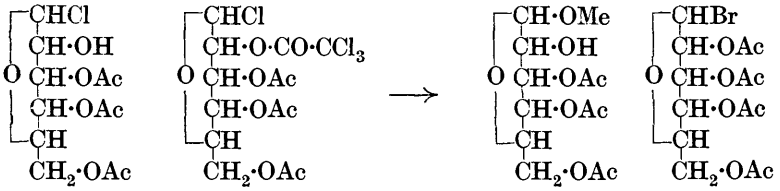
CLXXIII.—*Glucosides. Part III. The Abnormal Replacement of Halogen in Glucosyl Halides: The Formation of β-Glucosides from β-Glucosyl Chlorides.*

By Wilfred John Hickinbottom.

In continuation of previous work on the formation of glucosides from β-glucosyl chlorides (J., 1929, 1676), the action of sodium alkoxides on 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride (II) and on 3 : 4 : 6-triacetyl β-glucosyl chloride (I) has been examined. It would be expected, by analogy with the behaviour of 2 : 3 : 4 : 6-tetra-acetyl α-glucosyl bromide (IV) towards similar reagents (compare Zemplén and Kunz, *Ber.*, 1923, **56**, 1710), that glucoside formation would occur with the normal change in con-

figuration. Indeed, Pictet and Castan (*Helv. Chim. Acta*, 1921, **4**, 319) have stated that the glucosyl chloride, prepared by the addition of hydrogen chloride to α-glucosan—and identified by them as β-glucosyl chloride, since its tetra-acetate has the same melting point as Fischer and Armstrong's labile 2 : 3 : 4 : 6-tetra-acetyl β-glucosyl chloride—gives α-methylglucoside by reaction with a solution of sodium methoxide in methyl alcohol.



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

It was found, however, that β-glucosides were the principal products of the action of sodium alkoxides on 3 : 4 : 6-triacetyl β-glucosyl chloride and on 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride. These results are in direct contrast to the behaviour of the same β-glucosyl chlorides towards alcohols in presence of silver oxide or carbonate, or silver nitrate and pyridine. For comparison, the results are summarised in the following table :

2-Trichloroacetyl 3 : 4 : 6-*triacetyl* β-*glucosyl chloride.*

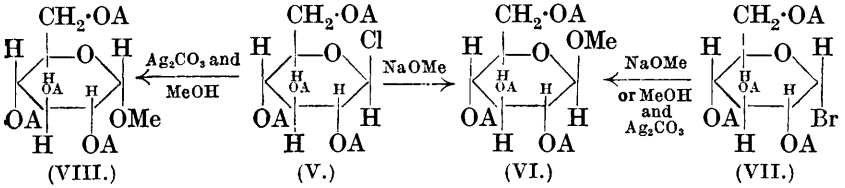
	Experimental conditions.	α- and β-Glucosides, %, in product. α.	β.
Brigl and Keppler (*Ber.*, 1926, **59**, 1588) Hickinbottom (*loc. cit.*)	Methyl alcohol and Ag_2O or Ag_2CO_3	70	30
Hickinbottom (*loc. cit.*)	Methyl alcohol, $AgNO_3$, and pyridine	90	10
	Methyl alcohol and NaOMe	15	85
	Ethyl alcohol and NaOEt	10	90

3 : 4 : 6-*Triacetyl* β-*glucosyl chloride.*

Hickinbottom (*loc. cit.*)	Methyl alcohol and Ag_2O or Ag_2CO_3	70	30
,, ,,	Methyl alcohol, $AgNO_3$, and pyridine	80	20
	Methyl alcohol and NaOMe	Approx. 100	

It is possible, therefore, to obtain either the α- or the β-glucoside from each of these glucosyl chlorides by selecting the appropriate conditions. On current conceptions, it is assumed that, in the usual replacement of halogen in glucosyl halides by the action of silver carbonate and alcohol, a change in configuration occurs

(VI and VIII). This applies both to the α- and to the β-series of glucosyl halides. It is then remarkable to find that both series of glucosyl halides yield glucosides of the same configuration by reaction with sodium alkoxides in alcohols. For instance, sodium methoxide in methyl alcohol produces β-methylglucosides (VI) from the β-glucosyl chlorides (V) used in the present investigation and also from 2 : 3 : 4 : 6-tetra-acetyl α-glucosyl bromide (VII).



