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Unexpected reductions of glycosyl spacer-armed phthalimides

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Abstract—An unusual reductive ring-opening reaction in the title compounds, of the phthalimide group with sodium hydride in anhydrous DMF is observed for the first time and the presumed mechanism is described in detail. An unexpected hydrogenation of the phthalimide group was also observed.

Keywords: Phthalimide; Benzylation; Hydrogenation; Reduction

1. Introduction

The phthaloyl group is widely used as an amino protecting group in carbohydrate and peptide chemistry. It is quite stable under various conditions and is usually removed with hydrazine hydrate in refluxing alcohol.[1] The phthalimide can be reduced by hydrogen-transfer reactions (such as zinc or tin in acetic acid, or hydrochloric acid) in low yield[2–5] and by $NaBH_4$.[6] Recently, however, we found specific phthalimides that are labile to reduction under classical conditions of benzylation and hydrogenation.

2. Results and discussion

2.1. Reduction by NaH in anhydrous DMF

We chose phthaloyl protection of a primary amino group in the synthesis of an oligosaccharide intermediate. After reduction of the azide group of compound **1**[7] by hydrogenation, the resulting amine was treated with phthalic anhydride to give the phthalimide **2**.[8] The 3′,4′-dihydroxyl function of **2** was then regioselectively protected with an isopropylidene group.[9] When compound **3** was treated with sodium hydride (1.2 equiv per OH group) and benzyl bromide (1.5 equiv per OH group) in anhydrous DMF, an unexpected reaction of the phthalimide group occurred. Compound **4** was isolated from the complex reaction mixture as the main product in 29% yield. Components more polar than **4** (>5 spots on TLC) were speculated to be products of incomplete benzylate (Scheme 1).

The hydride ion can attack one of the carbonyl carbons (transition state **B**) of the proposed intermediate **A** to give the delocalized amide anion (**D**), which is further *N*-benzylated to give the aldehyde (**E**). Reduction and benzylation of the aldehyde then occurred repeatedly and rapidly to give the product **4** (Scheme 1). The *O*-benzylated product of the delocalized amide anion (**D**) was not obtained from the reaction mixture, probably because of its disfavored thermodynamic stability.

Benzylation of **3** was incomplete under these conditions, although fully benzylated **4** could be isolated from the reaction mixture. The flexible aglycon may play a role in the benzylation of the carbohydrate moiety. When 1.0 equiv of NaH per hydroxyl group was used, compound **4** was isolated from the mixture in lower yield (16%); and when 1.5 equiv of NaH per hydroxyl group was used, compound **4** was obtained in higher yield (46%). Although the formation of **4** is related to the amount of NaH used, the reaction was still incomplete, even when a large excess of NaH was used.

