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An Alternative Preparation of *O*-Benzylidene Acetals. Part II

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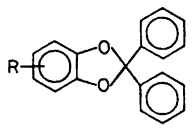
Some further examples of the preparation of *O*-benzylidene acetals by the treatment of diols with benzal halides in pyridine are given. The use of benzal bromide instead of benzal chloride results in milder reaction conditions. Benzylidene groups may be introduced into glycosides containing *O*-triphenylmethyl or *O*-acetyl groups in fair yields.

In 1930, Bradley *et al.* reported that the condensation of catechols with dichlorodiphenylmethane in the presence of pyridine yielded the ketal I.[1]



I

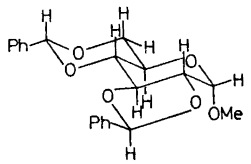
In a previous communication we reported the extension of this reaction to the condensation of glycosides with the appropriate disposition of two hydroxyl groups, with benzal chloride in pyridine at reflux temperature.[2] The various benzylidene acetals were obtained in acceptable yields. Since the reaction is irreversible, benzylidene acetals are obtainable which may be difficult to produce by the usual, acid-catalyzed procedures, *e.g.* in the synthesis of 1,3-dioxolan derivatives. In the present communication further examples of the scope and utility of this novel method for preparing benzylidene acetals are reported.

The use of benzal bromide instead of benzal chloride in the reaction was investigated by allowing 1.2 molar equivalents of each benzal halide to react with methyl α-D-glucopyranoside at reflux temperature. Each reaction was monitored by TLC. The lower reactivity of benzal chloride necessitated a longer reaction time. The product was obtained as the acetate and the yield

of methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside[3] was 69 % using benzal chloride as compared to 86 % using benzal bromide.

A product which can be isolated from the various benzylidenation reaction mixtures was obtained as follows. When benzal bromide in excess pyridine was refluxed for 5 – 6 h or allowed to stand at 50 – 60° during 24 h, a crystalline mass was deposited. This was filtered off and recrystallized from acetic acid. The product, which was not particularly hygroscopic, was soluble in water, soluble with difficulty in dimethyl sulphoxide, dimethyl formamide and pyridine. A solution in water gave a positive halogen test (aqueous silver nitrate-dissolution of the precipitate in aqueous ammonia). The properties are consistent with the product being dipyridiniumphenylmethane dibromide.[3a] Dissolution in water and osmometric molecular weight determination gave a molecular weight of 124. The expected molecular weight of dipyridiniumphenylmethane dibromide in water (ionization gives three particles per mol) is 136. Treatment of methyl α-D-glucopyranoside in pyridine at reflux temperature with dipyridiniumphenylmethane dibromide, followed by acetylation of the product with acetic anhydride, afforded a 59 % yield of methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside. While this does not prove the intermediary of the dipyridinium salt in the formation of the benzylidene derivative from the glycoside and a benzal halide in pyridine, the possibility of at least part of the product arising from the dipyridinium salt is clearly indicated. Other possible intermediates include bromophenylpyridiniummethane bromide.

In an effort to raise the yield of the 4,6-acetal beyond the 69 % reported above for the reaction of methyl α-D-glucopyranoside with benzal chloride in pyridine, the glucoside was treated with 2.2 molar equivalents of benzal chloride in pyridine. The product was treated with acetic anhydride in the usual manner. In addition to the expected product, methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside, a minor product was obtained in about 15 % yield. Isolation by TLC, examination by NMR and by elemental analysis showed the product to be methyl 2,3:4,6-di-*O*-benzylidene-α-D-glucopyranoside, II. The difference in chemical shifts (0.03 Hz) for the two

