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Contrasting reactivity of thioglucoside and selenoglucoside donors towards promoters: implications for glycosylation stereocontrol☆

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Abstract—The stereochemical outcome of glycosylation reactions with model thioglycosides and selenoglycosides proved to be dependent on the source of promoter iodonium ion, with iodine giving different results to *N*-iodosuccinimide (NIS) alone or *N*-iodosuccinimide/trimethylsilyltrifluoromethanesulfonate (NIS/TMSOTf). In contrast to armed thioglycosides, which anomerise, and disarmed thioglycosides, which do not react, both armed and disarmed selenoglycosides give rise to the corresponding glycosyl iodides when reacted with iodine. Further, whilst the single electron transfer agent DDQ alone is an ineffective promoter, in combination with iodine it produces better acetonitrile-assisted β-stereoselectivity with both thioglycosides and selenoglycosides than does tris(4-bromophenyl)aminium hexachloroantimonate (BAHA).

Keywords: Thioglycoside; Selenoglycoside; Glycosylation; Promoter; Mechanism

1. Introduction

In the past decades there has been an increasing awareness of the importance of carbohydrates in biological processes[2] and as a consequence, the demand for improved synthetic strategies towards oligosaccharides has grown.[3] Of the many classes of glycosyl donor building blocks, thioglycosides have probably received the most attention due to their inherent shelf stability and the ease of chemoselective activation.[4] In the early 1990s, selenoglycosides[4] were demonstrated to be more reactive than the corresponding thioglycosides towards a variety of promoter systems;[5] they are also effective in chemoselective glycosylation reactions employing armed/disarmed strategies.[6] As well as two electron activation with conventional promoters, such as NIS/TfOH or NIS/TMSOTf,[7] the single electron transfer (SET) activator tris(4-bromophenyl)aminium hexachloroantimonate (BAHA) has also been used to promote glycosylation reactions with thioglycosides[8] and selenoglycoside donors.[9] This laboratory has a longstanding interest in the use of molecular iodine and related reagents as promoters for glycosylation chemistry.[1] Iodine itself is a mild and effective activator of a variety of widely used glycosyl donor species, including glycosyl halides, thioglycosides, selenoglycosides, glycosyl trichloroacetimidates, phosphates and sulfoxides, and pentenyl glycosides.[10] It is generally assumed that iodine simply serves as a source of iodonium ion in such reactions, in much the same way as NIS does. Whilst iodine alone is able to activate reactive glycosyl donors, less reactive donors are activated when iodine is used in conjunction with DDQ, a versatile single electron oxidising agent.[11,12] Activation of thioglycosides with DDQ in the absence of iodine has not proved possible, demonstrating that the combination of the two reagents (I_2/DDQ) is key. The mechanism of thioglycosides activation by I_2/DDQ is not currently understood, but the SET properties of DDQ might be significant.

☆ Iodine: a versatile reagent in carbohydrate chemistry XVIX.[1]

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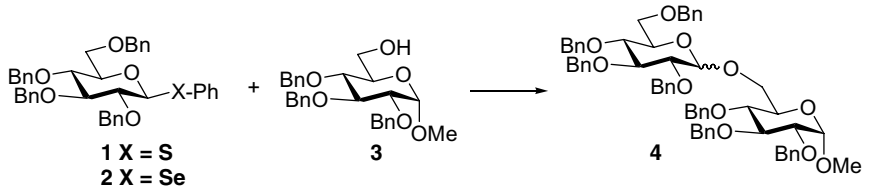
Table 1. Model iodonium ion-mediated glycosylation reactions with thioglycoside **1** and selenoglycoside **2**



Reagents and conditions	Thioglycoside **1**	Selenoglycoside **2**
NIS, CH_3CN	53%, $\alpha/\beta = 1/3$	64%, $\alpha/\beta = 1/5$
NIS, CH_2Cl_2	88%, $\alpha/\beta = 1/1$	32%, $\alpha/\beta = 1/1.2$
NIS, TMSOTf, CH_3CN	96%, $\alpha/\beta = 1/4.3$	83%, $\alpha/\beta = 1/5$
NIS, TMSOTf, CH_2Cl_2	97%, $\alpha/\beta = 1.3/1$	92%, $\alpha/\beta = 1/1.4$
I_2 (2 equiv), CH_3CN	88%, $\alpha/\beta = 1/2.8$	91%, $\alpha/\beta = 1/1.5$
I_2 (2 equiv), CH_2Cl_2	45%, $\alpha/\beta = 1/1.2$	52%, $\alpha/\beta = 2/1$

