150. *Deoxy-sugars. Part X. Some Methanesulphonyl and Toluene-p-sulphonyl Derivatives of α-Ethyl-2 : 3-dideoxy-D-glucoside.*

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The methanesulphonyl and toluene-*p*-sulphonyl esters of α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside and α-ethyl-2 : 3-dideoxy-D-glucoside have been prepared and their exchange reactions with sodium iodide in acetone studied. It has been shown that for the former compound, the ethylenic linkage between $C_{(2)}$ and $C_{(3)}$ exerts an activating influence on substituents at $C_{(4)}$.

It is well known that when 3 : 4 : 6-triacetyl glucal (I) is heated with water it loses an acetyl group and migration of the ethylenic linkage occurs, the product being 4 : 6-diacetyl ψ-glucal (II) (Bergmann, *Annalen*, 1925, **443**, 223). Recently, we used this product as an intermediate in a synthesis of 2-deoxy-D-ribose (Overend and Stacey, *J.*, 1949, 1358) and became interested in the mechanism of this change. The reaction is a fairly general one with acetylated glycals and occurs, not only in the glucose series, but also with galactose (Lohaus and Widmaier, *Annalen*, 1935, **520**, 301) and arabinose derivatives (Gehrke and Aichner, *Ber.*, 1927, **60**, 918).

When D-glucal was boiled with water, under conditions similar to those used for preparing diacetyl ψ-glucal from triacetyl glucal there was no migration of the double bond and the initial material was recovered unchanged. In a like manner when D-glucal was heated with water containing acetate ions it underwent no change. However, when glucal was heated under like conditions with acetic acid a reaction did occur and some of the glucal (20%) was converted into 2-deoxy-D-glucose which was isolated from the syrupy reaction product as its dibenzyl mercaptal (Overend, Stacey, and Staněk, *J.*, 1949, 2841). However the main product, which was very labile, was not isolated in crystalline form. From these preliminary experiments it appeared

that the ethylenic linkage between $C_{(1)}$ and $C_{(2)}$ in triacetyl glucal activated the acetyl substituent at $C_{(3)}$ so that gentle heating with water was sufficient to eliminate it, and the acidity consequently developed induced migration of the double bond. Recently, whilst working with methanesulphonyl and toluene-*p*-sulphonyl esters we have obtained some evidence of the activating influence of ethylenic linkages on substituents in molecules of this type.