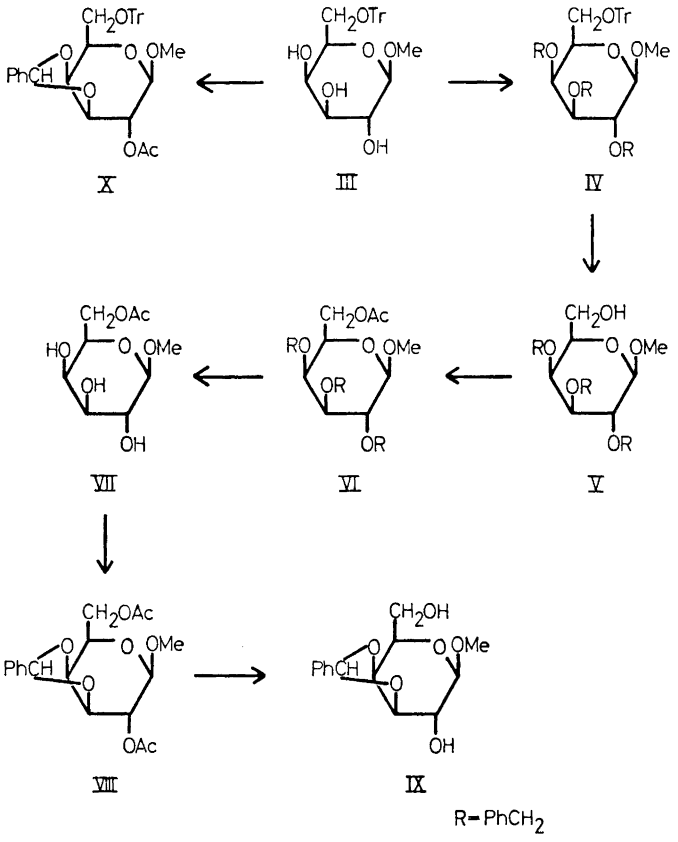


II

2,3-*O*-benzylidene methine protons was too small for deciding which stereoisomer[4] was present in the recrystallized product.

The synthetic utility of the benzylidenation method was demonstrated by the synthesis, in good yields, of 2-phenyl-1,3-dioxolan,[5] 4-methyl-2-phenyl-1,3-dioxolan,[6] 2-phenyl-1,3-dioxan,[7] and 2-phenyl-1,3-dioxepan.[8]

Methyl 3,4-*O*-benzylidene-β-D-galactopyranoside was required in connection with other studies. Its synthesis was deemed a suitable test for ascertaining whether benzylidene groups can be introduced into glycosides containing acetyl groups which in normal, acid-catalyzed benzylidenations may be prone to migration. Methyl 6-*O*-trityl-β-D-galactopyranoside (III) [9] was benzylated to



X III IV V VI VII VIII IX

yield the crystalline 2,3,4-tri-*O*-benzyl ether IV in 50 % yield. Detritylation of IV yielded crystalline methyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside V in 96 % yield. Acetylation of V afforded the crystalline 6-acetate VI in quantitative yield. Catalytic hydrogenation of VI afforded methyl 6-*O*-acetyl-β-D-galactopyranoside VII, crystalline and in nearly quantitative yield. The 6-acetate VII was benzylidenated with benzal bromide in refluxing pyridine. The product was acetylated with acetic anhydride in the same solvent. Work-up afforded crystalline VIII in a 20 % yield. The narrow m.p. range and the NMR spectrum indicated one stereoisomer only.[4] Examination of the crude reaction mixture revealed the presence of a minor amount of the other stereo-

somer, which was obtained in crystalline form following chromatographic purification. The chemical shifts for the benzylic protons indicated that the major stereoisomer of VIII isolated had an *endo* benzylic proton. A yield of 58 % of VIII, obtained as a crystalline mixture of isomers in which the one with an *endo* benzylic proton again predominated, was obtained by the benzylidenation of VII using benzal chloride instead of benzal bromide. Although, therefore, a higher yield of the product was obtained in the latter experiment, the two preparations are not directly comparable since in the latter one a higher proportion of the halide and modified reaction conditions were used. Deacetylation of VIII (*endo* or *exo*) afforded the corresponding stereoisomeric methyl 3,4-*O*-benzylidene-β-D-galactopyranosides (IX).

Due to their acid lability, the use of trityl groups as blocking groups in the molecule is precluded in acid catalyzed benzylidenations. The present method circumvents this difficulty. Methyl 6-*O*-trityl-β-D-galactopyranoside (III) was treated with benzal bromide in pyridine and then with acetic anhydride as usual. Methyl 2-*O*-acetyl-3,4,-*O*-benzylidene-6-*O*-trityl-β-D-galactopyranoside X was obtained in a yield of 27 %. In addition, a 7 % yield of methyl 2,6-di-*O*-acetyl-3,4-*O*-benzylidene-β-D-galactopyranoside was obtained, presumably arising through detritylation following the benzylidation.

