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Reactions of dodecamethylcyclohexasilane and polydimethylsilane with metal chlorides

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Abstract

The reactions of dodecamethylcyclohexasilane and high-molecular-weight polydimethylsilane with chlorides of I, II, IV–VI and VIII Group metals at high temperature in the absence of a solvent were studied. The interaction of $(Me_2Si)_6$ with metal chlorides proceeds with the cleavage of Si–Si and Si–C bonds with the formation of chloro derivatives of linear and cyclic permethyloligosilanes. The reactions of polydimethylsilane with metal chlorides afford mixtures of α,ω-dichlorooligosilanes, $Cl(Me_2Si)_nCl$ ($n = 2$–9). The influence of the reaction conditions (temperature, reaction time and the reagent ratio) on the composition and yields of the reaction products was examined.

Keywords: Dodecamethylcyclohexasilane; Polydimethylsilane; Metal chlorides; Chloro derivatives of oligosilanes

1. Introduction

Dichloro-substituted linear and cyclic permethyloligosilanes are convenient starting compounds for the synthesis of polymers or copolymers containing oligosilane fragments in a backbone [1–15]. α,ω-Dichloropermethyloligosilanes $Cl(Me_2Si)_nCl$ (**1**) have been prepared previously by chlorodemethylation of hexamethyldisilane $Me(SiMe_2)_2Me$ (dichlorodisilane **1a**) and octamethyltrisilane $Me(SiMe_2)_3Me$ (dichlorotrisilane **1b**) [16–19], chlorodephenylation of 1,4-diphenyloctamethyltetrasilane $Ph(SiMe_2)_4Ph$ (dichlorotetrasilane **1c**) [20] and 1,5-diphenyldecamethylpentasilane $Ph(SiMe_2)_5Ph$ (dichloropentasilane **1d**) [21], reductive coupling of Me_2SiCl_2 with SmI_2 (a mixture of dichlorosilanes **1a–c**) [22].

The method used most widely to prepare chloro-substituted linear and cyclic oligosilanes is the reaction of permethylcyclosilanes $(Me_2Si)_n$ ($n = 5$ or 6) with different chlorinating agents. Thus dichlorooligosilanes **1a–c** and dichlorohexasilane (**1e**) are prepared by treatment of dodecamethylcyclohexasilane $(Me_2Si)_6$ (**2**) with chlorinating agents, such as Cl_2 [23,24], $SOCl_2$, SCl_2 [25], PCl_5 [26] and gallium(III), tin(IV), titanium(IV) chlorides [27].

Chloro derivatives of cyclohexasilane **2** with the general formula $Cl_mSi_6Me_{12-m}$ (**2a–c** with $m = 1$–3, respectively) are prepared by chlorodemethylation of cyclosilane **2** on treatment with dry HCl in the presence of catalytic amounts of $AlCl_3$ (chlorocyclosilane **2a**) [28] or by the reaction of cyclosilane **2** with $SbCl_5$ (monochloro-, dichloro- and trichlorocyclosilanes **2a–c**) [2,27,29–31].

High-molecular-weight polydimethylsilane (**3**) is a convenient starting compound for the synthesis of dichlorooligosilanes **1**. However, the data of the synthesis of dichlorooligosilanes **1** by the reactions of polysilane **3** with chlorinating agents are scarce. Dichlorodisilane **1a** was prepared in 43% yield by passing chlorine through a suspension of polysilane **3** in CCl_4 at -20 °C [23]. A mixture of dichlorooligosilanes **1** was obtained by the reaction of polysilane **3** with $SnCl_4$ at high temperature [27]. However, the data on the compositions of the reaction products and the ratios between these products are lacking.

In the present study, with the aim of synthesizing dichlorooligosilanes **1** and chloro derivatives of cyclo-

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hexasilane **2**, we examined the reactions of cyclohexasilane **2** and polysilane **3** with chlorides of I, II, IV–VI and VIII Group metals in variable oxidation states (MCl_k) and investigated the influence of the reaction conditions on the conversion of cyclohexasilane **2** and polysilane **3**, the compositions of the reaction products and their yields.

2. Results and discussion

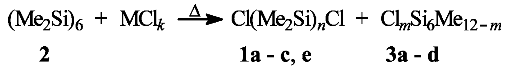
2.1. Reactions of cyclohexasilane 2 with metal chlorides

Previously [27], it was shown that the reaction of cyclosilane **2** with $SnCl_4$ in CH_2Cl_2 gives not only dichlorohexasilane **1e** as the major product but also its lower homologues **1a–c** formed upon cleavage of the Si–Si bond in oligomer **1e**. Later [9], it was found that the reaction of cyclosilane **2** with $SnCl_4$ is accompanied by not only Si–Si bond cleavage in cyclosilane **2** and dichlorohexasilane **1e** but also by cleavage of the Si–Me bonds in the initial cyclosilane **2** to give its monochloro **2a** and dichloro **2b** derivatives.

