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Note

A convenient synthesis of 6-amino-6-deoxy- and 6-deoxy-D-glucopyranose

RENÉ CSUK
Institute of Organic Chemistry, Technical University Graz, A-8010 Graz (Austria)
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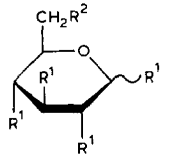
There are several approaches[1] for the synthesis of the title compounds, starting either from 1,2-*O*-isopropylidene-α-D-glucofuranose[2], methyl α-D-glucopyranoside[3–5], or D-glucuronic acid[6]. All of these syntheses are multi-step and elaborate. More-convenient syntheses are now described.

Treatment[7] of D-glucose with 4 mol. equiv. of *N*-trimethylsilylacetamide in refluxing pyridine gave 1,2,3,4-tetrakis(trimethylsilyl)-D-glucose (**1**). *N*-Trimethylsilylacetamide can be obtained easily[8] by the reaction of dry acetamide with chlorotrimethylsilane in dry benzene with triethylamine as acid scavenger.

Reaction[4] of **1** with triphenylphosphine and *N*-bromosuccinimide yielded the 6-bromo-6-deoxy derivative, which was treated in a one-pot reaction with sodium azide to yield the 6-azido-6-deoxy derivative. Hydrogenation in glacial acetic acid followed by *N*-acetylation then afforded 6-acetamido-6-deoxy-D-glucose (**2**, 56% overall yield).

Hydrogenolysis of the above crude 6-bromo-6-deoxy derivative in glacial acetic acid yielded 6-deoxy-D-glucose (**3**, 54% from D-glucose).



1 $R^1 = Me_3SiO$, $R^2 = OH$
2 $R^1 = OH$, $R^2 = NHAc$
3 $R^1 = OH$, $R^2 = H$

EXPERIMENTAL

General. — Melting points (Tottoli) are uncorrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter.

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*6-Acetamido-6-deoxy-*D*-glucose* (**2**). — To a solution of 1,2,3,4-tetrakis-(trimethylsilyl)-D-glucose (**1**; 5 g, 10.66 mmol) in anhydrous *N,N*-dimethylformamide (25 mL) were added *N*-bromosuccinimide (1.96 g, 11.01 mmol) and triphenylphosphine (2.88 g, 10.98 mmol), and the mixture was stirred for 3 h at 50° under nitrogen, then cooled, and treated with methanol (0.5 mL). To the filtered solution was added dry sodium azide (1.0 g, 15.39 mmol), and the mixture was stirred at 50° overnight and then concentrated *in vacuo*. The residue was triturated with ether (150 mL) to remove the triphenylphosphine oxide, and a solution in glacial acetic acid was hydrogenated in the presence of 10% Pd/C (0.1 g) at 1 atm. for 6 h. The mixture was filtered, and concentrated *in vacuo*, and to a solution of the amorphous residue in anhydrous pyridine (10 mL) was added acetic anhydride (1.13 mL, 12 mmol) slowly at 0°. After stirring for 3 h, the mixture was filtered through a short column of Celite (25 mL) and concentrated, and the residue was recrystallised from water–2-propanol, after decolorisation with charcoal (0.3 g), to afford **2** (1.48 g, 62.9%), m.p. 195–196°, $[\alpha]_D^{20}$ +32.2° (*c* 3.5, water); lit.[6] m.p. 197.5°, $[\alpha]_D^{24}$ +33.8° (*c* 3, water).

*6-Deoxy-*D*-glucose* (**3**). — To a solution of **1** (2.5 g, 5.33 mmol) in anhydrous *N,N*-dimethylformamide (15 mL) were added *N*-bromosuccinimide (1.0 g, 5.61 mmol) and triphenylphosphine (1.45 g, 5.53 mmol). The mixture was stirred for 3 h at 50° under nitrogen and then cooled, methanol (0.2 mL) was added, and the solvents were evaporated *in vacuo*. The residue was triturated with ether (100 mL) to yield a yellow oil, a solution of which in glacial acetic acid (10 mL) was hydrogenated over 10% Pd/C (0.1 g) at 1 atm. overnight. The catalyst was removed and the filtrate concentrated to afford a pale-yellow solid which was treated with charcoal (0.3 g) and Celite (0.3 g) in hot ethyl acetate to yield **3** (0.53 g, 60.6%), m.p. 145–146° (twice from ethyl acetate), $[\alpha]_D^{25}$ +73° (5 min) → +30° (3 h; *c* 1.5, water); lit.[2] m.p. 146°, $[\alpha]_D^{20}$ +30° (3 h; *c* 8.3, water).

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