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2,3-Unsaturated Allyl Glycosides as Glycosyl Donors for Selective α-Glycosylation

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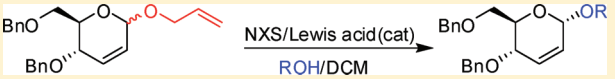
Supporting Information

ABSTRACT: In the presence of NBS and a catalytic amount of a Lewis acid, 2,3-unsaturated allyl glycosides [6-(allyloxy)-3,6-dihydro-2-(hydroxymethyl)-2*H*-pyran-3-ol] have been successfully used as versatile glycosyl donors for the stereoselective α-glycosylation of a variety of alcohols comprising sensitive functions such as acetonide, keto, nitro, and ester in 50−90% yields. The methodology offers an equally facile alternative to 4-pentenyl replacement in unsaturated sugars.



Stereoselective α-glycosylation has attracted considerable attention of researchers in the recent past[1] owing to a wide occurrence of α-linkage in a variety of natural products, be it more common disaccharides such as sucrose, maltose, trehalose, or less common kojibiose, nigerose, turanose, or medicinally important oligosaccharides,[2] glycosphingolipids,[3] phosphoglycans,[4] saponins,[5] antitumor vaccines,[6] etc. Therefore, the development of stereoselective glycosylation strategies continues to be an important goal for the synthetic chemists. The concept of "armed−disarmed" sugars introduced by Fraser-Reid has been one of the revolutionary ideas in this field.[7] Thus, by judicious positioning of electron-withdrawing/donating protecting groups at C-2, the selectivity and reactivity of glycosyl donors possessing a suitable leaving group at the anomeric position can be controlled. On the other hand, the absence of a stereodirecting group at C-2 makes the task of attaining high selectivity rather complicated.

The stereoselective glycosylation strategy in 2,3-unsaturated glycosides is of particular interest, as they have enjoyed a unique importance in carbohydrate chemistry due to the possibility of further functionalization;[8] therefore, they may be employed in the synthesis of 2-deoxy, 2,3-dideoxy, and allied structures occurring in innumerable natural products.[9] Surprisingly, the utilization of 2,3-unsaturated glycosides as glycosyl donors has been least exploited,[10] despite being valuable intermediates in the synthesis of biologically active molecules such as antibiotics,[11] nucleosides,[12] glycopeptide building blocks,[13] oligosaccharides,[14] and modified carbohydrates.[15] The 2,3-unsaturated glycosyl donors are relatively reactive under mild reaction conditions because of the stabilization of the oxocarbenium intermediate during the glycosylation reactions.[16]

Earlier, the 4-pentenyl group was also used as a protection of anomeric hydroxyl in sugars, which could be selectively deprotected with NBS in CH_3CN/H_2O.[17] Fraser-Reid et al.[18] in 1988 demonstrated that substituting water with an alcohol effectively leads to the replacement of 4-pentenyl protection and the formation of coresponding *O*-glycosides. In a further attempt to determine whether ω-alkenyl glycosides other than *n*-pentenyl could also be used as glycosyl donors, Rodebaugh and Fraser-Reid[19] observed that only the *n*-pentenyl group underwent oxidative hydrolysis, while all other homologues including *O*-allyl substitution gave bromohydrins. Later, Boons et al.[20]and Wang et al.[21] reported the use of substituted *O*-allyl glycosides as the donors; however, their method essentially involved prior activation (*i.e.*, ene migration) with metal complexes such as $(Ph_3P)_3RhCl$ and $Ir(COD)(PMePh_2)_2]$-PF_6 before effecting glycosylation.

Basically, O-allylation has generally been employed as a stable protection strategy in glycochemistry,[22] removable by suitable activators;[23] however, owing to its higher stability, its potential as a glycosyl donor has not been well exploited. In continuation of our interest in the development of new protection and glycosylation strategies,[24,25] we envisaged to explore the possibility of using *O*-allyl glycoside as a versatile glycosyl donor.

