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HYDROSILYLATION OF ALLYL ESTERS OF MONOSACCHARIDES

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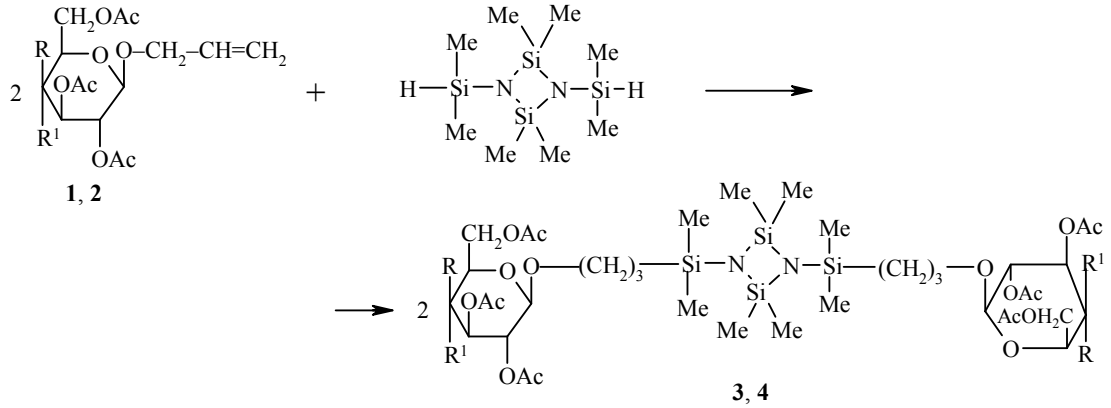
By hydrosilylation of 1-O-allyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranose and 1-O-allyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranose with 1,3-bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane in the presence of the catalyst $Co_2(CO)_8$, we have obtained 1,3-di[3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)propyldimethylsilyl]-2,2,4,4-tetramethylcyclodisilazane and 1,3-di[3-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)propyldimethylsilyl]-2,2,4,4-tetramethylcyclodisilazane. By deacetylation, we obtained 1,3-di[3-(β-D-glucopyranosyloxy)propyldimethylsilyl]-2,2,4,4-tetramethyl-cyclodisilazane.

Keywords: hydrosilylation, monosaccharides, allyl esters, cyclodisilazanes, deacetylation.

Synthesis of low-toxicity compounds has become important in biological and pharmacological studies, and so there is interest in using carbohydrates to modify linear and cyclolinear siloxanes, which may lead to a substantial change in the nature of the drug action [1-4].

We have studied the reaction of hydrosilylation of 1-O-allyl-2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranoses (**1**) and 1-O-allyl-2,3,4,6-tetra-O-acetyl-β-*D*-galactopyranoses (**2**) with 1,3-bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane. The reaction was carried out in dry chloroform with a mole ratio of the reacting components equal to 2.5:1 at a temperature of 60-65°C in the presence of the catalyst $Co_2(CO)_8$.

We obtained the corresponding 1,3-di[3-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (**3**) and 1,3-di[3-(2,3,4,6-tetra-O-acetyl-β-*D*-galactopyranosyloxy)-dimethylsilyl]-2,2,4,4-tetramethylcyclodisilazane (**4**).



