxyamination, epoxidation, or hydroxylation. The derivatives of 2,3-unsaturated glycosides can be used as important intermediates in glycopeptide blocks,[2] oligosaccharides,[3] modified

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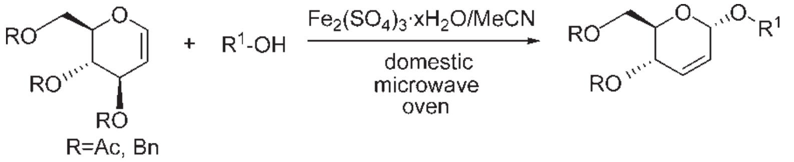
carbohydrates,[4] some important antibiotics,[5] nucleosides,[6] natural product–like compounds,[7] and various natural products.[8]

In recent years, more and more reagents have been described to form 2,3-unasturated-*O*-glycosides from glycals, such as montmorillonite K-10,[9] $SnCl_4$,[10] 2,3-dichloro-5,6-dicyano-1,4-quinone (DDQ),[11] $K_5CoW_{12}O_{40} \cdot 3H_2O$,[12] $InCl_3$,[13] $BF_3 \cdot OEt_2$,[14] $BiCl_3$,[15] $Dy(OTf)_3$,[16] $CeCl_3 \cdot 7H_2O$,[17] $ZnCl_2$,[18] $ZrCl_4$,[19] $FeCl_3$,[20] N-iodosuccinimide (NIS),[21] $Sc(OTf)_3$,[22] I_2,[23] $HClO_4$-SiO_2,[24] ceric ammonium nitrate (CAN),[25] $Bi(NO_3)_3 \cdot 5H_2O$,[26] $Fe(NO_3)_3 \cdot 9H_2O$,[26b] and $NbCl_5$.[27] However, some of the catalysts are very expensive and moisture sensitive. Furthermore, all these methods have some drawbacks of generality, varied stereoselectivity and yields, long reaction times, and harsh reaction conditions. Therefore, the search for newer and more economic synthetic methodologies with greater efficiency and convenient procedures continues.

Herein, we report the ferric sulphate hydrate–catalyzed, microwave-induced Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal and 3,4,6-tri-*O*-benzyl-D-glucal with alcohols in an open vessel, giving 2,3-unsaturated glycosides with high α-selectivity (Scheme 1).

In our experiment, per-*O*-acetylated/benzylated glucal in the presence of an alcohol was treated with 10 mol% of $Fe_2(SO_4)_3 \cdot xH_2O$ in anhydrous acetonitrile and irradiated with microwaves in an open vessel for a few minutes to afford the corresponding 2,3-unsaturated glycosides in good yields with very high α-selectivity as summarized in Table 1. $Fe_2(SO_4)_3 \cdot xH_2O$ used in the experiments was purchased from the Beijing Chemical Factory (A. R. grade). The moles of $Fe_2(SO_4)_3 \cdot xH_2O$ are calculated based on the formula: $M_{\mathrm{Fe2(SO4)3\ \cdot\ xH2O}} = 0.5 \times (W_{\mathrm{Fe2(SO4)3\ \cdot\ xH2O}} \times \mathrm{Fe(III)\%}/55.8)$.

As shown in Table 1, both peracetyl and perbenzyl glycals underwent the Ferrier reaction with primary and secondary alcohols to afford 2,3-unsaturated-*O*-glycosides in good yields with α-selectivity. However, in the literature most of the Ferrier reaction of 3,4,6-tri-*O*-acetyl-D-glucal gave 2,3-unsaturated glycosides as a mixture of α- and β-anomers except montmorillonite K-10[9b] and $NbCl_5$.[27] It is noteworthy that 3,4,6-tri-*O*-benzyl-D-glucal also underwent the Ferrier reaction under these conditions to afford the corresponding 2,3-unsaturated-*O*-glycosides in excellent yields with exclusively α-selectivity (entries 10–13). To the best of our knowledge, there was only CAN[25b] available for the Ferrier rearrangement of 3,4,6-tri-*O*-benzyl-D-glucal to form 2,3-unsaturated-*O*-glycosides. The reaction of perbenzyl glucal with



Scheme 1.

