Synthesis of Phenyl 2-Azido-2-deoxy-1-selenoglycosides from Glycals

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2-Amino-2-deoxyglycopyranosides are important compounds that are widely distributed in living organisms where they constitute building blocks of glycoconjugates (glycolipids, lipopolysaccarides, glycopeptides, etc.).[1-8] They are also present in glycosaminoglycans (heparin, heparan sulfate, dermatan sulfate, chondroitin sulfate, etc.),[9] in human milk,[10] in blood group substances,[11,12] and on cell surfaces, where they play an important role as receptor ligands for protein molecules such as enzymes,[13] antibodies,[14] and lectins,[15] and participate in antibody–antigen interactions.[4,16] The importance of these compounds has led to intense activity in the development of chemical methods for oligosaccharide synthesis with a special emphasis on the finding of simple, efficient, and selective procedures. There are in the literature many excellent reviews dealing with oligosaccharide synthesis, in general,[1,2,7,11,17] and in particular with the synthesis of oligosaccharides of 2-amino-2-deoxysugars.[18]

Different glycosyl donors have been applied in the construction of glycosidic bonds: glycosyl halides[7a,19] (used extensively in the so-called Koenigs–Knorr glycosylation and in the related procedures), glycosyl imidates,[1,17a] pent-4-enyl glycosides,[20] vinyl glycosides,[21] thioglycosides,[22] and recently, selenoglycosides.[23,24] Pinto[23] and van Boom[24] have introduced phenyl selenoglycosides as new glycosyl donors in glycosylation reactions. These phenyl selenoglycosides were easily prepared by treatment of peracetylated sugars with phenylselenol and $BF_3{\cdot}OEt_2$. The versatile glycosylation properties of these glycosides depend on the promoter and on the protective groups which allow the application of the "armed-disarmed" methodology[20,22c-e] and the chemoselective activation of one of the partners in the glycosylation of either two selenoglycosides or a selenoglycoside and a thioglycoside.

The 2-azido-2-deoxy derivatives of mono- and disaccharides are frequent intermediates in the synthesis of 2-amino-2-deoxy oligosaccharides. The azido function was shown to be a nonparticipating group that did not cause steric hindrance, and therefore, it can be used as the amino protective group of glycosyl donors in 1,2-cis-glycosylation reactions. Furthermore, reduction of the azido group can afford the free amino group. These azido derivatives have been prepared by azidonitration of glycals,[25] by addition of halogenoazides to glycals,[26] from 1,6-anhydro sugars either by opening of the corresponding 2,3-epoxide derivatives[27] or by substitution of 2-sulfonate[28] derivatives, and by diazotransfer of 2-amino-2-deoxyaldoses.[29] Of these methods, azidonitration is most widely used for the preparation of 2-azido analogues. It occurs by addition of ceric ammonium nitrate and sodium azide to protected glycals, regiospecifically affording epimeric mixtures of 2-azido-2-deoxy-1-*O*-nitropyranoses. The stereochemistry

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Scheme I

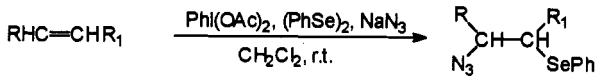


Table I. Azidophenylselenenylation of Glycals 1–4

glycal	time reaction (rt) (d)	products	yield[a] (%)
1a	2	**5a + 5b**[b]	74
1b	4	**5c + 5d**[b]	48
2	2	**6a + 6b**[c]	66
3	8	**8**	87
4	1	**9**	26
		10	47

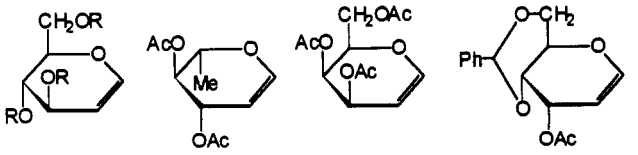
[a] Calculated on isolated products. [b] ~1:1 diastereomeric mixture. [c] ~1:2 diastereomeric mixture.

