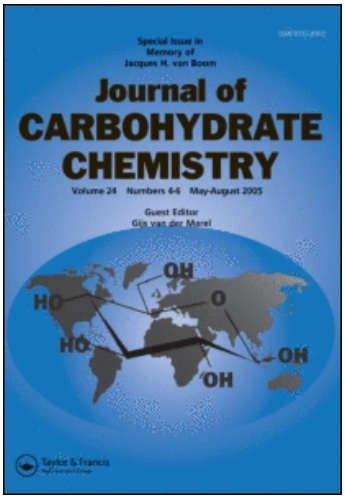

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Large-scale Synthesis of Per-*O*-acetylated Saccharides and Their Sequential Transformation to Glycosyl Bromides and Thioglycosides

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Large-scale Synthesis of Per-*O*-acetylated Saccharides and Their Sequential Transformation to Glycosyl Bromides and Thioglycosides

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This work describes a large-scale synthesis of per-*O*-acetylated mono- and disaccharides using a stoichiometric amount of acetic anhydride in the presence of $LiClO_4$ under solvent-free conditions. The peracetylated saccharides underwent subsequent anomeric bromination and thioglycosidation in one-pot to yield synthetically valuable building blocks.

Keywords Acetylation, $LiClO_4$, One-pot synthesis, Glycosyl bromides, Thioglycosides

INTRODUCTION

The acetylation of alcohols is an important organic transformation used in the laboratory to protect hydroxyl functionality in a multistep organic synthesis and to promote the isolation and identification of natural products bearing saccharide moiety.[1] It is also used in industry to prepare special chemicals. In carbohydrate chemistry, acetylated sugars are important starting materials for the synthesis of complex oligosaccharides and glycoconjugates.[2] This transformation is performed using acetic acid, acetyl chloride, or acetic anhydride as an acetylating reagent. The latter reagent is extensively used, and it invariably requires a catalyst to achieve a reasonable reaction rate.

Various catalysts were developed in recent years to catalyze the acylation of hydroxyl group(s), ranging from organic bases like pyridine and its derivatives DMAP[3] to trialkyl phosphines,[4] aminophosphanes superbases,[5] and novel ionic liquids.[6] Also, Lewis acids including $Ce(OTf)_2$,[7] $ZnCl_2$,[8] $FeCl_3$,[9] $V(O)(OTf)_2$,[10] $Sc(OTf)_3$,[11] $Cu(OTf)_2$,[12] $Zn(ClO_4)_2.6H_2O$,[13] Bronsted acids ($HClO_4$,[14] H_2SO_4[15]), heterogeneous catalysts (Montmorillonite K-10,[16] H-beta zeolite,[17] and zirconium sulfophenyl phosphonate[18]), and iodine[19] have been used as catalysts. Despite the availability of many catalysts, only a handful of catalysts have been employed to acetylate carbohydrates.[7–16,19] Additionally, only a few of these have been used in the large-scale synthesis of carbohydrate building blocks and intermediates.[9,12] For instance, pyridine, which acts both as a catalyst and a solvent, has been used for large-scale preparation, despite its known toxicity and malodorous nature.[20] It requires that acetic anhydride be used in excess by a large factor. Therefore, it involves inconvenient work-up and has a great disadvantage in terms of green chemistry. Similarly, the use of iodine and sodium acetate as a catalyst, in few cases, requires an excess of acetic anhydride.[18] The aforementioned limitations of the large-scale preparation of peracetylated carbohydrates lead to the need for a catalyst that is mild and suitable for

large-scale synthesis, works under near room temperature conditions, and has a simple work-up procedure.

