Reaction of 2,3:6,7-Di-*O*-isopropylidene-5-*O*-toluene-*p*-sulphonyl-D-*glycero*-D-*gulo*-heptofuranose with Sodium Methoxide: a Possible Case of Intramolecular Transtosylation

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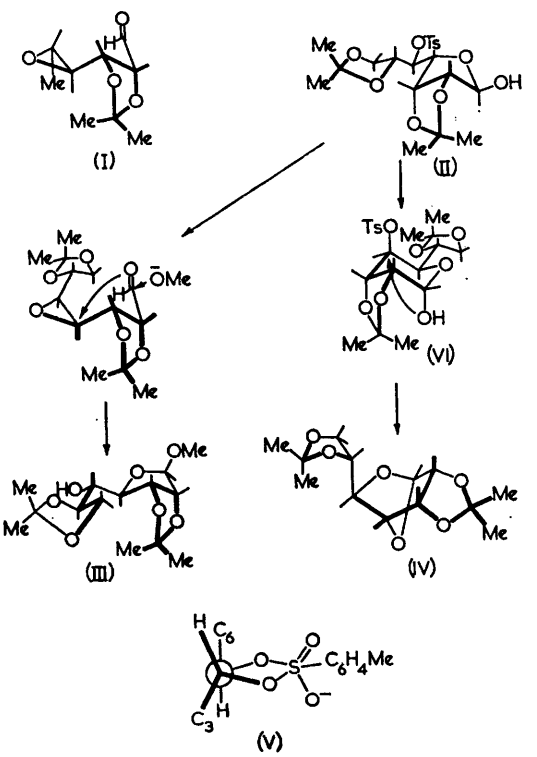
2,3-*O*-ISOPROPYLIDENE-5-*O*-TOLUENE-*p*-SULPHONYL-L-RHAMNOFURANOSE rapidly reacts with sodium methoxide at room temperature to give methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside[1] and it has been postulated[2] that the epoxide (I) is first formed and is subsequently attacked by methoxide ion. Under similar conditions, 2,3:6,7-di-*O*-isopropylidene-5-*O*-toluene-*p*-sulphonyl-D-*glycero*-D-*gulo*-heptose (II) [obtained as a chromatographically homogeneous syrup, $[\alpha]_D$ −7° (chloroform), by acid-catalysed acetonation of D-*glycero*-D-*gulo*-heptose followed by sulphonylation] reacted much less readily.

After 48 hr., two major products (*A* and *B*) were isolated by chromatography on silica gel. Product *A* (28%), b.p. 140—150° (bath)/0·1 mm. (slight decomp.), $[\alpha]_D$ −28·5° (chloroform), was identified as methyl 2,3:6,7-di-*O*-isopropylidene-β-D-*glycero*-L-*talo*-heptofuranoside (III) by the following evidence. It had a molecular weight of 304 (mass spectrometry) and the n.m.r. spectrum ($CDCl_3$ with internal tetramethylsilane) clearly demonstrated the presence of methoxyl (τ 6·40, 3 proton singlet) and diketal (τ 8·46, 8·50, 8·55, 8·63, singlets, 12 protons) groups. Complete acidic hydrolysis gave D-*glycero*-L-*talo*-heptose (identified chromatographically[3]). Graded acidic hydrolysis afforded a syrupy monoketal, with n.m.r. signals at τ 6·68 (OMe) and τ 8·59, 8·74 (CMe_2), which was converted into D-ribose following successive treatments with sodium periodate (2 mol.), sodium borohydride, and acid. Compound (III) presumably arises *via* a reaction sequence (II → III) similar to that suggested[2] for the rhamnose sulphonate.



The product *B* (15·5%), m.p. 117—118°, $[\alpha]_D$ −34° (chloroform), had a molecular weight of 272

and an elemental analysis corresponding to the molecular formula $C_{13}H_{20}O_6$. Acidic hydrolysis yielded D-*glycero*-D-*allo*-heptose, m.p. and mixed m.p. 90—93° (lit.,[4] m.p. 95—98°). Graded acidic hydrolysis gave a monoketal, m.p. 107—108°, $[\alpha]_D$ −21° (chloroform), which on treatment in succession with periodate (1 mol. consumed), borohydride, and acid was converted into D-allose (identified chromatographically). Further, the infrared spectrum (CCl_4) showed no absorptions for C=C, C=O, or OH groups. Thus, compound *B* must be 1,4-anhydro-2,3 : 6,7-di-*O*-isopropylidene-α-D-*glycero*-D-*allo*-heptopyranose (1,5-anhydro-2,3 : 6,7-di-*O*-isopropylidene-β-D-*glycero*-D-*allo*-heptofuranose) (IV). The n.m.r. spectrum of compound *B* is entirely consistent with structure (IV) showing signals at τ 4·59 [singlet, H(1)], 5·26, 5·73 [AB quartet, $J_{2,3}$ 5·7 c./sec., H(2) and H(3)], 5·28 [doublet, $J_{4,5}$ 3·8 c./sec., H(4)]: significantly, no coupling is observed between the protons H(1)—H(2) and H(3)—H(4) on the bicyclic ring system which subtend dihedral angles of *ca.* 90°.

Anhydro-compound (IV) differs from the original sulphonate (II) in that the configuration at C-4 is inverted and its formation is best accounted for in terms of a base-catalysed, intramolecular (*cf.*, refs. 5 and 7) sulphonyl group migration from C-5 to C-4 *via* a cyclic diester (*e.g.*, V). This process is presumably facilitated by steric hindrance to rotation about the C-4–C-5 bond. Subsequent intramolecular displacement of the sulphonate group at C-4 by the anomeric hydroxyl group in compound (VI) yields the anhydro-compound (IV) (*cf.*, ref. 6).

Migrations involving sulphonate groups are rare but migration of the sulphate group, to the equatorial hydroxymethyl group, occurs[7] with chondroitin 4-sulphate at elevated temperatures, presumably through a cyclic 4,6-diester.

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