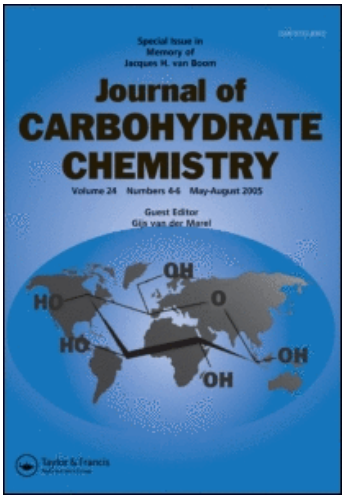

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CONVENIENT PREPARATION OF PERBENZYLATED 2-AZIDO AND 2-*N*-ACETYLAMINO-2-DEOXY-D-HEXONO-1,5-LACTONES BY OXIDATION OF THE CORRESPONDING LACTOLS

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ABSTRACT

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galacto, gluco and mannopyranoses (**1**, **2**, **3**) were oxidized with DMSO in the presence of acetic anhydride. From **1** and **2** the corresponding lactone derivatives were obtained in good yield (89-92%), whereas from **3**, glucono-1,5-lactone was obtained (92%) after complete epimerization at C-2. 2-*N*-Acetylamino-3,4,6-tri-*O*-benzyl-2-deoxy-D-galacto, gluco and mannopyranoses (**7**, **8**, **9**) were obtained from the corresponding 2-azido phenylselenoglycopyranosides (**13**, **14**, **15**) by reduction, *N*-acetylation and hydrolysis catalyzed by mercury trifluoroacetate. Oxidation of **7** and **8** by tetra-*n*-propylammonium tetra-oxoruthenate (VII) in the presence of 4-methylmorpholine-*N*-oxide afforded the corresponding lactones in good yield (90%) and high purity. Epimerization at C-2 occurred during oxidation of **9** and perbenzylated D-glucono-1,5-lactone (**11**) was obtained (90%).

INTRODUCTION

In the course of our research program devoted to the synthesis of 2-amino-2-deoxy-*C*-glycosides, perbenzylated 2-azido and 2-*N*-acetylamino-2-deoxy-D-hexono-1,5-lactones were needed. Several years ago, 2-*N*-acetylamino-3,4,6-tri-*O*-benzyl-2-

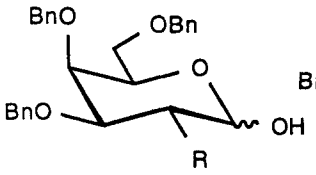
deoxy-D-glucono-1,5-lactone **11** was prepared by oxidation of the corresponding lactol **8**, with DMSO in the presence of acetic anhydride in 92% yield,[1] but the synthesis of the precursor **8** was long and difficult.[2] The same drawback was associated with the preparation of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-allono-1,5-lactone.[3] Therefore, other approaches to protected 2-azido-2-deoxy-D-hexono-1,5-lactones were recently examined including nucleophilic displacement by azide anion of 2-*O*-sulfonate lactones[4,5] and electrophilic azidation of 2-deoxy lactones.[6] In both cases limitations were encountered due to formation of an epimeric mixture at C-2,[4,5] or instability of the resulting 2-azido-2-deoxy-D-hexono-1,5-lactone under the reaction conditions.[6] Hence, the search for an alternative and more practical access to this class of compounds was undertaken and we report herein our results.

RESULTS AND DISCUSSION

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranose (**1**), 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose (**2**) and 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-mannopyranose (**3**) were readily prepared by azidophenylselenylation of perbenzylated D-galactal and D-glucal followed by hydrolysis.[7]

Since 4-methylmorpholine-*N*-oxide (NMO) in the presence of tetra-*n*-propylammonium perruthenate (TPAP) gave us good results for the oxidation of diversely protected glycopyranoses and glycofuranoses to lactones,[8] this system was first evaluated for the oxidation of azidolactols **1**, **2** and **3**. No azidolactone was formed under these conditions and slow decomposition of the starting material was observed.

