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THE SELECTIVE BENZOYLATION OF MONOSACCHARIDES

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ABSTRACT

The selective benzoylation of monosaccharides can be accomplished, with little or no anomerisation, to give synthetically useful benzoate derivatives. Thus, α-D-glucopyranose and α-D-mannopyranose 1,2,3,6-tetrabenzoates, β-L-arabinopyranose 1,2,3-tribenzoate, and α-D-xylopyranose 1,2,4-tribenzoate were prepared. Circular dichroism measurements have been used to confirm the structures of some of these benzoates. Attempted azide displacement of the sulphonate group in 1,2,3,6-tetra-*O*-benzoyl-4-*O*-methanesulphonyl-α-D-glucopyranose resulted in rearrangement to give 1,4-anhydro-β-D-galactopyranose tribenzoate, but normal displacement occurred for 1,2,3-tri-*O*-benzoyl-4-*O*-methanesulphonyl-β-L-arabinopyranose.

INTRODUCTION

Previous investigations in this[1,2] and other[3–6] laboratories have shown the usefulness of selective esterification (especially benzoylation) of pyranosides. Monosaccharides may also be converted in good yield into partially esterified derivatives, provided precautions are taken to minimise anomerisation. The ketoses sorbose and fructose have been converted into benzoate derivatives in which the anomeric hydroxyl group, being the most sterically hindered, is unesterified[7,8]; more recently, selective esterifications of some disaccharides have been reported[9,10].

Synthetic routes which utilise selective esterification can be shortened by using a monosaccharide instead of a glycoside as starting material, and anomeric acyloxy groups are more readily replaced by halogen than are alkoxy groups. We now report synthetically useful, selective benzoylations of some monosaccharide aldoses.

RESULTS AND DISCUSSION

Treatment of α-D-glucopyranose with 4.2 molar equivalents of benzoyl chloride in anhydrous pyridine at −35° gave a mixture containing mainly penta- and tetrabenzoates. α-D-Glucopyranose 1,2,3,6-tetrabenzoate (37%), contaminated with a

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trace of pentabenzoate, was crystallised from this mixture, and chromatography of the mother liquor on silica gel yielded another 13% of homogeneous tetrabenzoate. In contrast, an improved preparation of β-D-glucopyranose 1,2,3,6-tetrabenzoate was recently reported[11] which involved four steps from D-glucose. The structure of the tetrabenzoate was established by its conversion, *via* the crystalline α-bromide[12], into the methyl β-glycoside derivative, and by its p.m.r. spectrum. The protons that are α to a benzoyloxy group are normally the most deshielded of the pyranose protons, and the signal for H-4, the proton attached to the hydroxyl-substituted carbon, was a triplet (J 10 Hz) at τ 5.98, to high field of the other pyranose protons; H-1, H-2, and H-3 were the most deshielded pyranose protons. Thus, HO-4 of α-D-glucopyranose was the least reactive towards benzoylation, as for the methyl α-pyranoside[1].

Similar tetramolar benzoylation of α-D-mannopyranose gave a syrupy product from which a tetrabenzoate (51%) could be isolated by fractional crystallisation. This tetrabenzoate was expected to be the 1,2,3,6-tetrabenzoate, since HO-4 is the least reactive hydroxyl group in the selective benzoylation of methyl α-D-mannopyranoside[1]. The structure was confirmed by p.m.r. spectroscopy, but because H-2 and H-3 were very strongly coupled, and the signals for H-4, H-5, and H-6 overlapped, in the 100-MHz spectra, the praesodymium $(fod)_3$ shift reagent[13] was used. The addition of only 0.03 ml of a 20% solution of Pr $(fod)_3$ in deuteriochloroform to 0.1M tetrabenzoate was sufficient to separate the signals for H-2 and H-3, which then appeared as quartets. The most-shifted proton gave a triplet (J ~10 Hz) at τ 7.07, and was readily identified as H-4. Increasing the temperature to 54° reduced the line-width slightly, thus facilitating the measurement of coupling constants ($J_{1,2}$ 1.5, $J_{2,3}$ 3, $J_{3,4}$ 10, $J_{4,5}$ 9.5 Hz). The tetrabenzoate was expected to have the same (α) anomeric configuration as that of the starting material, and this was supported (but not proved) by the similar chemical shifts of H-5 (τ 5.75 and 5.68) in the D-mannose and α-D-glucose 1,2,3,6-tetrabenzoates, respectively.

