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CARBOHYDRATE MODIFIED POLYDIMETHYLSILOXANES. PART 1. SYNTHESIS AND CHARACTERIZATION OF CARBOHYDRATE SILANE AND SILOXANE BUILDING BLOCKS

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CARBOHYDRATE MODIFIED POLYDIMETHYLSILOXANES. PART 1. SYNTHESIS AND CHARACTERIZATION OF CARBOHYDRATE SILANE AND SILOXANE BUILDING BLOCKS

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ABSTRACT

A series of silanes containing carbohydrate residues usable as building blocks for the preparation of modified poly(dimethylsiloxane)s (PDMS) were synthesized. Allyl glycosides, allyl ethers and allyl amides of glucose, gluconic acid and glucuronic acid-γ-lactone with protected hydroxyl groups were reacted with diisopropoxymethylsilane in the presence of hydrosilylation catalysts yielding sugar substituted dialkoxysilanes. In addition, di- and trialkoxysilanes containing sugar residues were obtained by reaction of D(+)glucono-δ-lactone with 3-aminopropylsilanes. By hydrosilylation of tetramethylcyclotetrasiloxane with trimethylsilyl (TMS)-protected 3-O-allylglucose a glucose substituted cyclosiloxane was obtained and used in equilibration reactions for the synthesis of water soluble PDMS with pendant sugar moieties. However, the ring double bond of cellobial was found to be unaccessible for hydrosilylations.

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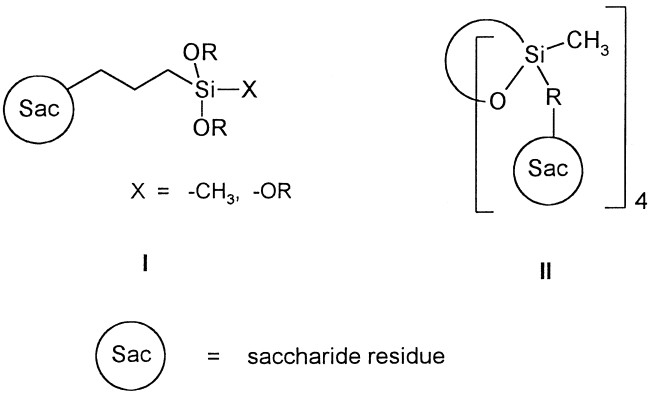
INTRODUCTION

Polymers consisting of a hydrophobic, but chemically and biologically stable, synthetic backbone and side chains of a natural hydrophilic saccharide residue ("glycopolymers") [1, 2], have attracted increasing interest in recent years, mainly with respect to very special applications in basic biochemical and biomedical research. Whereas numerous combinations of polyacryate, polymethacrylate and polystyrene backbones with saccharides have been investigated, PDMS have been scarcely considered, although their use as a hydrophobic backbone is of advantage because of their good chemical and thermal stability, high oxygen affinity, as well as biocompatibility. Such hydrophobic/hydrophilic hybrid polymers including linear as well as crosslinked PDMS types are expected to exhibit interesting properties useful in many applications, for example as amphiphilic polymers (nonionic silicone surfactants), surface modifiers or biocompatible materials. In addition, organofunctional silanes and siloxanes with hydroxyl groups are of interest as resin components for UV-curable resins based on silicone acrylates as well as for the preparation of inorganic-organic hybrid materials by the sol-gel process.

Reactions of sugars with chlorosilanes are well known, predominantly for protecting their hydroxyl groups and for analytical purposes. But, due to the hydrolytical sensitivity of the Si-O-C bonds, this reaction is not suitable for the synthesis of PDMS-based glycopolymers. In contrast, stable Si-C- bonds can be formed by hydrosilylation of compounds with carbon-carbon multiple bonds in the presence of Pt-, Pd-, Rh-, Ru-based catalysts [3]. The addition of hydrosilanes to unsaturated alcohols catalyzed by chloroplatinic acid gives rise to numerous side reactions such as the liberation of hydrogen and the associated formation of a silyl ether, or the β-addition to the C=C double bond. Thus, HO-groups of unsaturated alcohols are preferentially provided with a protective group which is removed after the addition reaction [4]. In addition, the reaction time and the formation of byproducts of the hydrosilylation is strongly influenced by the temperature, solvent and type of catalyst which has to be carefully selected in each case.

In previous work, we described silicone rubbers crosslinked by glucose or sucrose moieties [5-7]. Stadler *et al*. reported linear PDMS containing glucose-, or galactose residues [8-11] and very recently, the attachment of N-allyl-aldonoamides to PDMS was investigated extensively by the same authors with respect to the crucial role of the hydrosilylation catalyst [12].



Scheme 1.

Saccharide substituted low molecular silanes and siloxanes usable as building blocks for the preparation of modified PDMS have not been reported so far. Compared to the attachment of sugar derivatives to preformed reactive siloxane polymers such monomers and intermediates offer much more polymerization flexibility in the preparation of modified PDMS with special molecular architectures.

The first part of this series deals with the synthesis and characterisation of some low molecular silanes and siloxanes building blocks containing sugar residues, the basic structures of which are shown in Scheme 1. Type **I** monomers can be used for the synthesis of poly(siloxane)s by polycondensation or for sol-gel reactions, whereas type **II** monomers can be incorporated by equilibration reactions. In order to prevent side reactions due to the HO-groups and to get homogenous reaction media the saccharides generally have to be protected for the monomer syntheses as well as for polycondensations and equilibrations.

EXPERIMENTAL

General

D(+)-Glucose, D(+)-glucono-δ-lactone (**6**), D(+)-glucurono-γ-lactone, allyl alcohol, allylamine trimethylchlorosilane, and hexamethyldisilazane were obtained from Aldrich and used as received. All solvents were dried by common methods and distilled. 3-O-Allyl-1,2;5,6-di-O-isopropyliden-α-D(+)-glucofuranose (**1a**) [13], allyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (**1b**)[14], diiso-

propoxymethylsilane (**2**) [15], 1,2-O-isopropylidene glucofuranosidurono-6,3-lactone (**7**)[16], 3,4,6-tri-O-acetyl-D-glucal (**13a**) [17], 3,6,2´,3´,4´,6´-Hexa-O-acetyl-D-cellobial (**13b**) [17], the 3-aminoproplysilanes **8a-d** were prepared according to the literature [18]

The solution of Karstedt's catalyst [19] was obtained by heating a mixture of 0.25 g $Na_2PtCl_4.4.H_2O$, 0.25 g 2,4,6,8-tetramethyltetravinylcycotrisiloxane and 0.25 g $NaHCO_3$ in 1ml abs. ethanol to 75°C for 10 minutes under nitrogen atmosphere. The solvent was removed by a nitrogen stream and the residue was dissolved in 2.5 ml abs. benzene.

^{1}H-NMR and ^{13}C-NMR-Spectra were recorded on a Bruker AC-E-200 FT-NMR spectrometer

Allyl-2,3,4,6-tetra-O-trimethylsilyl-β-D-glucopyranoside (1c)

To get the pure β-isomer, **1c** was prepared by deacetylation of **1b** and subsequent silylation. 9.71 g (25 mmol) **1b** was dissolved in 100 ml 0,01 M $NaOCH_3$ in CH_3OH and stirred with 20 g strong acid ion exchanger (Lewatit SC 104® at room temperature for 2 hours. The ion exchanger was filtered off and the solvent was removed under reduced pressure. Yield: 4.5 g (82%) allyl-β-D-glucopyranoside.

