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Note

A convenient synthesis of 1,2-*O*-benzylidene and 1,2-*O*-ethylidene derivatives of carbohydrates

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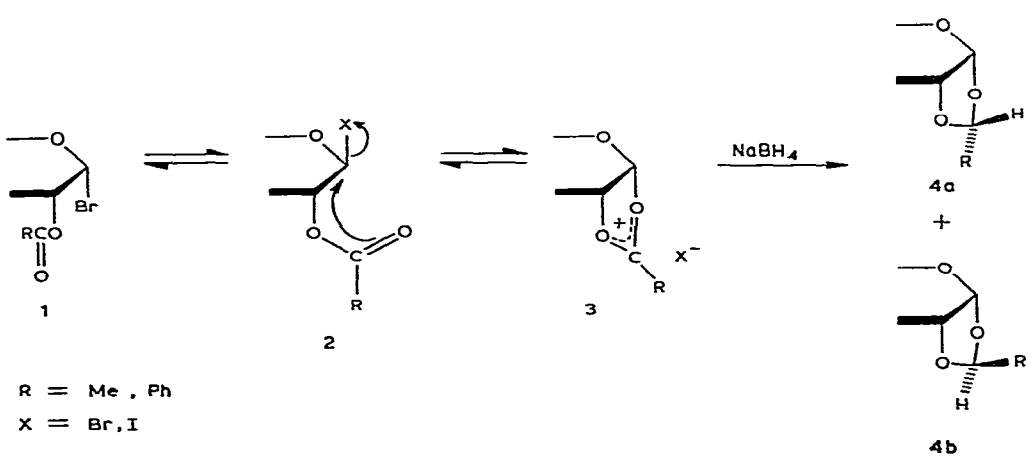
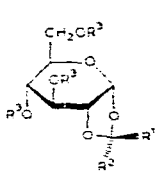
Alkylidene derivatives of sugars are widely employed[1,2] in synthesis and they are of interest for conformational studies of fused-ring heterocyclic systems.

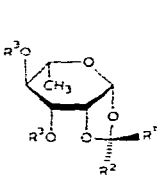
Two main methods for the synthesis of the title compounds involve (*a*) treatment of 1,2-*O*-alkoxyalkylidene sugar derivatives with an aldehyde or its acetal in *N*,*N*-dimethylformamide in the presence of toluene-*p*-sulfonic acid monohydrate and methyl orthoformate[3] and (*b*) interaction of 1,2-*trans*-acylglycosyl chlorides with sodium borohydride in *N*,*N*-dimethylformamide, 1,2-dimethoxyethane, or pyridine[4,5]. The necessary starting-compounds for these syntheses are usually obtainable from acylglycosyl bromides (1,2-*trans*-acylglycosyl chlorides can be prepared from 1,2-*trans*-peracetates as well[5,6]).

Having used the approach successfully to prepare 1,2-*O*-(1-cyanoalkylidene) derivatives of neutral sugars[7], we describe now a convenient access to 1,2-*O*-benzylidene and 1,2-*O*-ethylidene derivatives, starting from easily available, stable acylglycosyl bromides of type **1** (D-*gluco* and D-*galacto* series) and type **2** (D- and L-*manno* series) according to the scheme:

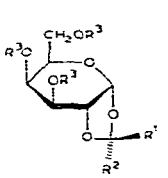




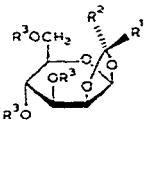
5a $R^1 = H, R^2 = Me, R^3 = H$
5b $R^1 = Me, R^2 = H, R^3 = H$
6a $R^1 = H, R^2 = Me, R^3 = Ac$
6b $R^1 = Me, R^2 = H, R^3 = Ac$
7a $R^1 = H, R^2 = Ph, R^3 = H$
7b $R^1 = Ph, R^2 = H, R^3 = H$
8a $R^1 = H, R^2 = Ph, R^3 = Ac$
8b $R^1 = Ph, R^2 = H, R^3 = Ac$
9a $R^1 = H, R^2 = Me, R^3 = Bz$
9b $R^1 = Me, R^2 = H, R^3 = Bz$
10a $R^1 = H, R^2 = Ph, R^3 = Bz$
10b $R^1 = Ph, R^2 = H, R^3 = Bz$



