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THE SYNTHESIS OF 2'-DEOXY-β-DISACCHARIDES: NOVEL APPROACHES*

MICHEL TRUMTEL, PAOLO TAVECCHIA†, ALAIN VEYRIÈRES, AND PIERRE SINAŸ‡
Ecole Normale Supérieure, Laboratoire de Chimie, UA 1110, 24 Rue Lhomond, 75231 Paris 05 (France)
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ABSTRACT

Benzylated 1,2-orthoacetates were converted by dry acetic acid into 1,2-*trans*-diacetates which behaved as excellent β-glycosyl donors with various non-acylated glycosyl acceptors in the presence of trimethylsilyl triflate. Deacetylation, followed by xanthation and then radical reduction with tributylstannane, led in high yields to the 2'-deoxy-β-disaccharides. In another approach, glycosylations were performed with various derivatives of *N*-formylglucosamine (β-acetate or α-trichloroacetimidate, in the presence of trimethylsilyl triflate; α-chloride in the presence of silver or stannous triflate) upon acceptors having different kinds of protecting groups. The resulting disaccharides were smoothly deaminated into the corresponding 2'-deoxy-β-disaccharides through intermediate isonitriles by radical reduction with tributylstannane. The β-stereocontrol in the glycosylation step was ensured by an intermediate oxazolinium ion. A β-trichloroacetimidate of *N*-phthaloylglucosamine was used as a more powerful glycosylating reagent in the case of acid-sensitive molecules, with the conversion of the *N*-phthaloyl into an *N*-formyl group being effected in a high yield after the glycosylation step.

INTRODUCTION

The search for highly stereoselective and high-yielding syntheses of glycosides and oligosaccharides is one of the classical topics of carbohydrate chemistry. 2-Deoxy-β-D-glycosides are important as components of various natural products of biological significance, such as the orthosomycin[1] group of antibiotics and a group of related cytostatics including chromomycin A_3[2], olivomycin A[3], and mithramycin[4] (aureolic acid).

Although various stereoselective methods for the synthesis of 2-deoxy-α-glycosides are available, the β anomers are not accessible readily. Attempts to pre-

*Presented at the IVth European Carbohydrate Symposium, Darmstadt, F.R.G., July 12–17, 1987.
†Present address: Lepetit Research Centre, Via R. Lepetit 34, I-21040 Gerenzano (VA), Italy.
‡Author for correspondence.

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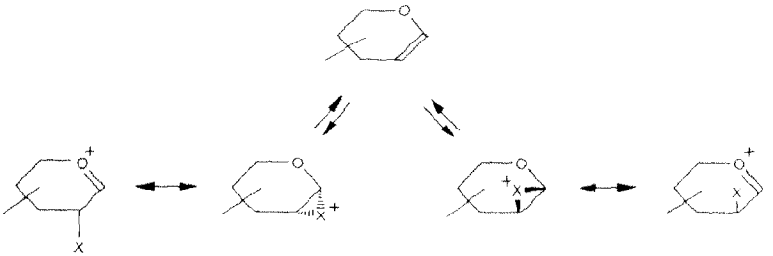
pare β-glycosides directly from the 2-deoxy sugar have not been satisfactory. The use of silver zeolite as a promoter for the activation of benzoylated 2-deoxy-α-D-glucopyranosyl bromide gave an αβ-mixture[5]. In order to obtain 2-deoxy-β-glycosides, it is advantageous to have an equatorial neighbouring group at C-2 which subsequently can be removed readily under mild conditions. Thus, 2-bromo-2-deoxy-α-D-glucopyranosyl bromides[6-8] can be converted selectively into 2-deoxy-β-glycosides under the appropriate conditions[8-10] in moderate yields. The stereochemistry of glycosylation can be controlled by an equatorial phenylthio group. Thus, in the elegant work of Nicolaou *et al.*[11] based on that of Acton *et al.*[12], the required 2-deoxy-2-phenylthioglucopyranosyl fluoride was obtained from the corresponding mannopyranosyl phenyl sulfide *via* a 1,2-migration triggered by diethylaminosulfur trifluoride (DAST). Electrophilic addition of a sulfur species at C-2 of a tri-*O*-benzyl-D-glycal has been studied. Ito and Ogawa[13] used a sulfenate ester, but the stereochemical outcome of the reaction was variable. The addition of phenylsulfenyl chloride to 3,4,6-tri-*O*-benzyl-D-glucal, followed by hydrolysis with sodium carbonate, afforded 3,4,6-tri-*O*-benzyl-2-deoxy-2-phenylthio-D-glucopyranose. Conversion into the 1-trichloroacetimidate gave an efficient β-glycosyl donor, although total β-stereocontrol was not achieved uniformly[14]. Similar β-selectivity was achieved with an equatorial phenylseleno group[15]. Reduction of the temporary group at C-2 was effected with tributylstannane or Raney nickel in ethanol.

The stereochemical outcome of the above reactions depends on the structure of the glycosyl donor, the acceptor, and the conditions of the reaction, especially the polarity of the solvent. This last point was illustrated clearly in the glycosyloxyselenation of glycals[15,16], which is not surprising since such 2-substituents as bromine, sulfur, or selenium give rise to species that undergo the equilibration[17] shown in the next Scheme.



X = Br, I, SPh, SePh

Thus, it is understandable that complete control of glycosylation stereochemistry, using these strategies, is not governed automatically by the configuration of an intermediate with a participating group at C-2 or by the kinetic, diastereofacial, selective formation of an intermediate onium ion.

Another approach involves selective deoxygenation at C-2 of a natural β-

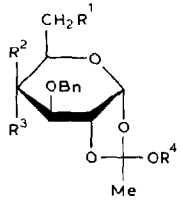
linked disaccharide[18], but the regioselective manipulation of protecting groups in disaccharides is not always straightforward.

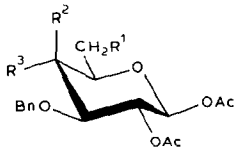
We now report on two fully stereoselective and general preparations of 2-deoxy-β-disaccharides where the stereochemical outcome of the glycosylation step is controlled by a neighboring *O*-acetyl or *N*-formyl group.

RESULTS AND DISCUSSION

The first method involves 1-*O*-acetyl-β-D-glycopyranoses having a 2-*O*-acetyl group (1,2-*trans*) and benzyl groups on the other positions. Provided that the glycosyl acceptor is not protected by *O*-acyl groups, HO-2′ in the product can be exposed, thereby allowing selective deoxygenation. Although benzylated orthoesters have been used as glycosyl donors[19,20], the yields and stereoselectivity have not been consistently high.

Benzylated 1,2-orthoesters react at room temperature with dry acetic acid to give exclusively the corresponding 1,2-*trans*-di-*O*-acetyl derivatives in high yield. The presence of traces of water in the acetic acid is detrimental[21]. Application of this method to the stereoselective synthesis of acetylated 1-*O*-acyl-β-D-glucopyranoses has been reported[22]. The 1,2-*trans*-di-*O*-acetyl derivatives **4**–**6** were obtained from the respective benzylated orthoesters **1**[19], **2**[23], and **3**[24]. A similar benzylated orthoester of L-quinovopyranose has been described[25]. Compound **5** has been prepared in moderate yield from a benzylated orthoester by another route[26].





1 $R^1 = R^3 = OBn, R^2 = H, R^4 = Me$
2 $R^1 = R^2 = OBn, R^3 = H, R^4 = Me$
3 $R^1 = R^2 = H, R^3 = OBn, R^4 = Et$

4 $R^1 = R^3 = OBn, R^2 = H$
5 $R^1 = R^2 = OBn, R^3 = H$
6 $R^1 = R^2 = H, R^3 = OBn$

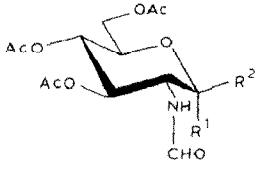
In the presence of trimethylsilyl trifluoromethanesulfonate, β-acetates react[27,28] with hydroxyl groups of acceptors to give β-linked di- and oligo-saccharides in high yields. In the presence of this reagent, **4**–**6** were excellent β-glycosyl donors at −20°. Thus, **4** reacted with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**13**) to give 85% of the disaccharide derivative **14**, with methyl 2-*O*-benzyl-6-deoxy-4-*O*-methyl-β-D-galactopyranoside[24] (**41**) to give 78% of **42**, and with phenyl 2,3-di-*O*-benzyl-6-deoxy-1-thio-β-D-glucopyranoside[24] (**50**) to give 75% of **51**. The *galacto* derivative **5** is an efficient β-D-galactosyl donor under such conditions[28] and reacted with methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[29] (**21**) and methyl 2,3,6-tri-*O*-

benzyl-α-D-glucopyranoside[30] (**29**) to give **22** (82%) and **30** (90%), respectively. The *quinovo*-diacetate **6** reacted with **50** to give 80% of **55**. No trace of α-linked disaccharides was isolated under these conditions.

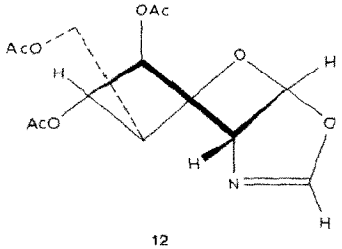
The disaccharide derivatives **14, 22, 30, 42, 51,** and **55** were deacetylated (sodium methoxide in methanol) to give, respectively, **15, 23, 31, 43, 52,** and **56**. These alcohols were converted into the corresponding disaccharide xanthates **16, 24, 32, 44, 53,** and **57** by treatment in tetrahydrofuran with sodium hydride, carbon disulfide, and a catalytic amount of imidazole, followed by reaction with methyl iodide. The radical reduction[31] of the xanthates by tributylstannane in the presence of azobisisobutyronitrile (AIBN) gave the protected 2-deoxy-β-disaccharides **17, 25, 33, 45, 54,** and **58**, respectively, in excellent yields. Thus, the availability of benzylated β-acetates of the types **4–6** opens the route to a simple, probably general, efficient, and stereospecific preparation of a variety of 2-deoxy-β-disaccharides. This approach is limited because acylated acceptors cannot be used.

In order to enlarge the scope of this strategy, another approach was developed, based on 2-amino-2-deoxy-D-glucose, where an *O*-acylated glycosyl donor or acceptor can be used.

Aliphatic or alicyclic isocyanides can be reduced smoothly with tributylstannane to the corresponding hydrocarbons[32]. Isocyanides can be obtained in high yields by dehydration of formamides. These two reactions are compatible with the common functional groups found in carbohydrate chemistry and they were applied in an efficient synthesis of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranose from 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-formamido-β-D-glucopyranose[33] (**7**). Benzyl 6-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-galactopyranoside (**37**), obtained by selective benzoylation of benzyl 2,4-di-*O*-benzyl-β-D-galactopyranoside[34], reacted with **7** at room temperature in the presence of trimethylsilyl triflate, to give 94% of the β-linked disaccharide derivative **38**. The reactions of **7** with the alcohols **21, 29,** and **41** gave the corresponding disaccharide derivatives **26, 34,** and **46** in yields of 64, 64, and 29%, respectively. Attempts to glycosylate **13** resulted in decomposition since the isopropylidene groups could not withstand the conditions of the reaction.



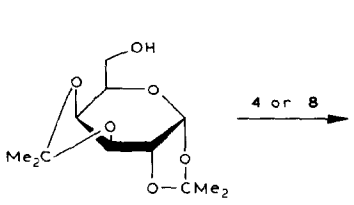
7 $R^1 = H, R^2 = OAc$
8 $R^1 = Cl, R^2 = H$
9 $R^1 = OH, R^2 = H$
10 $R^1 = OC{:}NHCCl_3, R^2 = H$
11 $R^1 = H, R^2 = OMe$



12

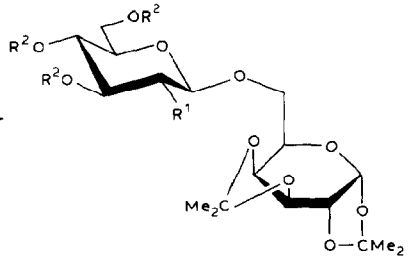
Although attempts[33] to prepare a chloro sugar from **7** led to syrups, treatment with a saturated solution of hydrogen chloride in acetyl chloride at room temperature gave 80% of the crystalline α-chloride **8**. Compound **8** reacted at room temperature in the presence of silver triflate with alcohols **13, 21, 29, 37,** and **41** to give the corresponding disaccharide derivatives **18, 26, 34, 38,** and **46** in yields of 83, 97, 15, 27, and 26%, respectively. The results with the primary alcohols **13** and **21** were excellent and the disappointing yield for the glycosylation of **41** by **8** was not improved significantly when stannous triflate was used as a promoter[35]. The low yields obtained on glycosylation of **41** by either **7** or **8** are attributed to the formation of an isomeric *O*-methyl-α-disaccharide. Glycosylation of **8** by methanol was best accomplished with stannous triflate[35] at room temperature, when 58% of the methyl β-glycoside **11** was obtained.