2.7 g (12 mmol) allyl-β-D-glucopyranoside and 9.85 g (61 mmol) hexamethyldisilazane were heated to reflux for 20 hours. The reaction mixture was filtered and excess disilazane was removed under reduced pressure. Yield: 4.0 g (64%)

^{1}H-NMR (DMSO-d_6) δ (ppm): 6.08-5.85 (m; 1H; CH=), 5.34-5.11 (m; 2H; $=CH_2$), 4.42-3.13 (m; 9H; H-1,2,3,4,5,6,6', =CH-C$\underline{H}_2$), 0.30-0.02 (m; 36H; 9(CH_3)

^{13}C-NMR (DMSO) δ (ppm): 134.50 (=CH), 117.39 (CH_2=), 102.38 (C-1), 79.04, 76.86, 76.35 (C-2,3,5), 71.92 (C-4), 70.04 (=CH-C$\underline{H}_2$), 62.48 (C-6), 2.64, 2.09, 1.55, 1.40, 1.05, 0.78, 0.6, -0.07 (Si-CH_3)

3-O-Allyl-1,2,4,6-tetra-O-trimethylsilyl-D-glucopyranose (1d)

1d was prepared by deprotection of **1a** and subsequent silylation. 10 ml conc. HCl was dropped into a dispersion of 12.6 g (42 mmol) **1a** in 150 ml water and stirred at room temperature for 1 hour. The solution was adjusted to pH 7 with 10% NaOH. After removal of water under reduced pressure the residue was stirred with 50 ml CH_3OH, filtered, and the solvent was distilled. Yield: 6.3 g (68%) 3-O-allyl-α-D-glucopyranose. A solution of 8.9 g (81 mmol) trimethyl-

chlorosilane in 30 ml n-hexane was dropped within one hour to a mixture of 4.5 g (20.4 mmol) 3-O-allyl-α-D-glucopyranose, 20 ml formamide and 6.6 g (81 mmol) pyridine at 0-5°C under nitrogen atmosphere and then stirred for 2 hours. The hexane phase was separated, the solvent was removed under reduced pressure, the residue was redissolved in *n*-hexane and purified by treatment with carbon black. Yield: 5.6 g (68 %).

^{1}H-NMR($CDCl_3$) δ (ppm): 6.02-5.81 (m; 1H; CH=), 5.33-5.06 (m; 2H; $=CH_2$), 4.50-3.10 (m; 9H; H-1,2,3,4,5,6,6', =CH-C$\underline{H}_2$), 0.23-0.08 (m; 36H; 9(CH_3).

^{13}C-NMR($CDCl_3$) δ (ppm): 135.36, 135.14 (=CH), 115.51, 115.15 (CH_2=), 97.88 (C-1(), 93.71 (C-1α), 85.03 (C-3β), 81.13 (C-3α), 77.21, 76.86, 74.99, 74.10, 73.77, 72.17, 70.63 (C-2,4,5 u. =CH-$\underline{C}H_2$),61.71 (C-6).

Allyl-D-glucofuranosidurono-6,3-lactone

8,8 g (50 mmol) D(+)-glucurono-γ-lactone, 10.0 g ion exchanger (Lewatit SC 104® and 50 ml allyl alkohol were stirred at 60°C for 4 hours. The ion exchanger was filtered off and excess allyl alcohol was distilled under reduced pressure. The residue was recrystallized from ethylacetate.

Yield: 5.9 g (55%.

Fp 106-108°C

Elemental analysis (%)	Calculated:	C 50,00	H 5,59
	Found:	C 49,42	H 5,41

^{1}H-NMR (DMSO-d_6) δ (ppm): 5.95–5.70 (m, ^{1}H, -CH=), 5.90 (d, 1H, C5-OH), 5.75 (d, 1H, CH_2-OH), 5.30–5.05 (m, 2H, $=CH_2$), 5.00 (s, 1H, H-1), 4.90–4.70 (m, 2H, H-3, H-4), 4.50 (t, 1H, H-5), 4.10 (d, 1H, H-2), 4.25–4.10 (m, 1H, H-α of -CH_2-), 3.95 – 3.80 (m, 1H, H-(α´ of -CH_2-).

^{13}C-NMR (DMSO-d_6) δ (ppm): 175.3 (C-6), 134.9 (-CH=), 117.0 (=CH2), 108.0 (C-1), 83.0 (C-3), 78.4 (C-2), 77.3 (C-4), 69.0 (C-5), 67.7 (-CH_2-).

Allyl-2,5-di-O-trimethylsilyl-D-glucofuranosid-urono-6,3-lactone (1e)

A solution of 5.0 g (46 mmol) trimethylchlorosilane in 23 ml n-hexane was dropped into a mixture of 4.5 g (21 mmol) **1** in 3,7 ml pyridine and 14 ml formamide at 0-5°C under nitrogen atmosphere and subsequently stirred at room temperature for 1.5 hours. The hexane phase was separated, the solvent was removed under reduced pressure. The residue was redissolved in n-hexane and purified by treatment with carbon black. Yield: 5.5 g (73 %).

^{1}H-NMR ($CDCl_3$) δ (ppm): 5.95–5.70 (m, 1H, -CH=), 5.30–5.10 (m, 2H, $=CH_2$), 5,00 (s, 1H, H-1), 4.90 (dd, 1H, H-4); 4.70 (d, 1H, H-3) 4.40–4.30 (m, H-2, H-5); 4.35–4.20 (m, 1H-α, $-CH_2-$) 3.95–3.80 (m, 1H-(α´ of $-CH_2-$), 0.35–0.05 (bs, 18H, Si-CH_3).

^{13}C-NMR ($CDCl_3$) δ (ppm): 173.6 (C-6), 133.5 (-CH=), 117.6 ($=CH_2$), 107.1 (C-1) 83.3 (C-3), 78.5 (C-2), 77.7 (C-4), 69.8 (C-5), 68.1 ($-CH_2-$), -0.1; -0.2 (Si-CH_3).

General Procedure for the Hydrosilylation of the Unsaturated Sugar Derivatives 1a-e

A solution of the allyl substituted sugar and an excess of **2** in toluene or o-xylene was heated to reflux in a nitrogen atmosphere and the catalyst solution was added. After the reaction time, the solutions were filtered and purified by treatment with carbon black and the solvent and unreacted **2** were distilled off under reduced pressure. The purity of liquid products was confirmed by gas chromatography, ^{1}H- and ^{13}C-NMR-spectroscopy in $CDCl_3$.

3a: 3.0 g (10 mmol) **1a**, 4.87 g (30 mmol) **2**, 0.2 ml catalyst solution, 20 ml o-xylene, 0.5 hours reflux. Yield: 4.0 g (87%).

