Glucosidation of Tetra-*O*-benzyl-α-D-glucose with Chlorosilane and Silver Sulfonate

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Glucosidation of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose with methanol or cyclohexanol in the presence of chlorosilane and silver sulfonate is described. As by-products, octa-*O*-benzyl-α,α- and -α,β-trehaloses are also formed. Possible reaction pathways are discussed.

The development of methods for the synthesis of glycosides has always been very important in carbohydrate chemistry.[1] The Fischer method[1] appears to have the methodological advantage that it can be performed by a direct dehydration between glycose and alcohol in the presence of an acid catalyst. Modified methods[2-4] using acid with a dehydrating agent have been developed for the glycosidation of appropriately protected precursors having a reducing hydroxyl group. Such methods suggested a novel glucosidation of a stable precursor, 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (**1**), with alcohol by using strongly dehydrating chlorosilanes,[5-7] which was investigated[8] as a part of our continuing studies.[9]

Results and Discussion

On treating **1** with methanol at 0 °C in dichloromethane containing dichlorodiphenylsilane (DCPS) and methanesulfonic acid as catalyst, methyl glucosides (**2a** and **2b**) of **1** were formed with a moderate efficiency. As the dehydration with DCPS and methanesulfonic acid was insufficient, the reaction was carried out with DCPS and silver methanesulfonate, from which more reactive bis(methylsulfonyloxy)diphenylsilane[10] was expected to be formed. The reaction proceeded well without addition of the acid.

A series of experiments were then done using stoichiometric amounts of **1** (αGOH), aglucon (methanol or cyclohexanol), chlorosilane, and silver sulfonate according to Eq. 1, where *n* denotes the number of chlorine atom(s) in the silanes and G represents a tetra-*O*-benzyl-D-glucopyranosyl moiety.

$$\alpha\mathrm{GOH} + \mathrm{ROH} + \frac{2}{n}\mathrm{R'_{4-n}SiCl_n} + 2\mathrm{R''SO_3Ag} \longrightarrow \mathrm{GOR} + \frac{2}{nx}\text{-}[\mathrm{R'_{4-n}SiO_{n/2}}]_x + 2\mathrm{R''SO_3H} + 2\mathrm{AgCl} \quad (1)$$

The results are shown in Table 1 and Fig. 1. Yields are based on the amounts of the products obtained on column chromatography, in reference to the amount of **1** charged. In every case, self-condensation products identified as octa-*O*-benzyl-α,α- and -α,β-trehaloses (**3a** and **3b**) and unchanged **1** were obtained on chromatography.

Treatment of **1** with DCPS and silver sulfonate without alcohol led to efficient self-condensations which can be described by Eq. 2, where GOG expresses the trehalose derivatives (**3a** and **3b**).

$$2\alpha\mathrm{GOH} + (\mathrm{C_6H_5})_2\mathrm{SiCl_2} + 2\mathrm{R''SO_3Ag} \longrightarrow \mathrm{GOG} + \frac{1}{x}\text{-}[(\mathrm{C_6H_5})_2\mathrm{SiO}]_x + 2\mathrm{R''SO_3H} + 2\mathrm{AgCl} \quad (2)$$

Results are shown in Table 2.

As shown in Fig. 1, DCPS was almost exhausted within 1 h and the amount of dimethoxydiphenylsilane (DMPS)[11] hardly exceeded 6%. Siloxanes[12] such as **4** and **5**[8,13] were detected by TLC throughout the reaction.

A filtrate of the reaction mixture of DCPS and silver methanesulfonate was able to condense **1** with methanol to give **2a** and **2b** as well as by-products **4** and **5**. Treatment of **4** with methanesulfonic acid in dichloromethane gave **2a** and **2b** in 78% yield, and **5** treated similarly gave **3a** and **3b** in 74% yield. DMPS with methanesulfonic acid in dichloromethane also transformed **1** into **2a** and **2b** in 63% yield. Consequently, the scheme of glucosidation of **1** with methanol in the presence of DCPS and silver methanesulfonate can be postulated as in Fig. 2, the bis(methylsulfonyloxy)-diphenylsilane formed reacts with methanol and **1** to