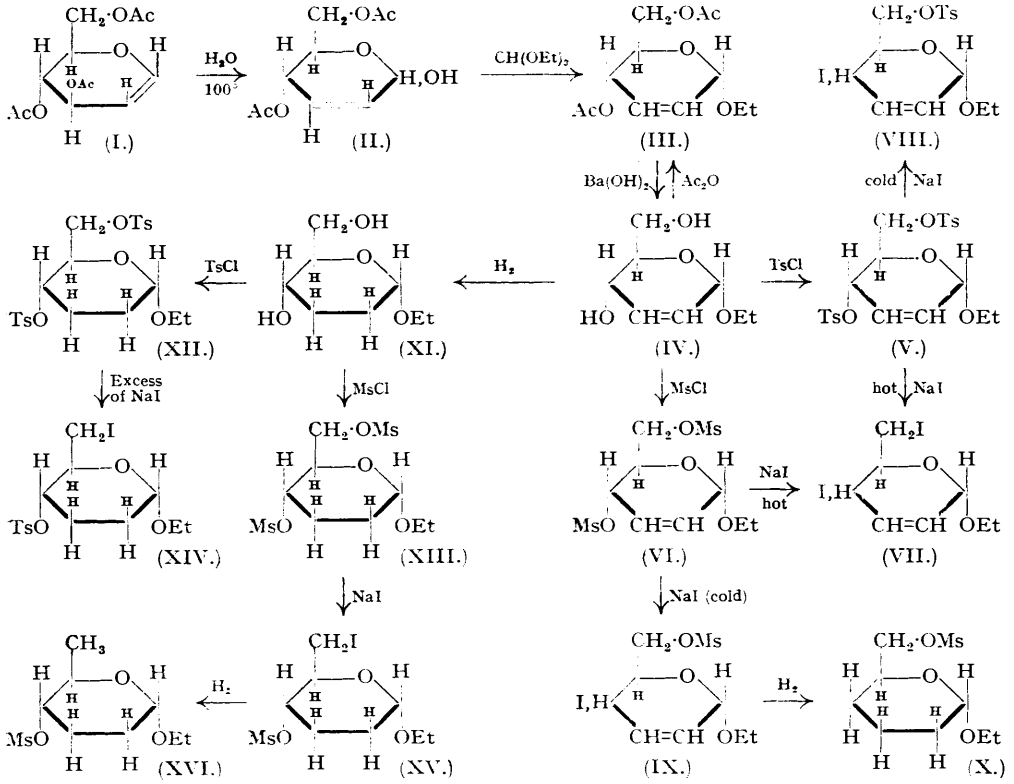
Generally, when a primary hydroxyl group is esterified with a toluene-*p*-sulphonyl or methanesulphonyl residue, the toluene-*p*-sulphonyloxy- or methanesulphonyloxy-group can be exchanged for iodine by the simple expedient of heating with sodium iodide in acetone or in a higher-boiling ketone. When a secondary hydroxyl group in a sugar derivative is similarly esterified, the residues are with a few exceptions not usually replaced. Helferich and Gnüchtel (*Ber.*, 1938, **71**, 712; see also Helferich and Jochinke, *Ber.*, 1940, **73**, 1049) did, however, convert 1 : 2 : 3 : 6-tetra-acetyl 4-methanesulphonyl D-glucose into its corresponding 4-iodo-4-deoxy-derivative by the usual procedure, and a further exception to the general rule was encountered when adjacent primary and secondary hydroxyl groups were esterified with toluene-*p*-sulphonyl residues, since treatment of these esters with sodium iodide in acetone resulted in the elimination of both toluene-*p*-sulphonyloxy-groups and formation of an unsaturated compound (Hahn, Ness, and Hudson, *J. Amer. Chem. Soc.*, 1944, **66**, 73). The toluene-*p*-sulphonyloxy-residues in the open-chain compounds *iso*mannide and *iso*sorbide (cf. Montgomery and Wiggins, *J.*, 1946, 393) are also exchanged although they are formed by esterification of secondary hydroxyl groups. In these compounds, however, the anhydro-rings may exert some influence. In this communication we describe further instances in unsaturated derivatives of sugars, of the exchange for iodine of methanesulphonyloxy- and toluene-*p*-sulphonyloxy-residues formed by appropriate esterification of secondary hydroxyl groups.

3 : 4 : 6-Triacetyl D-glucal (I) was heated with water and converted into 4 : 6-diacetyl 2 : 3-didehydro-2 : 3-dideoxy-D-glucose (diacetyl ψ-glucal) (II), which was immediately treated with ethyl orthoformate in ethanol to yield 4 : 6-diacetyl α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (III) previously described by Bergmann (*Annalen*, 1925, **443**, 223). Deacetylation of this with barium hydroxide yielded α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (IV) (Bergmann and Freudenberg, *Ber.*, 1931, **64**, 158). That no other change accompanied this deacetylation was apparent from the fact that (IV) could be acetylated smoothly with acetic anhydride to re-form (III). Moreover, (IV) was non-reducing to lead tetra-acetate in benzene solution, showing that it retained its pyranose structure. It formed a crystalline 4 : 6-*di*-p-*nitrobenzoate* which was a suitable derivative for characterisation. Treatment with toluene-*p*-sulphonyl chloride in dry pyridine afforded crystalline 4 : 6-*ditoluene*-p-*sulphonyl* α-*ethyl*-2 : 3-*didehydro*-2 : 3-*dideoxy*-D-*glucoside* (V); similarly with methanesulphonyl chloride a crystalline 4 : 6-*dimethanesulphonyl* derivative (VI) was obtained. When either the ditoluene-*p*-sulphonyl (V) or the dimethanesulphonyl derivative (VI) was heated with excess of sodium iodide in acetone at 110—115° for 3 hours, there was obtained crystalline 4 : 6-*di-iodo* α-*ethyl*-2 : 3-*dehydro*-2 : 3 : 4 : 6-*tetradeoxy*-D-*hexoside* (VII). When, however, the toluene-*p*-sulphonyl derivative (V) was kept for 3 days at 30° with 1·1 moles of sodium iodide in acetone, it gave a monoiodo monotoluene-*p*-sulphonyl derivative (VIII). By analogy with subsequent work this was probably 4-*iodo* 6-*toluene*-p-*sulphonyl* α-*ethyl*-2 : 3-*didehyrod*-2 : 3 : 4-*trideoxy*-D-*hexoside*, but, since it was unstable to the reduction process needed to establish its structure, we concentrated our attention on the corresponding methanesulphonyl derivative which was more stable to this treatment.

