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Note

The heterogeneous, catalytic, transfer hydrogenolysis of tri-*O*-benzyl derivatives of 1,6-anhydro-β-D-hexopyranoses

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Heterogeneous, catalytic, transfer hydrogenolysis[1] may result in enhanced selectivity in the deprotection of benzyl ethers of polyols and has been utilised in carbohydrate chemistry[2,3]. Our preliminary results[4] indicated that, in conformationally rigid molecules, benzyl groups may act as hydrogen donors and partially *O*-benzoylated derivatives could be obtained when the reaction was carried out in the presence of atmospheric oxygen. We now report on the complete series of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-hexopyranoses (**1–8**) in relation to the scope, limitations, and factors that influence this unusual reaction. This work is part of our study of the selectivity–activation of carbohydrate derivatives[5,6].

Treatment of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose[7] (**1**) with 10% Pd/C in refluxing 2-propanol for 5 h gave, after column chromatography, 1,6-anhydro-β-D-galactopyranose (**10**) and its 3-benzoate[8] (**9**, 70%). Shorter reaction time resulted in the isolation of 3,4-di-*O*-benzyl[9] (**11**) and 3-*O*-benzoyl-2-*O*-benzyl (**12**) derivatives. Acetylation of **9**, **11**, and **12** gave the corresponding acetyl derivatives **13–15**, respectively. Under the above conditions, (*a*) the *manno* isomer[10] gave, after 4 h, 1,6-anhydro-β-D-mannopyranose (**17**) and its 3-benzoate (**16**, 40%); (*b*) the *gulo* isomer **3** gave, after 7 h, 1,6-anhydro-β-D-gulopyranose (**19**), its 2-benzoate[11] (**18**, 40%), and its 3-benzoate (**20**, 10%); (*c*) the *allo* isomer[12] **4** gave, after 4 h, 1,6-anhydro-β-D-allopyranose (**24**, 30%), **4** (10%), its 2-benzoate (**21**, 15%), and a 2:1 mixture (40%) of the 3- (**22**) and 4-benzoate (**23**): (*d*) the *altro* isomer[13] **5** gave, after 24 h, 1,6-anhydro-β-D-altropyranose (**27**, 20%), its 3-benzoate (**25**, 25%), and its 4-benzoate[14] (**26**, 35%); (*e*) the *talo* isomer **6** gave, after 7 h, 1,6-anhydro-β-D-talopyranose (**29**, 20%), and two minor products, probably the 2- (**30**) and 4-benzoate (**31**); (*f*) the *ido* isomer **7** gave, after 48 h, 1,6-anhydro-β-D-idopyranose (**35**), its 3-benzoate (**32**, 18%), and a 2:3 mixture (47%) of its 2- (**33**) and 4-benzoate (**34**); (*g*) the *gluco* isomer[15] **8** gave only a partially benzylated derivative (30%), the structure of which was not determined, and 1,6-anhydro-β-D-glucopyranose (**36**).

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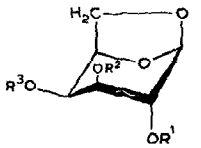

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9 $R^1 = R^3 =$ H, $R^2 =$ Bz
10 $R^1 = R^2 = R^3 =$ H
11 $R^1 =$ H, $R^2 = R^3 =$ Bzl
12 $R^1 =$ Bzl, $R^2 =$ Bz, $R^3 =$ H
13 $R^1 = R^3 =$ Ac, $R^2 =$ Bz
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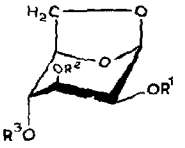
15 $R^1 =$ Bzl, $R^2 =$ Bz, $R^3 =$ Ac



2 $R^1 = R^2 = R^3 =$ Bzl
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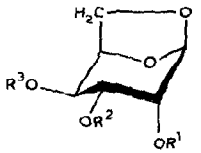
17 $R^1 = R^2 = R^3 =$ H



3 $R^1 = R^2 = R^3 =$ Bzl
18 $R^1 =$ Bz, $R^2 = R^3 =$ H
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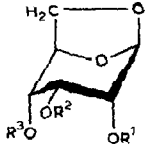
20 $R^1 = R^3 =$ H, $R^2 =$ Bz



