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3,5-Dinitrobenzoic acid catalyzed synthesis of 2,3-unsaturated *O*- and *S*-glycosides and tetrahydropyranylation of alcohols and phenols

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ABSTRACT

A simple procedure for the synthesis of 2,3-unsaturated glycosides in acetonitrile and tetrahydropyranylation of alcohols and phenols in dichloromethane in the presence of 3,5-dinitrobenzoic acid is described. A variety of alcohols and thiols are reacted with glycals to give the desired products in high yields with high α-selectivity.

2,3-Unsaturated glycopyranosides are a class of important chiral intermediates[1,2] in the synthesis of biologically active compounds such as glycopeptide building blocks,[3] oligosaccharides,[4] and modified carbohydrates.[5a] In addition 2,3-unsaturated glycosides have also been employed in the synthesis of antibiotics, nucleosides, and various natural products.[5] Because of the importance of 2,3-unsaturated glycosides, several reports have appeared in the literature. The synthesis of 2,3-unsaturated glycopyranosides is generally achieved by the treatment of corresponding glycal with an alcohol or thiol in the presence of a Lewis or a Brønsted acid. This reaction was discovered by Ferrier by using $BF_3{\cdot}Et_2O$ as a Lewis acid catalyst and is popularly known as the Ferrier rearrangement or Ferrier type I reaction.[2a] Apart from $BF_3{\cdot}Et_2O$ several other Lewis acid catalysts, oxidants or protic acids such as $ZnCl_2$,[6] H_3PO_4,[7] $InCl_3$,[8] $SnCl_4$,[9] $Yb(OTf)_3$,[10] $FeCl_3$,[11] montmorillonite K-10,[12] $Dy(OTf)_3$,[13] DDQ,[14] I_2,[15] $I(Coll)_2ClO_4$,[16] CAN,[17] $CeCl_3{\cdot}7H_2O$,[18] $HClO_4/SiO_2$,[19] MeOH·HCl,[20] and *N*-iodosuccinamide[21] have been reported to affect this rearrangement. All of these methods offer several advantages but some of them suffer drawbacks due to low yield, longer reaction times, harsh reaction conditions, and the use of air sensitive catalysts. Owing to the importance of the Ferrier rearrangement products, the introduction of new and efficient catalysts for this transformation is still in demand.

With an objective of developing a viable procedure for Ferrier rearrangement, we focused on finding a low cost and efficient catalyst that would give high yields and easy handling procedure under aerobic conditions. In continuation of our work on novel organocatalysts for organic transformations,[22] we became interested to use very cheap 3,5-dinitrobenzoic acid (3,5-DNBA, <$0.1 per gram) as organocatalyst for the aforementioned reaction. Though 3,5-DNBA has been used as an additive in many reactions,[23,24] it has not been used as a catalyst. In the present Letter, we describe the successful utilization of 3,5-DNBA as an organocatalyst for the Ferrier rearrangement of glycals and tetrahydropyranylation of various primary and secondary alcohols and phenols.

In our preliminary experiment, we allowed to stir a mixture of benzyl alcohol (1 mmol) and glucal **1** (1.1 mmol) in the presence of 3,5-DNBA (0.2 mmol) in CH_2Cl_2 at room temperature for 24 h. Under these conditions the reaction did not proceed. When we carried out the reaction at 80 °C in CH_3CN, the reaction underwent smoothly to give 2,3-unsaturated-*O*-glucopyranoside **3e** in 81% yield. However, the reaction with low catalyst loading (0.1 mmol) led to longer reaction times and resulted in the formation of glycoside **3e** in low yield. Having developed conditions in hand, the methodology was applied for alcohols such as allyl alcohol, propanol, butanol, and *iso*-butanol. The 3,5-DNBA catalyzed reactions of all these reactants proceeded smoothly under the same conditions to afford the corresponding *O*-glycosides **3a–d** in high yields (Scheme 1, Table 1). Similarly, the Ferrier rearrangement of galactal **2** provided the 2,3-unsaturated-*O*-galactopyranosides

