154. *Studies of Trifluoroacetic Acid. Part VII.* The Synthesis of 2-Benzoyl 4 : 6-Benzylidene Methyl-α-D-glucopyranoside and its Conversion into the Isomeric 3-Benzoate by an Acyl Migration.*

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Benzoylation of 4 : 6-benzylidene trifluoroacetyl α-methyl-D-glucoside (I) afforded 2-benzoyl 4 : 6-benzylidene 3-trifluoroacetyl α-methyl-D-glucoside (II). Ethanolysis or acidic hydrolysis of the latter gave 2-benzoyl (IX), and alkaline hydrolysis gave 3-benzoyl 4 : 6-benzylidene α-methyl-D-glucoside (III), which was formed also when the 2-benzoate (IX) was treated with dilute alkali; this is an example of a simple benzoyl migration from $C_{(2)}$ to $C_{(3)}$. The structures of these esters were established by toluenesulphonylation and by methylation.

Previous papers in this series have described investigations on trifluoroacetate esters, which undergo readily both alcoholysis and hydrolysis without concomitant Walden inversion, racemisation, or anhydro-ring formation (Bourne, Tatlow, and Tatlow, *J.*, 1950, 1367); these properties make them potentially very valuable as synthetic inter-

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mediates in the carbohydrate and allied fields. For instance, various groupings may be substituted at the free hydroxyl groups of partially trifluoroacetylated polyalcohols and the trifluoroacetyl residues then split off under very mild conditions, the fluoroacyl fragment being used as a readily removable " blocking " group. This new technique was illustrated by Bourne, Stacey, Tatlow, and Tatlow (*J.*, 1951, 826), who prepared 4 : 6-benzylidene trifluoroacetyl α-methyl-D-glucoside (I), acetylated the free hydroxy-group, and removed the trifluoroacetyl residue by alcoholysis. By varying the conditions of the acetylation, either the 2- or the isomeric 3-acetyl 4 : 6-benzylidene α-methylglucoside could be made; it was concluded that the trifluoroacetyl group can migrate readily. A similar approach was used by Butler, Lloyd, and Stacey to prepare 2 : 4-dimethyl L-rhamnose (unpublished results). Not only is this technique useful in general synthesis, but also the various partly esterified polyalcohols, which should now be more readily accessible, may well provide new information on acyl migrations.

This paper describes the benzoylation of 4 : 6-benzylidene trifluoroacetyl α-methyl-D-glucoside (I). Benzoyl chloride in pyridine gave a syrupy product (A) [later shown to be principally (II)] which resisted purification; however with dilute alkali (approx. 1 mol.), this afforded a crystalline benzoyl 4 : 6-benzylidene α-methyl-D-glucoside (III), from which 4 : 6-benzylidene α-methylglucoside was regenerated. Toluenesulphonylation of the benzoate (III) yielded the known 3-benzoyl 4 : 6-benzylidene 2-tosyl α-methyl-D-glucoside (IV) (Robertson and Griffith, *J.*, 1935, 1193), which with sodium methoxide gave the known 4 : 6-benzylidene 2 : 3-anhydro-α-methyl-D-mannoside (V) (*idem, ibid.*). Moreover, methylation of the ester (III) gave 3-benzoyl 4 : 6-benzylidene 2-methyl α-methyl-D-glucoside (VI), as was proved by its conversion into the known 4 : 6-benzylidene 2-methyl α-methyl-D-glucoside (VII) (Bourne, Stacey, Tatlow, and Tatlow, *loc. cit.*). Thus, the product (III) had its benzoate group located at position 3 of the glucose molecule (cf. later reactions in the 2-benzoate series).

