

Preparation of oligosilanes containing perhalogenated silyl groups ($-\text{SiX}_3$, $-\text{SiX}_2-$, $>\text{SiX}-$, $\text{X} = \text{Cl}, \text{Br}$) and their hydrogenation by stannanes

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Abstract

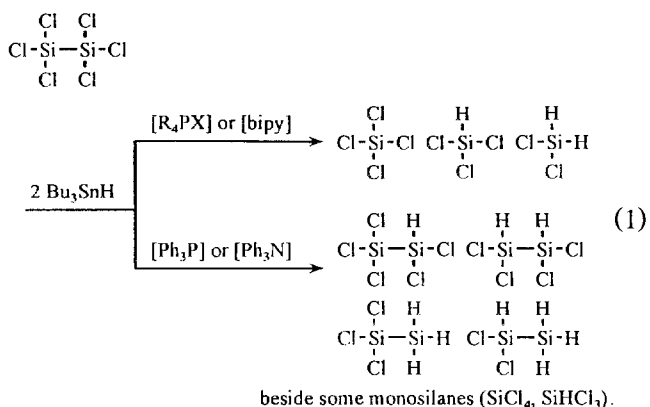
Starting from methylphenylsubstituted oligosilanes the disilanes $\text{SiX}_3-\text{SiX}_i\text{Me}_{3-i}$ ($i = 0, 1, 2$; $\text{X} = \text{Cl}, \text{Br}$), trisilanes $\text{SiX}_2(\text{SiX}_i\text{Me}_{3-i})$ ($i = 0, 1$) and branched tetrasilanes $\text{SiX}(\text{SiXMe}_2)_3$ were synthesized and their behavior towards the Lewis-base catalyzed hydrogenation by stannanes was investigated. In the case of methylchlorodisilanes $\text{SiCl}_3-\text{SiCl}_i\text{Me}_{3-i}$ Si-Si bond cleavage competes with the hydrogenation reaction. © 1997 Elsevier Science S.A.

Keywords: Silicon; Oligosilanes; Perhalogenated silyl groups

1. Introduction

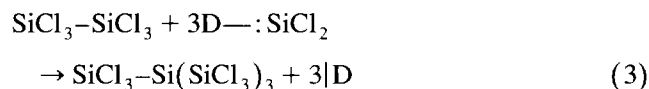
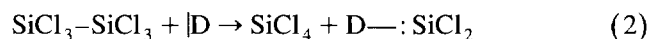
The Lewis-base catalyzed hydrogenation of methylchlorooligosilanes as well as methylbromooligosilanes with trialkylstannanes is a very useful method to provide partially as well as completely hydrogenated oligosilanes [1–3]. The formed product distribution depends on the starting molar ratio stannane: oligosilane, on the used catalyst and stannane.

But until now only few results are known about the hydrogenation of oligosilanes bearing completely halo-



gen substituted silicon units. Only the hydrogenation of hexachlorodisilane with tri-*n*-butylstannane has been investigated.

In the presence of a catalytically more active Lewis-base catalyst a cleavage of the Si-Si bond, presumably according to the mechanism described in Ref. [4] dominates followed by a partial hydrogenation of the primarily formed SiCl_4 [5]. The structure of the as formed higher oligosilanes was not investigated, but it is known from Refs. [6,7] that the Lewis-base catalyzed disproportionation of hexachlorodisilane leads to SiCl_4 and mainly $\text{Si}(\text{SiCl}_3)_4$:

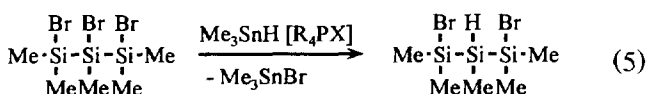
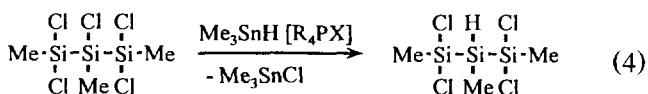


In this sense it was interesting to evaluate to which extend the disproportionation dominates the hydrogenation of other disilanes bearing one SiCl_3 unit ($\text{SiCl}_3-\text{SiCl}_i\text{Me}_{3-i}$) and to compare the results with those ones of the hydrogenation of methylbromodisilanes $\text{SiBr}_3-\text{SiBr}_i\text{Me}_{3-i}$. Furthermore the investigation of the hydrogenation reactions of some other oligosilanes having perhalogenated silyl groups (e.g. $\text{SiCl}_i\text{Me}_{3-i}-\text{SiCl}_2-\text{SiCl}_i\text{Me}_{3-i}$, $\text{SiCl}(\text{SiClMe}_2)_3$, $\text{cyclo}-(\text{SiCl}_2)_5$) should display, whether the disproportionation is a serious

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problem concerning only the hydrogenation of silanes bearing terminal SiX_3 units ($\text{X} = \text{Cl}, \text{Br}$) or not.

From the hydrogenation of trisilanes bearing one halogen substituent at the middle silicon atom ($-\text{SiXMe}-$ units) it is known [2,3,8] that this one is hydrogenated by stannanes at first.