All reactions conducted at room temperature for 30 min. Yields, which are unoptimised, relate to the combined isolated α/β mixture. The stereochemical outcome of the reaction was determined by integration of the ^{1}H NMR signals for the methyl aglycones of the anomers of **4**.[15]

Herein we report comparison of iodonium ion sources in the activation of model thioglycosides and selenoglycosides, along with studies on the activation of similar glycosyl donors under single electron transfer conditions. The aim of these studies was to assess the impact of the source of iodonium ion and SET agent on glycosyl donor activation and glycosylation stereocontrol, and to determine if, consequently, there are differences in the mechanism of activation of selenoglycosides and thioglycosides.

2. Results and discussion

2.1. Comparison of NIS, NIS/TMSOTf and iodine as promoters of model glycosylation reactions with thioglucoside and selenoglucoside donors

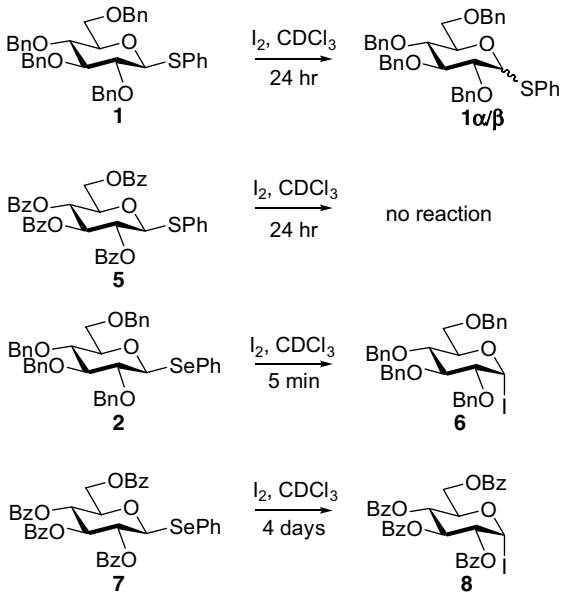
Glycosylation reactions with armed thioglycoside **1**[13] or armed selenoglycoside **2**[9] and the primary alcohol acceptor **3**[14] gave the corresponding 1,6-linked disaccharides **4**[15] in a manner that was both solvent and promoter-dependent (Table 1). One might reasonably expect that iodonium ion-promoted glycosylation reactions with both thioglycosides and selenoglycosides would favour β-glycoside formation more strongly in acetonitrile than in a non-participating solvent such as dichloromethane. It is generally accepted that solvent participation by acetonitrile shields the α-face of a glycosyl oxocarbenium ion by kinetically controlled formation of an α-glycosyl nitrilium ion, thus favouring the formation of a β-configured glycosidic linkage.[16]

Comparison of the reaction or donors **1** and **2** in acetonitrile and dichloromethane with NIS gives the expected result, with acetonitrile-based reactions favouring β-glycosylation whereas dichloromethane-based reactions give essentially no stereocontrol and much slower reaction (a feature typical of reactions involving polar or charged reaction intermediates) (Table 1). Broadly the same stereochemical outcomes are evident for the corresponding reactions with NIS/TMSOTf, but yields are higher. Whilst iodine gives good yields in acetonitrile with both donors, β-selectivity with respect to the corresponding reactions in dichloromethane is notably poorer than for the corresponding reactions with NIS and NIS/TMSOTf. This may be due to the generation of glycosyl iodides in situ, arising from participation of iodide released in the initial *S*-activation step. We were therefore drawn to investigate the diminished ®-selectivity observed in molecular iodine-promoted glycosylation in acetonitrile, and to assess the likely involvement, or otherwise, of glycosyl iodide intermediates.