Herein, we report the development of an alternate methodology applicable in 2,3-unsaturated α-glycosylation via *O*-allyl replacement, which is based on our earlier work on the preparation of tetrahydropyranylether as alcohol/thiol protecting group through a facile *O*-allyl replacement, under mild experimental conditions.[26] The present methodology is not only facile but also stereoselective for α-glycosylation of a large range of substrates and equally useful as an alternative to 4-pentenyl replacement. In this method, allyl glycosides such as 6-(allyloxy)-3-(benzyloxy)-2-((benzyloxy)methyl)-3,6-dihydro-2*H*-pyran (**1a**, **1b**) are used as versatile glycosyl donors in the presence of the promoter NBS. The simple procedures for the preparation of the allyl glycosides **1a** and **1b** are available in the literature.[27]

The present methodology has several advantages, including (i) economical availability and handling of *O*-allyl reagents, (ii) facile and stereoselective 2,3-unsaturated α-glycosylation through replacement of the *O*-allyl group in a single step under mild experimental conditions at ambient temperature, (iii) suitability even in the presence of other sensitive functionalities such as acetonide, ester, nitro, keto etc., (iv) nonreactivity of the endocyclic double bond under the stipulated reaction conditions.

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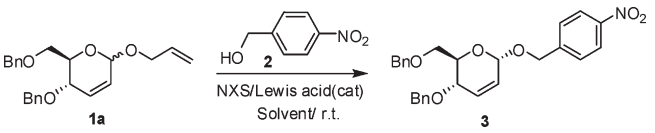
Table 1. Optimization of Reaction Conditions for Glycosylation of *p*-Nitrobenzyl Alcohol (1.5 equiv) with Allyl Glycoside (1a)



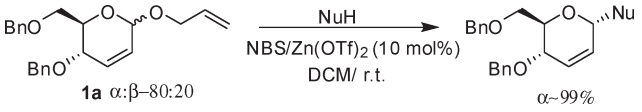
entry	NXS[a]	solvent	catalyst (10 mol %)	time (h)	yield[b] (%)
1	NBS	DCM		18	92
2	NBS	DCM	$Zn(OTf)_2$	8	90
3	NBS	DCM	$Yb(OTf)_2$	10	85
4	NBS	DCM	$Cu(OTf)_2$	12	80
5	NBS	DCM	$In(OTf)_3$	14	80
6	NBS	DCM	$BF_3(OEt)_2$	10	75
7	NBS	DCM	$InCl_3$	12	70
8	NBS	DCM	$TiCl_4$	10	50
9	NBS	DCM	$SnCl_4$	13	45
10	NBS	acetonitrile	$Zn(OTf)_2$	6	55
11	NBS	diethyl ether	$Zn(OTf)_2$	20	70
12	NBS	THF	$Zn(OTf)_2$	18	76
13	NBS	ionic liquid	$Zn(OTf)_2$	8	40
14	NIS	DCM	$Zn(OTf)_2$	8	78
15	NCS	DCM	$Zn(OTf)_2$	10	70

[a] Halogenating agents (1.2 equiv) were used. [b] Isolated yield.

The experimental conditions were optimized using *p*-nitrobenzyl alcohol as a model acceptor, being a relatively faster reactant. Thus, **1a** was treated with *p*-nitrobenzyl alcohol in the presence of halosuccinimide in different organic solvents with or without the addition of a small amount of a cocatalyst. The best results for the replacement of the *O*-allyl group were observed when NBS was used with $Zn(OTf)_2$ as a cocatalyst in DCM, giving the desired product (8 h) in 90% yield (Table 1, entry 2). In the absence of the cocatalyst, *O*-allyl replacement was effected in 18 h (92% yield). Thus, the addition of a Lewis acid cocatalyst (10 mol %) significantly reduced the reaction time but not the yields. The yields with other Lewis acids, such as $Yb(OTf)_2$, $Cu(OTf)_2$, $In(OTf)_3$, $BF_3 \cdot Et_2O$, $InCl_3$, $SnCl_4$, and $TiCl_4$, were comparatively low with longer reaction time, whereas NBS was found to be better than NIS and NCS. In all of the glycosylations, the α-stereoselectivity is very high (~99%) with 50−90% isolated yields. It may be emphasized here that the donor allyl glycosides, such as (2*R*,3*S*)/(2*R*,3*R*)-6-(allyloxy)-3,6-dihydro-2-(hydroxymethyl)-2*H*-pyran-3-ol (**1a**, **1b**) prepared via Ferrier rearrangement,[9c] are obtained as an α/β mixture of isomers in the approximate ratio of 80:20, which are directly transformed to α-glycosylated products by the present methodology.