of the addition favors the formation of an equatorial 2-azido derivative rather than an axial 2-epimer, although this depends on the configuration of the glycal. Thus, for the *lyxo*-glycals, the equatorial product is highly favored, leading to mixtures of 2-azido-2-deoxygalactose nitrates;[25a] conversely for the *arabino*-glycals, mixtures of 2-azido-2-deoxy-glucose and -mannose derivatives result.[7c,18,25c] When this procedure is employed in a glycosylation strategy, an additional transformation of the 2-azido-2-deoxy-1-*O*-nitropyranose derivative into an adequate glycosyl donor is required. Conversions to halides,[7a] trichloroacetimidates,[30] and *S*-xanthates[31] have been efficiently applied in the synthesis of oligosaccharides.

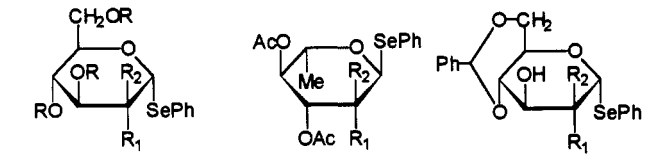
However, it would be desirable to have a method that permits a one-step preparation of 2-azido-2-deoxy glycosides bearing a leaving group with good glycosylating properties. Along these lines, the procedure for azido phenylselenylation of alkenes developed by Tingoli et al.[32] seemed promising. This involves a radical reaction that occurs when alkenes are treated with (diacetoxyiodo)-benzene, sodium azide, and diphenyl diselenide in dichloromethane at room temperature and that yields β-azido selenides with complete anti-Markovnikov regioselectivity (see Scheme I).

These results encouraged us to apply the same reaction to glycals because, if 2-azido-2-deoxy-1-selenoglycosides were obtained, it would be possible to combine the versatility of selenoglycoside glycosylations with the nonparticipating character of the azido group. We have examined as substrates 3,4,6-tri-*O*-acetyl-D-glucal (**1a**), 3,4,6-tri-*O*-benzyl-D-glucal (**1b**), 3,4-di-*O*-acetyl-L-rhamnal (**2**), 3,4,6-tri-*O*-acetyl-D-galactal (**3**), and 3-*O*-acetyl-4,6-*O*-benzylidene-D-allal (**4**). In all cases, the radical addition to these glycals proceeded with the expected regioselectivity and the corresponding 2-azido-2-deoxy-1-selenoglycosides were obtained.

For **1a** and **2**, the reaction with (diacetoxyiodo)benzene, sodium azide, and diphenyl diselenide in dichloromethane yielded a ≈1:1 mixture (determined by ^{1}H-NMR) of phenyl 2-azido-2-deoxy-1-selenoglycosides having *gluco* and *manno* configurations (**5a + 5b** and **6a + 6b**, respectively) (see Table I). These product mixtures could not be resolved by column chromatography. However, in the case of **5a + 5b**, Zemplén deacetylation followed by benzylidenation with α,α-dimethoxytoluene allowed the isolation of the



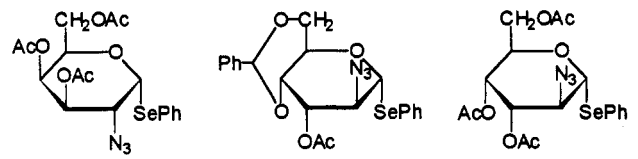
1a R = Ac **2** **3** **4**
1b R = Bn



5a R = Ac, R_1 = N_3, R_2 = H
5b R = Ac, R_1 = H, R_2 = N_3
5c R = Bn, R_1 = N_3, R_2 = H
5d R = Bn, R_1 = H, R_2 = N_3

