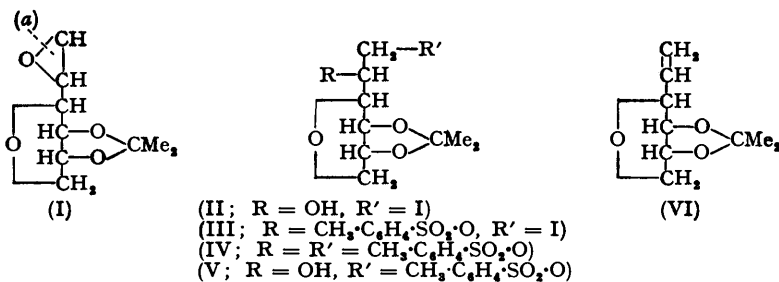


### 763. Mechanism of the Reaction of Terminal Vicinal Ditoluene-*p*-sulphonyl Hexitol Derivatives with Sodium Iodide in Acetone.

By A. B. FOSTER and W. G. OVEREND.

The reaction of terminal vicinal toluene-*p*-sulphonyloxy-residues in carbohydrates with sodium iodide in dry acetone to yield unsaturated products has been studied by using 1-toluene-*p*-sulphonyl and 1:2-ditoluene-*p*-sulphonyl derivatives of 3:6-anhydromannitol. A mechanism of the reaction is suggested which postulates the intermediate formation of an iodo-compound, with the iodine substituent located on the primary position, which on subsequent intramolecular transition produces the unsaturated derivative.

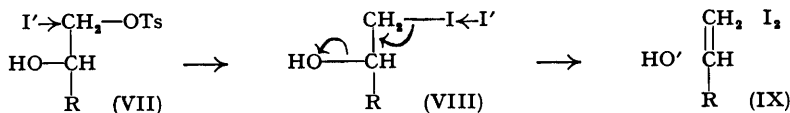
EXCEPTIONS to the rule formulated by Oldham and Rutherford, (*J. Amer. Chem. Soc.*, 1932, **54**, 366; see also Levene and Raymond, *J. Biol. Chem.*, 1933, **102**, 317) for distinguishing between primary and secondary toluene-*p*-sulphonyloxy-groups have been recorded. Thus, (a) the presence of an activating group adjacent to a secondary toluene-*p*-sulphonyl ester group facilitates an exchange reaction with sodium iodide in acetone; both the  $-\text{CH}=\text{CH}-$  (Laland, Overend, and Stacey, *J.*, 1950, 738) and the methylene groups (Foster and Overend, unpublished observations; cf. Foster, Overend, and Stacey, *J.*, 1951, 988) are effective in this respect. (b) The 2:5-ditoluene-*p*-sulphonyl esters of 1:4:3:6-dianhydro-mannitol and -sorbitol undergo similar exchange reactions (Wiggins and Wood, *J.*, 1951, 1180). In this case the unusual reactivity is attributed to the peculiar stereochemistry of these dianhydrohexitol derivatives, since it is found that the two sulphonyloxy-groups are replaced in the mannitol derivative whereas only one undergoes reaction in the sorbitol derivative. Moreover, this stereochemical explanation is supported by the fact that the corresponding derivative of L-idoitol does not undergo any exchange reaction. (c) Compounds, in particular carbohydrates, which contain terminal vicinal toluene-*p*-sulphonyl ester groups [*i.e.*,  $\cdot\text{CH}(\text{OTs})\cdot\text{CH}_2\cdot\text{OTs}$ ] react with sodium iodide in dry acetone to yield unsaturated products (cf., also, Bell, Friedman, and Williamson, *J.*, 1937, 252, and Raymond and Schroeder, *J. Amer. Chem. Soc.*, 1948, **70**, 2786). Elimination of both the toluene-*p*-sulphonyloxy-residues occurs and no iodo-derivative can be isolated. This investigation deals with some aspects of reaction (c).