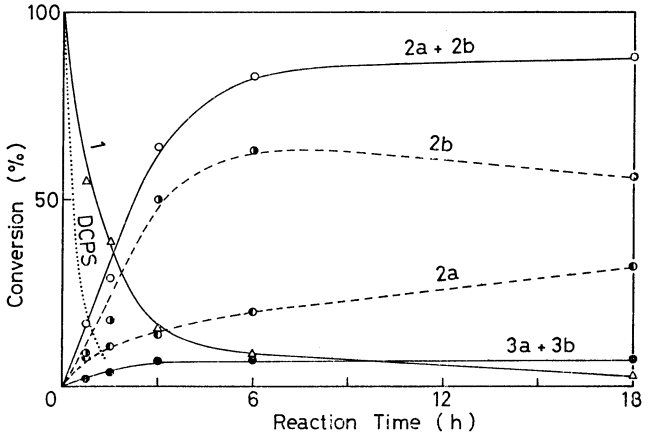


Fig. 1. Time-dependence of glucosidation of **1** with methanol in the presence of DCPS and silver methanesulfonate at 0 °C, plotted from the data of runs 1—5 in Table 1 except the GC data for DCPS (·····).

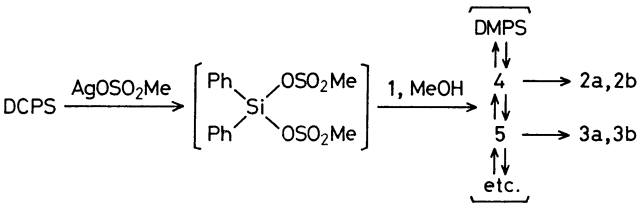


Fig. 2. A scheme of glucosidation of **1** with methanol in the presence of DCPS and silver methanesulfonate.

Table 1. Glucosidation[a] of tetra-*O*-benzyl-α-D-glucopyranose (**1**)

Run	R	*n*	R′	R″	Reaction time (h)	Yield (%) 2(2′)**a**+2(2′)**b**	(α/β)	**3a**+**3b**	**1**
1	Me	2	Ph	Me	0.5	17	(8/ 9)	2	55
2	Me	2	Ph	Me	1.5	29	(11/18)	4	39
3	Me	2	Ph	Me	3.0	64[b]	(14/50)[b]	8[b]	15[b]
4	Me	2	Ph	Me	6.0	83	(20/63)	7	8
5	Me	2	Ph	Me	18.0	88	(32/56)	7	3
6	Me	2	Me, Ph[c]	Me	3.0	43	(9/34)	8	45
7	Me	2	Me	Me	3.0	36	(10/26)	6	51
8	Me	1	Ph	Me	3.0	21	(9/12)	—[d]	58
9	Me	3	Ph	Me	3.0	75	(21/54)	8	8
10	Me	4	—	Me	3.0	73	(23/50)	7	11
11	Me	2	Ph	Tol[e]	3.0	44	(13/31)	2	26
12	Me	2	Ph	Pnp[f]	2.0	73	(18/55)	18	8
13	Ch	2	Ph	Me	3.0	55	(18/37)	28	10
14	Ch	2	Ph	Tol[e]	3.0	31	(12/19)	21	34
15	Ch	2	Ph	Pnp[f]	3.0	70	(54/16)	21	8

a) Reactions were carried out in dichloromethane at 0 °C according to Eq. 1. b) Revised data of Ref. 6. c) Dichloromethylphenylsilane. d) Not determined. e) $C_6H_4CH_3(p)$. f) $C_6H_4NO_2(p)$.

Table 2. Self-condensation[a] of tetra-*O*-benzyl-α-D-glucopyranose (**1**)

R″	Temp (°C)	Time (h)	Yield (%) **3a**+**3b**	(αα/αβ)	**1**
CH_3	0	6.5	68	(23/45)	15
$C_6H_4NO_2(p)$	0	4.5	80	(39/41)	12
CF_3	−20	0.33	70	(26/44)	16

a) Reactions were carried out in dichloromethane according to Eq. 2.