11a $R^1 = H, R^2 = Me, R^3 = H$
11b $R^1 = Me, R^2 = H, R^3 = H$
12a $R^1 = H, R^2 = Me, R^3 = Ac$
12b $R^1 = Me, R^2 = H, R^3 = Ac$
13a $R^1 = H, R^2 = Ph, R^3 = H$
13b $R^1 = Ph, R^2 = H, R^3 = H$
14a $R^1 = H, R^2 = Ph, R^3 = Ac$
14b $R^1 = Ph, R^2 = H, R^3 = Ac$



15a $R^1 = H, R^2 = Me, R^3 = H$
15b $R^1 = Me, R^2 = H, R^3 = H$
16a $R^1 = H, R^2 = Me, R^3 = Ac$
16b $R^1 = Me, R^2 = H, R^3 = Ac$



17a $R^1 = H, R^2 = Me, R^3 = H$
17b $R^1 = Me, R^2 = H, R^3 = H$
18a $R^1 = H, R^2 = Me, R^3 = Ac$
18b $R^1 = Me, R^2 = H, R^3 = Ac$

The presence of halogen ions in the reaction medium ensures equilibration[8] between **1** and highly reactive[9] **2**, which, in turn, is in equilibrium with cation **3**. Reduction of this cation affords, irreversibly, alkylidene derivatives **4** as a mixture of *R* (**4a**) and *S* (**4b**) isomers.

The following conditions were optimal. Acylglycosyl bromide **1** (or **2**) is treated with sodium borohydride (1.5 mol) in dry acetonitrile for 15–48 h at room temperature. No additional reagents are necessary for 1,2-*trans*-acylglycosyl bromides, whereas, for the less-reactive 1,2-*cis*-acylglycosyl bromides, the presence of tetrabutylammonium iodide (0.5 mol) is required. This procedure, with subsequent deacylation, gave the following diastereomeric pairs of 1,2-*O*-alkylidenehexopyranose derivatives with *gluco* (**5ab**, **7ab**), *galacto* (**15ab**), and *manno* configurations (**11ab**, **13ab**, **17ab**) in yields of 83–92% after column chromatography, which removes possible, minor 1,5-anhydrohexitol contaminants.

Acetylation of each of the aforementioned compounds and benzylation[10] of **5ab** and **7ab** afforded the respective, fully protected derivatives, individual (*R*)- and (*S*)-isomers being separated by chromatography.

The (*R*):(*S*) ratios were determined from the integrated intensities of the characteristic doublets of the acetal Me group or the benzylidene singlets in the p.m.r. spectra of the ethylidene and benzylidene derivatives, respectively.

The benzylidene derivatives were completely hydrolysed with aqueous 90% trifluoroacetic acid[11] for 2 h at room temperature. The ethylidene group was practically unaffected under these conditions, thus paralleling the stability of the 4,6-*O*-ethylidene group in D-galactopyranose derivatives[12]. Removal of the 1,2-*O*-ethylidene group required treatment with boiling, aqueous 80% acetic acid for 6 h. Also effective was mild acetolysis, which does not affect glycosidic bonds[12].

EXPERIMENTAL

Optical rotations were determined with a Perkin–Elmer 141 polarimeter at 22 ±2°. Melting points were determined with a Kofler apparatus and are uncorrected. P.m.r. spectra (internal Me_4Si) were recorded with Varian DA-60-IL and Tesla BS-497 (100 MHz, CSSR) spectrometers. Column chromatography was performed on Silica Gel L (40–100 μm, CSSR). T.l.c. was performed on Silica Gel L (5–40 μm, CSSR) with *A*, ethyl acetate; *B*, 2:1 benzene–ether; and *C*, 10:1 benzene–ether; and detection by charring with sulfuric acid. Acetonitrile was dried with $CaCl_2$, and distilled from $CaCl_2$ and then from CaH_2. Acetylglycosyl bromides were prepared as described[7,12], and benzoyl-glucosyl and -rhamnosyl bromides were prepared analogously from benzoylated D-gluco- and L-rhamno-pyranose, respectively. Solutions were concentrated *in vacuo* at 40°.

