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A COMPARISON OF BIS(TRIBUTYLTIN) OXIDE, POTASSIUM CYANIDE, AND POTASSIUM HYDROXIDE AS REAGENTS FOR THE REGIOSELECTIVE 1-*O*-DEACETYLATION OF FULLY ACETYLATED SUGARS*

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ABSTRACT

Treatments of fully acetylated sugars with bis(tributyltin) oxide in toluene at reflux, and with potassium cyanide or potassium hydroxide, or both, in mixtures of tetrahydrofuran and 2-propanol were found to be effective for regioselective 1-*O*-deacetylation of fully acetylated sugars.

INTRODUCTION

Glycosylation of alcohols, phenols, and nucleic acid bases has been accomplished by using 1-*O*-phenoxycarbonyl[2], 1-*O*-methoxycarbonyl[2], and 1-isourea sugar derivatives[3], each of which is derived from a corresponding sugar relative bearing a free anomeric hydroxyl group. Recently, 1-OH sugar derivatives were converted into the corresponding glycosyl chlorides and bromides by reaction with a Vilsmeier reagent[4], and into the trichloroacetimidates by reaction with trichloroacetonitrile[5] for the preparation of a glycosyl donor. Moreover, we have recently communicated a novel procedure for *C*-glycosylation involving the Lewis acid-catalyzed coupling-reaction of an enol silyl ether with a glycosyl fluoride, which was also prepared from the corresponding 1-OH sugar derivative by treatment with the adduct formed by hexafluoropropene and a secondary amine[6].

The peracylated 1-OH aldose derivatives commonly used were originally prepared from glycosyl halides by treatment with silver carbonate in aqueous acetone[7]; the instability of many of the halides and the expense of silver compounds suggested a need to develop more practical procedures for their preparation. The procedure involving treatment with hydrazine acetate is useful for pyranoses[8], but gives the corresponding hydrazone derivatives on application to aldofuranose acetates[9]. Piperidine effects regioselective 1-*O*-deacetylation of disaccharide derivatives under proper conditions[10], but monosaccharide acetates react further with

*Partial Protection of Carbohydrate Derivatives. Part 15. For Part 14, see ref. 1.

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TABLE I

REACTIONS OF 1,2,3,4,6-PENTA-*O*-ACETYL-α-D-GLUCOPYRANOSE (**1**) WITH ORGANOTIN COMPOUNDS[a]

Entry	*Organotin compound (mol. equiv.)*		*Reaction conditions*			*Yield (%) of*		*Recovery of* **1** *(%)*
			Solvent	*Reaction temp.*	*Reaction time*	**2**	**3**[b]	
1	$(Bu_3Sn)_2O$	(1.25)	$C_6H_5CH_3$	reflux	3.5 h	67	trace	19
2	$(Bu_3Sn)_2O$	(1.25)	C_6H_6	reflux	24 h	60	7	20
3	$(Bu_3Sn)_2O$	(1.25)	C_6H_6	room temp.	26 d	73	trace	6
4	$(Bu_3Sn)_2O$	(1.25)	C_6H_6 + MeOH (1 eq.)	reflux	10.5 h	61	6	6
5	$(Bu_3Sn)_2O$	(0.62)	EtOH	reflux	6.0 h	62	trace	7
6	$(Bu_2SnO)_n$	(1.25)	$C_6H_5CH_3$	reflux	7.0 h		no reaction	
7	$(Bu_2SnO)_n$	(1.11)	EtOH	reflux	2.0 h	28	—	3
8	Bu_3SnOCH_3	(1.25)	C_6H_6	reflux	6.0 h	49	5	6