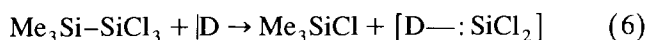


This regioselectivity should also result in the cases of oligomers having $-\text{SiX}_2-$ as well as $>\text{SiX}-$ units beside halogen substituents at the terminal silicon atoms.

2. Results and discussion

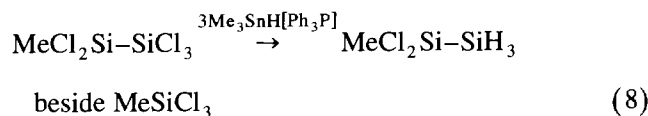
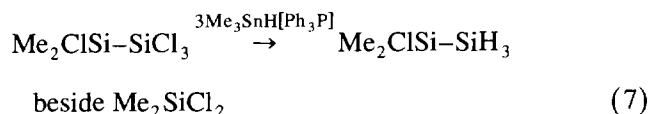
2.1. Hydrogenation of disilanes having one SiX_3 unit ($\text{X} = \text{Cl}, \text{Br}$)

All attempts to hydrogenate 1,1,1-trichlorotrimethyl-disilane with stannanes (Me_3SnH , Bu_3SnH) in presence of catalysts as Ph_3MePI , Ph_3P , bipy led only to a complete cleavage of the $\text{Si}-\text{Si}$ bond. Exclusively Me_3SiCl resulted as volatile product:



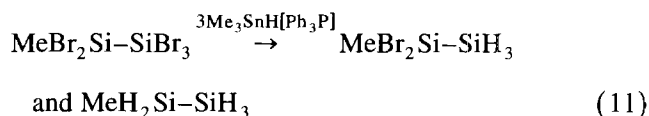
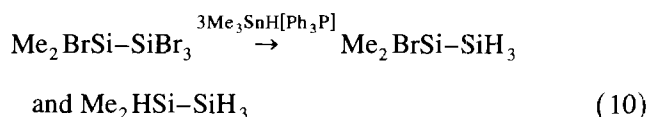
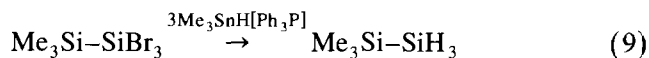
The structure of the eventually formed higher oligosilanes was not investigated yet.

Unlike this reaction the hydrogenation of 1,1,1,2-tetrachlorodimethyldisilane and pentachloromethyldisilane with Bu_3SnH (molar ratio 1:3) and Ph_3P as catalyst yielded partially hydrogenated disilanes and only little amounts (40% and 20%, respectively) of methylchloromonosilanes resulting from a disproportionation of the disilane:



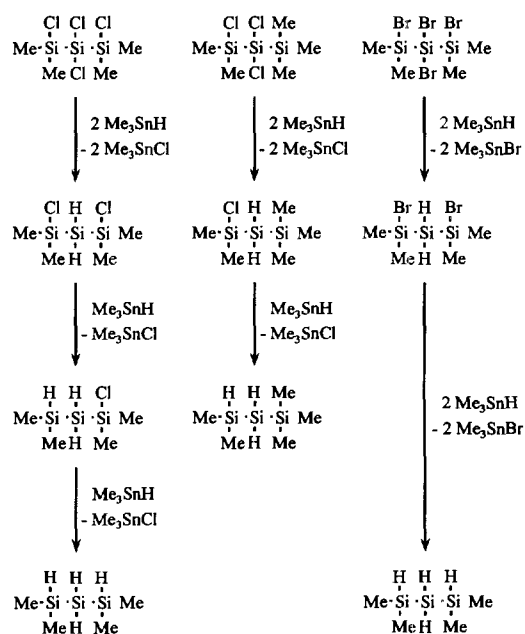
Not a trace of other partially hydrogenated disilanes could be indicated by means of ^{29}Si NMR spectroscopy.

If the hydrogenations were carried out with the analog methylbromodisilanes no $\text{Si}-\text{Si}$ bond cleavage could be observed:



These results exhibit, that the tendency of disilanes to give base catalyzed $\text{Si}-\text{Si}$ bond cleavage rises with the polarity of the $\text{Si}-\text{Si}$ bond rather than with an increase of the total number of electron withdrawing substituents. This conclusion parallels the observation in Ref. [4], where $\text{SiCl}_2\text{Me}-\text{SiClMe}_2$ is cleaved preferably to $\text{SiCl}_2\text{Me}-\text{SiCl}_2\text{Me}$ and $\text{SiClMe}_2-\text{SiClMe}_2$. Due to the less electron drawing effect of bromine substituents no $\text{Si}-\text{Si}$ bond cleavage occurs in methylbromodisilanes.

The hydrogenation in disilane molecules having one SiX_3 unit starts in all investigated examples exclusively at this group and leads only to the completely hydrogenated SiH_3 unit.



Scheme 1. Hydrogenation of the trisilanes $\text{SiX}_2(\text{SiXMe}_2)_2$, $\text{X} = \text{Cl}, \text{Me}/\text{Br}$.

