Photobromination of Carbohydrate Derivatives. Part 8.[1] Reaction of Furanose Derivatives with *N*-Bromosuccinimide. *X*-Ray Molecular Structure of 1-*O*-Acetyl-2,5,6-tri-*O*-benzoyl-4-hydroxy-3,4-*O*-(α-succinimidobenzylidene)-β-D-galactofuranose

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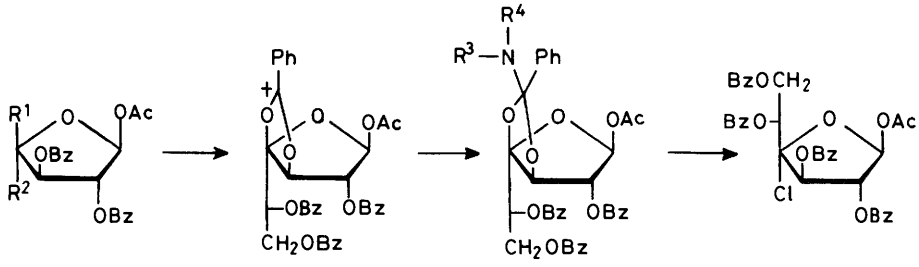
Photobromination of 1-*O*-acetyl-2,3,5,6-tetra-*O*-benzoyl-β-D-gluco-or -galacto-furanose with *N*-bromosuccinimide gives the title compound in good yield. This was characterised by *X*-ray diffraction analysis, and analogous products were obtained by use of *N*-bromophthalimide or *N*-bromoacetamide. Similar reaction of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose, pentabenzoyladenosine, and 1,2,3,4-tetra-*O*-acetyl-β-D-xylopyranose gave no such products but, instead, the corresponding 4-, 4-, and 5-bromide, respectively.

The title compound was efficiently converted into 1-*O*-acetyl-2,3,5,6-tetra-*O*-benzoyl-4-chloro-β-D-glucofuranose.

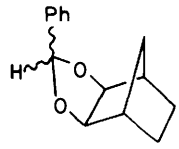
Previous studies in this series have been devoted to producing bromine-containing derivatives from a range of carbohydrate compounds by use of bromine radicals derived photochemically from either *N*-bromosuccinimide (NBS) or bromine. The latter, on occasions, leads to more efficient substitution reactions,[2,3] but since the hydrogen bromide formed as a by-product is not removed by the reagent (as is the case with NBS with which it gives bromine and succinimide[4]) compounds susceptible to reaction with hydrogen bromide can react further to give products containing more than one bromine atom.[5] With both reagents, however, the accessible primary products have been the same in all cases so far examined. In the preceding paper it is shown that some acylated furanosyl compounds undergo efficient substitution at C-4 when treated in carbon tetrachloride with bromine under bright light, and we now show that, whereas in some cases similar and even more efficient reaction can occur with NBS as radical source, in others entirely different products can be isolated.

When treated with bromine under bright light, the hexose esters (**1**) and (**2**) both gave good yields of the epimeric 4-bromo-products (**3**) and (**4**) with the D-*galacto*-isomer (**4**) predominating.[1] We now find, however, that when treated similarly with NBS these esters yield small amounts of these products and the main product is the benzylidene orthoester (**6**) which was isolated in 74% yield and characterised by *X*-ray diffraction analysis (see below). The related compound (**11**) with a 2-succinimido-1,3-dioxolane ring has been found amongst the products of treatment of the benzylidene acetal (**10**) with NBS.[6] It was thought to have arisen *via* the corresponding benzoxonium ion which suggests that compound (**6**) was similarly formed from the ion (**5**) which was produced by heterolysis of the bromides (**3**) and (**4**), and when these were heated with NBS without irradiation they were converted completely into the benzylidene product (**6**) to substantiate the proposal. Amides are known to react with benzoxonium ions to give *N*-acylorthoamides rather than products of *trans*-ring opening[7] as occurs, for example, with bromide ions, and in the same way as NBS reacted with the D-*gluco*-ester (**1**) to give compound (**6**), *N*-bromoacetamide and *N*-bromophthalimide gave the analogous orthoamides (**7**) and (**8**). With the former reagent the photobromination was carried out with cooling of the solution, and as well as compound (**6**) the D-*galacto*-bromide



	R^1	R^2		R^3	R^4	
(**1**)	-CH(OBz)CH_2OBz	H	(**5**)	(**6**)	-OCCH_2 CH_2CO-	(**9**)
(**2**)	H	-CH(OBz)CH_2OBz		(**7**)	H COMe	
(**3**)	-CH(OBz)CH_2OBz	Br		(**8**)	-OC CO-	
(**4**)	Br	-CH(OBz)CH_2OBz				

Scheme. Bz = benzoyl



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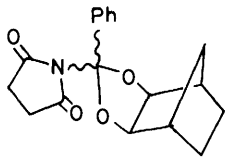
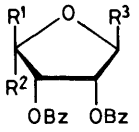
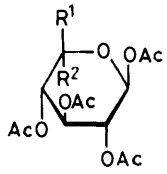


(11)

(4) was isolated from the products in appreciable proportions, again suggesting that the orthoamides are formed by way of 4-bromides.