Oxidation of **1** and **2** with DMSO in the presence of acetic anhydride proceeded smoothly and 2-azido lactones **4** and **5** were obtained in good yield (≈ 90%) and good purity. The structure of **4** was confirmed by NMR spectroscopy and comparison with literature data.[6] However, for lactone **5**, the values of coupling constants in $CDCl_3$ were too small for a $^4C_1$(D) conformation ($J_{2,3}$ = 2.90 Hz and $J_{3,4}$ = 1.60 Hz) and too large for a $^1C_4$(D) conformation ($J_{4,5}$ = 6.40 Hz). Consequently the configuration at C-2 was confirmed by reduction of **5** under catalytical hydrogenation conditions, followed by acetylation to give a compound whose ^{1}H NMR spectrum ($J_{1,2}$ = 3.50 Hz) was identical to that of 2-*N*-acetylamino-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose described by Hasegawa *et al.*[9]



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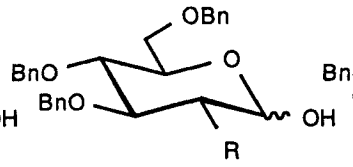

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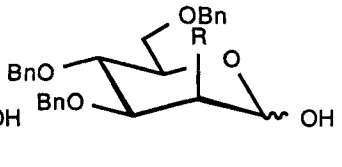

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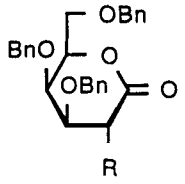

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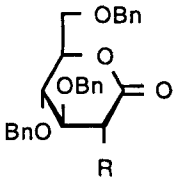

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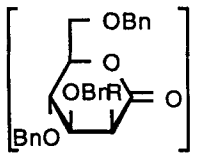
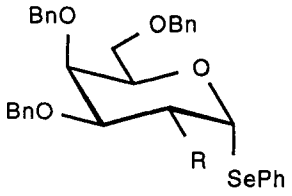
11 R = NHAc



6 R = N_3
12 R = NHAc



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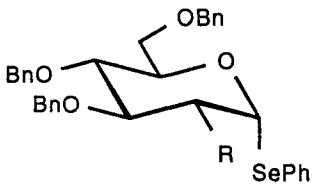

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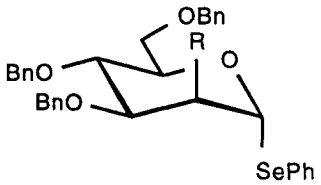
17 R = NHAc



15 R = N_3
18 R = NHAc

The observed small ^3J values were perhaps due to a distorted conformation of **5**, previously described for 3,4,6-tri-*O*-benzyl-2-deoxy-D-*arabino*-hexono-1,5-lactone with a $B_{2,5}$ conformation based on the ^1H NMR data.[6]

Treatment of the *manno* derivative **3** under the same conditions afforded the *glucono*-1,5-lactone **5** as a single product (92% yield). No *manno* isomer **6** could be detected by examination of the ^1H NMR spectrum of the crude reaction mixture. This epimerization was previously reported in the literature in the case of axially oriented azido group.[3,10] For example, Ali and Richardson[10] reported that oxidation of methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside with DMSO in acetic anhydride afforded methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-hex-3-ulopyranoside with inversion of the vicinal azido group from axial to equatorial

attachment. Several years later, Kuzuhara *et al.*[3] observed that oxidation of 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-altropyranose with a mixture of DMSO and acetic anhydride gave 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-allono-1,5-lactone with concomitant inversion of the azido group. Finally, although it does not allow the preparation of the 2-azido-2-deoxy-D-mannono-1,5-lactone, this epimerization is advantageous because the protected 2-azido-2-deoxy-D-glucono-1,5-lactone can be obtained by direct oxidation (without separation of the *manno* derivative) of the *gluco-manno* mixture obtained from azido-phenylselenylation of protected D-glucal derivative followed by hydrolysis.[7,12] For example, oxidation of a mixture of **2** and **3** (69 : 31) afforded exclusively **5** in 92% yield.