Cyclosilane **2** reacts with $TiCl_4$ in a similar way, i.e., with Si–Si and Si–Me bond cleavage in cyclosilane **2** to give dichlorooligosilanes **1a–c**, **e** and monochlorocyclosilane **2a** [9,27]. The reaction of cyclosilane **2** with $SnCl_4$ and $TiCl_4$ in CH_2Cl_2 proceeds slowly with a relatively low degree of conversion of the initial cyclic compound **2**. It was also shown [27] that in the absence of a solvent, the degree of conversion of cyclosilane **2** was 100% after 4 h, linear dichlorooligosilanes **1a–c**, **e** being formed as the only products.

In this respect, we studied the reaction of several main group metal chlorides and transition metal chlorides ($SnCl_4$, $SbCl_5$, $HgCl_2$, $CuCl_2$, $FeCl_3$, $TiCl_4$, $ZrCl_4$, $MoCl_5$, WCl_6) with cyclosilane **2** in the absence of a solvent at elevated temperatures. Under these conditions (Scheme 1, Table 1) cyclosilane **2** reacts with the above mentioned metal chlorides with cleavage of its Si–Si and Si–Me bonds to give linear and cyclic chloro-substituted permethyloligosilanes.

It should be noted that tin and mercury chlorides react with cyclosilane **2** mainly cleavage of the Si–Si bond giving predominantly linear dichlorooligosilanes **1a–c**, **e** (the content of chloro-substituted cyclosilanes **2a–c** in the products did not exceed 7.5%), the degree of conversion of cyclosilane **2** being rather high (80–100%). In the reactions of the rest of metal chlorides studied with cyclosilane **2**, the intensity of cleavage of the Si–Me bonds in the initial ring increases, which results in markedly higher proportions of chloro-substituted cyclosilanes in the products. Indeed, $ZrCl_4$ and WCl_6 react with cyclosilane **2** with the predominant formation of chloro-substituted cyclosilanes **2a–c**; polychlorinated cyclosilanes $Cl_mSi_6Me_{12-m}$ (**2d**, $m > 3$) are also formed. $CrCl_3$ and $FeCl_3$ proved to be the poorest chlorinating agents for cyclosilane **2**: the degree of conversion of **2** was $\leq 20\%$; however, even in those cases where the conversion of cyclosilane **2** in the reactions with metal chlorides was rather high, the yield of linear dichlorooligosilanes **1a–c**, **e** did not exceed 55%.



$$\underset{\mathbf{2}}{(Me_2Si)_6} + MCl_k \xrightarrow{\Delta} \underset{\mathbf{1a-c,\ e}}{Cl(Me_2Si)_nCl} + \underset{\mathbf{3a-d}}{Cl_mSi_6Me_{12-m}}$$

$n = 2$ (**a**), 3 (**b**), 4 (**c**), 6 (**e**);
$m = 1$ (**a**), 2 (**b**), 3 (**c**);
$m > 3$ (**d**)

Scheme 1.

Previously, it was shown [27] that the reaction of $SbCl_5$ with cyclosilane **2** in the presence of a solvent (CH_2Cl_2, $CHCl_3$, CCl_4) proceeds selectively with cleavage of only Si–Me bonds in the initial cyclosilane **2**, the Si–Si bonds remaining intact. When reproducing the procedure, we obtained almost analogous results (see Table 1, entry 6), namely, the content of the linear dichlorohexasilane **1e** in the reaction mixture was only 0.5%. Dichloro-substituted cyclosilane **2b** was formed as the major reaction product. As shown previously [2,27,29–31], this product was a mixture of structural isomers, namely, 1,3-dichlorocyclosilane (**2b′**) and 1,4-dichlorocyclosilane (**2b″**) (in ~1:1 ratio), which are, in turn, mixtures of *cis*- and *trans*-isomers (see Section 3, ^{29}Si-NMR spectra of cyclosilanes **2b′** and **2b″**). A very reactive chlorinating agent for cyclosilane **2** is $SbCl_5$. Treatment of cyclosilane **2** with $SbCl_5$ in a 1:2 ratio at 25 °C in the absence of a solvent bring about a vigorous exothermal reaction with 100% conversion of cyclosilane **2** over a period of several seconds; this gives not only chloro-substituted cyclosilanes **2a–d** but also linear dichlorooligosilanes **1a–c**, **e** (the ratio of linear to cyclic chloro-substituted oligisilanes was ~2:1). Thus, unlike the reaction in solutions, not only Si–Me but also Si–Si bonds of cyclosilane **2** are cleaved in the solvent-free reaction.