6a R_1 = H, R_2 = N_3
6b R_1 = N_3, R_2 = H

7a R_1 = N_3, R_2 = H
7b R_1 = H, R_2 = N_3



8 **9** **10**

benzylidene derivatives **7a** and **7b** by column chromatography. Galactal triacetate **3** led only to phenyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-1-seleno-α-D-galactopyranoside **8**, in high yield (see Table I). When this reaction was applied to glycal **4**, which has a benzylidene group, compound **9** was isolated together with a polar product that exhibited a ^{1}H-NMR spectrum indicating no C_6H_5CH proton but with signals for a C_6H_5COO function. When this product was deacylated and treated with acetic anhydride–pyridine, the 3,4,6-tri-*O*-acetyl derivative **10** was obtained. This product was also isolated when **9** was treated with trifluoroacetic acid followed by conventional acetylation. These results suggest that under the reaction conditions, compound **10** arises from a radical opening of the benzylidene group of compound **9** in a manner similar to the Hanessian–Hullar reaction.[33]

In the addition of halogenoazides to glycals it has been reported[26] that higher yields resulted when *O*-benzyl derivatives were used instead of the corresponding *O*-acetyl derivatives. Given this, we studied the reaction with glucal **1b**. The expected phenyl 2-azido-2-deoxyselenoglycosides **5a** and **5d** were obtained with similar stereoselectivity; however, the reaction time proved to be longer and the yield lower (see Table I).

The above results indicate that the azidophenylselenylation of the selected glycals is a regiospecific process. The reaction was shown to be stereoselective for the D-glucal and D-rhamnal derivatives **1a**, **1b**, and **2** and stererospecific for the D-galactal and D-allal derivatives **3** and **4**, respectively.

In summary, the glycal azidophenylselenylation is a procedure that allows the one-pot preparation of phenyl 2-azido-2-deoxy-selenoglycosides, regiospecifically and in high yield. Studies directed toward the application of these compounds as glycosyl donors are in progress in our laboratory.

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Experimental Section

General Details. 3,4,6-Tri-*O*-acetyl-D-galactal[34] and 3-*O*-acetyl-4,6-*O*-benzylidene-D-allal[35] were prepared according to the published procedure. All other reagents were purchased from Aldrich Chemical Co. Thin-layer chromatography was performed on precoated plates of silica gel 60 F_{254} (Merck) with detection by UV light, and the spots were visualized with a spray containing 5% sulfuric acid in ethanol followed by heating. Organic solutions were dried over Na_2SO_4. Column chromatography was performed on silica gel 60 (270–230 mesh, Merck). Optical rotations were measured at room temperature in $CHCl_3$ (c = 1). Infrared data were obtained with a Perkin-Elmer IR 983 spectrometer; only bands of spectral structural significance are listed. ^1H and ^{13}C NMR spectra of all products compounds were recorded in $CDCl_3$ at 300 MHz (Bruker AM300 instrument). Mass spectra data (m/z) were obtained by the chemical ionization mode using methane as the ionizing gas with a Hewlett-Packard 5988A instrument, and molecular weights were obtained with a Kratos MS-80-RFA instrument.

Phenyl 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-1-seleno-α-D-gluco- (5a) and α-D-mannopyranosides (5b). A mixture of 3,4,6-tri-*O*-acetyl-D-glucal (**1a**, 544 mg), diphenyl diselenide (762 mg), sodium azide (312 mg), and (diacetoxyiodo)benzene (919 mg) in methylene chloride (20 mL) was stirred at room temperature until TLC showed complete disappearance of the starting material (48 h). The mixture was poured on aqueous $NaHCO_3$ saturated solution, and extracted with methylene chloride. The organic layer was washed with water, dried, and evaporated. The crude product was purified by column chromatography using ethyl acetate–hexane (1:5) as eluant to get an inseparable mixture of the title compounds **5a** and **5b** (≈1:1 as shown the ^1H NMR) as a syrup (700 mg, 74%): IR (neat) 2105 (N_3), 1740 (CO) cm^{-1}; ^1H NMR δ 7.55 and 7.25 (2 m, 5H, Ph), 5.90 (d, ≈0.5 H, J = 5.5 Hz, H-1 of **5a**), 5.77 (d, ≈0.5 H, J = 1.5 Hz, H-1 of **5b**), 5.34 (t, ≈0.5 H, J ≈ 10 Hz, H-3 of **5a**), 5.28 (dd, ≈ 0.5 H, J ≈ 10 and 3.4 Hz, H-3 of **5b**), 5.25 and 5.01 (2t, 1H, J ≈ 10.2 Hz, H-4), 4.48 and 4.38 (2m, 1H, H-5), 4.33 (dd, ≈0.5 H, J = 3.4 and 1.5 Hz, H-2 of **5b**), 4.26 (dd, 1H, J = 12.3 and 5.1 Hz, H-6 of **5a** and **5b**) 4.02 (dd, ≈0.5 H, J = 10.2 and 5.5 Hz, H-2 of **5a**), 4.05 (dd, ≈0.5 H, J = 12.4 and 2.3 Hz, H-6′), 3.93 (dd, ≈0.5 H, J = 12.4 and 2.3 Hz, H-6′), 2.08, 2.06, 2.04, 2.03, 2.02, and 1.98 (6s, 9H, 3 OAc); ^{13}C NMR δ 170.5, 170.4, 169.9, 169.8, 169.7, 169.4 (6 CO), 134.8–127.4 (C_6H_5), 83.7, 82.5 (C-1), 72.8, 71.5, 71.2, 70.1, 68.4, 65.9 (C-3, 4, 5), 63.3, 62.2 (C-2), 62.0, 61.8 (C-6), 20.6 (3 *Me*CO).

