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Note

Selective mono-esterification and alkylation of 1,6-anhydro-β-D-glucopyranose *via* its dibutylstannylene derivative

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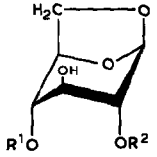
1,6-Anhydro-β-D-glucopyranose (**1**) has been shown to be a useful synthetic intermediate[1,2]. Its utility is enhanced because 2,4-disubstituted derivatives can be prepared selectively[3,4]. The availability of monosubstituted derivatives would further increase its usefulness. Previous attempts to introduce an ester group selectively at O-2 or O-4 have resulted in complex mixtures and very low yields[3,5–7]. The mono-*O*-benzyl derivatives have been obtained *via* several-step syntheses[4,8].

We particularly desired a method for the preparation of either 2- or 4-mono-*O*-substituted derivatives of **1** in order to shorten the route to 1,6:2,3-dianhydro-4-*O*-benzyl-β-D-allopyranose. We have used this compound as an intermediate in the synthesis of 3-*O*-substituted D-glucose derivatives[9] that affect the rates of growth of certain yeasts[10].

Since the original report by Moffatt *et al.*[11], dibutylstannylene acetals have



1 $R^1 = R^2 = H$
2 $R^1 = R^2 = SnBu_2$
3 $R^1 = COPh, R^2 = H$
4 $R^1 = H, R^2 = COPh$
5 $R^1 = Ts, R^2 = H$
6 $R^1 = H, R^2 = Ts$
7 $R^1 = Bn, R^2 = H$
8 $R^1 = H, R^2 = Bn$

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been shown to be extremely useful for the nucleophilic activation of hydroxyl groups and as reagents that can give regioselective esterification and alkylation of secondary hydroxyl groups[12]. Regioselective substitution has not yet been reported for a 1,3-diaxially related pair of hydroxyl groups. We now report that regioselective alkylation and esterification of the dibutylstannylene derivative of the 1,3-diaxially related diol unit of **1** occurs preferentially at O-4.

The dibutylstannylene derivative (**2**) of **1** was easily formed when **1** was refluxed with dibutyltin oxide in benzene. Reaction with 1.1 equiv. of benzoyl chloride at 10° yielded mainly mono-*O*-benzoyl products (74%), in contrast to the complex mixture obtained[3] from the direct benzoylation of **1**. The two mono-*O*-benzoyl derivatives obtained, namely, 1,6-anhydro-4-*O*-benzoyl-β-D-glucopyranose (**3**) and its 2-*O*-benzoyl analog (**4**) were separated, and identified by comparison of their physical constants with literature values[3,13]. Because the optical rotations of **3** in two solvents did not match those previously reported[3,13], more-extensive evidence is provided in support of the structure of **3**.

The mass spectrum indicated that **3** was indeed a mono-*O*-benzoyl derivative, and this conclusion is supported by the ^{1}H- and ^{13}C-n.m.r.-spectral data listed in Tables I–III. In particular, it was noticeable that the ^{1}H-n.m.r. spectra of all mono-substituted derivatives of **1** prepared here, including **3**, contain two sharp exchangeable doublets, each having integral intensities lying between 2.5 and 3.0 p.p.m. These doublets were assigned to the two OH hydrogen atoms of a mono-substituted derivative of **1**. The similarity of the chemical shifts for H-1, H-5, H-6, H-6′, C-1, C-5, and C-6 of **3** with those[14,15] of **1** and the other compounds prepared here (**4–8**) indicated that **3** maintained its 1,6-anhydro-β-D-glucopyranose frame. Support for the *gluco* stereochemistry comes from the absence of measurable

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS[a]

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C=O, CH_2, or CH_3*	*Phenyl*
1[b]	102.1	70.9	73.3	71.6	76.9	65.8		
3	102.1	70.1	71.4	73.3	74.3	65.8	165.6	133.6,129.7,128.6
4	99.8	72.0[c]	71.6[c]	72.0[c]	76.5	65.4	168.4	133.6,129.8,128.6
4[d]	99.1	73.8	71.1[c]	71.4[c]	76.5	65.2	165.4	133.5,129.6,129.4,128.7
5	101.9	69.9[c]	71.2[c]	78.5	74.7	65.4	21.7	145.5,132.9,130.1,127.8
6	99.5	77.0	70.7[c]	71.4[c]	76.3	65.6	21.7	145.6,132.6,130.1,127.9
7	102.1	70.4	69.9	76.9	74.4	65.4	71.4	137.2,128.5,128.1,127.8
7[e]	104.5	74.3	73.5	81.9	75.5	66.6	71.6	139.3,128.7,128.1,127.8
8	100.7	76.8	70.3[c]	70.8[c]	76.3	65.3	72.1	137.0,128.5,128.1,127.8

