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Trimethylaluminium promoted rearrangements of unsaturated sugars into cyclohexanes

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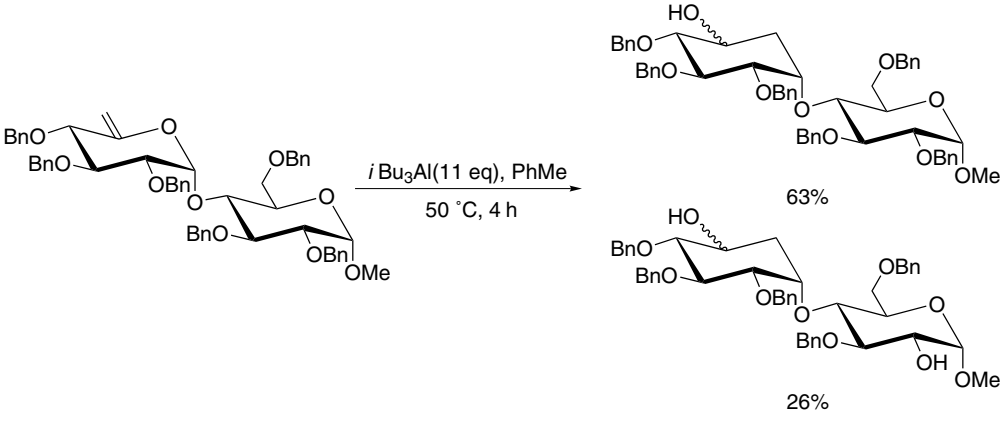
Abstract—Trimethylaluminium induces a stereoselective rearrangement of unsaturated glycosides into polyfunctionalised cyclohexanic rings containing a tertiary alcohol and retaining the anomeric group. In contrast with the previously used triisobutylaluminium, no de-*O*-benzylation reaction was observed.

1. Introduction

The glycoside to carbocycle conversion provides an attractive method for the synthesis of polyfunctionalised enantiomerically pure carbocyclic derivatives from readily available sugar precursors.[1,2] In the classical Ferrier-II reaction,[3] the transformation relies on the *exo*-cleavage of the glycosidic bond. In contrast, Al^iBu_3[4] (TIBAL) or $TiCl_3O^iPr$[5] assisted rearrangements preserve the anomeric group. This feature allowed us to extend this carbocyclisation to C-, S- or Se-glycosides[6] and, more importantly, to disaccharides.[7] During this work, we established that Ti(IV) was not suitable for the rearrangement of disaccharides, whereas Al^iBu_3 promoted the rearrangement of hexenopyranosides bearing a sugar aglycon, thereby providing an attractive synthesis of pseudo-disaccharides.[8] As shown in Scheme 1, Al^iBu_3 mediated rearrangement of particular disaccharides may be accompanied[7] by a de-*O*-benzylation side reaction,[9] due to the reducing properties of the reagent.



Scheme 1.

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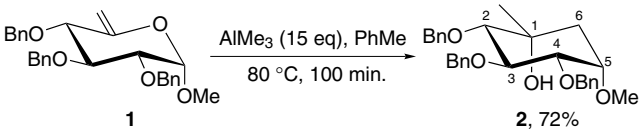
The secondary hydroxyl group, which is present in the cyclohexane moiety (see Scheme 1) also originates from a reduction of a transient ketone function.

Within the framework of a general program on the Al-mediated carbohydrate rearrangements, we report herein on the use of $AlMe_3$, an aluminium-based Lewis acid devoid of reducing properties.

2. Results and discussion

When hexenopyranoside **1**[10] was treated with 15 equiv of $AlMe_3$ at 80 °C, a single carbocyclic product **2** was formed in 72% yield (Scheme 2). The introduction of the methyl group is completely stereoselective and the *R* configuration of carbon 1 was unambiguously assigned from the X-ray crystallographic structure of compound **2**[11] (Fig. 1).



Scheme 2.