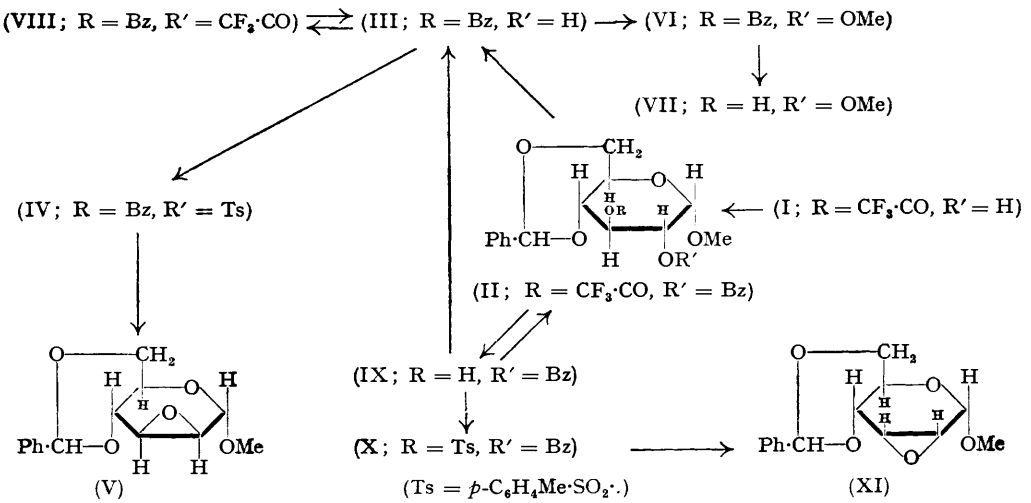
Because of the difficulty in isolating the precursor (A) of the benzoate (III), the latter was trifluoroacetylated (Bourne, Tatlow, and Tatlow, *loc. cit.*) to give 3-benzoyl 4 : 6-benzylidene 2-trifluoroacetyl α-methyl-D-glucoside (VIII), which, by ethanolysis or partial saponification, regenerated the 3-benzoate (III), complete saponification giving 4 : 6-benzylidene α-methylglucoside. Further examination of the mixed ester (VIII) revealed that in aqueous acetone the trifluoroacetyl residue was removed by autocatalytic acidic hydrolysis, the 3-benzoate (III) being formed. The benzylidene group was clearly more stable than is usual under acidic conditions, and so the possibility of removing preferentially the trifluoroacetyl group of syrup (A) by treatment with dilute acid was examined.

Under these conditions (A) afforded a second benzoyl 4 : 6-benzylidene α-methyl-glucoside (IX); this ester was formed also by alcoholysis of (A). Upon toluene-sulphonylation the new benzoate (IX) gave the known 2-benzoyl 4 : 6-benzylidene 3-tosyl α-methyl-D-glucoside (X) and thence 4 : 6-benzylidene 2 : 3-anhydro-α-methyl-D-alloside (XI) (Robertson and Griffith, *loc. cit.*). Methylation of the ester (IX) failed to give pure material, but hydrolysis of the product and examination by the filter-paper ionophoresis technique (Foster, *Chem. and Ind.*, 1952, 828, 1050; Foster and Stacey, *J. Appl. Chem.*, in the press) showed clearly the presence of 3-methyl glucose, no 2-methyl glucose being detected. The structure of the product (IX) was thus clearly established as 2-benzoyl 4 : 6-benzylidene α-methyl-D-glucoside.

Trifluoroacetylation of this benzoate (IX) yielded the corresponding 3-trifluoroacetate (II), complete saponification of which gave 4 : 6-benzylidene α-methylglucoside, whilst ethanolysis regenerated the 2-benzoate (IX). By partial saponification with dilute alkali, however, the isomeric 3-benzoate (III) was obtained. Thus it appeared that the principal constituent of the syrup (A) was 2-benzoyl 4 : 6-benzylidene 3-trifluoroacetyl α-methyl-D-glucoside (II), and indeed a slightly impure crystalline sample of this material was obtained in a fresh attempt to purify the syrup. That the crystalline substance was (II) and not (VIII) was evident from mixed m. p. determinations, from its specific rotation, and from the fact that alcoholysis yielded 2-benzoyl 4 : 6-benzylidene α-methylglucoside (IX). The above results could not be explained solely on the basis that syrup (A) was a mixture of

the isomers (VIII) and (II), because, from the same sample of (A), acidic hydrolysis gave (IX) in 45% yield, and alkaline hydrolysis afforded 67% of (III). It was apparent that the benzoyl group had migrated from $C_{(2)}$ to $C_{(3)}$ during the alkaline hydrolysis of (A), and this was confirmed when it was shown that 2-benzoyl 4 : 6-benzylidene α-methylglucoside (IX) was transformed readily into the 3-benzoate (III) by treatment in acetone with dilute aqueous sodium hydroxide, though it was unchanged in acidic or neutral media, in dry or wet pyridine, or by dry silver oxide in boiling ether.