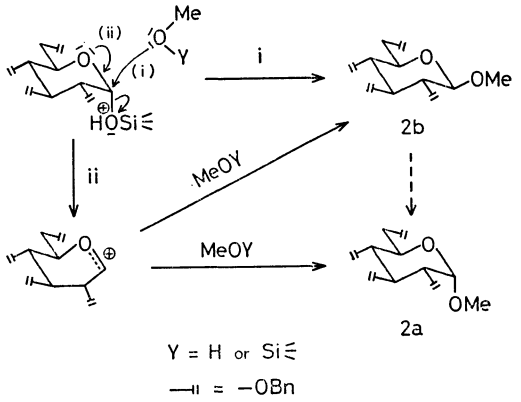


Fig. 3. Pathways of glucosidation of **1** with methanol in the presence of chlorosilane and silver sulfonate.

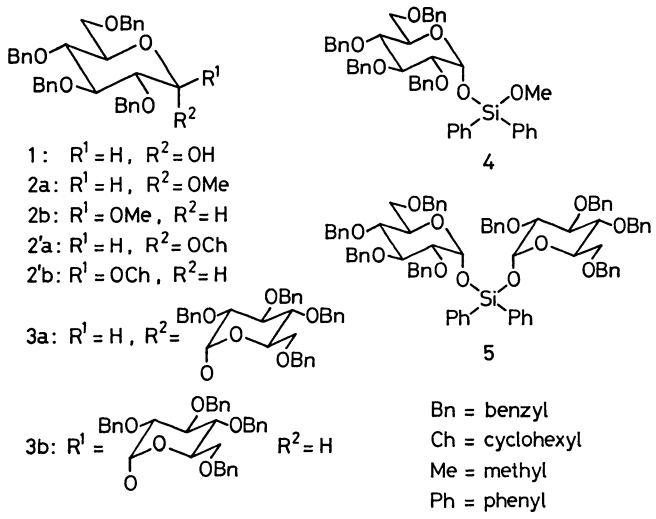
generate a mixture of methanesulfonic acid and siloxanes, such as DMPS, **4**, and **5**, the latters of which eventually produce the glucosides. Dimeric 1,3-dichloro-1,1,3,3-tetraphenyldisiloxane was also effective for the glucosidation of this kind. This suggests that a part of the glucosidation is likely to proceed by way of oligosiloxanes structurally related to **4** and **5**, which were actually detected in the reaction mixture.

The role of the liberated acid is essential for the glucosidation, since no glucosides, but only siloxanes **4** and **5**, formed when a base such as pyridine was first added to the reaction mixture.

An inefficient condensation of **1** and methanol with methanesulfonic acid alone proceeded to give **2a** and **2b** in 12 and 13% yields, respectively, indicating that the condensation of **1** and methanol with DCPS and silver methanesulfonate goes partly at least through a pathway i leading directly to **2b**, as shown in Fig. 3. Tables 1 and 2 show that ratios of **2a** to **2b** are mostly smaller than those of **3a** to **3b**, reflecting the idea that the less bulky methanol has more chances to take pathway i than the bulky **1** does.[14] The decrease of the amount of **2b** which accompanied the increase of that of **2a** occurred during a longer reaction period, as seen in Fig. 1, obviously indicating that a part of **2b** is isomerized into **2a** by the methanesulfonic acid generated. Actually, about 10% of **2b** was anomerized with two equivalents of methanesulfonic acid in dichloromethane at 0 °C within 3 h. No appreciable amount of the β,β-isomer[4] formed in the self-condensation reaction of **1**, suggesting that the α-configuration of **1** was mostly retained during the condensation reaction.

The results thus summarized in Table 1 allow the following remarks. Of the dichlorosilanes so far examined, DCPS was best for the glucosidation. The trends in the efficiency of the reaction appear to follow the order of stability of the siloxane[15] to be formed.