Trimolar benzoylation of β-L-arabinopyranose gave a product mixture in which a tribenzoate preponderated. This was isolated (57%) as a homogeneous syrup after column chromatography on silica gel, and was shown to be 1,2,3-tri-*O*-benzoyl-β-L-arabinopyranose by its n.m.r. spectrum. The most-deshielded pyranose protons were H-1, H-2, and H-3; the coupling constants ($J_{1,2}$ 3, $J_{2,3}$ 10, $J_{3,4}$ 3 Hz) were consistent with the $^4C_1$ chair conformation. A second tribenzoate was isolated in low yield in crystalline form, and shown to be the β-1,2,4-tribenzoate by n.m.r. spectroscopy. Crystalline 2,3-di-*O*-benzoyl-α-L-arabinopyranose was also isolated in low yield. Its n.m.r. spectrum showed two low-field quartets at τ 4.34 and 4.67, which were identified as originating from H-2 and H-3, respectively, from the coupling constants ($J_{1,2}$ 7.0, $J_{2,3}$ 9.8, $J_{3,4}$ 3.0 Hz).

α-D-Xylopyranose 1,2,4-tribenzoate, the major product of benzoylation of α-D-xylopyranose, was isolated in only 32% yield after column chromatography, because of the partial overlap with an isomeric tribenzoate. The minor tribenzoate crystallised from a mixture, and was shown to be α-D-xylopyranose 2,3,4-tribenzoate. Both structures were established by n.m.r. spectroscopy. In the spectrum of the

1,2,4-tribenzoate, the signal for H-3 was a triplet (τ 5.43, J 9 Hz) to high field of H-1, H-2, and H-4. In the spectrum of the 2,3,4-tribenzoate, the three most-deshielded pyranose protons were not H-2, H-3, and H-4. The anomeric proton resonated at τ 4.3 ($J_{1,2}$ 3.4 Hz) at lower field than H-2 and H-4, and showed partial coupling to HO-1; the anomeric substituent was thus hydroxyl and not benzoyloxy, as anomeric equatorial protons in 1-*O*-benzoylpyranoses resonate below τ 3.5 in deuteriochloroform. Anomerisation could be followed by n.m.r. measurements. H-3 was more deshielded in the α-anomer (by the *syn*-axial, anomeric hydroxyl group) than in the β-anomer.

Circular dichroism (c.d.) measurements have also been useful in establishing the structures of some of these monosaccharide benzoates. The very intense, split Cotton effects associated with vicinal dibenzoates led to the formulation of an appropriate chirality rule[14]. A similar rule was subsequently published[15] by Nakanishi and co-workers, who also showed that interactions between more-remote benzoate groups gave similar Cotton effects[16]. The c.d. curve of 2,3,4-tri-*O*-benzoyl-α-D-xylopyranose showed a net dibenzoate chirality[17] of zero, and this could be accommodated by only two structures, namely a pyranose 2,3,4-tribenzoate and the β-pyranose 1,2,3-tribenzoate, which were distinguished by n.m.r. Table I gives c.d. data on selected benzoates, the preferred conformations of which are known from n.m.r. data. The net dibenzoate chirality shown includes interactions between benzoate groups attached to vicinal carbon atoms and those between benzoate groups attached to alternate carbon atoms. There is an approximate correlation between the magnitude of $\Delta\varepsilon$ and the net dibenzoate chirality, except for the α-D-xylopyranose tetrabenzoate. The data in Table I suggest that it may not be possible to predict the magnitude of $\Delta\varepsilon$ for tetrabenzoates in which opposing dibenzoate interactions are present. The additivity of these interactions is being studied further.

