Synthesis of difunctional 1,4-dimethyl-1,4-disilacyclohexanes

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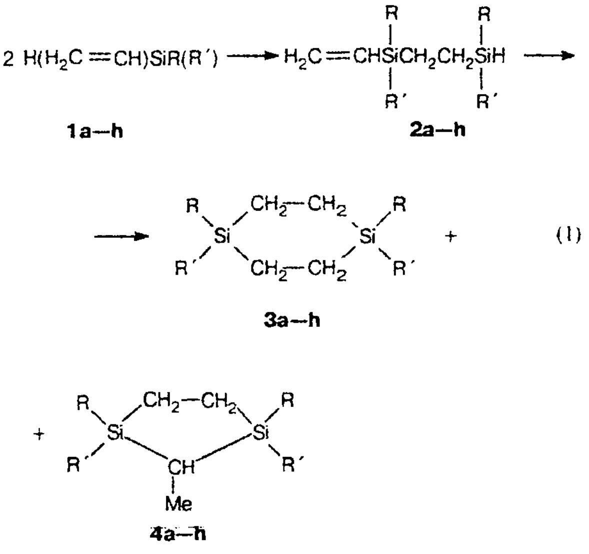
Transformations of $HVinSiCl_2$, HVinSi(Me)Cl, HVinSi(Me)Ph, and $HVinSi(Me)NEt_2$ in the presence of Pt catalyst were studied. In dilute solutions, the reaction gave a mixture of structural and stereoisomers of five- and six-membered disilacyclanes, resulting from intramolecular cyclization of the initially formed linear dimer. In the case of methyl(phenyl)disilacyclane, the structural isomers were separated and *trans*-1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohexane was isolated. The reaction of this product with HCl in the presence of $AlCl_3$ followed by hydrolysis resulted in the synthesis of *trans*-1,4-dichloro- and *trans*-1,4-dihydroxy-1,4-dimethyl-1,4-disilacyclohexanes. The structures of the structural and stereoisomers synthesized were confirmed by ^1H, ^{13}C, and ^{29}Si NMR and IR spectroscopies and mass spectrometry.

Key words: hydrosilylation, chlorination, hydrolysis, intramolecular cyclization, disilacycloalkanes, structural and stereoisomerism.

The purpose of this work was an attempt to prepare difunctional 1,4-diorgano-1,4-disilacyclohexanes, which could serve as the basis for the synthesis of cyclolinear polyorganocarbosiloxanes or polyorganocarbosilanes. These polymers present a certain interest as self-organizing systems and can be used to prepare monomolecular Langmuir films. No data on polymers with disilacyclohexane units in the chain can be found in the literature. Organodisilacyclanes are formed in 5–19% yields as by-products in the syntheses of linear polycarbosilanes by polyaddition of organovinylhydrosilanes in the presence of Pt catalysts.[1–10]

Based on IR spectra, organodisilacyclanes prepared from vinylhydrogensilanes **1a–d** *via* linear dimers **2a–d** (reaction (1)) were assumed[1] to have structures **3a–d** and **4d**. Later, it was found by NMR spectroscopy that they are mixtures of structural isomers, whose ratio depends on the substituents at the silicon atom.[2] In a study of stepwise hydrosilylation of dimethyl(divinyl)silane with chlorodimethylsilane followed by reduction of $ClMe_2SiCH_2CH_2SiMe_2Vin$ isolated in the first step, it has been shown that structural isomers are formed from dimethyl(vinyl)silane (**1a**) at the step of intramolecular cyclization; the ratio of five- to six-membered disilacyclanes is 70 : 30.[3] Compound **3a** was synthesized from bis(trimethylsilyl)ethane by elimination of $SiMe_4$ in the presence of $AlBr_3$ [4,5] and by methylation of tetrachlorodisilacyclohexane **3e**.[6] Crystalline compounds **3e,f** were isolated from the products of polyaddition of dichlorovinylsilane (**1e**) and chloro(phenyl)vinylsilane (**1f**) in 5 and 9% yield, respectively,[7] whereas chloro(methyl)vinylsilane (**1g**) and chloro(ethyl)vinylsilane form mixtures of structural isomers of disilacyclanes **3** and **4**.[7] However, based on the data on the reduction of the reaction mixture, it was concluded[8,9] that dichlorosilane **1e** is also converted into a mixture of isomers **3e** and **4e**. Note that 1,1,4,4-tetrafluoro-1,4-disilacyclohexane was obtained by hydrosilylation of diphenyldivinylsilane by diphenylsilane followed by chlorination and fluorination.[10]