When NBS was used as radical source for the photobromination of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**12**) no orthoamide was detected; instead, the reaction gave the same products as were formed using bromine—the 4-bromo-D-*ribo* and -L-*lyxo* compounds (**13**) and (**14**) in the ratio 60:40. To confirm that the hexose and pentose esters (**1**) and (**12**) behaved differently with NBS, parallel experiments were carried out under identical conditions, and the opportunity was taken to search for orthoamide derivatives amongst the products formed from tetra-*O*-acetyl-β-D-xylopyranose (**15**), which previously[5b]





	R^1	R^2	R^3
(**12**)	CH_2OBz	H	OAc
(**13**)	CH_2OBz	Br	OAc
(**14**)	Br	CH_2OBz	OAc
(**18**)	CH_2OBz	H	Dibenzoyladenin-9-yl
(**19**)	CH_2OBz	Br	Dibenzoyladenin-9-yl

	R^1	R^2
(**15**)	H	H
(**16**)	H	Br
(**17**)	Br	H

had yielded only 46% of the crystalline (5*S*)-bromide (**16**), by also submitting it to these reaction conditions. The anomaly was confirmed: the D-*gluco*-compound (**1**) gave the orthoamide (**6**) and the bromides (**4**) and (**3**) in the proportions 4:5:1, whereas the pentose esters (**12**) and (**15**) afforded only products of bromination at C-4 and C-5, respectively. From the compounds produced from tetra-*O*-acetyl-β-D-xylopyranose (**15**) the known (5*S*)-compound (**16**) was isolated as the preponderant component, but the previously undetected (5*R*)-epimer (**17**) was also obtained. Other pyranose compounds examined have given epimerically discrete bromides by way, we propose,[1] of intermediates with uncoupled electrons in axial orbitals, but since this D-xylopyranose peracetate exists in solution to an appreciable extent in both chair conformations,[8] it is consistent that axial hydrogen abstraction[9] from C-5 should give two configurationally and conformationally different radicals which lead to the two epimeric bromides.

Like the ribose ester (**12**), pentabenzoyladenosine (**18**) gave mixed products with NBS; bromination at C-4′ was again preponderant and was more selective than with bromine,[1] 40% of the 4′-bromonucleoside (**19**) being isolated by column chromatography.

It is not clear why orthoamide products were formed only in the cases of the hexofuranose esters (**1**) and (**2**), but it is noted that in compounds (**6**)—(**8**) the ester substituents at C-2 are *exo*-related to the bicyclic systems whereas, in the case of the analogous compounds which would be obtainable from the ribofuranose ester (**12**) and its nucleoside analogue (**18**), these substituents are in the destabilising *endo* situation.

The potential of the orthoamide derivative (**6**) as a precursor of 4-substituted D-glucofuranose compounds was illustrated by its reaction with dichloromethyl methyl ether in the presence of boron trifluoride with which it specifically gave the 4-chloride (**9**) which was structurally and configurationally characterised by comparative n.m.r. methods.[1] Whereas the monocyclic compounds of this series had two clearly separated sets of ester proton resonances centred near δ 7.4 and 7.9, the bicyclic compounds in which one of the benzoyl groups has been converted into the benzylidene system had more diffuse resonances over the range δ 7.0—8.2. With the D-*gluco*-chloride (**9**) available it was possible to characterise by ^1H n.m.r. methods[1] the products of irradiation of the D-glucose ester (**1**) in the presence of t-butyl hypochlorite[10] as a mixture of this D-glucose derivative (**9**) and its D-*galacto*-epimer (ratio 1:3).

