Branched-chain Sugars. VIII. On the Configuration of Branched-chain Sugars from Methyl 3-*O*-Benzoyl-4,6-*O*-benzylidene-α-D-*arabino*-hexopyranosid-2-ulose[1]

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Stereoselectivities in the Grignard, diazomethane and nitromethane reaction of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*arabino*-hexopyranosid-2-ulose (**1**) were examined. In contrast to the Grignard reaction of **1** using methylmagnesium iodide to give a single 2-*C*-methyl derivative (**4**), the diazomethane reaction followed by reduction afforded another epimer (**6**). The nitromethan condensation product (**10**) of **1** was converted into the corresponding 2-*C*-acetaminomethyl derivative (**13**). The NMR spectrum of 2-*O*-acetate of **4** and comparison of the optical rotations of **4**, **6**, **10** and **13** in cuprammonium solution indicated that **4** and others have D-*gluco*- and D-*manno*-configuration, respectively. Discussions were made on the stereoselectivties of these reactions.

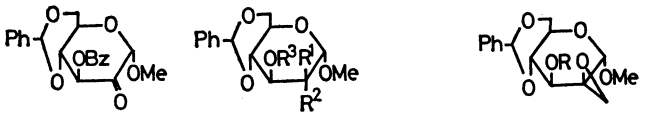
In a previous paper,[2] we reported that the Grignard and nitromethane reaction of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose gave D-*allo*-type branched-chain sugars, while diazomethane reaction afforded a D-*gluco*-type product. In this paper, these reactions of the corresponding 2-ulose were carried out, and the complemental stereoselectivities of the Grignard and diazomethane reaction and a new evidence for the stereoselectivity of nitromethane reaction are described.

Results and Discussion

The starting material; methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*arabino*-hexopyranosid-2-ulose (**1**) was synthesized in 87% yield by the oxidation of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside,[3] which was separated in 7% yield as a by-product in the selective synthesis of the corresponding 2-*O*-benzoate reported by Carey and Hodgson.[4] The structure of **1** was clearly supported by the presence of a sharp singlet of H_1 (δ 4.80) and a doublet of H_3 (δ 5.98, $J_{3,4}=10.0$) in the NMR spectrum.

Reaction of **1** with equimolar methyl magnesium iodide at room temperature gave the corresponding 2-*C*-methyl derivative (**2**) in 50% yield, which was then acetylated in the presence of acid catalyst to give 2-*O*-acetate (**3**) quantitatively. The chemical shift (δ 1.91) of methyl protons of the tertiary acetoxy group in **3** indicated that **3** has D-*gluco*-configuration.[5] Treatment of **2** in methanol with barium oxide gave the de-*O*-benzoylated product (**4**) in 37% yield.

On the other hand, reaction of **1** with diazomethane in benzene–ethanol–ether gave quantitatively the corresponding spiro-epoxide (**5**) which was characterized by the presence of an AB quartet of epoxy-methylene protons (δ 2.82 and 2.74, J=4.0) in the NMR spectrum. Reduction of **5** with lithium aluminium hydride gave the corresponding 2-*C*-methyl derivative (**6**) in 67% yield. The compound was determined to be 2-epimer of **4** from the physical constants and the optical rotation change in cuprammonium solution[6] (Table 1). Treatment of **5** with barium oxide in methanol gave the corresponding de-*O*-benzoylated product (**8**), and the ring-opening product; methyl 4,6-*O*-benzylidene-2-*C*-methoxymethyl-α-D-mannopyranoside (**7**). These results offer a new instance of the complemental stereoselectivity of the Grignard and diazomethane reactions.[2,7]



