### Siloxanes |Hot Paper|

# One-Step Synthesis of Siloxanes from the Direct Process Disilane Residue

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**Abstract:** The well-established Müller–Rochow Direct Process for the chloromethylsilane synthesis produces a disilane residue (DPR) consisting of compounds  $Me_nSi_2CI_{6-n}$  (n = 1-6) in thousands of tons annually. Technologically, much effort is made to retransfer the disilanes into monosilanes suitable for introduction into the siloxane production chain for increase in economic value. Here, we report on a single step reaction to directly form cyclic, linear, and cage-like siloxanes upon treatment of the DPR with a 5 M HCl in Et<sub>2</sub>O solution at about 120 °C for 60 h. For simplification of the Si–Si bond cleavage and aiming on product selectivity the grade of methylation at the silicon backbone is increased to  $n \ge 4$ . Moreover, the HCl/Et<sub>2</sub>O reagent is also suitable to produce siloxanes from the corresponding monosilanes under comparable conditions.

Production of monosilanes  $Me_nSiCl_{4-n}$  (n = 0-4) by the Müller-Rochow Direct Process (DP),<sup>[1]</sup> is one of the main pillars in silicon chemistry. The subsequent hydrolysis and condensation of dichlorodimethylsilane (Me<sub>2</sub>SiCl<sub>2</sub>) yields cyclic or linear siloxanes that are further polymerized to a wide range of polydimethylsiloxanes (PDMS).<sup>[2]</sup> The DP produces up to 10 weight percent of a residue (DPR),<sup>[3]</sup> mainly comprising a disilane fraction of mixed chloromethyldisilanes,  $Me_nSi_2CI_{6-n}$  (n = 1-6). More specifically, a typical mixture consists of 70-75% Cl<sub>2</sub>MeSi-SiMeCl<sub>2</sub> 1, 15–20% unsymmetrical Cl<sub>2</sub>MeSi–SiMe<sub>2</sub>Cl 2, 8–10% of CIMe<sub>2</sub>Si–SiMe<sub>2</sub>Cl 3, as well as low amounts of Me<sub>3</sub>Si–SiMe<sub>2</sub>Cl 4, and Me<sub>3</sub>Si-SiMe<sub>3</sub> 5.<sup>[4]</sup> A variety of procedures to recover valuable chloromethylsilane monomers by virtue of cleavage, redistribution, or disproportionation reactions were conceived to increase commercial benefit.<sup>[3-5]</sup> By means of their commercial value, these reports are mostly published in the patent literature as cited in the following section.

The historically preferred work up of the DPR to give monosilanes by thermally induced rearrangements requires heating of the mixture up to  $600 \,^{\circ}C$ ,<sup>[6]</sup> thus creating polymeric resins as byproducts. At lower temperatures, disproportionation reactions with catalytic amounts of amines<sup>[3,5,7]</sup> and ammonium or phosphonium chlorides<sup>[3,5,8]</sup> yields monosilanes, again with

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polysilanes as side products that either need further workup or have to be disposed. To overcome polysilane formation and for simplification of the disilane breakdown, a Si-Si bondcleavage reagent such as hydrogen chloride (HCI) is necessary, but requires harsh reaction conditions;<sup>[9]</sup> disilanes 3, 4, and 5 react only at  $T > 400 \,^{\circ}$ C to give the corresponding monosilanes.<sup>[10]</sup> Combinations of these processes use amines,<sup>[11]</sup> amides,<sup>[12]</sup> or ammonium chlorides<sup>[13]</sup> as catalysts for the HCl assisted Si-Si bond cleavage. Alternatively, AlCl<sub>3</sub> has also been discussed as catalyst for the HCl<sup>[14]</sup> or H<sub>2</sub><sup>[15]</sup> supported disilane cleavage. Moreover, transition-metal-catalyzed conversions of disilanes<sup>[16]</sup> into monosilanes in the presence of  $H_2^{[17]}$  and HCI,<sup>[18]</sup> in some cases in combination with amines or phosphines<sup>[19]</sup> or with allyl chloride, are reported in the literature.<sup>[20]</sup> Nevertheless, all processes listed lack the ability to fully convert highly methylated disilanes (3-5) to the respective monosilanes, but a few exceptions are reported.<sup>[5, 19b]</sup> In light of these findings, AICl<sub>3</sub> catalyzed methyl-chlorine exchange reactions for disilanes have been developed.<sup>[21]</sup> In these, the "non-cleavable" fraction (Me<sub>n</sub>Si<sub>2</sub>Cl<sub>6-n</sub>,  $n \ge 4$ ) is converted to the "cleavable" disilanes (n < 4) that are then transferred into the corresponding monomers. All of these cleavage processes are costly and account for reaction steps that give complicated product mixtures. That is why tons of DPR are sent to waste treatment or are simply burnt.