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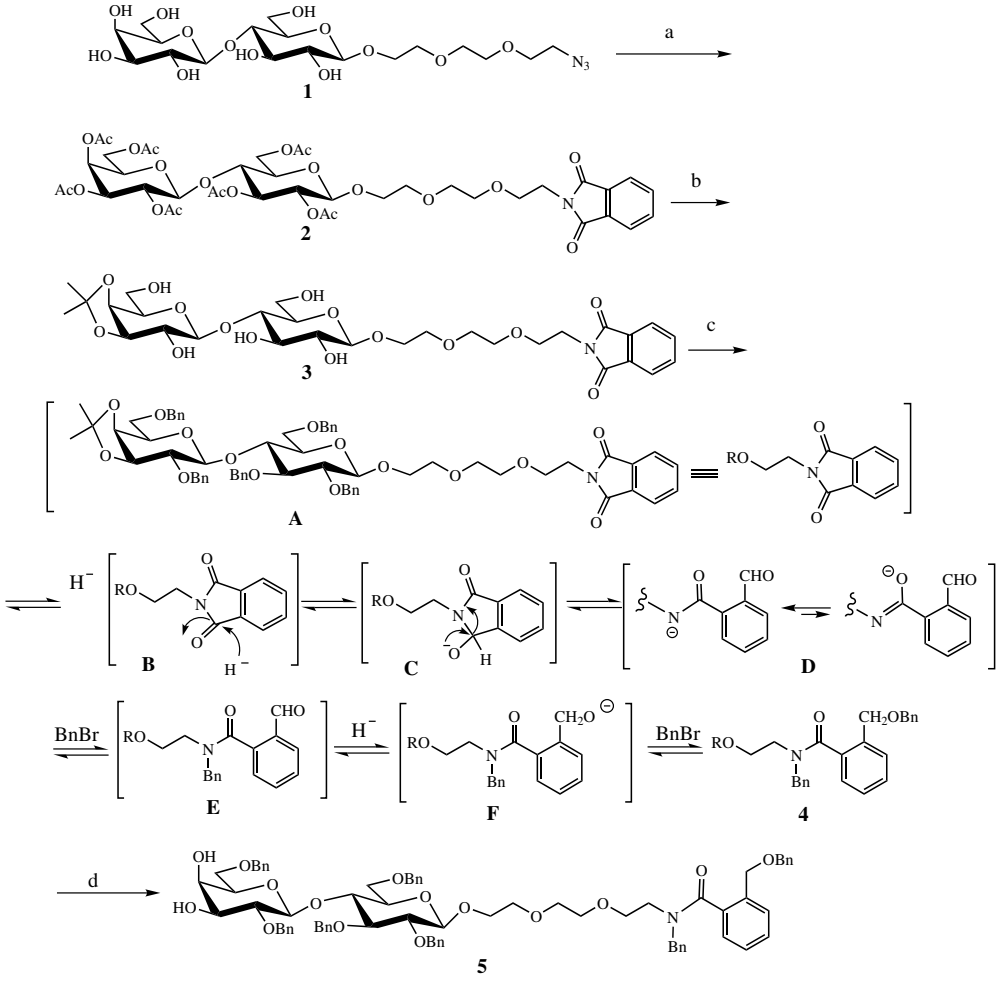


Scheme 1. Reagents and conditions: (a) (1) Pd–C, H_2, EtOAc–HOAc, 6 h; (2) phthalic anhydride, MeOH, rt, 24 h; (3) Ac_2O, pyridine, rt, overnight; (b) (1) NaOMe, MeOH, rt, 3 h; (2) 2,2-dimethoxypropane, TsOH, DMF, rt, 24 h; Et_3N, MeOH–H_2O, refluxing; (c) BnBr, NaH, DMF, 0 °C to rt, overnight; (d) CF_3CO_2H–H_2O (9:1), CH_2Cl_2, 0 °C, 30 min.

Compound **4** was obtained in slightly higher yield under these conditions. Compound **4** was observed even when the reaction was quenched with methanol after 2 h. This evidence indicates that the rate of reduction was comparable with the rate of benzylation.

To our knowledge, this is the first report of a phthalimide group that was reduced under the standard benzylation procedure.

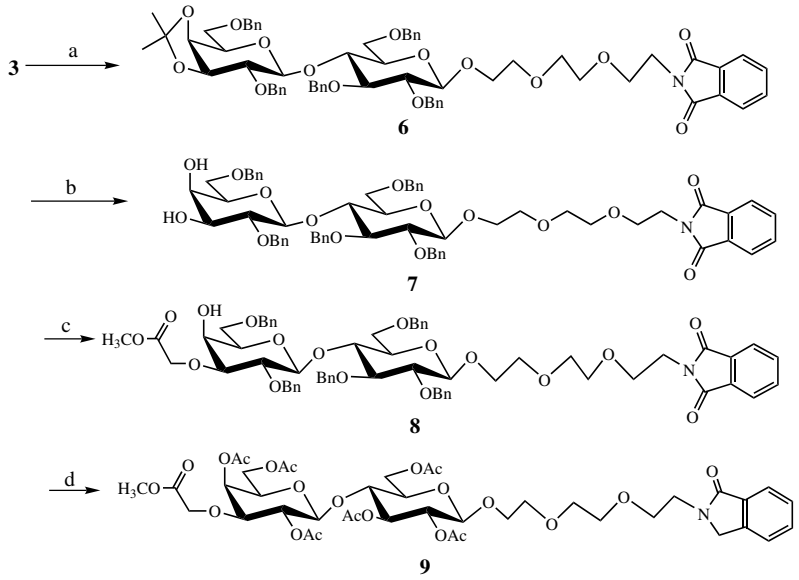
2.2. Phthalimide is reduced to a 2,3-dihydro-isoindol-1-one by hydrogenation