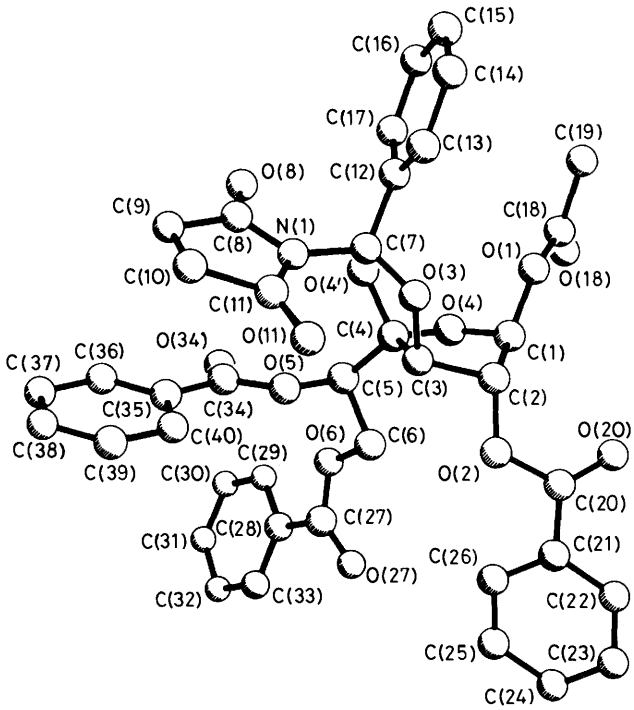


Figure. *X*-Ray crystal structure of 1-*O*-acetyl-2,5,6-tri-*O*-benzoyl-4-hydroxy-3,4-*O*-(α-succinimidobenzylidene)-β-D-galactofuranose (**6**)

X-Ray analysis of the orthoamide derivative (**6**) (Figure) showed that the succinimide group occupies the *exo*-site and that the furanose ring adopts a conformation close to $^3T_2$. Values for $J_{1,2}$ and $J_{2,3}$ of 0.8 and 0 Hz indicate that this is also close to the preferred conformation in solution.

Experimental

Unless otherwise indicated n.m.r. spectra were measured in deuteriochloroform using a Varian FT 80A instrument, and optical rotations were determined in chloroform within the concentration range 0.5—1.5%. Light petroleum refers to the fraction boiling in the range 60—80 °C.

1-O-*Acetyl*-2,5,6-*tri*-O-*benzoyl*-4-*hydroxy*-3,4-O-(α-*succinimidobenzylidene*)-β-D-*galactofuranose* (**6**).—A mixture of the D-*gluco*-β-acetate (**1**) (1.0 g) and NBS (0.83 g, 3 mol equiv.) was heated under reflux in carbon tetrachloride (40 ml) over a 275 W heat-lamp for 0.9 h. The solids were filtered off and the filtrate was evaporated to give a syrup which was fractionated

on a column of silica gel with light petroleum-ethyl acetate as eluant. Eluted first was the 4-bromo-D-*galacto*-compound (**4**) (0.17 g, 15%), characterised by ^{1}H n.m.r. spectroscopy, and this was followed by the *succinimido product* (**6**) (0.85 g, 74%). Recrystallisation from diethyl ether–light petroleum gave crystals, m.p. 159—160 °C; $[\alpha]_D$ −2° (Found: C, 65.3; H, 4.5; N, 2.1. $C_{40}H_{33}NO_{13}$ requires C, 65.3; H, 4.5; N, 1.9%); δ_H([$^2H_6$]Me_2CO) 1.63 (3 H, Ac), 2.42 (4 H, CH_2CO), 4.81 (1 H, dd, $J_{5,6}$ 8.2, $J_{6,6'}$ 11.8 Hz, 6-H), 5.04 (1 H, dd, $J_{5,6'}$ 3.5 Hz, 6'-H), 5.50 (1 H, s, 3-H), 5.52 (1 H, d, $J_{1,2}$ 0.7 Hz, 2-H), 6.08 (1 H, dd, 5-H), 6.57 (1 H, d, 1-H), and 7.2—8.0 (20 H, ArH); δ_C([$^2H_6$]Me_2CO) 29.2 (CH_2C=O), 63.7 (C-6), 70.5 (C-5), 80.4 (C-2), 86.2 (C-3), 101.9 (C-1), 116.2 (Ph–*C*–N), 117.9 (C-4), and 175.6 p.p.m. (N–C=O), and phenyl and ester resonances.

When the reaction was carried out as above with the D-*galacto*-β-acetate (**2**) (1 g) the 4-bromo-D-*galacto*-compound (**4**) and the succinimido-derivative (**6**) were isolated in 19 and 64% yield, respectively. When the D-*gluco*-ester (**1**) (0.1 g) was converted into the epimeric bromides (**3**) and (**4**) by irradiation in carbon tetrachloride (4 ml) and bromine (0.08 g) and the products were redissolved in this solvent (4 ml) and heated under reflux with NBS (0.12 g) in the dark for 1.3 h the only product observed (^{1}H n.m.r.) was the succinimido-compound (**6**).

