

Partial Desulphurisation of Sugar Thioacetals

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Reductive desulphurisation of sugar thioacetals with Raney nickel, as devised by Wolfrom and Karabinos¹, is a convenient method for the preparation of deoxyalditols. In the course of the study of a natural deoxyheptitol², we used this method to prepare the 1-deoxyheptitols from some heptose diethyl dithioacetals. Chromatographic examination of the reaction products sometimes revealed the presence of a component with an R_F -value intermediate between those of the starting material and the desired product. On further treatment with Raney nickel this component disappeared. It therefore seemed probable that the component was the 1-deoxy-1-thioethylheptitol and that 1-deoxy-1-thioalkylalditols in general could be prepared by controlled reductive desulphurisation of the corresponding sugar thioacetals with Raney nickel. This reduction has now been studied with two more easily available substances, the diethyl dithioacetals of D-galactose and D-mannose.

Different preparations of Raney nickel may differ in activity and this also decreases with the age of the preparation. Furthermore it is difficult to estimate the amount of Raney nickel used in a reaction accurately. The preferred procedure was therefore to treat the thioacetal with an insufficient quantity of Raney nickel, characterise the reaction products by paper chromatography and continue the treatment with fresh amounts of Raney nickel until the starting material had just disappeared on the chromatograms. In the two examples studied, the 1-deoxy-1-thioethylhexitol could then be isolated by crystallisation, and further amounts obtained by fractionation of the mother liquors on a cellulose column.

The 1-deoxy-1-thioethylhexitols prepared gave correct analyses and on further treatment with Raney nickel yielded the expected 1-deoxyhexitols. This, together with their mode of preparation, should prove their structures. It is believed that the described reductive desulphurisation of

sugar thioacetals is a general reaction and might find synthetic applications.

Experimental. Chromatograms were run on Whatman No. 1 filter papers, using 95 % aqueous acetone (v/v) as irrigant. A satisfactory separation was obtained in 30 min. The spots were developed with silver nitrate-sodium hydroxide³. Butan-1-ol, saturated with water, was used as irrigant in the cellulose column separations.

1-Deoxy-1-thioethyl-D-galactitol. A solution of D-galactose diethyl dithioacetal (10 g), in 70 % aqueous ethanol (150 ml) was refluxed on the steam bath. Successive amounts of Raney nickel W-2, prepared according to *Org. Syntheses*⁴ were added as slurries in anhydrous ethanol and the mixture was characterised by paper chromatography 15 min after each addition. When the starting material had disappeared, the mixture was cooled, the nickel removed by filtration and washed with ethanol and water. The combined filtrate and washings were concentrated to dryness and crystallised from water, yielding 1-deoxy-1-thioethyl-D-galactitol (2.48 g), m.p. 148–149°, $[\alpha]_D^{20} -3^\circ$ (c, 2.0 in pyridine) (Found: C 42.4; H 7.94; S 14.0. Calc. for $C_8H_{18}O_6S$: C 42.5; H 8.01; S 14.2).

Fractionation of the mother liquors on a cellulose column yielded further 1-deoxy-1-thioethyl-D-galactitol (1.08 g) and 1-deoxy-D-galactitol (1.20 g), m.p. 153–154°.

1-Deoxy-1-thioethyl-D-mannitol. D-Mannose diethyl dithioacetal (10 g) was treated as described above for the corresponding D-galactose derivative. The reaction product, on crystallisation from ethanol, yielded the 1-deoxy-1-thioethyl-D-mannitol (3.06 g) of m.p. 107–108°. An analytical sample melted at 114–115° and showed $[\alpha]_D^{20} +32^\circ$ (c, 2.0 in water). (Found: C 42.8; H 8.06; S 14.0. Calc. for $C_8H_{18}O_6S$: C 42.5; H 8.01; S 14.2).

Further amounts of the same substance (1.25 g) and 1-deoxy-D-mannitol (0.98 g) m.p. 121–122°, were obtained from the mother liquors after fractionation on a cellulose column.

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Received June 6, 1961.