TABLE I

Compound	$\Delta\varepsilon$[a]	*Net dibenzoate chirality*
β-L-Arabinopyranose tetrabenzoate	+71.5	+5
β-L-Arabinopyranose 1,2,3-tribenzoate	+35.5	+3
Methyl 6-deoxy-β-L-galactopyranoside tribenzoate[2]	−43	−3
β-L-Arabinopyranose 1,2,4-tribenzoate	+30	+2
α-D-Xylopyranose tetrabenzoate	+20	+2
α-L-Arabinopyranose 2,3-dibenzoate	+20.5[b]	+1
Methyl β-L-arabinopyranoside 2,3-dibenzoate[3b]	+21	+1
α-D-Xylopyranose 1,2,4-tribenzoate	+13	+1
α-D-Xylopyranose 2,3,4-tribenzoate	−1.0	0
Methyl 6-deoxy-α-D-glucopyranoside tribenzoate[2]	+4.4	0

[a]Of the two most-intense extrema, the one at higher wavelength (at 237 ±1 nm) was measured. Methanol was the solvent. [b]Unchanged after mutarotation.

The foregoing, partially benzoylated aldopyranoses are useful precursors for the synthesis of methyl ethers (under conditions that avoid ester migration[18]), and

deuterium- and tritium-labelled compounds (*via* the ulose derivatives[19]), but nucleophilic displacements of the sulphonate derivatives are not necessarily straightforward. Hexopyranose 4-sulphonate derivatives possessing anomeric acetoxy substituents rearrange to 1,4-anhydrides[20,21], probably *via* removal of AcO-1 as the first step. It was possible that this rearrangement would compete less effectively with the normal displacement reaction in pentopyranose 4-sulphonates and in derivatives containing an anomeric benzoyloxy substituent. To check these possibilities, we have examined the reactions of 1,2,3,6-tetra-*O*-benzoyl-4-*O*-methanesulphonyl-α-D-glucopyranose and 1,2,3-tri-*O*-benzoyl-4-*O*-methanesulphonyl-β-L-arabinopyranose with sodium azide in methyl sulphoxide. The glucose sulphonate, when heated with sodium azide in methyl sulphoxide at 75–80° for 7.5 h, gave crystalline 1,4-anhydro-β-D-galactopyranose 2,3,6-tribenzoate (72%). In contrast, the arabinose sulphonate underwent a slow displacement by azide, unchanged starting material and 4-azido-2,3-di-*O*-benzoyl-4-deoxy-α-D-xylopyranose being isolated after reaction for 1.5 h at 100°. Higher temperatures caused extensive decomposition of both sulphonates. Thus, a normal nucleophilic displacement was possible for the pentose 4-methanesulphonate.

EXPERIMENTAL

General. — Melting points, measured on a Kofler hot-stage, are corrected. N.m.r. spectra were recorded on a Varian HA-100 spectrometer with deuteriochloroform as solvent and tetramethylsilane as internal reference unless otherwise stated. First-order coupling constants were measured to ±0.2 Hz, and assignments were confirmed by spin decoupling. Optical rotations were made with a Perkin–Elmer 141 polarimeter at 20 ±2°, using chloroform as solvent unless otherwise stated. T.l.c. was performed on Kieselgel-G (Merck) and detection with (*a*) 5% sulphuric acid in ethanol at 120°, or (*b*) hydroxylamine solution followed by ferric chloride solution (for benzoates). BDH silica gel (60–120 mesh) was used for column chromatography.

Selective benzoylation. — Each monosaccharide was rapidly dissolved in dry pyridine at room temperature, and the solution was then rapidly cooled to −35°. Addition of benzoyl chloride to the stirred solution was commenced immediately, and the remaining procedure is that described in ref. 1.