1-O-*Acetyl*-2,5,6-*tri*-O-*benzoyl*-4-*hydroxy*-3,4-O-(α-*phthalimidobenzylidene*)-β-D-*galactofuranose* (**8**).—The D-*gluco*-β-acetate (**1**) (1.5 g) and *N*-bromophthalimide (2.0 g) were heated under reflux in carbon tetrachloride (60 ml) over the heat-lamp for 0.75 h. Isolation as for the succinimido-compound gave the D-*galacto*-bromide (**4**) (0.13 g, 8%) and the N-*phthalimido-derivative* (**8**) (1.34 g, 73%) which, on crystallisation from ethyl acetate–light petroleum, had m.p. 194.5—195.5 °C, $[\alpha]_D$ −25° (Found: C, 67.4; H, 4.3; N, 1.7. $C_{44}H_{33}NO_{13}$ requires C, 67.4; H, 4.2; N, 1.8%); δ_H([$^2H_6$]Me_2CO) 1.60 (3 H, Ac), 4.84 (1 H, dd, $J_{5,6}$ 8.0, $J_{6,6'}$ 11.7 Hz, 6-H), 5.06 (1 H, dd, $J_{5,6'}$ 3.7 Hz, 6'-H), 5.62 (1 H, s, 3-H), 5.76 (1 H, d, $J_{1,2}$ 0.7 Hz, 2-H), 6.17 (1 H, dd, 5-H), 6.60 (1 H, d, 1-H), and 6.9—8.0 (24 H, ArH); δ_C 63.8 (C-6), 71.3 (C-5), 80.5 (C-2), 86.1 (C-3), 101.9 (C-1), 116.1 (Ph–*C*–N), and 118.3 p.p.m. (C-4), and phenyl and ester resonances.

3,4,-O-(α-*Acetamido-benzylidene*)-1-O-*acetyl*-2,5,6-*tri*-O-*benzoyl*-4-*hydroxy*-β-D-*galactofuranose* (**7**).—A solution of the D-*gluco*-β-acetate (**1**) (1.0 g) and *N*-bromoacetamide was stirred in carbon tetrachloride (40 ml) in a cold-water-jacketted irradiation vessel under two 275 W heat-lamps for 17 h. Chloroform (40 ml) was added and the solution was washed successively with water, aqueous sodium thiosulphate, aqueous sodium hydrogen carbonate, and water and dried, and the solvent was removed to give a syrup which was fractionated by column chromatography (eluant light petroleum–ethyl actetate). The first material obtained was the D-*galacto*-bromide (**4**) (0.37 g, 33%) which was followed by the *acetamido-derivative* (**7**) as an oil (0.48 g, 44%), $[\alpha]_D$ −2° (Found: C, 65.1; H, 4.9; N, 1.8. $C_{38}H_{33}NO_{12}$ requires C, 65.6; H, 4.8; N, 2.0%); δ_H ([$^2H_6$]Me_2CO) 1.41 (OAc), 1.95 (NAc), 3.0 (1 H, s, NH), 4.79 (1 H, dd, $J_{5,6}$ 7.9, $J_{6,6'}$ 11.8 Hz, 6-H), 5.02 (1 H, dd, $J_{5,6'}$ 3.5 Hz, 6'-H), 5.33 (1 H, s, 3-H), 5.48 (1 H, d, $J_{1,2}$ 0.7 Hz, 2-H), 6.41 (1 H, d, 1-H), 6.49 (1 H, dd, 5-H), and 7.0—8.2 (20 H, ArH); δ_C([$^2H_6$]Me_2CO) 23.6 (NCOCH_3), 63.8 (C-6), 72.1 (C-5), 81.5 (C-2), 87.8 (C-3), 101.4 (C-1), 114.9 (Ph–*C*–N), 117.6 (C-4), and 170.3 p.p.m. (N–C=O), and phenyl and ester resonances.

1-O-*Acetyl*-2,3,5-*tri*-O-*benzoyl*-4-*bromo*-β-D-*ribofuranose* (**13**).—2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl acetate (**12**) (1 g) and NBS (1 g) were heated under reflux in carbon tetrachloride (80 ml) over the heat-lamp for 1.25 h. Solids were removed by filtration and the filtrate was diluted with chloroform (80 ml) and washed in turn with aqueous sodium thiosulphate, aqueous sodium hydrogen carbonate, and water, and dried. Removal of the solvent gave a syrup which was fractionated by flash chromatography[11] to give the 4-bromo-D-ribose compound (**13**) (0.64 g, 55%), $[\alpha]_D$ +19° (lit.,[1] +20°); the ^{1}H and ^{13}C n.m.r. spectra were identical with those previously reported.[1] This was followed by a compound (0.27 g, 30%) which, as before,[1] had the ^{1}H n.m.r. characteristics expected of 2,3,5-tri-*O*-benzoyl-D-*erythro*-pentos-4-ulose.

