247. 4 : 5-iso*Propylidene* 1 : 2-3 : 6-*Dianhydromannitol.*

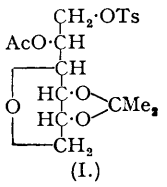
By A. B. Foster and W. G. Overend.

A new dianhydro-derivative of mannitol has been characterised, namely, 4 : 5-*iso*propylidene 1 : 2-3 : 6-dianhydromannitol. The ethylene oxide ring in this compound undergoes scission on treatment with water, hydrobromic acid, lithium aluminium hydride, methylmagnesium iodide, sodium methoxide, or methanolic ammonia, with the exclusive formation of $C_{(1)}$-substituted derivatives.

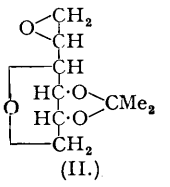
Dianhydro-derivatives of mannitol incorporating two butylene oxide rings (*e.g.*, 1 : 4-3 : 6-dianhydromannitol) or two ethylene oxide rings (*e.g.*, 1 : 2-5 : 6-dianhydromannitol) have been examined in considerable detail (Wiggins, *J.*, 1945, 4; 1946, 384). This paper describes some derivatives of a new dianhydromannitol containing a butylene oxide and an ethylene oxide anhydro-ring, namely, 1 : 2-3 : 6-dianhydromannitol.

When 2-acetyl 4 : 5-*iso*propylidene 1-toluene-*p*-sulphonyl 3 : 6-anhydromannitol (I), obtained from 4 : 5-*iso*propylidene 3 : 6-anhydromannitol (Foster and Overend, *J.*, 1951, in the press) by partial reaction with toluene-*p*-sulphonyl chloride and subsequent acetylation, was treated with sodium methoxide, it was converted into 4 : 5-*iso*propylidene 1 : 2-3 : 6-dianhydromannitol (II), evidence for the structure of which may be summarised as follows. The location of the toluene-*p*-sulphonyloxy-group at $C_{(1)}$ was established by treating (I) with sodium iodide in acetone under standard conditions, 0·87 mole of sodium toluene-*p*-sulphonate being precipitated. Since all

the hydroxyl groups in (I), other than those at $C_{(1)}$ and $C_{(2)}$, are protected by groups resistant to alkali, the newly formed anhydro-ring must bridge $C_{(1)}$ to $C_{(2)}$. Since $C_{(1)}$ is not an asymmetric centre the dianhydro-derivative retains the mannitol configuration.



(I.)



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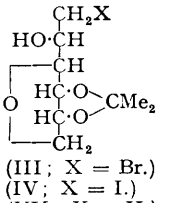
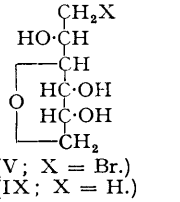
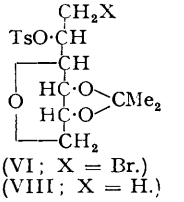


(III; X = Br.)
(IV; X = I.)
(VII; X = H.)
(X; X = NH_2.)
(XI; X = OMe.)



(V; X = Br.)
(IX; X = H.)



(VI; X = Br.)
(VIII; X = H.)

(Ts = *p*-$C_6H_4Me{\cdot}SO_2{\cdot}$)

In attempts to prepare 4 : 5-*iso*propylidene 1 : 2-3 : 6-dianhydromannitol (II) from 4 : 5-*iso*propylidene 1 : 2-ditoluene-*p*-sulphonyl 3 : 6-anhydromannitol by treatment with sodium methoxide, the starting material was recovered unchanged. A satisfactory explanation of this result has not yet been found and further experiments are in progress.

