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Electrochemical synthesis and X-ray crystal structures of β-D-2-phenylselenyl-1,3,4,6-tetra-*O*-acetylglucopyranose and α-D-2-phenylselenyl-1,3,4,6-tetra-*O*-acetylmannopyranose

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Abstract—Electrochemical acetoxyphenylselenation of 3,4-dihydro-2*H*-pyran and D-3,4,6-tri-*O*-acetylglucal was studied. The constant current electrolysis (50 mA) of dihydropyran and diphenyl diselenide in an acetic acid solution of tetramethylammonium chloride was performed at room temperature in an undivided cell using a graphite anode and an aluminum cathode and yielded *trans*-DL-2-acetoxy-3-phenylselenyltetrahydropyran (27%), in agreement with Markovnikov's rule. The analysis of the ^{1}H NMR spectral data showed that the acetoxy and phenylselenyl groups adopt axial positions in the most stable conformation of this compound due to the anomeric effect. Under the same conditions D-3,4,6-tri-*O*-acetylglucal afforded D-2-phenylselenyl-1,3,4,6-tetra-*O*-acetylglucopyranose and D-2-phenylselenyl-1,3,4,6-tetra-*O*-acetylmannopyranose, which were separated by column chromatography and isolated in 87% overall yield (isomer ratio 60:40). The structures of these compounds were established by spectral data. Single crystal X-ray structure determinations of the diastereomers are reported.

Keywords: Electrochemical acetoxyphenylselenation; 2-Substituted monosaccharides; Vinyl ethers; D-3,4,6-Tri-*O*-acetylglucal; X-ray analysis

1. Introduction

Glycals are extremely useful derivatives in carbohydrate chemistry because of the versatile reactivity of their enol ether functionality. Among 2-substituted monosaccharide derivatives, which can be synthesized from glycals those containing halogens,[1–7] sulfur, and selenium[8–16] are synthetically useful because they can be readily transformed to other derivatives. Saccharides containing a phenylselenyl group are particularly interesting, since this group can be removed by both reductive and oxidative methods, resulting in 2-deoxysugars or unsaturated sugars, respectively. Two principal methods are available to generate a phenylselenyl cation ($C_6H_5Se^{\oplus}$): from phenylselenyl halides and from diphenyl diselenide by anodic or chemical oxidation.[17] Since electrophilic addition of $C_6H_5Se^{\oplus}$ to the double bond of an unsaturated substrate obeys Markovnikov's rule, and the following attack of a nucleophile at the intermediate cation formed in the first step results in an *anti*-addition, it is possible to predict regiochemistry, and sometimes, stereochemistry of the product.

This reaction can be successfully applied in the synthesis of 2-phenylselenyl sugars from glycals.[14–20] Our experience in electrochemical phenylselenation of

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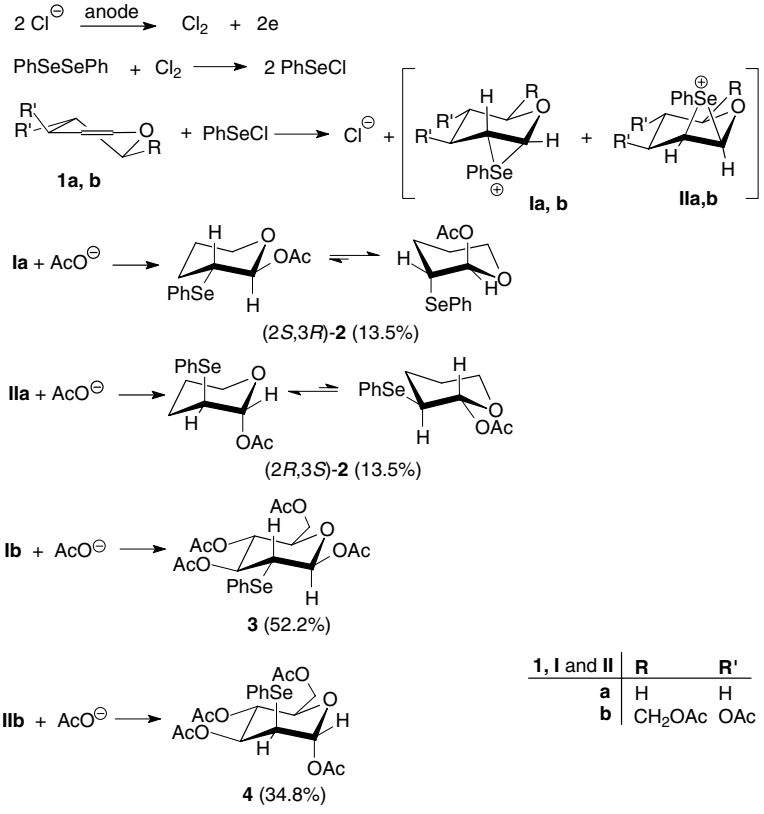
unsaturated compounds[21,22] as well as the literature on halogenophenylselenation and alkoxyphenylselenation of glycals[14–20] prompted us to examine the electrochemical conversion of D-3,4,6-tri-*O*-acetylglucal (**1b**) to 2-phenylselenyl derivatives of D-glucose and D-mannose in the presence of diphenyl diselenide. Here we report the results of our synthetic efforts.