The influence of the reaction conditions on the conversion of cyclosilane **2**, on the yield and composition of the reaction products and on the ratio between them was studied in relation to the reaction of **2** with $SnCl_4$. An increase in the reaction times (cf. entries 1–3, 4 and 5 in Table 1) results in a higher yield of linear dichlorooligosilanes **1a–c**, **e** and a lower content of chloro-substituted cyclosilanes **2a–c** in the reaction products. In addition, the content of short-chain linear oligomers **1a** and **1b** increases and the content of dichlorotetrasilane **1c** and dichlorohexasilane **1e** decreases. Evidently, this is due to an increase in the intensity of Si–Si bond cleavage in oligomers **1c** and **1e** following an increase in the reaction time. For equal reaction times, transition from 1:1 ratio of cyclosilane **2**

Table 1
Conditions and products of the reaction of cyclosilane **2** with metal chlorides MCl_k

Entry	MCl_k	**2**:MCl_k	T (°C)	t (h)	Composition of the reaction mixture (%) [a]								Yield of **1**	Conversion of **2**
					1a	**1b**	**1c**	**1e**	**2**	**2a**	**2b**	**2c**	(%) [b]	(%) [c]
1	$SnCl_4$	1:1	175	0.5	7.5	11.3	9.6	46.1	18.1	3.9	1.6	1.9	86.5	82.6
2	$SnCl_4$	1:1	175	1	9.0	14.8	11.3	44.3	14.2	3.4	1.4	1.6	87.2	86.5
3	$SnCl_4$	1:1	175	2	13.5	19.1	13.5	40.2	10.9	0.9	1.5	0.4	89.5	89.8
4	$SnCl_4$	1:2	175	1	29.9	34.7	25.8	1.5	0.4	2.0	0.8	4.9	78.9	99.5
5	$SnCl_4$	1:2	175	2	41.5	37.0	18.7	–	–	0.8	0.4	1.6	86.9	100
6	$SbCl_5$ [d]	1:1	25	2	–	–	–	0.5	2.8	5.4	89.3	2.0	0.5	97.2
7	$SbCl_5$	1:2	25	0.002	43.4	11.4	10.8	3.1	–	4.5	6.8	19.3 [e]	66.3	100
8	$HgCl_2$	1:2	210	2	30.0	40.8	21.9	2.1	1.8	0.7	1.1	1.6	86.6	98.2
9	$CuCl_2$	1:1	180	1	5.8	9.6	4.6	16.1	44.3	2.1	11.2	6.3	53.8	60.2
10	$CrCl_3$	1:2	210	2	0.1	0.3	0.4	2.6	89.7	0.2	6.7	–	33.0	10.3
11	$FeCl_3$	1:1	180	2	1.4	3.6	2.3	5.7	84.3	0.3	2.4	–	53.5	19.6
12	$TiCl_4$	1:1	175	3	8.0	9.2	9.3	28.4	21.2	2.2	16.4	5.3	55.5	81.3
13	$ZrCl_4$	1:1	200	2	1.9	1.9	2.2	23.4	25.7	6.4	16.2	19.0 [f]	27.3	80.2
14	$MoCl_5$	1:1	185	3	10.9	6.3	4.4	17.8	27.4	14.0	10.1	9.1	40.2	78.2
15	WCl_6	1:1	205	1	17.8	9.4	5.9	6.7	6.9	7.5	4.6	11.8 [g]	34.6	94.3

[a] Unidentified by-products were neglected.

[b] Total yield of oligomers **1a–c**, **e** from all reaction products (including unidentified ones) and in relation to the reacted cyclosilane **2** (according to GLC).

[c] Determined by GLC.

[d] The reaction was carried out in CCl_4.

[e] The reaction mixture contains 0.7% polychloro-substituted cyclosilanes **2d**.

[f] The reaction mixture contains 3.3% polychloro-substituted cyclosilanes **2d**.

[g] The reaction mixture contains 29.4% polychloro-substituted cyclosilanes **2d**.

to $SnCl_4$ to 1:2 ratio (cf. entries 2 with 4 and 3 with 5 in Table 1), allows one to attain virtually 100% conversion of cyclosilane **2** with simultaneous sharp decrease (to 0–1.5%) in the content of dichlohexasilane **1e** in the reaction products. In addition, the content of short-chain oligomers **1a** and **1b** increases two to threefold.