The well-known stability of butylene oxide anhydro-rings contrasts with the lability of their ethylene oxide analogues (see Peat, *Adv. Carbohydrate Chem.*, 1946, **2**, 37). The reactions of (II) which contains both types of anhydro-ring elegantly emphasise this difference. When 4 : 5-*iso*propylidene-1 : 2-3 : 6-dianhydromannitol (II) was boiled under reflux with acetone containing 0·14N-hydrobromic acid, 3 : 6-anhydro-1-bromo-1-deoxymannitol (V) and its 4 : 5-*iso*propylidene derivative (III) were obtained. The latter product resulted from the scission of the ethylene oxide ring by hydrobromic acid and was characterised as its 2-toluene-*p*-sulphonate (VI). Evidence for the location of the bromine atom at $C_{(1)}$ was obtained by catalytic hydrogenation, which eliminated the bromine atom and gave a syrupy deoxy-derivative (VII) [also characterised as its toluene-*p*-sulphonate (VIII)]. There was no reaction between (VIII) and sodium iodide in acetone under standard conditions, so that the toluene-*p*-sulphonyloxy-residue was located at $C_{(2)}$. Consequently, (VII) must have been 4 : 5-*iso*propylidene 3 : 6-anhydro-1-deoxymannitol, and (VIII) its 2-toluene-*p*-sulphonate. Since (III) was converted into (VII) by direct replacement of bromine by hydrogen it must have been 4 : 5-*iso*propylidene 3 : 6-anhydro-1-bromo-1-deoxymannitol. Since catalytic hydrogenation of (V) followed by introduction of *iso*propylidene and toluene-*p*-sulphonyl groups gave 4 : 5-*iso*propylidene 2-toluene-*p*-sulphonyl 3 : 6-anhydro-1-deoxymannitol (VIII) identical with that already described, its structure must be as stated, namely 3 : 6-anhydro-1-bromo-1-deoxymannitol. There was no evidence of the formation of 2-bromo-derivatives. Hydrolysis of (VII) with mineral acid gave syrupy 3 : 6-anhydro-1-deoxymannitol (IX).

The lability of the ethylene oxide ring in (II) is emphasised by the fact that it undergoes scission simply by boiling of its aqueous solution : the only product was 4 : 5-*iso*propylidene 3 : 6-anhydromannitol; no sorbitol derivative was detected.

In a similar manner, when (II) was treated with lithium aluminium hydride the only product isolated was 4 : 5-*iso*propylidene 3 : 6-anhydro-1-deoxymannitol (VII), characterised as its 2-toluene-*p*-sulphonate (VIII).

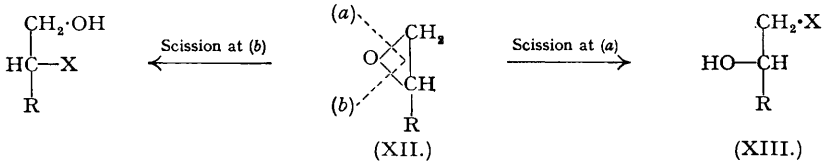
Grignard reagents have long been known to react with compounds containing ethylene oxide rings (Blaise, *Compt. rend.*, 1902, **134**, 557; Grignard, *ibid.*, 1903, **136**, 1260); for example, ethylene oxide and ethylmagnesium bromide give 2-bromoethanol. 4 : 5-*iso*Propylidene 1 : 2-3 : 6-dianhydromannitol (II) and methylmagnesium iodide in ether gave a crystalline compound containing iodine; catalytic hydrogenation of this substance, followed by reaction with toluene-*p*-sulphonyl chloride, gave 4 : 5-*iso*propylidene 2-toluene-*p*-sulphonyl 3 : 6-anhydro-1-deoxymannitol (VIII), indicating that the Grignard reaction gave 4 : 5-*iso*propylidene 3 : 6-anhydro-1-deoxy-1-iodomannitol (IV).

The reagents mentioned above, which are either acidic or neutral in character, exert no effect on the butylene oxide ring of (II), thereby demonstrating the difference in stability of the ethylene oxide and butylene oxide rings in this compound. The corresponding action of an alkaline reagent was shown by treatment of (II) with sodium methoxide. The syrupy compound isolated was designated as 1-methyl 4 : 5-*iso*propylidene 3 : 6-anhydromannitol (XI) since its crystalline toluene-*p*-sulphonate did not react with sodium iodide in acetone under standard conditions.

Treatment of (II) with methanolic ammonia at 120° afforded a syrupy amino-derivative, the

structure of which could not be conclusively proved but by analogy with other workers' results (Ohle *et al.*, *Ber.*, 1935, **68**, 2176; 1936, **69**, 1022, 1636; Wiggins, *J.*, 1946, 388) is provisionally designated as 4 : 5-*iso*propylidene 1-amino-3 : 6-anhydro-1-deoxymannitol (X).