2. Results and discussion

We have chosen the readily available and cheap 3,4-dihydro-2*H*-pyran (**1a**) as the model substrate for the initial investigations, due to its structural similarity to glycals, although glycals are more sterically hindered. An acetic acid solution of **1a**, diphenyl diselenide, and tetramethylammonium chloride was electrolyzed using an undivided cell supplied with a graphite anode and an aluminum cathode. The reaction was assumed to be finished after passing 4 F/mol charge through the solution when the yellow color of diphenyl diselenide disappeared. After chromatography we isolated a colorless liquid as the only stable product in 27% yield. On the basis of HRMS, IR, ^{1}H, and ^{13}C NMR spectral data this compound was identified as *trans*-2-acetoxy-3-phenylselenyl tetrahydropyran (**2**, Scheme 1).

We assume that the reaction proceeds by oxidation of chloride ions, at the anode, to chlorine (Cl_2) which oxidizes diphenyl diselenide, resulting in an in situ formation of phenylselenyl chloride (Scheme 1). This mechanism is supported by reports describing similar electrochemical phenylselenation of olefins and carbonyl compounds using bromide ions as the mediators.[23–25] Once formed, phenylselenyl chloride attacks the π-electronic system of the double bond of 3,4-dihydro-2*H*-pyran (**1a**). Since both sides of the double bond plane of the compound **1a** are sterically identical, two α-phenylselenyl cations (**Ia** and **IIa**) are formed in equal concentrations. The cations subsequently undergo nucleophilic attack by acetate ions yielding the final product *trans*-2-acetoxy-3-phenylselenyltetrahydropyran in racemic form (2*S*,3*R*-**2** and 2*R*,3*S*-**2**; Scheme 1).

The structure of compound **2** deserves some attention. Namely, bearing in mind the bulkiness of the acetoxy and phenylselenyl groups in comparison with the hydrogen atoms, these substituents could be expected to adopt equatorial positions in the most stable conformation. In this case both hydrogen atoms H-2 and H-3 must occupy axial positions. However, the relatively large chemical shift and the small coupling constant of the proton H-2 (δ 6.16 ppm, J 3.1 Hz) show that it occupies an equatorial position in the most stable conformation of compound **2**. Apparently, the equilibrium



1, I and II	R	R'
a	H	H
b	CH_2OAc	OAc

Scheme 1.

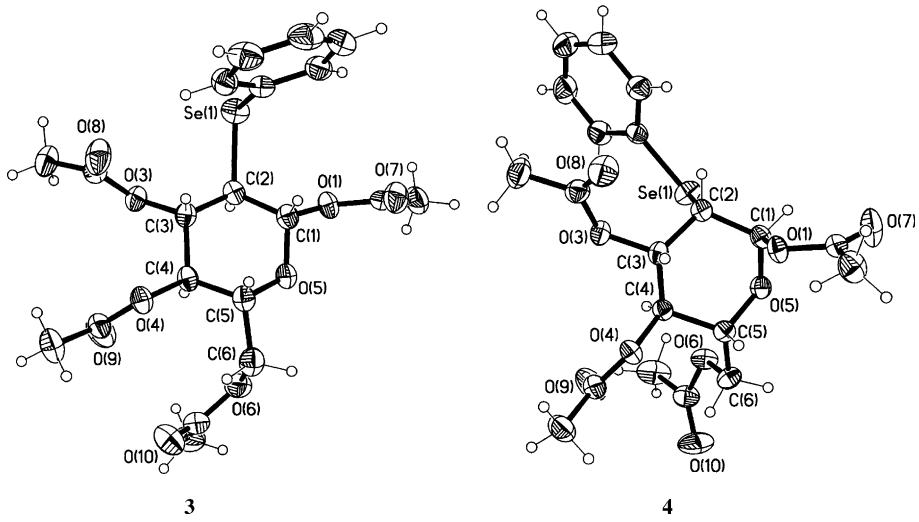


Figure 1. ORTEP plots of the molecular structures of **3** and **4**. Displacement ellipsoids are drawn at the 40% probability level.

between 'diequatorial' and 'diaxial' conformers of this compound is shifted quite to the latter, as a consequence of the anomeric effect.

