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Synthesis of α,ω-dichloropermethyloligosilanes by reactions of polydimethylsilane with metal chlorides

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The reactions of high-molecular-weight polydimethylsilane with metal chlorides in variable oxidation states at high temperature in the absence of a solvent afford mixtures of α,ω-dichloropermethyloligosilanes $Cl(Me_2Si)_mCl$ (m = 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.

Key words: polydimethylsilane, metal chlorides, α,ω-dichloropermethyloligosilanes.

Dichloro substituted linear permethyloligosilanes $Cl(Me_2Si)_mCl$ (**1**) are used as the starting compounds for the synthesis of various derivatives and copolymers containing oligosilane fragments in a polymeric chain. α,ω-Dichlorooligosilanes **1** have been prepared previously by chlorodemethylation of hexamethyldisilane $Me(SiMe_2)_2Me$ (dichlorodisilane **1a**) and octamethyltrisilane $Me(SiMe_2)_3Me$ (dichlorotrisilane **1b**),[1—4] chlorodephenylation of 1,4-diphenyloctamethyltetrasilane $Ph(Me_2Si)_4Ph$ (dichlorotetrasilane **1c**)[5] and 1,5-diphenyldecamethylpentasilane $Ph(Me_2Si)_5Ph$ (dichloropentasilane **1d**),[6] reductive coupling of Me_2SiCl_2 with SmI_2 (a mixture of dichlorosilanes **1a—c**),[7] and the reactions of permethylcyclosilanes $(Me_2Si)_n$ (n = 5 or 6) with different chlorinating agents.[8—13]

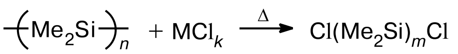
High-molecular-weight polydimethylsilane $—(Me_2Si)_n—$ (**2**) is a convenient starting compound for the synthesis of dichlorooligosilanes **1**. However, the data on the synthesis of α,ω-dichlorooligosilanes **1** by the reactions of polysilane **2** with chlorinating agents are scarce. Dichlorodisilane **1a** was prepared in 42.7% yield by passing Cl_2 through a suspension of polysilane **2** in CCl_4 at −20 °C.[8] A mixture of dichlorooligosilanes **1** was prepared[12] by the reaction of polysilane **2** with $SnCl_4$ at high temperature. 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**, we examined the reactions of high-molecular-weight polydimethylsilane **2** with chlorides of main group metals (Sn^{IV}, Sb^{V}) and transition metals (Hg^{II}, Cu^{II}, Cr^{III}, Fe^{III}, Ti^{IV}, Mo^{V}, W^{VI}) in variable oxidation states (MCl_k) and investigated the influence of the reaction conditions on the conversion of polysilane **2**, the compositions of the reaction products, and their yields.

Results and Discussion

The reactions of polysilane **2** with the above-mentioned metal chlorides in the absence of solvents at high temperature proceeded with the cleavage of the polysilane chain to form mixtures of homologs, *viz.*, α,ω-dichlorooligosilanes **1** (Scheme 1).

Scheme 1



$$\left(Me_2Si\right)_n + MCl_k \xrightarrow{\Delta} Cl(Me_2Si)_mCl$$

2 **1a—h** (m = 2—9)

The conversion of polysilane **2** was rather high (80—100%) in virtually all reactions. However, the reactions of polysilane **2** with transition metal chlorides (except for $HgCl_2$) afforded oligosilanes **1** in lower total yields (no higher than 55%, see Table 1) 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 **2** are attributable to the fact that these reactions, like those with cyclohexasilane $(Me_2Si)_6$ (**3**),[13] led not only to the cleavage of the Si—Si bonds in the starting polysilane **2** but also to the partial replacement of the Me groups by the Cl atoms both in polysilane **2** 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 previous study,[13] we found that $SbCl_5$ exhibits higher chemical activity as compared to $HgCl_2$ and $SnCl_4$. In the reactions with polysilane **2** and cyclosilane **3**,[13] antimony pentachloride behaved analogously to transition metal chlorides. In the

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Table 1. Reactions conditions and compositions of the products prepared from polysilane **2** and metal chlorides MCl_k