The efficiency of the reaction was also affected by the number, *n*. The order of the efficiency, 3—4> 2≫1, roughly correlates with the relative ease of the hydrolytic formation of polysiloxanes.[16] The high efficiencies favoring **2b** in the cases where $n \geqslant 2$ could partly be attributable to the direct pathway i in Fig. 3. The ratios of **2a** to **2b** increased progressively with the larger *n*; this seems to imply a generation of the glucosyl cation as indicated by pathway ii. The remarkably low yield of the glucosides with a fair increase of the anomer ratio in Run 8 may be due to

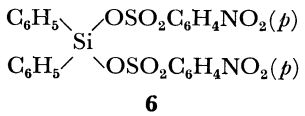


a steric effect caused by three phenyl groups on the silicon atom retarding the formation of the intermediary glucosylsiloxane which would afford the glucosides.

Silver arenesulfonates were also of use. The stronger liberated acid gave the greater efficiency. This was also observed in the self-condensation of **1**, as seen in Table 2. When silver trifluoromethanesulfonate was used, the self-condensation reaction had practically finished after 20 min at −20 °C.

As might be expected, the formation of self-condensation products became significant in the glucosidation of **1** with less reactive cyclohexanol, as shown in Table 1. Treatment with silver *p*-nitrobenzenesulfonate and DCPS yielded mostly **2'a**, agreeing with the fact that **2'b** is less resistant than **2b** to anomerization by acid.[17]

Finally, it should be mentioned that crystalline bis(*p*-nitrophenylsulfonyloxy)diphenylsilane (**6**) was successfully used as a reagent for glucosidation of **1** in a direct fashion :[18] a mixture of **1**, methanol, and **6** in dichloromethane furnished the glucosides, **2a** and **2b**, in 71% yield, favoring the latter.



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Experimental

Instruments used are the same as those previously described,[9] except for a DIP-180 (Japan Spectr.) for optical rotation.

Each aliquot of the reaction mixture was diluted with benzene, and powdered $NaHCO_3$ was added before application to TLC (silica gel No. 7731 (Merck)). Two kinds of solvent systems, consisting of benzene and butanone (solvent A) and of hexane and ethyl acetate (solvent B), were used for column chromatography (silica gel (Kanto Kagaku)), and each fraction was examined by TLC. GLC was carried out by a F6-D (Hitachi Perkin-Elmer): 10% Silicone SE-30 on Chromosorb W AW HMDS (80—100 mesh), 3 mm × 1 m (U-tube), 165 °C, 30 ml/min N_2.

Predistilled solvents and alcohols were stored over molecular sieves (Linde 3A). Silanes were distilled before use. Compound **1**,[19] whose C-13 NMR in $CDCl_3$ showed a single peak at 91.2 ppm, and silver sulfonate prepared from silver carbonate (Wako) and an appropriate sulfonic acid (Tokyo Kasei) were kept *in vacuo* over P_2O_5. Experiments were carried out at 0 °C, unless otherwise stated.

A General Procedure for the Preparation of 2(2')a and 2(2')b (Eq. 1). To a mixture of **1** (0.33 mmol) with alcohol (0.33 mmol) and silver sulfonate (0.67 mmol) in dichloromethane (0.9 ml), chlorosilane (0.67/*n* mmol, stated by Eq. 1) was added with stirring at 0 °C. The mixture was then diluted with benzene and an excess of $NaHCO_3$ was added with stirring. The filtrate was evaporated and chrmatographed over silica gel. Yields were based on the weight of fractions after removing the solvent and were reproducible within 5%. Reaction conditions and results are summarized in Table 1.

