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Bamford-Stevens reaction assisted synthesis of styrene *C*-glycosides

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ABSTRACT

Modification of carbohydrates and their analogs is hindered due to multi-step synthetic methodologies involving selective protection and deprotection of multiple hydroxyl groups present in the molecule. A highly efficient route for the synthesis of 1-phenyl-2-(β-D-glycopyranosyl)ethenes has been developed from native sugars, which neither requires protection/deprotection of the hydroxyl groups nor use of any metal/metal ions. The key step of the developed methodology is the use of Bamford-Stevens reaction which led to the formation of the desired compounds in moderate to high yields in three steps only.

GRAPHICAL ABSTRACT

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Introduction

C-Glycosides are a family of stable carbohydrate derivatives that have drawn the attention of chemists due to their interesting biological properties.[1–3] They are also used as precursors for the synthesis of *C*-glycoside mimics of glycolipids,[4] oligosaccharides,[5] glycoproteins,[6] and other natural and biologically active compounds.[7,8] The conformation of the native sugars and their *C*-glycosides have very little difference[9] but the pharmacological profile of *C*-glycosides vary significantly from its native *O*-glycosides as the glycosidic C–C bond is not cleavable under normal physiological conditions making them ideal surrogates of native *O*-glycosides as therapeutic agents.[10–13] In spite of various utility and natural origin of many *C*-glycosides,[14] their availability is often hedged by the report of complicated synthesis from corresponding native sugars.

The aim of this study is to develop an efficient metal free synthetic methodology for the preparation of styrene *C*-glycosides, which is a key intermediate molecule en-route to various natural and biologically active carbohydrate derivatives.[15–21] The synthesis of styrene *C*-glycosides reported earlier has been smeared either by inclusion of protection/deprotection steps, use of toxic transition metals or by formation of mixture

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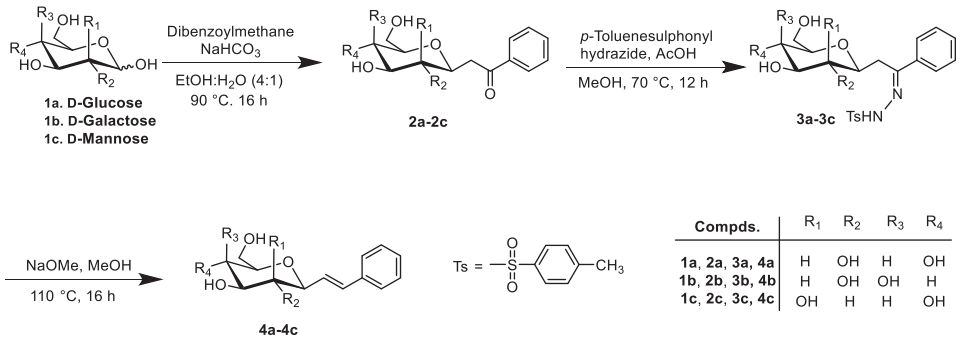
of α- and β-anomers or *E*-*Z* isomers.[22–29] Recently, Kaszás *et al.*, [22] have reported the synthesis of styrene *C*-glycoside by Pd-catalyzed cross coupling reaction of anhydro-aldose tosylhydrazone with benzyl bromides in moderate yields. However, one of the drawbacks of the reaction is the formation of mixture of compounds and the other is the multistep synthesis of starting aldehyde, *i.e.* anhydro-aldoses from native sugars that require protection/deprotection of multiple sugar hydroxyl groups too. Herein, we report the synthesis of (*E*)-1-phenyl-2-(β-D-glycopyranosyl)ethenes in 54–84% overall yields in three steps starting from unprotected hexose sugars. The developed methodology is convenient and efficient compared to the literature procedures where either transition metals or protection/deprotection chemistry has been used often leading to the formation of mixture of isomeric products. We have used Bamford-Stevens reaction,[30] which have recently attracted much interest in organic synthesis, in one of the crucial steps for the synthesis of 1-phenyl-2-(β-D-glycopyranosyl)ethenes.[31,32]