(5R)- *And* (5-S)-1,2,3,4-*Tetra*-O-*acetyl*-5-*bromo*-β-D-*xylopyranose* (**17**) *and* (**16**).—A suspension of 1,2,3,4-tetra-*O*-acetyl-β-D-xylopyranose (**15**) (1 g) and NBS (1.27 g) in carbon tetrachloride (40 ml) was heated under reflux over the heat-lamp for 1.6 h. The solids were removed by filtration, the filtrate was taken to dryness, and the resulting syrup was fractionated by flash chromatography to give 4 fractions. *Fraction* (i) was the (5R)-*bromide* (**17**) (0.41 g, 33%), $[\alpha]_D$ −92° (Found: Br, 21.1. $C_{13}H_{17}BrO_9$ requires Br, 20.1%); 2.01, 2.04, 2.16, and 2.18 (12 H, 4 s, Ac), 5.2—5.5 (3 H, m, 2-, 3-, and 4-H), and 6.1—6.25 (2 H, m, 1- and 5-H); δ_C 20.4 and 20.5 (COCH_3), 69.1, 70.1, and 77.3 (C-2, -3, and -4), 84.9 (C-5), and 91.6 p.p.m. (C-1), and ester C=O. *Fraction* (ii) was a 2:1 mixture of the (5*R*)- and (5*S*)-bromide (0.12 g, 36%). *Fraction* (iii) was the (5*S*)-bromide (**16**) (0.38 g, 30%), m.p. 132—137 °C (lit.,[5b] 135—140 °C); δ_H identical with literature data;[5b] δ_C 20.5 (COCH_3), 69.4, 69.7, and 70.4 (C-2, -3, and -4), 82.1 (C-5), and 89.9 p.p.m. (C-1), and ester C=O. *Fraction* (iv) (0.09 g) was recovered starting material.

Comparable Photobromination of 1-O-*Acetyl*-2,3,5,6-*tetra*-O-*benzoyl*-β-D-*glucofuranose* (**1**), 1-O-*Acetyl*-2,3,5-*tri*-O-*benzoyl*-β-D-*ribofuranose* (**12**), *and* 1,2,3,4-*Tetra*-O-*acetyl*-β-D-*xylopyranose* (**15**).—Each perester (0.23 mmol) was separately heated with NBS (3.6 mol equiv.) under reflux in carbon tetrachloride (7.5 ml) over the heat-lamp until each of the esters had just reacted completely (55, 45, 120 min respectively). After filtration, the filtrates were diluted with carbon tetrachloride, washed in the usual way, and dried to leave syrups which were examined by ^{1}H n.m.r. spectroscopy. The products were thus determined to be: from the D-glucose ester, the succinimido-compound (**6**) and the D-*galacto- and* D-*gluco*-bromide (**4**) and (**3**), 40:50:10; from the D-ribose ester, the D-*ribo*- and L-*lyxo*-bromide (**13**) and (**14**), 60:40; from the D-xylose ester, the (5*S*)- and (5*R*)-bromide (**16**) and (**17**), 60:40.

1,N-*Dibenzoyl*-2',3',5'-*tri*-O-*benzoyl*-4'-*bromoadenosine* (*Imine Tautomer*) (**19**).—The pentabenzoyl compound (**18**) (1.0 g) and NBS (1.3 g) were heated under reflux in carbon tetrachloride (40 ml) over the heat-lamp for 0.3 h. The solids were filtered off, chloroform (100 ml) was added to the filtrate, and the solution was washed and dried in the usual way. The solvent was then removed and the residue was fractionated by flash chromatography[11] to give the 4-bromo-derivative (0.43 g, 39%) which was identical (^{1}H n.m.r., t.l.c.) with the sample prepared by use of bromine.[1]

1-O-*Acetyl*-2,3,5,6-*tetra*-O-*benzoyl*-4-*chloro*-β-D-*glucofuranose* (**9**).—A solution of the succinimido-compound (**6**) (0.2 g) in carbon tetrachloride (6 ml) and dichloromethyl methyl ether (2 ml) at 0 °C under nitrogen was treated with boron trifluoride-diethyl ether (9 drops) and the mixture was stirred for 0.25 h at 0 °C and for 1.5 h at 20 °C. Aqueous sodium hydroxide was added to destroy the catalyst, and methylene dichloride (20 ml) was added to the organic phase which was washed with water and dried. Removal of the solvent gave the 4-*chloro-compound* (**9**) (0.18 g, 100%) which, after purification by preparative t.l.c., had $[\alpha]_D$ −4° (Found: C, 64.3; H, 4.8; Cl, 4.9. $C_{36}H_{29}ClO_{11}$ requires C, 64.2; H, 4.3; Cl, 5.3%). ^{1}H and ^{13}C Data have been reported elsewhere.[1]