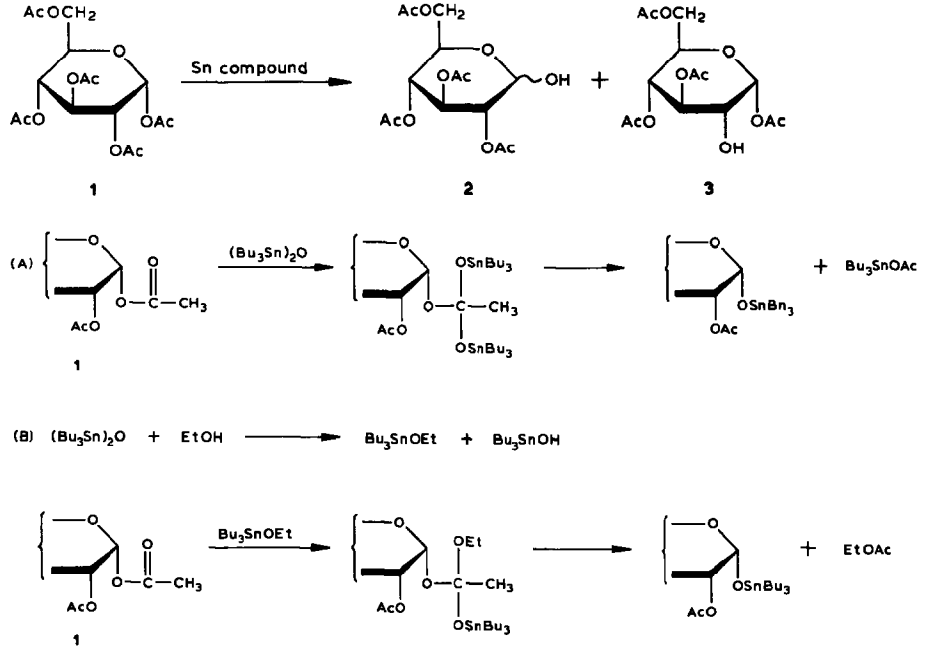
[a]All of the reactions were performed by using **1** (2.0 mmol) in a solvent (30 mL) under a nitrogen atmosphere. [b]The yield was determined by ^{1}H-n.m.r. spectroscopy.

piperidine, to give *N*-(3,4,6-tri-*O*-acetylglycosyl)piperidines[11]. Electrolytic methanolysis of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α- and -β-D-glucose was reported to bring about regioselective 1-*O*-deacetylation, affording 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucose in high yield[12]; however, on application to aldose acetates, this reaction gives a complex mixture[12].

Therefore, we set out to evaluate bis(tributyltin) oxide[13,14], potassium cyanide[15–17], and potassium hydroxide as reagents for regioselective 1-*O*-deacetylation of aldose peracetates; the results thus obtained are described herein.

RESULTS AND DISCUSSION

Reaction with organotin compounds. — Using 1,2,3,4,6-penta-*O*-acetyl-α-D-glucopyranose (**1**) as a model sugar derivative, it was treated with bis(tributyltin) oxide in slight excess as a potential agent in each of several solvents, either at room temperature or at reflux. Specific conditions and the results thus obtained are summarized in Table I. Bis(tributyltin) oxide gave the target compound, 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**2**), in good yields, accompanied by only small proportions of 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (**3**) (see Entries 1–5). The reaction gave almost the same results either in aprotic (Entries 1–3) or protic solvents (Entry 5), although it attained completion more quickly in the latter (*cf.*, Entries 2 and 5). The isolation of tributyltin acetate as a by-product (Entries 1–4) led to the assumption that the initial step of the reaction is addition of bis(tributyltin) oxide onto the 1-*O*-acetyl group of **1**, to give an adduct that might rearrange, with elimi-



Scheme 1.

TABLE II

REGIOSELECTIVE 1-*O*-DEACETYLATION OF PER-*O*-ACETYLALDOPYRANOSES BY BIS(TRIBUTYLTIN) OXIDE[a]

Entry	*Per-O-acetyl derivatives of*	*$(Bu_3Sn)_2O$ (mol. equiv.)*	*Reaction time (h)*	*Yield (%) of 1-OH sugar deriv.*	*Anomeric[b] ratio (α:β)*	*Recovery (%) of starting material*
1	α-D-glucopyranose	1.25	3.5	67	3.2:1	19
2	β anomer	1.25	2.5	93	3.2:1	4
3	α-D-mannopyranose	1.25	2	63	1:6	17
4	β anomer	1.25	2	71	1:6	4
5	α-D-galactopyranose	1.25	3	79	1.3:1	2
6	β anomer	1.25	2.5	86	1.3:1	5
7	β-D-xylopyranose	1.25	3	80	~α	5
8	β-D-ribofuranose	1.25	2.5	71	1:10	9
9	β-maltose	1.25	3	71	—	10
10	*N*-Ac-α-D-glucosamine	1.25	4	48	~α	23
11		1.0	5	49	~α	33
12	*N*-Ac-β-D-glucosamine	1.25	4.5	52	~α	16
13		1.0	5	59	~α	28
14	*N*-Ts-β-D-glucosamine	1.25	5	65	~α	15

