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Preparation and NMR spectroscopical investigations of (diethylamino)(methoxy)-methylchlorodi– and –trisilanes

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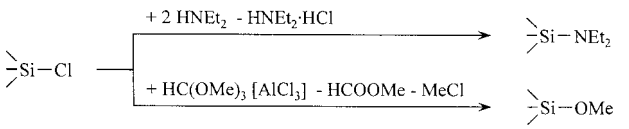
Abstract

Starting from the methylchlorodisilanes $SiClMe_2$–$SiClMe_2$, $SiCl_2Me$–$SiCl_2Me$ and methylchlorotrisilanes $SiClMe_2$–$SiClMe$–$SiClMe_2$ and $SiCl_2Me$–$SiClMe$–$SiCl_2Me$ the stepwise reaction with first $HC(OMe)_3/[AlCl_3]$ and second $HNEt_2$ leads to the formation of (diethylamino)(methoxy)-methylchlorooligosilanes. The products were investigated by means of ^{29}Si, ^{1}H NMR spectroscopy and GC/MS measurements. © 1998 Elsevier Science S.A.

Keywords: NMR spectroscopy; Methylchlorodisilanes; Methylchlorotrisilanes

1. Introduction

We have recently reported the synthesis of various (diethylamino)-methylchlorooligosilanes [1,2] as well as (methoxy)-methylchlorooligosilanes [3] starting from the corresponding methylchlorooligosilanes by reaction with diethylamine or trimethylorthoformiate/$AlCl_3$:



(1)

A detailed investigation of the stepwise substitution showed, that there is a high regioselectivity of both reactions. Especially in the case of aminations, the reaction can be carried out very well step by step, that means for instance:

$$SiCl_2Me - SiCl_2Me + 4HNEt_2 \xrightarrow{-2HNEt_2\cdot HCl}$$

$$SiClMe(NEt_2) - SiClMe(NEt_2)$$

and only traces of $Si_2Me_2Cl_3(NEt_2)$

and $Si_2Me_2Cl(NEt_2)_3$ (2)

The aim of this work was the combination of these reaction pathes and the preparation of the first (diethylamino)(methoxy)-methylchlorooligosilanes. Such compounds are interesting as model compounds for structures in polymer precursors of Si–NCO ceramics [4,5] and as synthons bearing different protecting groups for

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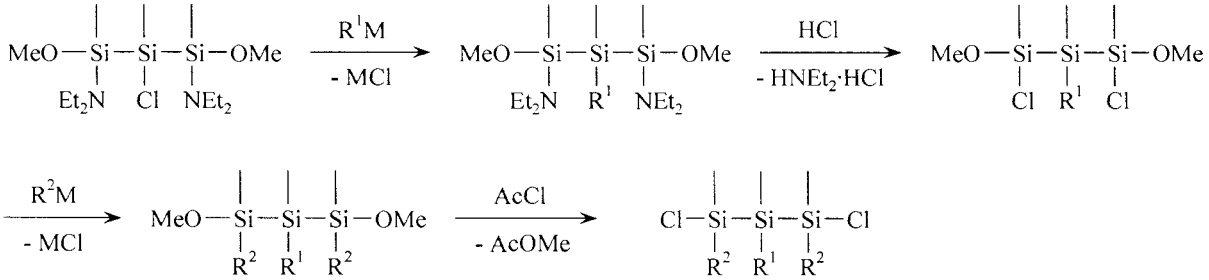
further reactions. Two protecting groups offer the possibility of a selective reintroduction of chlorine substituents after derivatizations with organometallic reagents:



(3)

The successful introduction of vinyl as well as allyl substituents into diethylaminosubstituted methylchlorodisilanes, for instance $SiClMe(NEt_2)$–$SiMe(NEt_2)_2$, was already investigated by us in Ref. [6].

Because of the different stability of Si–O and Si–N bonds during hydrolysis such compounds offer a higher variability in sol–gel processes than simple tetraalkoxysilanes.