In an alternative synthetic route, intermediate **3** was benzylated in the presence of Ag_2O powder[10] in anhydrous DMF (28.8% yield). After removal of the isopropylidene group of **6** by 90% TFA, the resulting diol **7** was treated with Bu_2SnO in refluxing toluene, and then with methyl bromoacetate under catalysis by tetra-*n*-butylammonium iodide (Bu_4NI) to afford the 3′-alkylated product (**8**).[11] Deprotection of the benzyl ether by hydrogenation over 10% Pd–C was performed in acetic acid. Acetylation gave, surprisingly the product **9**, fully characterized by ^1H NMR, ^{13}C NMR, 2D NMR, and TOF MS as a 2,3-dihydro-isoindol-1-one derivative. This unexpected hydrogenation of the phthalide took place in nearly quantitative yield (TLC) and suggests a novel method for preparing 2,3-dihydro-isoindol-1-one derivatives (Scheme 2).

3. Experimental

3.1. General methods

^1H and ^{13}C NMR spectra were recorded on either Varian VXR-300, or Jeol 300 spectrometers at ambient temperature. 2D NMR spectra were recorded on an Inova 500 spectrometer. Mass spectra were determined on a ZAB-HS spectrometer (FAB) or an LDI-TOF spectrometer (MALDI-TOF). Optical rotations were measured with an AA-10R automatic polarimeter. Solvents were dried and distilled conventionally. Column



Scheme 2. Reagents and conditions: (a) BnBr, Ag_2O, DMF, rt, 24 h; (b) CF_3CO_2H–H_2O, CH_2Cl_2, 0 °C; (c) (1) Bu_2SnO, toluene, reflux, 4 h; (2) $BrCH_2CO_2Me$, Bu_4NI, 80 °C, 2.5 h; (3) NaOMe, MeOH, rt, 3 h; (d) (1) Pd–C, H_2, AcOH, 36 h; (2) Ac_2O, pyridine, rt, 24 h.

chromatography was carried out on Silica Gel H (Haiyang Chemical Factory, Qingdao, Shandong, China). TLC was performed on Silica Gel GF_{254} (Haiyang Chemical Factory, Qingdao, Shandong, China) with detection by UV fluorescence quenching and by spraying with 10% H_2SO_4. 8-Azido-3,6-dioxaoctyl 4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (**1**) was prepared by literature methods.[7]

3.2. 8-Phthalimido-3,6-dioxaoctyl 4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (2)

A solution of the azide **1** (21.7 g, 36 mmol) in EtOAc (200 mL) and AcOH (100 mL) was treated with hydrogen (0.42 MPa) in the presence of 10% Pd–C (500 mg) for 6 h. After removal of insoluble materials through a pad of Celite, the filtrate was concentrated to give a colorless syrup, which was used in the next step without further purification.

To a solution of the foregoing amine acetate (22.3 g, 36.0 mmol) in dry MeOH (300 mL) were added Et_3N (9.5 mL, 75.0 mmol) and phthalic anhydride (6.0 g, 40.5 mmol). The mixture was stirred at room temperature for 24 h. After evaporation of MeOH under reduced pressure, Ac_2O (30 mL) and pyridine (30 mL) were added to the residue. The mixture was stirred at room temperature overnight, poured into ice–water (200 mL) and stirred vigorously for 2 h. The aq mixture was extracted with toluene (100 mL × 3). The combined extracts were then washed with aq saturated $NaHCO_3$ and brine, dried (Na_2SO_4), filtered, and concentrated. Column chromatography (3:2 petroleum ether–ether) of the residue afforded **2** (25.8 g, 79.9% for two steps) as a slightly yellow syrup, $[\alpha]_D$ −6.4 (*c* 1.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.85 (dd, 2H, *J* 3.0, *J* 5.7 Hz, Phth), 7.72 (dd, 2H, Phth), 5.34 (d, 1H, *J* 3.0 Hz), 5.22–5.08 (m, 2H), 4.98–4.85 (m, 2H), 4.55–4.47 (m, 3H), 4.16–4.05 (m, 4H), 3.92–3.54 (m, 14H), 2.15, 2.12, 2.06, 2.05, 2.04, 2.03, 1.97 (7s, 21H, 7×CH_3); ^{13}C NMR: δ 170.3, 170.3, 170.1, 170.0, 169.7, 169.6, 169.0, 168.2 (CO), 133.9, 132.1, 123.2 (Phth), 101.0, 100.6 (C-1, C-1′), 76.2, 72.7, 72.5, 71.6, 70.9, 70.6, 70.2, 70.0, 69.0, 67.9, 66.5, 62.0, 60.7, 60.3, 37.1, 21.0, 20.8, 20.8, 20.6, 20.6, 20.5 (7×*C*H_3CO); MALDI-TOF MS: Calcd for $C_{40}H_{51}NO_{22}$: *m*/*z* 897.3. Found: 898.2 $[M+H]^+$.