When 4 : 6-dimethanesulphonyl α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (VI) was kept at 18° for 5 days in the dark with sodium iodide in acetone it yielded 1 mole of sodium methanesulphonate together with a very unstable monoiodo monomethanesulphonyl α-ethyl-hexoside (IX). This rapidly liberated iodine when exposed to light or mild warming and so was immediately hydrogenated. A monomethanesulphonyl α-ethyl-trideoxy-hexoside was obtained. This could be either 6-*methanesulphonyl* α-*ethyl*-2 : 3 : 4-*trideoxy*-D-*glucoside* (X) or 4-methanesulphonyl α-ethyl-2 : 3 : 6-trideoxy-D-glucoside according to whether the methanesulphonyloxy-groups undergoing exchange had been formed by the esterification of a secondary or a primary hydroxyl group respectively. That it was, in fact, the former compound, was demonstrated by synthesising, by an alternative route, the 4-methanesulphonyl derivative, which proved to be different from (X).

Bergmann (*Annalen*, 1925, **443**, 236) showed that when α-ethyl 2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (IV) was reduced it yielded α-ethyl-2 : 3-dideoxy-D-glucoside (XI). This afforded crystalline 4 : 6-*ditoluene*-p-*sulphonyl* and 4 : 6-*dimethanesulphonyl* derivatives (XII and XIII). When (XII) was heated at 110° for 6 hours with excess of sodium iodide in acetone it gave

crystalline 6-*iodo* 4-*toluene*-p-*sulphonyl* α-*ethyl*-2 : 3 : 6-*trideoxy*-D-*glucoside* (XIV). Similarly, when 4 : 6-dimethanesulphonyl α-ethyl-2 : 3-dideoxy-D-glucoside (XIII) and sodium iodide in



acetone were heated at 110—120° for 6 hours, one mole of sodium methanesulphonate was precipitated and syrupy 6-iodo 4-methanesulphonyl α-ethyl-2 : 3 : 6-trideoxy-D-glucoside (XV) was formed. That these compounds were correctly designated was shown by the fact that further heating with excess of sodium iodide did not result in more exchange; moreover, the conditions employed for the exchange reactions were those designed to effect reaction between sodium iodide and toluene-*p*-sulphonyloxy- or methanesulphonyloxy-residues formed by appropriate esterification of a primary hydroxyl group (see also Overend and Stacey, *J.*, **1949**, 1235; Foster, Overend, Stacey, and Wiggins, *J.*, 1949, 2542). 6-Iodo 4-methanesulphonyl α-ethyl-2 : 3 : 6-trideoxy-D-glucoside (XV) darkened on being kept for a short time, so it was reduced immediately on isolation by shaking it in an atmosphere of hydrogen with Raney nickel and diethylamine (Haskins, Hann, and Hudson, *J. Amer. Chem. Soc.*, 1946, **68**, 628). The treatment yielded 4-*methanesulphonyl* α-*ethyl*-2 : 3 : 6-*trideoxy*-D-*glucoside* (XVI), which failed to react when heated at 115—120° for 5½ hours with sodium iodide in acetone, thereby indicating that the methanesulphonyl substituent was attached to a secondary hydroxyl group (Overend, Stacey, *et al.*, *loc. cit.*). On the other hand, the compound (X), provisionally designated as 6-methanesulphonyl α-ethyl-2 : 3 : 4-trideoxy-D-glucoside, afforded sodium methanesulphonate (53%; cf. Foster, Overend, Stacey, and Wiggins, *loc. cit.*) when subjected to the same treatment. This result indicated that the methanesulphonyl residue remaining in the compound (X) was attached at $C_{(6)}$ of the sugar.