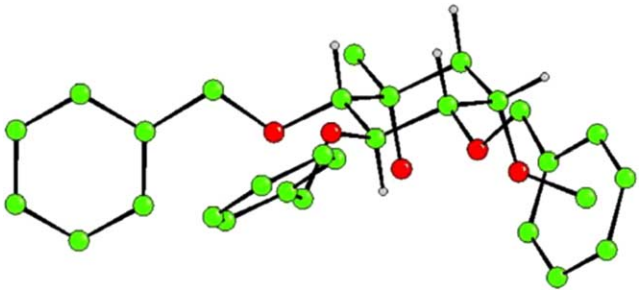


Figure 1.

We have previously shown that the allyl group was not removed during the Al^iBu_3-induced rearrangement.[12] We therefore synthesised the unsaturated sugar **4** starting from the known iodide **3**,[13] and treated it with $AlMe_3$. This reaction gave three separable compounds: the tertiary alcohol **5** (52%), the de-*O*-allylated product **6** (18%) and the unexpected side product **7** (15%) (Scheme 3).

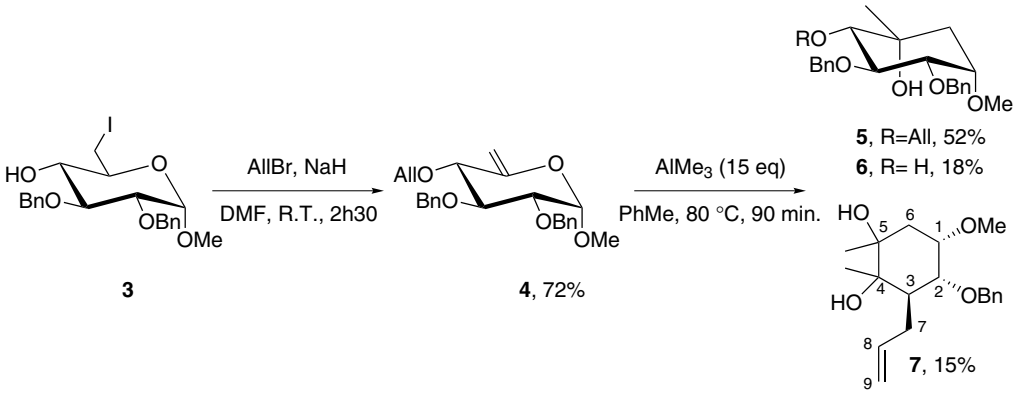
A plausible reaction mechanism leading to the cyclohexanic compound **7** is proposed in Scheme 4. The initially generated ketone **8** undergoes an elimination to afford the unsaturated ketone **9**, which is finally transformed into compound **7** through a Claisen rearrangement. The hexenopyranoside **4** was transformed into the ketone **8** in 73% yield by the action of 1 equiv of $TiCl_4$ at −78 °C. Treatment of this ketone with $AlMe_3$ gave a mixture of the alcohol **5** (32%) and of the product **7** (18%), which indicates the probable intermediacy of the ketone **8** in all those reactions.

We next treated the disaccharide **10**[7] with $AlMe_3$ (15 equiv) at 60 °C for 2 h and observed the formation of the rearranged product **11** in 75% yield, as a single isomer (Scheme 5). No de-*O*-benzylation was observed in this case (compare with Scheme 1).