^{1}H-NMR ($CDCl_3$) δ (ppm): 5.87 (d; 1H; H-1), 4.50 (d; 1H; H-2), 4.32 (t; 1H; H-5), 4.21-3.92 (m; 7H; H-4,6,6', O-CH_2, 2C<u>H</u>-$(CH_3)_2$), 3.83 (d, 1H; H-3), 1.70-1.52 (m; 2H; Si-CH_2-C<u>H</u>$_2$), 1.47, 1.40, 1.34 u. 1.32 (4s; 12H; 2C-(C<u>H</u>$_3)_2$), 1.14, 1.11 (2s 12H; 2CH-(C<u>H</u>$_3)_2$), 0.61-0.50 (m; 2H; Si-CH_2), 0.10 (s; 3H; Si-CH_3).

^{13}C-NMR ($CDCl_3$) δ (ppm): 111.84 u. 109.02 (C_q),105.44 (C-1), 83.06, 82.69, 81.35 (C-2,3,4), 77.92, 76.65 (C-5, O-CH_2), 67.36 (C-6), 64.86 (<u>C</u>H-$(CH_3)_2$), 16.98, 26.24, 25.57 (C-(<u>C</u>H$_3)_2$), 25.90, 25.68 (CH-(<u>C</u>H$_3)_2$), 23.55 (Si-CH_2-<u>C</u>H$_2$), 11.05 (Si-CH_2), -3.78 (Si-CH_3).

3b:1.9 g (5 mmol) **1b**, 2.4 g (15 mmol) **2**, 0.2 ml catalyst solution, 10 ml o-xylene, 5 hour reflux. Yield: 2.7 g (98%).

^{1}H-NMR ($CDCl_3$) δ (ppm): 5.21-4.88 (m; 3H; H-2,3,4), 4.48 (d; 1H; H-1), 4.30-3.32 (m; 7H; H-5,6,6', O-CH_2, 2C<u>H</u>-$(CH_3)_2$), 2.10-1.90 (4s; 12H; 4CH_3), 1.68-1.48 (m; 2H; Si-CH_2-C<u>H</u>$_2$), 1.21-1.03 (m; 12H; 2CH-(C<u>H</u>$_3)_2$), 0.57-0.42 (m; 2H; Si-CH_2), 0.10 (s; 3H; Si-CH_3).

^{13}C-NMR ($CDCl_3$) δ (ppm): 170.81, 170.43, 169.55, 169.41 (C=O), 105.66 (C-1), 73.03, 72.71, 71.86, 71.49 (C-2,3,5, O-CH_2), 68.57 (C-4), 64.85 (<u>C</u>H-$(CH_3)_2$), 62.11 (C-6), 25.86, 25.64 (CH-(<u>C</u>H$_3)_2$), 23.30 (Si-CH_2-<u>C</u>H$_2$), 20.77 (Acetyl-CH_3), 10.81 (Si-CH_2), -3.80 (Si-CH_3).

3c: 1.5. g (1 mmol) **1c**, 1,6. g (10 mmol) **2**, 0.1 ml catalyst solution, 10 ml o-xylene, 0.5 hour reflux. Yield: 1.75 g (82%).

^{1}H-NMR ($CDCl_3$) δ (ppm): 4.20-3.13 (m; 11H; H-1,2,3,4,5,6,6', O-CH_2, 2C<u>H</u>-$(CH_3)_2$,), 1.74-1.52 (m; 2H; Si-CH_2-C<u>H</u>$_2$), 1.20 (d; 12H; 2CH-(C<u>H</u>$_3)_2$), 0.67-0.54 (m; 2H; Si-CH_2), 0.23-0.10 (m; 39H; 13Si-CH_3).

^{13}C-NMR ($CDCl_3$) δ (ppm): 102.95 (C-1), 78.91, 76.59, 76.32 (C-2,3,5), 71.80 (C-4 u. O-CH_2), 68.57 (C-4), 64.44 (<u>C</u>H-$(CH_3)_2$), 62.44 (C-6), 25.91 (CH-(<u>C</u>H$_3)_2$), 23.46 (Si-CH_2-<u>C</u>H$_2$), 11.28 (Si-CH_2), 1.57, 1.06, 0.21, -0.30 (TMS-Si-CH_3), -3.75 (Si-CH_3).

3d: 1.0 g (2 mmol) **1d**, 0.66 g (4 mmol) **2**, 0.1 ml catalyst solution, 5 ml o-xylene, 0.5 hours reflux. Yield: 1.3 g (98%).

^{1}H-NMR ($CDCl_3$) δ (ppm): 4.48-3.05 (m; 11H; H-1,2,3,4,5,6,6', O-CH_2, 2(C<u>H</u>-$(CH_3)_2$), 1.25-1.07 (m; 2H; Si-CH_2-C<u>H</u>$_2$), 1.18, 1.14 (2s; 12H; 2(CH-(C<u>H</u>$_3)_2$), 0.57-0.40 (m; 2H; Si-CH_2), 0.23-0.08 (m; 39H; 13 (Si-CH_3).

^{13}C-NMR ($CDCl_3$) δ (ppm): 98.29 (C-1β), 94.07 (C-1α), 85.81 (C-3β), 81.76 (C-3α), 77.65, 76.62, 76.38, 74.74, 72.45, 71.22, 71.11 (C-2,4,5, O-<u>C</u>H$_2$), 64.62 (<u>C</u>H-$(CH_3)_2$), 62.12 (C-6), 25.89, 25.67 (CH-(<u>C</u>H$_3)_2$), 23.86 (Si-CH_2-<u>C</u>H$_2$), 10.78 (Si-CH_2), 1.59, 0.95, 0.72, 0.49, 0.31, -0.17, -0.30 (TMS-Si-CH_3), -3.83 (Si-CH_3).

3e: 2.4 g (6.5 mmol) **1e**, 1.1 g (6.5 mmol) **2**, 4 mg $Rh(PC_6H_5)_3Cl$ (solution in toluene), 40 ml toluene, 100°C, 17 hours. Yield: 3.2 g (93%)

^{1}H-NMR ($CDCl_3$) δ (ppm): 5.00–4.75, (m, 2H, H-1, H-3), 4.75–4.60 (d, 1H, H-3), 4.50–4.25 (m, 2H, H-2, H-5), 4.15 (m, 2H, -O-C<u>H</u>-$(CH_3)_2$), 3.85–3.70 (m, 1H, H-α of -CH_2-), 3.35–3.15 (m, 1H, H-α´ of -CH_2-), 1.70–1.40 (m, 2H, Si-C<u>H</u>$_2$-CH_2-), 1.30–1.00 (m, 12H, -O-CH-(C<u>H</u>$_3)_2$), 0.65–0.40 (m, 2H, Si-CH_2-C<u>H</u>$_2$-), 0.35 0.00 (bs, 21H, Si-CH_3).

N-Allyl-gluconic Acid Amide (4a)

A mixture of 7.13 g (40 mmol) D(+)-glucono-δ-lactone and 2.86 g (40 mmol) allylamine was refluxed in 50 ml methanol for 15 minutes. The solution was cooled and the precipitated white crystals were dried under reduced pressure.

Yield: 6.7 g (67.2 %). Fp.:120-21°C

Elemental analysis ($C_9H_{17}NO_6$, %)

Calculated:	C 45.95	H 7.28	N 5.95
Found:	C 46.16	H 6.96	N 5.87

IR (KBr) (cm^{-1}): 3400 (O-H, N-H), 2922 (C-H), 1667, 1653, 1640 (C=O, C=C), 1541 (N-H bending).