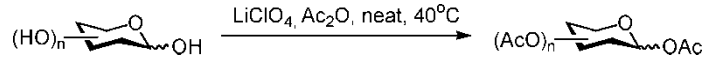
RESULTS AND DISCUSSION

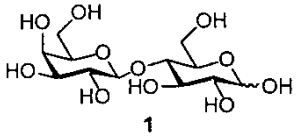
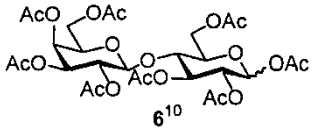
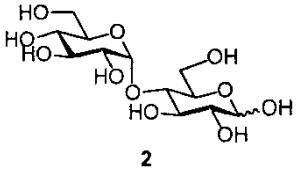
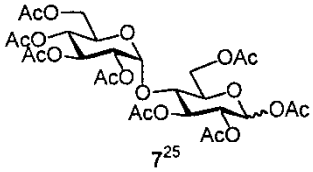
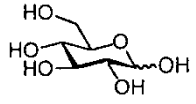
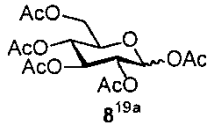
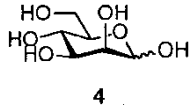
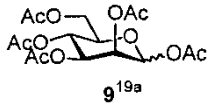
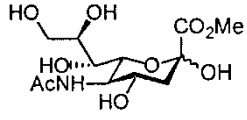
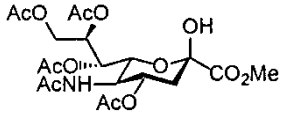
Our previous investigation demonstrated that $LiClO_4$ is a mild catalyst for the preparation of peracetylated sugars.[21] In this report we reveal that the current procedure is suitable for multi-gram scale (20 g) synthesis. The reaction requires only 1.05 equiv of acetic anhydride and 0.1 equiv of $LiClO_4$ per OH group and involves a simple work-up procedure of only neutralization with aqueous $NaHCO_3$ and filtration to give products, usually in the form of solids. These per-*O*-acetylated products could be further transformed into useful glycosyl bromides and thioglycoside derivatives in a one-pot synthetic sequence.

Initially, lactose (**1**, Table 1) was treated with acetic anhydride (1.05 equiv per OH) in the presence of $LiClO_4$ (10 mol% per OH) at 40°C for 12 h, giving per-acetylated lactose **6** as a white solid in a 92% yield upon addition of the reaction mixture to aq $NaHCO_3$ solution (1.4 equiv per OH) and filtration. Similarly, maltose (**2**) and glucose (**3**) were subjected to the above acetylation conditions to yield the corresponding per-*O*-acetylated derivatives **7** and **8** as white solids in yields of 93% and 71%, respectively. More of compound **8** was obtained by extracting the filtrate using ethyl acetate, affording a combined yield of 94%. However, per-*O*-acetylated mannose derivative **9**, being syrupy, had to be isolated by extraction and was obtained in a yield of 91%. When the methyl ester of sialic acid (**5**) was used, only 4,7,8,9 tetra-*O*-acetyl sialic acid **10** was obtained. Therefore, this work provides a very reliable method for preparing this important sialic acid donor precursor. All the per-*O*-acetylated derivatives in Table 1 have been characterized by NMR and the spectra data were consistent with those reported in the literature (see Table 1). No furanosyl isomers of the above per-*O*-acetylated sugars were detected while α/β pyranosyl derivatives were observed.

Glycosyl bromides are popular donors in Königs-Knorr glycosylation. Thus, an attempt was made to develop a one-pot-two-step transformation process to synthesize the 1-bromo-sugar derivatives from unprotected sugars. Although the peracetylated derivatives were isolated in the initial experiments to determine the feasibility of multi-gram synthesis, they need not be isolated in case they are to be subjected to further functional group transformation at the anomeric center.[22] Accordingly, mannose (**4**) was converted to the bromo-derivative **15** in 97% yield (entry 4, Table 2) by sequential per-*O*-acetylation ($LiClO_4$ in Ac_2O, 40°C, 12 h) and bromination (HBr/AcOH, 0°C, 1 h) in a one-pot-two-step synthesis. Similarly, peracetylated bromo-derivatives **12**–**14** and **16** were obtained in near quantitative yields in one-pot sequential reactions (Table 2). The yields reported in Table 2 are greater than or comparable

Table 1: Acetylation of saccharides catalyzed by $LiClO_4$.



Entry	Substrate	Product	Yield (%)[a]
1	 **1**	 **6**[10]	92
2	 **2**	 **7**[25]	93
3	 **3**	 **8**[19a]	94
4	 **4**	 **9**[19a]	91
5	 **5**	 **10**[26]	95

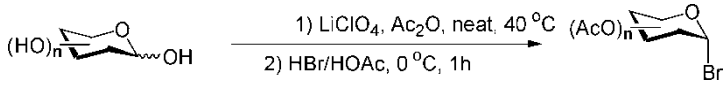
[a]Yield of crude product with purity higher than 95% according to ^{1}H NMR spectroscopy.

