The Nitrous Acid Deamination of Methyl 4-Amino-4-deoxy-2,3-*O*-isopropylidene-α-L-talo- and -mannopyranosides

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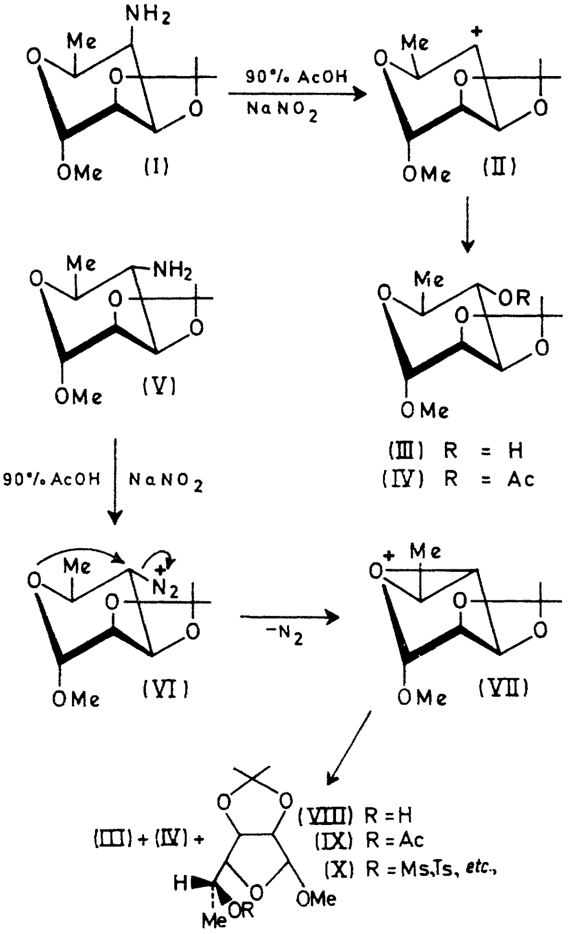
Summary Deamination of the L-*talo*-amine (I) with sodium nitrite in 90% acetic acid afforded the L-mannopyranosides (III) and (IV), whereas similar deamination of the L-*manno*-amine (V) gave (III), (IV), and rearrangement products (VIII) and (IX) possessing the D-*allo*-configuration.

CONSIDERABLE interest has developed in rearrangement reactions which may accompany nucleophilic displacements on carbohydrate sulphonates[1] and the deamination of amino-sugars.[2] In extending our investigations,[1c] we have examined the deamination of the title amino-sugar derivatives. In each case, the products of deamination were identified by g.l.c., by isolation, and, where necessary, by conversion into known derivatives.

Deamination of the axial amine (I)[3] with sodium nitrite in 90% acetic acid at 0° gave methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (III)[4] (32%), the 4-acetate (IV) (57%), m.p. 68—69°, $[\alpha]_D$ − 16° (*c* 1, $CHCl_3$), and an unidentified compound (*ca.* 11%), which was readily distinguishable (g.l.c.) from the epimeric L-talopyranoside derivatives. These products are presumed to arise by solvent attack on the carbonium ion (II) formed from the diazonium intermediate.[5] The absence of products of retained configuration must be ascribed to steric hindrance to the approach of solvent molecules from the *axial* direction.

Corresponding deamination of the equatorial amine (V)[6] afforded a mixture of four products, which were identified (g.l.c.) as (III), (IV), methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (VIII),[7] and the 5-acetate (IX). After treatment of the products with boiling methanolic sodium methoxide, the alcohols (III) and (VIII) were isolated from a mixture in which the latter slightly preponderated. The products can be considered to arise from the oxonium ion (VII) formed with participation of the ring oxygen atom on solvolysis of the diazonium intermediate (VI). Solvent attack at C-4 of the ion (VII) would yield the pyranosides (III) and (IV), whereas attack at C-5 would furnish the rearrangement products (VIII) and (IX).

Certain displacement reactions on methyl 6-deoxy-2,3-*O*-isopropylidene-α-L(D)-mannopyranoside 4-sulphonates are also postulated[8] to proceed by a concerted rearrangement involving participation by the ring oxygen atom. One notable difference, however, is the formation[1a] of talofuranoside derivatives, which are often isolated as the major products from the displacement reactions. It has been suggested[8] that the talofuranoside derivatives could arise through direct displacements on allofuranoside sulphonates [*e.g.*, (X)] formed by the collapse of ion-pair intermediates.



The deamination experiment would also suggest that such rearranged sulphonates are the main precursors of the talofuranosides observed in the displacement reactions.

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