The benzylidenation method presented in this and in the previous paper [2] clearly is of synthetic utility. Being irreversible it may be used for the synthesis of dioxolan derivatives which are not readily accessible in acid-catalyzed, reversible reactions. Benzylidene groups may be introduced into molecules containing acid-labile (trityl) and base-labile (acetyl) groups. The synthesis of methyl 3,4-*O*-benzylidene-6-*O*-trityl-β-D-galactoside affords easy access to 2-substituted galactose derivatives. A similar synthesis of 4-substituted mannoses *via* an analogous synthesis of methyl 2,3-*O*-benzylidene-6-*O*-trityl-α-D-mannopyranoside is clearly indicated.

Although the benzylidenation reaction would seem to be irreversible, the thermodynamically most stable product is obtained in each instance.

EXPERIMENTAL

Concentrations were performed at reduced pressure. Melting points are corrected. Optical rotations were determined at room temperature (20 – 22°) with a Perkin-Elmer 141 polarimeter. NMR spectra were recorded with a Varian A-60 A spectrometer using t tramethylsilane as internal reference. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane. Pertinent parts of the spectra are given below. The remainder of the spectra was invariably in accordance with the presumed structures. TLC was performed on silica gel (Merck DC-Fertigplatten Kieselgel F_{254} for analytical and 2 mm PSC-Fertigplatten Kieselgel F_{254} for preparative separations). Benzylidenations were generally followed by TLC using ethyl acetate as solvent. GLC was run on a Perkin-Elmer F11 instrument fitted with a 6′ × 1/4″ glass column, packed with 3 % ECNSS-M on Gas Chrom Q, 100/120 mesh. The nitrogen flow rate was 30 ml/min.

*Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside.*[3] (a) Methyl α-D-glucopyranoside (0.5 g) and benzal chloride (0.4 ml) in pyridine (10 ml) were refluxed for 8 h and then cooled. Acetic anhydride (3 ml) was added. After standing overnight at room temperature the solution was poured into water and extracted with chloroform. The combined chloroform phases were shaken with water, aqueous sodium bicarbonate and water. After drying over magnesium sulphate and filtration the solution was concentrated

to dryness. Pyridine was removed by co-distillation with toluene. The product was purified by TLC (solvent, chloroform:ethyl ether 9:1) to yield 0.63 g of product, m.p. 95 – 100°.

(b) Methyl α-D-glucopyranoside (0.5 g) and benzal bromide (0.75 g) in pyridine (10 ml) were refluxed for 1 h, acetylated and worked up as described under (a). The yield of product was 0.78 g, m.p. 95 – 100°.

Dipyridiniumphenylmethane dibromide.[3a] Refluxing of benzal bromide in excess pyridine for 5 – 6 h, or keeping the same solution at 50 – 60° during about 24 h produced a crystalline deposit. The product after recrystallization from acetic acid had m.p. 233 – 237°.

Methyl α-D-glucopyranoside (0.5 g) and dipyridiniumphenylmethane dibromide (1.0 g) in pyridine (10 ml) were refluxed for 5 h, acetylated and worked up as described above. The yield of methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside was 0.54 g, m.p. 95 – 100°.

*Methyl 2,3:4,6-di-*O*-benzylidene-α-D-glucopyranoside.* Methyl α-D-glucopyranoside (1.0 g) and benzal chloride (1.5 ml) in pyridine (15 ml) were refluxed for 8 h. The product was acetylated as described above. TLC on the reaction mixture revealed the presence of the expected methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside and, in addition, the presence of a minor component (10 – 20 %) with higher mobility on TLC. This latter product was obtained in a pure state by TLC (solvent, chloroform:ethyl ether 9:1). Recrystallization from methanol afforded material with m.p. 157 – 161°, $[\alpha]_D + 55°$ (c, 0.3 in chloroform). (Found: C 67.9; H 5.95. $C_{21}H_{22}O_6$ requires: C 68.1; H 5.99.) NMR ($CDCl_3$), mixture before crystallization, δ 3.53 (3 H) singlet, methoxyl; δ 5.63 (1 H) singlet, 4,6-*O*-benzylidene methine proton; δ 6.17 and δ 7.20 (1 H), singlets, equal intensity, 2,3-*O*-benzylidene methine protons; δ 7.42 (10 H) multiplets, aromatic.

