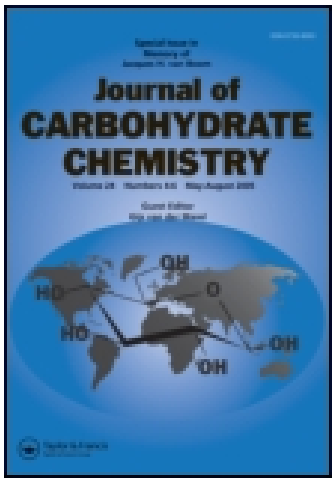

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Reactions of Nucleophiles with Reactive Intermediates in the 3,4,6-Tri-O-benzyl-d-glucal-TfOH-n-Bu_4NI Reaction System

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Reactions of Nucleophiles with Reactive Intermediates in the 3,4,6-Tri-*O*-benzyl-D-glucal–TfOH–*n*-Bu_4NI Reaction System

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ABSTRACT

The unique reactive intermediate formed in the 3,4,6-tri-*O*-benzyl-D-glucal–TfOH (triflic acid)–*n*-Bu_4NI reaction system (in dichloromethane) reacted with nucleophiles in a regio- and stereoselective manner. These selectivities resulted in hitherto unknown compounds, such as benzyl 4,6-di-*O*-benzyl-2,3-dideoxy-3-iodo-α-glucopyranoside, which was obtained in the presence of an iodide ion as a nucleophile. The corresponding 2-deoxy α-glycosides were obtained exclusively in the corresponding reaction with hydroxylic nucleophiles.

Key Words: Carbohydrates; Glucal; Reactive intermediates; Nucleophiles; Iodosugars; 2-deoxyglycopyranosides.

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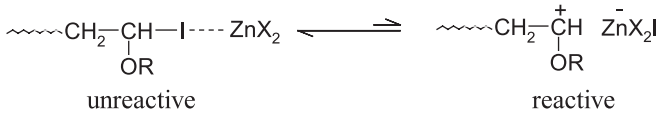
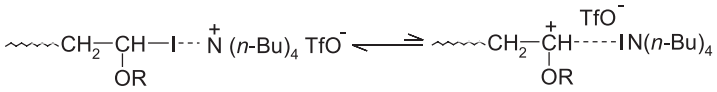
INTRODUCTION

Specific combinations of protonic acids with either Lewis acids (e.g., HI–ZnX_2,[1–4] RCO_2H–MX_n[2]) or Lewis bases (e.g., TfOH–Me_2S[3]), function as effective initiating systems for the living cationic polymerization of alkyl vinyl ethers[1–11] and other electron-rich vinyl monomers.[12–14] Such polymerizations are characterized by absence of termination of any kind and by a very narrow molecular weight distribution of the polymers formed. These characteristics are due to a combination of two built-in features—$R_i \gg R_p$ (i—initiation, p—propagation) and a very low equilibrium concentration of the reactive species of the growing chain ends. Thus, for example, the following is such an equilibrium for the HI (hexane solution)—ZnX_2 initiated polymerization of alkyl vinyl ethers (Eq. 1):



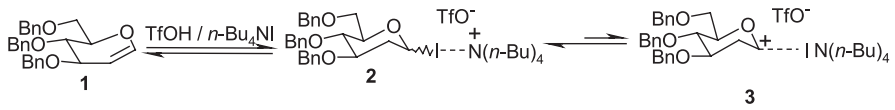
(1)

We have recently shown that a TfOH–*n*-Bu_4NI mixture is an effective initiation system for the living cationic polymerization of isobutyl vinyl ether (IBVE) (in CH_2Cl_2 at $-23°C$).[15] It was suggested that the following equilibrium mixture of growing chain ends was involved in the propagation steps of that polymerization (Eq. 2):[16,17]



(2)

Our working hypothesis was that the reaction of 3,4,6-tri-*O*-benzyl-D-glucal (**1**) with TfOH in the presence of *n*-Bu_4NI might result in an analogous equilibrium mixture (Eq. 3):



(3)

It was the purpose of the present research to apply the experimental and mechanistic approach which afforded the TfOH–*n*-Bu_4NI-initiated living cationic polymerizations of *i*-butyl vinyl ether, to reactions of glycals (represented by the glucal derivative **1**) with various nucleophiles. We have assumed that the analogous glucal-involved equilibrium mixture (Eq. 3) might result in specific/selective reaction pathways, in the presence of nucleophiles.

RESULTS AND DISCUSSION

Reactions of **1** with nucleophiles in the **1**–TfOH–*n*-Bu_4NI reaction system were studied. Nucleophiles of three different types were used—an iodide salt (the *n*-Bu_4NI), a nucleophilic olefin (CH_2═CH–OR, R = *i*-Bu) and hydroxylic compounds.

