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Note

Synthesis of phenyl 2-azido-2-deoxy-1-selenoglycosides from disaccharidic glycals

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Phenyl selenoglycosides have been recognized as versatile glycosyl donors for the construction of glycosidic bonds [1]. In search of new donors of this kind, we have recently applied to glycals the azidophenylselenation of alkenes developed by Tingoli et al. [2]. Thus, reaction of a number of monosaccharidic glycals with (diacetoxyiodo)benzene, sodium azide, and diphenyl selenide regiospecifically produced phenyl 2-azido-2-deoxy-1-selenoglycosides in high yields and with a high degree of stereoselectivity [3]. These new azido derivatives should be valuable as synthons in 2-amino-2-deoxy-glycoside synthesis. We have now extended this chemistry to disaccharides, namely, the peracetylated glycals of cellobiose [4] (**1a**), lactose [5] (**1b**), and maltose [6] (**1c**) in order to prepare compounds potentially useful for block synthesis of oligosaccharides containing 2-amino-2-deoxy sugars.

The reactions were performed using the conditions previously described [3]. In all cases, an inseparable mixture of the corresponding phenyl 2-azido-2-deoxy-1-selenodisaccharide anomers **2** and **3** was obtained. These mixtures gave satisfactory microanalyses for $C_{30}H_{37}N_3O_{14}Se \cdot H_2O$.The major product in each case was the α anomer **2a–c** (δ H-1 at 5.72 ± 0.2, d, $J_{1,2}$ 1.5 ± 0.2 Hz; δ C-1 at 82.0 ± 0.3), and the minor product was the β anomer **3a–c** (δ H-1 at 5.55 ± 0.07, d, $J_{1,2}$ 3.1 ± 0.5 Hz; δ C-1 at 89.9 ± 0.1). The proportions of anomers in the mixtures were determined by ^{1}H NMR as $\approx$ 2:1 for **2a/3a**, $\approx$ 13:1 for **2b/3b**, and $\approx$ 6:1 for

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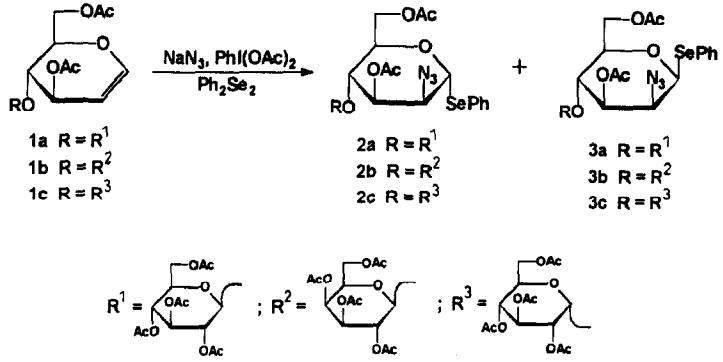

2c/3c. In all cases, the reactions were slower and afforded lower yields (22% for **2a/3a**, 45% for **2b/3b**, and 33% for **2c/3c**) as compared to monosaccharidic glycals [11], but the same regiospecificity and similar stereoselectivity were observed. Research directed toward the use of these compounds as glycosyl donors is in progress in our laboratory.

1. Experimental

General procedure.—A mixture of glycal (1 mmol), diphenyl diselenide (2.3 mmol), sodium azide (5.5 mmol), and (diacetoxyiodo)benzene (2.6 mmol) in dry CH_2Cl_2 (50mL/mmol) was stirred under Ar at room temperature. The reaction time was 21 days for **1a** and 8 days for **1b–c**. The mixture was poured into satd aq $NaHCO_3$, and extracted with CH_2Cl_2. The organic layer was washed with water, dried, and evaporated. The crude product was purified by column chromatography using 4:1 ether–hexane as eluent.

