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SYNTHESIS AND REACTIONS OF *tert*-BUTYLDIPHENYLSILYL ETHERS OF SUCROSE*

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ABSTRACT

The reaction of sucrose with 1.1 mol. equiv. of *tert*-butyldiphenylsilyl (*t*-BDPS) chloride in pyridine in the presence of 4-dimethylaminopyridine gave the crystalline 6′-*t*-BDPS ether **1** in 49% yield, without recourse to column chromatography. Compound **1** was transformed into the 4,6,1′-trichloride by using sulphuryl chloride. When the silylation reaction of sucrose was performed with 3 mol. equiv. of the reagent, chromatography gave the crystalline 6,6′-di-*t*-BDPS ether and the 6,1′,6′-tri-*t*-BDPS ether **9** in yields of 78 and 18.7%, respectively. Compound **9** was obtained as the major product on treatment of sucrose with 4.6 mol. equiv. of the silylating reagent. Removal of the silyl protecting-group in 6,6′-di-*O*-*tert*-butyldiphenylsilylsucrose hexabenzoate, using tetrabutylammonium fluoride, proceeded smoothly, but with 4→6 migration of the benzoate.

INTRODUCTION

The need for selective protection of hydroxyl groups in sucrose has led us to investigate the use of *tert*-butyldiphenylsilyl chloride. The value of this reagent for preferentially blocking primary hydroxyl groups in sugar derivatives has been recognised[2]. The *O*-*tert*-butyldiphenylsilyl group is much more stable towards acid and hydrogenolysis than the related silyl and trityl ethers[2]. The fact that trityl, tetrahydropyranyl, benzyl, and other silyl ethers and acetals can be preferentially removed in the presence of *tert*-butyldiphenylsilyl ethers makes this derivative an important synthetic intermediate in carbohydrate chemistry. We now describe the synthesis and reactions of 6′-mono-, 6,6′-di-, and 6,1′,6′-tri-*t*-BDPS ethers of sucrose.

RESULTS AND DISCUSSION

The reaction of sucrose with 1.1 mol. equiv. of *tert*-butyldiphenylsilyl chloride in pyridine in the presence of a catalytic amount of 4-dimethylaminopyridine at room

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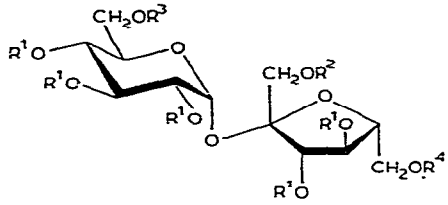
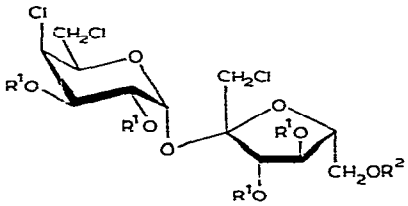
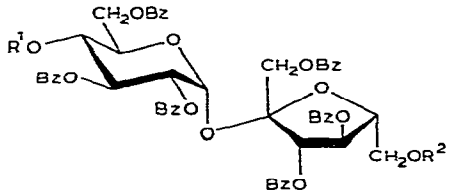
temperature for 4 h gave the crystalline 6′-*t*-BDPS ether **1** in 49% yield. T.l.c. revealed that **1** was the only monosilyl ether present, and the remainder of the product mixture contained sucrose and some 6,6′-di-*t*-BDPS ether **2**. These results are consistent with the findings of Franke and Guthrie[3], who investigated the reaction of sucrose with 0.65 mol. equiv. of *tert*-butyldimethylsilyl chloride in pyridine and obtained the corresponding 6′-, 6,6′-di-, and 6,1′,6′-tri-*O*-*tert*-butyldimethylsilyl ethers in yields of 10.5, 36.4, and 33.5%, respectively. Monosubstitution at C-6 and C-1′ under the conditions employed was not observed[3]. These results and ours clearly show that HO-6′ in sucrose is the most reactive site towards silylation. To explain the formation of **2**, despite the presence of excess of sucrose, it can be argued, as suggested by Franke and Guthrie[3], that once **1** is formed, the reaction proceeds more rapidly, because of its solubility, and is only limited by the supply of reagent.