^{1}H-NMR (DMSO-d_6+D_2O): 7.77 (bs; 1H; NH), 5.92-5.70 (m; 1H; CH=), 5.37-5.00 (m; 2H; =CH_2), 4.11-3.91 (m; 2H; NH-C$\underline{H}_2$), 3.83-3.32 (m; 11H; H-2,3,4,5,6,6', 5×OH)

^{13}C-NMR (DMSO-d_6): 172.69 (C=O), 135.55 (CH=), 115.35 (=CH_2), 74.03, 72.81, 71.90 70.54 (C-2,3,4,5), 63.71 (C-6), 40.97 (NH-CH_2).

N-Allyl-penta-trimethylsilyl-gluconic Acid Amide (4b)

4.70 g (20 mmol) **4a** and 28.3 g (175 mmol) hexamethyldisilazane were heated to reflux for 72 hours under nitrogen atmosphere. The reaction mixture was filtered, the excess disilazane was removed under reduced pressure and the residue was fractionated.

Yield: 11.7 g (86%), Bp: 131-35°C/0.015 mbar

^{1}H-NMR($CDCl_3$): 5.96-5.73 (m; 1H; CH=), 5.28-5.10 (m; 2H; =CH_2), 4.30-3.42 (m; 8H; NH-C$\underline{H}_2$, H-2,3,4,5,6,6'), 0.22-0.02 (m; 54H; Si-CH_3).

^{13}C-NMR($CDCl_3$): 171.92 (C=O), 134.39 (CH=), 116.87 (=CH_2), 77.82, 75.55, 74.04, 72.64 (C-2,3,4,5), 64.28 (C-6), 41.66 (NH-CH_2), 0.98, 0.86, 0.76, 0.38, 0.39 (Si-CH_3).

N-(3-Diisopropoxymethylsilyl-)propyl-penta-O-trimethylsilyl-gluconic Acid Amide (5)

A solution of 2.00 g (3.35 mmol) **4b** and 1.62 g (10 mmol) 2 was in 10 ml o-Xylene was heated to reflux under nitrogen atmosphere. and 0,05 ml catalyst solution was added. After refluxing for 30 minutes. The solvent was removed under reduced pressure.

Yield: 2,5 g (97%)

Elemental analysis ($C_{31}H_{75}NO_8Si_6$, %)

Calculated:	C 49.09	H 9.97	N 1.85
Found:	C 49.26	H 9.61	N 1.75

^{1}H-NMR ($CDCl_3$): 6.58 (bs; 1H; NH), 4.24-3.00 (m; 10H; H-2,3,4,5,6,6', N-CH_2, 2(C$\underline{H}$-(CH_3)$_2$), 1.68-1.50 (m; 2H; Si-CH_2-C$\underline{H}_2$), 1.23-1.14 (m; 12H; 2(CH-(C$\underline{H}_3$)$_2$), 0.68-0.54 (m; 2H; Si-CH_2), 0.26-0.09 (m; 48H; 16(Si-CH_3).

^{13}C-NMR($CDCl_3$): 171.99 (C=O),77.26, 76.01, 73.93, 72.54 (C-2,3,4,5), 64.95 ($\underline{C}$H-(CH_3)$_2$), 64.19 (C-6), 41.90 (NH-CH_2), 25.92 25.70 (CH-($\underline{C}$H$_3$)$_2$),

23.74 (Si-CH_2-$\underline{C}H_2$), 12.54 (Si-CH_2), 1.06, 0.92, 0.49, -0.34 (TMS-Si-CH_3)-3.74 (Si-CH_3).

General Procedure for the Reaction of D(+)-glucono-δ-Lactone (6) with Aminosilanes

A mixture of **6** and the aminosilane was refluxed in methanol under nitrogen atmosphere for 30 minutes. The solvent was removed under reduced pressure and the residual crystals were dried.

9a: 7.13 g (40 mmol) **6**, 7.65 g (40 mmol) **8a**, 70 ml methanol. Yield: 12.67 g (86 %)

Fp. 103-104°C.

^{1}H-NMR (DMSO+D_2O): 7.63 (bs; 1H; NH), 4.70-3.30 (m; 11H; H-2,3,4,5,6,6', 5OH), 3.69 (q; 4H; 2(O-CH_2), 3.13-2.94 (m; 2H; NH-C$\underline{H}_2$), 1.54-1.32 (m; 2H; NH-CH_2-C$\underline{H}_2$), 1.10 (t; 6H; 2(O-CH_2-C$\underline{H}_3$), 0.58-0.40 (m; 2H; Si-CH_2), -0.02 (s; 3H; Si-CH_3).

^{13}C-NMR (DMSO):172.21 (C=O), 73.60, 72.39, 71.42, 70.05 (C-2,3,4,5), 63.31 (C-6).

57.37 (O-CH_2), 41.06 (NH-CH_2), 22.69 (NH-CH_2-$\underline{C}H_2$), 18.26 (O-CH_2-$\underline{C}H_3$), 10.6 (Si-CH_2), -4.95 (Si-CH_3).

9b: 0.534 g (3 mmol) **6**, 0.658 g (3 mmol) **8b**, 5 ml methanol. Yield: 1.19 g (100%).

^{1}H-NMR (DMSO+D_2O):7.70 (bs; 1H; NH), 4.70-3.30 (m; 13H; H-2,3,4,5,6,6', 5OH, 2C$\underline{H}$-(CH_3)$_2$), 3.17-3.00 (m; 2H; NH-C$\underline{H}_2$), 1.55-1.38 (m; 2H; NH-CH_2-C$\underline{H}_2$), 1.18, 1.14 (2s; 12H; 2CH-(C$\underline{H}_3$)$_2$), 0.58-0.43 (m; 2H; Si-CH_2), 0.10 (s; 3H; Si-CH_3).

^{13}C-NMR (DMSO): 172.58 (C=O),73.99, 72.98, 71.80, 70.41 (C-2,3,4,5), 64.58 ($\underline{C}$H-(CH_3)$_2$), 63.69 (C-6), 41.54 (NH-CH_2), 25.98 (CH-($\underline{C}H_3$)$_2$), 23.28 (NH-CH_2-$\underline{C}H_2$), 12.05 (Si-CH_2), -3.57 (Si-CH_3).

9c: 7.1 g (40 mmol) **6**, 8.9 g (40 mmol) **8c**, 70 ml methanol. Yield: 15.1 g (94 %).

^{1}H-NMR (DMSO+D_2O):7.62 (bs; 1H; NH), 4.40-3.30 (m; 11H; H-2,3,4,5,6,6', 5OH), 3.72 (q; 6H; 3(O-CH_2), 3.13-2.97 (m; 2H; NH-C$\underline{H}_2$), 1.55-1.38 (m; 2H; NH-CH_2-C$\underline{H}_2$), 1.13 (t; 9H; 3(CH_3), 0.60-0.43 (m; 2H; Si-CH_2).

^{13}C-NMR (DMSO):172.23 (C=O), 73.59, 72.40, 71.42, 70.06 (C-2,3,4,5), 63.32 (C-6), 57.63 (O-CH_2), 40.94 (NH-CH_2), 22.64 (NH-CH_2-$\underline{C}H_2$), 18.10 (CH_3), 7.23 (Si-CH_2).

