Base catalysed hydrogenation of methylbromooligosilanes with trialkylstannanes, identification of the first methylbromohydrogenoligosilanes

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Abstract

The Lewis base catalysed hydrogenation of methylchlorooligsilanes with trialkylstannanes can also be applied to the hydrogenation of methylbromooligosilanes. In this way methylbromohydrogenoligosilanes were prepared for the first time. Methylbromotrisilanes with an > SiBrMe middle group (e.g. $SiBrMe_2-SiBrMe-SiBrMe_2$) are hydrogenated first at this silicon atom under formation of an > SiHMe group (e.g. $SiBrMe_2-SiHMe-SiBrMe_2$). Brominated silanes containing a quarternary $Si(Si)_4$ unit (e.g. $Si(SiBrMe_2)_4$) do not react with trialkylstannanes.

Keywords: Silane; Hydrogenation; Stannanes; Nuclear magnetic resonance; Oligosilanes

1. Introduction

Oligosilanes containing methyl, bromine and hydrogen substituents simultaneously are unknown until now. The hydrogenation of methylbromooligosilanes with $LiAlH_4$ in etheral solvents leads to the formation of the completely hydrogenated methylhydrogenoligosilanes only.

Recently, we have investigated the partial hydrogenation of $SiCl_4$, methylchloromono- and -oligosilanes (Si_2-Si_6) by trialkylstannanes in the presence of a Lewis base catalyst [1–4]. We were able to show that the hydrogenation by trialkylstannanes takes place at the silicon atom with the highest acceptor strength first. The acceptor strength increases with the number of silyl and chlorine substituents, e.g. in the order:

$$SiCl_2Me-SiClMe-SiCl_2Me > SiCl_2Me-SiCl_2Me >$$
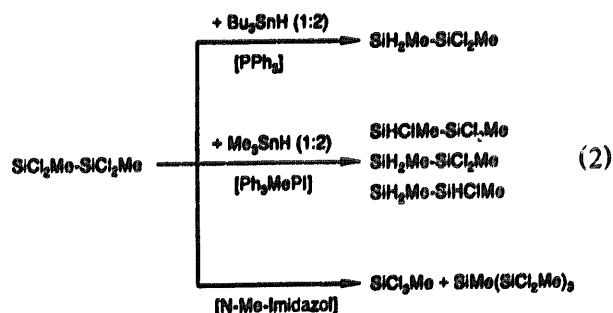$$SiClMe_2-SiClMe_2 > SiCl_3Me > SiCl_2Me_2$$
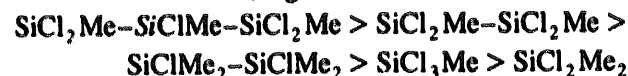
This series was confirmed by our MO calculations (see Table 1) and can also be concluded from the stability of 2.2' bipy adducts of mono-, di- and trisilanes [6].

The first step of the overall reaction is the attack of the Lewis base catalyst at the silicon atom, forming a hypervalent silicon atom and stretching the silicon halogen bond. In a second step, this species reacts with the stannane to give hydrogenated silane and trialkylhalostannane (X = Cl, Br):

(1)
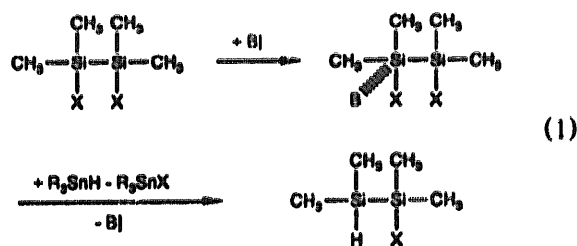
The obtained product spectrum of silanes can be influenced by a variation of both the stannane and the Lewis base used, e.g.:

(2)

Table 1
LUMO energies of methylchlorosilanes (STO 3-21 G$^{(**)}$) [5]

Compound	LUMO energy (eV)
SiCl$_2$Me–SiClMe–SiCl$_2$Me	2.25 *
SiCl$_2$Me–SiCl$_2$Me	3.01
SiCl$_2$Me–SiClMe$_2$	3.28
SiClMe$_2$–SiClMe$_2$	3.75
SiClMe$_2$–SiMe$_3$	4.28
SiCl$_3$Me	4.47

* The LUMO is mainly localized at the middle silicon atom.

Addition of N-methylimidazole leads immediately to a disproportionation of the disilane [7].

2. Results and discussion

The hydrogenation of the disilanes SiBrMe$_2$–SiMe$_3$ (1), SiBrMe$_2$–SiBrMe$_2$ (2), SiBr$_2$Me–SiBr$_2$Me (3), trisilanes SiBrMe$_2$–SiMe$_2$–SiBrMe$_2$ (4), SiBrMe$_2$–SiBrMe–SiBrMe$_2$ (5), isotetrasilanes SiMe(SiBrMe$_2$)$_3$ (SiMe$_3$)$_{3-i}$, i = 1, 2, 3 (6a, 6b, 6c), SiMe(SiBr$_2$Me)$_3$ (7) and neopentasilanes Si(SiBrMe$_2$)$_i$(SiMe$_3$)$_{4-i}$, i = 1, 2, 3, 4, (8a, 8b, 8c, 8d) was investigated.

