Preliminary communication

The deamination of methyl 5-amino-5,6-dideoxy-2,3-O-isopropylidene- α -L talo- and - β -D-allo-furanosides with nitrous acid

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We have recently attributed¹ the formation of ring-contracted products on deamination of methyl 4-amino-4,6-dideoxy-2,3-O-isopropylidene- α -L-mannopyranoside to the intermediacy of the bicyclic oxonium ion 1 rather than to that of the open carbonium ion 2. In foreseeing the need to distinguish between the reactions of the intermediates 1 and 2, we have generated the latter ion by deamination of both methyl 5-amino-5,6-dideoxy-2,3-O-isopropylidene- α -L-talofuranoside (3) and the diastereoisomeric β -D-allofuranoside amine 4. The amines 3 [b.p. 68–70° (bath)/0.5 mmHg, $[\alpha]_D-54°$ (c 1, methanol)] and 4 [b.p. 48–50° (bath)/0.35 mmHg, $[\alpha]_D-72 \pm 2°$ (c 1, chloroform)] were prepared by reduction of the corresponding azides² and were purified by either preparative g.Lc. or t.Lc.

Deamination of the L-talo-amine 3 with nitrous acid in 90% acetic acid at $ca. 0^{\circ}$ gave 5 (2.9%), 6 (26.4%), 7 and 8 (together 12.3%), and 9 (43.5%), as well as



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a number of unidentified minor products. Identification of compounds 5–8 was achieved by g.l.c.-mass spectrometry and by comparison (mass spectrometry, g.l.c., t.l.c.) with authentic compounds¹. In the case of methyl 5,6-dideoxy-2,3-O-isopropylidene- β -D-*ribo*-hex-5-enofuranoside (9) [b.p. 41–43° (bath)/0.15 mmHg, $[\alpha]_D-58 \pm 1^\circ$ (c 1, chloroform), v_{max}^{film} 1650 cm⁻¹ (C=C, weak)], a rigorous characterisation was effected by elemental analysis and n.m.r. spectroscopy following its isolation from the products obtained after deacetylation; the n.m.r. spectrum clearly demonstrated the presence of a vinylic system (as a modified ABX pattern) and was distinct from that of the isomeric unsaturated sugar³ 12 $(J_{5.6}, 7$ Hz).

The products similarly identified from deamination of the D-allo-amine 4 were 5 (12.55%), 6 (25.8%), 7 and 8 (together 20.4%), 9 (7.7%), 10 (14.1%), and 11 (17.5%); there were also two very minor products. An authentic sample of the rearranged product 6-deoxy-2,3-O-isopropylidene-5-O-methyl-L-talofuranose (11) was obtained for comparative purposes either by solvolysis⁴ of methyl 5-O-(p-bromobenzenesulphonyl)-6-deoxy-2,3-O-isopropylidene- β -D-allofuranoside or by successive methylation and debenzylation of benzyl 6-deoxy-2,3-O-isopropylidene- α -L-talofuranoside⁵ [m.p. 85–86°, [α]_D -71 ± 1° (c 0.35, chloroform)]. The identity of the rearranged acetate 10 was inferred from mass-spectral data and reasonably follows from the presence of 11 among the other products of deamination.



There are several features of these deaminations worthy of note. Firstly, it is apparent that the reactions of carbonium ion 2 depend upon the structure of the diastereoisomeric amine from which it is derived. Analogous results have been obtained in the deamination of other diastereoisomeric amines and have been attributed⁶ to the operation of conformational factors on the intermediate diazonium ion*. It is interesting to note that migration of the glycoside methoxyl group to C-5 occurs

^{*} It is generally assumed that $C - N_2$ heterolysis primarily occurs from the most-populated, ground-state conformation of the diazonium ion and that the carbonium ion so formed reacts before significant rotation about the adjacent carbon-carbon bond takes place. If these conditions pertain, the carbonium ion derived from diastereoisomeric amines will be formed and react in distinctly individual conformations. Only when interconversion between the conformers of the carbonium ion is fast compared with the rate of reaction can the same set of products be expected.

only with the β -D-allo-amine 4; in this respect, the deamination resembles the solvolysis of the corresponding sulphonate⁴ and presumably involves^{1,7} the formation of the oxonium ion 13. Finally, the presence of the terminal unsaturated sugar 9 may be diagnostic for the carbonium ion 2, in which case the absence of this unsaturated sugar from the products of deamination of methyl 4-amino-4,6-dideoxy-2,3-O-isopropylidene- α -L-mannopyranoside¹ is significant. This and other aspects of the work will be discussed in detail in a subsequent publication.

All new compounds gave satisfactory elemental analyses and spectroscopic data.

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