The interesting fact emerges from this work that, contrary to expectation, when 4 : 6-dimethanesulphonyl α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (VI) is kept with sodium iodide in acetone, the methanesulphonyloxy-group formed by exterification of the secondary hydroxyl group exchanges for iodine before that formed by esterification of the primary hydroxyl group. Similar results are obtained with the toluene-*p*-sulphonyl esters of α-ethyl-2 : 3-di-

dehydro-2 : 3-dideoxy-D-glucoside. The ethylenic linkage between $C_{(2)}$ and $C_{(3)}$ clearly confers lability on the substituent on the hydroxyl group of the adjacent carbon atom 4. This is analogous to the elimination of an acetyl group when triacetyl glucal is boiled with water. In this case the acetyl group eliminated is that at $C_{(3)}$ which has an adjacent ethylenic linkage between $C_{(1)}$ and $C_{(2)}$.

Experimental.

4 : 6-*Diacetyl* α-*Ethyl*-2 : 3-*didehydro*-2 : 3-*dideoxy*-D-*glucoside*.—3 : 4 : 6-Triacetyl D-glucal (10 g.) and water (200 c.c.) were heated under reflux for 15 minutes. Water was then removed at 40°, and the residue was dried by distilling ethanol over it. A yellow syrup remained which strongly reduced Fehling's solution. This was heated under reflux with ethyl orthoformate (6·4 g.) and absolute ethanol (10 c.c.) for 50 minutes. Ammonium chloride (50 mg.) was added during the reaction. The ethanol and excess of ethyl orthoformate were removed by evaporation *in vacuo*, and the residue crystallised. It recrystallised from 96% ethanol as colourless needles (2·0 g.), m. p. 78—79°, $[\alpha]_D^{17}$ +106·7° (*c*, 2·1 in benzene). Bergmann (*Annalen*, 1925, **443**, 223) reports m. p. 81—82° and $[\alpha]_D^{20}$ +102·7° in benzene for this compound.

α-*Ethyl*-2 : 3-*didehydro*-2 : 3-*dideoxy*-D-*glucoside*.—4 : 6-Diacetyl α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (1·4 g.) was kept with barium hydroxide (3·58 g.) in water (35 c.c.) for 24 hours at room temperature. The excess of barium hydroxide was neutralised with carbon dioxide, and the solution centrifuged. The filtrate was evaporated, and the residue extracted with ethanol (3 × 100 c.c.). Solvent was removed from the extract, and the residue was recrystallised from benzene, forming colourless needles (0·64 g.), m. p. 90—93° (unchanged after repeated recrystallisation). After recrystallisation from ethyl acetate, the m. p. was 94—97°. Sublimation of the material (70°/15 mm.) afforded needles, m. p. 96—97°, $[\alpha]_D^{20}$ +99·5° (*c*, 0·54 in ethanol) (Found : C, 54·95; H, 8·0. Calc. for $C_8H_{14}O_4$: C, 55·2; H, 8·0%). Bergmann and Freudenberg (*Ber.*, 1931, **64**, 158) give m. p. 100—101°, $[\alpha]_D^{20}$ 100·3° in ethanol for this compound. It was not oxidised by lead tetra-acetate in benzene but could be reacetylated with acetic anhydride to yield 4 : 6-diacetyl α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside in 80% yield.

4 : 6-*Di*-p-*nitrobenzoyl* α-*Ethyl*-2 : 3-*didehydro*-2 : 3-*dideoxy*-D-*glucoside*.—α-Ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (50 mg.) was dissolved in dry pyridine (0·5 c.c.), and *p*-nitrobenzoyl chloride (130 mg., 2·12 mols.) was added. After 18 hours at room temperature, the solution was poured into water (25 c.c.). The solid which separated was recrystallised from 96% ethanol, and 4 : 6-*di*-p-*nitrobenzoyl* α-*ethyl*-2 : 3-*didehydro*-2 : 3-*dideoxy*-D-*glucoside* was obtained as colourless needles (100 mg.), m. p. 129—130°, $[\alpha]_D^{19}$ +109·5° (*c*, 0·66 in benzene) (Found : C, 55·7; H, 4·5; N, 6·1. $C_{22}H_{20}O_{10}N_2$ requires C, 55·9; H, 4·3; N, 5·9%).