Wanderings of acyl groups in esterified polyhydroxy-compounds often occur, as was noticed by Fischer (*Ber.*, 1920, **53**, 1621), and many examples of this effect are now known. Migrations during methylations with the Purdie reagents are quite common (*e.g.*, Haworth, Hirst, and Teece, *J.*, 1930, 1405; 1931, 2858), but only a few cases have been reported so far of the direct conversion of a simple acylated sugar into an isomer which was itself isolated (cf. Josephson, *Svensk Kem. Tidskr.*, 1929, **41**, 99; *Ber.*, 1930, **63**, 3089; Ohle, *Ber.*, 1924, **57**, 403; Helferich and Klein, *Annalen*, 1926, **450**, 219; 1927, **455**, 173;



Helferich, Bredereck, and Schneidmüller, *ibid.*, 1927, **458**, 111; Helferich and Müller, *Ber.*, 1930, **63**, 2142). The transformation, herein reported, of 2-benzoyl 4 : 6-benzylidene α-methylglucoside into the 3-benzoate is an example of a direct acyl migration to an adjacent, apparently more stable, position. The benzoyl residue in this reaction follows the usual behaviour of migrating acyl groups in glucose derivatives; such changes are mostly catalysed by alkali (Hirst and Peat, *Ann. Reports*, 1934, **31**, 172) and the migration is normally away from the potential reducing group (Brown, Hough, and Jones, *J.*, 1950, 1125).

Mechanisms advanced to explain acyl migration have usually invoked acid ortho-esters as intermediates (see Fischer, *loc. cit.*; Helferich *et al.*, *locc. cit.*; and the review by Pacsu, *Adv. Carbohydrate Chem.*, 1945, **1**, 77). Recently, Doerschuk (*J. Amer. Chem. Soc.*, 1952, **74**, 4202) showed by using radioactive tracers that an acyl migration from $C_{(2)}$ to $C_{(1)}$ in glycerol monopalmitate was an intramolecular process; an ortho-ester seems the likeliest transition state. We have made infra-red measurements (in collaboration with R. R. Randle) on 2-benzoyl, 3-benzoyl, and 2 : 3-dibenzoyl 4 : 6-benzylidene α-methyl-D-glucoside and found that all three gave bands at the characteristic carbonyl stretching frequency, affording strong evidence that they possessed orthodox acyl groups and that neither monobenzoate was itself a cyclic ortho-ester. The work of Reeves however (*ibid.*, 1949, **71**, 215; *Adv. Carbohydrate Chem.*, 1951, **6**, 107) has shown that, although the hydroxyl groups on $C_{(2)}$ and $C_{(3)}$ in glucose derivatives are *trans*, owing to the conformation of the pyranose ring the C–O bonds are not usually directed at 180° to each other but at a smaller angle, thus enabling cuprammonium complexes to be formed. Hence, though the two monobenzoates (IX) and (III) may not exist normally as ortho-esters, the formation

of such a transitory intermediate from the 2-benzoate (IX), by addition of the hydroxyl group of $C_{(3)}$ across the benzoate carbonyl function, would appear to be possible; ring scission to give the more stable 3-benzoate (III) could then occur.

