PRELIMINARY COMMUNICATION

Denitration of Primary Nitromethyl Groups in *C*-Glycopyranosylnitromethanes *via C*-Glycopyranosylmethanal Diethyl Dithioacetals

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Nitro compounds, noncarbohydrate as well as carbohydrate, are valuable intermediates due to their activating properties for carbon—carbon bond formation. Removal of the nitro group in a following step is a recent strategy in organic synthesis and is widely used for synthesis of complex natural products with various functional groups [1].

The nitro group of tertiary nitro compounds can be easily replaced by hydrogen on treatment with tributyltin hydride (TBTH) and catalytic amount of azobisisobutyronitrile (AIBN) in boiling benzene [2, 3]. Under these conditions, also a nitro group in an allyl or benzyl position or in a vicinal position to a keto or ester group is readily denitrated [4]. Inactivated secondary nitroalkyl groups are less reactive and a large excess of TBTH in boiling toluene is required providing mostly moderate yields of denitrated products [2, 5].

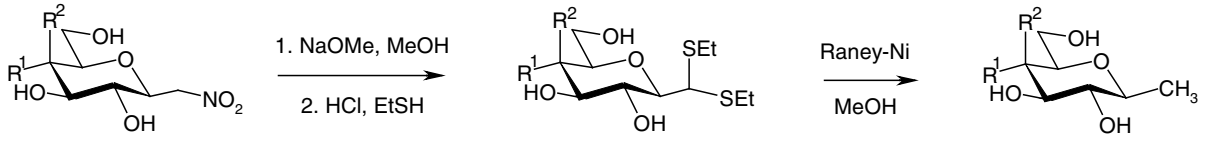
Primary nitro groups are much more resistant to the direct replacement by hydrogen. There is only one report on denitration of the primary nitro groups as a result of treatment with TBTH, *viz.* in the presence of 1,1′-azobis(cyclohexanecarbonitrile) (ABCN) [6]. However, a study of behaviour of a series of *C*-glycosylnitromethanes under treatment with TBTH in boiling benzene in the presence of ABCN has shown that the corresponding *C*-glycosylmethanal oximes are high-yield products of the transformation [7]. This reduction to the corresponding aldehyde oxime is selective to the primary nitro groups and remains secondary nitro groups unreacted [8].

Recently, we have described an extension of the Nef reaction to *C*-glycosylnitromethanes. The corresponding *C*-glycosylmethanal dialkyl acetals are the products of the transformation of the intermediate *C*-glycosylmethyl-hydrogennitronates in acidified low alcohols [9].

Here we report on an analogous acid-catalyzed solvolysis of the *C*-glycopyranosylmethyl-hydrogennitronate group with ethanethiol affording *C*-glycopyranosylmethanal diethyl dithioacetals, what introduces a new transformation of the primary nitromethyl group. Application of a known desulfurization of dialkyl dithioacetals with freshly activated Raney nickel [10, 11] enables then a two-step denitration of the primary nitromethyl group of *C*-glycopyranosylnitromethanes, which is reported here as well.

C-*β*-D-Glucopyranosylnitromethane (2,6-anhydro-1-deoxy-1-nitro-D-*glycero*-D-*gulo*-heptitol, [12], *Ia*, Scheme 1) was stirred in a 0.35 M-sodium methoxide in MeOH at r.t. for 24 h. The mixture was cooled at 0 °C and an HCl solution in EtSH (made of acetyl chloride in EtSH) was added so that a final 0.5 M-HCl solution in EtSH—MeOH ($\varphi_r = 2 : 1$) was obtained. After stirring for 2 h at 10—15 °C, the reaction mixture was deionized (strongly acidic cation-exchange resin in the H^+ form, strongly basic anion-exchange resin in the OH^- form) and the filtrate was concentrated to a solid sirup of *C*-*β*-D-glucopyranosylmethanal diethyl dithioacetal (2,6-anhydro-D-*glycero*-D-*gulo*-heptose diethyl dithioacetal, *IIa*) obtained in a 77 % yield. Subsequent treatment of *IIa* with a freshly prepared Raney nickel in methanol resulted in a quantitative formation of *C*-*β*-D-glucopyranosylmethane (2,6-anhydro-1-deoxy-D-*glycero*-D-*gulo*-heptitol, *IIIa*).

Analytical and spectroscopic data, compound *IIa*: [α] (D, 20 °C, MeOH, $\rho = 7.5$ g dm^{-3}) = −22.7°; ^{13}C NMR (75.47 MHz, CD_3OD), δ: 85.4, 82.2, 79.7, 72.7, 71.9 (C-2—C-6), 63.2 (C-7), 53.2 (C-1), 26.6, 26.3



Ia, Ib *IIa, IIb* *IIIa, IIIb*

a: R^1 = OH, R^2 = H

b: R^1 = H, R^2 = OH

Scheme 1

(CH_2), 15.0 ($2CH_3$). Compound *IIIa*: [α] (D, 20 °C, MeOH, $\rho = 10.0$ g dm^{-3}) = + 11.0°; ^{13}C NMR (75.47 MHz, CD_3OD), δ: 81.6, 79.7, 77.2 (2 ×), 72.2 (C-2—C-6), 63.2 (C-7), 18.4 (C-1).

Similar conversions were accomplished from the starting *C*-β-D-galactopyranosylnitromethane (2,6-anhydro-7-deoxy-7-nitro-L-*glycero*-L-*galacto*-heptitol, [12], *Ib*, Scheme 1), and the corresponding *C*-β-D-galactopyranosylmethanal diethyl dithioacetal (2,6-anhydro-D-*glycero*-L-*manno*-heptose diethyl dithioacetal, *IIb*) and *C*-β-D-galactopyranosylmethane (2,6-anhydro-7-deoxy-L-*glycero*-L-*galacto*-heptitol, *IIIb*) were obtained subsequently. Thus, in both cases, a substitution of a nitro group with a hydrogen atom was achieved in two steps and good overall yields in these primary nitromethyl groups.

Our work to develop this synthetic method for other *C*-glycosylnitromethanes and to extend it also to inactivated secondary nitroalkyl groups is in progress.

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