4 : 6-*Ditoluene*-p-*sulphonyl* α-*Ethyl*-2 : 3-*didehydro*-2 : 3-*dideoxy*-D-*glucoside*.—α-Ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (0·75 g.) was kept at room temperature for 18 hours with toluene-*p*-sulphonyl chloride (0·7 g.) in dry pyridine (0·5 c.c.). The mixture was poured into water, and the precipitated solid filtered off. Recrystallisation from 90% ethanol afforded the *ditoluene*-p-*sulphonyl* derivative (0·12 g.) as colourless needles, m. p. 119—120°, $[\alpha]_D^{15}$ +59° (*c*, 2·16 in benzene) (Found : C, 54·5; H, 5·5; S, 13·0. $C_{22}H_{26}O_8S_2$ requires C, 54·7; H, 5·4; S, 13·2%).

4 : 6-*Dimethanesulphonyl* α-*Ethyl*-2 : 3-*didehydro*-2 : 3-*dideoxy*-D-*glucoside*.—α-Ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (0·75 g.), methanesulphonyl chloride (1·15 g., 0·78 c.c.), and dry pyridine (0·5 c.c.) were kept together at 0° for 75 hours. The mixture was worked up in the usual manner, and after recrystallisation from 85% ethanol 4 : 6-*dimethanesulphonyl* α-*ethyl*-2 : 3-*didehydro*-2 : 3-*dideoxy*-D-*glucoside* (0·72 g.) was obtained as colourless needles, m. p. 71—72°, $[\alpha]_D^{20}$ +87·7° (*c*, 1·46 in acetone) (Found : C, 36·4; H, 5·9. $C_{10}H_{18}O_8S_2$ requires C, 36·4; H, 5·5%).

α-*Ethyl*-2 : 3-*dideoxy*-D-*glucoside*.—α-Ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (0·4 g.), dissolved in dry methanol (20 c.c.), was hydrogenated at room temperature in the presence of platinic oxide (100 mg.). The solution was filtered, and the methanol evaporated. The residue crystallised from benzene–light petroleum as colourless needles (0·35 g., 83%), m. p. 67—69° $[\alpha]_D^{20}$ +140·6° (*c*, 0·69 in water) (Found : C, 54·4; H, 8·99. Calc. for $C_8H_{16}O_4$: C, 54·5; H, 9·1%). Bergmann (*loc. cit.*) reports m. p. 72—72·5°, $[\alpha]_D^{20}$ +137·8° in water for this compound.

4 : 6-*Ditoluene*-p-*sulphonyl* α-*Ethyl*-2 : 3-*dideoxy*-D-*glucoside*.—α-Ethyl-2 : 3-dideoxy-D-glucoside (0·25 g.), toluene-*p*-sulphonyl chloride (0·66 g.), and dry pyridine (1·5 c.c.) were kept at room temperature for 60 hours. The mixture was poured into water, and the product isolated in the usual manner. After recrystallisation from ethanol 4 : 6-*ditoluene*-p-*sulphonyl* α-*ethyl*-2 : 3-*dideoxy*-D-*glucoside* (0·5 g.) was obtained as colourless needles, m. p. 58—60°, $[\alpha]_D^{20}$ +85° (*c*, 0·89 in benzene) (Found : C, 54·6; H, 5·9. $C_{22}H_{28}O_8S_2$ requires C, 54·5; H, 5·8%).

