Carbohydrate Research, 244 (1993) 237–246
Elsevier Science Publishers B.V., Amsterdam

Electrosyntheses of disaccharides from phenyl or ethyl 1-thioglycosides *

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(Received December 30th, 1991; accepted June 17th, 1992)

ABSTRACT

Constant current electrolyses of the glycosyl donors phenyl and ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside in dry acetonitrile in the presence of various primary and secondary sugar alcohols, performed in an undivided cell, gave β-linked disaccharide derivatives selectively in good yields. Phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside gave the β-glucosides exclusively in good to moderate yields.

INTRODUCTION

The efficient preparation of oligosaccharides is a central problem in carbohydrate chemistry. Most of the reported glycosylation processes rely on S_N1-type reactions at the anomeric centre, i.e., the generation of a reactive intermediate oxycarbenium ion pair from an appropriate activated glycosyl donor. *S*-Glycosides have attracted considerable attention in this context mainly due to their stability during various chemical transformations. The activation of 1-thioglycosides involves the formation of a reactive sulfonium intermediate, taking advantage of the well-known affinity of the sulfide group for soft electrophiles[1] or the use of heavy metal salts[2]. Anomeric sulfoxides[3] or sulfones[4] have also been used in glycosylation reactions.

Oxycarbenium ions may also be generated by the so-called $S_{ON}1$ type reaction[5]. Photostimulated one-electron-transfer reactions of aryl[6] and thioaryl[7] glycosides in

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* Part of this work has been reported: XII$^{\text{èmes}}$ Journées de la Chimie et de la Biochimie des Glucides, May 21–23, 1990, Avignon, Abstr. C1; EUROCARB VI, September 8–13, 1991, Edinburgh, Abstr. B136.

$$\begin{array}{ll} \text{Gly–SPh} & \longrightarrow [\text{Gly–SPh}]^{+\cdot} + e^- \\ [\text{Gly–SPh}]^{+\cdot} & \longrightarrow \text{Gly}^+ + \text{PhS}^\cdot \\ \text{Gly}^+ + \text{ROH} & \longrightarrow \text{Gly–OR} + \text{H}^+ \\ \text{PhS}^\cdot & \longrightarrow 0.5\ (\text{PhS})_2 \\ \hline \text{Gly–SPh} + \text{ROH} & \longrightarrow \text{Gly–OR} + 0.5(\text{PhS})_2 + \text{H}^+ + e^- \end{array}$$

Scheme 1.

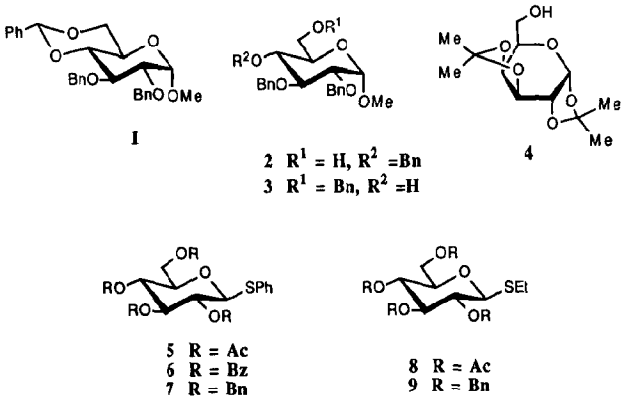
acetonitrile in the presence of simple primary alcohols gave glycosides via $S_{ON}1$ processes, but the potential for synthesis appeared to be limited. Noyori and Kurimoto[8] subsequently discovered that one-electron anodic oxidation of aryl glycosides resulted in a more useful methodology. It is known[9] that alkyl phenyl sulfides (Ph–S–R) are easily anodically oxidised[10] to provide a radical cation $(Ph–S–R)^{+\cdot}$ which may undergo S–R bond cleavage to give a thiyl radical (Ph–S$^\cdot$) and a cation (R^+). Such a reaction pathway is controlled by the stability of (R^+) and should be particularly favoured for glycosyl phenyl sulfides (Gly–SPh) since glycosyl cations are stabilised by the neighboring oxygen atom.

We[11] and others[12] discovered that electro-oxidative generation of oxycarbenium species from phenyl 1-thioglycosides resulted in electroglycosylation (Scheme 1). Phenyl 1-thioglycosides are prepared easily and have lower oxidation potentials than aryl glycosides[8]. Following our preliminary communication on electroglycosylation[11], we now report details and improvements of the original procedure.