Treatment of **7** with benzylamine[36] in tetrahydrofuran gave 84% of the hemiacetal **9**, which reacted with trichloroacetonitrile in the presence of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene[37] (DBU) to give 95% of the α-tri-

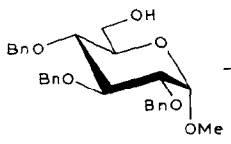


13

4 or 8

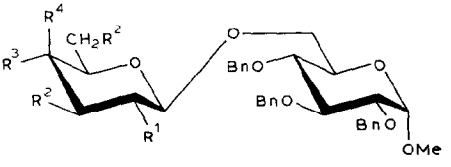


14 R^1 = OAc, R^2 = Bn
15 R^1 = OH, R^2 = Bn
16 R^1 = OC:SSMe, R^2 = Bn
17 R^1 = H, R^2 = Bn
18 R^1 = NHCHO, R^2 = Ac
19 R^1 = NC, R^2 = Ac
20 R^1 = H, R^2 = Ac

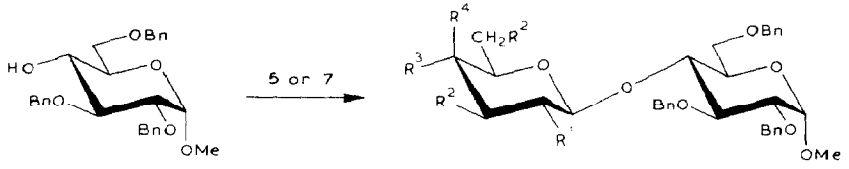


21

5 or 8

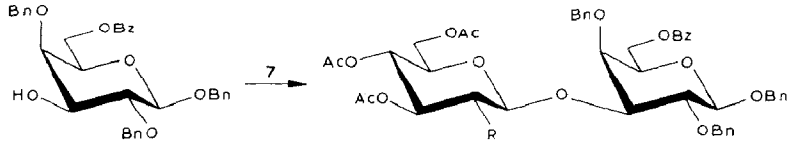


22 R^1 = OAc, R^2 = R^4 = OBn, R^3 = H
23 R^1 = OH, R^2 = R^4 = OBn, R^3 = H
24 R^1 = OC:SSMe, R^2 = R^4 = OBn, R^3 = H
25 R^1 = R^3 = H, R^2 = R^4 = OBn
26 R^1 = NHCHO, R^2 = R^3 = OAc, R^4 = H
27 R^1 = NC, R^2 = R^3 = OAc, R^4 = H
28 R^1 = R^4 = H, R^2 = R^3 = OAc



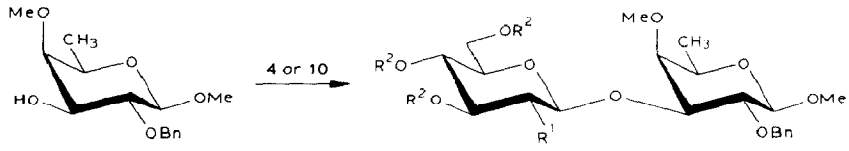
29

30 R^1 = OAc, R^2 = R^4 = OBn, R^3 = H
31 R^1 = OH, R^2 = R^4 = OBn, R^3 = H
32 R^1 = OC(:SSMe), R^2 = R^4 = OBn, R^3 = H
33 R^1 = R^3 = H, R^2 = R^4 = OBn
34 R^1 = NHCHO, R^2 = R^3 = OAc, R^4 = H
35 R^1 = NC, R^2 = R^3 = OAc, R^4 = H
36 R^1 = R^4 = H, R^2 = R^3 = OAc



37

38 R = NHCHO
39 R = NC
40 R = H

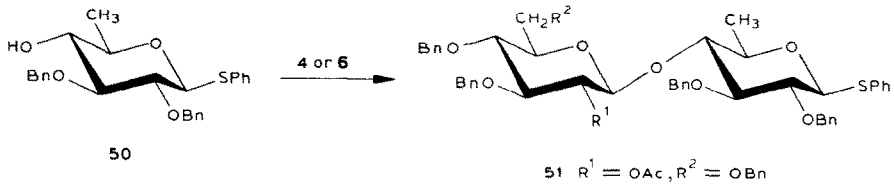


41

42 R^1 = OAc, R^2 = Bn
43 R^1 = OH, R^2 = Bn
44 R^1 = OC(:SSMe), R^2 = Bn
45 R^1 = H, R^2 = Bn
46 R^1 = NHCHO, R^2 = Ac
47 R^1 = NC, R^2 = Ac
48 R^1 = H, R^2 = Ac
49 R^1 = NPhth, R^2 = Ac

chloroacetimidate **10**. Reaction of **10** with **41** in the presence of trimethylsilyl triflate at room temperature gave 54% of the disaccharide derivative **46**.

The β-stereocontrol observed in the glycosylations performed with derivatives of 2-deoxy-2-formamido-D-glucose can be attributed to an intermediate oxazolinium ion. Indeed, 86% of the oxazoline **12** could be isolated when the chloride **8** was treated with silver triflate for 4 h at room temperature. The ^{1}H-n.m.r. spectrum of **12** showed coupling constants similar to those of 2-methyl- or 2-phenyl-1,3-oxazolines, and, particularly, a long-range coupling between H-2 and H-4 (1.1 Hz) involving a planar W arrangement where H-2,4 are pseudo-equatorial[38].



50

51 R^1 = OAc, R^2 = OBn
52 R^1 = OH, R^2 = OBn
53 R^1 = OC : SSMe, R^2 = OBn
54 R^1 = H, R^2 = OBn
55 R^1 = OAc, R^2 = H
56 R^1 = OH, R^2 = H
57 R^1 = OC : SSMe, R^2 = H
58 R^1 = R^2 = H

The ^{1}H-n.m.r. spectra reveal that various derivatives of 2-deoxy-2-formamido-D-glucose exist in solution in both the *cis* and *trans* configurations about the central C–N bond[39]. Two formyl H signals are present at δ 8.0–8.3 ($CDCl_3$); one (bs) at lower field corresponds to the *trans* rotamer and the other (d, J ~11 Hz) to the *cis*-rotamer. H-1 usually gives two distinct signals in the mixture of rotamers.

The 2-deoxy-2-formamido disaccharide derivatives **18, 26, 34, 38,** and **46** were converted into the corresponding 2-deoxy-2-isocyano derivatives **19** (85%), **27** (92%), **35** (88%), **39** (97%), and **47** (92%) by dehydration with phosphorus oxychloride and triethylamine in dichloromethane[40]. The radical reduction of the isocyano derivatives by tributylstannane in refluxing toluene gave the corresponding 2-deoxy-disaccharide derivatives **20** (96%), **28** (97%), **36** (74%), **40** (87%), and **48** (86%).

A drawback of this methodology is the sluggishness of the glycosylation reaction, which results in low yields for such acid-sensitive molecules as **41**. In order to circumvent this difficulty, **41** was treated with the more powerful glycosylating reagent 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate[41], readily prepared from 2-amino-2-deoxy-D-glucose. In the presence of a catalytic amount of trimethylsilyl triflate, the reaction occurred almost instantaneously at −70° to give 93% of the disaccharide derivative **49**. Sequential removal of the *O*-acetyl groups by transesterification and the *N*-phthaloyl group by hydrazinolysis[42], followed by *N*-formylation and then *O*-acetylation, gave 85% of **46**.

The disaccharide derivatives **58** and **48** are key intermediates in the synthesis of orthosomycin fragments. Thus, **58** has been converted (92%) into the corresponding crystalline glycal[43].

The numerous glycosylation reactions described above consistently gave β-linked disaccharides exclusively.

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi Model 510 capillary apparatus and are uncorrected. Optical rotations were measured at 20 ±2° with a Perkin–Elmer Model 241 polarimeter. C.i. (ammonia)-mass spectra were obtained with a Nermag R10-10 spectrometer. Elemental analyses were performed at the University Pierre et Marie Curie (Paris VI). ^{1}H-N.m.r. spectra were recorded with Cameca 250 and Bruker AM-400 spectrometers for solutions in $CDCl_3$ or C_6D_6 (internal Me_4Si). ^{13}C-N.m.r. spectra were recorded at 100.57 MHz with a Bruker AM-400 spectrometer for solutions in $CDCl_3$, adopting 77.0 p.p.m. for the central line of $CDCl_3$. Assignments were aided by the J-MOD technique[44,45]. Reactions were monitored by t.l.c. on Silica Gel 60 F_{254} (Merck) and detection by charring with sulfuric acid. Flash column chromatography[46] was performed on Silica Gel 60 (230–400 mesh, Merck).

*General procedure for the conversion of 1,2-orthoacetates into 1,2-*trans*-di-O-acetyl derivatives.* — A solution of 1,2-orthoacetate (1 mmol) in glacial acetic acid was stirred for 1 h at room temperature under argon and then concentrated, and toluene was evaporated several times from the residue. The residue was a nearly pure 1,2-*trans*-di-*O*-acetyl derivative, slightly contaminated with products resulting from the hydrolysis of the starting material. The polar by-products were conveniently removed by filtration through silica gel.

*1,2-Di-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-*D*-glucopyranose* (**4**). — 3,4,6-Tri-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-α-D-glucopyranose[19] (**1**; 507 mg, 1 mmol) reacted with acetic acid to give **4** (454 mg, 85%), isolated as a syrup, $[\alpha]_D$ +25.5° (*c* 0.9, chloroform), R_F 0.35 (50:1 dichloromethane–acetone); ^{1}H-n.m.r. ($CDCl_3$): δ 7.42–7.16 (m, 15 H, 3 Ph), 5.64 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 5.15 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.82 and 4.68 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.79 and 4.56 (2 d, 2 H, J_{gem} 10.5 Hz, OCH_2Ph), 4.65 and 4.50 (2 d, 2 H, J_{gem} 12 Hz, OCH_2Ph), 3.90–3.68 (m, 4 H, H-3,4,6a,6b), 3.62 (ddd, 1 H, $J_{4,5}$ 10, $J_{5,6a}$ 2.5, $J_{5,6b}$ 3.5 Hz, H-5), 2.08 and 1.93 (2 s, each 3 H, 2 OAc).

Anal. Calc. for $C_{31}H_{34}O_8$: C, 69.65; H, 6.41. Found: C, 69.94; H, 6.57.

*1,2-Di-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-*D*-galactopyranose* (**5**). — 3,4,6-Tri-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-α-D-galactopyranose[23] (**2**; 507 mg, 1 mmol) reacted with acetic acid to give **5** (449 mg, 84%), isolated as a syrup, $[\alpha]_D$ +23° (*c* 1, chloroform), R_F 0.61 (4:1 toluene–ethyl acetate); ^{1}H-n.m.r. ($CDCl_3$): δ 7.46–7.15 (m, 15 H, 3 Ph), 5.62 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 5.50 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.96 and 4.62 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.70 and 4.52 (2 d, 2 H, J_{gem} 12.5 Hz, OCH_2Ph), 4.44 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.02 (d, 1 H, $J_{3,4}$ 2.5 Hz, H-4), 3.77–3.56 (m, 4 H, H-3,5,6a,6b), 2.06 and 2.01 (2 s, each 3 H, 2 OAc).

Anal. Calc. for $C_{31}H_{34}O_8$: C, 69.65; H, 6.41. Found: C, 69.40; H, 6.37.

*1,2-Di-*O*-acetyl-3,4-di-O-benzyl-6-deoxy-β-*D*-glucopyranose* (**6**). — 3,4-Di-*O*-benzyl-6-deoxy-1,2-*O*-(1-ethoxyethylidene)-α-D-glucopyranose[24] (**3**; 414 mg, 1 mmol) reacted with acetic acid to give **6** (394 mg, 92%), m.p. 112–113° (from

ethanol), $[\alpha]_D$ +24° (*c* 1, chloroform), R_F 0.57 (4:1 toluene–ethyl acetate); ^{1}H-n.m.r. ($CDCl_3$): δ 7.49–7.29 (m, 10 H, 2 Ph), 5.66 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 5.13 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.89 and 4.69 (2 d, 2 H, J_{gem} 11 Hz, OCH_2Ph), 4.86 and 4.71 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 3.73 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.62 (dq, 1 H, $J_{4,5}$ 9.5, $J_{5,Me}$ 6.0 Hz, H-5), 3.34 (dd, 1 H, H-4), 2.11 and 1.95 (2 s, each 3 H, 2 OAc), 1.34 (d, 3 H, CH_3-6).

Anal. Calc. for $C_{24}H_{28}O_7$: C, 67.28; H, 6.59. Found: C, 67.15; H, 6.56.

*General procedure for glycosylation with 1,2-*trans*-di-O-acetyl derivatives.* — A solution of the 1,2-*trans*-di-*O*-acetyl glycosyl donor (1 mmol) and the alcoholic acceptor (1 mmol) in dry dichloromethane (40 mL) was stirred for 1 h at room temperature in the presence of activated powdered molecular sieves (4 Å, 2 g) under argon, then cooled at −20°. Trimethylsilyl triflate (0.2 mL, 1 mmol) was added, and the mixture was stirred at −20° for ~20 min, the reaction being monitored by t.l.c. The mixture was neutralized at −20° with triethylamine (~0.15 mL), then allowed to reach room temperature, diluted with dichloromethane, and filtered. The filtrate was washed successively with dilute hydrochloric acid, water, aqueous sodium hydrogencarbonate, and water, dried ($MgSO_4$), and concentrated.