[OA = OH or OAc]

These observations appear to find a parallel in the behaviour of the α- and β-penta-acetyl glucoses, which normally give the same tetra-acetyl glucosyl halide by the action of hydrogen halides. It is certain, when hydrogen chloride is used, that the first products have different configurations, but under the experimental conditions 2 : 3 : 4 : 6-tetra-acetyl β-glucosyl chloride isomerises to the more stable α-glucosyl chloride (Schlubach, Stadler, and Wolf, *Ber.*, 1928, **61**, 293; compare Fischer and Armstrong, *Ber.*, 1901, **34**, 2894).

A somewhat similar explanation may account for the anomalous formation of β-glucosides from β-glucosyl chlorides, namely, that by the action of the sodium alkoxides the β-glucosyl chlorides are isomerised to α-glucosyl chlorides, which then react in the normal way to give β-glucosides. This explanation was advanced by Fischer and Armstrong (*loc. cit.*) to account for the non-formation of α-phenylglucoside from the unstable 2 : 3 : 4 : 6-tetra-acetyl β-glucosyl chloride. Their view was supported by the observation that the β-glucosyl chloride was converted completely into the α-glucosyl chloride in an ethereal solution in contact with powdered hydrated sodium carbonate, or the wet sodium compound of glucose.

It appears at first sight that the extension of this hypothesis to account for the formation of β-glucosides from the β-glucosyl chlorides examined in the present work would be justifiable. A fuller consideration of the experimental facts, however, indicates that it can only be accepted if certain assumptions are made.

Although no accurate determinations of the velocity of the reaction between sodium methoxide or ethoxide and 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride have been made owing

to the occurrence of comparatively slow side reactions, qualitative observations of the density of the precipitate of sodium chloride obtained when the reaction is carried out in ethyl alcohol indicate that glucoside formation occurs very quickly, and for 0·5*N*-solutions it is practically complete within a few minutes after mixing. Evidently, if the isomerisation hypothesis of Fischer and Armstrong holds, isomerisation must be complete or almost so before any replacement occurs; the isomerisation must therefore be extremely rapid. 2-Trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride, however, is comparatively stable and does not isomerise readily. For instance, it does not change in non-hydroxylic solvents which bring about the conversion of 2 : 3 : 4 : 6-tetra-acetyl β-glucosyl chloride into the α-isomeride. Further, the addition of a trace of a methyl-alcoholic solution of sodium methoxide to an acetone solution of 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride does not cause any change of rotation over a period of 25 minutes. A drop of 20% aqueous sodium hydroxide added to an acetone solution of the β-glucoside brings about a change of $[\alpha]_D$ only from +8° to +13° after 48 hours at room temperature. Further, a xylene solution of the β-glucosyl chloride may be kept in contact with an excess of dry, finely powdered sodium methoxide (free from methyl alcohol) at room temperature for 20 hours without any marked change in the rotation or without any serious amount of glucoside formation; indeed the greater part of the β-glucosyl chloride may be recovered unchanged. Micheel and Micheel (*Ber.*, 1930, **63**, 392) have shown that anhydrous trimethylamine has no action on 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride in benzene at room temperature, and only a small action after 4 hours' heating at 100°.

The alcohol does not appear to be responsible for the isomerisation, since the rate of change of rotation in methyl alcohol is slow compared with the rate of replacement of the halogen (Hickinbottom, *loc. cit.*).

If the isomerisation hypothesis is to be retained, there must be assigned to the sodium alkoxide in the alcohol a catalytic power which is not possessed by the dry alkoxide, nor by the alcohol alone, nor by small quantities of the alcoholic methoxide in acetone.

An alternative hypothesis is to assume that addition to the glucosyl chloride may occur, and that the subsequent behaviour of the compound formed is determined by such factors as electron distribution, polarity, and steric configuration as well as by the relative energies of the systems.

It is known that the relative proportions of α- and β-glucosides obtained by the replacement of the halogen of the glucosyl halides

may be varied very considerably. For instance, although sodium alkoxides react with 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride to give β-glucosides, sodium phenoxide gives a comparatively high proportion of the α-phenylglucoside—approximately 60% of the total product.