Suitable compounds for this study were prepared by treating 4:5-isopropylidene 1:2:3:6-dianhydromannitol (I) (Foster and Overend, *J.*, 1951, 1132) with hydriodic acid or methylmagnesium iodide, both of which yielded 4:5-isopropylidene 3:6-anhydro-1-deoxy-1-iodo-mannitol (II) by scission of the epoxide ring at (a). (II) readily afforded a 2-toluene-*p*-sulphonyl derivative (III). With an excess of toluene-*p*-sulphonyl chloride in dry pyridine 4:5-isopropylidene 3:6-anhydromannitol (Foster and Overend *J.*, 1951, 680) gave the 1:2-ditoluene-*p*-sulphonyl derivative (IV) whereas the use of 1 mol. of the same reagent at 0° afforded 4:5-isopropylidene 1-toluene-*p*-sulphonyl 3:6-anhydromannitol (V).

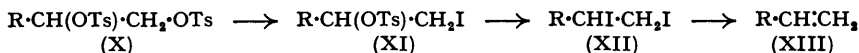
The nature of the reaction of carbohydrate derivatives containing the grouping  $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OTs}$  (*e.g.*, V) with sodium iodide in acetone was outlined by Friedman and Williamson (*loc. cit.*) who recorded that 1:2-isopropylidene 6-toluene-*p*-sulphonyl D-glucose could be converted into a derivative of D-glucose (5:6-didehydro-5:6-dideoxy-D-glucose). Similarly 6-toluene-*p*-sulphonyl 1:4-anhydrosorbitol afforded 1:4-anhydrosorbitoleen (Raymond and Schroeder, *loc. cit.*). It is probable that these reactions proceed in two stages:

(1) anionic attack at the terminal carbon atom in (VII) results in replacement of the toluene-*p*-sulphonyloxy-group by iodine to give (VIII); (2) anionic attack at the iodine atom in (VIII)

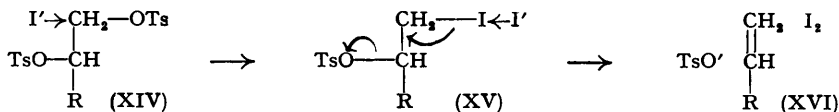


results in an intramolecular displacement with the ejection of a hydroxyl ion, formation of molecular iodine, and the establishment of an ethylenic linkage (IX). In support of this view it was shown that treatment of 4 : 5-*isopropylidene* 1-toluene-*p*-sulphonyl 3 : 6-anhydromannitol (V) with sodium iodide (1.2 mols.) in dry acetone at 80—90° for 3 hours resulted in 91.2% replacement of the toluene-*p*-sulphonyloxy-residue by iodine, and 4 : 5-*isopropylidene* 3 : 6-anhydro-1-deoxy-1-iodomannitol (II) was obtained [cf. (VII) → (VIII)]. (II) on treatment with sodium iodide (1.2 mols.) in dry acetone at 140—145° for 12 hours did not undergo any further reaction, but, by increasing the molar proportion of sodium iodide (to 8.8 mols.) and heating at 210—220° for 12 hours, iodine was liberated and 4 : 5-*isopropylidene* 3 : 6-anhydromannitoleen (VI) was formed [cf. (VIII) → (IX)]. Thus the conversion (VII) → (IX) may be readily differentiated into two stages of which the first stage may be effected with greater ease.

The reactions of derivatives containing the grouping  $\cdot\text{CH}(\text{OTs})\cdot\text{CH}_2\cdot\text{OTs}$  with sodium iodide in acetone differ from those described above since they proceed more readily and it is not possible to isolate intermediate compounds. The first example of this type of reaction was encountered by Levene and Mehlretter (*Enzymologia*, 1937, 4, 232) who found that all the toluene-*p*-sulphonyloxy-groups in 1 : 2 : 3-tritoluene-*p*-sulphonyl D-glycerol were eliminated and an unsaturated product resulted (see also Tipson and Cretcher, *J. Org. Chem.*, 1943, 8, 95; Hann, Ness, and Hudson, *J. Amer. Chem. Soc.*, 1944, 66, 73; Karrer, Schick, and Schwyzer, *Helv. Chim. Acta*, 1948, 31, 784; Karrer and Davis, *ibid.*, p. 1611; Owen and Bladon, *J.*,