6-O-(2-O-Acetyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**14**). — Glycosylation of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**13**; 260 mg, 1 mmol) with **4** (535 mg, 1 mmol), followed by column chromatography (8:1 toluene–ethyl acetate), gave **14** (625 mg, 85%), isolated as a syrup, $[\alpha]_D$ −34° (*c* 1.1, chloroform); lit.[19]: $[\alpha]_D$ −31° (*c* 0.05–1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.44–7.19 (m, 15 H, 3 Ph), 5.54 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.03 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 9.0 Hz, H-2′), 4.81 and 4.71 (2 d, 2 H, J_{gem} 11 Hz, OCH_2Ph), 4.81 and 4.57 (2 d, 2 H, J_{gem} 12 Hz, OCH_2Ph), 4.67 and 4.58 (2 d, 2 H, J_{gem} 12 Hz, OCH_2Ph), 4.60 (dd, 1 H, $J_{6a,6b}$ 8.0, $J_{5,6a}$ 2.5 Hz, H-6a), 4.46 (d, 1 H, H-1′), 4.30 (dd, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 4.21 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 4.09 (dd, 1 H, $J_{5',6'a}$ 3.5, $J_{6'a,6'b}$ 11.5 Hz, H-6′a), 3.95 (ddd, 1 H, $J_{4',5'}$ 7.0, $J_{5',6'b}$ 2.0 Hz, H-5′), 3.80–3.60 (m, 5 H, H-3,4,3′,4′,6′b), 3.50 (m, 1 H, H-5), 2.02 (s, 3 H, OAc), 1.51, 1.43, 1.32, and 1.31 (4 s, each 3 H, 2 CMe_2).

Anal. Calc. for $C_{41}H_{50}O_{12}$: C, 67.01; H, 6.86. Found: C, 66.88; H, 6.90.

Methyl 3-O-(2-O-acetyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2-O-benzyl-6-deoxy-4-O-methyl-β-D-galactopyranoside (**42**). — Glycosylation of methyl 2-*O*-benzyl-6-deoxy-4-*O*-methyl-β-D-galactopyranoside[24] (**41**; 282 mg, 1 mmol) with **4** (535 mg, 1 mmol), followed by column chromatography (97:3, then 19:1 dichloromethane–acetone), gave **42** (594 mg, 78.5%), m.p. 136° (ethanol), $[\alpha]_D$ +12° (*c* 1, chloroform); ^{1}H-n.m.r. (400 MHz) (C_6D_6): δ 7.49–7.03 (m, 20 H, 4 Ph), 5.48 (m, 1 H, $J_{1',2'}$ 8.0 Hz, H-2′), 5.05 and 4.45 (2 d, 2 H, J_{gem} 11 Hz, OCH_2Ph), 4.72 and 4.68 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.72 and 4.65 (2 d, 2 H, J_{gem} 12 Hz, OCH_2Ph), 5.01 (d, 1 H, H-1′), 4.34 (m, 2 H, OCH_2Ph), 4.17 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.99 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 3.85 (dd, 1 H, $J_{5',6'a}$ 3.0, $J_{6'a,6'b}$ 10 Hz, H-6′a), 3.67 (s, 3 H, OMe), 3.63 (m, 3 H, H-3,3′,5′), 3.55 (dd, 1 H, $J_{5',6'b}$ 5.0 Hz, H-6′b),

3.37 (m, 4 H, OMe, H-4'), 3.31 (dd, 1 H, $J_{3,4}$ 3.0, $J_{4,5}$ 0.5 Hz, H-4), 3.16 (dq, 1 H, $J_{5,Me}$ 6.5 Hz, H-5), 1.63 (s, 3 H, OAc), 1.22 (d, 3 H, CH_3-6).

Anal. Calc. for $C_{44}H_{52}O_{11}$: C, 69.82; H, 6.93. Found: C, 69.70; H, 6.90.

Phenyl 4-O-(2-O-acetyl-3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-2,3-di-O-benzyl-6-deoxy-1-thio-β-D-glucopyranoside (**51**). — Glycosylation of phenyl 2,3-di-*O*-benzyl-6-deoxy-1-thio-β-D-glucopyranoside[24] (**50**; 437 mg, 1 mmol) with **4** (535 mg, 1 mmol), followed by column chromatography (19:1 toluene–ethyl acetate), gave **51** (683 mg, 75%), m.p. 129–130° (from ethanol), $[\alpha]_D$ +22° (*c* 1.2, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.61–7.17 (m, 30 H, 6 Ph), 5.18–4.51 (m, 10 H, H-1,1', 4 OCH_2Ph), 5.04 (dd, 1 H, $J_{1',2'}$ 8.5, $J_{2',3'}$ 9.5 Hz, H-2'), 4.38 (s, 2 H, OCH_2Ph), 3.78–3.34 (m, 9 H, H-2,3,4,5,3',4',5',6'a,6'b), 1.96 (s, 3 H, OAc), 1.35 (d, 3 H, $J_{5,Me}$ 6.0 Hz, CH_3-6).

Anal. Calc. for $C_{55}H_{58}O_{10}S$: C, 72.50; H, 6.42. Found: C, 72.63; H, 6.46.

Methyl 6-O-(2-O-acetyl-3,4,6-tri-O-benzyl-β-D-galactopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**22**). — Glycosylation of methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[29] (**21**; 465 mg, 1 mmol) with **5** (535 mg, 1 mmol), followed by column chromatography (17:3 toluene–ethyl acetate), gave **22** (845 mg, 82%), m.p. 117° (ethyl acetate–hexane), $[\alpha]_D$ +10° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.48–7.20 (m, 30 H, 6 Ph), 5.49 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 10 Hz, H-2'), 4.42 (d, 1 H, H-1'), 3.35 (s, 3 H, OMe), 1.96 (s, 3 H, OAc).

Anal. Calc. for $C_{57}H_{62}O_{12}$: C, 72.90; H, 6.65. Found: C, 72.85; H, 6.65.

Methyl 4-O-(2-O-acetyl-3,4,6-tri-O-benzyl-β-D-galactopyranosyl)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (**30**). — Glycosylation of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[30] (**29**; 465 mg, 1 mmol) with **5** (535 mg, 1 mmol), followed by column chromatography (24:1 dichloromethane–acetone), gave **30** (845 mg, 90%), isolated as a syrup, $[\alpha]_D$ +9° (*c* 1.3, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.46–7.15 (m, 30 H, 6 Ph), 5.33 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 10 Hz, H-2'), 3.38 (s, 3 H, OMe), 1.95 (s, 3 H, OAc).

Anal. Calc. for $C_{57}H_{62}O_{12}$: C, 72.90; H, 6.65. Found: C, 72.86; H, 6.82.

Phenyl 4-O-(2-O-acetyl-3,4-di-O-benzyl-6-deoxy-β-D-glucopyranosyl)-2,3-di-O-benzyl-6-deoxy-1-thio-β-D-glucopyranoside (**55**). — Glycosylation of **50** (437 mg, 1 mmol) with **6** (428 mg, 1 mmol), followed by column chromatography (19:1 toluene–ethyl acetate), gave **55** (644 mg, 80%), m.p. 150–151° (from ethanol), $[\alpha]_D$ +25° (*c* 0.9, chloroform); ^{1}H-n.m.r. (400 MHz, C_6D_6): δ 7.82–7.08 (m, 25 H, 5 Ph), 5.47 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 9.5 Hz, H-2'), 5.34 and 4.95 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 5.02 and 4.90 (2 d, 2 H, J_{gem} 11 Hz, OCH_2Ph), 4.86 and 4.45 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.76 and 4.73 (2 d, 2 H, J_{gem} 12 Hz, OCH_2Ph), 4.75 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 4.55 (d, 1 H, H-1'), 3.72–3.05 (m, 5 H, H-2,3,4,3',4'), 3.28 and 3.23 (2 dq, 2 H, $J_{4,5} = J_{4',5'} = 9.5$, $J_{5,Me} = J_{5',Me} = 6.0$ Hz, H-5,5'), 1.84 (s, 3 H, OAc), 1.41 and 1.23 (2 d, each 3 H, CH_3-6,6').

Anal. Calc. for $C_{48}H_{52}O_9S$: C, 71.62; H, 6.51. Found: C, 71.32; H, 6.46.

General procedure for O-deacetylation of disaccharides. — A solution of the protected disaccharide (1 mmol) in anhydrous methanol (30 mL; dry 1,4-dioxane

was added when the mixture was not homogeneous) was treated with sodium (a few mg) at room temperature under argon. The reaction was monitored by t.l.c. (1–3 h). After the starting material had disappeared, the solution was neutralized with IR-120 (H^+) ion-exchange resin, filtered, and then concentrated to give a quantitative yield of *O*-deacetylated disaccharide.

1,2:3,4-Di-O-*isopropylidene-6*-O-*(3,4,6-tri*-O-*benzyl*-β-D-*glucopyranosyl)*-α-D-*galactopyranose* (**15**). — *O*-Deacetylation of **14** gave **15** (100%) as a syrup. An analytical sample, prepared by column chromatography (4:1 toluene–ethyl acetate), had $[\alpha]_D$ −42° (*c* 0.6, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.49–7.16 (m, 15 H, 3 Ph), 5.61 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.07 and 4.84 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.89 and 4.53 (2 d, 2 H, J_{gem} 11 Hz, OCH_2Ph), 4.65 and 4.56 (2 d, 2 H, J_{gem} 12 Hz, OCH_2Ph), 4.64 (dd, 1 H, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 8.0 Hz, H-6a), 4.37 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.36 (dd, 1 H, $J_{1,2}$ 5.0, $J_{2,3}$ 2.5 Hz, H-2), 4.26 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 4.14 (dd, 1 H, $J_{5',6'a}$ 3.5, $J_{6'a,6'b}$ 11 Hz, H-6′a), 4.06 (ddd, 1 H, $J_{4',5'}$ 8.0, $J_{5',6'b}$ 2.0 Hz, H-5′), 3.83–3.61 (m, 6 H, H-3,4,2′,3′,4′,6′b), 3.52 (m, 1 H, H-5), 1.56, 1.47, 1.35, and 1.33 (4 s, each 3 H, 2 CMe_2).

Anal. Calc. for $C_{39}H_{48}O_{11}$: C, 67.61; H, 6.98. Found: C, 67.37; H, 7.04.

Methyl 2-O-*benzyl-6-deoxy-4*-O-*methyl-3*-O-*(3,4,6-tri*-O-*benzyl*-β-D-*glucopyranosyl)*-β-D-*galactopyranoside* (**43**). — *O*-Deacetylation of **42** gave crystalline **43** (100%). An analytical sample, prepared by column chromatography (4:1 toluene–ethyl acetate), had m.p. 149–150° (ethanol), $[\alpha]_D$ +10° (*c* 0.9, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.48–7.23 (m, 20 H, 4 Ph), 5.02–4.46 (m, 9 H, 4 OCH_2Ph, H-1′), 4.24 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1), 3.78–3.45 (m, 9 H, H-2,3,5,2′,3′,4′,5′,6′a,6′b), 3.63 and 3.56 (2 s, each 3 H, 2 OMe), 3.43 (d, 1 H, $J_{3,4}$ 2.0 Hz, H-4), 2.79 (s, 1 H, OH), 1.30 (d, 3 H, $J_{5,Me}$ 6.5 Hz, CH_3-6).

Anal. Calc. for $C_{42}H_{50}O_{10}$: C, 70.57; H, 7.05. Found: C, 70.45; H, 6.97.

Phenyl 2,3-di-O-*benzyl-6-deoxy-4*-O-*(3,4,6-tri*-O-*benzyl*-β-D-*glucopyranosyl)*-1-*thio*-β-D-*glucopyranoside* (**52**). — *O*-Deacetylation of **51** gave crystalline **52** (100%). An analytical sample, prepared by column chromatography (9:1 toluene–ethyl acetate), had m.p. 97–99° (from ethanol), $[\alpha]_D$ +20° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.63–7.19 (m, 30 H, 6 Ph), 5.14–4.52 (m, 10 H, H-1,1′, 4 OCH_2Ph), 4.43 (s, 2 H, OCH_2Ph), 3.69–3.39 (m, 10 H, H-2,3,4,5,2′,3′,4′,5′,6′a,6′b), 2.41 (s, 1 H, OH), 1.44 (d, 3 H, $J_{5,Me}$ 6.0 Hz, CH_3-6).

Anal. Calc. for $C_{53}H_{56}O_9S \cdot 0.5\ H_2O$: C, 72.49; H, 6.54. Found: C, 72.53; H, 6.44.

Methyl 2,3,4-tri-O-*benzyl-6*-O-*(3,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl)*-α-D-*glucopyranoside* (**23**). — *O*-Deacetylation of **22** gave crystalline **23** (100%). An analytical sample, prepared by column chromatography (8:1 toluene–ethyl acetate), had m.p. 77–78° (from ethanol), $[\alpha]_D$ +6° (*c* 0.8, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.46–7.26 (m, 30 H, 6 Ph), 4.25 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 3.38 (s, 3 H, OMe).