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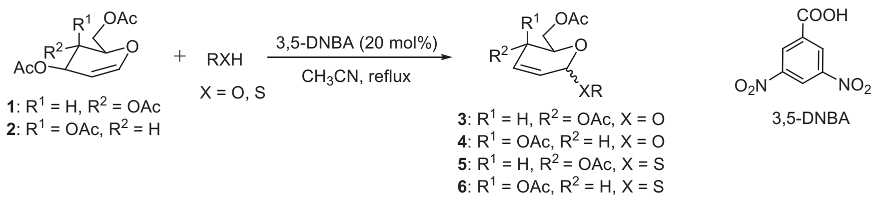
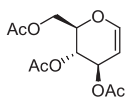
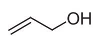
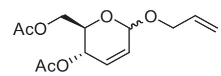
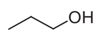
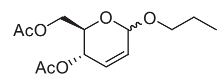
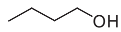
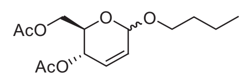
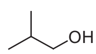
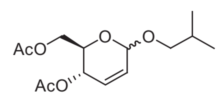
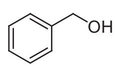
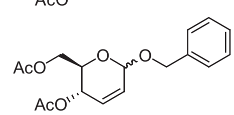
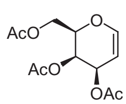
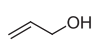
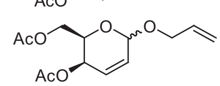
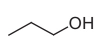
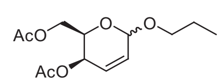
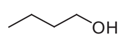
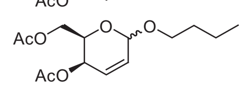
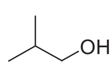
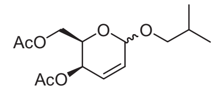
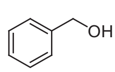
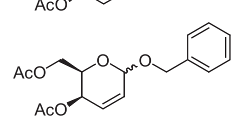
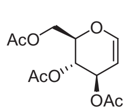
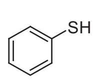
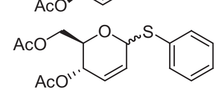
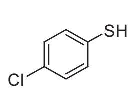
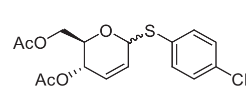
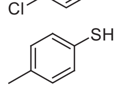
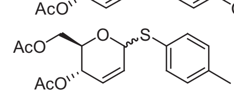
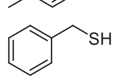
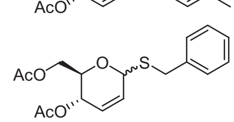


Scheme 1. Synthesis of 2,3-unsaturated glycopyranosides by using alcohols and thiols in the presence of organocatalyst 3,5-DNBA.

Table 1
Ferrier rearrangement of 2,3-tri-*O*-acetyl-D-glycals with alcohols and thiols in the presence of 3,5-DNBA

Entry	Substrate	Alcohol/thiol	Time (h)	Product		
				Glycoside	Yield[a] (%)	α/β[b]
1	 **1**		2	 **3a**	86	5:1
2	**1**		2	 **3b**	84	6:1
3	**1**		2.5	 **3c**	86	4:1
4	**1**		2.5	 **3d**	82	8:1
5	**1**		2	 **3e**	81	10:1
6	 **2**		2	 **4a**	89	6:1
7	**2**		2	 **4b**	82	9:1
8	**2**		2.5	 **4c**	86	14:1
9	**2**		2.5	 **4d**	80	12:1
10	**2**		2	 **4e**	87	22:1
11	 **1**		1.5	 **5a**	91	6:1
12	**1**		2	 **5b**	86	7:1
13	**1**		1.5	 **5c**	89	13:1
14	**1**		1	 **5d**	95	17:1

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