Table 1

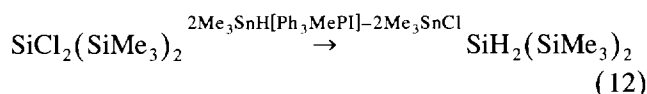
NMR data of the disilanes $\text{SiX}_3\text{-SiX}_i\text{Me}_{3-i}$, $\text{X} = \text{Cl, Br, H}$; $i = 0, 1, 2$ (chemical shifts in ppm and coupling constants in Hz)

Compound	δ_{SiA}	δ_{SiB}	$^1J_{\text{SiSi}}$	$\delta_{\text{HSi}^{\wedge}\text{H}}$	$\delta_{\text{HSi}^{\text{B}}\text{H}}$	δ_{HCH_3}
$\text{Si}^{\text{A}}\text{Cl}_3\text{Si}^{\text{B}}\text{Me}_3$	17.54	-7.15 ^a	115.7			0.25
$\text{Si}^{\text{A}}\text{Cl}_3\text{Si}^{\text{B}}\text{ClMe}_2$	7.82	15.67	150.6			0.60
$\text{Si}^{\text{A}}\text{Cl}_3\text{Si}^{\text{B}}\text{Cl}_2\text{Me}$	-0.22	14.01	245.6			0.95
$\text{Si}^{\text{A}}\text{Br}_3\text{Si}^{\text{B}}\text{Me}_3$	-3.40	-1.38				0.28
$\text{Si}^{\text{A}}\text{Br}_3\text{Si}^{\text{B}}\text{BrMe}_2$	-18.64	10.90	127			0.78
$\text{Si}^{\text{A}}\text{Br}_3\text{Si}^{\text{B}}\text{Br}_2\text{Me}$	-29.19	0.54				1.25
$\text{Si}^{\text{A}}\text{H}_3\text{Si}^{\text{B}}\text{Me}_3$	-98.07	-17.09		3.17		0.11
$\text{Si}^{\text{A}}\text{H}_3\text{Si}^{\text{B}}\text{HMe}_2$	-98.47	-40.56		$3.19 \text{ } ^3J_{\text{HH}}: 2.4$	3.95	$0.10 \text{ } ^3J_{\text{HH}}: 5$
$\text{Si}^{\text{A}}\text{H}_3\text{Si}^{\text{B}}\text{H}_2\text{Me}^{\text{b}}$	-100.67	-70.12		$3.25 \text{ } ^3J_{\text{HH}}: 3.1$	3.69	$0.07 \text{ } ^3J_{\text{HH}}: 4.9$
$\text{Si}^{\text{A}}\text{H}_3\text{Si}^{\text{B}}\text{ClMe}_2$	-95.24	21.40		3.24		0.39
$\text{Si}^{\text{A}}\text{H}_3\text{Si}^{\text{B}}\text{BrMe}_2$	-93.35	13.53		$3.36 \text{ } ^1J_{\text{SiH}}: -196$		0.48
$\text{Si}^{\text{A}}\text{H}_3\text{-Si}^{\text{B}}\text{Cl}_2\text{Me}$	-90.68	29.99		$3.29 \text{ } ^1J_{\text{SiH}}: -204$		0.57
$\text{Si}^{\text{A}}\text{H}_3\text{Si}^{\text{B}}\text{Br}_2\text{Me}$	-86.06	13.01		3.56		0.88

^a $^1J_{\text{SiC}}: 49.2$ Hz.^b ^{29}Si and ^1H NMR data already known from Ref. [12].

2.2. Hydrogenation of trisilanes containing a $-\text{SiX}_2-$ unit

The hydrogenation of $\text{SiCl}_2(\text{SiMe}_3)_2$ with Me_3SnH provides pure $\text{SiH}_2(\text{SiMe}_3)_2$. Any cleavage of Si–Si bonds could not be observed:

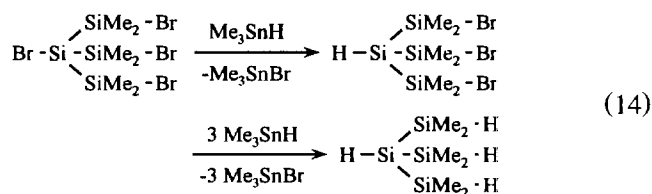
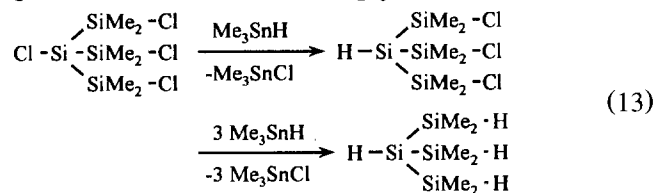


Our attempts to produce $\text{SiHCl}(\text{SiMe}_3)_2$ failed. The hydrogenation of $\text{SiCl}_2(\text{SiMe}_3)_2$ with one equivalent Me_3SnH yields a mixture of 50% $\text{SiCl}_2(\text{SiMe}_3)_2$ and 50% $\text{SiH}_2(\text{SiMe}_3)_2$.