(**1**) (**2**) $R^1=CH_3$ $R^2=OH$ $R^3=Bz$ (**5**) R=Bz
(**3**) $R^1=CH_3$ $R^2=OAc$ $R^3=Bz$ (**8**) R=H
(**4**) $R^1=CH_3$ $R^2=OH$ $R^3=H$
(**6**) $R^1=OH$ $R^2=CH_3$ $R^3=H$
(**7**) $R^1=OH$ $R^2=CH_2OCH_3$ $R^3=H$
(**9**) $R^1=OH$ $R^2=CH_2NO_2$ $R^3=Bz$
(**10**) $R^1=OH$ $R^2=CH_2NO_2$ $R^3=H$
(**11**) $R^1=OH$ $R^2=CH_2NO_2$ $R^3=Ac$
(**12**) $R^1=OH$ $R^2=CH_2NH_2$ $R^3=H$
(**13**) $R^1=OH$ $R^2=CH_2NHAc$ $R^3=H$

Reaction of **1** with nitromethane in tetrahydrofuran at room temperature gave the corresponding 2-*C*-nitromethyl derivative (**9**) and its de-*O*-benzoylated product (**10**) in 12% and 63% yield, respectively. Acid catalyzed acetylation of **10** gave only 3-*O*-acetate (**11**) in 80% yield. Catalytic hydrogenation of **10** gave the corresponding 2-*C*-aminomethyl derivative (**12**), which was then converted into 2-*C*-acetamidomethyl derivative (**13**) quantitatively. In order to determine the configuration of the nitromethane condensation product, optical rotations of **10** and **13** in cuprammonium solution were measured, together with **4** and **6**. The results shown in Table 1 clearly indicate that the epimeric correlation between the Grignard and nitromethane reaction products and also the same configuration of the nitromethane and diazomethane reaction products. From these results, the stereoselectivity of nucleophilic additions indicated that the Grignard reagent attacked the carbonyl group from the less hindered site, while diazomethane and nitromethane from the hindered site.

Excepting a few instances in which an additive attractive factor to magnesium atom is included in the substrate,[8] the same stereoselectivity between the

Table 1. Rotational change of compounds **4**, **6**, **10** and **13** in cuprammonium solution

Compound	$[\alpha]_D^{50\%\ MeOH}$		$[\alpha]_D^{Cupra\ A}$
4	+136°	⟶	+ 60°
6	+ 84°	⟶	+248°
10	+ 94°	⟶	+148°
13	+ 34°	⟶	+144°

Grignard reagent and simple catalytic reductions are generally accepted. As was pointed out in our previous paper,[2] the stereoselectivity of diazomethane reaction is mainly controlled by the attractive force between vicinal (or neighboring) axial-hydroxyl oxygens and diazomethylene cation of zwitterionic intermediate, and consequently, the Grignard and diazomethane reactions show sometimes complemental stereoselectivities.

Concerning the nitromethane condensation, it is known that the stereoselectivity is the same as the reduction or the Grignard reaction in the cases of methyl 4,6-*O*-benzylidene-2-substituted-α-D-*arabino*-hexopyranosid-3-uloses,[2] methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosid-2-ulose,[9] 1,2;5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose,[10] while, reversely in the case of methyl 6-deoxy 3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-2-ulose.[11] Consequently, the last instance and the result obtained here imply the exceptional stereoselectivity of nitromethane condensation. However, it is known that nitromethane condensation gave the epimeric mixtures in various ratios depending upon the conditions used.[9,12] Moreover, similar phenomena in the addition of nucleophiles to enoses[13] and a furanos-3-ulose[14] are explained by isomerization of the kinetically-controlled product into thermodynamically-controlled product. A similar interpretation will be applied to the result of the nitromethane reaction.

In order to pursue the kinetically-controlled D-*gluco*-type product, the reaction was carried out at a lower temperature (−20 °C——78 °C) under monitoring with TLC. The starting material (R_f=0.46 with the solvent system; benzene/acetone=8/1) changed into a compound of R_f=0.18, and then gradually into **9** (R_f=0.35). However, the amount of the intermediate product (R_f=0.18) gradually diminished during the treatment of the reaction mixture at room temperature even after acidification, whereas that of **9** increased. Moreover, the intermediate product isolated with preparative TLC was always contaminated with the monohydrate of **1**. In one instance, a doublet of H_3 (δ 5.04, $J_{3,4}$=11.0) and a quartet of $C_{2'}$-methylene (δ 4.75 and 4.54, J=10.0) and a singlet of H_1 (δ 5.14) were observed in the NMR spectrum of such a product, in addition to the signals of the monohydrate. These chemical shifts are higher than that of **9** (H_3; δ 5.85; $J_{3,4}$=11.0, $C_{2'}$-methylene; δ 4.98 and 4.81, J=11.7, H_1; δ 5.20), and seems to be rational to assign to D-*gluco*-type product.

