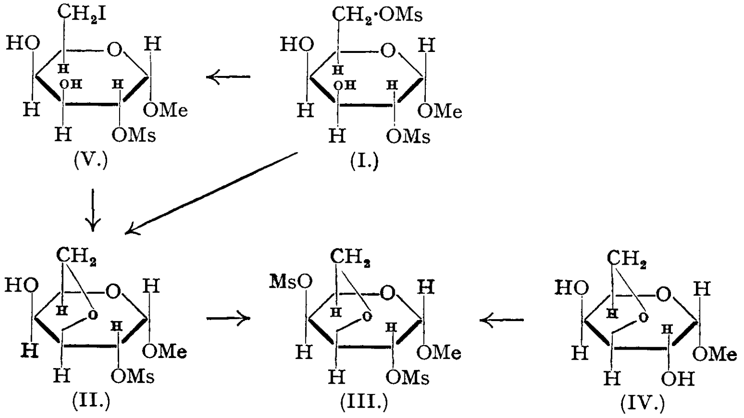
535. *Methanesulphonyl Derivatives of* D-*Galactose.*

By A. B. Foster, W. G. Overend, M. Stacey, and L. F. Wiggins.

The preparation is described of some dimethanesulphonyl derivatives of D-galactose in which one of the methanesulphonyl groups is attached to the primary hydroxyl group. Replacement of the " methanesulphonyloxy " groups by iodine atoms has been studied. Several new derivatives of D-galactose are also recorded.

It is well established that when a toluene-*p*-sulphonyl group is attached to a primary alcoholic group in aldohexoses (Oldham and Rutherford, *J. Amer. Chem. Soc.*, 1932, **54**, 366) and aldopentofuranoses (Levene and Raymond, *J. Biol. Chem.*, 1933, **102**, 317) the toluene-*p*-sulphonyloxy-group is readily replaced by iodine when the substance is treated under standard conditions with sodium iodide in acetone, whilst similar groups attached at other positions are unaffected under these conditions. This reaction has been widely used in both synthetic and structural studies in the sugar series. In a similar manner, a methanesulphonyl group attached to a primary alcoholic group in such sugars also undergoes replacement when treated with sodium iodide in acetone. In certain circumstances, however, replacement is possible, by similar methods, when the methanesulphonyl group is attached to a secondary hydroxyl group. For example, Helferich and Gnüchtel (*Ber.*, 1938, **71**, 712) report that 1 : 2 : 3 : 6-tetra-acetyl 4-methanesulphonyl glucose on treatment with sodium iodide in acetone solution affords 1 : 2 : 3 : 6-tetra-acetyl 4-iodo-4-deoxyglucose in good yield.

Recently we became interested in the latter reaction since it was a potential method of synthesis of iodinated deoxy-sugars and thence of other deoxy-sugar derivatives (cf. Newth, Overend, and Wiggins, *J.*, 1947, 10; Kent, Stacey, and Wiggins, this vol., p. 1232; Overend and Stacey, *ibid.*, p. 1235). We have now further investigated this reaction by preparing some dimethanesulphonyl derivatives of D-galactose having one methanesulphonyl group attached



[Ms = Me·SO$_2$]

to the primary hydroxyl group of the sugar, and by studying the effect of heating these derivatives with sodium iodide in dry acetone.

α-Methyl-D-galactoside was converted into 3 : 4-*iso*propylidene α-methyl-D-galactoside by being shaken with acetone containing a few drops of concentrated sulphuric acid (cf. Wiggins, *J.*, 1944, 525). Acetylation of this with acetic anhydride in pyridine afforded crystalline 2 : 6-*diacetyl* 3 : 4-iso*propylidene α-methyl-*D*-galactoside.* In a similar manner *p*-nitrobenzoylation yielded the 2 : 6-*di-*p*-nitrobenzoate.* When 3 : 4-*iso*propylidene α-methyl-D-galactoside was treated with methanesulphonyl chloride in pyridine it gave 2 : 6-*dimethanesulphonyl* 3 : 4-iso*propylidene α-methyl-*D*-galactoside.* The *iso*propylidene group was removed by treatment with methanolic hydrogen chloride, 2 : 6-*dimethanesulphonyl α-methyl-*D*-galactoside* (I) being obtained in quantitative yield. With N-sodium hydroxide in ethanol this afforded a crystalline methanesulphonyl derivative of an anhydromethylhexoside, which was shown to be 2-*methanesulphonyl* 3 : 6-*anhydro-α-methyl-*D*-galactoside* (II) since further treatment with methanesulphonyl chloride yielded 2 : 4-*dimethanesulphonyl* 3 : 6-*anhydro-α-methyl-*D*-galactoside* (III), identical with that obtained from 3 : 6-anhydro-α-methyl-D-galactoside (IV) (Haworth, Jackson, and Smith, *J.*, 1940, 620). Neither 2-methanesulphonyl 3 : 6-anhydro-α-methyl-D-galactoside nor 2 : 4-dimethanesulphonyl 3 : 6-anhydro-α-methyl-D-galactoside was changed when heated at 110—115° for 5 hours with sodium iodide in acetone.