α-D-*Glucopyranose 1,2,3,6-tetrabenzoate.* — A solution of α-D-glucose (2.5 g) in dry pyridine (150 ml) was treated with benzoyl chloride (6.7 ml) to give a syrupy product which crystallised on the addition of ethanol. T.l.c. showed that the solid contained two components (tetra- and penta-benzoates). Fractional crystallisation from ethanol and aqueous ethanol yielded α-D-glucopyranose pentabenzoate (2.1 g), m.p. 155–157° (lit.[22] m.p. 157°), and 1,2,3,6-tetra-*O*-benzoyl-α-D-glucopyranose (3.1 g, 37%) containing a trace of pentabenzoate. Chromatography of the mother liquor on a silica gel column with benzene–ethyl acetate (7:3) gave 1.1 g of homogeneous tetrabenzoate (total yield, 50%). The first tetrabenzoate sample obtained had m.p. 112–119°, and, after recrystallisation from benzene–light petroleum (b.p. 60–80°), m.p. 167–169°, $[\alpha]_D$ +180°. All subsequent preparations had the latter m.p.

N.m.r. data: τ 1.8–2.8 (20 H, Ar*H*), 3.24 (*d*, 1 H, *J* 3.5 Hz, H-1), 4.01 (*t*, 1 H, *J* 10 Hz, H-3), 4.45 (*q*, 1 H, *J* 10 and 3.5 Hz, H-2), 5.17 (*q*, 1 H, *J* 12.5 and 3.5 Hz, H-6), 5.48 (*q*, 1 H, *J* 12.5 and 2 Hz, H-6'), 5.68 (*m*, 1 H, H-5), 5.98 (*m*, 1 H, H-4; *t*, *J* 10 Hz after D_2O exchange), 6.22 (*m*, 1 H, OH; absent after D_2O exchange).

Anal. Calc. for $C_{34}H_{28}O_{10}$: C, 68.45; H, 4.7. Found: C, 69.0; H, 4.5.

A portion of the glucose tetrabenzoate, when treated with hydrogen bromide in glacial acetic acid and chloroform, gave the α-glycosyl bromide (62%), m.p. 161–162° [from ether–light petroleum (b.p. 40–60°)], $[\alpha]_D$ +188° (lit.[12] m.p. 163–164°, $[\alpha]_D$ +194°). The glycosyl bromide was converted by a standard Koenigs–Knorr reaction, into methyl 2,3,6-tri-*O*-benzoyl-β-D-glucopyranoside (60%), m.p. 151–152°, $[\alpha]_D$ +76° (lit.[12] m.p. 145–146°).

1,2,3,6-Tetra-O-benzoyl-4-O-methanesulphonyl-α-D-glucopyranose. — A solution of 1,2,3,6-tetra-*O*-benzoyl-α-D-glucopyranose (170 mg) in pyridine (3 ml) was treated with methanesulphonyl chloride (0.1 ml). After 17 h, the reaction mixture was poured into ice–water (200 ml), and the product (193 mg) was isolated by chloroform extraction in the usual way, and recrystallised from ethanol to give the sulphonate (170 mg, 88%), m.p. 221–223°, $[\alpha]_D$ +167°. N.m.r. data: τ 1.9–2.8 (20 H, ArH), 3.2–5.5 (7 H, pyranose H), 7.07 (*s*, 3 H, $MeSO_2$).

Anal. Calc. for $C_{35}H_{30}O_{12}S$: C, 62.3; H, 4.45. Found: C, 62.1; H, 4.2.

