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2-*O*-ACETYL-3,4-DI-*O*-BENZYL-6-*O*-(*tert*-BUTYLDIPHENYLSILYL)-D-GLUCOPYRANOSYL CHLORIDE AS A D-GLYCOSYL DONOR*

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ABSTRACT

2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-D-glucopyranosyl chloride, prepared from 6-*O*-(*tert*-butyldiphenylsilyl)-1,2-*O*-(1-ethoxyethylidene)-α-D-glucopyranose in two steps, was treated separately with allyl alcohol, cyclohexanol, and benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside, to give the corresponding allyl and cyclohexyl glycosides, and benzyl 2-acetamido-4-*O*-[2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α- and -β-D-glucopyranosyl]-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside, respectively. The yields and relative proportions of the α- and β-D anomers in the products depended on the conditions of the condensation reaction.

INTRODUCTION

The trisaccharide **1** is a component of the carbohydrate "core" of the *N*-glycoproteins[1]. Compound **1**, unlike the analog **2** containing an α-D-Man*p*-(1→3)-residue, does not occur in human mannosidosis urine[2], but is needed for the preparation of certain biosynthetic intermediates. In previous syntheses of *N*-glycoprotein "core" oligosaccharides[3], we utilized a D-glucosyl halide as the precursor of the β-D-Man*p*-(1→4)- residue. This approach has the advantage that the coupling reaction to form the (1→4) linkage is expected to be stereospecific when the D-glucosyl

α-D-Man*p*-(1→6)-β-D-Man*p*-(1→4)-D-GlcNAc

1

α-D-Man*p*-(1→3)-β-D-Man*p*-(1→4)-D-GlcNAc

2

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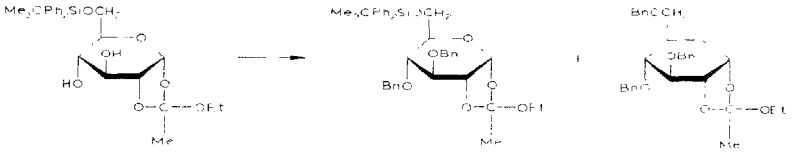
donor contains a participating 2-*O*-acetyl group. The resulting β-D-glucoside is readily converted into a β-D-mannoside by 2-*O*-deacetylation, oxidation, and borohydride reduction[3,4].

For the synthesis of **1**, the D-glucosyl "donor" must have a "temporary" protecting group[5] at O-6, and "persistent" groups at O-3 and -4. To fulfil these requirements, 2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α,β-D-glucopyranosyl chloride (**7**) has been synthesized, and the ability of **7** to glycosylate compounds containing OH groups having various degrees of reactivity has been investigated.

The *tert*-butyldiphenylsilyl (*t*BuPh$_2$Si) group was chosen because of (*a*) the ease of formation of *tert*-butyldiphenylsilyl derivatives[6,7] and the strong selectivity of the group for primary alcoholic groups, (*b*) the ease of detection on chromatographic plates, the *tert*-butyldiphenylsilyl group having a very strong u.v. absorbance, (*c*) the occurrence of characteristic, proton resonances in the n.m.r. spectrum, and (*d*) the ease of removal by treatment with fluoride ion[6,7].

RESULTS AND DISCUSSION

6-*O*-(*tert*-Butyldiphenylsilyl)-1,2-*O*-(1-ethoxyethylidene)-α-D-glucopyranose[7] (**3**) was best converted into the 3,4-di-*O*-benzyl derivative **4** by brief treatment with benzyl bromide and sodium hydride at 0°. During this benzylation, an unavoidable side-reaction was the base-catalyzed hydrolysis of the *t*BuPh$_2$Si group, followed by benzylation to yield the tri-*O*-benzyl derivative **5**. When other reagents, such as barium oxide–barium hydroxide, were tried, or when the reaction was performed at higher temperature[8], the formation of **5** was enhanced. The lability of the *tert*-butyldiphenylsilyl group had been observed in related work[7].