The methylbromooligosilanes 1 [8], 2 [9], 3 [10], 4, 5 [11] and 6c [12], were already known. The prepared products were characterized by means of ^{29}Si, ^{1}H NMR and GC MS. The identification and quantification of the formed hydrogenation products were carried out by means of ^{29}Si and ^{1}H NMR spectroscopy. The NMR data are summarized in Table 2(a)=(c).

The trends of the ^{29}Si chemical shifts of the tertiary as well as the quarternary silicon atoms are demonstrated in Figs. 1–3.
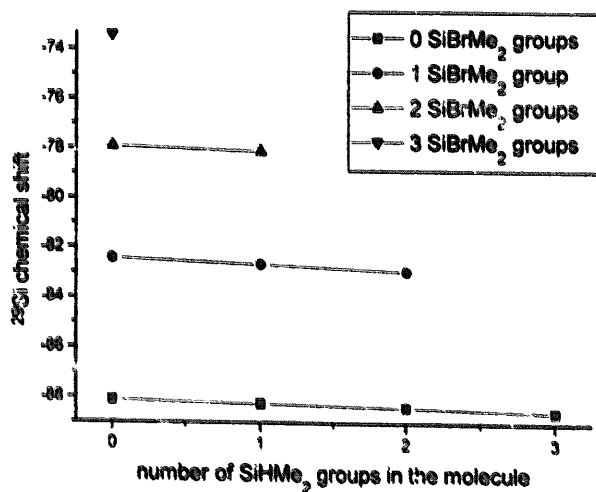
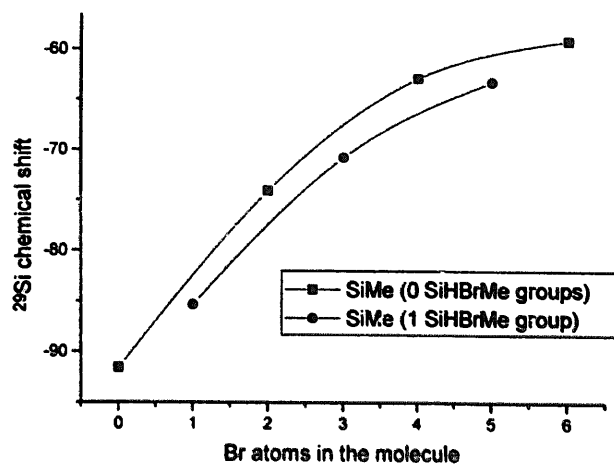Fig. 2. ^{29}Si NMR chemical shift (ppm) of the tertiary SiMe group in the compounds SiMe(SiH$_2$Me)$_x$(SiHBrMe)$_y$(SiBr$_2$Me)$_{3-x-y}$.

2.1. Hydrogenation of SiBrMe$_2$SiMe$_3$ (1) and SiBrMe$_2$–SiBrMe$_2$ (2)

Reaction of 1 with Bu$_3$SnH in a 1:1 molar ratio led to pure SiHMe$_2$–SiMe$_3$, whereas hydrogenation of 2 in a 1:1 molar ratio resulted in a mixture containing 75 mol% SiHMe$_2$–SiBrMe$_2$ besides 2 and SiHMe$_2$–SiHMe$_2$. A similar result was achieved by using Me$_3$SnH instead of Bu$_3$SnH (68 mol% SiHMe$_2$–SiBrMe$_2$).

2.2. Hydrogenation of SiBr$_2$Me–SiBr$_2$Me (3)

The hydrogenation of 3 was carried out with two molar ratios 3:Bu$_3$SnH. Table 3 shows the relative amounts of the hydrogenated disilanes after condensation into a trap.

Compared with SiCl$_2$Me–SiCl$_2$Me (14), the formation of the asymmetrically double hydrogenated product SiH$_2$Me–SiX$_2$Me is not so much favored. Whereas the hydrogenation of 14 with Bu$_3$SnH (1:2 molar ratio) in the presence of Ph$_3$P yielded only SiH$_2$Me–SiX$_2$Me

Fig. 1. ^{29}Si NMR chemical shift (ppm) of the tertiary SiMe group in the compounds SiMe(SiHMe$_2$)$_x$(SiBrMe$_2$)$_y$(SiMe$_3$)$_{3-x-y}$.
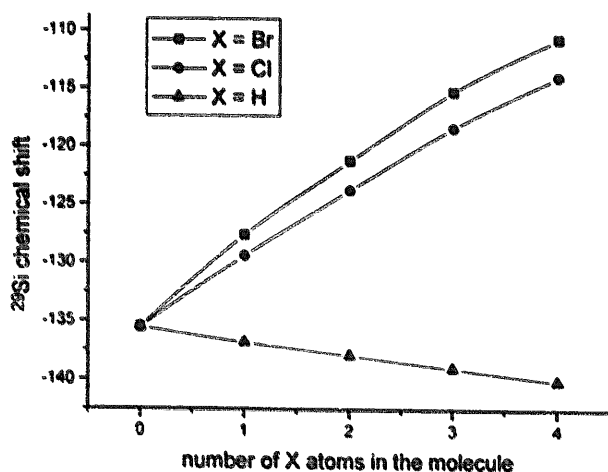
Fig. 3. ^{29}Si NMR chemical shift (ppm) of the quarternary silicon atom in the compounds Si(SiXMe$_2$)$_x$(SiMe$_3$)$_{4-x}$ with X = Br, Cl [15] and H.