Treatment of 2 : 6-dimethanesulphonyl α-methyl-D-galactoside with sodium iodide in acetone at 115° for 30 hours gave sodium methanesulphonate corresponding to 96·4% of that required for the complete exchange of one methanesulphonyloxy-group and a product which contained iodine and sulphur. The syrupy reaction product subsequently isolated must therefore be either 2-*methanesulphonyl* 6-*iodo-α-methyl-*6-*deoxy-*D*-galactoside* (V) or 6-methanesulphonyl 2-iodo-α-methyl-2-deoxy-D-galactoside. That it was in fact the former was proved by treatment of the syrupy product with N-sodium hydroxide in ethanol which led to loss of the iodine and the formation of 2-methanesulphonyl 3 : 6-anhydro-α-methyl-D-galactoside (II) in 65% yield. Thus it is confirmed that replacement of a primary methanesulphonyloxy-group by an iodine atom is effected easily but that the corresponding replacement of a secondary group is not. In fact the replacement of a secondary methanesulphonyloxy-group under these conditions does not appear to be a general reaction but is specific for a few compounds only. That both primary toluene-*p*-sulphonyloxy- and methanesulphonyloxy-groups can be quantitatively replaced by iodine if the time of heating is sufficiently prolonged was also demonstrated. For this purpose, 6-toluene-*p*-sulphonyl 1 : 2-3 : 4-di*iso*propylidene D-galactose (Freudenberg *et al.*, *Ber.*, 1922, **55**, 934; 1923, **56**, 2119) and 6-methanesulphonyl 1 : 2-3 : 4-di*iso*propylidene D-galactose (Helferich, Dressler, and Griebel, *J. pr. Chem.*, 1939, **153**, 285) were prepared. Removal of the *iso*propylidene groups from the latter compound gave 6-*methanesuphonyl* D-*galactose* which was isolated either as the *diethyl* or the *dibenzyl mercaptal.* Both 6-toluene-*p*-sulphonyl and 6-methanesulphonyl di*iso*propylidene D-galactose, when heated with sodium iodide in acetone, afforded 1 : 2-3 : 4-di*iso*propylidene 6-iodo-6-deoxy-D-galactose (Freudenberg and Raschig, *Ber.*, 1927, **60**, 1634) in 91 and 93% yield, respectively.

Compound.	Weight, g.	Weight of NaOTs or NaOMs formed, g.*	Exchange, %.	Exchange corr. for solubility of NaOTs or NaOMs, %.*
2 : 6-Ditoluene-*p*-sulphonyl 3 : 4-*iso*propylidene α-methyl-D-galactoside	1·084	0·058	13·7	17·9
2 : 6-Ditoluene-*p*-sulphonyl α-methyl-D-galactoside	1·004	0·370	87·2	91·2
2 : 6-Dimethanesulphonyl 3 : 4-*iso*propylidene α-methyl-D-galactoside	0·78	0·022	6·97	8·9
2 : 6-Dimethanesulphonyl α-methyl-D-galactoside	0·70	0·201	85	87·5
6-Toluene-*p*-sulphonyl 1 : 2-3 : 4-di*iso*propylidene D-galactose	0·818	0·083	19·6	23·9
6-Methanesulphonyl 1 : 2-3 : 4-di*iso*propylidene D-galactose	0·676	0·022	9·32	11·9
6-Toluene-*p*-sulphonyl D-galactose	0·67	0·275	72·0	76·8
6-Toluene-*p*-sulphonyl 3 : 4-*iso*propylidene D-galactal	0·645	0·034	9·25	13·8
6-Methanesulphonyl 3 : 4-*iso*propylidene D-galactal	0·480	0·018	8·39	11·2

* NaOTs and NaOMs = sodium toluene-*p*- and methane-sulphonate, respectively.