Scission of non-terminal ethylene oxide rings by acidic, neutral, and alkaline reagents is well known, and may occur on either side of the ring-oxygen atom, affording a mixture of two isomeric products. On the other hand, however, the reaction of terminal ethylene oxide rings (XII) with similar reagents (generic formula, R'–X) leads to unidirectional scission of the ring



(XII.) (XIII.)

at (*a*) and products with the substituents in a terminal position (XIII). This is supported by the observations of numerous workers but a discordant note was struck by Swern, Billen, and Knight (*J. Amer. Chem. Soc.*, 1949, **71**, 1152) who claimed that the ethylene oxide ring in propylene oxide underwent scission on both sides of the ring oxygen when treated with allyl alcohol in the presence of an acid catalyst. The experiments outlined earlier are in opposition to this and support the postulate of unidirectional scission.

Experimental.

2-*Acetyl* 4 : 5-iso*Propylidene* 1-*Toluene*-p-*sulphonyl* 3 : 6-*Anhydromannitol*.—A solution of 4 : 5-*iso*propylidene-3 : 6-anhydromannitol (1·0 g.), prepared by Foster and Overend's method (*J.*, 1951, in the press), in dry pyridine (8 c.c.) was cooled to 0° and treated during 1 hour with toluene-*p*-sulphonyl chloride (1·0 mol., 0·95 g.). The mixture was kept at 0° for a further hour and then at room temperature overnight. Freshly distilled acetic anhydride (2 c.c.) was next added and the mixture set aside at room temperature for a further day. Dilution with water caused separation of the crystalline *product* which after recrystallisation from aqueous methanol was obtained as colourless needles (1·27 g.), m. p. 95—96°, $[\alpha]_D^{20}$ −23·2° (*c*, 0·52 in methanol) (Found: C, 53·9; H, 6·1. $C_{18}H_{24}O_8S$ requires C, 54·0; H, 6·0%).

Reaction of the Foregoing Derivative with Sodium Iodide in Acetone.—2-Acetyl 4 : 5-*iso*propylidene 1-toluene-*p*-sulphonyl 3 : 6-anhydromannitol (0·2 g.) and sodium iodide (1·5 mols., 0·112 g.) in dry acetone (10 c.c.) were heated in a sealed tube at 115—120° for 4 hours. The precipitated sodium toluene-*p*-sulphonate (85 mg.) which was collected in a sintered-glass funnel, washed with dry acetone, and dried at 130° for 30 minutes, corresponded to 87·6% of the amount for complete exchange of one toluene-*p*-sulphonyloxy-group.

Action of Sodium Methoxide on the Foregoing Toluene-p-*sulphonyl Derivative*.—A solution of 2-acetyl 4 : 5-*iso*propylidene 1-toluene-*p*-sulphonyl 3 : 6-anhydromannitol (1·11 g.) in chloroform (10 c.c.) was shaken vigorously with sodium methoxide (from sodium, 0·24 g., and methanol, 5 c.c.) at room temperature for 20 minutes. It was then diluted with chloroform (50 c.c.) and washed thrice with water. The dried ($MgSO_4$) chloroform solution was evaporated and the straw-coloured residue (0·56 g.) distilled. 4 : 5-iso*Propylidene* 1 : 2-3 : 6-*dianhydromannitol* (0·4 g.) was obtained as a colourless mobile liquid, b. p. 75—85° (bath-temp.)/0·01 mm., n^{21} 1·4558, $[\alpha]_D^{20}$ −64° (*c*, 0·53 in methanol). It crystallised on refrigeration but could not be satisfactorily recrystallised; it had m. p. 27—28° (Found: C, 57·1; H, 7·7. $C_9H_{14}O_4$ requires C, 58·0; H, 7·5%).

Non-reaction of Sodium Methoxide with 4 : 5-iso*Propylidene* 1 : 2-*Ditoluene*-p-*sulphonyl* 3 : 6-*Anhydromannitol*.—Under the conditions described by Richtmyer and Hudson (*J. Amer. Chem. Soc.*, 1941, **63**, 1730), 4 : 5-*iso*propylidene 1 : 2-ditoluene-*p*-sulphonyl 3 : 6-anhydromannitol (0·95 g.) (Foster and Overend, *loc. cit.*) was dissolved in chloroform (13 c.c.), cooled to 0°, and treated with a solution of sodium (0·2 g.) in dry methanol (5 c.c.) also cooled to 0°. The mixture was set aside at 0° for 3 days and then at room temperature for a further day. It was then diluted with chloroform (50 c.c.), washed thrice with water, dried ($MgSO_4$), and freed from solvent. The crystalline residue (0·9 g.) was recrystallised from ethanol, being obtained in colourless needles, m. p. 123—124° alone or on admixture with the starting material.