	a	b	c	d	e	f	g	h
R	Me	Et	Ph	Me	Cl	Ph	Me	Me
R′	Me	Et	Ph	Ph	Cl	Cl	Cl	NEt_2

We studied three possible approaches to the synthesis of difunctional diorganodisilacyclohexanes. One of them

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is based on the preparation of 1,1,4,4-tetrachloro-1,4-disilacyclohexane (**3e**) followed by Grignard phenylation. Upon homohydrosilylation of dichlorovinylsilane (**1e**) in the presence of a Pt complex of tetramethyldivinyldisiloxane (Carsted catalyst) in hexane, we obtained products (18%) which partially crystallized during distillation. Judging by the ^{1}H NMR spectroscopy and GLC data, the crystals separated by filtration represented compound **3e** of 90% purity. The liquid product was found to be a mixture of isomers **4e** and **3e** in 85 : 15 ratio. However, the reaction of this mixture with phenylmagnesium bromide did not give compound **3f**.

We further studied homohydrosilylation of diethylamino(methyl)vinylsilane (**1h**) in the presence of the Carsted catalyst and $H_2PtCl_6 \cdot 6H_2O$ both in solution and without a solvent. The reaction in hexane gave 5% distillable products. According to GLC, the product isolated by distillation was a mixture of three compounds. The chemical shifts and absorption bands observed in the ^{1}H NMR and IR spectra correspond to the $SiCH_2CH_2Si$, SiCH(Me)Si, CH_2=CHSi, and HSi groups, indicating the presence of three structural isomers **2h**—**4h**, *i.e.*, intramolecular hydrosilylation in solution does not occur completely. We were unable to separate the isomers by conventional techniques. Even under rigorous conditions (7 h at 200—215 °C), intramolecular hydrosilylation in block did not occur to completion, and unreacted Si—Vin and Si—H groups remained in the polymer.

The third approach to the synthesis of difunctional diorganocyclohexanes studied here is based on homohydrosilylation of chloro(methyl)vinylsilane (**1g**) in a 10% hexane solution in the presence of the Carsted catalyst. This gave volatile products (17%); judging by the ^{1}H NMR spectrum, they were a mixture of isomers **4g** and **3g** in 65 : 35 ratio, which is consistent with the published data.[7]

Comparison of published data with those obtained in this study shows that the structural isomers can be separated for R′ = Cl and Ph, because in these cases, isomer **3** predominates. We decided to separate isomers **3d** and **4d**, in view of the fact that the majority of organosilicon compounds with phenyl substituents exhibit an enhanced tendency for crystallization.

We studied the influence of the concentration of the solution (in hexane or toluene) and the type of Pt catalyst used (H_2PtCl_6, Carsted catalyst, metallic and bimetallic Pt and Pt/Pd colloids in a polystyrene—4-vinylpyridine block copolymer micelle) on the yield and the composition of the cyclic products of homohydrosilylation of methyl(phenyl)vinylsilane (**1d**). According to ^{1}H and ^{13}C NMR spectra, the type of the catalyst does not influence significantly the quantitative or qualitative composition of the resulting structural and stereoisomers. Dilution of the reaction mixture increases the yield of distillable products to 35—40%. According to ^{1}H NMR spectra, the products distilled after the synthesis in a 1% hexane—toluene solution contained up to 1.5% linear dimer **2d** apart from isomers **3d** and **4d**. The reaction in a 10% solution afforded up to 30% of a mixture of disilacyclanes **3d** and **4d** without linear isomer **2d**. Analysis of the ^{1}H NMR spectra of this mixture shows that the δ 0.16—0.37 region has five signals due to the methyl groups at the silicon atoms; of these signals, three low-field signals correspond to the five-membered disilacyclane **4d**. This assignment was based on the integrals of the three doublets due to the protons of the methyl group attached to the CH group, occurring at 0.811—0.831, 1.007—1.026, and 1.190—1.209 ppm. Two high-field signals corresponding to the protons of the Me groups at the silicon atoms belong apparently to two stereoisomers, *cis*- and *trans*-1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohexane (**3d**).