When D-galactal was shaken with acetone containing zinc chloride it gave crystalline 3 : 4-*iso*propylidene D-galactal. Treatment of this with toluene-*p*-sulphonyl chloride in pyridine yielded 6-*toluene*-p-*sulphonyl* 3 : 4-iso*propylidene* D-*galactal* and with methanesulphonyl chloride the corresponding 6-*methanesulphonyl* derivative was obtained. Attempts to prepare 3 : 4-*iso*propylidene 6-iodo-6-deoxy-D-galactal from either of these, by treatment with sodium iodide in dry acetone, were unsatisfactory. In both cases reaction occurred to a small extent (see below) but it was not possible to isolate pure 3 : 4-*iso*propylidene 6-iodo-6-deoxy-D-galactal. From these experiments it is clear that there is no great difference in the ease of replacement by iodine of primary toluene-*p*-sulphonyloxy and methanesulphonyloxy groups. It is of some interest to record that we have observed that in the galactose series an exchange of either of these sulphur-containing residues by iodine proceeds only to a small extent (*ca.* 10%) when the derivative carries one *iso*propylidene group at $C_{(3)}$:$C_{(4)}$ whereas it is almost quantitative (under identical conditions) when the protecting group is removed. The compounds listed in the table were heated with sodium iodide in dry acetone; all the samples were heated in the same bath for the same length of time, and the solutions were equimolecular with respect to each other (see p. 2546). The extent of the exchange reaction was determined by weighing the sodium toluene-*p*-sulphonate or methanesulphonate precipitated. Solubilities of these salt in acetone at 18° were 0·12 and 0·04 g. per 100 c.c., respectively, and in the figures quoted in the table these are taken into account. The results show that other groups attached to the sugar molecule exercise a shielding effect on the toluene-*p*-sulphonyl and methanesulphonyl residues and that this effect is greater for the latter smaller group.

EXPERIMENTAL.

3 : 4-iso*Propylidene* α-*Methyl*-D-*galactoside*.—Dry α-methyl-D-galactoside (16·3 g.) was dissolved in acetone (750 c.c.) containing concentrated sulphuric acid (6 c.c.), and the solution was shaken for 4 days. The acid was then neutralised with anhydrous sodium carbonate, and the acetone removed by evaporation in the presence of a small amount of sodium carbonate. The residue was distilled and 3 : 4-*iso*propylidene α-methyl-D-galactoside obtained as a colourless syrup, b. p. 145—155°/0·001 mm. Trituration of the syrup with light petroleum (b. p. 60—80°) induced crystallisation. The solid (10·2 g.), recrystallised from light petroleum, had m. p. 103—104°, $[\alpha]_D^{20}$ +135° in acetone.

2 : 6-*Dimethanesulphonyl* 3 : 4-iso*Propylidene* α-*Methyl*-D-*galactoside*.—3 : 4-*iso*Propylidene α-methyl-D-galactoside (3 g.) was dissolved in dry pyridine (12 c.c.) and treated with methanesulphonyl chloride (2·3 mols., 3·5 g.). The reaction mixture was set aside for 4—5 hours (longer periods are inadvisable owing to the separation of tarry materials) and then poured into water (300 c.c.). A brown oil separated which slowly crystallised. Recrystallisation from aqueous methanol gave 2 : 6-*bismethanesulphonyl* 3 : 4-iso*propylidene* α-*methyl*-D-*galactoside* (2·6 g.) as fine rosettes of colourless needles, m. p. 122—123° $[\alpha]_D^{20}$ +135·5° (*c*, 0·68 in pyridine) (Found : C, 36·9; H, 5·9; S, 16·4. $C_{12}H_{22}O_{10}S_2$ requires C, 36·9; H, 5·7; S, 16·4%).