Azido lactones **4** and **5**, although reported to be instable,[6] were obtained as stable compounds which could be kept in a freezer for several months without decomposition.

For the preparation of perbenzylated 2-*N*-acetylamino-2-deoxy lactones (**10, 11** and **12**), corresponding 2-*N*-acetylamino lactols **7, 8** and **9** were needed. These lactols were obtained by reduction and acetylation of corresponding 2-azido-2-deoxy selenoglycosides (**13, 14** and **15**),[7] followed by hydrolysis of the selenoglycosides.

For the reduction of the azido group of **13, 14** and **15**, rather than using an excess of 1,3-propanedithiol (5 equiv)[11] as in our previous work,[12] a catalytic amount (0.2 equiv) of this reagent was employed in the presence of sodium borohydride and triethylamine in propan-2-ol.[13] Acetylation of the crude product afforded 2-*N*-acetylamino-2-deoxy-selenoglycosides (**16, 17, 18**) which were transformed into the 2-*N*-acetylamino-2-deoxy-glycopyranoses (**7**, **8** and **9**) by hydrolysis catalyzed by mercury trifluoroacetate (≈ 90% yield).

This sequence of reactions allowed the preparation of **7** from 3,4,6-tri-*O*-benzyl-D-galactal in 58% overall yield[14] and of **8** from 3,4,6-tri-*O*-benzyl-D-glucal in 44.5% overall yield.[15]

For these perbenzylated 2-*N*-acetylamino-2-deoxy lactols the best results were obtained with NMO in the presence of catalytic amount of TPAP and the 2-*N*-acetylamino-2-deoxy lactones **10** and **11** were obtained directly in analytical purity in good yield (90%). Under these conditions epimerization at C-2 was also observed with the *manno* derivative **9** and the glucono-1,5-lactone **11** was obtained as a single product.

However, when lactols **7** to **9** were oxidized with DMSO in acetic anhydride, further recristallizations were needed to give analytically pure lactones **10** and **11** in 56% yield.

EXPERIMENTAL

General methods Optical rotations were measured on a Perkin-Elmer 141 polarimeter in a 10 cm cell at 22 °C. IR spectra were recorded with a Unicam spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AGH 250 spectrometer. Chemical shifts are given in ppm with tetramethylsilane as internal standard. Analytical TLC was performed on Merck aluminium precoated plates of silica gel 60 F - 254 with detection by UV and spraying with 6 N H_2SO_4 and heating about 2 min at 300 °C. Merck silica gel 60 (300 - 400) and anhydrous solvents were employed for column chromatography. Elemental analyses were performed at the "Service de microanalyse" of the Université Pierre et Marie Curie.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactono-1,5-lactone (4). Compound **1** (475 mg, 1 mmol) was dissolved in a mixture of DMSO (3 mL) and acetic anhydride (3 mL). After stirring at room temperature for 12 h, the mixture was diluted with EtOAc (10 mL) and washed with H_2O (3 x 10 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure to give **4** (421 mg, 89%) as an oil: R_f 0.58 (1 : 1 hexane-ether); $[\alpha]_D$ +65.2° (*c* 1, $CHCl_3$); lit.[6] $[\alpha]_D$ + 63° (*c* 0.6, $CHCl_3$); IR 1780, 2119 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.58 (m, 2H, $J_{6,6'}$ = 9.20 Hz, H-6, H-6'), 3.62 (dd, 1H, $J_{3,4}$ = 2.70 Hz, H-3), 4.09 (m, 1H, H-4), 4.25 (ddd, 1H, $J_{4,5}$ = 1.70 Hz, $J_{5,6}$ = 7.50 Hz, H-5), 4.53 (d, 1H, $J_{2,3}$ = 10.04 Hz, H-2), 4.35-4.90 (m, 6H, $3CH_2$ benzyl), 7.10-7.50 (m, 15H, Arom). ^{13}C NMR ($CDCl_3$) δ 62.2 (C–2); 68.0 (C–6); 71.8 (C–4); 72.6, 72.7, 74.9 (CH_2 benzyl); 78.6 (C–5); 79.5(C–3); 127.8, 127.8, 128.0, 128.1, 128.8 (C-Arom); 137.0, 137.4 (C-ipso); 168.2 (C-1).