Besides compound **2** we also observed by TLC two more products which were unstable. From the chromatographic behavior, ^{1}H NMR spectrum, and GC–MS analysis, one of them could be an oligomer (at least dimer), containing both equatorial and axial hydrogen atoms connected to the acetal carbon atoms.

Electrochemical acetoxyphenylselenation of 3,4,6-tri-*O*-acetylglucal (**1b**) gives a different picture. Since the steric situations on both sides of the double bond plane of this compound are not equal, and taking into account that it already contains three chiral carbon atoms, theoretically several diastereomeric products are possible, all of them being glucose or mannose derivatives. Our results show that the reaction proceeded exclusively as an *anti*-addition, following Markovnikov's rule (via intermediate cations **Ib** and **IIb**), and only two products were obtained, β-D-2-phenylselenyl-1,3,4,6-tetra-*O*-acetylglucopyranose (**3**) and α-D-2-phenylselenyl-1,3,4,6-tetra-*O*-acetylmannopyranose (**4**) in 87% overall yield. The ratio of the two diastereomers **3**/**4** was 60:40 as determined by ^{1}H NMR.

The structures of compounds **3** and **4** were established by IR, ^{1}H, ^{13}C NMR, and HRMS spectral data. Thus, the doublet at 5.70 ppm with a coupling constant of 9.6 Hz indicates an axial H-1 proton in **3**. On the other hand, in the spectrum of compound **4** a doublet is observed at 6.42 ppm with a coupling constant of 1.7 Hz, which confirms that the hydrogen atom occupies an equatorial position. Of course, the equilibria between the conformers of **3** and **4** are shifted to the more stable ones, with a higher number of bulky substituents in equatorial positions. Also, all singlets attributed to the equatorial acetyl groups of both **3** and **4** are located in a narrow region between 1.99 and 2.13 ppm, whereas the singlet of the axial group in **4** (positioned at C-1) is shifted upfield (1.75 ppm).

An unambiguous confirmation was provided by the X-ray crystal analysis. The molecular structures of compounds **3** and **4** and the numbering scheme for the atoms are shown in Figure 1, and selected bond lengths, bond angles, and torsion angles are given in Table 1. It can be concluded that different configurations at C-1 and C-2 of the two diastereomers induce different conformations of the pyranose rings. Thus, when comparing the acetal C–O bond lengths, the endocyclic C-1–O-5

Table 1. Selected bond lengths, bond angles, and torsion angles of compounds **3** and **4**

	3	**4**
Bond lengths (Å)		
O(1)–C(1)	1.425(4)	1.453(3)
O(5)–C(5)	1.437(4)	1.437(3)
O(5)–C(1)	1.419(4)	1.406(4)
C(1)–C(2)	1.519(5)	1.518(4)
C(2)–C(3)	1.519(4)	1.529(4)
C(3)–C(4)	1.511(4)	1.506(4)
C(4)–C(5)	1.526(4)	1.539(4)
C(5)–C(6)	1.493(5)	1.498(4)
Se(1)–C(2)	1.968(3)	1.971(3)
Bond angles (deg)		
O(5)–C(5)–C(4)	107.3(2)	111.7(2)
C(1)–O(5)–C(5)	112.4(2)	114.6(2)
O(5)–C(1)–C(2)	111.9(3)	111.1(2)
C(6)–C(5)–C(4)	115.6(3)	112.6(2)
O(5)–C(5)–C(6)	108.3(3)	107.1(2)
O(5)–C(1)–O(1)	103.9(2)	109.2(2)
O(1)–C(1)–C(2)	108.4(3)	107.0(2)
C(1)–C(2)–Se(1)	112.5(2)	105.1(2)
C(3)–C(2)–Se(1)	113.1(2)	113.4(2)
Torsion angles (deg)		
O(5)–C(1)–C(2)–Se(1)	−179.8(2)	−64.4(3)
O(1)–C(1)–C(2)–Se(1)	−65.8(3)	176.5(2)

bond in **3** is significantly longer than in the diastereomer **4** (1.419 Å vs 1.406 Å). Although the axial C-2–Se bond in **4** is only slightly longer than the equatorial one in **3** (1.971 Å vs 1.968 Å), the exocyclic acetal C–O bonds are significantly different from each other (axial in **4** 1.453 Å vs equatorial in **3** 1.425 Å). Also, the rings' C–O–C bond angles are different (112.4° in **4** vs 114.6° in **3**). Calculated torsion angles H–C-1–C-2–H in **3** and **4** are 173.90° and −60.34°, respectively, which is in agreement with the coupling constants observed in the ^{1}H NMR spectra (9.6 Hz vs 1.7 Hz, respectively).