2 : 6-*Diacetyl* 3 : 4-iso*Propylidene* α-*Methyl*-D-*galactoside*.—3 : 4-*iso*Propylidene α-methyl-D-galactoside (0·5 g.) was dissolved in dry pyridine (5 c.c.) and freshly distilled acetic anhydride was added. The solution was kept at room temperature for 20 hours and then poured into water. The solution was extracted with chloroform, and the extract washed with water and dried ($MgSO_4$). The solvent was evaporated and the resulting straw-coloured syrup crystallised by trituration with ethanol. Recrystallisation from ethanol afforded 2 : 6-*diacetyl* 3 : 4-iso*propylidene* α-*methyl*-D-*galactoside* as colourless prisms, m. p. 116—117°, $[\alpha]_D^{20}$ +142° in acetone (Found : C, 53·2; H, 7·2. $C_{14}H_{22}O_8$ requires C, 52·8; H, 6·9%).

2 : 6-*Di*-(p-*nitrobenzoyl*) 3 : 4-iso*Propylidene* α-*Methyl*-D-*galactoside*.—*p*-Nitrobenzoyl chloride (2·2 mols., 0·86 g.) was added to a solution of 3 : 4-*iso*propylidene α-methyl-D-galactoside (0·5 g.) in dry pyridine (6 c.c.). The solution was set aside at room temperature for 2 days. On pouring the solution into water (50 c.c.) the product separated as an oil which solidified overnight. The solid was triturated with an aqueous solution of potassium carbonate to remove any unchanged acid chloride and then dried. The *di*-p-*nitrobenzoate* had only slight solubility in methanol and ethanol, but recrystallised from acetone to form prisms, m. p. 171—173°, $[\alpha]_D^{20}$ +85·8° (*c*, 1·31 in acetone) (Found : C, 54·2; H, 4·9; N, 5·5. $C_{24}H_{24}O_{12}N_2$ requires C, 54·1; H, 4·5; N, 5·3%).

2 : 6-*Ditoluene*-p-*sulphonyl* 3 : 4-iso*Propylidene* α-*Methyl*-D-*galactoside*.—3 : 4-*iso*Propylidene α-methyl-D-galactoside (2·6 g.) was dissolved in dry pyridine (12 c.c.) and treated with toluene-*p*-sulphonyl chloride (2·2 mols., 5 g.) for 24 hours at room temperature. The mixture was poured into water, and the product isolated in the usual manner. After being recrystallised (aqueous ethanol) the ditoluene-*p*-sulphonyl derivative (2·8 g.) had m. p. 147—148° and $[\alpha]_D^{18}$ +111·5° in pyridine (cf. Rao and Smith, *J.*, 1944, 231, who report m. p. 148° and $[\alpha]_D$ +115°).

2 : 6-*Dimethanesulphonyl* α-*Methyl*-D-*galactoside*.—(a) *Employing anhydrous methanolic hydrogen chloride.* 2 : 6-Dimethanesulphonyl 3 : 4-*iso*propylidene α-methyl-D-galactoside (1 g.) was dissolved in 1% methanolic hydrogen chloride (100 c.c.), and the solution gently boiled under reflux. The reaction was shown polarimetrically to be complete in 1·5 hours. The solution was neutralised with dry silver carbonate, and filtered, and the filtrate boiled with charcoal to remove colloidal silver. The filtrate was evaporated to dryness, leaving a crystalline residue which did not reduce Fehling's solution. The resultant 2 : 6-*bismethanesulphonyl* α-*methyl*-D-*galactoside*, recrystallised from methanol, had m. p. 145—146°, $[\alpha]_D^{20}$ +110° in pyridine (Found : C, 31·0; H, 5·6; S, 18·2. $C_9H_{18}O_{10}S_2$ requires C, 30·9; H, 5·2; S, 18·3%).

(b) *Employing aqueous-methanolic hydrogen chloride.* The *iso*propylidene compound (1 g.) was dissolved in methanol (50 c.c.) containing 5N-hydrochloric acid (2·0 c.c.), and the solution was boiled under reflux. The reaction was followed polarimetrically and was complete in 2 hours. The product was isolated as above and 2 : 6-dimethanesulphonyl α-methyl-D-galactoside was obtained, having m. p. 145—146°. In both experiments the yield was quantitative.

2 : 6-*Ditoluene*-p-*sulphonyl α-Methyl*-D-*galactoside.*—2 : 6-Ditoluene-*p*-sulphonyl 3 : 4-*iso*propylidene α-methyl-D-galactoside (1·8 g.) was dissolved in methanol (50 c.c.) containing 5N-hydrochloric acid (3 c.c.), and the solution was heated under reflux for 5 hours. The product, isolated in the usual manner and recrystallised from methanol (1·2 g.), had m. p. 148—149° and $[\alpha]_D^{20}$ +63·2° in pyridine (Rao and Smith, *loc. cit.*, give m. p. 148° and $[\alpha]_D$ +68° in pyridine).

