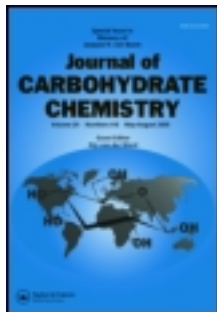


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Rajib Panchadhayee^a & Anup Kumar Misra^a

^a Division of Molecular Medicine, Bose Institute, A.J.C. Bose Centenary Campus, P-1/12, C.I.T. Scheme VII-M, Kolkata, 700054, India

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***N*-Bromosuccinimide-Mediated Conversion of Allyl Glycosides to Glycosyl Hemiacetals**

Rajib Panchadhayee and Anup Kumar Misra

Division of Molecular Medicine, Bose Institute, A.J.C. Bose Centenary Campus, P-1/12, C.I.T. Scheme VII-M, Kolkata 700054, India

A novel reaction condition has been developed for the hydrolysis of differentially functionalized allyl glycosides to their corresponding glycosyl hemiacetal derivatives in the presence of *N*-bromosuccinimide (NBS). The reaction condition is exceptionally fast, mild, and compatible with most of the functional groups used in the oligosaccharide synthesis, and yields were excellent.

Keywords Allyl glycoside; *N*-Bromosuccinimide; Glycosyl hemiacetal; Hydrolysis

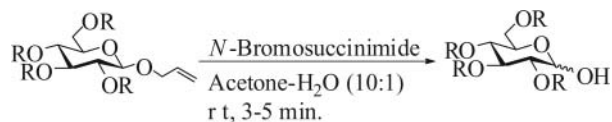
INTRODUCTION

1-Hydroxy sugars or glycosyl hemiacetal derivatives are useful intermediates for the synthesis of complex oligosaccharides.^[1,2] They can be used directly in the dehydrative glycosylation reactions^[3] or can be converted to reactive glycosyl donors^[4–6] to be used in the oligosaccharides or natural product synthesis.^[7,8] Because of their usefulness, a number of reports appeared in the literature dealing with the preparation of glycosyl hemiacetal derivatives, which include (a) removal of the anomeric acetyl group using hazardous hydrazine salts^[9] or organic bases^[10] or acidic conditions^[11]; (b) hydrolysis of alkyl glycosides^[12] and oxidative removal of 4-methoxyphenyl glycosides^[13]; and (c) hydrolysis of thioglycoside derivatives using a variety of thiophilic reagents.^[14–20] Hydrolysis of thioglycoside derivatives has been found to be beneficial over other methods due to the less toxic and mild reaction conditions as well as compatibility of other functional groups present in the sugar skeleton.

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Address correspondence to Anup Kumar Misra, Division of Molecular Medicine, Bose Institute, A.J.C. Bose Centenary Campus, P-1/12, C.I.T. Scheme VII-M, Kolkata 700054, India. E-mail: akmisra69@gmail.com

Suitably functionalized allyl glycosides have been used as glycosyl acceptors in the synthesis of several complex oligosaccharides.^[21] In a multistep oligosaccharide synthetic strategy the anomeric allyl group has been used as a temporary protecting group that can be removed after glycosylation to generate hemiacetal derivatives for their use in the next step. Conventionally, removal of the allyl group is carried out using expensive palladium or rhodium salts^[22], in a two-step reaction sequence involving the isomerization of the *O*-allyl group to the more labile *O*-propenyl group in the presence of expensive iridium salt^[23]; or using irradiation^[24] followed by hydrolysis of the resulting *O*-propenyl group using *N*-bromosuccinimide (NBS). In some cases the removal of the anomeric allyl group became exceptionally problematic because of the functional groups present in the substrates and thereby required special reaction conditions.^[25,26] However, many of these methods for the removal of the allyl group suffer from limitations such as use of expensive reagents, incompatibility with acidic functional groups, relatively low yield, and sometimes harsh reaction conditions. In this context, it would be useful to develop an economically convenient mild reaction protocol for the preparation of glycosyl hemiacetal derivatives having sensitive protecting groups. Although NBS has been used to remove allyl ether under the special reaction conditions mentioned earlier, we disclose herein a novel metal-free reaction condition for the preparation of functionalized glycosyl hemiacetal derivatives by direct NBS-mediated hydrolysis of allyl glycosides, avoiding the use of expensive reagents or stringent reaction conditions (Sch. 1).