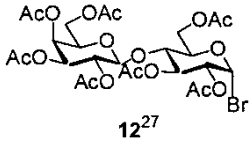
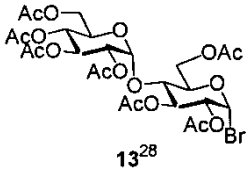
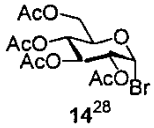
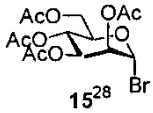
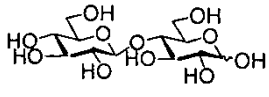
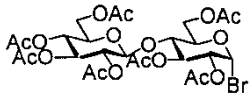
to the best reported in the literature.[23] Notably, the lower product yields in Table 1 than those in Table 2 may be due to the loss of product during the procedures of $NaHCO_3$ work-up and filtration.

Encouraged by the near quantitative yields in sequential one-pot synthesis of peracetylated bromo-derivatives, we next explored similar one-pot synthesis of per-*O*-acetylated thioglycosides, which are also known to be an important class of glycosyl donors[24] (Table 3). In a manner similar to that associated with the synthesis of 1-bromo-sugar derivatives, mannose (**4**) was converted into fully acetylated sugar by $LiClO_4$-mediated peracetylation, followed by the addition of two equiv of BF_3Et_2O and 1.1 equiv of *p*-thiocresol, to form thioglycoside **21** (entry 4, Table 3) in 83% yield. Other sugars (see Table 3) also gave good yields, of between 67% and 80%, of the corresponding thioglycosides.

Here, it should be noted that the results in Tables 1 to 3 lead one to believe that the sequential one-pot per-*O*-acetylation and bromination or

Table 2: One-pot synthesis of per-*O*-acetylated glycosyl bromides.



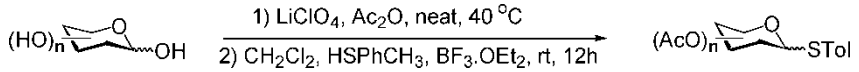
Entry	Substrate	Product	Yield (%)[a]
1	1	 **12**[27]	99
2	2	 **13**[28]	98
3	3	 **14**[28]	98
4	4	 **15**[28]	97
5	 **11**	 **16**[29]	99

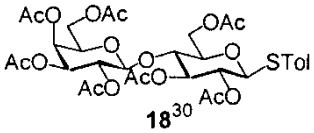
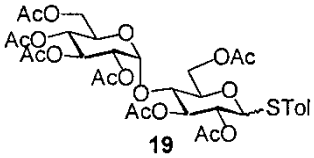
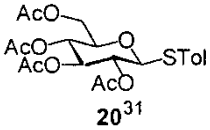
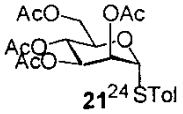
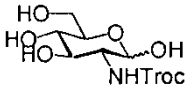
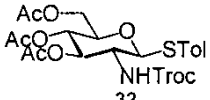
[a]Yield of crude product with purity higher than 97% according to ^{1}H NMR spectroscopy.

thioglycosidation reactions are wider in scope and may be applicable to other saccharides. However, our previous results[21] indicated that the isomerization from pyranose to furanose occurs in the case of some monosaccharides during the peracetylation. This may be considered as a limitation in the one-pot-two-step synthesis reported here. Although we and others never had any accident while using $LiClO_4$, perchlorate salts are known to be explosive and must be handled with caution.[21]

In conclusion, a practical and mild method based on $LiClO_4$-catalyzed solvent-free per-*O*-acetylation was developed for the multi-gram synthesis of peracetylated saccharides, which are important building blocks in the synthesis of complex oligosaccharides and glycoconjugates. The flexibility of this method for further sequential transformations to glycosyl bromides and thioglycosides was demonstrated. Therefore, this method may be applied to other sugars for such sequential transformations in carbohydrate chemistry.

Table 3: One-pot synthesis of per-*O*-acetylated thioglycosides.



Entry	Substrate	Product	Yield (%)[a]
1	1	 **18**[30]	78
2	2	 **19**	80[b]
3	3	 **20**[31]	67
4	4	 **21**[24]	83
5	 **17**	 **22**[32]	66

[a]Isolated yield.
[b](α/β) = 1:5.5, 19α ($J_{H1,2}$ = 4.0 Hz), 19β ($J_{H1,2}$ = 10.0 Hz).

EXPERIMENTAL

General Methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-400 or 500 MHz spectrometer. Assignment of ^{1}H NMR spectra was achieved using 2D methods (COSY). Chemical shifts were expressed in ppm using residual $CDCl_3$ as reference. High-resolution mass spectra were obtained by means of a Micromass (Autospec) mass spectrometer. Analytical thin-layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254). Silica gel 60 (E. Merck Co.) was employed for all flash chromatography. All reactions were carried out in oven-dried glassware (120°C) under an atmosphere of nitrogen unless indicated otherwise. All solvents were dried and distilled by standard techniques.