2-*Methanesulphonyl* 3 : 6-*Anhydro-α-methyl*-D-*galactoside.*—2 : 6-Bismethanesulphonyl α-methyl-D-galactoside (1·8 g.) was dissolved in ethanol (20 c.c.) containing N-sodium hydroxide (6 c.c.), and the solution heated at 65—70° for 2 hours. The solution became orange-yellow on heating. After being neutralised (phenolphthalein) with carbon dioxide, the solution was evaporated to dryness, the crystalline residue was extracted twice with hot acetone, and the combined extracts were evaporated to dryness. The residue recrystallised from ethanol formed colourless rods of 2-*methanesulphonyl* 3 : 6-*anhydro-α-methyl*-D-*galactoside* (1·0 g.), m. p. 142—143°, $[\alpha]_D^{20}$ +88° in pyridine (Found : C, 38·7; H, 5·7; S, 11·8. $C_8H_{14}O_7S,0{\cdot}5C_2H_5{\cdot}OH$ requires C, 38·9; H, 6·1; S, 11·6%).

Treatment of 2-*Methanesulphonyl* 3 : 6-*Anhydro-α-methyl*-D-*galactoside with Sodium Iodide in Acetone.*—The anhydro-compound (0·25 g.), dissolved in dry acetone (10 c.c.), was heated with sodium iodide (1·25 mols., 0·2 g.) in a sealed tube at 110—115° for 5 hours. No separation of sodium methanesulphonate occurred. Prolongation of the heating for 40 hours produced no effect. Evaporation of the solution and crystallisation of the residue gave unchanged 2-methanesulphonyl 3 : 6-anhydro-α-methyl-D-galactoside (0·21 g.), m. p. 143°.

2 : 4-*Dimethanesulphonyl* 3 : 6-*Anhydro-α-methyl*-D-*Galactoside.*—(a) *From* 3 : 6-*anhydro-α-methyl*-D-*galactopyranoside.* 3 : 6-Anhydro-α-methyl-D-galactopyranoside (0·1 g.) (prepared by the method of Haworth, Jackson, and Smith, *J.*, 1940, 620) was dissolved in dry pyridine (7 c.c.), methanesulphonyl chloride (2·3 mols., 0·12 g.) added at 0°, and the solution kept for 18 hours. Thereafter it was poured into water (25 c.c.), 2 : 4-*dimethanesulphonyl* 3 : 6-*anhydro-α-methyl*-D-*galactoside* (0·08 g.) separating. On recrystallisation from ethanol it formed fine needles, m. p. 112—114°, $[\alpha]_D^{20}$ +62·3° (*c*, 0·71 in pyridine) (Found : C, 32·6; H, 4·9. $C_9H_{16}O_9S_2$ requires C, 32·5; H, 4·8%).

(b) *From* 2-*methanesulphonyl* 3 : 6-*anhydro-α-methyl*-D-*galactoside.* 2-Methanesulphonyl 3 : 6-anhydro-α-methyl-D-galactoside (0·25 g.) was dissolved in dry pyridine (2 c.c.) and treated with methanesulphonyl chloride (1·25 mols., 0·5 g.) at room temperature. The product was isolated as above and showed m. p. 113—114°.

Treatment of 2 : 4-*Dimethanesulphonyl* 3 : 6-*Anhydro-α-methyl*-D-*galactoside with Sodium Iodide in Acetone.*—This substance (0·35 g.) was heated at 110—115° for 5 hours with sodium iodide in acetone but was recovered unchanged (0·33 g.).