Starting with $\text{SiX}_2(\text{SiXMe}_2)_2$ ($\text{X} = \text{Cl, Br}$) the reaction with two equivalents Me_3SnH leads exclusively to $\text{SiH}_2(\text{SiXMe}_2)_2$. A stepwise hydrogenation of the terminal Si–halogen bonds occurs, if more stannane is added. This course was also observed for $\text{SiMe}_3\text{-SiCl}_2\text{-SiClMe}_2$ (in mixture with $\text{SiCl}_2(\text{SiClMe}_2)_2$ and parallels the results of the hydrogenation of trisilanes bearing a $-\text{SiXMe}-$ unit [2,3] (Scheme 1). Ph_3MePI was used as a catalyst.

2.3. Hydrogenation of isotetrasilanes containing a tertiary $>\text{SiX}-$ unit

As expected, the hydrogenation of $\text{SiX}(\text{SiXMe}_2)_3$ ($\text{X} = \text{Cl, Br}$) with one equivalent Me_3SnH (Ph_3MePI as catalyst) provides $\text{SiH}(\text{SiXMe}_2)_3$ exclusively. Reaction with an excess of Me_3SnH yields the completely hydrogenated molecule $\text{SiH}(\text{SiHMe}_2)_3$:



2.4. Hydrogenation of cyclo- $(\text{SiCl}_2)_5$

The reaction of cyclo- $(\text{SiCl}_2)_5$ with Me_3SnH (Ph_3MePI as catalyst) results in a stepwise hydrogenation of SiCl_2 units to SiH_2 units. The assignment of the ^{29}Si NMR signals especially in the SiCl_2 region was very difficult and only possible by comparison of the spectra of mixtures with different molar ratios $\text{Me}_3\text{SnH}:\text{Si}_5\text{Cl}_{10}$ (1:2, 1:4, 1:6, 1:8). Any formation of products containing SiHCl units was not indicated in the ^{29}Si NMR spectra (no signal in the expected chemical shift range for $-\text{SiHCl}-$). The dominating product in the stepwise hydrogenation is 1,1,3,3-tetrachlorocyclopentasilane, whereas 1,1,2,2,3,3,4,4-octachlorocyclopentasilane could not be detected. With an excess of Me_3SnH the previously known [9] $(\text{SiH}_2)_5$ is formed.

2.5. NMR measurements

Even though the investigated methylchlorodisilanes and methylbromodisilanes are relatively small and sim-

Table 2
NMR data of further methylbromodisilanes

Compound	δ_{SiA}	δ_{SiB}	$^1J_{\text{SiSi}}$	δ_{HA}	δ_{HB}
$\text{Si}^{\text{A}}\text{BrMe}_2\text{Si}^{\text{B}}\text{Me}_3$ ^a	17.97	-17.71	92	0.48	0.11
$\text{SiBrMe}_2\text{-SiBrMe}_2$ ^a	10.47			0.54	
$\text{Si}^{\text{A}}\text{Br}_2\text{Me-Si}^{\text{B}}\text{Me}_3$	23.92	-11.49	103	1.04	0.20
$\text{Si}^{\text{A}}\text{Br}_2\text{Me-Si}^{\text{B}}\text{BrMe}_2$	11.11	8.38		1.11	0.68
$\text{SiBr}_2\text{Me-SiBr}_2\text{Me}$ ^a	2.84			1.18	

^a NMR data already published in Ref. [3].

Table 3

NMR data of the trisilanes $\text{SiX}_i\text{Me}_{3-i}-\text{SiX}_2-\text{SiX}_j\text{Me}_{3-j}$, X = Cl, Br, H; $i = 0, 1$; $j = 0, 1$

