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Note

An improved preparation of benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside

G. J. F. CHITTENDEN
Microbiological Chemistry Research Laboratory, Department of Organic Chemistry, The University, Newcastle upon Tyne, NE1 7RU (Great Britain)

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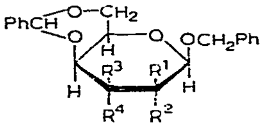
Treatment of benzyl 4,6-*O*-benzylidene-β-D-galactopyranoside (**1**) with one equivalent of benzoyl chloride in pyridine–dichloromethane at 0° gives[1] the 3-benzoate **2** as the main product. Thin-layer chromatography (t.l.c.) of the crude product showed the presence of unreacted diol **1**, the 2,3 dibenzoate, and the 2-benzoate **3**. Some diol **1** (35–40%) remained unreacted and was recovered from the mixture. The yield of **2**, allowing for this, was 64–78%. Treatment of **2** with dilute alkali gave the 2-benzoate **3** in 81% yield.

Recently[2], the usefulness of *N*-benzoylimidazole[3] as a selective acylating agent for carbohydrate derivatives was reported. Treatment of the diol **1** with this reagent gave **2** in excellent yield (89–93%). T.l.c. of the crude product indicated only trace amounts of unreacted **1** and the 2-benzoate **3**. The product **2** was characterised as the known[1] sulphonate **4**.



1 $R^1 = R^4 = H$; $R^2 = R^3 = OH$
2 $R^1 = R^4 = H$; $R^2 = OH$; $R^3 = OBz$
3 $R^1 = R^4 = H$; $R^2 = OBz$; $R^3 = OH$
4 $R^1 = R^4 = H$; $R^2 = OTs$; $R^3 = OBz$
5 $R^1 = R^3 = OH$; $R^2 = R^4 = H$

The usefulness of **2** as an intermediate in preparing 2,3-anhydro derivatives of D-talose and D-gulose has been illustrated[1], and, recently, it has been converted[4] into derivatives of D-talose, in high yield, by a methyl sulphoxide–metal hydride, oxidation–reduction sequence. The preparation of **2** demonstrated here makes it an attractive starting material for these otherwise not readily available derivatives. Thus, the conversion **1**→**5** can now be effected[4] in an overall yield of ~50%.

EXPERIMENTAL

Silica gel G (Merck) was used for t.l.c. with benzene–ether (4:1) as the developing solvent; compounds were detected by exposure to iodine vapour.

*Benzoylation of benzyl 4,6-*O*-benzylidene-β-D-galactopyranoside.* — Recrystallized imidazole (6.81 g, 0.1 mole) dissolved in purified chloroform (75 ml) was treated with a solution of redistilled benzoyl chloride (7.03 g, 50 mmoles) in chloroform (25 ml), slowly with stirring at 5°. The mixture was filtered to remove imidazole hydrochloride which was subsequently washed with chloroform (25 ml). The combined filtrate and washings were then added to a solution of the diol **1** (17.92 g, 50 mmoles) in chloroform (200 ml), and the mixture was heated for 18 h under reflux. After being extracted with saturated, aqueous sodium hydrogen carbonate (50 ml) and water (2 × 50 ml), the solution was dried (Na_2SO_4) and evaporated, and the residue was recrystallized from propan-2-ol to give the 3-benzoate **2** (20.6–21.5 g, 89–93%), m.p. and mixed m.p. 178–179°, $[\alpha]_D^{21}$ +64.4° (*c* 1.2, chloroform); lit.[1] m.p. 179–180°, $[\alpha]_D^{22}$ +64.6°.

Treatment[1] of **2** with toluene-*p*-sulphonyl chloride in pyridine gave the sulphonate **4** (79%), m.p. and mixed m.p. 170–172°, $[\alpha]_D^{21}$ +89° (*c* 1, chloroform); lit.[1] m.p. 171–172°, $[\alpha]_D^{21}$ +89.5°.

REFERENCES

1 G. J. F. Chittenden and J. G. Buchanan, *Carbohyd. Res.*, 11 (1969) 379.
2 F. A. Carey and K. O. Hodgson, *Carbohyd. Res.*, 12 (1970) 463.
3 H. A. Staab, *Angew. Chem.*, 74 (1962) 407.
4 G. J. F. Chittenden, *Carbohyd. Res.*, 15 (1970) 101.