Treatment of 2 : 6-*Dimethanesulphonyl α-Methyl*-D-*galactoside with Sodium Iodide in Acetone.*—The compound (2 g.) in dry acetone (20 c.c.) containing sodium iodide (2·4 mols., 2 g.) was heated at 115° for 30 hours. Sodium methanesulphonate (0·65 g.) corresponding to 96·4% of that required for complete exchange of one methanesulphonyl group was precipitated. This was removed and the filtrate evaporated. The syrupy residue did not crystallise. It was freed from sodium iodide by prolonged leaching with water and gave positive tests for sulphur and iodine and presumably contained 2-methanesulphonyl 6-iodo-α-methyl-6-deoxy-D-galactoside. A portion (1 g.) of this was heated at 70—75° for 2 hours with ethanol (10 c.c.) containing N-sodium hydroxide (3 c.c.). The solution was then neutralised with carbon dioxide and evaporated to dryness. The residue was extracted with acetone, and the extract evaporated to dryness. The product was dissolved in ethanol, filtered from a small amount of insoluble material, and set aside. 2-Methanesulphonyl 3 : 6-anhydro-α-methyl-D-galactoside (0·45 g., 65%) separated, having m. p. 142—143° alone or in admixture with an authentic specimen.

6-*Methanesulphonyl*-D-*galactose Dibenzyl Mercaptal.*—1 : 2-3 : 4-Di*iso*propylidene 6-methanesulphonyl D-galactose, prepared according to Helferich, Dressler and Griebel (*loc. cit.*), had m. p. 122° and $[\alpha]_D$ −63·8° in acetone, −61·0° in chloroform. This compound (2·5 g.) was dissolved in glacial acetic acid (15 c.c.) and 50% (by volume) aqueous acetic acid (15 c.c.), and the solution was maintained at 80°. The reaction was followed polarimetrically, and after 15 hours the solution was carefully evaporated under reduced pressure at 40°, affording a yellow syrup which strongly reduced Fehling's solution. This material (1·8 g.) was treated with concentrated hydrochloric acid (2 c.c.) and toluene-ω-thiol (2 c.c.), first at 0° then at room temperature. The mixture became solid after being shaken for 2 hours and was then filtered. The solid was washed with water and, recrystallised from ethanol–acetone, yielded fine needles of 6-*methanesulphonyl* D-*galactose dibenzyl mercaptal* (0·5 g.), m. p. 129—130° (decomp.), $[\alpha]_D^{20}$ −16·9° in pyridine (Found : C, 51·8; H, 5·9; S, 19·6. $C_{21}H_{28}O_7S_3$ requires C, 51·6; H, 5·7; S, 19·6%). 6-*Methanesulphonyl* D-*galactose diethyl mercaptal* was similarly obtained and had m. p. 111—112°, $[\alpha]_D^{21}$ +7·2° (*c*, 1·11 in pyridine) (Found : C, 35·8; H, 6·4; S, 25·3. $C_{11}H_{24}O_7S_3$ requires C, 36·2; H, 6·6; S, 26·4%).

6-*Toluene*-p-*sulphonyl* 1 : 2-3 : 4-*Di*iso*propylidene* D-*Galactose.*—1 : 2-3 : 4-Di*iso*propylidene D-galactose was converted into its 6-toluene-*p*-sulphonyl derivative by a modification of the method of Freudenberg *et al.* (*Ber.*, 1922, **55**, 934; 1923, **56**, 2119). 1 : 2-3 : 4-Di*iso*propylidene D-galactose (52 g.) was dissolved in dry pyridine (100 c.c.), and toluene-*p*-sulphonyl chloride (1·5 mols., 58 g.) was added at room temperature. The mixture was kept at 60° for 4—5 hours and then poured into water. An oil separated which rapidly crystallised. After being recrystallised from methanol it had m. p. 89—91°, $[\alpha]_D$ −63·4° in chloroform, −54·5° in acetone. Yield, 60 g.

1 : 2-3 : 4-*Di*iso*propylidene* 6-*Iodo*-6-*deoxy*-D-*galactose.*—(*a*) 6-Methanesulphonyl 1 : 2-3 : 4-di*iso*propylidene D-galactose (2 g.) in acetone solution (20 c.c.) containing sodium iodide (1 g.) was heated at 130—135° for 40 hours. Sodium methanesulphonate separated (0·66 g., corresponding to 93% of that required for complete exchange) and was removed by filtration. The solution was evaporated to

dryness, and the residue leached with a small amount of water to remove excess of sodium iodide. The residue was thoroughly dried. It slowly crystallised. Recrystallised from methanol it afforded 1 : 2-3 : 4-di*iso*propylidene 6-iodo-6-deoxy-D-galactose (2·0 g., 93%), m. p. 72°, $[\alpha]_D^{20}$ −45·9° (*c*, 1·42 in acetone), −51·7° (*c*, 1·16 in chloroform), in agreement with the constant given by Freudenberg and Raschig (*Ber.*, 1927, **60**, 1634).