The above reactions support the earlier suggestion (Bourne, Stacey, Tatlow, and Tatlow, *loc. cit.*) that the monotrifluoroacetate, m. p. 210°, is the 3-isomer (I). However, the trifluoroacetyl group does not appear to migrate during benzoylations as it does during acetylations in pyridine, despite the fact that the 3-benzoate (III) is more stable than its isomer (IX). Benzoylation of the trifluoroacetate (I) with benzoic acid–trifluoroacetic anhydride (Bourne, Stacey, Tatlow, and Tedder, *J.*, 1949, 2976), in trifluoroacetic acid as solvent, gave a product which was the same as that obtained from the pyridine reaction, but in poorer yield; separation from residual benzoic acid was difficult. It seems reasonable that the fluoroacyl group should not migrate during benzoylation in pyridine, since, although the 3-benzoate is the more stable isomer, Robertson and Griffith (*loc. cit.*) treated 4 : 6-benzylidene α-methylglucoside in pyridine with benzoyl chloride ($1\frac{1}{4}$ mol.) and obtained an inseparable mixture of benzoates, from which a little 2-benzoyl 3-tosyl compound (X) could be made; if the benzoyl group will not substitute preferentially on $C_{(3)}$ under these conditions it is hardly likely to cause even the mobile trifluoroacetyl group to move. It is noteworthy that, of the carboxyl monoesters of 4 : 6-benzylidene α-methylglucoside, the 3-benzoate, 3-acetate, and 3-trifluoroacetate are apparently the more stable isomers, though the 2-tosyl ester is formed preferentially (*idem, ibid.*; Bolliger and Prins, *Helv. Chim. Acta*, 1945, **28**, 465).

Experimental

Unless otherwise stated, all operations involving trifluoroacetates were conducted with dry reagents under anhydrous conditions. Values of [α] refer to chloroform solutions.

4 : 6-*Benzylidene Trifluoroacetyl* α-*Methyl*-D-*glucoside*.—Prepared as described previously (Bourne, Stacey, Tatlow, and Tatlow, *loc. cit.*) this compound had m. p. 210°, $[\alpha]_D^{19}$ +117·0° (*c*, 1·42).

3-*Benzoyl* 4 : 6-*Benzylidene* α-*Methyl*-D-*glucoside from* 4 : 6-*Benzylidene Trifluoroacetyl* α-*Methylglucoside*.—Freshly distilled benzoyl chloride (2·3 c.c.) was added to 4 : 6-benzylidene trifluoroacetyl α-methylglucoside (6·24 g.) in pyridine (25 c.c.). After 95 hours at room temperature, the product was distilled under diminished pressure with several portions of carbon tetrachloride, the residue was extracted with warm ether (3 × 50 c.c.), and the filtered extracts were concentrated *in vacuo*. To the syrupy residue in acetone (170 c.c.), 0·1N-sodium hydroxide was added rapidly until the solution was just alkaline to phenolphthalein (180 c.c. of alkali required). After 1 hour the precipitate was filtered off, and acetone was distilled from the filtrate under diminished pressure, yielding more solid. The combined precipitates were washed, dried, and recrystallised from ethyl alcohol–light petroleum (b. p. 60—80°), to give 3-*benzoyl* 4 : 6-*benzylidene* α-*methyl*-D-*glucoside* (4·10 g.), m. p. 217—218°, $[\alpha]_D^{19}$ +33·5° (*c*, 2·55) (Found : C, 65·5; H, 5·9; OMe, 8·0; Ph·CO, 27·2. $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7; OMe, 8·0; Ph·CO, 27·2%).

To determine the benzoyl content the ester (*ca.* 1 g.) was kept for about 4 hours in ethyl-alcoholic sodium ethoxide (10 c.c.; 0·825N), water (2 c.c.) was added, and after 12 hours further the solution was back-titrated against hydrochloric acid (1·5N). Alcohol was distilled *in vacuo* from the titration liquors and the resulting precipitate recrystallised from water, affording 4 : 6-benzylidene α-methylglucoside (67%), m. p. and mixed m. p. 165—166° (Found : C, 59·6; H, 6·4. Calc. for $C_{14}H_{18}O_6$: C, 59·55; H, 6·4%).

