The Reaction of Methyl 2,3-Anhydro-β-D-*ribo*-pyranoside with Cyanide Ion: an Apparent *cis*-Opening of an Epoxide Ring

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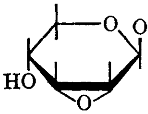
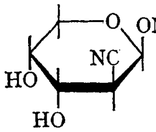
TREATMENT of methyl 2,3-anhydro-β-D-*ribo*-pyranoside (I) with sodium cyanide in aqueous solution buffered at pH 8·0—8·5, at 100°, gave a mixture of products, from which two isomeric crystalline cyano-deoxy-sugars could be isolated in 40% yield by column chromatography on silica gel. These compounds were expected to be the 2-cyano-2-deoxy-D-*arabino*- and 3-cyano-3-deoxy-D-*xylo*-derivatives (II) and (III), formed by nucleophilic attack of cyanide ion at C-2 and C-3, with *trans*-opening of the epoxide ring. However, neither sugar was oxidised by periodate, thus ruling out

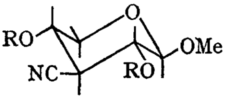
(II). Ring contraction to a furanoside was unlikely under the reaction conditions, which was confirmed by the stability of both glycosides in 1·0N-hydrochloric acid at room temperature. Both compounds showed the expected nitrile infrared band at 2250 cm.$^{-1}$. Both sugars therefore appeared to be 3-cyano-3-deoxy pyranosides, and further evidence proved them to be the *xylo*- and *ribo*-isomers (III) and (IV), m.p. 127—128°, $[\alpha]_D$ −52 (28% yield), and m.p. 115—116°, $[\alpha]_D$-117 (12% yield), respectively. Acetylation of these compounds in pyridine yielded the di-*O*-acetates (V) and (VI), whose 100 Mc./sec. ^{1}H n.m.r. spectra clearly indicate the assigned *xylo*- and *ribo*-configurations; in particular, for (V), $J_{2,3} = J_{3,4} =$ 6·7 c./sec., indicating an axial–axial arrangement for H-2, H-3, and H-4, whereas for (VI), these coupling constants are both equal to 4·3 c./sec., compatible with equatorial–axial proton coupling. Furthermore, catalytic hydrogenation of (IV), followed by acetylation, furnished the tri-acetyl derivative (VII), whose ^{1}H n.m.r. spectrum showed $J_{2,3}$, $J_{3,4}$ = 2·0—3·0 c./sec.



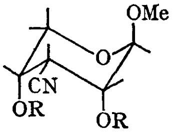
(I)



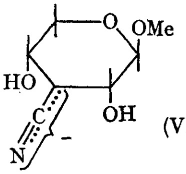
(II)



(III) R=H
(V) R=Ac



(IV) R=H
(VI) R=Ac



(VIII)

The unexpected formation of (IV), suggesting an improbable *cis*-opening of the epoxide ring in (I), may be explained by a base-catalysed isomerisation of the initially-formed *xylo*-isomer (III), involving the mesomeric anion (VIII). Accordingly, either (III) or (IV) yielded the same isomeric mixture under the reaction conditions, or simply on heating in aqueous sodium hydrogen carbonate solution. An analogous, more ready, isomerisation has been reported recently with 3-deoxy-3-nitroglycopyranosides, which are interconverted by alkali at room temperature.[1]

The ease of formation of (VIII) may be attributed to the combined influence of the cyanide group and the inductively electron-attracting hydroxyl groups, which indicates that under such circumstances cleavage of epoxide rings may not necessarily yield products with *trans*-related substituents.

Satisfactory analyses were obtained for all the compounds described.

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[1] H. H. Baer and F. Kienzle, *Annalen*, 1966, **695**, 192.