[a] P.p.m. downfield relative to the central peak of chloroform-*d* at 77.0 p.p.m. in chloroform-*d* at 90.8 MHz. [b] From ref. 14. [c] Assignments may have to be interchanged. [d] In dimethyl sulfoxide-d_6, referenced to the solvent central line as 39.56 p.p.m. [e] In pyridine-d_5, referenced to the central C-3 line as 123.5 p.p.m.

TABLE II

^{1}H-N.M.R. CHEMICAL SHIFTS[a]

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*OH-3*	*OH-2 or OH-4*	*CH_2 or CH_3*	*Phenyl*
3	5.548	3.637	3.954	4.948	4.743	3.852	4.304	2.971	2.588		7.462,7.601, 8.048
4	5.630	4.827	3.962	3.724	4.646	3.838	4.396	2.732	2.692		7.464,7.604, 8.042
5	5.458	3.501	3.744	4.402	4.607	3.743	4.120	2.998	2.652	2.460	7.36–7.39, 7.81–7.85
6	5.320	4.220	3.872	3.610	4.560	3.729	4.140	2.910	2.956	2.458	7.36–7.38, 7.81–7.84
7	5.482	3.415	3.917	3.435	4.616	3.717	4.116	2.701	2.823	4.662	7.33–7.36
8	5.496	3.346	3.917	3.606	4.557	3.748	4.173	2.470	2.999	4.692, 4.534	7.31–7.37

[a]P.p.m. downfield from internal Me_4Si in chloroform-*d* at 361.05 MHz.

TABLE III

^{1}H-N.M.R. COUPLING CONSTANTS (Hz)

Compound	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{2,OH-2}$	$J_{3,OH-3}$	$J_{4,OH-4}$
3	5.52	0.67	−7.75	10.83	6.50	
4	5.59	[a]	−7.48		5.83	10.66
5	5.54	0.62	−7.96	10.57	6.58	
6	5.53	0.72	−7.54		5.73	9.83
7	5.45	[a]	−7.57	11.23	7.29	
8	5.36	[a]	−7.59		7.42	11.56

[a] Not observed.

coupling constants between H-1 to H-5 in the ^{1}H-n.m.r. spectrum in **3**, as in the spectra of other derivatives with this stereochemistry[1]. The location of the benzoyl group was established by means of a combination of ^{1}H- and ^{13}C-n.m.r. spectroscopy. In the ^{1}H-n.m.r. spectra, the signals of H-1, H-5, H-6, and H-6′ were readily assigned from their chemical shifts (H-1) or appearance due to coupling (H-5, H-6, H-6′), or to lack of it (H-1). Of the signals for the remaining skeletal protons, two were coupled to the signals of OH protons with different sized coupling constants, while one was not coupled and was farther downfield. Selective decoupling experiments were used to correlate each of the proton signals to the signals of the directly bonded carbon atoms. Comparison of the ^{13}C-n.m.r. chemical shifts of **3** with those of **1** allowed unambiguous assignment of structure. The conversion of a hydroxyl group into a benzoate group is known[15,16] to cause the signal of the directly attached carbon atom to be shifted downfield by 1.5–4 p.p.m. and those of the adjacent carbon atoms to be shifted upfield by 1–5 p.p.m. The signals of C-1 in the spectra of

1 and **3** have the same shifts. Thus, the benzoyl group in **3** cannot be attached to O-2. The signal of C-5 in the spectrum of **3**, in comparison to that for **1**, was shifted upfield by 2.6 p.p.m., suggesting that the benzoyl group in **3** is attached to O-4. The signal for the carbon atom bearing the benzoate group can be assigned through correlation with the downfield proton signal that was not coupled to an OH proton; the value observed was 73.3 p.p.m. Because the shift of C-3 was 73.3 p.p.m. in the spectrum of **1**, the observed shift is not consistent with a structure having a benzoyl group attached to O-3. Further support for the 4-*O*-benzoyl structure is supplied by the chemical shifts of the remaining carbon atoms. The signal of C-3 is shifted upfield by 1.9 p.p.m., while that of C-2 is relatively unaffected (upfield shift, 0.8 p.p.m.).