4 : 6-*Dimethanesulphonyl* α-*Ethyl*-2 : 3-*dideoxy*-D-*glucoside*.—α-Ethyl-2 : 3-dideoxy-D-glucoside (0·3 g.), methanesulphonyl chloride (0·32 c.c.), and dry pyridine (0·5 c.c.) were kept at 0° for 12 hours. The mixture was then poured into water, and the oil which separated was extracted with chloroform. The extract was washed with dilute sulphuric acid (2%) and then water, and dried ($MgSO_4$). Evaporation of the solvent yielded a syrup which crystallised when triturated with water. Recrystallisation of the solid from 90% ethanol yielded the *dimethanesulphonyl* derivative (0·14 g.) as colourless needles, m. p. 68—69°, $[\alpha]_D^{20}$ +118·7° (*c*, 1·11 in acetone) (Found : C, 36·4; H, 5·8. $C_{10}H_{20}O_8S_2$ requires C, 36·2; H, 6·0%).

6-*Iodo* 4-*Toluene*-p-*sulphonyl* α-*Ethyl*-2 : 3 : 6-*trideoxy*-D-*glucoside*.—4 : 6-Ditoluene-*p*-sulphonyl α-ethyl-2 : 3-dideoxy-D-glucoside (0·3 g.), sodium iodide (0·252 g.), and dry acetone (12 c.c.) were heated in a sealed tube at 110° for 6 hours. Sodium toluene-*p*-sulphonate was precipitated. This was collected by filtration, washed with anhydrous acetone, dried, and weighed (0·130 g. = 100% replacement of one toluene-*p*-sulphonyl group). The acetone solution was evaporated, and the residue treated with chloroform and water. The chloroform layer was washed with dilute sodium thiosulphate solution, dried ($MgSO_4$), and evaporated. The residue slowly crystallised and was recrystallised from 80% ethanol. 6-*Iodo* 4-*toluene*-p-*sulphonyl* α-*ethyl*-2 : 3 : 6-*trideoxy*-D-*glucoside* (0·2 g.) was obtained as

colourless needles, m. p. 58—59°, $[\alpha]_D^{17}$ +88·8° (*c*, 0·39 in benzene) (Found: C, 40·3; H, 5·2; I, 29·1. $C_{15}H_{21}O_5SI$ requires C, 40·8; H, 4·9; I, 28·8%).

4 : 6-*Di-iodo* α-*Ethyl*-2 : 3-*dehydro*-2 : 3 : 4 : 6-*tetradeoxy*-D-*hexoside*.—(*a*) 4 : 6-Ditoluene-*p*-sulphonyl α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (0·72 g.) and dry sodium iodide (0·6 g.) in dry acetone (17 c.c.) were heated together at 110—115° for 3 hours. (Milder exchange conditions yielded only syrupy products.) The amount of sodium toluene-*p*-sulphonate formed (0·55 g.), after filtration, washing with acetone and drying, corresponded to 93% replacement of both toluene-*p*-sulphonyl residues. The acetone was evaporated, and the residue extracted with chloroform (50 c.c.). The extract was washed with dilute sodium thiosulphate solution and dried ($MgSO_4$). After evaporation of the chloroform, the residue partly crystallised. This was recrystallised from 80% ethanol and 4 : 6-*di-iodo* α-*ethyl*-2 : 3-*dehydro*-2 : 3 : 4 : 6-*tetradeoxy*-D-*hexoside* (0·12 g.) was obtained as colourless needles, m. p. 97—98°, $[\alpha]_D^{15}$ −364·8° (*c*, 1·88 in chloroform) (Found: C, 24·6; H, 3·1; I, 63·1. $C_8H_{12}O_2I_2$ requires C, 24·3; H, 3·0; I, 63·5%). This compound was very unstable, and iodine was liberated even after 1 day in the dark. Decomposition was complete in 10 days.

(*b*) 4 : 6-Dimethanesulphonyl α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (0·3 g.), sodium iodide (0·3 g.), and dry acetone were heated at 105—110° for 3 hours. The sodium methanesulphonate formed corresponded to 93% replacement of both methanesulphonyl groups. The product was isolated as above but showed no tendency to crystallise. It was dissolved in benzene (10 c.c.) and run through a short column of alumina, which was then washed with benzene (20 c.c.); 5 c.c. portions (*a*, *b*, *c*, and *d*) were collected; (*a*), (*c*), and (*d*) when evaporated gave syrupy products, but (*b*) yielded crystals which recrystallised from 80% ethanol (0·0279 g.) as colourless needles, m. p. 97—98° alone or in admixture with the di-iodo-compound described above.

