

# Photolysis of 1-azido-1-deoxyalditols

## Preparation of D-mannose

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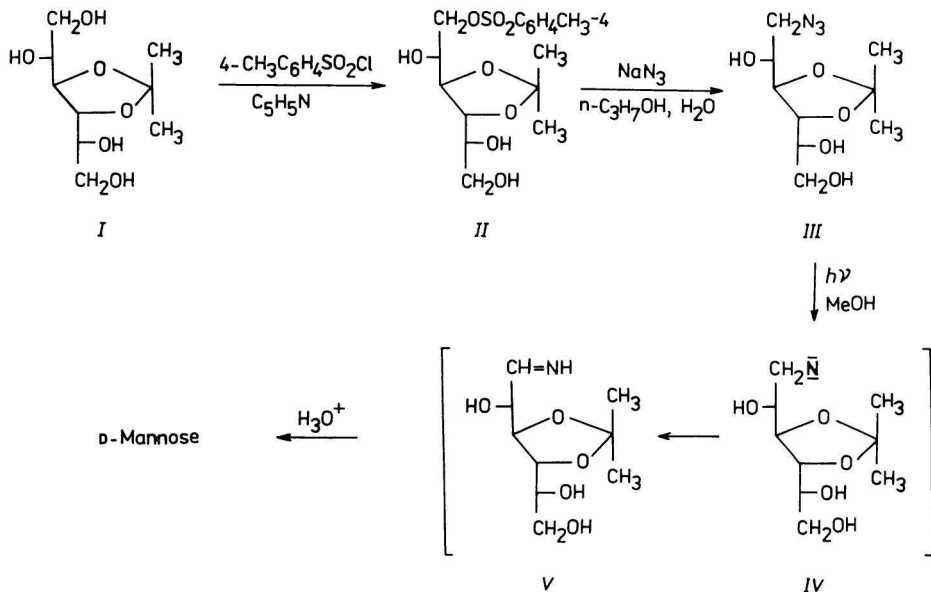
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3,4-*O*-Isopropylidene-1-*O*-(4-methylbenzenesulfonyl)-D-mannitol has been prepared by partial tosylation of the starting 3,4-*O*-isopropylidene-D-mannitol. This derivative was treated with sodium azide to give 1-azido-1-deoxy-3,4-*O*-isopropylidene-D-mannitol, which on photolysis and subsequent acid hydrolysis afforded D-mannose.

Посредством парциального тозилрования исходного 3,4-*O*-изопропилиден-D-маннитола получен 3,4-*O*-изопропилиден-1-*O*-(4-метилбензосульфо)-D-маннитол. В результате действия азиды натрия на полученное соединение образовался 1-азидо-1-дезоксид-3,4-*O*-изопропилиден-D-маннитол, из которого после фотолиза и последующего кислотного гидролиза была получена D-манноза.

Conversion of the primary hydroxyl group to aldehyde group, generally utilized in preparation of omega-aldehyde derivatives of saccharides, is relatively well developed. Such conversion can be achieved by several synthetic procedures of catalytic oxidation [1] as well as by utilization of various oxidizers [2—4]. Another approach to the solution of this problem is photochemical conversion of suitable derivatives, for example photochemical oxidation of *O*-pyruvoyl derivatives [5] or photolysis of azidodeoxy derivatives, in combination with subsequent hydrolysis of the aldimine formed by rearrangement of the alkylnitrene photolytic product [6].

In the present work we have shown the possibility of applying the last procedure to simple conversion of alditols to aldoses with the same number of carbon atoms. This method in an unambiguous process does not require protection of hydroxyl groups. The starting 3,4-*O*-isopropylidene-D-mannitol (*I*, Scheme 1) was sufficiently soluble in pyridine, owing to the 3,4-*O*-isopropylidene group. 3,4-*O*-Isopropylidene-1-*O*-(4-methylbenzenesulfonyl)-D-mannitol (*II*) was prepared in a relatively low (ca. 35 %) yield by classical partial tosylation of the derivative *I* with equimolar amount of tosyl chloride. This crystalline derivative was unstable (losing the tosyl group on standing) similarly as the other noncrystalline reaction product, 3,4-*O*-isopropylidene-1,6-bis-*O*-(4-methylbenzenesulfonyl)-D-mannitol [7]. Quantitative decomposition of the derivative *III* in methanol was



Scheme 1

achieved by photolysis within 4 h under the conditions used. It is known that photolysis of primary alkyl azides results in the corresponding aldimines which are formed presumably from the primary photolytic product, alkylnitrene, by rearrangement of the  $\alpha$ -proton to the nitrene nitrogen atom [8]. In our case the product of photolysis was obviously the alkylnitrene derivative IV, providing the aldimine V (Scheme 1) which on subsequent hydrolysis with strong acid cation exchanger afforded D-mannose in 55 % yield.

The synthetic pathway presented for conversion of D-mannitol to D-mannose provides another method for preparation of aldoses from alditols. Works on utilization of this procedure for preparation of further aldoses are in progress.

## Experimental

Specific optical rotations were measured on a Perkin—Elmer 141 polarimeter, elemental analysis was performed on a Perkin—Elmer 240 analyzer, infrared spectra were recorded on a Perkin—Elmer 457 spectrophotometer, and melting points were obtained on a Kofler block.  $^{13}\text{C}$  NMR spectra were measured on a Bruker AM-300 spectrometer in  $\text{C}^2\text{H}_5\text{O}^2\text{H}$  at room temperature. The data for *O*-(4-methylbenzenesulfonyl) derivatives [9] and *O*-isopropylidene derivatives of alditols [10] were used to assign the individual signals.