Methyl 2,3,4,6-Tetra-O-benzyl-α- and -β-D-glucopyranosides (2a and 2b). A mixture of **1** (180 mg), methanol (14 μl), silver methanesulfonate (136 mg), and DCPS (69 μl) in dichloromethane (0.9 ml) was stirred for 3 h. The processed mixture of products was chromatographed. After elution of **4** and **5** (R_f=0.75 and 0.67, solvent A (40 : 1), respectively) with solvent A (80 : 1), **2b**, **2a**, and then **3a** (R_f=0.55, 0.45, and 0.40, solvent A (40 : 1)) were eluted with solvent A (40 : 1), followed by the elutions of **3b** (R_f=0.30, solvent A (40 : 1)) with solvent A (20 : 1) and of **1** with solvent A (10 : 1). On recrystallization from hexane, **2b** was obtained as colorless needles : 92 mg (50%), mp 74—75 °C, $[\alpha]_D^{20}$ +14° (*c* 1.0, dioxane) [lit,[20] mp 68—69 °C, $[\alpha]_D^{20}$ +11° (*c* 5.3, dioxane)]. Found: C, 75.20; H, 6.92%. Calcd for $C_{35}H_{38}O_6$: C, 75.79; H, 6.90%. Syrupy **2a** (26 mg, 14%) had a NMR spectrum ($CDCl_3$)[21] identical with that of **2a**[20] prepared from methyl α-D-glucopyranoside. Syrupy **3a** (6 mg, 3%) had an R_f value identical with that of **3a** prepared from α,α-trehalose. On recrystallization from hexane, **3b** was obtained as colorless needles : 9 mg (5%), mp 100—101 °C, with an IR spectrum (KBr) identical with that of **3b** prepared as noted below. Crystalline **1** (27 mg, 15%) was recovered.

Glucosidation by the Filtrate of the Reaction Mixture of DCPS and Silver Methanesulfonate. A mixture of silver methanesulfonate (149 mg, 2.2 eq.) and DCPS (76 μl, 1.1 eq.) in dichloromethane (1.8 ml) was stirred for 2 h. Then the resulting mixture was filtered onto **1** (180 mg) kept in a cooling bath. Methanol (14 μl, 1 eq.) was immediately added and the resulting mixture was stirred for 3 h to give **2a** (28 mg, 15%) and **2b** (23 mg, 17%). Fractions containing **4** and **5** were eluted prior to the appearance of **2a** and **2b** on the chromatography.

Evaporation of the solvent from the above-mentioned filtrate (NMR(CH_2Cl_2)δ=3.05 (s, CH_3SO_3Si)[22]) gave a clear syrup, which rapidly turned into a white paste in air.

Glucosidation with DCPS and Methanesulfonic Acid. Treatment of a mixture of **1** (180 mg), methanol (14 μl, 1 eq.), and DCPS (69 μl, 1 eq.) in dichloromethane (0.9 ml) with methanesulfonic acid (1.0—2.0 eq.) for 3 h gave **2a** and **2b**. The following data were obtained : [the acid used, **2a**, **2b**] 22 μl (1.0 eq.), 13 mg (7%), 24 mg (13%); 33 μl (1.5 eq.), 22 mg (12%), 37 mg (20%); and 44 μl (2.0 eq.), 32 mg (17%), 46 mg (25%).

Glucosidation with DMPS and Methanesulfonaic Acid. A mixture of **1** (180 mg) and DMPS (38 μl, 1 eq.) in dichloromethane (0.9 ml) was treated with methanesulfonic acid (44 μl, 2 eq.) to afford **2a** (44 mg, 24%) and **2b** (72 mg, 39%), after 3 h.

Glucosidation with Methanesulfonic Acid. A solution of **1** (180 mg) in dichloromethane (0.9 ml) containing methanol (14 μl, 1 eq.) was treated with methanesulfonic acid (44 μl, 2 eq.) for 3 h to give **2a** (22 mg, 12%) and **2b** (24 mg, 13%).

*Glucosidation with Bis(p-nitrophenylsulfonyloxy)diphenylsilane (**6**).* A mixture of silver *p*-nitrobenzenesulfonate (51.5 mg) and DCPS (18 μl) in acetone (0.5 ml) was stirred at 27 °C for 1 h. Filtration and evaporation gave **6** : hygroscopic prisms, mp 98—101 °C, IR (KBr) 1435 (C_6H_5Si),[23] 1520, 1365 cm^{-1} (NO_2). Found: N, 4.44%. Calcd for $C_{24}H_{28}N_2O_{10}S_2Si$: N, 4.77%.