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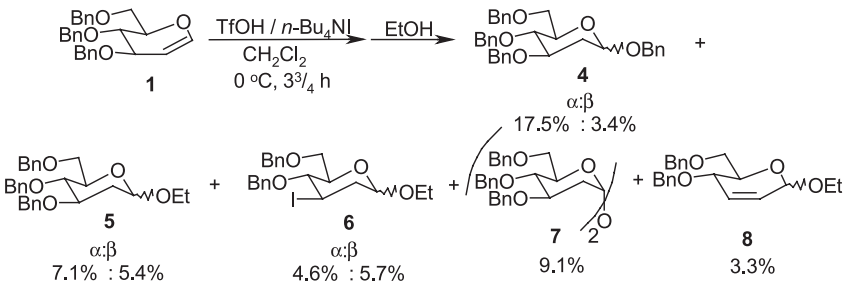
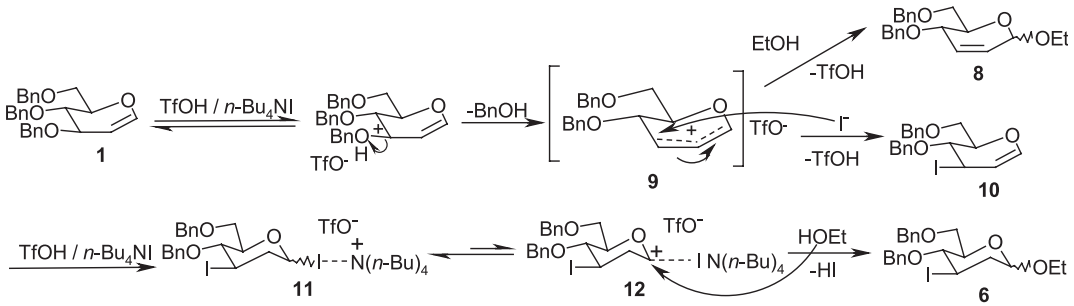
A cooled solution (−42 °C) of *n*-Bu_4NI and TfOH in CH_2Cl_2 was added to a solution of **1** in dichloromethane at 0°C, followed by quenching the reaction mixture with ethanol after the required reaction period. The ratio of the concentrations of the reactants used was [TfOH]:[*n*-Bu_4NI]:[**1**] = 1:2:1. A complex mixture of products was obtained, eight of which (total yield 56% based on **1**) were isolated, purified and their structure determined or confirmed (Eq. 4):



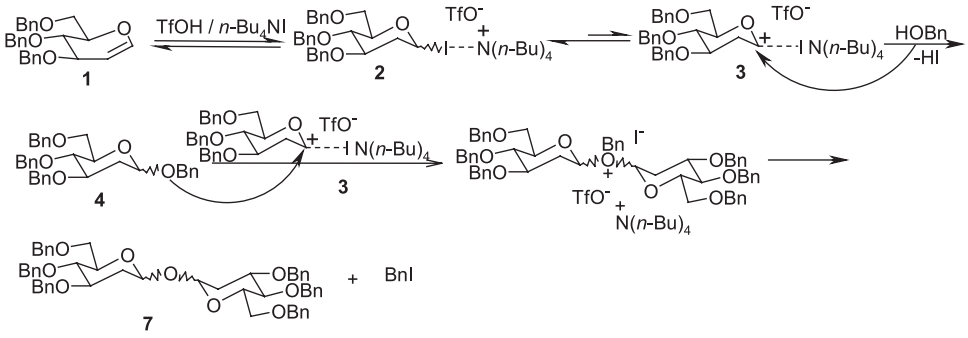
(4)

Possible reaction pathways leading to the formation of these products are detailed below (Schemes 1 and 2).

We suggest (Schemes 1 and 2) that several types of reactive intermediates are involved in the formation of the products isolated. One is the oxaallyl cation salt **9** (cf. Scheme 1), and the others are the carbocation salts **3** and **12** formed by the addition reaction TfOH to the glucal derivatives **1** and **10**, respectively, in the presence of *n*-Bu_4 NI (cf. Schemes 1 and 2). The anticipated specificity of the *n*-Bu_4NI-solvated carbocation triflate salts **3** and **12** in their reactions with nucleophiles, has been realized (for this reaction system) by the unique regiospecific and stereospecific formation of a hitherto unreported iodosaccharide - ethyl 2,3-dideoxy-3-iodoglycoside derivative **6** (Scheme 1) and by the formation of the 2,2′-dideoxy-α,α-trehalose derivative **7** (Scheme 2). It should be noted that the benzyl alcohol involved in the formation of the trehalose derivative **7** (Scheme 2) was produced in the reaction leading to the formation of the oxaallyl cation salt **9** (Scheme 1).

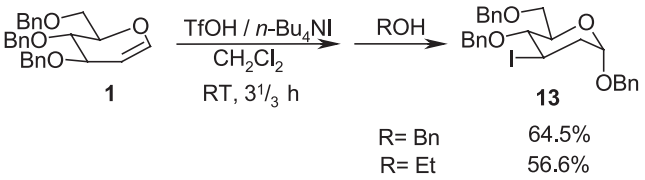


Scheme 1. Formation of alkyl 2,3-dideoxy-3-iodoglycoside in the **1**-TfOH-n-Bu_4NI reaction system.



Scheme 2. Formation of the 2,2′-dideoxy-α,α-trehalose derivative **7** in the **1**-TfOH-n-Bu_4NI reaction system.

