2,3-Thioanhydropentofuranosides

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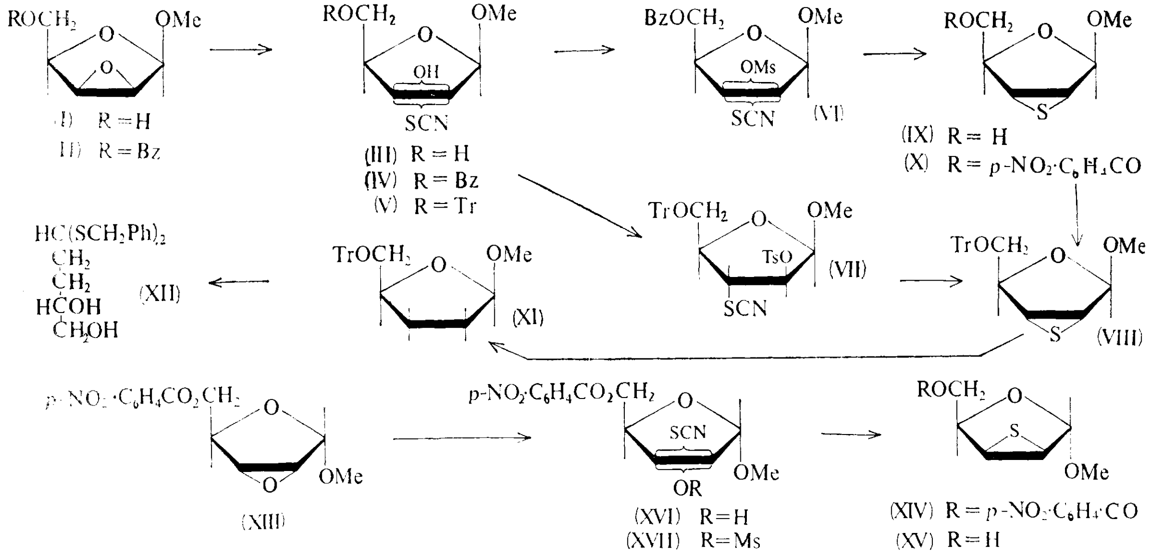
THE 2,3-anhydropentofuranosides have been extremely useful intermediates in the synthesis of unusual sugars and nucleosides.[1] Their sulphur counterparts, the 2,3-thioanhydropentofuranosides, which might be expected also to have considerable synthetic utility, have not been reported although attempts to prepare them have been described.[2] This communication details successful approaches to both the 2,3-thioanhydroribofuranosides and the 2,3-thioanhydrolyxofuranosides.

Reaction of the epoxide (I)[3] with ammonium thiocyanate in tetrahydrofuran under reflux gave a mixture (III) of thiocyano-sugars. The n.m.r. spectrum of the bis-*p*-nitrobenzoate of (III) indicated a ratio of 3-thiocyanate to 2-thiocyanate of about 7:3. Tritylation of (III) yielded the mixture (V) from which, after treatment with toluene-*p*-sulphonyl chloride in pyridine, the crystalline 2-tosylate (VII) was obtained, m.p. 151—154°, $[\alpha]_D$ − 76° ($CHCL_3$).† Reaction of (VII) with sodium methoxide[4] under reflux gave an excellent yield of the furanose episulphide (VIII), m.p. 134—136·5°, $[\alpha]_D$ − 55° ($CHCl_3$). Compound (VIII) was desulphurized to (XI), isolated as an oil, which was converted into the dibenzyl dithioacetal (XII), m.p. 70—71°, $[\alpha]_D$ − 23° ($CHCl_3$), whose constants were in satisfactory agreement with those reported for the L-enantiomer.[5]

Alternatively, the benzoylated epoxide (II) was converted with ammonium thiocyanate into the mixture (IV) whose n.m.r. spectrum suggested that two-thirds of the ring-opening occurred at C-3. Mesylation of (IV) afforded (VI) as a gum which could be converted into the episulphide (IX) with sodium methoxide. The crystalline *p*-nitrobenzoate (X), m.p. 115—117°, $[\alpha]_D$ − 77° ($CHCl_3$), was hydrolysed in aqueous methanol with dilute base to give (IX) as a mobile liquid, after evaporative distillation, $[\alpha]_D$ − 138° ($CHCl_3$). Tritylation of (IX) yielded (VIII).

The epithiolyxoside (XV) was prepared similarly. The blocked epoxide (XIII)[6]‡ was opened with



Tr = trityl, Ts = toluene-*p*-sulphonyl; Ms = methanesulphonyl.

† Satisfactory analytical data were obtained for the crystalline compounds and for (IX) and (XV).

‡ The β-anomer corresponding to (XIII) could not be opened with thiocyanate ion even in dimethylformamide at 110°. The α-anomer corresponding to (I) also was much less reactive to ammonium thiocyanate than (I).

ammonium thiocyanate in refluxing tetrahydrofuran to (XVI), the mesylate of which was converted with base into (XV). The crystalline *p*-nitrobenzoate (XIV), m.p. 86—87°, $[\alpha]_D + 12°$ ($CHCl_3$), was hydrolysed to (XV) which, after evaporative distillation, had $[\alpha]_D + 27°$ ($CHCl_3$).

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