9d: 0.9 g (5 mmol) **6**, 1.32g (5 mmol) **8d**, 10 ml methanol. Yield: 1.9 g (88 %).

^{1}H-NMR (DMSO+D_2O): 7.70 (bs; 1H; NH), 4.70-3.30 (m; 14H; H-2,3,4,5,6,6', 5OH ,3C<u>H</u>-$(CH_3)_2$), 3.16-3.02 (m; 2H; NH-C<u>H_2</u>), 1.54-1.41 (m; 2H; NH-CH_2-C<u>H_2</u>), 1.18, 1.14 (2s; 18H; 3CH-(C<u>H_3</u>)$_2$), 0.60-0.43 (m; 2H; Si-CH_2).

^{13}C-NMR (DMSO): 172.30 (C=O), 73.99, 72.97, 71.81, 70.42 (C-2,3,4,5), 64.65 (<u>C</u>H-$(CH_3)_2$), 63.70 (C-6), 41.45 (NH-CH_2), 25.74 (CH-(<u>C</u>$H_3)_2$), 23.27 (NH-CH_2-<u>C</u>H_2), 9.12 (Si-CH_2).

1,2-O-Isopropylidene-N-(3-diisopropoxymethylsilyl)-propyl-glucuronic Acid Amide (10)

1.9 g (9 mmol) 7 and 1.9 g (9 mmol) 8b were stirred in 50 ml toluene at 60°C for 2 hours. The solvent was removed under reduced pressure, the residue was purified by treatment with carbon black. Yield: 3.7 g (98 %).

^{1}H-NMR (DMSO-d_6): 8.05 (m, 1H, CO-NH), 5.85 (d, 1H, H-1), 5.70 u. 5.50 (m, 2H, C3-OH, C5-OH), 4.40 (d, 1H, H-2, H-3, H-4, H-5), 4.20–4.00 (m, 3H, H-2, H-3, H-4, H-5), 4.10 (m, 2H,CH-CH_3,) 3.20–3.00 (m, 2H, N-CH_2-), 1.55–1.35 (m, 2H, Si-CH2-CH2), 1.40 u. 1.25 (s, 6H, C-CH_3), 1.15 u. 1.10 (s, 12H, CH-CH_3), 0.60–0.45 (m, 2H, Si-CH_2), 0.10 (s, 3H, Si-CH_3).

2,4,6,8-Tetramethyl-tetra-(1,2-4,6-tetratrimethylsilyl-3-O-propylgluco-pyra-nosyl)-cyclootetrasiloxane (12a)

0.36 g (1.50 mmol) **11** and 0.1 ml 0,05% $H_2PtCl_6.6H_2O$ solution in isopropanol were added to 3.0 g (5.88 mmol) **1d** at 90°C and stirred for 30 minutes. The product was dissolved in chloroform and treated with carbon black. After filtration the solvent was removed under reduced pressure and the residue was stirred at 100°/0,003 mbar for 8 hours to remove unreacted **11**. Yield: 3.2 g (95%)

^{1}H-NMR ($CDCl_3$): 0.0–0.2 (m; -Si-CH_3; 156 H), 0.3–0.5 (m; -Si-CH_2-; 8 H), 1.45–1.8 (m; -CH_2-C<u>H_2</u>-CH_2-; 8 H), 3.0–3.8 (m; H^2, H^3, H^4, H^6, -C<u>H_2</u>-O-, 32 H), 4.4 (d; H^1; 4 H).

Elemental analysis ($C_{88}H_{208}O_{28}Si_{20}$, %)

Calculated:	C 46.43	H 9.20
Found:	C 45.97	H 9.30

2,4,6,8-Tetramethyl-tetra-(3-O-propylglucopyranosyl)-cyclootetrasiloxane (12b)

1.91 g (0.84 mmol) **12a** was refluxed in 100 ml methanol/water (1:1) for 48 hours. The foaming solution was distilled carefully to yield 0.6 g (36%) yellow crystalline residue.

Fp 112-116°C

^{1}H-NMR ($CDCl_3$): 0.0–0.2 (m; -Si-CH_3; 120 H), 0.3–0.6 (m; -Si-CH_2-; 8 H), 1.45–1.8 (m; -CH_2-C<u>H</u>$_2$-CH_2-; 8 H), 3.0–4.0 (m; H^2, H^3, H^4, H^6, -C<u>H</u>$_2$-O-, -OH; 36 H), 4.4 and 4.9 (d; $H^{1(\alpha,\beta)}$; 4 H).

Elemental Analysis ($C_{40}H_{80}O_{28}Si_4$, %)

Calculated:	C 42.84	H 7.19
Found:	C 41.97	H 6.90

Isopropyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-6-O-acetyl-2,3-di-deoxy-α-D-*erythro*-hex-2-enopyranoside (14)

A solution of 5 g (8.92 mmol) **13b** in 25 ml dichloromethane was cooled to 0-5°C under nitrogen atmosphere and 0.5 ml bortrifluorid-etherate was added. After stirring for 25 minutes. a solution of 0.91 g (8.97 mmol) triethylamine in 15 ml dichloromethan was added and the mixture was shaken with 100 ml water. The organic phase was separated, dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was dissolved in methanol, precipitated with water, filtered and dried. Yield: 4.6 g (92 %)

Fp.: 111-113°C

Elemental Analysis: ($C_{25}H_{36}O_{14}$,%)

Calculated:	C 53.57	H 6.47
Found:	C 53.14	H 6.47

^{1}H-NMR ($CDCl_3$): 6.1 (d, 1 H, H-2), 6.25 (ddd, 1 H, H-3), 5.25-4.95 (m, 4 H, H-1,2´,3´,4´), 4.65 (d, 1 H, H-1´), 4.35-3.9 (m, 6 H, -O-C<u>H</u>$(CH_3)_2$, H-4,6a,6b,6a´,6b´), 3.8-3.6 (m, 2 H, H-5,5´),2.2-1.95 (m, 15 H, CH_3- Acetyl), 1.25, 1.2 (2 d, je 3 H, (C<u>H</u>$_3)_2$CH-).

^{13}C-NMR ($CDCl_3$): 170.72, 170.60, 170.24, 169.36 (5 > C=O), 130.97 (C-3), 127.69 (C-2), 101.61 (C-1´), 92.70 (C-1), 73.47, 72.68, 71.70, 71.30, 70.49, 68.24, 67.18 (C-4,5,2´,3´,4´,5´, -O-<u>C</u>H$(CH_3)_2$), 63.15 (C-6), 61.86 (C-6´), 23.48, 21.91 (-O-CH(<u>C</u>H$_3)_2$), 20.81, 20.69, 20.56 (5 CH_3- Acetyl).

Allyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-6-O-acetyl-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside (15)

15 was prepared according to the procedure for the preparation of 14 from 4 g (7.13 mmol) 13b, 0.95 g (16.4 mmol) allylalcohol, 20 ml dichloromethane, 0.4 ml bortrifluoride-etherat and 0.73 g (7.17 mmol) triethylamine. Yield: 3.74 g (93.9%).