[a]All of the reactions were performed on the per-*O*-acetylaldose (1–2 mmol) in toluene (30 mL) at reflux under a nitrogen atmosphere. [b]These were calculated from ^{1}H-n.m.r. spectra of products from acetylation of the anomeric mixture of 1-OH aldose acetates, using Ac_2O–pyridine at 0°. The symbol ~α indicates product that appeared to be solely α anomer.

nation of tributyltin acetate, to give the corresponding tributyltin 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl oxide; the latter should be hydrolyzed during work-up of the reaction, to give **2**, as depicted in Scheme A. The reaction in ethanol (Entry 5) gave no tributyltin acetate; this case may involve a mechanism induced by tributyltin ethoxide [instead of bis(tributyltin) oxide, from which the ethoxide should be formed by reaction with the solvent, as depicted in Scheme B]. To test this argument, **1** was treated with tributyltin methoxide in benzene (Entry 8), but the yield of **2** was lowered to 49%; t.l.c. of the resulting mixture revealed several more-polar spots, in addition to the spot of **2**, which indicated more extensive *O*-deacetylation. Tributyltin methoxide was thus too reactive to permit performing regioselective *O*-deacetylation in aromatic hydrocarbon solvents. Dibutyltin oxide was tested, and also found to be unsatisfactory for this reaction; t.l.c. indicated no reaction in toluene at reflux (Entry 6), whereas, in ethanol at reflux, an intense color developed, and t.l.c. showed the formation of highly polar products (Entry 7).

Based on the foregoing results, the treatment with bis(tributyltin) oxide in toluene at reflux under a nitrogen atmosphere was selected for testing with other aldose acetate derivatives, in order to determine its effectiveness for regioselective 1-*O*-deacetylation of a wider range of examples; the results are summarized in Table II. Peracetates of α- and β-D-glucopyranose, α- and β-D-mannopyranose, α- and β-D-galactopyranose, β-D-xylopyranose, β-D-ribofuranose, and β-maltose gave the corresponding 1-OH derivatives in yields ranging from 63 to 93%. ^{1}H-N.m.r. spectroscopy of each resulting mixture demonstrated that formation of isomeric

derivatives occurred in no more than traces. Reactions of β anomers (Entries 2, 4, and 6) were more facile, and proceeded with higher regioselectivity, than those of the corresponding α anomers (Entries 1, 3, and 5). The derivatives of D-glucosamine (Entries 10–14) are less reactive, and recovery of unchanged materials increased, even though the reaction time was prolonged, as shown in Table II; as before, β anomers (Entries 12 and 13) are more reactive than the corresponding α anomers (Entries 10 and 11). The reaction of the *N*-acetyl derivative (Entries 10 and 12) with 1.25 mol. equiv. of bis(tributyltin) oxide unexpectedly gave large proportions of tributyltin acetate, and was shown by t.l.c. to afford significant proportions of highly polar products. Lessening of the proportion of bis(tributyltin) oxide to 1.0 mol. equiv. gave slightly improved regioselectivity in the formation of the desired 1-OH derivative, but recovery of starting material also increased (Entries 11 and 13).

For comparison with the acetates, a reaction using 1,2,3,4,6-penta-*O*-benzoyl-α-D-glucopyranose was performed; because of lower reactivity, this required a longer period (24 h). Interestingly, a small proportion of 1,2,3,6-tetra-*O*-benzoyl-α-D-glucopyranose, bearing a free hydroxyl group at C-4, was additionally formed in this reaction.

Proportions of the anomers in each resulting mixture were deduced on the basis of ^{1}H-n.m.r. spectra of the corresponding peracetates obtained through acetylation performed under conditions (Ac_2O–C_5H_5N at 0°) that have been reported to bring about no significant anomerization[18]. Each of the anomers in the mixtures of peracetate obtained from the acetylation of the 1-OH derivatives gave, by and large, the same proportion, regardless of the anomeric configuration of the starting peracetate of D-glucose, D-mannose, D-galactose, or 2-acetamido-2-deoxy-D-glucose; equilibration of the anomers of the 1-OH sugar derivatives may have occurred during the work-up or during chromatographic separation on silica gel.