α-D-Mannopyranose 1,2,3,6-tetrabenzoate. — A solution of α-D-mannose (0.5 g) in dry pyridine (10 ml) was treated with benzoyl chloride (1.34 ml). The syrupy product crystallised from ethanol to give a mixture of penta- and tetra-benzoates. Recrystallisation from chloroform–light petroleum (b.p. 60–80°) gave 1,2,3,6-tetra-*O*-benzoyl-α-D-mannopyranose (0.85 g, 51%), m.p. 182–184°, $[\alpha]_D$ +34.5°. N.m.r. data: τ 1.8–2.8 (20 H, Ar*H*), 3.44 (*d*, 1 H, *J* 1.5 Hz, H-1), ~4.08 (*m*, 2 H, H-2,3), 5.07 (*q*, 1 H, *J* 12 and 2.5 Hz, H-6), 5.48 (*q*, 1 H, *J* 12 and 2 Hz, H-6'), 5.57 (*m*, 1 H, H-4), ~5.75 (*m*, 1 H, H-5), 7.50 (*d*, 1 H, *J* 4.5 Hz, OH; absent after D_2O exchange); on addition of $Pr(fod)_3$, the following upfield shifts (p.p.m.) were obtained: H-1 0.84, H-2 0.9, H-3 1.29, H-4 1.50, H-5 ~0.57, H-6 1.01, H-6' 0.60, and OH 1.8.

Anal. Calc. for $C_{34}H_{28}O_{10}$: C, 68.45; H, 4.7. Found: C, 68.3; H, 5.05.

Trimolar benzoylation of L-arabinose. — Treatment of β-L-arabinopyranose (4 g) dissolved in pyridine (300 ml) with benzoyl chloride (9.6 ml, 3.1 equiv.), followed by the usual work-up, gave a syrup (11.5 g). A portion (4.1 g) was eluted from silica gel with ether–light petroleum (b.p. 60–80°) (1:3) to give β-L-arabinopyranose tetrabenzoate (0.28 g), m.p. 157–158.5° (from ethanol), $[\alpha]_D$ +293° (lit.[23] m.p. 153°, $[\alpha]_D$ +301°), and then crystalline 1,2,4-tri-*O*-benzoyl-β-L-arabinopyranose (0.25 g) followed by syrupy 1,2,3-tri-*O*-benzoyl-β-L-arabinopyranose (2.5 g). Ether–light petroleum (1:1) eluted a dibenzoate fraction (0.21 g) which crystallised to give 2,3-di-*O*-benzoyl-α-L-arabinopyranose (0.13 g).

The 1,2,4-tribenzoate had m.p. 231–233° (from ether), $[\alpha]_D$ +200°. N.m.r. data (acetone-d_6): τ 1.8–2.1 (*m*, 6 H, Ar*H*), 2.3–2.7 (*m*, 9 H, Ar*H*), 3.22 (*d*, 1 H, *J* 3.8 Hz, H-1), 4.28 (*q*, 1 H, *J* 3.8 and 10.0 Hz, H-2), 4.31 (*m*, 1 H, H-4), 5.2 (*m*, 2 H, H-3 and

OH; after D_2O exchange 5.19, *q*, 1 H, *J* 3.8 and 10.0 Hz, H-3), 5.52 (*q*, 1 H, *J* 1 and 13 Hz, H-5), 5.90 (*q*, 1 H, *J* 2 and 13 Hz, H-5').

Anal. Calc. for $C_{26}H_{22}O_8$: C, 67.5; H, 4.8. Found: C, 67.5; H, 4.5.

The 1,2,3-tribenzoate had $[\alpha]_D$ +211°. N.m.r. data: τ 1.8–2.2 (*m*, 6 H, Ar*H*), 2.4–2.8 (*m*, 9 H, Ar*H*), 3.25 (*d*, 1 H, *J* 3.0 Hz, H-1), 3.96 (*q*, 1 H, *J* 3.0 and 10.4 Hz, H-2), 4.17 (*q*, 1 H, *J* 3.0 and 10.4 Hz, H-3), 5.51 (*m*, 1 H, H-4), 5.74 (*bd*, 1 H, *J* 12.5 Hz, H-5), 5.97 (*q*, 1 H, *J* 2.0 and 12.5 Hz, H-5'), 7.5 (*bs*, 1 H, OH; removed by D_2O exchange).