3,4,6-Tri-O-*acetyl-1,2*-O-[(R)- *and* (S)-*ethylidene*]-α-D-*glucopyranose* (**6a** *and* **6b**). — A mixture of tetra-*O*-acetyl-α-D-glucopyranosyl bromide (4.1 g, 10 mmol), sodium borohydride (600 mg, 15 mmol), and tetrabutylammonium iodide (2 g, 5 mmol) in acetonitrile (15 mL) was stirred for 20 h at room temperature. The mixture was diluted with chloroform (100 mL), washed with water (3 × 100 mL), filtered through cotton, and concentrated to dryness. The residue was treated with 0.1M methanolic sodium methoxide (15 mL) for 2 h at room temperature, and then concentrated, and the residue was subjected to column chromatography (gradient elution: chloroform → 9:1 chloroform–methanol), to give an isomeric mixture **5ab** (1.9 g, 92%) as a chromatographically homogeneous, colourless syrup, $[\alpha]_D$ +44.0° (*c* 3, methanol), R_F 0.49 (solvent *A*). This product was treated with 1:2 acetic anhydride–pyridine (9 mL) for 15 h at room temperature. Ethanol (3 mL) was added and, after 1 h, the mixture was diluted with chloroform (100 mL), washed with water (3 × 100 mL), and concentrated to dryness. The residue was dried *in vacuo*, to give syrupy **6ab** (2.35 g, 77%), $[\alpha]_D$ +36.0° (*c* 4.6, chloroform). P.m.r. data (CCl_4): δ 1.28 and 1.44 (2 d, 3 H, *J* 5 Hz each, ethylidene Me of **6b** and **6a** in the ratio 1:2), 1.97, 2.02, 2.04, and 2.05 (4 s, 9 H, 3 AcO).

Anal. Calc. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.60; H, 6.09.

Column chromatography (gradient elution benzene → 7:3 benzene–ether) of the mixture gave **6a** as a syrup, $[\alpha]_D$ +21.4° (*c* 4.5, chloroform), R_F 0.45 (solvent *B*); lit.[4] $[\alpha]_D^{20}$ +25° (chloroform); and **6b** as a syrup, $[\alpha]_D$ +67.5° (*c* 4.2, chloroform), R_F 0.49; lit.[4] $[\alpha]_D^{20}$ +74° (chloroform).

3,4,6-Tri-O-*acetyl-1,2*-O-[(R)- *and* (S)-*ethylidene*]-α-D-*galactopyranose* (**16a** *and* **16b**). — A mixture of tetra-*O*-acetyl-α-D-galactopyranosyl bromide (2.05 g, 5 mmol), sodium borohydride (950 mg, 25 mmol), tetrabutylammonium iodide (920 mg, 2.5 mmol), and acetonitrile (10 mL) was stirred for 24 h at room temperature. The mixture was worked-up as described above, to give a colourless, syrupy mixture (940 mg, 91%) of **15a** [R_F 0.42 (solvent *A*)] and **15b** (R_F 0.49), $[\alpha]_D$ +74.5° (*c* 1.9, methanol). Acetylation, as described above, afforded a syrupy mixture of **16a** and **16b** in the ratio 5:2 (p.m.r. data), $[\alpha]_D$ +93.0° (*c* 2.6, chloroform).

Anal. Calc. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.61; H, 5.86.

Column chromatography, as described above, gave **16a** as a syrup, $[\alpha]_D$ +96.0° (*c* 2.8, chloroform), R_F 0.47 (solvent *B*). P.m.r. data (CCl_4): δ 1.45 (d, 3 H, *J* 5 Hz, ethylidene Me), 2.03 (×2), 2.07 (2 s, 9 H, 3 AcO), and 5.45 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1). Eluted second was **16b** as a syrup, $[\alpha]_D$ +88.0° (*c* 2, chloroform), R_F 0.49. P.m.r. data (CCl_4): δ 1.35 (d, 3 H, *J* 5 Hz, ethylidene Me), 2.02 (×2), 2.07 (2 s, 9 H, 3 AcO), and 5.50 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1).

