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Preparative scale synthesis of *O*-glycosides and of a disaccharide by electrochemical oxidation of phenyl *S*-glycosides

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O-glycosides were synthesized by electrochemical oxidation of phenyl *S*-glycosides in the presence of primary alcohols in acetonitrile. Similarly, a β-linked disaccharide was obtained selectively by oxidation of phenyl *S*-glycoside in the presence of a sugar alcohol. Electrosyntheses were performed under controlled potential or at constant current, in an undivided cell, on a large scale. 1 to 60 g of phenyl *S*-glycosides in 0.5 to 1 dm^3 of acetonitrile were converted with chemical yields in the range of 65–75%.

1. Introduction

The easy, efficient and selective production of oligosaccharides is an important challenge in carbohydrate chemistry [1, 2]. Thioglycosides are now attracting a great deal of attention as glycosyl donors. They are stable under a variety of chemical transformations and can be selectively activated by thiophilic reagents to provide efficient glycosylating species. The hereto reported activations of thioglycosides mainly rely on the formation of reactive sulfonium intermediate [3–16] or the use of heavy metal salt [17–21]. Toxicity, difficulty in handling and the high cost associated with most of the promoters may well be a limitation to large scale synthesis. Tris(4-bromophenyl) ammoniummyl hexachloroantimonate (TBPA$\cdot^+$), a stable commercial crystalline radical cation which is easy to handle, has also been used by one of us [22] as a suitable promoter in acetonitrile.

It was shown that phenyl *S*-glycosides can be transformed into disaccharides [23, 24] and *O*-glycosides [23–25] or under mild electrochemical oxidation in acetonitrile.

$$\text{Gly–SPh} + \text{ROH} \longrightarrow \text{Gly–OR} + \tfrac{1}{2}\text{PhSSPh} + \text{H}^+ + \text{e}^-$$

This reaction is based upon the one-electron oxidation of alkyl phenyl sulphides Ph–S–R, to the corresponding radical cations Ph–S–R$\cdot^+$ [26–29]. In the case of phenyl *S*-glycosides, cleavage of the S–R bond selectively affords thiyl radicals PhS$\cdot$ and the cation R^+, strongly stabilized by the neighbouring oxygen atom. This cation can then undergo a nucleophilic attack by an alcohol to provide *O*-glycosides:

$$\begin{aligned}
&\text{Gly–SPh} &&\longrightarrow \text{Gly–SPh}\cdot^+ + \text{e}^-\\
&\text{Gly–SPh}\cdot^+ &&\longrightarrow \text{Gly}^+ + \text{PhS}\cdot\\
&\text{Gly}^+ + \text{ROH} &&\longrightarrow \text{Gly–OR} + \text{H}^+\\
&\text{PhS}\cdot &&\longrightarrow \tfrac{1}{2}(\text{PhS})_2\\
\hline
&\text{Gly–SPh} + \text{ROH} &&\longrightarrow \text{Gly–OR} + \tfrac{1}{2}(\text{PhS})_2 + \text{H}^+ + \text{e}^-
\end{aligned}$$

We have previously established the feasibility of this procedure at a millimole scale [23, 24]; we now report some examples of electrolyses performed on larger scales, showing that the electrosynthesis of disaccharide and *O*-glycosides is actually operative under preparative conditions.

2. Experimental details

Controlled potential electrolyses were carried out using a Tacussel PJT 35-2X potentiostat. Constant current electrolyses were carried out using a stabilized power supply Sodilec PB Autorange (60 V, 3 A).

HPLC analyses were performed on a LKB apparatus equipped with a UV detector set at 254 nm and a reverse phase column (RP8, 10 μm, 250 mm × 4 mm). ^{1}H and ^{13}C n.m.r. were recorded on a Brüker AC-250 and Brüker AM-400 spectrometers. Optical rotations were measured at 20 ± 2° C with a Perkin–Elmer Model 241 polarimeter. C.I. ammonia mass spectra were performed on a Nermag R 10–10 spectrometer. Melting points were determined with a Büchi Model 510 capillary apparatus.

Electrolyses were carried out under anhydrous conditions.