Phenyl 2-Azido-4,6-*O*-benzylidene-2-deoxy-1-seleno-α-D-gluco (7a) and -α-D-mannopyranosides (7b). The mixture of **5a** + **5b** (549 mg) was deacetylated in methanolic 0.06 M $NaOCH_3$ solution (10 mL) during 10 h at 4 °C. After deonization by cation exchange the solution was evaporated. The residue was dissolved in dry acetonitrile (20 mL) and treated with α,α-dimethoxytoluene (5 mL) at rt and *p*-toluenesulfonic acid (20 mg) for 2 h. After concentration at 35 °C to half of the volume to complete the acetalation the reaction mixture was carefully neutralized with triethylamine. The solution was evaporated and the product chromatographed on a column with ether:hexane = 4:1 as eluent. Eluted first was **7b** (205 mg) isolated as a syrup: $[\alpha]_D$ +114°; IR (neat) 3474 (OH), 2106 (N_3); ^1H NMR δ 7.60–7.20 (m, 10H, 2 C_6H_5), 5.74 (d, 1H, J = 0.8 Hz, H-1), 5.54 (s, 1H, PhC*H*), 4.23 (m, 1H, H-5), 4.22–4.14 (m, 2H, H-3,6), 4.12 (dd, 1H, J = 3.9 and 0.8 Hz, H-2), 3.95 (t, 1H, $J_{3,4} \approx J_{4,5} \approx$ 9.1 Hz, H-4), 3.80 (t, 1H, $J_{5,6} + J_{6,6'}$ = 21 Hz, H-6′) and 3.48 (bs, 1H, OH); ^{13}C NMR δ 136.9–126.4 (2 C_6H_5), 102.2 (PhC*H*), 83.8 (C-1), 69.2, 66.2, 65.9 (C-2,3,4,5), and 68.0 (C-6); MS (calcd mass for $C_{19}H_{19}N_3O_7Se$ 433.0540) obsd m/e 433.054.

Eluted second was **7a** (200 mg) isolated as a solid: mp 112–114 °C; $[\alpha]_D$ +233°; IR (Nujol) 3402 (OH), 2100 (N_3); ^1H NMR δ 7.63–7.25 (m, 10H, 2 C_6H_5), 5.84 (d, 1H, J = 5.4 Hz, H-1), 5.54 (s, 1H, PhC*H*), 4.28 (dt, 1H, $J_{4,5} \approx J_{5,6} \approx$ 9.5 Hz, $J_{5,6'}$ = 5 Hz, H-5), 4.15 (dd, 1H, J = 10.3 and 5.0 Hz, H-6), 3.99 (t, 1H, $J_{2,3} \approx J_{3,4}$ ≈ 9.5 Hz, H-3), 3.86 (dd, 1H, J = 9.7 and 5.4 Hz, H-2), 3.72 (t, 1H, $J_{5,6'} \approx J_{6,6'} \approx$ 10.3, H-6′), 3.57 (t, 1H, $J_{3,4} \approx J_{4,5} \approx$ 9.5 Hz, H-4) and 3.0 (bs, 1H, OH); ^{13}C NMR δ 136.8–126.4 (2 C_6H_5), 102.2 (PhC*H*), 84.9 (C-1), 81.3, 71.7, 64.9, 64.6 (C-2,3,4,5), and 68.4 (C-6); MS m/e (rel intensity) 434 (M^+, 90), 432 (M^+, 49), 406 (100), 356 (25), 300 (21), 248 (46). Anal. Calcd for $C_{19}H_{19}N_3O_4Se$: C, 58.82; H, 4.43; N, 9.73. Found: C, 52.57; H, 4.30; N, 9.68.