Fp.: 110-113 °C

Elemental analysis ($C_{25}H_{34}O_{14}$ %)

Calculated:	C 53.76	H 6.14
Found	C 54.02	H 6.27

^{1}H-NMR ($CDCl_3$): 6.1 (d,1 H, H-2), 6.0-5.85 (m, 1 H, -C<u>H</u>=CH_2), 5.75 (ddd, 1 H, H-3), 5.35-4.9 (m, 6 H, =CH_2, H-1,2´,3´,4´), 4.65 (d, 1 H, H-1´), 4.35-3.95 (m, 8 H, H-4,5,6a,6b,6a´,6b´, -O-C<u>H</u>$_2$-CH=CH_2), 3.75-3.6 (m, 1 H, H-5´), 2.2-1.9 (m, 15 H, CH_3-).

^{13}C-NMR ($CDCl_3$): 170.62, 170.52, 170.16, 169.30, 169.24 (5 > C=O), 134.09 (-<u>C</u>H=CH_2), 131.40 (C-3), 127.00 (C-2), 117.25 (-CH=<u>C</u>H_2), 101.58 (C-1´), 93.51 (C-1), 73.29, 72.63, 71.71, 71.26, 69.08, 68.22, 67.38 (C-4,5, 2´,3´,4´,5´, -O-<u>C</u>H_2-CH=CH_2), 62.96 (C-6), 61.82 (C-6´), 20.80, 20.65, 20.52 (5 CH_3-).

1-O-(Diisopropoxymethylsilyl)-propyl-4-O-(2,3,4,6-tetra-O-acetyl-gluco-pyranosyl)-6-O-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (16)

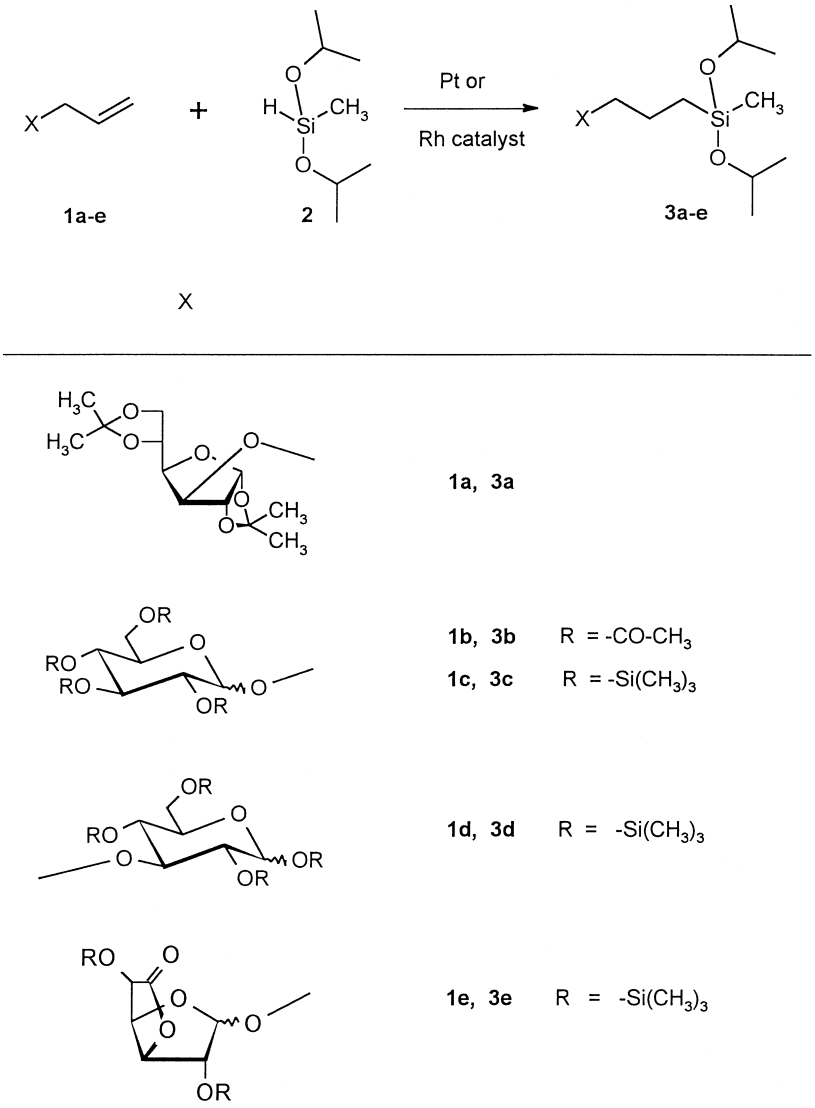
A solution of 0.86 g (1.54 mmol) **15**, 0.25 g (1.54 mmol) **2** and 4 drops of Karstedt's catalyst was stirred at 80°C under nitrogen for 18 hours. The solvent was removed under reduced pressure to yield pure **15**. Yield: 1.11 g (100 %)

^{1}H-NMR ($CDCl_3$): 6.05 (d, 1 H, H-2), 5.75 (d, 1 H, H-3), 5.25-4.9 (m, 4 H, H-1,2´,3´,4´), 4.6 (d, 1 H, H-1´), 4.3-3.9 (m, 7 H, H-4,6a,6b,6a´,6b´, -O-C<u>H</u>$(CH_3)_2$), 3.9-3.3 (m, 4 H, -O-C<u>H</u>$_2$-CH_2-CH_2-Si-, H-5,5´), 2.2-1.95 (m, 15 H, CH_3- Acetyl), 1.75-1.5 (m, 2 H, -O-CH_2-C<u>H</u>$_2$-CH_2-Si-), 1.15 (d, 12 H, (C<u>H</u>$_3)_2$CH-), 0.55 (dd, 2 H, -CH_2-Si-), 0.1 (s, 2 H, CH_3-Si-).

^{13}C-NMR ($CDCl_3$): 170.64, 170.51, 170.16, 169.31, 169.25 (5 >C=O), 131.15 (C-3), 127.14 (C-2), 101.70 (C-1´), 94.31 (C-1), 74.45, 73.66, 73.36, 72.66, 71.70, 71.23, 68.22, 67.27, 64.63 (C-4,5,2´,3´,4´,5´, 2x -O-<u>C</u>H$(CH_3)_2$, -O-<u>C</u>H_2-CH_2-CH_2-Si), 63.02 (C-6), 61.83 (C-6´), 25.65, 25.44 (2x -O-CH(<u>C</u>$H_3)_2$), 21.39, 20.81, 20.64, 20.52 (5 CH_3- Acetyl, -O-CH_2-<u>C</u>H_2-CH_2-Si), 11.00 (-O-CH_2-CH_2-<u>C</u>H_2-Si), -4.02 (CH_3-Si).