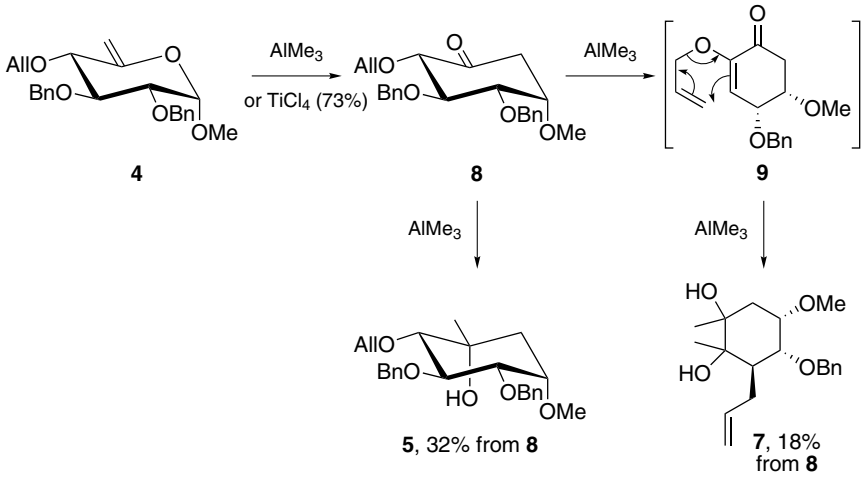
Indeed, as shown in Scheme 6, the selective de-*O*-benzylation of the model perbenzylated glucose derivative **12**[14] is much slower with $AlMe_3$ than with Al^iBu_3,[9] but still allows the regioselective access to the free hydroxyl in position 2 after a prolonged reaction time.

3. Conclusion

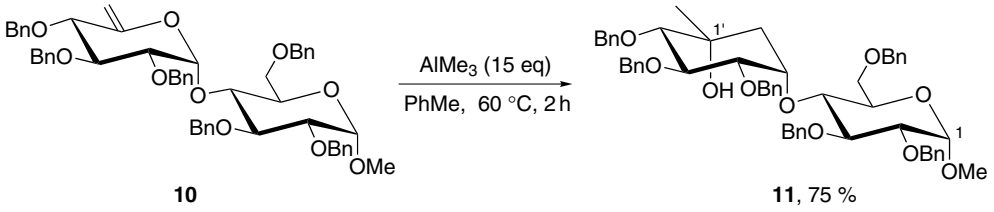
In summary, we have delineated a novel stereoselective access to polyhydroxylated cyclohexanes containing a tertiary alcohol promoted by $AlMe_3$, starting from 6-deoxy-hex-5-eno-pyranosides. Compared to previous syntheses of related compounds[15–17] total stereoselection both at C-1 and C-5 was observed, as well as retention of the aglycon allowing transformations of a disaccharide such as **10**. Furthermore, in comparison with the Al^iBu_3-mediated rearrangement on disaccharides, this version leads to tertiary alcohols without de-*O*-benzylation side reaction.



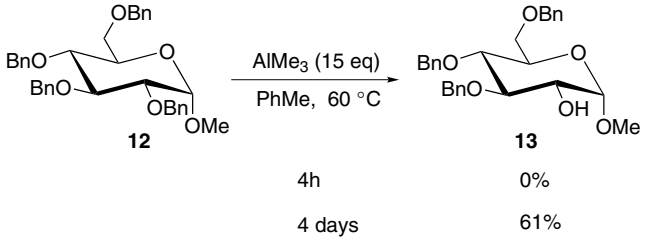
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

4. Experimental

General: Solvents were freshly distilled from Na/benzophenone (THF, toluene), or P_2O_5 (CH_2Cl_2). Reactions were carried under Ar, unless stated otherwise. Melting points were recorded on a Büchi 510 apparatus and are uncorrected. Optical rotations were measured on a Perkin Elmer 241 digital polarimeter with a path length of 1 dm. Mass spectra were recorded on a Nermag R10-10 spectrometer, using chemical ionisation with ammonia. Elemental analyses were performed by the Service d'Analyse de l'Université Pierre et Marie Curie, 75252 Paris Cedex 05, France. NMR spectra were recorded on a Brüker AM-400 (400 and 100.6 MHz, for ^1H and ^{13}C, respectively) or Brüker AC-250 (250 and 63 MHz, for ^1H and ^{13}C, respectively) using TMS as internal standard. TLC was performed on silica gel 60 F_{254} (Merck) and developed by charring with concd H_2SO_4. Flash column chromatography was performed using silica gel 60 (230–400 mesh, Merck). Trimethylaluminium was purchased from Aldrich as a 2 M solution in toluene.