1950, 598; Foster and Overend, *loc. cit.*). It was suggested by Owen and Bladon (*loc. cit.*) that the reaction proceeded in three stages, (X) → (XIII), and that it would not be possible to isolate the intermediate (XII). The second suggestion was based on previous work by Finkelstein (*Ber.*, 1910, 43, 1528) and by Büllman (*Rec. Trav. chim.*, 1916, 36, 313; 1917, 37, 245) who showed that vicinal di-iodo-compounds could not be prepared by the action of sodium iodide in acetone on the corresponding dibromo- or dichloro-derivatives, unsaturated products being invariably obtained. An alternative mechanism, however, may account for the results: Anionic attack at the primary carbon atom in (XIV) may result in a normal iodine exchange,



to afford (XV). Thereafter anionic attack at the iodine atom in (XV) causes an intramolecular displacement resulting in the release of the toluene-*p*-sulphonate ion, formation of molecular iodine, and establishment of an ethylenic linkage (XVI) [cf. (VII) → (VIII) → (IX)]. The action of sodium iodide, sodium trifluoroacetate, and sodium salicylate in acetone on 4 : 5-*isopropylidene* 1 : 2-ditoluene-*p*-sulphonyl 3 : 6-anhydromannitol (IV) and 4 : 5-*isopropylidene* 2-toluene-*p*-sulphonyl 3 : 6-anhydro-1-deoxy-1-iodomannitol (III) provided evidence in support of this. The product in each case with sodium iodide was 4 : 5-*isopropylidene* 3 : 6-anhydromannitoleen (VI). The results summarized in Table I show that the conversion (III) → (VI) [in the general case (XV) → (XVI)] proceeds at room temperature, whereas under similar conditions (IV) [in the general case (XIV)] is unaffected.

These results explain our previous failure to obtain (III) by treatment of (IV) with sodium iodide in acetone under very mild conditions (Foster and Overend, *loc. cit.*), since the conditions necessary to effect the conversion (IV) → (III) are those under which (III) when formed would be converted rapidly into (VI). Hence, in derivatives of the type  $\text{R}\cdot\text{CH}(\text{OTs})\cdot\text{CH}_2\cdot\text{OTs}$  the second stage of their reaction with sodium iodide in acetone is the readier whereas in derivatives of the type  $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OTs}$  the first stage is the readier.

It follows that if the mechanism suggested above, (XIV)  $\longrightarrow$  (XVI), is valid, then it should be possible to effect the second stage, (XV)  $\longrightarrow$  (XVI), by the anion of any sodium salt which is soluble in acetone. Most of the common sodium salts are either of low solubility or insoluble in acetone and hence a wide investigation was not possible. It was feasible however to examine the action of sodium trifluoroacetate and sodium salicylate. The results shown in Table II demonstrate that both have a pronounced effect on (III). Furthermore, in reactions on a

TABLE I.  
*Extent (%) of exchange reaction on treatment of (III) and (IV) with sodium iodide in acetone (see Experimental).*

Compound	Reaction conditions				Method of determination *
	15—20° 30 hrs.	130—135° 1 hr.	100—105° 5 hrs.	130—135° 6 hrs.	
4 : 5- <i>iso</i> Propylidene 1 : 2-ditoluene- <i>p</i> -sulphonyl 3 : 6-anhydromannitol (IV)	—	32.6	45.8	64.0	A
	—	36.5	50.7	68.4	B
4 : 5- <i>iso</i> Propylidene 2-toluene- <i>p</i> -sulphonyl 3 : 6-anhydro-1-deoxy-1-iodo-mannitol (III)	38.6	48.2	59.2	—	A
	37.8	52.6	60.1	—	B

\* A, % exchange determined from the wt. of sodium toluene-*p*-sulphonate pptd. B, % exchange determined by titration of the liberated iodine.