Anal. Calc. for $C_{55}H_{60}O_{11}$: C, 73.64; H, 6.74. Found: C, 73.49; H, 6.79.

Methyl 2,3,6-tri-O-*benzyl-4*-O-*(3,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl)*-α-

D-*glucopyranoside* (**31**). — *O*-Deacetylation of **30** gave **31** (100%) as a syrup. An analytical sample, prepared by column chromatography (4:1 toluene–ethyl acetate), had $[\alpha]_D$ +8.5° (*c* 1.2, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.43–7.19 (m, 30 H, 6 Ph), 4.48 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 3.37 (s, 3 H, OMe), 2.98 (s, 1 H, OH).

Anal. Calc. for $C_{55}H_{60}O_{11}$: C, 73.64; H, 6.74. Found: C, 73.41; H, 6.78.

*Phenyl 2,3-di-O-benzyl-6-deoxy-4-O-(3,4-di-O-benzyl-6-deoxy-β-*D*-glucopyranosyl)-1-thio-β-*D*-glucopyranoside* (**56**). — *O*-Deacetylation of **55** gave crystalline **56** (100%), m.p. 106–108° (from ethanol), $[\alpha]_D$ +21° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.59–7.15 (m, 25 H, 5 Ph), 5.08–4.59 (m, 8 H, 4 OCH_2Ph), 4.64 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 4.50 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1'), 3.68–3.13 (m, 8 H, H-2,3,4,5, 2',3',4',5'), 2.47 (s, 1 H, OH), 1.44 and 1.20 (2 d, 6 H, $J_{5,Me} = J_{5',Me}$ = 6.0 Hz, CH_3-6,6').

Anal. Calc. for $C_{46}H_{50}O_8S \cdot 0.5\ H_2O$: C, 71.57; H, 6.65. Found: C, 71.62; H, 6.53.

General procedure for preparation of disaccharide xanthates. — Sodium hydride (80 mg of a 60% dispersion in oil, 2 mmol) was added to an ice-cooled solution of disaccharide alcohol (1 mmol) and imidazole (14 mg, 0.2 mmol) in dry tetrahydrofuran (60 mL). The mixture was stirred for 1 h at room temperature under argon, and carbon disulfide (0.6 mL, 10 mmol) was then added. Stirring was continued for 20 min, and methyl iodide (0.6 mL, 10 mmol) was added. The reaction was monitored by t.l.c. (4:1 toluene–ethyl acetate). Methanol was added at 0° to destroy the excess of sodium hydride. The mixture was concentrated, the residue was taken up in ether, and the extract was washed successively with water, dilute hydrochloric acid, and water, dried ($MgSO_4$), and concentrated.

*1,2:3,4-Di-O-isopropylidene-6-O-[3,4,6-tri-O-benzyl-2-O-(methylthio)thiocarbonyl-β-*D*-glucopyranosyl]-α-*D*-galactopyranose* (**16**). — Xanthation of **15**, followed by column chromatography (9:1 toluene–ethyl acetate), gave **16** (82%), $[\alpha]_D$ −62° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.42–7.20 (m, 15 H, 3 Ph), 6.08 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 9.0 Hz, H-2'), 5.53 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 4.84 and 4.57 (2 d, 2 H, J_{gem} 11 Hz, OCH_2Ph), 4.73 (m, 2 H, OCH_2Ph), 4.66 and 4.58 (2 d, 2 H, J_{gem} 12.5 Hz, OCH_2Ph), 4.65 (d, 1 H, H-1'), 4.58 (dd, 1 H, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 8.0 Hz, H-6a), 4.30 (dd, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 4.23 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 4.08 (dd, 1 H, $J_{5',6'a}$ 5.0, $J_{6'a,6'b}$ 11 Hz, H-6'a), 3.98–3.51 (m, 7 H, H-3,4,5,3',4',5',6'b), 2.59 (s, 3 H, SMe), 1.52, 1.43, 1.33, and 1.30 (4 s, each 3 H, 2 CMe_2).

Anal. Calc. for $C_{41}H_{50}O_{11}S_2$: C, 62.90; H, 6.44. Found: C, 63.03; H, 6.57.

*Methyl 2-O-benzyl-6-deoxy-4-O-methyl-3-O-[3,4,6-tri-O-benzyl-2-O-(methylthio)thiocarbonyl-β-*D*-glucopyranosyl]-β-*D*-galactopyranoside* (**44**). — Xanthation of **43**, followed by column chromatography (9:1 toluene–ethyl acetate), gave **44** (100%), $[\alpha]_D$ −20° (*c* 0.7, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.52–7.20 (m, 20 H, 4 Ph), 6.14 (m, 1 H, $J_{1',2'}$ 8.0 Hz, H-2'), 5.06 (d, 1 H, H-1'), 4.93–4.52 (m, 8 H, 4 OCH_2Ph), 4.22 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.86–3.39 (m, 8 H, H-2,3,5,3',4',5', 6'a,6'b), 3.60 and 3.54 (2 s, each 3 H, 2 OMe), 3.35 (dd, 1 H, $J_{3,4}$ 3.0, $J_{4,5}$ 0.5 Hz, H-4), 2.59 (s, 3 H, SMe), 1.27 (d, 3 H, $J_{5,Me}$ 6.5 Hz, CH_3-6).

Anal. Calc. for $C_{44}H_{52}O_{10}S_2$: C, 65.65; H, 6.51. Found: C, 65.50; H, 6.59.

*Phenyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(methylthio)-thiocarbonyl-β-*D*-glucopyranosyl]-1-thio-β-*D*-glucopyranoside* (**53**). — Xanthation of **52**, followed by column chromatography (19:1 toluene–ethyl acetate), gave **53** (95%), $[\alpha]_D$ −13° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.61–7.16 (m, 30 H, 6 Ph), 6.08 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 9.0 Hz, H-2′), 5.15–4.49 (m, 9 H, H-1′, 4 OCH_2Ph), 4.66 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 4.40 (s, 2 H, OCH_2Ph), 3.79 (dq, 1 H, $J_{4,5}$ 9.0, $J_{5,Me}$ 6.0 Hz, H-5), 3.69–3.33 (m, 8 H, H-2,3,4,3′,4′,5′,6′a,6′b), 2.61 (s, 3 H, SMe), 1.38 (d, 3 H, CH_3-6).

Anal. Calc. for $C_{55}H_{58}O_9S_3$: C, 68.87; H, 6.09. Found: C, 68.82; H, 6.14.

*Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(methylthio)thiocarbonyl-β-*D*-galactopyranosyl]-α-*D*-glucopyranoside* (**24**). — Xanthation of **23**, followed by column chromatography (toluene, then 16:1 toluene–ethyl acetate), gave **24** (99%), $[\alpha]_D$ −4° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.43–7.24 (m, 30 H, 6 Ph), 6.41 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 10 Hz, H-2′), 4.36 (d, 1 H, H-1′), 3.32 (s, 3 H, OMe), 2.44 (s, 3 H, SMe).

Anal. Calc. for $C_{57}H_{62}O_{11}S_2$: C, 69.35; H, 6.33. Found: C, 69.46; H, 6.37.

*Methyl 2,3,6-tri-*O*-benzyl-4-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(methylthio)thiocarbonyl-β-*D*-galactopyranosyl]-α-*D*-glucopyranoside* (**32**). — Xanthation of **31**, followed by column chromatography (16:1 toluene–ethyl acetate), gave **32** (96%), $[\alpha]_D$ −3° (*c* 0.6, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.41–7.17 (m, 30 H, 6 Ph), 6.32 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 10 Hz, H-2′), 3.37 (s, 3 H, OMe), 2.59 (s, 3 H, SMe).

Anal. Calc. for $C_{57}H_{62}O_{11}S_2$: C, 69.35; H, 6.33. Found: C, 69.21; H, 6.46.

*Phenyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-[3,4-di-*O*-benzyl-6-deoxy-2-*O*-(methylthio)thiocarbonyl-β-*D*-glucopyranosyl]-1-thio-β-*D*-glucopyranoside* (**57**). — Xanthation of **56**, followed by column chromatography (toluene), gave **57** (100%), m.p. 140° (from ethanol), $[\alpha]_D$ −14° (*c* 0.3, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.51–7.09 (m, 25 H, 5 Ph), 5.98 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 9.5 Hz, H-2′), 5.04–4.52 (m, 9 H, 4 OCH_2Ph, H-1′), 4.59 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 3.78–3.20 (m, 7 H, H-2,3,4,5, 3′,4′,5′), 2.58 (s, 3 H, SMe), 1.36 and 1.16 (2 d, 6 H, $J_{5,Me}$ = $J_{5',Me}$ = 6.0 Hz, CH_3-6,6′).

Anal. Calc. for $C_{48}H_{52}O_8S_3$: C, 67.58; H, 6.14. Found: C, 67.62; H, 6.31.

General procedure for radical reduction of disaccharide xanthates. — A solution of disaccharide xanthate (1 mmol) in dry toluene (70 mL) was added dropwise to a refluxing solution of tributyltin hydride (2.7 mL, 10 mmol) in dry toluene (35 mL) containing α,α′-azobisisobutyronitrile (40 mg). The reaction was monitored by t.l.c. and was usually complete in <3 h under reflux. The mixture was cooled, then concentrated.

*1,2:3,4-Di-*O*-isopropylidene-6-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-arabino-hexopyranosyl)-α-*D*-galactopyranose* (**17**). — Reduction of **16** (783 mg, 1 mmol), followed by column chromatography (9:1 toluene–ethyl acetate), gave **17** (582 mg, 86%), $[\alpha]_D$ −47° (*c* 0.5, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.45–7.22 (m, 15 H, 3 Ph), 5.61 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 4.94 and 4.57 (2 d, 2 H, J_{gem} 11 Hz, OCH_2Ph), 4.73 and 4.60 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.67 and 4.56 (2 d, 2 H, J_{gem} 12.5

Hz, OCH_2Ph), 4.62 (dd, 1 H, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 8.0 Hz, H-6a), 4.54 (dd, 1 H, $J_{1',2'e}$ 2.0, $J_{1',2'a}$ 9.5 Hz, H-1'), 4.34 (dd, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 4.25 (dd, 1 H, $J_{5,.6b}$ 2.0 Hz, H-6b), 4.12 (dd, 1 H, $J_{5',6'a}$ 3.5, $J_{6'a,6'b}$ 11 Hz, H-6'a), 4.03 (m, 1 H, H-5'), 3.80–3.52 (m, 5 H, H-3,4,3',4',6'b), 3.43 (m, 1 H, H-5), 2.49 (ddd, 1 H, $J_{2'e,3'}$ 5.0, $J_{2'e,2'a}$ 12.5 Hz, H-2'*e*), 1.67 (ddd, 1 H, $J_{2'a,3'}$ 12 Hz, H-2'*a*), 1.55, 1.45, 1.34, and 1.32 (4 s, each 3 H, 2 CMe_2).

Anal. Calc. for $C_{39}H_{48}O_{10}$: C, 69.21; H, 7.15. Found: C, 69.15; H, 7.35.

*Methyl 2-*O*-benzyl-6-deoxy-4-*O*-methyl-3-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-arabino-hexopyranosyl)-β-*D*-galactopyranoside* (**45**). — Reduction of **44** (805 mg, 1 mmol), followed by column chromatography (17:3 toluene–ethyl acetate), gave **45** (573 mg, 82%), m.p. 95° (from dichloromethane–hexane), $[\alpha]_D$ +2° (*c* 0.8, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.44–7.26 (m, 20 H, 4 Ph), 4.94 and 4.56 (2 d, 2 H, J_{gem} 11 Hz, OCH_2Ph), 4.93 and 4.58 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.68 (dd, 1 H, $J_{1',2'e}$ 2.0, $J_{1',2'a}$ 10 Hz, H-1'), 4.66 and 4.62 (2 d, 2 H, J_{gem} 12 Hz, OCH_2Ph), 4.64 and 4.60 (2 d, 2 H, J_{gem} 11 Hz, OCH_2Ph), 4.22 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.80–3.34 (m, 9 H, H-2,3,4,5,3',4',5',6'a,6'b), 3.63 and 3.56 (2 s, each 3 H, 2 OMe), 2.33 (ddd, 1 H, $J_{2'e,2'a}$ 12.5, $J_{2'e,3'}$ 5.0 Hz, H-2'*e*), 1.62 (ddd, 1 H, $J_{2'a,3'}$ 9.5 Hz, H-2'*a*), 1.29 (d, 3 H, $J_{5,Me}$ 6.5 Hz, CH_3-6).

Anal. Calc. for $C_{42}H_{50}O_9$: C, 72.18; H, 7.21. Found: C, 72.27; H, 7.45.

*Phenyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-arabino-hexopyranosyl)-1-thio-β-*D*-glucopyranoside* (**54**). — Reduction of **53** (959 mg, 1 mmol), followed by column chromatography (19:1 toluene–ethyl acetate), gave **54** (734 mg, 86%), m.p. 128–129° (from ethanol), $[\alpha]_D$ +10° (*c* 0.6, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.64–7.17 (m, 30 H, 6 Ph), 5.17–4.53 (m, 10 H, H-1,1', 4 OCH_2Ph), 4.45 (m, 2 H, OCH_2Ph), 3.70–3.31 (m, 9 H, H-2,3,4,5,3',4',5',6'a,6'b), 2.35 (ddd, 1 H, $J_{1',2'e}$ 2.5, $J_{2'e,2'a}$ 12.5, $J_{2'e,3'}$ 4.5 Hz, H-2'*e*), 1.63 (ddd, 1 H, $J_{1',2'a}$ 10, $J_{2'a,3'}$ 9.5 Hz, H-2'*a*), 1.34 (d, 3 H, $J_{5,6}$ 6.0 Hz, CH_3-6).

Anal. Calc. for $C_{53}H_{56}O_8S$: C, 74.62; H, 6.62. Found: C, 74.41; H, 6.55.

*Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-lyxo-hexopyranosyl)-α-*D*-glucopyranoside* (**25**). — Reduction of **24** (987 mg, 1 mmol), followed by column chromatography (50:1 dichloromethane–ethyl acetate), gave **25** (881 mg, 100%), m.p. 100° (from ethanol), $[\alpha]_D$ +7° (*c* 0.9, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.43–7.25 (m, 30 H, 6 Ph), 4.24 (dd, 1 H, $J_{1',2'a}$ 9.5, $J_{1',2'e}$ 2.0 Hz, H-1'), 3.35 (s, 3 H, OMe), 2.12 (ddd, 1 H, $J_{2'e,2'a}$ 12, $J_{2'a,3'}$ 10 Hz, H-2'*a*), 1.94 (ddd, 1 H, $J_{2'e,3'}$ 3.5 Hz, H-2'*e*).

Anal. Calc. for $C_{55}H_{60}O_{10}$: C, 74.98; H, 6.86. Found: C, 74.73; H, 6.71.

*Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-lyxo-hexopyranosyl)-α-*D*-glucopyranoside* (**33**). — Reduction of **32** (987 mg, 1 mmol), followed by column chromatography (9:1 toluene–ethyl acetate), gave **33** (705 mg, 80%), $[\alpha]_D$ −3° (*c* 1.1, chloroform); ^{1}H-n.m.r. (C_6D_6): δ 7.64–7.07 (m, 30 H, 6 Ph), 4.75 (dd, 1 H, $J_{1',2'e}$ 2.0, $J_{1',2'a}$ 10 Hz, H-1'), 3.19 (s, 3 H, OMe), 2.45 (ddd, 1 H, $J_{2'e,2'a}$ 12.5, $J_{2'a,3'}$ 10 Hz, H-2'*a*), 2.09 (ddd, 1 H, $J_{2'e,3'}$ 3.5 Hz, H-2'*e*).

Anal. Calc. for $C_{55}H_{60}O_{10}$: C, 74.98; H, 6.86. Found: C, 74.90; H, 7.05.

Phenyl 2,3-di-O-benzyl-6-deoxy-4-O-(3,4-di-O-benzyl-2,6-dideoxy-β-D-arabino-hexopyranosyl)-1-thio-β-D-glucopyranoside (**58**). — Reduction of **57** (853 mg, 1 mmol), followed by column chromatography (24:1 toluene–ethyl acetate), gave **58** (598 mg, 80%), m.p. 136–138° (from ethanol), $[\alpha]_D$ +6° (*c* 0.8, chloroform); ^{1}H-n.m.r. (C_6D_6): δ 7.64–6.86 (m, 25 H, 5 Ph), 5.20 and 4.47 (2 d, 2 H, J_{gem} 11 Hz, OC*H*$_2$Ph), 4.86 and 4.80 (2 d, 2 H, J_{gem} 11 Hz, OC*H*$_2$Ph), 4.86 and 4.75 (2 d, 2 H, J_{gem} 11 Hz, OC*H*$_2$Ph), 4.63 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 4.41 and 4.32 (2 d, 2 H, J_{gem} 12 Hz, OC*H*$_2$Ph), 4.36 (dd, 1 H, $J_{1',2'e}$ 2.0, $J_{1',2'a}$ 10 Hz, H-1′), 3.60–2.97 (m, 7 H, H-2,3,4,5,3′,4′,5′), 2.19 (ddd, 1 H, $J_{2'e,2'a}$ 12, $J_{2'e,3'}$ 5.0 Hz, H-2′*e*), 1.68 (ddd, 1 H, $J_{2'a,3'}$ 10 Hz, H-2′*a*), 1.22 and 1.20 (2 d, 6 H, $J_{5,Me} = J_{5',Me}$ = 6.0 Hz, CH_3-6,6′).

Anal. Calc. for $C_{46}H_{50}O_7S$: C, 73.97; H, 6.75. Found: C, 73.56; H, 6.92.

3,4,6-Tri-O-acetyl-2-deoxy-2-formamido-α-D-glucopyranosyl chloride (**8**). — A stream of dry hydrogen chloride was passed through a suspension of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-formamido-β-D-glucopyranose[33] (**7**; 3.75 g, 10 mmol) in acetyl chloride (60 mL), with stirring and cooling at 0°, until a clear solution was obtained. The reaction mixture was left overnight at room temperature, then concentrated. The residue crystallized from dichloromethane–benzene to give **8** (2.82 g, 80%), m.p. 105–107° (dec.), $[\alpha]_D$ +106° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.15 (bd s, 0.9 H, CHO, *trans*), 8.03 (d, 0.1 H, $J_{CHO,NH}$ 11.0 Hz, CHO, *cis*), 6.27 (d, 1 H, $J_{2,NH}$ 9.0 Hz, NH, *cis* and *trans*), 6.20 (d, 0.9 H, $J_{1,2}$ 3.5 Hz, H-1, *trans*), 6.15 (d, 0.1 H, $J_{1,2}$ 3.5 Hz, H-1, *cis*), 5.37 (dd, 1 H, $J_{3,4}$ 9.5, $J_{4,5}$ 10.5 Hz, H-4), 5.22 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-3), 4.64 (ddd, 1 H, H-2), 4.39–4.09 (m, 3 H, H-5,6a,6b), 2.19 (s, 3 H, OAc), 2.09 (s, 6 H, 2 OAc).

Anal. Calc. for $C_{13}H_{18}ClNO_8$: C, 44.39; H, 5.15; N, 3.98. Found: C, 43.72; H, 5.32; N, 3.75.

3,4,6-Tri-O-acetyl-2-deoxy-2-formamido-α,β-D-glucopyranose (**9**). — Benzylamine (0.52 mL, 4.8 mmol) was added at room temperature to a suspension of **7** (450 mg, 1.2 mmol) in dry tetrahydrofuran (5 mL). The mixture was stirred overnight at room temperature, by which time **7** had dissolved. The solution was neutralized with IR-120 (H^+) resin, filtered, and concentrated. Column chromatography (5:3 dichloromethane–acetone) of the residue gave **9** (334 mg, 84%) as a white foam, $[\alpha]_D$ +52° (*c* 1, chloroform); $\nu_{max}^{CHCl_3}$ 3410 (NH), 3380 (OH), 1750 (OAc), 1690 (NCHO) cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 8.18 (bd s, CHO, *trans*), 8.02 (d, $J_{CHO,NH}$ 11.5 Hz, CHO, *cis*), 6.50 (m, 1 H, NH), 5.43–5.27 (m, 1 H, H-4), 5.29 (d, $J_{1,2}$ 3.5 Hz, H-1, *trans*), 5.22–5.01 (m, 1 H, H-3), 4.91 (d, $J_{1,2}$ 3.5 Hz, H-1, *cis*), 4.44–4.03 (m, 4 H, H-2,5,6a,6b), 2.31 (bd s, 1 H, OH), 2.17–1.96 (9 H, 3 OAc).

Anal. Calc. for $C_{13}H_{19}NO_9$: C, 46.83; H, 5.75; N, 4.20. Found: C, 46.21; H, 5.85; N, 4.01.

3,4,6-Tri-O-acetyl-2-deoxy-2-formamido-α-D-glucopyranosyl trichloroacetimidate (**10**). — 1,8-Diazabicyclo[5.4.0]undec-7-ene (15 μL, 0.1 mmol) was added at 0° to a stirred mixture of **9** (346 mg, 1.03 mmol), trichloroacetonitrile (0.21 mL, 2.07 mmol), and activated powdered molecular sieves (4 Å, 100 mg) in dry dichloromethane (2 mL). This mixture was stirred for 30 min at 0°; t.l.c. (5:4 hexane–

acetone) then showed the disappearance of **9** and the presence of one compound (R_F 0.8). The reaction mixture was directly poured onto the top of a column of silica gel equilibrated in 250:200:9 hexane–acetone–triethylamine. Elution with the same solvent gave **10** (469 mg, 95%) as a white foam, $[\alpha]_D$ +87° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 9.00 (s, 0.1 H, CCl_3C:NH, *cis*), 8.91 (s, 0.9 H, CCl_3C:NH, *trans*), 8.24 (bd s, 0.9 H, CHO, *trans*), 8.16 (d, 0.1 H, $J_{CHO,NH}$ 11.5 Hz, CHO, *cis*), 6.46 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.90 (m, 1 H, NH), 5.48–5.19 (m, 2 H, H-3,4), 4.69 (ddd, 1 H, $J_{2,3}$ 10, $J_{2,NH}$ 9.5 Hz, H-2), 4.35–4.11 (m, 3 H, H-5,6a,6b), 2.10, 2.09, and 2.07 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{15}H_{19}Cl_3N_2O_9$: C, 37.71; H, 4.01; N, 5.86. Found: C, 37.65; H, 4.07; N, 5.76.

*(3,4,6-Tri-*O*-acetyl-1,2-dideoxy-α-*D*-glucopyrano)-[2,1-*d*]-2-oxazoline* (**12**). — Silver triflate (154 mg, 0.6 mmol) was added to a mixture of **8** (176 mg, 0.5 mmol) and activated powdered molecular sieves (4 Å, 300 mg) in dry dichloromethane (2 mL) at −20° under argon. The mixture was stirred for 1 h at −20°, then 4 h at room temperature. T.l.c. (5:4 hexane–acetone) showed the disappearance of **8**, and the presence of two compounds, **12** and some hydrolysis product. The mixture was neutralized with triethylamine, then poured onto the top of a column of silica gel equilibrated in 250:200:3 hexane–acetone–triethylamine. Elution with the same solvent gave **12** (135 mg, 86%), $[\alpha]_D$ +23° (*c* 1.4, chloroform); $\nu_{max}^{CHCl_3}$ 1760, 1640, 1380 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 7.20 (d, 1 H, $J_{2,N=CH}$ 2.5 Hz, N=CH), 6.08 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 5.36 (dd, 1 H, $J_{3,4}$ 2.2, $J_{2,3}$ 2.8 Hz, H-3), 4.96 (ddd, 1 H, $J_{4,5}$ 9.0, $J_{2,4}$ 1.1 Hz, H-4), 4.29–4.12 (m, 3 H, H-2,6a,6b), 3.64 (m, 1 H, H-5), 2.15, 2.12, and 2.10 (3 s, each 3 H, 3 OAc); mass spectrum: *m/z* 333 (M^+ + 18), 316 (M^+ + 1).

Anal. Calc. for $C_{13}H_{17}NO_8$: C, 49.51; H, 5.44; N, 4.44. Found: C, 49.36; H, 5.52; N, 4.30.

*Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-formamido-β-*D*-glucopyranoside* (**11**). — Stannous triflate (208 mg, 0.5 mmol) was added to a mixture of **8** (176 mg, 0.5 mmol), anhydrous methanol (0.2 mL), and activated powdered molecular sieves (4 Å, 400 mg) in dry dichloromethane (2 mL) at 0°. The mixture was stirred at room temperature under argon for 66 h, then neutralized with saturated aqueous sodium hydrogencarbonate (2 mL), and filtered. The organic layer was separated and concentrated. Column chromatography (5:4 hexane–acetone) of the residue gave **11** (100 mg, 58%), m.p. 131–132° (from hexane–acetone), $[\alpha]_D$ −11° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.24 (d, 0.4 H, $J_{CHO,NH}$ 1.5 Hz, CHO, *trans*), 8.04 (d, 0.6 H, $J_{CHO,NH}$ 11.0 Hz, CHO, *cis*), 6.60 (dd, 0.4 H, $J_{2,NH}$ 9.5 Hz, NH, *cis*), 6.43 (dd, 0.6 H, $J_{2,NH}$ 9.0 Hz, NH, *trans*), 4.66 (d, 0.4 H, $J_{1,2}$ 8.0 Hz, H-1, *trans*), 4.37 (d, 0.6 H, $J_{1,2}$ 8.0 Hz, H-1, *cis*), 3.58 (s, 1.2 H, OMe, *cis*), 3.54 (s, 1.8 H, OMe, *trans*), 2.13–2.01 (9 H, 3 OAc).

Anal. Calc. for $C_{14}H_{21}NO_9$: C, 48.41; H, 6.09; N, 4.03. Found: C, 48.48; H, 6.09; N, 3.96.