4.1. (1*R*,2*S*,3*R*,4*S*,5*S*)-2,3,4-Tribenzyloxy-5-methyloxy-1-hydroxy-1-methyl cyclohexane 2

Trimethylaluminium (17.8 mL, 35.6 mmol, 2 M in toluene) was added to a stirred solution of **1**[10] (1.06 g, 2.23 mmol) in anhydrous toluene (10 mL) at room temperature under argon. The mixture was heated at 80 °C for 100 min, when TLC (AcOEt/cyclohexane, 3:7) indicated completion of the reaction. The mixture was cooled to 0 °C and toluene saturated with water (20 mL), then water (20 mL) were added dropwise over 15 min. AcOEt (50 mL) was added at room temperature and the aqueous layer was extracted with AcOEt (2 × 100 mL). Combined extracts were dried ($MgSO_4$), filtered and the solvent was removed in vacuo. The residue was purified by flash chromatography (cyclohexane/AcOEt, 3:1) to afford **2** (789 mg, 72%), as a colourless oil.

2: $[\alpha]_D^{20} = -0.7$ (*c* 2.4, $CHCl_3$); mp 48–52 °C (hexane); δ_H (400 MHz, $CDCl_3$) 7.41–7.30 (m, 15H, H arom.), 5.03 (d, 1H, $J = 11.2$ Hz, CHPh), 5.02 (d, 1H, $J = 10.5$ Hz, CHPh), 4.92 (d, 1H, $J = 10.5$ Hz, CHPh), 4.84 (d, 1H, $J = 11.9$ Hz, CHPh), 4.76 (d, 1H, $J = 11.9$ Hz, CHPh), 4.73 (d, 1H, $J = 11.2$ Hz, CHPh), 4.16 (t, 1H, $J_{3,2} = J_{3,4} = 9.6$ Hz, H-3), 4.12 (br s, 1H, OH), 3.72 (q, 1H, $J = 3$ Hz, H-5), 3.54 (s, 3H, OMe), 3.49 (dd, 1H,

H-4), 3.19 (d, 1H, H-2), 2.15 (dd, 1H, $J_{6a,5} = 3.5$ Hz, $J_{6a,6b} = 15.2$ Hz, H-6a), 1.32 (dd, 1H, $J_{6b,5} = 2.5$ Hz, H-6b), 1.17 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$) 138.8, 138.4, 138.3 (3 C arom. quat.), 128.7–127.5 (15 C arom.), 85.5 (C-2), 82.8 (C-4), 80.9 (C-3), 78.3 (C-5), 76.0, 75.9, 73.0 (3× *C*HPh), 73.5 (C-1), 58.9 (OMe), 35.8 (C-6), 26.3 (C-7); m/z 480 $(M+NH4)^+$; Anal. Calcd for $C_{29}H_{34}O_5$: C, 75.28; H, 7.42; found. C, 75.29; H, 7.50.

4.2. Methyl 2,3-di-O-benzyl-4-O-allyl-6-deoxy-α-D-xylo-hex-5-enopyranoside 4

Methyl 2,3-di-O-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside[13] **3** (500 mg, 1.0 mmol) was dissolved in anhydrous DMF (4 mL), allyl bromide (0.18 mL, 2.0 mmol) and sodium hydride (210 mg, 5.0 mmol, 60% in mineral oil) were then added. After 2 h 30 min of stirring at room temperature, TLC (toluene/AcOEt, 9:1) indicated completion of the reaction. Excess NaH was quenched by MeOH (3 mL). The solvent was removed in vacuo and the residue was partitioned between DCM (50 mL) and water (50 mL). The aqueous layer was extracted with DCM (2×50 mL) and the combined extracts were washed with brine (50 mL), dried ($MgSO_4$), filtered and the solvent was removed in vacuo. The residue was purified by flash chromatography (AcOEt/cyclohexane: 1/7) to afford **4** (296 mg, 72%), as a colourless oil.