After some period at room temperature, crystals (10—12%) precipitate from a mixture of disilacyclanes **3d** and **4d**. According to GLC data, this substance becomes chromatographically pure after recrystallization. Single crystals grown from a solution proved to be systematic twins, which precluded their complete X-ray diffraction study. The differential scanning calorimetry (DSC) curves of the crystal of **3d** exhibit one peak, matched by the melting point at 93 °C.

Since the X-ray diffraction study did not allow us to find out which of the spatial isomers had been isolated as crystals, we attempted to elucidate their structure more precisely using a semiempirical method based on the use of increments for some organocyclotetrasiloxanes found by ^{1}H NMR spectroscopy.[13] The ^{1}H NMR spectrum of a mixture of disilacyclanes **3d** and **4d** recorded in a CCl_4—C_6D_6 mixture, in addition to complex multiplets at δ 7.1—7.5 and 0.8—1.3 due to the protons of the phenyl and methylene groups, exhibits two singlets at δ 0.223 and 0.178 with a ratio of integral intensities of 1.0 : 0.3, corresponding to the protons of the methylsilyl groups of the *cis*- and *trans*-isomers of **3d**. The crystalline product isolated from the mixture exhibits a high-field ^{1}H NMR signal at δ 0.178 due to the methylsilyl groups. Data on the increments for a phenyl group and a hydrogen atom can be found in the literature but no data for methyl groups have been reported. However, in view of the fact that the protons of two methyl groups at one silicon atom in the two stereoisomers of planar organocyclotetrasiloxanes are indistinguishable and are identical for *cis*- and *trans*-isomers, it can be assumed with a high degree of certainty that the effects of the methyl group and the hydrogen atoms attached directly to silicon on the chemical shifts of the protons of the Me groups attached to the neighboring silicon atom are nearly identical. In this case, an estimate of chemical shifts by the increment scheme[13] shows that the signal of the methyl group in the *trans*-isomer should be shifted upfield from the corresponding signal of the *cis*-isomer by 0.045 ppm. Based on this fact, we believe that the crystalline product that we isolated is the *trans*-isomer of **3d**.

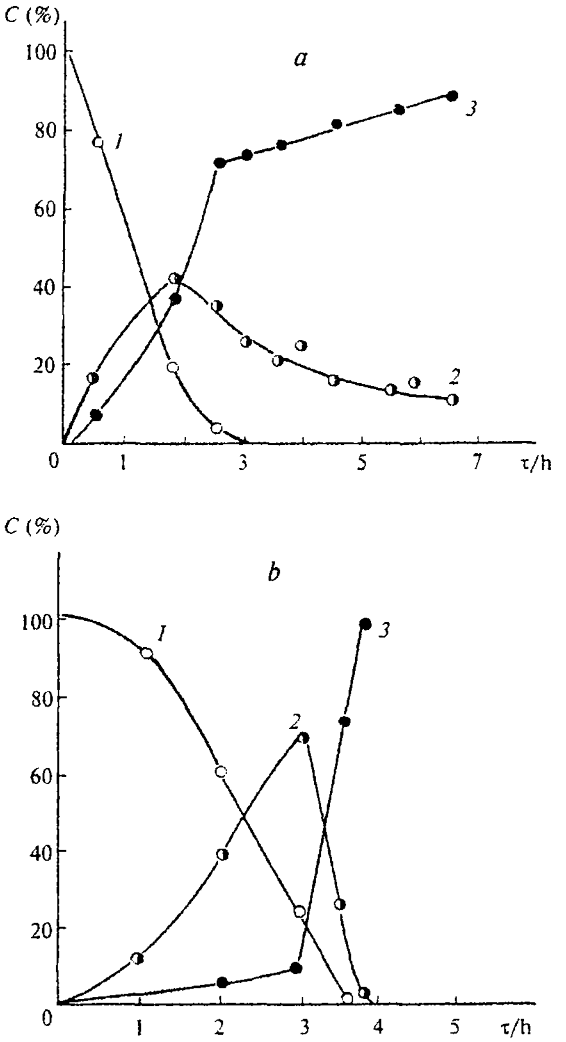
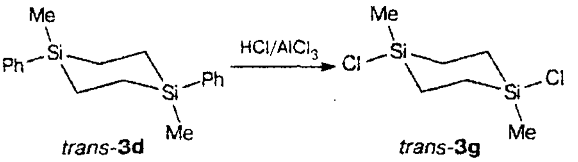