Reactions catalyzed by metal salts. — In a separate series of experiments, potassium cyanide, which had been shown by Mori and co-workers[15] to be a useful

TABLE III

REGIOSELECTIVE 1-*O*-DEACETYLATION OF PER-*O*-ACETYLALDOPYRANOSES BY POTASSIUM CYANIDE[a]

Entry	*Per-O-acetyl derivative of*	*Reaction time (days)*	*Yield (%) of 1-OH sugar deriv.*	*Recovery (%) of starting material*
1	α-D-glucopyranose	3	63	18
2	β-D-glucopyranose	4	97	2
3	α-D-mannopyranose	4	90	7
4	β-D-mannopyranose	4	99	—
5	α-D-galactopyranose	3	58	18
6	β-D-galactopyranose	5	72	14

[a]All of the reactions were performed by using an aldopyranose acetate (1 mmol) and KCN (20 mg, 0.3 mol. equiv.) in 1:1 95% aqueous 2-propanol–tetrahydrofuran (20 mL) at room temperature.

TABLE IV

REGIOSELECTIVE 1-*O*-DEACETYLATION OF PER-*O*-ACETYLALDOPYRANOSES BY POTASSIUM HYDROXIDE[a]

Entry	*Per-O-acetyl derivative of*	*Reaction time (min)*	*Yield (%) of 1-OH sugar deriv.*	*Recovery (%) of starting material*
1	α-D-glucopyranose	15	72	9
2	β-D-glucopyranose	15	93	4
3	α-D-mannopyranose	8	89	—
4	β-D-mannopyranose	10	99	—
5	α-D-galactopyranose	15	72	10
6	β-D-galactopyranose	5	80	4
7	*N*-Ac-α-D-glucosamine	40	93	4
8	α-cellobiose[b]	60	83	8

[a]All of the reactions were performed by using an aldopyranose acetate (1 mmol) and potassium hydroxide (80 mg, 1.4 mol. equiv.) in 1:1 95% aqueous 2-propanol–tetrahydrofuran (6 mL) at room temperature. [b]The solvent system used for this reaction was 1:1 95% aqueous 2-propanol–chloroform (12 mL).

reagent for transesterifications, and by El-Schenawy and Schuerch[16] and Paulsen and his co-workers[17] for *O*-deacylations of oligosaccharides, was applied to regioselective 1-*O*-deacetylation of six different peracetylated sugars. Compound **1** was chosen as the model reactant and subjected to treatment with potassium cyanide (0.3 mol. equiv.) at room temperature in 1:19 water–methanol, –ethanol, –propanol, and –2-propanol, respectively; all the reactions were monitored by t.l.c. and the last solvent was found to be the best for the reaction. Addition of tetrahydrofuran was found to enhance the solubility of **1**, and, under optimized conditions, peracetylated sugars were treated with 0.3 mol. equiv. of potassium cyanide in 1:1 95% aqueous 2-propanol–tetrahydrofuran; the results thus obtained are summarized in Table III. In each example, the reaction mixture was a heterogeneous suspension in the initial stage of the reaction, but gradually turned into a homogeneous solution. The reactions of **1** (Entry 1) and 1,2,3,4,6-penta-*O*-acetyl-α-D-galactopyranose (Entry 5) gave the corresponding 1-OH sugar derivatives in a lower yield, compared with the other examples (Entries 2, 3, 4, and 6), and a similar pattern was observed in reactions involving potassium hydroxide instead of potassium cyanide (*cf.*, Table IV); such a trend, within this series of sugars, might have arisen from stereochemical differences which affect the reactivity of the 1-*O*-acetyl group. Formation of the corresponding 2-OH derivatives in the reactions of **1** and 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (Entries 1 and 2) was revealed by ^{1}H-n.m.r. spectroscopy.

In the reaction, potassium cyanide may effect the deacetylation catalytically, or undergo solvolysis to generate potassium hydroxide or 2-propoxide, which could, in principle, catalyze *O*-deacetylation. To test such a possibility, we attempted to effect regioselective 1-*O*-deacetylation of the peracetylated sugars under catalysis by potasium hydroxide; the results thus obtained, and the conditions

used, are summarized in Table IV. The reactions displayed considerable regioselectivity, giving the corresponding 1-OH sugar derivatives in 70–99% yields, and, moreover, the reaction times were very short (8–15 min) in the presence of 1.4 mol. equiv. of potassium hydroxide; at longer reaction times, the two exceptions, which are less reactive than the others, gave the desired products, respectively, in excellent yields (Entries 7 and 8). Moreover, the ^{1}H-n.m.r. spectrum of each resulting mixture revealed that formation of the corresponding 2-OH derivatives occurred in only traces. Therefore, it was concluded that (*a*) it is practical to perform regioselective 1-*O*-deacetylation by potassium hydroxide owing to its simplicity, short reaction time, and high regioselectivity, and (*b*) hydrolysis of cyanide is not significant to its catalysis of 1-*O*-deacetylation.