2. Results and discussion

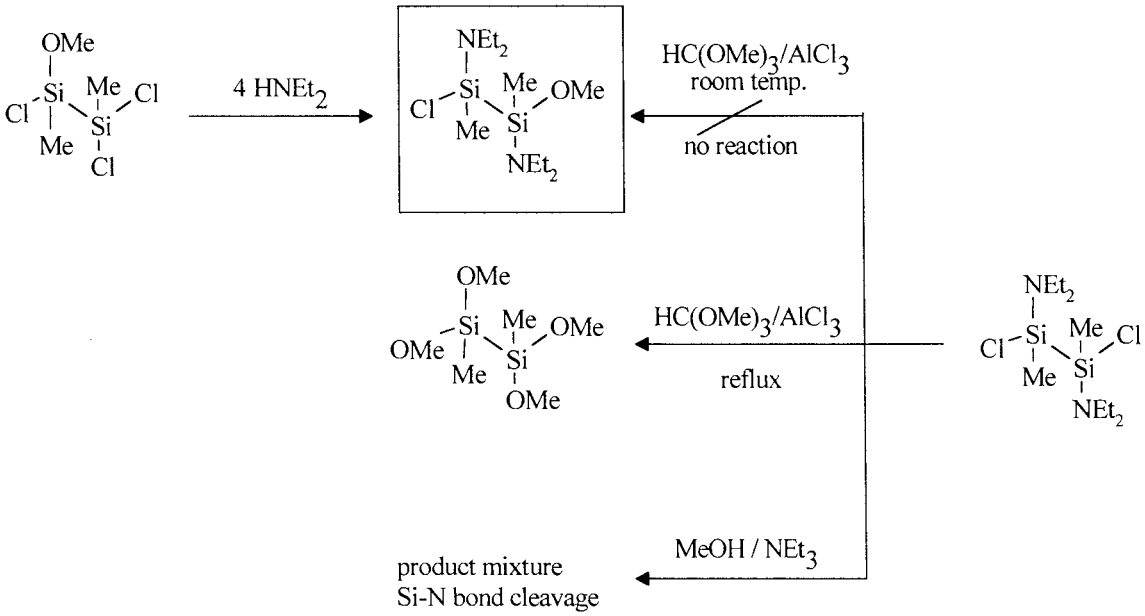
Various methods and reaction conditions were investigated to prepare (diethylamino)(methoxy)-methylchlorooligosilanes (Scheme 1). The only successful method was to synthesize the (methoxy)-methylchlorooligosilanes first and than adding the $HNEt_2$ to obtain silanes containing diethylamino, methoxy, methyl and chloro substituents. Attempts applying the opposite order failed. Since the introduction of OMe substituents via the standard route $R_3Si–Cl + MeOH + NEt_3$ is less selective than the reaction with $HC(OMe)_3$ in presence of $AlCl_3$ [3], the first was only used, if all Si–Cl bonds should be exchanged for OMe substituents.

Because the Si–O-bond is the most stable in this system, the reaction of (diethylamino)-methylchlorooligosilanes with either $HC(OMe)_3$/, [$AlCl_3$] or $MeOH/NEt_3$ results in a cleavage of Si–N bonds and only product mixtures. The corresponding methoxymethyloligosilane yields, if an excess of $HC(OMe)_3$ or MeOH was used.

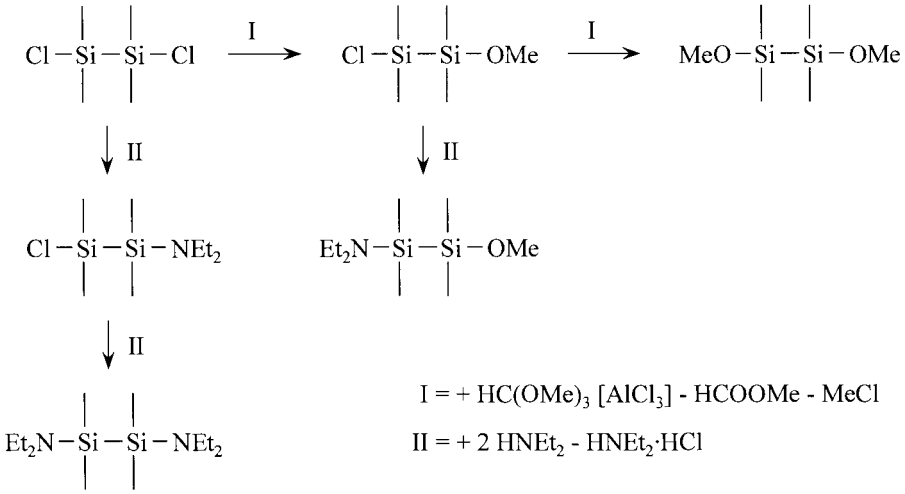
Whereas a great number of the substitution reactions take an expected course, some surprises occurred, especially if the educts are highly halogenated oligosilanes.

2.1. (Diethylamino)(methoxy)-methylchlorodisilanes

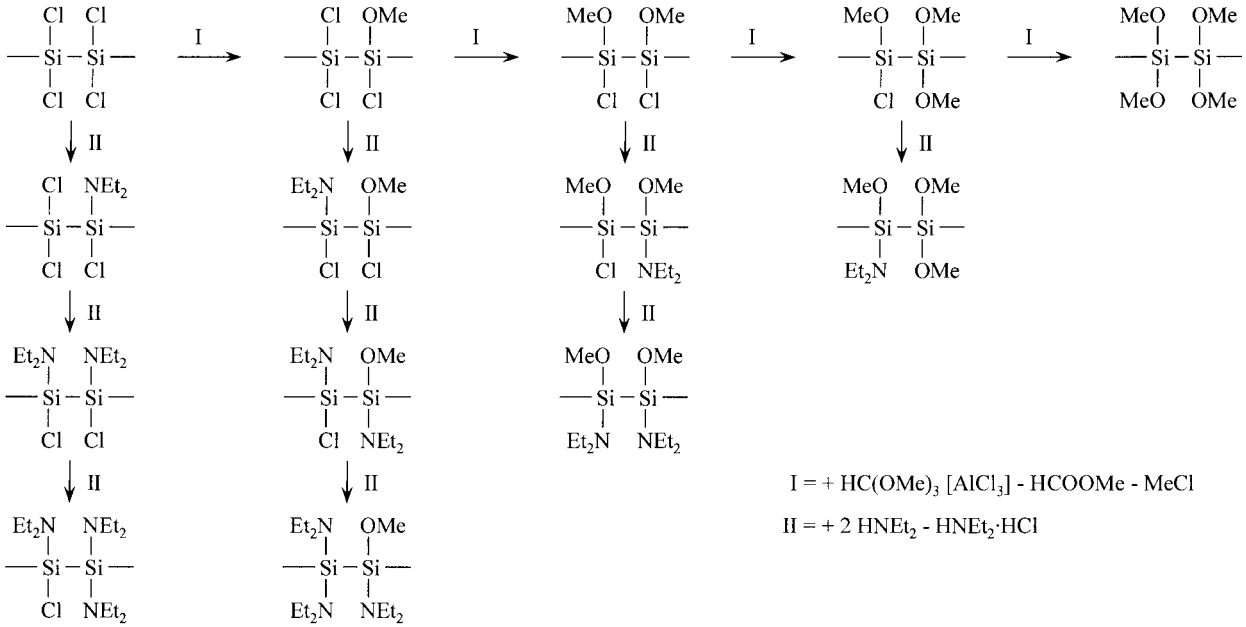
Starting from 1,2-dichlorotetramethyldisilane only one compound can be prepared, which contains simultaneously methoxy and diethylamino substituents, Scheme 2.