Fig. 1. Curves for the conversion (*1*) of *trans*-**3d** (*a*) and a mixture of isomers **3d** and **4d** (*b*) and accumulation of chloro(dimethyl)phenyldisilacyclanes (*2*) and dichloro(dimethyl)disilacyclanes (*3*) at room temperature; $[AlCl_3]$ = 25.0 mol.% (*a*) and 27.5 mol.% (*b*).

Study of the reaction of *trans*-**3d** and a mixture of structural and stereoisomers **3d** and **4d** with gaseous HCl in the presence of $AlCl_3$ in benzene at room temperature showed that the amount of $AlCl_3$ and the flow rate of HCl influence the rate of the reaction. The reaction affords monochlorinated dimethyl(phenyl)disilacycloalkane and then the dichlorinated derivative (Fig. 1). In the presence of 5—10 mol.% $AlCl_3$, the phenyl groups were not completely substituted by chlorine atoms over a period of 10 h, and when the proportion of the catalyst was >40 mol.%, replacement of the methyl groups and even ring opening in silacyclanes also occurred. The mass spectrum of the product of more extensive chlorination was found to exhibit a peak with *m/z* 232, whereas that of the product obtained under milder conditions contained a peak with *m/z* 212.

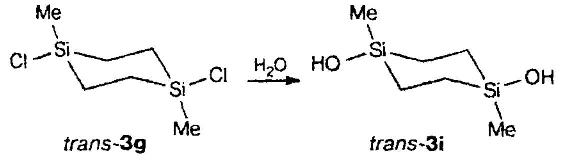
When the crystalline isomer *trans*-**3d** is treated with HCl and $AlCl_3$, crystalline dichloride **3g** is formed.



(2)

During storage, crystals partially precipitate from the products formed upon treatment of the isomer mixture with HCl in the presence of $AlCl_3$. Judging by the ^1H NMR spectrum, the crystals correspond to dichloride **3g** formed from the individual isomer *trans*-**3d**.

Hydrolysis of the crystalline dichloride **3g** in a neutral medium afforded a crystalline compound, which was identified as 1,4-dihydroxy-1,4-dimethyl-1,4-disilacyclohexane (**3i**) based on ^1H, ^{13}C, and ^{29}Si NMR and IR spectra.



(3)

The isomer mixture of chlorinated derivatives **3g** and **4g** was converted into a mixture of dihydroxy derivatives **3i** and **4i**.