Noteworthy, monosilanes obtained from the DPR are mainly used for the subsequent siloxane production process. A DPR conversion to directly give siloxanes could therefore highly improve the economic value of the existing process technologies. That is the very basis to disclose a new concept to fully convert the DPR to a mixture of cyclic (**D**), linear (**L**), and cage-like (**T**) methylsiloxanes (Figure 1).<sup>[22]</sup> This approach involves the



Figure 1. Cyclic, linear, and cage-like methylsiloxanes.

cleavage of disilanes by HCl dissolved in diethyl ether (Et\_2O) as the active reagent.  $\ensuremath{^{[23]}}$ 

To gain more detailed insight into siloxane formation, model disilanes 1, 3, 4, and 5 for the DPR were subsequently reacted with the  $HCI/Et_2O$  reagent. In initial experiments, disilane

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1 ( $\delta^{29}$ Si = +17.7 ppm, cf. SI for details) was treated with a solution of HCl in  $Et_2O$  ( $\approx 5 \text{ M}$ ) at room temperature, resulting only in the formation of trace amounts of MeSiCl<sub>3</sub>. However, by carrying out the reaction in a sealed glass ampule at 100 °C for 20 h, a substantial conversion of 1 was achieved. The product mixture consisted of ethoxylated monosilanes (EtO)<sub>n</sub>SiMeCl<sub>3-n</sub> (n = 1, 2) and  $(EtO)_2Si(H)CI$  besides the disilane  $CI_2MeSi-SiMe$ -Cl(OEt)  $(\delta^{29}Si = +19.2, -0.6 \text{ ppm})^{[24]}$  as main product. The ethoxylation of 1 is quantitative at 125°C (14 h); the main product is then the doubly substituted disilane EtOCIMeSi-Si-MeClOEt ( $\delta^{29}$ Si = +2.2, +1.6 ppm,<sup>[24]</sup> two diastereomers). To gain further insight into the silicon ethoxylation, a corresponding reaction of solely HCl and Et<sub>2</sub>O at 120 °C proved the EtOH and EtCl formation. In a concurrent reaction, EtOH formed Et<sub>2</sub>O and H<sub>2</sub>O by an HCl catalyzed condensation reaction (see the Supporting Information).<sup>[25]</sup> From that it is viable that the Si-Cl functionalities of disilane 1 and the initially formed monosilanes MeSiCl<sub>3</sub> and Me(H)SiCl<sub>2</sub> are easily ethoxylated under these conditions. Further heating over 65 h lead to a quantitative conversion of the product mixture; all Si-Cl and Si-Si bonds were converted into either Si-O-Si or Si-OEt moieties. The complex product mixture consisted of linear and cyclic ethoxymethylsiloxanes, as well as of octamethylocta- (T8) and decamethyldecasilsesquioxane (T10). The former are obviously precursors for the subsequent silsesquioxane formation, whereby every Si-Si and Si-Cl bond is subject to alcoholysis and/or hydrolysis followed by condensation to exclusively form cage-like Si-O-Si bond motifs (Scheme 1a).

(a) 
$$Cl_2MeSi-SiMeCl_2 \xrightarrow{HCl} T8 - T10$$
  
(b)  $ClMe_2Si-SiMe_2Cl \xrightarrow{HCl} D3 - D7$   
(c)  $Me_3Si-SiMe_2Cl \xrightarrow{HCl} D3 - D6 / L2 - L7$   
(d)  $Me_3Si-SiMe_3 \xrightarrow{HCl} L2$ 

Scheme 1. a) Conversion of 1 to silsesquioxanes. b) Cleavage of 3 with subsequent condensation to cyclic dimethylsiloxanes D3-D7. c) Reaction of 4 to a mixture of D3-D6 and L2-L7, d) Conversion of 5 to L2.