TABLE II  
*Action of sodium trifluoroacetate and sodium salicylate in acetone on (III). Extent (%) of exchange reaction.*

Mannitol derivative	Reactions conditions		Method of determination *
	CF <sub>3</sub> ·CO <sub>2</sub> Na, 120—130° for 3 hours	<i>o</i> -HO·C <sub>6</sub> H <sub>4</sub> ·CO <sub>2</sub> Na, 120—130° for 5 hours	
4 : 5- <i>iso</i> Propylidene 1-iodo- .....	43.4	77.1	A
2-Toluene- <i>p</i> -sulphonyl 3 : 6-anhydro-1-deoxy- .....	15.4	21.9	B

\* A and B as in Table I.

larger scale it was possible to isolate the well-authenticated 4 : 5-*isopropylidene* 3 : 6-anhydromannitoleen in each case. These salts had no effect on the 1 : 2-ditoluene-*p*-sulphonyl derivative (IV), suggesting that their reaction with (III) is by anionic attack at the iodine atom [cf. (XV)]. Moreover, it may be seen from Table II that the discrepancies between the values determined by the methods A and B are 28% and 55.2% respectively for the sodium trifluoroacetate and the sodium salicylate, whereas in Table I for sodium iodide they do not exceed 5% which is near the limit of experimental error. The reasons for these discrepancies are not completely understood but, with the sodium trifluoroacetate, attack by the trifluoroacetate ion on the iodine atom in (III) by the mechanism we have suggested would yield CF<sub>3</sub>·CO·OI which is known to decompose readily (cf. Henne and Zinner, *J. Amer. Chem. Soc.*, 1951, 73, 1362) and would be expected to give rise to some molecular iodine together with other products containing iodine. In the case of the action of sodium salicylate on (III), in addition to the unsaturated product 4 : 5-*isopropylidene* 3 : 6-anhydromannitoleen (VI), a second, unidentified substance was obtained, having m. p. 68—69°, which did not contain iodine or sulphur or an ethylenic linkage and was optically inactive; this compound may be one of the breakdown products of HO·C<sub>6</sub>H<sub>4</sub>·CO·OI.

From our results it seems that the mechanism of the reaction of terminal vicinal ditoluene-*p*-sulphonyl derivatives with sodium iodide in dry acetone is not completely explained by the three-stage reaction [(X)  $\longrightarrow$  (XIII)] suggested by Owen and Bladon (*loc. cit.*) which involves a vicinal di-iodo-intermediate derivative. It appears that the alternative mechanism now suggested, *i.e.*, (XIV)  $\longrightarrow$  (XVI), offers a more satisfactory explanation of the conversion of 4 : 5-*isopropylidene* 1 : 2-ditoluene-*p*-sulphonyl 3 : 6-anhydromannitol (IV) into 4 : 5-*isopropylidene* 3 : 6-anhydromannitoleen (VI) by the action of sodium iodide in acetone.

#### EXPERIMENTAL.

*Action of Methylmagnesium Iodide on 4 : 5-isoPropylidene 1 : 2-3 : 6-Dianhydromannitol.*—To a boiling ethereal solution of methylmagnesium iodide [prepared from magnesium (0.3 g.), methyl iodide (0.75 c.c.) and dry ether (5 c.c.)], a solution of 4 : 5-*isopropylidene* 1 : 2-3 : 6-dianhydromannitol (1.0 g.) in dry ether (10 c.c.) was added gradually during 30 minutes. After a further 3 hours the ethereal

solution was poured into ice-cold dilute sulphuric acid, and the aqueous layer extracted with chloroform (3 × 30 c.c.). The combined extracts were washed with dilute aqueous sodium hydrogen carbonate, dried (MgSO<sub>4</sub>), and evaporated. The syrupy residue gradually crystallized and recrystallization from light petroleum (b. p. 40–60°) gave 4 : 5-isopropylidene 3 : 6-anhydro-1-deoxy-1-iodomannitol (1.2 g.) as colourless prisms, m. p. 75–76°,  $[\alpha]_D^{20} -44.6^\circ$  (c, 0.99 in chloroform) (Found : C, 34.2; H, 4.9; I, 40.6. C<sub>9</sub>H<sub>15</sub>O<sub>4</sub>I requires C, 34.4; H, 4.8; I, 40.4%).