Scheme 1.



Scheme 2. Derivatives of 1,2-dichlorotetramethyldisilane.

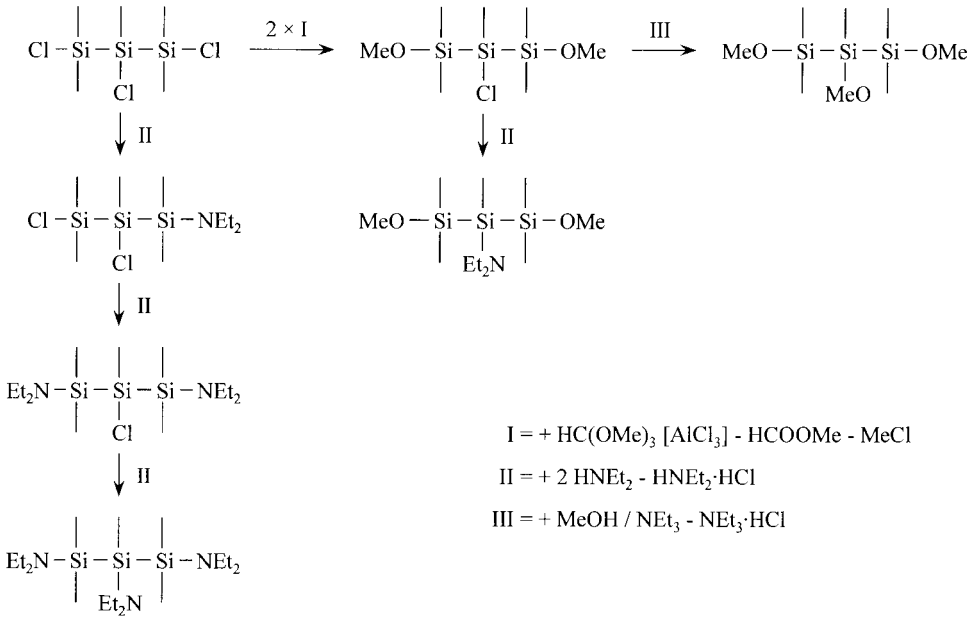


Scheme 3. Derivatives of 1,1,2,2-tetrachlorodimethyldisilane.

Table 1
^{29}Si NMR shifts of (diethylamino)(methoxy)-methylchlorodisilanes[a]

