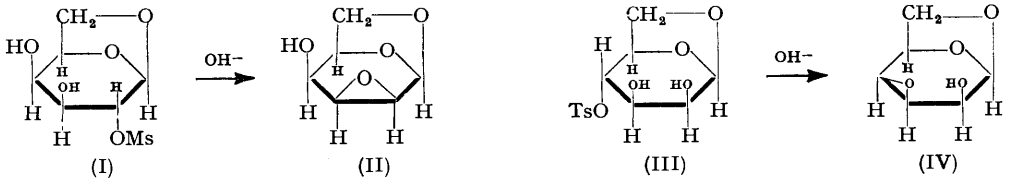
87. O-*Toluene*-p-*sulphonyl Derivatives of* 1 : 6-*Anhydro*-β-D-*altrose and their Behaviour towards Alkali.**

By F. H. Newth.

1 : 6-Anhydro-2-*O*-toluene-*p*-sulphonyl- and 1 : 6-anhydro-3 : 4-di-*O*-toluene-*p*-sulphonyl-β-D-altrose resist conversion into epoxides. 1 : 6-Anhydro-3-*O*-toluene-*p*-sulphonyl-β-D-altrose, prepared by selective acylation of the equatorial hydroxyl group in 1 : 6-anhydro-2-*O*-benzoyl-β-D-altrose, reacts but gives 1 : 6-3 : 4-dianhydro-β-D-altrose rather than 1 : 6-2 : 3-dianhydro-β-D-mannose. The conformational aspects of epoxide formation are considered.

It is well known that a sugar epoxide is formed easily and in good yield by alkaline hydrolysis of a sulphonyloxy-group vicinal to a *trans*-hydroxy-group. However, two derivatives of 1 : 6-anhydro-β-D-altrose containing the *trans*-hydroxy-*O*-toluene-*p*-sulphonyl system have now been found which are inert. The only hexose anhydrides so far known which possess a 1 : 6-anhydro-ring in addition to the epoxide group are 1 : 6-2 : 3- and 1 : 6-3 : 4-dianhydro-β-D-talose (II and IV). They are readily formed from 1 : 6-anhydro-2-*O*-methanesulphonyl-β-D-galactose (I) and 1 : 6-anhydro-4-*O*-toluene-*p*-sulphonyl-β-D-mannose (III) (James, Smith, Stacey, and Wiggins, *J.*, 1946, 625; Hann and Hudson, *J. Amer. Chem. Soc.*, 1942, **64**, 925, 2435), and cleavage of either by alkali gives a mixture in which that isomer predominates whose configuration has the diaxial relationship. A primary objective of this work was to provide further examples in this series to support the general application of Fürst and Plattner's rule to the fission of sugar epoxides (Mills, cited by Newth and Homer, *J.*, 1953, 989; see also Bose, Chaudhuri, and Bhattacharyya, *Chem. and Ind.*, 1953, 869; Newth, *ibid.*, p. 1257; Cookson, *ibid.*, 1954, 223, 1512; Angyal, *ibid.*, p. 1230). Success in this was limited to one other dianhydro-β-D-hexose, but the properties of the sulphonic esters of 1 : 6-anhydro-β-D-altrose mentioned above have necessitated a fuller consideration of the geometry of epoxide formation.



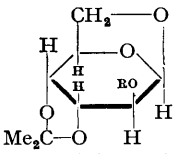
(I) (II) (III) (IV)

(Ms = $CH_3 \cdot SO_2$; Ts = p-$C_6H_4Me \cdot SO_2$)

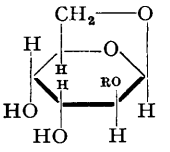
A convenient source of substituted altrose derivatives is 1 : 6-anhydro-3 : 4-*O*-*iso*propylidene-β-D-altrose (V) (Newth and Wiggins, *J.*, 1950, 1734). This is easily acylated and the 2-*O*-toluene-*p*-sulphonyl (VI) and the 2-*O*-methanesulphonyl derivative (VII) are hydrolysed to the corresponding sulphonyl derivatives (VIII and IX) of 1 : 6-anhydro-β-D-altrose under mildly acidic conditions. Each of these compounds has the correct configuration for epoxide formation and would be expected to yield 1 : 6-2 : 3-dianhydro-β-D-allose (X) on treatment with alkali. They were, however, recovered unchanged after being subjected to hot alkoxide or hydroxide as is usually employed—1 : 6-anhydro-2-chloro-2-deoxy-β-D-altrose (Newth and Wiggins, *loc. cit.*) showed a similar resistance. By prolonged and vigorous treatment with sodium methoxide 1 : 6-anhydro-2-*O*-toluene-*p*-sulphonyl-β-D-altrose gave an intractable resin; under such conditions, any epoxide (X) would certainly be decomposed, and the conformation (VIII*a*) would also permit a concerted displacement of the type observed by Henbest and Clayton (*Chem. and Ind.*, 1953, 1315) with 3β-*O*-toluene-*p*-sulphonyloxycholestan-5α-ol and 3α-*O*-toluene-*p*-sulphonyloxycoprostan-5β-ol, and by Smith (*ibid.*, 1955, 92) in the formation of 2-deoxy-D-ribose from 3-*O*-methanesulphonyl-D-glucopyranose (XI).