When glucoside formation is effected from 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride or 3 : 4 : 6-triacetyl β-glucosyl chloride in an alcoholic suspension of silver oxide or silver carbonate, the product obtained is α-glucoside with about 30% of β; the proportion of α can be increased if the silver carbonate is replaced by silver nitrate and pyridine. Further, it is possible to obtain some α-glucosides from 2 : 3 : 4 : 6-tetra-acetyl α-glucosyl bromide by reaction in presence of quinoline, the formation of α-glucoside being apparently determined by the nature of the hydroxy-compound reacting.

These facts, together with observations on the opening of the ethylene-oxide ring in 3 : 4 : 6-triacetyl glucose anhydride, indicate that the reagents employed to effect glucoside formation determine, to some extent at least, the nature of the product.

Although it would be possible to explain these results by assuming that each reagent has its own isomerising effect, it seems more probable that the effect is determined by some factor such as preliminary addition.

In the reaction between sodium methoxide or ethoxide and 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride in equimolecular proportion in alcoholic solution, the trichloroacetyl group is split off and a 3 : 4 : 6-triacetyl β-alkylglucoside (III) is produced. This reaction provides an alternative method of preparing these compounds, which hitherto have only been obtained from 3 : 4 : 6-triacetyl β-glucosyl chloride or by the reaction of 3 : 4 : 6-triacetyl glucose anhydride with alcohols. It is an additional example of the comparative instability of the trichloroacetyl group in position 2 (Brigl, *Z. physiol. Chem.*, 1921, **116**, 1; Hickinbottom, *loc. cit.*).

Experimental.

Action of Sodium Methoxide in Methyl Alcohol on 2-Trichloroacetyl 3 : 4 : 6-Triacetyl β-Glucosyl Chloride.—Formation of 3 : 4 : 6-triacetyl β-methylglucoside. The sodium methoxide used in these experiments was prepared by dissolving sodium in freshly distilled, dry methyl alcohol to yield an approximately 0·5*N*-solution. The concentration was determined accurately by titration against standard acid.

A measured volume of this solution, diluted with methyl alcohol,

was added to 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride so that the glucosyl chloride and sodium methoxide were present in equimolecular proportion. The changes in specific rotation (calc. on the glucosyl chloride) were as follows ($c = 5{\cdot}23$; $l = 2$):

t (mins.) ...	2	3	4	8	14	42	62	88
$[\alpha]_D^{21{\cdot}5°}$.....	+27·3°	28·8°	27·3°	26·8°	24·2°	20·7°	19·2°	20·0° (const.)

A number of other determinations of the change of rotation, also made at room temperature, were in general agreement with those recorded above: $[\alpha]_D$ +27—30° about 2 minutes after mixing, changing to a constant end value between +14° and +25°.

The solutions obtained were clear and neutral to moist litmus. Evaporation under diminished pressure at room temperature, followed by repeated extraction of the residue with boiling chloroform to eliminate inorganic salts, and subsequent evaporation of the chloroform, yielded the product of the reaction as a colourless transparent gum. It slowly solidified in a vacuum desiccator to a crystalline mass (A).

The inorganic residue remaining after the extraction with chloroform was sodium chloride. In one or two experiments it contained a small quantity of acetate.

The crystalline mass (A) was not entirely free from lower-melting compounds. The products from two typical experiments showed $[\alpha]_D$ +32·7° ($c = 1{\cdot}65$) and $[\alpha]_D$ +37·6° ($c = 1{\cdot}78$) in ethyl alcohol. On deacetylation with alcoholic ammonia a mixture of α- and β-glucosides resulted. From the two specimens for which the specific rotations are recorded above, methylglucosides were obtained which, after removal of amides and drying at 78°/12 mm., had $[\alpha]_D$ −6° ($c = 1{\cdot}38$) and $[\alpha]_D$ +4° ($c = 2{\cdot}63$) in water. These values correspond to mixtures of β-methylglucoside containing 14% and 19% respectively of α-methylglucoside. Crystallisation of the crude glucoside from alcohol furnished pure β-methylglucoside, $[\alpha]_D$ −32° in water ($c = 1{\cdot}07$), m. p. 107—108° (alone or mixed with a genuine specimen of β-methylglucoside). The presence of α-methylglucoside was established by adding ether to a concentrated alcoholic solution of the product of deacetylation of the crude product (A). Two forms of crystal, which could be separated mechanically, were deposited on keeping. The greater part consisted of stout transparent prisms of β-methylglucoside. A few aggregates of small needles were also present, and after further purification from absolute alcohol these were identified as α-methylglucoside by melting point and rotation.