Whereas the use of bis(tributyltin) oxide, potassium cyanide, and potassium hydroxide enabled us to prepare 1-OH derivatives of aldose acetates, potassium hydroxide is the most useful of the three, because its action is much faster; however, in circumstances where this reagent proves unsuitable, bis(tributyltin) oxide and potasisum cyanide are satisfactory alternatives.

EXPERIMENTAL

General. — Melting points were determined in a Micro-melting-point apparatus (Yanagimoto Co., Ltd.), and are uncorrected. Specific rotations were determined with a JASCO DIP-4 apparatus. ^{1}H-N.m.r. spectra were recorded with a Varian T-60, EM-360, or EM-390 spectrometer for solutions in deuteriochloroform containing tetramethylsilane as the internal standard, unless otherwise specified. 1,2,3,4,6-Penta-*O*-acetyl-α- (**1**)[19] and -β-D-glucopyranose[19], 1,2,3,4,6-penta-*O*-acetyl-α-[20] and -β-D-mannopyranose[21], 1,2,3,4,6-penta-*O*-acetyl-α-[19] and -β-D-galactopyranose[22], 1,2,3,4-tetra-*O*-acetyl-β-D-xylopyranose[8], 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-[19] and -β-D-glucopyranose[23], 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-(*p*-toluenesulfonamido)-β-D-glucopyranose[24], 1,2,3,4,6-penta-*O*-benzoyl-α-D-glucopyranose[25], 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose[21], and 1,2,3,6-tetra-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-glucopyranose (1,2,3,6,2′,3′,4′,6′-octa-*O*-acetyl-β-maltose)[8] were prepared (from sugars commercially available), according to the respective methods reported. 1,2,3,6-Tetra-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranose (1,2,3,6,2′,3′,4′,6′-octa-*O*-acetyl-α-cellobiose) and organotin compounds were commercially obtained. Column chromatography was conducted on Wakogel C-300.

*2,3,4,6-Tetra-*O*-acetyl-*D*-glucopyranose* (**2**) *(Representative procedures for 1-*O*-deacetylation).* — *(a) Procedure through bis(tributyltin) oxide.* Compound **1** (781 mg, 200 mmol) was heated in toluene at reflux under a nitrogen atmosphere with bis(tributyltin) oxide (1.474 g, 2.43 mmol). The resulting mixture was evaporated *in vacuo*, and the residue was chromatographed by successively using 200 mL each of 100:0, 98:2, 96:4, 94:6, 92:8, 90:10, 88:12, 85:15, 80:20, 75:25, 70:30, 65:35,

60:40, and 50:50 (v/v) benzene–ethyl acetate as the eluants, to give tributyltin acetate (288 mg, 41% yield), **1** (149 mg, 19% recovery), and **2** (465 mg, 67% yield), in turn.

Compound **2** was a syrup, $[\alpha]_D^{15}$ +71° (*c* 1.14, chloroform) {lit.[8] $[\alpha]_D^{20}$ +74° (*c* 1.95, chloroform); lit.[26] m.p. 123–126°, $[\alpha]_D$ +30.8° (chloroform); lit.[27] α anomer, m.p. 100°, $[\alpha]_D^{20}$ +135.6° (chloroform), +142.2→+80.4° (ethanol); lit.[28] β anomer (two forms), m.p. 120–122°, $[\alpha]_D^{20}$ +40° (*c* 1.6, chloroform), +32.6→+79° (*c* 1.9, ethanol), and m.p. 138–140°, $[\alpha]_D^{20}$ +18.8° (*c* 1.7, chloroform), −4.2→+75° (*c* 1.9, ethanol); lit.[7b] α anomer, m.p. 99–100°, $[\alpha]_D^{18}$ +135.1° (*c* 4.4, chloroform), $[\alpha]_D^{20-23}$ +139.4→+80.3° (*c* 4.0, 95% ethanol), β anomer, m.p. 137.5–138°, $[\alpha]_D^{18}$ +14.8° (*c* 4.1, chloroform), $[\alpha]_D^{24-26}$ −3.0→+80.2° (*c* 3.37, 95% ethanol)}; ^{1}H-n.m.r.: δ 4.5–5.8 (m, 5 H, H-1,2,3,4, and O*H*), 3.5–4.5 (m, 3 H, H-5,6,6'), and 2.07, 2.03, and 2.00 (3s, 12 H, 4 Ac).