Scheme 1: *N*-Bromosuccinimide (NBS)-mediated hydrolysis of allyl glycoside for the preparation of glycosyl hemiacetal derivatives.

RESULTS AND DISCUSSION

During the synthesis of oligosaccharides^[27] using suitably protected allyl glycoside as the glycosyl acceptor under the thioglycoside activation condition in the presence of *N*-iodosuccinimide (NIS) and trifluoromethane sulfonic acid (TfOH) combination, we isolated a considerable amount of unwanted product, which was characterized as the hemiacetal derivative generated from the allyl glycoside. Taking this clue from the earlier experiments, allyl glycoside (**1**) was allowed to react separately with NBS and NIS in the presence and absence of an acid in different solvents, for example, CH₂Cl₂, CH₃CN-H₂O (9:1), acetone-H₂O (10:1), THF. It was observed that the use of 1.1 equiv. of NBS in acetone-H₂O can form hemiacetal derivative in excellent yield from the corresponding

allyl glycosides without requiring any acid as activator at room temperature in 3 minutes. Although NIS was almost equally effective for this transformation, we opted to use economically cheaper NBS. However, NBS has some limitation because of its tendency for radical reactions. To expand the scope of the reaction, a series of differentially protected allyl glycoside was transformed into corresponding hemiacetal derivative in excellent yield (Sch. 1, Table 1) following similar reaction conditions. Use of $\text{CH}_3\text{CN-H}_2\text{O}$ (9:1) as solvent can furnish similar yield of the product, but acetone- H_2O has been used because of its cheap availability. Most of the functional groups used in the protection of hydroxy groups of the carbohydrate backbone (i.e., benzylidene, isopropylidene acetal, benzyl, 4-methoxybenzyl, benzoyl, acetyl, *tert*-butyldiphenylsilyl, etc.) remain unaffected under the reaction condition. Although NBS has been used in the oxidative opening of benzylidene acetal under the Hanessian-Hullar reaction condition, it has no effect on the benzylidene acetal using the present reaction condition. A comparative study on the effect of solvent and halogenating agents on the formation of hemiacetal derivatives is presented in Table 2. Using α - and β -allyl glycosides, similar results were obtained.

We presumed that bromonium ion (Br^+) generated from NBS and the allyl group are in a close proximity to form an addition product, which after hydrolysis resulted in the glycosyl hemiacetal derivatives from the allyl glycoside.

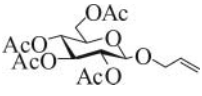
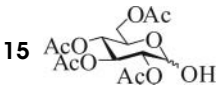
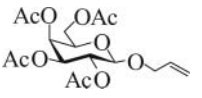
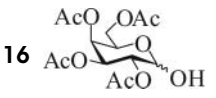
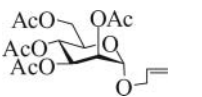
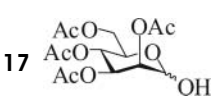
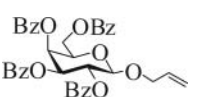
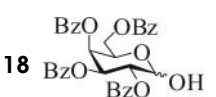
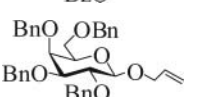
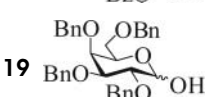
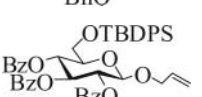
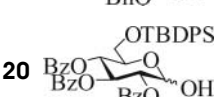
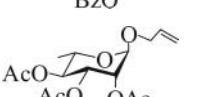
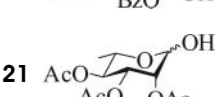
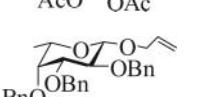
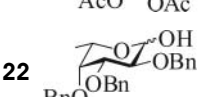