(60–70%) besides **14** and SiH_2Me-SiH_2Me [2], **3** yielded all possible hydrogenated products SiY_2Me-SiY_2Me (Y = H, Br).

A further difference between **3** and **14** could be obtained in the behavior towards N-methylimidazole: whereas **14** immediately disproportionates into $SiCl_3Me$ and higher oligosilanes, no reaction was observed with **3** at room temperature.

2.3. Hydrogenation of $SiMe_2(SiBrMe_2)_2$ (4) and $SiBrMe(SiBrMe_2)_2$ (5)

In accordance with the hydrogenation of $SiMe_2(SiClMe_2)_2$, the reaction of **4** with Me_3SnH (1:1) yields the monohydrogenated product $SiHMe_2$-$SiMe_2$-$SiBrMe_2$ in about 60% yield besides **4** and $SiMe_2(SiHMe_2)_2$.

Table 2
NMR data (chemical shifts in ppm and coupling constants in Hz)

(a) Methylbromohydrogendi- and -trisilanes

Compound		$\delta_{Si}/{}^1J_{SiSi}$	$\delta_H SiMe/{}^3J_{HH}$	$\delta_H SiH/{}^1J_{SiH}$
$Si^A BrMe_2$-$Si^B Me_3$	A:	17.97/92.2	0.482	
	B:	-17.71	0.110	
$Si^A HMe_2$-$Si^B Me_3$	A:	-39.10/84.6 [13]	0.17/4.7	3.78/-173
	B:	-18.90	0.16	
$SiBrMe_2$-$SiBrMe_2$		10.47	0.539	
$Si^A HMe_2$-$Si^B BrMe_2$	A:	-38.00	0.135/4.45	3.90/-187
	B:	17.74	0.521	
$SiHMe_2$-$SiHMe_2$		-39.02/82.6 [14]	0.15/4.7	3.90/-172
$SiBr_2Me$-$SiBr_2Me$		2.84	0.931	
$Si^A HBrMe$-$Si^B Br_2Me$	A:	-21.04		
	B:	18.20		
$Si^A H_2Me$-$Si^B Br_2Me$	A:	-57.52	0.08/4.74	3.80
	B:	19.54		
$SiHBrMe$-$SiHBrMe$		-15.40 and -16.00		
$Si^A H_2Me$-$Si^B HBrMe$	A:	-64.37/77.0	0.081/4.86	3.72
	B:	-9.61	0.522/4.14	4.59
SiH_2Me-SiH_2Me		-67.74	0.22 /5.1	3.57/-186 $^2J_{SiH}$: 7.3/ $^3J_{SiH}$: 3.6
$Si^A Me_2(Si^B BrMe_2)_2$	A:	-42.60/79	0.216	
	B:	19.62	0.614	
$Si^A HMe_2$-$Si^B Me_2$-$Si^C BrMe_2$	A:	-37.51	0.168/4.52	3.904
	B:	-44.69	0.181	
	C:	21.45	0.582	
$Si^A Me_2(Si^B HMe_2)_2$	A:	-47.52/72	0.158	
	B:	-36.72	0.153/4.58	3.92/-174
$Si^A BrMe(Si^B BrMe_2)_2$	A:	-10.90/84	0.790	
	B:	12.17	0.738, 0.753	
$Si^A HMe(Si^B BrMe_2)_2$	A:	-66.03	0.277/5.05	3.672
	B:	18.61	0.712	
$Si^A HMe_2$-$Si^B HMe$-$Si^C BrMe_2$	A:	-37.62		
	B:	-69.44		
	C:	20.75		
$Si^A HMe(Si^B HMe_2)_2$	A:	-73.48/70	0.2	3.29/-164
	B:	-37.29	0.147/4.47	3.93/-174

(b) Methylbromohydrogenisotetrasilanes

Compound		$\delta_{Si}/{}^1J_{SiSi}$	$\delta_H SiMe/{}^3J_{HH}$	$\delta_H SiH/{}^1J_{SiH}$
$Si^A Me(Si^B BrMe_2)(Si^C Me_3)_2$	A:	-82.42		
	B:	24.57	0.680	
	C:	-12.46	0.197	
$Si^A Me(Si^B HMe_2)(Si^C Me_3)_2$	A:	-88.24		
	B:	-34.80		
	C:	-12.28		
$Si^A Me(Si^B BrMe_2)_2(Si^C Me_3)$	A:	-77.90		
	B:	22.28/64.5	0.740	
	C:	-12.10	0.256	
$Si^A Me(Si^B HMe_2)(Si^C BrMe_2)$ $(Si^D Me_3)$	A:	-82.67		
	B:	24.09		
	C:	-35.29		
	D:	-12.23		

Table 2 (continued)