3.3. 8-Phthalimido-3,6-dioxaoctyl 4-*O*-(3,4-di-*O*-isopropylidene-β-D-galactopyranosyl)-β-D-glucopyranoside (3)

To a solution of compound **2** (19.6 g, 21.8 mmol) in dry MeOH (400 mL) was added NaOMe (0.11 g, 2.0 mmol). After stirring at rt for 3 h, the mixture was neutralized with H^+ cation-exchange resin, filtered, and concentrated to give a pale-yellow syrup (12.8 g, 97.7%).

A mixture of the deacetylated product (10.5 g, 17.4 mmol), 2,2-dimethoxypropane (20 mL), and *p*-toluenesulfonic acid hydrate (350 mg, 1.8 mmol) in dry DMF (80 mL) was stirred at rt for 24 h. The mixture was neutralized with Et_3N and evaporated to dryness in vacuo. The residue was dissolved in MeOH–H_2O (10:1, 150 mL, v/v) and refluxed for 4 h. TLC indicated that the intermediate (R_f 0.67, 20:1 $CHCl_3$–MeOH) was converted into the desired product (R_f 0.18, 20:1 $CHCl_3$–MeOH). Column chromatography (100:4:1 $CHCl_3$–MeOH–Et_3N) afforded **3** (9.40 g, 84.0%) as a yellow foam, $[\alpha]_D$ +32.8 (*c* 0.62, $CHCl_3$); ^{1}H NMR ($CDCl_3$+D_2O): δ 7.84 (dd, 2H, *J* 3.3, *J* 5.4 Hz, Phth), 7.22 (dd, 2H, Phth), 4.73 (m, 1H), 4.48 (d, 1H, *J* 8.1 Hz,

H-1 or H-1′), 4.34 (d, 1H, *J* 7.8 Hz, H-1 or H-1′), 4.14–3.90 (m, 3H), 3.88–3.78 (m, 8H), 3.73–3.41 (m, 12H, $OCH_2CH_2OCH_2CH_2OCH_2CH_2N$), 1.49, 1.30 (2s, 6H, $2CH_3$); ^{13}C NMR: δ 168.3 (2×C=O), 134.0, 132.1, 123.3 (Phth), 110.3 [$(CH_3)_2C$], 103.0, 102.9 (C-1, C-1′), 79.8, 79.4, 74.9, 74.6, 74.1, 73.9, 73.3, 70.3, 70.1, 68.8, 67.9, 62.1, 61.6, 37.3, 28.0, 26.2 (2×CH_3). FAB MS: Calcd for $C_{29}H_{41}NO_{15}$: *m*/*z* 643.2. Found: 682.3 $[M+K]^+$.

3.4. 8-[*N*-Benzyl,*N*-(2-benzyloxymethylbenzoyl)]-6-dioxaoctyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,6-di-*O*-benzyl-3,4-di-*O*-isopropylidene-β-D-galactopyranosyl)-β-D-glucopyranoside (4)