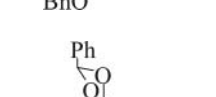
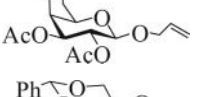
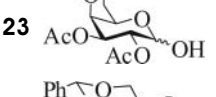
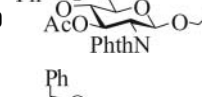
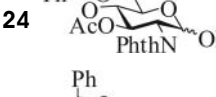
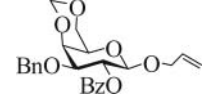
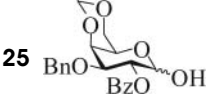
In summary, a novel, metal-free mild reaction condition has been developed for the direct hydrolysis of allyl glycosides in the presence of NBS. This finding can also explain the low-yielding glycosylation reactions using functionalized allyl glycoside as glycosyl acceptor under iodonium ion-mediated thioglycoside activation conditions. Use of readily available reagents, without requirement of heavy metallic salts, high boiling solvents, or expensive Lewis acid additives, makes this exceptionally fast reaction protocol for the preparation of glycosyl hemiacetal derivatives an attractive alternative to the existing methods.

EXPERIMENTAL

General Procedure

All reactions were monitored by thin layer chromatography over silica gel-coated TLC plates. The spots on TLC were visualized by warming ceric sulphate (2% $\text{Ce}(\text{SO}_4)_2$ in 2N H_2SO_4)-sprayed plates in hot plate. Silica gel 230–400 mesh was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance DRX 500 MHz using CDCl_3 as solvents and TMS as internal reference unless stated otherwise. Chemical shift value is expressed in δ ppm. ESI-MS were recorded on a Micromass Quattro II triple

Table 1: Hydrolysis of allyl glycosides using *N*-bromosuccinimide (NBS)^a at room temperature

Thioglycosides	Products	Time (min)	Yield (%) (α/β)	Ref
1 	15 	3	90 (2:1)	(14)
2 	16 	<2	92 (3:1)	(14)
3 	17 	3	90 (5:1)	(14)
4 	18 	5	88 (2:1)	(14)
5 	19 	5	82 (2:1)	(14)
6 	20 	5	80 (3:1)	(16)
7 	21 	<2	90 (4:1)	(14)
8 	22 	<2	85 (3:1)	(14)
9 	23 	3	86 (2:1)	—
10 	24 	5	90 (1:3)	(18)
11 	25 	5	82 (3:1)	—
12 	26 	3	80 (2:1)	—

(Continued on next page)

Table 1: Hydrolysis of allyl glycosides using *N*-bromosuccinimide (NBS)^a at room temperature (*Continued*)

Thioglycosides	Products	Time (min)	Yield (%) (α/β)	Ref
13	27	5	88 (3:1)	(16)
14	28	5	82 (2:1)	(16)

NPhth, *N*-phthalimido; MBn, 4-methoxybenzyl.
^a1.1 equiv. of NBS was used in acetone-H₂O (10:1).

quadrupole mass spectrometer. Commercially available grades of organic solvents of adequate purity are used in many reactions.

Typical Experimental Protocol for The Preparation of Glycosyl Hemiacetal Derivatives

To a solution of functionalized allyl glycoside (1 mmol) in acetone-H₂O (2 mL; 10:1, v/v) was added NBS (1.1 mmol) at 0 to 5°C and the reaction mixture was allowed to stir at the same temperature for the appropriate time (Table 1). The reaction mixture was diluted with CH₂Cl₂ (20 mL) and the organic layer was washed with 5% Na₂S₂O₃ and H₂O, dried (Na₂SO₄), and evaporated to dryness. The crude product was purified over SiO₂ using hexane-EtOAc as eluant to give pure glycosyl hemiacetal derivative. An inseparable anomeric mixture of hemiacetal derivative was formed in every case; the ratio was determined from the integration of their ¹H NMR spectra. ¹H NMR and ¹³C NMR spectra of the known glycosyl hemiacetal derivatives matched with the data reported in the cited references. Spectral data for new compounds,