Action of Hydrobromic Acid on 4 : 5-iso*Propylidene* 1 : 2-3 : 6-*Dianhydromannitol*.—A solution of the dianhydro-compound (1·8 g.) in acetone–water (125 c.c.; 7 : 3) containing 2N-hydrobromic acid (7·5 c.c.) was boiled under reflux for 5 hours. The acid was neutralised by lead carbonate, and the insoluble lead residues were collected and washed with hot acetone. The filtrate was evaporated under diminished pressure until the acetone had been completely removed, and the remaining aqueous solution was thrice extracted with ether (total volume, 100 c.c.). Evaporation of the ethereal solution yielded a syrupy fraction A, and of the aqueous solution a syrupy fraction B.

Identification of Fraction A.—This fraction could not be crystallised. Distillation yielded a homogeneous, colourless, viscous liquid (1·39 g.), b. p. 115—120° (bath-temp.)/0·01 mm., which gave positive tests for halogen. It was 4 : 5-iso*propylidene* 3 : 6-*anhydro*-1-*bromo*-1-*deoxymannitol* and had n^{18} 1·4970 and $[\alpha]_D^{20}$ −42·1° (*c*, 0·99 in methanol) (Found: C, 40·8; H, 5·6. $C_9H_{15}O_4Br$ requires C, 40·4; H, 5·6%).

The 1-bromo-derivative (100 mg.) in dry pyridine (0·5 c.c.) was treated with toluene-*p*-sulphonyl chloride (1·5 mols.; 100 mg.) at 40° for 12 hours. Dilution with water afforded 4 : 5-iso*propylidene* 2-*toluene*-p-*sulphonyl* 3 : 6-*anhydro*-1-*bromo*-1-*deoxymannitol* (80 mg.) as fine colourless needles (from aqueous methanol), m. p. 86—87°, $[\alpha]_D^{20}$ −82·5° (*c*, 0·27 in ethanol) (Found : C, 46·0; H, 4·9; S, 7·7. $C_{16}H_{21}O_6BrS$ requires C, 45·6; H, 5·0; S, 7·6%).

Hydrogenation of Fraction A.—A solution of the 1-bromo-derivative (1·29 g.) in methanol (20 c.c.) was shaken in an atmosphere of hydrogen at a slight over-pressure in the presence of Raney nickel (2 g.) and diethylamine (0·4 g.). Hydrogen (90 c.c.; 1·3 mols.) was rapidly absorbed and after 2 hours the catalyst was collected and washed with hot methanol, and the combined filtrate and washings were evaporated to dryness, yielding a syrupy residue. From this was obtained 4 : 5-iso*propylidene* 3 : 6-*anhydro*-1-*deoxymannitol* (0·6 g.) as a colourless mobile liquid, b. p. 78—82° (bath-temp.)/0·01 mm., n^{22} 1·4554, $[\alpha]_D^{21}$ −62·9° (*c*, 1·09 in methanol) (Found : C, 56·7; H, 8·5. $C_9H_{16}O_4$ requires C, 57·4; H, 8·5%).

The 1-deoxy derivative (0·1 g.) gave, as in the foregoing case, the 2-*toluene*-p-*sulphonate* (0·115 g.), as colourless prisms (from aqueous methanol), m. p. 70—71°, $[\alpha]_D^{20}$ −70·1° (*c*, 0·54 in chloroform) (Found : C, 56·2; H, 6·4. $C_{16}H_{22}O_6S$ requires C, 56·1; H, 6·4%).

Iodine non-exchange. 4 : 5-*iso*Propylidene 2-toluene-*p*-sulphonyl 3 : 6-anhydro-1-deoxymannitol (30 mg.) and an excess of sodium iodide (50 mg.) were heated in dry acetone (2 c.c.) at 110—115° for 4 hours. There was no precipitation of sodium toluene-*p*-sulphonate.