RESULTS AND DISCUSSION

The initial glycosylation reactions were conducted at room temperature under nitrogen in a divided cell equipped with a woven carbon anode and a platinum-gauze cathode. In order to neutralise the acid produced (Scheme 1), dry potassium carbonate was added to the anodic compartment, which also contained the glycosyl donor and the acceptor. The solvent was acetonitrile (containing tetrabutylammonium tetrafluoroborate as the supporting electrolyte), which is known to be particularly suitable for one-electron oxidation of sulfides[13] and to promote β-selectivity[14].

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[15] (**1**), used to prepare the model alcohols methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[16] (**2**) and methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[17] (**3**), was prepared conveniently on a large scale and in a yield of 80% in a one-pot operation from methyl α-D-glucopyranoside. This modified procedure used *N*,*N*-dimethylformamide as the solvent both for the formation[18] of the benzylidene acetal and for the subsequent benzylation. The primary alcohol **2** was prepared by a slight modification of the well-established regioselective ring cleavage of the benzylidene acetal in **1** with the $LiAlH_4$–$AlCl_3$ reagent[16b]. It is beneficial in large-scale reactions to



reduce the proportions of $LiAlH_4$ (1.5 instead of 4.7 equiv) and $AlCl_3$ (2 instead of 4 equiv). The secondary alcohol **3** was prepared from **1** through a regioselective reductive ring cleavage with $NaBH_3CN$ (4 equiv) and $HBF_4 \cdot Et_2O$. The use of this acid instead of hydrogen chloride in ether[17b] was advantageous.

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside[19] (**5**) and ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside[20] (**8**) were prepared easily in bulk from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose according to the procedure of Ferrier and Furneaux[21], chloroform being replaced by dichloromethane. *O*-Deacetylation of **5** gave phenyl 1-thio-β-D-glucopyranoside which was benzylated (NaH, BnBr and *N*,*N*-dimethylformamide) to give phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[2a,22] (**7**) and benzoylated (BzCl and pyridine) to give phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside[21,23] (**6**). Similarly, *O*-deacetylation of **8** followed by benzylation gave ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[24] (**9**).

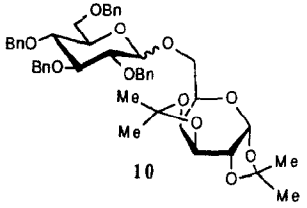
Entries 1 and 2 (Table I), with the primary alcohol 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**4**) as the acceptor and **5** and **7** as the donors, clearly demonstrate the feasibility of electro-oxidative glycosylation but the yields of the

TABLE I

Electrochemical glycosylation in a divided cell [a]

Entry	Donor	Acceptor	Product	α:β	Yield (%)
1	**7**	**4**[31]	**10**[32]	1:4	63
2	**5**	**4**	**11**[33]	0:1	50
3	**9**	**2**	**13**[34]	6:1	84

[a] Electrolyses were carried out at constant current at room temperature in a 0.1 M tetrabutylammonium tetrafluoroborate solution in acetonitrile (entries 1 and 2) or in dichloromethane (entry 3). Dry potassium carbonate (1.2 mmol), *S*-glycoside (1.2 mmol) and alcohol (1.4 mmol) for entries 1 and 2, *S*-glycoside (1.0 mmol) and alcohol (1.0 mmol) for entry 3, were added to the anodic compartment.



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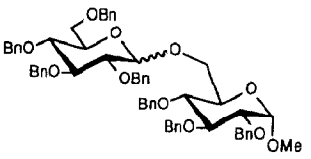

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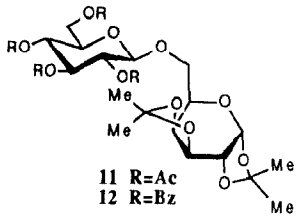

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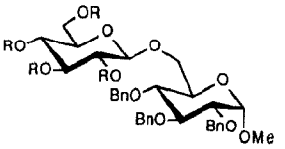
12 R=Bz



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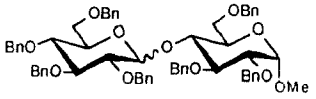
15 R=Bz



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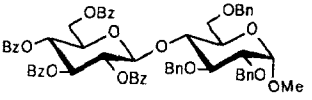

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disaccharide derivatives were relatively low (50–63%). The donor **5** did not condense with the moderately reactive secondary alcohol **3**.