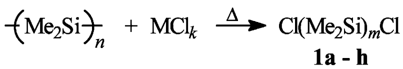
2.2. Reactions polysilane 3 with metal chlorides

The reaction of polysilane **3** with the above mentioned metal chlorides in the absence of a solvent at high temperature proceeds with the cleavage of the polysilane chain to form a mixture of homologs, viz., dichlorooligosilanes **1** (Scheme 2).

The conversion of polysilane **3** was rather high (80–100%) in virtually all reactions (Table 2). However, the reactions of polysilane **3** with transition metal chlorides (except for $HgCl_2$) afforded oligosilanes **1** in lower total yields (no higher than 55%) as compared to those obtained in the reactions of main group metal chlorides (except for $SbCl_5$). Apparently, the relatively low yields of oligosilanes **1** obtained in the reactions of transition metal chlorides with polysilane **3** are attributable to the fact that these reactions, like those with cyclohexasilane **2**, led not only to the cleavage of the Si–Si bonds in the initial polysilane **3** but also to the partial replacement of the Me groups by Cl atoms both in polysilane **3** and the resulting oligosilanes **1**. As a result, the reaction mixtures contained large amounts of by-products with a consequent decrease in the yield of the target products.

It should be noted that, as in our investigation described above, we found that $SbCl_5$ exhibits higher chemical activity as compared to the rest of metal chlorides. The reaction of polysilane **3** with $SbCl_5$ was completed in several seconds at room temperature and was accompanied by heat evolution. In addition, in the reactions with polysilane **3** $SbCl_5$ behaved analogously to transition metal chlorides: conversion of polysilane **3** was 100%, whereas the yield of oligosilanes **1** was only 54%.

The highest yields of dichlorooligosilanes **1** were achieved in the reactions with the use of $SnCl_4$ and $HgCl_2$ as chlorinating agents (see Table 2). It was established that variation of conditions of the reaction between polysilane **3** and these metal chlorides makes it possible to control to certain extent the length of oligomer chain in the resulting dichlorooligosilanes **1**. It was found that a decrease polysilane **3**: metal chloride ratio in the reactions performed at the same temperature over the same period of time (cf. entries 1, 5 and 8 and also entries 10, 14 and 15 in Table 2) led to an increase in the conversion of polysilane **3**, a rise in the amount of short-chain oligosilanes **1a**, **b** and a decrease in the amount of long-chain oligosilanes **1d**–**h**. An analogous effect was observed when the reaction temperature or the duration of the process was increased. The highest yields of long-chain oligosilanes **1d**–**h** were achieved when polysilane **3** and $SnCl_4$ were taken in a ratio of 2:1 and the reaction was carried out at 125 °C (entry 2). However, the conversion of polysilane **3** in the latter case was only 56%. According to the data from GLC and ^{29}Si-NMR spectroscopy, none of the reactions under study afforded dichlorooligosilanes **1** with $m > 9$. The optimum reaction conditions, which allow one to attain a high conversion of polysilane **3** and to obtain long-chain dichlorooligosilanes **1d**–**h** in high yields, are as follows: the reaction temperature is 180 °C, the reaction time is 3 h and polysilane **3** to $SnCl_4$ ratio is 4:1 (for $SnCl_4$); the corresponding conditions for $HgCl_2$ are 180 °C, 2 h and 2:1.



$$-\!\!(Me_2Si)_n\!\!- + MCl_k \xrightarrow{\Delta} \underset{\textbf{1a - h}}{Cl(Me_2Si)_mCl}$$

m = 2 (**a**), 3 (**b**), 4 (**c**), 5 (**d**), 6 (**e**), 7 (**f**), 8 (**g**), 9 (**h**)

Scheme 2.

The procedure for the synthesis of dichlorooligosilanes **1** based on the reactions of polysilane **3** with metal chlorides has advantages over known procedures. Thus, this procedure makes it possible to prepare dichlorooligosilanes **1** containing more than six Si atoms in the oligomer chain, dichloropentasilane **1d** (which has been previously prepared from difficultly accessible $(Me_2Si)_5$ or $Ph(Me_2Si)_5Ph$) is generated rather easily and insoluble unfusible polysilane **3**, which is formed as a by-product in the synthesis of cyclosilanes [32,33], is utilized.