1 $R^1 = R^2 = R^3 = H$, $R^4 = t\text{-BuPh}_2\text{Si}$
2 $R^1 = R^2 = H$, $R^3 = R^4 = t\text{-BuPh}_2\text{Si}$
3 $R^1 = R^2 = R^3 = Ac$, $R^4 = t\text{-BuPh}_2\text{Si}$
4 $R^1 = R^2 = R^3 = Bz$, $R^4 = t\text{-BuPh}_2\text{Si}$
8 $R^1 = R^2 = R^3 = Ac$, $R^4 = H$
9 $R^1 = H$, $R^2 = R^3 = R^4 = t\text{-BuPh}_2\text{Si}$
10 $R^1 = R^2 = Ac$, $R^3 = R^4 = t\text{-BuPh}_2\text{Si}$
11 $R^1 = R^2 = Bz$, $R^3 = R^4 = t\text{-BuPh}_2\text{Si}$
14 $R^1 = Bz$, $R^2 = R^3 = R^4 = t\text{-BuPh}_2\text{Si}$
15 $R^1 = Ac$, $R^2 = R^3 = R^4 = t\text{-BuPh}_2\text{Si}$



5 $R^1 = Ac$, $R^2 = t\text{-BuPh}_2\text{Si}$
6 $R^1 = R^2 = H$
7 $R^1 = R^2 = Ac$



12 $R^1 = R^2 = H$
13 $R^1 = H$, $R^2 = Tr$

Conventional acetylation of **1** with acetic anhydride and pyridine gave the hepta-acetate **3**, and benzoylation with benzoyl chloride in pyridine afforded the corresponding heptabenzoate **4**. The ^{1}H-n.m.r. spectra of **3** and **4** (Table I) showed clearly that only one silyl group was present, but its location could not be determined from the spectra. Hence, **1** was converted into the 6′-*t*-BDPS 4,6,1′-trichloride **5** by treatment with sulphuryl chloride in a mixture of pyridine and chloroform followed

TABLE I

^{1}H-N.M.R. DATA: FIRST-ORDER CHEMICAL SHIFTS (τ) AND COUPLING CONSTANTS (Hz) AT 100 MHz[a]

Compound	3[b]	4[b]	5[c]	7[b]	10[b]	11[b]	12	12[d]	13	13[d]	14	15
H-1	4.38 d	3.90–4.12	4.00 d	4.12 d	4.42 d	3.98 d	3.89 d	3.89 d		3.95 d		4.44 d
H-2	5.22 dd	4.60 dd	4.79 dd	4.76 dd	5.24 dd	4.60 dd	4.76 dd	4.68 dd	4.71 dd	4.67 dd	4.62 dd	5.15 dd
H-3	4.60 t	3.81 t	4.61 dd	4.62 dd		3.85 t		3.95 t	4.22 t	3.93 t		
H-4	5.00 t	4.28 t	5.16 dd	5.19 dd				4.54 t		4.54 t		
H-5			5.29 td	5.42 td								
H-3′	4.46 d	3.90–4.12	4.28 d	4.28 d		4.05 d					3.70 d	4.12 d
H-4′	4.58 t		4.11 t	4.45 t		4.07 t						
Aromatic	2.26–2.80	1.78–3.0	2.23–2.71		2.33–2.90	1.90–3.08	1.7–2.2		1.93–3.08	2.90–3.05	1.82–3.16	2.24–3.00
tert-butyl	8.91 s	8.98 s	8.91 s		9.00 s	8.96 s					8.90 s	8.94 s
						9.01 s					8.95 s	8.97 s
OAc	7.86–8.05		7.87–8.00	7.82–7.94	7.93–8.20							7.98–8.22
$J_{1,2}$	3.5	3.5	3.5	3.5	3.5	3.5	3.0	3.0	3.5	3.5	3.5	3.5
$J_{2,3}$	10.0	10.0	10.5	10.5	10.0	9.0	10.0	10.0	10.0	10.0	9.5	10.0
$J_{3,4}$	9.5	10.0	3.0	3.0		9.0		10.0	10.0	10.0		
$J_{4,5}$	9.5	10.0	1.2	1.2						10.0		
$J_{5,6}$	—	—	5.5	5.5								
$J_{5,6}$	—	—	8.5	9.0								
$J_{3',4'}$	5.0		8.0	7.0		7.0						
$J_{4',5'}$	5.0		7.5	7.0		7.0						