3. Experimental

All chemicals used were commercially available and were used as received. Acetic acid and the solvents used were purified by distillation. IR measurements were carried out with a Perkin–Elmer 457 grating FT instrument. NMR spectra were recorded on a Varian Gemini (200 MHz) spectrometer, using $CDCl_3$ as the solvent. Chemical shifts are expressed in ppm using Me_4Si as an internal standard. Mass spectra were measured with a MAT 95 (FAB) spectrometer. Melting points were determined on a Kofler hot-plate apparatus. Diffraction intensity data were measured using a NONIUS Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å); data reduction with DENZO-SMN,[26] no absorption correction, structure solution with SHELXS86, refinement on F^2 with SHELXL97,[27] hydrogen atoms calculated and refined in the riding model with isotropic displacement parameters. A Uniwatt Beha Labor-Netzgerät (NG 394) was used as a direct current source for the electrolysis. A cylindrical glass vessel equipped with a magnetic stirrer, a graphite stick (as anode; $\varnothing = 1$ cm), and an Al spiral (as cathode; $\varnothing = 2.5$ cm) was used as the cell.

3.1. General procedure for electrochemical acetoxyphenylselenation

One millimole of the corresponding substrate (272 mg of **1b**; in the case of **1a**, however, an excess of 0.5 mL was used), 0.5 mmol (156 mg) of diphenyl diselenide, and tetramethylammonium chloride (200 mg) were dissolved in freshly distilled glacial acetic acid (10 mL). The solution was placed in the electrolytic cell, vigorously stirred at room temperature, and electrolyzed at constant current (50 mA). The electrolysis was stopped after the yellow color of the diselenide had disappeared (2 h, ~4 F/mol charge). The solvent was removed by rotary evaporation, H_2O (15 mL) was added to the residue, and the mixture was extracted with three portions of diethyl ether (3×15 mL). The organic layers were collected, washed successively with a saturated aqueous solution of $NaHCO_3$ (40 mL), brine (40 mL), and H_2O (40 mL), and dried with anhydrous Na_2SO_4 over night. After evaporation of the solvent, the crude reaction mixture was subjected to column chromatography using silica gel 60 (15 g, particle size 0.063–20 mm, Fluka). The elution was monitored by TLC (silica gel 60 F_{254}, layer thickness 2 mm, Merck). The first band was diphenyl diselenide (only traces), and the following ones were phenylselenated products.

3.1.1. DL-*trans*-2-Acetoxy-3-phenylselenyltetrahydropyran (2). Chromatography with toluene–ethyl acetate (9:1) gave **2** (81 mg, 27% based on the starting PhSeSePh) as a colorless liquid: R_f 0.59; IR (KBr): 3058, 2948, 2883, 2852, 2373, 1750, 1686, 1655, 1638, 1578, 1561, 1545, 1536, 1309, 1478, 1449, 1437, 1372, 1325, 1302, 1279, 1235, 1221, 1167, 1111, 1075, 1040, 1013, 992, 940, 901, 870, 830, 741, 693, 671, 623, 602, 523, 471, 449 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.65–2.15 (m, 4H, H-4, and H-5), 2.10 (s, 3H, $COCH_3$), 3.31 (m, 1H, H-3), 3.66 (m, 1H, H-6) 3.80 (m, 1H, H-6), 6.16 (d, J 3.1 Hz, 1H, H-2); ^{13}C NMR ($CDCl_3$): δ 21.2, 26.7, 26.9, 43.9, 61.3, 92.6, 128.2, 128.9, 129.4, 135.0, 169.9; HR-MS (FAB): m/z 300.0260, $C_{13}H_{16}O_3Se$ requires 300.0259.

