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Preliminary communication

Stereoselective hydrogenolysis of *exo*- and *endo*-2,3-benzylidene acetals of hexopyranosides

ANDRÁS LIPTÁK, PÉTER FÜGEDI, and PÁL NÁNÁSI

Institute of Biochemistry, L. Kossuth University, H-4010, Debrecen (Hungary)

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The reagent formed[1] from $LiAlH_4$ and $AlCl_3$ can cleave cyclic acetals and ketals to give hydroxy ether derivatives[2–4].

When applied to benzylidene acetals of carbohydrates[5–7], benzyl ether derivatives are formed which may be useful for further transformations. We have shown[6] that the direction of cleavage of the 4,6-*O*-benzylidene ring of hexopyranosides on reaction with the $LiAlH_4$–$AlCl_3$ reagent is determined by the size of the substituents near the dioxane ring. However, for 3,4-*O*-benzylidenepyranosides, the direction of cleavage of the dioxolane ring depends on the configuration of the acetal carbon atom[8]. We now report a similar finding for 2,3-*O*-benzylidenepyranosides.

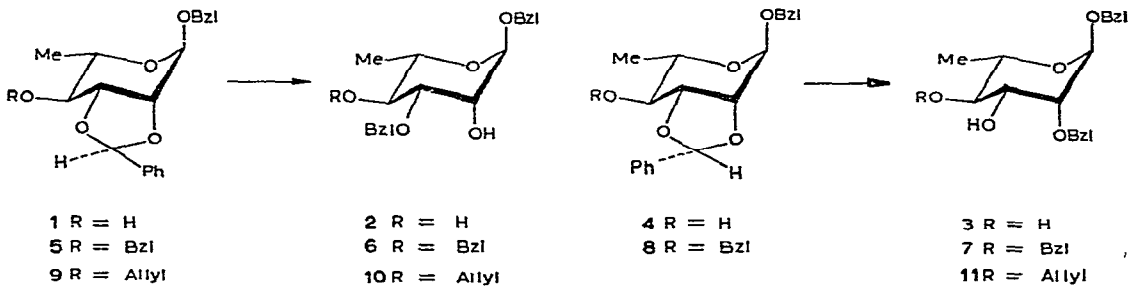
Pyranosides containing a *cis*-2,3-diol grouping can be converted by reaction with benzaldehyde into diastereoisomeric 2-phenyl-1,3-dioxolane derivatives, and configuration at the acetal carbon atom can be assigned by n.m.r. spectroscopy[9,10].

The following compounds were treated with 1.1 mol of $LiAlH_4$–$AlCl_3$ in ether–dichloromethane (1:1) at 45°.

Benzyl *exo*-2,3-*O*-benzylidene-α-L-rhamnopyranoside {1, m.p. 132–133°, $[\alpha]_D$ –67° (*c* 0.42, chloroform), $\delta_{CH.Ph}$ 6.00; 4-acetate, m.p. 103–104°, $[\alpha]_D$ –55° (*c* 0.55, chloroform), $\delta_{CH.Ph}$ 6.19} gave benzyl 3-*O*-benzyl-α-L-rhamnopyranoside {2, 98% (determined by g.l.c.), $[\alpha]_D$ –48° (*c* 0.5, chloroform)} as a syrup {2,4-diacetate, m.p. 93–94°, $[\alpha]_D$ –11° (*c* 0.71, chloroform)} and benzyl 2-*O*-benzyl-α-L-rhamnopyranoside {3, 2%, m.p. 73–74°, $[\alpha]_D$ –39° (*c* 0.88, chloroform)}. On treatment with periodate, 3 reacted but 2 was resistant.

Benzyl *endo*-2,3-*O*-benzylidene-α-L-rhamnopyranoside {4, syrup, $[\alpha]_D$ –68° (*c* 1.18, chloroform), $\delta_{CH.Ph}$ 5.86} gave 2 and 3 in the ratio 2:98.

Benzyl 4-*O*-benzyl-*exo*-2,3-*O*-benzylidene-α-L-rhamnopyranoside {5, m.p. 124–125°, $[\alpha]_D$ –81° (*c* 0.96, chloroform), $\delta_{CH.Ph}$ 5.87} gave syrupy benzyl 3,4-di-*O*-benzyl-α-L-rhamnopyranoside {6, 94%, $[\alpha]_D$ –58° (*c* 0.6, chloroform)} and benzyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside {7, 6%, $[\alpha]_D$ –42° (*c* 0.64, chloroform)}. The ratio of 6 and 7 was 18:82 when the ring-cleavage reaction was applied to benzyl 4-*O*-benzyl-*endo*-2,3-*O*-

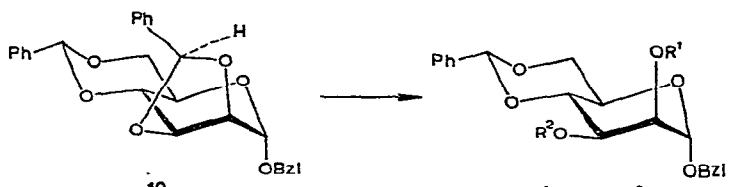


1 R = H
5 R = Bzl
9 R = Allyl

2 R = H
6 R = Bzl
10 R = Allyl

4 R = H
8 R = Bzl

3 R = H
7 R = Bzl
11 R = Allyl



12

13 R^1 = H, R^2 = Bzl
14 R^1 = Bzl, R^2 = H

benzylidene-α-L-rhamnopyranoside {8, m.p. 53–54°, $[\alpha]_D$ –57° (*c* 0.88, chloroform), $\delta_{CH.Ph}$ 5.76}.

Benzyl 4-*O*-allyl-*exo*-2,3-*O*-benzylidene-α-L-rhamnopyranoside {9, m.p. 68–69°, $[\alpha]_D$ –46° (*c* 0.97, chloroform), $\delta_{CH.Ph}$ 6.00} yielded syrupy benzyl 4-*O*-allyl-3-*O*-benzyl-α-L-rhamnopyranoside {**10**, ~85% (t.l.c.), $[\alpha]_D$ –56° (*c* 0.76, chloroform)} and the 2-*O*-benzyl derivative {**11**, ~15%, $[\alpha]_D$ –28° (*c* 0.56, chloroform)}.

Benzyl *exo*-2,3:4,6-di-*O*-benzylidene-α-D-mannopyranoside[11] {**12**, m.p. 188–189°, $[\alpha]_D$ +30° (*c* 1.2, chloroform), $\delta_{CH.Ph}$ 6.22 and 5.56} gave benzyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside {**13**, 76%, m.p. 88–89°, $[\alpha]_D$ +55° (*c* 1.4, chloroform), $\delta_{CH.Ph}$ 5.51} and benzyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside[12] {**14**, ~1%, m.p. 97–98°, $[\alpha]_D$ +39° (*c* 0.2, chloroform)}.

The above results establish that the direction of the hydrogenolytic ring-cleavage of 2,3-*O*-benzylidenepyranosides is determined by the configuration at the acetal carbon atom. For the *exo* isomers, the reagent mainly attacks the *axial* oxygen atom of the dioxolane ring, yielding a derivative containing *axial* hydroxyl and *equatorial* *O*-benzyl groups. For the *endo* isomers, mainly the *equatorial* oxygen atom is attacked, giving derivatives with *equatorial* hydroxyl and *axial* *O*-benzyl groups.

The possibility for reductive ring-cleavage of a dioxolane ring in the presence of a dioxane ring (4,6-benzylidene acetal) or allyl ether groups may prove useful in synthesis, for example, of complex oligosaccharides of biological importance.

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