Non-anomeric 2-deoxy iodosugars, although quite uncommon, are useful intermediates in carbohydrate synthesis.[18–30] There is a single report on the preparation of a 3-iodo-2,3-dideoxy saccharide from 3,4,6-tri-*O*-benzyl-D-galactal, in a synthesis consisting of several steps.[31] 2,3-Dideoxy-3-iodo glycosides might be useful precursors in carbohydrate synthesis for the preparation of such compounds as 2,3-dideoxy glycosides, 2-deoxy-3,4-epoxyglycosides, etc. It was therefore of interest to try to convert the observed one-pot low-yield direct formation of the alkyl 2,3-dideoxy-3-iodoglycoside **6** into a practical preparation, applying the **1**–TfOH–*n*-Bu_4NI reaction system. A variety of experimental conditions were screened in this regard. It was found that performing the reaction (Eq. 5) at room temperature, instead of 0 °C, resulted in a dramatic change. The target compound, benzyl 4,6-di-*O*-benzyl-2,3-dideoxy-3-iodo-α-D-glucopyranoside (**13**), was formed as the major product. Quenching the reaction mixture with either EtOH or BnOH had almost no effect on the yield of **13** (Eq. 5):



(5)

This clearly indicated that the formation of **13** in this thermodynamically-controlled reaction was completed before the addition of the alcoholic quencher. The stereospecificity of the nucleophilic attack of the iodide anion on the oxaallylic cation salt **9**, which resulted in retention of the configuration of the C-3 position, could be due to a neighboring group participation of the C-4 benzyloxy group (Scheme 3).

As mentioned above, the TfOH–*n*-Bu_4NI mixture was an effective initiator for the living cationic polymerization of isobutyl vinyl ether.[15] We therefore expected that the reaction of the reactive intermediate(s) formed in the **1**–TfOH–*n*-Bu_4NI reaction mixture with CH_2═CH–OR would result in a *C*-glycosidation reaction. To this end, iso-butyl vinyl ether was added to a cooled (−23 °C) **1**–TfOH–*n*-Bu_4NI mix-

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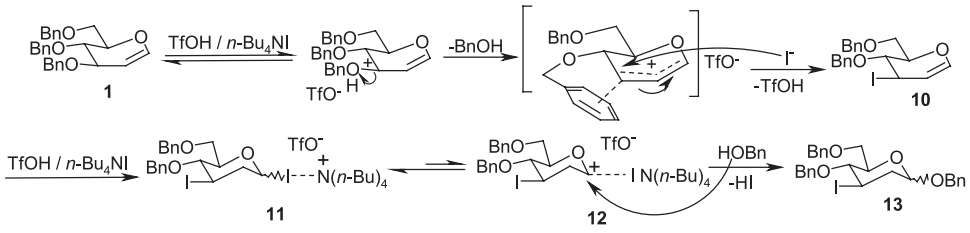
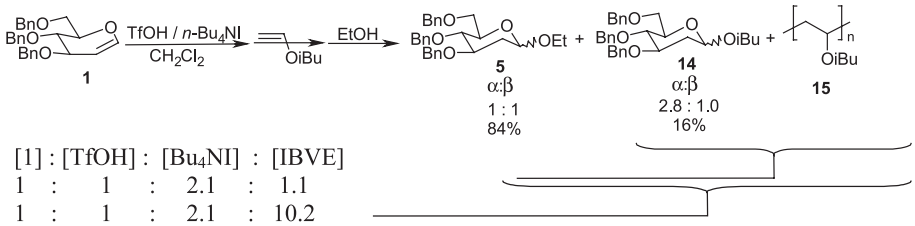


Scheme 3. The stereospecific formation of the iodo sugar **13**.

ture dissolved in dichloromethane. The reaction mixture was quenched with EtOH. The ratio of concentrations of the reactants used was [**1**]:[TfOH]:[n-Bu_4NI]: [IBVE] = 1:1:2.1:1.1. The only products obtained under these conditions were the ethyl and isobutyl 2-deoxy glycosides **5** (84%) and **14** (16%), respectively. Poly (IBVE) was obtained, in addition, when the above ratio of concentrations was 1:1:2.1:10.2. The poly (IBVE) obtained had no sugar moiety end group, indicating that a *C*-glycosidation reaction did not occur (Eq. 6):

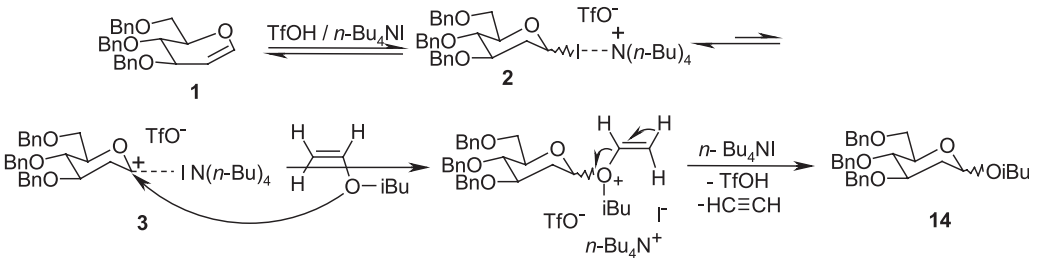


(6)

Formation of the ethyl glycoside **5** was presumably due to reaction of the quencher ethanol with the reactive intermediate **3** (cf. Scheme 2). The high yield of **5** and the low yield of **14** indicates the *i*-butyl glycoside **14** indicated that the formation of **14** is relatively slow and that the reactive intermediate **3** is quite stable under the experimental conditions applied.

Formation of the isobutyl 2-deoxyglycoside **14** pointed to the selectivity features of reactive intermediate in the **2**–**3** equilibrium mixture (cf. Scheme 2) demonstrated in its reactions with nucleophiles. We suggest that the reaction leading to the formation of **14** took place in this case exclusively via the etheric oxygen of the IBVE rather than via its electron-rich double bond. The following is a plausible mechanism for the unusual formation of an alkyl 2-deoxy glycoside in the acid-catalyzed reaction of a glucal with an alkyl vinyl ether (Scheme 4). It should be noted that Ferrier-type rearrangement products were not detected.

