The Allyl Ether as a Protecting Group in Carbohydrate Chemistry. Part VI.[1] The Allyl Ether as a 'Temporary' Protecting Group in Oligosaccharide Synthesis

By **Patricia A. Gent** and **Roy Gigg,*** Laboratory of Lipid and General Chemistry, National Institute for Medical Research, Mill Hill, London NW7 1AA

Allyl 2.3.4-tri-*O*-benzyl-6-*O*-but-2-enyl-α-D-galactopyranoside was treated with chloro(tristriphenylphosphine)-rhodium(I) to give predominantly the corresponding prop-1-enyl glycoside. The prop-1-enyl group was removed by hydrolysis and the free sugar was converted into 2.3.4-tri-*O*-benzyl-6-*O*-but-2-enyl-α-D-galactopyranosyl chloride. which was condensed with benzyl 2.3.4-tri-*O*-benzyl-α-D-galactopyranoside to give an α-linked disaccharide in high yield. The but-2-enyl group was removed to give benzyl 6-*O*-(2.3.4-tri-*O*-benzyl-α-D-galactopyranosyl)-2.3.4-tri-*O*-benzyl-α-D-galactopyranoside. a suitable intermediate for the synthesis of trisaccharides. The fully benzylated derivatives of benzyl 6-*O*-(α- and β-D-galactopyranosyl)-α-D-galactopyranose were also prepared. 6-*O*-Allyl-2.3.4-tri-*O*-benzyl-D-glucopyranose was prepared and the allyl group was removed by isomerisation with chloro(tristriphenylphosphine)rhodium(I) and subsequent acidic hydrolysis.

In Part V [1] we outlined a general method of oligosaccharide synthesis in which benzyl groups were used for 'persistent' [2] blocking and allyl groups (including 2- and 3-methylallyl groups) for 'temporary' [2] blocking. We described a route to some α-linked disaccharides in which 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride and some tri-*O*-benzyl derivatives of benzyl-α-D-galactopyranoside were used as aglycones. For the success of the general method it was necessary to show that it was possible to prepare glycosyl halides containing allyl groups and we have now investigated the preparation of a partially benzylated, partially allylated galactosyl chloride and its use in the synthesis of an α-linked disaccharide by the general methods described in the previous paper.[1]

We chose to investigate the preparation of 2,3,4-tri-*O*-benzyl-6-*O*-but-2-enyl-α-D-galactopyranosyl chloride (6) as a model glycosyl chloride, and for this purpose allyl 6-*O*-but-2-enyl-α-D-galactopyranoside (1) [3] was converted into the benzyl ether (2). In a preliminary communication [4a] we have shown that the but-2-enyl group is isomerised much more slowly than the allyl group by chloro(tristriphenylphosphine)rhodium(I), and that compound (2) can be converted into the prop-1-enyl glycoside (3) in good yield by the rhodium complex. Hydrolytic removal of the prop-1-enyl group of compound (3) by mercury(II) chloride [5] gave the free sugar (4), which was purified by chromatography on neutral

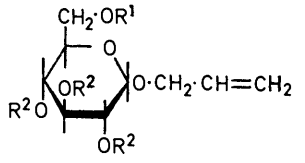
[1] Part V, P. A. Gent and R. Gigg, *J.C.S. Perkin I*, 1974, 1446.
[2] P. J. Pfäffli, S. H. Hixon, and L. Anderson, *Carbohydrate Res.*, 1972, **23**, 195.
[3] P. A. Gent, R. Gigg, and R. Conant, *J.C.S. Perkin I*, 1972, 1535.
[4] (*a*) P. A. Gent and R. Gigg, *J.C.S. Chem. Comm.*, 1974, 277; (*b*) E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1973, **38**, 3224.
[5] R. Gigg and C. D. Warren, *J. Chem. Soc.* (*C*), 1968, 1903.

alumina and obtained as a syrup. For characterisation, compound (4) was reduced with sodium borohydride and the 2,3,4-tri-*O*-benzyl-6-*O*-but-2-enyl-D-galactitol obtained was treated with potassium t-butoxide in dimethyl sulphoxide to remove [3] the but-2-enyl group and give the known [6] 2,3,4-tri-*O*-benzyl-D-galactitol.

