

The Reaction of Sulphur Ylids with Methyl Glycopyranosiduloses

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ONE route for the preparation of branched-chain glycosides involves epoxidation of glycopyranosiduloses with diazomethane followed by cleavage of the epoxide either with lithium aluminium hydride to give a glycoside with a *C*-methyl substituent,¹ or with alkali to give a *C*-hydroxymethyl substituent.² The reaction with diazomethane leads to a mixture of isomeric epoxides and also, under appropriate conditions, can result in ring expansion of the glycoside.³ Consequently an alternative method for the epoxidation of glycopyranosiduloses has been examined, namely treatment with dimethylsulphoxonium methylide.

Methyl 4,6-*O*-benzylidene-2-deoxy- α -D-*erythro*-hexopyranosid-3-ulose¹ when treated with dimethylsulphoxonium methylide afforded a spiro-epoxide (I) (65%), m.p. 123—124°, $[\alpha]_D + 154^\circ$ (EtOAc) which was cleaved with lithium aluminium hydride in ether to give a methyl 4,6-*O*-benzylidene-2-deoxy-3-*C*-methyl- α -D-hexopyranoside (II), m.p. 124—125°, $[\alpha]_D + 120^\circ$ (EtOH), which was shown to be identical (mixed m.p., infrared spectrum) with a sample of methyl 4,6-*O*-benzylidene-2-deoxy-3-*C*-methyl- α -D-*ribo*-hexopyranoside, m.p. 125.5—126°, $[\alpha]_D + 121^\circ$ (EtOH), kindly provided by Dr. B. Flaherty of this laboratory.

From the n.m.r. spectrum[†] of the epoxide (I) an unambiguous proton count of 18 was obtained. The assignment of signals was as follows: the five protons at τ 2.60 were clearly the phenyl protons and the singlet at τ 4.45 was due to the acetal proton. The doublet at τ 5.18 (1 proton) and the 4 protons at τ 5.6—6.3 were assigned respectively to the anomeric proton and to H-4, H-5, H-6 *eq.* and H-6 *ax.* The two sharp doublets at τ 7.0 (1 proton) and τ 7.54 (1 proton) were assigned to the protons of the epoxide ring (these were 13 c./sec. and 18 c./sec. up-field from the corresponding doublets of the C-3 epimer). The 3 protons in the singlet at τ 6.63 were those of the methoxy-group, and H-2 *ax.* and H-2 *eq.* gave rise respectively to the quartets at τ 7.6 (1 proton) and 8.4 (1 proton). All splittings were consistent with formulation of the epoxide as (I). The n.m.r. spectrum of compound (II) gave a proton count of 20: the two sharp doublets assigned to the epoxide ring had disappeared and a singlet at τ 8.73 (3 protons) was due to the methyl group at C-3.

From the reaction of methyl 3,4-*O*-isopropylidene- β -L-*erythro*-pentopyranosidulose⁴ and dimethylsulphoxonium methylide a mixture of epoxides (A) (80%) was obtained which on

[†] N.m.r. spectra were obtained for solutions in CDCl₃ and Me₄Si was used as an internal standard.

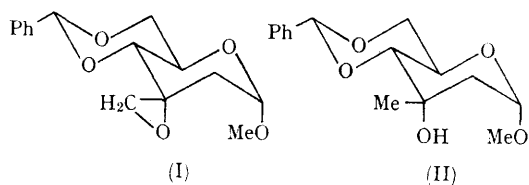
successive mild hydrolysis with alkali and acid gave methyl 2-C-hydroxymethyl- β -L-ribose and -arabino-
side, identified by comparison on paper chromatograms (solvent systems: ethyl methyl ketone saturated with water, or n-butanol-ethanol-water, 4:1:5, v/v) with authentic samples prepared from the pentopyranosidulose by treatment with diazomethane and subsequent hydrolysis, according to the method of Overend and Williams.²

Reduction of the mixture (A) with lithium aluminium hydride in ether gave a clear syrup (80%). The major component (*ca.* 75% of the mixture), b.p. 60°/0.1 mm., $[\alpha]_D + 113^\circ$ (CHCl₃) was partially hydrolyzed to afford crystalline methyl 2-C-methyl- β -L-arabinopyranoside, m.p. 100°, $[\alpha]_D + 130^\circ$ (EtOH). Burton *et al.*⁴ give m.p. 100°, $[\alpha]_D + 124^\circ$ (EtOH) for this compound, and the L-ribo-epimer has m.p. 58–59°, $[\alpha]_D + 174^\circ$ (MeOH).⁵

To establish the generality of the reaction, a furanoid derivative, namely 5-O-benzoyl-1,2-O-isopropylidene- α -D-erythro-pentofuranos-3-ulose,⁶ has been treated with the methylide and it has

been found that epoxidation proceeds in normal fashion.

Corey and Chaykovsky⁷ have noted that, with cyclic carbonyl compounds, dimethylsulphoxonium methylide gives preferentially an equatorial addition product but on the other hand treatment of cyclic ketones with dimethylsulphonium methylide results in axial addition.⁷ With the above "oxo-sugars" we find that their reaction with dimethylsulphonium methylide is more complex than with dimethylsulphoxonium methylide, but these reactions will be reported later.



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⁵ R. J. Ferrier, W. G. Overend, G. A. Rafferty, H. M. Wall, and N. R. Williams, unpublished results.

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⁷ E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, 87, 1353.