3-*Benzoyl* 4 : 6-*Benzylidene* 2-*Tosyl* α-*Methyl*-D-*glucoside*.—3-Benzoyl 4 : 6-benzylidene α-methylglucoside (1·22 g.) in pyridine (4·5 c.c.) was treated with toluene-*p*-sulphonyl chloride (0·96 g.) for 14 days at room temperature and the product isolated in the usual way. Recrystallisation from ethyl alcohol afforded the 2-tosyl derivative (1·50 g.), m. p. 212—214°, $[\alpha]_D^{19}$ +49·3° (*c*, 3·70) (Found : C, 62·2; H, 5·2; S, 6·2; OMe, 5·7. Calc. for $C_{28}H_{28}O_9S$: C, 62·2; H, 5·2; S, 5·9; OMe, 5·7%). Robertson and Griffith (*loc. cit.*) gave m. p. 212—213°, $[\alpha]_D^{15}$ +51·6° (*c*, 2·88).

This diester, treated with sodium methoxide, gave 4 : 6-benzylidene 2 : 3-anhydro-α-methyl-D-mannoside (65%), m. p. and mixed m. p. 145—146°, $[\alpha]_D^{18}$ +103·2° (*c*, 1·90) (Found : C, 63·5; H, 5·9; OMe, 12·0. Calc. for $C_{14}H_{16}O_5$: C, 63·6; H, 6·1; OMe, 11·7%). Robertson and Griffith (*loc cit.*) cited m. p. 146—147°, $[\alpha]_D^{15}$ +107° (*c*, 1·61).

3-*Benzoyl* 4 : 6-*Benzylidene* 2-*Methyl* α-*Methyl*-D-*glucoside*.—Silver oxide (2·9 g.) was added

to 3-benzoyl 4 : 6-benzylidene α-methylglucoside (1·095 g.) in methyl iodide (30 c.c.), and the mixture was refluxed for 18 hours. The solvent was distilled, the residue was extracted with boiling chloroform, the filtered extracts were evaporated, and the residue was remethylated as before. Isolation as above gave, after recrystallisation from ethyl alcohol, 3-*benzoyl* 4 : 6-*benzylidene* 2-*methyl* α-*methyl*-D-*glucoside* (0·84 g.), m. p. 167—168°, $[\alpha]_D^{19}$ +29·2° (*c*, 3·76) (Found : C, 65·7; H, 5·8; OMe, 15·2; Ph·CO, 26·4. $C_{22}H_{24}O_7$ requires C, 66·0; H, 6·0; OMe, 15·5; Ph·CO, 26·25%).

From the titration liquors of the benzoyl determination (see above) there was isolated 4 : 6-benzylidene 2-methyl α-methylglucoside (73%), recrystallised from ethyl alcohol–light petroleum (b. p. 60—80°), m. p. and mixed m. p. 167—168° (depressed in admixture with the starting material), $[\alpha]_D^{15}$ +74·5° (*c*, 1·18) (Found : C, 60·5; H, 6·7; OMe, 20·5. Calc. for $C_{15}H_{20}O_6$: C, 60·8; H, 6·8; OMe, 20·95%). Bourne, Stacey, Tatlow, and Tatlow (*loc. cit.*) gave m. p. 168°, $[\alpha]_D^{17}$ +78·9° (*c*, 1·19 in EtOH).

3-*Benzoyl* 4 : 6-*Benzylidene* 2-*Trifluoroacetyl* α-*Methyl*-D-*glucoside*.—(a) *Preparation.* 3-Benzoyl 4 : 6-benzylidene α-methylglucoside (1·28 g.) was heated at 50° for 10 minutes with trifluoroacetic anhydride (16·0 c.c.) and sodium trifluoroacetate (0·28 g.); the mixture was distilled under diminished pressure with several portions of carbon tetrachloride, and the residue was extracted with boiling light petroleum (100 c.c. in all; b. p. 60—80°). The filtered extracts, when cool, deposited a solid which, after three recrystallisations from light petroleum (b. p. 40—60°), gave 3-*benzoyl* 4 : 6-*benzylidene* 2-*trifluoroacetyl* α-*methyl*-D-*glucoside* (0·795 g.), m. p. 130—132°, $[\alpha]_D^{19}$ +25·9° (*c*, 1·30) (Found : C, 57·3; H, 4·3; F, 11·8. $C_{23}H_{21}O_8F_3$ requires C, 57·3; H, 4·4; F, 11·8%).

