Reaction of the Si–Cl bond with trialkyl orthoformates
Preparation of alkoxy-substituted silanes

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Abstract

Trialkyl orthoformates in the presence of aluminium chloride represent quite useful reagents to generate silicon alkoxides from chlorosilanes. 3-Cyanopropyltrichlorosilane and 2-[(2-trichlorosilyl)ethyl]-pyridine give the triethoxy compounds 3-cyanopropyltriethoxysilane and 2-[(2-triethoxysilyl)ethyl]-pyridine respectively. Via this route, in methylchlorooligosilanes a partial or complete exchange of the chlorine substituents for alkoxy groups occurs depending on the starting molar ratio of silane:HC(OR)$_3$ (R = Me, Et). SiCl$_2$Me groups react to SiClMe(OR) first before SiMe(OR)$_2$ groups are formed. (Si)$_2$SiClMe units are not affected by HC(OR)$_3$. © 1997 Elsevier Science S.A.
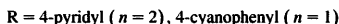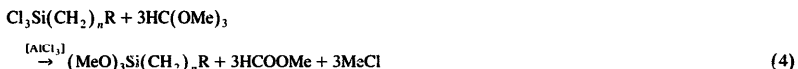
1. Introduction

Alkoxy-substituted oligosilanes have been prepared previously by the reaction of the chloro-substituted or bromo-substituted oligosilanes with the corresponding alcohol in the presence of a base, usually triethylamine [1–3]:

$$SiClMe_2\text{–}SiClMe_2 + 2MeOH + 2NEt_3$$

$$\rightarrow SiMe_2(OMe)\text{–}SiMe_2(OMe) + 2[HNEt_3]Cl \qquad (1)$$

$$SiBrMe(SiBrMe_2)_2 + 3MeOH + 3NEt_3$$

$$\rightarrow SiMe(OMe)[SiMe_2(OMe)]_2 + 3[HNEt_3]Cl \qquad (2)$$

The formation of partially substituted oligosilanes during these reactions was not observed.

Shorr [4] and Grüniger and Calzaferri [5] showed that the AlCl$_3$-catalysed reaction of trichlorosilanes with trimethyl orthoformate leads to alkoxy-substituted silanes:

$$MeHSiCl2 + 2HC(OEt)_3$$

$$\xrightarrow{[AlCl_3]} MeHSi(OEt)_2 + 2HCOOEt + 2EtCl \qquad (3)$$

$$Cl_3Si(CH_2)_nR + 3HC(OMe)_3$$

$$\xrightarrow{[AlCl_3]} (MeO)_3Si(CH_2)_nR + 3HCOOMe + 3MeCl \qquad (4)$$

R = 4-pyridyl (n = 2), 4-cyanophenyl (n = 1)

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Starting from trichlorosilanes this kind of alkoxylation offers an easy access to interesting components in sol gel processes of film preparation on silica carriers.

We also tried to transfer this method to the preparation of alkoxide derivatives from chloro-substituted oligosilanes. This should also lead to partially substituted oligosilanes, depending on the starting molar ratio of silane:trialkyl orthoformate.

2. Results and discussion

Cyanopropyltrichlorosilane and 2-[(2-trichlorosilyl)ethyl]-pyridine react quite well with triethyl orthoformate in the presence of aluminium chloride to their ethoxy derivatives (Eqs. (5) and (6); Table 1):

