Formation of 1,4-Anhydropyranoses from 1-*O*-Acetyl-6-deoxy-2,3-*O*-isopropylidene-4-*O*-methylsulphonyl-α-L-manno- and talo-pyranose

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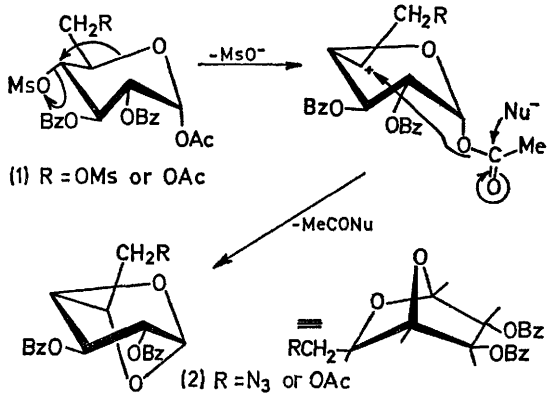
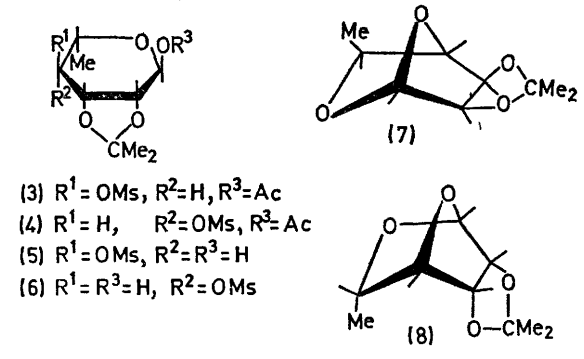
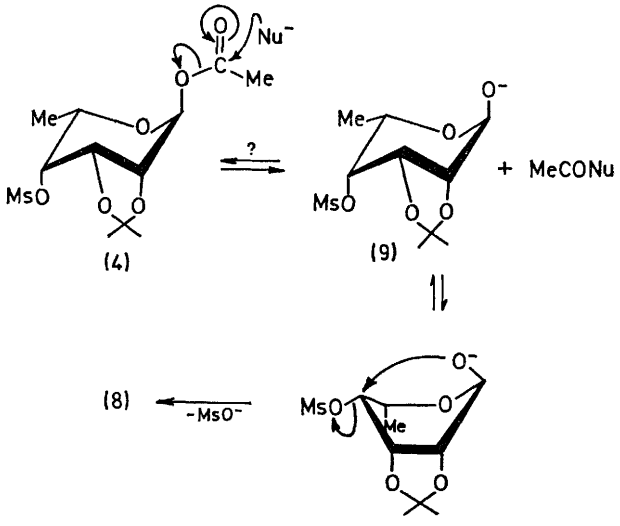
Summary 1-*O*-Acetyl-6-deoxy-2,3-*O*-isopropylidene-4-*O*-methylsulphonyl-α-L-mannopyranose (**3**) and the epimeric L-talopyranose derivative (**4**) yield the 1,4-anhydropyranoses (**7**) and (**8**), respectively, on treatment with sodium azide in hot *NN*-dimethylformamide; a possible general mechanism is suggested for these and related reactions.

IT has been shown[1] that α-D-glucopyranose derivatives (*e.g.* **1**) with a sulphonyloxy-group at C-4 and an acetoxy-group at C-1 are converted into 1,4-anhydro-β-D-galactopyranose derivatives (**2**) on treatment with sodium azide in aprotic solvents. We have performed similar reactions





on the title methanesulphonates (**3**) {m.p. 120—121°, $[\alpha]_D$ − 10° (*c* 1, $CHCl_3$)} and (**4**) {m.p. 111—112° (decomp.), $[\alpha]_D$ − 16° (*c* 1, $CHCl_3$)}, prepared by acetylation of the parent alcohols (**5**)[2] and (**6**).[3] The main products obtained on treatment of the acetates (**3**) and (**4**) with sodium azide in DMF at 140° for 2—4 h were the 1,4-anhydropyranoses (**7**, > 90%) and (**8**, *ca.* 60%), respectively, which were identified by comparison (mixed m.p. and/or t.l.c., g.l.c., n.m.r. spectroscopy) with authentic compounds.[2,3] Once again, the 1-acetoxy-derivatives behave differently from the corresponding methyl glycopyranosides[4,5] in these reactions.



SCHEME

Richardson *et al.*[1] have suggested that the conversion of (**1**) into (**2**) might involve a ring contraction in the displacement of the sulphonyloxy-group, but have pointed out the difficulty in rationalizing the contrasting behaviours of methyl glycopyranoside 4-sulphonates[6] and the corresponding 1-acetoxy-derivatives by this mechanism. While a ring-contraction mechanism can also be envisaged for the conversion (**3**) → (**7**), such a mechanism is unable, for steric reasons, to explain the conversion (**4**) → (**8**). In the latter instance, it is reasonable to conclude that the anhydro-sugar (**8**) results from nucleophilic attack on the 1-acetoxy-group to produce the oxyanion (**9**), which undergoes intramolecular displacement of the sulphonyloxy-group (Scheme).† The ready conversion of the alcohol (**6**) into the anhydro-sugar (**8**) under mild basic conditions[3] can be cited in support of this mechanism. A mechanism involving initial deacylation at C-1 merits serious consideration for the other reactions [(**1**) → (**2**) and (**3**) → (**7**)] since it removes the need to invoke unprecedented steric and/or electronic effects militated by a ring-contraction mechanism.[1]‡ There

† This mechanism assumes an intrinsically greater reactivity of the 1-acetoxy-group towards nucleophilic attack (see ref. 7). Several candidates can be considered for effecting deacetylation at C-1, but discussion on this point is reserved for a forthcoming publication.

‡ Since the ring-contraction mechanism requires nucleophilic attack on the 1-acetoxy-group at some stage, the main point at issue is whether a ring contraction need be invoked as the first stage of the sequence. Professor J. G. Buchanan[8] has also suggested a mechanism for the reaction (**1**) → (**2**) similar to that suggested in the Scheme and has noted that the reaction is more rapid than authenticated ring contractions.[4]

are precedents for the formation of 1,4-anhydro-sugars from the alcohol (**5**)[2] and related D-glucopyranose derivatives[9] under relatively mild basic conditions. The different behaviours of the glycosides and 1-acetoxy-derivatives noted above may merely reflect the susceptibility of the latter towards cleavage at the outset of the reaction.

We thank Professor J. G. Buchanan for valued discussion and the University of Dundee for financial support.

(*Received, 29th December* 1972; *Com.* 2149.)

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