3,4,6-Tri-O-*acetyl-1,2*-O-[(R)- *and* (S)-*benzylidene*]-α-D-*glucopyranose* (**8a** *and* **8b**). — A mixture of tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (4.6 g, 6.8 mmol), sodium borohydride (400 mg, 10.5 mmol), tetrabutylammonium iodide (1.3 g, 3.5 mmol), and acetonitrile (15 mL) was stirred for 48 h at room temperature. Work-up, as described above, afforded a chromatographically homogeneous mixture **7ab** (1.67 g, 87%), $[\alpha]_D$ +43.0° (*c* 1.5, methanol), R_F 0.53 (solvent *A*). Acetylation, as described above, gave **8ab** (2.28 g, 95%), $[\alpha]_D$ + 43.0° (*c* 3, chloroform), **ab**-ratio 7:2 (p.m.r. data).

Anal. Calc. for $C_{19}H_{22}O_9$: C, 57.86; H, 5.62. Found: C, 57.37; H, 5.66.

Column chromatography, as described above, gave **8a** as a syrup, $[\alpha]_D$ +50.0° (*c* 1.9, chloroform), R_F 0.56 (solvent *B*); lit.[4] $[\alpha]_D^{20}$ +56° (chloroform). P.m.r. data (CCl_4): δ 1.96 (× 2), 2.05 (2 s, 9 H, 3 AcO), 5.60 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 5.80 (s, 1 H, PhC*H*), and 7.40–7.45 (m, 5 H, Ph). Eluted second was **8b**, m.p. 108–110° (from ether–hexane), $[\alpha]_D$ +48.4° (*c* 3, chloroform), R_F 0.61; lit.[4] m.p. 112–113°, $[\alpha]_D^{20}$ +48° (chloroform). P.m.r. data (CCl_4): δ 2.03 (s, 9 H, 3 AcO), 5.54 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 6.33 (s, 1 H, PhC*H*), and 7.33 (s, 5 H, Ph).

3,4,6-Tri-O-*acetyl-1,2*-O-[(S)- *and* (R)-*ethylidene*]-β-D-*mannopyranose* (**18a** *and* **18b**). — D-Mannopyranose penta-acetate (2.26 g, 5.8 mmol) was conventionally converted[7,12] into the glycosyl bromide, which was stirred with sodium borohydride (1.1 g, 29 mmol) in acetonitrile (15 mL) for 20 h at room temperature. The mixture was worked-up, as described for **6ab**, to give chromatographically homogeneous **17ab** (1.0 g, 83%) as a syrup, $[\alpha]_D$ +4.2° (*c* 2, methanol), R_F 0.42 (solvent *A*). Acetylation afforded a 5:1 (p.m.r. data) mixture (1.34 g) of **18a** + **18b**, $[\alpha]_D$ −12.6° (*c* 2.7, chloroform).

Anal. Calc. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.49; H, 5.91.

Column chromatography (gradient elution: benzene → 7:3 benzene–ether) gave **18a**, m.p. 113–115° (from ether-hexane), $[\alpha]_D$ −17.8° (*c* 1.2, chloroform), R_F 0.36 (solvent *B*). P.m.r. data ($CDCl_3$): δ 1.51 (d, 3 H, *J* 5 Hz, ethylidene Me), 2.03 (× 2), and 2.09 (2 s, 9 H, 3 AcO). Eluted second was **18b**, m.p. 89–91° (from ether–hexane), $[\alpha]_D$ +3.4° (*c* 1.7, chloroform), R_F 0.39. P.m.r. data ($CDCl_3$): δ 1.33 (d, 3 H, *J* 5 Hz, ethylidene Me), 1.98, 2.01, 2.05 (3 s, 9 H, 3 AcO), and 5.33 (d, 1 H, $J_{1,2}$ 2.5 Hz, H-1).

3,4-Di-O-*acetyl-1,2*-O-[(R)- *and* (S)-*ethylidene*]-β-L-*rhamnopyranose* (**12a** *and* **12b**). — L-Rhamnopyranose tetra-acetate (2.16 g, 6.5 mmol) was conventionally converted[7,12] into the glycosyl bromide, which was treated with sodium borohydride (1.24 g, 32.5 mmol) in acetonitrile (15 mL) for 20 h at room temperature. The mixture

was worked-up as described for **6ab**, to give, after chromatography, **11ab** (1.1 g, 87%) as a colourless syrup, $[\alpha]_D$ +15.7° (*c* 2.2, methanol), R_F 0.58 (solvent *A*). Acetylation, as described above, gave a 6:1 mixture of **12a** and **12b** (p.m.r. data) as a chromatographically homogeneous syrup (1.54 g, 97%), $[\alpha]_D$ +25.6° (*c* 3.1, chloroform), R_F 0.50 (solvent *B*). P.m.r. data (CCl_4): δ 1.16 (d, 3 H, $J_{6,5}$ 6 Hz, rhamnose Me), 1.33 (d, *J* 5 Hz, ethylidene Me in **12b**), 1.46 (d, *J* 5 Hz, ethylidene Me in **12a**), 1.98 and 2.03 (2 s, 6 H, 2 AcO).