$$\text{N}\equiv\text{C}\diagup\diagdown\diagup\diagdown\underset{\text{Cl}}{\overset{\text{Cl}}{\text{Si}}}\text{—Cl}\quad\xrightarrow[-3\ \text{HCOOEt}-3\ \text{EtCl}]{3\ \text{HC(OEt)}_3\ [\text{AlCl}_3]}\quad\text{N}\equiv\text{C}\diagup\diagdown\diagup\diagdown\underset{\text{OEt}}{\overset{\text{OEt}}{\text{Si}}}\text{—OEt} \tag{5}$$
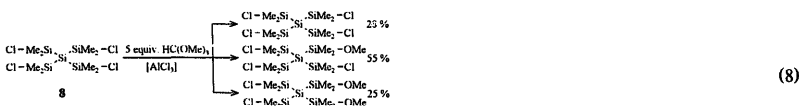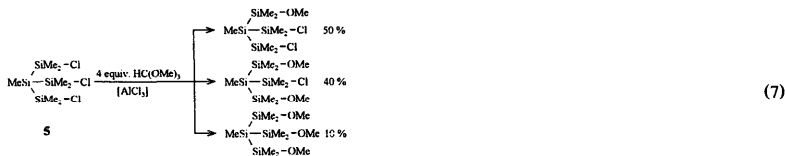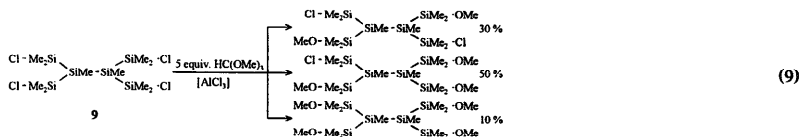
$$\tag{6}$$

The formed alkoxides could be immobilized onto silica gel and the resulting solids represent heterogeneous catalysts for the Lewis-base-catalysed disproportionation of methylchlorodisilanes as described in Ref. [6].

In order to estimate the reactivity of different chloro-substituted silyl groups (–SiClMe$_2$, –SiCl$_2$Me, –SiClMe–) in oligosilanes, the behaviour of the methylchlorooligosilanes SiClMe$_2$–SiClMe$_2$ (1), SiCl$_2$Me–SiCl$_2$Me (2), SiClMe(SiClMe$_2$)$_2$ (3), SiClMe(SiCl$_2$Me)$_2$ (4), SiMe(SiClMe$_2$)$_3$ (5), SiMe(SiClMe$_2$)$_2$(SiMe$_3$) (5a), SiMe(SiClMe$_2$)(SiMe$_3$)$_2$ (5b), SiMe(SiCl$_2$Me)$_3$ (6), (SiCl$_2$Me)$_2$SiMe–SiClMe–SiCl$_2$Me (7), Si(SiClMe$_2$)$_4$ (8), (SiClMe$_2$)$_2$SiMe–SiMe(SiClMe$_2$)$_2$ (9) and (SiCl$_2$Me)$_2$SiMe–SiMe(SiCl$_2$Me)$_2$ (10) toward HC(OMe)$_3$ in the presence of AlCl$_3$ was investigated. The alkoxy-substituted oligosilanes formed could be detected by means of ^{29}Si and ^{1}H NMR spectroscopy, which allows a clear identification also in product mixtures. The NMR spectroscopy results are summarized in Tables 2–6. The NMR data of the methylchlorooligosilanes used have already been published [2,3,6–9].

2.1. Reaction of oligosilanes bearing –SiClMe$_2$ groups

Whereas 1 reacts with HC(OMe)$_3$ to give either SiMe$_2$(OMe)–SiClMe$_2$ or the completely substituted product SiMe$_2$(OMe)–SiMe$_2$(OMe) depending on the starting molar ratio (1:1, 1:2), the reactions of 5, 8 and 9 with HC(OMe)$_3$ lead only to mixtures of partially substituted products even if an excess of HC(OMe)$_3$ is used:

$$\tag{7}$$

$$\tag{8}$$

$$
\begin{array}{ccc}
\text{Cl–Me}_2\text{Si} & \diagdown & \text{SiMe}_2\cdot\text{Cl} \\
 & \text{SiMe–SiMe} & \\
\text{Cl–Me}_2\text{Si} & \diagup & \text{SiMe}_2\cdot\text{Cl} \\
 & \mathbf{9} &
\end{array}
\xrightarrow[\text{[AlCl}_3\text{]}]{\text{5 equiv. HC(OMe)}_3}
$$