*Benzyl 6-*O*-benzoyl-2,4-di-*O*-benzyl-β-*D*-galactopyranoside* (**37**). — A solu-

tion of benzyl 2,4-di-*O*-benzyl-β-D-galactopyranoside[34] (2.25 g, 5 mmol) in pyridine (4 mL) was added at room temperature to a solution of benzoyl cyanide (983 mg, 7.5 mmol) in dry dichloromethane (20 mL). The reaction mixture was stirred for 24 h at room temperature under argon. Methanol (2 mL) was added, and stirring continued for 1 h. The solution was concentrated, the residue was taken up in dichloromethane, and the extract was washed successively with saturated aqueous sodium hydrogencarbonate, ice-cold dilute hydrochloric acid, and water, then dried, and concentrated. Column chromatography (3:1 hexane–acetone) of the residue gave **37** (1.23 g, 44%), m.p. 77° (from di-isopropyl ether), $[\alpha]_D$ −38° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.03 and 7.70–7.22 (2 m, 2 and 18 H, 4 Ph), 5.00 and 4.68 (2 d, 2 H, J_{gem} 12.5 Hz, OCH_2Ph), 5.06, 4.93, 4.77, and 4.72 (4 d, 4 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.60 (dd, 1 H, $J_{5,6a}$ 6.5, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.50 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1), 4.41 (dd, 1 H, $J_{5,6b}$ 7.0 Hz, H-6b), 3.92 (m, 1 H, H-4), 3.84–3.67 (m, 3 H, H-2,3,5), 2.39 (bd s, 1 H, OH); ($CDCl_3$ + CCl_3CONCO): δ 8.10 (s, 1 H, NH), 8.02 and 7.65–7.19 (2 m, 2 and 18 H, 4 Ph), 4.48 and 4.90 (2 d, 2 H, J_{gem} 12.5 Hz, OCH_2Ph), 4.91 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 3.0 Hz, H-3), 4.73–4.60 (m, 5 H, 2 OCH_2Ph and H-6a), 4.58 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.40 (dd, 1 H, $J_{5,6b}$ 7.0, $J_{6a,6b}$ 11.0 Hz, H-6b), 4.09 (dd, 1 H, H-4), 3.91 (dd, 1 H, H-2), 3.87 (m, 1 H, H-5).

Anal. Calc. for $C_{34}H_{34}O_7$: C, 73.61; H, 6.19. Found: C, 73.46; H, 6.16.

General procedure for glycosylations with β-acetate **7**. — Trimethylsilyl triflate (2.5–4.0 mmol) was added with stirring to a mixture of **7** (2 mmol), alcohol (1 mmol), and activated powdered molecular sieves (4 Å, 2 g) in dry dichloromethane (10 mL) at −20° under argon. The reaction mixture was allowed to reach room temperature, and stirring was continued until t.l.c. indicated the reaction to be complete (6–48 h). The mixture was neutralized with saturated aqueous sodium hydrogencarbonate (10 mL); the water layer was extracted with dichloromethane (10 mL), and the combined dichloromethane extracts were dried ($MgSO_4$), then concentrated.

General procedure for glycosylations with α-chloride **8**. — Silver triflate or stannous triflate (2 mmol) was added with stirring to a mixture of **8** (1.7 mmol), alcohol (1 mmol), and activated powdered molecular sieves (4 Å, 1.3 g) in dry dichloromethane (7 mL) at −20° under argon. The mixture was allowed to reach room temperature, and stirred until reaction was complete (24–48 h), with further additions of **8** and the catalyst being made if required. Work-up was effected as described for reactions with **7**.

General procedure for glycosylations with α-trichloroacetimidate **10**. — Trimethylsilyl triflate (1.2 mmol) was added with stirring to a mixture of **10** (1.2 mmol), alcohol (1 mmol), and activated powdered molecular sieves (4 Å, 2 g) in dry dichloromethane (10 mL) at −20° under argon. The mixture was allowed to reach room temperature, and stirred until reaction was complete (24 h). Further additions of **10** and trimethylsilyl triflate were made if required with cooling at −10°. Work-up was effected as described for reactions with **7** (neutralization of the reaction mixture could be done with triethylamine, giving rise to the formation of *O*-trimethylsilyl derivative if alcohol was still present).

1,2:3,4-Di-O-isopropylidene-6-O-(3,4,6-tri-O-acetyl-2-deoxy-2-formamido-β-D-glucopyranosyl)-α-D-galactopyranose (**18**). — Glycosylation of **13** (260 mg, 1 mmol) with **8** (586 mg, 1.7 mmol) in the presence of silver triflate gave, after column chromatography (4:1 chloroform–acetone), **18** (478 mg, 83%), m.p. 143–144° (from hexane–acetone), $[\alpha]_D$ −67° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.25 (d, 0.8 H, $J_{CHO,NH}$ 1.0 Hz, CHO, *trans*), 8.06 (d, 0.2 H, $J_{CHO,NH}$ 11.5 Hz, CHO, *cis*), 6.17 (d, 0.8 H, $J_{2,NH}$ 8.5 Hz, NH, *trans*), 5.92 (d, 0.2 H, $J_{2,NH}$ 10.5 Hz, NH, *cis*), 5.65 (d, 0.8 H, $J_{1,2}$ 5.0 Hz, H-1, *trans*), 5.60 (d, 0.2 H, $J_{1,2}$ 5.0 Hz, H-1, *cis*), 5.26–5.06 (m, 2 H), 4.80 (d, 1 H, $J_{1',2'}$ 8.5 Hz, H-1′), 4.64 (dd, 1 H, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 8.0 Hz, H-6a), 4.44–3.38 (m, 9 H), 2.16–2.00 (9 H, 3 OAc), 1.60–1.28 (12 H, 2 C*Me*$_2$); ^{13}C-n.m.r. ($CDCl_3$): δ 101.92 and 101.01 (C-1′), 96.01 and 96.16 (C-1).

Anal. Calc. for $C_{25}H_{37}NO_{14}$: C, 52.17; H, 6.47; N, 2.43. Found: C, 51.99; H, 6.48; N, 2.60.

Reaction of **13** with **7** in the presence of trimethylsilyl triflate only gave rise to decomposition products.

Methyl 2-O-benzyl-6-deoxy-4-O-methyl-3-O-(3,4,6-tri-O-acetyl-2-deoxy-2-formamido-β-D-glucopyranosyl)-β-D-galactopyranoside (**46**). — Glycosylation of **41** (282 mg, 1 mmol) with **10** (812 mg, 1.7 mmol) in the presence of trimethylsilyl triflate gave, after column chromatography (20:3 dichloromethane–acetone), **46** (383 mg, 64%), m.p. 202–208° (dec.) (from hexane–acetone), $[\alpha]_D$ +2° (*c* 1, chloroform); ^{13}C-n.m.r. ($CDCl_3$): δ 109.39 and 104.44 (C-1′), 101.60 and 101.46 (C-1).

Anal. Calc. for $C_{28}H_{39}NO_{13}$: C, 56.26; H, 6.59; N, 2.34. Found: C, 56.40; H, 6.60; N, 2.36.

Reaction of **41** with **7** in the presence of trimethylsilyl triflate gave **46** in 29% yield.

Reaction of **41** with **8** in the presence of silver triflate or stannous triflate gave **46** in 26 and 34% yields, respectively. In the presence of mercury cyanide at room temperature, no reaction occurred.

Methyl 2,3,4-tri-O-benzyl-6-O-(3,4,6-tri-O-acetyl-2-deoxy-2-formamido-β-D-glucopyranosyl)-α-D-glucopyranoside (**26**). — Glycosylation of **21** (464 mg, 1 mmol) with **8** (586 mg, 1.7 mmol) in the presence of silver triflate gave, after column chromatogaphy (10:7 hexane–acetone), **26** (756 mg, 97%), m.p. 185–186° (from ethanol), $[\alpha]_D$ +12° (*c* 1, chloroform); ^{13}C-n.m.r. ($CDCl_3$ + C_6D_6): δ 101.20 and 100.16 (C-1′); 97.81 and 97.78 (C-1).

Anal. Calc. for $C_{41}H_{49}NO_{14}$: C, 63.14; H, 6.33; N, 1.79. Found: C, 62.95; H, 6.32; N, 1.92.

Reaction of **21** with **7** in the presence of trimethylsilyl triflate gave **26** in 64% yield.

Methyl 2,3,6-tri-O-benzyl-4-O-(3,4,6-tri-O-acetyl-2-deoxy-2-formamido-β-D-glucopyranosyl)-α-D-glucopyranoside (**34**). — Glycosylation of **29** (464 mg, 1 mmol) with **7** (750 mg, 2 mmol) in the presence of trimethylsilyl triflate gave, after column chromatography (3:2 ethyl acetate–hexane), **34** (499 mg, 64%), m.p. 160–162° (from methanol), $[\alpha]_D$ −28° (*c* 1, chloroform); ^{13}C-n.m.r. ($CDCl_3$): δ 100.23 and 100.13 (C-1′), 98.30 and 98.20 (C-1).

Anal. Calc. for $C_{41}O_{49}NO_{14}$: C, 63.14; H, 6.33; N, 1.79. Found: C, 63.27; H, 6.33; N, 1.95.

Reaction of **29** with **8** in the presence of silver triflate gave **34** in 15% yield.

Benzyl 6-O-benzoyl-2,4-di-O-benzyl-3-O-(3,4,6-tri-O-acetyl-2-deoxy-2-formamido-β-D-glucopyranosyl)-β-D-galactopyranoside (**38**). — Glycosylation of **37** (555 mg, 1 mmol) with **7** (750 mg, 2 mmol) in the presence of trimethylsilyl triflate gave, after column chromatography (3:2 hexane–acetone), **38** (818 mg, 94%), m.p. 157–159° (from ethanol), $[\alpha]_D$ −55° (*c* 1, chloroform); ^{13}C-n.m.r. ($CDCl_3$): δ 102.06, 101.97, 101.93 (C-1 and C-1′).

Anal. Calc. for $C_{47}H_{51}NO_{15}$: C, 64.89; H, 5.90; N, 1.60. Found: C, 64.86; H, 5.87; N, 1.70.

Reaction of **37** with **8** in the presence of silver triflate gave **38** in 27% yield.

General procedure for dehydration of formamido-disaccharides. — Phosphorus oxychloride (0.2 mL, 2 mmol) was added with stirring to a solution of the formamido-disaccharide (1 mmol) and triethylamine (0.6 mL, 4 mmol) in dry dichloromethane (20 mL) at −30° under argon. The mixture was allowed to reach room temperature, and stirred until the starting material had disappeared, further additions of phosphorus oxychloride and triethylamine being eventually made. The mixture was then poured directly onto the top of a column of silica gel, and the isocyanide was eluted with an appropriate solvent.

1,2:3,4-Di-O-isopropylidene-6-O-(3,4,6-tri-O-acetyl-2-deoxy-2-isocyano-β-D-glucopyranosyl)-α-D-galactopyranose (**19**). — Dehydration of **18**, followed by column chromatography (2:1 hexane–acetone), gave **19** (85%), $[\alpha]_D$ −28° (*c* 1, chloroform), $\nu_{max}^{CHCl_3}$ 2160 (–NC), 1760 (OAc) cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 5.60 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.37 (dd, 1 H, $J_{3',4'} = J_{4',5'}$ = 10.0 Hz, H-4′), 4.98 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-3′), 4.87 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.66 (dd, 1 H, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 8.0 Hz, H-6a), 4.40–4.27 (m, 3 H), 4.20–3.88 (m, 4 H), 3.77 (ddd, 1 H, $J_{5',6'b}$ 9.5 Hz, H-5′), 3.68 (dd, 1 H, H-2′), 2.12, 2.10, and 2.05 (3 s, each 3 H, 3 OAc), 1.56 and 1.46 (2 s, each 3 H, CMe_2), 1.39 (s, 6 H, CMe_2).

Anal. Calc. for $C_{25}H_{35}NO_{13}$: C, 53.84; H, 6.33; N, 2.51. Found: C, 53.96; H, 6.34; N, 2.68.

Methyl 2-O-benzyl-6-deoxy-4-O-methyl-3-O-(3,4,6-tri-O-acetyl-2-deoxy-2-isocyano-β-D-glucopyranosyl)-β-D-galactopyranoside (**47**). — Dehydration of **46**, followed by column chromatography (2:1 hexane–acetone), gave **47** (92%), $[\alpha]_D$ +34° (*c* 1, chloroform), $\nu_{max}^{CHCl_3}$ 2160 (–NC), 1760 (OAc) cm^{-1}; ^{1}H-n.m.r. (C_6D_6): δ 7.78–7.14 (m, 5 H, Ph), 5.34 (dd, 1 H, $J_{3',4'}$ 9.5, $J_{4',5'}$ 10.5 Hz, H-4′), 5.07 (m, 2 H, OCH_2Ph), 5.03 (dd, 1 H, $J_{2',3'}$ 10.5 Hz, H-3′), 4.80 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.25 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.12 (dd, 1 H, $J_{5',6'a}$ 4.0, $J_{6'a,6'b}$ 12.5 Hz, H-6′a), 4.09 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.01 (dd, 1 H, $J_{5',6'b}$ 2.5 Hz, H-6′b), 3.70 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 3.51 (s, 3 H, OMe), 3.45 (dd, 1 H, H-2′), 3.42 (s, 3 H, OMe), 3.26–3.15 (m, 2 H, H-4,5), 2.92 (ddd, 1 H, H-5′), 1.72, 1.69, and 1.67 (3 s, each 3 H, 3 OAc), 1.25 (d, 3 H, $J_{5,Me}$ 6.5 Hz, CH_3-6).