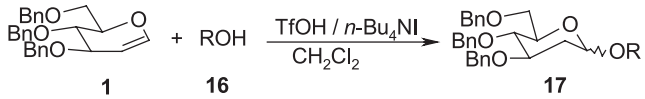
The quantitative and exclusive conversion of the glucal **1** to the mixture of the derived ethyl and isobutyl 2-deoxyglycosides **5** and **14**, respectively (cf. Eq. 6), led us to apply hydroxylic compounds to react as nucleophiles in the **1**–TfOH–n-Bu_4NI reaction system, for preparing 2-deoxyglycosides directly from the glucal **1**. Protonic and Lewis acid-catalyzed reactions of hydroxylic compounds with glycals to affect their direct conversion to the derived 2-deoxyglycosides, have been reported in a few



Scheme 4. Formation of the iso-butylglycoside in the **1**-TfOH-n-Bu_4NI-CH_2=CH-OR. (R = iso-butyl).

cases.[32–38] It should be mentioned in this regard that 2-deoxy-glycosides are significant structural moieties of sugar-containing natural products and bioactive materials.[39–42]

Thus, the reaction of **1** with each of several hydroxylic compounds (**16**) was carried out in methylene chloride at low temperature (Eq. 7). The ratio of concentrations of the reactants used was [**1**]:[TfOH]:[Bu_4NI]:[ROH] = 1:1:2:3. Catalytic amounts of TfOH and *n*-Bu_4NI were also effective. The reactions performed resulted in most cases (cf. Table 1) in the corresponding 2-deoxyglycosides with a high α stereoselectivity. No Ferrier-type rearrangement products were detected (Eq. 7). The resulsts are summarized in Table 1.



(7)

This reaction system turned out to be an efficient new route (in addition to the few existing ones[32–38]) for the direct acid-catalyzed one-pot conversion of glucals to the derived 2-deoxyglycosides, and might be applicable as well to other glycals.

In conclusion, it was demonstrated that carbocation salts formed by reacting 3,4,6-tri-*O*-benzyl-D-glucal **1** with a specific combination of a protonic acid (TfOH) and a Lewis acid (*n*-Bu_4NI), which was effective in initiating a living cationic polymerization of alkyl vinyl ethers, reacted with nucleophiles in unique regioselective and stereospecific reaction pathways. The preliminary results obtained point to an interesting potential for a novel chemistry of glycals in their reactions with nucleophiles in the presence of other specific combinations of protonic and Lewis acids, which are effective in inducing living cationic polymerizations of alkyl vinyl ethers.

EXPERIMENTAL

General methods. ^1H and ^{13}C NMR spectra were obtained on Bruker AC-200 (200 MHz), Bruker AC-250 Cryospec (250 MHz), Bruker ARX-500 (500 MHz) and Bruker DRX-600 (600 MHz) spectrometers, in $CDCl_3$, downfield from tetramethylsilane as internal standard. Values of chemical shifts (δ) and couplings (J) are given in ppm and Hz, respectively. FABMS were obtained using a Finnigan MAT 312 Mass Spectrometer

(70 ev) and the EIMS were obtained using a Finnigan MAT 8430 Mass Spectrometer (70 ev). Silica gel 60 (Baker: 0.04–0.063 mm or ICN: 0.03–0.063 mm) was used for flash chromatography. All solvents were purified and dried by standard methods.

The 3,4,6-tri-*O*-benzyl-D-glucal (1)–TfOH–*n*-Bu_4NI reaction system. The reaction was carried out using two two-neck flasks equipped with an argon inlet, a rubber septum and magnetic stirring, under strictly dry conditions. Tetrabutylammonium iodide (1.779 g, 4.815 mmol) was introduced to one of the two flasks, followed by 5.0 mL of dry dichloromethane. The solution was cooled to − 42 °C. Triflic acid (0.20 mL, 2.26 mmol) was injected into the cooled solution, resulting in a colour change to yellow. A portion of the mixture (0.63 mL, 0.224 mmol of TfOH, 3.06 mmol *n*-Bu_4NI) was injected into the second flask, which contained a solution of 3,4,6-tri-*O*-benzyl-D-glucal (**1**) (0.257 g, 0.618 mmol) in 13.0 mL of dry dichloromethane, at 0 °C. The mixture in the second flask was stirred for 3.75 h at 0 °C followed by quenching with ethyl alcohol (0.20 mL, 3.43 mmol). Stirring was continued for 0.5 h at 0 °C, a saturated solution of sodium thiosulfate added, and the mixture was brought to room temperature. Dichloromethane was added, and the mixture was washed with a saturated sodium thiosulfate solution followed by extraction of the aqueous layer with dichloromethane. The combined extracts were washed with a saturated solution of sodium hydrogen carbonate and then with water, dried over magnesium sulfate and filtered. The solvent was removed from the filtrate under reduced pressure. The residue was subjected to flash chromatography on two different silica gel columns using as eluents petroleum ether: ethyl acetate, 9:1 and 8:2, respectively. Not all the products comprising the crude residue were isolated and their structure confirmed.

The following are the ^1H NMR, ^{13}C NMR and MS data of the new products which were isolated.