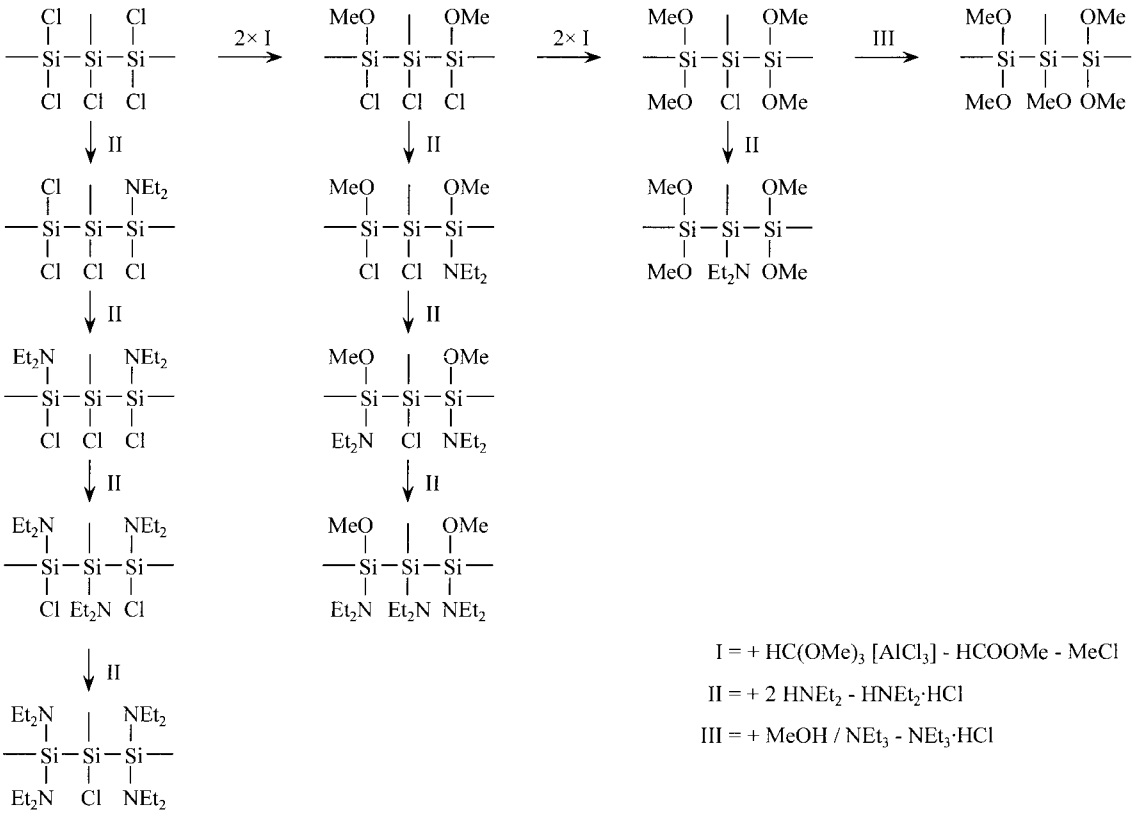
Compound	δ/ppm	
	Si^A	Si^B
$Me_3Si^A–Si^BMe_2Cl$ [7]	−18.2 ($^1J_{SiSi}$: 94.0)	22.9
$Me_3Si^A–Si^BMe_2(NEt_2)$	−22.3 ($^1J_{SiSi}$: 96.4)	−3.2
$ClMe_2Si–SiMe_2Cl$ [4]	17.2	
$(NEt_2)Me_2Si^A–Si^BMe_2Cl$	−5.7	17.6
$(NEt_2)Me_2Si–SiMe_2(NEt_2)$	−6.2	
$(OMe)Me_2Si^A–Si^BMe_2(NEt_2)$	13.5	−7.4
$(OMe)ClMeSi^A–Si^BMeCl(NEt_2)$	8.3/6.7[b]	−0.9/−1.2[b]
$(OMe)(NEt_2)MeSi^A–Si^BMeCl(NEt_2)$	−8.8	3.3/2.4[b]
$(OMe)(NEt_2)MeSi^A–Si^BMe(NEt_2)_2$	−4.8	−12.9
$(OMe)ClMeSi^A–Si^BMe(OMe)(NEt_2)$	11.2/10.8[b]	−10.1/−10.3[b]
$[(OMe)(NEt_2)MeSi^A–]_2$	−6.5/−6.6[b]	
$(OMe)_2MeSi^A–Si^BMe(OMe)(NEt_2)$	−3.6	−8.6

[a] NMR data of the series $SiMeCl_i(OMe)_{2-i}–SiMeCl_j(OMe)_{2-j}$ are published in Ref. [3] and $SiMeCl_i(NEt_2)_{2-i}–SiMeCl_j(NEt_2)_{2-j}$ in Ref. [1].
[b] Two diastereomers.



Scheme 4. Derivatives of 1,2,3-trichloropentamethyltrisilane.

More interesting is the stepwise substitution of 1,1,2,2-tetrachlorodimethyldisilane, Scheme 3. In the case of one methoxy substitutent, the first diethylamino group enters the molecule as expected at the other silicon atom. But surprisingly, the second diethylamino group is introduced selectively at the SiMeCl(OMe) site, probably because of steric hindrance at the SiMeCl(NEt_2) unit. Despite the fact, that it was impossible to obtain SiMe(NEt_2)$_2$–SiMe(NEt_2)$_2$ by reaction of $SiCl_2$Me–$SiCl_2$Me with an excess of $HNEt_2$, all



Scheme 5. Derivatives of 1,1,2,3,3-pentachlorotrimethyltrisilane.

Table 2
^{29}Si NMR shifts of (diethylamino)-methylchlorotrisilanes

Compound	δ/ppm		
	Si^A	Si^B	Si^C
$(Me_3Si^A)_2Si^BMeCl$ [8]	−15.0	9.9	
$(Me_3Si^A)_2Si^BMe(NEt_2)$	−19.5	−13.4	
$(ClMe_2Si^A)_2Si^BMeCl$ [9]	19.5	−0.7	
$ClMe_2Si^A–Si^BMeCl–Si^CMe_2(NEt_2)$	20.3	0.3	−3.3
$[(NEt_2)Me_2Si^A]_2Si^BMeCl$	−2.7	2.0	
$[(NEt_2)Me_2Si^A]_2Si^BMe(NEt_2)$	−4.1	−18.1	
$(Cl_2MeSi^A)_2Si^BMeCl$ [4]	23.8	−4.9	
$Cl_2MeSi^A–Si^BMeCl–Si^CMeCl(NEt_2)$	26.3	−4.3	2.5
$[Cl(NEt_2)MeSi^A]_2Si^BMeCl$	3.8/4.1/5.2/5.4[a]	−4.9/−4.6/−4.0[a]	
$[Cl(NEt_2)MeSi^A]_2Si^BMe(NEt_2)$	−2.0/−2.4/−8.6/−8.8[a]	−19.7/−20.5/−21.3[a]	
$[(NEt_2)_2MeSi^A]_2Si^BMeCl$	−7.6 $^1J_{SiSi}$: 98 Hz	0.9	

[a] Several diastereomers.