[a]Key: d, doublet; dd, double doublet; t, triplet; td, triple doublet; s, singlet. The resonances due to H-5,5′ (with the exception of **5** and **7**) and H-6,6′ appeared as a complex, overlapped multiplet in the region τ 5.0–6.5. [b]In $CDCl_3$. [c]In CD_3COCD_3. [d]In $CDCl_3$ after addition of trichloroacetyl isocyanate.

by dechlorosulphation and acetylation. The mass spectrum of **5** showed peaks at m/z 503 (3:1 doublet) and 283 (9:6:1 triplet) due to the fructofuranosyl and hexopyranosyl cations, respectively. In the ^{1}H-n.m.r. spectrum of **5** (Table I), the resonance due to H-4 appeared as a double doublet at τ 5.16, indicating that one of the chlorine atoms is located at C-4. The coupling constants ($J_{1,2}$ 3.5, $J_{2,3}$ 10.5, $J_{3,4}$ 3.0, and $J_{4,5}$ 1.2 Hz) are in agreement with the α-D-*galacto* configuration and $^4C_1$ conformation for the hexopyranosyl ring in **5**. Desilylation of **5** with tetrabutylammonium fluoride, followed by de-esterification with a catalytic amount of sodium methoxide in methanol, gave the 4,6,1′-trichloride **6**. The physical constants of **6** are different from those of 1,6-dichloro-1,6-dideoxy-β-D-fructofuranosyl 4-chloro-4-deoxy-α-D-galactopyranoside[4]. Conventional acetylation of **6** gave the corresponding penta-acetate **7**. The mass spectrum of **7** showed peaks at m/z 307 (3:1 doublet) and 283 (9:6:1 triplet) due to the fructofuranosyl and hexopyranosyl cations, respectively, clearly indicating that the *tert*-butyldiphenylsilyl group in **1** is located at C-6′. The ^{1}H-n.m.r. spectrum of **7** is different from the spectra of 1,6-dichloro-1,6-dideoxy-β-D-fructofuranosyl 4-chloro-4-deoxy-α-D-galactopyranoside penta-acetate[4] and 6-chloro-6-deoxy-β-D-fructofuranosyl 4,6-dideoxy-α-D-galactopyranoside penta-acetate[5]. The coupling constants of **7** (Table I) are in agreement with the α-D-*galacto* configuration and $^4C_1$ conformation for the hexopyranosyl ring. Further proof of the structure of **1** was obtained by desilylation of **3** which afforded the hepta-acetate **8**, whose physical properties are identical with those of a standard sample[6–8].

The reaction of sucrose with 3 mol. equiv. of *tert*-butyldiphenylsilyl chloride gave, after column chromatography, crystalline **2** and the 6,1′,6′-tri-*t*-BDPS ether **9** in yields of 78.3 and 18.5%, respectively. Compound **2** was transformed into the corresponding hexa-acetate **10** and the hexabenzoate **11** by conventional esterification. The structures of **10** and **11** were supported by their ^{1}H-n.m.r. spectra (Table I). Chemical proof of the structure of **11** was achieved by conversion into the 6′-trityl ether **13**. 6,6′-Di-*O*-*tert*-butyldiphenylsilylsucrose hexabenzoate (**11**), on treatment with tetrabutylammonium fluoride in tetrahydrofuran, gave a mixture containing the 4,6′-dihydroxy compound **12** as the major product and a slightly faster moving, minor product which was probably the 6,6′-dihydroxy compound. No attempt was made to purify this product. In the ^{1}H-n.m.r. spectrum of impure **12**, the absence of resonance due to H-4 in the region τ 4.0–4.9 indicated the presence of a hydroxyl group at C-4. The formation of **12** suggested that the desilylation at C-6 in **11** was followed by 4→6-benzoyl migration. Similar results were obtained by Franke and Guthrie[3] when 6,6′-di-*O*-*tert*-butyldimethylsilylsucrose hexabenzoate was desilylated. Treatment of **12** with 4 mol. equiv. of trityl chloride in pyridine at 80° for 60 h gave, after column chromatography, the 6′-trityl ether **13** in 75% yield. Although the signals due to H-4 were not allocated in the ^{1}H-n.m.r. spectrum of **13**, their absence from the region τ 4.0–4.9 revealed the presence of a hydroxyl group at C-4. Addition of trichloroacetyl isocyanate to a solution of **13** in deuteriochloroform led to the appearance in the ^{1}H-n.m.r. spectrum of a singlet at τ 1.61 due to an imino proton,

and also caused the re-appearance of signals for H-4 at τ 4.54, which confirmed that the hydroxyl group in **13** is located at C-4.