Phenyl 3,4-Di-*O*-acetyl-2-azido-2,6-dideoxy-1-seleno-α-L-gluco- (6a) and -α-L-mannopyranoside (6b). A mixture of 3,4-di-*O*-acetyl-L-rhamnal (**2**, 727 mg), diphenyl diselenide (1,3 g), sodium azide (530 mg), and (diacetoxyiodo)benzene (1.6 g) in methylene chloride (55 mL) was stirred at room temperature for 2 days. The reaction mixture was worked up as indicated for compounds **5a** + **5b**. The crude product was purified by column chromatography using ether:hexane = 1:3 → 1:1 as eluant yielding 890 mg (66%) of **6a** + **6b** (≈1:2 as shown the ^1H NMR) as a syrup: IR (neat) 2108 (N_3), 1750 (CO) cm^{-1}; ^1H NMR δ 7.55–7.25 (m, 5 H, 2 C_6H_5), 5.83 (d, ≈0.33 H, J = 5.4 Hz, H-1 of **6a**), 5.68 (d, ≈0.66 H, J = 1.4 Hz, H-1 of **6b**), 5.22 (t, ≈0.33 H, J ≈ 9.5 Hz, H-3 of **6a**), 5.13 (t, ≈0.66 H, J ≈ 9.6 Hz, H-4 of **6b**), 4.78 (t, ≈0.33 H, J ≈ 9.5 Hz, H-4 of **6a**), 4.34 (dd, ≈0.66 H, J = 3.7 and 1.4 Hz, H-2 of **6b**), 4.30 (m, ≈ 0.33 H, H-5 of **6a**), 4.19 (m, ≈0.66 H, H-5 of **6b**), 4.00 (dd, ≈0.33 H, J = 9.3 and 5.4 Hz, H-2 of **6a**), 2.08, 2.07, 2.06, 2.04 (4s, 6 H, 2 AcO), 1.21 (d, ≈2 H, J = 6.2 Hz, H-6 of **6b**), and 1.13 (d, ≈1 H, J = 6.2 Hz, H-6 of **6a**); ^{13}C NMR δ 170.0, 169.7 (2 CO), 134.6–128.1 (C_6H_5), 83.9, 82.6, (C-1), 73.6, 72.9, 71.5, 70.8, 69.7, 68.4 (C-3,4,5), 63.8, 62.7 (C-2), 20.7, 20.6 (2 *Me*CO), and 17.2, 17.0 (C-6); MS m/e (rel intensity) 413 (M^+ + 1, 2), 371 (17), 256 (100); MS (calcd mass for $C_{16}H_{19}N_3O_5Se$ 413.0489) obsd m/e 433.0471.