Si–Cl bonds are substituted by NEt_2 in the series $Si_2Me_2Cl_i(OMe)_{4-i}$ $i = 1–3$. This should be explained by the steric overcrowding of a disilane bearing four bulky NEt_2 groups rather than by a decrease of the reactivity of the remaining Si–Cl bond.

The ^{29}Si NMR data of (diethylamino)(methoxy)-methylchlorodisilanes are summarized in Table 1.

2.2. (Diethylamino)(methoxy)-methylchlorotrisilanes

2-Chloroheptamethyltrisilane reacts with two equivalents $HNEt_2$ to pure 2-diethylaminoheptamethyltrisilane.

The reaction of 1,2,3-trichloropentamethyltrisilane with both, $HC(OMe)_3$ and $HNEt_2$ yields in a preferred substitution of the terminal Si–Cl bonds. This observation is also true during the formation of (diethylamino)(methoxy)methylchlorotrisilanes, Scheme 4. No products with terminal $SiMe_2Cl$ site and a central $>SiMeY$ (Y = OMe, NEt_2) unit could be obtained. The introduction of a OMe substituent at the central Si atom succeeds only by treatment of the chlorosilane with MeOH–NEt_3.

More complicated are the reaction paths of 1,1,2,3,3-pentachlorotrimethyltrisilane, Scheme 5. The stepwise reaction of this trisilane with $HNEt_2$ results first in a substitution of one Si–Cl bond at each terminal $SiMeCl_2$ unit. Secondly a transformation of the central $>SiMeCl$ site into $SiMe(NEt_2)$ takes place. Surprisingly, the reaction with an excess of $HNEt_2$ yields a product were the central $>SiMeCl$ site is recovered. No formation of the completely substituted product $[SiMe(NEt_2)_2]_2SiMe(NEt_2)$ occurs, due to steric overcrowding. The transformation of $[SiMeCl(NEt_2)]_2SiMe(NEt_2)$ into $[SiMe(NEt_2)_2]_2SiMeCl$ shows very clear, that diethylamino substituents at silicon are kinetically labil. These reactions are rather thermodynamically than kinetically controlled.

If at least two Si–Cl bonds were transformed into Si–OMe groups, all remaining chlorine substituents can be exchanged for NEt_2, but the terminal Si–Cl bonds are more reactive.

The ^{29}Si NMR data of (diethylamino)-methylchlorotrisilanes are summarized in Table 2, ^{29}Si NMR data of (diethylamino)(methoxy)-methylchlorotrisilanes are given in Table 3.

To sum it up it can be said, that $SiCl_2Me$ sites show the highest reactivity towards $HNEt_2$ as well as towards $HC(OMe)_3/[AlCl_3]$ mixture, followed by SiClMe(OMe)

Table 3
^{29}Si NMR shifts of (diethylamino)(methoxy)-methylchlorotrisilanes

Compound	δ/ppm			$^1J_{SiSi}$ [Hz]
	Si^A	Si^B	Si^C	
$[(OMe)Me_2Si^A]_2Si^BMe(NEt_2)$	14.4	−20.6		93.8
$[(OMe)Me_2Si^A]_2Si^BMe(OMe)$	14.0	6.5		94.9
$(OMe)(NEt_2)MeSi^A–Si^BMeCl–Si^CMeCl(OMe)$	−4.5/−4.7[a]	−6.3	5.8/4.6[a]	
$[(OMe)(NEt_2)MeSi^A]_2Si^BMeCl$	−3.8/−3.9[a]	−4.3		
$[(OMe)(NEt_2)MeSi^A]_2Si^BMe(NEt_2)$	−2.3/−2.6/−2.9[a]	−23.4/−22.6/−24.4[a]		
$[(OMe)_2MeSi^A]_2Si^BMe(NEt_2)$	−0.9	−26.7		
$[(OMe)_2MeSi^A]_2Si^BMe(OMe)$	−2.40	−0.90		120.1

[a] Several diastereomers.

Table 4
Preparation and analytical data of (diethylamino)-methylchlorodi– and –trisilanes