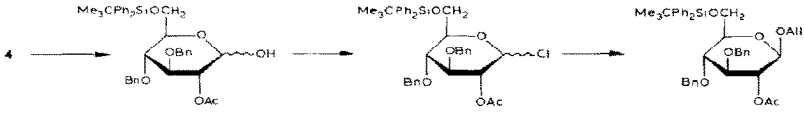
3 **4** **5**

In an attempt to convert **4** directly into the desired glycosyl chloride **7**, it was treated with chlorotrimethylsilane[9], but examination of the reaction mixture by t.l.c. indicated that the yields of **7** were very poor. Therefore, **4** was converted into **6** by stirring with a cation-exchange resin, and **6** was converted into **7** by treatment with the Vilsmeier reagent, namely, chloro-*N*,*N*-dimethylformamidium chloride[10]. As observed in our work and in other laboratories, chloride formation with this reagent is usually complete[7,11] within 10–15 min at room temperature, but, in the

case of **6**, a prolonged reaction time (24 h), or an elevated temperature (80°) was necessary.

Once formed, however, the glycosyl chloride **7** was unusually stable. Thus, when a solution of **7** in ($^2H_1$)chloroform was kept at room temperature in an n.m.r. tube, in the presence of D_2O, no change in the ^{1}H-n.m.r. spectrum could be observed during two weeks. Furthermore, when **7** was treated with silver nitrate in the presence of aqueous methanol, hydrolysis to give **6** occurred very slowly (~2 h for complete reaction). The slow formation, and unexpected stability, of **7** are presumably an effect of the steric bulk of the *tert*-butyldiphenylsilyl group.

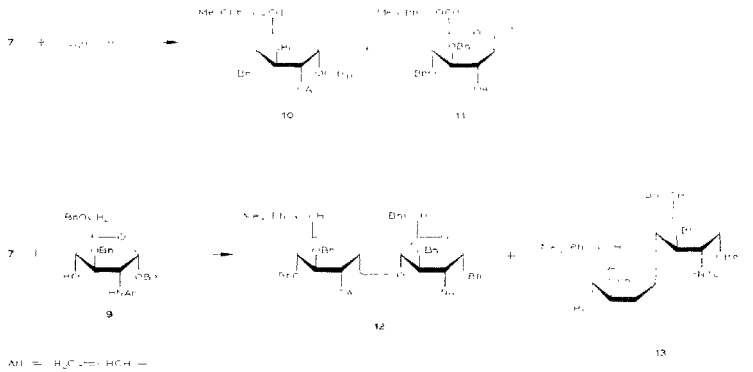
Initial experiments to explore the usefulness of **7** as a glycosyl donor employed "aglycons" having either primary or secondary hydroxyl groups with various degrees of steric accessibility. The reactions were conducted at room temperature in the presence of mercury dibromide or mercuric cyanide as[12] the "catalyst", with 1,2-dichloroethane as the solvent. In every instance, the yield of glycoside was very poor, and most of the **7** remained unchanged. However, successful results were obtained when the temperature was raised. Thus, when **7** was treated overnight with allyl alcohol in the presence of mercury dibromide at 60°, a satisfactory yield of the β-D-glucoside **8** was obtained, but, when **7** was employed to glycosylate cyclohexanol, again in the presence of mercury dibromide, two products (**10** and **11**) were isolated by preparative-layer chromatography, in a combined yield of 95%. The ^{1}H-n.m.r. spectra showed that **10** and **11** were the α- and β-D-glucosides, respectively.