4 $R^1 = R^2 = R^3 =$ Bzl
21 $R^1 =$ Bz, $R^2 = R^3 =$ H
22 $R^1 = R^3 =$ H, $R^2 =$ Bz
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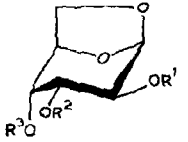
24 $R^1 = R^2 = R^3 =$ H



5 $R^1 = R^2 = R^3 =$ Bzl
25 $R^1 = R^3 =$ H, $R^2 =$ Bz
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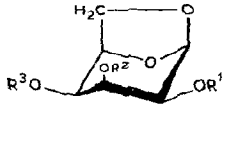
27 $R^1 = R^2 = R^3 =$ H



6 $R^1 = R^2 = R^3 =$ Bzl
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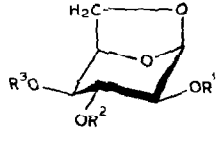
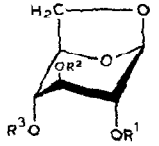
29 $R^1 = R^2 = R^3 =$ H
30 $R^1 =$ Bz, $R^2 = R^3 =$ H
31 $R^1 = R^2 =$ H, $R^3 =$ Bz



7 $R^1 = R^2 = R^3 =$ Bzl
32 $R^1 = R^3 =$ H, $R^2 =$ Bz
33 $R^1 =$ Bz, $R^2 = R^3 =$ H
34 $R^1 = R^2 =$ H, $R^3 =$ Bz
35 $R^1 = R^2 = R^3 =$ H



8 $R^1 = R^2 = R^3 =$ Bz
36 $R^1 = R^2 = R^3 =$ H

The foregoing results indicate, as noted previously[4], that *O*-benzyl groups can act as hydrogen donors in heterogeneous, catalytic, transfer hydrogenolysis and that probably there are stereochemical requirements for the reaction. However, the observation[4] that benzoates are formed only when the benzyl groups are vicinal-*cis* is in error since all possible *O*-benzoylated derivatives were isolated after the hydrogenolysis of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-idopyranose (**7**). As benzoyl migration may occur during the hydrogenolysis, the mechanism of hydrogen transfer is difficult to determine. However, the above results seem to indicate that axial *O*-benzyl groups are better hydrogen donors than equatorial groups and that no hydrogen donation from an axial group takes place in the absence of a *cis*-group, as demonstrated with the *gluco* isomer **8**.

EXPERIMENTAL

General. — Melting points were measured in capillary tubes and are uncorrected. T.l.c. was performed on silica gel GF_{254} (Merck) with detection by charring with sulfuric acid. Column chromatography was performed on Merck Type I (70–230 mesh) silica gel. N.m.r. spectra (^1H, 300 MHz; ^{13}C, 75 and 20 MHz) were recorded with Varian XL-300 and Bruker WP-80 spectrometers. Optical rotations were determined with a Perkin–Elmer 141 polarimeter.

*1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-*D*-gulopyranose* (**3**). —2,3,4-Tri-*O*-acetyl-1,6-anhydro-β-D-gulopyranose[8] was deacetylated with sodium methoxide in methanol, and the deacetylated product was benzylated with benzyl bromide and sodium hydride under the usual conditions to give **3**, isolated as a syrup, $[\alpha]_D^{25}$ −13° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.36–7.25 (m, 15 H, 3 Ph), 5.30 (d, 1 H, $J_{1,2}$ ~2 Hz, H-1), 4.81–4.60 (m, 6 H, 3 PhCH_2), 4.42 (t, 1 H, $J_{4,5} \simeq J_{5,6exo} \simeq$ 4.4 Hz, H-5), 4.00–3.97 (m, 2 H, H-2, H-6*endo*), 3.72–3.68 (m, 2 H, H-3,4), 3.58–3.54 (dd, 1 H, H-6*exo*).

Anal. Calc. for $C_{27}H_{28}O_5$: C, 74.99; H, 6.59. Found: C, 74.69; H, 6.61.