Anal. Calc. for $C_{12}H_{18}O_7$: C, 52.55; H, 6.56. Found: C, 52.65; H, 6.93.

Crystallisation from ether–hexane gave **12ab** with the same isomer ratio and m.p. 77–79°, $[\alpha]_D$ +33.0° (*c* 0.9, chloroform).

*3,4-Di-*O*-acetyl-1,2-*O*-[(R)- and (S)-benzylidene]-β-*L*-rhamnopyranose* (**14a** *and* **14b**). — Tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide (3.24 g, 6 mmol) was stirred with sodium borohydride (950 mg, 25 mmol) in acetonitrile (10 mL) for 15 h at room temperature. Work-up as described for **6ab** gave a chromatographically homogeneous mixture **13ab** (1.25 g, 83%), $[\alpha]_D$ +41.2° (*c* 3.1, chloroform), R_F 0.68 (solvent *A*). Acetylation, as described above, gave a 10:1 mixture of **14a** and **14b** (1.61 g, 98%), $[\alpha]_D$ +122° (*c* 3.2, chloroform).

Anal. Calc. for $C_{17}H_{20}O_7$: C, 60.71; H, 5.96. Found: C, 60.79; H, 6.13.

Column chromatography (gradient elution: benzene → 7:3 benzene–ether) gave **14a**, m.p. 118–120° (from benzene–hexane), $[\alpha]_D$ +140° (*c* 1.5, chloroform), R_F 0.59 (solvent *B*). P.m.r. data ($CDCl_3$): δ 1.23 (d, 3 H, $J_{6,5}$ 6 Hz, rhamnose Me), 1.99 and 2.02 (2 s, 6 H, 2 AcO), 5.53 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 5.91 (s, 1 H, PhC*H*), and 7.21–7.68 (m, 5 H, Ph). Eluted second was **14b**, m.p. 134–135° (from ether–hexane), $[\alpha]_D$ +1.8° (*c* 3, chloroform), R_F 0.67. P.m.r. data ($CDCl_3$): δ 1.30 (d, 3 H, $J_{6,5}$ 6 Hz, rhamnose Me), 2.05 and 2.08 (2 s, 6 H, 2 AcO), 5.55 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 6.36 (s, 1 H, PhC*H*), and 7.38 (s, 5 H, Ph).

*3,4,6-Tri-*O*-benzyl-1,2-*O*-[(R)- and (S)-ethylidene]-α-D-glucopyranose* (**9a** *and* **9b**). — To a solution of **5ab** (1.4 g, 6.8 mmol) in *N*,*N*-dimethylformamide (20 mL) was added sodium hydride (970 mg, 42 mmol), and the mixture was stirred for 0.5 h at room temperature. Benzyl chloride (3.7 mL, 32 mmol) was added and, after 15 h, the mixture was treated with methanol (5 mL) for 1 h, and then diluted with chloroform (100 mL) and washed with water (4 × 100 mL). The organic layer was filtered through cotton and concentrated, and the residue was subjected to chromatography (gradient elution: benzene → 9:1 benzene–ether), to give **9ab** (2 g, 61%), $[\alpha]_D$ +58.5° (*c* 3.4, chloroform).

Anal. Calc. for $C_{29}H_{32}O_6$: C, 73.10; H, 6.72. Found: C, 73.15; H, 6.71.

Individual isomers were isolated by rechromatography, to give **9a** as a syrup, $[\alpha]_D$ +30.5° (*c* 2.6, chloroform), R_F 0.31 (solvent *C*). P.m.r. data (CCl_4): δ 1.37 (d, 3 H, *J* 5 Hz, ethylidene Me), 5.41 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), and 7.11–7.20 (m, 15 H, aromatic protons). Eluted second was **9b**, m.p. 73–74° (from ether–hexane), $[\alpha]_D$ +83.0° (*c* 1.3, chloroform), R_F 0.43. P.m.r. data (CCl_4): δ 1.28 (d, 3 H, *J* 5 Hz, ethylidene Me), 5.50 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), and 7.11–7.20 (m, 15 H, 3 Ph).