Compound		$\delta_{Si}/$ $^1J_{SiSi}$	δ_H SiMe/ $^3J_{HH}$	δ_H SiH/ $^1J_{SiH}$
$Si^A Me(Si^B HMe_2)_2(Si^C Me_3)$	A:	−88.38		
	B:	−34.91/61		
	C:	−12.16		
$Si^A Me(Si^B BrMe_2)_3$	A:	−73.33/68	0.355	
	B:	20.40	0.804	
$Si^A Me(Si^B HMe_2)(Si^C BrMe_2)_2$	A:	−78.10		
	B:	22.28		
	C:	−35.46		
$Si^A Me(Si^B HMe_2)_2(Si^C BrMe_2)$	A:	−82.92		
	B:	23.60		
	C:	−35.29		
$Si^A Me(Si^B HMe_2)_3$	A:	−88.56/62	0.17	
	B:	−34.8	0.19/4.5	4.05
$Si^A Me(Si^B Br_2Me)_3$	A:	−59.15/79.5	0.570	
	B:	14.70	1.393	
$Si^A Me(Si^B HBrMe)(Si^C Br_2Me)_2$	A:	−63.12	0.522	
	B:	−9.35	0.963/3.94	4.854
	C:	17.15	1.354	
$Si^A Me(Si^B H_2Me)(Si^C Br_2Me)_2$	A:	−62.90	0.465	
	B:	−63.71	0.383/4.84	3.800/ − 197
	C:	19.94/74.8	1.301	
$Si^A Me(Si^B H_2Me)(Si^C HBrMe)$	A:	−70.74	0.417	
$(Si^D Br_2Me)_2$	B:	−63.92	0.343	3.77
	C:	−6.04	0.869/3.72	4.792
	D:	22.44	1.260	
$Si^A Me(Si^B H_2Me)_2(Si^C Br_2Me)$	A:	−74.06	0.375	
	B:	−63.03/65	0.325/4.88	3.740/ − 191
	C:	25.44	1.217	
$Si^A Me(Si^B H_2Me)_2(Si^C HBrMe)$	A:	−85.3		
	B:	−63.0		
	C:	−2.31		
$Si^A Me(Si^B H_2Me)_3$	A:	−91.54/61.8	0.284	
	B:	−62.45	0.228/4.86	3.70/ − 196

(c) Methylbromo- und methylhydrogenneopentasilanes

Compound		$\delta_{Si}/$ $^1J_{SiSi}$	δ_H SiMe/ $^3J_{HH}$	δ_H SiH
$Si^A(Si^B BrMe_2)(Si^C Me_3)_3$	A:	−127.62		
	B:	24.95	0.701	
	C:	−9.74	0.248	
$Si^A(Si^B BrMe_2)_2(Si^C Me_3)_2$	A:	−121.23		
	B:	23.50	0.735	
	C:	−8.99	0.288	
$Si^A(Si^B BrMe_2)_3(Si^C Me_3)$	A:	−115.22		
	B:	21.85	0.775	
	C:	−8.24	0.328	
$Si^A(Si^B BrMe_2)_4$	A:	−110.57/57		
	B:	20.02	0.809	
$Si^A(Si^B HMe_2)(Si^C Me_3)_3$	A:	−136.78		
	B:	−33.49	0.280/4.4	4.199
	C:	−9.56	0.232	
$Si^A(Si^B HMe_2)_2(Si^C Me_3)_2$	A:	−137.88		
	B:	−33.44	0.280/4.4	4.193
	C:	−9.20	0.232	
$Si^A(Si^B HMe_2)_3(Si^C Me_3)$	A:	−139.00		
	B:	−33.40	0.278/4.4	4.187
	C:	−8.73	0.230	
$Si^A(Si^B HMe_2)_4$	A:	−140.07		
	B:	−33.35	0.276/4.4	4.175

Table 3
Hydrogenation of 3 with Bu₃SnH in the presence of Ph₃MePI

Molar ratio	Amount of					
3:Bu₃SnH	SiBr₂Me–SiBr₂Me	SiHBrMe–SiBr₂Me	SiH₂Me–SiBr₂Me	SiHBrMe–SiHBrMe	SiH₂Me–SiHBrMe	SiH₂Me–SiH₂Me
1:2	15%	12%	19%	9%	34%	11%
1:3	—	6%	7%	—	18%	69%

Starting with 5 the monohydrogenated product SiHMe(SiBrMe₂)₂ can be obtained in 80% yield besides some unreacted 5 and the two-fold hydrogenated compound SiHMe₂–SiHMe–SiBrMe₂. As was shown earlier for SiClMe(SiClMe₂)₂ [3], no hydrogenation products like SiHMe₂–SiBrMe–SiBrMe₂ (first attack at a terminal silicon atom) were found.

Hydrogenation of 5 with Me₃SnH in a molar ratio of 1:2 yields about 60% SiHMe₂–SiHMe–SiBrMe₂ besides SiHMe(SiBrMe₂)₂ and SiHMe(SiHMe₂)₂.

2.4. Hydrogenation of SiMe(SiBrMe₂)ᵢ(SiMe₃)₃₋ᵢ, i = 1, 2, 3 (6a–c)

Starting from pure SiMe(SiBrMe₂)₃ (6c) the hydrogenation with Me₃SnH in molar ratios 1:1 and 1:2 gave mixtures of SiMe(SiHMe₂)ₓ(SiBrMe₂)₃₋ₓ (x = 0 to 3) containing SiMe(SiHMe₂)(SiBrMe₂)₂ and SiMe(SiHMe₂)₂(SiBrMe₂) respectively as main product (60–70%).

