

NMR Spectroscopic Investigation of the Reaction between Tetrachlorodimethyldisilane and Diethylamine for the Synthesis of Chloro- and Amino-functionalized Methyldisilanes

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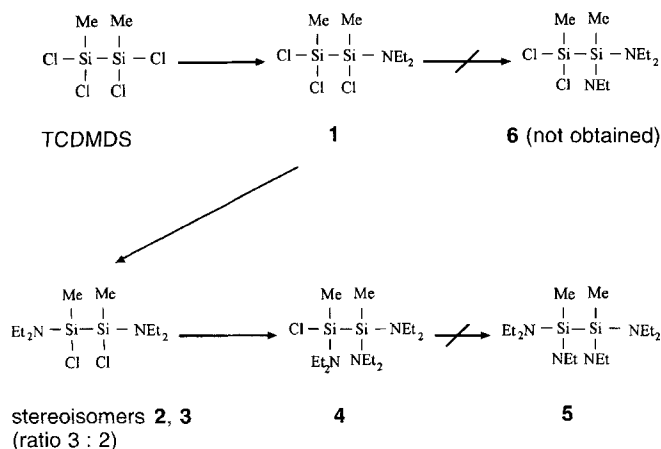
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The formation of aminochloromethyl substituted disilanes from (1,1,2,2)tetrachlorodimethyldisilane (TCDMDS) and diethylamine (Et_2NH) is of interest both from synthetic aspects and from an NMR point of view. It represents also an easy way to synthesize variously substituted (amino)chloromethyldisilanes and it gives not only the possibility to obtain the chemical shifts of mixed substituted silicon atoms. Those compounds allow further reactions of the remaining chloro function. Finally the newly obtained aminodisilanes can be converted into the corresponding chlorodisilanes [1].

The disilanes which can possibly be formed by the reaction of Et_2NH and TCDMDS are summarized in Scheme 1. By increasing the ratio of Et_2NH /TCDMDS from 1:1 to 9:1 we detected 4 different (amino)chloromethyldisilanes. Using quantitative ^{29}Si and ^{13}C NMR spectroscopic investigations the compounds formed were identified (Tab.1, 2) and the composition of the mixtures determined (Fig. 1). We did not find the nonsymmetrical twofold substituted product, but exclusively the stereoisomers of the symmetrical substituted



Scheme 1

1,2-dichloro-1,2-bis(diethylamino)dimethyldisilane (**2, 3**) in a ratio 3:2. This behaviour can be explained by a decrease of the electrophilicity of the substituted silicon atom and possibly by a controlling influence of Et_2NH . The diethylamino group already bonded to silicon and bridged with two other Et_2NH molecules over hydrogen bonds may act as a chelate ligand in the transition state favouring the 1,2-substitution. Also the completely substituted product (1,1,2,2-tetrakisdiethylamino-dimethyldisilane) **5** was never observed in a reaction mixture in spite of the excess of Et_2NH up to 9:1. A similar behaviour was observed by J. Lipovitz *et al.* in the case of disilazane [2].

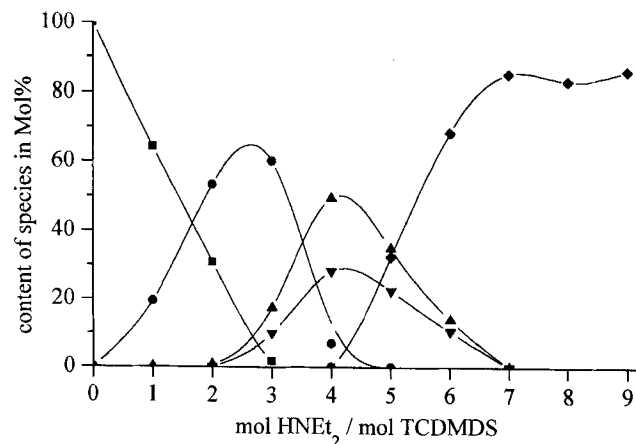


Fig. 1 Composition dependence of the reaction mixture on the molar ratio diethylamine/tetrachlorodimethyldisilane (TCDMDS);