Results and discussion

Three hexoses, *i.e.* D-glucose (**1a**), D-galactose (**1b**), and D-mannose (**1c**) were selectively converted to β-*C*-glycosyl benzoylmethane (**2a**, **2b,** and **2c**, respectively) on treatment with 1,3-diphenylpropan-1,3-dione (dibenzoylmethane) in the presence of sodium bicarbonate ($NaHCO_3$) at 90 °C in ethanol:water mixture (4:1), in quantitative yields, except in case of D-galactose (71% yield).[25,33] The β-configuration of benzoyl methyl group in compounds **2a-c** has been proved by NOE spectroscopy, which has also been supported by literature reports.[25,33] The refluxing of compounds **2a-c** with *p*-toluenesulphonyl hydrazide in the presence of catalytic amount of glacial acetic acid at 70 °C in methanol afforded 1-phenyl-2-(β-D-glycopyranosyl)ethylidene *p*-toluoylsulfonyl hydrazide (**3a-c**) in 87–94% yields. It was envisaged that Bamford–Stevens reaction can be used for the synthesis (*E*)-1-phenyl-2-(β-D-glycopyranosyl)ethenes (**4a-c**) from the corresponding hydrazides **3a-c** *via* the formation of diazo-intermediate followed by generation of carbocation and in turn the formation of the desired products in basic condition (Scheme 1).

The Bamford-Stevens reaction condition with respect to the use of base and solvent for the efficient synthesis of (*E*)-1-phenyl-2-(β-D-glycopyranosyl)ethenes (**4a-c**) was optimized by the conversion of 1-phenyl-2-(β-D-galactopyranosyl)ethylidene



Scheme 1. Bamford–Stevens reaction assisted synthesis of styrene *C*-glycosides **4a-c**.

Table 1. Optimization of Bamford–Stevens reaction condition for the conversion of hydrazide **3b** to styrene *C*-glycoside **4b**.

Entry	Base	Solvent	Additive	T (°C)	Time (h)	Yield (%)
1.	Et_3N	DMF	–	110	30	nr[a]
2.	DBU	DMF	–	110	30	nr[a]
3.	KOH	1,4-Dioxane	–	110	12	9
4.	KOH	MeOH	H_2O	70	16	20
5.	KOH	MeOH	H_2O	110	24	20
6.	K_2CO_3	1,4-Dioxane	–	110	16	5
7.	K_2CO_3	MeOH	H_2O	110	16	10
8.	NaOMe	1,4-Dioxane	–	110	16	20
9.	NaOMe	MeOH	H_2O	70	16	30
10.	NaOMe	MeOH	H_2O	110	16	89
11.	MeLi	THF	–	−40	3	nr[b]
12.	MeLi	THF	–	0	3	nr[b]
13.	*n*BuLi	THF	–	−40	3	nr[b]
14.	*n*BuLi	THF	–	0	3	nr[b]

Reaction conditions unless otherwise specified: base (10 equiv.); additive = 0.1 equiv.; nr[a] = no reaction; nr[b] = inseparable mixture.

p-toluoylsulfonyl hydrazide (**3b**) to (*E*)-1-phenyl-2-(*β*-D-galactopyranosyl)ethene (**4b**) as a model reaction in sealed reaction vessel (Table 1). It was observed that the use of organic bases, such as triethylamine (Et_3N) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in DMF failed to initiate the conversion of hydrazide **3b** into alkene **4b** even after a prolonged heating at 110 °C (Table 1, entries 1–2). However, application of inorganic bases, such as potassium hydroxide (KOH) and potassium carbonate (K_2CO_3) either in 1,4-dioxane or in aqueous methanol initiated the formation of alkene from hydrazide, but to a very less extent which is of no practical utility (Table 1, entries 3–7). Likewise, the use of sodium methoxide (NaOMe) in dioxane at 110 °C and in aqueous methanol at 70 °C did not lead to an appreciable improvement in the yield of *C*-styryl galactoside. However, employment of NaOMe in aqueous methanol at 110 °C led to the conversion of hydrazide to (*E*)-1-phenyl-2-(*β*-D-galactopyranosyl)ethenes (**4b**) in 89% yield (Table 1, entries 8–10). The application of optimized Bamford-Stevens reaction condition on 1-phenyl-2-(*β*-D-glucopyranosyl)ethylidene *p*-toluoylsulfonyl hydrazide (**3a**) and 1-phenyl-2-(*β*-D-mannopyranosyl)ethylidene *p*-toluoylsulfonyl hydrazide (**3c**) led to the formation of (*E*)-1-phenyl-2-(*β*-D-glucopyranosyl)ethene (**4a**) and (*E*)-1-phenyl-2-(*β*-D-mannopyranosyl)ethenes (**4c**) in 89 and 84% yields, respectively. The trans geometry of the double bond, *i.e.* exclusive formation of (*E*)-1-phenyl-2-(*β*-D-glycopyranosyl)ethenes (**4a-c**) was revealed by the coupling constant of two double bond protons ($J = 16.0$ Hz).