To an ice-cold solution of compound **3** (1.30 g, 2.0 mmol) in dry DMF (30 mL) was added NaH (60%, 0.48 g, 12.0 mmol) and benzyl bromide (1.80 mL, 15.0 mmol). The temperature of the mixture was allowed to rise to rt and it was stirred overnight. An excess of MeOH was added dropwise to quench the reaction. The clear solution was diluted with water (50 mL) and extracted with toluene (30 mL × 3). The extracts were combined and washed with brine (50 mL × 2), dried (Na_2SO_4), and concentrated. Column chromatography (5:1 petroleum ether–EtOAc) of the residue afforded **4** (750 mg, 29.0%) as a yellow syrup, $[\alpha]_D$ +25.0 (*c* 0.96, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.98 (m, 1H), 7.51–7.10 (m, 38H), 4.91–4.61 (m, 8H), 4.54–4.27 (m, 8H), 4.08–3.49 (m, 20H), 3.39–3.18 (m, 6H), 1.37, 1.32 (2s, 6H, $2CH_3$); ^{13}C NMR ($CDCl_3$): δ 171.1 (CO), 138.9, 138.6, 138.3, 138.1, 138.0, 137.6, 136.6, 135.6, 132.8, 132.6, 130.7, 130.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.2, 109.7 [$(CH_3)_2C$], 103.8, 102.5 (C-1, C-1′), 82.8, 82.7, 81.6, 80.5, 80.0, 79.3, 76.4, 76.2, 75.3, 75.2, 75.0, 74.8, 73.5, 73.4, 73.3, 73.1, 72.8, 71.9, 70.5, 70.2, 53.5, 48.2, 47.7, 43.7, 27.9, 26.4 [$(CH_3)_2C$]. MALDI-TOF MS: Calcd for $C_{78}H_{87}NO_{15}$: *m*/*z* 1277.6. Found: 1278.7 $[M+H]^+$, 1316.8 $[M+Na]^+$.

3.5. 8-[*N*-Benzyl,*N*-(2-benzyloxymethylbenzoyl)]-6-dioxaoctyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,6-di-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (5)

To an ice-cold solution of compound **4** (380 mg, 0.3 mmol) in CH_2Cl_2 (15 mL) was added CF_3CO_2H–H_2O (5.0 mL, 9:1, v/v). The mixture was stirred for 45 min and diluted with 20 mL of CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ solution and brine, dried (Na_4SO_4), and concentrated. Column chromatography (2:1 petroleum ether–EtOAc) of the residue afforded **5** (320 mg, 87.0%) as a pale-yellow syrup, $[\alpha]_D$ +30.6 (*c* 0.85, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.00 (m, 1H), 7.48–7.12 (m, 38H), 4.98–4.55 (m, 7H), 4.46–4.36 (m, 6H), 4.05–3.92 (m, 3H), 3.87 (s, 2H, $PhCH_2$), 3.83–3.19 (m, 24H); ^{13}C NMR ($CDCl_3$): δ 171.2 (CO), 139.2, 138.7, 138.4, 138.2, 138.1, 137.5, 136.7, 132.6, 132.4, 130.5, 128.9, 128.5, 128.4, 128.3, 128.2, 128.2, 128.0, 127.7, 127.5, 127.5, 127.1, 127.0, 103.9, 102.5 (C-1, C-1′), 82.7, 81.7, 80.1, 76.5, 75.1, 74.8, 74.7, 73.6, 73.5, 73.2, 73.0, 70.6, 70.5, 70.3, 69.0, 68.8, 68.7, 68.4, 53.5, 52.2, 48.3, 47.5. MALDI-TOF MS: Calcd for $C_{75}H_{83}NO_{15}$: *m*/*z* 1237.6. Found: 1238.3 $[M+H]^+$.

3.6. 8-Phthalimido-3,6-dioxaoctyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,6-di-*O*-benzyl-3,4-di-*O*-isopropylidene-β-D-galactopyranosyl)-β-D-glucopyranoside (6)