* Part of this work was communicated at the Amer. Chem. Soc. 126th Meeting, New York, September, 1954.

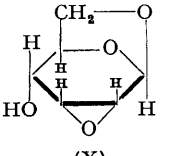
A potential intermediate for the formation of 1 : 6-2 : 3-dianhydro-β-D-mannose (XII) was prepared by the following sequence. 1 : 6-Anhydro-2-*O*-benzoyl-3 : 4-*O*-*iso*propylidene-β-D-altrose (XIII), formed nearly quantitatively from the 2-hydroxy-compound (V), was converted by mild acid into 1 : 6-anhydro-2-*O*-benzoyl-β-D-altrose (XIV). When this was treated with toluene-*p*-sulphonyl chloride in pyridine, 1 : 6-anhydro-2-*O*-benzoyl-3 : 4-di-*O*-toluene-*p*-sulphonyl-β-D-altrose (XV) was formed, together with some of the 3-toluene-



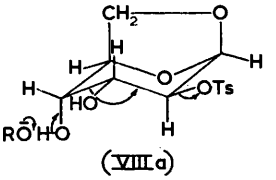
(V) R = H
(VI) R = Ts
(VII) R = Ms
(XIII) R = Bz



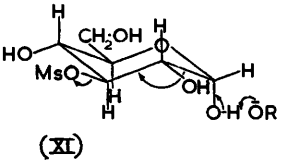
(VIII) R = Ts
(IX) R = Ms
(XIV) R = Bz



(X)

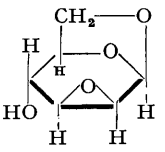


(VIIIa)

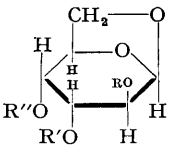


(XI)

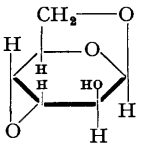
p-sulphonate (XVI). The latter was the sole product when only one mol. of sulphonyl chloride in dilute pyridine at 0° was employed. Sodium methoxide in methanol at 18° removed only the benzoyl group, giving 1 : 6-anhydro-3-*O*-toluene-*p*-sulphonyl-β-D-altrose (XVII), which was not oxidised by sodium metaperiodate, showing the toluene-*p*-sulphonyl group to be at position 3.



(XII)



(XV) R = Bz; R′ = R″ = Ts
(XVI) R = Bz; R′ = Ts; R″ = H
(XVII) R = R″ = H; R′ = Ts
(XXIII) R = H; R′ = R″ = Ts



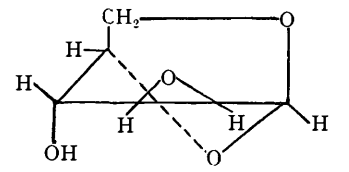
(XVIII)

The preferential formation of the 3-toluene-*p*-sulphonate might be expected since the 3-hydroxyl group in 1 : 6-anhydro-2-*O*-benzoyl-β-D-altrose is equatorial and that at $C_{(4)}$ is axial (cf. VIII*a*). An equatorial is esterified faster than an axial hydroxyl group since, in the latter case, the transition state is subject to more steric hindrance. de la Mare (in Klyne's " Progress in Stereochemistry," Vol. I, Butterworths Ltd., London, 1954, p. 61) has pointed out that this applies specifically to the formation of carboxylates and the formation of a sulphonic ester might be subject to different influences but the example here given suggests that this is not so.