There is an alternative approach to generate diazo intermediate from suitable hydrazides, such as 1-phenyl-2-(*β*-D-galactopyranosyl)ethylidene *p*-toluoylsulfonyl hydrazide (**3b**) utilizing organolithium compounds which in turn can be converted into styrene *C*-galactoside as per Shapiro reaction.[34] Thus, hydrazide **3b** in dry THF was treated with methyl lithium/*n*-butyl lithium at -40 °C and also at 0 °C, but the reaction did not yield the desired product. This might happen because of the presence of free hydroxyl groups on sugar moiety of hydrazides (Table 1, entries 11–14).

The structures of all the synthesized compounds **2a-c**, **3a-c,** and **4a-c** were unambiguously established on the basis of their spectral (IR, ^1H & ^{13}C NMR and HRMS) data

analysis (See Supplementary Material). The structures of known compounds **2a**-**c** were confirmed on the basis of comparison of their spectral data with those reported in the literature.[25,33]

Conclusion

We have developed a simple, efficient and eco-friendly route for exclusive synthesis of (*E*)-1-phenyl-2-(*β*-D-glycopyranosyl)ethenes from native sugars using Bamford-Stevens reaction in one of the crucial steps. The developed methodology does not require any protection/deprotection step(s) or metal ion-catalysis and is selective to afford the *trans* product only.

Experimental

All reactions were performed under normal atmospheric conditions. Commercial chemicals, reagents and solvents were purchased from local commercial sources and used without any further purification. R_f values are reported for analytical TLC using the specified solvents and 0.25 mm silica gel $60F_{254}$ plates that were visualized by UV irradiation or by charring with 5% alcoholic sulfuric acid solution (5% conc. H_2SO_4 in EtOH). Solvents were removed under reduced pressure using rotary evaporator, followed by further drying of the residual solvents under high vacuum. Column chromatography was performed on silica gel (100–200 mesh). The IR spectra were recorded on a Perkin-Elmer model 2000 FT-IR spectrometer by making KBr disk for solid samples and neat for liquid samples. The ^{1}H- and ^{13}C-NMR spectra were recorded on Jeol Delta 400 MHz and 100.6 MHz spectrometer, respectively using tetramethylsilane (TMS) as internal standard. The chemical shift values are on δ scale and the coupling constant (J) are in Hz. ^{1}H NMR spectra in CD_3OD were referenced at $\delta = 3.31$ ppm. The ^{13}C NMR spectra in CD_3OD were referenced at $\delta = 49.00$ ppm. The following abbreviations were used to designate signal multiplicity, s = singlet, d = doublet, t = triplet, m = multiplet. HRMS analysis was carried out using Agilent G6530AA LC Q-TOF mass spectrometer using ESI method. The optical rotation was measured on a Rudolph Autopol II automatic polarimeter using 589 nm wavelength's light.

Synthesis of 1-phenyl-2-(β-D-glucopyranosyl)ethylidene p-toluoylsulfonyl hydrazide (3a)

Compound **2a** (500 mg, 1.77 mmol) was taken in two necked round bottom flask and dissolved in methanol (5 mL) followed by addition of glacial acetic acid (10 mg, 0.17 mmol). The reaction was refluxed for 15 min at 70 °C before the stepwise addition of *p*-toluenesulphonyl hydrazide (363 mg, 1.9 mmol) dissolved in methanol (5 mL). The reaction was stirred under refluxing condition for 12 h. After complete disappearance of the starting material on TLC, reaction mixture was concentrated under reduced pressure and purified by column chromatography using 7% methanol in DCM as eluent to give hydrazide **3a**, which was obtained as colorless oil (755 mg) in 94% yield; IR (KBr, ν_{max}/cm^{-1}): 3352, 2918, 2850, 1598, 1072; ^{1}H NMR (400 MHz, CD_3OD): δ 2.42 (s, 3H),

2.88–3.0 (m, 3H), 3.12–3.19 (dd, 1 H, $J = 14.2$, 8.5 Hz), 3.45–3.62 (m, 5H), 7.29–7.34 (m, 3H), 7.39 (d, 2 H, $J = 8.0$ Hz), 7.59–7.65 (m, 2H), 7.90 (d, 2 H, $J = 8.0$ Hz).; ^{13}C NMR (100.6 MHz, CD_3OD) δ 20.24, 29.43, 60.91, 66.40, 71.08, 74.59, 75.66, 80.40, 126.23, 127.94, 128.19, 129.29, 129.41, 135.96, 136.40, 144.10, 153.20; HRMS (ESI) $m/z = 451.1533$ (calculated for $C_{21}H_{27}N_2O_7S$ $[M + H]^+ = 451.1539$).

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