Efficient Method for Synthesis of *C*-β-D-Glucopyranosylmethanaloxime

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In recent years, the utility of nitro compounds in carbohydrate chemistry has been extended due to their outstanding properties to be used for carbon—carbon bond formation. Therefore, efficient methods for transformations or replacing the nitro group by hydrogen are required. In 1981, *Ono* [1] discovered that the nitro group in tertiary nitro compounds is replaced by hydrogen on treatment with tributyltin hydride (TBTH) in the presence of a radical initiator azoisobutyronitrile (AIBN). At more drastic conditions and using a large excess of TBTH, the method can be applied also to the denitration of secondary nitro compounds [2, 3]. However, primary nitro groups were originally considered to be inert to this procedure [3]. Now, we report on a simple conversion of easily available *C*-β-D-glucopyranosylnitromethane (2,6-anhydro-D-*glycero*-D-*gulo*-heptitol, *I*) [4] derived from D-glucose to the corresponding oxime under the denitration conditions (Scheme 1).

Treatment of per-*O*-acetylated *C*-β-D-glucopyranosylnitromethane in refluxing benzene with TBTH in the presence of 1,1′-azobis(cyclohexanecarbonitrile) (ABCN) gave (*E*)-*C*-β-D-glucopyranosylmethanaloxime (*II*) in a 90 % yield. The reduction product *II* was readily separable from tin compounds by passing through silica gel using a mixture of hexane—ethyl acetate (φ_r = 3 2). The same reduction product was formed when AIBN instead of ABCN was used under otherwise the same reaction conditions.

Analytical and spectroscopic data for compound *II*: M.p. = 155—157 °C; ^{1}H NMR spectrum (300.13 MHz, acetone-d_6), δ: 10.40 (s, 1H, OH), 7.25 (d, 1H, $J_{1,2}$ = 7.1 Hz, H-1), 5.35 (dd, 1H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.3 Hz, H-4), 5.06 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-3), 5.04 (dd, 1H, $J_{5,6}$ = 10.1 Hz, H-5), 4.24 (dd, 1H, H-2), 4.20 (dd, 1H, $J_{6,7a}$ = 5.2 Hz, $J_{7a,7b}$ = 12.4 Hz, H-7a), 4.10 (dd, 1H, $J_{6,7b}$ = 2.4 Hz, H-7b), 3.97 (ddd, 1H, H-6), 2.01, 2.00, 1.96, 1.93 (4s, 12H, 4 Me of Ac). ^{13}C NMR spectrum (acetone-d_6), δ: 170.7, 170.3, 170.0, 169.9 (4 CO of Ac), 146.7 (C-1), 76.4 (C-2), 75.3 (C-6), 74.1 (C-4), 70.6 (C-3), 69.4 (C-5), 63.1 (C-7), 20.6 (4 Me of Ac).

Our work to develop this synthetic method and to elucidate the mechanism of the conversion is in progress.

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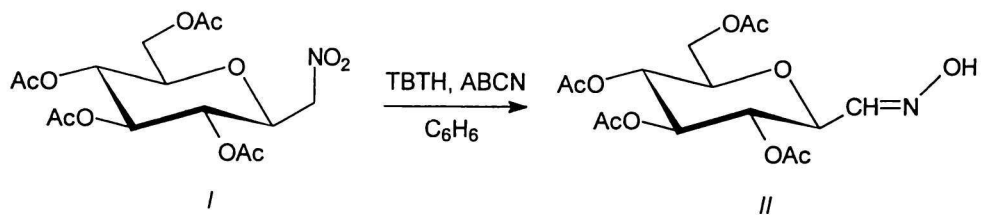

I *II*

Scheme 1