The 2,3-dibenzoate had m.p. 134.5–135.5°, $[\alpha]_D$ +106 (7 min) → +135° (equil.). N.m.r. data (acetone-d_6): τ 1.9–2.1 (*m*, 4 H, Ar*H*), 2.4–2.7 (*m*, 6 H, Ar*H*), 4.06 (*d*, 1 H, *J* 6.8 Hz, OH-1; removed by D_2O exchange), 4.34 (*q*, 1 H, *J* 7.0 and 9.8 Hz, H-2), 4.67 (*q*, 1 H, *J* 3.0 and 9.8 Hz, H-3), 5.01 (*t*, 1 H, *J* 7 Hz, H-1; *d* after D_2O exchange), 5.42 (*d*, 1 H, *J* 4.5, HO-4; removed by D_2O exchange), 5.68 (*m*, 1 H, H-4), 5.94 (*q*, 1 H, *J* 2.6 and 12.4 Hz, H-5), 6.16 (*q*, 1 H, *J* 1.5 and 12.4 Hz, H-5').

Anal. Calc. for $C_{19}H_{18}O_7$: C, 63.6; H, 5.05. Found: C, 63.6; H, 4.7.

*Derivatives of 1,2,3-tri-*O*-benzoyl-β-*L*-arabinopyranose.* — (*a*) *4-Phenylcarbamate.* After reaction of the 1,2,3-tribenzoate (150 mg) with phenyl isocyanate (0.5 ml) in dry toluene (3 ml) and dry pyridine (1 ml) at room temperature overnight, water (5 ml) was added, and the mixture was stirred for 1 h. Filtration and concentration gave a syrup which was extracted with chloroform (20 ml). The chloroform layer was washed with water, dried ($MgSO_4$), and concentrated to give the syrupy carbamate (180 mg), $[\alpha]_D$ +188°. N.m.r. data: τ 1.9–3.0 (*m*, 21 H, Ar*H*+NH), 3.2–6.0 (6 H, pyranose H).

Anal. Calc. for $C_{33}H_{27}NO_9$: C, 68.15; H, 4.65; N, 2.4. Found: C, 67.9; H, 4.65; N, 2.7.

(*b*) *4-Methanesulphonate.* Reaction of the tribenzoate (150 mg) with methanesulphonyl chloride in pyridine, in the usual way, gave the 4-methanesulphonate as a syrup (155 mg), $[\alpha]_D$ +201°. N.m.r. data: τ 1.9–2.9 (15 H, Ar*H*), 6.93 (*s*, 3 H, $MeSO_2$).

Trimolar benzoylation of D-*xylose.* — Treatment of α-D-xylopyranose (2 g) dissolved in pyridine (50 ml) with benzoyl chloride (4.8 ml, 3.1 equiv.), followed by the usual work-up, gave a syrup (5.9 g), which was eluted from silica gel with ether–light petroleum (b.p. 60–80°) (1:3) to give, in the following order, α-D-xylopyranose tetrabenzoate (0.7 g), m.p. 119–121°, $[\alpha]_D$ +149° (lit.[24] m.p. 119–120°, $[\alpha]_D$ +149.5°); a tribenzoate fraction (2.8 g), which crystallised from di-isopropyl ether to give 2,3,4-tri-*O*-benzoyl-α-D-xylopyranose (0.45 g); syrupy 1,2,4-tri-*O*-benzoyl-α-D-xylopyranose (2.0 g, 32%).

The 2,3,4-tribenzoate had m.p. 181–183°; $[\alpha]_D$ +24° (5 min), +24° (4 h). N.m.r. data: τ 1.9–2.2 (6 H, Ar*H*), 2.5–2.8 (9 H, Ar*H*), 3.78 (*t*, 1 H, *J* 9.5 Hz, H-3), 4.30 (*bd*, 1 H, *J* 3.4 Hz, H-1; sharp *d* after D_2O exchange), ~4.6 (*m*, 1 H, H-4), 4.70 (*q*, 1 H, *J* 3.4 and 9.8 Hz, H-2), 5.87 (*d*, 2 H, *J* 7.8 Hz, H-5), 6.3 (*bs*, 1 H, OH; removed by D_2O exchange); after anomerisation, the spectrum also showed, *inter alia*, signals at τ 4.10 (*t*, *J* 9 Hz, H-3 of β-anomer), 5.00 (*d*, *J* 7 Hz, H-1 of β-anomer).