6 **7** **8**

When **7** was coupled with benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside[3a] (**9**), the OH-4 group of which is very unreactive, in the presence of the same solvent and catalyst as for cyclohexanol, a mixture of α- and β-D-glucosyl disaccharides, **12** and **13**, respectively, was obtained. The anomeric assignments were based on optical rotation and high-field, ^{1}H-n.m.r. spectra, and the α-D anomer was the major product. This was surprising in view of the low polarity of the solvent (1,2-dichloroethane) and the expected neighboring-group participation of the AcO-2 group in the glycosylation, factors expected to favor formation of the 1,2-*trans*-glycoside[12]. However, loss of stereochemical control had been observed when mercuric salts were employed as glycosylation catalysts[12-14], especially when the hydroxyl group of the "aglycon" was weakly reactive.

Fortunately, stereochemical control could be restored to this reaction by changing the catalyst to silver trifluoromethanesulfonate (triflate), in which case, **7** was reactive at room temperature, and only the desired β-D-glucoside was isolated,



in satisfactory yield (48%). This result is consistent with previous results with silver triflate[3,15], but recently the formation of a mixture of anomers was observed when silver triflate was employed to promote the formation of β-D-(1→4)-linked disaccharides[16].

EXPERIMENTAL

General methods. — Melting points were determined with a Mettler FP-2 hot-stage equipped with a microscope, and correspond to "corrected melting points". Optical rotations were determined in 1-dm, semimicro tubes with a Perkin–Elmer No. 141 polarimeter. I.r. spectra were recorded with a Perkin–Elmer spectrophotometer Model 237. ^{1}H-N.m.r. spectra were recorded at 60 MHz with a Varian T-60 spectrometer, for solutions in ($^2H_1$)chloroform containing tetramethylsilane as an internal standard, unless stated otherwise. The high-field, ^{1}H-n.m.r. spectra were recorded, at the NSF Northeast Regional NMR Facility at Yale University, at 500 MHz with a WM-500 spectrometer for solutions in ($^2H_1$)chloroform. 1,2-Dichloroethane was dried by distillation in the presence of phosphorus pentaoxide, and addition of molecular sieve 3A (Fisher Scientific Co., Pittsburgh, PA 15219) that had been predried for 24 h at 200°. Toluene was dried by treatment with dry molecular sieve 3A, followed by addition of calcium hydride in lump form (Fisher Scientific Co.). Other solvents were dried by treatment with molecular sieve 3A. Nitrogen was dried by passing it through at least two traps of calcium chloride. Solid compounds were dried by adding dry toluene and evaporating *in vacuo* for several hours. Glycosylations were performed in tubes that had been predried for several hours at 200° under dry nitrogen. The microanalyses were performed by Dr. W. Manser, CH-8704 Zurich, Switzerland, and by Galbraith Laboratories, Inc. Knoxville, TN 37921.

Chromatographic methods. — All proportions of solvents are v/v. Column chromatography was performed on Silica gel 60 (0.05–0.2 mm, 70–325 mesh; E. Merck AG, Darmstadt, Germany). T.l.c. and preparative t.l.c. were performed on precoated plates of silica gel. For t.l.c., plates 0.25-mm thick (F254, Merck) were cut into pieces ~6 cm long and ~2 cm wide. The protected sugars were detected by u.v. absorption, and by spraying with 1:1:18 anisaldehyde–sulfuric acid–ethanol[17] and heating the plate to 125°.

Unsaturation was detected by spraying with a solution of 1% potassium permanganate in 2% aqueous sodium hydrogencarbonate. Preparative t.l.c. was performed on plates 1-mm (LS 254 Schleicher and Schuell) and 2-mm thick (F254, Merck). The desired compounds were detected by u.v. absorption, and extracted by stirring with 5:1 chloroform–methanol for several hours.