Experimental

All melting points were uncorrected. The solutions were evaporated under reduced pressure at a bath temperature not exceeding 50 °C. Optical rotations were measured in a 0.5-dm tube with a Carl Zeiss LEP-Al polarimeter. IR spectra were recorded with a Hitachi Model EPI-G2 spectrometer. NMR spectra were taken with JEOL 4H-100 spectrometer in deuteriochloroform containing TMS as an internal reference. Chemical shifts and coupling constants were recorded in δ and Hz units, and IR frequencies in cm^{-1}.

*Methyl 3-O-Benzoyl-4,6-O-benzylidene-α-D-*arabino*-hexopyranosid-2-ulose (**1**).* The starting material, methyl 3-*O*-benzoyl 4,6-*O*-benzylidene-α-D-glucopyranoside was obtained, from the mother liquor of the corresponding 2-*O*-benzoate prepared by the method of Carey and Hodgson,[4] in 7% yield which was recrystallized from acetone (mp 216—218 °C). The structure was confirmed by elemental analysis and the NMR spectrum of the corresponding 3-*O*-acetate (mp 154 °C, lit,[3] mp 153—154 °C); NMR: 1.9—2.8 (Ph, m), 5.82 (H_3; t, $J_{2,3}$=9.2), 5.48 (methine H; s), 5.11 (H_2; q; $J_{2,3}$=10.0), 4.96 (H_1; d, $J_{1,2}$=4.0), 4.31 ($H_{5,6e}$=4.0), 3.98 (H_5; sex, $J_{5,6a}$=10.0), 3.78 (H_1; t, $J_{4,5}$=9.2), 3.86 (H_{6a}; t, $J_{6a,6e}$=9.2), 3.42 (OMe), 1.96 (OAc).

A solution of the starting material (5.0 g, 12.9 mmol) in DMSO (50 ml) and acetic anhydride (30 ml) was kept at room temperature for 10 h, and then poured into ice-water. The resulting solution was neutralized with 2 M potassium carbonate, and then extracted with chloroform. Treatment of the chloroform extract in a usual manner gave a sirup, which was crystallized and recrystallized from acetone–water to give needles (4.5 g, 86.9%) of the monohydrate of **1**. Mp 136—137 °C; $[\alpha]_D^{17}$ +36.4° (*c* 0.75, $CHCl_3$); IR; 3530 and 3500 (OH), 1720 (ester).

Found: C, 63.08; H, 5.45%. Calcd for $C_{21}H_{20}O_7 \cdot H_2O$; C, 62.68; H, 5.51%.

Dehydration of the above hydrate at 100 °C/15 mmHg for 2 h gave again a sirupy **1**. $[\alpha]_D^{16}$ +35.0° (*c* 1.15, $CHCl_3$); IR: 1750 (C=O), 1720 (ester); NMR: 2.0—2.8 (Ph; m), 5.98 (H_3; d, $J_{3,4}$=10.0), 5.53 (methine H; s), 4.80 (H_1: s), 4.44 (H_{6e}; q, $J_{6a,6e}$=11.5), 4.26 (H_5: sex, $J_{5,6e}$=4.2), 4.05 (H_4; t, $J_{4,5}$=10.0), 3.83 (H_{6a};t,$J_{5,6a}$=11.5), 3.47 (OMe).

Found; C, 65.26; H. 5.35%. Calcd for $C_{21}H_{20}O_7$; C, 65.61; H, 5.24%.