2.2. Investigation of iodine-promoted activation of thioglucoside and selenoglucoside donors by ^{1}H NMR spectroscopy

The behaviour of both armed thio- and seleno-glycoside donors **1** and **2**, as well as their disarmed counterparts **5**[17] and **7**,[18] in the presence of iodine was studied directly by NMR spectroscopy. In previous studies,[19] we have shown that reaction of armed, benzyl ether protected thioglycosides with iodine results in (intermolecular) thioglycoside epimerisation.[†] We could find no evidence for glycosyl iodide formation, which may reflect the reversibility of C–S bond formation, with the equilibrium favouring the thioglycosides. Further, disarmed, ester protected thioglycosides did not react with iodine.[19] These earlier observations were borne out by the current NMR study of the reaction of thioglycosides **1** and **5** with iodine (Scheme 1), as judged by monitoring anomeric proton ^{1}H NMR signals.[19]

[†] The observation of thioglycoside epimerisation follows on from an earlier work.[20]



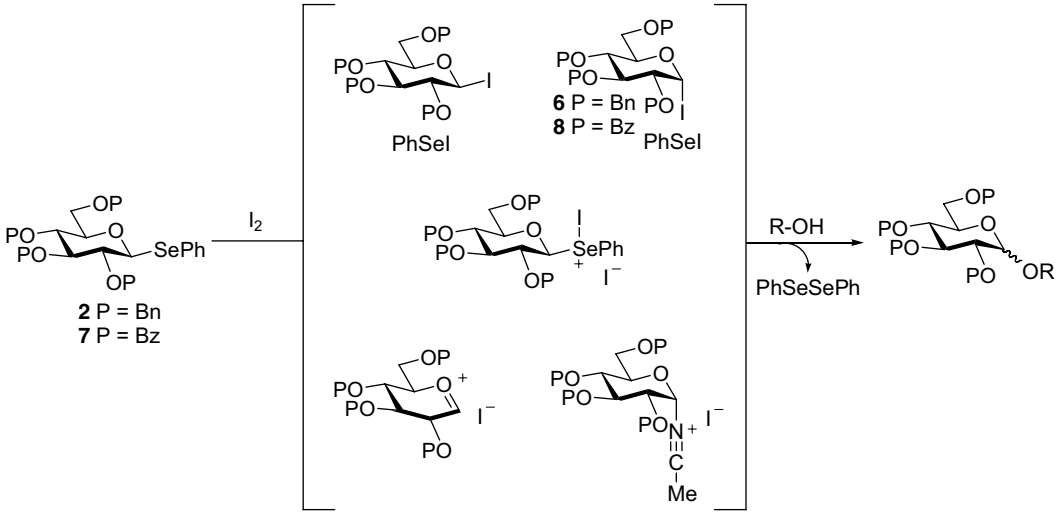
Scheme 1. Reaction of selenoglycosides and thioglycosides with iodine under NMR conditions.

In contrast to the reactivity of thioglycosides, armed selenide donor **2** was transformed within 5 min into the corresponding α-glycosyl iodide **6**,[21,22] which decomposed at prolonged reaction times. The disarmed donor selenide **7** reacted much slower with iodine; after four days it also gave an α-glycosyl iodide product, **8**. Known iodide **8**[22,23] proved to be reasonably stable and was obtained from the NMR reaction by flash column chromatography in 45% isolated yield. During the reaction of selenides **2** and **7** with iodine, no anomerisation of the β-selenide was detectable by ^{1}H NMR spectroscopy, in contrast to the corresponding reaction of armed thioglycoside **1**. This suggests that the iodine-mediated activation process is potentially reversible for thioglycosides, but seems not to be so for selenoglycosides; once the C–Se bond is cleaved it is not reformed.