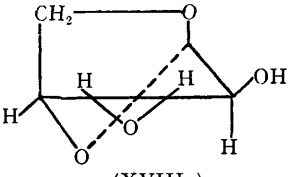
1 : 6-Anhydro-3-*O*-toluene-*p*-sulphonyl-β-D-altrose was unaffected by one mol. of sodium methoxide in boiling methanol after 4 hr. but with higher alkoxide concentration, a low yield of a dianhydrohexose, $C_6H_8O_4$, was obtained. Intramolecular displacement of the toluene-*p*-sulphonate anion from $C_{(3)}$ by the hydroxyl anion at $C_{(2)}$ must lead to the formation of 1 : 6-2 : 3-dianhydro-β-D-mannose (XII) but a second intramolecular nucleophilic displacement by the 4-hydroxyl group which is *trans* to the 2 : 3-epoxide group is possible. The dianhydride therefore could be either (XII) or 1 : 6-3 : 4-dianhydro-β-D-altrose (XVIII) and its identity was decided by fission of the epoxide ring. The isomer (XII) would give derivatives of D-altrose and D-glucose whereas the 1 : 6-3 : 4-dianhydride (XVIII) would give derivatives of D-idose and D-mannose. In each case D-glucose and D-mannose would be expected to predominate since these have the diaxial relationship when the 1 : 6-ring is

retained. Treatment with sodium hydroxide gave an ambiguous result since the interconversion (XII) ⇌ (XVIII) is possible. Dilute sulphuric acid on the other hand gave only one product which paper chromatography showed to be either 1 : 6-anhydro-β-D-glucose or 1 : 6-anhydro-β-D-mannose (the hydrolytic conditions did not open the 1 : 6-anhydro-ring), and a distinction in favour of 1 : 6-anhydro-β-D-mannose was made by paper ionophoresis. The compound, $C_6H_8O_4$, is therefore 1 : 6-3 : 4-dianhydro-β-D-altrose and acidic fission of its epoxide yields mainly the diaxial isomer in conformity with Fürst and Plattner's rule.

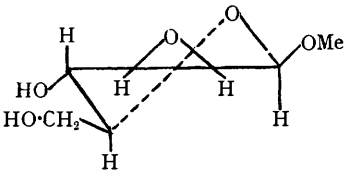
Examples of this isomerisation are already known. Lake and Peat (*J.*, 1939, 1069) found that the chief product, methyl 2 : 3-anhydro-β-D-mannopyranoside (XIX), from the reaction of methyl 2-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside with sodium methoxide



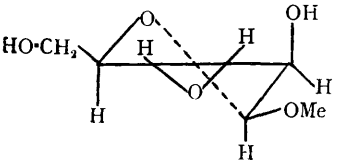
(XII*a*)



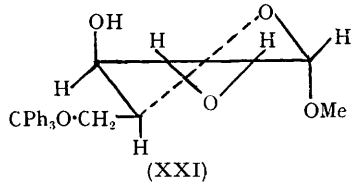
(XVIII*a*)



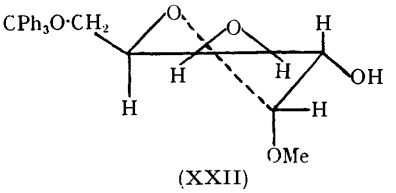
(XIX)



(XX)



(XXI)



(XXII)

(In XVIII*a*, XX, and XXII the tetrahydropyran ring is shown rotated through 60° to the right. Because of the half-chair conformation, all groups will be either e′ or a′.)

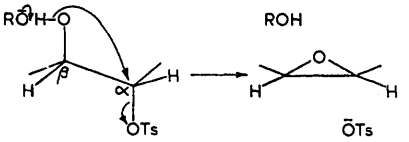
is always accompanied by some methyl 3 : 4-anhydro-β-D-altropyranoside (XX). More recently Buchanan (*Chem. and Ind.*, 1954, 1484) showed that methyl 2 : 3- (XXI) and 3 : 4-anhydro-6-*O*-trityl-α-D-galactopyranoside (XXII) are formed from methyl 4-*O*-toluene-*p*-sulphonyl-6-*O*-trityl-α-D-glucoside by alkali. There is at present no indication as to which epoxide predominates in this reaction mixture. [A similar intramolecular process accounts for the formation of methyl 3 : 6-anhydro-β-D-gluco-furanoside and -pyranoside from methyl 2 : 3-anhydro-β-D-allo-furanoside and -pyranoside (Ohle and Wilcke, *Ber.*, 1938, **71**, 2316; Peat and Wiggins, *J.*, 1938, 1088; see also Peat, *Adv. Carbohydrate Chem.*, 1946, **2**, 51).]