Anal. Calc. for $C_{28}H_{37}NO_{12}$: C, 58.01; H, 6.44; N, 2.41. Found: C, 58.04; H, 6.57; N, 2.36.

Methyl 2,3,4-tri-O-benzyl-6-O-(3,4,6-tri-O-acetyl-2-deoxy-2-isocyano-β-D-glucopyranosyl)-α-D-glucopyranoside (**27**). — Dehydration of **26**, followed by column chromatography (2:1 hexane–acetone), gave **27** (92%), $[\alpha]_D$ +34° (*c* 1, chloroform), $\nu_{max}^{CHCl_3}$ 2160 (NC), 1760 (OAc) cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 7.50–7.30 (m, 15 H, 3 Ph), 5.34 (dd, 1 H, $J_{3',4'}$ 10.5, $J_{4',5'}$ 9.5 Hz, H-4'), 4.98 (dd, 1 H, $J_{2',3'}$ 10.5 Hz, H-3'), 4.67 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.46 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.29 (dd, 1 H, $J_{5',6'a}$ 4.5, $J_{6'a,6'b}$ 12.5 Hz, H-6'a), 4.20–4.00 (m, 3 H), 3.90–3.55 (m, 6 H), 3.44 (s, 3 H, OMe), 2.14, 2.07, and 2.05 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{41}H_{47}NO_{13}$: C, 64.63; H, 6.23; N, 1.83. Found: C, 64.52; H, 6.26; N, 1.99.

Methyl 2,3,6-tri-O-benzyl-4-O-(3,4,6-tri-O-acetyl-2-deoxy-2-isocyano-β-D-glucopyranosyl)-α-D-glucopyranoside (**35**). — Dehydration of **34**, followed by column chromatography (2:1 hexane–acetone), gave **35** (88%), $[\alpha]_D$ +14° (*c* 1.1, chloroform), $\nu_{max}^{CHCl_3}$ 2150 (NC), 1755 (OAc) cm^{-1}; ^{1}H-n.m.r. (C_6D_6): δ 7.56–7.06 (m, 15 H, 3 Ph), 5.28 (dd, 1 H, $J_{3',4'}$ 9.5, $J_{4',5'}$ 10.5 Hz, H-4'), 5.09 and 4.92 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 5.02 (dd, 1 H, $J_{2',3'}$ 10.5 Hz, H-3'), 4.63, 4.55, 4.41, and 4.35 (4 d, 4 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.24 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 3.98 (m, 1 H), 3.78 (dd, 1 H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 12.5 Hz, H-6a), 3.67 (dd, 1 H, $J_{5,6b}$ 1.0 Hz, H-6b), 3.53 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.0 Hz, H-2), 3.28 (dd, 1 H, H-2'), 3.11 (s, 3 H, OMe), 1.69, 1.67, and 1.65 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{41}H_{47}NO_{13}$: C, 64.63; H, 6.23; N, 1.83. Found: C, 64.59; H, 6.23; N, 1.98.

Benzyl 6-O-benzoyl-2,4-di-O-benzyl-3-O-(3,4,6-tri-O-acetyl-2-deoxy-2-isocyano-β-D-glucopyranosyl)-β-D-galactopyranoside (**39**). — Dehydration of **38**, followed by column chromatography (2:1 hexane–acetone), gave **39** (97%), $[\alpha]_D$ −25° (*c* 1, chloroform); $\nu_{max}^{CHCl_3}$ 2150 (–NC), 1770, 1730 cm^{-1}; ^{1}H-n.m.r. (C_6D_6): δ 8.22 and 7.77–7.09 (2 m, 2 and 18 H, 4 Ph), 5.31 (dd, 1 H, $J_{3',4'}$ 9.5, $J_{4',5'}$ 10.5 Hz, H-4'), 5.14–4.86 (m, 5 H, H-3' and OCH_2Ph), 4.73 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.69–4.59 (m, 3 H, H-6a and OCH_2Ph), 4.51 (dd, 1 H, $J_{5,6b}$ 6.0, $J_{6a,6b}$ 11.0 Hz, H-6b), 4.44 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1'), 4.24 (dd, 1 H, $J_{2',3'}$ 9.5 Hz, H-2'), 4.15 (dd, 1 H, $J_{5',6'a}$ 4.5, $J_{6'a,6'b}$ 12.5 Hz, H-6'a), 3.94 (dd, 1 H, $J_{5',6'b}$ 2.0 Hz, H-6'b), 3.90 (m, 1 H, H-4), 3.66 (dd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 3.0 Hz, H-3), 3.55 (ddd, 1 H, H-5), 3.39 (dd, 1 H, H-2), 2.92 (ddd, 1 H, H-5'), 1.73, 1.71, and 1.66 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{47}H_{49}NO_{14}$: C, 66.25; H, 5.80; N, 1.64. Found: C, 66.24; H, 5.82; N, 1.65.

General procedure for the radical reduction of isocyano-disaccharides. — A solution of the isocyano-disaccharide (1 mmol) in dry toluene (10 mL) was added dropwise to a refluxing solution of tributyltin hydride (10 mmol) and α,α'-azobis-isobutyronitrile (160 mg) in toluene (4 mL). The reaction was monitored by t.l.c. and was usually complete after 10 min. The mixture was cooled, then concentrated.

1,2:3,4-Di-O-isopropylidene-6-O-(3,4,6-tri-O-acetyl-2-deoxy-β-D-arabino-hexopyranosyl)-α-D-galactopyranose (**20**). — Reduction of **19**, followed by column chromatography (2:1 hexane–acetone), gave **20** (96%), m.p. 115° (from di-iso-

propyl ether), $[\alpha]_D$ −68° (*c* 1, chloroform); ^{1}H-n.m.r. (400 MHz) (C_6D_6): δ 5.56 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.24 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 10.0$ Hz, H-4′), 5.06 (ddd, 1 H, $J_{2'a,3'}$ 12.0, $J_{2'e,3'}$ 5.5 Hz, H-3′), 4.47 (dd, 1 H, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 8.0 Hz, H-6a), 4.38 (dd, 1 H, $J_{5',6'a}$ 4.0, $J_{6'a,6'b}$ 12.0 Hz, H-6′a), 4.30 (dd, 1 H, $J_{1',2'a}$ 9.5, $J_{1',2'e}$ 2.0 Hz, H-1′), 4.21 (dd, 1 H, $J_{5,6b}$ 4.0 Hz, H-6b), 4.20 (dd, 1 H, $J_{1,2}$ 5.0, $J_{2,3}$ 2.0 Hz, H-2), 4.16 (ddd, 1 H, $J_{4,5}$ 7.0 Hz, H-5), 4.03 (dd, 1 H, $J_{5',6'b}$ 2.5 Hz, H-6′b), 3.93–3.87 (m, 2 H, H-3,4), 3.13 (ddd, 1 H, H-5′), 2.25 (ddd, 1 H, $J_{2'a,2'e}$ 12.5 Hz, H-2′*e*), 1.78 (ddd, 1 H, H-2′*a*), 1.75, 1.72, and 1.63 (3 s, each 3 H, 3 OAc), 1.50, 1.47, 1.16, and 1.08 (4 s, each 3 H, 2 CMe_2).

Anal. Calc. for $C_{24}H_{36}O_{13}$: C, 54.11; H, 6.82. Found: C, 54.03; H, 6.77.

*Methyl 2-*O*-benzyl-6-deoxy-4-*O*-methyl-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-arabino-hexopyranosyl)-β-*D*-galactopyranoside* (**48**). — Reduction of **47**, followed by column chromatography (20:1 dichloromethane–acetone), gave **48** (86%), $[\alpha]_D$ +0.2° (*c* 1, chloroform); ^{1}H-n.m.r. (C_6D_6): δ 7.50–7.17 (m, 5 H, Ph), 5.28 (dd, 1 H, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.5 Hz, H-4′), 5.11 (ddd, 1 H, $J_{2'a,3'}$ 11.5, $J_{2'e,3'}$ 5.0 Hz, H-3′), 5.05 and 4.58 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.81 (dd, 1 H, $J_{1',2'a}$ 9.5, $J_{1',2'e}$ 2.0 Hz, H-1′), 4.32 (dd, 1 H, $J_{5',6'a}$ 4.0, $J_{6'a,6'b}$ 12.5 Hz, H-6′a), 4.25 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.14 (dd, 1 H, $J_{5',6'b}$ 2.5 Hz, H-6′b), 3.97 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 3.71 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 3.58 and 3.45 (2 s, each 3 H, 2 OMe), 3.31 (dd, 1 H, $J_{4,5}$ 0.5 Hz, H-4), 3.23 (m, 1 H, $J_{5,Me}$ 6.5 Hz), 3.09 (ddd, 1 H, H-5′), 2.39 (ddd, 1 H, $J_{2'a,2'e}$ 12.5 Hz, H-2′*e*), 1.76 (ddd, 1 H, H-2′*a*), 1.76, 1.72, and 1.08 (3 s, each 3 H, 3 OAc), 1.36 (d, 3 H, CH_3-6).

Anal. Calc. for $C_{27}H_{38}O_{12}$: C, 58.46; H, 6.91. Found: C, 58.52; H, 7.05.

*Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-arabino-hexopyranosyl)-α-*D*-glucopyranoside* (**28**). — Reduction of **27**, followed by column chromatography (2:1 hexane–acetone), gave **28** (97%), $[\alpha]_D$ +20° (*c* 1.2, chloroform); ^{1}H-n.m.r. (400 MHz) (C_6D_6): δ 7.37–7.05 (m, 15 H, 3 Ph), 5.24 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 10.0$ Hz, H-4′), 5.07 (ddd, 1 H, $J_{2'a,3'}$ 12.0, $J_{2'e,3'}$ 5.0 Hz, H-3′), 5.05, 4.94, 4.78, and 4.59 (4 d, 4 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.66 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.52 and 4.46 (2 d, 2 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.37 (dd, 1 H, $J_{5',6'a}$ 4.5, $J_{6'a,6'b}$ 12.0 Hz, H-6′a), 4.26 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.0$ Hz, H-3), 4.15 (dd, 1 H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.08 (dd, 1 H, $J_{5',6'b}$ 2.5 Hz, H-6′b), 4.07 (dd, 1 H, $J_{1',2'a}$ 9.5, $J_{1',2'e}$ 2.5 Hz, H-1′), 3.96 (ddd, 1 H, $J_{5,6b}$ 5.5, $J_{4,5}$ 10.0 Hz, H-5), 3.61 (dd, 1 H, H-4), 3.60 (dd, 1 H, H-6b), 3.57 (dd, 1 H, H-2), 3.20 (ddd, 1 H, H-5′), 3.16 (s, 3 H, OMe), 2.18 (ddd, 1 H, $J_{2'a,2'e}$ 12.5 Hz, H-2′*e*), 1.79 (ddd, 1 H, H-2′*a*), 1.72, 1.70, and 1.61 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{40}H_{48}O_{13}$: C, 65.19; H, 6.57. Found: C, 65.22; H, 6.64.

*Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-arabino-hexopyranosyl)-α-*D*-glucopyranoside* (**36**). — Reduction of **35**, followed by column chromatography (40:1 dichloromethane–acetone), gave **36** (74%), $[\alpha]_D$ +6° (*c* 1.6, chloroform); ^{1}H-n.m.r. (400 MHz) (C_6D_6): δ 7.50–7.02 (m, 15 H, 3 Ph), 5.25 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.5$ Hz, H-4′), 5.20 and 4.91 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 5.05 (ddd, 1 H, $J_{2'a,3'}$ 12.0, $J_{2'e,3'}$ 5.5 Hz, H-3′), 4.70 (dd, 1 H, $J_{1',2'a}$ 10.0, $J_{1',2'e}$ 2.0

Hz, H-1'), 4.63 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.56, 4.51, 4.41, and 4.32 (4 d, 4 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.34 (dd, 1 H, $J_{5',6'a}$ 4.0, $J_{6'a,6'b}$ 12.0 Hz, H-6'a), 4.17 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.0$ Hz, H-3), 4.13 (dd, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 3.87 (dd, 1 H, $J_{5',6'b}$ 2.0 Hz, H-6'b), 3.80 (m, 1 H, H-5), 3.57 (dd, 1 H, $J_{5,6a}$ 3.5, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.53 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 3.52 (dd, 1 H, H-2), 3.19 (ddd, 1 H, H-5'), 3.13 (s, 3 H, OMe), 2.24 (ddd, 1 H, $J_{2'a,2'e}$ 12.5 Hz, H-2'*e*), 1.76 (ddd, 1 H, H-2'*a*), 1.70, 1.68, and 1.65 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{40}H_{48}O_{13}$: C, 65.19; H, 6.57. Found: C, 65.17; H, 6.66.

