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## Preliminary communication

# Regioselective hydrogenolysis of benzyl glycosides

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We have described the selective hydrogenolysis of benzyl ether groups in the presence of benzylidene acetals by using a catalytic (Pd–C) hydrogen-transfer system with ammonium formate as the hydrogen donor[1]. We now report the application of the method for the selective hydrogenolysis of benzyl glycosides. *O*-Benzylated sugars with the anomeric hydroxyl group unsubstituted are useful compounds especially in the synthesis of glycosides and oligosaccharides[2]. These compounds are prepared usually by acid hydrolysis of glycosides, but this method is not applicable to disaccharide derivatives because the inter-glycosidic bond would be cleaved.

Benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-gluco-, galacto-, and manno-pyranoside undergo catalytic hydrogen transfer with loss of BnO-1 (see Table I). The reactions were monitored by t.l.c. (Kieselgel 60; 1:2 benzene–ethyl acetate), since prolonged reaction

TABLE I

Hydrogenolysis of benzyl glycosides

| *Starting material* | *Product* | *Time (h)* | *Yield (%)* |
|---|---|---|---|
| Benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside[5] | 2,3,4,6-tetra-*O*-benzyl-D-glucose[6] | 12 | 75 |
| | | 24 | 63[a] |
| Benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside[6] | 2,3,4,6-tetra-*O*-benzyl-D-galactose[6] | 10 | 80 |
| Benzyl 2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranoside[6] | 2,3,4,6-tetra-*O*-benzyl-D-mannose[6] | 15 | 68 |
| Benzyl 2,3,4-tri-*O*-benzyl-α-L-arabinopyranoside[6] | 2,3,4-tri-*O*-benzyl-L-arabinose[6] | 0.5 | 35 |
| Benzyl 2,3,4-tri-*O*-benzyl-β-L-arabinopyranoside[b] | 2,3,4-tri-*O*-benzyl-L-arabinose[6] | 0.5 | 10 |
| | | 5 | 73 |
| Benzyl 2,3,6,2',3',4',6'-hepta-*O*-benzyl-β-D-lactoside[c] | 2,3,6,2',3',4',6'-hepta-*O*-benzyl-D-lactose[7] | 20 | 67 |
| Benzyl 2,3,6,2',3',4',6'-hepta-*O*-benzyl-β-D-maltoside[d] | 2,3,6,2',3',4',6'-hepta-*O*-benzyl-D-maltose[8] | 10 | 65 |

[a] A mixture of tri-*O*-benzyl derivatives was separated (yield, 10%). [b] M.p. 61–62°, $[\alpha]_{546}^{20}$ +108° (chloroform). [c] M.p. 74–76°, $[\alpha]_{546}^{20}$ + 0.1° (chloroform). [d] Syrup, $[\alpha]_{546}^{20}$ +0.2° (chloroform).

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caused hydrogenolysis of the other benzyl groups and complex mixtures of products were formed (see Table I).

Typically, a solution of the substrate (0.16 mmol) and ammonium formate (2.5 mmol) in methanol (5–10 mL) was stirred in the presence of 10% Pd–$Al_2O_3$ (160 mg) and then filtered, the catalyst was washed with alcohol (5 mL), and the combined filtrate and washings were concentrated. Chromatography (silica gel, benzene–ether) of the syrupy residue then gave the product, the structure of which was proved by n.m.r. spectroscopy and by comparison with known compounds.

Under the above conditions, the inter-glycosidic bond of the benzyl β-glycosides of hepta-*O*-benzyl-lactose and -maltose were not cleaved and BnO-1 was removed (Table I).

The reactivity of benzyl glycosides depends upon the configuration at the anomeric centre. Thus, benzyl 2,3,4-tri-*O*-benzyl-α-L-arabinopyranoside (BnO-1 equatorial) was converted into 2,3,4-tri-*O*-benzyl-L-arabinopyranose within 30 min, whereas the reaction of the β-glycoside (BnO-1 axial) was much slower; after 30 min, only 8% of the substrate had reacted.

Benzylation of sugars under conditions of phase-transfer catalysis[4], coupled with the above procedure, is a useful route to protected derivatives having HO-1 unsubstituted.

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