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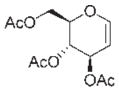
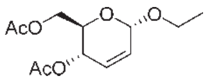
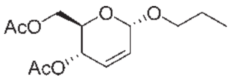
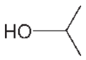
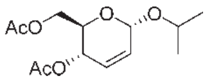
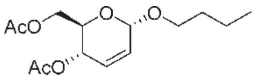
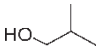
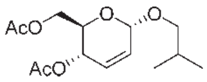
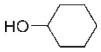
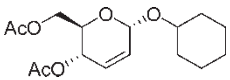
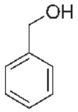
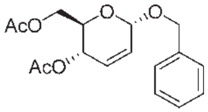
Table 1. $Fe_2(SO_4)_3 \cdot xH_2O$-catalyzed, microwave-assisted synthesis of 2,3-unsaturated Ferrier rearranged products

Entry	Substrate	Alcohol	Product	Time[a] (min)	Yield (%)[b]
1				5	89
2				5	92
3				6	88
4				7	93
5				5	91
6				8	90
7				7	88

(*continued*)

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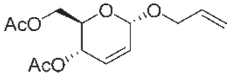
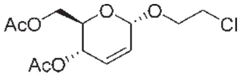
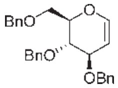
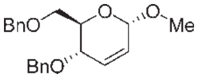
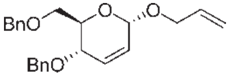
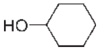
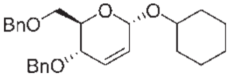
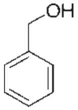
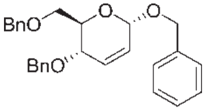
Table 1. Continued

Entry	Substrate	Alcohol	Product	Time[a] (min)	Yield (%)[b]
8				9	92
9				7	91
10		CH_3OH		5	87
11				6	88
12				4	84
13				6	86

[a] All reactions were irradiated at middle low level in a domestic microwave oven (2450 MHz, 700 W).

[b] Isolated yields; all products were characterized by ^{1}H NMR and only α observed.

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methanol, allyl alcohol, and cyclohexanol in the presence of CAN, formed 2-deoxy products as the major products along with the Ferrier products in yields of 38%, 23%, and 18%, respectively. In all cases, various α/β ratios of the glyosides were observed; α products were the major ones. In our methodology, $Fe_2(SO_4)_3 \cdot xH_2O$-catalyzed Ferrier rearrangement of 3,4,6-tri-*O*-benzyl-D-glucal with methanol, allyl alcohol, and cyclohexanol gave 2,3-unsaturated α-glycosides as the only products in excellent yields of 87%, 88%, and 84%, respectively. No formation of 2-deoxy hexopyranosides was observed.

In addition, we have found that $Fe_2(SO_4)_3 \cdot xH_2O$ can be reused several times without loss of activity by filtering the catalyst, washing with acetone, and drying. Take ethanol for example: the yields of glycosides promoted by catalyst recovered four times were 89%, 87%, 85%, and 86%, respectively.

In summary, in this article we describe an efficient, economic, ecofriendly method for the synthesis of *O*-glycosides from glycals and alcohols using a catalytic amount of ferric sulphate hydrate under mild reaction conditions. Our present methodology has the following advantages: (a) the catalyst, $Fe_2(SO_4)_3 \cdot xH_2O$, can be easily recovered and reused. (b) The reaction has short reaction times and generally good yields. (c) The catalyst is nontoxic and friendly to the environment. In conclusion, we have developed a mild and ecofriendly approach to the 2,3-unsaturated glycosides.

EXPERIMENTAL

^1H NMR spectra were recorded on a Bruker AC-400 NMR spectrometer in solutions of $CDCl_3$ using tetramethylsilane as the internal standard. Acetonitrile was distilled from P_2O_5 followed by distillation from CaH_2 prior to use. All reagents were obtained from commercial sources and used without further purification.

General Procedure

To a mixture of glycal (0.5 mmol) and alcohol (1.5 mmol) in anhydrous acetonitrile (1–2 mL), $Fe_2(SO_4)_3 \cdot xH_2O$ (0.05 mmol) was added, and the mixture was irradiated with microwaves at the medium low level (2450 MHz, 700 W) for the specified period of time in an open vessel. The reaction was monitored using thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The products were purified by silica-gel column chromatography and characterized by ^1H NMR spectroscopy; the spectroscopic data are comparable with the literature data (1–9,[26b] 10–12,[25b] and 13.[28]) The catalyst can be reused for several times without loss of activity.

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