3. Experimental

3.1. General comments

All reactions were monitored by GLC. The GLC analysis was carried out on a LKhM-8MD chromatograph (a 0.3 × 100 cm stainless steel column; 5% SE-30 on Chromaton N-AW-DMCS; a thermal conductivity detector; the temperature was increased from 30 to 300 °C with a rate of 12° min^{-1}; helium as the carrier gas). GC/MS measurements were performed on a Kratos-MS-890 instrument (a 15 m × 0.32 mm capillary column; SE-30 liquid phase; helium as the carrier gas; the temperature was programmed to rise from 30 to 270 °C at a rate of 12° min^{-1}; ionization energy was 70 eV). ^{29}Si-NMR spectra (79.46 MHz) were recorded on a Bruker WP-400 SY spectrometer. Samples were dissolved in $CDCl_3$ and Me_4Si was used as internal standard. Elemental analysis were performed by the Laboratory of Microanalysis of the Institute of Organoelement Compounds.

All reactions were carried out under an atmosphere of argon. Cyclosilane **2** was prepared by catalytic depoly-

Table 2
Conditions and products of the reaction of polysilane **3** with metal chlorides MCl_k

Entry	MCl_k	**3**:MCl_k [a]	T (°C)	t (h)	$Cl(Me_2Si)_mCl/\Sigma^{8}_{m=2}Cl(Me_2Si)_mCl$ (%) at different m							Conversion of **3**	Yield of **1a**–**g**
					2	**3**	**4**	**5**	**6**	**7**	**8**	(%) [b]	(%) [c]
1	$SnCl_4$	4:1	180	3	13.2	31.1	26.4	18.0	7.4	2.7	1.2 [d]	87.2	95.5
2	$SnCl_4$	2:1	125	3	13.7	30.4	20.7	14.3	8.8	6.7	5.4 [d]	56.6	80.8
3	$SnCl_4$	2:1	180	1	22.1	41.3	20.9	12.4	3.3	Traces	—	100	87.3
4	$SnCl_4$	2:1	180	2	26.4	44.3	21.9	6.6	0.8	—	—	100	88.3
5	$SnCl_4$	2:1	180	3	27.3	45.3	23.3	3.7	0.4	—	—	100	90.5
6	$SnCl_4$	2:1	210	0.5	34.8	37.6	16.3	9.1	2.2	—	—	100	82.4
7	$SnCl_4$	1:1	180	1	11.0	46.1	35.3	7.4	0.2	—	—	100	87.1
8	$SnCl_4$	1:1	180	3	15.0	49.7	29.5	5.8	—	—	—	100	89.9
9	$SbCl_5$	2:1	20	0.003	49.4	22.0	17.6	7.3	2.4	1.3	—	100	54.2
10	$HgCl_2$	2:1	180	2	6.5	47.6	27.6	12.4	4.9	1.0	Traces	94.3	91.9
11	$HgCl_2$	2:1	230	0.5	16.4	47.3	23.4	10.9	2.0	Traces	–	97.2	93.4
12	$HgCl_2$	2:1	230	2	28.8	53.2	17.3	0.7	Traces	–	–	100	92.9
13	$HgCl_2$	1:1	180	0.5	25.7	54.7	16.9	2.4	0.3	Traces	–	96.1	94.6
14	$HgCl_2$	1:1	180	2	37.9	53.3	8.8	–	–	–	–	100	92.3
15	$HgCl_2$	1:2	180	2	42.8	51.2	6.0	–	–	–	–	100	90.5
16	$HgCl_2$	1:2	230	0.5	43.6	51.8	4.6	–	–	–	–	100	82.5
17	$HgCl_2$	1:2	230	2	45.0	52.9	2.4	–	–	–	–	100	85.9
18	$CuCl_2$	1:1	180	1	46.2	30.0	13.4	6.9	1.7	1.2	0.6 [c]	97.3	46.2
19	$CrCl_3$	2:1	210	2	3.9	29.5	20.8	17.4	11.7	9.3	7.4 [d]	38.3	53.9
20	$FeCl_3$	1:1	180	1	52.0	30.2	12.2	4.5	1.1	–	–	100	51.0
21	$TiCl_4$	2:1	180	3	35.6	22.0	20.4	16.9	5.1	–	–	100	55.5
22	$MoCl_5$	2:1	200	1	54.5	30.6	14.9	–	–	–	–	100	24.5
23	WCl_6	2:1	200	1	75.9	16.1	8.0	–	–	–	–	77.9	55.4

[a] With respect to the $-SiMe_2-$ unit.

[b] In all experiments, we used polysilane **3** from the same preparation. Its conversion was determined after separation of the precipitate and dissolution of the metal chloride salt in the corresponding solvent.

[c] In relation to the reacted polysilane **3**.