Compounds **6**,[10] **7**,[25] **8–9**,[19a] **10**,[26] **12**,[27] **13–15**,[28] **16**,[29] **18**,[30] **20**,[31] **21**,[24] and **22**[32] have previously been reported, and our prepared samples

showed consistent ^{1}H and ^{13}C NMR spectral data to the structural assignments.

Method A: General Procedure for Per-*O*-acetylation

Round-bottom flask (1 L) was charged with D-glucose (20 g, 111.0 mmol), $LiClO_4$ (5.9 g, 55.6 mmol), and Ac_2O (55.0 mL, 582.6 mmol) and the flask was placed in an oil bath at 40°C. Stirring was continued at this temperature under nitrogen atmosphere until the completion of reaction as monitored by TLC. After cooling the reaction flask to room temperature, its contents were poured slowly into a ice-cold aq $NaHCO_3$ solution (48.9 g in 500 mL H_2O) under vigorous stirring. A white solid was precipitated immediately (except in the case of D-mannose). It was filtered through Buchner funnel and washed with cold water (50 mL × 3). The solid was then subjected to high vacuum until completely dry.

Method B: General Procedure for Per-*O*-acetylation

A mixture of D-mannose (20 g), Ac_2O (55.0 mL, 582.6 mmol), and $LiClO_4$ (5.9 g, 55.6 mmol) was stirred at 40°C (oil bath temperature). The progress of the reaction was followed by TLC. Once the reaction was complete, the reaction mixture was diluted with ethyl acetate (500 mL) and washed with water (80 mL). The aqueous layer was separated and extracted with ethyl acetate (250 mL × 2). The combined organic layer was washed successively with saturated aq $NaHCO_3$ (100 mL × 2) and brine (100 mL), and dried (Na_2SO_4) and concentrated to give almost pure per-*O*-acetylated saccharide **9**.

General Procedure for One-pot Synthesis of Per-*O*-acetylated Glycosyl Bromides

A mixture of the sugar (27.75 mmol), Ac_2O (1.05 equiv per OH), and $LiClO_4$ (0.1 equiv per OH) was stirred at 40°C (oil bath temperature). The progress of the reaction was followed by TLC. Once the reaction was complete, the reaction mixture was cooled to 0°C and 33% HBr/HOAc (21 mL, 86.18 mmol) was added. The mixture was stirred for 1 h and then poured onto ice (80 g). The resulting mixture was extracted with CH_2Cl_2 (80 mL × 3). The organic layer was successively washed with cold saturated $NaHCO_3$ (50 mL × 2) and brine (50 mL), and dried (Na_2SO_4) and concentrated to give pure peracetylated glycosyl bromide.

General Procedure for One-pot Synthesis of Per-*O*-acetylated Thioglycosides

Per-*O*-acetylation of saccharide (from 1 g starting sugar) was carried out as described above. When reaction was complete according to TLC, CH_2Cl_2 (1 mL), *p*-thiocresol (1.2 equiv), and $BF_3 \cdot Et_2O$ (2 equiv) were sequentially added to the reaction mixture at room temperature. The mixture was allowed to stir for 12 h. The reaction was diluted with CH_2Cl_2 and washed successively with water and saturated $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and concentrated in vacuum. Purification of the residues was performed by either flash column chromatography or recrystallization from EtOAc-hexane to give the desired thioglycoside.