It is important to consider the factors which could determine the direction of these interconversions. The conformations of the three pairs of isomers are shown in their respective formulæ and it is perhaps significant that the chief product (XVIII*a* and XIX) in the first two pairs is that in which the free hydroxyl group is equatorial. This suggests that the conformation determines which isomer will predominate inasmuch as the epoxide group is attacked more easily by an axial than by an equatorial hydroxyl group. On this basis one would expect methyl 3 : 4-anhydro-6-*O*-trityl-α-D-galactoside to be the chief product in the mixture (XXI, XXII). Nucleophilic activity of the 2- and 4-hydroxyl groups must also be considered and that at $C_{(2)}$, with its neighbouring aldehydic $C_{(1)}$, will be subject to an electronic pull by that centre. Its anion will consequently have reduced nucleophilic character relative to that at $C_{(4)}$ and would be less inclined to attack the

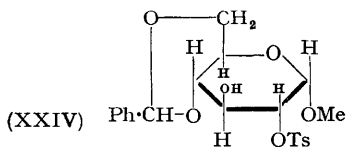
neighbouring epoxide. If this were a primary effect it would mean that a 3 : 4-epoxide should always be the chief product, but the predominance of (XIX) over (XX) contradicts this. In the absence of reaction rates and reliable product analysis no more can be said at present than that conformation appears to exert the greater influence.

To return to the behaviour of the 3-*O*-toluene-*p*-sulphonyl group attached to 1 : 6-anhydro-β-D-altrose, it was found that in contrast to (XVII), 1 : 6-anhydro-3 : 4-di-*O*-toluene-*p*-sulphonyl-β-D-altrose (XXIII) was unaffected by sodium methoxide in boiling methanol for 20 hr. In order to rationalise the inertness of (XXIII) and 1 : 6-anhydro-2-*O*-toluene-*p*-sulphonyl-β-D-altrose compared with 1 : 6-anhydro-3-*O*-toluene-*p*-sulphonyl-β-D-altrose, it is necessary to consider general conformational aspects of the formation of sugar epoxides.

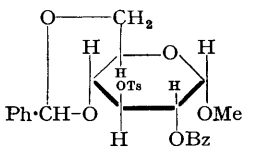
The base-catalysed reaction of a *trans*-1 : 2-diol mono-*O*-toluene-*p*-sulphonate to give an epoxide is almost certain to involve an intramolecular S_N2 process :



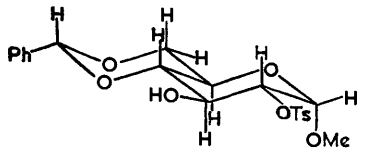
and in a six-membered ring, according to present views, the diaxial condition will permit maximum participation since C_α, C_β, the O of OH and O of OTs are coplanar. This is certainly true in the analogous bimolecular ionic elimination reaction of 1 : 2-dihalides, where no elimination occurs if both *trans*-substituents are rigidly held in equatorial positions as in methyl 11α : 12β-dibromo-3α : 9β-epoxycholanate (Barton and Rosenfelder, *J.*, 1951, 1048). Such an extreme difference is not observed in the formation of epoxides in the carbohydrate field where both diequatorial and diaxial systems react smoothly. The diequatorial condition is found in methyl 4 : 6-*O*-benzylidene-2-*O*-toluene-*p*-sulphonyl-α-D-glucoside (XXIV) and methyl 2-*O*-benzoyl-4 : 6-*O*-benzylidene-3-*O*-toluene-



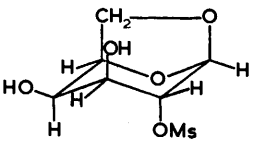
(XXIV)



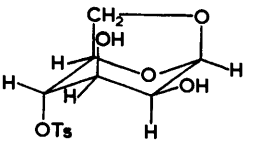
(XXV)



(XXIVa)



(Ia)



(IIIa)

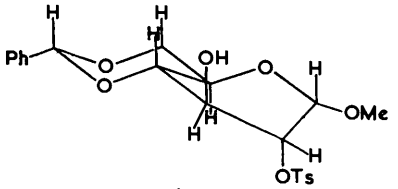
p-sulphonyl-α-D-glucoside (XXV) which give the 2 : 3-*manno*- and 2 : 3-*allo*-epoxide (Robertson and Griffith, *J.*, 1935, 1193). [It should be noted that in (XXV) the 2-*O*-benzoyl group is directly hydrolysed and does not participate in the reaction as it would under acidic solvolytic conditions (Winstein, Hanson, and Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 812).] The esters (XXIV) and (XXV) are formed by selective acylation at $C_{(2)}$ of methyl 4 : 6-*O*-benzylidene-α-D-glucoside, a compound in which the C 1 conformation has been demonstrated by Reeves (*J. Amer. Chem. Soc.*, 1949, **71**, 215) and the *trans*-ring junction makes this a rigid structure about $C_{(4)}/C_{(5)}$ as shown in (XXIV*a*).