[d] Traces ($<0.1\%$) of dichlorononasilane **1h** ($m = 9$).

merization of polysilane **3** as described in Ref. [9]. Polysilane **3** was obtained according to a modified procedure [34]. Immediately prior to the use, $TiCl_4$, $SnCl_4$ and $SbCl_5$ were distilled in an N_2 flow, while the other metal chlorides were used as received. CCl_4 was dried by distillation over P_2O_5 in an N_2 flow.

*3.2. Reaction of cyclosilane **2** with $SnCl_4$ (typical procedure) (Table 1, entry 2)*

Cyclosilane **2** (34.9 g, 0.1 mol) was placed in an ampoule equipped with a branch for reactant introduction and a Teflon stopcock, $SnCl_4$ (26.1 g, 0.1 mol) was added and the ampoule was placed in an oil bath preheated to 175 °C. The reaction mixture was kept at this temperature with vigorously stirring for 1 h. The ampoule was cooled and 50 ml of anhydrous CCl_4 was added. The $SnCl_2$ precipitate was filtered off and washed with CCl_4 (2×10 ml). The solvent was evaporated and the residue was analyzed by GLC (see Table 1). Fractionation of the residue gave:

5.6 g (10.0% relative to the reacted cyclosilane **2**) of dichlorodisilane **1a**. B.p.: 148–148.5 °C. ^{29}Si-NMR: δ 17.21;

8.1 g (16.5%) of dichlorotrisilane **1b**. B.p.: 84–85 °C (10 Torr). ^{29}Si-NMR: δ 24.98 (ClSi), −43.71 (ClSi*Si*);

5.7 g (12.7%) of dichlorotetrasilane **1c**. B.p.: 111–112 °C (5 Torr). ^{29}Si-NMR: δ 26.26 (ClSi), −42.68 (ClSi*Si*).

After evaporation of lower dichlorooligosilanes **1a–c**, the initial cyclosilane **2** and chloro-substituted cyclosilanes **2a** and **2b** were removed by sublimation. Distillation of the residue gave 20.8 g (49.5%) of dichlorohexasilane **1e**. B.p.: 166–167 °C (1 Torr), m.p. 45–46 °C. ^{29}Si-NMR: δ 26.35 (ClSi), −40.90 (ClSi*Si*), −39.95 (ClSiSi*Si*).

Entries 1, 3–5 and 7–15 were carried out in a similar way (entry 7 without heating) except that the residue after removal of CCl_4 was not fractionated but was analyzed by GLC.

*3.3. Reaction of cyclosilane **2** with $SbCl_5$ (Table 1, entry 6)*

A solution of $SbCl_5$ (11.8 g, 39.4 mmol) in 30 ml of anhydrous CCl_4 was added dropwise to a solution of cyclosilane **2** (10.0 g, 28.7 mmol) in 50 ml of anhydrous CCl_4 cooled to 0 °C. The reaction mixture was vigorously stirred for 2 h at 20 °C. The precipitate was filtered off and washed with anhydrous hexane (2×10 ml). The solvents were removed on a rotary evaporator and the initial cyclosilane **2** and the reaction products (chloro-substituted cyclosilanes **2a–c**) were extracted from the residue with anhydrous hexane (3×10 ml). Acetonitrile (6 ml) was added to the resulting solution for deactivation of antimony compounds and the hexane solution of the reaction products was separated using a separating funnel. Hexane was removed on a rotary evaporator. The initial cyclosilane **2** and monochloro-substituted cyclosilane **2a** were removed from crystalline residue by sublimation (80 °C, 1 Torr). The residue after sublimation was recrystallized from anhydrous pentane to give 6.7 g (60%) of a mixture of 1,3-(**2b′**) and 1,4-dichlorocyclosilane (**2b″**) isomers (~ 1:1). ^{29}Si-NMR: δ:

2b′ (*cis*-, *trans*-isomers): 15.42, 14.90 (SiCl), −37.05, −37.62 (ClSi*Si*SiCl), −38.94, −39.36 (Si*Si*SiCl), −42.48, −44.59 (Si*Si*Si);

2b″ (*cis*-, *trans*-isomers): 15.60, 15.13 (SiCl), −39.66, −39.92 (ClSi*Si₂*SiCl).