A mixture of **1** (90 mg) and **6** (98 mg) in dichloromethane (0.9 ml) and methanol (7 μl) was stirred. *p*-Nitrobenzenesulfonic acid soon deposited. After 3 h, the reaction mixture was diluted with benzene, filtered, and chromatographed to give **2a** (11.1 mg, 14%), **2b** (54.2 mg, 57%), **3a**+**3b** (14.3 mg, 16%), and **1** (8.5 mg, 9%).

Glucosidation with 1,3-Dichloro-1,1,3,3-tetraphenyldisiloxane[24] and Silver p-Nitrobenzenesulfonate. A mixture of **1** (90 mg), the siloxane (75 mg), and silver *p*-nitrobenzenesulfonate (103 mg) in dichloromethane (0.45 ml) and methanol (7 μl) was stirred for 3 h to give **2a** (17 mg, 18%), **2b** (35 mg, 38%), **3a**+**3b** (18 mg, 20%), and **1** (4 mg, 5%).

*Conversion of **4** into **2a** and **2b** with Methanesulfonic Acid.* A solution of **4** (47 mg) in dichloromethane (0.24 ml) was treated with methanesulfonic acid (8.2 μl, 2 eq.) for 3 h to give **2a** (8.3 mg, 24%) and **2b** (19 mg, 54%).

*Anomerization of **2b** with Methanesulfonic Acid.* A mixture of **2b** (46 mg) and methanesulfonic acid (11 μl, 2 eq.) in dichloromethane (0.23 ml) was stirred for 3 h to give **2a** (4.7 mg, 10%) and **2b** (36.5 mg, 79%).

*Cyclohexyl 2,3,4,6-Tetra-O-benzyl-α- and -β-D-glucopyranosides (**2'a** and **2'b**).* A mixture of **1** (180 mg), cyclohexanol (35 μl), silver methanesulfonate (136 mg), and DCPS (69 μl) in dichloromethane (0.9 ml) was stirred for 3 h. The processed mixture of products was chromatographed. After elution with the solvent A (80 : 1), a mixture of **2'a** and **2'b** appeared with solvent A (40 : 1), followed by **3a** and **3b** (49 mg, 28%) with solvent A (20 : 1), and unchanged **1** (18 mg, 10%) with solvent A (10 : 1). The mixture of **2'a** and **2'b** was separated by chromatography with solvent B (3 : 1) to afford **2'b** and then **2'a**. On recrystallization from diisopropyl ether, **2'b** was obtained as colorless needles : 77 mg (37%), mp 104—105 °C, $[\alpha]_D^{20}$ +8°(*c* 1.0, $CHCl_3$). Syrupy **2'a** (38 mg, 18%), $[\alpha]_D^{20}$ +43°(*c* 1.0, $CHCl_3$), showed a NMR spectrum identical with that of **2'a** prepared in the alternative fashion described below. Found: for **2'a**, C, 76.74; H, 7.25%. For **2'b**, C, 77.17; H, 7.64%. Calcd for $C_{40}H_{46}O_6$: C, 77.14; H, 7.45%.

*Alternative Synthesis of **2'a**.* A mixture of cyclohexyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside[25] (92 mg), KOH (260 mg), and benzyl chloride (3 ml) was heated at 110 °C for 5.5 h. Filtration and evaporation gave a yellow syrup which was chromatographed over silica gel. After one elution with solvent A (100 : 1), another with solvent A (40 : 1) furnished **2'a** (73 mg, 60%), $[\alpha]_D^{20}$ +41° (*c* 2.3, $CHCl_3$). Found: C, 76.14; H, 7.25%. Calcd for $C_{40}H_{46}O_6$: C, 77.14; H, 7.45%.

*Octa-O-benzyl-α,α- and -α,β-trehaloses (**3a** and **3b**).* To a stirred mixture of **1** (180 mg, 0.33 mmol) and silver methanesulfonate (64 mg, 0.03 mmol) in dichloromethane (0.9 ml), DCPS (35 μl, 0.17 mmol) was added; the resulting mixture was stirred for 6.5 h. The processed mixture of products was chromatographed. After one elution with solvent A (80 : 1), **3a** was eluted again with solvent A (40 : 1). Further elution with solvent A (20 : 1) gave **3b**. **3a** was colorless syrup, 41 mg, (23%), $[\alpha]_D^{20}$ +84° (*c* 1.0, $CHCl_3$), having a NMR spectrum identical with that of the sample prepared as given below. On recrystallization from hexane, **3b** was obtained as colorless needles : 80 mg (45%), mp 100—101 °C, $[\alpha]_D^{20}$ +52° (*c* 1.0, $CHCl_3$); its IR and NMR spectra were identical with those of the sample prepared as given below.