The diaxial condition is found in 1 : 6-anhydro-2-*O*-methanesulphonyl-β-D-galactose (I*a*) and 1 : 6-anhydro-4-*O*-toluene-*p*-sulphonyl-β-D-mannose (III*a*) where the 1 C conformation is held firm by the 1 : 6-anhydro-ring. Even in the absence of quantitative data, the preparative conditions employed show that the esters (I) and (III) are converted more easily into epoxides than are (XXIV) and (XXV) although the latter pair must not be

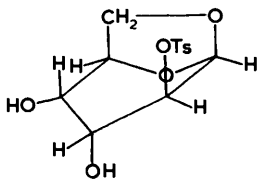
considered inert. There is, unfortunately, no 2- or 3-*O*-toluene-*p*-sulphonyl derivative of methyl 4 : 6-*O*-benzylidene-α-D-altroside (diaxial) for comparison with (XXIV) and (XXV), but a partial comparison shows that methyl 4 : 6-*O*-benzylidene-2-deoxy-2-iodo-α-D-altroside (Richards and Wiggins, *J.*, 1953, 2442) is very easily converted into the 2 : 3-*allo*-epoxide.

Ottar (*Acta Chem. Scand.*, 1947, **1**, 283) has shown by election diffraction that 1 : 2-epoxy*cyclo*hexane has a half-chair conformation similar to that of *cyclo*hexene, and Cookson (*loc. cit.*) first portrayed sugar epoxides in this way, illustrated here by the series (XII*a*, XVIII*a*—XXII). [Reeves (*J. Amer. Chem. Soc.*, 1950, **72**, 1499) stated erroneously that epoxides can only be accommodated in a boat form of the pyranose ring; this would be impossible in compounds such as (II) and (IV)].

There is no difficulty in envisaging the process of 2 : 3-epoxide formation from a diaxial system when $C_{(2)}$ and $C_{(3)}$ move in opposite directions to acquire trigonal character and so become coplanar with $C_{(1)}$ and $C_{(4)}$. Reaction in the diequatorial system cannot be formulated so simply and Barton and Rosenfelder's finding (*loc. cit.*) suggests that a structural modification must occur before reaction. Models show that the C 1 (XXIV*a*) and the 1 C conformation and (VIII*a*) are easily transformed into the boat conformations B 2 and 3 B (Reeves, *loc. cit.*), (XXIV*b*) and (VIII*b*), without disturbing the point of ring



(XXIV*b*)



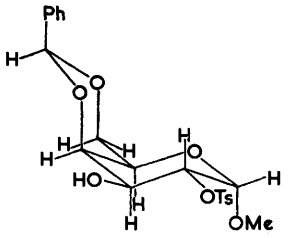
(VIII*b*)

fusion and, by comparison with *cyclo*hexane, only about 5 kcal. should be necessary for this change. The OH and the OTs group are seen to be coplanar and are now in a position to react as a diaxial system. It is recognised that the epoxide conformation is half-way in the chair–boat conversion and that $C_{(2)}$ and $C_{(3)}$ will have to move again in the reverse direction to become coplanar with $C_{(1)}$ and $C_{(4)}$. For this reason the true boat form may never be reached. It is convenient, however, to formulate this extreme condition since in its attainment steric interactions are apparent which readily explain different activities and permit predictions. In passing from chair to boat conformation there will be steric interaction between vicinal groups when one is axial and the other equatorial since they will have to move past each other. In the final boat form there will be interaction between1 : 2-, 1 : 3-, and 1 : 4-axial groups. Such hindrance in the *O*-toluene-*p*-sulphonyl derivatives of 1 : 6-anhydro-β-D-altrose is considerable. In the change (VIII*a* ⟶ VIII*b*) the 3-hydroxyl group has to pass the 4-hydroxyl group, and the toluenesulphonyloxy-group will then show severe interaction with $O_{(1)}$ and $C_{(6)}$. 1 : 6-Anhydro-3 : 4-di-*O*-toluene-*p*-sulphonyl-β-D-altrose (XXIII) will also show a severe OTs/OTs interaction as the groups pass and, in the boat form, $OH_{(2)}/O_{(1)}$ and $OH_{(2)}/C_{(6)}$ interactions. It is considered that these factors are sufficient to prevent reaction under normal conditions. On the other hand, 1 : 6-anhydro-3-*O*-toluene-*p*-sulphonyl-β-D-altrose (XVII) does react and, although steric interaction is almost the same, the $OTs/OH_{(4)}$, $OH_{(2)}/O_{(1)}$, and $OH_{(2)}/C_{(6)}$ interactions could show the fine difference which distinguishes the compound from (VIII) and (XXIII).