*1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-*D*-talopyranose* (**6**). — Prepared from 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-talopyranose[16], as indicated for **3**, **6**, isolated as a syrup, had $[\alpha]_D^{25}$ −18° (*c* 0.36, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.38–7.25 (m, 15 H, 3 Ph), 5.40 (s, 1 H, H-1), 4.93–4.57 (m, 6 H, 3 PhCH_2), 4.55 (d, 1 H, $J_{6endo,6exo}$ ~4.6 Hz, H-6*endo*), 4.40 (t, 1 H, $J_{4,5} \simeq J_{5,6exo} \simeq$ 4.4 Hz, H-5), 4.17 (t, 1 H, $J_{2,3} \simeq J_{3,4} \simeq$ 4.4 Hz, H-3), 3.71 (t, 1 H, H-6*exo*), 3.60 (t, 1 H, H-4), 3.38 (dd, 1 H, $J_{1,2}$ ~1.6 Hz, H-2).

Anal. Calc. for $C_{27}H_{28}O_5$: C, 74.99; H, 6.59. Found: C, 74.97; H, 6.80.

*1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-*D*-idopyranose* (**7**). — Conventional deacetylation of 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-idopyranose[17] and benzylation of the product gave **7**, isolated as a syrup, $[\alpha]_D^{25}$ −30° (*c* 0.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.30 (m, 15 H, 3 Ph), 5.29 (d, 1 H, $J_{1,2}$ ~1.6 Hz, H-1), 4.68 (m, 6 H, 3 PhCH_2), 4.38 (t, 1 H, $J_{4,5} \simeq J_{5,6exo} \simeq$ 4.5 Hz, H-5), 4.13 (d, 1 H, H-6*endo*), 3.73 (m, 3 H, H-3,4,6*exo*), 3.47 (dd, 1 H, $J_{2,3}$ ~7.7 Hz, H-2).

Anal. Calc. for $C_{27}H_{28}O_5$: C, 74.99; H, 6.59. Found: C, 74.70; H, 6.70.

General method of catalytic, transfer hydrogenolysis. — A solution of the 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-hexopyranose (0.2 g, 0.46 mmol) in 2-propanol (10 mL) was added to a stirred suspension of 10% Pd/C (1 g) in refluxing 2-propanol (10 mL), and the mixture was boiled under reflux for the times indicated. The catalyst was collected and washed with 2-propanol and water, the combined filtrate and washings were concentrated, and the residue was fractionated by column chromatography.

(*a*) *1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose* (**1**). Hydrogenolysis of **1** (ref. 7) for 5 h and subsequent column chromatography (7:5 hexane–ethyl acetate) gave, first, **9** (85 mg, 70%), m.p. 146–148°, $[\alpha]_D^{20}$ −22° (*c* 0.4, chloroform); lit.[8] m.p. 145–147°, $[\alpha]_D^{20}$ −25° (*c* 0.8, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 8.03–7.42 (m, 5 H, Ph), 5.44 (s, 1 H, H-1), 5.37 (dd, 1 H, $J_{2,3}$ ~1.2, $J_{3,4}$ ~5 Hz, H-3), 4.47 (t, 1 H, $J_{4,5} \simeq J_{5,6exo} \simeq 4.5$ Hz, H-5), 4.39–4.36 (m, 2 H, H-4,6*endo*), 3.86 (d, 1 H, H-2), 3.76 (dd, 1 H, $J_{6endo,6exo}$ ~5.6 Hz, H-6*exo*), 3.11 (d, 1 H, OH), 2.90 (d, 1 H, OH); ^{13}C, δ 101.12, 76.76 (2 C), 74.16, 72.42, 65.12, 63.76.

When the reaction was stopped after 3 h, chromatography (7:3 hexane–ethyl acetate) of the mixture gave **11** and **12**. Compound **12** (30 mg, 20%) was isolated as a syrup, $[\alpha]_D^{20}$ −64° (*c* 0.24, chloroform); ν_{max} 3450 (OH), 1720 cm^{-1} (C=O). N.m.r. data ($CDCl_3$): ^1H, δ 8.02–7.32 (m, 10 H, 2 Ph), 5.46 (dd, 1 H, $J_{2,3}$ ~1.1, $J_{3,4}$ ~5.3 Hz, H-3), 5.39 (s, 1 H, H-1), 4.86–4.64 (m, 2 H, PhCH_2), 4.50 (t, 1 H, $J_{4,5} \simeq J_{5,6exo} \simeq 5.6$ Hz, H-5), 4.35 (m, 1 H, H-4), 4.36 (d, 1 H, $J_{6exo,6endo}$ ~6.5 Hz, H-6*endo*), 3.75 (dd, 1 H, H-6*exo*), 3.59 (t, 1 H, $J_{1,2}$ ~1.1 Hz, H-2); ^{13}C, δ 133.6, 129.8 (3 C), 129.1, 128.7 (4 C), 128.1 (3 C), 100.2 (C-1), 76.7 (2 C), 74.2, 72.4, 70.3, 65.1, 63.7.

