Nucleophilic Displacements on Talopyranoside 4-Sulphonate Derivatives

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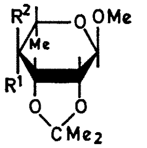
Summary The azide displacement reaction on methyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranoside (V) yielded the azide (IX) and the unsaturated sugars (VII) and (VIII) in the approximate ratio of 4 : 5 : 1.

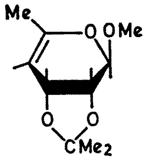
IT is surprising that methyl 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-L-talopyranoside (I) and the corresponding iodide (II) appear to undergo vastly different reactions with sodium azide in *NN*-dimethylformamide. Whereas the methanesulphonate (I) gave[1] the azide (III) and the unsaturated sugar (IV), a compound presumed to be the iodide (II) was reported[2,3] to afford ring-contracted products. The structure assigned[4] to the iodide has been questioned and its re-assignment[5] as methyl 5,6-dideoxy-5-iodo-2,3-*O*-isopropylidene-β-D-allofuranoside reasonably accounts for the differences observed in the displacement reactions.

In continuing our investigations, we find that both the talopyranoside 4-methanesulphonates (V) and (VI) yielded unsaturated sugars, in addition to the product of S_N2 displacement, on reaction with sodium azide in boiling *NN*-dimethylformamide. Methyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranoside (V), m.p. 109—110°, $[\alpha]_D$ − 83° (*c* 1, $CHCl_3$), for example, afforded methyl 4,6-dideoxy-2-*O*-methyl-3-methoxy-α-L-*threo*-hex-3-enopyranoside (VII, *ca.* 50%), b.p. 40—42°/0·05 mm., $[\alpha]_D$ − 213° (*c* 1, CCl_4), ν_{max} 1673 cm^{-1} (C=C); methyl 4,6-dideoxy-2,3-di-*O*-methyl-β-D-*erythro*-hex-4-enopyranoside (VIII, *ca.* 10%), b.p. 33—35°/0·05 mm., $[\alpha]_D$ − 288° (*c* 1·2, $CHCl_3$), ν_{max} 1670 cm^{-1} (C=C); and methyl 4-azido-4,6-dideoxy-2,3-di-*O*-methyl-α-L-mannopyranoside (IX, *ca.* 40%), b.p. 60—62°/0·05 mm., $[\alpha]_D$ − 131° (*c* 1, CCl_4), ν_{max} 2100 cm^{-1} (N_3).

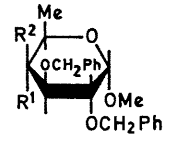
The structure of the azide (IX) was readily established since it was indistinguishable from that obtained on methylation of the well-characterised[1] methyl 4-azido-4,6-dideoxy-α-L-mannopyranoside. The olefinic nature of the other products was apparent from mass spectrometry, and infrared and n.m.r. spectroscopy. The location of the double bond followed from the appearance of the C(5)-Me resonance as a doublet at τ 8·70 ($J_{5,6}$ 6 Hz) and as a singlet at τ 8·26 in the n.m.r. spectra of (VII) and (VIII), respectively.



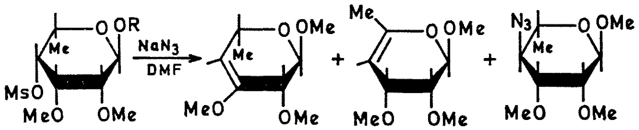
(I) R¹ = OMs, R² = H
(II) R¹ = I, R² = H
(III) R¹ = H, R² = N₃



(IV)



(X) R¹ = H, R² = OMs
(XI) R¹ = N₃, R² = H



(V) R = Me
(VI) R = CH₂Ph
(VII)
(VIII)
(IX)

Chromatographic and spectroscopic evidence suggested that only the unsaturated sugars were formed on reaction of methanesulphonate (V) with the more basic benzoate ion.

It is interesting to note that the azide (XI) is formed[6] from the D-galactopyranoside 4-methanesulphonate (X) in virtually quantitative yield. The L-enantiomer of (X) differs configurationally from the methanesulphonate (V) at C-2 and the competing elimination processes are evidently enhanced when the substituent on this carbon atom is β-*cis*-axial to the sulphonyloxy group.

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[1] J. S. Brimacombe, O. A. Ching, and M. Stacey, *J. Chem. Soc.* (*C*), 1969, 1270.

[2] A. I. Usov, K. S. Adamyants, and N. K. Kochetkov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1968, 2546.

[3] "Carbohydrate Chemistry," 1969, vol. 2 (*Chem. Soc. Specialist Periodical Rep.*), p. 82.

[4] K. S. Adamyants, N. K. Kochetkov, and A. I. Usov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1967, 1311.

[5] K. Kefurt, J. Jary, and Z. Samek, *Chem. Comm.*, 1969, 213.

[6] C. L. Stevens, P. Blumbergs, F. A. Daniher, D. H. Otterbach, and K. G. Taylor, *J. Org. Chem.*, 1966, **31**, 2822.