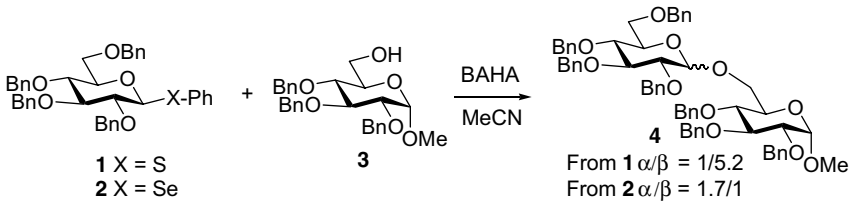
Glycosyl iodides **6** and **8** might serve as intermediates in iodine-mediated glycosylation reactions with glycosylselenides **2** and **7**, respectively. It is possible that glycosyl iodides formed in situ react directly with acceptor alcohols, or indeed with further molecular iodine present in the reaction mixture. Such processes can, on occasion, give rise to α-glycosylation, even in the presence of a C-2 participating group, presumably due to the intermediacy of a transient β-glycosyl iodide intermediate.[24] This notion parallels the in situ generation of labile β-linked armed glycosyl iodides, which ultimately gives rise to an α-selective glycosylation process.[25] In addition, the generation of β-linked armed glycosyl bromides from selenides has been successfully exploited in iterative glycosylation chemistry.[26] Bearing in mind the poor β-stereocontrol for iodine-promoted reaction of armed thioglycoside **1** with sugar primary alcohol **3** in acetonitrile (Table 1), iodide **6** might also be formed transiently during the activation of donor **1**. Taken together, these observations suggest that the nucleophilic iodide generated in iodine-promoted glycosylation reactions may out-compete the nucleophilicity of acetonitrile solvent, thus interfering with solvent-mediated stereocontrol of the glycosylation process (Scheme 2).

2.3. Single electron transfer agents as promoters of model glycosylation reactions with thioglucoside and selenoglucoside donors

Looking to promoters with a fundamentally different mode of action, the single electron transfer agent tris(4-bromophenyl)aminium hexachloroantimonate (BAHA) has also been used to promote glycosylation reactions with thioglycoside[8] and selenoglycoside[9] donors. Literature reports of the reactions of thioglycoside **1** and

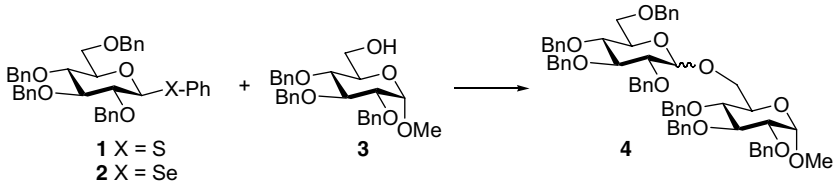


Scheme 2. Potential intermediates in iodine-promoted activation of selenoglycosides.



Scheme 3. BAHA-promoted SET-based glycosylation with thioglycoside **1**[8] and selenoglycoside **2**.[9]

Table 2. Model SET-based glycosylation reactions with thioglycoside **1** and selenoglycoside **2**



Reagents and conditions	Thioglycoside **1**	Selenoglycoside **2**
BAHA (1.5 equiv), CH_3CN	84%, $\alpha/\beta = 1/4.6$	62%, $\alpha/\beta = 1/2$
BAHA (1.5 equiv), CH_2Cl_2	79% $\alpha/\beta = 1.1/1$	87% $\alpha/\beta = 1.5/1$
DDQ (2 equiv), CH_3CN	No disaccharide	No disaccharide
I_2 (1.5 equiv), DDQ (1.5 equiv), CH_3CN	87%, $\alpha/\beta = 1/5$	79%, $\alpha/\beta = 1/5$
I_2 (1.5 equiv), DDQ (1.5 equiv), CH_2Cl_2	32%, $\alpha/\beta = 1/3.4$	26%, $\alpha/\beta = 1/1.5$

All reactions conducted at room temperature for 30 min. Yields, which are unoptimised, relate to the combined isolated α/β mixture. The stereochemical outcome of the reaction was determined by integration of the ^{1}H NMR signals for the methyl aglycones of the anomers of **4**.[15]

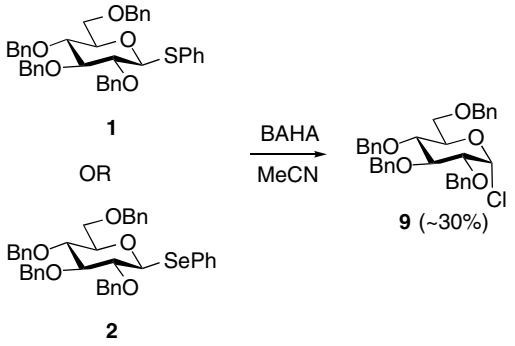
selenoglycoside **2** with acceptor primary alcohol **3** in acetonitrile show a marked donor-dependence in the stereoselectivity of the process: reaction with thioglycoside **1** gives pronounced β-selectivity, as expected,[16] but reaction with selenoglycoside **2** gives only a very modest excess of the β-glycoside **4**[8,9] (Scheme 3). The intriguing difference in stereoselectivity prompted us to compare the activation of both classes of glycosyl donor under single electron transfer (SET) conditions.