Phenyl 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-1-selenogalactopyranoside (8). A mixture of 3,4,6-tri-*O*-acetyl-D-galactal[34] (**3**, 544 mg), diphenyl diselenide (1.1 g), sodium azide (450 mg), and (diacetoxyiodo)benzene (1.4 g) in methylene chloride (50 mL) was stirred at rt for 8 days. The reaction mixture was worked up as indicated for compounds **5a** + **5b**. The crude product was purified by column chromatography using ether:hexane = 1:1 as eluant yielding 817 mg (87%) of **8** isolated as a solid mp 122–124 °C; $[\alpha]_D$ +240°; IR (Nujol) 2113 (N_3), 1751 (CO) cm^{-1}; ^1H NMR δ 7.60–7.30 (m, 5 H, 2 C_6H_5), 6.00 (d, 1 H, J = 5.4 Hz, H-1), 5.46 (dd, 1 H, J = 3.2 and 1.3 Hz, H-4), 5.11 (dd, 1H, J = 10.8 and 3.2 Hz, H-3), 4.66 (dt, 1 H, J = 6.5 and 1.3 Hz, H-5), 4.25 (dd, 1 H, J = 10.8 and 5.4 Hz, H-2), 4.06 (dd, 1 H, J = 11.4 and 6.0 Hz, H-6), 4.00 (dd, 1 H, J = 11.4 and 7.0 Hz, H-6′), and 2.14, 2.05, 1.96 (3 s, 9 H, 3 AcO); ^{13}C NMR δ 170.4, 170.0, 169.8 (3 CO), 134.8–127.6 (C_6H_5), 84.2 (C-1), 71.2, 69.1, 67.3 (C-3,4,5), 61.6 (C-6), 58.8 (C-2), and 20.7 (2 *Me*CO); MS m/e (rel intensity) 471 (M+ + 1, 3), 314 (100). Anal. Calcd for $C_{18}H_{21}N_3O_7Se$: C, 45.96; H, 4.50; N, 8.93. Found: C, 46.03; H, 4.53; N, 9.18.

Phenyl 3-*O*-Acetyl-2-azido-4,6-benzylidene-2-deoxy-1-seleno-α-D-altropyranoside (9) and Phenyl 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-1-seleno-α-D-altropyranoside (10). A mixture of 3-*O*-acetyl-4,6-*O*-benzylidene-D-allal (**4**,[35] 276 mg), diphenyl diselenide (375 mg), sodium azide (312 mg), and (diacetoxyiodo)-benzene (900 mg) in methylene chloride (15 mL) was stirred at rt for 1 day. The reaction mixture was worked up as indicated for compounds **5a** + **5b**. The crude product was purified by column chromatography using ether:hexane = 1:1 as eluant. Eluted first was **9** (122 mg, 26%) as a syrup: $[\alpha]_D$ +134°; IR (neat) 2105 (N_3), 1750 (CO) cm^{-1}; ^1H NMR δ 7.68–7.35 (m, 10 H, 2 C_6H_5), 5.71 (s, 1 H, H-1), 5.63 (s, 1 H, PhC*H*), 5.32 (t, 1 H, J ≈ 3.0 Hz, H-3), 4.72 (dt, 1 H, J = 10 and 1.5 Hz, H-5), 4.40 (d, 1H, J = 3 Hz, H-2), 4.38 (dd, 1 H, J = 10.0 and 5.1 Hz, H-6), 4.09 (dd, 1 H, J = 9.8 and 3.0 Hz, H-4), 3.86 (t, 1 H, J ≈ 10.3 Hz, H-6′), and 2.26 (s, 3 H, AcO); ^{13}C NMR δ 169.6 (CO), 137.0–126.1 (2 C_6H_5), 102.1 (PhC*H*), 82.7 (C-1), 74.2, 67.6, 63.0, 62.1 (C-2,3,4,5), 68.7 (C-6), and 21.1 (MeCO); MS (calcd mass for $C_{21}H_{21}N_3O_6Se$ 475.0646) obsd m/e 475.0583.

Eluted second was a mixture of products (200 mg) which was deacetylated in methanolic 0.06 M $NaOCH_3$ (10 mL) during 3 h at rt. After deionization by cation exchange the solution was evaporated. The crude product was conventionally acetylated with Ac_2O–pyridine (2:2 mL). Conventional workup followed by purification in a column chromatography using ether:hexane = 1:2 as eluant gave **10** (220 mg, 47% with respect to **4**), isolated as a syrup: $[\alpha]_D$ +122°; IR (neat) 2108 (N_3), 1750 (CO) cm^{-1}; ^1H NMR δ 7.62–7.22 (m, 5 H, C_6H_5), 5.69 (bs 1 H, H-1), 5.30 (t, 1