4: $[\alpha]_D^{20} = -16$ (c 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.42–7.30 (m, 10H, H arom.), 6.00 (ddt, 1H, $J_{B,Ca} = 17.3$ Hz, $J_{B,Cb} = 10.5$ Hz, $J_{B,A} = 5.7$ Hz, H–B), 5.36 (ddt, 1H, $J_{Ca,Cb} = J_{Ca,A} = 1.6$ Hz, H–Ca), 5.24 (ddt, 1H, $J_{Cb,A} = 1.3$ Hz, H–Cb), 4.91 (s, 2H, 2 CHPh), 4.87 (d, 1H, $J = 12.2$ Hz, CHPh), 4.85 (br s, 1H, H-6a), 4.73 (br s, 1H, H-6b), 4.71 (d, 1H, $J = 12.2$ Hz, CHPh), 4.65 (d, 1H, $J_{1,2} = 3.4$ Hz, H-1), 4.29 (dt, 2H, $J = 12.7$ Hz, 2 H–A), 3.95 (t, 1H, $J_{3,2} = J_{3,4} = 9.3$ Hz, H-3), 3.82 (dt, 1H, $J_{4,6} = 2.1$ Hz, H-4), 3.61 (d, 1H, H-2), 3.46 (s, 3H, OMe); δ_C (100 MHz, $CDCl_3$) 153.8 (C-5), 138.6, 138.1 (2 C arom. quat.), 134.4 (C–B), 128.4–127.6 (10 C arom.), 117.3 (C–C), 99.0 (C-1), 96.6 (C-6), 81.1 (C-3), 79.1, 79.0 (C-2 and C-4), 75.8, 73.6 (2 *C*HPh), 73.3 (C–A), 55.4 (OMe); m/z 414 $(M+NH4)^+$, 397 $(M+H)^+$; Anal. Calcd for $C_{24}H_{28}O_5$: C, 72.70; H, 7.12; found. C, 72.72; H, 7.16.

4.3. Rearrangement of hexenopyranoside 4 into (1*R*,2*S*,3*R*,4*S*,5*S*)-2-allyloxy-3,4-dibenzyloxy-5-methyloxy-1-hydroxy-1-methyl cyclohexane 5, (1*R*,2*S*,3*R*,4*S*,5*S*)-3,4-dibenzyloxy-5-methyloxy-1,2-dihydroxy-1-methyl cyclohexane 6 and cyclohexane 7

Trimethylaluminium (12.5 mL, 25 mmol, 2 M in toluene) was added to a stirred solution of **4** (650 mg, 1.64 mmol) in anhydrous toluene (7 mL) at room temperature under argon. The mixture was heated at 80 °C for 90 min, when TLC (AcOEt/cyclohexane, 3:7) indicated completion of the reaction. The mixture was cooled to 0 °C and toluene saturated with water (20 mL), then water (20 mL) were added dropwise over 15 min. AcOEt (50 mL) was added at room temperature and the aqueous layer was extracted with AcOEt (2×100 mL). Combined extracts were dried ($MgSO_4$), filtered and the solvent was removed in vacuo. The residue was purified by flash chromatography (graduent cyclohexane/AcOEt, 5:1 to 3:1) to afford **7** (79 mg, 15%), further elution afforded **5** (351 mg, 52%) and then **6** (110 mg, 18%).