Isolation of 3 : 4 : 6-*triacetyl* β-*methylglucoside* (III). Extraction of the solid (A) with ether left a gummy residue which showed

little sign of crystallising. The ethereal solution on slow spontaneous evaporation deposited aggregates of prismatic needles, which after crystallisation from carbon tetrachloride or alcohol were obtained pure; m. p. 93—94°, $[\alpha]_D$ +20° in ethyl alcohol ($c = 4{\cdot}5$) (Found: C, 49·0; H, 6·4; OMe, 9·6. Calc. for $C_{13}H_{20}O_9$: C, 48·6; H, 6·4; OMe, 9·6%). The analysis corresponds to triacetyl methylglucoside, and the constants are in good agreement with those recorded for 3 : 4 : 6-triacetyl β-methylglucoside prepared from 3 : 4 : 6-triacetyl glucose anhydride (Hickinbottom, J., 1928, 3144). The substance did not depress the melting point of an authentic specimen of 3 : 4 : 6-triacetyl β-methylglucoside, and yielded 2 : 3 : 4 : 6-tetra-acetyl β-methylglucoside on acetylation.

Action of an Excess of Sodium Methoxide in Methyl Alcohol on 2-Trichloroacetyl 3 : 4 : 6-Triacetyl β-Glucosyl Chloride.—A freshly prepared solution (0·404*N*) of sodium methoxide (1·154 mols.) in dry methyl alcohol was added to 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride (0·5421 g.; 1 mol.). The solution was rapidly diluted with dry methyl alcohol to 25 c.c. The following changes in rotation at room temperature were observed ($l = 2{\cdot}0$; $c = 2{\cdot}17$):

t (mins.)	2	4	6	10	12	14	17
α_D	+0·94°	0·66°	0·45°	0·29°	0·25°	0·20°	0·13°

t (mins.)	19	23	29	54	88	1080	
α_D	+0·10°	0·03°	−0·10°	−0·28°	−0·35°	−0·54°	(const.)

The solution was neutral after 24 hours. The final value, calculated on the assumption that only β-methylglucoside is present, is $[\alpha]_D$ −31·2°.

The product obtained on evaporation, however, did not consist entirely of β-methylglucoside. After solution of the glucosides in absolute alcohol and filtration to remove mineral matter, no appreciable amount of β-methylglucoside could be separated, even after concentration of the alcoholic solution and nucleation with β-methylglucoside. A determination of the acetyl content by hydrolysis with alcoholic potash showed that the product consisted largely of monoacetyl β-methylglucoside (Found: Ac, 13·2. Calc. for $C_7H_{13}O_6Ac$: Ac, 18·4%). It is evident that extensive deacetylation is brought about even in the cold by the action of a slight excess of sodium methoxide.

Action of a Solution of Sodium Ethoxide in Ethyl Alcohol on 2-Trichloroacetyl 3 : 4 : 6-Triacetyl β-Glucosyl Chloride.—The formation of 3 : 4 : 6-triacetyl β-ethylglucoside. The β-glucosyl chloride (1·1393 g.) was mixed with sodium ethoxide (1 mol.) in ethyl alcohol at room temperature, and the solution diluted to 25 c.c. No readings of the change of rotation were taken owing to the precipit-

ation of sodium chloride. After 24 hours, the solution was neutral to moist litmus, and after filtration had α_D +0·21° (l = 0·5); hence $[\alpha]_D$ +9°, calculated on the glucosyl chloride, or $[\alpha]_D$ +11°, calculated on triacetyl ethylglucoside.

Saturation of the solution with dry ammonia at room temperature, and subsequent evaporation after 20 hours, followed by extraction with ether to remove trichloroacetamide, and then drying at 78°/12 mm., left a mixture of ethylglucosides, $[\alpha]_D$ −14° in water (c = 1·95; l = 0·5). The solution was almost indifferent to Fehling's solution, and showed no detectable mutarotation after 24 hours. This value of the specific rotation corresponds to a mixture of 91% of β-ethylglucoside and 9% of α-ethylglucoside. The presence of β-ethylglucoside as the major constituent of the mixture was also demonstrated by acetylation, whereby 2 : 3 : 4 : 6-tetra-acetyl β-ethylglucoside was obtained which, after one crystallisation from alcohol, melted, alone or mixed with a genuine specimen, at 103—104°.