*Benzyl 6-O-benzoyl-2,4-di-O-benzyl-3-O-(3,4,6-tri-O-acetyl-2-deoxy-β-*D*-arabino-hexopyranosyl)-β-*D*-galactopyranoside* (**40**). — Reduction of **39**, followed by column chromatography (100:3 dichloromethane–acetone), gave **40** (87%), $[\alpha]_D$ −49° (*c* 2.3, chloroform); ^{1}H-n.m.r. (400 MHz) (C_6D_6): δ 8.16 and 7.45–7.04 (2 m, 2 and 18 H, 4 Ph), 5.20 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.5$ Hz, H-4'), 5.08 and 4.99 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 5.05 (ddd, 1 H, $J_{2'a,3'}$ 11.5, $J_{2'e,3'}$ 5.5, $J_{3',4'}$ 9.5 Hz, H-3'), 4.91 and 4.61 (2 d, 2 H, J_{gem} 12.0 Hz, OCH_2Ph), 4.72 and 4.53 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.69 (dd, 1 H, $J_{5,6a}$ 6.5, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.66 (dd, 1 H, $J_{1',2'a}$ 9.5, $J_{1',2'e}$ 2.0 Hz, H-1'), 4.47 (dd, 1 H, $J_{5,6b}$ 6.0 Hz, H-6b), 4.41 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.29 (dd, 1 H, $J_{5',6'a}$ 4.5, $J_{6'a,6'b}$ 12.0 Hz, H-6'a), 4.08 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.07 (dd, 1 H, $J_{5',6'b}$ 2.0 Hz, H-6'b), 3.99 (dd, 1 H, $J_{3,4}$ 3.0, $J_{4,5}$ 0.5 Hz, H-4), 3.61 (dd, 1 H, H-3), 3.52 (ddd, 1 H, H-5), 3.10 (ddd, 1 H, H-5'), 2.34 (ddd, 1 H, $J_{2'a,2'e}$ 12.5 Hz, H-2'*e*), 1.74 (m, 1 H, H-2'*a*), 1.74, 1.71, and 1.67 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{46}H_{50}O_{14}$: C, 66.80; H, 6.10. Found: C, 66.77; H, 6.21.

*Methyl 2-O-benzyl-6-deoxy-4-O-methyl-3-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-β-*D*-galactopyranoside* (**49**). — A mixture of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate[41] (580 mg, 1 mmol), **41** (282 mg, 1 mmol), and activated powdered molecular sieves (4 Å, 1 g) in dry dichloromethane (10 mL) was stirred for 1 h at room temperature under argon, then cooled at −78°. Trimethylsilyl triflate (40 μL, 0.2 mmol) was added. T.l.c. (7:3 hexane–acetone) showed that the reaction was completed within a few min. The mixture was neutralized at −78° with triethylamine, then allowed to reach room temperature, and filtered. The filtrate was washed with water and then concentrated, and toluene was evaporated several times from the residue. The residue crystallized from ethanol–water to give **49** (651 mg, 93%), m.p. 164–166°, $[\alpha]_D$ +40° (*c* 1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.86–7.10 (m, 9 H, aromatic), 5.89 (dd, 1 H, $J_{2',3'}$ 10.5, $J_{3',4'}$ 9.0 Hz, H-3'), 5.74 (d, 1 H, $J_{1',2'}$ 8.5 Hz, H-1'), 5.23 (dd, 1 H, $J_{4',5'}$ 10 Hz, H-4'), 4.55 and 4.18 (2 d, 2 H, J_{gem} 11.5 Hz, OCH_2Ph), 4.41 (dd, 1 H, H-2'), 4.14 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.79 (ddd, 1 H, $J_{5',6'a}$ 3.0, $J_{5',6'b}$ 4.0 Hz, H-5'), 3.74 (dd, 1 H, $J_{6'a,6'b}$ 10 Hz, H-6'a), 3.56 and 3.41 (2 s, each 3 H, 2 OMe), 2.12, 2.07, and 1.88 (3 s, each 3 H, 3 OAc), 1.29 (d, 3 H, $J_{5,Me}$ 6.0 Hz, CH_3-6).

Anal. Calc. for $C_{35}H_{41}NO_{14}$: C, 60.08; H, 5.91; N, 2.00. Found: C, 59.68; H, 5.91; N, 2.03.

Conversion of the N-*phthaloyl disaccharide* **49** *into the* N-*formyl disaccharide* **46**. — A solution of **49** (700 mg, 1 mmol) in 0.1M sodium methoxide in methanol (20 mL) was stirred at room temperature under argon. T.l.c. (5:1 chloroform–methanol) showed the deacetylation to be completed after 35 min. The mixture was neutralized with Amberlite IR-120 (H^+) resin, filtered, and then concentrated. The crude residue was dissolved in ethanol (10 mL) and treated with hydrazine hydrate (0.15 mL, 3 mmol) at reflux. A precipitate appeared gradually, and t.l.c. (5:1 chloroform–methanol) showed the dephthaloylation to be finished after 2 h. The mixture was cooled, then concentrated. The crude residue was dissolved in 2:1 1,4-dioxane–water (20 mL) and treated with *p*-nitrophenyl formate (335 mg, 2 mmol) at room temperature for 24 h. T.l.c. (3:3:1 2-propanol–ethyl acetate–water) then showed the *N*-formylation to be incomplete. 1,4-Dioxane was evaporated, and the aqueous residue was extracted with ether to remove the *p*-nitrophenol and then concentrated. The residue was dissolved in 1:1 1,4-dioxane–water, and treated again with *p*-nitrophenyl formate (335 mg, 2 mmol) for 40 h at room temperature. The mixture was worked-up as previously, and the residue was acetylated with 13:2 pyridine–acetic anhydride (15 mL) for 90 min at room temperature. Solvents were evaporated, and t.l.c. (17:3 dichloromethane–acetone) showed the residue to be nearly pure **46**. Crystallization from ethanol or dichloromethane–hexane gave **46** (508 mg, 85%) identical to the product described above.

REFERENCES

1 D. E. Wright, *Tetrahedron*, 35 (1979) 1207–1237.
2 M. Miyamoto, Y. Kawamatsu, K. Kawashima, M. Shinohara, K. Tanaka, S. Tatsuoka, and K. Nakanishi, *Tetrahedron*, 23 (1967) 421–437.
3 Yu. A. Berlin, S. E. Esipov, and M. N. Kolosov, *Khim. Prir. Soedin.*, 5 (1969) 567–572; *Chem. Abstr.*, 73 (1970) 25823r.
4 G. P. Bakhaeva, Yu. A. Berlin, E. F. Boldyreva, O. A. Chuprunova, M. N. Kolosov, V. S. Soifer, T. E. Vasiljeva, and I. V. Yartseva, *Tetrahedron Lett.*, (1968) 3595–3598.
5 P. J. Garegg, S. Köpper, P. Ossowski, and J. Thiem, *J. Carbohydr. Chem.*, 5 (1986) 59–65.
6 A. Fogh, I. Lundt, C. Pedersen, and P. Rasmussen, *Acta Chem. Scand., Ser. B*, 31 (1977) 768–770.
7 K. Bock, I. Lundt, and C. Pedersen, *Carbohydr. Res.*, 90 (1981) 7–16.
8 J. Thiem, M. Gerken, and K. Bock, *Justus Liebigs Ann. Chem.*, (1983) 462–470.
9 K. Bock, I. Lundt, and C. Pedersen, *Carbohydr. Res.*, 130 (1984) 125–134.
10 J. Thiem and M. Gerken, *J. Carbohydr. Chem.*, 1 (1983) 229–249.
11 K. C. Nicolaou, T. Ladduwahetty, J. L. Randall, and A. Chucholowski, *J. Am. Chem. Soc.*, 108 (1986) 2466–2467.
12 K. J. Ryan, E. M. Acton, and L. Goodman, *J. Org. Chem.*, 36 (1971) 2646–2657.
13 Y. Ito and T. Ogawa, *Tetrahedron Lett.*, 28 (1987) 2723–2726.
14 R. Preuss and R. R. Schmidt, *Synthesis*, (1988) 694–697.
15 M. Perez and J.-M. Beau, *Tetrahedron Lett.*, 30 (1989) 75–78.
16 G. Jaurand, J.-M. Beau, and P. Sinaÿ, *J. Chem. Soc., Chem. Commun.*, (1981) 572–573.
17 K. Tatsuta, K. Fujimoto, M. Kinoshita, and S. Umezawa, *Carbohydr. Res.*, 54 (1977) 85–104.
18 J. Thiem and H. Karl, *Chem. Ber.*, 113 (1980) 3039–3048.
19 H. B. Boren, G. Ekborg, K. Eklind, P. J. Garegg, A. Pilotti, and C.-G. Swahn, *Acta Chem. Scand.*, 27 (1973) 2639–2644.
20 J.-C. Jacquinet and P. Sinaÿ, *Tetrahedron*, 32 (1976) 1693–1697.
21 R. U. Lemieux and J. D. T. Cipera, *Can. J. Chem.*, 34 (1956) 906–910.

22 K. HONMA AND A. HAMADA, *Chem. Pharm. Bull.*, 24 (1976) 1165–1168.
23 J.-R. POUGNY, M. A. M. NASSR, N. NAULET, AND P. SINAŸ, *Nouv. J. Chim.*, 2 (1978) 389–395; H. F. VERNAY, E. S. RACHAMAN, R. EBY, AND C. SCHUERCH, *Carbohydr. Res.*, 78 (1980) 267–273.
24 M. TRUMTEL, A. VEYRIÈRES, AND P. SINAŸ, *Int. Carbohydr. Symp., 14th, Stockholm*, 1988, B36.
25 S. KAMIYA, S. ESAKI, AND N. SHIBA, *Agric. Biol. Chem.*, 47 (1983) 2929–2931.
26 S. HANESSIAN, T. J. LIAK, AND D. M. DIXIT, *Carbohydr. Res.*, 88 (1981) C14–C19.
27 T. OGAWA, K. BEPPU, AND S. NAKABAGASHI, *Carbohydr. Res.*, 93 (1981) C6–C9.
28 H. PAULSEN AND M. PAAL, *Carbohydr. Res.*, 135 (1984) 53–69.
29 R. EBY AND C. SCHUERCH, *Carbohydr. Res.*, 34 (1974) 79–90; B. BERNET AND A. VASELLA, *Helv. Chim. Acta*, 62 (1979) 1990–2016.
30 J. M. KÜSTER AND I. DYONG, *Justus Liebigs Ann. Chem.*, (1975) 2179–2189.
31 D. H. R. BARTON AND S. W. MCCOMBIE, *J. Chem. Soc., Perkin Trans. 1*, (1975) 1574–1585; W. HARTWIG, *Tetrahedron*, 39 (1983) 2609–2645.
32 D. H. R. BARTON, G. BRINGMANN, G. LAMOTTE, W. B. MOTHERWELL, R. S. H. MOTHERWELL, AND A. E. A. PORTER, *J. Chem. Soc., Perkin Trans. 1*, (1980) 2657–2664.
33 C. G. GREIG, D. H. LEABACK, AND P. G. WALKER, *J. Chem. Soc.*, (1961) 879–883.
34 S. DAVID, C. A. JOHNSON, AND A. VEYRIÈRES, *Carbohydr. Res.*, 28 (1973) 121–124.
35 A. LUBINEAU AND A. MALLERON, *Tetrahedron Lett.*, 26 (1985) 1713–1716; A. LUBINEAU, J. LE GALLIC, AND A. MALLERON, *Tetrahedron Lett.*, 28 (1987) 5041–5044.
36 B. HELFERICH AND W. PORTZ, *Chem. Ber.*, 86 (1953) 604–612.
37 M. NUMATA, M. SUGIMOTO, K. KOIKE, AND T. OGAWA, *Carbohydr. Res.*, 163 (1987) 209–225.
38 C. FOCES-FOCES, F. H. CANO, M. BERNABÉ, S. PENADES, AND M. MARTIN-LOMAS, *Carbohydr. Res.*, 135 (1984) 1–11.
39 L. A. LAPLANCHE AND M. T. ROGERS, *J. Am. Chem. Soc.*, 86 (1964) 337–341.
40 U. SCHÖLLKOPF, R. SCHRÖDER, AND D. STAFFORST, *Justus Liebigs Ann. Chem.*, (1974) 44–53; G. D. HARTMAN AND L. M. WEINSTOCK, *Org. Synth.*, 59 (1979) 182–190.
41 G. GRUNDLER AND R. R. SCHMIDT, *Carbohydr. Res.*, 135 (1985) 203–218.
42 D. R. BUNDLE AND S. JOSEPHSON, *Can. J. Chem.*, 57 (1979) 662–668.
43 A. FERNANDEZ-MAYORALAS, A. MARRA, M. TRUMTEL, A. VEYRIÈRES, AND P. SINAŸ, *Carbohydr. Res.*, 188 (1989) 81–95.
44 C. LE COQ AND J.-Y. LALLEMAND, *J. Chem. Soc., Chem. Commun.*, (1981) 150–152.
45 D. L. RABENSTEIN AND T. T. NAKASHIMA, *Anal. Chem.*, 51 (1979) 1465A.
46 W. C. STILL, M. KAHN, AND A. MITRA, *J. Org. Chem.*, 43 (1978) 2923–2925.