

Catalytic Oxidation of a Primary Hydroxyl Group in the Presence of an Epoxide Bridge

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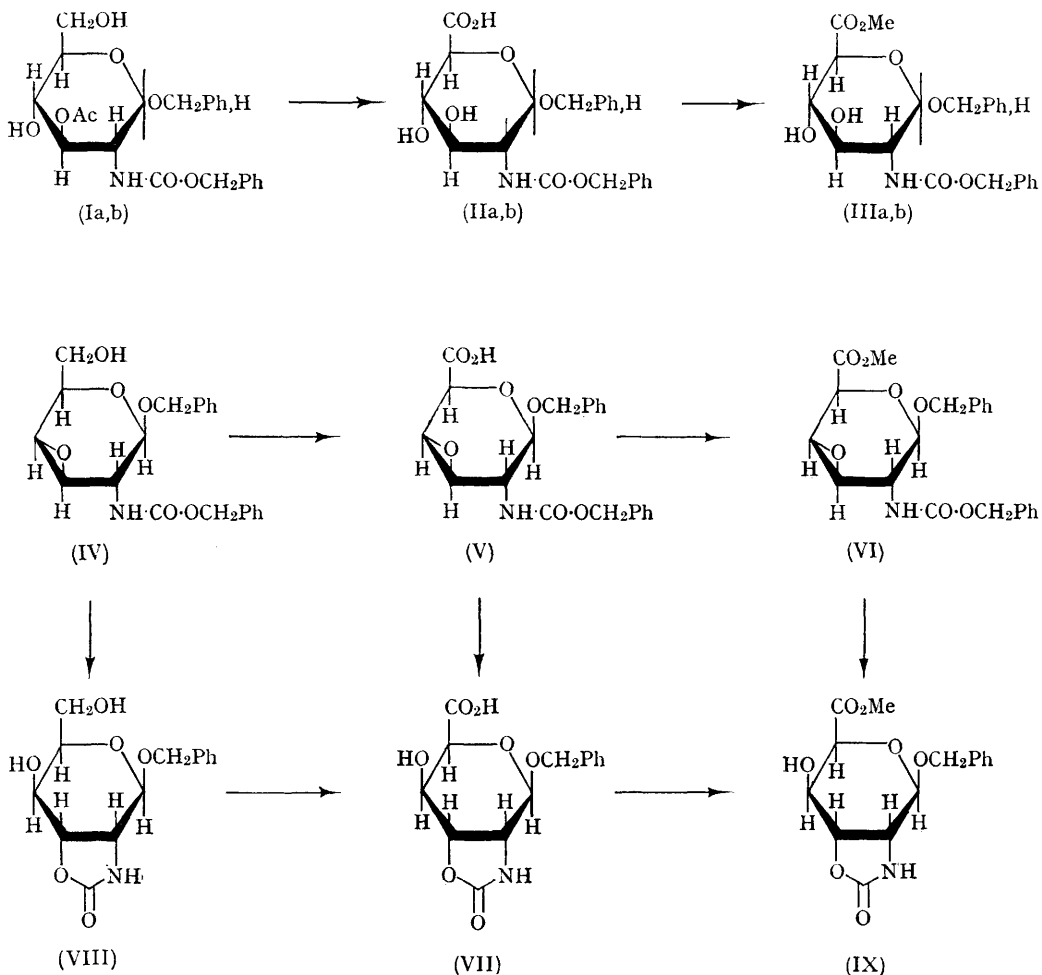
WHILE investigating intermediates for the purpose of preparing D-gulosaminuronic acid derivatives, attempts were made to oxidize both the α - and the β -anomeric benzyl 3-O-acetyl-2-benzyloxycarbonylamido-2-deoxy-D-glucosides (Ia, Ib) over Pt, using oxygen, at 80°. At the pH of about 8 required for this oxidation (obtained by adding NaHCO₃), it was found that the 3-O-acetyl group is completely solvolyzed from the uronic acid product by an apparent interaction of the carboxyl group *via* a mechanism which is still unclear, giving benzyl 2-benzyloxycarbonylamido-2-deoxy- α - and - β -D-glucosiduronic acids² (IIa, IIb) respectively. Both

products were confirmed through their methyl esters (IIIa, IIIb).

Subsequently, it was found that benzyl 3,4-anhydro-2-benzyloxycarbonylamido-2-deoxy- β -D-galactoside (IV), which can be obtained by a procedure analogous to that used in preparing the α -anomer,³ can be oxidized smoothly in 60% yield under the above conditions, without disturbing the epoxide blocking ring, giving benzyl 3,4-anhydro-2-benzyloxycarbonylamido-2-deoxy- β -D-galactopyranosiduronic acid (V), m.p. 131°, $[\alpha]_D^{26} -151^\circ$ (*c*, 1·1, pyridine). Compound (IV) was thus fully as stable in the oxidation as is the 3,4-unblocked

sugar. The acid (V) could be converted into the methyl ester, (VI), m.p. 177—178°, $[\alpha]_D^{26} -137^\circ$ (c, 1.3, pyridine), quantitatively by reaction with diazomethane, and by aqueous acetic acid to benzyl β -D-gulopyranosiduronic acid-(2',3':4,5)-oxazolid-2-one (VII), which was obtained as a

characterized as its methyl ester (IX), m.p. 145—146°, $[\alpha]_D^{21} -125^\circ$ (c, 1.1, pyridine), obtained in 13% yield from (VIII) and in 78% yield from (V). Treatment of (VI) with aqueous acetic acid also validated this series of reactions by giving (IX).



gum. The same gum was obtained also by converting (IV) through treatment with aqueous acetic acid into benzyl β -D-gulopyranosido-(2',3':4,5)-oxazolid-2-one (VIII), m.p. 115° (dec.), $[\alpha]_D^{23} -101^\circ$ (c, 2.6, pyridine), which was then oxidized over platinum as before. The gum (VII) was

The stability of the epoxide ring toward the conditions of catalytic oxidation appears to provide another useful property which may prove to be of value in a variety of synthetic problems.

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¹ H. Weidmann and H. K. Zimmerman, *Annalen*, 1961, **639**, 198.

² S. M. Block, P. H. Gross, H. Weidmann, and H. K. Zimmerman, *Annalen*, in the press.

³ P. H. Gross, K. Brendel, and H. K. Zimmerman, *Annalen*, 1964, **680**, 155.