The ratio of **3** to **4** obtained was 86:14; thus, the reaction was quite regioselective. Direct benzoylation yielded equal amounts of **3** and **4**. Benzoylation of **2** conducted in 1,2-dimethoxyethane as the solvent in the presence of triethylamine[17] gave a similar yield of mono-*O*-benzoyl derivatives (73%) having a similar composition.

Mono-*O*-*p*-toluenesulfonylation of **2** in 1,2-dimethoxyethane in the presence of triethylamine yielded 75% of mono-*O*-*p*-tolylsulfonyl derivatives with the ratio of **5**:**6** being 65:35. Compounds **5** and **6** were identified from their physical properties[3]. Again, the proportions of mono-*O*-*p*-tolylsulfonyl derivatives obtained were much greater than given by direct reaction with **1**, and considerable selectivity was obtained, although not as much as for benzoylation.

Mono-*O*-benzylation was performed by using the procedure of David *et al.*[18], with benzyl bromide in benzene in the presence of tetrabutylammonium iodide at reflux. The yield of mono derivatives (61%) was lower than obtained for esterification. The two products (**7** and **8**) were separated. The preference for the 4-*O*-substituted derivative **7** was again significant (ratio 68:32). The physical properties of **8** were identical to literature values[4]. The optical rotation of **7** was the same as that previously observed[8], but the m.p. obtained here was higher, 70–71°, *vs.* 54–56° (ref. 8). As discussed for **3**, the structure of **7** could be unambiguously established from its ^{1}H- and ^{13}C-n.m.r.-spectral data. A two dimensional, ^{1}H–^{13}C-n.m.r. correlation experiment was performed in order to verify the ^{13}C-n.m.r. assignments (see Table I), and hence confirm the structure assigned to **7**. Because this compound was shown to be the 4-*O*-benzyl derivative, a different polymorph must have been obtained here than earlier[8].

Benzylation of **2** in 1,4-dioxane without added iodide gave a somewhat lower yield (50%) of mono-*O*-benzyl derivatives[19]. The regiospecificity obtained under these conditions was nor reported, although the two products were separated[19]. The ^{13}C-n.m.r. shifts reported[19] for **7** in pyridine-d_5 were identical to those obtained here. However, the assignments made[19] for C-3 and for the benzyl primary carbon atom have now been interchanged on the basis of the coupled spectrum recorded here. The change in solvent from chloroform-*d* caused large (< 5 p.p.m.) chemical-shift changes for C-1, C-2, C-3, and C-4. It was observed that reaction of **2** with benzyl bromide in *N*,*N*-dimethylformamide, conditions often used with dibutylstan-

nylene acetals[12,19], was much slower than under the conditions reported.

The origin of the selectivity observed for **2** is uncertain. There is considerable evidence that most carbohydrate dibutylstannylene acetals in non-polar solvents exist as dimers with pentacoordinate tin[12,20,21]. It has been argued that the apically bound oxygen atoms, normally the most electronegative, are more reactive[12]. Thus, if stereochemical factors are equal, the more electronegative atom, normally O-2 would be expected to react faster. However, O-2 and O-4 are here close to being stereochemically equivalent, and O-4 is the more reactive.