3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl-(1 → 1)-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (7αα). 0.0238 g (0.028 mmol, 9.1%) of **7αα** was obtained as the α–α isomer, as a colorless viscous oil. The spectral data of **7αα** is given hereby: ^1H NMR (600 MHz, α–α isomer) δ: 1.72 (ddd, 1H, $J_{2ax,2eq} \approx J_{2ax,3} \approx 12.9$ Hz, $J_{2ax,1} = 2.2$ Hz, H-2_{ax}), 2.14 (ddd, 1H, $J_{2eq,3} = 4.8$ Hz, H-2_{eq}), 3.64 (dd, 1H, $J_{4,3} \approx J_{4,5} \approx 9.1$ Hz, H-4), 3.65 (dd, 1H, $J_{6',6} = 10.5$ Hz, $J_{6',5} = 2.2$ Hz, H-6′), 3.72 (bd, 1H, H-5), 3.76 (dd, 1H, $J_{6,5} = 3.75$ Hz, H-6), 3.94 (ddd, 1H, H-3), 4.52 (d, 1H, J = 11.9 Hz, *CH*$_2$Ph), 4.53 (d, 1H, J = 10.2 Hz, *CH*$_2$Ph), 4.61 (d, *CH*$_2$Ph, 1H), 4.63 (d, J = 10.9 Hz, *CH*$_2$Ph, 1H), 4.65 (d, *CH*$_2$Ph, 1H), 4.99 (d, 1H, *CH*$_2$Ph), 5.23 (d, 1H, H-1), 7.20–7.35 (m, 30H, 6Ph); ^{13}C NMR (600 MHz) δ: 35.04 (C-2), 68.81 (C-6), 71.49 (C-5), 71.79 (*CH*$_2$Ph), 73.50 (*CH*$_2$Ph), 75.16 (*CH*$_2$Ph), 77.20 (C-3), 78.12 (C-4), 92.79 (C-1), 127.60–128.41 (Ph), 138.14 (Ph), 138.40 (Ph), 138.54 (Ph).

HR-FABMS Calcd for $C_{54}H_{58}NaO_9$: 873.397854. Obs. $MNa^+ = 873.400790$.

Ethyl 4,6-Di-*O*-benzyl-2,3-dideoxy-3-iodo-α-D-glucopyranoside (6α). 0.0136 g (0.028 mmol, 4.6%) of **6α** was obtained as the α isomer, as a colorless viscous oil. The spectral data of **6α** is given hereby: ^1H NMR (200 MHz, α isomer) δ: 1.16 (t, 3H, $J_{1'',1'} = 7.1$ Hz, H-1″), 2.46 (ddd, 1H $J_{2ax,2eq} \approx J_{2ax,3} = 13.3$ Hz, $J_{2ax,1} = 3.4$ Hz, H-2_{ax}), 2.57 (ddd, 1H, $J_{2eq,3} = 5.5$ Hz, $J_{2eq,1} = 1.3$ Hz, H-2_{eq}), 3.41 (dq, 1H, $J_{1'b,1'a} = 9.5$ Hz, Hz, H-1′b), 3.57–3.87 (m, 5H, H-1′a, H-4, H-5, 2H-6), 4.40–4.61 (3H), 4.40–4.61 (m,

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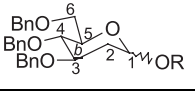
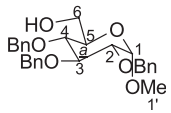
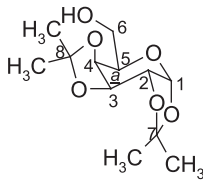
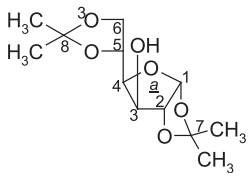
Table 1. The glycosidation of 3,4,6-tri-*O*-benzyl-D-glucal—experimental conditions and results.

Entry	ROH [equiv]	TfOH (equiv)	Bu_4NI (equiv)	Time (h)	Temperature (°C)		Yield (%)	α:β[a]
1	Cholesterol, **16a** [3]	0.15	0.3	1.25	0	**17a**[b,43]	65.9	2:1
2	EtOH, **16b** [3]	1	2	2	−23	**5**[c,d,44]	100	1:1
3	 **16c** [3]	1	2	2	−23	**17c**[c,43,45-47]	47.5	1:0
4	 **16d** [3]	1	2	2	−23	**17d**[c,43,48]	67.1	12:1
5	 **16e** [3]	1	2	2	−23	**17e**[c,45]	11.1	1:0
6	BnOH, **16f** [3]	1	2	2	−23	**4a**[45]	82.1	1:0

H-3), 4.42 (d, J = 12.1 Hz, CH_2Ph), 4.51 (d, J = 10.0 Hz, CH_2Ph), 4.68 & 4.71 (d, 2H, CH_2Ph; bs, H-1), 4.94 (d, 1H, CH_2Ph, 1H), 7.26–7.39 (m, 10H, 2Ph); ^{13}C NMR (200 MHz) δ: 14.96 (C-1″), 26.77 (C-3), 47.90 (C-2), 62.62 (C-1′), 69.29 (C-6), 72.59 (C-5), 73.72 (CH_2Ph), 74.63 (CH_2Ph), 79.90 (C-4), 97.42 (C-1), 127.84–128.40 (Ph), 137.75 (Ph), 137.86 (Ph).

HR FABMS Calcd for $C_{22}H_{27}INaO_4$: 505.085181. Obs. MNa^+ = 505.084370.