Table 1. Atomic co-ordinates ($\times 10^4$) of non-hydrogen atoms of compound (**6**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(1)	4 137(3)	576(2)	7 457(4)	C(14)	6 727(2)	−259(2)	5 675(5)
O(2)	1 907(3)	460(2)	6 101(4)	C(15)	7 118(2)	−360(2)	6 838(5)
O(3)	3 935(3)	−323(2)	5 540(4)	C(16)	6 601(2)	−588(2)	7 803(5)
O(4)	3 032(3)	−54(2)	8 116(3)	C(17)	5 691(2)	−714(2)	7 604(5)
O(4′)	3 838(3)	−818(2)	7 316(4)	C(18)	4 506(5)	751(3)	8 532(7)
O(5)	2 214(3)	−1 336(2)	6 697(4)	C(19)	5 495(7)	843(4)	8 409(11)
O(6)	792(3)	−982(2)	8 458(4)	C(20)	1 629(4)	1 003(3)	5 927(6)
O(8)	4 812(4)	−1 864(2)	7 073(6)	C(21)	646(3)	1 048(2)	5 894(5)
O(11)	3 615(4)	−1 013(3)	3 638(5)	C(22)	274(3)	1 577(2)	5 637(5)
O(18)	4 081(4)	818(3)	9 469(5)	C(23)	−661(3)	1 650(2)	5 661(5)
O(20)	2151(3)	1 381(2)	5 822(5)	C(24)	−1 224(3)	1 195(2)	5 942(5)
O(27)	−460(3)	−658(3)	7 612(7)	C(25)	−852(3)	666(2)	6 200(5)
O(34)	2 075(4)	−2 012(2)	8 186(5)	C(26)	84(3)	593(2)	6 176(5)
N(1)	4 272(3)	−1 298(2)	5 480(5)	C(27)	−84(5)	−986(3)	8 301(9)
C(1)	3 192(4)	455(3)	7 499(6)	C(28)	−519(4)	−1 403(2)	9 111(7)
C(2)	2 880(4)	373(3)	6 154(6)	C(29)	−51(4)	−1 655(2)	10 094(7)
C(3)	3 017(4)	−249(3)	5 946(6)	C(30)	−477(4)	−2 058(2)	10 839(7)
C(4)	3 016(4)	−502(3)	7 247(5)	C(31)	−1 372(4)	−2 209(2)	10 601(7)
C(5)	2 247(4)	−900(3)	7 644(6)	C(32)	−1 840(4)	−1 957(2)	9 618(7)
C(6)	1 334(4)	−615(3)	7 713(6)	C(33)	−1 414(4)	−1 554(2)	8 873(7)
C(7)	4 341(4)	−761	6 198(6)	C(34)	2 119(5)	−1 881(3)	7 112(8)
C(8)	4 561(5)	−1 803(3)	6 025(9)	C(35)	2 047(4)	−2 265(2)	6 042(6)
C(9)	4 487(5)	−2 249(3)	5 035(9)	C(36)	2 088(4)	−2 842(2)	6 300(6)
C(10)	4 252(5)	−1 955(3)	3 857(8)	C(37)	2 032(4)	−3 234(2)	5 329(6)
C(11)	3 999(5)	−1 360(3)	4 259(7)	C(38)	1 934(4)	−3 048(2)	4 101(6)
C(12)	5 299(2)	−613(2)	6 442(5)	C(39)	1 892(4)	−2 471(2)	3 844(6)
C(13)	5 817(2)	−385(2)	5 477(5)	C(40)	1 949(4)	−2 080(2)	4 814(6)

Table 2. Selected intramolecular bond distances and angles for compound (**6**)[a] with e.s.d.s in parentheses

Atoms	Distance (Å)	Atoms	Distance (Å)
O(1)–C(1)	1.429(7)	O(27)–C(27)	1.207(11)
O(1)–C(18)	1.340(9)	O(34)–C(34)	1.194(10)
O(2)–C(2)	1.456(7)	N(1)–C(7)	1.489(8)
O(2)–C(20)	1.363(8)	N(1)–C(8)	1.398(10)
O(3)–C(3)	1.436(7)	N(1)–C(11)	1.378(9)
O(3)–C(7)	1.391(8)	C(1)–C(2)	1.525(9)
O(4)–C(1)	1.394(8)	C(2)–C(3)	1.503(9)
O(4)–C(4)	1.412(7)	C(3)–C(4)	1.518(8)
O(4)′–C(4)	1.430(7)	C(4)–C(5)	1.537(8)
O(4)′–C(7)	1.417(7)	C(5)–C(6)	1.513(8)
O(5)–C(5)	1.448(7)	C(7)–C(12)	1.484(7)
O(5)–C(34)	1.371(8)	C(8)–C(9)	1.499(12)
O(6)–C(6)	1.427(8)	C(9)–C(10)	1.482(12)
O(6)–C(27)	1.307(8)	C(10)–C(11)	1.520(12)
O(8)–C(8)	1.192(11)	C(18)–C(19)	1.486(12)
O(11)–C(11)	1.201(10)	C(20)–C(21)	1.459(8)
O(18)–C(18)	1.196(9)	C(27)–C(28)	1.464(11)
O(20)–C(20)	1.187(8)	C(34)–C(35)	1.467(10)