Hydrogenation of syrupy **3a** over Pd-black in a mixture of aq ethanol and dioxane containing acetic acid, followed by heating with acetic anhydride and sodium acetate, gave octa-*O*-acetyl-α,α-trehalose: mp 94—97 °C, $[\alpha]_D^{20}$ +163° (*c* 1.0, $CHCl_3$) [lit,[26] mp 98—100 °C, $[\alpha]_D^{22}$ +160° (*c* 1.0, $CHCl_3$)]. Found: C, 49.26; H, 5.57%. Calcd for $C_{20}H_{38}O_{19}$: C, 49.56; H, 5.60%. Similar treatment of **3b** gave octa-*O*-acetyl-α,β-trehalose: mp 138—140 °C, $[\alpha]_D^{20}$ +78° (*c* 1.0, $CHCl_3$) [lit,[26] mp 140—142 °C, $[\alpha]_D^{22}$ +84.5° (*c* 0.68, $CHCl_3$)]. Found: C, 49.54; H, 5.65%. Calcd for $C_{20}H_{38}O_{19}$: C, 49.56; H, 5.60%.

Reaction conditions and results of analogous self-condensations of **1** stated by Eq. 2 using other silver sulfonates are shown in Table 2.

*Conversion of **5** into **3a** and **3b** with Methanesulfonic Acid.* A solution of **5** (156 mg) in dichloromethane (0.78 ml) was treated with methanesulfonic acid (19 μl, 1 eq.) for 4 h to afford **3a** (20 mg, 22%) and **3b** (67 mg, 51%).

*Alternative Synthesis of **3a**.* Crystalline α,α-trehalose dihydrate (Wako, 96.3 mg) was dried *in vacuo* at 90 °C and then heated with benzyl chloride (0.9 ml), crushed KOH (0.71 g), and Drierite (0.7 g) in *N*,*N*-dimethylformamide (1 ml) at 60 °C for 5 h. After filtration and evaporation, chromatography over silica gel with solvent A (gradient, 80 : 1→40 : 1) afforded **3a** (151 mg, 56%), $[\alpha]_D^{20}$ +88° (*c* 1.3, $CHCl_3$). Found; C, 76.42; H, 6.61%. Calcd for $C_{68}H_{70}O_{11}$: C, 76.81; H, 6.64%.

*Alternative Synthesis of **3b**.* A mixture of acetobromoglucose (94 mg), **1** (108 mg), $Hg(CN)_2$ (50 mg), and $HgBr_2$ (72 mg) in nitromethane (1 ml) was stirred at room temperature for 70 h. The product (132 mg) was treated with sodium methoxide (10 ml, 0.02 M) and then benzylated with benzyl bromide (0.25 ml) in *N*,*N*-dimethylformamide (0.5 ml) in the presence of BaO (0.2 g) and $Ba(OH)_2 \cdot 8H_2O$ (0.1 g).[27] After removal of insoluble material by filtration and evaporation *in vacuo* at 98 °C, the residue obtained was chromatographed over silica gel with solvent A (gradient, 100 : 1→30 : 1) to give **3b** (69 mg, 32%). Recrystallization from hexane afforded **3b** : Colorless needles, mp 100—101 °C, $[\alpha]_D^{20}$ +53° (*c* 1.4, $CHCl_3$). Found: C, 76.93; H, 6.62%. Calcd for $C_{68}H_{70}O_{11}$: C, 76.81; H, 6.64%.