Anal. Calcd for $C_{27}H_{27}N_3O_5$: C, 68.48; H, 5.74; N, 8.87 Found: C, 68.69; H, 5.53; N, 9.01.

2-Azido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucono-1,5-lactone (5). Oxidation of **2** or **3** or a mixture of **2** and **3** (475 mg, 1 mmol) as described for **1** gave **5** (435 mg, 92%) as an oil: R_f 0.53 (1 : 1 hexane-ether); $[\alpha]_D$ +17.6° (*c* 0.72, CH_2Cl_2); IR 1780, 2119 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.58 (d, 2H, H-6, H-6'), 3.82 (dd, 1H, $J_{4,5}$ = 6.40 Hz, H-4), 3.98 (dd, 1H, $J_{3,4}$ = 1.60 Hz, H-3), 4.05 (d, 1H, $J_{2,3}$ = 2.90 Hz, H-2), 4.24 (ddd, 1H, $J_{5,6}$ = 2.00 Hz, H-5), 4.25-4.60 (m, 6H, $3CH_2$ benzyl), 7.10-7.50 (m, 15H, Arom). ^{13}C NMR ($CDCl_3$) δ 58.7 (C–2); 68.4 (C–6); 71.7, 72.3 (CH_2 benzyl); 73.2 (C–4); 77.9 (C–3); 79.2 (C–5); 127.5, 127.7, 127.8, 128.0, 128.1, 128.3 (C-Arom); 136.3, 237.2 (C-ipso); 166.6 (C-1).

Anal. Calcd for $C_{27}H_{27}N_3O_5$: C, 68.48; H, 5.74; N, 8.87. Found: C, 68.69; H, 5.53; N, 9.01.

2-*N*-Acetylamino-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucose. A solution of **5** (40 mg, 0.084 mmol) in methanol (1.5 mL) was hydrogenated at atmospheric pressure over 10% palladium on charcoal (80 mg) for 15 h at room temperature. The catalyst was filtered off using Celite and the solids were washed with methanol. After solvent evaporation, the crude product was treated with acetic anhydride (112 μL) and pyridine (250 μL) at room temperature. After 15 h, pyridine was evaporated and the residue was filtered through silica gel using hexane-EtOAc (1 : 1) as eluent to give 21 mg (64%) of the title compound as a solid: mp 142-144 °C, $[\alpha]_D$ +98° (*c* 1, $CHCl_3$); lit.[9] mp 139 °C, $[\alpha]_D$ +94° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.87 (s, 3H, Ac), 1.98 (s, 3H, Ac), 1.99 (s, 3H, Ac), 2.02 (s, 3H, Ac), 2.13 (s, 3H, Ac), 3.88-4.04 (m, 2H, H-5, H-6), 4.13-4.23 (dd, 1H, $J_{5,6'}$ = 4.00 Hz, $J_{6,6'}$ = 12.40 Hz, H-6'), 4.34-4.50 (m, 1H, H-2), 5.08-5.25 (m, 2H, H-3, H-4); 5.59 (d, 1H, $J_{2,NH}$ = 9.00 Hz, NH), 6.10 (d, 1H, $J_{1,2}$ = 3.60 Hz, H-1). ^{13}C NMR ($CDCl_3$) δ 21.7, 21.8, 22.1, 24.2 (CH_3); 52.1 (C-2); 62.6 (C-6); 68.6 (C-5); 70.8, 71.8 (C-3, C-4); 91.8 (C-1); 169.8, 170.2, 171.1, 171.8, 172.8 (C=O).