*3,4-Di-O-benzyl-6-O-(*tert*-butyldiphenylsilyl)-1,2-O-(1-ethoxyethylidene)-α-*D*-glucopyranose* (**4**). — Sodium hydride (50% oil suspension; 800 mg, ~16 mmol) was washed with dry hexane (30 × 2 mL), and suspended in *N,N*-dimethylformamide (25 mL). The suspension was cooled to 0°, and benzyl bromide (2.5 g, 16 mmol) and a solution of 6-*O*-(*tert*-butyldiphenylsilyl)-1,2-*O*-(1-ethoxyethylidene)-α-D-glucopyranose[7] (**3**; 4.4 g, 8.0 mmol) in *N,N*-dimethylformamide were added. The mixture was stirred for 30 min at 0°, the excess of sodium hydride was decomposed at 0° with methanol (~1 mL), and the mixture evaporated *in vacuo*. The residue was extracted with chloroform (100 mL), the extract washed with water (2 × 100 mL), dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel with 90:10:1 hexane–ethyl acetate–triethylamine, to give syrupy **4** (3.7 g, 55%); $[\alpha]_D^{27}$ +19.5° (*c* 1.14, chloroform); R_F 0.70 (2:1 hexane–ethyl acetate); ν_{max}^{NaCl} 3080, 3040, 2940, 2860, 1100, 820, 730, and 680 cm^{-1}; ^{1}H-n.m.r.: δ 8.01–7.50 (m, 20 H, arom.), 5.89 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 3.61 (q, 2 H, $J_{CH_2CH_3}$ 7 Hz, CH_2CH_3), 1.66 (s, 3 H), 1.21 (t, 3 H, methyl, J_{CH_3,CH_2} 7 Hz, CH_3CH_2), and 1.08 (s, 9 H, CMe_3).

Anal. Calc. for $C_{40}H_{48}O_7Si$: C, 71.82; H, 7.23. Found: C, 71.74; H, 7.22.

The second product isolated from the chromatograph was the known 3,4,6-tri-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-1,2-*O*-(1-ethoxyethylidene)-α-D-glucopyranose (**5**; 1.2 g, 18%); $[\alpha]_D^{28}$ +30° (*c* 4.02, chloroform); lit.[18] $[\alpha]_D^{20}$ +35° (*c* 1.5, chloroform); R_F 0.65 (1:2 ethyl acetate–hexane); ^{1}H-n.m.r.: δ 7.75–7.08 (m, 15 H, arom.), 5.85 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 3.61 (q, 2 H, J_{CH_2,CH_3} 7 Hz, CH_2CH_3), 1.7 (s, 3 H, CH_3CO_3), and 1.2 (t, 3 H, $J_{CH_3CH_2}$ 7 Hz, CH_3CH_2).

*2-O-Acetyl-3,4-di-O-benzyl-6-O-(*tert*-butyldiphenylsilyl)-α,β-*D*-glucopyranose* (**6**). — To a solution of **4** (1 g, 1.50 mmol) in 95% ethanol (10 mL) was added Bio-Rad AG 50W-X8 (200–400 mesh) cation-exchange resin (1 g). The suspension was stirred for 5 min, and filtered, and the filtrate was evaporated at room temperature. The residue was chromatographed on silica gel (50 g) with 3:2 hexane–ethyl acetate, to give **6** (920 mg, 96%); m.p. 88° (1:1 ethyl acetate–hexane), $[\alpha]_D^{27}$ +41° (*c* 1.03, chloroform); R_F 0.21 (3:1 hexane–ethyl acetate); ν_{max}^{NaCl} 3450 (br.), 3060, 3040, 2940, 2870, 1760, 1421, 1380, 1362, 1234, 1112, 820, 750, 725, and 624 cm^{-1};

^{1}H-n.m.r.: δ 8.14–7.30 (m, 20 H, arom.), 5.56 (m, 1 H, H-1α,β), 3.00 (br., 1 H, OH, disappeared in D_2O), 2.08 (s, 3 H, COCH_3), and 1.1 (s, 9 H, CMe$_3$).

Anal. Calc. for $C_{38}H_{44}O_7Si$: C, 71.22; H, 6.92. Found: C, 71.20; H, 7.05.