Phenyl 3,6-di-O-acetyl-2-azido-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-1-seleno-α,β-D-mannopyranoside (**2a** *and* **3a**).—IR: υ^{nujol} 2110 (N_3), 1744 (CO) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.59 and 7.30 (2 m, 5 H, Ph), 5.72 (d, *J* 1.7 Hz, H-1 of **2a**), 5.54 (t, *J* 9.9 Hz, H-3′ of **3a**), 5.47 (d, *J* 3.6 Hz, H-1 of **3a**), 5.32 (dd, *J* 9.1 and 3.7 Hz, H-3 of **2a**), 5.17 (t, *J* 9.4 Hz, H-3′ of **2a**), 5.09 (t, *J* 9.8 Hz, H-4′ of **3a**), 5.08 (t, *J* 9.7 Hz, H-4′ of **2a**), 4.96 (dd, *J* 9.4 and 7.9 Hz, H-2′ of **2a**), 4.91 (dd, *J* 10.2 and 3.6 Hz, H-3 of **3a**), 4.74 (d, *J* 8.0 Hz, H-1′ of **3a**), 4.57 (d, *J* 7.9 Hz, H-1′ of **2a**), 4.40 (dd, *J* 11.9 and 1.9 Hz, H-6 of **2a**), 4.42–3.97 (several m, H-4–6 of **2a** and **3a** and H-2 of **3a**), 4.29 (dd, *J* 3.7 and 1.9 Hz, H-2 of **2a**), 3.78–3.75 (m, H-5′ of **3a**), 3.72 (ddd, *J* 9.9, 4.9, and 2.2 Hz, H-5′ of **2a**), and 2.13–2.00 (10 s, AcO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 100.8 (C-1′ of **2a** and **3a**), 90.0 (C-1 of **3a**), 82.3 (C-1 of **2a**), 74.3, 72.7, 71.7, 71.4, 71.1, 67.8, 63.4, 61.9, 61.7, (C-2–6,2′–6′) of **2a**), 71.9, 70.8, 69.6, 68.3, 67.1, and 61.7 (signals of minor intensity corresponding to **3a**).

Phenyl 3,6-di-O-acetyl-2-azido-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-1-seleno-α,β-D-mannopyranoside (**2b** *and* **3b**).—IR: υ^{nujol} 2109 (N_3), 1750 (CO) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.52 and 7.32 (2 m, 5 H, Ph), 5.71 (d, *J* 1.5 Hz, H-1 of **2b**), 5.55 (d, *J* 3.6 Hz, H-1 of **3b**), 5.37 (d, *J* 3.6 Hz, H-4′ of **2b**), 5.32 (dd, *J* 9.0 and 3.8 Hz, H-3 of **2b**), 5.16 (dd, *J* 10.2 and 8.1 Hz, H-2′ of **2b**), 4.99 (dd, *J* 10.2 and 3.7 Hz, H-3′ of **2b**), 4.62 (d, *J* 7.5 Hz, H-1′ of **3b**), 4.55 (d, *J* 8.0 Hz, H-1′ of **2b**), 4.40–3.90 (several m, H-4–6,5′,6′ of **2b** and **3b** and H-2 of **3b**), 4.30 (bd, *J* 3.5 Hz, H-2 of **2b**), and 2.16–1.97 (10 s, AcO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 101.2 (C-1′ of **2b** and **3b**), 89.8 (C-1 of **3b**), 82.2 (C-1 of **2b**), 74.1, 71.6, 71.4, 70.8, 70.5, 68.9, 66.5, 63.1, 62.0, 60.9 (C-2–6,2′–6′ of **2b**), 71.3, 70.7, 66.6, and 61.0 (signals of minor intensity corresponding to **3b**).

Phenyl 3,6-di-O-acetyl-2-azido-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-1-seleno-α,β-D-mannopyranoside (**2c** and **3c**).—IR: υ^{KBr} 2109 (N_3), 1747 (CO) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.60 and 7.32 (2 m, 5 H, Ph), 5.74 (d, *J* 1.7 Hz, H-1 of **2c**), 5.62 (d, *J* 2.6 Hz, H-1 of **3c**), 5.55 (d, *J* 4.1 Hz, H-1′ of **2c**), 5.54 (d, *J* 5.0 Hz, H-1′ of **3c**), 5.41 (dd, *J* 10.4 and 9.6 Hz, H-3′ of **2c**), 5.38 (dd, *J* 10.3 and 9.6 Hz, H-3′ of **3c**), 5.23 (dd, *J* 9.0 and 3.8 Hz, H-3 of **2c**), 5.20 (dd, *J* 4.3 and 7.8 Hz, H-3 of **3c**), 5.08 (t, $J \approx 9.8$ Hz, H-4′ of **2c**), 5.07 (t, $J \approx 10.0$ Hz, H-4′ of **3a**), 4.90 (dd, *J* 10.5 and 4.1 Hz, H-2′ of **2c**), 4.89 (m, H-2′ of **3c**), 4.50–3.98 (several m, H-4–6 of **2c** and **3c** and H-2 of **3c**), 4.29 (dd, *J* 3.7 and 1.7 Hz, H-2 of **2c**), and 2.18–1.96 (10 s, AcO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 95.7 (C-1′ of **2c** and **3c**), 89.8 (C-1 of **3c**), 81.8 (C-1 of **2c**), 74.3, 71.2, 70.4, 70.1, 69.3, 68.4, 67.9, 62.7, and 61.3, (C-2–6,2′–6′ of **2c**), 73.5, 71.7, 70.8, 69.8, 69.4, and 68.3 (signals of minor intensity corresponding to **3c**).

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