Anal. Calcd for $C_{16}H_{23}NO_{10}$: C, 49.35; H, 5.95; N, 3.59. Found: C, 49.29; H, 5.92; N, 3.45.

Phenyl 2-*N*-acetylamino-3,4,6-tri-*O*-benzyl-2-deoxy-1-seleno-α-D-galactopyranoside (16). To a stirred solution of **13** (150 mg, 0.24 mmol) in *i*-PrOH (750 μL), 1,3-propanedithiol (5 μL, 0.048 mmol), Et_3N (67 μL, 0.48 mmol) and sodium borohydride (37 mg, 0.48 mmol) were added. After stirring at 45 °C for 4 h, TLC indicated completion of the reaction. Solvent was evaporated and the crude product was dissolved in anhydrous pyridine (144 μL) and acetic anhydride (72 μL, 3 mmol) was added. After work-up, the crude product was chromatographed on silica gel (elution with 60 : 1 dichloromethane-methanol) to give known **16** [12] (134 mg, 87%).

Phenyl 2-*N*-acetylamino-3,4,6-tri-*O*-benzyl-2-deoxy-1-seleno-α-D-glucopyranoside (17). Reduction and acetylation of **14** (0.24 mmol) as above followed by chromatography (elution with 60 : 1 dichloromethane-methanol) gave **17** (125.6 mg, 81.6%) as a solid: mp 147-149 °C; R_f 0.43 (60 : 1 dichloromethane-methanol); $[\alpha]_D$ +103.4° (*c* 1, CH_2Cl_2); IR 1550, 1660, 3324 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (s, 3H, CH_3), 3.40-3.65 (m, 2H, $J_{5,6}$ = 2.10 Hz, $J_{6,6'}$ = 11.0 Hz, H-3, H-6), 3.70-3.80 (m, 2H, $J_{5,6'}$ = 6.10 Hz, H-4, H-6'), 4.10 (m, 1H, $J_{4,5}$ = 9.40 Hz, H-5), 4.20 (ddd, 1H, $J_{2,3}$ = 8.00 Hz, H-2), 4.35-4.80 (m, 6H, $3CH_2$ benzyl), 5.00 (d, 1H, $J_{2,NH}$ = 7.90 Hz, NH), 5.85 (d, 1H, $J_{1,2}$ = 4.70 Hz, H-1), 7.00-7.60 (m, 20H, Arom).

Anal. Calcd for $C_{35}H_{37}NO_5Se$: C, 66.65; H, 5.91; N, 2.22. Found: C, 66.68; H, 6.01; N, 2.28.

Phenyl 2-*N*-acetylamino-3,4,6-tri-*O*-benzyl-2-deoxy-1-seleno-α-D-mannopyranoside (18). Reduction of **15** (0.24 mmol) and acetylation as described for **13** and **14** followed by chromatography (elution with 60 : 1 dichloromethane-methanol) gave **18** (131 mg, 85%) as a syrup: R_f 0.43 (60 : 1 dichloromethane-methanol); $[\alpha]_D$ +51.4° (*c* 1, CH_2Cl_2); IR 1550, 1660, 3324 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (s, 3H, CH_3), 3.40-3.90 (m, 2H), 4.20-4.80 (m, 10H), 5.75 (s, 1H, H-1), 5.90 (d, 1H, $J_{2,NH}$ = 8.40 Hz, NH), 7.00-7.50 (m, 20H, Arom).

Anal. Calcd for $C_{35}H_{37}NO_5Se$: C, 66.65; H, 5.91; N, 2.22. Found: C, 66.78; H, 5.94; N, 2.22.