*Methoxydiphenyl(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyloxy)silane (**4**) and Bis(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyloxy)diphenylsilane (**5**).* A mixture of **1** (180 mg, 0.33 mol), pyridine (93 μl, 0.67 mmol), silver *p*-toluenesulfonate (186 mg, 0.67 mmol), and DCPS (69 μl, 0.33 mmol) in 1,2-dichloroethane (0.9 ml) was stirred at 0 °C for 1 h. Methanol (14 μl, 0.33 mmol) was then added to the mixture. After stirring for 3 h, the mixture was treated with an excess of sodium acetate, filtered, evaporated, and then chromatographed over silica gel. After one elution with benzene, another with solvent A (100 : 1) gave **4** as a syrup: 53 mg (24%), $[\alpha]_D^{20}$ +47° (*c* 0.9, $CHCl_3$), IR (film) 1422 cm^{-1} (C_6H_5Si),[23] NMR ($CDCl_3$) δ=3.61 (3H, s, OCH_3), 5.48 (1H, d, anomeric H, J=3.2 Hz), 7.1—7.5 (phenyl), and 7.6—7.8 (4H, m, H's β to Si in $=Si(C_6H_5)_2$.[28] Found: C, 74.86; H, 6.44%. Calcd for $C_{47}H_{48}O_7Si$: C, 74.97; H, 6.43%.

Elution with solvent A (80 : 1) gave **5** as a syrup: 74 mg (35%), $[\alpha]_D^{20}$ +64° (*c* 1.0, $CHCl_3$), IR(film) 1432 cm^{-1} (C_6H_5Si),[23] NMR($CDCl_3$) δ=5.54 (1H, d, anomeric H, J= 3.0 Hz), 7.0—7.4 (phenyl), and 7.6—7.8 (2H, m, H's β to Si in $=Si(C_6H_5)_2$ [28]). Found: C, 75.55; H, 6.34%. Calcd for $C_{80}H_{80}O_{12}Si$: C, 76.16; H, 6.39%.

Isolation of Hexaphenylcyclotrisiloxane. The mixture of

Run 3 was poured onto a column of silica gel, and eluted with benzene. On evaporation, crystals were obtained (28 mg, 43%), mp 188—189 °C, [lit,[29] 190 °C], whose IR(KBr)[30] was identical with that of a sample prepared by the known procedure.[29]

Examination of Volatile Components in the Reaction Mixture of Run 3. Aliquots of the supernatant were injected into the GLC-apparatus without quenching to give the data: ([reaction time, DMPS (3.8 min), DCPS(4.4 min)] 8 min, 3%, 74%; 15 min, 5%, 48%; 45 min, 6%, 20%, and 60 min, 4%, 10%.

Examination of the Fractions Containing Siloxanes.[31] The reaction mixture of Run 2 (**1**, 180 mg) quenched with excess benzene and powdered $NaHCO_3$ was poured onto a column of silica gel, which was eluted with solvent A (100 : 1) to give a syrup (94 mg). Rechromatography with solvent B (gradient, 100 : 1→10 : 1) afforded three fractions: A, B, and C. The fastest-moving fraction A (19 mg) was a mixture (*ca.* 1 : 2) of **4** (NMR(CCl_4) δ=3.57 (s, OCH_3)) and 1-methoxy-3-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyloxy)-1,1,3,3-tetraphenyldisiloxane (NMR(CCl_4) δ=3.45 (s, OCH_3), 5.40(d, anomeric H, J=4 Hz), overlapping to that of **4**). Fraction B (23 mg) had a NMR spectrum consistent with the structure of 1,5-bis(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-1,1,3,3,5,5-hexaphenyl trisiloxane (NMR(CCl_4) δ= 5.23 (d, anomeric H, J=4 Hz), 7.5—7.7 (6H, m, H's β to Si in $=Si(C_6H_5)_2$[28]). The slowest-moving fraction C (13 mg) was a mixture of (1 : 1) of **5** (NMR(CCl_4) δ=5.47 (d, anomeric H, J=4 Hz)) and 1,3-bis(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyloxy)-1,1,3,3-tetraphenyldisiloxane (NMR (CCl_4) δ=5.23 (d, anomeric H, J=2 Hz), 7.5—7.7 (m, H's β to Si in $=Si(C_6H_5)_2$[28]).

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