To a solution of compound **3** (5.80 g, 9.0 mmol) in dry DMF (80 mL) were added freshly prepared Ag_2O powder (18.6 g, 90 mmol) and BnBr (10.8 mL, 90 mmol). The suspension was treated by ultrasonic irradiation for 15 min before being stirred in dark for 24 h at rt. After removal of the solid through a pad of Celite, the filtrate was diluted with toluene (200 mL), washed with brine, dried ($CaCl_2$), and concentrated. Column chromatography (2:1 petroleum ether–EtOAc) of the residue afforded **6** (2.52 g, 28.8%) as a pale-yellow syrup, $[\alpha]_D$ +25.8 (*c* 1.55, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.78–7.64 (m, 4H, Phth), 7.51–7.19 (m, 25H, 5 Ph), 4.90–4.84 (m, 2H), 4.77–4.62 (m, 3H), 4.55–4.26 (m, 5H), 4.01–3.91 (m, 4H), 3.88–3.31 (m, 22H), 1.36, 1.32, (2s, 6H, $2CH_3$); ^{13}C NMR ($CDCl_3$): δ 168.2 (2×C=O), 139.0, 138.7, 138.5, 138.34, 138.2, 133.9, 132.1, 123.2 (Phth), 128.5, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 127.7, 127.5, 127.4, 127.2 (CH of 5 Ph), 109.7 [$(CH_3)_2C$], 103.8, 101.8 (C-1, C-1′), 82.8, 81.6, 80.6, 79.3, 77.2, 76.8, 76.5, 76.3, 75.4, 74.3, 75.4, 75.0 74.7, 73.6, 73.3, 73.2, 73.1, 71.9, 70.5, 70.3, 70.0, 68.9, 68.9, 68.2, 67.9, 37.2, 29.0, 27.9 (2×CH_3). MALDI-TOF MS: Calcd for $C_{64}H_{71}NO_{15}$: *m*/*z* 1093.5. Found: 1132.2 $[M+K]^+$.

3.7. 8-Phthalimido-3,6-dioxaoctyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,6-di-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (7)

To an ice-cold solution of compound **6** (640 g, 0.59 mmol) in CH_2Cl_2 (15 mL) was added CF_3CO_2H–H_2O (5.0 mL, 9:1, v/v). The mixture was stirred for 0.5 h and diluted with 35 mL of CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ solution and brine, dried (Na_4SO_4), and concentrated. Column chromatography (7:3 petroleum ether–EtOAc) of the residue afforded **7** (550 mg, 89.3%) as a pale-yellow syrup, $[\alpha]_D$ +105.0 (*c* 1.08, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.80 (dd, 2H, *J* 3.0, *J* 9.0 Hz, Phth), 7.65 (dd, 2H, Phth), 7.52–7.20 (m, 25H, 5 Ph), 4.98–4.74 (m, 3H), 4.70–4.55 (m, 3H), 4.45–4.35 (m, 4H), 4.02–3.92 (m, 3H), 3.86–3.79 (m, 4H), 3.69–3.34 (m, 19H); ^{13}C NMR ($CDCl_3$): δ 168.2 (C=O), 129.0, 138.6, 138.3, 138.1, 137.9, 133.8, 132.0, 128.4, 128.3, 128.2, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6,127.6, 127.5, 127.5, 127.4, 127.2, 126.9, 123.1

(Phth, 5×Ph), 103.7, 102.5 (C-1, C-1′), 82.6, 81.5, 79.9, 76.4, 75.1, 74.9, 74.8, 74.6, 73.4, 73.1, 72.8, 70.4, 70.3, 69.9, 68.9, 68.7, 68.6, 68.2, 67.8, 37.1. MALDI-TOF MS: Calcd for $C_{61}H_{67}NO_{15}$: m/z 1053.4. Found: 1092.6 $[M+K]^+$.

3.8. 8-Phthalimido-3,6-dioxaoctyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,6-di-*O*-benzyl-3-*O*-methoxycarbonylmethylene-β-D-galactopyranosyl)-β-D-glucopyranoside (8)