***p*-Tolyl *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-1-thio-α-D-glucopyranoside (19α).** Yield 12.3%; syrup; ^{1}H NMR ($CDCl_3$, 500 MHz): 2.02, 2.04 (x 2), 2.08, 2.09, 2.10, 2.11 (s, 3H x 7, CH_3CO), 2.34 (s, 3H, $SC_6H_4CH_3$), 3.92 (dd, 1H, $J_{4',3'} = 8.0$ Hz, $J_{4',5'} = 9.7$ Hz, H-4′), 4.02 (ddd, 1H, $J_{5,6a} = 2.2$ Hz, $J_{5,6b} = 3.7$ Hz, $J_{5,4} = 9.9$ Hz, H-5), 4.07, (dd, 1H, $J_{6a,5} = 2.2$ Hz, $J_{6a,6b} = 12.5$ Hz, H-6a), 4.25 (m, 2H, H-6b, H-6′a), 4.36 (dd, 1H, $J_{6'b,5'} = 2.5$ Hz, $J_{6'b,6'a} = 12.2$ Hz, H-6′b), 4.54 (ddd, 1H, $J_{5',6'b} = 2.5$ Hz, $J_{5',6'a} = 5.3$ Hz, $J_{5',4'} = 9.7$ Hz, H-5′), 4.90 (dd, 1H, $J_{2,1} = 4.0$ Hz, $J_{2,3} = 10.5$ Hz, H-2), 5.01 (dd, 1H, $J_{2',1'} = 5.7$ Hz, $J_{2',3'} = 9.5$ Hz, H-2′), 5.08 (t, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4), 5.39 (dd, 1H, $J_{3,4} = 9.9$ Hz, $J_{3,2} = 10.5$ Hz, H-3), 5.40 (d, 1H, $J_{1,2} = 4.0$ Hz, H-1), 5.42 (dd, 1H,$J_{3',4'} = 8.0$ Hz, $J_{3',2'} = 9.5$ Hz, H-3′), 5.70 (d, 1H, $J_{1',2'} = 5.7$ Hz, H-1′), 7.13 (d, $J = 8.0$ Hz, 2H, $SC_6H_4CH_3$), 7.37 (d, $J = 8.0$ Hz, 2H, $SC_6H_4CH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz); 20.81, 20.85, 20.88, 20.92, 21.12, 21.33, 61.76, 62.36, 63.24, 65.16, 68.26, 68.77, 69.61, 70.18, 71.22, 72.60, 73.71, 85.38, 96.10, 128.92, 130.15, 133.00, 138.43, 169.68, 169.85, 170.13, 170.18, 170.69, 170.77, 170.85; HRMS (FAB) Calcd for $C_{33}H_{43}O_{17}S$ $[M + H]^+$, 743.2221. Found: 743.2226.

***p*-Tolyl *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (19β).** Yield 67.7%; white solid. mp. 125–126°C; ^{1}H NMR ($CDCl_3$, 400 MHz): 1.99, 2.00, 2.03, 2.04, 2.07, 2.10, 2.14 (s, 3H × 7, CH_3CO), 2.36 (s, 3H, $SC_6H_4CH_3$), 3.69 (m, 1H, H-5), 3.93 (m, 2H, H-4, H-5′), 4.04 (dd, 1H, $J_{6'a,\ 5'} = 2.1$ Hz, $J_{6'a,6'b} = 12.3$ Hz, H-6′a), 4.20 (dd, 1H, $J_{6a,5} = 4.6$ Hz, $J_{6a,6b} = 12.1$ Hz, H-6a), 4.24 (dd, 1H, $J_{6'b,\ 5'} = 4.0$ Hz, $J_{6'b,6'a} = 12.3$ Hz, H-6′b), 4.54 (dd, 1H, $J_{6b,5} = 2.5$ Hz, $J_{6b,6a} = 12.1$ Hz, H-6b), 4.66 (d, 1H, $J_{1,2} = 10.0$ Hz, H-1), 4.77 (dd, 1H, $J_{2,3} = 9.0$ Hz, $J_{2,1} = 10.0$ Hz, H-2), 4.84 (dd, 1H, $J_{2',1'} = 4.0$ Hz, $J_{2',3'} = 10.4$ Hz, H-2′), 5.04 (dd, 1H, $J_{4',5'} = 9.7$ Hz, $J_{4',3'} = 10.0$ Hz, H-4′), 5.27 (t, 1H, $J_{3,2} = J_{3,4} = 9.0$ Hz, H-3), 5.34 (dd, 1H, $J_{3',4'} = 10.0$ Hz, $J_{3',2'} = 10.4$ Hz, H-3′), 5.39 (d, 1H, $J_{1',2'} = 4.0$ Hz, H-1′), 7.12 (d, 2H,

$J = 8.0$ Hz, $SC_6H_4CH_3$), 7.39 (d, 2H, $J = 8.0$ Hz, $SC_6H_4CH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) 20.73, 20.83, 20.90, 20.98, 21.07, 21.29, 21.35, 61.69, 62.97, 68.22, 68.68, 69.50, 70.16, 70.84, 72.60, 76.26, 76.7, 85.31, 95.71, 127.33, 129.82, 134.25, 139.00, 169.60, 169.71, 169.81, 170.35, 170.51, 170.71, 170.80; HRMS (FAB) Calcd for $C_{33}H_{43}O_{17}S$ $[M + H]^+$, 743.2221. Found: 743.2229.

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