Compound	δ_{Si}	$^1J_{\text{SiSi}}$	$\delta_{\text{H}} \text{SiMe}/$ $^3J_{\text{HH}}$	$\delta_{\text{H}} \text{SiH}$
$\text{Si}^{\text{A}}\text{Cl}_2(\text{Si}^{\text{B}}\text{Me}_3)_2$ ^a	A: 34.51	76	0.211	
	B: -11.42			
$\text{Si}^{\text{A}}\text{H}_2(\text{Si}^{\text{B}}\text{Me}_3)_2$ ^a	A: -103.88	69	0.195	2.67
	B: -14.12			
$\text{Si}^{\text{A}}\text{Cl}_2(\text{Si}^{\text{B}}\text{ClMe}_2)-$ $(\text{Si}^{\text{C}}\text{Me}_3)$	A: 23.37			
	B: 17.45			
	C: -9.67			
$\text{Si}^{\text{A}}\text{H}_2(\text{Si}^{\text{B}}\text{ClMe}_2)-$ $(\text{Si}^{\text{C}}\text{Me}_3)$	A: -101.09			2.91
	B: 26.7			
$\text{Si}^{\text{A}}\text{H}_2(\text{Si}^{\text{B}}\text{HMe}_2)-$ $(\text{Si}^{\text{C}}\text{Me}_3)$	A: -104.62		-2.9 ^b	2.74
	B: -38.10			
	C: -13.93			
$\text{Si}^{\text{A}}\text{Cl}_2(\text{Si}^{\text{B}}\text{ClMe}_2)_2$ ^a	A: 13.44	98	0.599	
	B: 17.38			
$\text{Si}^{\text{A}}\text{H}_2(\text{Si}^{\text{B}}\text{ClMe}_2)_2$	A: -97.91		0.545	3.15
	B: 24.52			
$\text{Si}^{\text{A}}\text{H}_2(\text{Si}^{\text{B}}\text{HMe}_2)-$ $(\text{Si}^{\text{C}}\text{ClMe}_2)$	A: -101.52		-2.7 ^b	2.98
	B: -38.41			
	C: 26.21			
$\text{Si}^{\text{A}}\text{Br}_2(\text{Si}^{\text{B}}\text{BrMe}_2)_2$	A: -4.31	90	0.54	
	B: 9.15			
$\text{Si}^{\text{A}}\text{H}_2(\text{Si}^{\text{B}}\text{BrMe}_2)_2$	A: -94.62		0.220/4.3	3.98
	B: 17.33			
$\text{Si}^{\text{A}}\text{H}_2(\text{Si}^{\text{B}}\text{HMe}_2)_2$	A: -105.81	68	-2.85 ^b	2.81
	B: -38.01			

^a ²⁹Si NMR shifts and ¹J_{SiSi} already given in Ref. [10].

^b Coupling constant ³J_{Hi-Si^A-Si^B-H}.

ple molecules as far as we know no ²⁹Si NMR chemical shifts has been reported until now. Only ¹H NMR data of $\text{SiCl}_3-\text{SiCl}_i\text{Me}_{3-i}$ ($i = 0, 1, 2$) has been given in Ref. [10]. In order to complete the NMR data of the series of methylbromodisilanes 1,1-dibromotetramethyl-

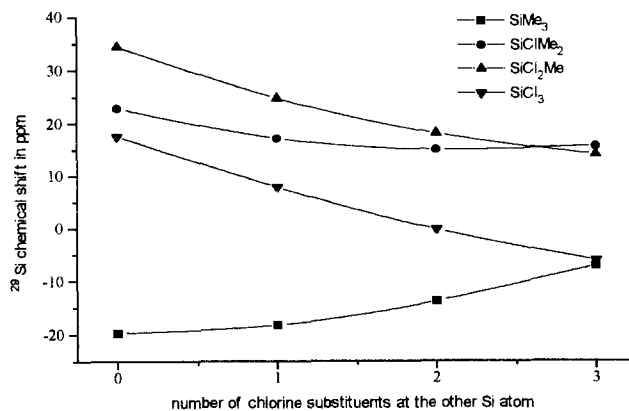


Fig. 1. ²⁹Si NMR chemical shifts in methylchlorodisilanes $\text{SiCl}_i\text{Me}_{3-i}-\text{SiCl}_j\text{Me}_{3-j}$.

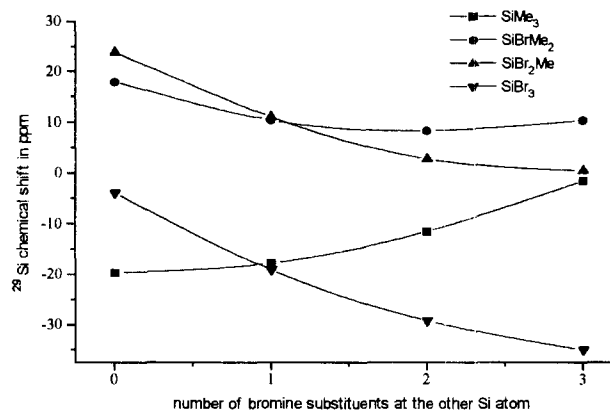


Fig. 2. ²⁹Si NMR chemical shifts in methylbromodisilanes $\text{SiBr}_i\text{Me}_{3-i}-\text{SiBr}_j\text{Me}_{3-j}$.

disilane and 1,1,2-tribromotrimethyldisilane were prepared, too. Tables 1 and 2 show the results of our NMR measurements of disilanes.

The found NMR data of trisilanes, Table 3, fit well the trends of previously published data for instance in Ref. [11].

The substitution of a methyl group by a hydrogen atom causes an upfield shift on the neighbour Si atom, the opposite signal moving happens if a methyl group is substituted by a halogen atom. (See Figs. 1–3.)

3. Experimental

3.1. Preparation of methylphenyloligosilanes

1,1-diphenyltetramethyldisilane and 1,1,1-triphenyltrimethyldisilane were prepared according to Ref. [14].

NMR: $\text{SiPh}_2\text{Me}-\text{SiMe}_3$: δ_{Si} : -21.3 ppm, -18.3 ppm, δ_{H} : 0.22 ppm (9H), 0.66 ppm (3H), 7.2–7.6 ppm (10H); $\text{SiPh}_3-\text{SiMe}_3$: δ_{Si} : -20.6 ppm, -18.6 ppm, δ_{H} : 0.23 ppm (9H), 7.2–7.6 ppm (15H).

