The Formation of 4-Thio-L-arabinofuranose Derivatives by Ring Contraction of 1,2-O-Isopropylidene-3,4-di-O-methanesulphonyl-5-thio-α-D-xylopyranose

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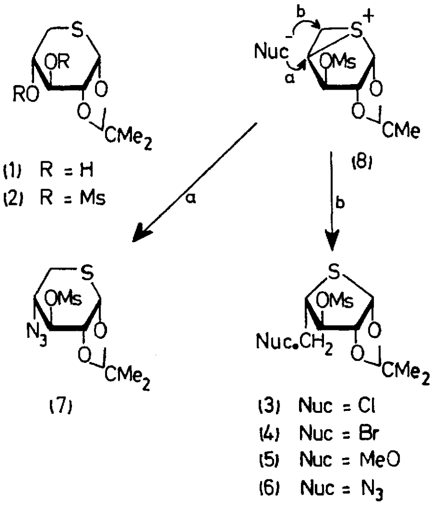
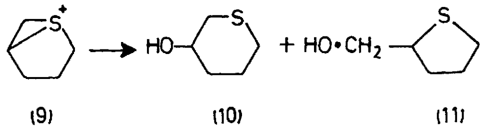
Summary 1,2-*O*-Isopropylidene-3,4-di-*O*-methanesulphonyl-5-thio-α-D-xylopyranose has been synthesised and reacts readily with nucleophiles to give 5-substituted-1,2-*O*-isopropylidene-3-*O*-methanesulphonyl-4-thio-β-L-arabinofuranoses; the structure of the 5-chloro-compound was determined by *X*-ray crystallography.

RECENTLY a number of examples of ring contractions of pyranosides to furanosides, resulting from displacements or solvolyses of 4-*O*-sulphonate esters or deaminations of 4-amino-4-deoxy derivatives, have been reported.[1] These have mostly involved hexoses and a recently reported[2] deamination of methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-α-D-lyxopyranoside is the only example recorded in the pentose series. We now report a case involving a 5-thiopentopyranose sulphonate.





Toluene-*p*-sulphonylation of 1,2-*O*-isopropylidene-5-thio-α-D-xylopyranose (**1**)[3] leads to extensive decomposition but low temperature methanesulphonylation in dichloromethane gave a crystalline dimesylate (**2**) which rapidly decomposed[4] at room temperature. In methanol containing triethylamine hydrochloride the dimesylate (**2**) was smoothly converted into 5-chloro-5-deoxy-1,2-*O*-isopropylidene-3-*O*-methanesulphonyl-4-thio-β-L-arabinofuranose (**3**) whose structure was confirmed by *X*-ray crystallography.

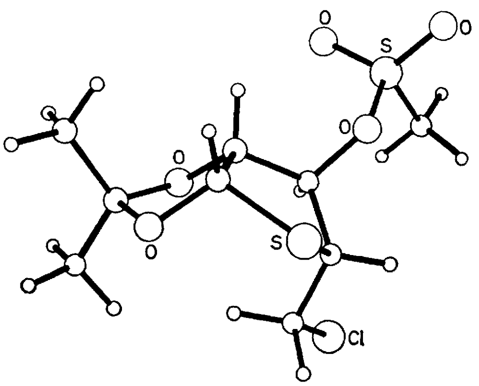


FIGURE. Structure of 5-chloro-5-deoxy-1,2-*O*-isopropylidene-3-methanesulphonyl-4-thio-β-L-arabinofuranose (**3**).

Crystal data: $C_9H_{15}ClO_5S_2$, $M = 302{\cdot}8$, orthorhombic, $a = 8{\cdot}426(9)$, $b = 9{\cdot}029(14)$, $c = 17{\cdot}806(21)$ Å, $U = 1354{\cdot}7$ Å^3, $D_c = 1{\cdot}48$, $Z = 4$, $D_m = 1{\cdot}46$, space group $P\,2_12_12_1$. Intensity data were collected on a Hilger-Watts Y290 circle diffractomer with Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å), giving 1519 independent reflections with $I > 3\sigma(I)$. The structure was solved by direct methods and refined to $R = 3{\cdot}36\%$. Full details will be reported elsewhere. The molecular structure is shown in the Figure.

The dimesylate (**2**) reacted readily with other nucleophiles, *e.g.*, bromide, methoxide, and azide ions to give the 4-thio-L-arabinofuranoses (**4**), (**5**), and (**6**) respectively whose ^{1}H n.m.r. spectra closely resembled that of (**3**). In the reaction with azide ion an additional product was isolated whose ^{1}H n.m.r. spectrum indicated it to be 4-azido-4-deoxy-1,2-*O*-isopropylidene-3-*O*-methanesulphonyl-5-thio-α-D-xylopyranose (**7**).

These ring contractions and, in the last case, a displacement with retention of configuration, clearly proceed *via* the episulphonium ion (**8**), formed by intramolecular displacement by the ring sulphur atom at the C(4) mesylate group in the dimesylate (**2**). Attack on the episulphonium ion (**8**) occurs preferentially at the primary position and is undoubtably influenced by the formation of a furanose ring bearing a *cis*-acetal group, a particularly favourable system in carbohydrate chemistry,[5] and a feature shared by the other reported pentose case.[2] The unsubstituted episulphonium ion (**9**) undergoes solvolytic opening mainly at the secondary position giving the tetrahydrothiopyran (**10**) (82%) and the tetrahydrothiophen (**11**) (18%) as the minor product.

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