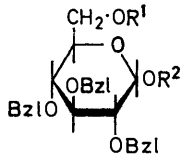
We looked at various methods for the conversion of the free sugar (4) into the chloride (6). Thionyl chloride in the presence of zinc chloride, which was a useful reagent for the preparation of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride,[1,7] produced some decomposition presumably due to reaction with the but-2-enyl group. The chloride (6) was however readily prepared by treating the crystalline *p*-nitrobenzoate (5) with hydrogen chloride in ether–dichloromethane and the n.m.r. spectrum indicated that it was the α-isomer.

The chloride (6) was condensed with benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside [1] (2 mol. equiv.) in the presence of tetraethylammonium chloride and triethylamine in dichloromethane at 80° [1] during 17 h and the product was chromatographed on alumina to obtain a disaccharide fraction (*ca.* 70%, based on chloride) which was shown by t.l.c. to contain two isomers in the ratio *ca.* 9 : 1. The pure α-linked protected disaccharide (7) was obtained by crystallisation. The but-2-enyl group was cleaved from compound (7) by the action of potassium t-butoxide in dimethyl sulphoxide [3] to give the crystalline alcohol (8), which is a suitable intermediate for elaboration into a trisaccharide. A portion of compound (8) was converted into the methyl ether (9), which was hydrogenated over palladium–charcoal, and the product was hydrolysed with acid. Chromatography indicated the presence of both galactose and 6-*O*-methylgalactose running concurrently with authentic standards.

The protected disaccharide (8) was also hydrogenolysed to give 6-*O*-(α-D-galactopyranosyl)-D-galactose (10), with properties similar to those reported previously,[8-10] and which on reduction with sodium borohydride and subsequent acetylation gave crystalline 6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-1,2,3,4-tetra-*O*-acetyl-D-galactitol.[9] The alcohol (8) was benzylated to give the crystalline fully benzylated α-linked disaccharide (11), which was prepared for comparison with the corresponding β-linked disaccharide (14), obtained as follows. Benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside [1] and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide were condensed under Koenigs–Knorr conditions to give compound (12), which was deacylated

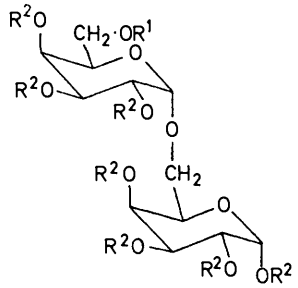


(16) $R^1 = CPh_3$, $R^2 = H$
(17) $R^1 = CPh_3$, $R^2 = Bzl$
(18) $R^1 = H$, $R^2 = Bzl$

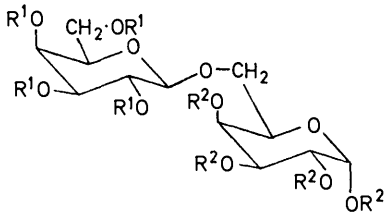


(19) $R^1 = H$, $R^2 = OCH{=}CHMe$
(20) $R^1 = CH_2{\cdot}CH{=}CH_2$, $R^2 = CH{=}CHMe$
(21) $R^1 = CH_2{\cdot}CH{=}CH_2$, $R^2 = H$
(22) $R^1 = CH{=}CHMe$, $R^2 = H$
(23) $R^1 = R^2 = H$

Bzl = CH_2Ph



(7) $R^1 = CH_2{\cdot}CH{=}CHMe$, $R^2 = Bzl$
(8) $R^1 = H$, $R^2 = Bzl$
(9) $R^1 = Me$, $R^2 = Bzl$
(10) $R^1 = R^2 = H$
(11) $R^1 = R^2 = Bzl$



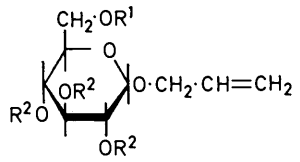
(12) $R^1 = Ac$, $R^2 = Bzl$
(13) $R^1 = H$, $R^2 = Bzl$
(14) $R^1 = R^2 = Bzl$
(15) $R^1 = R^2 = H$

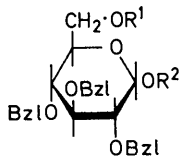
Bzl = CH_2Ph

[6] R. Gigg and C. D. Warren, *J. Chem. Soc.*, 1965, 2205.
[7] V. D. Grob, T. G. Squires, and J. R. Vercelotti, *Carbohydrate Res.*, 1969, **10**, 595.
[8] T. R. Ingle and B. V. Bhide, *J. Indian Chem. Soc.*, 1958, **35**, 516.
[9] M. J. Clancy and W. J. Whelan, *Arch. Biochem. Biophys.*, 1967, **118**, 724.
[10] R. U. Lemieux, K. James, and T. L. Nagabhushan, *Canad. J. Chem.*, 1973, **51**, 42.