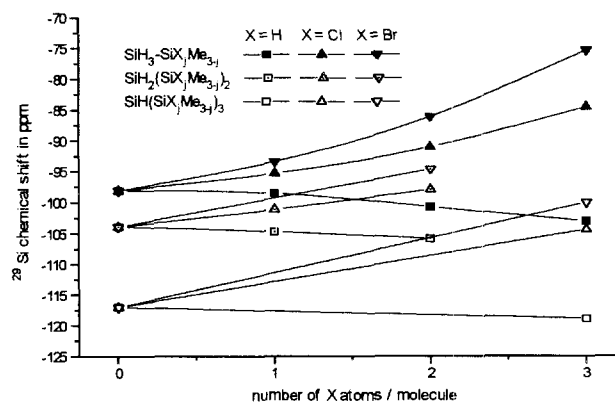


Fig. 3. ²⁹Si NMR chemical shifts of $\text{SiH}_i(\text{SiX}_j\text{Me}_{3-j})_{4-i}$, $i = 1, 2, 3$.

Table 4
NMR data of the isotetrasilanes $\text{Si}^{\text{A}}\text{X}(\text{Si}^{\text{B}}\text{CMe}_2)_3$, X = Cl, H/Br, H

Compound	$\delta_{\text{Si}^{\text{A}}}$	$^1J_{\text{Si}^{\text{A}}\text{Si}^{\text{B}}}$	$\delta_{\text{Si}^{\text{B}}}$
$\text{Si}^{\text{A}}\text{Cl}(\text{Si}^{\text{B}}\text{ClMe}_2)_3$	-24.38	77	22.12
$\text{Si}^{\text{A}}\text{H}(\text{Si}^{\text{B}}\text{ClMe}_2)_3$	-104.32	69	26.09
$\text{Si}^{\text{A}}\text{H}(\text{Si}^{\text{B}}\text{HMe}_2)_3$	-118.91		-35.54
$\text{Si}^{\text{A}}\text{Br}(\text{Si}^{\text{B}}\text{BrMe}_2)_3$	-40.09		12.71
$\text{Si}^{\text{A}}\text{H}(\text{Si}^{\text{B}}\text{BrMe}_2)_3$	-100.00		18.09

3.1.1. 2,2-diphenylhexamethyltrisilane

A mixture of 20 g Ph_2SiCl_2 and 200 g Me_3SiCl was added to 3.46 g Li powder in 100 ml dried tetrahydrofuran. After stirring over night the mixture was filtered from LiCl. Excess Me_3SiCl and THF were separated from the residue of $\text{SiPh}_2(\text{SiMe}_3)_2$ by distillation.

Yield: 27 g (66%), GC/MS (*m/e*, rel. int.): 328 (M^+ , 47), 313 ($\text{Si}_3\text{Me}_5\text{Ph}_2$, 12), 255 ($\text{Si}_2\text{Me}_3\text{Ph}_2$, 100), 225 (Si_2MePh_2 , 9), 197 (SiMePh_2 , 53), 178 ($\text{Si}_2\text{Me}_3\text{Ph}$, 67), 163 ($\text{Si}_2\text{Me}_2\text{Ph}$, 66), 135 (SiMe_2Ph , 87), 105 (SiPh , 28), 73 (SiMe_3 , 35).

NMR: δ_{Si} : -38.7 ppm (SiPh_2), -16.0 ppm (SiMe_3).

3.1.2. Tris-(trimethylsilyl)-phenylsilane

A mixture of 25 g PhSiCl_3 and 250 g Me_3SiCl was added to 6.9 g Li powder in 100 ml dried tetrahydrofuran. After stirring over night the mixture was filtered from LiCl and fractionated to yield 27 g (50%) $\text{SiPh}(\text{SiMe}_3)_3$. B.p. 200–210°C/0.6 kPa.

GC/MS (*m/e*, rel. int.): 324 (M^+ , 31), 309 ($\text{Si}_4\text{Me}_8\text{Ph}$, 10), 251 ($\text{Si}_3\text{Me}_6\text{Ph}$, 12), 236 ($\text{Si}_3\text{Me}_5\text{Ph}$, 15), 221 ($\text{Si}_3\text{Me}_4\text{Ph}$, 8), 191 ($\text{Si}_3\text{Me}_2\text{Ph}$, 23), 174 (Si_3Me_6 , 100), 159 (Si_3Me_5 , 37), 135 (SiMe_2Ph , 78), 73 (SiMe_3 , 96).

NMR: δ_{Si} : -76.8 ppm (SiPh), -12.8 ppm (SiMe_3)
 $^1J_{\text{SiSi}}$: 62 Hz, δ_{H} : 0.21 ppm (27H), 7.2–7.7 ppm (5H).