Treatment of sucrose with 4.6 mol. equiv. of the silylating reagent at 65° for 51 h gave, after conventional benzoylation and column chromatography, 6,1′,6′-tri-*O*-*tert*-butyldiphenylsilylsucrose pentabenzoate (**14**) in 80.4% yield. De-esterification of **14** with a catalytic amount of sodium methoxide in methanol afforded the 6,1′,6′-*t*-BDPS ether **9**. Although the resonances due to most of the ring protons in the ^{1}H-n.m.r. spectra of **14** and the corresponding penta-acetate **15** were unresolved, the general pattern of the spectra was in agreement with their structures.

EXPERIMENTAL

For general experimental details, see Part XXIV[9].

The reaction of sucrose with 1.1 mol. equiv. of tert-*butyldiphenylsilyl chloride.* — A solution of sucrose (1.4 g) in dry pyridine (30 ml) was stirred with 4-dimethylaminopyridine (40 mg) and *tert*-butyldiphenylsilyl chloride (1.1 ml) at room temperature for 4 h. T.l.c. (butyl acetate–pyridine–water, 5:3:1) then showed one major and one minor fast-moving product together with sucrose. The mixture was poured into ice–water and extracted with ethyl acetate, dried (Na_2SO_4), and evaporated to dryness. Two crystallisations of the residue from ether gave 6′-*O*-*tert*-butyldiphenylsilylsucrose (**1**; 1.2 g, 49%), m.p. 192–195°, $[\alpha]_D$ +44° (*c* 1, methanol).

Anal. Calc. for $C_{28}H_{40}O_{11}Si$: C, 57.9; H, 6.9. Found: C, 57.7; H, 6.95.

The mother liquor was concentrated and eluted from a column of silica gel (100 g) with ethyl acetate–acetone–water (10:10:0.1), to afford 6,6′-di-*O*-*tert*-butyldiphenylsilylsucrose (**2**; 0.2 g, 6%), m.p. 212–213° (from ether–light petroleum), $[\alpha]_D$ +26° (*c* 1, methanol).

Anal. Calc. for $C_{44}H_{58}O_{11}Si_2$: C, 64.55; H, 7.1. Found: C, 63.8; H, 7.0.

Conventional acetylation of **1** with acetic anhydride in pyridine gave the hepta-acetate **3** (93%), $[\alpha]_D$ +50° (*c* 1.7, chloroform).

Anal. Calc. for $C_{42}H_{54}O_{18}Si$: C, 57.65; H, 6.2. Found: C, 57.85; H, 6.5.

Conventional benzoylation of **1** with benzoyl chloride in pyridine gave the heptabenzoate **4** (78%), m.p. 85–89° (ethanol), $[\alpha]_D$ +39° (*c* 1, chloroform).

Anal. Calc. for $C_{77}H_{68}O_{18}Si$: C, 70.65; H, 5.2. Found: C, 69.9; H, 5.15.

*6-*O*-*tert*-Butyldiphenylsilyl-1-chloro-1-deoxy-β-*D*-fructofuranosyl 4,6-dichloro-4,6-dideoxy-α-*D*-galactopyranoside tetra-acetate* (**5**). — A solution of **1** (2.5 g) in pyridine (6.3 ml) and chloroform (6.5 ml) was treated dropwise with sulphuryl chloride (7.4 ml, 8 mol. equiv.) at −70° for 2 h. The mixture was diluted with chloroform (5 ml) and stirred at 50°. The reaction was monitored by t.l.c., using the following procedure: a small sample was diluted with an equal amount of methanol, neutralised with sodium carbonate, and treated with a few drops of 4% aqueous, methanolic (1:1) sodium iodide. After 5 h, all of the starting material was consumed and one major, fast-moving product was formed. The reaction was worked-up as described for the t.l.c. sample. The insoluble matter was filtered off and the filtrate

concentrated to a syrup which was then taken up in pyridine (10 ml) and treated with acetic anhydride (2 ml) at 40° for 45 min. The solution was concentrated by co-distillation with toluene and the residue was eluted from a column of silica gel with ethyl acetate–light petroleum (1:3), to yield **5** as a syrup (2.1 g, 60.7%), $[\alpha]_D$ +72° (*c* 0.8, chloroform).