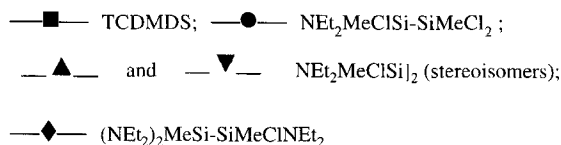


Table 1 ^{29}Si -NMR chemical shifts (δ) and coupling constants (1J) of the aminosilanes 1–4

compound	$\delta_{\text{Si}^{\text{A}}}$ /ppm	$\delta_{\text{Si}^{\text{B}}}$ /ppm	J_{SiSi} /Hz	$^1J_{\text{SiC}}$ /Hz
$\text{Me}(\text{NEt}_2)\text{ClSi}^{\text{A}}\text{-Si}^{\text{B}}\text{MeCl}_2$ (1)	-1.8	21.2	161.3	54.7
$[\text{Me}(\text{NEt}_2)\text{ClSi}]_2$ (2)	2.1			
$[\text{Me}(\text{NEt}_2)\text{ClSi}]_2$ (3)	-0.05			
$\text{Me}(\text{NEt}_2)_2\text{Si}^{\text{A}}\text{-Si}^{\text{B}}\text{Me}(\text{NEt}_2)\text{Cl}$ (4)	-12.5	4.6	149.8	53.1

Table 2 ^{13}C NMR chemical shifts (δ) of the aminodisilanes 1–4

compound	δ_{C} /ppm	relative intensity	assignment
$\text{Me}(\text{NEt}_2)\text{ClSi}^{\text{A}}\text{-Si}^{\text{B}}\text{MeCl}_2$ (1)	0.01	1	$\text{Si}^{\text{A}}\text{-CH}_3$
	6.70	1	$\text{Si}^{\text{B}}\text{-CH}_3$
	15.11	2	$\text{N}\sim\text{CH}_3$
	40.45	2	N-CH_2
$[\text{Me}(\text{NEt}_2)\text{ClSi}]_2$ (2)	1.59	1	Si-CH_3
	14.88	2	$\text{N}\sim\text{CH}_3$
	40.76	2	N-CH_2
$[\text{Me}(\text{NEt}_2)\text{ClSi}]_2$ (3)	1.72	1	Si-CH_3
	14.90	2	$\text{N}\sim\text{CH}_3$
	40.30	2	N-CH_2
$\text{Me}(\text{NEt}_2)_2\text{Si}^{\text{A}}\text{-Si}^{\text{B}}\text{Me}(\text{NEt}_2)\text{Cl}$ (4)	-0.77	1	$\text{Si}^{\text{A}}\text{-CH}_3$
	3.18	1	$\text{Si}^{\text{B}}\text{-CH}_3$
	14.70	2	$\text{Si}^{\text{A}}\text{-N}\sim\text{CH}_3$
	14.91	2	$\text{Si}^{\text{A}}\text{-N}\sim\text{CH}_3^{\text{a}}$
	15.09	2	$\text{Si}^{\text{B}}\text{-N-CH}_2^{\text{a}}$
	39.55	2	$\text{Si}^{\text{A}}\text{-N-CH}_2$
	39.61	2	$\text{Si}^{\text{A}}\text{-N-CH}_2$
	40.46	2	$\text{Si}^{\text{B}}\text{-N-CH}_2$

^a) no unambiguous assignment possible

Fig. 1 shows the composition of the mixtures in dependence on the molar ratio $\text{Et}_2\text{NH}/\text{TCDMDS}$ under equilibrium conditions. Because of the time dependence of the reaction it is important to stir the mixture at least for 24 h to get reproducible results. We always added the Et_2NH to the TCDMDS. One experiment with reversed order of adding resulted in the same yield after a longer reaction period. The yield graphs (Fig. 1) demonstrate that the reaction proceeds step by step. That means, until the lower substituted species is formed in a high amount (65–80%) the further conversion into the higher substituted compound does not start.

From Fig. 1 it is evident that the pure compounds **1** and **4** can be prepared easily by picking out a suitable ratio $\text{Et}_2\text{NH}/\text{TCDMDS}$. So after a reaction period of 24 h the mixture was filtered and the filtrate was fractionated. By doing this it was possible to isolate the aminosilanes **1** and **4**. In the case of **2** and **3** the synthesis was more complicated. In every batch containing **2** and **3** in a good yield **1** and **4** are also obtained. We were able to isolate **2** and **3** from **1** and **4** by the method mentioned above, but the separation of **2** from **3** was not possible by a simple distillation.