2-O-Acetyl-3,4-di-O-benzyl-6-O-(tert-butyldiphenylsilyl)-α,β-D-glucopyranosyl chloride (**7**). — Compound **6** (200 mg, 0.31 mmol) and chloro-*N,N*-dimethylformamidium chloride[10] (200 mg, 1.5 mmol) were stirred with dry 1,2-dichloroethane (5 mL) in a sealed tube under dry nitrogen for 2 h at 80°. The tube was cooled, and opened under dry nitrogen, and the solvent was flushed out. Dry toluene was added (5 mL) and the excess of reagent was removed by filtration through silica gel under dry nitrogen in a Pasteur pipet. The filtrate was evaporated, and the resulting **7** (180 mg, 87%) was used without purification: R_F 0.68 (1:3 hexane–ethyl acetate); ^{1}H-n.m.r.: δ 8.16–7.3 (m, 20 H, arom.), 6.53 (d, 1 H, $J_{1,2}$ 4 Hz, H-1α), 2.08 (s, 3 H, COCH_3), and 1.1 (s, 9 H, CMe$_3$).

Allyl 2-O-acetyl-3,4-di-O-benzyl-6-O-(tert-butyldiphenylsilyl)-β-D-glucopyranoside (**8**). — Allyl alcohol (0.5 mL, 430 mg, 7.36 mmol), mercury dibromide (200 mg), dry molecular sieve 3A (~150 mg), and 1,2-dichloroethane (2 mL) were stirred in a sealed tube for 2 h. A solution of chloride **7** (120 mg, 0.18 mmol) in dry 1,2-dichloroethane (1 mL) was injected into the tube through the stopper, without opening, and the mixture was stirred overnight at 60°. After being cooled, the tube was opened, the mixture filtered, and the filtrate successively washed with 70% potassium iodide and water, dried ($MgSO_4$), filtered, and evaporated. The residue was chromatographed on a plate of silica gel with 3:1 hexane–ethyl acetate, to give **8** as a syrup (78 mg, 65%): $[\alpha]_D^{27}$ +3° (*c* 0.20, chloroform); R_F 0.57 (3:1 hexane–ethyl acetate); ν_{max}^{NaCl} 3080, 3050, 2950, 2880, 1760, 1420, 1370, 1125, 1050, 825, 735, and 680 cm^{-1}; ^{1}H-n.m.r.: δ 7.77–7.17 (m, 20 H, arom.), 5.89 (oct., 1 H, CH_2-CH_X=CH_AH$_B$), 5.27 (dd, 1 H, $J_{A,X}$ 17.29, $J_{A,B}$ 1.5 Hz, vinylic *trans* H$_A$), 5.18 (dd, $J_{B,X}$ 10.45, $J_{B,A}$ 1.5 Hz, vinylic *cis* H$_B$), 5.06 (dd, 1 H, $J_{2,1}$ 7.96 Hz, H-2), 4.85 (dd, 2 H, CH_2C$_6$H$_5$), 4.71 (dd, 2 H, CH_2C$_6$H$_5$), 4.43 (d, 1 H, $J_{1,2}$ 7.96 Hz, H-1), 4.34 (dd, 1 H, CH_2-CH=CH$_2$), 4.09 (dd, 1 H, CH_2-CH=CH$_2$), 3.94 (d, 2 H, H-6), 3.87 (t, 1 H, $J_{3,2}$ 9.4 Hz, H-3), 3.69 (t, 1 H, $J_{4,3}$ 9.4 Hz, H-4), 3.36 (dt, 1 H, $J_{5,4}$ 9.4, $J_{5,6}$ 2.8 Hz, H-5), 1.99 (s, 3 H, COCH_3), and 1.07 (s, 9 H, CMe$_3$). The compound was detected on t.l.c. plates by u.v. absorption, by a violet-green spot with the anisaldehyde spray-reagent, and by a yellow spot with the permanganate spray-reagent.

Anal. Calc. for $C_{41}H_{44}O_7Si$: C, 72.39; H, 7.01. Found: C, 72.39; H, 6.99.