Repetition of the literature BAHA-mediated glycosylation reactions (Scheme 3) confirmed the previously reported results, that is, good ®-selectivity for reaction with thioglycoside **1** and poor stereoselectivity when the selenoglycoside **2** was used (Table 2).

The use of DDQ alone in an attempt to effect SET-mediated donor activation did not provide any disaccharide product from reactions with either the thioglycoside **1** or selenoglycoside **2** and primary alcohol **3**. However, DDQ-promoted activation of selenoglycoside **2**, but not thioglycoside **1**, in the presence of 4 M equiv of methanol did give rise to anomeric methyl glucosides (27%, $\alpha/\beta = 1/4$), as judged by monitoring methyl aglycone ^{1}H NMR signals.[27] The poor yield of methyl glycosides in these reactions is accompanied by substantial hemiacetal formation.

We have previously reported the use of I_2/DDQ for activation of glycosyl halides,[11] and noted the potential of the same reagent combination for the activation of *S*-*p*-methoxybenzyl thioglycosides.[12] Although iodine-promoted glycosylation in acetonitrile gives rather poor ®-selectivity (Table 1), addition of DDQ to the iodine-promoted glycosylation of primary alcohol **3** with either thioglycoside **1** of selenoglycoside **2** gave the ®-linked disaccharide **4** in high yield and with greater stereoselectivity than in either the corresponding iodine- or NIS/TMSOTf-mediated processes (Table 2).[‡] These results indicate that activation with I_2/DDQ follows a different reaction pathway than activation with iodine alone. It seems unlikely that this particular process involves a single electron transfer process; more likely, the DDQ serves to oxidise iodide, generated in the activation process, to iodine, so preventing glycosyl iodide and facilitating α-glycosyl nitrilium ion formation. Interference from nucleophilic counter-ions has previously been noted in glycosyl sulfoxide activation with ICl, which generates glycosyl chlorides.[28] Similarly, the activation of thioglycosides with dimethyl(methylthio)sulfonium tetrafluoroborate[29] and the electrochemical activation of chalcoglycosides in the presence of tetrafluoroborate ions as supporting electrolyte[30] both generate glycosyl fluorides. As for iodine-promoted reactions in dichloromethane, I_2/DDQ-promoted glycosylation in this solvent is slow.

[‡] Attempts to activate armed thioglycosides with iodine in the presence of more potent oxidising agents such as CAN did not meet with successful glycoside synthesis. The nucleophilic nitrate counter-ion intercepted activated intermediates to give anomeric α-nitrates (P. Cura and R. A. Field, unpublished observations).



Scheme 4. Reaction of armed and armed donors with BAHA.

As noted above, we were conscious of the potential for interference from counter-ions present in glycosylation reactions. Armed thioglycoside **1** and selenoglycoside **2** were therefore reacted with BAHA in the absence of an acceptor alcohol with a view to evaluate the impact of the $SbCl_6^-$ counter-ion present in the BAHA complex. Activation of thioglycoside **1** or selenoglycoside **2** with BAHA in acetonitrile gave a complex mixture of compounds, the dominant species being the known α-glycosyl chloride **9**[31] (Scheme 4) accompanied by hemiacetal and other unidentified degradation products.

Transient glycosyl chloride formation might therefore occur in situ during BAHA-promoted glycosylation. However, if this is the case, the reversibility of C–S bond formation must, presumably, permit regeneration of thioglycoside from glycosyl chloride in a manner that is not evident for the corresponding selenoglycoside.