(b) *Complete saponification.* The diester was hydrolysed by the process suggested by Bourne, Tatlow, and Tatlow (*loc. cit.*) for trifluoroacetyl determinations, excess of alkali being used (Found : N-alkali uptake 4·14 c.c./g. $C_{23}H_{21}O_8F_3$ requires N-alkali uptake 4·15 c.c./g.). The titration liquors afforded 4 : 6-benzylidene α-methylglucoside, m. p. and mixed m. p. 163—164°.

(c) *Partial saponification.* When the diester (0·152 g.) in acetone (7 c.c.) was made just alkaline to phenolphthalein by the rapid addition of 0·0444N-sodium hydroxide (7·35 c.c.), a colourless solid was deposited, which, after recrystallisation from ethyl alcohol–light petroleum (b. p. 60—80°), gave 3-benzoyl 4 : 6-benzylidene α-methylglucoside (0·092 g.), m. p. and mixed m. p. 215—217° (Found : C, 65·4; H, 5·8%).

(d) *Ethanolysis.* A solution of the diester (0·193 g.) in dry ethyl alcohol (10 c.c.) was kept for 24 hours at 15°. The deposited solid was 3-benzoyl 4 : 6-benzylidene α-methylglucoside (0·124 g.), m. p. and mixed m. p. 216—217° (Found : C, 65·2; H, 5·9%).

(e) *Acidic hydrolysis.* To the ester (0·207 g.) in acetone (4·0 c.c.), water (3·0 c.c.) was added dropwise, the solution rapidly becoming acid. After 30 minutes, water (4·0 c.c.) was added and the precipitate of 3-benzoyl 4 : 6-benzylidene α-methylglucoside filtered off, washed, and dried (yield 55%; m. p. and mixed m. p. 216—217°).

2-*Benzoyl* 4 : 6-*Benzylidene* α-*Methyl*-D-*glucoside from* 4 : 6-*Benzylidene Trifluoroacetyl* α-*Methylglucoside*.—The trifluoroacetate (1·50 g.), pyridine (6·5 c.c.), and freshly distilled benzoyl chloride (0·52 c.c.) were kept at 15° for 75 hours. The solution was then poured slowly into ice-water (200 c.c.) which was mechanically stirred and kept slightly acid by the simultaneous addition of 2N-hydrochloric acid. The precipitate was filtered off, washed, dried, and recrystallised from light petroleum (b. p. 60—80°) containing a little ethyl alcohol, to give 2-*benzoyl* 4 : 6-*benzylidene* α-*methyl*-D-*glucoside* (0·615 g.), m. p. 165—166°, $[\alpha]_D^{21}$ +109·5° (*c*, 2·09) (Found : C, 65·6; H, 6·0; OMe, 8·4; Ph·CO, 27·3. $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7; OMe, 8·0; Ph·CO, 27·2%). The m. p. was depressed on admixture with the 3-benzoyl isomer.

From the titration liquors of the acyl determination (Bourne, Tatlow, and Tatlow, *loc. cit.*) there was isolated 4 : 6-benzylidene α-methylglucoside (42%), m. p. and mixed m. p. 161—162°.

2-*Benzoyl* 4 : 6-*Benzylidene* 3-*Tosyl* α-*Methyl*-D-*glucoside*.—The 2-benzoate (0·100 g.), pyridine (0·50 c.c.) and toluene-*p*-sulphonyl chloride (0·088 g.), after 90 hours at 15° and isolation as usual, afforded 2-benzoyl 4 : 6-benzylidene 3-tosyl α-methylglucoside (0·107 g.), m. p. 188—189° (recrystallised from ethyl alcohol), $[\alpha]_D^{21}$ +88·5° (*c*, 1·60) (Found : C, 62·5; H, 5·2; S, 6·1. Calc. for $C_{28}H_{28}O_9S$: C, 62·2; H, 5·2; S, 5·9%). Robertson and Griffith (*loc. cit.*) gave m. p. 184—186°, $[\alpha]_D$ +83·8° (*c*, 4·24). The m. p. was depressed in admixture with the 3-benzoyl 2-tosyl isomer.