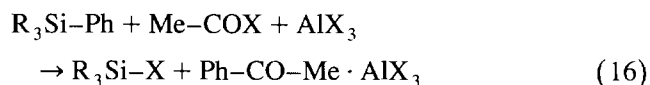
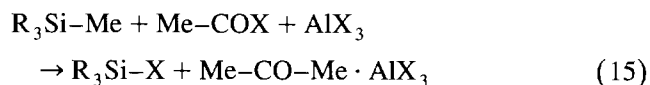
3.1.3. Decaphenylcyclopentasilane

126.5 g Ph_2SiCl_2 were added to 6.9 g Li powder in 200 ml THF. After stirring over night the mixture was filtered and THF removed in vacuo. The residue was dissolved in toluene, filtered and the toluene removed in vacuo to yield 48 g (53%) $\text{Si}_5\text{Ph}_{10}$. ^{29}Si NMR: one signal at -34 ppm (-34.4 ppm [13]).

3.2. Preparation of methylchlorooligosilanes and methylbromooligosilanes

All methylchlorooligosilanes as well as methylbromooligosilanes were prepared starting from phenylmethyloligosilanes by action of acetyl chloride plus aluminiumchloride or acetyl bromide plus aluminiumbromide, respectively. After the conversion was complete, n-hexane was added to extract the as formed halogenated oligosilane out of the residue of acetone

and acetophenone aluminiumhalogenide complex (X = Cl, Br):



Because Si–Ph bonds are much more reactive towards acetyl halide than Si–Me bonds, all Si–Ph bonds were transformed first.

The hexane phase was separated and the solvent could easily be removed from the desired silane by condensation in vacuo.

The NMR data of the products are summarized in Tables 1–5.

3.2.1. 1,1,1-trichlorotrimethyldisilane, 1,1,1,2-tetrachlorodimethyldisilane and pentachloromethylidisilane

8.5 g $\text{SiPh}_3\text{SiMe}_3$, 10.25 g AlCl_3 and 6.0 g acetyl chloride yielded, after working up as described, 2.9 g (55%) pure $\text{SiCl}_3\text{SiMe}_3$ (b.p. 70°C/3 kPa).

The same reaction, carried out with 13.5 g AlCl_3 and 8.0 g acetyl chloride at 50°C (2 h) led to 2 g (35%) $\text{SiCl}_3-\text{SiClMe}_2$ (after distillation).

Pentachloromethylidisilane can also be prepared from $\text{SiPh}_3\text{SiMe}_3$ with AlCl_3 and acetylchloride (starting molar ratio 1 : 6 : 6, 10 h at 120°C, yield 30%), but more conveniently it can be obtained from $\text{SiCl}_2\text{Ph}-\text{SiCl}_2\text{Me}$ as it will be published in Ref. [15].

Table 5
NMR data of cyclopentasilanes $\text{Si}_5\text{H}_i\text{Cl}_{10-i}$, $i = 0, 4, 6, 8, 10$

compound	$\delta_{\text{Si}^{\text{A}}}$	δ_{H}
a)	-1.8	-
A: -83.5 B: 3.0 C: 8.9		4.00
A: -89.2 B: -78.7 C: 12.8		A: 3.78 B: 3.91
A: -107.5 B: -87.1 C: 14.4		A: 3.49 B: 3.74 $^3J_{\text{HH}}$: 3.8
a)	-105.7	3.46

^a ^{29}Si NMR shifts already published in Ref. [13].

3.2.2. 1,1-dibromotetramethyldisilane

The reaction of 5.5 g $\text{SiPh}_2\text{Me-SiMe}_3$ with 10.7 g AlBr_3 and 4.9 g acetylbromide at room temperature provided after the usual work up and distillation 2.0 g (36%) $\text{SiBr}_2\text{Me-SiMe}_3$ (b.p. $50^\circ\text{C}/0.8\text{ kPa}$, m.p. 40°C).

3.2.3. 1,1,2-tribromotrimethyldisilane

Bromination of 4.2 g Si_2Me_6 with 22.9 g AlBr_3 and 10.6 g acetyl bromide (1 h at 120°C) yielded after distillation 7.55 g (77%) of a crystalline product containing 80% $\text{SiBr}_2\text{Me-SiBrMe}_2$ beside 10% $\text{SiBrMe}_2\text{-SiBrMe}_2$ and $\text{SiBr}_2\text{Me-SiBr}_2\text{Me}$ (10%).

3.2.4. 1,1,1-tribromotrimethyldisilane, 1,1,1,2-tetra-bromodimethyldisilane and pentabromomethyldisilane

The reaction of 2.0 g $\text{SiPh}_3\text{SiMe}_3$ with (a) 5.6 g AlBr_3 and 2.6 g acetylbromide at room temperature, (b) 7.5 g aluminiumbromide and 3.5 g acetyl bromide at 50°C and (c) 9 g aluminiumbromide and 4.2 g acetylbromide (10 h at 120°C) yielded (a) 1.5 g (73%) $\text{SiBr}_3\text{SiMe}_3$, (b) 1.8 g (74%) $\text{SiBr}_3\text{SiBrMe}_2$ (m.p. $65\text{--}68^\circ\text{C}$) and (c) 2.0 g (70%) $\text{SiBr}_3\text{SiBr}_2\text{Me}$ (m.p. 83°C).