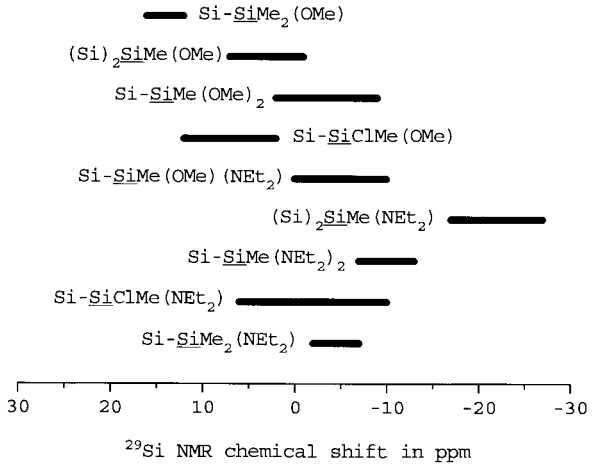
Compound	Starting compound	Molar ratio silan/$HNEt_2$	Additional analytical data (^{29}Si NMR see Table 2)
$Me_3Si^A–Si^BMe_2(NEt_2)$	$Me_3Si–SiMe_2Cl$	1:2	^{1}H NMR: 0.05 (Si^AMe_3), 0.11 (Si^BMe_2), 0.97 *M* (N ~ Me), 2.80 *M* (N–CH_2) $^3J_{HH}$: 6.9 Hz; ^{13}C NMR: −1.5 (Si^AMe_3), −0.8 (Si^BMe_2), 16.2 (N ~ Me), 41.3 (N–CH_2) $^1J_{SiAC}$: 42.9 Hz, $^1J_{SiBC}$: 46.9 Hz; GC/MS: 203 (M^+, 24), 188 (M^+–Me, 25), 130 ($SiMe_2NEt_2$, 100), 73 ($SiMe_3$, 95)
$(NEt_2)Me_2Si^A–Si^BMe_2Cl$	$ClMe_2Si–SiMe_2Cl$	1:2	^{1}H NMR: 0.22 (Si^AMe_2), 0.42 (Si^BMe_2), 0.98 *M* (N ~ Me), 2.82 *M* (N–CH_2); ^{13}C NMR: −1.6 (Si^AMe_2), 2.9 (Si^BMe_2), 16.2 (N ~ Me), 41.3 (N–CH_2)
$(NEt_2)Me_2Si–SiMe_2(NEt_2)$	$ClMe_2Si–SiMe_2Cl$	1:4	^{1}H NMR: 0.12 ($SiMe_2$), 0.98 *M* (N ~ Me), 2.82 *M* (N–CH_2) $^3J_{HH}$: 7.1 Hz ^{13}C NMR: 0.2 ($SiMe_2$), 16.2 (N ~ Me), 41.3 (N–CH_2) $^1J_{SiC}$: 38.5 Hz
$[Si^AMe_3]_2Si^BMe(NEt_2)$	$[SiMe_3]_2SiMeCl$	1:2	^{1}H NMR: 0.10 (Si^AMe_3), 0.18 (Si^BMe), 0.97 *M* (N ~ Me), 2.80 *M* (N–CH_2) $^3J_{HH}$: 7.1 Hz
$[Si^AMe_2(NEt_2)]Si^BClMe–[Si^CMe_2Cl]$	$(SiMe_2Cl)_2SiMeCl$	1:2	^{1}H NMR: 0.32 (Si^AMe_2), 0.63 (Si^BMe), 0.56 (Si^CMe_2), 1.01 *M* (N ~ Me), 2.84 *M* (N–CH_2) $^3J_{HH}$: 6.7 Hz
$[Si^AMe_2(NEt_2)]_2Si^BMeCl$	$(SiMe_2Cl)_2SiMeCl$	1:4	^{1}H NMR: 0.25 (Si^AMe_2), 0.53 (Si^BMe), 1.00 *M* (N ~ Me), 2.84 *M* (N–CH_2)
$[Si^AMe_2(NEt_2)]_2Si^BMe(NEt_2)$	$(SiMe_2Cl)_2SiMeCl$	1:8	Only in mixture with $[SiMe_2(NEt_2)]_2SiMeCl$
$[Si^AMeCl(NEt_2)]Si^BClMe–[Si^CMeCl_2]$	$(SiMeCl_2)_2SiMeCl$	1:2	^{1}H NMR: 0.65 (Si^AMe), 0.74 (Si^BMe), 0.92 (Si^CMe), 1.03 *M* (N ~ Me), 2.92 *M* (N–CH_2)
$[Si^AMeCl(NEt_2)]_2Si^BMeCl$	$(SiMeCl_2)_2SiMeCl$	1:4	^{1}H NMR: 0.67 (Si^AMe), 0.76/0.77 (Si^BMe), 1.08 *M* (N ~ Me), 3.0 *M* (N–CH_2), element. anal.: C: 35.18%, H: 7.91, N: 7.60% (calc. for $C_{11}H_{29}Cl_3N_2Si_3$: C: 34.76%, H: 7.69%, N: 7.37%)
$[Si^AMeCl(NEt_2)]_2Si^BMe(NEt_2)$	$(SiMeCl_2)_2SiMeCl$	1:6	^{1}H NMR: 0.29 (Si^BMe), 0.58/0.61 (Si^A Me), 1.05 *M* (N ~ Me), 2.93 *M* (N–CH_2)
$[Si^AMe(NEt_2)_2]_2$ Si^BMeCl	$(SiMeCl_2)_2SiMeCl$	1:15	^{1}H NMR: 0.27 (Si^AMe), 0.64 (Si^BMe), 1.01 *M* (N ~ Me), 3.0 *M* (N–CH_2); GC/MS: 452 (M^+, 0.5), 379 (M^+–2Et–Me, 1), 307 (M^+–NEt_4Me, 1), 230 ($Si_2Me_2(NEt_2)_2$, 35), 187 ($Si_2Me_3(NEt_2)_2$, 100), 158 ($Si_2Me_2NEt_2$, 16), 116 (37)

Table 5
Preparation and analytical data of (diethylamino)(methoxy)-methylchlorodisilanes