By the usual method, the 3-tosyl 2-benzoate was converted into 4 : 6-benzylidene 2 : 3-anhydro-α-methyl-D-alloside (71%), m. p. and mixed m. p. 199—200°, $[\alpha]_D^{19}$ +144·5° (*c*, 0·82), for which Robertson and Griffith gave m. p. 199—200°, $[\alpha]_D^{15}$ +140·4° (*c*, 2·21).

Conversion of 2-*Benzoyl* 4 : 6-*Benzylidene* α-*Methyl*-D-*glucoside into the Isomeric* 3-*Benzoate.*—To the 2-benzoate (0·086 g.) in acetone (5·0 c.c.), 0·044N-sodium hydroxide (5·1 c.c.) was added. A precipitate formed immediately, and after addition of water (4·0 c.c.) it was filtered off, washed, and dried; it was 3-benzoyl 4 : 6-benzylidene α-methylglucoside (0·056 g.), m. p. and mixed m. p. 217—218°, $[\alpha]_D^{14}$ +33·4° (*c*, 0·78) (Found : C, 65·5; H, 5·7%).

The 2-benzoate was recovered unchanged after 24 hours at 15° in dry or aqueous pyridine, and after 48 hours with dry silver oxide in refluxing ether.

2-*Benzoyl* 4 : 6-*Benzylidene* 3-*Trifluoroacetyl* α-*Methyl*-D-*glucoside.*—(a) *Preparation.* 2-Benzoyl 4 : 6-benzylidene α-methylglucoside (0·497 g.), trifluoroacetic anhydride (8·0 c.c.), and sodium trifluoroacetate (0·16 g.) were refluxed for 15 minutes, and the mixture was then distilled *in vacuo* with several portions of carbon tetrachloride. The residual syrup was extracted with boiling light petroleum (b. p. 60—80°), the filtered extracts were concentrated, and the syrup crystallised from light petroleum (b. p. 60—80°) to give 2-*benzoyl* 4 : 6-*benzylidene* 3-*trifluoroacetyl* α-*methyl*-D-*glucoside* (0·371 g.), m. p. 135—138°, $[\alpha]_D^{17}$ +123·5° (*c*, 0·68) (Found : C, 57·1; H, 4·4; F, 12·3. $C_{23}H_{21}O_8F_3$ requires C, 57·3; H, 4·4; F, 11·8%). In admixture with the 3-benzoyl 2-trifluoroacetyl isomer the m. p. was 105—110°.

(b) *Complete saponification.* This was carried out as for the other isomer (Found : N-alkali uptake, 4·31 c.c./g. $C_{23}H_{21}O_8F_3$ requires N-alkali uptake, 4·15 c.c./g.), the titration liquors yielding 4 : 6-benzylidene α-methylglucoside, m. p. and mixed m. p. 161—162°.

(c) *Partial saponification.* The mixed ester (0·102 g.) in acetone (4·0 c.c.) was treated with 0·048N-sodium hydroxide until the solution was just alkaline to phenolphthalein (4·71 c.c. required). Water (10 c.c.) was added, and the resulting solid was reprecipitated from acetone (1·5 c.c.) by 0·048N-sodium hydroxide (3·0 c.c.). After being washed and dried the product, 3-benzoyl 4 : 6-benzylidene α-methylglucoside (0·067 g.), had m. p. and mixed m. p. 217—218° (Found : C, 65·7; H, 5·9%).