*3.4. Reaction of polysilane **3** with $SnCl_4$ (typical procedure) (Table 2, entry 1)*

Polysilane **3** (40.0 g, 0.688 mol) was placed in an argon-filled tube equipped with an inlet pipe for the introduction of reagents, a Teflon stopcock and a magnetic stirrer. Then $SnCl_4$ (44.8 g, 0.172 mol) was added. The tube was placed in an oil bath preheated to 180 °C and kept for 3 h with vigorously stirring. The reaction mixture was cooled and 50 ml of anhydrous CCl_4 was added. The precipitate of $SnCl_2$ and unreacted polysilane **3** were filtered off and washed with anhydrous CCl_4 (3×10 ml). The precipitate was treated with acetone to dissolve $SnCl_2$. Polysilane **3** was filtered off and dried at 60 °C in vacuo to a constant weight. Polysilane **3** was obtained in a yield of 5.1 g (conversion was 87.2%). The solvent was distilled off from the solution of dichlorooligosilanes **1** in CCl_4 and the residue was analyzed by GLC (see Table 2). Fractionation of the residue gave:

5.4 g (10.1% relative to the reacted polysilane **3**) of dichlorodisilane **1a**. B.p.: 147.5–148 °C. ^{29}Si-NMR: δ 17.23;

13.0 g (27.9%) of dichlorotrisilane **1b**. B.p.: 85–86 °C (10 Torr). ^{29}Si-NMR: δ 24.95 (ClSi), −43.77 (ClSi*Si*);

11.0 g (25.5%) of dichlorotetrasilane **1c**. B.p.: 110–111 °C (5 Torr). ^{29}Si-NMR: δ 26.22 (ClSi), −42.62 (ClSi*Si*);

7.6 g (18.3%) of dichloropentasilane **1d**. B.p.: 95–96 °C (0.5 Torr). ^{29}Si-NMR: δ 26.26 (ClSi), −41.65 (ClSi*Si*), −41.12 (ClSiSi*Si*);

3.1 g (7.8%) of dichlorohexasilane **1e**. B.p.: 139–141 °C (0.5 Torr). ^{29}Si-NMR: δ 26.21 (ClSi), −40.89 (ClSi*Si*), −40.01 (ClSiSi*Si*);

1.1 g (2.9%) of dichlorotetradecamethylheptasilane **1f**. B.p.: 179–181 °C (0.5 Torr). Anal. Calc. for $C_{14}H_{42}Cl_2Si_7$: C, 35.18; H, 8.86; Cl, 14.83; Si, 41.13%. Found: C, 35.44; H, 8.63; Cl, 14.27; Si, 40.78%. ^{29}Si-NMR: δ 26.37 (ClSi), −41.05 (ClSi*Si*), −39.80 (ClSiSi*Si*), −37.91 (ClSiSiSi*Si*). MS: *m/e* (rel. int.,%) 463 [M^+−Me, 0.8], 325 ($Si_5Me_{10}Cl$, 11.8), 267 (Si_4Me_8Cl, 100), 209 (Si_3Me_6Cl, 35.4), 174 (Si_3Me_6, 11.1), 173

($Si_3Me_5CH_2$, 13.5), 159 (Si_3Me_5, 11.5), 131 (Si_2Me_5, 28.2), 116 (Si_2Me_4, 9.2), 115 ($Si_2Me_3CH_2$, 7.5), 73 ($SiMe_3$, 55.6);

0.5 g (1.3%) of dichlorohexadecamethyloctasilane **1g**. B.p.: 185–187 °C (0.06 Torr). Anal. Calc. for $C_{16}H_{48}Cl_2Si_8$: C, 35.84; H, 9.02; Cl, 13.23; Si, 41.91%. Found: C, 35.41; H, 8.85; Cl, 12.98; Si, 41.43%. ^{29}Si-NMR: δ 26.43 (ClSi), −40.89 (ClSi*Si*), −39.67 (ClSiSi*Si*), −37.69 (ClSiSiSi*Si*).

According to the GLC data, the residue was a mixture of dichlorooctasilane **1g** and dichlorooctadecamethylnonasilane **1h** in a ratio of 1:1.4.

Entries 2–23 were carried out in analogously (entry 9 without heating) but the residues obtained after the removal of CCl_4 were analyzed by GLC rather than distilled (see Table 2).

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References

[1] F.K. Mitter, G. Pollhammer, E. Hengge, J. Organomet. Chem. 314 (1986) 1.

[2] F.K. Mitter, E. Hengge, J. Organomet. Chem. 332 (1987) 47.

[3] E. Hengge, P.K. Jenkner, Z. Anorg. Allg. Chem. 560 (1988) 27.

[4] E. Hengge, P. Gspaltl, A. Spielberger, J. Organomet. Chem. 479 (1994) 165.

[5] K. Kumar, M.H. Litt, J. Polym. Sci., Part C Polym. Lett. 26 (1988) 25.