In order to carry out electrolyses without proton accumulation, the use of an *undivided* electrochemical cell was investigated (see Scheme 2). The protons liberated by reaction at the anode were reduced to hydrogen at the cathode. A nickel cathode was used in order to reduce protons selectively, in the presence of diphenyl disulfide. The apparatus is relatively simple and is represented in Fig. 1. The electrolyses were carried out at a constant current.

The replacement of tetrabutylammonium tetrafluoroborate by lithium tetrafluoroborate as supporting electrolyte facilitated the isolation of the disaccharide derivatives, and the addition of 3A molecular sieves kept the medium anhydrous and neutralised the residual acidity.

As indicated in Table II, the electrochemical glycosylation of **2–4** with **7** and **9** under these conditions were more satisfactory. The β-selectivity of the reaction could be improved significantly by decreasing the temperature (entries 5 and 6), a feature which is now observed consistently when a reactive α-nitrilium intermediate is involved[14]. Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**9**) reacted with primary (entries 8 and 9) or secondary (entry 10) alcohols in acetonitrile to give β-glycosides selectively in good yields (75–86%). Although **9** reacted with methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**2**) in dichloromethane to give selectively an α-linked disaccharide derivative, the electrolysis needed to be carried out

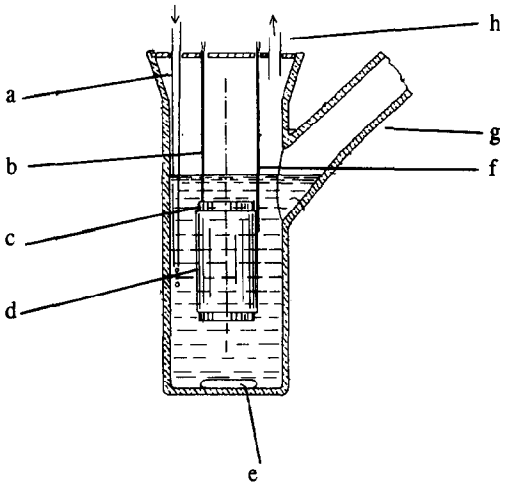

Fig. 1. Undivided cell for electroglycosylation: a, nitrogen bubbler inlet; b, cathode lead; c, cathode; d, anode; e, stirring bar; f, anode lead; g, side neck for sampling and filling; h, nitrogen outlet.

in a divided cell (Table I, entry 3). Secondary alcohols were found to be unreactive towards **9** in dichloromethane and, in the presence of collidine, the electrolysis afforded 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl fluoride, resulting from a nucleophilic attack on Gly^+ by BF_4^-. This reaction may offer an economic entry to glycosyl fluorides, which are usually prepared from elaborate reagents[25].

Glycosylation with acylated phenyl 1-thioglycosides was then reinvestigated using an undivided cell (Table III). Thus, **5** reacted with the primary alcohol **2** (entry 11) but not with the secondary alcohol **3** (entry 12). In contrast, **6** was an effective glycosyl donor (entries 13–15) with the acceptors **2–4**, a trend which is now established in this field[26]. Compound **6** is poorly activated[27] by tris(4-bromophenyl)ammoniumyl hexachloroantimonate ($TBPA^{+\cdot}$ $SbCl_6^-$), a well-known one-electron oxidising agent. In the $TBPA^{+\cdot}$-mediated process, a complex or an adduct with the thioglycoside is formed initially and an inner-sphere mechanism has been postulated[28]. Such a process is probably hampered with **6** due to steric hindrance. In the alternative electrochemical process, one electron is abstracted from the sulfur atom by an outer-sphere mechanism. Thus, a combination of chemical and electrochemical one-electron oxidative glycosylation may be of value for the preparation of disaccharide donors.

Anode: $Gly\text{–}SPh + ROH \longrightarrow Gly\text{–}OR + 0.5\ (PhS)_2 + H^+ + e^-$

Cathode: $H^+ + e^- \longrightarrow 0.5\ H_2$

$$Gly\text{–}SPh + ROH \longrightarrow Gly\text{–}OR + 0.5\ (PhS)_2 + 0.5\ H_2$$

Scheme 2.