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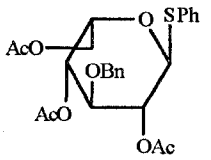
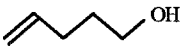
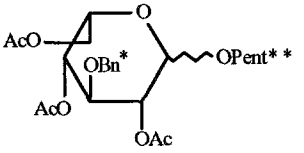
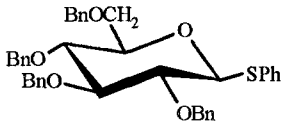
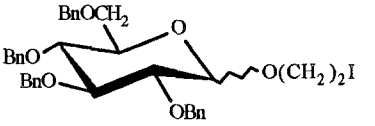
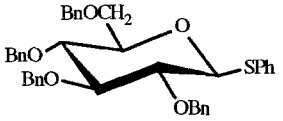
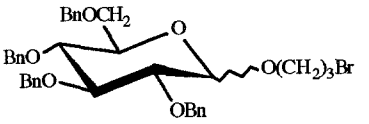
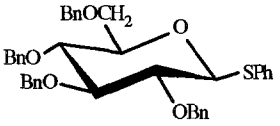
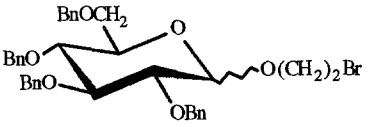
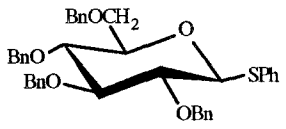
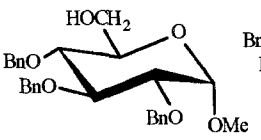
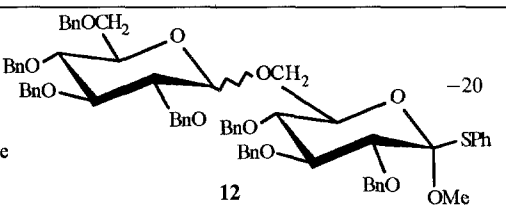
Table 1. Electrochemical glycosylation from phenyl S-glycosides

Entry	*Donor*	*Acceptor*	*Glycoside*	*T* °C	*Yield isolated*	α/β
1	 **1**[a]	 **2**	 **3**	20	75%	1/1
2	**1**[b]	**2**	**3**	20	60%	1/1
3	 **4**	$HO(CH_2)_2I$ **5**	 **6**	−20	77%	1/4
4	 **4**	$HO(CH_2)_3Br$ **7**	 **8**	−20	73%	1/4
5	 **4**	$HO(CH_2)_2Br$ **9**	 **10**	−20	76%	1/4
6	 **4**[c]	 **11**	 **12**	−20	62%[e]	1/25
7	**4**[d]	**11**	**12**	−20	52%[e]	1/25

(a) 20 g of 1. (b) 60 g of 1. (c) The electrolysis was performed at controlled potential. (d) The electrolysis was performed at constant current. (e) Pure isolated β isomer.
* Bn = Ph-CH_2. ** Pent = CH_2=CH-$(CH_2)_3$.

Acetonitrile (Janssen, distilled over CaH_2 or HPLC grade solvent, Chromoptic, dried by filtration through neutral Al_2O_3) was stored over 0.3 nm molecular sieves.

Two cells (0.5 dm^3 or 1 dm^3) were used according to the amount of starting materials and the temperature. In both cells, the electrodes were two concentric conducting cylinders isolated by a separator [30, 31]. The anode (outer electrode) was made of carbon woven (Carbone Lorraine TGM 389) separated from the cathode (inner electrode, nickel foam Metapore PPI 100 laminated of 0.5 mm thickness) by a plastic grid wrapped around the cathode.

This cylindric configuration presents several advantages. The plastic grid allows good diffusion of the species in the solution and maintains a short distance between the electrodes, so that the ohmic drop is minimized. The apparent anode areas were 3 and 0.9 dm^2 for the 1 dm^3 cell and the 0.5 dm^3 cell respectively. The apparent cathode areas were, respectively, 2.5 and 0.7 dm^2. The 1 dm^3 cell was used for electrolyses performed at room temperature while the 0.5 dm^3 cell was used for electrolyses carried out at low temperature.