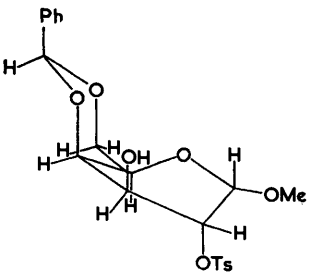
This concept may be applied to methyl 4 : 6-*O*-benzylidene-2-*O*-toluene-*p*-sulphonyl-α(and β)-D-galactoside (XXVI). Although Reichstein and his co-workers found that both the α- and the β-form were converted into methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene-D-taloside when boiled with sodium methoxide (*Helv. Chim. Acta*, 1945, **28**, 1, 226, 1164), Wiggins (*J.*, 1944, 522) observed that with cold sodium methoxide the β-form gave 78% of the anhydride after 15 min. while there was no reaction with the α-form. The chair conformation of the α-form is shown in (XXVI*a*) and it can be seen that there will be interactions on passing to (XXVI*b*) which will be similar to those in the 1 : 6-anhydro-β-D-altrose series. This example, however, is not so easy to interpret since the ring fusion at

$C_{(4)}/C_{(5)}$ is *cis* and this permits the pyranose ring to become 1 C in conformation (XXVI*c*). Even if this were so the β- and the α-anomer could still show different steric interactions to account for the behaviour which Wiggins observed.

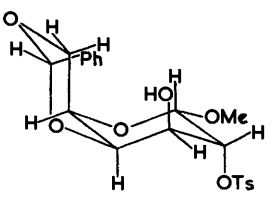
Further consideration of steric interactions would suggest that methyl 4 : 6-*O*-benzylidene-2-*O*-toluene-*p*-sulphonyl-β-D-glucoside should react faster than the α-form which itself should react more slowly than the 3-toluene-*p*-sulphonate. Rate measurements, however, are required before these steric effects can be fully assessed.



(XXVI*a*)



(XXVI b)



(XXVI c)

Experimental

1 : 6-*Anhydro*-2-O-*toluene*-p-*sulphonyl*-β-D-*altrose*.—1 : 6-Anhydro-3 : 4-*O*-*iso*propylidene-2-*O*-toluene-*p*-sulphonyl-β-D-altrose (10 g.; Newth and Wiggins, *loc. cit.*) was boiled with 20% acetic acid (100 ml.) for 2 hr. On cooling, 1 : 6-*anhydro*-2-O-*toluene*-p-*sulphonyl*-β-D-*altrose* (8·5 g.) separated which, recrystallised from ethanol–water, had m. p. 129—130°, $[\alpha]_D^{17}$ −148·5° (*c*, 1·05 in EtOH) (Found: C, 49·4; H, 5·1. $C_{13}H_{16}O_7S$ requires C, 49·4; H, 5·1%). Acetylation (acetic anhydride–pyridine) yielded the 3 : 4-*di*-O-*acetate*, m. p. 139—140° (from ethanol), $[\alpha]_D^{20}$ −142·5° (*c*, 1·27 in $CHCl_3$) (Found: C, 51·0; H, 5·0. $C_{17}H_{20}O_9S$ requires C, 51·0; H, 5·0%).

1 : 6-*Anhydro*-2-O-*methanesulphonyl*-3 : 4-O-iso*propylidene*-β-D-*altrose*.—1 : 6-Anhydro-3 : 4-*O*-*iso*propylidene-β-D-altrose (2 g.) in pyridine (10 ml.) was treated with methanesulphonyl chloride (0·87 ml., 1·1 mol.) for 15 hr. The mixture was poured into water, and 1 : 6-*anhydro*-2-O-*methanesulphonyl*-3 : 4-O-iso*propylidene*-β-D-*altrose*, recrystallised from methanol, had m. p. 158—159° (1·7 g.), $[\alpha]_D^{23}$ −162° (*c*, 0·99 in $CHCl_3$) (Found: C, 43·2; H, 5·7. $C_{10}H_{16}O_7S$ requires C, 42·9; H, 5·7%).

1 : 6-*Anhydro*-2-O-*methanesulphonyl*-β-D-*altrose*.—The *iso*propylidene derivative (1·7 g.) was boiled in ethanol (60 ml.) and 0·5N-sulphuric acid (30 ml.) for 2 hr. The acid was neutralised with barium hydroxide and, after removal and washing of the inorganic precipitate, the solution was evaporated to dryness. The residue, recrystallised from ethanol, afforded 1 : 6-*anhydro*-2-O-*methanesulphonyl*-β-D-*altrose* (1·3 g.), m. p. 138—140°, $[\alpha]_D^{23}$ −186·4° (*c*, 0·77 in EtOH) (Found: C, 35·1; H, 5·2. $C_7H_{12}O_7S$ requires C, 35·0; H, 5·0%). The 3 : 4-*di*-O-*acetate*, recrystallised from ethanol, had m. p. 139°, $[\alpha]_D^{18}$ −157·5° (*c*, 0·95 in $CHCl_3$) (Found: C, 40·6; H, 5·0. $C_{11}H_{16}O_9S$ requires C, 40·7; H, 4·9%).