4-*Iodo* 6-*Toluene*-p-*sulphonyl* α-*Ethyl*-2 : 3-*didehydro*-2 : 3 : 4-*trideoxy*-D-*hexoside*.—4 : 6-Ditoluene-*p*-sulphonyl α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (0·5 g.), dry acetone (15 c.c.), and dry sodium iodide (0·175 g. ≡ 1·1 mols.) were kept in a stoppered flask, protected from light, at 18° for 9 days. The reaction mixture became yellow owing to liberated iodine, and sodium toluene-*p*-sulphonate (0·15 g. ≡75% replacement of one toluene-*p*-sulphonyloxy-group) was precipitated (Found: C, 43·3; H, 3·6. Calc. for $C_7H_7O_3SNa$: C, 43·4; H, 3·6%).

After separation of this salt, the acetone was evaporated, and the residue extracted with chloroform. After being washed with 1% sodium thiosulphate, the extract was dried ($MgSO_4$) and the solvent evaporated. The only crystalline material which could be isolated from the residue was unchanged 4 : 6-ditoluene-*p*-sulphonyl α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (0·04 g.), m. p. 119—120°. If the temperature at which the exchange was carried out was raised to 25°, then sodium toluene-*p*-sulphonate equivalent to 83% replacement was obtained. At 30°, however, complete replacement was effected. The unsaturated ditoluene-*p*-sulphonyl derivative (0·2 g.), sodium iodide (0·061 g.), and dry acetone (5·5 c.c.) were kept together in a stoppered flask protected from light at 30° for 3 days. The product was isolated in the usual manner and a syrup was obtained (0·146 g.). This was purified by passage through a column of alumina, and a straw-coloured syrup (0·096 g.) was obtained: $[\alpha]_D^{20}$ −59·6° (*c*, 1·5 in benzene) (Found: C, 40·9; H, 4·4; OEt, 9·96. $C_{15}H_{19}O_5SI$ requires C, 41·1; H, 4·3; OEt, 10·28%). This syrupy *compound* was unstable and on storage liberated much iodine in 2 days. Attempts to hydrogenate the ethylenic linkage resulted in the uptake of more than 1 mol. of hydrogen even at room temperature.

6-*Methanesulphonyl* α-*Ethyl*-2 : 3 : 4-*trideoxy*-D-*glucoside*.—4 : 6-Dimethanesulphonyl α-ethyl-2 : 3-didehydro-2 : 3-dideoxy-D-glucoside (0·595 g.), sodium iodide (0·29 g. = 1·2 mols.), and dry acetone (10 c.c.) were kept together at 18° for 5 days in absence of light. Sodium methanesulphonate (0·19 g.) separated and was removed by filtration. The product was isolated in the usual manner (0·60 g.) and purified by passage through a column of alumina. A syrup was obtained which was very unstable and sensitive to light and mild heating. It readily liberated iodine and so, as soon as it was isolated, it was hydrogenated in methanol (15 c.c.) containing diethylamine (0·36 c.c.) and a trace of water. Raney nickel was used as catalyst and the mixture was shaken at room temperature for 3·5 hours in an atmosphere of hydrogen at 20 mm. over-pressure. The solution was filtered, and the solvent evaporated. The residue was treated with chloroform and water. The aqueous layer gave a strong positive test for iodide ions. The chloroform layer was dried ($MgSO_4$), and the solvent evaporated. A pale yellow syrup remained (0·33 g.) which gave a positive test for sulphur and a negative test for iodine and had $[\alpha]_D^{20}$ +65·3° (*c*, 2·45 in acetone). It was 6-*methanesulphonyl* α-*ethyl*-2 : 3 : 4-*trideoxy*-D-*glucoside* (Found: C, 45·4; H, 7·3; S, 12·8. $C_9H_{18}O_5S$ requires C, 45·4; H, 7·5; S, 13·4%).