2.1. *General procedure*

The cell was loaded with the reactants, the supporting electrolyte, $LiBF_4$, activated 0.3 nm molecular sieves and finally with the solvent. The selected current or potential was applied and the electrolysis was performed until complete consumption of phenyl *S*-glycoside. The composition of the solution as a function of the charge passed through the cell was monitored by thin layer chromatography and by HPLC. Although oxidation of the phenyl *S*-glycoside requires one faraday per mole, an average of 2.4 faraday per mole was necessary to entirely convert

the phenyl *S*-glycoside because oxidation of the side product (diphenyldisulphide) occurred.

The *O*-glycosides and the disaccharide were then characterized by ^1H and ^{13}C n.m.r., mass spectrometry and compared with literature data. The new compounds were further characterized by elemental analyses. The α/β ratio was determined from integration of the corresponding protons by ^1H n.m.r.

2.2. *Electrosynthesis of compound* **3**: *Pent-4-enyl 2,4,6-tri-O-acetyl-3-O-benzyl-(α,β)-L-idopyranoside from compound* **1** [*32*]. (*Table 1, entries 1 and 2*)

1 (20 g, 0.04 mol), **2** (36 mL, 0.33 mol), $LiBF_4$ (6 g), activated 0.3 nm molecular sieves (10 g), acetonitrile (900 ml) were introduced into the 1 dm^3 cell. The suspension had been stirred under argon for 30 min before starting the electrolysis. The electrolysis was performed at a controlled potential of +1.7 V vs SCE with an initial current of 0.6 A. The reaction was completed in over 15 h. The mixture was then filtered through Celite and concentrated. The residue was treated with acetic anhydride/pyridine (1/2 v/v) overnight, concentrated and taken up with dicholoromethane and water. The organic layer was dried ($MgSO_4$) and concentrated. **3** (14 g, 75%) was isolated by flash chromatography on a silica gel column (cyclohexane/ethyl acetate 3/1 v/v) as a colourless syrup.

An electrolysis was also performed on 60 g of **1** (entry 2) corresponding to an initial current of 1.8 A to give **3** (33 g, 60%). **3** was isolated as a mixture α/β 1/1:

^1H n.m.r. (250 MHz, $CDCl_3$, TMS) δ: 7.39–7.25 (m, 5H, Ph); 5.90–5.72 (m, 1H, $CH=CH_2$); 5.07–5.05 (m, 1H, H-4α and H-4β); 5.03–4.94 (m, 2.5H, H-1α, $CH=CH_2$); 4.87–4.82 (m, 1.5H, H-1β, H-2α and H-2β); 4.80 and 4.65 (2d, 1H, J 12Hz, CH_2Ph); 4.71 (s, 1H, CH_2Ph); 4.52–4.43 (m, 0.5H, H-5β); 4.31–4.11 (m, 1.5H, H-5α and H-6a); 3.92–3.86 (m, 1H, H-6b); 3.80–3.67 (m, 2H, H-3α, H-3β, $OCHaHbCH_2$); 3.59–3.40 (m, 1H, $OCHaHbCH_2$); 2.20–2.01 (m, 11H, CH_2–$CH=CH_2$ and 3OAc), 1.85–1.66 (m, 2H, $CH_2CH_2CH_2$).
MS m/z: M + 18 = 482.
Anal. calcd for $C_{24}H_{32}O_9$ (464.51) C: 62.06; H: 6.94. Found C: 62.36; H: 6.67

2.3. *Electrosynthesis of compound* **6**: *2-iodoethyl 2,3,4,6-tetra-O-benzyl-(α,β)-D-glucopyranoside from compound* **4** [*33, 34*]. (*Table 1, entry 3*)

The 0.5 dm^3 cell was loaded with dry CH_3CN (400 ml), $LiBF_4$ (6 g), 0.3 nm molecular sieves (8 g), **4** (6.32 g, 10 mmol) and **5** (1.39 g, 10 mmol) and cooled to −20° C. The suspension had been stirred for 30 min., under argon. The exhaustive electrolysis was performed at a constant potential of 1.7 V vs SCE, corresponding to an initial current of 100 mA.