2-Phenyl-1,3-dioxolan.[5] Ethylene glycol (6.2 g) and benzal chloride (16.2 g) in pyridine (50 ml) were refluxed for 3 h. The solution was diluted with light petroleum (60 – 80°). Precipitated pyridine hydrochloride was filtered off. The filtrate was shaken several times with water, dried over sodium sulphate, filtered, dried and concentrated. The residue was distilled at 105 – 120° and 15 mmHg to yield 9.2 g, $n_D^{25} = 1.5265$ (lit. $n_D^{25} = 1.5270$). NMR (CCl_4): δ 3.93 (4 H), narrow multiplet, δ 5.78 (1 H), singlet, benzylidene, δ 7.40, multiplet, aromatic.

2-Phenyl-4-methyl-1,3-dioxolan.[6] (a) Propane-1,2-diol (7.6 g) and benzal chloride (21 g) in pyridine (70 ml) were refluxed overnight and worked up as described above. The product was vacuum distilled at 115 – 130° at 15 mmHg to yield 12.9 g of a stereoisomeric mixture. (Found: C 73.0; H 7.21. Calc. for $C_{10}H_{12}O_2$: C 73.1; H 7.37.) NMR (CCl_4): two isomers in similar proportions, δ 1.23 and 1.33 (3 H), doublets, methyl, δ 3.28 – 3.73 (1 H), multiplet, δ 3.83 – 4.55 (2 H), multiplet, δ 5.80 and δ 5.98 (1 H), singlets, benzylidene, δ 7.45 (5 H), multiplet, aromatic, $n_D^{25} = 1.5108$ (lit. $n_D^{27} = 1.5089$).

(b) Propane-1,2-diol (7.6 g), benzaldehyde (10.6 g) and *p*-toluenesulphonic acid (0.5 g) in toluene were refluxed with the separation of water (Dean and Stark apparatus) for 2 h. The solution was neutralized with barium carbonate and worked up to yield 9.5 g of a mixture indistinguishable (NMR) from that obtained in (a). $n_D^{25} = 1.5132$ (lit. $n_D^{27} = 1.5089$).

2-Phenyl-1,3-dioxan.[7] Propane-1,3-diol (7.6 g) and benzal chloride (16.2 g) in pyridine (50 ml) were refluxed for 3 h and worked up as described above. The product was recrystallized from light petroleum (40 – 60°) to yield 9.5 g, m.p. 41 – 44° (lit. 49 – 51°).

2-Phenyl-1,3-dioxepan.[8] Butane-1,4-diol (4.5 g) and benzal chloride (8.0 g) in pyridine (50 ml) were refluxed for 5 h and worked up as described above. The product was distilled at 135° and 14 mmHg to yield 4.2 g, $n_D^{25} = 1.5299$. NMR (CCl_4): δ 1.68 (4 H), multiplet, δ 3.78 (4 H), multiplet, δ 5.69 (1 H), singlet, benzylidene, δ 7.42 (5 H), multiplet, aromatic. (Found: C 74.0; H 7.84. Calc. for $C_{11}H_{14}O_2$: C 74.1; H 7.92.)

*Methyl 2,3,4-tri-*O*-benzyl-6-*O*-triphenylmethyl-β-D-galactopyranoside (IV).* Methyl 6-*O*-triphenylmethyl-β-D-galactopyranoside (III)[9] (24.5 g), benzyl chloride (200 g) and powdered sodium hydroxide (60 g) were vigorously stirred for 4 h at 130 – 140°. Methanol was added and the mixture allowed to stand with stirring during 2 h. The product was partitioned between chloroform and water. The chloroform phase was concentrated at a final bath temperature of 70° and then concentrated several times at this temperature following additions of water. The residue was concentrated at 140° and 0.1 mmHg in order to remove dibenzyl ether. The final residue crystallized from ethyl ether:light

petroleum (40 – 60°), 19.7 g, m.p. 125 – 128°. The crude material was sufficiently pure for use in the next step. A small quantity was recrystallized from methanol to yield material with m.p. 135 – 136°, $[\alpha]_D$ + 2.5° (*c*, 1.0 in chloroform). (Found: C 79.8: H 6.65. $C_{47}H_{46}O_6$ requires: C 79.9; H 6.56.) NMR ($CDCl_3$): δ 3.58 (3 H), singlet, methoxyl, δ 4.65 (4 H) and δ 4.73 (2 H), benzyl, δ 7.3 – 7.7 (30 H), multiplets, aromatic.