RESULTS AND DISCUSSION

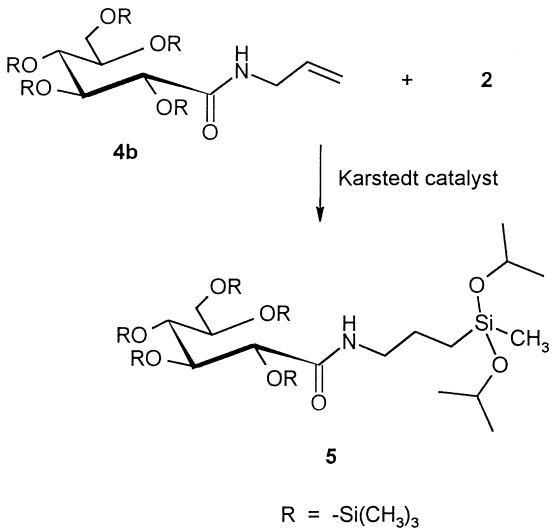
Diisopropoxymethylsilane (**2**) was reacted with allyl derivatives of glucose protected by isopropylidene- (**1a**) acetyl- (**1b**) and trimethylsilyl (TMS) (**1c, 1d**) groups under standard hydrosilylation conditions. No reactions or low yields were obtained with common Speier's catalyst ($H_2PtCl_6.6H_2O$), whereas a



Scheme 2.

Pt-complex prepared from Na_2PtCl_4 and tetramethyltetravinyl-cyclotetra-siloxane as catalyst (Karstedt's catalyst) afforded the dialkoxysilanes **3a-e** in 82-95% yields, (Scheme 2).

Hydrosilylation of TMS protected allyl-D-glucofuranosidurono-6,3-lactone (**1e**) with **2** in the presence of Karstedt's catalyst yielded a mixture of **3e** and hydrogenated **1e**, whereas with $Rh(PC_6H_5)_3Cl$ (Wilkinson's catalyst) only < 5%



Scheme 3.

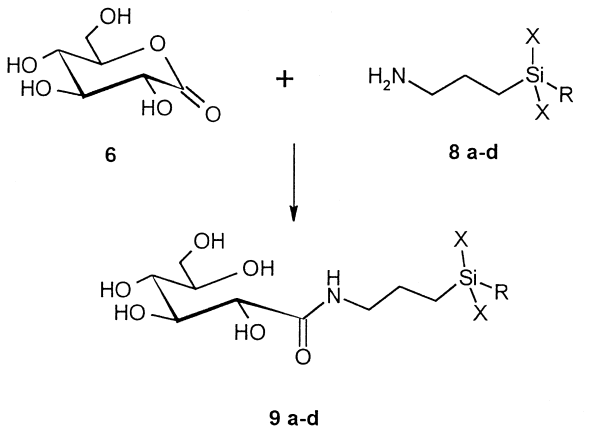
of this byproduct was formed. The monomer **3e** enables the incorporation of reactive sugar lactone residues into silicones.

Dialkoxysilanes containing gluconic acid amide residues were obtained by two different synthetic routes:

N-allyl gluconic acid amide (**4a**) was converted to the TMS protected derivative **4b** by reaction with hexamethyldisilazane and subsequently hydrosilylated with **2** yielding the gluconamide substituted diisopropoxysilane **5** in 97% yield (Scheme 3). Very recently, it was reported that due to the amide structure aldonic acid amides can be hydrosilylated only with a special prepared bis (dialkylsulfido)platinum(II) catalyst. We found that Karstedt's catalyst is also suitable for the hydrosilylation of such amides in almost quantitative yields.

Similar gluconic- and glucuronic acid amide substituted alkoxysilanes could be prepared by reaction of unprotected D(+)-glucono-δ-lactone (**6**) or isopropylidene protected D(+)-glucofuranosidurono-6,3-lactone (**7**) with various 3-aminopropyl-silanes (**8a-d**, Scheme 4). Thus the dialkoxysilanes **9a** (86%), **9b** (98%), **10** (98%) and the trialkoxysilanes **9c** (95%) and **9d** (88%) were obtained.

Equilibration reactions of cyclic siloxanes, for example octamethylcyclotetrasiloxane (OMCTS) are among the major routes to PDMS. For the introduction of functional groups by this reaction appropriate functionalized cyclosiloxanes are required. For this purpose the glucose substituted cyclosiloxane **12a** was prepared from 2,4,6,8-tetramethylcyclotetrasiloxane (**11**) and TMS-

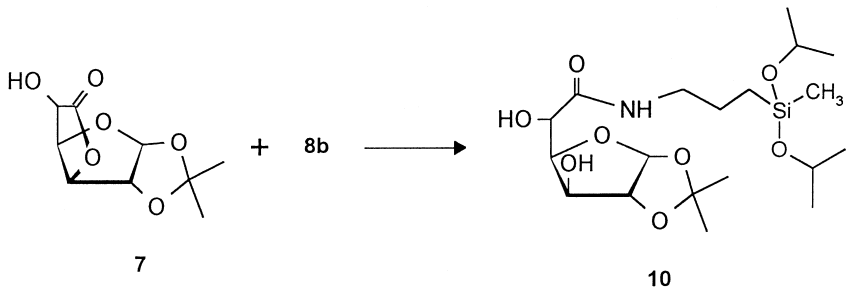


8a, 9a R = $-CH_3$, X = $-OC_2H_5$

8b, 9b R = $-CH_3$, X = $-OCH(CH_3)_2$

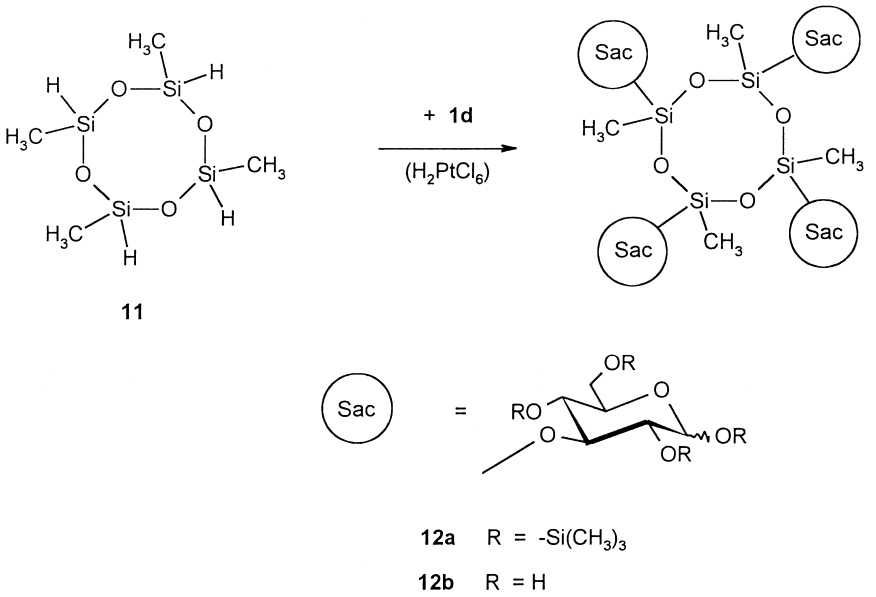
8c, 9c R = X = $-OC_2H_5$

8d, 9d R = X = $-OCH(CH_3)_2$



Scheme 4.