[6] J. Chojnowski, J. Kurjata, S. Rubinsztajn, M. Ścibiorek, in: A.R. Bassindale, P.P. Gaspar (Eds.), Frontiers of Organosilicon Chemistry, The Royal Society of Chemistry, Cambridge, 1991, p. 70.

[7] J. Chojnowski, W. Fortuniak, N. Gladkova, M. Pluta, M. Ścibiorek, B. Zavin, J. Inorg. Organomet. Polym. 5 (1995) 7.

[8] J. Kurjata, M. Ścibiorek, W. Fortuniak, J. Chojnowski, Organometallics 18 (1999) 1259.

[9] A.I. Chernyavskii, B.G. Zavin, Izv. Akad. Nauk, Ser. Khim. (1997) 1513. [Russ. Chem. Bull. 46 (1997) 1449 (English translation)].

[10] N.A. Chernyavskaya, V.I. Aleksinskaya, A.I. Chernyavskii, Izv. Akad. Nauk, Ser. Khim. (1998), 544. (Russ. Chem. Bull. 47 (1998) 526 (English translation)).

[11] A.I. Chernyavskii, A.I. Belokon', N.A. Chernyavskaya, V.I. Aleksinskaya, B.G. Zavin, Yu.S. Nekrasov, Izv. Akad. Nauk, Ser. Khim. (1999) 1729. (Russ. Chem. Bull. 48 (1998) 1707 (English translation)).

[12] A. Kleewein, H. Stiiger, Monatsh. Chem. 130 (1999) 69.

[13] A.I. Chernyavskii, N.A. Chernyavskaya, V.I. Aleksinskaya, B.G. Zavin, J. Organomet. Chem. 579 (1999) 328.

[14] A.I. Chernyavskii, D.Yu. Larkin, N.A. Chernyavskaya, Izv. Akad. Nauk, Ser. Khim. (2002) 165. (Russ. Chem. Bull., Int. Ed. 51 (2002) 175).

[15] A.I. Chernyavskii, E.G. Kononova, M.I. Buzin, N.A. Chernyavskaya, Izv. Akad. Nauk, Ser. Khim., [Russ. Chem. Bull., Int. Ed. 52, (2003) 952].

[16] M. Kumada, M. Yamaguchi, Y. Yamamoto, I. Nakajima, K. Shina, J. Org. Chem. 21 (1956) 1264.

[17] M. Kumada, M. Ishikawa, J. Organomet. Chem. 1 (1963) 153.

[18] H. Sakurai, R. Tominaga, T. Watanabe, M. Kumada, Tetrahedron Lett. (1966) 5493.

[19] M. Ishikawa, M. Kumada, H. Sakurai, J. Organomet. Chem. 23 (1970) 63.

[20] M. Kumada, M. Ishikawa, S. Maeda, J. Organomet. Chem. 2 (1964) 478.

[21] M. Kumada, M. Ishikawa, S. Sakamoto, S. Maeda, J. Organomet. Chem. 17 (1969) 223.

[22] B.G. Zavin, A.I.Chernyavskii, Ya.S. Vygodskii, N.E. Brandukova, Dokl. Akad. Nauk 336 (1994) 365. (Dokl. Chem. 336 (1994) 97 (English translation)).

[23] P.K. Sen, D. Ballard, H. Gilman, J. Organomet. Chem. 15 (1968) 237.

[24] W. Wojnowski, C.J. Hurt, R. West, J. Organomet. Chem. 124 (1977) 271.

[25] P.K. Jenkner, A. Spielberger, E. Hengge, J. Organomet. Chem. 427 (1992) 161.

[26] H. Gilman, S. Inoue, J. Org. Chem. 29 (1964) 3418.

[27] B. Derczewski, W. Wojnowski, J. Prakt. Chem. 332 (1990) 229.

[28] M. Ishikawa, M. Kumada, Synth. Inorg. Met.-Org. Chem. 1 (1971) 191.

[29] E. Hengge, M. Eibl, J. Organomet. Chem. 428 (1992) 335.

[30] A. Spielberger, P. Gspaltl, H. Siegl, E. Hengge, K. Gruber, J. Organomet. Chem. 499 (1995) 241.

[31] M. Eibl, U. Katzenbeisser, E. Hengge, J. Organomet. Chem. 444 (1993) 29.

[32] E. Carberry, R. West, J. Am. Chem. Soc. 91 (1969) 5440.

[33] R. West, L. Brough, W. Wojnowski, Inorg. Synth. 19 (1979) 265.

[34] J.P. Wesson, T.C. Williams, J. Polym. Sci. Part A 17 (1979) 2833.