Methoxy-group Migration in the Hydrolysis of the 4-Nitrobenzene-*p*-sulphonates of Methyl β-D-Xylopyranoside and Methyl β-D-Glucopyranoside

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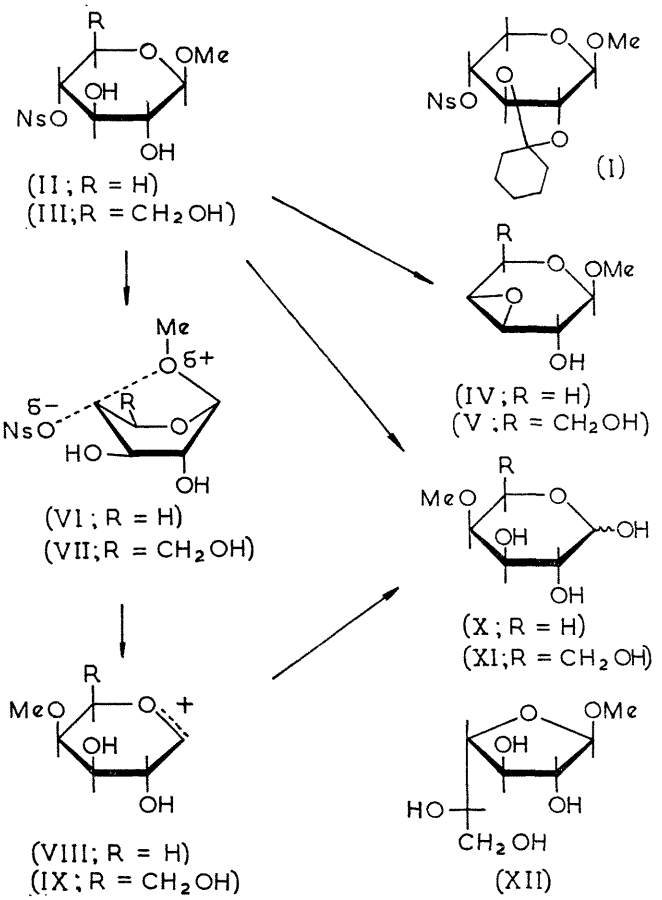
Summary One of the products of hydrolysis of methyl 4-*O*-nitrobenzene-*p*-sulphonyl-β-D-xylopyranoside, at pH 5, is 4-*O*-methyl-L-arabinose, while the corresponding β-D-glucopyranoside yields both 4-*O*-methyl-D-galactose and methyl α-L-altrofuranoside as products.

As part of a study of sugar nitrobenzene-*p*-sulphonates[1,2] we have examined the hydrolysis of methyl 4-*O*-nitrobenzene-*p*-sulphonyl-β-D-xylopyranoside (II), which was prepared as follows. Methyl β-D-xylopyranoside was treated with 1,1-dimethoxycyclohexane (1·4 mol.) in dimethylformamide at 75°/0·1 mm., using toluene-*p*-sulphonic acid as catalyst, to give a mixture of the two isomeric *O*-cyclohexylidene acetals,[3] consisting mainly of one isomer, as shown by t.l.c. After reaction of the mixture of acetals with nitrobenzene-*p*-sulphonyl chloride in pyridine a crystalline sulphonate (I), m.p. 132°, $[\alpha]_D$ − 60·6° ($CHCl_3$) was isolated in 69% overall yield. Hydrolysis of the sulphonate (I) with aqueous acetic acid afforded the required diol (II) (79%), m.p. 62—65°, $[\alpha]_D$ −66·5° (EtOAc), shown to be the 4-sulphonate by conversion into the epoxide (IV) with sodium methoxide in methanol.[4]

When the sulphonate (II) was heated at 100° in water containing sodium acetate (2 mol.) and acetic acid (1 mol.), t.l.c. indicated that reaction was complete in 1·5 hr. Paper chromatography and g.l.c.[5] showed that the major products were methyl 3,4-anhydro-α-L-arabinopyranoside (IV) (*ca.* 40%), together with 4-*O*-methyl-L-arabinose (X) (*ca.* 30%), and methyl α-L-arabinopyranoside (*ca.* 15%). The sugar (X) was identified, after separation from other components by chromatography on Deacidite FF SRA 63 (HSO_3^- form) resin,[6] by conversion into methyl 4-*O*-methyl-β-L-arabinopyranoside m.p. 112—114°, indistinguishable from an authentic sample.[7]

Several cases of alkoxy-group migration in the carbohydrate series have been reported.[8] In the present case the formation of the sugar (X) must involve a boat-like transition state (VI) similar to that encountered in the acetolysis of *trans*-4-methoxycyclohexyl toluene-*p*-sulphonate.[9] Migration of the methoxy-group is promoted by the mesomeric effect of the pyranose ring oxygen with the formation of the glycosyl cation (VIII).

The hydrolysis of the β-D-glucoside (III) has been studied from the point of view of methoxy-group migration and ring-contraction.[2] The sulphonate (III) m.p. 140—a 43°, $[\alpha]_D$ −35° (EtOAc), was prepared from methyl



Ns = *p*-$O_2N{\cdot}C_6H_4{\cdot}SO_2$—

2,3-di-*O*-*p*-nitrobenzoyl-4-*O*-nitrobenzene-*p*-sulphonyl-6-*O*-triphenylmethyl-β-D-glucopyranoside by careful treatment with sodium methoxide in methanol, followed by detritylation under acidic conditions. Among the products of hydrolysis of the sulphonate (II) in water at pH 5 were

methyl 3,4-anhydro-β-D-galactopyranoside (V) (*ca.* 50%), 4-*O*-methyl-D-galactose (XI) and methyl α-L-altrofuranoside (XII), which were isolated in crystalline form and identified by comparison with authentic compounds.[2,10]

Formation of the sugar (XI) is to be expected by analogy with the β-xyloside (II). The transition state (VII) should be energetically very similar to (VI), since the hydroxymethyl group in (VII) is equatorial, having an eclipsing interaction only with an oxygen lone-pair. The resulting glycosyl cation (IX) leads to the sugar (XI). The formation of the furanoside (XII) is analogous to the behaviour of methyl 4-*O*-nitrobenzene-*p*-sulphonyl-α-D-glucopyranoside,[2] and it is interesting that in both the α- and β-series only the L-altrofuranoside isomer [as in (XII)] is formed, with no detectable C-5 epimer.[2,8c] No ring contraction to a furanoside was observed in the hydrolysis of the xyloside.

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