Hydrogenation of a mixture of 58% 6b besides 28% 6a and 14% 6c with Me₃SnH in a molar ratio 6a–c:stannane of 1:1 has shown that 6c was hydrogenated most easily. 70% of the initial 6c was converted into SiMe(SiHMe₂)₂(SiBrMe₂) and 30% into SiMe(SiHMe₂)₃. 6b was hydrogenated to SiMe(SiHMe₂)(SiBrMe₂)(SiMe₃) (75%) and SiMe(SiHMe₂)₂(SiMe₃) (15%). 5% remained as 6b. Only 20% of the total content of 6a was hydrogenated to SiMe(SiHMe₂)(SiMe₃)₂, 80% was recovered.

In summary, the product mixture contained approximately 75% isotetrasilanes bearing one bromine atom, 3% bearing two bromine atoms and 22% isotetrasilanes without any bromine atom.

2.5. Hydrogenation of SiMe(SiBr₂Me)₃ (7)

The hydrogenation of 7 was carried out with several molar ratios 7:Me₃SnH. Table 4 shows the results in the cases of molar ratios 1:2 and 1:4.

In comparison to the hydrogenation of SiMe(SiCl₂Me)₃ with Me₃SnH in the presence of Ph₃MePI [3], the amount of silanes containing SiHXMe groups is much less. No products bearing two or three SiHBrMe groups could be detected. As Table 4 indicates, the compounds SiMe(SiH₂Me)(SiBr₂Me)₂ and SiMe(SiH₂Me)₂(SiBr₂Me) respectively can be prepared in approximately 60% yield.

2.6. Hydrogenation of Si(SiBrMe₂)ᵢ(SiMe₃)₄₋ᵢ, i = 1, 2, 3, 4 (8a–d)

The brominated neopentasilanes 8a–d as well as the chlorinated compounds Si(SiClMe₂)ᵢ(SiMe₃)₄₋ᵢ did not react with stannanes. Reaction with LiAlH₄ in Et₂O led to the completely hydrogenated species Si(SiHMe₂)ᵢ-(SiMe₃)₄₋ᵢ. Probably steric hindrance prevents the attack of the Lewis base at the silicon atom of the SiXMe₂ group directly attached to the quarternary silicon atom. This conclusion was also confirmed by the selective single hydrogenation of the hexasilane (SiClMe₂)₃Si–SiClMe–SiClMe₂ to (SiClMe₂)₃Si–SiClMe–SiHMe₂ with Me₃SnH in the presence of Ph₃MePI [15].

3. Experimental details

All preparations were carried out under an argon atmosphere using standard Schlenk techniques.

Table 4
Hydrogenation of 7 with Bu₃SnH in the presence of Ph₃MePI

Molar ratio	Amount of						
7:Me₃SnH	SiMe(Si Br₂Me)₃	SiMe(Si HBrMe)(SiBr₂Me)₂	SiMe(Si H₂Me)(SiBr₂Me)₂	SiMe(Si H₂Me)(SiHBrMe)(SiBr₂Me)	SiMe(Si H₂Me)₂(SiBr₂Me)	SiMe(Si H₂Me)₂(SiHBrMe)	SiMe(Si H₂Me)₃
1:2	10%	12%	57%	11%	9%	—	—
1:4	—	—	13%	14%	61%	5%	7%

The NMR data were recorded with a Bruker MSL 300 spectrometer (^{1}H: 300.13 MHz, ^{29}Si: 59.627 MHz). Samples were dissolved in toluene and filled into 7 mm glass ampoules, which could be introduced into 10 mm NMR tubes charged with CDCl$_3$ as external lock substance. All chemical shift data are relative to internal TMS. ^{29}Si chemical shifts of SiBrMe$_2$ and SiBr$_2$Me groups can vary by about ±0.5 ppm in different solutions of the same compound. The given values, however, are related to the differences in δ_{Si} of brominated silyl groups of different compounds in the same spectrum.

The amounts of hydrogenation products were determined from the intensities of the ^{29}Si NMR signals.

Mass spectra were obtained with a HP 5971 (ionization energy 70 eV).

3.1. Preparation of the brominated oligosilanes

3.1.1. Bromopentamethyldisilane (1) and 1,2-dibromotetramethyldisilane (2)

1 and 2 were prepared by bromination of Si$_2$Me$_6$ with CH$_3$COBr and AlBr$_3$ according to Ref. [16].

2. GC MS m/e (intensity of the major peak in the isotopic pattern due to $^{79/81}$Br, $^{28/29/30}$Si and $^{12/13}$C): 276 (M$^+$, 19), 261 (Si$_2$Me$_3$Br$_2$, 3), 197 (Si$_2$Me$_4$Br, 7), 139 (SiMe$_2$Br, 100), 109 (20), 73 (SiMe$_3$, 80), 58 (SiMe$_2$, 52).

3.1.2. 1,1,2,2-Tetrabromodimethyldisilane (3)

5 g (34 mmol) Si$_2$Me$_6$ was heated with 17 g (137 mmol) CH$_3$COBr and 37 g (137 mmol) AlBr$_3$ to 120°C for 3 h under stirring. After cooling to room temperature, 50 ml hexane was added. The upper phase was separated and fractionated to give 10 g (25 mmol) colorless crystalline needles of 3 (m.p. 96.5°C [10]). The product is extremely air sensitive and turned dark brown within some minutes when the tube was opened.