A variety of alcohols produced corresponding α-glycosides when treated with *O*-allyl glycoside **1a** under optimized reaction conditions in the presence of NBS (Table 2). The primary, secondary, and benzylic alcohols were conveniently glycosylated at room temperature. The reagent system is mild enough to be used with natural products comprising other sensitive multifunctional groups. We encountered no difficulty in the glycosylation of monoacetonide of glycerol, diacetonides of sugars, 1-phenyl ethanol, and furfuryl alcohol, comprising acid-sensitive functionalities (Table 2, entries 5−10), effecting smooth transformations without the formation of side products. Moreover, the 2,3-unsaturated glycosides of natural biomolecules such as podophyllotoxin **4** and 11-keto-β-boswellic acid **5** can easily be used as precursors to generate semisynthetic libraries of bioactive molecules (Figure 1).

Table 2. Glycosylation of Alcohols Including Natural Products with Allyl Glycoside (1a, Synthesized from Glucal[27])



entry	NuH[a]	product[b]	time (h)	yield[c] (%)
1	2	**3**	8	90
2	4	**23**	24	70
3	5	**24**[d]	30	65
4	6	**25**	10	90
5	7	**26**	20	60
6	8	**27**	12	70
7	9	**28**	10	80
8	10	**29**	15	50
9	11	**30**	6	75
10	12	**31**	18	85
11	13	**32**	8	90
12	14	**33**	10	80
13	15	**34**	10	80
14	16	**35**	12	78
15	17	**36**	8	84
16	18	**37**	12	88
17	19	**38**	13	91
18	20	**39**	8	90
19	21	no reaction		
20	22	no reaction		

[a] Nucleophile (1.5 molar equiv) was used. [b] Affording only the α-anomers in all cases. [c] Isolated yields. [d] Natural mixture (1:2) of positional isomers.

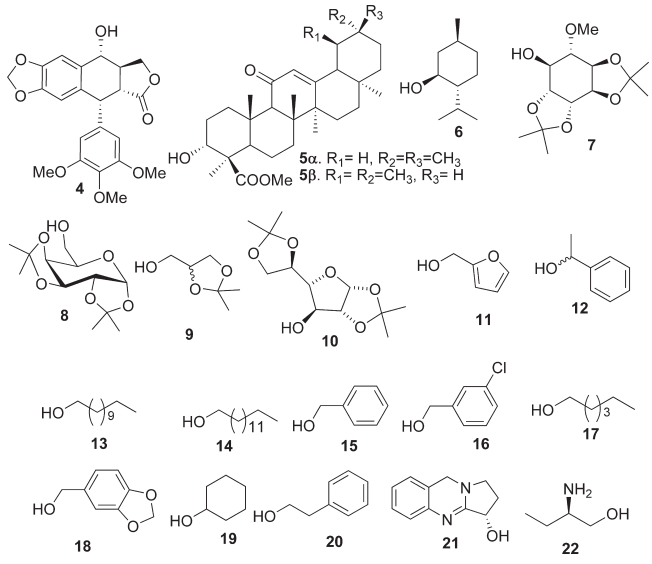


Figure 1. Nucleophiles used for glycosylation.

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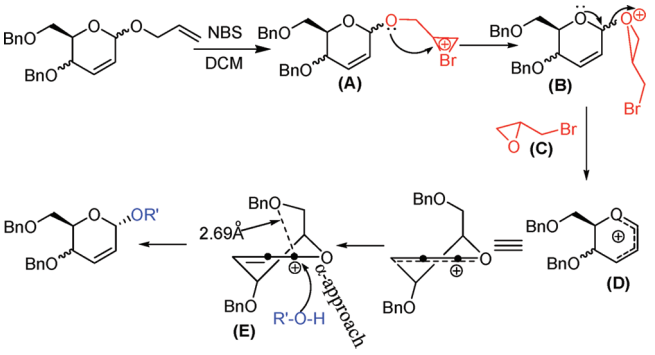
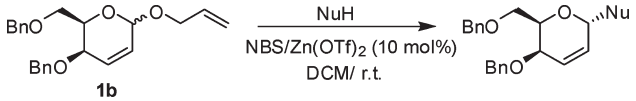


Figure 2. Plausible mechanism of replacement of *O*-allyl group by alcohols.

