1,3,4,6-Tetra-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranose from D-Glucosamine

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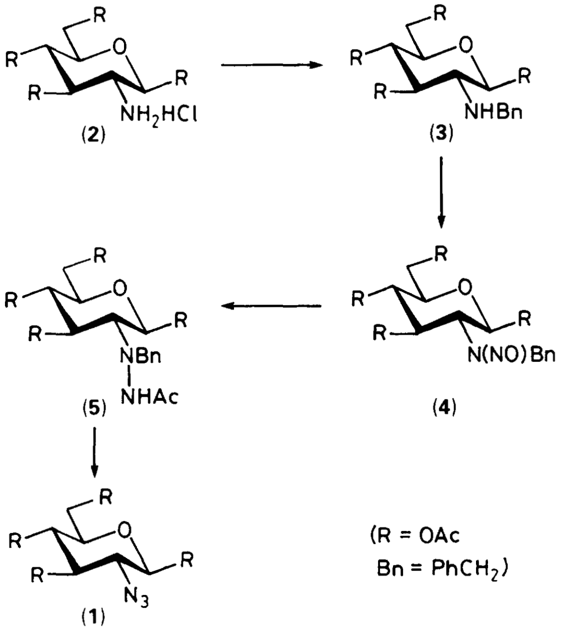
A new method which is quick and efficient has been developed for the preparation of the above azido compound (**1**) from 1,3,4,6-tetra-*O*-acetyl-2-*N*-benzyl-2-deoxy-β-D-glucopyranose.

2-Azido-2-deoxy-D-glucopyranose derivatives have been extensively used during the synthesis of complex oligosaccharides containing α-linked *N*-acetyl-D-glucosamine moieties.[1] These have been prepared by azido-nitration,[2,3] or chloroazidation[4] of D-glucal derivatives, by stereo- and regio-specific ring opening of the 'Cerny epoxide,'[5] with sodium azide and by the regioselective triflation (triflate = trifluoromethane) of 1,6-anhydro-D-mannopyranose followed by acetylation and subsequent treatment with sodium azide.[6]

In this communication, we report the preparation of (**1**) from 1,3,4,6-tetra-*O*-acetyl-2-*N*-benzyl-2-deoxy-β-D-glucopyranose (**3**). Compound (**3**) can be prepared from 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride (**2**) by treatment with benzyl bromide either under phase transfer conditions or in the presence of anhydrous K_2CO_3 in *N*,*N*-dimethylformamide. Thus, a dispersion of compound (**2**) in CH_2Cl_2 and water was stirred overnight with benzyl bromide (2 M) in the presence of Bu_4NI (2 M). Compound (**3**) was isolated from the organic layer by column chromatography from a dry silica gel column along with a small quantity of syrupy 1,3,4,6-tetra-*O*-acetyl-2-*N*,*N*-dibenzyl-2-deoxy-β-D-glucopyranose $[\alpha]_D^{22}$ +17° (*c* 2.2, chloro-



form). Alternatively, and more efficiently, (**3**) was prepared by stirring a solution of (**2**) in *N*,*N*-dimethylformamide containing anhydrous K_2CO_3 (5 M) and benzyl bromide (2 M). Column chromatographic purification afforded (**3**), m.p. 81—82 °C, $[\alpha]_D^{22}$ +23° (*c* 2.4, chloroform). Nitrosation[7] of (**3**) was carried out in CH_2Cl_2 with N_2O_4 (5 min) in the presence of anhydrous NaOAc. The reaction mixture was filtered and the filtrate washed with cold aqueous sodium hydrogen carbonate solution and water, dried, filtered, and the filtrate was evaporated to afford almost quantitatively, (**4**), m.p. 118—119 °C, $[\alpha]^{22}_D$ −10.8° (*c* 1.3, chloroform). Compound (**4**) was reduced with Zn–AcOH in the presence of acetic anhydride to afford, after a basic work up and column purification, compound (**5**) (67—75%), m.p. 138—139 °C, $[\alpha]_D^{22}$ +22.5° (*c* 1.4, chloroform). Hydrogenation of (**5**) in ethanol containing toluene-*p*-sulphonic acid (1 M) was carried out under atmospheric pressure using 10% Pd–C, to afford the debenzylated product, 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-(1′-*N*-acetyl hydrazino)-β-D-glucopyranose, syrup, $[\alpha]_D^{22}$ +116.3° (*c* 1.8, chloroform). The debenzylated material was acetylated (pyridine–acetic anhydride) and the crude product was refluxed with isoamyl nitrite in tetrahydrofuran containing a trace quantity of water. After 16 h a major product had formed, which was isolated by column chromatography, to afford compound (**1**)[4] as a syrup (49—55% overall yield), $[\alpha]_D^{22}$ + 4.3° (*c* 1.2, chloroform). NMR data δ_H ($CDCl_3$): 5.6 (d, 1 H, $J_{1,2}$ 8.8 Hz, H-1), 5.1 (m, 2 H, H-3,4), 4.1—4.3 (2dd, 2 H, H-6a, 6b), 3.8 (m, 1 H, H-5), 3.7 (t with fine splittings, 1 H, H-2).

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