*Methyl 2,3,4-tri-*O*-benzyl-β-*D*-galactopyranoside (V).* The above 6-*O*-trityl derivative (19.7 g) in 200 ml 80 % aqueous acetic acid was kept on a boiling water bath for 10 min and then concentrated. The residue crystallized upon the addition of water. Triphenylmethanol crystallized out on dissolving the mass in the minimum amount of hot methanol and then standing at + 5° overnight. Following filtration, the mother liquor was concentrated and the residue crystallized from ethyl ether:light petroleum (60 – 80°). Recrystallization from the same solvents yielded 12.5 g, m.p. 92 – 95°, slightly contaminated with triphenylmethanol (TLC). A small quantity was recrystallized from cyclohexane to yield material with m.p. 103 – 105°, $[\alpha]_D$ – 22° (*c*, 0.7 in chloroform). (Found: C 72.2; H 6.98. $C_{28}H_{32}O_6$ requires: C 72.4; H 6.94.) NMR ($CDCl_3$); δ 1.7 – 2.3 ppm (1 H), broad singlets, hydroxyl, δ 3.57 (3 H), singlet, methoxyl, δ 4.7 – 5.0, three signals (6 H), benzyl, δ 7.46 (15 H), narrow multiplet, aromatic.

*Methyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-*D*-galactopyranoside (VI).* Methyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (12.1 g) was acetylated with acetic anhydride (25 ml) in pyridine (50 ml) on a boiling water bath for 15 min and then poured into water (1000 ml whereupon the product crystallized. Filtration and drying in a vacuum over (in turn) silica gel, concentrated sulphuric acid and sodium hydroxide pellets yielded 13.1 g, m.p. 139 – 141°. Recrystallization of a small amount from methanol yielded material with m.p. 142 – 143°, $[\alpha]_D$ – 21° (*c*, 0.9 in chloroform). (Found: C 71.0; H 6.92. $C_{30}H_{34}O_7$ requires: C 71.1; H 6.77.) NMR ($CDCl_3$): δ 1.98 (3 H), singlet, acetoxy, δ 3.58 (3 H), singlet, methoxyl, δ 7.43 (15 H), aromatic.

*Methyl 6-*O*-acetyl-β-*D*-galactopyranoside (VII).* Methyl 6-*O*-acetyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (7.8 g) was hydrogenated with palladium on carbon in methanol: ethyl acetate (1:1, 100 ml) to yield a material which crystallized from methanol:ethyl acetate, 3.7 g, m.p. 142 – 145°, $[\alpha]_D$ – 14° (*c*, 0.4 in ethanol) and $[\alpha]_D$ – 1.1° (*c*, 0.4 in water). The material was homogeneous on thin layer chromatography (solvent ethyl acetate:methanol:water 80:15:5) and paper chromatography (solvent water-saturated butanone). (Found: C 45.7; H 6.99. $C_9H_{16}O_7$ requires: C 45.8; H 6.83.) NMR in CD_3OD showed CH_3 in acetoxyl and CH_3 in methoxyl in a ratio of 1:1.

*Methyl 2,6-di-*O*-acetyl-3,4-*O*-benzylidene-β-*D*-galactopyranosides (VIII).* (a) Methyl 6-*O*-acetyl-β-D-galactopyranoside (3.2 g) and benzal bromide (4.1 g) in pyridine (75 ml) were refluxed for 1.75 h. More benzal bromide (0.5 g) was added and the solution was refluxed for another 0.25 h. The solution was allowed to cool. Acetic anhydride (10 ml) was added to the still warm solution which was allowed to stand during 1 – 2 h. The solution was partitioned between water and benzene. The combined benzene solutions were washed with aqueous sodium bicarbonate and then water, dried over sodium sulphate, filtered and concentrated. To the residue was added toluene and the solution was concentrated. Part of the material crystallized from ether:light petroleum (40 – 60°). Recrystallization from ethanol yielded 1.0 g (20 %), m.p. 130 – 132°, $[\alpha]_D$ + 19° (*c*, 0.5 in chloroform). (Found: C 59.0; H 6.06. $C_{18}H_{22}O_8$ requires: C 59.0; H 6.05.) The NMR indicated the presence of one stereoisomer only ($CDCl_3$): δ 2.11 (3 H) and δ 2.17 (3 H), singlets, acetoxy, δ 3.58 (3 H), singlet, methoxyl, δ 6.31 (1 H), singlet, benzylidene, δ 7.51 (5 H), multiplet, aromatic.