2-*N*-Acetylamino-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactopyranose (7). A solution of **16** (102 mg, 0.16 mmol) in THF/H_2O (160/160 μL) was treated at room temperature with mercury trifluoroacetate (0.24 mmol). After 30 min the mixture was diluted with EtOAc (5 mL), and washed with sat. K_2CO_3 (5 mL). The aqueous layer was extracted with EtOAc (2 x 5 mL). The combined EtOAc layer was washed with 5% aq Na_2S (5 mL). The aqueous layer was reextracted with EtOAc (2 x 5 mL) and the organic layer was washed with H_2O until neutral pH, dried over $MgSO_4$, filtered and concentrated. The crude product, purified by column chromatography on silica gel (elution with 30 : 1 dichloromethane-methanol), gave **7** as a solid (72.3 mg, 91%): mp 179-181 °C ; R_f 0.55 (30 : 1 dichloromethane-methanol); IR 1550, 1660, 3324 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.85 (s, 3H, CH_3), 3.40-3.60 (m, 4H, H-2, H-3, H-6, OH), 3.70 (dd, 1H, $J_{6,6'}$= 10.20 Hz, $J_{5,6'}$ = 2.50 Hz, H-6'), 4.00 (s, 1H, H-4), 4.10 (m, 1H, H-5), 4.35-5.25 (m, 7H, H-1, $3CH_2$ benzyl), 5.40 (d, 1H, $J_{2,NH}$ = 8.20 Hz, NH), 7.10-7.40 (m, 15H, Arom).

Anal. Calcd for $C_{29}H_{33}NO_6$: C, 70.86; H, 6.77; N, 2.85. Found: C, 70.59; H, 6.74; N, 2.71.

2-*N*-Acetylamino-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose (8). Hydrolysis of **17** (116 mg, 0.18 mmol) as described for **16** followed by chromatography on silica gel (elution with 30 : 1 dichloromethane-methanol) gave **8** as a solid (79.5 mg, 88%): mp 199-202 °C; R_f 0.53 (30 : 1 dichloromethane-methanol); IR 1550, 1660, 3324 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (s, 3H, CH_3), 3.30-3.70 (m, 4H, H-4, H-6, H-6', OH), 3.80 (m, 1H, H-2), 3.90-4.20 (m, 2H, H-3, H-5), 4.50-5.15 (m, 7H, H-1, $3CH_2$ benzyl), 5.40 (d, 1H, $J_{2,NH}$ = 8.90 Hz, NH), 7.10-7.40 (m, 15H, Arom).

Anal. Calcd for $C_{29}H_{33}NO_6$: C, 70.86; H, 6.77; N, 2.85. Found: C, 70.79; H, 6.80; N, 2.82.

2-*N*-Acetylamino-3,4,6-tri-*O*-benzyl-2-deoxy-D-mannopyranose (9). Hydrolysis of **18** (102 mg, 0.16 mmol) as described for **16** and **17** followed by

chromatography on silica gel (elution with 30 : 1 dichloromethane-methanol) gave **9** as an oil (72.3 mg, 91%): R_f 0.52 (30 : 1 dichloromethane-methanol); IR 1550, 1660, 3324 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95 (s, 3H, CH_3), 3.30-3.80 (m, 5H, H-2, H-4, H-6, H-6', OH), 3.95 (m, 1H, $J_{4,5}$ = 9.70 Hz, $J_{5,6}$ = 5.80 Hz, $J_{5,6'}$ = 3.60 Hz, H-5), 4.15 (dd, 1H, $J_{2,3}$ = 4.60 Hz, $J_{3,4}$ = 9.20 Hz, H-3), 4.35-4.85 (m, 6H, $3CH_2$ benzyl), 5.20 (s, 1H, H-1), 5.80 (d, 1H, $J_{2,NH}$ = 8.60 Hz, NH), 7.00-7.40 (m, 15H, Arom).

Anal. Calcd for $C_{29}H_{33}NO_6$: C, 70.86; H, 6.77; N, 2.85. Found: C, 70.76; H, 6.84; N, 2.96.