and benzylated to give the fully benzylated β-linked disaccharide (14) as a syrup. Hydrogenolysis of compound (14) gave 6-*O*-(β-D-galactopyranosyl)-D-galactose (15).[11]

An alternative route to 6-*O*-allyl-2,3,4-tri-*O*-benzyl derivatives of glycopyranoses was investigated with D-glucose. A mixture of the anomers of allyl D-glucopyranoside [12] was converted into the trityl ethers (16), and these were converted into the benzyl ethers (17); acidic hydrolysis of compounds (17) gave the anomers of allyl 2,3,4-tri-*O*-benzyl-D-glucopyranoside (18).





(16) $R^1 = CPh_3$, $R^2 = H$
(17) $R^1 = CPh_3$, $R^2 = Bzl$
(18) $R^1 = H$, $R^2 = Bzl$

Bzl = CH_2Ph

(19) $R^1 = H$, $R^2 = CH{=}CHMe$
(20) $R^1 = CH_2{\cdot}CH{=}CH_2$, $R^2 = CH{=}CHMe$
(21) $R^1 = CH_2{\cdot}CH{=}CH_2$, $R^2 = H$
(22) $R^1 = CH{=}CHMe$, $R^2 = H$
(23) $R^1 = R^2 = H$

Isomerisation [13] of the anomers (18) with potassium t-butoxide in dimethyl sulphoxide gave the corresponding anomeric mixture of prop-1-enyl glycosides (19). Allylation of compounds (19) gave the anomers (20), which were hydrolysed with dilute acid to give crystalline 6-*O*-allyl-2,3,4-tri-*O*-benzyl-D-glucopyranose (21). This route is also applicable to the preparation of the corresponding 6-*O*-but-2-enyl and 6-*O*-2-methylallyl ethers.

We have shown [4a] that chloro(tristriphenylphosphine)-rhodium(I) does not abstract carbon monoxide from the aldehyde group of free sugars under the conditions required for the isomerisation of allyl ethers. Compound (21) was therefore characterised by isomerisation [4a] with the rhodium complex to the prop-1-enyl ether (22), which was subsequently hydrolysed with dilute acid to give the known [14] 2,3,4-tri-*O*-benzyl-D-glucopyranose (23). Base is usually added during isomerisations with the rhodium complex [4b] to prevent hydrolysis of the vinyl ethers in the reaction medium. However in this case base was not added (because of its possible deleterious effect on the free sugar) and the prop-1-enyl group was removed to a considerable extent during the reaction. Carbon monoxide is abstracted [4b] from the propionaldehyde (liberated on hydrolysis of the prop-1-enyl ether) by the rhodium complex to give a catalytically less active rhodium complex; this could account for the long time required for the isomerisation.

EXPERIMENTAL

Solvents were evaporated off under reduced pressure. Optical rotations were measured at 22—24° with a Bendix Automatic Polarimeter. T.l.c. was carried out on microscope slides coated with silica gel G. The light petroleum used had b.p. 40—60° unless otherwise stated. Potassium t-butoxide was obtained from Courtorch Chemicals Ltd., Marsworth, Herts.