An interesting feature of the ^{1}H-n.m.r. spectra of **3**–**8** in chloroform-*d* is the large and differing magnitudes of the OH proton coupling constants. The signal of OH-3 always had a smaller coupling constant (5.7–7.3 Hz) than that of OH-2 or OH-4 (9.8–11.6 Hz). Large coupling constants for OH-2 have similarly been observed for chloroform-*d* solutions of 3,4-di-*O*-substituted derivatives of 1,6-anhydro-β-D-glucopyranose[9,22]. Karplus-type relationships have been developed for H–C–O–H fragments[23]. The values obtained here for OH-2 and OH-4 are consistent with the predominant H–C–O–H orientations as being *anti*. In contrast, the magnitudes of the coupling constants observed for OH-3 suggest that there is not any preference for particular C-3–O-3 rotamers. In the solid state, **1** has OH-2 *anti* to H-2, and it was suggested[24] that weak intramolecular hydrogen-bonds to O-4 and O-5 stabilize this orientation. Crystals of 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose exist[25] in a conformation having OH-4 *anti* to H-4, whereas those of the hydrochloride of this compound have neither OH-2 nor OH-4 *anti* to a hydrogen atom[26]. Seib *et al.*[4,22] have used i.r. frequency measurements to indicate that, in dilute carbon tetrachloride solutions, mono- and di-*O*-alkyl derivatives of **1** form intramolecular hydrogen-bonds. For the compounds having OH-2 or OH-4, or both, free, the intramolecular hydrogen-bonds persist in chloroform solutions, causing the large coupling constants observed here and earlier[9,22], but disappear[22] in dimethyl sulfoxide-d_6. Because alcohol–dimethyl sulfoxide hydrogen-bond strengths are[27] on the order of 3–4 kcal.mol^{-1}, the hydrogen bonds in these compounds must be weaker.

EXPERIMENTAL

General methods. — Most general methods were as described in re. 28. T.l.c. was performed on 0.2-mm thick Merck Silica Gel 60F-254 on aluminium sheets cut to be 7 cm long.

General procedure for preparation of the dibutylstannylene derivatives (**2**) *of 1,6-anhydro-β-D-glucopyranose* (**1**). — A mixture of **1** (0.810 g, 5 mmol) and dibutyltin oxide (1.25 g, 5 mmol) in benzene (50 mL) was refluxed for 12 h in an apparatus equipped for the azeotropic removal of water. Evaporation under diminished pressure gave the crude stannylene derivative **2**, which was used without purification.

Benzoylation of **2**. — A solution of benzoyl chloride (0.65 mL, 5.5 mmol) in

benzene (50 mL) was added dropwise during 0.5 h to a vigorously stirred mixture of **2** (5 mmol) and powdered molecular sieves 4A (3 g) in benzene (50 mL) at 10°. After being stirred for 2 h at 10°, the mixture was filtered. The filtrate was diluted with dichloromethane (150 mL), and the solution was washed with water (2 × 50 mL), dried ($MgSO_4$), and evaporated. The resulting syrup was separated by column chromatography on silica gel, using a solvent gradient changing from 1:1 to 4:1 ethyl acetate–chloroform. The first fraction contained a mixture of di-*O*-benzoyl derivatives and benzoyl chloride. The second fraction was solid 1,6-anhydro-4-*O*-benzoyl-β-D-glucopyranose (**3**) (729 mg, 55%). Recrystallization from a mixture of acetone, ether, and petroleum ether (b.p. 30–60°) gave flakes; m.p. 130–131° (lit.[3] m.p. 123–126°), $[\alpha]_D^{23}$ −117° (*c* 1.07, chloroform), −118.7° (*c* 1.40, methanol) (lit.[3,13] −87° (chloroform), −85° (methanol)); *m/z*: 248 (1.2%, $M^+ - H_2O$), 123 (16%), 105 (100%, +COPh), 77 (23%), and 70 (11%). A mixed fraction (200 mg) was followed by another solid, namely, 1,6-anhydro-2-*O*-benzoyl-β-D-glucopyranose (**4**; 60 mg, 5%), that was recrystallized from the same solvent mixture to give fine needles; m.p. 164–165° (lit.[3] m.p. 162–164°); $[\alpha]_D^{23}$ +30.4° (*c* 0.98, methanol) (lit.[3] +28°); ^{13}C-n.m.r. spectroscopy indicated that the mixed fraction consisted of **3** and **4** in the ratio of 5:3. Thus, the overall product ratio of **3** to **4** was 86:14. For ^{1}H- and ^{13}C-n.m.r. data for **3** and **4**, see Tables I–III.