Anal. Calc. for $C_{14}H_{20}O_{10}$: C, 48.28; H, 5.79. Found: C, 48.30; H, 5.85.

Tributyltin acetate obtained here was identical with a sample obtained commercially [m.p. 82–84°, no depression on admixture]; ^{1}H-n.m.r.: δ 0.5–2.4 (m, 27 H, 3 Bu), and 2.02 (s, 3 H, COC*H*$_3$).

(b) Procedure through potassium cyanide. To a suspension of potassium cyanide (16 mg, 0.3 mol. equiv.) in a mixture of 95% aqueous 2-propanol (10 mL) and tetrahydrofuran (10 mL) was added **1** (391 mg, 1 mmol), and the mixture was stirred at room temperature. After 3 days, water was added, the solution was extracted with chloroform (20 mL × 3), and the extracts were combined, washed with water, dried (anhydrous sodium sulfate), and evaporated *in vacuo*. The residue was chromatographed as before, to give **1** (71 mg, 18% yield) and **2** (219 mg, 63% yield), in turn.

(c) Procedure through potassium hydroxide. Compound **1** (422 mg, 1.08 mmol) was added to a mixture of 95% aqueous 2-propanol (3 mL) and tetrahydrofuran (3 mL) containing potassium hydroxide (90 mg, 1.4 mol. equiv.), and the mixture was stirred at room temperature. After 15 min, water was added, and the mixture was extracted with chloroform (10 mL × 3). The extracts were combined, washed with water, dried (anhydrous sodium sulfate), and evaporated *in vacuo*; the residue was chromatographed as before, to give **1** (37 mg, 9% yield) and **2** (274 mg, 73% yield), in turn.

*1,3,4,6-Tetra-*O*-acetyl-α-*D*-glucopyranose* (**3**). — Compound **1** (788 mg, 2.02 mmol) and bis(tributyltin) oxide (1.470 g, 2.47 mmol) were heated in benzene (30 mL) at reflux under a nitrogen atmosphere for 24 h. The mixture was evaporated *in vacuo*, and chromatography of the residue as before gave fractions containing tributyltin acetate (408 mg, 58% yield), **1** (76 mg, 20% recovery), **2** (410 mg), a mixture of **2** and **3** (31 mg, which was determined to contain 12 mg of **2** and 19 mg of **3** by ^{1}H-n.m.r. spectroscopy), and **3** (29 mg), in turn.

Compound **3** [m.p. 98–100° (from methanol)] was identical, by mixture melting-point and ^{1}H-n.m.r. spectroscopy, with an authentic sample prepared according to a literature procedure[29].

1,2,3,6-Tetra-O-*benzoyl*-α-D-*glucopyranose and 2,3,4,6-tetra*-O-*benzoyl*-D-*glucopyranose*. — 1,2,3,4,6-Penta-*O*-benzoyl-α-D-glucopyranose (1.407 g, 2.01 mmol) and bis(tributyltin) oxide (1.499 g, 2.51 mmol) were heated in toluene (30 mL) at reflux under a nitrogen atmosphere for 24 h. The mixture was evaporated to a residue that was purified by chromatography, using 300 mL each of 100:0, 99:1, 98:2, 96:4, 94:6, 90:10, 85:15, and 80:20 (v/v) benzene–ethyl acetate successively, to give fractions containing a mixture of the starting material and tributyltin benzoate (918 mg), the 4-OH compound (115 mg, 10% yield), and the 1-OH compound (714 mg, 60% yield), in turn.

The 4-OH compound was a crystalline powder; m.p. 167–170° (from diethyl ether), $[\alpha]_D^{15}$ +155° (*c* 1.12, chloroform) (lit.[30] m.p. 167–169°, $[\alpha]_D$ +180°).

The 1-OH compound was isolated as needles, m.p. 89–92° (from diethyl ether), $[\alpha]_D^{15}$ +65° (*c* 1.21, chloroform) {lit.[26] m.p. 117–120°, $[\alpha]_D^{20}$ +72.4° (chloroform); lit.[31] m.p. 114–116°, $[\alpha]_D^{18}$ +90.1° (*c* 0.2, chloroform)}; ^{1}H-n.m.r.: δ 6.9–8.2 (m, 20 H, 4 Bz), 5.5–6.7 (m, 3 H, H-1,3,4), 5.92 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.5 Hz, H-2), and 4.2–5.1 (m, 4 H, H-5,6,6′, and O*H*).