2,3,4-Tri-O-benzyl-6-O-but-2-enyl-1-O-p-nitrobenzoyl-β-D-galactopyranose (5).—Allyl 6-*O*-but-2-enyl-α-D-galactopyranoside (1) [3] (6·3 g) was treated with an excess of benzyl chloride and sodium hydride in dimethylformamide at 55° for 1·5 h. T.l.c. (ether–light petroleum, 1 : 2) then indicated conversion of compound (1) into the product (2) (R_F 0·4), which was isolated in the usual way and chromatographed on alumina. Elution with ether–light petroleum (1 : 2) gave first the product (2) contaminated with some less polar impurity (7·8 g), and then pure compound (2) (5·8 g) as a syrup. Compound (2) (5·3 g), ethanol (160 ml), benzene (70 ml), water (23 ml), diazabicyclo[2.2.2]octane (0·94 g), and chloro(tristriphenylphosphine)rhodium(I) (0·13 g) [4a] were mixed at 20° and the solution was then heated under reflux for 3·25 h. T.l.c. (ether–light petroleum, 1 : 2) then indicated the presence of *ca.* 10% starting material (2) (R_F 0·4), a major product (3) (R_F 0·5), and *ca.* 10% of another product (due to isomerisation of both allyl and but-2-enyl groups [4a]) (R_F 0·7). The mixture was cooled, diluted with water, and extracted with ether; the extract was washed with saturated potassium chloride solution, acidified to *ca.* pH 2 with hydrochloric acid, then washed with saturated potassium chloride solution, dried ($MgSO_4$), and evaporated. Mercury(II) chloride (3·8 g) was added to a solution of the crude product (5·4 g) in acetone–water (9 : 1; 100 ml) and the solution was kept at 20° for 0·5 h. T.l.c. (ether–light petroleum, 1 : 1) then indicated the presence of a major product (R_F 0·4) with minor contaminants (R_F 0 and 0·8). The products were isolated in the usual way [5] and chromatographed on alumina. Elution with ether–light petroleum (2 : 1) removed the non-polar contaminant [starting material (2)] and elution with ether–methanol (32 : 1) gave 2,3,4-tri-*O*-benzyl-6-*O*-but-2-enyl-D-galactopyranose (4) (3 g) as a syrup.

For characterisation, compound (4) (200 mg; R_F 0·6 in ether–light petroleum, 2 : 1) was reduced with sodium borohydride in ethanol to give 2,3,4-tri-*O*-benzyl-6-*O*-but-2-enyl-D-galactitol (R_F 0·4). Glacial acetic acid was added to decompose the excess of borohydride and the ethanol was evaporated off. Water and ether were added to the residue and the ethereal extract was dried ($MgSO_4$) and evaporated. Dimethyl sulphoxide (10 ml) and potassium t-butoxide (500 mg) were added to the product and the solution was kept at 40° for 2 h; t.l.c. then indicated

[11] V. M. Parikh and J. K. N. Jones, *Canad. J. Chem.*, 1966, **44**, 1531.

[12] E. A. Talley, M. D. Vale, and E. Yanovsky, *J. Amer. Chem. Soc.*, 1945, **67**, 2037; J. B. Fraser, L. N. Owen, and G. Shaw, *Biochem. J.*, 1947, **41**, 328.

[13] J. Gigg and R. Gigg, *J. Chem. Soc.* (*C*), 1966, 82.

[14] G. Zemplén, Z. Csürös, and S. Angyal, *Ber.*, 1937, **70**, 1848.

complete removal of the but-2-enyl group to give 2,3,4-tri-*O*-benzyl-D-galactitol (R_F 0·1). The solution was diluted with water and extracted with ether; the product, recrystallised from chloroform–light petroleum (b.p. 60—80°), had m.p. 116—118°, mixed m.p. (with material prepared previously [6] and recrystallised from the same solvent mixture) 115—117°, $[\alpha]_D$ −7° (*c* 1 in $CHCl_3$) {lit.,[6] m.p. 111°, $[\alpha]_D$ −9° (*c* 1 in $CHCl_3$)}. A solution of *p*-nitrobenzoyl chloride (1·8 g) in dry dichloromethane (4·6 ml) was added to a solution of 2,3,4-tri-*O*-benzyl-6-*O*-but-2-enyl-D-galactopyranose (4) (3 g) in dry dichloromethane (23 ml) containing dry pyridine (1 ml). The mixture was stirred at 20° for 6 h; t.l.c. (ether–light petroleum, 1 : 1) then showed conversion of the starting material (R_F 0·4) into the product (R_F 0·8). The product was isolated in the usual way and recrystallised from ethanol to give 2,3,4-*tri*-O-*benzyl*-6-O-*but*-2-*enyl*-1-O-p-*nitrobenzoyl*-β-D-*galactopyranose* (5) (2·3 g), m.p. 94—97°, $[\alpha]_D$ −40° (*c* 0·9 in $CHCl_3$) (Found: C, 69·8; H, 5·9; N, 2·4. $C_{38}H_{39}NO_9$ requires C, 69·8; H, 6·0; N, 2·1%).