5: $[\alpha]_D^{20} = +7.5$ (c 0.8, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.41–7.30 (m, 10H, H arom.), 6.04 (dddd, 1H, $J_{B,Ca} = 16$ Hz, $J_{B,Cb} = 10.3$ Hz, $J_{B,A'} = 6.3$ Hz, $J_{B,A} = 5.7$ Hz, H–B), 5.29 (dq, 1H, $J_{Ca,Cb} = J_{Ca,A} = 1.6$ Hz, H–Ca), 5.19 (dq, 1H, $J_{Cb,A} = 1.3$ Hz, H–Cb), 4.95 (d, 1H, $J = 10.5$ Hz, CHPh), 4.91 (d, 1H, $J = 10.5$ Hz, CHPh), 4.81 (d, 1H, $J = 11.9$ Hz, CHPh), 4.75 (d, 1H, $J = 11.9$ Hz, CHPh), 4.49 (ddt, 1H, $J_{A,A'} = 12.2$ Hz, H–A), 4.49 (ddt, 1H, H–A′), 4.14 (br s, 1H, OH), 4.07 (t, 1H, $J_{3,2} = J_{3,4} = 9.7$ Hz, H-3), 3.72 (q, 1H, $J_{5,4} = J_{5,6} = 3$ Hz, H-5), 3.54 (s, 3H, OMe), 3.45 (dd, 1H, H-4), 3.08 (d, 1H, H-2), 2.17 (dd, 1H, $J_{6a,5} = 3.4$ Hz, $J_{6a,6b} = 15.2$ Hz, H-6a), 1.34 (dd, 1H, $J_{6b,5} = 2.5$ Hz, H-6b), 1.27 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$), 138.8, 138.3 (2 C arom. quat.), 135.4 (C–B), 128.4–127.6 (10 C arom.), 117.0 (C–C), 85.5 (C-2), 82.7 (C-4), 80.8 (C-3), 78.4 (C-5), 76.0 (*C*HPh), 75.2 (C–A), 73.5 (C-1), 73.0 (*C*HPh), 58.9 (OMe), 35.7 (C-6), 26.3 (C-7); m/z 430 $(M+NH4)^+$; Anal. Calcd for $C_{25}H_{32}O_5$: C, 72.75; H, 7.83; found. C, 72.68; H, 7.93.

6: $[\alpha]_D^{20} = -6.4$ (c 0.7, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.46–7.30 (m, 10H, H arom.), 4.97 (d, 1H, $J = 10.9$ Hz, CHPh), 4.91 (d, 1H, $J = 10.9$ Hz, CHPh), 4.81 (d, 1H, $J = 11.9$ Hz, CHPh), 4.73 (d, 1H, $J = 11.9$ Hz, CHPh), 4.08 (br s, 1H, OH-5), 3.83 (t, 1H, $J_{3,2} = J_{3,4} = 9.2$ Hz, H-3), 3.74 (dt, 1H, $J_{5,4} = J_{5,6b} = 2.8$ Hz, $J_{5,6a} = 3.6$ Hz, H-5), 3.55 (s, 3H, OMe), 3.47 (dd, 1H, H-4), 3.33 (t, 1H,$J = 8.4$ Hz, H-2), 2.61 (bd, 1H, 6.9 Hz, OH-2), 2.20 (dd, 1H, $J_{6a,5} = 3.9$ Hz, $J_{6a,6b} = 15.2$ Hz, H-6a), 1.42 (dd, 1H, $J_{6b,5} = 2.2$ Hz, H-6b), 1.28 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$), 138.8, 138.2 (2 C arom. quat.), 128.6–127.6 (10 C arom.), 82.0 (C-4), 81.3 (C-3), 78.5 (C-5), 78.4 (C-2), 75.8 (*C*HPh), 75.1 (C-1), 73.0 (*C*HPh), 59.0 (OMe), 35.7 (C-6), 25.8 (C-7); m/z 390 $(M+NH4)^+$; Anal. Calcd for $C_{22}H_{28}O_5$: C, 70.94; H, 7.58; found. C, 70.81; H, 7.75.