3.2.5. 2,2-dichlorohexamethyltrisilane

The chlorination of 23 g $\text{SiPh}_2(\text{SiMe}_3)_2$ with 22.6 g AlCl_3 and 13.4 g acetyl chloride at room temperature provided after distillation 6.2 g (36%) pure $\text{SiCl}_2(\text{SiMe}_3)_2$ (b.p. $50^\circ\text{C}/0.6\text{ kPa}$). GC/MS (*m/e*, rel. int.): 244 (M^+ , 5), 229 ($\text{Si}_3\text{Me}_5\text{Cl}_2$, 3), 209 ($\text{Si}_3\text{Me}_6\text{Cl}$, 1), 151 ($\text{Si}_2\text{Me}_4\text{Cl}$, 4), 136 ($\text{Si}_2\text{Me}_3\text{Cl}$, 39), 131 (Si_2Me_5 , 9), 93 (SiMe_2Cl , 8), 73 (SiMe_3 , 100).

This mass spectrum differs significantly from that of 1,3-dichlorohexamethyltrisilane (prepared as described in Ref. [16]): 244 (M^+ , 1), 229 ($\text{Si}_3\text{Me}_5\text{Cl}_2$, 2), 209 ($\text{Si}_3\text{Me}_6\text{Cl}$, 5), 151 ($\text{Si}_2\text{Me}_4\text{Cl}$, 47), 131 (Si_2Me_5 , 7), 116 (Si_2Me_4 , 29), 93 (SiMe_2Cl , 14), 73 (SiMe_3 , 100).

3.2.6. 1,2,2,3-tetrachlorotetramethyltrisilane and 1,2,2-trichloropentamethyltrisilane

3.0 g $\text{SiCl}_2(\text{SiMe}_3)_2$ were chlorinated with 6 g AlCl_3 and 3.5 g acetyl chloride and yielded after working up 2.7 g (77%) $\text{SiCl}_2(\text{SiClMe}_2)_2$ as oily residue. Repetition of this reaction with 4.7 g AlCl_3 and 2.75 g acetyl chloride provided 2.5 g of a mixture of 70% $\text{SiCl}_2(\text{SiClMe}_2)_2$ with 30% $\text{SiClMe}_2\text{-SiCl}_2\text{-SiMe}_3$.

3.2.7. Tris-(chlorodimethylsilyl)-chlorosilane and tris-(bromodimethylsilyl)-bromosilane

These isotetrasilanes could be obtained from tris-(trimethylsilyl)-phenylsilane:

5.25 g $\text{SiPh}(\text{SiMe}_3)_3$, 12 g AlCl_3 and 6.25 g acetylchloride provided 3 g (54%) $\text{SiCl}(\text{SiClMe}_2)_3$.

4.7 g $\text{SiPh}(\text{SiMe}_3)_3$, 21.6 g AlBr_3 and 8 g acetyl bromide yielded 4 g (53%) $\text{SiBr}(\text{SiBrMe}_2)_3$.

3.2.8. Decachlorocyclopentasilane

15 g $\text{Si}_5\text{Ph}_{10}$ were reacted with 32 g aluminiumchloride and 17.5 g acetyl chloride (1 h at 75°C and 10 h at room temperature) to yield 3.5 g (43%) $\text{Si}_5\text{Cl}_{10}$.

3.3. Hydrogenations with stannanes

The hydrogenations of disilanes were carried out with Bu_3SnH . So the hydrogenated disilanes as well as formed monosilanes could easily be separated from the catalyst and the formed Bu_3SnX ($\text{X} = \text{Cl}, \text{Br}$) by condensation of the silanes into a trap in vacuo at room temperature. Ph_3P was used as catalyst, because it was known from the hydrogenation of Si_2Cl_6 that this base is suitable for the hydrogenation of SiCl_3 groups.

In all other hydrogenation reactions (trisilanes, isotetrasilanes as well as cyclopentasilanes) Me_3SnH was used together with Ph_3MePI as catalyst. The formed Me_3SnX have relatively simple $^1\text{H NMR}$ spectra and can easily be removed from high boiling oligosilanes by condensation in vacuo at room temperature. In a typical experiment an amount of 0.5–1 g of the oligosilane was mixed in the desired molar ratio with Me_3SnH or Bu_3SnH at room temperature and a trace of the catalyst (1 mol% of the oligosilane) was added. The reaction with stannanes were almost quantitative, that means all R_3SnH was converted into R_3SnX ($\text{X} = \text{Cl}, \text{Br}$) as could be detected by $^{119}\text{Sn NMR}$ spectroscopy. The isolable yields of hydrogenated oligosilanes were in the range 80–100%.

Me_3SnH was freshly prepared from Me_3SnCl and LiAlH_4 in tetraglyme. Bu_3SnH was commercially available from Merck.

3.4. NMR measurements

All NMR measurements were carried out with a BRUKER MSL 300 spectrometer (^{29}Si : 59.627 MHz, ^1H : 300.13 MHz). TMS was used as internal standard.

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