2,3,4-*Tri*-O-*benzyl*-6-O-*but*-2-*enyl*-α-D-*galactopyranosyl Chloride* (6).—Dry ether (20 ml) saturated with hydrogen chloride was added to a solution of the *p*-nitrobenzoate (5) (2·25 g) in dry dichloromethane (30 ml) and dry hydrogen chloride was passed through the solution for 3 h. T.l.c. (ether–light petroleum, 1 : 2) then showed almost complete conversion of the starting material (R_F 0·3) into a product (R_F 0·7). The solvents were evaporated off and dry dichloromethane (5 ml) was added to the residue. The crystalline *p*-nitrobenzoic acid was filtered off and washed with dry dichloromethane and the combined filtrate and washings were evaporated. The residue was taken up in light petroleum and chromatographed on neutral silica gel (B.D.H.; 60—120 mesh); elution with light petroleum gave the *chloride* (6) (1·7 g) as a syrup, $[\alpha]_D$ +116·8° (*c* 0·9 in CH_2Cl_2) (Found: C, 71·0; H, 6·5. $C_{31}H_{35}ClO_5$ requires C, 71·15; H, 6·7%), τ 6·1 (d, $J_{1,2}$ 3·5 Hz) (indicating the α-anomer).

Benzyl 6-O-(2,3,4-*Tri*-O-*benzyl*-6-O-*but*-2-*enyl*-α-D-*galactopyranosyl*)-2,3,4-*tri*-O-*benzyl*-α-D-*galactopyranoside* (7).—2,3,4-Tri-*O*-benzyl-6-*O*-but-2-enyl-α-D-galactopyranosyl chloride (1·7 g, 3·25 mmol), benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside [1] (3·64 g, 6·7 mmol), triethylamine (0·92 ml, 6·6 mmol), dry tetraethylammonium chloride (0·54 g, 3·3 mmol), and dry dichloromethane (4 ml) were sealed in an ampoule under vacuum and kept at 80° for 17 h.[1] T.l.c. (ether–light petroleum, 1 : 1) indicated the presence of a major product (R_F 0·5) and the benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (R_F 0·2) but no chloride (6) (R_F 0·9). The mixture was processed in the usual way [1] and the products (5·8 g) were chromatographed on alumina. Elution with benzene gave the disaccharide fraction (2·3 g) and elution with benzene–methanol (32 : 1) gave first a mixture of the disaccharide and benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (1·1 g) and then the pure benzyl tri-*O*-benzylglycoside (1·5 g). T.l.c. showed that the disaccharide fraction consisted of two products in the ratio *ca.* 9 : 1. A portion (2 g) of the disaccharide fraction was recrystallised from ethyl acetate–light petroleum (b.p. 60—80°) to give the *α-linked disaccharide* (7) (1·8 g), m.p. 124—126°, $[\alpha]_D$ +66·8° (*c* 0·93 in $CHCl_3$) (Found: C, 76·8; H, 6·7. $C_{65}H_{70}O_{11}$ requires C, 76·0; H, 6·9%).

Benzyl 6-O-(2,3,4-*Tri*-O-*benzyl*-α-D-*galactopyranosyl*)-2,3,4-*tri*-O-*benzyl*-α-D-*galactopyranoside* (8).—A mixture of potassium t-butoxide (100 mg) and compound (7) (1 g) in dry dimethyl sulphoxide was stirred at 20° for 1·5 h. T.l.c. (ether–light petroleum, 2 : 1) indicated the presence of a major product (R_F 0·5), a little starting material (7) (R_F 0·8) and a minor product (R_F 0·3). The product (0·93 g) was isolated in the usual way and chromatographed on alumina. Elution with ether removed the starting material (7) and ether–methanol (99 : 1) eluted the product (0·75 g) (R_F 0·5), a portion of which crystallised from methanol gave the *alcohol* (8), m.p. 101·5—103°, $[\alpha]_D$ +60·5° (*c* 1 in $CHCl_3$) (Found: C, 75·1; H, 6·7. $C_{61}H_{64}O_{11}$ requires C, 75·3; H, 6·6%). A portion of compound (8) was treated with methyl iodide and sodium hydride in refluxing benzene and the methyl ether (9) formed was treated in methanol with hydrogen in the presence of 10% palladium–charcoal. The hydrogenation product was treated with N-hydrochloric acid at 100° for 1 h; t.l.c. of the solution on an Eastman chromagram sheet of polyamide (K541 V) in propan-1-ol–ethyl acetate–water (5 : 1 : 1) showed the presence of galactose (R_F 0·34) and 6-*O*-methylgalactose (R_F 0·58) running concurrently with authentic standards. Compound (8) was hydrogenated in methanol over 10% palladium–charcoal to give 6-*O*-(α-D-galactopyranosyl)-D-galactose (10), $[\alpha]_D$ +141·8° (*c* 0·52 in H_2O; final value) {lit.,[8] $[\alpha]_D^{28}$ +142·5° (*c* 0·5 in H_2O); lit.,[9] $[\alpha]_D$ +156°; lit.,[10] $[\alpha]_D^{22}$ +149° (*c* 0·36 in H_2O)}. The disaccharide (10) was reduced with sodium borohydride and the crude product acetylated with acetic anhydride in pyridine to give 6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-1,2,3,4-tetra-*O*-acetyl-D-galactitol, m.p. 144—146° [from ethyl acetate–light petroleum (b.p. 60—80°)], $[\alpha]_D$ +63·5° (*c* 0·5 in $CHCl_3$) {lit.,[9] m.p. 139—140°, $[\alpha]_D$ +66° ($CHCl_3$)}.