Atoms	Angle (°)	Atoms	Angle (°)
C(1)–O(1)–C(18)	115.7(5)	C(7)–N(1)–C(8)	119.6(6)
C(2)–O(2)–C(20)	115.9(5)	C(7)–N(1)–C(11)	127.0(6)
C(3)–O(3)–C(7)	110.2(4)	C(8)–N(1)–C(11)	113.3(6)
C(1)–O(4)–C(4)	109.8(4)	O(1)–C(1)–O(4)	110.8(5)
C(4)–O(4′)–C(7)	110.7(4)	O(1)–C(1)–C(2)	106.9(5)
C(5)–O(5)–C(34)	116.5(5)	O(4)–C(1)–C(2)	106.7(5)
C(6)–O(6)–C(27)	119.3(6)	O(2)–C(2)–C(1)	108.5(5)
O(2)–C(2)–C(3)	105.4(5)	C(9)–C(10)–C(11)	104.5(7)
C(1)–C(2)–C(3)	102.9(5)	O(11)–C(11)–N(1)	126.3(7)
O(3)–C(3)–C(2)	107.0(5)	O(11)–C(11)–C(10)	126.5(7)
O(3)–C(3)–C(4)	103.3(5)	N(1)–C(11)–C(10)	107.2(6)
C(2)–C(3)–C(4)	104.5(5)	C(7)–C(12)–C(13)	119.1(5)
O(4)–C(4)–O(4′)	110.1(4)	C(7)–C(12)–C(17)	120.9(5)
O(4)–C(4)–C(3)	108.0(5)	O(1)–C(18)–O(18)	123.2(7)
O(4)–C(4)–C(5)	106.9(5)	O(1)–C(18)–C(19)	111.8(7)
O(4)′–C(4)–C(3)	104.7(5)	O(18)–C(18)–C(19)	125.0(8)
O(4)′–C(4)–C(5)	107.1(5)	O(2)–C(20)–O(20)	121.9(6)

Table 2. *contd.*

Atoms	Angle (°)	Atoms	Angle (°)
C(3)–C(4)–C(5)	119.8(5)	O(2)–C(20)–C(21)	111.8(5)
O(5)–C(5)–C(4)	105.5(5)	O(20)–C(20)–O(20)	126.3(6)
O(5)–C(5)–C(6)	108.8(5)	C(20)–C(21)–C(22)	117.6(5)
C(4)–C(5)–C(6)	113.6(5)	C(20)–C(21)–C(26)	122.3(5)
O(6)–C(6)–C(5)	104.9(5)	O(6)–C(27)–O(27)	122.1(7)
O(3)–C(7)–O(4′)	105.8(5)	O(6)–C(27)–C(28)	111.4(7)
O(3)–C(7)–N(1)	110.2(5)	O(27)–C(27)–C(28)	126.4(7)
O(3)–C(7)–C(12)	109.0(5)	C(27)–C(28)–C(29)	121.2(6)
O(4′)–C(7)–N(1)	108.6(5)	C(27)–C(28)–C(33)	118.8(6)
O(4′)–C(7)–C(12)	112.1(5)	O(5)–C(34)–O(34)	124.2(7)
N(1)–C(7)–C(12)	111.0(5)	O(5)–C(34)–C(35)	109.7(6)
O(8)–C(8)–N(1)	126.3(7)	O(34)–C(34)–C(35)	126.0(6)
O(8)–C(8)–C(9)	127.2(7)	C(34)–C(35)–C(36)	116.7(6)
N(1)–C(8)–C(9)	106.5(7)	C(34)–C(35)–C(40)	123.3(6)
C(8)–C(9)–C(10)	106.9(7)		

[a] Phenyl group atoms were fixed (see text) with C–C 1.395 Å, and H–C–C, C–C–C angles of 120°.

1-O-*Acetyl*-2,3,5,6-*tetra*-O-*benzoyl*-4-*chloro*-β-D-*galacto*- and *gluco-furanose*.—A solution of the D-*gluco*-β-acetate (**1**) (0.2 g) and t-butyl hypochlorite (0.5 ml) in benzene (3 ml), after having nitrogen passed through it for 0.3 h, was irradiated with the heat-lamp for 2 h during which more hypochlorite was added (2 × 0.5 ml). The volatile compounds were removed and the residue was purified by preparative t.l.c. and shown by ^{1}H n.m.r. to contain the D-*gluco* and the D-*galacto* chlorides in the ratio 1:3.

X-*Ray Crystal Analysis of Compound* (**6**).—*Crystal data*. $C_{40}H_{33}NO_{13}$, orthorhombic, $a = 14.797(2)$, $b = 23.671(3)$, $c = 10.716(2)$ Å, $U = 3\,754(1)$ Å^3, $Z = 4$, $D_c = 1.30$ g cm^{-3}. Space group $P2_12_12_1$, μ(Mo-K_α) = 1.1 cm^{-1}. Intensities were collected on a Nicolet R3M four-circle diffractometer at 20 °C with graphite monochromatized Mo-K_α radiation using variable 2θ scan rates with a minimum of 4 degrees min^{-1}.