Product	Starting compound	Molar ratio silan/$HNEt_2$	Additional analytical data (^{29}Si NMR see Table 1)
$(OMe)Me_2Si^A–Si^BMe_2(NEt_2)$	$(OMe)Me_2Si–SiMe_2Cl$	1:2	^{1}H NMR: 0.19 (Si^AMe_2), 0.12 (Si^BMe_2), 0.98 *M* (N ~ Me), 2.82 *M* (N–CH_2), $^3J_{HH}$: 7.1 Hz, 3.48 (OMe)
$(OMe)ClMeSi^A–Si^BMeCl(NEt_2)$	$(OMe)ClMeSi–SiMeCl_2$	1:2	^{1}H NMR: 0.595, 0.599 (Si^BMe^*), 0.617, 0.635 (Si^AMe^*), 1.10 (N ~ Me), 2.96 (N–CH_2) ($^3J_{HH}$: 7.0 Hz), 3.57 (OMe) *: two diastereomers
$(OMe)(NEt_2)MeSi^A–Si^BMeCl(NEt_2)$	$(OMe)ClMeSi–SiMeCl_2$	1:4	
$(OMe)(NEt_2)MeSi^A–Si^BMe(NEt_2)_2$	$(OMe)ClMeSi–SiMeCl_2$	1:6	GC/MS: 333 (M^+, 1), 318 (M^+–Me, 1), 245 (5), 217 (23), 187 ($SiMe(NEt_2)_2$, 100), 171 (23), 146 ($SiMe(NEt_2)OMe$, 8), 116 (43), 114 (16), 75 (6)
$(OMe)ClMeSi^A–Si^BMe(OMe)(NEt_2)$	$[SiMeCl(OMe]_2$	1:2	
$[(OMe)(NEt_2)MeSi–]_2$	$[SiMeCl(OMe]_2$	1:4	^{1}H NMR: 0.16 (SiMe), 1.05 (N ~ Me), 2.96 (N–CH_2) ($^3J_{HH}$: 6.8 Hz), 3.40 (OMe); GC/MS: 292 (M^+, 4), 277 (M^+–Me, 3), 220 (M^+–NEt_2, 9), 206 (43), 204 (81), 176 (72), 146 ($SiMe(NEt_2)OMe$, 100),135 (22), 75 (55)
$(OMe)_2MeSi^A–Si^BMe(OMe)(NEt_2)$	$(OMe)_2MeSi–SiMeCl(OMe)$	1:2	^{1}H NMR: 0.188 (Si^BMe), 0.204 (Si^AMe),1.03 (N ~ Me), 2.96 (N–CH_2), 3.42 (Si^BOMe), 3.53 (Si^AOMe)

Table 6
Preparation and analytical data of (diethylamino)(methoxy)-methylchlorotrisilanes

Product	Starting compound	Molar ratio silan/$HNEt_2$	Additional analytical data (^{29}Si NMR see Table 3)
$[(OMe)Me_2Si^A]_2Si^BMe(NEt_2)$	$[(OMe)Me_2Si]_2SiMeCl$	1:2	^{1}H NMR: 0.217 (Si^AMe), 0.230 (Si^BMe_2), 0.99 (N ~ Me), 2.85 ($N–CH_2$) ($^3J_{HH}$: 6.7 Hz), 3.37 (OMe)
$[(OMe)Me_2Si^A]_2Si^BMe(OMe)$	$[(OMe)Me_2Si]_2SiMeCl$	MeOH/NEt_3	^{1}H NMR: 0.21 (Si^AMe), 0.40 (Si^BMe), 3.4 (OMe)
$(OMe)(NEt_2)MeSi^A–Si^BMeCl–Si^CMeCl(OMe)$	$[(OMe)ClMeSi]_2SiMeCl$	1:2	^{1}H NMR: 0.34 (Si^AMe), 0.65/0.67 (Si^CMe), 0.72/0.73 (Si^BMe), 1.08 (N ~ Me), 2.98 ($N–CH_2$) ($^3J_{HH}$: 6.8 Hz), 3.59 (OMe)
$[(OMe)(NEt_2)MeSi^A]_2Si^BMeCl$	$[(OMe)ClMeSi]_2SiMeCl$	1:4	^{1}H NMR: 0.280, 0.299 (Si^AMe), 0.619 (Si^BMe), 1.05 (N ~ Me), 2.95 ($N–CH_2$), ($^3J_{HH}$: 7.0 Hz) 3.44, 3.46 (OMe) GC/MS: 308 (M^+–2OMe, 19), 301 (16), 267 (M^+–OMe–NEt_2, 26), 263 (M^+–Cl–NEt_2, 23), 248 (M^+–Cl–Me–NEt_2, 30), 192 (65), 188 (46), 158 ($Si_2Me_2(NEt_2)$, 28), 146 (SiMe(OMe)(NEt), 100), 133 (36), 89 ($SiMe_2(OMe)$, 28), 75 ($SiMe(OMe)_2$, 61), 59 (SiOMe, 83)
$[(OMe)(NEt_2)MeSi^A]_2Si^BMe(NEt_2)$	$[(OMe)ClMeSi]_2SiMeCl$	1:6	^{1}H NMR: 0.19/0.23 (Si^AMe), 0.26/0.30 (Si^BMe), 1.03 (N ~ Me), 2.87 and 2.95 ($N–CH_2$), 3.37/3.38 (OMe)
$[(OMe)_2MeSi^A]_2SiMe^B(NEt_2)$	$[(OMe)_2MeSi]_2SiMeCl$	1:2	^{1}H NMR: 0.16 (Si^AMe), 0.40 (Si^BMe), 0.99 (N ~ Me), 2.98 ($N–CH_2$), 3.52 (Si^AOMe)
$[(OMe)_2MeSi^A]_2Si^BMe(OMe)$	$[(OMe)_2MeSi]_2SiMeCl$	MeOH/NEt_3	^{1}H NMR: 0.159 (Si^AMe), 0.404 (Si^BMe), 3.42 (Si^BOMe), 3.50 (Si^AOMe)