7: δ_H (400 MHz, $CDCl_3$) 7.40–7.35 (15H, H arom.), 6.00 (dddd, 1H, $J_{8,9a} = 17.2$ Hz, $J_{8,9b} = 9.9$ Hz, $J_{8,7} = 9.1$ Hz, $J_{8,7} = 5.6$ Hz, H-8), 5.19 (bd, 1H, H-9a), 5.19 (bd, 1H, H-9b), 4.72 (d, 1H, $J = 11.5$ Hz, CHPh), 4.55 (d, 1H, $J = 11.5$ Hz, CHPh), 4.51 (br s, 1H, OH), 3.88 (q, 1H, $J_{1,2} = J_{1,6} = 3$ Hz, H-1), 3.71 (dd, 1H, $J_{2,3} = 12.6$ Hz, H-2), 3.51 (s, 3H, OMe), 2.81–2.72 (m, 1H, H-7a), 2.46 (ddd, 1H, $J_{7a,7b} = 14.8$ Hz, $J = 11.1$ Hz, $J = 3.5$ Hz H-7b), 2.34 (dt, 1H, $J_{3,2} = 11.6$ Hz, $J_{3,7a} = J_{3,7b} = 4.2$ Hz, H-3), 1.97 (dd, 1H, $J_{6a,6b} = 14.9$ Hz, $J_{6a,1} = 3.5$ Hz, H-6a), 2.17 (dd, 1H, $J_{6a,1} = 3.4$ Hz, H-6b), 1.36 (s, 3H, CH_3), 1.17 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$), 138.6 (C-8), 138.2 (C arom. quat.), 128.4, 127.9, 127.7 (5 C arom.), 116.3 (C-9), 78.6, 74.3 (C-4, C-5), 77.5 (C-2), 76.9 (C-1), 71.4 (*C*HPh), 58.3 (OMe), 40.7 (C-3), 34.4 (C-6), 30.0 (C-7), 22.8, 21.6 (2 Me); m/z 338 $(M+NH4)^+$, 321 $(M+H)^+$; Exact Mass calcd. for $C_{19}H_{29}O_4$: 321.2066 $(M+H)^+$; found. 321.206.

4.4. (2*S*,3*R*,4*S*,5*S*)-2-Allyloxy-3,4-tribenzyloxy-5-methyloxy cyclohexanone 8

$TiCl_4$ (34 μL, mmol) was added to a cooled (−78 °C) solution of **4** (73 mg, mmol) in dry dichloromethane (1 mL), under argon. The reaction mixture was stirred at −78 °C for 2 h, and then poured into a stirred ice-cold solution of $NaHCO_3$. The aqueous layer was extracted with DCM (2×10 mL). Combined extracts were dried ($MgSO_4$), filtered and the solvent was removed in vacuo. The residue was purified by flash chromatography (cyclohexane/AcOEt, 4:1) to afford **8** (53 mg, 73%), as a white solid.

8: $[\alpha]_D^{20} = -41$ (*c* 1.0, $CHCl_3$); mp 61 °C (cyclohexane/ethyl acetate); δ_H (400 MHz, $CDCl_3$) 7.42–7.30 (m, 10H, H arom.), 5.99 (dddd, 1H, $J_{B,Ca} = 16$ Hz, $J_{B,Cb} = 10.3$ Hz, $J_{B,Ab} = 6.3$ Hz, $J_{B,Aa} = 5.7$ Hz, H–B), 5.35 (dq, 1H, $J_{Ca,Cb} = J_{Ca,A} = 1.6$ Hz, H–Ca), 5.23 (dq, 1H, $J_{Cb,A} = 1.3$ Hz, H–Cb), 4.92 (d, 1H, $J = 10.5$ Hz, CHPh), 4.88 (d, 1H, $J = 10.5$ Hz, CHPh), 4.87 (d, 1H, $J = 12.1$ Hz, CHPh), 4.79 (d, 1H, $J = 11.9$ Hz, CHPh), 4.41 (ddt, 1H, $J_{Aa,Ab} = 12.2$ Hz, H–Aa), 4.11 (ddt, 1H, H–Ab), 4.10 (t, 1H, $J_{3,2} = J_{3,4} = 8.8$ Hz, H-3), 3.98 (d, 1H, H-2), 3.83–3.78 (m, 2H, H-4 H-5), 3.42 (s, 3H, OMe), 2.79 (dd, 1H, $J_{6a,5} = 4.1$ Hz, $J_{6a,6b} = 14.5$ Hz, H-6a), 2.36 (dd, 1H, $J_{6b,5} = 1,4$ Hz, H-6b); δ_C (100 MHz, $CDCl_3$) 203.7 (C-1), 138.4, 138.1 (2 C arom. quat.), 134.3 (C–B), 128.4–127.7 (10 C arom.), 117.6 (C-C), 85.4 (C-2), 82.2 (C-3), 82.7, 75.3 (C-4 or C-5), 76.0 (*C*HPh), 73.0 (*C*HPh), 72.7 (C–A), 57.3 (OMe), 40.4 (C-6); *m*/*z* 414 $(M+NH4)^+$; Anal. Calcd for $C_{24}H_{28}O_5$: C, 72.69; H, 7.13; found. C, 72.51; H, 7.16.