Anal. Calc. for $C_{26}H_{22}O_8$: C, 67.5; H, 4.8. Found: C, 67.4; H, 4.35.

The 1,2,4-tribenzoate had $[\alpha]_D$ +88°. N.m.r. data: τ 1.92–2.2 (6 H, Ar*H*), 2.4–2.8 (9 H, Ar*H*), 3.36 (*d*, 1 H, *J* 3.5 Hz, H-1), 4.61 (*q*, 1 H, *J* 3.5 and 9.0 Hz, H-2), 4.68 (*sex*, 1 H, H-4), 5.43 (*t*, 1 H, *J* 9 Hz, H-3), 5.85 (*q*, 1 H, *J* 5.7 and 11.0 Hz, H-5-*eq*), 6.06 (*q*, 1 H, *J* 10.0 and 11.0 Hz, H-5-*ax*), 7.1 (*bs*, 1 H, OH; removed by D_2O exchange).

Reaction of methanesulphonates with sodium azide in methyl sulphoxide. — (*a*) *Glucose derivative.* A solution of 1,2,3,6-tetra-*O*-benzoyl-4-*O*-methanesulphonyl-α-D-glucopyranose (118 mg) in dry methyl sulphoxide (2.4 ml) containing sodium azide (80 mg) was heated at 75–80° for 7.5 h. T.l.c. then indicated the formation of one product. The reaction mixture was poured into ice–water (200 ml), and ether extraction (3 × 80 ml) gave, after drying ($MgSO_4$) and concentration of the extract, a solid (60 mg) which, on recrystallisation from methanol, yielded 1,4-anhydro-2,3,6-tri-*O*-benzoyl-β-D-galactopyranose, m.p. 141–143°, $[\alpha]_D$ +117°. N.m.r. data: τ 1.8–2.1 (6 H, Ar*H*), 2.4–2.7 (9 H, Ar*H*), 3.99 (*d*, 1 H, *J* 2 Hz, H-1), 4.82 (*m*, 2 H, H-2,3), 5.07 (*m*, 1 H, H-4), 5.69 (*m*, 3 H, H-5,6,6′); this spectrum closely resembled that of the 6-*O*-acetyl-2,3-di-*O*-benzoyl analogue[20].

Anal. Calc. for $C_{27}H_{22}O_8$: C, 68.4; H, 4.65. Found: C, 67.95; H, 4.8.

(*b*) *Arabinose derivative.* A solution of 1,2,3-tri-*O*-benzoyl-4-*O*-methanesulphonyl-β-L-arabinopyranose (145 mg) in dry methyl sulphoxide (3 ml) containing sodium azide (97 mg) was heated at 100° for 1.5 h. T.l.c. then revealed two components. The reaction mixture was poured into ice–water (200 ml), and ether extraction (3 × 80 ml) gave, after drying ($MgSO_4$) and concentration of the extract, a syrup. Elution from silica gel with ether–light petroleum (b.p. 60–80°) (1:3) gave first 4-azido-1,2,3-tri-*O*-benzoyl-4-deoxy-α-D-xylopyranose (35 mg), $[\alpha]_D$ +185°, ν_{max} (Nujol) 2120 cm^{-1} (azide). N.m.r. data: τ 1.9–2.2 (6 H, Ar*H*), 2.4–2.8 (9 H, Ar*H*), 3.31 (*d*, 1 H, *J* 3.6 Hz, H-1), 3.99 (*bt*, 1 H, *J* ~9 Hz, H-3), 4.51 (*q*, 1 H, *J* 3.6 and 10.0 Hz, H-2), 6.0 (*m*, 3 H, H-4,5,5′), and then starting material (45 mg) identified by n.m.r.

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