The IR spectra of the isolated compounds **3d,g,i** exhibit absorption bands at ν ~1000 (vw), 1070, and 1120 cm^{-1}, typical of stretching and deformation vibrations of bonds in the $Si—CH_2—CH_2—Si$ group.[5]

The replacement of Cl at a silicon atom (by, *e.g.*, an OH group) is known to be accompanied in most cases by inversion[14,15]; however, in sterically hindered molecules retention of the configuration can also be observed.[16] It was found previously that during the hydrolysis of dichlorocyclosiloxanes, configuration at the silicon atom does not change.[17] Since the chlorination and the subsequent hydrolysis in disilacyclohexane **3d** can involve two centers, Si—Ph and Si—Cl, double inversion would result in a final configuration of the products of transformation of disilacyclohexane **3d** *via* reactions (2) and (3) being identical to the initial configuration. If only one center is inverted, the other stereoisomer is formed. When isomer mixtures are introduced in reactions (2) and (3), dichloro and dihydroxy derivatives of disilacyclohexane **3g** and **3i** are formed as two stereoisomers, whose ^1H NMR spectra are characterized by signals of the methyl group protons at δ 0.410 (*trans*-**3g**) and 0.444 (*cis*-**3g**) or 0.032 (*trans*-**3i**) and 0.023 (*cis*-**3i**); the ratios of integral intensities are 0.5 : 1.0 and 0.8 : 1.0, respectively. The crystalline isomer *trans*-**3d** was converted into dichloro and dihydroxy derivatives (*trans*-**3g** and *trans*-**3i**), in which the proportions of the minor isomer did not exceed 5%, and the methyl group protons of the major isomer were manifested in the ^{1}H NMR spectra as singlets at δ 0.410 and 0.031, respectively. Since the content of the minor isomer was insignificant, it can be concluded that both reactions (2) and (3) occur with retention of the configuration. Thus, the crystalline products isolated in these reactions are *trans*-isomers.

Thus, we succeeded in isolating the individual isomer *trans*-**3d** from the mixture of methyl(phenyl)disilacycloalkanes obtained and in preparing the *trans*-isomers of difunctional dimethyldisilacyclohexanes **3g,i** based on it; these products can be used to prepare various cyclolinear polycarbosiloxanes and polycarbosilanes.

Experimental

IR spectra were recorded on a Specord M-82 spectrophotometer. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were measured on a Bruker AMX-400 spectrometer (400.13 MHz) using Me_4Si as the external standard. The ^{29}Si NMR spectra were recorded in the absence of the Overhauser effect; the delay between the pulses was 25 s. Chromatographic analysis was carried out on an LKhM-80 instrument (a 3 m×3 mm column, SE-30 on Chromaton, helium as the carrier gas, flow rate 30 mL min^{-1}, injector temperature 270 °C, katharometer as the detector, programmed increase in the column temperature from 50 to 300 °C). GC/MS analysis was carried out using a Kratos MS 890 mass spectrometer (UK) (70 eV, temperature of the ionization chamber 250 °C) equipped with a Carlo Erba Meda Series gas chromatograph with a capillary column (15 m) coated with a methylsiloxane elastomer. The operation mode was as follows: 4 °C min^{-1} from 30 to 400 °C, 10 °C min^{-1} up to 250 °C, and 15 min at 250 °C; helium at a flow rate of 2 mL min^{-1} was used as the carrier gas.

Dichlorovinylsilane was prepared by disproportionation of trichlorovinylsilane and phenylsilane in the presence of Bu^n_3N by a known procedure,[11] yield 61.5%, b.p. 67—68 °C.

Phenylsilane was prepared by the reduction of $PhSiCl_3$ with lithium aluminum hydride by a known procedure[1]; yield 74.0%, b.p. 120 °C, n_D^{20} 1.513.

Diethylamino(methyl)vinylsilane was prepared by partial amination of dichloro(methyl)vinylsilane followed by the reduction of chloro(diethylamino)(methyl)vinylsilane by lithium aluminum hydride, yield 57.0%, b.p. 135—138 °C, n_D^{20} 1.4250. Found (%): C, 58.0; H, 11.31; N, 9.81; Si, 20.2. $C_7H_{17}NOSi$. Calculated (%): C, 58.67; H, 11.95; N, 9.78; Si, 19.60.