3.1.3. 1,3 Dibromohexamethyltrisilane (4)

A three-necked flask equipped with a dropping funnel, stirrer and reflux condensor was charged with 13 g (50 mmol) AlBr$_3$ and a solution of 4 g (20 mmol) Si$_3$Me$_8$ in dried n-hexane. Under stirring, 5.5 g (45 mmol) CH$_3$COBr diluted in 10 ml hexane was added dropwise. After stirring overnight the upper phase containing hexane, 4 and traces of AlBr$_3$ was separated from the yellow-brown high viscous residue. After adding 0.1 ml acetone the aluminiumbromide precipitated as acetone complex. The filtered solution was fractionated to give 4 g (12 mmol) 4 (b.p. 95°C/0.6 kPa).

GC MS: 334 (M$^+$, 0.5), 319 (Si$_3$Me$_5$Br$_2$, 1), 255 (Si$_3$Me$_6$Br, 1.5), 197 (Si$_2$Me$_4$Br, 45), 139 (SiMe$_2$Br, 9), 131 (Si$_2$Me$_5$, 6), 116 (Si$_2$Me$_4$, 33), 73 (SiMe$_3$, 100).

3.1.4. 1,2,3-Tribromopentamethyltrisilane (5)

(a) 2-Phenylheptamethyltrisilane. A three-necked flask equipped with a dropping funnel, stirrer and reflux condensor was charged with a liquid alloy of 42 g (1.07 mol) potassium and 6 g (0.26 mol) sodium. A mixture of 40 g (0.21 mol) PhMeSiCl$_2$ and 200 g (1.84 mol) Me$_3$SiCl was added dropwise under vigorous stirring. After complete addition and further stirring for 2 h the silanes were filtered from the blue mixture of KCl, NaCl and residual sodium potassium alloy. The residue was washed twice with dried hexane and the combined filtrates were fractionated to give 15 g (0.10 mol) Si$_2$Me$_6$ (b.p. 112–113°C), 15 g (0.056 mol) SiPhMe(SiMe$_3$)$_2$ (9) (b.p. 80°C/6 Pa) and 12.5 g residue of (SiPhMe–SiMe$_3$)$_2$ (10) with a small amount of SiMe$_3$–SiPhMe–SiClPhMe (11).

9. GC MS: 266 (M$^+$, 34), 251 (Si$_3$Me$_6$Ph, 12), 193 (Si$_2$Me$_4$Ph, 100), 178 (Si$_2$Me$_3$Ph, 17), 163 (Si$_2$Me$_2$Ph, 18), 135 (SiMe$_2$Ph, 78), 116 (Si$_2$Me$_4$, 22), 105 (SiPh, 12), 73 (SiMe$_3$, 54). ^{29}Si NMR: − 15.79 ppm (SiMe$_3$), − 46.45 ppm (SiPhMe).

10. GC MS: (two signals with the same MS due to the two diastereotops) 386 (M$^+$, 22), 371 (Si$_4$Me$_7$Ph$_2$, 5), 313 (Si$_3$Me$_5$Ph$_2$, 14), 236 (Si$_3$Me$_5$Ph, 84), 221 (Si$_3$Me$_4$Ph, 17), 193 (Si$_2$Me$_4$Ph, 70), 135 (SiMe$_2$Ph, 100), 105 (SiPh, 16), 73 (SiMe$_3$, 59). ^{29}Si NMR: − 14.44/− 14.61 ppm (SiMe$_3$), − 43.87 ppm (SiPhMe).

11. GC MS: 348 (M$^+$, 9), 333 (Si$_3$Me$_4$Ph$_2$Cl, 8), 240 (Si$_2$Me$_2$Ph$_2$, 93), 225 (Si$_2$MePh$_2$, 39), 197 (SiMePh$_2$, 70), 193 (Si$_2$Me$_4$Ph, 73), 135 (SiMe$_2$Ph, 100), 105 (SiPh, 32), 73 (SiMe$_3$, 54).

(b) 5. 7 g (26 mmol) 9 was brominated with 12.3 g (100 mmol) CH$_3$COBr and 28 g (105 mmol) AlBr$_3$ in the same manner as described above for the preparation of 4. Yield 5 g (12.5 mmol) 5, b.p. 95°C/0.6 kPa.

5. GC MS: 400 (M$^+$, 2), 385 (Si$_3$Me$_4$Br$_3$, 0.5), 319 (Si$_3$Me$_5$Br$_2$, 1.5), 276 (Si$_2$Me$_4$Br$_2$, 1), 261 (Si$_2$Me$_3$Br$_2$, 11), 197 (Si$_2$Me$_4$Br, 32), 182 (Si$_2$Me$_3$Br, 73), 139 (SiMe$_2$Br, 32), 109 (18), 73 (SiMe$_3$, 100).

3.1.5. Bromination of tris-(trimethylsilyl)-methylsilane to 6a–c

1.5 g (5.7 mmol) SiMe(SiMe$_3$)$_3$ was brominated once with 2.9 g (24 mmol) CH$_3$COBr and 6.4 g (24 mmol) AlBr$_3$ and in a second experiment with 1.5 g (12.5 mmol) CH$_3$COBr and 3.5 g (12.5 mmol) AlBr$_3$. The first yielded 1.5 g (3.3 mmol) 6c and the second 1.5 g of a mixture of 58 mol% 6b, 28 mol% 6a and 14 mol% 6c after working up in the same way as already described.