*Methyl 3-O-Benzoyl-4,6-O-benzylidene-2-C-methyl-α-D-gluco-pyranoside (**2**).* To a solution of methylmagnesium iodide in ether (5 ml) prepared from magnesium turnings (60 mg, 2.47 mmol) and methyl iodide (5 ml) was added **1** (1 g, 2.6 mmol) in benzene (5 ml), and the reaction mixture was refluxed for 1.5 h, poured into cold ammonium chloride solution, and the resulting solution was extracted with methylene chloride. The extract was washed with water and evaporated to give a white powder which was crystallized from methanol–petroleum ether. Yield, 510 mg(49%). Mp 150—152 °C; $[\alpha]_D^{22}$ +17.6° (*c* 0.5, 50% MeOH); IR: 3610 (OH), 1750 (ester), 1595 (Ph); NMR: 8.2—7.2 (Ph; m), 5.67 (H_3; d, J=10.5), 5.51 (methine; s), 4.48 (H_1, s), 4.33 (H_{6e}; q, $J_{6e,5}$=4.0, $J_{6e,6a}$=10.0), 4.10—3.65 (H_4, H_5, H_{6a}; m), 3.46 (OMe), 2.74 (OH, broad s), 1.44 (*C*-Me; s).

Found; C, 66.18; H, 6.08%. Calcd for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04%.

Acetylation of **2** with acetic anhydride in the presence of catalytic amount of *p*-toluenesulfonic acid gave the corresponding 2-*O*-acetate (**3**) in a quantitative yield, which was recrystallized from ethanol–hexane. Mp 163—165 °C; $[\alpha]_D^{22}$ +32.7° (*c* 0.5, acetone); IR: 1730 and 1720 (ester), 1600 (Ph); NMR: 8.2—7.2 (PH; m), 5.86 (H_3; d, $J_{3,4}$=10.0), 5.49 (methine; s), 5.46 (H_1; s), 4.30 (H_{6a}; q, $J_{6e,5}$=4.0, $J_{6a,6e}$=9.0), 4.15—3.65 (H_4, H_5, H_{6a}; m), 3.39 (OMe), 1.91 (OAc), 1.76 (*C*-Me; s).

Found: C, 65.29; H, 6.19%. Calcd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92%.

Methyl 4,6-O-Benzylidene-2-C-methyl-α-D-glucopyranoside (4). A suspension of **2** (400 mg, 1 mmol) and barium oxide (400 mg, 2.5 mmol) in methanol (20 ml) was refluxed for 30 min, filtered, and then evaporated. The residue was extracted with methylene chloride, and the extract was treated in a usual manner to give a sirup which was purified on a silica gel column (benzene/methanol/etheyl actate=5/1/1). The purified sirup (110 mg, 37.2%) crystallized slowly on standing. Mp 55—56 °C; $[\alpha]_D^{21}$ +92.2° (*c* 0.25, 50% MeOH); IR: 3450 (OH); NMR: 7.6—7.2 (Ph, m), 5.46 (methine, s), 4.36 (H_1; s), 4.22 (H_{6e}; q, $J_{6e,5}$=2.5, $J_{6e,6a}$=7.5), 3.95—3.3 (H_3, H_4, H_5, H_{6a}; m), 3.37 (OMe), 3.05 and 2.75 (2×OH; each broad s), 1.28 (*C*-Me, s).

Found: C, 60.54; H, 6.78%. Calcd for $C_{15}H_{20}O_6$; C, 60.80; H, 6.80%.

Methyl 2,2'-Anhydro-3-O-benzoyl-4,6-O-benzylidene-2-C-hydroxymethyl-α-D-mannopyranoside (5). To a suspension of **1** (200 mg, 0.52 mmol) in benzene (40 ml)–ethanol (6 ml) was added dropwise a solution of diazomethane (1 mmol) in ether (30 ml) at O °C. With proceeding the reaction, the mixture turned to be homogeneous. After standing the mixture at 0 °C for 3 h, the solution was evaporated, and the resulting sirup crystallized gradually. The crystals were recrystallized from ethanol to give colourless needles in a quantitative yield. Mp 144 °C; $[\alpha]_D^{22}$ +13.1° (*c* 1.0, acetone); IR: 1720 (ester), 1590 and 710 (Ph); NMR: 8.12—7.22 (Ph and PhCO; m), 6.01 (H_3; d, $J_{3,4}$=10.0), 4.34 (H_{6e}; q, $J_{6e,6a}$=8.8, J_{6e}=3.7), 4.23 (H_1, s), 4.10 (H_4; t, $J_{4,5}$=8.2), *ca.* 4.08 (H_5, m), 3.88 (H_{6a}; q, $J_{6a,5}$=9.8), 3.41 (OMe), 2.82 and 2.74 (CH_2; ABq, J=4.0).