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H, J = 3.6 Hz, H-3), 5.19 (dd, 1 H, J = 9.8 and 3.3 Hz, H-4), 4.68 (ddd, 1 H, J = 9.8, 5.2 and 2.4 Hz, H-5), 4.34 (dd, 1 H, J = 12.2 and 5.2 Hz, H-6), 4.19 (dd, 1 H, J = 12.2 and 2.4 Hz, H-6'), 4.13 (dd, 1 H, J = 4.2 and 1.6 Hz, H-2), and 2.20, 2.07, 2.02 (3 s, 9 H, 3 AcO); ^{13}C NMR δ 170.7, 169.3, 169.2 (3 CO), 133.6–128.2 (C_6H_5), 82.5 (C-1), 67.7, 64.8, 62.5 (C-2,3,4,5), 62.3 (C-6), and 20.9, 20.7, 20.6 (3 *Me*CO); MS *m/e* (rel intensity) 472, 470 (M^+ + 1, 5 and 3), 444, 442 (3 and 1), 429, 427 (25 and 12), 314 (100).

Phenyl 2-Azido-2-deoxy-3,4,6-tri-*O*-benzyl-1-seleno-α-D-gluco- (5c) and -α-D-mannopyranosides (5d). A mixture of 3,4,6-tri-*O*-benzyl-D-glucal[26] (1b, 544 mg), diphenyl diselenide (500 mg), sodium azide (200 mg), and (diacetoxyiodo)benzene (600 mg) in methylene chloride (50 mL) was stirred at rt for 4 days. The reaction mixture was worked up as indicated for compounds **5a + 5b**. The crude product was purified by column chromatography using ether:hexane (1:10) as eluant. Eluted first was **5d** (206 mg, 25%) as a syrup: $[\alpha]_D$ +81°; IR (neat) 2104 (N_3) cm^{-1}; ^{1}H NMR δ 7.55–7.15 (m, 20 H, 4 C_6H_5), 5.78 (d, 1 H, J = 1.4 Hz, H-1), 4.76 (bs, 2 H, PhCH_2), 4.73 (AB system, 2 H, J = 10.7, $\delta\nu$ = 100 Hz, PhCH_2), 4.57 (AB system, 2 H, J = 12.0 Hz, $\delta\nu$ 50 Hz, PhCH_2), 4.18 (dd, 1 H, J = 3.0 and 1.4 Hz, H-2), 4.05–3.90 (m, 3 H, H-3,4,5), 3.81 (dd, 1 H, J = 10.9 and 4.5 Hz, H-6) and 3.71 (dd, 1 H, J = 10.9 and 1.8 Hz, H-6'); ^{13}C NMR δ 138.2–127.6 (4 C_6H_5), 83.8 (C-1), 80.3, 74.6, 74.5 (C-3,4,5), 75.4, 73.4, 72.8 (3 PhCH_2), 68.6 (C-6), and 63.7 (C-2).

Eluted second was **5c** (180 mg, 22%) as a syrup: $[\alpha]_D$ +101°; IR (neat) 2108 (N_3) cm^{-1}; ^{1}H NMR δ 7.65–7.12 (m, 20 H, 4 C_6H_5), 5.92, (d, 1 H, J = 5.2 Hz, H-1), 4.90–4.40 (several m, 6 H, 3 PhCH_2), 4.28 (m, 1 H, H-5), 3.95–3.75 (m, 4 H, H-2,3,4,6) and 3.58 (dd, 1 H, J = 10.08 and 2.0 Hz, H-6'). ^{13}C NMR δ 137.9–127.7 (4 C_6H_5), 85.3 (C-1), 82.8, 78.0, 73.5, (C-3,4,5), 75.8, 75.1, 73.8 (3 $PhCH_2$), 68.2 (C-6), and 64.8 (C-2).

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Supplementary Material Available: ^{1}H NMR and ^{13}C spectra for compounds **5a + 5b, 5d, 6a + 6b, 9,** and **10** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.