Cyclohexyl 2-O-acetyl-3,4-di-O-benzyl-6-O-(tert-butyldiphenylsilyl)-α- (**10**) *and -β-D-glucopyranoside* (**11**). — Cyclohexanol (0.5 mL, 5.27 mmol), mercury dibromide (200 mg), dry molecular sieve 3A (100 mg), and 1,2-dichloroethane (2 mL) were stirred under dry nitrogen in a sealed tube for 2 h. A solution of chloride **7** (100 mg, 156 μmol) in 1,2-dichloroethane (1 mL) was injected into the tube through the stopper, without opening, and the mixture was stirred overnight at 60°. The tube was cooled to room temperature and the mixture was filtered. Chloroform (10 mL) was added to the filtrate and the organic solution was washed with 10% potassium iodide, dried (calcium chloride), and evaporated. Toluene was

added and evaporated under high vacuum, to remove cyclohexanol. The residue was chromatographed on two 1-mm plates of silica gel (3:1 hexane–ethyl acetate), to give **10** (64 mg, 65%), **11** (31 mg, 30%), and the product of hydrolysis (**4**; ~10 mg).

Compound **10**: $[\alpha]_D^{28}$ +57° (*c* 0.10, chloroform); R_F 0.67 (3:1 hexane–ethyl acetate); ν_{max}^{NaCl} 3070, 3020, 2940, 2865, 1760, 1430, 1385, 1230, 1120, 820, 730, and 690 cm^{-1}; ^{1}H-n.m.r.: δ 7.76–7.15 (m, 20 H, arom.), 5.21 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.83 (4 H, AB, 2 $CH_2C_6H_5$), 4.79 (dd, 1 H, $J_{2,1}$ 3.8, $J_{2,3}$ 9.9 Hz, H-2), 4.62 (d, 1 H, $J_{5,4}$ 10.7 Hz, H-5), 4.06 (t, 1 H, H-3), 3.89 (very close AB, 2 H, H-6), 3.69 (t, 1 H, H-4), 3.54 (hept, 1-H, H-1 of C_6H_{11}), 2.05 (s, 3 H, $COCH_3$), 1.06 (s, 9 H, CMe_3), and 2.04–0.88 (several br. peaks, 10 H, 10 H of C_6H_{11}).

Anal. Calc. for $C_{42}H_{54}O_7Si$: C, 72.17; H, 7.79. Found: C, 72.23; H, 7.66.

Compound **11**: $[\alpha]_D^{28}$ +3° (*c* 0.22, chloroform); R_F 0.60 (3:1 hexane–ethyl acetate); ν_{max}^{NaCl} 3070, 3020, 2950, 2860, 1760, 1420, 1380, 1220, 1110, 820, 730, and 690 cm^{-1}; ^{1}H-n.m.r.: δ 7.76–7.17 (m, 20 H, arom.), 5.00 (dd, 1 H, $J_{2,1}$ 7.9, $J_{2,3}$ 9.4 Hz, H-2), 4.77 (two close AB systems, 4 H, 2 $CH_2C_6H_5$), 4.46 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 3.93 (dAB, 2 H, $J_{6a,6b}$ 11.2 Hz, H-6a,6b), 3.81 (t, 1 H, H-4), 3.69 (t, 1 H, H-3), 3.64 (hept, 1 H, H-1 of C_6H_{11}), 1.99 (s, 3 H, $COCH_3$), 1.07 (s, 9 H, CMe_3), and 1.77–0.90 (several br. peaks, 10 H, 10 H of C_6H_{11}).

Anal. Calc. for $C_{42}H_{54}O_7Si$: C, 72.17; H, 7.79. Found: C, 72.23; H, 7.66.