Identification of Fraction B.—Fraction B (0·62 g.) gave a positive test for halogen and was soluble in water; it was essentially 3 : 6-anhydro-1-bromo-1-deoxymannitol. The syrup (0·6 g.) was shaken in methanol (20 c.c.) under hydrogen at a slight over-pressure in the presence of Raney nickel (1 g.). Hydrogen (50 c.c.) was rapidly absorbed and after 2 hours the catalyst was collected and washed with hot methanol, and the combined filtrate and washings were evaporated to dryness. The syrupy residue so obtained (0·34 g.) was shaken in acetone (50 c.c.) containing concentrated sulphuric acid (0·1 c.c.) for 24 hours. Neutralisation with sodium carbonate and evaporation afforded a syrup (0·35 g.). Treatment of this in dry pyridine (1·5 c.c.) with toluene-*p*-sulphonyl chloride (1·4 mols.; 0·5 g.) at room temperature for 24 hours, followed by dilution with water and recrystallisation of the solid product, gave 4 : 5-*iso*propylidene 2-toluene-*p*-sulphonyl 3 : 6-anhydro-1-deoxymannitol (0·4 g.), m. p. 70—71° alone or on admixture with the compound derived from fraction A.

Hydrolysis of 4 : 5-iso*Propylidene* 3 : 6-*Anhydro*-1-*deoxymannitol.*—A solution of the *iso*propylidene derivative (0·32 g.) in methanol (25 c.c.) containing 5N-hydrochloric acid (3 c.c.) was boiled under reflux. The hydrolysis was followed polarimetrically and shown to be complete in 1·5 hours. The acid was neutralised with silver carbonate, and the silver residues were removed in the usual manner. Evaporation of the solution gave a syrup which was purified by passage in methanol through a column of alumina (3 × 1 cm.). Evaporation of the eluate gave 3 : 6-*anhydro*-1-*deoxymannitol* as a colourless syrup, n^{18} 1·4757, $[\alpha]_D^{20}$ −34·0° (*c*, 0·74 in methanol) (Found : C, 48·5; H, 8·3. $C_6H_{12}O_4$ requires C, 48·6; H, 8·1%).

Action of Water on 4 : 5-iso*Propylidene* 1 : 2-3 : 6-*Dianhydromannitol.*—A solution of the dianhydro-compound (0·2 g.) in water (10 c.c.) was boiled under reflux for 8 hours. Evaporation of the solvent under diminished pressure gave a syrup which was dried over phosphoric oxide *in vacuo*. Recrystallisation from ethyl acetate–light petroleum (b. p. 60—80°) gave a product, m. p. 83—84° alone or on admixture with authentic 4 : 5-*iso*propylidene 3 : 6-anhydromannitol (Foster and Overend, *loc. cit.*).

Action of Lithium Aluminium Hydride on 4 : 5-iso*Propylidene* 1 : 2-3 : 6-*Dianhydromannitol.*—The dianhydro-compound (0·8 g.) in dry ether (20 c.c.) was added gradually to a mixture of finely powdered lithium aluminium hydride (1·3 g.) and ether (40 c.c.). The whole was boiled under reflux for 3 hours and then treated with ice-cold sulphuric acid until acidic to litmus. Excess of acid was neutralised with sodium carbonate, and the precipitated inorganic material collected and washed with acetone. The combined filtrate and washings were extracted four times with an equal volume of chloroform, and the combined extracts dried ($MgSO_4$) and evaporated to dryness. Distillation of the syrupy residue gave 4 : 5-*iso*propylidene 3 : 6-anhydro-1-deoxymannitol (0·55 g.) as a colourless mobile liquid, b. p. 80—85° (bath-temp.)/0·01 mm., n^{18} 1·4560, $[\alpha]_D^{20}$ −61° (*c*, 0·83 in methanol). Treatment of the substance (0·1 g.) in dry pyridine (0·4 c.c.) with toluene-*p*-sulphonyl chloride (0·15 g.) at room temperature for 20 hours, followed by working up in the usual manner, gave a crystalline substance, m. p. 70—71° alone or on admixture with 4 : 5-*iso*propylidene 2-toluene-*p*-sulphonyl 3 : 6-anhydro-1-deoxymannitol described above.

Action of Methylmagnesium Iodide on 4 : 5-iso*Propylidene* 1 : 2-3 : 6-*Dianhydromannitol.*—To a 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 the dianhydro-compound (1·0 g.) in dry ether (10 c.c.) was added gradually during 30 minutes, with continual refluxing of the mixture. After a further 3 hours the ethereal solution was poured into ice-cold dilute sulphuric acid, and the aqueous layer extracted with chloroform (3 times; total volume 90 c.c.). The combined extracts were washed with dilute aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. The syrupy residue gradually crystallised and recrystallisation from light petroleum (b. p. 40—60°) gave 4 : 5-iso*propylidene* 3 : 6-*anhydro*-1-*deoxy*-1-*iodomannitol* (1·2 g.) as colourless prisms, m. p. 75—76°, $[\alpha]_D^{20}$ −44·6° (*c*, 0·99 in chloroform) (Found : C, 34·2; H, 4·9; I, 40·6. $C_9H_{15}O_4I$ requires C, 34·4; H, 4·8; I, 40·4%).