6a. GC MS: 328 (M$^+$, 0.5), 313 (Si$_4$Me$_8$Br, 8), 255 (Si$_3$Me$_6$Br, 7), 240 (Si$_3$Me$_5$Br, 3), 189 (Si$_3$Me$_7$, 6), 174 (Si$_3$Me$_6$, 100), 159 (Si$_3$Me$_5$, 30), 131 (Si$_2$Me$_5$, 33), 73 (SiMe$_3$, 85).

6b. GC MS: 392 (M$^+$, 0.1), 377 (Si$_4$Me$_7$Br$_2$, 4), 319 (Si$_3$Me$_5$Br$_2$, 2), 313 (Si$_4$Me$_8$Br, 1), 304 (Si$_3$Me$_4$Br$_2$,

0.5), 269 (Si$_3$Me$_7$Br, 1), 255 (Si$_3$Me$_6$Br, 27), 240 (Si$_3$Me$_5$Br, 75), 197 (Si$_2$Me$_4$, 7), 139 (SiMe$_2$Br, 10), 131 (Si$_2$Me$_5$, 45), 116 (Si$_2$Me$_4$, 29), 73 (SiMe$_3$, 100).

6c. GC MS: 443 (Si$_4$Me$_6$Br$_3$, 2), 377 (Si$_4$Me$_7$Br$_2$, 3), 319 (Si$_3$Me$_5$Br$_2$, 65), 240 (Si$_3$Me$_5$Br, 28), 197 (Si$_2$Me$_4$Br, 20), 137 (SiMe$_2$Br, 19), 131 (Si$_2$Me$_5$, 58), 116 (Si$_2$Me$_4$, 23), 73 (SiMe$_3$, 100).

3.1.6. Tris-(dibromomethylsilyl)-methylsilane (7)

(a) SiMe(SiH$_2$Me)$_3$ (12). 5 g (13 mmol) SiMe(SiCl$_2$-Me)$_3$ was added dropwise to a solution of 1.5 g (40 mmol) LiAlH$_4$ in 50 ml dried Et$_2$O. After stirring for 2 h the mixture was carefully hydrolyzed with 50 ml diluted H$_2$SO$_4$ at 0 °C. The organic layer was separated and dried over anhydrous CaCl$_2$. The ether was removed in vacuum giving a residue of 1.5 g (8.4 mmol) pure **12**.

12. GC MS: 178 (M$^+$, 5), 163 (Si$_4$Me$_3$H$_6$, 4), 132 (Si$_3$Me$_3$H$_3$, 100), 115 (Si$_3$Me$_2$H, 8), 101 (Si$_2$Me$_3$, 15), 86 (Si$_2$Me$_2$, 30), 73 (SiMe$_3$, 18), 69 (22), 59 (SiMe$_2$H, 19), 45 (SiMeH$_2$, 16), 43 (SiMe, 22).

(b) 7. 1 g (5.6 mmol) **12** was diluted with 3 ml n-octane, 10 g (39.5 mmol) CHBr$_3$ was added and the mixture was heated up to 120 °C for 72 h. At this point a ^{29}Si NMR spectrum showed a composition of 73 mol% **7** and 27 mol% SiMe(SiBr$_2$Me)$_2$(SiHBrMe). Further heating of the mixture and removal of octane, formed CH$_2$Br$_2$ and residual CHBr$_3$ in vacuum led to 3.3 g (5 mmol) pure **7**.

3.1.7. Bromination of tetrakis-(trimethylsilyl)-silan to 8a–d

Starting from Si(SiMe$_3$)$_4$, bromination with CH$_3$-COBr and AlBr$_3$ in the described manner yielded pure **8d** (molar ratio silane:CH$_3$COBr:AlBr$_3$ 1:5:5) as colorless crystals or a mixture of 2 mol% **8a**, 34 mol% **8b**, 54 mol% **8c** and 10 mol% **8d** (molar ratio silane:CH$_3$COBr:AlBr$_3$ 1:2.5:2.5) as a partially crystallized product.

8a. GC MS: 371 (Si$_5$Me$_{10}$Br, 13), 313 (Si$_4$Me$_8$Br, 4), 255 (Si$_3$Me$_6$Br, 2), 232 (Si$_4$Me$_8$, 100), 217 (Si$_4$Me$_7$, 3), 173 (13), 158 (22), 131 (Si$_2$Me$_5$, 16), 99 (Si$_3$Me, 11), 73 (SiMe$_3$, 90).

8b. GC MS: 435 (Si$_5$Me$_9$Br$_2$, 10), 371 (Si$_5$Me$_{10}$Br, 1), 362 (Si$_4$Me$_6$Br$_2$, 3), 313 (Si$_4$Me$_8$Br, 9), 298 (Si$_4$Me$_7$Br, 100), 283 (Si$_4$Me$_6$Br, 3), 255 (Si$_3$Me$_6$Br, 13), 174 (Si$_3$Me$_6$, 17), 159 (Si$_3$Me$_5$, 15), 144 (Si$_3$Me$_4$, 22), 131 (Si$_2$Me$_5$, 23), 73 (SiMe$_3$, 88).