Chloro(methyl)vinylsilane was prepared by the reaction of diethylamino(methyl)vinylsilane with dichloro(methyl)vinylsilane similarly to chlorodimethylsilane by a previously described procedure,[12] yield 59.5%, b.p. 62—64 °C. Ref. 18: b.p. 60 °C.

Chloro(methyl)(phenyl)vinylsilane was synthesized from $MeVinSiCl_2$ by the Grignard reaction with PhMgBr, yield 57.0%, b.p. 86—87 °C (10 Torr), n_D^{20} 1.5270. Ref. 1: b.p. 79—80 °C (3—4 Torr).

Methyl(phenyl)vinylsilane was prepared by the reduction of chloro(methyl)(phenyl)vinylsilane by lithium aluminum hydride, yield 84%, b.p. 54—55 °C (8 Torr), n_D^{20} 1.5125. Ref. 1: b.p. 56—57 °C (7 Torr).

Homohydrosilylation of methyl(phenyl)vinylsilane (1d). A 0.1 *N* solution of $H_2PtCl_6 \cdot 6H_2O$ (0.08 g) in THF was added to a solution of methyl(phenyl)vinylsilane (32.0 g, 0.21 mol) in 150 mL of toluene and 100 mL of hexane, the mixture was refluxed for 10 h, and the solvent was evaporated. Fractionation gave 9.8 g (31.0%) of a mixture of isomers **3d** and **4d**, b.p. 126—134 °C ($1 \cdot 10^{-2}$ Torr). Ref. 1: b.p. 135—137 °C (0.26 Torr). ^{1}H NMR (CCl_4—$CDCl_3$ 5 : 1),* δ: 0.107 (q, 1 H, CH, *J* = 7.6 Hz); 0.223 (s, 6 H, 2 CH_3Si, was assigned to *cis*-**3d**); 0.274, 0.299, 0.345 (all s, 6 H, 2 $\underline{CH_3}Si$); 0.361 (q, 1 H, CH, *J* = 6.8 Hz); 0.649 (q, 1 H, CH, *J* = 7.6 Hz); 0.775 (d, 3 H, CH_3, *J* = 6.8 Hz); 0.890—1.327 (m, 4 H, 2 CH_2Si); 0.998 (d, 3 H, CH_3, *J* = 7.6 Hz); 1.198 (d, 3 H, CH_3, *J* = 7.6 Hz); 7.100—7.550 (m, 5 H, H arom.). At –20 °C, 0.7 g of crystals precipitated from the resulting isomer mixture, m.p. 94—96 °C (from Pr^iOH or hexane); the crystalline compound was identified as *trans*-1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohexane (**3d**). ^{1}H NMR (CCl_4—C_6D_6), δ: 0.178 (s, 6 H, 2 CH_3Si); 1.020—1.125 (m, 8 H, 4 ring CH_2); 7.22—7.26, 7.46—7.49 (m, 10 H, 2 C_6H_5Si). ^{13}C NMR ($CDCl_3$—CCl_4), δ: −4.29 (4 ring CH_2); 7.73 (2 CH_3); 127.91—129.02 (C_p arom.); 138.59 (C_m, C_o arom.); 138.27 (C(Ph)—Si). ^{29}Si NMR (C_6D_6—CCl_4), δ: −5.12 (s, 2 Si).

Homohydrosilylation of dichlorovinylsilane 1e. A mixture of dichlorovinylsilane (**1e**) (16.0 g, 0.125 mol), 110 mL of hexane, and $1 \cdot 10^{-4}$ mol.% Pt (Carsted catalyst) was refluxed for 3 h. The solution was decanted from the resulting polymer; fractionation gave 2.7 g (17.5%) of a product with b.p. 88—92 °C (10 Torr), which partially crystallized during fractionation. Crystals (1.5 g), m.p. 75 °C, were filtered off; according to GLC and the ^{1}H NMR spectrum, they contained >90% tetrachloride **3e**. ^{1}H NMR (CCl_4—$CDCl_3$), δ: 1.52 (s, 8 H, 4 ring CH_2). The liquid fraction contained compound **4e** (80%) and tetrachloride **3e** (20%). The ^{1}H NMR spectrum of **4e** ($CDCl_3$—CCl_4), δ: 0.983 (q, 1 H, $\underline{CH}$—CH_3, *J* = 7.3 Hz); 1.317, 1.337 (d, 3 H, $\underline{CH_3}$—CH, *J* = 7.3 Hz); 1.467 (s, 4 H, 2 ring CH_2).