Isolation of 3 : 4 : 6-*triacetyl* β-*ethylglucoside.* The filtered solution resulting from the action of sodium ethoxide (1 mol.) on 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride in alcohol had $[\alpha]_D$ +4° (c = 4·78), calculated on the original glucosyl chloride, and $[\alpha]_D$ +6°, calculated on triacetyl ethylglucoside. It was evaporated under reduced pressure, and the dry residue extracted with ether. The ethereal solution deposited, on spontaneous evaporation, needles, m. p. 105—110°, which were contaminated by a small quantity of a substance having the odour of an ester. After three crystallisations from ethyl alcohol, the solid melted at 119—120°, and was identified by its m. p., mixed m. p., and specific rotation as 3 : 4 : 6-triacetyl β-ethylglucoside (Hickinbottom, *loc. cit.*).

Action of Sodium Phenoxide and Phenol on 2-*Trichloroacetyl* 3 : 4 : 6-*Triacetyl* β-*Glucosyl Chloride.*—Sodium phenoxide solution was prepared by the action of metallic sodium on an excess of molten phenol, precautions being taken to exclude moisture. The crystalline compound which separated on cooling, and probably consisted of the additive compound of phenol and sodium phenoxide (compare Gentsch, D.R.-P. 156761), was dissolved in sufficient dry acetone to give an approximately 0·5N-solution. The concentration of phenoxide was determined accurately by titration.

2-Trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride (0·7816 g.) was treated with sodium phenoxide (1 mol.), and the solution made up to 25 c.c. with acetone. A precipitate of sodium chloride formed rapidly. After 2 hours the filtered solution had $[\alpha]_D$ +33°, calculated on the basis of the glucosyl chloride, and this value did not alter during 48 hours. The filtered solution was evaporated, and

the residue heated at 100°/15 mm. to remove phenol. A brownish gum was obtained, $[\alpha]_D$ +106·5° in benzene ($c = 2{\cdot}16$; $l = 0{\cdot}5$). After deacetylation with alcoholic alkali, a mixture of phenylglucosides remained, $[\alpha]_D$ +88° in water ($c = 1{\cdot}48$; $l = 0{\cdot}5$). Acetylation of the glucosides gave a brownish mixture of the tetra-acetyl phenylglucosides, $[\alpha]_D$ +95° in benzene ($c = 1{\cdot}35$; $l = 0{\cdot}5$). This value corresponds to a mixture containing approximately 64% of tetra-acetyl α-phenylglucoside and 36% of the β-isomeride. Crystallisation of the crude mixture from alcohol furnished pure 2 : 3 : 4 : 6-tetra-acetyl α-phenylglucoside, m. p. 110—112° alone or mixed with an authentic specimen. $[\alpha]_D$ +168° in benzene.

Action of a Solution of Sodium Methoxide in Methyl Alcohol on 3 : 4 : 6-Triacetyl β-Glucosyl Chloride.—Sodium methoxide (1 mol.) in methyl-alcoholic solution (0·6683*N*) was diluted with methyl alcohol and added to 0·6655 g. of pure 3 : 4 : 6-triacetyl β-glucosyl chloride (m. p. 154°). The solution was made up to 25 c.c. as rapidly as possible: 4 minutes after mixing, $[\alpha]_D$ (calc. on the glucosyl chloride) was −7·5°, and it fell to a constant value of $[\alpha]_D$ −22·5° on keeping over-night at room temperature. The solution then contained no free glucosyl chloride. It was evaporated under diminished pressure, and the residue extracted repeatedly with boiling ethyl acetate. Evaporation of the extract left a transparent colourless gum which was inactive towards boiling Fehling's solution. Deacetylation of the gum with alcoholic ammonia at room temperature left a product which consisted very largely of β-methylglucoside, $[\alpha]_D$ −32° in water ($c = 1{\cdot}57$; $l = 0{\cdot}5$). The identification as β-methylglucoside was established by its m. p., mixed m. p., and specific rotation, after crystallisation from absolute alcohol.