Table 3. Selected torsion angles for compound (**6**). The torsion angle of the bonded atoms A–X–Y–B is the angle between the planes A–X–Y and X–Y–B and is positive if clockwise when viewed down the bond X–Y

Atoms	Angle (°)	Atoms	Angle (°)
C(18)–O(1)–C(1)–O(4)	−74.5	C(8)–N(1)–C(7)–O(3)	−173.9
C(18)–O(1)–C(1)–C(2)	169.6	C(8)–N(1)–C(7)–O(4′)	−58.4
C(1)–O(1)–C(18)–O(18)	−1.9	C(8)–N(1)–C(7)–C(12)	−110.1
C(20)–O(2)–C(2)–C(1)	87.4	C(7)–N(1)–C(8)–C(9)	−174.7
C(20)–O(2)–C(2)–C(3)	−162.9	C(11)–N(1)–C(8)–C(9)	1.3
C(2)–O(2)–C(20)–O(20)	0.3	C(8)–N(1)–C(11)–C(10)	−8.9
C(7)–O(3)–C(3)–C(2)	133.0	O(1)–C(1)–C(2)–O(2)	−158.9
C(7)–O(3)–C(3)–C(4)	23.1	O(1)–C(1)–C(2)–C(3)	89.7
C(3)–O(3)–C(7)–O(4′)	−22.3	O(4)–C(1)–C(2)–O(2)	82.5
C(3)–O(3)–C(7)–N(1)	95.0	O(4)–C(1)–C(2)–C(3)	−28.9
C(3)–O(3)–C(7)–C(12)	−143.0	C(1)–C(2)–C(3)–O(3)	−87.0
C(4)–O(4)–C(1)–O(1)	−91.8	C(1)–C(2)–C(3)–C(4)	22.2
C(4)–O(4)–C(1)–C(2)	24.3	O(3)–C(3)–C(3)–O(4′)	−14.6
C(1)–O(4)–C(4)–O(4′)	104.1	O(3)–C(3)–C(4)–C(5)	−134.7
C(1)–O(4)–C(4)–C(3)	−9.6	C(2)–C(3)–C(4)–O(4)	−9.1
C(1)–O(4)–C(4)–C(5)	−139.8	O(4′)–C(4)–C(5)–C(6)	175.6
C(7)–O(4′)–C(4)–O(4)	−113.9	O(5)–C(5)–C(6)–O(6)	80.9
C(7)–O(4′)–C(4)–C(3)	2.0	O(4′)–C(7)–C(12)–C(17)	20.2
C(7)–O(4′)–C(4)–C(5)	130.2	N(1)–C(7)–C(12)–C(17)	−101.5
C(4)–O(4′)–C(7)–O(3)	12.0	N(1)–C(8)–C(9)–C(10)	7.1
C(4)–O(4′)–C(7)–N(1)	−106.3	C(8)–C(9)–C(10)–C(11)	−11.8
C(4)–O(4′)–C(7)–C(12)	130.8	C(9)–C(10)–C(11)–N(1)	12.7
C(34)–O(5)–C(5)–C(4)	136.2	O(2)–C(20)–C(21)–C(22)	−175.7
C(34)–O(5)–C(5)–C(6)	−101.5	O(6)–C(27)–C(28)–C(33)	−165.8
C(27)–O(6)–C(6)–C(5)	−152.9	O(5)–C(34)–C(35)–C(36)	170.3
C(6)–O(6)–C(27)–O(27)	−5.8		

A total of 1 723 reflections with $3.0 \leqslant 2\theta \leqslant 46.5°$ were measured with intensities greater than 3.0 times their standard deviation. The intensities were corrected for Lorentz and polarization factors and the structure was solved by direct methods. All calculations were performed using G. M. Sheldrick's SHELXTL and SHELX-76; the former was supplied with the Nicolet diffractometer. Structure solution was partially successful using the random phase routine RANT in SHELXTL. The structure was solved independently using the PDP8-E programmes.[12]

All hydrogen atoms except those of the acetyl group and the benzene rings were located and refined isotropically. The phenyl groups, particularly C(28)—C(33), and C(35)—C(40), showed signs of some disorder but no useful modelling of this could be established. All phenyl groups were therefore refined as rigid C_6H_5 groups, with C–C, C–H 1.395, 0.95 Å respectively, and appropriate hexagonal geometry. All non-hydrogen atoms were refined with anisotropic thermal parameters. Refinement entailed blocked full matrix least-squares minimizing the quantity $\Sigma\omega\Delta^2$ where Δ was $(|F_o| - |F_c|)$ and ω were modified statistical weights: $[\sigma^2(F) + 0.0005\,F^2]^{-1}$. Scattering curves for neutral atoms were taken from International Tables.[13] The final residuals R, R_w are 0.048, 0.054 respectively.

Atomic co-ordinates, bond lengths and angles (non-hydrogen), and selected torsion angles are given in Tables 1—3. Observed and calculated structure factors, additional bond lengths, weighted mean planes, all thermal parameters, and hydrogen co-ordinates are listed in Supplementary Publication No. SUP 23913 (18 pp).

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