protected 3-O-allylglucose (**1d**) using $H_2PtCl_6.6\ H_2O$ as catalyst (Scheme 5). This hydrosilylation was performed without solvent and can be controlled by the molar ratio of the reactants. Less than four moles of **1d** per mole of **11** results in mixtures of partially substituted cyclosiloxanes, an excess of **1d** yields the fully substituted product **12a** from which unreacted **1d** was difficult to remove. Thus a molar ratio of 1:3.9 moles of **1d** were used giving almost pure **12a** after removal of unreacted **11**, as was demonstrated by ^{1}H-NMR-spectroscopy. The TMS protected cyclosiloxane **12a** can be converted to the hydrophilic water soluble cyclosiloxane **12b** by treatment with methanol/water, but advantageously



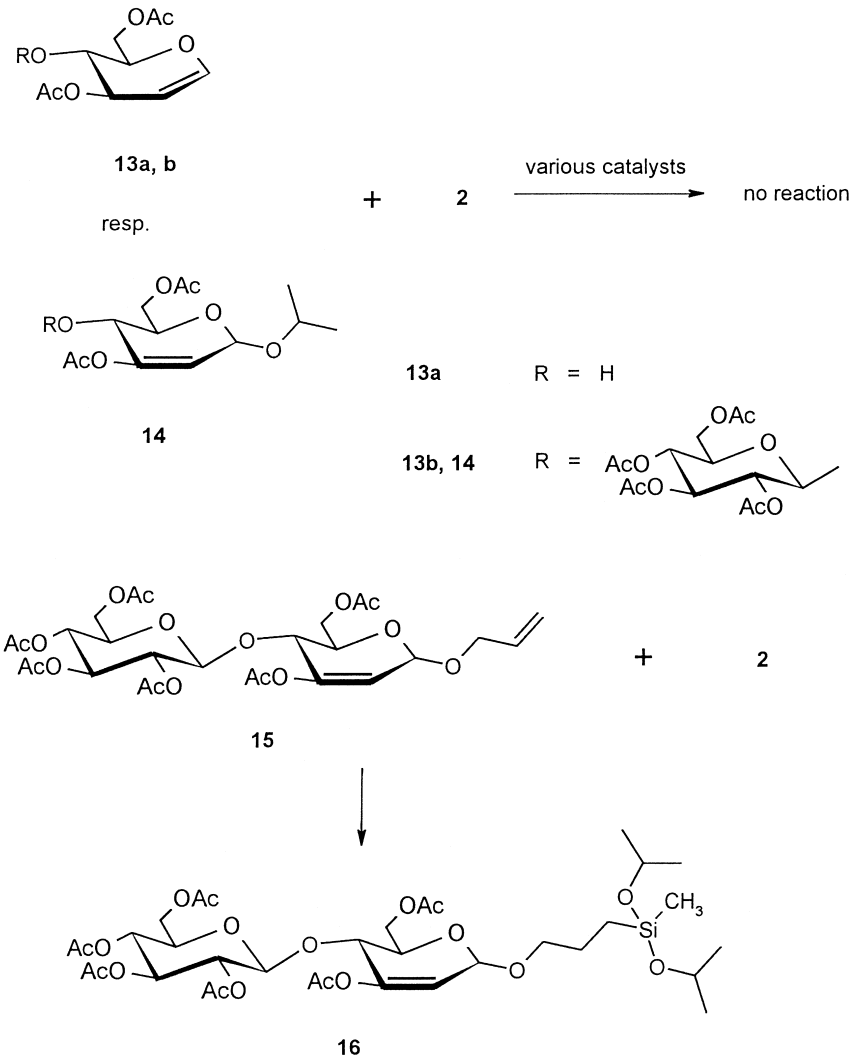
Scheme 5.

12a can be used for equilibration reactions due to its better solubility in apolar media.

In addition, acetylated glycals were used as easily available unsaturated sugar derivatives for the hydrosilylation experiments. For this purpose, 3,4,6-tri-O-acetylglucal (**13a**) and 3,6,2',3',4',6'-hexa-O-acetylcellobial (**13b**) were prepared by reduction of the acetylated bromides in quantitative yield according to the literature.

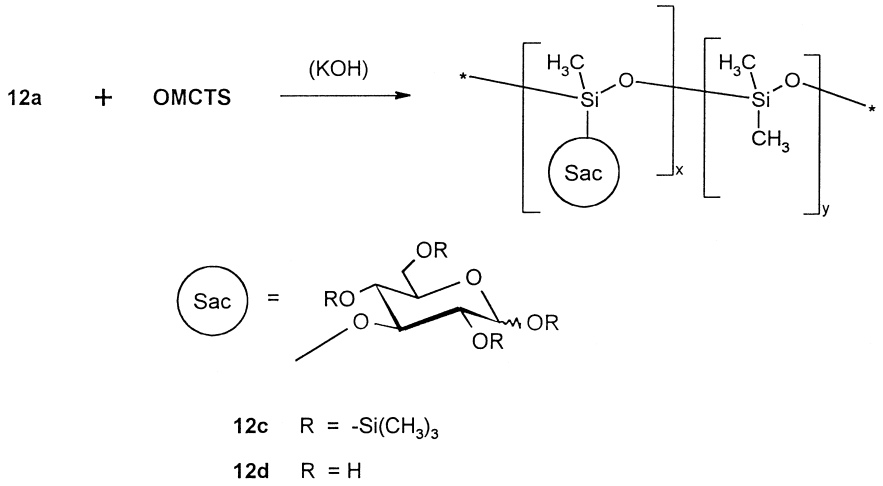
However, all attempts for the hydrosilylation of **13a** and **13b** with **2** using various catalysts (H_2PtCl_6, Karstedt's catalyst, $(Ph_3P)_2PdCl_2$, and $(Ph_3P)_3$ RhCl) and under various reaction conditions failed. Also, the unsaturated isopropyl cellobioside **14** obtained from **13b** and isopropanol failed to react with **2** (Scheme 6). The lack of reactivity of these sugar derivatives having double bonds in the ring may be attributed to the vinyl ether structure in **13a,b** resp. sterical hindrance in **14**, since reaction of **2** with the allyl cellobioside **15** in the presence of Karstedt's catalyst yielded 95% of the expected alkoxysilane **16**. Other catalysts resulted in mixtures of **16** and its hydrogenated product.

Preliminary equilibration reactions of the functional cyclosiloxane **12a** with OMCTS demonstrated the possibility to prepare polysiloxanes with pen-



Scheme 6.

dant glucose residues, the degree of substitution of which can be adjusted by the molar ratio of the reactants (Scheme 7). Thus a PDMS containing 11 mmol glucose residues/g was prepared (**12c**) and after splitting the TMS-groups by treatment with methanol/water a hygroscopic solid **12d** was obtained the aqueous solution of which was shown to have a surface tension of about 30 mN/m. Condensation reactions of the di- and trialkoxysilanes **3c** or **9c** resulted cross-linked polymers.



Scheme 7.

The results of these investigations and properties of the sugar modified linear and crosslinked polysiloxanes will be presented more detailed in forthcoming papers.

CONCLUSION

Previously unreported silane monomers containing carbohydrate residues were prepared by hydrosilylation of allyl ethers of carbohydrates with dialkoxysilanes and OCTMS as well as by reaction of sugar lactones with aminopropylsilanes. The choice of the appropriate catalyst was found to be essential for the reactivity and yields in these hydrosilylation reactions. The monomers are useful for the preparation of linear and crosslinked poly(siloxane)s containing hydrophilic residues as well as for sol-gel reactions.

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