Attempted Formation of 1 : 6-2 : 3-*Dianhydro*-β-D-*allose*.—1 : 6-Anhydro-2-*O*-toluene-*p*-sulphonyl-β-D-altrose and 1 : 6-anhydro-2-*O*-methanesulphonyl-β-D-altrose were recovered unchanged after they had been treated with boiling 0·5N-sodium methoxide solution (1 equiv.) for 5 hr. or N-sodium hydroxide (1 equiv.) at 95° for 6 hr. 1 : 6-Anhydro-2-*O*-toluene-*p*-sulphonyl-β-D-altrose was also recovered unchanged after treatment in boiling butan-1-ol with a solution from sodium (1 atom equiv.) in butan-1-ol. When this compound was heated with a solution of sodium methoxide (3 equiv.) at 120° for 22 hr. and the resulting dark brown solution neutralised, a highly coloured resin was obtained which could not be characterised. 3 : 4-Di-*O*-acetyl-1 : 6-anhydro-2-*O*-toluene-*p*-sulphonyl- and -2-*O*-methanesulphonyl-β-D-altrose were deacetylated quantitatively when their chloroform solutions were treated with sodium methoxide (3 equiv.) in methanol for 16 hr. 1 : 6-Anhydro-2-chloro-2-deoxy-β-D-altrose was recovered after its treatment with 0·5N-sodium hydroxide (1 equiv.) at 18° for 20 hr.

1 : 6-*Anhydro*-2-O-*benzoyl*-3 : 4-O-iso*propylidene*-β-D-*altrose*.—1 : 6-Anhydro-3 : 4-*O*-*iso*propylidene-β-D-altrose (6·45 g.) in pyridine (50 ml.) was treated with benzoyl chloride (4·9 g., 1·1 mol.). The mixture was poured into water after 15 hr. and the precipitate removed and washed with water. 1 : 6-*Anhydro*-2-O-*benzoyl*-3 : 4-O-iso*propylidene*-β-D-*altrose* (7·3 g.), recrystallised from

ethanol, had m. p. 95—96°, $[\alpha]_D^{20}$ −212·6° (*c*, 1·17 in $CHCl_3$) (Found : C, 62·7; H, 5·9. $C_{16}H_{18}O_6$ requires C, 62·7; H, 5·8%).

1 : 6-*Anhydro*-2-O-*benzoyl*-β-D-*altrose*.—The 3 : 4-*O*-*iso*propylidene derivative (4·5 g.) was boiled with 20% acetic acid (100 ml.) for 2 hr. The solution was evaporated and 1 : 6-*anhydro*-2-O-*benzoyl*-β-D-*altrose* (3·9 g.) separated which, recrystallised from ethanol, had m. p. 203—204°, $[\alpha]_D^{20}$ −220·5° (*c*, 0·84 in $COMe_2$) (Found : C, 58·6; H, 5·3. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3%). The 3 : 4-*di*-O-*acetate* had m. p. 117—118° (from ethanol), $[\alpha]_D^{18}$ −203° (*c*, 2·98 in $CHCl_3$) (Found : C, 58·3; H, 5·3. $C_{17}H_{18}O_8$ requires C, 58·3; H, 5·1%).

1 : 6-*Anhydro*-2-O-*benzoyl*-3 : 4-*di*-O-*toluene*-p-*sulphonyl*-β-D-*altrose*.—1 : 6-Anhydro-2-*O*-benzoyl-β-D-altrose (3·0 g.) in pyridine (30 ml.) was treated with toluene-*p*-sulphonyl chloride (4·75 g., 2·2 mol.) for 20 hr. When the mixture was then poured into water, 1 : 6-*anhydro*-2-O-*benzoyl*-3 : 4-*di*-O-*toluene*-p-*sulphonyl*-β-D-*altrose* separated which, recrystallised from ethanol (4·4 g., 70%), had m. p. 187—188°, $[\alpha]_D^{20}$ −214° (*c*, 0·92 in $CHCl_3$) (Found : C, 56·3; H, 4·4; S, 11·4. $C_{27}H_{26}O_{10}S_2$ requires C, 56·4; H, 4·5; S, 11·2%). The residue from the mother-liquors, recrystallised from ethanol, had m. p. 176—177° (0·8 g.), $[\alpha]_D^{18}$ −238° (*c*, 2·22 in $CHCl_3$), and was 1 : 6-*anhydro*-2-O-*benzoyl*-3-O-*toluene*-p-*sulphonyl*-β-D-*altrose* (Found : C, 57·2; H, 5·1; S, 7·7. $C_{20}H_{20}O_8S$ requires C, 57·2; H, 5·1; S, 7·6%). This derivative was obtained quantitatively when 1 : 6-anhydro-2-*O*-benzoyl-β-D-altrose (166 mg.) was treated with toluene-*p*-sulphonyl chloride (118 mg.) in pyridine at 0° for 48 hr. Benzoylation of 1 : 6-anhydro-2-*O*-benzoyl-3-*O*-toluene-*p*-sulphonyl-β-D-altrose gave the 2 : 4-*di*-O-*benzoate*, m. p. 125° (from ethanol), $[\alpha]_D^{18}$ −215° (*c*, 0·92 in $CHCl_3$) (Found : C, 61·9; H, 4·7. $C_{27}H_{24}O_9S$ requires C, 61·8; H, 4·6%).

