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HYDROFORMYLATION OF CARBOHYDRATE EPOXIDES

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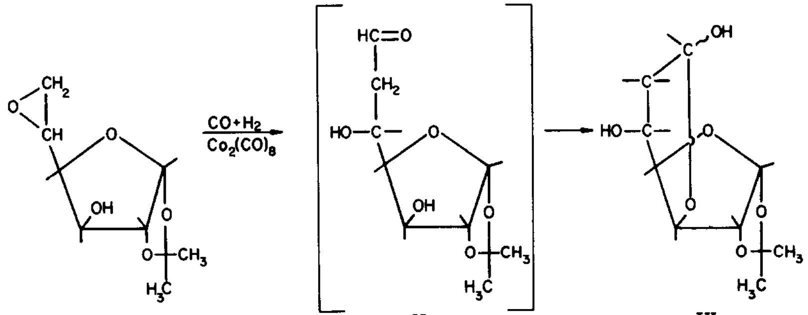
In a previous communication (1) we reported the application of the oxo reaction (2) in the direct conversion of glycals into anhydrodeoxyaldoses. We have now extended this reaction to the carbohydrate epoxides in an analogous way to that recently reported for the hydroformylation of propylene oxide and cyclohexene oxide (3,4).

The general procedure used at the present time is as follows. A solution of 2.4 g. of 5,6-anhydro-1,2-O-isopropylidene-α-D-gluco-furanose (I), dicobalt octacarbonyl (0.3 g) and anhydrous benzene (50 ml) is allowed to react with a mixture of 70 atm. of reagent carbon monoxide and 70 atm. of hydrogen at a temperature of 100-105° for about 2 hr. Filtration of the reaction mixture afforded crystalline product IV in 78 % yield and work-up of the filtrate as described previously (5) yielded crystalline compound III in 14 % yield. Substance IV was



I

II
+
III

IV

recrystallized from ethanol-ethyl acetate, m.p. 159-160°, $[\alpha]_D^{22}$+60° (*c* 2, water). [Found: C, 51.71; H, 6.96; mol. wt. 232 (the base peak in the mass spectrum is at M^+-15 (loss of CH_3); I.R. no carbonyl peak; Calcd. for $C_{10}H_{16}O_6$: C, 51.71; H, 6.90; mol. wt. 232]. Crude IV had an initial $[\alpha]_D^{22}$+39° which mutarotated to +60° after 3 hr. Substance IV was homogenous (R_f 0.71) by chromatography (6), gave an n.m.r. spectrum (multiplet at 7.7 τ equal to two methylenic hydrogens and multiplets at 4.25 and 4.82 τ equal to one anomeric C_7-H) in agreement with the assigned structure. Compound IV is therefore 6-deoxy-1,2-O-isopropylidene-α-D-*gluco*-heptodialdo-1,4-furanose-3,7-pyranose. Presumably compound IV was formed from the *aldehydo* intermediate II.

Further confirmation of the structure of compound IV was obtained by n.m.r. and elemental analysis (all satisfactory) of the following derivatives:

(1) 6-deoxy-1,2-O-isopropylidene-α-D-*gluco*-heptodialdo-1,4-furanose semicarbazone monohydrate, $C_{11}H_{16}N_3.H_2O$; m.p. 190-191°; $[\alpha]_D^{20}$-9° (*c* 1, water); R_f 0.36.

(2) 6-deoxy-1,2-O-isopropylidene-α-D-*gluco*-heptodialdo-1,4-furanose phenylhydrazone, $C_{16}H_{22}N_2O_5$; m.p. 134-135° $[\alpha]_D^{22}$-33° (*c* 2, chloroform).

(3) 5,7-di-O-acetyl-6-deoxy-1,2-O-isopropylidene-α-D-*gluco*-heptodialdo-1,4-furanose-3,7-pyranose (C-7-OAc is β). $C_{14}H_{20}O_8$; m.p. 176-177°; $[\alpha]_D^{22}$+42° (*c* 2, chloroform) R_f 0.73; n.m.r. H-7 at 4.36 τ (J 1,2,2 = 12 c.p.s.).

Compound III, recrystallized from benzene, m.p. 98-100°; R_f 0.86, was not characterized because of the difficulty of removing a trace of an impurity.

Hydroformylation of 5-O-acetyl-2,3-anhydro-β-D-ribofuranoside and of methyl 2,3-anhydro-4,6-O-benzylidene-α-D-mannopyranoside yielded branched chain sugars; the nature of these products are under investigation and will be the subject of a future communication.

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(6) Data refer to Silica Gel G activated at 100° with methyl ethyl ketone-water azeotrope as the developing solvent. Homogeneity of each substance was checked by T.L.C. by at least four different tests using different solvent systems.