Action of Sodium Phenoxide on 3 : 4 : 6-Triacetyl β-Glucosyl Chloride.—A solution (0·4161*N*) of sodium phenoxide (1 mol.) in acetone containing free phenol was added to 3 : 4 : 6-triacetyl β-glucosyl chloride (0·5364 g.), and the solution diluted rapidly to 25 c.c. The separation of sodium chloride commenced in less than a minute after mixing. Filtration after 18 hours gave a solution having $[\alpha]_D$ +50°, calculated on the basis of the glucosyl chloride. In another experiment, with 0·5031 g. of β-glucosyl chloride in 25 c.c. of acetone containing 1 mol. of sodium phenoxide, there resulted a solution which had $[\alpha]_D$ +49° after being kept for 50 hours at room temperature. Both solutions were faintly alkaline to moist litmus. They were combined, and the acetone was removed under reduced pressure. The residue, after being heated at 100°/15 mm. to remove phenol, was a light brown, transparent gum, $[\alpha]_D$ +42° in alcohol ($c = 1{\cdot}62$; $l = 0{\cdot}5$).

Acetylation of this residue in pyridine furnished a product having,

after the usual treatment to remove pyridine, $[\alpha]_D$ +40° in benzene ($c = 2{\cdot}1$). This value corresponds to a mixture of approximately 65% of the tetra-acetyl β-phenylglucoside and 35% of the α-isomeride. Crystallisation from alcohol gave pure 2 : 3 : 4 : 6-tetra-acetyl β-phenylglucoside, m. p. 125—126°, $[\alpha]_D$ −28° in benzene.

Action of Sodium Methoxide in Methyl Alcohol on 2 : 3 : 4 : 6-*Tetra-acetyl α-Glucosyl Bromide.*—In order to compare the behaviour of the β-glucosyl halides towards sodium methoxide with that of the α-glucosyl halides the action of sodium methoxide in methyl alcohol on 2 : 3 : 4 : 6-tetra-acetyl α-glucosyl bromide was followed polarimetrically.

Sodium methoxide (1 mol.) in methyl-alcoholic solution (0·4*N*) was added to 1·1969 g. of 2 : 3 : 4 : 6-tetra-acetyl α-glucosyl bromide at room temperature, and methyl alcohol then added to make the volume up to 50 c.c. The changes in rotation were :

t (mins.) ...	1·5	3	5	8	45	1135
a_D ($l = 0{\cdot}5$)	−0·01°	−0·05°	−0·07°	−0·09°	−0·13°	−0·15°(const.)

The solution after acetylation yielded tetra-acetyl β-methyl-glucoside.

The Stability of 2-*Trichloroacetyl* 3 : 4 : 6-*Triacetyl* β-*Glucosyl Chloride.*—Attempts were made to effect the isomerisation of 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride by the action of traces of alkali or sodium methoxide in acetone.

A solution of the β-glucosyl chloride in dry acetone ($[\alpha]_D$ +8°; $c = 4{\cdot}41$; $l = 0{\cdot}5$), treated with 2 drops of 0·5*N*-solution of sodium methoxide in methyl alcohol, showed no change in rotation after being kept at room temperature for 25 minutes. The subsequent addition of 1 drop of 5*N*-sodium hydroxide gave a solution which had $[\alpha]_D$ +10·5° after 24·5 hours and $[\alpha]_D$ +13·1° after 47·5 hours. The tube contained a small deposit, presumably sodium chloride. The solution, however, on evaporation gave unchanged β-glucosyl chloride.

A suspension of an excess of sodium methoxide (*e.g.*, 2 mols.) in dry xylene free from methyl alcohol had only a slow action on 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride. After 17 hours, with intermittent shaking, the filtered solution had $[\alpha]_D$ +17°, calculated on the basis of the glucosyl chloride. Evaporation under reduced pressure gave a residue which partly crystallised, and from which a large proportion of unchanged β-glucosyl chloride was isolated.

The addition of 1 drop of concentrated hydrochloric acid to an acetone solution of 2-trichloroacetyl 3 : 4 : 6-triacetyl β-glucosyl chloride ($c = 4{\cdot}4$) brought about a change in specific rotation from +7·2° to +9·6° after 92 hours. The solution had become

darker in colour. On evaporation it yielded a somewhat impure product, m. p. 120—125°, from which the pure β-glucosyl chloride, m. p. 135—136°, was obtained by one crystallisation from ethyl alcohol.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, April 3rd,* 1930.]