1 : 6-*Anhydro*-3-O-*toluene*-p-*sulphonyl*-β-D-*altrose*.—1 : 6-Anhydro-2-*O*-benzoyl-3-*O*-toluene-*p*-sulphonyl-β-D-altrose (0·56 g.) in chloroform (5 ml.) was treated with a solution from sodium methoxide (from 70 mg. of sodium ; 2·2 mol.) in methanol (5 ml.). Excess of alkali was neutralised with carbon dioxide after 16 hr. and the solution evaporated. The dry residue was extracted with acetone and the crystalline residue from this extract was 1 : 6-*anhydro*-3-O-*toluene*-p-*sulphonyl*-β-D-*altrose* (185 mg.), m. p. 144—145° (from acetone–ether), $[\alpha]_D^{28}$ −168·5° (*c*, 1·18 in MeOH) (Found : C, 49·2; H, 4·9. $C_{13}H_{16}O_7S$ requires C, 49·4; H, 5·0%). It was not oxidised by aqueous sodium metaperiodate.

Treatment of 1 : 6-*Anhydro*-3-O-*toluene*-p-*sulphonyl*-β-D-*altrose with Sodium Methoxide*.—The compound (750 mg.) was boiled for 2 hr. in a solution of methanol (20 ml.) containing sodium (140 mg., 2·5 mol.). The dark mixture was neutralised with carbon dioxide and then evaporated and the residue extracted with ethyl acetate. The crystalline *dianhydride* (70 mg.) obtained from this extract, recrystallised from ethyl acetate, had m. p. 158°, $[\alpha]_D^{20}$ −108° (*c*, 0·75 in $COMe_2$) (Found : C, 50·2; H, 5·7. $C_6H_8O_4$ requires C, 50·0; H, 5·6%). 1 : 6-Anhydro-3-*O*-toluene-*p*-sulphonyl-β-D-altrose was unaffected by the above treatment with only 1 atom equiv. of sodium.

The dianhydride was identified as 1 : 6-3 : 4-*dianhydro*-β-D-*altrose* by acidic hydrolysis (2·8 mg. in 0·2 ml. of 0·1N-sulphuric acid at 80° for 2 hr.). Paper chromatography of the product (pyridine–ethyl acetate–water, 1 : 2 : 2, top layer) showed it to be 1 : 6-anhydro-β-D-glucose or -mannose [lead tetra-acetate spray reagent (Buchanan, Dekker, and Long, *J.*, 1950, 3162)]. Paper ionophoresis (0·1M-sodium tetraborate, 200 v for 5 hr.) distinguished the product as 1 : 6-anhydro-β-D-mannose. Authentic specimens of 1 : 6-anhydro-β-D-altrose, -β-D-glucose, -β-D-idose, and -β-D-mannose were used as markers.

1 : 6-*Anhydro*-3 : 4-*di*-O-*toluene*-p-*sulphonyl*-β-D-*altrose*.—To a solution of 1 : 6-anhydro-2-*O*-benzoyl-3 : 4-di-*O*-toluene-*p*-sulphonyl-β-D-altrose (4·4 g.) in chloroform (50 ml.), sodium methoxide (from 0·4 g. of sodium) in methanol (25 ml.) was added at 0°. Within 15 min. the sparingly soluble product which had separated was removed and washed with water. To this was added a further small amount obtained on evaporating the chloroform layer. 1 : 6-*Anhydro*-3 : 4-*di*-O-*toluene*-p-*sulphonyl*-β-D-*altrose*, recrystallised from ethanol, had m. p. 209°, $[\alpha]_D^{20}$ −147° (*c*, 0·73 in $CHCl_3$) (Found : C, 51·1; H, 4·7. $C_{20}H_{22}O_9S$ requires C, 51·1; H, 4·7%). The compound was unaffected by boiling 2·5M-sodium methoxide for 20 hr.

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