The reaction mixture was filtered through Celite and concentrated. A solution of the residue in dichloromethane was washed with water, dried ($MgSO_4$) and concentrated. The residue was chromatographed (eluent : cyclohexane/ethyl acetate 6/1) to afford **6** (5.34 g, 77%) as an α: β 1/4 mixture.
β isomer:
mp 67–68° C (pentane/hexane/ethyl acetate)
$[\alpha]_D$ + 9° (c 1.0, $CHCl_3$)
^1H n.m.r. (250 MHz, $CDCl_3$, TMS) δ: 7.44–7.13 (m, 20H, Ph); 5.08–4.52 (m, 8H, OCH_2Ph); 4.46 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1); 4.23–4.15 (m, 1H, H-5); 3.92–3.27 (m, 10H, H-2,3,4,5,6a,6b, OCH_2, CH_2I).
^{13}C n.m.r. (62 MHz, $CDCl_3$, TMS) δ: 138.49, 138.37, 137.99, 137.99 (4C, Ph); 128.33–127.54 (*C*H,Ph); 103.46 (C-1); 84.50, 82.03, 77.62, 74.81 (C-2,3,4,5); 75.62, 74.94, 74.81, 73.42, 70.41, 68.75 (4 CH_2Ph, C-6, OCH_2CH_2I); 2.52 (CH_2I).
MS m/z: M + 18 = 712.
Anal. Calcd, C: 62.25; H: 5.66. Found C: 62.54; H: 5.73.

2.4. *Electrosynthesis of compound* **8**: *3-bromopropyl 2,3,4,6-tetra-O-benzyl-(α,β)-D-glucopyranoside from compound* **4** (*Table 1, entry 4*)

The 0.5 dm^3 cell was loaded with dry CH_3CN (400 ml), $LiBF_4$ (6 g) 0.3 nm molecular sieves (8 g), **4** (6.32 g, 10 mmol) and **7** (1.53 g, 11 mmol) and cooled to −20° C.

The electrolysis was performed as described above to give **8** (4.96 g, 73%) as an α: β 1/4 mixture.
β isomer:
m.p. 74–75° C (pentane/cyclohexane/ethyl acetate)
$[\alpha]_D$ + 8.6° (c 1.0, $CHCl_3$).
^1H n.m.r. (250 MHz, $CDCl_3$, TMS) δ: 7.41–7.13 (m, 20H, Ph); 4.98–4.54 (m, 8H, $4CH_2Ph$); 4.43 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1); 4.12–4.04 (m, 1H, H-5); 3.79–3.44 (m, 9H, H-2,3,4,6a,6b, OCH_2, CH_2Br); 2.28–2.12 (m, 2H, CH_2).
^{13}C n.m.r. (62 MHz, $CDCl_3$, TMS) δ: 138.48, 138.26, 138.04, 137.99 (4C, Ph); 129.3–127.5 (*C*H, Ph); 103.49 (C-1); 84.62, 82.18, 77.72, 74.76 (C-2,3,4,5); 75.61, 74.91, 74.85, 73.40, 68.74, 67.24 (4 CH_2Ph, C-6, OCH_2); 32.82, 30.31 (CH_2CH_2Br).
MS m/z: M + 18 = 678, 680.
Anal. Calcd. C: 67.17; H: 6.25. Found C: 66.90; H: 6.26.

2.5. *Electrosynthesis of compound* **10**: *2-bromoethyl 2,3,4,6-tetra-O-benzyl-(α,β)-D-glucopyranoside from compound* **4** (*Table 1, entry 5*)

The 0.5 dm^3 cell was loaded with dry CH_3CN (400 ml), $LiBF_4$ (6 g), 0.3 nm molecular sieves (8 g), **4** (6.32 g, 10 mmol) and **9** (1.35 g, 10 mmol) and cooled to −20° C.