*3,4,6-Tri-*O*-benzyl-1,2-*O*-[(R)- and (S)-benzylidene]-α-D-glucopyranose* (**10a**

and **10b**). — A solution of **7ab** (400 mg, 1.5 mmol) in *N*,*N*-dimethylformamide (10 mL) was treated with sodium hydride (240 mg, 10 mmol) and benzyl chloride (1 mL, 8 mmol) as described above, to give, after chromatography, **10ab** (760 mg, 94%), $[\alpha]_D$ +49.5° (*c* 2.3, chloroform).

Anal. Calc. for $C_{34}H_{34}O_6$: C, 75.83; H, 6.31. Found: C, 76.09; H, 6.11.

Individual isomers were isolated by rechromatography, to give **10a** as a syrup, $[\alpha]_D$ +57.5° (*c* 3.6, chloroform), R_F 0.48 (solvent *C*). P.m.r. data (CCl_4): δ 5.43 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 5.58 (s, 1 H, PhC*H*), and 7.00 (s, 20 H, 4 Ph). Eluted second was **10b**, $[\alpha]_D$ +45.0° (*c* 3.3, chloroform), R_F 0.59. P.m.r. data (CCl_4): δ 5.60 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 6.02 (s, 1 H, PhC*H*), and 7.10–7.33 (m, 20 H, 4 Ph).

Removal of the 1,2-O-benzylidene group. — (*a*) A solution of **8ab** (360 mg, 0.9 mmol) in aqueous 90% trifluoroacetic acid (4 mL) was kept at room temperature for 2 h and then concentrated to dryness, and the residue was treated with acetic anhydride–pyridine, as for **6ab**, to give α,β-D-glucopyranose penta-acetate (360 mg, 100%), $[\alpha]_D$ +57.5° (*c* 3.6, chloroform). P.m.r. data (CCl_4): δ 5.61 (d, $J_{1,2}$ 8 Hz, H-1β) and 6.17 (d, $J_{1,2}$ 4 Hz, H-1α); α,β-ratio 3:2.

(*b*) The mixture **10ab** (420 mg, 0.78 mmol) was treated with trifluoroacetic acid as described above, and the residue was dried *in vacuo*, to give 3,4,6-tri-*O*-benzyl-D-glucose (320 mg, 90%), R_F 0.73 (solvent *A*). Crystallisation from ethanol afforded material with m.p. 83–85° and $[\alpha]_D$ +53.1° (*c* 3.1, chloroform); lit.[13] m.p. 85–86° (from ethanol), $[\alpha]_D$ +57.1° (chloroform).

Removal of the 1,2-O-ethylidene group. — (*a*) The mixture **9ab** (350 mg, 0.73 mmol) was treated with boiling, aqueous 80% acetic acid (10 mL) for 6 h. The hydrolysate was concentrated to dryness and the residue was subjected to chromatography (gradient elution: ethyl acetate → 19:1 ethyl acetate–ethanol), to give 3,4,6-tri-*O*-benzyl-D-glucose (300 mg, 91%).

(*b*) The mixture **6ab** (350 mg, 1.1 mmol) was treated with acetic anhydride (3 mL) and a solution of conc. sulfuric acid (0.1 mL) in acetic acid (25 mL). After 20 h at room temperature, the mixture was diluted with water (1.5 mL), kept at 80° for 30 min, and then concentrated. Toluene–ethanol–heptane (5:1:1, 2 × 10 mL) was distilled from the residue, which was then treated with acetic anhydride (1 mL) for 2 h at room temperature. Water (30 mL) was added, and the mixture was shaken for 1 h and extracted with chloroform (2 × 25 mL). The combined extracts were washed successively with water (2 × 35 mL), saturated, aqueous sodium hydrogencarbonate (2 × 50 mL), and water (35 mL), and concentrated to give α,β-D-glucopyranose penta-acetate (360 mg, 88%), $[\alpha]_D$ +54.5° (*c* 3.8, chloroform).

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