Scheme 6. General Si NMR chemical shift ranges of the investigated silyl groups.

sites. The reaction of $SiClMe(NEt_2)$ units with $HNEt_2$ is limited by a steric overcrowding. Si–Cl bonds at linear Si–*Si*ClMe–Si units show only low or no reactivity towards $HNEt_2$ and $HC(OMe)_3/[AlCl_3]$, respectively.

2.3. ^{29}Si NMR measurements

^{29}Si NMR spectroscopy is the most powerful tool to characterize oligomeric silanes. But unfortunately only very few data for amino as well as alkoxy substituted oligosilanes are known until now. So this work should also give a contribution to a better insight into ^{29}Si NMR general chemical shift ranges of amino as well as alkoxy substituted oligosilanes. Scheme 6 shows the general chemical shift ranges for the investigated Si sites.

This information is very helpful for the assignment of Si–C–N–O polymers. So the base catalyzed disproportionation of methylchlorodisilanes leads over methylchlorooligosilanes [4] to methylchloropolysilanes which can be spun into green fibers. After curing with ammonia, primary amines or traces of water vapour their pyrolysis gives SiC fibers [10]. Aim of this crosslinking which has to make the green fibers infusible should be the generation of amino as well as oxo substituted Si sites $Si_xSi(CH_3)Cl_y(N<)_{3-x-y}$ or $Si_xSi(CH_3)Cl_y(O^-)_{3-x-y}$ near the surface. But until now the signals of the ^{29}Si NMR spectra could not be assigned to judge the curing stage of such polymer products. It seems now that Si–$SiCl_2$Me groups of the polysilane were converted by ammonia into Si–*Si*ClMe–N< and Si–*Si*Me(–N<)$_2$ whereas linear Si–*Si*ClMe–Si units of the polymer were not affected. This finding parallels our results discussed above for methylchlorodi– and –trisilanes.

3. Experimental

3.1. General comments

All ^{29}Si, ^{13}C and ^{1}H NMR spectra were recorded on a Bruker MSL 300 using the IGATED pulse sequence (C, Si) with TMS or Si_2Me_6 (δ_{Si} −19.68 ppm, used if signals near 0 ppm were expected) as internal standard and $CDCl_3$ as solvent. GC/MS measurements were carried out on a Hewlett Packard 5971. Ionisation energy: 70 eV; Column: 30 m × 0.25 mm × 0.25 μm coated with phenylmethylpolysiloxane. Flow: Helium 0.5 ml/min. Because of the high injection and column temperature the GC/MS investigations succeeded only for relatively stable compounds. The more reactive chlorocompounds gave reactions on the column.

3.2. Preparation of (diethylamino)methylchlorotrisilanes

The (diethylamino)methylchlorotrisilanes were prepared by the reaction of bis(dichloromethylsilyl)chloromethylsilane [4] or bis(chlorodimethylsilyl)chloromethylsilane [9], respectively, and diethylamine in various molar ratios. Diethylamine were added dropwise to a solution of 1 g methylchlorotrisilane in 50 ml dry *n*-hexane. The mixture was stirred for 24 h before the formed $HNEt_2^*HCl$ was filtered off. The solvents and volatiles were evaporated from the resulting filtrate. The products were investigated by means of NMR spectroscopy.

3.3. Preparation of methoxymethylchlorodi– and –trisilanes

The preparation of the (methoxy)-methychlorosilanes was carried out by the reaction of the corresponding methychlorooligosilanes with $HC(OMe)_3$–$AlCl_3$ as described in [3].

3.4. Preparation of (diethylamino)(methoxy)-methylchlorodi– and –trisilanes

Starting from the corresponding (methoxy)-methychlorooligosilanes, diluted in dried *n*-hexane, the addition of the given molar ratio diethylamine yielded after working up, as described above for the preparation of (diethylamino)-methychlorotrisilanes the desired (diethylamino)(methoxy)-methychlorodi– and –trisilanes (Tables 4–6).

3.5. Preparation of 1,2,3-trimethoxypertamethyltrisilane and 1,1,2,3,3-pentamethoxytrimenthyl-trisilane

About 3.5 mmol (approx. 1 g) $[SiMe_2(OMe)]_2SiMeCl$ or $[SiMe(OMe)_2]_2SiMeCl$, respectively, were stirred

with 10 ml *n*-hexane, 4 mmol (0.13 g) dried methanol and 3.5 mmol (0.35 g) triethylamine for 1 h. The mixture was filtered from the precipitated NEt_3^*HCl and the solvent evaporated to yield $[SiMe_2(OMe)]_2SiMe(OMe)$ or $[SiMe(OMe)_2]_2SiMe(OMe)$ in approximately 90% yield. Both compounds are already known [11,12], but were prepared on different routes.

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