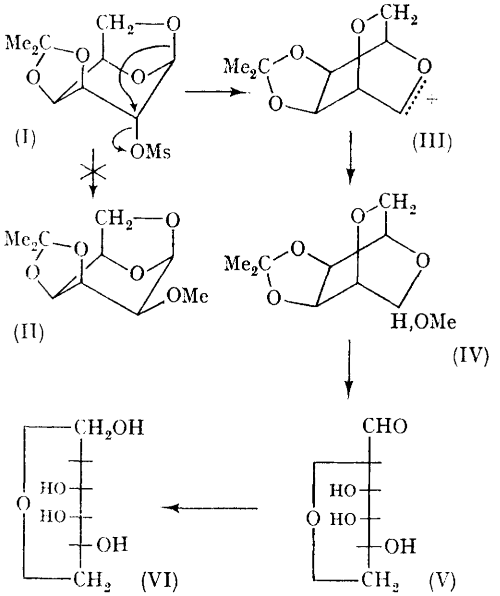
Formation of Methyl 2,6-Anhydro-3,4-*O*-isopropylidene-α- and -β-D-talopyranosides by an Intramolecular Displacement in the Methanolysis of 1,6-Anhydro-3,4-*O*-isopropylidene-2-*O*-methanesulphonyl-β-D-galactopyranose

By N. A. HUGHES

(*Department of Organic Chemistry, University of Newcastle upon Tyne*)

IN 1959 it was reported[1] that solvolysis of 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-methanesulphonyl-β-D-galactopyranose (I) in methanol containing potassium fluoride dihydrate at 130° for 15 hr. gave 1,6-anhydro-3,4-*O*-isopropylidene-2-*O*-methyl-β-D-talopyranose (II). This result seemed unlikely; the anhydro-compound (I) should experience considerable steric hindrance in an S_N2 displacement reaction. A much more probable course of reaction would be an intramolecular displacement from the C-1–C-6 oxygen atom, ideally placed in a *trans*-diaxial relationship in the sulphonate group. The resultant carboxonium ion (III) could then react with methanol to give a mixture of anomers of methyl 2,6-anhydro-3,4-*O*-isopropylidene-D-talopyranoside

(IV). A number of related reactions have been described recently.[2]



This has been shown to be the case. Repetition of the solvolysis under the conditions described earlier gave two isomeric products. The major product (68%), m.p. 77—79°, $[\alpha]_D$ −70·1°, appeared to be identical with that described earlier (m.p. 72—73°, $[\alpha]_D$ −75·1°), the minor product (8%) had m.p. 85—87°, $[\alpha]_D$ + 52·5°. The mass spectra of the two products were virtually superimposable and the n.m.r. spectra indicated the presence of an *O*-methyl group and an isopropylidene group in each compound. Complete acidic hydrolysis of either of the products (IV) gave a reducing compound, presumably (V) or a hemi-acetal form, which when reduced with sodium borohydride gave 1,5-anhydro-D-altritol (2,6-anhydro-D-talitol) (VI) identical in all respects with an authentic sample[3] (kindly provided by Dr. N. K. Richtmyer). From a consideration of optical rotations the major product is probably the *β*- or *exo*-anomer and the minor product the α- or *endo*-anomer (the structurally related methyl 2,6-imino-2,6-dideoxy-3,4-*O*-isopropylidene-α-D-talopyranoside[4] has $[\alpha]_D$ + 65·1°).

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