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LETTERS TO THE EDITOR

Shortest Route to 2-Deoxyaldonic Acids

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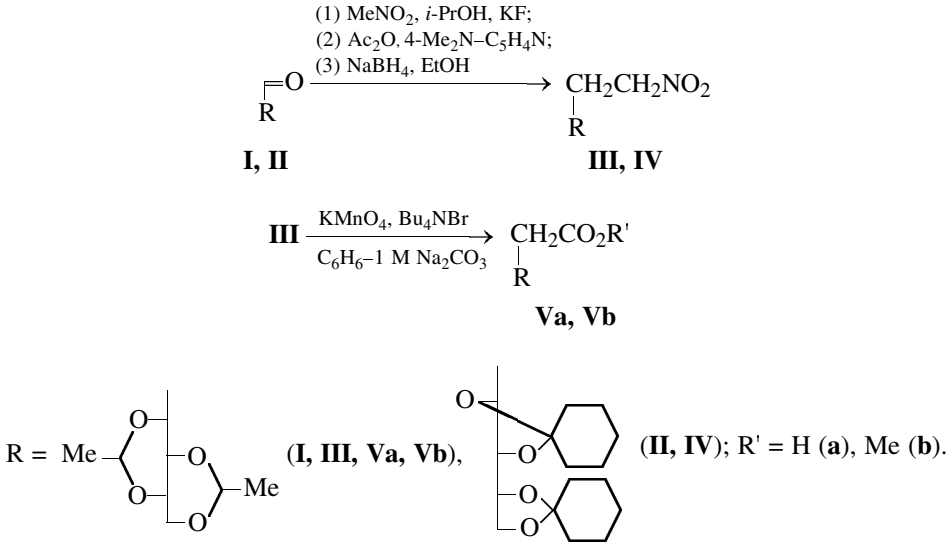
The search for new, still unrealized synthetic routes to higher biologically important carbohydrate derivatives is not infrequently hindered by facile and effective procedures for synthesis of 2-deoxyaldonic acids with alkali-resistant protective groups.

In the present work we suggest such a procedure that involves 1-C-nitromethylpolyols as potential sources of carbonyl-containing carbohydrate derivatives. Previously we reported a one-pot synthesis of the base nitro derivative **III** [1]. The universality of this new methods of reductive nitromethylation of aldoses like **I** and **II** we confirmed by the synthesis of dicyclohexylidene-D-*arabino*-hexitol (**IV**) in a yield of 62%.



The oxidation of compound **III** with $KMnO_4$ into 2-deoxy acid **Va** under conditions of phasetransfer catalysis, like with 5-C-nitromethyl derivatives of furanoses [2]. Permanganate ions are fairly effectively transferred into the organic phase, and the reaction is complete in 3 h. Acid **Va** was isolated in quantitative yield and additionally characterized as methyl ester **Vb**. The latter was obtained by treatment of acid **Va** with ethereal diazomethane with subsequent column chromatofgraphy on Silochrom in $CHCl_3$.

The elemental analyses were consistent with the proposed structures.

1,2-Dideoxy-1-nitro-3,4:5,6-di-*O*-cyclohexylidene-D-*arabino*-hexitol (IV). Yield 62%, syrup-like material, R_f 0.6 (Silochrom, $CHCl_3$–C_6H_6, 1 : 1 v/v). IR spectrum, ν, cm^{-1}: 1547 (NO_2). ^1H NMR spectrum, ν, ppm: 1.4–1.6 m (20H, $2C_6H_{10}$); 2.2, 2.5 d.m (2H, HC_2), 3.5–4.1 m (5H, $HC^{3\text{-}6,6'}$), 4.6 t (2H, CH_2NO_2).

2-Deoxy-3,5:4,6-di-*O*-ethylidene-L-*xylo*-hexonic

acid (Va). Yield 82%, colorless crystals, mp 173–175°C (from toluene), R_f 0.3 (Silochrom, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3100 (OH), 1710 (CO). ^1H NMR spectrum, ν, ppm: 1.4 m (6H, 2MeCH); 2.8 d (2H, HC^2), 3.6–4.2 m (5H, $HC^{3\text{-}6,6'}$), 4.7, 4.8 d.q (2H, 2MeCH), 10.0 br.s (1H, CO_2H).

Methyl 2-deoxy-3,5:4,6-di-*O*-ethylidene-L-*xylo*-hexonoate (Vb). Yield 75%, syrup-like material, R_f 0.7 (Al_2O_3, $CHCl_3$), 0.6 (Silochrom, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1740 (CO_2Me). ^1H NMR spectrum, ν, ppm: 1.4 m (6H, 2*Me*CH), 2.7 m (2H, HC^2), 3.55–4.15 m (8H, OMe, $HC^{3\text{-}6,6'}$), 4.7, 4.8 d.q (2H, 2MeC*H*).

The IR spectra were measured on an IR-75 spectrometer in thin films. The 1H NMR spectra were obtained on a Bruker DPX-250 instrument (250 MHz) in $CDCl_3$, internal reference HMDS. Thin-layer and column chromatography were performed on Silochrom C-80 (0.2–0.35mm) and Al_2O_3.

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