Anal. Calc. for $C_{34}H_{28}O_{10}$: C, 68.45; H, 4.73. Found: C, 68.18; H, 4.83.

2,3,4,6-Tetra-O-*acetyl*-D-*mannopyranose* formed granular crystals, m.p. 94.5–97.5° (from diethyl ether), $[\alpha]_D^{15}$ +22° (*c* 1.0, chloroform) {lit.[26a] m.p. 90–94°, $[\alpha]_D$ +23.5° (chloroform); lit.[32] m.p. 94°, $[\alpha]_D^{20}$ +25.5° (chloroform)}; ^{1}H-n.m.r.: δ 4.7–5.6 (m, 5 H, H-1,2,3,4 and O*H*), 3.6–4.5 (m, 3 H, H-5,6,6′), and 2.16, 2.10, 2.06, and 2.00 (4 s, 4 × 3 H, 4 Ac).

Anal. Calc. for $C_{14}H_{20}O_{10}$: C, 48.27; H, 5.79. Found: C, 48.31; H, 5.77.

2,3,4,6-Tetra-O-*acetyl*-D-*galactopyranose* was isolated as a powder, m.p. 103–108° (from diethyl ether), $[\alpha]_D^{15}$ +74° (*c* 1.09, chloroform) {lit.[26a] m.p. 124–125°, $[\alpha]_D$ +27.5° (chloroform); lit.[33] α anomer, m.p. 143–146°, $[\alpha]_D^{22}$ +135–136→ +69.5° (*c* 2, ethanol–water); lit.[34] α anomer, m.p. 133°, $[\alpha]_D^{21}$ +144° (*c* 0.98, chloroform); lit.[35] β anomer, m.p. 112°, 127–128° (in dealkalinated glass), $[\alpha]_D^{20}$ +23.3° (*c* 5.0, chloroform); lit.[36] β anomer, m.p. 125–126°, $[\alpha]_D^{24}$ +26° (*c* 1.0, chloroform)}; ^{1}H-n.m.r.: δ 3.7–5.6 (8 H, H-1,2,3,4,5,6,6′, and O*H*), and 2.19, 2.13, 2.10, and 2.04 (4 s, 4 × 3 H, 4 Ac).

Anal. Calc. for $C_{14}H_{20}O_{10}$: C, 48.27; H, 5.79. Found: C, 48.20; H, 5.78.

2,3,4-Tri-O-*acetyl*-D-*xylopyranose* had m.p. 137–139° (from diethyl ether), $[\alpha]_D^{15}$ +63° (*c* 1.35, chloroform) {lit.[26a] m.p. 132–135°, $[\alpha]_D$ −4.5→ +38° (chloroform); lit.[8] α anomer, m.p. 160°, $[\alpha]_D$ +67° (*c* 1.25, chloroform)→ +33.5° (addition of a trace of trifluoroacetic acid); lit.[37] α anomer, m.p. 135–137°, m.p. 155° (in dealkalinated glass), $[\alpha]_D^{21}$ +71.1° (*c* 4, chloroform); β anomer, m.p. 136–137.5°, m.p. 149° (in dealkalinated glass), $[\alpha]_D^{20}$ −34.4° (*c* 6.5, chloroform)}; ^{1}H-n.m.r.: δ 4.6–5.7 (m, 5 H, H-1,2,3,4, and O*H*), 3.80 (d, 2 H, $J_{4,5}$ and $J_{4,5'}$ 8 Hz, H-5,5′), 2.09, and 2.04 (2 s, 3 H and 6 H, 3 Ac).

Anal. Calc. for $C_{11}H_{16}O_8$: C, 47.83; H, 5.84. Found: C, 47.87; H, 5.71.

2-Acetamido-3,4,6-tri-O-*acetyl-2-deoxy*-D-*glucopyranose* was a syrup, $[\alpha]_D^{15}$ +46° (*c* 1.01, chloroform) {lit.[38] α anomer, m.p. 65–75°, $[\alpha]_D^{20}$ +49.4° (*c* 2.1,

chloroform), +50.4→+26.9° (*c* 0.5, water)}; ^{1}H-n.m.r.: δ 6.06 (br. d, 1 H, $J_{2,NH}$ 9.5 Hz, N*H*), 4.95–5.6 (m, 3 H, H-1,3,4), 4.85 (br. s, 1 H, O*H*), 4.0–4.5 (m, 4 H, H-2,5,6,6'), 2.18, 2.09, 2.04, and 1.98 (4 s, 4 × 3 H, 4 Ac).