Benzyl 6-O-(2,3,4,6-*Tetra*-O-*benzyl*-α-D-*galactopyranosyl*)-2,3,4-*tri*-O-*benzyl*-α-D-*galactopyranoside* (11).—Compound (8) (195 mg) was treated with benzyl chloride and sodium hydride in tetrahydrofuran under reflux for 3 h. T.l.c. (ether–light petroleum, 1 : 1) then showed complete conversion of compound (8) (R_F 0·3) into the product (R_F 0·7), which was isolated in the usual way and recrystallised from ethyl acetate–methanol to give the *fully benzylated disaccharide* (11) (147 mg), m.p. 112—114°, $[\alpha]_D$ +61° (*c* 1 in $CHCl_3$) (Found: C, 76·85; H, 6·6. $C_{68}H_{70}O_{11}$ requires C, 76·8; H, 6·6%).

Benzyl 6-O-(2,3,4,6-*Tetra*-O-*benzyl*-β-D-*galactopyranosyl*)-2,3,4-*tri*-O-*benzyl*-α-D-*galactopyranoside* (14).—Solvent (*ca.* 20 ml) was distilled from a solution of benzyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside [1] (0·75 g) in dry nitromethane (30 ml) and dry benzene (30 ml) and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (0·75 g) and mercury(II) cyanide (0·5 g) were then added to the solution, which was kept at 40° for 22 h. T.l.c. (ether–light petroleum, 2 : 1) indicated the presence of a major product (R_F 0·25) and a small quantity of the benzyl tri-*O*-benzylglycoside (R_F 0·4) but no bromide (R_F 0·5). Bromide (0·8 g) was added and after 1 h the product (2·4 g) was isolated in the usual way [1] and chromatographed on neutral alumina. Elution with ether gave compound (12) (1·4 g) (R_F 0·25); this was dissolved in dry methanol and N-sodium methoxide in methanol (2 ml) was added. After 0·5 h, t.l.c. (chloroform–methanol, 9 : 1) showed a major product (R_F 0·5) with minor contaminants and the material was chromatographed on silica gel (B.D.H.; 60—120 mesh). Elution with chloroform–methanol (99 : 1) removed contaminants and elution with chloroform–methanol (19 : 1) gave the major product (13) (0·77 g). This was treated with benzyl

chloride and sodium hydride in dimethylformamide at 20° for 4·5 h; t.l.c. (ether–light petroleum, 1 : 1) then showed a major product (R_F 0·6) with less polar contaminants. The crude material was chromatographed on alumina. Ether–light petroleum (1 : 1) eluted the contaminants and the β-*linked disaccharide* (14) (0·68 g) was eluted with ether and obtained as a syrup, $[\alpha]_D$ +25·7° (*c* 0·56 in $CHCl_3$) (Found: C, 77·0; H, 6·6. $C_{68}H_{70}O_{11}$ requires C, 76·8; H, 6·6%). Compound (14) was hydrogenated in ethyl acetate–methanol (1 : 1) over 10% palladium–charcoal to give 6-*O*-(β-D-galactopyranosyl)-D-galactose (15), $[\alpha]_D$ +28·1° (*c* 0·73 in H_2O; final value) {lit.,[11] $[\alpha]_D^{23}$ +26 ⟶ +35·2° (48 h) (*c* 1·5 in H_2O)}.