Ethyl 4,6-Di-*O*-benzyl-2,3-dideoxy-3-iodo-β-D-glucopyranoside (6β). 0.0170 g (0.035 mmol, 5.7%) of **6β** was obtained as the β isomer, as a colorless viscous oil. The spectral data of **6β** is given hereby: ^{1}H NMR (200 MHz, α isomer) δ: 1.23 (t, 3H, $J_{1'',1'}$ = 7.1 Hz, H-1″), 2.36 (dt, 1H, $J_{2ax,2eq} \approx J_{2ax,3} \approx$ 13.1 Hz, $J_{2ax,1}$ = 9.2 Hz, H-2_{ax}), 2.61 (ddd, 1H, $J_{2eq,3}$ = 4.8 Hz, $J_{2eq,1}$ = 1.8 Hz, H-2_{eq}), 3.38 (ddd, 1H, $J_{5,4}$ = 9.1 Hz, $J_{5,6} \approx J_{5,6'} \approx$ 1.9 Hz, H-5), 3.52 (dq, 1H, $J_{1'b,1'a}$ = 9.4 Hz, H-1′b), 3.67–3.83 (m, 3H, H-4, 2H-6), 3.93 (dq, 1H, H-1′a), 4.14 (ddd, 1H, $J_{3,4}$ = 10.2 Hz, H-3), 4.40 (dd, 1H, H-1), 4.50 (d, 1H, J = 10.2 Hz, CH_2Ph), 4.56 (d, 1H, J = 12.5 Hz, CH_2Ph), 4.56 (d, 1H, CH_2Ph), 4.93 (d, 1H, CH_2Ph), 7.26–7.35 (m, 10H, 2Ph); ^{13}C NMR δ: 15.16 (C-1″), 26.21 (C-3), 44.64 (C-2), 64.82 (C-1′), 69.29 (C-6), 73.65 (CH_2Ph), 74.87 (CH_2Ph), 77.68 (C-5), 79.76 (C-4), 100.92 (C-1), 127.72–128.38 (Ph), 137.64 (Ph), 138.07 (Ph).

HR-FABMS Calcd for $C_{22}H_{27}INaO_4$: 505.085181. Obs. MNa^+ = 505.084132.

Ethyl 2,3-Dideoxy-4,6-bis-*O*-benzyl-α-D-*erythro*-hex-2-enopyranoside (8). 0.0072 g (0.020 mmol, 3.3%) of **8** was obtained as a mixture of α and β isomers, together with **4**, as a colorless viscous oil. The molar ratio of **8** and **4** were deduced from the ^{1}H NMR spectrum of the mixture. The obtained mass and yield were calculated from the molar ratio of **8** and **4** and from the mixture's mass. The spectral data of the α-isomer of **8**, was in accordance with that reported.[4,49]

Benzyl 4,6-Di-*O*-benzyl-2,3-dideoxy-3-iodo-α-D-glucopyranoside (13). The reaction was carried out using two two-neck flasks equipped with an argon inlet, a rubber septum and magnetic stirring, under strictly dry conditions. Tetrabutylammonium iodide (1.073 g, 2.095 mmol) was introduced to one of the flasks, followed by 3.0 mL of dry dichloromethane, and the solution was cooled to −42 °C. Triflic acid (0.13 mL, 1.47 mmol) was injected into the cooled solution changing its colour to yellow. The obtained mixture (2.0 mL, 0.94 mmol of TfOH, 1.34 mmol of *n*-Bu_4NI) was injected into the second flask which contained 3,4,6-tri-*O*-benzyl-D-glucal (1) (0.3925 g, 0.942 mmol) dissolved in 14.0 mL of dry dichloromethane at room temperature. The mixture in the second flask which turned brown, was stirred for 3 h at room temperature and was then quenched with benzyl alcohol (0.15 mL, 1.44 mmol). Stirring was continued for 0.5 h and the reaction mixture was subjected to the same workup described above to give the crude product (viscous liquid).

Notes to Table 1:

[a]Determined by ^{1}H NMR.

[b]Reported in the reference cited, including ^{1}H NMR.

[c]Reported in the reference cited, spectral data not included.

[d] ^{1}H NMR data in the reference is given for the L-isomer.

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The crude product was subjected to flash chromatography using a petroleum ether: ethyl acetate mixture (9:1, respectively) as eluent, to yield 0.331 g (0.608 mmol, 64.5%) of **13** as colorless viscous oil, which solidified at −20°C to a white solid (mp 73–74°C). The spectral features of the product are as follows: ^{1}H NMR (200 MHz, α isomer) δ: 2.49 (ddd, 1H, $J_{2ax,2eq} \approx J_{2ax,3} \approx 13.4$Hz, $J_{2ax,1} = 3.4$ Hz, H-2ax), 2.62 (ddd, 1H, $J_{2eq,3} = 5.3$ Hz, $J_{2eq,1} = 1.4$ Hz, H-2eq), 3.61 (bd, 1H, $J_{6,6'} = 9.2$ Hz, H-6), 3.75–3.88 (m, 3H, H-4, H-5, H-6′), 4.43 (d, 1H, J = 10.0 Hz, CH_2Ph), 4.44–4.52 (m, 1H, H-3), 4.44 (d, 1H, J = 11.8 Hz, CH_2Ph), 4.53 (d, 1H, J = 12.0 Hz, CH_2Ph), 4.64 (d, 1H, CH_2Ph), 4.71 (d, 1H, CH_2Ph), 4.77 (bd, 1H, H-1), 4.94 (d, 1H, CH_2Ph), 7.22–7.42 (m, 15H, 3Ph); ^{13}C NMR (200 MHz) δ: 26.50 (C-3), 43.45 (C-2), 68.93 (C-6/CH_2Ph), 69.13 (C-6/CH_2Ph), 72.83 (C-5), 73.67 (CH_2Ph), 74.61 (CH_2Ph), 79.77 (C-4), 97.05 (C-1), 128.42–128.86 (Ph), 137.38 (Ph), 137.65 (Ph), 137.81 (Ph).