30 % 50 % 10 % (9)

Using a mixture of 70% **5a** with 15% **5** and 15% **5b** (molar ratio silanes:HC(OMe)₃ = 1:2) it can be demonstrated that **5** is more reactive than **5a** (and **5a** is more reactive than **5b**). Whereas **5** reacts to an average mixture of

Table 1
NMR data and refractive indices of the triethoxysilanes

Compound	δ_{Si} (ppm)	δ_{H} (ppm)	n_{D}^{30}
NC–(CH₂)₃–Si(OC₂H₅)₃	−47.94	0.60 CH_2Si (t, 2 H); 1.02 OCH₂CH_3 (t, 9 H); 1.59 CH₂CH_2CH₂ (m, 2 H); 2.22 NC–CH_2 (t, 2 H); 3.50 OCH_2 (q, 6 H)	1.4166
NC₅H₄–(CH₂)₂–Si(OC₂H₅)₃ [a]	−48.31	0.42 CH_2Si (t, 2 H); 0.48 OCH₂CH_3 (t, 9 H); 2.33 py–CH_2 (t, 2 H); 3.13 OCH_2 (q, 6 H); 6.72, 7.24, 7.88 py (2 H, 1 H, 1 H)	1.4867

[a] δ_C (ppm): 9.3 CH₂Si ($^1J_{SiC}$ = 96.6 Hz); 16.9 OCH₂CH₃; 28.5 py-CH₂; 56.9 OCH₂; 121.0, 122.5 C-3/C-5; 138.5 C-4; 144.4 C-6; 160.4 C-2.

Table 2
NMR data of methylchloroalkoxydisilanes

Compound	δ_{Si} (ppm)		δ_{H} (ppm)			
	A	B	Me (A)	Me (B)	OMe (A)	OMe (B)
Si^{A}Me₂(OMe)–Si^{B}ClMe₂	11.98	17.64	0.21	0.53		
[SiMe₂(OMe)]₂	12.0		0.19			
Si^{A}ClMe(OMe)–Si^{B}Cl₂Me	2.55	19.16	0.664	0.930		
[SiClMe(OMe)]₂		4.55/5.19^a		0.588/0.598^a		3.656
Si^{A}Me(OMe)₂–Si^{B}Cl₂Me	−12.36	21.88	0.318	0.856		
Si^{A}Me(OMe)₂–Si^{B}ClMe(OMe)	−9.75	8.28	0.238	0.516	3.548	
[SiMe(OMe)₂]₂	−6.32		0.158		3.484	
Si^{A}ClMe(OEt)–Si^{B}Cl₂Me	−0.32^b	19.00	0.626	0.880		O–CH₂ 3.864^d CH₃ 1.228
[SiClMe(OEt)]₂		1.78/2.40^a		0.556/0.545^a		O–CH₂ 3.84^d CH₃ 1.20
Si^{A}Me(OEt)₂–Si^{B}Cl₂Me	−16.32	21.93	0.230	0.495		
Si^{A}Me(OEt)₂–Si^{B}ClMe(OEt)	−13.83^c	5.62				
[SiMe(OEt)₂]₂	−10.29		0.151			O–CH₂ 3.784^e CH₃ 1.196

[a] Two diastereomers.
[b] $^1J_{SiSi}$ = 159.6 Hz.
[c] $^1J_{SiSi}$ = 168.0 Hz.
[d] $^3J_{HH}$ = 6.7 Hz.
[e] $^3J_{HH}$ = 6.8 Hz.