TABLE II

Electrochemical glycosylation in an undivided cell with donors having no participating substituent at C-2

Entry	Donor	Acceptor	Product	Temp. (°C)	$\alpha:\beta$	Yield (%)
4	**7**	**4**	**10**	20	1:4.5	89
5	**7**	**2**	**13**	20	1:3	75
6	**7**	**2**	**13**	−30	1:22	73
7	**7**	**3**	**16**[35]	20	1:3	73
8	**9**	**4**	**10**	20	1:4	86
9	**9**	**2**	**13**	20	1:3.5	80
10	**9**	**3**	**16**	20	1:3	75

The above data show that electrolysis of phenyl or ethyl 1-thioglycosides in the presence of alcohols is an effective method for the selective preparation of β-linked disaccharides.

EXPERIMENTAL

General methods.—Melting points were determined with a Büchi Model 510 capillary apparatus and are uncorrected. Optical rotations were measured at $20 \pm 2°$ with a Perkin–Elmer Model 241 polarimeter. CI(ammonia)-mass spectra were obtained with a Nermag R10-10 spectrometer. ^{1}H NMR spectra were recorded with Cameca 250 and Brüker AM-400 spectrometers for solutions in $CDCl_3$ (internal Me_4Si). Reactions were monitored by TLC on Silica Gel 60 F_{254} (Merck) and detection by charring with H_2SO_4. HPLC was performed on an LKB 2152 apparatus with a UV detector (254 nm) equipped with a reverse-phase column (Lichrosorb RP8, 10 μm, 250 × 4 mm). Flash-column chromatography was performed on Silica Gel 60 (230–400 mesh, Merck). Acetonitrile and CH_2Cl_2 were distilled from CaH_2 under N_2 and stored over activated 3A molecular sieves. Tetrabutylammonium tetrafluoroborate was obtained from the hydrogensulfate by treatment with sodium tetrafluoroborate in water, crystallised from EtOAc–light petroleum, and dried under vacuum. Lithium tetrafluoroborate (Janssen) was used without purification. 3A Molecular sieves were activated by heating at 200°C under vacuum and powdered before use.

TABLE III

Electrochemical glycosylation in an undivided cell with donors having a participating group at C-2

Entry	Donor	Acceptor	Product	Yield (%)
11	**5**	**2**	**14**[36]	73
12	**5**	**3**	–	0
13	**6**	**4**	**12**[37]	73
14	**6**	**2**	**15**[14b]	67
15	**6**	**3**	**17**[38]	45

Methyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**1**).—A mixture of methyl α-D-glucopyranoside (50 g, 0.25 mol), benzaldehyde dimethyl acetal (48 mL, 1.3 equiv), camphorsulfonic acid (0.7 g), and *N*,*N*-dimethylformamide (200 mL) was stirred at 100°C under vacuum (water aspirator) for 2 h. The resulting solution was cooled to 0°C, and benzyl bromide (70 mL, 1.2 equiv) and *N*,*N*-dimethylformamide (300 mL) were added, followed by NaH (60% in oil, 24 g, 1.2 equiv) portionwise during 2 h. After 15 h at room temperature, MeOH (100 mL) was added, stirring was continued for 1 h, and the solution was then concentrated under vacuum. The residue was treated with CH_2Cl_2 (500 mL) and water (500 mL). The organic layer was separated, washed with water, dried ($MgSO_4$), and concentrated. The residue was crystallised from hexane to afford **1** (93 g, 80%), mp 96°C; lit.[15] mp 99°C (from MeOH), 93°C (from aq MeOH), 96–98°C (from aq EtOH).

Methyl 2,3,6-tri-O-benzyl-α-D-glucopyranoside (**3**).—$HBF_4 \cdot Et_2O$ (37 mL, 4 equiv) was added to a cold (0°C) suspension of $NaBH_3CN$ (16.3 g, 4 equiv) and **1** (30 g, 0.065 mol) in dry oxolane (150 mL). Stirring was continued at 0°C for 15 min, aq 10% $NaHCO_3$ (100 mL) was added, the solution was diluted with ether, the aqueous layer was extracted with ether, and the combined organic layers were dried ($MgSO_4$) and concentrated. Column chromatography (2:1 hexane–EtOAc) of the residue gave **3** (21.11 g, 70%); $[\alpha]_D$ + 14° (*c* 1.1, $CHCl_3$); lit.[17a] $[\alpha]_D$ + 12°.