A solution of the iodo-compound (0·3 g.) in methanol (30 c.c.) was shaken in an atmosphere of hydrogen at a slight overpressure in the presence of Raney nickel (0·5 g.) and diethylamine (0·5 c.c.); rapid absorption of hydrogen occurred and after 1 hour the catalyst was collected and washed with methanol. Evaporation of the combined filtrate and washings gave a syrupy residue from which

4 : 5-*iso*propylidene 3 : 6-anhydro-1-deoxymannitol (0·1 g.) was obtained as a colourless mobile liquid, b. p. 75—80° (bath temp.)/0·01 mm., n^{21} 1·4550, $[\alpha]_D^{20}$ −60° (*c*, 1·0 in methanol).

Treatment of the 1-deoxy-derivative with toluene-*p*-sulphonyl chloride in the usual manner gave a crystalline product, m. p. 70—71° alone or on admixture with authentic 4 : 5-*iso*propylidene 2-toluene-*p*-sulphonyl 3 : 6-anhydro-1-deoxymannitol described above.

Action of Sodium Methoxide on 4 : 5-iso*Propylidene* 1 : 2-3 : 6-*Dianhydromannitol.*—A solution of the dianhydro-compound (0·84 g.) in methanol (30 c.c.) in which sodium (0·6 g.) had been dissolved was boiled under reflux for 30 hours. The solution was diluted with chloroform (100 c.c.), washed twice with water, dried ($MgSO_4$), and evaporated. Distillation of the syrupy residue thereby obtained gave 1-methyl 4 : 5-*iso*propylidene 3 : 6-anhydromannitol (0·69 g.) as a colourless hygroscopic liquid, n^{18} 1·4585, $[\alpha]_D^{20}$ −47·3° (*c*, 0·76 in methanol). The hygroscopic nature of this substance did not facilitate good analytical results (Found : C, 53·5; H, 8·6. Calc. for $C_{10}H_{18}O_5$: C, 55·0; H, 8·3%) but its identity was substantiated on conversion into its toluene-*p*-sulphonate. Toluene-*p*-sulphonyl chloride (1·5 mols., 0·45 g.) was added to a solution of the methyl derivative (0·3 g.) in dry pyridine (1·5 c.c.) and the mixture set aside at 35° for 18 hours. Dilution with water afforded a syrupy product which solidified on storage. Recrystallisation from aqueous methanol gave 1-*methyl* 4 : 5-iso*propylidene* 2-*toluene*-p-*sulphonyl* 3 : 6-*anhydromannitol* (0·3 g.) as colourless prisms, m. p. 82—83°, $[\alpha]_D^{20}$ −51·5° (*c*, 0·805 in chloroform) (Found : C, 54·6; H, 6·3. $C_{17}H_{24}O_7S$ requires C, 54·8; H, 6·5%).

Iodine non-exchange. A solution of the forgoing toluene-*p*-sulphonyl derivative (0·2 g.) in dry acetone (10 c.c.) containing sodium iodide (0·5 g.) was heated at 125—130° for 10 hours. There was no precipitation of sodium toluene-*p*-sulphonate.

Action of Methanolic Ammonia on 4 : 5-iso*Propylidene* 1 : 2-3 : 6-*Dianhydromannitol.*—The dianhydro-compound (0·25 g.) was treated with methanol (10 c.c.), saturated at 0° with ammonia, at 110—120° for 20 hours. The solution was evaporated to dryness, and the brown syrupy residue dissolved in ethanol and passed down a column of activated alumina (3 × 1 cm.), which removed coloured impurities. Evaporation of the eluate gave 4 : 5-iso*propylidene* 1-*amino*-3 : 6-*anhydro*-1-*deoxymannitol* (0·24 g.) as a viscous straw-coloured syrup, n^{15} 1·4610, $[\alpha]_D^{20}$ −36·9° (*c*, 0·52 in ethanol) (Found : C, 53·3; H, 8·0. $C_9H_{17}O_4N$ requires C, 53·2; H, 8·4%).

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