(*b*) 6-Toluene-*p*-sulphonyl 1 : 2-3 : 4-di*iso*propylidene D-galactose (4 g.), heated in dry acetone (30 c.c.) containing dry sodium iodide (1·2 mols., 1·7 g.) at 115° for 20 hours, afforded the same 6-iodo-6-deoxy-derivative (4·4 g., 91%).

3 : 4-iso*Propylidene* D-*Galactal.*—D-Galactal (1·0 g.) was dissolved in acetone (50 c.c.) containing zinc chloride (5 g.), and the mixture was shaken mechanically for 5 days. It was then poured into a concentrated aqueous solution of sodium carbonate (75 c.c.), so that the final mixture was alkaline to litmus. The precipitated zinc carbonate was filtered off and well washed with acetone, and the filtrate concentrated in a vacuum until most of the acetone had been removed. The remaining aqueous solution was extracted thrice with ether (70 c.c. portions), and the combined ethereal extracts dried ($MgSO_4$) and evaporated to dryness. A pale straw-coloured syrup (0·82 g.) which did not reduce Fehling's solution but rapidly decolorised bromine-water was obtained. It distilled as a colourless oil, b. p. 110—112°/0·1 mm., n_D^{20} 1·4814, which crystallised from light petroleum in colourless needles. It was 3 : 4-iso*propylidene* D-*galactal* (0·7 g.), m. p. 41—43°, $[\alpha]_D^{20}$ +13·8° (*c*, 1·62 in acetone) (Found : C, 58·1; H, 7·8. $C_9H_{14}O_4$ requires C, 58·1; H, 7·5%).

6-*Toluene*-p-*sulphonyl* 3 : 4-iso*Propylidene* D-*Galactal.*—3 : 4-*iso*Propylidene D-galactal (5·3 g.) was dissolved in dry pyridine (21·2 c.c.), and toluene-*p*-sulphonyl chloride (1·5 mols., 7·95 g.) was added. The solution was kept for 2 days at room temperature and then poured into water (1 l.). The product separated as a colourless oil which, after being washed with water by decantation, gradually crystallised. The solidified product was triturated with water and dried. 6-*Toluene*-p-*sulphonyl* 3 : 4-iso*propylidene* D-*galactal* (7 g.), recrystallised from methanol, formed colourless needles, m. p. 81—83°, $[\alpha]_D^{24}$ +22° in chloroform (Found : C, 56·9; H, 6·1; S, 9·8. $C_{16}H_{20}O_6S$ requires C, 56·5; H, 5·9; S, 9·4%).

6-*Methanesulphonyl* 3 : 4-iso*Propylidene* D-*Galactal.*—3 : 4-*iso*Propylidene D-galactal (1·35 g.) was dissolved in dry pyridine (6 c.c.), and methanesulphonyl chloride (1·5 mols., 1·2 g.) was added with cooling. The solution was kept for 5 hours and then poured into water (50 c.c.). The aqueous layer was extracted 3 times with chloroform. The extract was washed twice with water, several times with ice-cold 0·05N-hydrochloric acid, and finally with sodium hydrogen carbonate solution. After being dried ($MgSO_4$), the solution was evaporated to a straw-coloured syrup which crystallised on being stirred with aqueous methanol. The 6-*methanesulphonyl* 3 : 4-iso*propylidene* D-*galactal*, recrystallised from aqueous methanol, formed long colourless needles, m. p. 131—133° (softening at 98—99°), $[\alpha]_D^{20}$ +16·3° (*c*, 1·6 in acetone) (Found : C, 45·1; H, 6:2. $C_{10}H_{16}O_6S$ requires C, 45·5; H, 6·1%).

Comparative Iodine Exchange Experiments.—The compounds listed in the table were used, and the quantities were those which were equivalent to 0·3 g. of sodium iodide. In each case the volume of acetone solution was 15 c.c. The time of heating was 5½ hours (at 115—125°). The amount of sodium toluenesulphonate or methanesulphonate precipitated was collected in a sintered-glass crucible, washed with dry acetone, and dried for 1 hour at 120° before weighing. The results are reported in the table.

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A. E. Hills Laboratories, University of Birmingham,
Edgbaston, Birmingham, 15.

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