4.5. Methyl 4-[(1*R*,2*S*,3*R*,4*S*,5*S*)-2,3,4-tribenzyloxy-1,5-dihydroxy-5-methyl-cyclohexyl]-2,3,4-*O*-benzyl-α-D-glucopyranoside 11

Trimethylaluminium (0.57 mL, 1.14 mmol, 2 M in toluene) was added to a stirred solution of **10**[7] (100 g, 0.11 mmol) in anhydrous toluene (1 mL) at room temperature under argon. The mixture was heated at 60 °C for 2 h, when TLC (AcOEt/cyclohexane, 3:7) indicated completion of the reaction. The mixture was cooled to 0 °C and toluene saturated with water (2 mL), then water (5 mL) were added dropwise over 15 min. AcOEt (5 mL) was added at room temperature and the aqueous layer was extracted with AcOEt (2×10 mL). Combined extracts were dried ($MgSO_4$), filtered and the solvent was removed in vacuo. The residue was purified by flash chromatography (cyclohexane/AcOEt, 3:1) to afford **11** (76 mg, 75%), as a colourless oil.

11: $[\alpha]_D^{20} = +33.5$ (*c* 0.8, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.39–7.09 (m, 30H, H arom.), 5.02 (d, 1H, $J = 11.6$ Hz, CHPh), 4.93 (d, 1H, $J = 11.6$ Hz, CHPh), 4.88 (d, 1H, $J = 11.2$ Hz, CHPh), 4.72 (d, 1H, $J = 12.1$ Hz, CHPh), 4.71 (d, 2H, $J = 12.0$ Hz, 2 CHPh), 4.63 (d, 1H, $J = 12.0$ Hz, CHPh), 4.62 (d, 1H, $J_{1,2} = 3.6$ Hz, H-1), 4.60 (d, 1H, $J = 11.2$ Hz, CHPh), 4.59 (d, 1H, $J = 12.1$ Hz, CHPh), 4.49 (d, 1H, $J = 12.0$ Hz, CHPh), 4.36 (d, 1H, $J = 11.2$ Hz, CHPh), 4.27 (d, 1H, $J = 11.2$ Hz, CHPh), 4.22–4.18 (m, 1H, H-5′), 4.01 (t, 1H, $J_{4,3} = J_{4,5} = 9.6$ Hz, H-4), 3.99 (bt, 1H, $J_{3',2'} = J_{3',4'} = 8.2$ Hz, H-3′), 3.87 (t, 1H, $J_{3,2} = 9.3$ Hz, H-3), 3.83–3.67 (m, 4H, H-5, H-6, OH), 3.55 (dd, 1H, H-2), 3.41 (s, 3H, OMe), 3.11 (bd, 1H, H-4′), 3.09 (d, 1H, H-2′), 1.90 (dd, 1H, $J_{6'a,5'} = 5.0$ Hz, $J_{6'a,6'b} = 14.6$ Hz, H-6′a), 1.23 (bd, 1H, H-6′b), 1.13 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$), 139.1, 138.7, 138.6, 138.3, 138.0, 137.5 (6 C arom. quat.), 128.4–126.9 (30 C arom.), 97.9 (C-1), 84.8 (C-2′), 82.4 (C-4′), 81.1 (C-3), 79.8 (C-2), 79.7 (C-3′), 76.1 (C-4), 75.9, 75.3 (2 *C*HPh), 74.8 (C-5′), 74.3, 73.6, 73.4, 72.7 (4 *C*HPh), 70.1 (C-5), 68.7 (C-6), 55.2 (OMe), 37.9 (C-6′), 26.4 (Me); *m*/*z* 912 $(M+NH4)^+$; Anal. Calcd for $C_{56}H_{62}O_{10}$: C, 75.14; H, 6.98; found. C, 75.12; H, 7.11.

References and notes

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