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Preliminary communication

Nucleophilic displacements on methyl 2,3-*O*-isopropylidene-α-D(L)-lyxopyranoside 4-sulphonates and deamination of the corresponding 4-amino sugar

JOHN S. BRIMACOMBE, JONATHAN MINSHALL and LESLIE C. N. TUCKER

Chemistry Department, The University, Dundee DD1 4HN (Great Britain)

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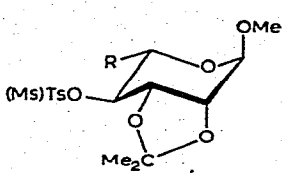
The formation[1] of ring-contracted products from displacements on methyl 6-deoxy-2,3-*O*-isopropylidene-L (or D)-mannopyranoside 4-sulphonates (**1a**) with ionic nucleophiles (*e.g.* N_3^-) can be ascribed[2] to intramolecular participation by the ring-oxygen atom. Direct S_N2 displacements on the sulphonate **1a** are assumed[3] to be impeded by a β-diaxial interaction between the incoming nucleophile and O–2. Although a similar steric situation is encountered in methyl 2,3-*O*-isopropylidene-4-*O*-toluene-*p*-sulphonyl-α-L-lyxopyranoside (**1b**), the inverted azide **2*** (~ 48.5%) is obtained[4] when **1b** is treated with sodium azide in *N,N*-dimethylformamide. Neither this reaction nor a comparable S_N2 displacement with thiolbenzoate[5] has attracted any comment. Re-investigation of the azide displacement on the enantiomeric sulphonate D-**1b** has shown that the unsaturated sugar **3** (~ 51.5%), b.p. 61–63°/12 mmHg, $[\alpha]_D$ +180° (*c* 1.9, chloroform), is also formed; **3** is more conveniently prepared by treating the sulphonate with 1,5-diazabicyclo[5.4.0]-undec-5-ene. A change from the $^4C_1$ conformation (the antipode of **1b**) is necessary for the displacement and elimination reactions on the sulphonate D-**1b**. These pathways are clearly favoured over that involving participation by the ring-oxygen atom (*cf.* the displacements on **1a**[1]) and undoubtedly reflect the easier conformational changes in pentopyranosides compared with hexopyranosides.

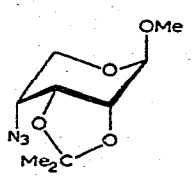
A comparison of the above displacement with the deamination of methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-α-D-lyxopyranoside (**4**) is particularly apposite, since the transition state for heterolysis of the diazonium ion intermediate will exhibit reactant-like characteristics[6,7]. On treatment at 0° with sodium nitrite in 90% acetic acid, the lyxopyranoside amine **4****, b.p. 48–50°/0.25 mmHg, $[\alpha]_D$ +56° (*c* 2.5, chloroform), yielded

*Characterization of the azide **2** was effected by its conversion into derivatives of 4-acetamido-4-deoxy-D-ribose that were also prepared by another route. The yield of **2** was determined by g.l.c.

The amine **4 was prepared either by way of an azide displacement on methyl 2,3-*O*-isopropylidene-4-*O*-toluene-*p*-sulphonyl-β-L-ribopyranoside, or by reduction of methyl 2,3-*O*-isopropylidene-β-L-*erythro*-pentopyranosid-4-ulose oxime and separation of the epimeric amines formed. Details of the preparation of these and other compounds mentioned will be provided when our results are published in full.



1 a R = Me
b R = H



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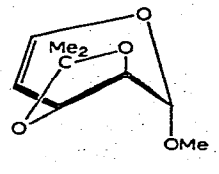

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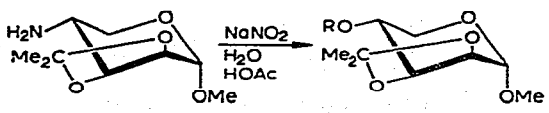

4

5 a R = H
b R = Ac
c R = Ts

6 a R = H
b R = Ac
c R = Ts

7

four products that were identified (by g.l.c.) as methyl 2,3-*O*-isopropylidene-α-D-lyxo-pyranoside[5] (**5a**, 26.2%), the corresponding 4-acetate **5b** (34.5%), and the ring-contracted compounds methyl 2,3-*O*-isopropylidene-β-L-ribofuranoside[8] (**6a**, 18.4%) and the corresponding 5-acetate[9] **6b** (21.3%). Deacetylation of the deamination products and toluene-*p*-sulphonylation of the separated alcohols gave the sulphonates **5c**, m.p. 105–106°, $[\alpha]_D$ −13° (*c* 2, chloroform) {lit. (L- enantiomer)[5], m.p. 104–105°, $[\alpha]_D$ +11.5° (*c* 1, chloroform)}, and **6c**, m.p. 82–83°, $[\alpha]_D$ +33° (*c* 0.7, ethanol) {lit. (D enantiomer)[10], m.p. 83–84°, $[\alpha]_D$ −35.5° (*c* 1, ethanol)}, which were indistinguishable (m.p. and i.r. spectroscopy) from authentic samples.

The products of deamination can be considered to arise *via* the bicyclic oxonium ion **7** resulting from participation of one of the lone pairs of electrons on the ring-oxygen atom with the carbocationic centre developed on heterolysis of the diazonium-ion intermediate. Solvent attack on the oxonium ion **7** at C–4 and C–5 would furnish the observed pyranosidic and furanosidic products, respectively. The expected, mechanistic correspondence between the deaminations of the D-lyxopyranoside amine **4** and the homologous rhamnopyranoside amine[6] is clearly realized, although, as noted earlier, totally different pathways are followed in displacements on the corresponding sulphonates **1a** and **1b**.

Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds reported.

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