HR-FABMS Calcd for $C_{27}H_{29}INaO_4$: 567.100831. Obs. MNa^+ = 567.099747.

The reaction of 3,4,6-tri-*O*-benzyl-D-glucal with isobutyl vinyl ether in the presence of *n*-Bu$_4$NI–TfOH. The reaction setup consisted of two flasks as described above. A mixture of TfOH (0.2 mL, 2.26 mmol) and *n*-Bu$_4$NI (1.77 g, 4.81 mmol) dissolved in dichloromethane (5 mL) cooled to − 42°C was prepared as described above. 1 mL of this solution (0.43 mmol of TfOH, 0.93 mmol of *n*-Bu$_4$NI) was injected into the second flask which contained a solution of 3,4,6-tri-*O*-benzyl-D-glucal (**1**) (0.198 g, 0.474 mmol) in dichloromethane (12 mL) at − 23°C. The mixture was stirred for 15 min at − 23°C and isobutyl vinyl ether (0.065 mL, 0.498 mmol) was injected to it over 5–10 min. Stirring was continued for 2.25 h at − 23°C, ethanol added (0.15 mL, 2.57 mmol) and then workup was carried out as described above. The crude product obtained was flash chromatographed (eluent: petroleum ether: ethylacetate 9:1) to yield two main products: a) ethyl 3,4,6-tri-*O*-benzyl-2-deoxy-α/β-D-*arabino*-hexopyranoside (**5**), a colourless viscous liquid, (0.185 g, 0.400 mmol, 84%) as a 1:1 mixture of the α and β isomers, b) isobutyl 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (**14α**) (0.028 g, 0.050 mmol 11.8%) and the β-isomer (**14β**) (0.008 g, 0.016 mmol, 3.4%).

Poly(isobutyl vinyl ether), –[CH$_2^1$CH^2(OCH$_2^3$CH^4(CH$_3$)$_2^5$)]$_n$– (15). ^{1}H NMR (200 MHz) δ: 0.90 (d, 6H, $J_{5,6} = 5.9$ Hz, 6H-5), 1.32–2.00 (m, 3H, H-4, 2H-1), 2.98–3.31 (m, 2H, 2H-3), 3.35–3.7 (m, 1H, H-2).

General procedure for the preparation of 2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosides in the 1–*n*-Bu$_4$NI–TfOH–ROH reaction system. Two two-neck flasks equipped with an argon inlet, a rubber septum and magnetic stirring were assembled under strictly dry conditions. Tetra *n*-butyl ammonium iodide (1.667 g, 4.513 mmol) and dichloromethane (4.7 mL) were introduced into one of the flasks which was then kept at −42 °C. 3,4,6-Tri-*O*-benzyl-D-glucal **1** (0.200 g, 0.481 mmol), the hydroxyl compound ROH (1.463 mmol) and dichloromethane (13.0 mL) were introduced into the second flask and the mixture kept at −23 °C. Triflic acid (0.05 mL, 0.565 mmol) was then injected into the first flask. The mixture in this flask turned yellow. One mL of this mixture was injected into the second flask and the mixture was stirred for 2 h at −23 °C. The reaction mixture was then quenched with a saturated solution of sodium thiosulfate, dichloromethane added, the aqueous layer extracted by dichloromethane.

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The combined organic layers were washed with water, dried over anhydrous magnesium sulfate, filtered and the solvent removed from the filtrate. The residue was subjected to flash chromatography on a silica gel column. The ROH (**16a–f**) substrates used, the derived 2-deoxy glycosides (**17a–f**) obtained and their yields are detailed in the Results and Discussion section. The following are hitherto unreported spectral data of the **17**-type products obtained (cf. Table 1).