Table 3
NMR data of methylchloroalkoxytrisilanes

Compound	δ_{Si} (ppm)		
	A	B	C
Si^{A}ClMe[Si^{B}Me₂(OMe)](Si^{C}ClMe₂)	−0.10	14.11	20.04
Si^{A}ClMe[Si^{B}Me₃(OMe)]₂	0.08	14.39	
Si^{A}Me(OMe)[Si^{B}Me₂(OMe)]₂ [2]	6.5	14.0	$^1J_{SiSi}$ = 94.9 Hz
Si^{A}ClMe[Si^{B}ClMe(OMe)](Si^{C}Cl₂Me)	−5.80	8.08/9.18^a	25.43
Si^{A}ClMe[Si^{B}ClMe(OMe)]₂	−7.72	8.36/9.44^a	
Si^{A}ClMe[Si^{B}Me(OMe)₂][Si^{C}ClMe(OMe)]	−7.45	−5.55	10.90/12.28^a
Si^{A}ClMe[Si^{B}Me(OMe)₂]₂	−7.71	−4.20	

[a] Several diastereomers.

Table 4
NMR data of methylchloroalkoxyisotetrasilanes

Compound	δ_{Si} (ppm)			
	A	B	C	D
$Si^A Me[Si^E Me_2(OMe)](Si^D Me_3)_2$	−89.38	22.05		−12.90
$Si^A Me[Si^B Me_2(OMe)(Si^C ClMe_2)(Si^D Me_3)$	−85.32	20.97	29.32	−12.94
$Si^A Me[Si^B Me_2(OMe)]_2(Si^D Me_3)$	−91.29	21.66		−13.29
$Si^A Me[Si^B Me_2(OMe)](Si^C ClMe_2)_2$	−80.82	20.08	27.64	
$Si^A Me[Si^B Me_2(OMe)]_2(Si^C ClMe_2)$	−86.56	20.68	28.78	
$Si^A Me[Si^B Me_2(OMe)]_3$	−93.1	21.36		
$Si^A Me[Si^C ClMe(OMe)(Si^D Cl_2Me)_2$	−68.60		15.59	32.83
$Si^A Me[Si^C ClMe(OMe)]_2(Si^D Cl_2Me)^a$	−74.48/ −74.68		17.31	34.80/ 34.68
$Si^A Me[Si^C ClMe(OMe)]_3$ ^{a}	−81.43/ −81.73		19.15/ 19.05	
$Si^A Me[Si^B Me(OMe)_2][Si^C ClMe(OMe)]_2$ ^{a}	−87.66/ −87.89	2.96	21.24/ 21.38	
$Si^A Me[Si^B Me(OMe)_2]_2[Si^C ClMe(OMe)]$	−93.63	4.72	23.26	
$Si^A Me[Si^D Me(OMe)_2]_3$	−101.30	6.02		
$Si^A Me[Si^B Me(OEt)_2]_3$	−101.61	2.62		

^{a} Several diastereomers; data in one row belong to the same diastereomer.

Table 5
NMR data of methylchloroalkoxypentasilanes

Compound	δ_{Si} (ppm)				δ_H (ppm)		
	A	B	C	D	B	C	OMe
$Si^A[Si^B Me_2(OMe)](Si^C ClMe_2)_3$	−119.82	21.58	28.53		0.423	0.602	3.12
$Si^A[Si^B Me_2(OMe)]_2(Si^C ClMe_2)_2$	−126.22	22.25	29.59		0.414	0.585	3.12
$Si^A Me[Si^B Me(OMe)_2]_2-Si^C ClMe-Si^D Me(OMe)_2$	−87.93	5.20/ 5.25^a	−4.39	7.55			

^{a} Diastereotopic silicon atoms.