(d) *Ethanolysis.* The 2-benzoate 3-trifluoroacetate (0·091 g.) was kept in dry ethyl alcohol (6·0 c.c.) at 15° for 22 hours; the rotation had then fallen to a constant value. The solution was evaporated, and the residue crystallised from light petroleum (b. p. 60—80°) containing a little ethyl alcohol, to give 2-benzoyl 4 : 6-benzylidene α-methylglucoside (0·056 g.), m. p. and mixed m. p. 165—166°.

Isolation of 2- *and* 3-*Benzoyl* 4 : 6-*Benzylidene* α-*Methyl*-D-*glucoside from the Same Benzoylation Experiment.*—A mixture of trifluoroacetyl 4 : 6-benzylidene α-methylglucoside (1·20 g.), pyridine (5·0 c.c.), and benzoyl chloride (0·40 c.c.) was kept for 48 hours at 15°, then poured into dilute hydrochloric acid, and the precipitate collected, washed, and dried. One portion was recrystallised from light petroleum to give the 2-benzoate (45%), m. p. and mixed m. p. 164—165°, and a second portion, after treatment in acetone with dilute alkali as before, afforded the 3-benzoate (67%), m. p. and mixed m. p. 216°.

Attempted Methylation of 2-*Benzoyl* 4 : 6-*Benzylidene* α-*Methyl*-D-*glucoside.*—This compound, methylated as described previously, gave only an impure amorphous material, which after treatment with sodium ethoxide in ethyl alcohol gave a second product, which could not be purified. Accordingly, this material was hydrolysed by treatment at 60° with dilute hydrochloric acid–acetone, the solution was evaporated and the residual syrup, after distillation *in vacuo* with several portions of water, was dissolved in water and subjected to filter-paper ionophoresis as described by Foster and Stacey (*locc. cit.*); a 0·2M-borate buffer (pH 10) and a potential difference of 900 v (final current 35—40 milliamp.) for 3 hours were employed, reference compounds being run simultaneously. An aniline hydrogen phthalate spray revealed that the main constituent was 3-methyl glucose (M_G value 0·80), traces of glucose being present also; no 2-methyl glucose (M_G value 0·23) was detected.

Attempted Isolation of 2-*Benzoyl* 4 : 6-*Benzylidene* 3-*Trifluoroacetyl* α-*Methyl*-D-*glucoside from the Benzoylation Process.*—4 : 6-Benzylidene trifluoroacetyl α-methylglucoside, benzoylated as before (p. 738), gave a syrup which crystallised after nucleation with the authentic 2-benzoate 3-trifluoroacetate. Recrystallisation from light petroleum (b. p. 60—80°) gave, first, a little unchanged starting material, and then a fluorine-containing product, m. p. 120—125°, depressed in admixture with the 3-benzoate 2-trifluoroacetate but not with the 2-benzoate 3-trifluoroacetate, $[\alpha]_D^{15}$ +114·0° (*c*, 2·02); after 20 hours at 15° in methyl alcohol it gave 2-benzoyl 4 : 6-benzylidene α-methylglucoside (60%), m. p. and mixed m. p. 164—165°.

Infra-red Investigation of the Benzoates of 4 : 6-*Benzylidene* α-*Methyl*-D-*glucoside* (with R. R. Randle).—Using a Grubb–Parsons spectrometer with a rock-salt prism and the Nujol mull technique, the following carbonyl stretching frequencies ($cm.^{-1}$) were recorded : (*a*) 2-benzoyl 4 : 6-benzylidene α-methylglucoside 1732, (*b*) the isomeric 3-benzoate 1726,

(*c*) 2 : 3-dibenzoyl 4 : 6-benzylidene α-methylglucoside (m. p. 151—152°; Ohle and Spencker, *Ber.*, 1928, **61**, 2387) 1732. Strong evidence is thus afforded for the presence of orthodox benzoate ester groups in all three products, since these frequencies accord well with those of other benzoates [*e.g.*, Hartwell, Richards, and Thompson (*J.*, 1948, 1436) gave 1727 cm.$^{-1}$ for liquid methyl benzoate]; if either monobenzoate possessed an ortho-ester structure the characteristic carbonyl frequency would be absent.

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