*Action of Hydriodic Acid on 4 : 5-isoPropylidene 1 : 2-3 : 6-Dianhydromannitol.*—A solution of dianhydro-compound (2.49 g.) in acetone (87 c.c.) and water (37 c.c.) containing hydriodic acid (0.35 c.c.; 43%) was boiled under reflux for 1.5 hours. Thereafter the solution was neutralised with lead carbonate, and the insoluble residues collected and well washed with acetone. The filtrate was evaporated to small bulk and extracted with ether (3 times; total volume, 100 c.c.). The combined extracts after being dried (MgSO<sub>4</sub>) were evaporated to 20 c.c. Coloured impurities were removed by shaking with charcoal. Evaporation to dryness gave a colourless syrup which after dissolution in ether—light petroleum (b. p. 60–80°) yielded large colourless prisms (2.6 g.), m. p. 75–76°,  $[\alpha]_D^{20} -43.2^\circ$  (c, 1.62 in chloroform). These were 4 : 5-isopropylidene 3 : 6-anhydro-1-deoxy-1-iodomannitol (mixed m. p.).

4 : 5-isoPropylidene 2-Toluene-p-sulphonyl 3 : 6-Anhydro-1-deoxy-1-iodomannitol.—4 : 5-isoPropylidene 3 : 6-anhydro-1-deoxy-1-iodomannitol (6.42 g.) in dry pyridine (26 c.c.) was treated at room temperature for 3 days with toluene-p-sulphonyl chloride (6.5 g., 1.65 mols.). On dilution of the mixture with water an oily product separated which gradually solidified. This was collected and dissolved in chloroform. The solution was washed successively with ice-cold dilute hydrochloric acid and dilute aqueous sodium hydrogen carbonate and dried (MgSO<sub>4</sub>). On evaporation a residue was obtained which after recrystallization from aqueous methanol afforded 4 : 5-isopropylidene 2-toluene-p-sulphonyl 3 : 6-anhydro-1-deoxy-1-iodomannitol (5.25 g.) as colourless prisms, m. p. 90–91°,  $[\alpha]_D^{20} -65.4^\circ$  (c, 1.7 in chloroform) (Found : C, 41.6; H, 4.5; S, 7.2. C<sub>16</sub>H<sub>21</sub>O<sub>7</sub>S requires C, 41.0; H, 4.5; S, 6.8%).

4 : 5-isoPropylidene 1 : 2-Ditoluene-p-sulphonyl 3 : 6-Anhydromannitol.—This substance, prepared according to the method of Foster and Overend (*loc. cit.*), had m. p. 125–126° and  $[\alpha]_D^{20} -31.7^\circ$  in chloroform.

4 : 5-isoPropylidene 1-Toluene-p-sulphonyl 3 : 6-Anhydromannitol.—4 : 5-isoPropylidene 3 : 6-anhydromannitol (1.0 g.) (Foster and Overend, *loc. cit.*) in dry pyridine (10 c.c.) at 0° was treated with toluene-p-sulphonyl chloride (0.94 g., 0.98 mol.) gradually during 2 hours. Thereafter the mixture was set aside at room temperature for 24 hours and then poured into water (250 c.c.). The crystalline product which separated was collected and well washed with water. Recrystallization from aqueous methanol afforded the 1-toluene-p-sulphonyl derivative (0.95 g.) as colourless needles, m. p. 133–134°,  $[\alpha]_D^{20} -21.8^\circ$  (c, 1.2 in chloroform) (Found : C, 53.9; H, 6.2. C<sub>16</sub>H<sub>22</sub>O<sub>7</sub>S requires C, 53.6; H, 6.1%).