Found: C, 66.13; H, 5.62%. Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57%.

Methyl 4,6-O-Benzylidene-2-C-methyl-α-D-mannopyranoside (6). To a solution of **5** (200 mg, 0.5 mmol) in ether (20 ml) was added lithium aluminium hydride (60 mg), and the mixture was stood at room temperature for 1 h. The excess hydride was carefully decomposed with water, and the water layer was extracted with ether. The combined ether extract was washed with water, dried, and evaporated to give a colorless needles which were recrystallized from ethanol-hexane. Yield, 100 mg (67.2%); mp 149—150 °C; $[\alpha]_D^{22}$ +39.1° (*c* 0.5, 50% MeOH); IR: 3450 and 3370 (OH), 1450 and 700 (Ph).

Found: 61.14; H, 6.78%. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80%.

Methyl 2,2'-Anhydro-4,6-O-benzylidene-2-C-hydroxymethyl- (8) and 4,6-O-benzylidene-2-C-methoxymethyl-α-D-mannopyranoside (7). A suspension of **5** (200 mg, 0.5 mmol) and barium oxide (200 mg, 1.25 mmol) in methanol (20 ml) was refluxed for 30 min, filtered, and then evaporated. A solution of the residue in methylene chloride was washed with water, dried, and evaporated to give a sirup which showed two spots on tlc (R_f=0.4 and 0.2; benzene/methanol/ethyl acetate=5/1/1). The two products were separated on a silica gel column, to give **8** (R_f=0.4; 35 mg, 23.7%) and **7** R_f=0.2; 30 mg, 18.3%).

Compound **8**: mp 160—162 °C; $[\alpha]_D^{21}$ +77.4° (*c* 0.25, CH_2Cl_2); IR: 3300 (OH), 3000 (epoxy methylene); NMR: 7.5—7.2 (Ph; m), 5.52 (methine; s), 4.35—4.15 (H_{6e}, H_4; m), 4.19 (H_1; s) 3.77 (H_5; sex, $J_{6e,5}$=4.0, $J_{5,6a}$=$J_{5,4}$=10.0), 3.82 (H_3; d, $J_{3,4}$=9.5), 3.16 (H_{6a}; t, $J_{6a,6e}$=8.0), 3.36 (OMe), 3.13 and 2.70 (CH_2; ABq, J=5.0), 2.05 (OH).

Found; C, 61.09; H, 6.35%. Calcd for $C_{15}H_{18}O_6$: C, 61.21; H, 6.17%.

Compound **7**: mp 163—165 °C; $[\alpha]_D^{22}$ +50.6° (*c* 0.58, CH_2Cl_2); IR: 3470 (OH); NMR: 7.5—7.2 (Ph, m), 5.53 (methine, s), 4.55 (H_1; s), 4.3—4.2 (H_4), 3.9—3.75 (H_{6e}, H_{6a}, H_5, H_3; m), 3.70 and 3.51 (CH_2; ABq, J=11.0), 3.36 and 3.35 (2×OMe), 3.08 and 2.85 (2×OH).

Found: C, 58.69; H, 6.68%. Calcd for $C_{16}H_{22}O_7$; C, 58.88; H, 6.80%.