Table 6
NMR data of methylchloroalkoxyhexasilanes

Compound	δ_{Si} (ppm)				
	A	B	C	D	E
$\{Si^A Me[Si^C ClMe_2][Si^D Me_2(OMe)]\}_2$	−79.15/ −79.26^b		29.30/ 29.54^b	21.41/ 21.46^b	
$Si^A Me[Si^C Me_2(OMe)]_2-Si^a Me[Si^D ClMe_2][Si^E Me_2(OMe)]$	−85.35	−79.34	21.85/ 21.95^a	29.94	21.68
$\{Si^A Me[Si^C Me_2(OMe)]_2\}_2$	−85.41		22.16		
$\{Si^A Me[Si^C Me(OMe)_2]_2\}_2$	−90.45		6.72		

^{a} Diastereotopic silicon atoms.
^{a} Two diastereomers.

$SiMe(SiMe_2OMe)_{2.2}(SiClMe_2)_{0.8}$. **5a** yields an average of $SiMe(SiMe_2OMe)_{1.2}(SiClMe_2)_{0.8}(SiMe_3)$ and **5b** an average of $SiMe(SiMe_2OMe)_{0.5}(SiClMe_2)_{0.5}(SiMe_3)_2$. All possible substitution products could be identified (Table 4).

2.2. Reaction of oligosilanes bearing −SiCl_2Me groups

The substitution of Si–Cl bonds in **2** by the action of $HC(OR)_3$ was investigated in more detail. Fig. 1 shows the product distribution found for the reaction of **2** with $HC(OMe)_3$ by variation of the molar ratio $2/HC(OMe)_3$.

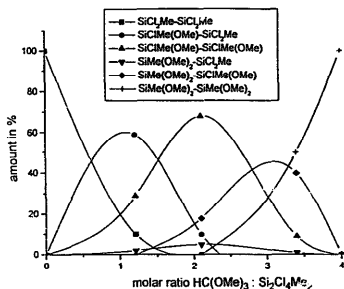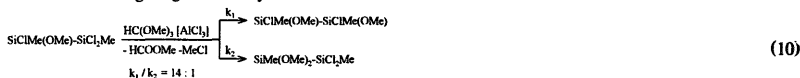Fig. 1. Product distribution of the reaction of SiCl$_2$Me–SiCl$_2$Me with HC(OMe)$_3$ and its dependence on the starting molar ratio of formic acid ester:disilane.

Remarkable is the high regioselectivity of the second substitution:

$$\text{SiClMe(OMe)-SiCl}_2\text{Me} \xrightarrow[\substack{-\text{HCOOMe -MeCl} \\ k_1/k_2 = 14:1}]{\text{HC(OMe)}_3 \ [\text{AlCl}_3]} \begin{cases} \xrightarrow{k_1} \text{SiClMe(OMe)-SiClMe(OMe)} \\ \xrightarrow{k_2} \text{SiMe(OMe)}_2\text{-SiCl}_2\text{Me} \end{cases} \tag{10}$$

A completely analogous product distribution of ethoxy-substituted disilanes can be observed, if HC(OEt)$_3$ is used instead of HC(OMe)$_3$.

The reaction of **6** with HC(OMe)$_3$ proceeds very similarly. Fig. 2 shows the observed reaction product distribution dependence on the starting molar ratio of **6**/HC(OMe)$_3$. No products bearing –SiCl$_2$Me and –SiMe(OMe)$_2$ groups simultaneously were detected in this case. The completely substituted isotetrasilanes SiMe[SiMe(OR)$_2$]$_3$ (R = Me, Et) can easily be prepared in the pure state using a slight excess of HC(OR)$_3$. Analogously, the treatment of **10** with HC(OMe)$_3$ leads to [(MeO)$_2$MeSi]$_2$SiMe–SiMe[SiMe(OMe)$_2$]$_2$.