Anal. Calc. for $C_{36}H_{45}Cl_3O_{12}Si$: C, 53.8; H, 5.6; Cl, 13.15. Found: C, 53.3; H, 5.5; Cl, 13.7.

1-Chloro-1-deoxy-β-D-fructofuranosyl 4,6-dichloro-4,6-dideoxy-α-D-galactopyranoside (**6**). — A solution of **5** (2.5 g) in tetrahydrofuran (150 ml) was treated with tetrabutylammonium fluoride (1.3 g) at room temperature for 3 h. T.l.c. (benzene–ethyl acetate, 3:1) then showed only one major and traces of several slow-moving products, which was due to partial deacetylation. The mixture was concentrated, taken up in methanol (20 ml), and treated with a catalytic amount of M sodium methoxide in methanol at room temperature for 3 h. T.l.c. (butyl acetate–pyridine–water, 5:3:1) then showed a slow-moving product. The solution was deionised by shaking with Biodeminrolit mixed-bed (CO_3^{2-}) resin, filtered, and concentrated, and the residue was eluted from a short column of silica gel (50 g) with acetone–ethyl acetate–water (10:10:0.1), to give **6** (630 mg, 51%), $[\alpha]_D$ +22° (*c* 1.3, methanol).

Anal. Calc. for $C_{12}H_{19}Cl_3O_8$: C, 36.3; H, 4.8; Cl, 26.6. Found: C, 35.8; H, 4.85; Cl, 26.9.

Conventional acetylation of **6** (250 mg) with pyridine (10 ml) and acetic anhydride (1 ml) gave the penta-acetate **7** (200 mg, 52.5%), $[\alpha]_D$ +34° (*c* 2.6, chloroform).

Anal. Calc. for $C_{22}H_{29}Cl_3O_{13}$: C, 43.5; H, 4.8; Cl, 17.4. Found: C, 44.0; H, 5.0; Cl, 16.45.

2,3,4,6,1',3',4'-Hepta-O-acetylsucrose (**8**). — A solution of **3** (400 mg) in dry tetrahydrofuran (20 ml) was stirred with tetrabutylammonium fluoride (260 mg) at room temperature for 4 h. The solution was concentrated, taken up in chloroform, and washed with water. The organic layer was dried (Na_2SO_4) and concentrated. Elution of the syrupy residue from a column of silica gel (50 g) with ether–light petroleum (1:1) gave **8** (230 mg, 78%), m.p. and mixture m.p. 158–160° (from ether); lit.[6–8] m.p. 158–160°. The ^{1}H-n.m.r. spectrum was identical with that of an authentic sample[8].

The reaction of sucrose with 3 mol. equiv. of tert-*butyldiphenylsilyl chloride.* — A solution of sucrose (13.6 g) in dry pyridine (300 ml) was stirred with 4-dimethylaminopyridine (400 mg) and *tert*-butyldiphenylsilyl chloride (22 ml) at room temperature for 3 h. The reaction mixture was then treated with an additional amount of the silylating reagent (10 ml) at 55–60° for 24 h. T.l.c. (butyl acetate–pyridine–water, 5:3:1) showed two, fast-moving, major products. The solution was concentrated by co-distillation with toluene, and the resulting syrup was eluted from a column of silica gel (500 g) with ethyl acetate–acetone–water (10:10:0.1), to give 6,1',6'-tri-*O-tert*-butyldiphenylsilylsucrose (**9**; 7.9 g, 18.7%), $[\alpha]_D$ +17° (*c* 1.2, chloroform).

Anal. Calc. for $C_{60}H_{76}O_{11}Si_3$: C, 68.2; H, 7.2. Found: C, 67.9; H, 7.5.

Further elution of the column gave the 6,6′-di-*t*-BDPS ether **2** (22.5 g, 78%), whose physical properties were identical with those of the sample obtained previously.

Conventional acetylation of **2** (2.45 g) with acetic anhydride (5.7 ml) and pyridine (50 ml) gave 6,6′-di-*O*-*tert*-butyldiphenylsilylsucrose hexaacetate (**10**, 3 g, 92.5%), m.p. 107–110° (acetone–light petroleum), $[\alpha]_D$ +54° (*c* 1.2, chloroform).