2-*N*-acetylamino-3,4,6-tri-*O*-benzyl-2-deoxy-D-galactono-1,5-lactone (10). To a solution of **7** (60 mg, 0.12 mmol) in dichloromethane (1.2 mL), were added 3Å molecular sieves (30 mg) and NMO (21 mg, 0.18 mmol). After stirring at room temperature for 10 min, TPAP (6.2 mg, 0.018 mmol) was added. After completion of the oxidation (1 h), the mixture was filtered through Celite, and concentrated under reduced pressure to give **10** (54 mg, 90%) as a solid: mp 138-141 °C; R_f 0.71 (30 : 1 dichloromethane-methanol); $[\alpha]_D$ +89.4° (*c* 1, CH_2Cl_2); IR 1550, 1660, 1780, 3324 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (s, 3H, CH_3), 3.55-3.75 (2dd, 2H, $J_{5,6}$ = 5.80 Hz, $J_{5,6'}$ = 3.71 Hz, $J_{6,6'}$ = 9.10 Hz, H-6, H-6'), 3.95 (dd, 1H, $J_{2,3}$ = 9.70 Hz, H-2), 4.10 (dd, 1H, $J_{3,4}$ = 2.20 Hz, H-3), 4.20 (s, 1H, H-4), 4.30-4.90 (m, 6H, $3CH_2$ benzyl), 6.30 (d, 1H, $J_{2,NH}$ = 6.80 Hz, NH), 7.10-7.50 (m, 15H, Arom). ^{13}C NMR ($CDCl_3$) δ 22.9 (CH_3); 54.6 (C-2); 67.6 (C-6); 71.3 (C-4); 72.4, 74.0, 75.1 (CH_2 benzyl); 77.3 (C-5); 77.9 (C-3); 128.3, 128.4, 128.5, 128.8, 128.8, 129.0 (C-Arom); 137.9, 138.2 (C-ipso); 169.0 (C=O); 171.3 (C-1).

Anal. Calcd for $C_{29}H_{31}NO_6$: C, 71.15; H, 6.38; N, 2.86. Found: C, 70.98; H, 6.19; N, 3.01.

2-*N*-acetylamino-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucono-1,5-lactone (11). Oxidation of **8** or **9** (60 mg, 0.12 mmol) as described for **7** gave **11** (54 mg, 90%) as a solid: mp 140-141 °C; R_f 0.73 (30 : 1 dichloromethane-methanol); $[\alpha]_D$ +125.7° (*c* 1, CH_2Cl_2); lit.[1] mp 141-142 °C, $[\alpha]_D$ +123.3° (*c* 0.94, $CHCl_3$); IR 1550, 1660, 1780, 3324 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (s, 3H, CH_3), 3.70 (m, 2H, H-6, H-6'), 4.00 (m, 3H), 4.30-4.85 (m, 7H, $3CH_2$ benzyl, H-5), 6.00 (d, 1H, $J_{2,NH}$ = 5.10 Hz, NH), 7.10-7.40 (m, 15H, Arom). ^{13}C NMR ($CDCl_3$) δ 23.0 (CH_3); 56.0, 76.5, 80.2 (C-2, C-3, C-4); 68.2 (C-6); 78.9 (C-5); 74.0, 75.1 (CH_2 benzyl); 128.3, 128.4, 128.6, 128.9 (C-Arom); 138.0, 138.4 (C-ipso); 169.3 (C=O); 171.0 (C-1).

Anal. Calcd for $C_{29}H_{31}NO_6$: C, 71.15; H, 6.38; N, 2.86. Found: C, 71.32; H, 6.42; N, 2.87.

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14. Compound **7** was previously prepared from 2-*N*-acetylamino-2-deoxy-D-galactopyranose in 16% overall yield.[2]
15. Compound **8** was previously prepared from 2-*N*-acetylamino-2-deoxy-D-glucopyranose in 49% overall yield.[2]