Phenyl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-glucopyranoside (**6**).—Phenyl 1-thio-β-D-glucopyranoside (6.0 g, 0.022 mol), prepared by *O*-deacetylation of **5** (MeONa–MeOH), was treated with benzoyl chloride (40 mL, 1.2 equiv) in pyridine (70 mL) for 15 h. Methanol was added, the solution was concentrated, and the residue was treated with water and CH_2Cl_2. The organic extract was dried ($MgSO_4$) and concentrated. The residue was crystallised from acetic acid to afford **6** (12 g, 80%); mp 166°C; lit.[21] mp 167–168°C.

Electrochemical equipment—Cyclic voltammetry was performed in a 15-mL three-electrode air-tight cell. The working electrode consisted of a vitreous carbon disc 2 mm in diameter. The reference electrode was a standard calomel electrode (Tacussel) separated from the solution by a bridge (3 mL) filled with a solution of tetrabutylammonium tetrafluoroborate in acetonitrile (or CH_2Cl_2) identical to that used in the cell. The counter electrode was a platinum spiral with an apparent surface area of 1 cm^2 located within 5 mm of, and facing, the working electrode. The potential-wave-form-signal generator was an EG & G PAR Model 175. The potentiostat used in cyclic voltammetry was home made[29]. Cyclic voltammetry was performed at a scan rate of 200 mV/s. A potentiostat Tacussel PJT 35-2 was used for preparative electrosyntheses when performed at constant potential, and a stabilised power supply (Sodilec 60V, 2A) was used for preparative electrosyntheses carried out at constant current. The cells and electrodes are described below. The charge consumed during the electrosyntheses was determined by integrating the electrolysis current as a function of time with a Tacussel IG5LN coulometer.

Electroglycosylation—(a) In a divided cell. The three-electrode air-tight cell

consisted of two (30 mL) compartments separated by fritted glass (No. 5). Each compartment was stirred with a Teflon-coated magnetic bar. The working electrode consisted of a (10 cm^2) woven carbon (Carbone Lorraine TGM 389) electrode placed parallel to, and 2 cm from, the fritted glass. The cathode consisted of a platinum grid with an apparent surface area of ca. 7 cm^2. The reference electrode/bridge was identical with that described above and was placed in the anolyte near the working electrode. The two compartments were each filled with 30 mL of the appropriate solvent containing the supporting electrolyte (0.1 M). 2-Chloronaphthalene (1 mL) was added to the catholyte as the reagent to be reduced. Electrolyses in entries 1 and 2 of Table I were carried out at constant current (50 mA) at room temperature in acetonitrile (0.1 M tetrabutylammonium tetrafluoroborate). Dry K_2CO_3 (1.2 mmol), phenyl 1-thioglycoside (1.2 mmol), and the alcohol **3** (1.4 mmol) were added to the anodic compartment. For entry 3 in Table 1, 3A powdered molecular sieves were used instead of K_2CO_3.

(b) In an undivided cell. The electrolyser[30] is represented in Fig. 1. The two concentric electrodes consist of an external cylindrical woven carbon anode 30 cm^2 in area and a cylindrical internal nickel-foam cathode 25 cm^2 in area, separated by a polyethylene grid and mounted as close as possible in order to minimise the ohmic drop.

The electrolyser was charged with acetonitrile (60 mL) containing 0.1 M lithium tetrafluoroborate followed by the alcohol (1 mmol), the glycosyl donor (1 mmol), and activated powdered 3A molecular sieves (4 g). The mixture was stirred for 30 min and the electrolyses were then carried out at a constant current of 50 mA until complete disappearance of the starting materials as monitored by HPLC and/or TLC. Although the glycosylation required the theoretical consumption of one Faraday per mol, the complete disappearance of the starting materials generally occurred after the consumption of 2.5 Faradays per mole due to the concomitant oxidation of the RSSR (R = Ph or Et) generated during the glycosylation (Scheme 1).

The electrolysed solution was filtered and concentrated. Chromatography (EtOAc–cyclohexane) of the residue afforded the disaccharide derivative (α,β-mixture or β form) which was characterised by ^1H and ^{13}C NMR, and mass spectroscopy by comparison to the authentic samples and data from the literature. The α,β-ratio was determined by integration of the signals for H-1′ and/or MeO. No preparative separation of the α and β anomers, using column chromatography, was carried out although such a separation is possible (see the corresponding references).

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