Thin-layer chromatography was carried out on Silufol plates (Lachema, Brno) in the elution system *S*<sub>1</sub>: benzene—methanol (volume ratio = 6 : 1). Nonfiltered light of medium-pressure 125 W mercury discharge lamp RVL-125 (Tesla, Holešovice) with removed luminophore was used for irradiation.

### 3,4-*O*-Isopropylidene-1-*O*-(4-methylbenzenesulfonyl)-*D*-mannitol (*II*)

3,4-*O*-Isopropylidene-*D*-mannitol (*I*) ([11], 7 g; 31.5 mmol) was dissolved in pyridine (70 cm<sup>3</sup>) and 4-methylbenzenesulfonyl chloride (6 g; 31.5 mmol) dissolved in pyridine (15 cm<sup>3</sup>) was added with stirring at 0 °C within 20 min. The temperature of the reaction mixture was allowed to equalize with room temperature during 4 h stirring and the mixture was put aside for 48 h. Then pyridine was distilled off at reduced pressure, the distillation residue was dissolved in chloroform and shaken with aqueous solutions of potassium hydrogen sulfate and sodium hydrogen carbonate. The chloroform solution was dried over anhydrous sodium sulfate, evaporated and the residue was crystallized from the mixture of benzene—hexane (volume ratio = 5 : 1) to give *II* (*m* = 4.9 g; yield = 41 %) with the admixture of 3,4-*O*-isopropylidene-1,6-bis-*O*-(4-methylbenzenesulfonyl)-*D*-mannitol; TLC-*R*<sub>f</sub>: 0.30 (*II*), 0.49 (di-*O*-tosyl derivative). After two crystallizations from the same mixture of solvents chromatographically pure *II* with m.p. = 55—56 °C and  $[\alpha]_D^{20}$  (20 °C, methanol,  $\rho = 20 \text{ g dm}^{-3}$ ) = +31.3° was obtained. <sup>13</sup>C NMR,  $\delta$ /ppm: 145.55, 133.32, 130.10, and 128.23 (6 aryl C), 109.95 (acetal C), 71.12 (C-1), 73.40 and 72.15 (C-2 and C-5), 80.06 and 79.22 (C-3 and C-4), 63.68 (C-6), 26.42 (2CH<sub>3</sub>-acetal), 20.71 (CH<sub>3</sub>-aryl).

For C<sub>16</sub>H<sub>24</sub>O<sub>8</sub>S (*M*<sub>r</sub> = 376.43) *w*<sub>i</sub>(calc.): 51.05 % C, 6.43 % H, 8.52 % S; *w*<sub>i</sub>(found): 51.23 % C, 6.58 % H, 8.80 % S.

### 1-Azido-1-deoxy-3,4-*O*-isopropylidene-*D*-mannitol (*III*)

The title compound was prepared by the modified procedure [12]. The mixture of solutions of *II* (2.6 g; 6.9 mmol) in 1-propanol (42 cm<sup>3</sup>) and sodium azide (2 g; 30.7 mmol) in water (15 cm<sup>3</sup>) was heated at 100 °C for 5 h. The reaction mixture was evaporated to dryness at 40 °C and the residue was extracted with acetone (3 × 50 cm<sup>3</sup>). The pooled acetone extracts were evaporated to give a crude sirupy *III* (*m* = 1.5 g; yield = 88 %); TLC-*R*<sub>f</sub>: 0.30 (*II*), 0.49 (di-*O*-tosyl derivative). After two crystallizations from the same Silica gel L 40—100 μm in the elution system *S*<sub>1</sub> gave the chromatographically pure sirupy *III* with  $[\alpha]_D^{20}$  (20 °C, methanol,  $\rho = 20 \text{ g dm}^{-3}$ ) = +37.4°. IR,  $\tilde{\nu}$ /cm<sup>-1</sup>: 2120 (N<sub>3</sub>). <sup>13</sup>C NMR,  $\delta$ /ppm: 109.80 (acetal C), 54.25 (C-1), 73.52 and 72.70 (C-2 and C-5), 80.32 and 80.05 (C-3 and C-4), 63.65 (C-6), 26.45 (2CH<sub>3</sub>-acetal).

For C<sub>9</sub>H<sub>17</sub>N<sub>3</sub>O<sub>5</sub> (*M*<sub>r</sub> = 247.25) *w*<sub>i</sub>(calc.): 43.72 % C, 6.93 % H, 16.99 % N; *w*<sub>i</sub>(found): 44.03 % C, 7.21 % H, 16.66 % N.

### Photolysis of *III* and isolation of *D*-mannose

The solution of *III* (1 g) in methanol (400 cm<sup>3</sup>) placed in the external jacket of the three-jacket quartz reactor (Kavalier, Sázava) and bubbled with nitrogen during 4 h was

irradiated from the inner vessel of the reactor. The temperature of the reaction mixture was 25—30 °C and the heat of the discharge lamp was carried away by water circulating through the inner jacket of the reactor. Methanol was distilled off from the reaction mixture at reduced pressure, water (20 cm<sup>3</sup>) and Dowex 50 W in H<sup>+</sup> form (3 g) were added to the residue and the mixture was refluxed for 3 h. Then the cation exchanger was filtered off, washed with water (5 × 10 cm<sup>3</sup>) and the filtrate was evaporated to give a sirup ( $m = 0.5$  g; yield = 68 %) which on crystallization from the mixture of methanol—ethanol (volume ratio = 1 : 6) afforded D-mannose ( $m = 0.1$  g) with m.p. = 130—131 °C and  $[\alpha]_D^{20}$  (D, 20 °C, water,  $\rho = 21$  g dm<sup>-3</sup>) = +13.8°. Another amount of D-mannose ( $m = 0.3$  g, i.e. total 0.4 g; total yield = 55 %) was obtained by purification through phenylhydrazone of D-mannose [13].

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