6-O-*Allyl*-2,3,4-*tri*-O-*benzyl*-D-*glucopyranose* (21).—A solution of the anomeric mixture of allyl D-glucopyranosides [12] (5 g) and triphenylmethyl chloride (8 g) in dry pyridine (30 ml) was kept at 20° for 24 h; t.l.c. (toluene–acetone, 1 : 2) then showed complete conversion of the starting material (R_F 0·1) into the trityl ethers (16) (R_F 0·8). The solution was diluted with water and the product was extracted with ethyl acetate. The extract was washed with ice-cold N-hydrochloric acid and saturated potassium chloride solution and dried (K_2CO_3). The extract was evaporated to give the crude trityl ethers (16), which were treated with benzyl chloride and sodium hydride in dimethylformamide to give the benzyl ethers (17) (R_F 0·75 in toluene–acetone, 2 : 1). The product was isolated in the usual way and treated with N-hydrochloric acid–acetone (1 : 10; 100 ml) at reflux for 2 h; t.l.c. (ether–light petroleum, 1 : 1) then showed the presence of the alcohols (18) (R_F 0·35 and 0·45) and triphenylmethanol (R_F 0·9). The acid was neutralised with an excess of sodium hydrogen carbonate and the solvents were evaporated off. The residue was extracted with ether and the extract dried (K_2CO_3) and evaporated, and the products were chromatographed on silica gel. Elution with ether–light petroleum (1 : 1) first gave the triphenylmethanol and then the allyl glycosides (18) (8 g). Compounds (18) were isomerised [13] with potassium t-butoxide in dimethyl sulphoxide; t.l.c. (ether–light petroleum, 1 : 1) showed conversion of the allyl glycosides (18) (R_F 0·35 and 0·45) into the prop-1-enyl glycosides (19) (R_F 0·45 and 0·55). The solution was diluted with water and extracted with ether and the prop-1-enyl glycosides (19) were treated with an excess of allyl bromide and sodium hydride in benzene at reflux to give the prop-1-enyl 6-*O*-allyl-2,3,4-tri-*O*-benzyl-D-glucopyranosides (20) (R_F 0·7). Compounds (20) were isolated in the usual way and treated with N-hydrochloric acid–acetone (1 : 9; 100 ml) at reflux for 30 min to give the free sugar (21) (R_F 0·3). The product was isolated in the usual way and recrystallised from acetate–light petroleum (b.p. 60—80°) and from ethyl methanol–water (10 : 1) to give 6-O-*allyl*-2,3,4-*tri*-O-*benzyl*-D-*glucopyranose* (21), m.p. 132—134°, $[\alpha]_D$ +11·7° (*c* 1 in $CHCl_3$) (Found: C, 73·9; H, 7·1. $C_{30}H_{34}O_6$ requires C, 73·4; H, 7·0%). Compound (21) (500 mg) in ethanol–benzene–water (7 : 3 : 1) (25 ml) containing chloro(tristriphenylphosphine)-rhodium(I) (100 mg) was heated under reflux for 10 h; t.l.c. (ether–light petroleum, 1 : 1) then showed conversion of the anomers of compound (21) (R_F 0·3) into the anomers of 2,3,4-tri-*O*-benzyl-6-*O*-prop-1-enyl-D-glucopyranose (22) (R_F 0·4 and 0·55) together with some hydrolysis product, 2,3,4-tri-*O*-benzyl-D-glucopyranose (R_F 0·1). The solution was filtered and the solvents evaporated off, and the residue (still containing rhodium derivatives) was taken up in N-hydrochloric acid–acetone (1 : 9; 50 ml) and heated under reflux for 15 min. T.l.c. then showed complete removal of the prop-1-enyl group. The solution was diluted with water and the acetone was evaporated off. Ether was added to the aqueous residue and the mixture was filtered (to remove rhodium derivatives); the ethereal layer was separated, washed with water, dried ($MgSO_4$), and evaporated. The product was recrystallised from chloroform–light petroleum (b.p. 60—80°) and aqueous ethanol to give 2,3,4-tri-*O*-benzyl-D-glucopyranose, m.p. 90—92°, $[\alpha]_D$ +15·2 ⟶ +16·6° (final) (*c* 1 in EtOH) {lit.,[14] m.p. 90—91°, $[\alpha]_D$ +19·6° ⟶ +18·8° (EtOH)}.

We thank Mr. R. Conant and Mr. N. Schunmann for technical assistance.

[4/712 *Received*, 8*th April*, 1974]