Anal. Calc. for $C_{20}H_{20}O_6$: C, 67.39; H, 5.66. Found: C, 67.27; H, 5.29.

Compound **11** (30 mg, 20%) had m.p. 68–70°, $[\alpha]_D^{20}$ −35° (*c* 0.5, chloroform), lit.[9] m.p. 70–71°, $[\alpha]_D^{23}$ −36.9° (*c* 0.8, chloroform). Acetylation of **11** gave **14**. N.m.r. data ($CDCl_3$): ^1H, δ 7.39–7.27 (m, 10 H, 2 Ph), 5.39 (s, 1 H, H-1), 4.96 (s, 1 H, H-2), 4.86–4.61 (m, 2 H, PhCH_2), 4.55 (d, 1 H, $J_{6exo,6endo}$ ~6.6 Hz, H-6*endo*), 4.55–4.39 (m, 2 H, PhCH_2), 4.47 (t, 1 H, $J_{4,5} \simeq J_{5,6exo} \simeq 3.7$ Hz, H-5), 3.82–3.76 (m, 2 H, H-3,4), 3.68 (dd, 1 H, H-6*exo*), 2.1 (s, 3 H, CH_3); ^{13}C, δ 128.48 (3 C), 128.30 (3 C), 127.60 (3 C), 99.47 (C-1), 74.39, 73.03, 72.75, 72.74, 70.80, 70.41, 64.70, 20.95.

(*b*) *1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-gulopyranose* (**3**). After 7 h, chromatography (7:4 hexane–ethyl acetate) of the product mixture gave **18** and **20**. Compound **18** (48 mg, 40%) had m.p. 147–150°, $[\alpha]_D^{20}$ +92° (*c* 0.48, chloroform); lit.[11] m.p. 151–152°, $[\alpha]_D^{25}$ +96° (*c* 0.3, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 8.08–7.39 (m, 5 H, Ph), 5.52 (d, 1 H, $J_{1,2}$ ~2.2 Hz, H-1), 5.22 (dd, 1 H, $J_{2,3}$ ~4.1 Hz, H-2), 4.48 (t, 1 H, $J_{4,5} \simeq J_{5,6exo} \simeq 4.6$ Hz, H-5), 4.04 (d, 1 H, $J_{6endo,6exo}$ ~7.8 Hz, H-6*endo*), 3.98–3.96 (m, 2 H, H-3,4), 3.63 (dd, 1 H, H-6*exo*).

Compound **20** (12 mg, 10%) had m.p. 136–139°, $[\alpha]_D^{20}$ +20° (*c* 0.3, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 8.08–7.42 (m, 5 H, Ph), 5.47 (d, 1 H, $J_{1,2}$ ~2.4 Hz, H-1), 5.04 (dd, 1 H, $J_{2,3}$ ~4.7, $J_{3,4}$ ~9.2 Hz, H-3), 4.54 (t, 1 H, $J_{4,5} \simeq$

$J_{5,6exo} \simeq 4.6$ Hz, H-5), 4.24–4.11 (m, 3 H, H-2,4,6*endo*), 3.74 (dd, 1 H, $J_{6endo,6exo}$ ~7.1 Hz, H-6*exo*).

Anal. Calc. for $C_{13}H_{14}O_6$: C, 58.62; H, 5.30. Found: C, 58.70; H, 5.82.

(*c*) *1,6-Anhydro-2,3,4-tri*-O-*benzyl*-β-D-*allopyranose*[12] (**4**). After 4 h, column chromatography (3:2 hexane–ethyl acetate) of the product mixture gave **21** and a 2:1 mixture of **22** and **23**. Compound **21** (10 mg, 15%) was isolated as a syrup, $[\alpha]_D^{20}$ +18° (*c* 0.25, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 8.05–7.46 (m, 5 H, Ph), 5.66 (d, 1 H, $J_{1,2}$ ~2.5 Hz, H-1), 5.22 (m, 1 H, H-2), 4.75 (m, 1 H, H-5), 4.04 (t, 1 H, $J_{2,3} \simeq J_{3,4} \simeq 4.4$ Hz, H-3), 3.90–3.83 (m, 3 H, H-4,6*endo*,6*exo*).