3. Summary and conclusions

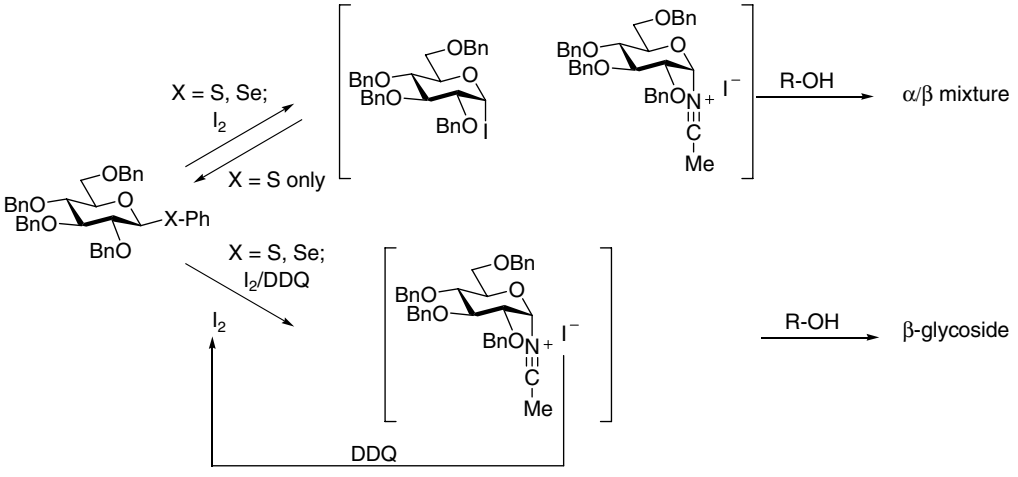
The stereochemical outcome of glycosylation reactions with model thioglycosides and selenoglycosides is dependent on the source of promoter iodonium ion, with iodine giving different results to NIS alone or NIS/TMSOTf. Subsequent comparison of the activation of thioglycosides and selenoglycosides revealed that they follow different reaction pathways. In contrast to armed thioglycosides, which anomerise, and disarmed thioglycosides, which do not react, both armed and disarmed selenoglycosides give rise to the corresponding glycosyl iodides on reaction with iodine. Further, whilst DDQ alone is an ineffective promoter, in combination with iodine it produces better acetonitrile-assisted β-stereoselectivity with both thioglycosides and selenoglycosides than does the established single electron transfer agent BAHA. However, the mechanism of iodine/DDQ action is likely not a SET process, but instead the DDQ serves to oxidise released iodide back to iodine, so prevention in situ glycosyl iodide generation, which may compete with α-glycosyl nitrilium ion formation (Scheme 5). In practical terms, use of iodine in conjunction with DDQ is at least as effective as NIS or NIS/TMSOTf in effecting acetonitrile-assisted β-glycosylation reactions.

Overall, it seems likely that, irrespective of the type of promoter used, the reversibility of C–S and the irreversibility of C–Se bond cleavage during glycosylation is the dominant factor that distinguishes the chemistry of thioglycosides from that of selenoglycosides. This may well account for differences in the stereochemical outcome of reactions employing these classes of glycosyl donor.

4. Experimental

4.1. Materials and general methods

Reactions were carried out in dry solvents using septa and syringes for addition of reagents. Dry CH_2Cl_2 and CH_3CN were prepared by distillation from CaH_2, CH_3OH was distilled from $Mg(OCH_3)_2$ and stored over



Scheme 5. Mechanism to account for differences in iodine and I_2/DDQ-promoted glycosylation in CH_3CN.

3 Å molecular sieves. TLC was performed on pre-coated aluminium plates (Silica Gel 60 F_{254}, Merck). Spots were visualised by exposure to UV light or by immersion in 5% ethanolic H_2SO_4 followed by heating to 150 °C. Solutions of reaction products were dried over $MgSO_4$ and solvents were evaporated under reduced pressure at 25–40 °C. Column chromatography was performed on silica gel (40–70 μm, BDH-Merck). Optical rotations were measured at 25 °C using a Perkin–Elmer 141 polarimeter. ^1H and ^{13}C NMR spectra were recorded at 24 °C with a Varian Unity Plus spectrometer at 400 and 100 MHz, respectively, using TMS as an internal standard. Accurate electrospray ionisation mass spectra (HR ESI-MS) were obtained using positive ionisation mode on a Finnigan MAT 900 XLT mass spectrometer.