The mother liquor was examined by TLC (chloroform:ethyl ether 7:3). In addition to the isomeric methyl 6-*O*-acetyl-3,4-*O*-benzylidene-β-D-galactopyranoside described below, it contained another benzylidene derivative, presumably the 4,6-linked isomer. Deacetylation and fractional crystallization yielded 130 mg material which upon reacetylation yielded the other 3,4-*O*-benzylidene derivative, m.p. 114 – 115°, $[\alpha]_D$ + 31° (*c*, 0.25 in chloroform). (Found: C 58.8; H 6.18. $C_{18}H_{22}O_8$ requires: C 59.0; H 6.05.) NMR ($CDCl_3$): δ 3.55 (3 H), singlet, methoxyl, δ 6.00 (1 H), singlet, benzylidene (values taken from NMR on mixture with above stereoisomeric 3,4-benzylidene derivative).

(b) Methyl 6-*O*-acetyl-β-D-galactopyranoside (VII) (1.77 g) and benzal chloride (1.61 g) in pyridine (25 ml) were refluxed for 5 h. More benzal chloride (1.61 g) was added and the mixture refluxed during a further 3 h. The product was acetylated by the addition of acetic anhydride (5 ml) and worked up as described above under (a). The crude crystal-

line product was washed with light petroleum (60 – 80°) in order to remove excess benzal chloride. The remaining product (2.74 g) was purified by passage through a silica gel column (25 g silica gel, solvent, chloroform:ethyl ether 9:1). The product crystallized from ethyl ether:light petroleum to yield 1.60 g of product, m.p. 113 – 117°. NMR showed the presence of both stereoisomers of VIII (see above for NMR parameters), the one with an *endo* benzylidene methine proton predominating.

Methyl 3,4-O-benzylidene-β-D-galactopyranosides (IX). Methyl 2,6-di-*O*-acetyl-3,4-*O*-benzylidene-β-D-galactopyranoside (1.0 g, m.p. 130 – 132°) was deacetylated in methanol (60 ml) containing methanol saturated with ammonia (12 ml) at room temperature overnight. Concentration and recrystallization from ethyl acetate gave 0.55 g, m.p. 139 – 141°, $[\alpha]_D$ +18° (*c*, 0.40 in ethanol). (Found: C 59.7; H 6.57. $C_{14}H_{18}O_6$ requires: C 59.6; H 6.43.) NMR ($CDCl_3$): δ 3.58 (3 H), singlet, methoxyl, δ 6.15 (1 H), benzylidene, δ 7.42 (5 H), multiplet, aromatic (values taken from mixture of stereoisomers).

Deacetylation of the mother liquor from the preparation of methyl 2,6-di-*O*-acetyl-3,4-*O*-benzylidene-β-D-galactopyranoside and fractional crystallization as described under (a) above yielded the stereoisomeric IX, m.p. 165 – 168° (softening at about 130°), $[\alpha]_D$ −11° (*c*, 0.34 i ethanol). (Found: C 59.4; H 6.60. $C_{14}H_{18}O_6$ requires: C 59.6; H 6.43.) NMR ($CDCl_3$): δ 3.57 (3 H), singlet, methoxyl, δ 5.97 (1 H), benzylidene, δ 7.45 (5 H), aromatic (values taken from mixture of stereoisomers).

Methyl 2-O-acetyl-3,4-O-benzylidene-6-O-triphenylmethyl-β-D-galactopyranosides (X). Methyl 6-*O*-triphenylmethyl-β-D-galactopyranoside [9] (12.0 g) and benzal bromide (7.5 g) in pyridine (50 ml) were refluxed for 2.5 h. Acetic anhydride (25 ml) was added and the product was worked up as described in the above benzylidenation. A crude yield of 12 g benzylidene derivative was obtained. This was added to the top of a 300 g silica gel column which was eluted with chloroform:ethyl ether 9:1. A fraction containing 1.55 g pure material was obtained (see below) and 5.9 g of material which by preparative TLC was shown to contain 45 % of the desired product, bringing the total yield of the product to 27 %. The material crystallized after further purification, m.p. 68 – 77°, $[\alpha]_D$ −5° (*c*, 0.5 in chloroform). The isomer distribution by NMR was 4:1. (Found for the stereoisomeric mixture: C 74.4; H 6.28. $C_{35}H_{34}O_7$ requires: C 74.2; H 6.05.) NMR ($CDCl_3$): δ 2.05 and 2.12 (major) (3 H), acetoxy, δ 5.87 and 6.19 (major) (1 H), benzylidene.

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