Table 3. Glycosidation of Alcohols with Allyl Glycoside (1b, Synthesized from Galactal[27])



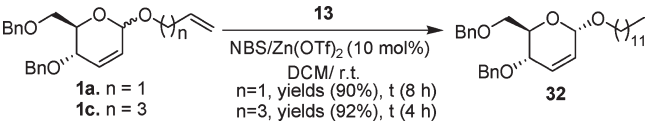
entry	NuH[a]	product[b]	time (h)	yield[c] (%)
1	6	**40**	12	80
2	14	**41**	12	75
3	15	**42**	11	75

[a] Nucleophile (1.5 molar equiv) was used. [b] Affording only the α-anomers in all cases. [c] Isolated yields.

In the case of the methyl ester of 11-keto-boswellic acid (Table 2, entry 3) as a substrate, which is an inseparable natural mixture of two positional isomers **5α** and **5*β*** (in the ratio 1:2),[28] the formation of two corresponding products in the same natural ratio was observed (each with ~99% α-O-glycosylation as elucidated by NMR; see Supporting Information). Besides, the smooth glycosidation of carbohydrate-based products such as **27** and **29** provides a facile entry into the synthesis of disaccharides and related analogues. The racemic 1-phenyl ethanol furnished a 1:1 mixture of two diastereomeric α-glycosides (Table 2, entry 10). Predictably, the reactions with amino alcohols such as the alkaloid vasicine and 2-aminobutanol did not proceed as the free amino group prevented the formation of the halonium ion intermediate **A** (Table 2, entries 19 and 20), thereby lending support to the proposed mechanism (Figure 2).

The distinction between α- and *β*-isomers has been a difficult task in 2,3-unsaturated glycoside due to the twisted chair conformation of 3,4-glucals, resulting in the close chemical shifts (δ) and coupling constants (J) for the anomeric proton and carbon. Therefore, 1,4,6-tri-*O*-benzyl glucal anomers were prepared through Ferrier rearrangement (as α and *β* mixture) and by the present method. In the course of these studies, it was observed that in the α-isomer of 1,4,6-tri-*O*-benzyl glucal, the chemical shift values for ^{1}H and ^{13}C are δ 5.1, J = 2.0 Hz and δ 94.0, respectively, whereas in the *β*-isomer, these values are δ 5.2, J = 1.5 Hz, and δ 95.0, respectively[29] (see Supporting Information). The formation of the α-glycosylated product was also unambiguously established through NOESY experiments wherein the correlation a between H-1 and H-5 was conspicuously absent as expected (see the Supporting Information).

Scheme 1. Comparison of the Reactivity of 1a and 1c



The versatility of the present methodology was further explored by applying it to the allyl glycoside (**1b**, 2*R*,3*R*)-6-(allyloxy)-3,6-dihydro-2-(hydroxymethyl)-2*H*-pyran-3-ol) obtained from galactal. As expected, **1b** on treatment with nucleophiles **6**, **14**, and **15** resulted in the formation of products **40**, **41**, and **42**, respectively (75−80% yield) with high α-stereoselectivity (Table 3).

In order to compare the reactivities of 2,3-unsaturated allyl glycoside (**1a**) and 2,3-unsaturated 4-pentenyl glycoside (**1c**) as a glycosyl donors, reactions with dodecyl alcohol (**13**) as a nucleophile was performed under the same reaction conditions as shown in Table 2 (entry 11) (Scheme 1). The reaction with **1c** completed faster (4 h) compared to that of **1a** (8 h), with almost similar yields and the formation of exlusively α-anomers (>99%).

Neighboring group participation (NGP) has long been used to control the stereochemistry of chemical reactions.[30] Functional groups at positions more distant from the anomeric center can also influence the stereoselectivity;[31] however, the role of NGP in these processes still remains a contentious issue.[32] In the present reaction, it is apparent that the NGP (6-benzyloxy) is the dominant factor rather than other known interactions for stereoselective glycosylation. The plausible mechanism for the cleavage of the *O*-allyl bond (Figure 2) is based on analogy to a report by Wang et al.[21] for the glycosylation using allyl glycosyl donor and also derived from the proposed mechanisms of 4-penten-1-ol replacement by Fraser-Reid et al.[33] and stereoselective synthesis of unsaturated α-*O*-glycosides by Nagaraj et al.[16] Thus, the initial formation of bromonium ion (**A**) at the terminal allylic double bond is followed by its facile elimination as epibromohydrin, due to the formation of a more stable delocalized carbenium (**D**). The carbenium (**D**) is stabilized not only by an endocyclic double bond and the ring oxygen but also by the remote oxygen atom of the C-6 benzyloxy group (bond distance = 2.69 Å from anomeric carbon; see Supporting Information) exerting anchimeric assistance through the formation of (**E**), thereby sterically blocking the upper face for the attack and directing the nucleophile's approach from the α face, resulting in the formation of α-product. The influence of the C-6 benzyloxy group (NGP) in directing the α-stereoselectivity was further established unequivocally when 4,6-di-*O*-benzyloxy in **1a** was replaced with 4,6-di-*O*-TBS derivative only to afford a mixture of α/*β* (5.5:1) isomers during glycosylation (see Supporting Information).