3.1.2. β-D-2-Phenylselenyl-1,3,4,6-tetra-*O*-acetylglucose (3). Chromatography with toluene–ethyl acetate (7:3) gave **3** (254 mg, 52.5% based on the starting substrate **1b**) as colorless crystals: R_f 0.44; mp 100.0–101.5 °C; $[\alpha]_D^{20}$ +60.55 ($CHCl_3$, c 2.626 mg/mL); IR (KBr): 3051, 2973, 2941, 2884, 1751, 1577, 1476, 1438, 1377, 1219, 1102, 1049, 1037, 957, 922, 900, 840, 747, 696, 639, 602, 543, 486, 458, 418 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.99 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 3.29 (dd, J 9.6, J 11.1 Hz, 1H, H-2), 3.67–3.74 (m, 1H, H-5), 4.03 (dd, J 2.1, J 12.5 Hz, 1H, H-6), 4.31 (dd, J 4.5, J 12.5 Hz, 1H, H-6), 4.99–5.17 (m, 2H, H-3, and H-4), 5.70 (d, J 9.6 Hz, 1H, H-1), 7.27–7.34 (m, 3H, ArH), 7.54–7.59 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 20.2, 20.3, 20.7, 46.3, 61.2, 68.7, 71.8, 71.9, 93.2, 126.1, 128.3, 129.0, 135.3, 168.3, 169.3, 169.5, 170.2; HR-MS (FAB): m/z 488.0574, $C_{20}H_{24}O_9Se$ requires 488.0580.

3.1.3. α-D-2-Phenylselenyl-1,3,4,6-tetra-*O*-acetylmannose (4). Chromatography with toluene–ethyl acetate (7:3) gave **4** (170 mg, 34.8% based on the starting substrate **1b**) as colorless crystals: R_f 0.31; mp 107.5–108 °C; $[\alpha]_D^{20}$ +47.25 ($CHCl_3$, c 2.730 mg/mL); IR (KBr): 3049, 2994, 2968, 2939, 1744, 1578, 1478, 1460, 1438, 1371, 1231, 1218, 1173, 1132, 1088, 1050, 1012, 970, 931, 793, 744, 691, 646, 607, 565, 545, 515, 465, 435, 409 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.75, (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 2.13 (s, 3H, $COCH_3$), 3.89 (dd, J 1.7, J 4.4 Hz, H-2), 4.19 (m, 3H, H-4, H-5, and H-6), 5.33–5.54 (m, 2H, H-3, and H-6),

6.42 (d, J 1.7 Hz, 1H, H-1), 7.27–7.32 (m, 3H, ArH), 7.58–7.62 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 20.1, 20.4, 20.5, 20.7, 46.4, 61.9, 66.3, 70.2, 70.8, 93.9, 128.0, 128.2, 129.1, 134.4, 168.3, 169.2, 170.0, 170.5; HR-MS (FAB): m/z 488.0579, $C_{20}H_{24}O_9Se$ requires 488.0580.

3.1.4. Crystal structure analysis of β-D-2-phenylselenyl-1,3,4,6-tetra-*O*-acetylglucose (3). Orthorhombic crystals were grown at room temperature by slow evaporation of a $CHCl_3$ solution. A crystal of $0.35\times0.21\times0.12$ mm dimension was analyzed. $C_{20}H_{24}O_9Se$, $M = 487.35$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 7.8739(2)$ Å, $b = 9.1910(3)$ Å, $c = 30.7223(8)$ Å, $V = 2223.34(11)$ Å^3, $Z = 4$, $\rho_c = 1.456$ g/cm^3, $\mu = 1.736$ mm^{-1}, $T = 233$ K, 9897 reflections collected, 3282 independent reflections ($R_{int} = 0.043$), 2870 reflections with $I > 2\sigma(I)$, 276 parameters refined, Flack parameter $x = -0.003(9)$; $R_1 = 0.0306$, w$R_2 = 0.0617$ ($I > 2\sigma(I)$); $R_1 = 0.0408$, w$R_2 = 0.0647$ (all data).

3.1.5. Crystal structure analysis of α-D-2-phenylselenyl-1,3,4,6-tetra-*O*-acetylmannose (4). Orthorhombic crystals were grown at room temperature by slow evaporation of a $CHCl_3$ solution. A crystal of $0.4\times0.18\times0.13$ mm dimension was analyzed. $C_{20}H_{24}O_9Se$, $M = 487.35$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 7.8223(2)$ Å, $b = 14.6982(4)$ Å, $c = 19.1655(5)$ Å, $V = 2203.53(10)$ Å^3, $Z = 4$, $\rho_c = 1.469$ g/cm^3, $\mu = 1.751$ mm^{-1}, $T = 233$ K, 11,172 reflections collected, 3071 independent reflections ($R_{int} = 0.034$), 2824 reflections with $I > 2\sigma(I)$, 276 parameters refined, Flack parameter $x = 0.002(8)$; $R_1 = 0.0248$, w$R_2 = 0.0559$ ($I > 2\sigma(I)$); $R_1 = 0.0300$, w$R_2 = 0.0577$ (all data).

The absolute structures of both compounds were determined by the method described by Flack.[28] Crystallographic data for the structures of **3** and **4** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 198394 and 198395, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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