Methyl 3-O-Benzoyl-4,6-O-benzylidene-2-C-nitromethyl-α-D-mannopyranoside (9). To a solution of nitromethane (5 ml) in tetrahydrofuran (5 ml) were added successively sodium methoxide (Na; 0.07 mmol) and **1** (1 g, 2.6 mmol) with stirring, and the resulting solution was stirred for 6.5 h at room temperature, neutralized with acetic acid (70%), extracted with chloroform. The extract was washed with water, dried, and evaporated to give colorless prisms which were recrystallized from ethanol, and **9** was separated from the corresponding de-*O*-benzoylated compound (**10**) by fractional crystallization from ethanol. Yield, 140 mg (12.1%); mp 221—223 °C; $[\alpha]_D^{22}$ +90.0° (*c* 1.0, acetone); IR: 3450 (OH), 1750 (ester), 1545 (NO_2); NMR; 8.10—7.20 (Ph and PhCO; m), 5.85 (H_3; d, $J_{3,4}$=11.0), 5.49 (CH_2; s), 5.20 (H_1; S), 4.98 and 4.81 (CH_2; ABq, J=11.7), 4.35 (H_{6e}; q, $H_{6a,6e}$=10.0, $J_{6e,5}$=5.0), 4.02 (H_5; m), 3.82 (H_4; t, $J_{4,5}$=11.0), 3.60 (H_{6a}; t, $J_{6a,5}$=10.0), 3.52 (OMe), 3.16 (OH).

Found: C, 59.66; H, 5.25; N, 3.17%. Calcd for $C_{22}H_{23}NO_9$: C, 59.32; H, 5.21; N, 3.14%.

Methyl 4,6-O-Benzylidene-3-C-nitromethyl-α-D-mannopyranoside (10): Yield, 55.5 mg (62.5%); mp 244—245 °C; $[\alpha]_D^{22}$ +40.0° (*c* 1.0, acetone); IR: 3500 and 3400 (OH), 1560 (NO_2).

Found: C, 52.80; H, 5.60; N, 3.91%. Calcd for $C_{15}H_{19}NO_8$: C, 52.78; H, 5.61; N, 4.10%.

Methyl 3-O-Acetyl-4,6-O-benzylidene-2-C-nitromethyl-α-D-mannopyranoside (11). Acid Catalyzed acetylation of **10** (100 mg) at room temperature and recrystallization of the product from ethanol–hexane gave the 3-*O*-acetate in 80.1% (90 mg) yield. Mp 196—197 °C; $[\alpha]_D^{22}$ +22.8° (*c* 0.5, acetone); IR: 3400 (OH), 1708 (ester), 1542 (NO_2); NMR: 7.5—7.25 (Ph; m), 5.51 (methine, s), 5.35 (H_3; d, J=10.0), 4.76 (H_1; s), 4.72 and 4.43 (CH_2; ABq, J=12.0), 4.4—3.8 (H_4, H_5, H_{6a}, H_{6e}; m), 3.43 (OMe), 2.10 (OAc), 1.63 (OH).

Found: C, 52.99; H, 5.47; N, 3.60%. Calcd for $C_{17}H_{21}NO_9$: C, 53.26; H, 5.52; N, 3.65%.

Methyl 2-C-Aminomethyl-4,6-O-benzylidene-α-D-mannopyranoside (12). Hydrogenation of **10** (500 mg) in ethanol in the presence of palladium-charcoal (10%), and cryrestallization of the product from ethanol–hexane gave prisms in 57% (260 mg) yield. Mp 170 °C; $[\alpha]_D^{22}$ +55.2° (*c* 1.0, acetone); IR: 3500 and 3600 (OH), 3290 (NH_2).

Found: C, 57.98; H, 6.87; N, 4.63%. Calcd for $C_{15}H_{21}NO_6$: C, 57.86; H, 6.80; N, 4.50%.

Methyl 2-C-Acetamidomethyl-4,6-O-benzylidene-α-D-mannopyranoside (13). Acetylation of **12** with acetic anhydride in ethanol and recrystallization of the product from ethanol–hexane gave the *N*-acetate in a quantitative yield. Mp 204—205 °C; $[\alpha]_D^{22}$ +34.0° (*c* 0.5, 50% MeOH); IR: 3540 (OH), 3300 (NH), 1635 and 1540 (amide).

Found: C, 58.31; H, 6.69; N, 3.79%. Calcd for $C_{17}H_{23}NO_7$: C, 57.78; H, 6.56; N, 3.96%.

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