Homohydrosilylation of chloro(methyl)vinylsilane 1g. A mixture of chloro(methyl)vinylsilane (**1g**) (2.3 g, 0.03 mol), $2.3 \cdot 10^{-4}$ mol.% Pt (Carsted catalyst), and 20 mL of hexane was refluxed for 4 h. Fractionation gave 2.5 g (17.0%) of a product, b.p. 90—95 °C (10 Torr), which was identified relying on the ^{1}H NMR spectrum as a mixture of isomers **4g** and **3g** in 65 : 35 ratio. ^{1}H NMR (CCl_4—C_6D_6), δ: 0.088 (q, 1 H, ring CH, *J* = 7.6 Hz); 0.516, 0.558 (both s, 6 H, 2 $\underline{CH_3}$—Si); 1.175 (d, 3 H, $C\underline{H_3}$—CH, *J* = 7.6 Hz); 0.880—1.340 (m, 4 H, 2 ring CH_2 + 3 H, disilacyclopentane CH_3, assigned to compound **4g**).

Reactions of 1,4-dimethyl-1,4-diphenyl-1,4-disilacyclohexane (3d) and a mixture of 3d and 4d with HCl in the presence of $AlCl_3$. *A.* An HCl stream was passed through a suspension of *trans*-**3d** (0.245 g, $8.1 \cdot 10^{-4}$ mol) and $AlCl_3$ (0.027 g, 25 mol.%) in 1.6 mL of dry benzene. Every 30 min, samples for GLC were taken (see Fig. 1, *a*). After 7 h, the supply of HCl was terminated, and the reaction mixture was frozen and sublimed *in vacuo*. The solid remainder was dissolved in CCl_4, the solution was filtered in a flow of argon, the solvent was evaporated *in vacuo*, and the residue was dried to a constant weight to give 0.128 g (74.9%) of crystals with m.p. 60—68 °C, which were identified as *trans*-1,4-dichloro-1,4-dimethyl-1,4-disilacyclohexane (*trans*-**3g**). ^{1}H NMR ($CDCl_3$—CCl_4), δ: 0.410 (s, 6 H, 2 CH_3—Si); 1.033—1.205 (m, 8 H, 4 ring CH_2). IR (KBr), ν/cm^{-1}: 1180 ($SiCH_2CH_2Si$); 1260 (CH_3Si). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 212 $[M]^+$ (80), 197 $[M - CH_3]^+$ (30), 184 $[M - CH_3 - CH]^+$ (100).

B. A similar procedure starting from *trans*-**3d** (1.42 g) and $AlCl_3$ (0.175 g, 27 mol.%) gave in 2 h dichloride *trans*-**3g**, yield 85%, m.p. 72.0 °C.

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* The ratio of CCl_4 to deuterated solvent was 5 : 1 in all cases.

C. HCl was passed in a similar way through a suspension of a mixture of isomers **3d** and **4d** (10 g) and $AlCl_3$ (1.24 g, 27.5 mol.%) in 65 mL of C_6H_6. Every hour samples for GLC were taken (see Fig. 1, *b*). The reaction mixture was frozen, and HCl and some of the benzene were removed. The solutions obtained in three experiments were combined and cooled, and the precipitated crystals were filtered off and washed with benzene to give 1.8 g (7.5%) of crystals with m.p. 72.0 °C, which were identified as *trans*-**3g** relying on the ^1H NMR spectrum.