2.3. Reaction of oligosilanes bearing –SiClMe– units with –SiCl$_2$Me or –SiClMe$_2$ groups

Surprisingly, the reactions of **3** or **4** lead only to substitution products in which the –SiClMe– unit remains, whereas in some other types of reaction (Lewis-base-catalysed disproportionation [6], Lewis-base-catalysed hydro-

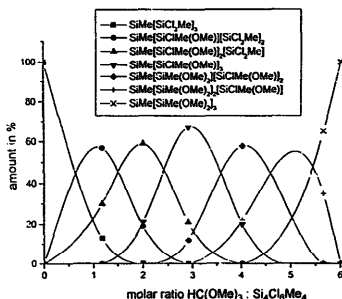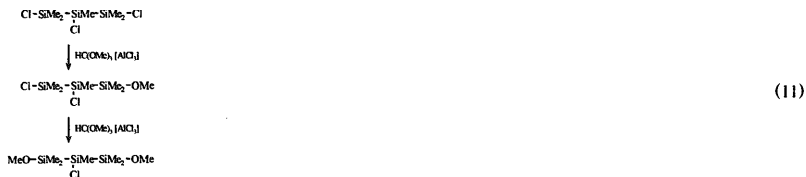Fig. 2. Product distribution of the reaction of SiMe(SiCl$_2$Me)$_3$ with HC(OMe)$_3$ and its dependence on the starting molar ratio of formic acid ester:tetrasilane.

genation by stannanes [7]) the silicon–chlorine bond on the middle silicon atom exhibits the highest reactivity. Even if an excess of $HC(OMe)_3$ is used, a conversion into the completely substituted products $SiMe(OMe)[SiMe_2(OMe)]_2$ or $SiMe(OMe)[SiMe(OMe)_2]_2$ does not succeed:

$$Cl-SiMe_2-\underset{\underset{Cl}{|}}{SiMe}-SiMe_2-Cl$$

$$\downarrow \text{HC(OMe)}_3 \text{ [AlCl}_3\text{]}$$

$$Cl-SiMe_2-\underset{\underset{Cl}{|}}{SiMe}-SiMe_2-OMe \qquad (11)$$

$$\downarrow \text{HC(OMe)}_3 \text{ [AlCl}_3\text{]}$$

$$MeO-SiMe_2-\underset{\underset{Cl}{|}}{SiMe}-SiMe_2-OMe$$

$$\underset{Cl}{\overset{Cl}{>}}SiMe-\underset{\underset{Cl}{|}}{SiMe}-SiMe\underset{Cl}{\overset{Cl}{<}}$$

$$\downarrow \text{HC(OMe)}_3 \text{ [AlCl}_3\text{]}$$

$$\underset{Cl}{\overset{Cl}{>}}SiMe-\underset{\underset{Cl}{|}}{SiMe}-SiMe\underset{Cl}{\overset{OMe}{<}}$$

$$\downarrow \text{HC(OMe)}_3 \text{ [AlCl}_3\text{]}$$

$$\underset{Cl}{\overset{MeO}{>}}SiMe-\underset{\underset{Cl}{|}}{SiMe}-SiMe\underset{Cl}{\overset{OMe}{<}} \qquad (12)$$

$$\downarrow \text{HC(OMe)}_3 \text{ [AlCl}_3\text{]}$$

$$\underset{Cl}{\overset{MeO}{>}}SiMe-\underset{\underset{Cl}{|}}{SiMe}-SiMe\underset{OMe}{\overset{OMe}{<}}$$

$$\downarrow \text{HC(OMe)}_3 \text{ [AlCl}_3\text{]}$$

$$\underset{MeO}{\overset{MeO}{>}}SiMe-\underset{\underset{Cl}{|}}{SiMe}-SiMe\underset{OMe}{\overset{OMe}{<}}$$

Analogously, the reaction of **7** with an excess of $HC(OMe)_3$ produces only $[(MeO)_2MeSi]_2SiMe–SiClMe–SiMe(OMe)_2$, in the pure state.

3. Experimental

3.1. Preparation of methylchlorooligosilanes

1, **2** and **3** were prepared as described in Refs. [10,8,11].