To a solution of compound **7** (1.79 g, 1.7 mmol) in absolute toluene (100 mL) was added Bu_2SnO (0.60 g, 1.4 mmol). The suspension was heated to reflux over a Dean–Stark apparatus for 4 h and 60 mL of the solvent were distilled out. The temperature of the clear solution was allowed to drop to 80 °C, methyl bromoacetate (1.5 mL, 10 mmol) and Bu_4NI (0.63 g, 1.7 mmol) were added, and the solution was stirred for 2.5 h. The mixture was concentrated under reduced pressure and the residue was re-dissolved in a solution of 0.05 M NaOMe in dry MeOH (100 mL). After stirring at rt for 2.5 h, the mixture was neutralized with H^+ cation-exchange resin, filtered, and concentrated. Column chromatography (3:1 petroleum ether–EtOAc) of the residue afforded **8** (1.42 g, 82.7%) as a yellow syrup, $[\alpha]_D$ −72.0 (c 0.85, $CHCl_3$); IR (cm^{-1}): 3482 (–OH), 1744 (C=O); ^1H NMR ($CDCl_3$): δ 7.80 (dd, 2H, J 3.0, J 9.0 Hz, Phth), 7.65 (dd, 2H, Phth), 7.48–7.22 (m, 25H, 5 Ph), 5.00–4.90 (m, 2H), 4.77–4.69 (m, 4H), 4.57–4.36 (m, 7H), 4.16–3.92 (m, 4H), 3.78 (s, 3H, OCH_3), 3.74–3.20 (m, 21H); ^{13}C NMR ($CDCl_3$): δ 172.0, 168.2 (3CO), 139.0, 138.7, 138.5, 138.3, 138.2, 133.9, 132.1, 128.3, 128.3, 128.2, 128.2, 128.0, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 127.2, 123.2 (5×Ph, Phth), 103.8, 102.4 (C-1, C-1′), 84.1, 82.7, 81.6, 79.4, 77.2, 75.4, 75.2, 75.0, 74.7, 73.5, 73.1, 72.7, 70.6, 70.6, 70.0, 69.0, 68.4, 68.2, 66.5, 52.1, 50.6 (OCH_3), 37.2. MALDI-TOF MS: Calcd for $C_{64}H_{71}NO_{17}$: m/z 1125.5. Found: 1148.6 $[M+Na]^+$, 1164.5 $[M+K]^+$.

3.9. 8-(2,3-Dihydro-isoindol-1-one-2-yl)-3,6-dioxaoctyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,4,6-tri-*O*-acetyl-3-*O*-methoxycarbonylmethyl-β-D-galactopyranosyl)-β-D-glucopyranoside (9)

To a solution of compound **8** (2.25 g, 2.0 mmol) in HOAc (20 mL) was added 10% Pd–C (200 mg). The suspension was treated with H_2 (0.42 MPa) for 36 h. TLC indicated that the starting material had been converted completely into the desired product. The solid was filtered off and the filtrate was concentrated.

A solution of the hydrogenation product (20 mg, 30 μmol) in pyridine (1 mL) and Ac_2O (1 mL) was stirred at rt for 24 h. An excess of MeOH was added to consume the remaining Ac_2O. The mixture was evaporated to dryness and the residue was subjected to column chromatography (3:4 petroleum ether–EtOAc) to give **9** (25 mg, 93%) as a colorless thick syrup, $[\alpha]_D$ +5.2 (c 0.80, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.86–7.44 (m, 4H), 5.39 (d, 1H, J 3.0 Hz, H-4′), 5.18 (t, 1H, J 9.5 Hz, H-3), 5.01 (dd, 1H, J 7.5 Hz, J 9.5 Hz, H-2′), 4.87 (dd, 1H, J 8.0, 9.5 Hz, H-2), 4.55 (s, 2H, $ArCH_2N$), 4.52 (d, 1H, J 8.0 Hz, H-1), 4.88 (dd, 1H, J 1.5, 11.5 Hz, H-6a), 4.55 (d, 1H, J 8.0 Hz, H-1′), 4.14–4.05 (m, 5H, H-3′, H-6b, H-6a′, CH_2), 3.89–3.73 (m, 6H), 3.72 (s, 3H, OCH_3), 3.69–3.56 (m, 10H), 2.142, 2.137, 2.10, 2.08, 2.04, 2.02 (6s, 18H, 6×Ac); ^{13}C NMR ($CDCl_3$): δ 170.4, 170.4, 170.3, 170.1, 169.7, 169.7, 168.5 (7×C=O), 141.8, 132.7, 131.2, 127.8, 123.6, 122.6, 101.1 (C-1′), 100.6 (C-1), 78.2 (C-6′), 76.3 (C-6), 72.9 (C-3), 72.7, 71.6 (C-2), 70.6 (C-2′), 70.6, 70.5, 70.3, 70.1, 70.0, 69.1, 66.0, 65.0 (C-4′), 62.1 (C-6), 61.2, 51.8 ($ArCH_2N$), 51.6 (OCH_3), 42.3 (OCH_2CH_2N), 20.9, 20.8, 20.8, 20.7 (CH_3CO). MALDI-TOF MS: Calcd for $C_{41}H_{55}NO_{22}$: m/z 913.3. Found: 914.3 $[M+H]^+$.

Acknowledgements

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