p-Toluenesulfonylation of **2**. — To a solution of **2** (5 mmol) in 1,2-dimethoxyethane (50 mL) were added triethylamine (0.77 mL, 5.5 mmol) and powdered 4A molecular sieves (3 g), followed by a solution of *p*-toluenesulfonyl chloride (1.048 g, 5.5 mmol) in 1,2-dimethoxyethane (20 mL). The mixture was stirred vigorously for 2 days and then filtered. The filtrate was diluted with dichloromethane (150 mL), and the solution was washed with water (2 × 50 mL), dried ($MgSO_4$), and evaporated. The residue was separated by column chromatography on silica gel using 7:3 chloroform–tetrahydrofuran as the eluant. The first component was 1,6-anhydro-2,4-di-*O*-*p*-tolylsulfonyl-β-D-glucopyranose (136 mg); m.p. 96–98°, lit.[1] m.p. 116–118°; $[\alpha]_D^{23}$ −44.5° (*c* 0.98, chloroform), lit.[1] −43°. The second component was 1,6-anhydro-4-*O*-*p*-tolylsulfonyl-β-D-glucopyranose (**5**; 678 mg, 43%), which was recrystallized from acetone, ether, and petroleum ether (b.p. 30–60°) to give needles, m.p. 125° (lit.[3] m.p. 125–127°); $[\alpha]_D^{23}$ −57.2° (*c* 1.03, chloroform) (lit.[3] −53°). A mixture (228 mg) was followed by a third pure fraction (273 mg, 17%) that was recrystallized from the same solvent to give thick prisms of 1,6-anhydro-2-*O*-*p*-tolylsulfonyl-β-D-glucopyranose (**6**); m.p. 116–118° (lit.[3] m.p. 116–119°); $[\alpha]_D^{23}$ −44.9° (*c* 1.13, chloroform) (lit.[1] −48°). The mixed fraction consisted of **5** and **6** in the ratio of 3:5 (as measured by ^{13}C-n.m.r. spectroscopy), giving an overall ratio of **5**:**6** of 65:35. For ^{1}H- and ^{13}C-n.m.r. data for **5** and **6**, see Tables I–III.

Benzylation of **2**. — To a solution of **2** (5 mmol) in benzene (50 mL) were added powdered 4A molecular sieves (3 g), tetrabutylammonium iodide (1.85 g, 5 mmol), and benzyl bromide (0.66 mL, 5.5 mmol), and the mixture was refluxed for 48 h, cooled, and filtered. The filtrate was diluted with dichloromethane (150 mL)

washed with water (2 × 50 mL), dried ($MgSO_4$), and evaporated to a syrup that was found to consist of three di-*O*-benzyl derivatives, two mono-*O*-benzyl derivatives, and a trace of **1**. The residue was separated by column chromatography on silica gel using 4:1 ethyl acetate–chloroform as the eluant. The first fraction, a syrup (360 mg), contained the di-*O*-benzyl derivatives. The second fraction (340 mg, 27%) crystallized from ether, to give colorless crystals of 1,6-anhydro-4-*O*-benzyl-β-D-glucopyranose (**7**); m.p. 70–71°; (lit.[8] m.p. 54–56°); $[\alpha]_D^{23}$ −42.3° (*c* 1.19, ethanol) (lit.[8] −43°). A mixed fraction (280 mg) was followed by a syrup (150 mg, 12%) that crystallized from ether–petroleum ether b.p. (30–60°), to give colorless crystals of 1,6-anhydro-2-*O*-benzyl-β-D-glucopyranose (**8**); m.p. 74–76° (lit.[4] m.p. 73–74°); $[\alpha]_D^{23}$ −58.9° (*c* 1.01, ethanol) (lit.[4] −64°). The mixed fraction, when separated by column chromatography as above, was found to contain **7** (160 mg) and **8** (80 mg). Thus, the overall product ratio of **7**:**8** was 68:32, and the overall yields for **7** and **8** were 40 and 18%. For ^1H- and ^{13}C-n.m.r. data for **7** and **8**, see Tables I–III.

A reaction conducted exactly as above, but using tetrabutylammonium bromide (1.61 g, 5 mmol) instead of the iodide, required three days to achieve completion, and yielded 58% of monosubstituted products having a similar composition.

A reaction conducted as in the preceding paragraph but using 1,2-dimethoxyethane as the solvent also took three days before all of the starting material had reacted.

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