1, **2**

3, **4**

1, **3** R = H, R^1 = OAc; **2**, **4** R = OAc, R^1 = H

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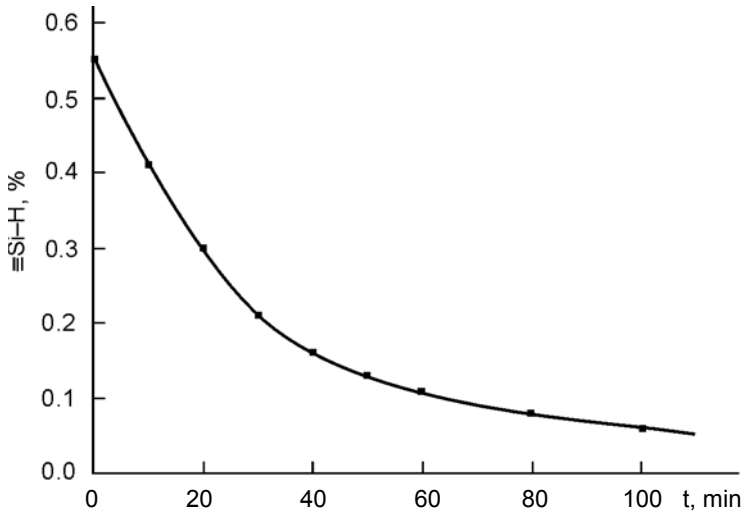
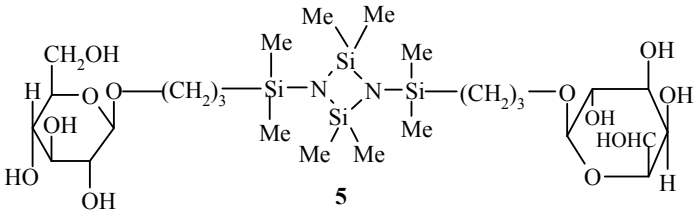


Fig. 1. Amount of active hydrogen on the silicon atom *vs*. hydrosilylation reaction time for compound **1**.

The reaction mainly occurs according to Farmer's rule, although a small amount of the Markovnikov addition product is also formed. The mixture was separated on a column (hexane–chloroform system, 3:2, silica gel L 50/100). The course of the reaction was monitored from the decrease in active hydrogen on the silicon over time (Fig. 1). We have established that in 1.5 h, the hydrogen in the ≡Si–H group is completely removed, which is supported by the IR spectrum, where in the 2165 cm^{-1} region there is no characteristic absorption for ≡Si–H bonds.

By deacetylation of compound **3** in absolute methanol in the presence of sodium methoxide, we obtained 1,3-di[3-β-*D*-glucopyranosyloxy)dimethylsilyl]-2,2,4,4-tetramethylcyclodisilazane (**5**).



5

EXPERIMENTAL

The IR spectra were obtained on a UR-20 in KBr disks. The ^1H NMR spectrum was taken on a Bruker WM-250 spectrometer (250 MHz); the ^{13}C NMR spectrum was taken on a Bruker AM-300 spectrometer (75 MHz) in $CDCl_3$. The purity of the compounds obtained and the R_f values were determined on Silufol UV-254. The optical rotation was measured on an SU-3 general-purpose saccharimeter at 20±2°C.

1,3-Di[3-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyloxy)propyldimethylsilyl]-2,2,4,4-tetramethyl-cyclodisilazane (3). 1,3-Bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (1.15 g, 5 mmol) in dry chloroform (20 ml) and $Co_2(CO)_8$ (0.15 g) were added dropwise to a solution of compound **1** (4.85 g, 12.5 mmol) in dry chloroform (25 ml). The reaction was carried out under a nitrogen atmosphere with constant stirring for 1.5 h (60-65°C). After cooling and separating on a column (2:1 benzene–chloroform system, silica