*Benzyl 2-acetamido-4-*O*-[2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-(tert-butyldiphenylsilyl)-α-* (**12**) *and -β-*D*-glucopyranosyl]-3,6-di-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (**13**). — (*a*) *With mercury dibromide as catalyst.* Dry glycoside[3a] **9** (200 mg, 0.42 mmol), molecular sieve 3A (150 mg), and dry mercury dibromide (200 mg) in 1,2-dichloroethane (2 mL) were stirred under dry nitrogen in a sealed tube for 2 h. A solution of chloride **7** (100 mg, 0.15 mmol) in 1,2-dichloroethane (1 mL) was injected into the tube through the stopper, without opening, and the mixture was stirred overnight at 80°. More chloride **7** (100 mg) in 1,2-dichloroethane was injected into the tube, and the mixture was stirred for a further 48 h at 80°. The tube was cooled to room temperature, and the mixture was filtered. Chloroform was added to the filtrate, and the organic solution was washed with 10% potassium iodide, dried (calcium chloride), and evaporated. The residue was chromatographed on silica gel (30 g) with 1:1 hexane–ethyl acetate, to give the starting material **9** (128 mg) and fractions that, according to ^{1}H-n.m.r. spectroscopy, contained *tert*-butyl and *N*- and *O*-acetyl groups. These fractions were combined (60 mg) and chromatographed on a 1-mm plate of silica gel with 1:1 hexane–ethyl acetate, to give **12** (38 mg, 23%) and **13** (10 mg, 6%).

Compound **12**; $[\alpha]_D^{27}$ +90° (*c* 0.56, chloroform); R_F 0.49 (1:1 hexane–ethyl acetate); $\nu_{max}^{CHCl_3}$ 3040, 2940, 2860, 1760, 1680, 1380, 1250, 1110, 870, 730, and 680 cm^{-1}; ^{1}H-n.m.r.: δ 7.73–7.06 (m, 35 H, arom.), 5.52 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1'), 5.20 (d, 1 H, $J_{NH,2}$ 9.23 Hz, NH), 4.92 (dd, 1 H, H-2'), 4.3 (m, 1 H, H-2), 1.89 (s, 3 H, $OCOCH_3$), 1.73 (s, 3 H, $NHCOCH_3$), and 1.05 (s, 9 H, CMe_3).

Anal. Calc. for $C_{67}H_{75}NO_{12}Si \cdot H_2O$: C, 71.06; H, 6.85; N, 1.23. Found: C, 71.24; H, 6.97; N, 1.22.

Compound **13**: $[\alpha]_D^{27}$ +45° (*c* 0.36, chloroform); R_F 0.55 (1:1 hexane–ethyl acetate); ν_{max}^{NaCl} 3080, 3040, 2930, 2850, 1110, 820, 730, and 680 cm^{-1}; ^{1}H-n.m.r.: δ 7.73–7.06 (m, 35 H, arom.), 5.03 (dd, 1 H, $J_{2',3'}$ 9.5, $J_{2',1'}$ 8.0 Hz, H-2'), 4.50 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 3.16 (m, 1 H, H-5'), 1.96 (s, 3 H, OCOCH_3), 1.71 (s, 3 H, NHCOCH_3), and 1.00 (s, 9 H, CMe_3).

Anal. Calc. for $C_{67}H_{75}NO_{12}Si$: C, 72.21; H, 6.78; N, 1.26. Found: C, 72.20; H, 6.73; N, 1.34.

(b) With silver triflate as catalyst. Dry glycoside[3a] **9** (125 mg, 0.26 mmol), silver triflate (125 mg), and molecular sieve 3A (100 mg) in dry 1,2-dichloroethane (2 mL) were stirred under dry nitrogen in a sealed tube protected from light for 1 h. The tube was cooled to −70° (acetone–Dry Ice), and the chloride **7** (82 mg, 0.13 mmol) in 1,2-dichloroethane (1 mL) was injected into the tube through the stopper, without opening. The mixture was stirred for 48 h at room temperature, filtered, and chromatographed on two 1-mm plates of silica gel (1:1 hexane–ethyl acetate), to give **13** (62 mg, 46%), identical to the product described under (*a*). No **12** could be detected.

ACKNOWLEDGMENTS

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