*Stability of 4 : 5-isoPropylidene 2-Toluene-p-sulphonyl 3 : 6-Anhydro-1-deoxy-1-iodomannitol.*—The toluene-p-sulphonyl derivative (100 mg.) in dry acetone (5 c.c.) was heated at 130–135° for 4 hours. The solution remained colourless throughout this period. Evaporation of the acetone solution gave unchanged starting material (80 mg.), m. p. 89–90°.

*Action of Sodium Iodide in Acetone on the Foregoing Toluene-p-sulphonyl Derivatives.*—(a) 4 : 5-isoPropylidene ditoluene-p-sulphonyl 3 : 6-anhydromannitol. A solution of the ditoluene-p-sulphonyl derivative (3.0 g.) and sodium iodide (3.0 g.) in dry acetone (25 c.c.) was heated for 3 hours at 110–115°. The sodium toluene-p-sulphonate precipitated (2.13 g.) corresponded to 91.8% of the theoretical for the exchange of two toluene-p-sulphonyloxy-residues. The filtrate after removal of the sodium salt was diluted with chloroform (75 c.c.), freed from iodine by washing with dilute sodium thiosulphate solution, dried (MgSO<sub>4</sub>), and evaporated. Distillation of the residue gave 4 : 5-isopropylidene 3 : 6-anhydromannitoleen (0.7 g.) as a colourless liquid, b. p. 65–75° (bath-temp.)/0.05 mm.,  $[\alpha]_D^{17} +87.5^\circ$  (c, 1.0 in methanol) (*cf.* Foster and Overend, *loc. cit.*).

(b) 4 : 5-isoPropylidene 2-toluene-p-sulphonyl 3 : 6-anhydro-1-deoxy-1-iodomannitol. The mono-toluene-p-sulphonyl derivative (1.5 g.) in dry acetone (10 c.c.) containing sodium iodide (1.0 g., 2 mols.) was heated at 115–120° for 4 hours. The sodium toluene-p-sulphonate precipitated (0.591 g.) corresponded to 95.1% of that expected for the complete exchange of the toluene-p-sulphonyloxy-group. The filtrate, treated as above, gave 4 : 5-isopropylidene 3 : 6-anhydromannitoleen (0.45 g.), b. p. 65–70° (bath-temp.)/0.05 mm.,  $n_D^{16} 1.5166$ ,  $[\alpha]_D^{20} +84^\circ$  (c, 1.2 in chloroform).

(c) 4 : 5-isoPropylidene 1-toluene-p-sulphonyl 3 : 6-anhydromannitol. A solution of the toluene-p-sulphonyl derivative (0.72 g.) in dry acetone (10 c.c.), containing sodium iodide (0.36 g., 1.2 mols.) was heated at 80–90° for 4 hours. The sodium toluene-p-sulphonate precipitated (0.353 g.) corresponded to 91.2% of that expected for the complete exchange of the toluene-p-sulphonyloxy-residue. The filtrate after removal of the sodium salt was evaporated to dryness and extracted with boiling light petroleum (b. p. 60–80°) whence crystals of 4 : 5-isopropylidene 3 : 6-anhydro-1-deoxy-1-iodomannitol (0.52 g.) separated, having m. p. 75–76° alone or on admixture with the authentic material described above.

(d) 4 : 5-isoPropylidene 3 : 6-anhydro-1-deoxy-1-iodomannitol. The iodo-derivative (2.0 g.) in dry acetone (15 c.c.) containing sodium iodide (9 mols., 8.6 g.) was heated at 210–215° for 12 hours. The solution was then diluted with chloroform (50 c.c.) and freed from iodine by washing with dilute aqueous sodium thiosulphate, dried (MgSO<sub>4</sub>), and evaporated. Distillation of the residue gave 4 : 5-isopropylidene 3 : 6-anhydromannitoleen (0.54 g.), b. p. 75–80° (bath-temp.)/0.05 mm.,  $n_D^{19} 1.5160$ ,  $[\alpha]_D^{20} +80.2^\circ$  (c, 1.51 in chloroform).