5: 11 g $SiMe(SiMe_3)_3$ were dissolved in 30 ml hexane. To this solution were added 21.5 g $AlCl_3$ and 12.5 g acetyl chloride under stirring. After reacting for 3 h at room temperature the upper layer was isolated. The fractionated distillation gave 8 g of pure $SiMe(SiClMe_2)_3$ (b.p. 110–120 °C/0.7 kPa, solidifies at ambient temperature).

5a: the same reaction as described above, but adding $AlCl_3$ and acetyl chloride in a molar ratio 1:2:2, yields 7 g of a mixture of 70% **5a** besides 15% **5** and **5b** (b.p. 100–110 °C/0.6 kPa, solidifies below 40 °C); for more details see Ref. [7].

8: in the same way as described above, the reaction of 3.7 g $Si(SiMe_3)_4$ with 7.7 g $AlCl_3$ and 4.5 g acetyl chloride gave, after removal of hexane in vacuum, 3.6 g of a crystalline residue of **8**.

9: analogously, the reaction of 4 g $(SiMe_3)_3SiMe–SiMe(SiMe_3)_2$ with 7 g $AlCl_3$ and 4 g acetyl chloride produced 2 g of a crystalline residue of **9**. In this case the reaction must be carried out at 0 °C to avoid skeletal rearrangements of the silane. The same reaction at 50 °C yields $(Si^A ClMe_2)_3 Si^B–Si^C ClMe–Si^D ClMe_2$ (δ_{Si}/ppm: A 27.60, B −109.92, C 10.60, D 20.82).

4, **6**, **7** and **10**: 900 g **2** were Lewis-base-catalysed disproportionated with a fixed catalyst as described in Ref. [6]. The mixture of **2**, **4**, **6**, **7** and **10** formed could be fractionated to give pure **4** (40 g, b.p. 215–220 °C), **6** (45 g, b.p. 120 °C/0.8 kPa, solidifies), **7** (25 g, b.p. 120 °C/13 Pa) and **10** (6 g, b.p. 160 °C/13 Pa).

3.2. Reaction of trichlorosilanes with trialkyl orthoformates

44.55 g (0.3 mol) HC(OEt)$_3$ were added at 50 °C to a mixture of 20.27 g (0.1 mol) 3-cyanopropyltrichlorosilane and 0.05 g AlCl$_3$. A vigorous reaction occurred and the mixture was refluxed for 6 h. After removal of the volatiles in vacuum the 3-cyanopropyltriethoxysilane was isolated by distillation: b.p. 114–117 °C/1.1 kPa; yield 19.45 g (84%).

To a mixture of 23.5 g (0.0977 mol) 2-[(2-trichlorosilyl)ethyl]-pyridine and 0.05 g AlCl$_3$ were added 43.4 g (0.293 mol) HC(OEt)$_3$ over 15 min. After the vigorous reaction had ceased the mixture was refluxed for 14 h. After having removed the volatiles the 2-[(2-triethoxysilyl)ethyl]-pyridine was distilled in vacuo: b.p. 140–143 °C/0.9 kPa; yield 19.2 g (73%).

3.3. Reaction of chloro-substituted oligosilanes with trialkyl orthoformates

First, a few milligrams AlCl$_3$ and, second, the calculated amount of either HC(OMe)$_3$ or HC(OEt)$_3$ were added to the methylchlorooligosilane. The course of the reaction can be followed by the evolution of gaseous MeCl or EtCl respectively. After standing overnight the product mixture was diluted with hexane and filtered from the precipitation of AlCl$_3$. In the cases of disilane derivatives the products were isolated by fractional distillation, otherwise the products were obtained by removal of the volatiles in vacuum: SiMe(OMe)$_2$–SiMe(OMe)$_2$, b.p. 117 °C; SiMe(OEt)$_2$–SiMe(OEt)$_2$, b.p. 92–93 °C/2.5 kPa.

3.4. NMR measurements

All NMR spectra were recorded on a Bruker MSL 300. TMS was used as internal standard.

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