4-*Methanesulphonyl* α-*Ethyl*-2 : 3 : 6-*trideoxy*-D-*glucoside*.—4 : 6-Dimethanesulphonyl α-ethyl-2 : 3-dideoxy-D-glucoside (0·13 g.) and sodium iodide in dry acetone (0·07 g. in 10 c.c.) were heated at 115—120° for 6 hours. Separation of sodium methanesulphonate (0·044 g. ≡ 95·6% replacement of 1 methanesulphonyloxy-group) commenced immediately, and replacement seemed easier to effect than with toluene-*p*-sulphonyl esters. The solid was filtered off, and the filtrate was evaporated to dryness. Water and chloroform were added to the residue, and the chloroform layer was separated, washed (dilute sodium thiosulphate solution), and dried ($MgSO_4$). Evaporation of the solvent afforded some syrup, which was dissolved in methanol (10 c.c.) containing diethylamine (0·1c.c.) and shaken with Raney nickel in an atmosphere of hydrogen at a slight over-pressure. When the uptake of hydrogen ceased, the solution was filtered and evaporated. The residue was treated with water and chloroform. The aqueous layer gave a strong positive test for iodide ions. The chloroform layer was dried ($MgSO_4$), and the solvent evaporated. A yellow syrup (0·087 g.) remained which was free from iodine. It was 4-*methanesulphonyl* α-*ethyl*-2 : 3 : 6-*trideoxy*-D-*glucoside*, $[\alpha]_D^{20}$ +122·9° (*c*, 2·17 in acetone) (Found: C, 46·1; H, 7·5; OEt, 18·7. $C_9H_{18}O_5S$ requires C, 45·4; H, 7·5; OEt, 18·9%).

Exchange Experiments.—(*a*) 4-Methanesulphonyl α-ethyl-2 : 3 : 6-trideoxy-D-glucoside (0·063 g.) was heated with sodium iodide (0·063 g.) in dry acetone (7·0 c.c.) at 115—120° for 5½ hours. No sodium methanesulphonate was formed and the initial materials could be recovered. (*b*) 6-Methanesulphonyl α-ethyl-2 : 3 : 4-trideoxy-D-glucoside (0·178 g.) and sodium iodide (0·12 g.) in acetone (9 c.c.) were heated together under identical conditions. Sodium methanesulphonate (0·047 g.) was precipitated

and was collected, washed with dry acetone, dried, and weighed. It corresponded to 53% replacement of the methanesulphonyloxy-residue in the initial material.

Experiments with Glucal.—(*a*) Glucal (1 g.) was boiled with water (12 c.c.) for 15 minutes. There was no change in optical rotation ($[\alpha]_D$ −7·5°) and the D-glucal could be recovered unchanged. (*b*) Glucal (0·5 g.) was dissolved in water (6 c.c.) containing crystalline sodium acetate (0·5 g.), and the solution boiled for 30 minutes. There was no change in optical rotation, and the solution developed no reducing power to Fehling's solution. (*c*) Glucal (1·08 g.) was dissolved in water (40 c.c.) containing acetic acid (0·040 g.), and the solution boiled. The change in optical rotation was followed polarimetrically :

Time (mins.)	0	20	40	60	80
$[\alpha]_D^{20}$	−7·8°	+3·9°	+10·4°	+16·6°	+16·6°

The solution soon rapidly restored the colour to Schiff's reagent. After neutralisation and evaporation, toluene-ω-thiol was added to the syrup together with concentrated hydrochloric acid. The product was isolated as described by Overend, Stacey, and Staněk (*J.*, 1949, 2841) and 2-deoxy-D-glucose dibenzyl mercaptal (20%), m. p. 147—148°, was obtained but no derivative of 2 : 3-didehydro-2 : 3-deoxy-D-glucose.

Certain of the analyses were carried out by Drs. Weiler and Strauss (Oxford). Our thanks are due to the British Empire Cancer Campaign (Birmingham Branch) for financial assistance. One of us (S. L.) thanks the University of Oslo for the award of a Familien Stillesen's grant which enabled him to take part in this work.

CHEMISTRY DEPARTMENT,
THE UNIVERSITY, BIRMINGHAM, 15. [*Received, December 10th*, 1949.]