Table 2: Optimization of the reaction condition for the formation of glycosyl hemiacetal derivative (**15**) from allyl glycoside (**1**)

Entry	Substrate	Catalyst	Solvent	Time (min)	Yield (%)
1	1	NBS	CH ₂ Cl ₂	30	85
2	1	NBS	CH ₃ CN-H ₂ O	5	88
3	1	NBS	Acetone-H ₂ O	3	90
4	1	NIS	CH ₃ CN-H ₂ O	15	85
5	1	NIS	Acetone-H ₂ O	15	90
6	1	I ₂	Acetone-H ₂ O	45	82

which were not reported earlier, are presented below. Although both α - and β -anomers formed under the reaction conditions, spectral data for the major isomer are presented for the sake of simplicity.

2,3-Di-O-acetyl-4,6-O-benzylidene- α -D-galactopyranose (23)

^1H NMR (CDCl_3 , 300 MHz): δ 7.48–7.33 (m, 5 H, Ar-H), 5.46 (s, 1 H, PhCH), 5.32–5.29 (m, 1 H, H-2), 4.94 (dd, $J = 10.4$, 3.4 Hz, 1 H, H-3), 4.53 (d, $J = 3.4$ Hz, 1 H, H-1), 4.32 (br s, 1 H, H-4), 3.85–3.77 (m, 2 H, H-6_{a,b}), 3.50–3.49 (m, 1 H, H-5), 2.09 (s, 6 H, 2 COCH₃); ESI-MS: calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_8$: m/z 352.12; found: m/z 335.1 [$\text{M}-\text{H}_2\text{O}+1$].

2-O-benzoyl-3-O-benzyl-4,6-O-benzylidene- α -D-galactopyranose (25)

^1H NMR (CDCl_3 , 300 MHz): δ 8.02–7.17 (m, 15 H, Ar-H), 5.59–5.54 (m, 1 H, H-2), 5.46 (s, 1 H, PhCH), 4.67 (d, $J = 12.4$ Hz, 1 H, PhCH_{2a}), 4.58 (d, $J = 9.0$ Hz, 1 H, H-1), 4.56 (d, $J = 12.4$ Hz, 1 H, PhCH_{2b}), 4.20 (br s, 1 H, H-4), 4.03–4.01 (m, 1 H, H-3), 3.76–3.69 (m, 2 H, H-6_{a,b}), 3.39–3.37 (m, 1 H, H-5); ESI-MS: calcd. for $\text{C}_{27}\text{H}_{26}\text{O}_7$: m/z 462.17; found: m/z 445.1 [$\text{M}-\text{H}_2\text{O}+1$].

2-O-acetyl-4,6-O-benzylidene-3-O-(4-methoxybenzyl)- α -D-galactopyranose (26)

^1H NMR (CDCl_3 , 300 MHz): δ 7.51–6.80 (m, 9 H, Ar-H), 5.46 (s, 1 H, PhCH), 5.32–5.26 (m, 1 H, H-2), 4.58–4.43 (m, 2 H, MeOPhCH₂), 4.52 (d, $J = 3.0$ Hz, 1 H, H-1), 4.30–4.27 (m, 1 H, H-3), 4.15 (br s, 1 H, H-4), 3.87–3.84 (m, 2 H, H-6_{a,b}), 3.79 (s, 3 H, OCH₃), 3.57–3.55 (m, 1 H, H-5); ESI-MS: calcd. for $\text{C}_{23}\text{H}_{26}\text{O}_8$: m/z 430.16; found: m/z 413.1 [$\text{M}-\text{H}_2\text{O}+1$].

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