The proposed mechanism also received support from the experiments of α-O-glycosylation of *O*-allyl glycoside obtained from galactal **1b** (Table 3). Thus, the replacement of the *O*-allyl group in **1b** to the corresponding α-*O*-glycoside was also effected stereoselectively, giving predominantly α-products (Table 3). Thus, it is evident that in both the sugars (**1a** and **1b**), the C-6 benzyloxy group plays a vital role in determining the stereochemical outcome.

It may be emphasized here that the direct replacement of the allyl group by a nucleophile in a saturated carbohydrate ring in a single step is unfavorable under the stipulated experimental

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conditions. The presence of the 2,3 double bond possibly facilitates the elimination of both the α and β leaving groups (**C**) through antiperiplanar arrangements with respect to the lone pair on the ring oxygen, owing to its distorted/pseudochair flipping conformations, as postulated for saturated sugars by Deslongchamps.[34] The stabilization of resulting intermediates (**D** and **E**) through delocalization involving four atoms may also be responsible for facile elimination of the allyl group.

In summary, we have for the first time demonstrated the use of *O*-allyl glycosides as donors in a facile and stereoselective α-O-glycosylation of alcohols in a single step under mild experimental conditions. The stabilities of the sensitive groups such as acetonide, keto, nitro, ester, etc. toward the reagent system are the added advantages. The *O*-allyl glycoside may well serve as an easy and economical substitute to pentenyl glycosides as a glycosyl donor in 2,3-unsaturated sugar systems. Moreover, due to the presence of a double bond, the glycosylated products can easily be structurally modified to other useful bioactive molecules. The reagent system is also applicable for the glycosylation of various natural products.

EXPERIMENTAL SECTION

Typical Procedure for the Synthesis of (2*R*,3*S*)-6-(4-Nitrobenzyloxy)-3-(benzyloxy)-2-((benzyloxy)methyl)-3,6-dihydro-2*H*-pyran (3): NBS (116.7 mg, 0.655 mmol) and $Zn(OTf)_2$ (10 mol %, 20 mg) were successively added to a solution of allyl glycoside **1a** (200 mg, 0.546 mmol) and *p*-nitrobenzyl alcohol **2** (125.4 mg, 0.819 mmol) in DCM (3 mL) and the solution was stirred for 8 h at rt. The reaction mixture after extraction with diethyl ether, usual workup, and purification through column chromatography on alumina afforded pure compound **3** as an oily liquid in 90% yield: $[\alpha]^{25}_{D}$ +13.1 (*c* 3.2 $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (m, 2H), 7.49 (m, 2H), 7.29 (m, 10H), 6.13 (d, 1H, *J* = 10.3 Hz), 5.85 (m, 1H), 5.14 (d, 1H, *J* = 1.6 Hz), 4.89 (d, 1H, *J* = 13.1 Hz), 4.43−4.69 (m, 5H), 4.17 (m, 1H), 3.94 (m, 1H), 3.69 (dd, 1H, *J* = 10.6 Hz, 4.2 Hz), 3.60 (dd, 1H, *J* = 10.6 Hz, 4.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 145.8, 137.9, 137.8, 131.3, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 125.9, 123.6, 94.5, 73.4, 71.2, 70.2, 69.6, 68.8, 68.7; ESI-MS $(M + Na)^+$ 484. Anal. Calcd for $C_{27}H_{27}NO_6$: C, 70.27; H, 5.90; N, 3.03. Found: C, 70.67; H, 5.88; N, 3.05.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, characterization data, and copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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