Anal. Calc. for $C_{13}H_{14}O_6$: C, 58.62; H, 5.30. Found: C, 58.34; H, 5.51.

The mixture (48 mg, 40%) of **22** and **23** could not be fractionated. ^1H-N.m.r. data ($CDCl_3$): **22**, δ 5.56 (d, $J_{1,2}$ ~2.7 Hz, H-1), 5.12 (t, $J_{2,3} \simeq J_{3,4} \simeq 3.8$ Hz, H-3), 4.70 (ddd, $J_{4,5}$ ~2.8, $J_{5,6endo}$ ~0.8, $J_{5,6exo}$ ~5.1 Hz, H-5), 4.12 (ddd, $J_{2,4}$ ~1.5 Hz, H-4), 4.06 (m, H-2), 3.92 (dd, $J_{6endo,6exo}$ ~8.1 Hz, H-6*endo*), 3.85 (dd, H-6*exo*); **23**, δ 5.59 (d, $J_{1,2}$ ~2.7 Hz, H-1), 5.24 (ddd, $J_{2,4}$ ~1.0, $J_{3,4}$ ~4.6, $J_{4,5}$ ~2.6 Hz, H-4), 4.82 (ddd, $J_{5,6exo}$ ~5.0, $J_{5,6endo}$ ~1.0 Hz, H-5), 4.02 (t, $J_{2,3}$ ~4.6 Hz, H-3), 3.89 (dd, $J_{6endo,6exo}$ ~8.1 Hz, H-6*endo*), ~3.7 (m, H-2).

(*d*) *1,6-Anhydro-2,3,4-tri*-O-*benzyl*-β-D-*altropyranose*[13] (**5**). After 24 h, column chromatography (3:2 hexane–ethyl acetate) of the product mixture gave **25** and **26**. Compound **25** (30 mg, 25%) had m.p. 133–135°, $[\alpha]_D^{20}$ −128° (*c* 0.3, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 8.12–7.43 (m, 5 H, Ph), 5.49 (d, 1 H, $J_{1,2}$ ~1.8 Hz, H-1), 5.08 (dd, 1 H, $J_{2,3}$ ~9.0, $J_{3,4}$ ~4.4 Hz, H-3), 4.69 (m, 1 H, H-5), 4.19 (dd, 1 H, $J_{4,5}$ ~2.6 Hz, H-4), 3.98 (dd, 1 H, H-2), 3.93–3.86 (m, 2 H, H-6*endo*,6*exo*).

Anal. Calc. for $C_{13}H_{14}O_6$: C, 58.62; H, 5.30. Found: C, 58.71; H, 5.33.

Compound **26** (42 mg, 35%) had m.p. 138–140°, $[\alpha]_D^{20}$ −210° (*c* 0.5, dimethyl sulfoxide); lit.[14] m.p. 139.5°, $[\alpha]_D^{25}$ −213.9° (*c* 1, dimethyl sulfoxide). N.m.r. data ($CDCl_3$): ^1H, δ 8.08–7.40 (m, 5 H, Ph), 5.44 (d, 1 H, $J_{1,2}$ ~1.7 Hz, H-1), 5.31 (dd, 1 H, $J_{3,4}$ ~4.8, $J_{4,5}$ ~2.6 Hz, H-4), 4.73 (dd, 1 H, $J_{5,6exo}$ ~4.4 Hz, H-5), 3.99 (dd, 1 H, $J_{2,3}$ ~8.6 Hz, H-3), 3.85–3.75 (m, 3 H, H-2,6*endo*,6*exo*).