1,4-Dihydroxy-1,4-dimethyl-1,4-disilacyclohexane (3i) and 1,3-dihydroxy-1,2,3-trimethyl-1,3-disilacyclopentane (4i). *A.* A mixture of H_2O (0.0219 g, $1.22 \cdot 10^{-3}$ mol), $PhNH_2$ (0.119 g, $1.28 \cdot 10^{-3}$ mol), and Et_2O (2.3 mL) was cooled to −6 °C, and a solution of *trans*-**3g** (0.1284 g) in 1 mL of Et_2O was added dropwise with stirring. After 1 h, the precipitate of $PhNH_2 \cdot HCl$ was filtered off, the ether was evaporated, and the crystalline residue was recrystallized from an ether—pentane (1 : 1) mixture and then from a benzene—ether (8 : 1) mixture to give 0.008 g (7.4%) of *trans*-**3i** as needle crystals, m.p. 158—162 °C. Found (%): C, 41.20; H, 7.06; Si, 32.02. $C_6H_{16}O_2Si_2$. Calculated (%): C, 41.16; H, 9.16; Si, 31.84. IR (KBr), ν/cm^{-1}: 1070—1120 (CH_2—CH_2). ^1H NMR (CD_3CO—CCl_4), δ: 0.032 (s, 3 H, $\underline{CH}_3$Si); 0.757 (m, 8 H, 4 ring CH_2); 4.042 (s, 1 H, $\underline{H}$OSi). ^{13}C NMR (CD_3CO—CCl_4), δ: 2.23 (4 ring CH_2); 9.64 (2 CH_3Si). ^{29}Si NMR (CD_3CO—CCl_4), δ: 10.57 (s, 2 Si).

B. A mixture of isomers **3g** and **4g** (11.52 g, 0.054 mol) in 50 mL of Et_2O was added dropwise at 0—4 °C over a period of 1 h to a mixture of $PhNH_2$ (11.05 g, 0.119 mol), H_2O (1.9 g, 0.108 mol), and ether (40 mL). The precipitate of $PhNH_2 \cdot HCl$ was filtered off. The solution was washed with water, the aqueous layer was separated, and the solvent was evaporated in a vacuum of a water-jet pump to give 10 g of a product; the product was dissolved in an ether—hexane mixture (1 : 3). Cooling of the solution gave 1.8 g of crystals with m.p. 156—159 °C, which were identified as *trans*-**3i**. The ^1H NMR spectrum of the mixture of stereoisomers remaining after the separation of crystals (CD_3CO—CCl_4), δ: for **4i**, 0.049 (s, 9 H, 3 CH_3Si, $\underline{CH}_3$CH); 0.092 (s, 9 H, 2 $C\underline{H}_3$Si, $C\underline{H}_3$CH); 0.116 (s, 9 H, 3 CH_3Si, CH_3CH); 1.049, 1.063 (both d, 3 H, CH_3CH, *J* = 7.6 Hz); for *cis*-**3i**, 0.023 (s, 3 H, 2 CH_3Si); the signals of the two stereoisomers of **4i** have identical chemical shifts and spin-spin coupling constants: 4.183, 4.216, 4.250, 4.273 (all s, 1 H, $\underline{H}$OSi).

Homohydrosilylation of diethylamino(methyl)vinylsilane (1h). A mixture of **1h** (6.5 g, 0.045 mol) and Pt ($1 \cdot 10^{-4}$ mol.%) in 150 mL of hexane was refluxed for 7 h to give a mixture of isomers **2h**—**4h** (0.30 g, 5.0%), b.p. 89—90 °C (3 Torr). IR (KBr), ν/cm^{-1}: 2115 (Si—H); 1405 (Si—Vin); 1177 ($SiCH_2CH_2Si$). ^1H NMR ($CDCl_3$—CCl_4), δ: 5.727—6.229 (m, 3 H, CH_2=CHSi); 3.476—3.534 (m, 1 H, CH_2=C$\underline{H}$Si); 3.462 (s, 1 H, SiH); 1.014, 1.006, 0.997 (all s, 3 H, $C\underline{H}_3$—CH); 0.988, 0.979 (both s, 6 H, $C\underline{H}_3$—Si).

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