Run	MCl_k	MCl_k : **2** ratio[b]	T/°C	Time/h	$Cl(Me_2Si)_mCl/\sum_{m=2}^{8} Cl(Me_2Si)_mCl$ (%) at different m							Conversion of **2**	Yields[a] of **1a—g**
					2	3	4	5	6	7	8	%	
1	$HgCl_2$	1 : 2	180	2	6.5	47.6	27.6	12.4	4.9	1.0	Traces	94.3	91.9
2	$HgCl_2$	1 : 2	230	0.5	16.4	47.3	23.4	10.9	2.0	Traces	—	97.2	93.4
3	$HgCl_2$	1 : 2	230	2	28.8	53.2	17.3	0.7	Traces	—	—	100	92.9
4	$HgCl_2$	1 : 1	180	0.5	25.7	54.7	16.9	2.4	0.3	Traces	—	96.1	94.6
5	$HgCl_2$	1 : 1	180	2	37.9	53.3	8.8	—	—	—	—	100	92.3
6	$HgCl_2$	2 : 1	180	2	42.8	51.2	6.0	—	—	—	—	100	90.5
7	$HgCl_2$	2 : 1	230	0.5	43.6	51.8	4.6	—	—	—	—	100	82.5
8	$HgCl_2$	2 : 1	230	2	45.0	52.6	2.4	—	—	—	—	100	85.9
9	$SnCl_4$	1 : 4	180	3	13.2	31.1	26.4	18.0	7.4	2.7	1.2[c]	87.2	95.5
10	$SnCl_4$	1 : 2	125	3	13.7	30.4	20.7	14.3	8.8	6.7	5.4[c]	56.6	80.8
11	$SnCl_4$	1 : 2	180	1	22.1	41.3	20.9	12.4	3.3	Traces	—	100	87.3
12	$SnCl_4$	1 : 2	180	2	26.4	44.3	21.9	6.6	0.8	—	—	100	88.3
13	$SnCl_4$	1 : 2	180	3	27.3	45.3	23.3	3.7	0.4	—	—	100	90.5
14	$SnCl_4$	1 : 2	210	0.5	34.8	37.6	16.3	9.1	2.2	—	—	100	82.4
15	$SnCl_4$	1 : 1	180	1	11.0	46.1	35.3	7.4	0.2	—	—	100	87.1
16	$SnCl_4$	1 : 1	180	3	15.0	49.7	29.5	5.8	—	—	—	100	89.9
17	$SbCl_5$	1 : 2	20	0.003	49.4	22.0	17.6	7.3	2.4	1.3	—	100	54.2
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	$CrCl_3$	1 : 2	210	2	3.9	29.5	20.8	17.4	11.7	9.3	7.4[c]	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	$TiCl_4$	1 : 2	180	3	35.6	22.0	20.4	16.9	5.1	—	—	100	55.5
22	$MoCl_5$	1 : 2	200	1	54.5	30.6	14.9	—	—	—	—	100	24.5
23	WCl_6	1 : 2	200	1	75.9	16.1	8.0	—	—	—	—	77.9	55.4

[a] With respect to consumed polysilane **2**.

[b] With respect to the $—SiMe_2—$ unit.

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

reactions with $SbCl_5$, the conversion of polysilane **2** was 100%, whereas the yield of oligosilanes **1** was only 54%. In addition, unlike all known reactions with metal chlorides, the reaction of polysilane **2** with $SbCl_5$ was completed in several seconds at room temperature and was accompanied by heat evolution.

The highest yields of dichlorooligosilanes **1** were achieved in the reactions with the use of Hg^{II} and Sn^{IV} chlorides as chlorinating agents (see Table 1). It was found that an increase in the metal chloride : polysilane **2** ratio in the reactions performed at the same temperature over the same period of time (*cf.* runs *1*, *5*, and *6* and also runs *9*, *13*, and *16* in Table 1) led to an increase in the conversion of polysilane **2**, 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 $SnCl_4$ and polysilane **2** were taken in a ratio of 1 : 2 and the reactions were carried out at 125 °C (run *10*). However, the conversion of polysilane **2** 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 with $m > 9$. The optimum reaction conditions, which allow one to attain a high conversion of polysilane **2** 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 the $SnCl_4$ to polysilane **2** ratio is 1 : 4 (for $SnCl_4$); the corresponding conditions for $HgCl_2$ are 180 °C, 2 h, and 1 : 2.

The procedure for the synthesis of dichlorooligosilanes **1** based on the reactions of polysilane **2** with metal chlorides has advantages over other known procedures. Thus, this procedure makes it possible to prepare dichlorooligosilanes **1** containing more than six Si atoms in the oligomeric 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 infusible polysilane **2**, which is formed as a by-product in the synthesis of cyclosilanes,[14] is utilized.