Methyl (3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-(1 → 6)-(2,3,4-tri-*O*-benzyl-α-D-glucopyranoside)(17c).[43,45–47] ^{1}H NMR (500 MHz): δ =1.67 (ddd, 1H, $J_{2axb,2eqb}$ = 12.9 Hz, $J_{2axb,3b}$ = 11.7 Hz, $J_{2axb,1b}$ = 3.4 Hz, H-2_{ax}b), 2.29 (dd, 1H, $J_{2eqb,3b}$ = 4.9 Hz, H-2_{eq}b), 3.34 (s, 3H, H-1′a), 3.47–3.82 (m, 9H, H-2a, H-4a, H-5a, 2H-6a, H-4b, H-5b, 2H-6b), 3.93 (ddd, 1H, $J_{3b,4b}$ = 8.9 Hz, H-3b), 3.99 (dd, 1H, $J_{3a,4a} \approx J_{3a,2a} \approx$ 9.3 Hz, H-3a), 4.40 (d, 1H, J = 12.1 Hz, CH_2Ph), 4.47 (d, 1H, J = 11.0 Hz, CH_2Ph), 4.54 (d, 1H, J = 11.1 Hz, CH_2Ph), 4.56 (d, 1H, J = 12.1 Hz, CH_2Ph), 4.59–4.64 (m, 3H, 2CH_2Ph, H-1a), 4.67 (d, 1H, J = 12.8 Hz, CH_2Ph), 4.78 (d, 1H, CH_2Ph), 4.79 (d, 1H, J = 10.6 Hz, CH_2Ph), 4.86 (d, 1H, CH_2Ph), 4.90 (d, 1H, CH_2Ph), 4.98 (bs, H-1b), 4.99 (d, CH_2Ph), (4.98–4.99: 2H), 7.13–7.35 (m, 30H, 6Ph); ^{13}C NMR (200 MHz): δ = 35.37 (C-2b), 55.06 (C-1′a), 65.79 (C-6a/b), 68.97 (C-6a/b), 69.89 (C-5a/b), 71.04 (C-5a/b), 71.70 (CH_2Ph), 73.26 (CH_2Ph), 73.44 (CH_2Ph), 74.82 (2CH_2Ph), 75.72 (CH_2Ph), 77.27 & 77.96 & 78.30 (C-4b, C-3b, C-4a), 80.23 (C-2a), 82.23 (C-3a), 97.81 (C-1b), 97.97 (C-1a), 127.50–128.34 (Ar), 138.29 (Ar), 138.45 (Ph), 138.67 (Ph), 138.83 (Ph).

HR-FABMS Calcd for $C_{55}H_{60}NaO_{10}$: 903.408419. Obs. MNa^+ = 903.408619.

3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl-(1 → 6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (17d).[43,48] ^{1}H NMR (200 MHz): δ = 1.33 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.73 (ddd, 1H, $J_{2axb,2eqb} \approx J_{2axb,3b} \approx$ 12.8 Hz, $J_{2axb,1b}$ = 3.6 Hz, H-2_{ax}b), 2.33 (dd, 1H, $J_{2eqb,3b}$ = 4.8 Hz, H-2_{eq}b), 3.49–3.84 (m, 6H, 2H-6a, H-4b, H-5b, 2H-6b), 3.91–4.05 (m, 2H, H-5a, H-3b), 4.22 (dd, 1H, $J_{4a,3a}$ = 8.1 Hz, $J_{4a,5a}$ = 1.6 Hz, H-4a), 4.31 (dd, 1H, $J_{2a,1a}$ = 5.0 Hz, $J_{2a,3a}$ = 2.4 Hz, H-2a), 4.46–4.71 (m, 6H H-3a, 5CH_2Ph), 4.88 (d, 1H, J = 10.7 Hz, CH_2Ph), 5.02 (bd, 1H, H-1b), 5.51 (1H, d, H-1a), 7.14–7.37 (15H, m, 3Ph); ^{13}C NMR (200 MHz): δ = 24.62 (CH_3), 24.97 (CH_3), 26.06 (CH_3), 26.16 (CH_3), 35.50 (C-2b), 65.47 (C-6a), 65.79 (C-5a), 68.92 (C-6b), 70.76 & 71.07 (C-3a, C-4a, C-3b, C-5b), 71.82 (CH_2Ph), 73.51 (CH_2Ph), 74.92 (CH_2Ph), 77.70 (C-4b), 78.35 (C-2a), 96.40 (C-1b), 97.32 (C-1a), 108.56 (C-7a), 109.34 (C-8a), 127.57–128.33 (Ph), 138.29 (Ph), 138.70 (Ph), 138.86 (Ph).

HR-FABMS Calcd for $C_{39}H_{48}NaO_{10}$: 699.314518. Obs. MNa^+ = 699.315523.

3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl-(1 → 3)-1,2:3,4-di-*O*-isopropylidene-α-D-glucofuranoside (17e).[45] ^{1}H NMR (200 MHz) δ: 1.25 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.71 (1H, ddd, $J_{2axb,2eqb} \approx J_{2axb,3b} \approx$ 12.8 Hz, $J_{2axb,1b}$ = 3.4 Hz, H-2_{ax}b), 2.27 (dd, 1H, $J_{2eqb,3b}$ = 4.2 Hz, H-2_{eq}b), 3.42–4.29 (m, 10H, H-3a, H-4a, H-5a, 2 H-6a, H-3b, H-4b, H-5b, 2H-6b), 4.48–4.71 (m, 6H, 5CH_2Ph, H-2a (1H, d, $J_{2a,1a}$ = 3.6 Hz)), 4.89 (d, 1H, J = 10.6 Hz, CH_2Ph), 5.24 (bd, 1H, H-1b), 5.81 (d, 1H, H-1a), 7.15–7.35 (m, 15H, 3Ph); ^{13}C NMR (200 MHz): δ = 25.47 (CH_3), 26.92 (CH_3), 38.84 (C-2a), 67.79 (C-6a), 69.03 (C-6b),

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71.81 (C-5), 71.94 (CH_2Ph), 72.58 (C-5a), 73.66 (CH_2Ph), 75.28 (CH_2Ph), 77.31 (C-3b), 78.23 (C-3a/4b), 80.34 (C-3a/4b), 81.42 (C-4a), 83.85 (C-2a), 98.78 (C-1b), 105.36 (C-1a), 109.18 (C-7, C-8), 127.75–128.49 (Ph), 135.81 (Ph), 138.13 (Ph).

HR-FABMS Calcd for $C_{39}H_{48}NaO_{10}$: 699.316923. Obs. MNa^+ = 699.315842.

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