Anal. Calc. for $C_{14}H_{21}NO_9$: C, 48.41; H, 6.09; N, 4.03. Found: C, 48.29; H, 6.11; N, 3.89.

*3,4,6-Tri-*O*-acetyl-2-deoxy-2-(*p*-toluenesulfonamido)-*D*-glucopyranose* had m.p. 159–161° (from benzene), $[\alpha]_D^{15}$ +33° (*c* 0.86, chloroform) {lit.[39] α anomer, m.p. 159–160°, $[\alpha]_D^{21}$ +70.9° (chloroform)}; ^{1}H-n.m.r.: δ 7.71 (d, 2 H, *J* 8.4 Hz, H-2,6 of *p*-tosyl group), 7.24 (d, 2 H, H-3,5 of *p*-tosyl group), 5.67 (br. d, 1 H, $J_{2,NH}$ 9.5 Hz, N*H*), 4.5–5.5 (m, 4 H, H-1,3,4, and O*H*), 3.0–4.5 (m, 4 H, H-2,5,6,6'), 2.40 (br. s, 3 H, C*H*$_3$-Ph), 2.06, 1.99, and 1.96 (3 s, 3 × 3 H, 3 Ac).

Anal. Calc. for $C_{19}H_{25}NO_{10}S$: C, 49.67; H, 5.48; N, 3.05; S, 6.98. Found: C, 49.74; H, 5.42; N, 3.25; S, 6.90.

*2,3,5-Tri-*O*-acetyl-*D*-ribofuranose* was a syrup, $[\alpha]_D^{15}$ +11° (*c* 1.21, chloroform) {lit.[40] $[\alpha]_D^{20}$ +45° (*c* 1.0, water) (α anomer:β anomer = 1.9)}; ^{1}H-n.m.r.: δ 4.8–5.6 (m, 3 H, H-1,2,3), 3.8–4.6 (m, 4 H, H-4,5,5', and O*H*), 2.12, 2.08, and 2.06 (3 s, 3 × 3 H, 3 Ac).

Anal. Calc. for $C_{11}H_{16}O_8$: C, 47.83; H, 5.84. Found: C, 47.79; H, 5.87.

*2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-*D*-glucopyranose* had m.p. 179–180° (from ethanol), $[\alpha]_D^{15}$ +86° (*c* 1.04, chloroform) {lit.[8] m.p. 191°, $[\alpha]_D^{20}$ +73.5→+112° (*c* 1, pyridine), $[\alpha]_D^{20}$ +77° (*c* 1, chloroform)→+108° (addition of a trace of trifluoroacetic acid); lit.[10] β anomer, m.p. 188°, $[\alpha]_D^{22}$ +84→+114° (*c* 0.91, pyridine)}; ^{1}H-n.m.r.: δ 3.5–5.7 (m, 15 H, glucopyranosyl ring-protons and O*H*), and 2.15, 2.11, 2.06, 2.03, and 2.02 (5 s, 3 H, 3 H, 6 H, 6 H, and 3 H, in turn, 7 Ac).

Anal. Calc. for $C_{26}H_{36}O_{18}$: C, 49.06; H, 5.70. Found: C, 49.08; H, 5.51.

*2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-*D*-glucopyranose* was a crystalline powder, m.p. 170–190° (from ethanol), $[\alpha]_D^{15}$ +27° (*c* 1.15, chloroform) {lit.[8] α anomer, m.p. 208–210°, $[\alpha]_D^{20}$ +34.5→+22.5° (*c* 1, pyridine); lit.[10] α anomer, m.p. 209°, $[\alpha]_D^{22}$ +33.4→+23° (*c* 2.2, pyridine)}; ^{1}H-n.m.r.: δ 3.36–5.57 (m, 15 H, glucopyranosyl ring-protons and O*H*), and 2.12, 2.07, 2.03, 2.01, 1.98, and 1.96 (6 s, 3 H, 3 H, 3 H, 6 H, 3 H, and 3 H, in turn, 7 Ac).

Anal. Calc. for $C_{26}H_{36}O_{18}$: C, 49.06; H, 5.70. Found: C, 49.15; H, 5.73.

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