*Comparative Iodine Exchange Experiments.*—In the comparative experiments (Tables I and II), 4 : 5-isopropylidene 2-toluene-p-sulphonyl 3 : 6-anhydro-1-deoxy-1-iodomannitol and 4 : 5-isopropylidene 1 : 2-ditoluene-p-sulphonyl 3 : 6-anhydromannitol were used in equimolecular quantities (100 and 110 mg. respectively). The volume of acetone was constant (5 c.c.) and the molar proportions of the

various salts were as follows: sodium iodide 1.1 (35 mg.) and 2.2 mols. (70 mg.) respectively; sodium trifluoroacetate 1.1 (32 mg.) and 2.2 mols. (64 mg.) respectively; sodium salicylate 1.1 (38 mg.) and 2.2 mols. (76 mg.) respectively.

In estimating the extent of the exchange reaction the precipitated sodium toluene-*p*-sulphonate was collected in a small sintered-glass funnel, washed with dry acetone, and dried at 100–110° for 30 minutes before being weighed. The corresponding filtrate was diluted with water and the free iodine titrated with 0.05*N*-sodium thiosulphate.

*Action of Sodium Trifluoroacetate in Acetone on 4:5-isoPropylidene 2-Toluene-p-sulphonyl 3:6-Anhydro-1-deoxy-1-iodomannitol.*—The toluene-*p*-sulphonyl derivative (1.5 g.) in dry acetone (15 c.c.) containing sodium trifluoroacetate (1.5 mols., 0.72 g.) was heated at 130–135° (aluminium block) for 6 hours. The precipitated sodium toluene-*p*-sulphonate (0.60 g.), collected in the usual manner, corresponded to 96.5% of that expected for the complete release of the toluene-*p*-sulphonyloxy-residue. Titration of the filtrate with 0.05*N*-sodium thiosulphate (27 c.c.) indicated that 39.7% of the iodine was present in the form of free iodine. Thereafter the mixture was diluted with water (40 c.c.) and extracted with chloroform (3 × 50 c.c.). The combined extracts were dried (MgSO<sub>4</sub>) and evaporated and the residue was distilled. 4:5-isoPropylidene 3:6-anhydromannitoleen (0.26 g.) was obtained, having b. p. 70–75° (bath-temp.)/0.05 mm.,  $n_D^{20}$  1.5165,  $[\alpha]_D^{20} + 82.3^\circ$  (*c*, 1.1 in chloroform).

*Action of Sodium Salicylate in Acetone on 4:5-isoPropylidene 2-Toluene-p-sulphonyl 3:6-Anhydro-1-deoxy-1-iodomannitol.*—A solution of the toluene-*p*-sulphonyl derivative (1.5 g.) in dry acetone (15 c.c.) containing sodium salicylate (1.5 mols.; 0.76 g.) was heated at 130–135° (aluminium block) for 6 hours. Sodium toluene-*p*-sulphonate (0.57 g.), corresponding to 91.7% of that expected for the complete release of the toluene-*p*-sulphonyloxy-residue, was collected in the usual way. Titration of the filtrate with 0.05*N*-sodium thiosulphate (30.7 c.c.) indicated that 47.9% of the iodine was present as free iodine. The iodine-free filtrate was diluted with water and extracted with chloroform (3 × 50 c.c.), and the combined extracts were dried (MgSO<sub>4</sub>) and evaporated to dryness. The straw-coloured syrup thereby obtained partly crystallized. The crystals were collected (0.18 g.) and after recrystallization from aqueous methanol were obtained as colourless feathery needles, m. p. 68–69°,  $[\alpha]_D^{20} \pm 0.0^\circ$  (*c*, 1.0 in chloroform) and did not contain sulphur, iodine, or an ethylenic linkage (Found: C, 62.3; H, 5.1%). This substance is so far unidentified. The residual syrup on distillation yielded 4:5-isopropylidene 3:6-anhydromannitoleen (0.24 g.), b. p. 70–75° (bath-temp.)/0.05 mm.,  $n_D^{20}$  1.5158,  $[\alpha]_D^{20} + 84.6^\circ$  (*c*, 1.5 in chloroform).

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