8c. GC MS: 501 (Si$_5$Me$_8$Br$_3$, 5), 435 (Si$_5$Me$_9$Br$_2$, 2), 399 (Si$_4$Me$_3$Br$_3$, 1), 377 (Si$_4$Me$_7$Br$_2$, 14), 362 (Si$_4$Me$_6$Br$_2$, 100), 319 (Si$_3$Me$_5$Br$_2$, 4), 298 (Si$_4$Me$_7$Br, 3), 255 (Si$_3$Me$_6$Br, 26), 240 (Si$_3$Me$_5$Br, 8), 197 (Si$_2$Me$_4$Br, 6), 174 (Si$_3$Me$_6$, 39), 159 (Si$_3$Me$_5$, 7), 139 (SiMe$_2$Br, 13), 131 (Si$_2$Me$_5$, 20), 116 (Si$_2$Me$_4$, 15), 73 (SiMe$_3$, 90).

8d. GC MS: 580 (M$^+$, 0.1), 565 (Si$_5$Me$_7$Br$_4$, 1), 501

(Si$_5$Me$_8$Br$_3$, 2), 443 (Si$_4$Me$_6$Br$_3$, 48), 377 (Si$_4$Me$_7$Br$_2$, 2), 362 (Si$_4$Me$_6$Br$_2$, 24), 319 (Si$_3$Me$_5$Br$_2$, 13), 304 (Si$_3$Me$_4$Br$_2$, 14), 289 (Si$_3$Me$_3$Br$_2$, 1), 255 (Si$_3$Me$_6$Br, 24), 240 (Si$_3$Me$_5$Br, 3), 197 (Si$_2$Me$_4$Br, 11), 174 (Si$_3$Me$_6$, 11), 139 (SiMe$_2$Br, 23), 131 (Si$_2$Me$_5$, 20), 116 (Si$_2$Me$_4$, 26), 73 (SiMe$_3$, 100).

Hydrogenation of **8a–d** with excess LiAlH$_4$ in Et$_2$O and working up as described above for the hydrogenation of SiMe(SiCl$_2$Me)$_3$ led to the completely hydrogenated silanes Si(SiHMe$_2$)$_i$(SiMe$_3$)$_{4-i}$, $i = 1$, 2, 3, 4 (**13a–d**) as colorless liquids. **13d** was already known [17].

13a. GC MS: 306 (M$^+$, 1.5), 291 (Si$_5$Me$_{10}$H, 3), 232 (Si$_4$Me$_8$, 88), 217 (Si$_4$Me$_7$, 25), 173 (Si$_4$Me$_4$H, 13), 158 (Si$_4$Me$_3$H, 25), 144 (Si$_3$Me$_4$, 20), 129 (Si$_3$Me$_3$, 9), 73 (SiMe$_3$, 100), 59 (SiMe$_2$H, 20).

13b. GC MS: 292 (M$^+$, 1), 277 (Si$_5$Me$_9$H$_2$, 4), 232 (Si$_4$Me$_8$, 18), 218 (Si$_4$Me$_7$H, 75), 203 (Si$_4$Me$_6$H, 17), 173 (Si$_4$Me$_4$H, 8), 159 (Si$_3$Me$_5$, 22), 144 (Si$_3$Me$_4$, 83), 129 (Si$_3$Me$_3$, 15), 73 (SiMe$_3$, 100), 59 (SiMe$_2$H, 26).

13c. GC MS: 278 (M$^+$, 1), 263 (Si$_5$Me$_8$H$_3$, 3), 218 (Si$_4$Me$_7$H, 62), 204 (Si$_4$Me$_6$H$_2$, 72), 189 (Si$_4$Me$_5$H$_2$, 15), 159 (Si$_3$Me$_5$, 12), 157 (Si$_4$Me$_3$, 11), 144 (Si$_3$Me$_4$, 74), 130 (Si$_3$Me$_3$H, 26), 73 (SiMe$_3$, 100), 59 (SiMe$_2$H, 40).

13d. GC MS: 264 (M$^+$, 0.5), 249 (Si$_5$Me$_7$H$_4$, 2), 204 (Si$_4$Me$_6$H$_2$, 100), 189 (Si$_4$Me$_5$H$_2$, 12), 175 (Si$_3$Me$_6$H, 7), 159 (Si$_3$Me$_5$, 8), 157 (Si$_4$Me$_3$, 8), 144 (Si$_3$Me$_4$, 80), 130 (Si$_3$Me$_3$H, 45), 73 (SiMe$_3$, 70), 59 (SiMe$_2$H, 54).

3.2. Hydrogenations with trialkylstannanes

The hydrogenations of **1–3** were carried out by adding Bu$_3$SnH and Ph$_3$MePI as catalyst. So the hydrogenated disilanes could easily be separated from the catalyst and the formed Bu$_3$SnBr by condensation of the silanes into a trap in vacuum at room temperature.

In all other cases (hydrogenation of **4–8**) trimethylstannane was used together with Ph$_3$MePI. After conversion into Me$_3$SnBr (b.p. 163 °C) which has a relatively simple ^{1}H NMR spectrum, it can easily be removed from highly boiling methylbromohydrogenoligosilanes by condensation in vacuum at ambient temperatures.

Me$_3$SnH (b.p. 60 °C) was freshly prepared from Me$_3$SnCl and LiAlH$_4$ in diglyme. Bu$_3$SnH was commercially available from Merck.

Acknowledgements

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