(*e*) *1,6-Anhydro-2,3,4-tri*-O-*benzyl*-β-D-*talopyranose* (**6**). Debenzylation of **6** gave, after 7.5 h, a mixture that was eluted with 3:2 hexane–ethyl acetate to give a 4:1:1 mixture (40 mg, 35%) of **28**, **30**, and **31** that could not be fractionated. ^1H-N.m.r. data ($CDCl_3$): **28**, δ 5.67 (tt, $J_{2,3} \simeq J_{3,4} \simeq 4.7$, $J_{1,3} \simeq J_{3,5} \simeq 1.1$ Hz, H-3), 5.34 (d, $J_{1,2}$ ~1.7 Hz, H-1), 4.36 (t, $J_{4,5} \simeq J_{5,6exo} \simeq 4.4$ Hz, H-5), 4.35 (d, $J_{6endo,6exo}$ ~7.1 Hz, H-6*endo*), 4.19 (t, H-4), 3.80 (m, H-2), 3.74 (dd, H-6*exo*); **30**, δ 5.48 (t, $J_{1,2} \simeq J_{1,3} \simeq 1.5$ Hz, H-1), 4.94 (dd, $J_{2,3}$ ~4.7 Hz, H-2), 4.44 (t, $J_{4,5} \simeq J_{5,6exo} \simeq 4.7$ Hz, H-5), 4.31 (d, $J_{6endo,6exo}$ ~7.9 Hz, H-6*endo*), 3.95 (t, $J_{3,4}$ ~4.7 Hz, H-4), 3.74 (dd, H-6*exo*); **31**, δ 5.34 (H-1), 5.14 (t, $J_{3,4} \simeq J_{4,5} \simeq 4.7$ Hz, H-4), 4.51 (t, $J_{5,6exo}$ ~4.7 Hz, H-5), 4.48 (d, $J_{6endo,6exo}$ ~7.6 Hz, H-6*endo*), 4.25 (t, $J_{2,3}$ ~4.7 Hz, H-3), 3.68 (dd, H-6*exo*).

(*f*) *1,6-Anhydro-2,3,4-tri*-O-*benzyl*-β-D-*idopyranose* (**7**). After 48 h, column chromatography (7:5 hexane–ethyl acetate) of the product mixture gave **32** and a

2:3 mixture of **33** and **34**. Compound **32** (21 mg, 18%) was isolated as a syrup, $[\alpha]_D^{20}$ −66° (*c* 0.4, chloroform). N.m.r. data: ^{1}H, δ 8.05–7.40 (m, 5 H, Ph), 5.39 (d, 1 H, $J_{1,2}$ ~2.1 Hz, H-1), 4.89 (t, 1 H, $J_{2,3} \simeq J_{3,4} \simeq$ 10 Hz, H-3), 4.53 (t, 1 H, $J_{4,5} \simeq J_{5,6} \simeq$ 4.7 Hz, H-5), 4.23 (d, 1 H, $J_{6exo,6endo}$ ~8.1 Hz, H-6*endo*), 4.03 (dd, 1 H, H-6*exo*), 3.79 (m, 2 H, H-2,4).

Anal. Calc. for $C_{13}H_{14}O_6$: C, 58.62; H, 5.30. Found: C, 58.78; H, 5.42.

The mixture (56 mg, 47%) of **33** and **34** could not be fractionated. ^{1}H-N.m.r. data ($CDCl_3$): **33**, δ 5.49 (d, $J_{1,2}$ ~1.6 Hz, H-1), 4.83 (dd, $J_{2,3}$ ~8.2 Hz, H-2), 4.50 (t, $J_{4,5} \simeq J_{5,6exo} \simeq$ 4.4 Hz, H-5), 4.14 (d, $J_{6exo,6endo}$ ~7.8 Hz, H-6*endo*); **34**, δ 5.39 (d, $J_{1,2}$ ~1.7 Hz, H-1), 5.10 (dd, $J_{3,4}$ ~8.2, $J_{4,5}$ ~4.5 Hz, H-4), 4.68 (t, $J_{4,5} \simeq J_{5,6exo} \simeq$ 4.5 Hz, H-5), 4.09 (d, $J_{6exo,6endo}$ ~7.8 Hz, H-6*endo*), 3.65 (dd, $J_{2,3}$ ~8.2 Hz, H-2).

(*g*) *1,6-Anhydro-2,3,4-tri-O-benzyl-β-D-glucopyranose*[15] (**8**). After 3 h, column chromatography (7:5 hexane–ethyl acetate) of the product mixture gave a benzylated compound (20 mg, 30%) and **36**.

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