Experimental

All NMR-spectra were recorded on a BRUKER MSL 300 spectrometer at 59,627 MHz (^{29}Si) with TMS as internal standard and 75,47 MHz (^{13}C) with CDCl_3 ($\delta=77$ ppm referred to TMS) as internal standard. The composition of the mixtures was determined by integrating the ^{29}Si NMR spectra, using the IGATED pulse sequence. For the synthesis dry *n*-hexane, dry Et_2NH and TCDMDS, prepared as described in [3], were used. Every preparation was carried out under inert atmosphere (Ar) using standard schlenk techniques.

Preparation of the reaction mixture for NMR-measurements

To a solution of 1 ml TCDMDS (0,00557 mol) in dry *n*-hexane (20 ml) a solution of diethylamine in *n*-hexane (5 ml) was added dropwise over a period of approx. 30–40 min at room temperature. The amount of diethylamine was varied from 0,00557 mol (0,58 ml, ratio 1:1) to 0,050 mol (5,23 ml, ratio 9:1). The mixtures were stirred for 25 h and filtered. The *n*-hexane was removed and the residue measured in CDCl_3 .

Chloro-1,2,2-tris(diethylamino)dimethyldisilane (4)

A solution of 72,1 ml (50,5 g, 0,69 mol) diethylamine in 50 ml *n*-hexane was added slowly to a solution of 15,5 ml (19,7 g, 0,0863 mol) TCDMDS in 200 ml *n*-hexane at 0 °C (ice bath). The mixture was stirred for about 36 h. Because of the high amount of diethylamine hydrochloride formed approx. 200 ml *n*-hexane were added and the mixture was filtered through glass fibre. The filtrate was concentrated and distilled under reduced pressure to give 16,1 g (55,4% yield) of **4** as a colourless liquid. $C_{14}H_{36}ClN_3Si_2$ (338,1) Found (calc.): C 50,0 (49,8), H 10,9 (10,7), N 12,3 (12,4), Cl 10,6 (10,5), Si 16,7 (16,6); GCMS: 337 (M^+) 187 ($M^+ - (Et_2N)_2SiMe$) 116 ($M^+ - (Et_2N)SiMe$) 72 (Et_2N). *b.p.* 120 °C/1,5 torr.

1,2-Tris-chloro-diethylaminodimethyldisilane (1)

This compound was obtained in 16% yield in the same manner as above from 31 ml (39,4 g, 0,17 mol) TCDMDS/100 ml *n*-hexane and 32,5 ml (22,74 g, 0,31 mol) diethylamine (ratio 1,8:1). $C_6H_{16}NCl_3Si_2$ (264,7) Found (calc.): GCMS: 265 (M^+) 250 ($M^+ - Me$) 228 ($M^+ - Cl$) 193 ($M^+ - Et_2N$) 150 ($M^+ - Cl_2MeSi$) 113 ($M^+ - (Et_2N)ClMeSi$) 72 (Et_2N). *b.p.* 60 °C/1,5 torr

1,2-Dichloro-1,2-bis(diethylamino)dimethyldisilane (2,3)

The procedure was the same as described above for compound **4**. From the reaction of 15,5 ml (19,7 g; 0,086 mol) TCDMDS with 35,9 ml (25,1 g; 0,34 mol) Et_2NH (ratio 5:1) 14,2 g pure

compound (55% yield) was obtained by fractional distillation under reduced pressure.

$C_{10}H_{26}Cl_2N_2Si_2$ (301,4) Found (calc.): C 39,3 (39,8), H 8,7 (8,7), N 9,4 (9,3), Cl 24,1 (23,5), Si 18,7 (18,6); GCMS: 300 (M^+) 228 ($M^+ - Cl_2$) 192; 150 ($M^+ - (Et_2N)MeClSi$) 100 ($(Et_2N)Si$) 72 (Et_2N). *b.p.* 75 °C/1,5 torr.

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