gel L 50/100), a chromatographically pure product was obtained in a yield of 5.91 g (61.7%); mp 152-153°C. R_f 0.61 (2:1 benzene–chloroform system). $[\alpha]_D^{18}$ +98° (*c* 0.52, chloroform). IR spectrum, ν, cm^{-1}; 690 (Si–C); 1120, 1030 (C–O–C); 1715 (C=O); 920 (Si–N); 1460 (CH_3). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.35 (1H, d, $J_{1,2}$ = 8, H-1); 5.55 (1H, d, $J_{1,2}$ = 4, H-1'); 4.38 (1H, dd, $J_{2,1}$ = 8.1; $J_{2,3}$ = 9.4, H-2); 4.78 (1H, dd, $J_{2,1}$ = 4; $J_{2,3}$ = 10.6, H-2'); 5.67 (1H, dd, $J_{3,2}$ = 9.4; $J_{3,4}$ = 10, H-3); 5.60 (1H, dd, $J_{3,2}$ = 10.6; $J_{3,4}$ = 9.8, H-3'); 4.22-4.28 (dd, $J_{4,3}$ = 10; $J_{4,5}$ = 12.3, H-4); 5.29-5.30 (dd, $J_{4,3}$ = 9.8; $J_{4,5}$ = 9.9, H-4'); 3.62-3.68 (1H, m, H-5); 3.90-4.00 (1H, m, H-5'); 4.80-4.10 and 4.11-4.14 (2H, d, H-6 and H-6', $C\underline{H}_2OCOCH_3$); 3.55-3.60 and 3.78-3.84 (2H, 2m, RO–$C\underline{H}_2$–CH_2–CH_2–SiR_3); 1.85-1.90 and 1.92-1.98 (2H, 2m, RO–CH_2–$C\underline{H}_2$–CH_2–SiR_3); 1.62-1.70 and 1.73-1.82 (2H, 2m, RO–CH_2–CH_2–$C\underline{H}_2$–SiR_3); 1.05-1.10 (24H, m, 8Si–$C\underline{H}_3$); 2.13-2.18 (21H, m, 7CO–$C\underline{H}_3$). Found, %: C 48.73; H 7.02; N 2.41; Si 10.33. $C_{42}H_{74}N_2O_{20}Si_4$. Calculated, %: C 48.55; H 7.12; N 2.72; Si 10.79.

1,3-Di[3-(2,3,4,6-tetra-O-acetyl-β-*D*-galactopyranosyloxy)propyldimethylsilyl]-2,2,4,4-tetramethylcyclodisilazane (4) were obtained similarly from compound **2** (4.85 g, 12.5 mmol) and 1,3-bis(dimethylsilyl)-2,2,4,6-tetramethylcyclodisilazane (1.31 g, 5 mmol) with a yield of 4.92 g (51%); mp 160-161.5°C, R_f 0.73 (2:1 benzene–chloroform system), $[\alpha]_D^{17}$ +102° (*c* 0.81 chloroform). IR spectrum, ν, cm^{-1}: 1700 (C=O); 710 (Si–C); 1020, 1050, 1110, (C–O–C); 1445 (CH_3). ^{13}C NMR spectrum, δ, ppm: 170.00-175.88 (RO–$\underline{C}O$–CH_3); 20.62 (RO–CO–$\underline{C}H_3$); 70.82-71.05 (RO–$\underline{C}H_2$–CH_2–CH_2–SiR_3); 29.38-29.73 (RO–CH_2–$\underline{C}H_2$–CH_2–SiR_3); 20.78-22.72 (RO–CH_2–CH_2–$\underline{C}H_2$–SiR_3); 8.05-13.40 (Si–CH_3); 91.90 and 100.88 ($C_{(1)}$ and $C_{(1')}$); 60.98 and 61.80 ($C_{(6)}$ and $C_{(6')}$); 66.80-77.51 ($C_{(2\text{-}5)}$ and $C_{(2'\text{-}5')}$). Found, %: C 48.94; H 7.53; N 2.43; Si 10.02. $C_{42}H_{74}N_2O_{20}Si_4$. Calculated, %: C 48.55; H 7.12; N 2.72; Si 10.79.

Deacetylation. A suspension of compound **3** (1.038 g, 1 mmol) in absolute methanol (20 ml) was heated for 10 min in a water bath with a 0.1 N solution of sodium methoxide (1.5 ml) and the solution obtained was allowed to stand overnight. The mixture was filtered and the filtrate was concentrated using a water-jet aspirator, and ether was added to the residual mass until crystals separated out. The crystals were filtered out and recrystallized from hexane. Yield of compound **5** 0.23 g (34%); mp 170-171°C, R_f 0.51 (2:1 chloroform–methanol system), $[\alpha]_D^{17}$ +62° (*c* 0.47, water). IR spectrum, ν, cm^{-1}: 3580-3650 (OH); 1220-1248 (Si–CH_3); 1000, 1150 (C–O–C); 1390-1410 (–CH_2–), 915 (Si–N). Found, %: N 4.0; Si 15.9. $C_{26}H_{58}N_2O_{12}Si_4$. Calculated, %: N 3.81; Si 15.29.

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