The electrolysis was performed as described above to give **10** (4.92 g, 76%) as an α: β 1/4 mixture.
β isomer:
mp 74.5–75.5° C (hexane/ethyl acetate)

$[\alpha]_D$ + 12 (c 0.77, $CHCl_3$).
^1H n.m.r. (250 MHz, $CDCl_3$, TMS) δ: 7.43–7.15 (m, 20H, Ph) 5.00–4.57 (m, 8H, 4 CH_2Ph); 4.51 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1); 4.34–4.24 (m, 1H, H-5); 3.98–3.50 (m, 9H, H-2,3,4,6a,6b, OCH_2, CH_2Br).
^{13}C n.m.r. (62 MHz, $CDCl_3$, TMS) δ: 138.57, 138.42, 138.06, 138.06 (4C, Ph); 128.40–127.62 (CH, Ph); 103.74 (C-1); 84.57, 82.07, 77.69, 74.91 (C-2, 3, 4, 5), 75.71, 75.02, 74.88, 73.50, 69.69, 68.84 (4 CH_2Ph, C-6, OCH_2); 30.3 (CH_2Br).
MS m/z: M + 18 = 664 and 666.
Anal. Calc. C: 66.77; H: 6.07. Found C: 66.87; H: 6.02.

2.6. *Electrosynthesis of compound* **12**: *methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside from compounds* **4** *and* **11** [*35, 36*] (*Table 1, entries 6 and 7*)

The 0.5 dm^3 cell was loaded with dry CH_3CN (400 ml), $LiBF_4$ (6 g), 0.3 nm molecular sieves (8 g), **4** (3.6 g, 5 mmol) and **11** (2.32 g, 5 mmol) and cooled to −20° C. The electrolysis was performed as described above at a constant current of 100 mA. The reaction mixture was filtered through Celite and concentrated. A solution of the residue in dichloromethane was washed with water, dried ($MgSO_4$) and concentrated. The residue was crystallized in ethanol to give the β isomer in a pure form (2.55 g, 52%) (entry 7). Physical data were in agreement with those previously reported [37]. The electrolysis was also performed at a controlled potential of 1.7 V vs SCE and yielded the pure β isomer (3.05 g, 62%) (entry 6).

3. Results and discussion

The results presented in the Table 1 (entries 1–5) indicate that the electrochemical oxidation process is an advantageous method for large scale glycosylation. Thus *O*-glycosides were synthesized in high yield by electrochemical oxidation of phenyl *S*-glycosides in the presence of primary alcohols: 4-penten-1-ol, 2-iodoethanol, 3-bromopropanol and 2-bromoethanol. The reactions were performed on 10 to 40 mmoles of phenyl *S*-glycosides. This last point is of particular interest owing to the difficulties in using large quantities of reactants in usual glycosylation reactions.

The use of woven carbon as the anode was of particular interest: first, this is a cheap material and secondly, the large area of this anode minimized the eventual poisoning of the anode by electrogenerated sulphur containing compounds. Poisoning of the anode was observed for example in the case of platinum electrodes. Nickel was chosen as material for the cathode because it easily reduces protons. So the protons produced at the anode were reduced at the cathode, preventing the reduction of the reactants and the products.

As expected a diminution of the temperature favours the formation of the β isomer in the glucose series (entries 3–7). The observed β-stereoselectivity is in agreement with the hypothesis of the formation of an α-nitrilium intermediate by acetonitrile trapping of the cation [38–42]. Since residual water could react with the glycosyl cation as a nucleophile, activated molecular sieves were necessary to minimize the formation of tetrabenzylglucopyranose. $LiBF_4$ was chosen as the supporting electrolyte because its high solubility in water allowed easy extraction of the crude products by dichloromethane, without simultaneous extraction of the supporting electrolyte.

Electrochemical oxidation allows the synthesis of *O*-glycosides and especially disaccharides by an easy and nonexpensive method. The oxidation potentials of phenyl *S*-glycosides are considerably lower than those of the corresponding phenyl *O*-glycosides [43]. Thus the electroglycosylation of phenyl *S*-glycosides is particularly attractive due to its compatibility with various protecting groups, the latter would be oxidized at larger potentials. The procedure with phenyl *S*-glycosides appears compatible with the use of highly functionalized acceptors and glycosyl donors.

4. Conclusion

Electrochemical glycosylation based on oxidation of phenyl *S*-glycosides was adapted to large scale preparative conditions. This method is an easy and attractive alternative to chemical glycosylations that are known to be difficult and costly on a large scale. Since *O*-glycosides are expected to have potential applications in glycobiology, such a route to glycosylations appears desirable.

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