The following known compounds were prepared according to standard literature procedures and/or are products of the experiments reported herein: phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**1**);[13] phenyl 2,3,4,6-tetra-*O*-benzyl-1-seleno-β-D-glucopyranoside (**2**);[9] methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**3**);[14] methyl 2,3,4,6-tri-*O*-benzyl-α/β-1,6-D-glucopyranosyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**4**);[15] phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (**5**);[17,32] 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl iodide (**6**);[21,22] phenyl 2,3,4,6-tetra-*O*-benzoyl-1-seleno-β-D-glucopyranoside (**7**);[18] 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl iodide (**8**);[22,23] 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl chloride (**9**).[31]

4.2. General procedures

4.2.1. NMR analysis. The stereochemical outcome of the reactions detailed in Tables 1 and 2 was assessed by integration of ^1H NMR signals for the methyl aglycones of the anomers of disaccharides **4** at 3.32 (β) and 3.35 (α) ppm.[15] Epimerisation of thioglycosides was judged by monitoring anomeric proton ^1H NMR signals at 5.39 and 4.58 ppm for α- and β-thioglycosides **1**, respectively,[19] and 4.85 ppm for thioglycoside **5**.[31]

4.2.2. Glycosylation reactions with NIS/TMSOTf or iodine. Donor **1** or **2** (0.22 mmol) and acceptor **3** (0.17 mmol) were dissolved in CH_2Cl_2 or CH_3CN (1 mL), 4 Å molecular sieves (0.10 g) were added and the reaction mixture was stirred under nitrogen for 30 min. NIS (1.1 mmol) and TMSOTf (0.02 mmol) [or solid iodine (0.44 mmol)] were added and the progress of the reaction was followed by TLC (EtOAc/hexane, 1/4, v/v). When the reaction was complete, the mixture was diluted with EtOAc (10 mL), washed with aq $NaHCO_3$ solution (2×5 mL), aq $Na_2S_2O_3$ solution (2×5mL) and brine (5 mL), dried ($MgSO_4$) and concentrated. Purification by column chromatography (EtOAc/hexane, 0/1 → 1/4, v/v) gave an α/β mixture of disaccharides **4**.

4.2.3. NMR studies on the reaction of glycosyl donors with I_2. Solid I_2 (0.1 mmol) was added to a solution of thioglycoside or selenoglycoside (0.05 mmol) in $CDCl_3$ (0.7 mL). The reaction was followed by ^1H NMR spectroscopy at 400 MHz.

4.2.4. Activation of selenoglycosides with DDQ in MeCN. Selenoglycoside (0.43 mmol) and DDQ (0.85 mmol) were dissolved in CH_3CN (2 mL) and the resulting mixture was stirred for 16 h. The reaction mixture was diluted with CH_2Cl_2 (15 mL), washed with H_2O and brine, dried ($MgSO_4$), concentrated and purified by column chromatography.

4.2.5. Activation of selenoglycosides with BAHA in MeCN. Selenoglycoside (0.16 mmol) and BAHA (0.32 mmol) were dissolved in CH_3CN (1 mL) and the resulting mixture was stirred for 8 h. The reaction mixture was cooled to 0 °C, neutralised with Et_3N, filtered through Celite, concentrated and purified by column chromatography.

4.2.6. Glycosylation reactions with BAHA or I_2/DDQ. Donor **1** or **2** (0.40 mmol) and acceptor **3** (0.32 mmol) were dissolved in CH_2Cl_2 or CH_3CN (2 mL), 4 Å molecular sieves (15 mg) were added and the reaction mixture was stirred under nitrogen for 30 min. BAHA (1.21 mmol) [or I_2 (0.6 mmol) and DDQ (0.6 mmol)] was added and the progress of the reaction was followed by TLC (EtOAc/hexane, 1/4, v/v). When reaction was complete, the mixture was cooled to 0 °C, neutralised with Et_3N, filtered through Celite and concentrated. Purification by column chromatography (EtOAc/hexane, 0/1 → 1/4, v/v) gave an α/β mixture of disaccharides **4**.

Acknowledgements

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