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Note

On the nature of the side-products formed during the hydrogenolysis of 1,6:2,3-dianhydro-4-*O*-benzyl-β-D-mannopyranose

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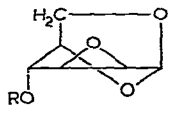
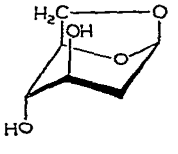
Trnka and Černý reported[1] that the hydrogenolysis of 1,6:2,3-dianhydro-4-*O*-benzyl-β-D-mannopyranose (**1**) over 10% Pd/C in ethanol, to give 1,6:2,3-dianhydro-β-D-mannopyranose (**2**), was 98% complete after 4 h at 40°. We observed that when hydrogen was bubbled through an ethanolic solution of **1** (1 g) in the presence of 10% Pd/C (0.3 g) at 40° for 4 h then, in addition to the main product **2** (R_F 0.58; t.l.c., silica gel, chloroform–methanol, 10:3), a minor product (R_F 0.38) was also formed which was isolated (preparative t.l.c., silica gel) and identified as 1,6-anhydro-2-deoxy-β-D-*arabino*-hexopyranose[2,3] (**3**), $[\alpha]_D^{20}$ −119° (*c* 1.1, water). ^{1}H-N.m.r. data (CD_3OD, internal Me_4Si): δ 5.47 (broad s, 1 H, $J_{1,2eq}$ ~1.5, $J_{1,2ax}$ 2.0, $J_{1,3}$ ~1.3 Hz, H-1), 4.43 (broad d, 1 H, $J_{4,5}$ ~1.0, $J_{5,6}$ 1.0, $J_{5,6'}$ 5.9, $J_{3,5}$ ~1.3 Hz, H-5), 4.25 (dd, 1 H, $J_{6,6'}$ 7.0, $J_{5,6}$ 1.0 Hz, H-6), 3.75 (m, 1 H, $J_{2eq,3}$ ~1.3, $J_{2ax,3}$ 5.5, $J_{3,4}$ ~1.3, $J_{1,3}$ ~1.3 Hz, H-3), 3.64 (dd, 1 H, $J_{5,6'}$ 5.9, $J_{6,6'}$ 7.0 Hz, H-6'), 3.57 (broad s, 1 H, $J_{3,4}$ ~1.3, $J_{4,5}$ ~1.0 Hz, H-4), 2.07 (m, 1 H, $J_{1,2ax}$ 2.0, $J_{2,2}$ 14.6, $J_{2ax,3}$ 5.5 Hz, H-2*ax*), and 1.69 (broad d, 1 H, $J_{1,2eq}$ ~1.5, $J_{2,2}$ 14.6, $J_{2eq,3}$ ~1.3 Hz, H-2*eq*).



1 R = Bzl
2 R = H



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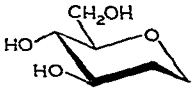

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After prolonged reaction (another 8 h at 40°), a third product (R_F 0.26) could be isolated (preparative t.l.c., silica gel; crystallisation from methanol–chloroform) and identified as 1,5-anhydro-2-deoxy-D-*arabino*-hexitol[4,5] (**4**), m.p. 84–86° $[\alpha]_D^{20}$ +17° (*c* 1.1, water). ^{1}H-N.m.r. data (CD_3OD, internal Me_4Si): δ 3.82 (m, 1 H, $J_{1eq,2eq}$ 1.6, $J_{1eq,2ax}$ 4.8, $J_{1eq,1ax}$ 11.5 Hz, H-1*eq*), 3.75 (dd, 1 H, $J_{5,6}$ 2.0, $J_{6,6'}$ 11.6

Hz, H-6), 3.54 (dd, 1 H, $J_{5,6'}$ 5.6, $J_{6,6'}$ 11.6 Hz, H-6'), 3.43 (m, 1 H, $J_{2eq,3}$ 4.8, $J_{2ax,3}$ 11.0, $J_{3,4}$ 8.0 Hz, H-3), 3.35 (m, 1 H, $J_{1ax,2eq}$ 2.0, $J_{1ax,2ax}$ 12.2, $J_{1eq,1ax}$ 11.5 Hz, H-1*ax*), 3.07 (dd, 1 H, $J_{3,4}$ 8.0, $J_{4,5}$ 9.2 Hz, H-4), 3.03 (m, 1 H, $J_{4,5}$ 9.2, $J_{5,6}$ 2.0, $J_{5,6'}$ 5.6 Hz, H-5), 1.81 (m, 1 H, $J_{1eq,2eq}$ 1.6, $J_{1ax,2eq}$ 2.0, $J_{2eq,2ax}$ 12.8, $J_{2eq,3}$ 4.8 Hz, H-2*eq*), and 1.50 (m, 1 H, $J_{1eq,2ax}$ 4.8, $J_{1ax,2ax}$ 12.2, $J_{2eq,2ax}$ 12.8, $J_{2ax,3}$ 11.0 Hz, H-2*ax*).

The formation of **3** from **1** is the first example of reductive cleavage of an oxirane during hydrogenolysis over Pd/C. Chemical (*e.g.*, $LiAlH_4$) and catalytic (using Raney nickel) reductive-cleavage of oxirane rings is widely exemplified. Moreover, the catalytic reductive-cleavage of the oxirane ring in 1,6:2,3-anhydromannose derivatives usually gives[2,6] similar proportions of 2- and 3-deoxy derivatives. Only the 2-deoxy derivative **3** was formed from **1**. Reductive cleavage of the 1,6-anhydro ring in the conversion **1**→**4** is also noteworthy. Compound **4** has been obtained by hydrogenation of D-glucal[4] and as a side-product in the hydrogenolysis[5] of methyl α-D-glucopyranoside over CuCr oxide at 220°. Since, in **3**, there is no electronegative group on C-2 which can stabilise the 1,6-anhydro bridge, hydrogenolysis is possible[3,7,8].

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