Experimental

The GLC-mass spectrometric analysis was performed on a Kratos MS-890 instrument (15 m × 0.32 mm capillary column, SE-30 liquid phase, helium as the carrier gas, ionizing voltage was 70 eV, the temperature was increased from 30 to 250 °C with a rate of 10 °C min^{-1}). The GLC analysis was carried out on an LKhM-8MD chromatograph (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 °C min^{-1}, helium as the carrier gas). The ^{29}Si NMR spectra were recorded on Bruker WP-200 SY (39.76 MHz) and Bruker WP-400 SY (79.46 MHz) spectrometers with Me_4Si as the internal standard.

Polydimethylsilane **2** was prepared according to a modified procedure.[**15**] Chlorides $TiCl_4$, $SnCl_4$, and $SbCl_5$ were distilled in an N_2 flow immediately before use. The remaining metal chlorides were used without purification. Carbon tetrachloride was dried by distillation in an N_2 flow over P_2O_5.

Reaction of polysilane 2 with $SnCl_4$ (see Table 1, run *9*). Polysilane **2** (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 intense stirring. The reaction mixture was cooled and then anhydrous CCl_4 (50 mL) was added. The precipitate of $SnCl_2$ and unconsumed polysilane **2** were filtered off and washed with anhydrous CCl_4 (2×10 mL). The precipitate was treated with acetone to dissolve $SnCl_2$. Polysilane **2** was filtered off and dried at 60 °C *in vacuo* to a constant weight. Polysilane **2** 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 1). Fractionation of the residue afforded compounds **1a—g**.

Dichlorodisilane (1a), the yield was 5.4 g (10.1% with respect to consumed polysilane **2**), b.p. 147.5—148 °C. ^{29}Si NMR (CCl_4), δ: 17.23.

Dichlorotrisilane (1b), the yield was 13.0 g (27.9%), b.p. 85—86 °C (10 Torr). ^{29}Si NMR (CCl_4), δ: 24.95 ($SiMe_2Cl$); −43.77 ($SiMe_2$).

Dichlorotetrasilane (1c), the yield was 11.0 g (25.5%), b.p. 110—112 °C (5 Torr). ^{29}Si NMR (CCl_4), δ: 26.22 ($SiMe_2Cl$); −42.62 ($SiMe_2$).

Dichloropentasilane (1d), the yield was 7.6 g (18.3%), b.p. 95—96 °C (0.5 Torr). ^{29}Si NMR (CCl_4), δ: 26.26 ($SiMe_2Cl$); −41.12 (Si_bMe_2), −41.65 (Si_cMe_2).

Dichlorohexasilane (1e), the yield was 3.1 g (7.8%), b.p. 139—142 °C (0.5 Torr). ^{29}Si NMR (CCl_4), δ: 26.21 ($SiMe_2Cl$); −40.89 (Si_bMe_2); −40.02 (Si_cMe_2).

Dichlorotetradecamethylheptasilane (1f), the yield was 1.1 g (2.9%), b.p. 178—181 °C (0.5 Torr). Found (%): C, 35.44; H, 8.63; Cl, 14.27; Si, 40.78. $C_{14}H_{42}Cl_2Si_7$. Calculated (%): C, 35.18; H, 8.86; Cl, 14.83; Si, 41.13. ^{29}Si NMR (CCl_4), δ: 26.37 ($SiMe_2Cl$); −41.05 (Si_bMe_2); −39.80 (Si_cMe_2); −37.91 (Si_dMe_2). MS, *m/z* (I_{rel} (%)): 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).

Dichlorohexadecamethyloctasilane (1g), the yield was 0.5 g (1.3%), b.p. 185—187 °C (0.06 Torr). Found (%): C, 35.41; H, 8.85; Cl, 12.98; Si, 41.43. $C_{16}H_{48}Cl_2Si_8$. Calculated (%): C, 35.84; H, 9.02; Cl, 13.23; Si, 41.91. ^{29}Si NMR (CCl_4), δ: 26.43 ($SiMe_2Cl$); −40.89 (Si_bMe_2); −39.67 (Si_cMe_2); −37.69 (Si_dMe_2).

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

Runs *1—8* and *1—23** were carried out analogously (run *17* without heating) but the residues obtained after the removal of CCl_4 were analyzed by GLC rather than distilled (see Table 1).

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* In all experiments, we used polysilane **2** from the same preparation. Its conversion was determined after separation of the precipitate and dissolution of the metal chloride salt in the corresponding solvent.