Anal. Calc. for $C_{56}H_{70}O_{17}Si_2$: C, 62.5; H, 6.5. Found: C, 63.0; H, 6.0.

Conventional benzoylation of **2** (2.45 g) with benzoyl chloride (4.2 ml) and pyridine (50 ml) gave 6,6′-di-*O*-*tert*-butyldiphenylsilylsucrose pentabenzoate (**11**; 3.8 g, 88.6%), $[\alpha]_D$ +8.75° (*c* 1.2, chloroform).

Anal. Calc. for $C_{86}H_{82}O_{17}Si_2$: C, 71.6; H, 5.7. Found: C, 70.8; H, 6.0.

2,3,6,1′,3′,4′-Hexa-O-benzoyl-6′-O-tritylsucrose (**13**). — A solution of **11** (1.3 g) in dry tetrahydrofuran (50 ml) was stirred with tetrabutylammonium fluoride (1.04 g) at room temperature for 4 h. The mixture was evaporated to a syrup, taken up in dichloromethane, and washed with water (3 × 50 ml). The dried (Na_2SO_4) extract was concentrated to a syrup, and washed by decantation with light petroleum (3 × 20 ml) to remove *tert*-butyldiphenylsilyl alcohol. The resulting solid **12** (0.789 g, 89%) was dissolved in pyridine (50 ml) and treated with trityl chloride (1.1 g) at 80° for 60 h. The mixture was poured into iced water and extracted with dichloromethane (2 × 50 ml), and the extract was washed successively with water, aqueous sodium hydrogencarbonate, and water. The organic layer was dried (Na_2SO_4) and concentrated, and the resulting syrup was eluted from a column of silica gel with light petroleum–ethyl acetate (4:1), to give **13** as a syrup (0.76 g, 75%), $[\alpha]_D$ +44° (*c* 0.55, chloroform).

Anal. Calc. for $C_{73}H_{60}O_{17}$: C, 72.5; H, 5.0. Found: C, 72.2; H, 4.8.

The reaction of sucrose with 4.6 mol. equiv. of tert-*butyldiphenylsilyl chloride.* — A solution of sucrose (10.26 g) in dry pyridine (300 ml) was stirred with 4-dimethylaminopyridine (400 mg) and *tert*-butyldiphenylsilyl chloride (26 ml) at room temperature for 3 h. More *tert*-butyldiphenylsilyl chloride (5 ml) was added, and the mixture was heated at 55–60° for 24 h, treated with more silylating reagent (5 ml), and heated for a further 24 h. T.l.c. (butyl acetate–pyridine–water, 5:3:1) showed two fast-moving products. The reaction mixture was treated with benzoyl chloride (30 ml) at 0°, and then stored at room temperature for 3 h. T.l.c. (benzene–ethyl acetate, 6:1) showed a major and a minor fast-moving component. The solution was diluted with dichloromethane and washed with aqueous sodium hydrogencarbonate and water. The organic layer was dried (Na_2SO_4) and concentrated, and the resulting syrup was eluted from a column of silica gel (500 g) with light petroleum–ethyl acetate (4:1), to give **14** (39 g, 80.4%), m.p. 122–124° (from acetone–light petroleum), $[\alpha]_D$ +14° (*c* 1.65, chloroform).

Anal. Calc. for $C_{95}H_{96}O_{16}Si_3$: C, 72.3; H, 6.1. Found: C, 72.55; H, 5.8.

Debenzoylation of **14** (5 g) was carried out by treating its solution in dry methanol (50 ml) and dichloromethane (20 ml) with a catalytic amount of sodium methoxide at room temperature for 5 h. The solution was deionised by shaking with Biodeminrolit mixed-bed resin (CO_3^{2-} form) and concentrated, to give **9** (2.9 g,

86.6%), whose optical rotation values were identical with those of the sample prepared previously.

Conventional acetylation of **9** with acetic anhydride and pyridine gave **15** (85%), $[\alpha]_D$ +43° (*c* 1.1, chloroform).

Anal. Calc. for $C_{70}H_{86}O_{16}Si_3$: C, 66.35; H, 6.8. Found: C, 66.7; H, 7.2.

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