This proposed reaction sequence was clearly proven by treating MeSiCl<sub>3</sub> with a solution of HCl in Et<sub>2</sub>O under comparable conditions to solely give silsesquioxanes (MeSiO<sub>3/2</sub>)<sub>n</sub> (n=8, 10, 12; see the Supporting Information).<sup>[26]</sup>

As expected, the reaction of **3** with the HCl/Et<sub>2</sub>O reagent quantitatively gives the cyclic siloxanes **D3** up to **D7** after 64 h at 120 °C (Scheme 1b, see the Supporting Information); the cleavage of the Si–Si bond in **3** generates Me<sub>2</sub>SiCl<sub>2</sub> equivalents,<sup>[27]</sup> which, upon ethoxylation and hydrolysis, form cyclic siloxanes by Si–Cl/Si–OEt/Si–OH condensation. A reaction of an authentic sample of Me<sub>2</sub>SiCl<sub>2</sub> with HCl/Et<sub>2</sub>O (120 °C for 67 h) confirms these findings; Me<sub>2</sub>SiCl<sub>2</sub> was fully converted into **D3**– **D7**. For the condensation reaction to occur, an initial ethoxylation of Me<sub>2</sub>SiCl<sub>2</sub> is necessary. Thus, samples of neat Me<sub>2</sub>Si(OEt)<sub>2</sub>, as well as dissolved in Et<sub>2</sub>O, were heated to 120 °C for 70 h, but no condensation was detected. However, when the diethoxysilane was heated in an atmosphere of HCl, substitution and condensation occurred, giving a mixture of the ethoxylated monosilane Me<sub>2</sub>Si(OEt)Cl and the disiloxane (EtO)Me<sub>2</sub>Si–O– SiMe<sub>2</sub>(OEt), besides low amounts of the cyclic siloxanes **D3**, **D4**, and **D5**. Additionally EtOH and Et<sub>2</sub>O were detected as reaction products. In accordance to our findings, the HCI/Et<sub>2</sub>O reagent strongly assists condensation reactions, because the reaction with Me<sub>2</sub>Si(OEt)<sub>2</sub> at 120 °C (65 h) cleanly produced the cyclosiloxanes **D3** up to **D7** (see the Supporting Information).<sup>[28]</sup>

Si–Si bond cleavage of the unsymmetrical disilane **4** yields a mixture of cyclic and linear siloxanes; HCl cleavage results in the preliminary formation of Me<sub>3</sub>SiH and Me<sub>2</sub>SiCl<sub>2</sub> or Me<sub>3</sub>SiCl and Me<sub>2</sub>Si(H)Cl. Si–H chlorination and Si–Cl ethoxylation followed by condensation give both, the linear siloxanes L2–L7, and the cyclic counterparts D3–D6, competitively (Scheme 2, see the Supporting Information).



Scheme 2. Simplified reaction cascade for the formation of linear and cyclic siloxanes from disilane 4.

As shown in Scheme 2, the proposed reaction pathway involves the HCl assisted cleavage of the Si–Si bond to form Si– H and Si–Cl moieties, but a Si–H formation was not observed.<sup>[27,29]</sup> Similar products as obtained from **4** were formed from an equimolar mixture of Me<sub>2</sub>SiCl<sub>2</sub> and Me<sub>3</sub>SiCl as starting materials. Product formation to predominantly give linear siloxanes uses Me<sub>3</sub>SiCl in molar excess, while the formation of cyclic siloxanes dominates when Me<sub>2</sub>SiCl<sub>2</sub> is used in surplus (see the Supporting Information).

Accordingly, from pure disilane **5** and an HCl/Et<sub>2</sub>O solution, **L2** was formed almost exclusively (120°C, 70 h), indicating a Si–Si bond cleavage to subsequently give Me<sub>3</sub>SiX (X=Cl, OEt, OH) that condense to **L2** (Scheme 1 d). Me<sub>3</sub>SiCl was detected as main product in the mixture obtained at 100°C (15 h, see the Supporting Information). This result clearly shows the high synthetic potential of the HCl/Et<sub>2</sub>O reagent for the Si–Si bond cleavage in highly methylated disilanes.

For simulation of an industrial DPR mixture, the disilanes 1, 3, 4, and 5 were mixed in a corresponding molar ratio and treated with a solution of HCl in  $Et_2O$  for 64 h at 120 °C. The mixture was completely consumed to give a wide range of linear (L2–L5) and cyclic (D3–D7) siloxanes, as well as the aforementioned silsesquioxanes (see the Supporting Information), and thus confirm our findings with defined chloromethyl mono- and disilanes.

Reactions with an authentic industrial DPR sample yielded a qualitatively similar complex product mixture, arising due to the multifunctionalities at the silicon centers after the Si–Si bond cleavage; a cleavage of the Si–CH<sub>3</sub> moiety is basically not observed.<sup>[30]</sup> As demonstrated for DPR model disilanes and stated before, the product composition of the HCl/Et<sub>2</sub>O assisted Si–Si bond cleavage largely depends on the degree of the

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methylation at the silicon center. To increase the product selectivity to give pure siloxanes, it is, thus, necessary to reduce the chlorine functionalities at the silicon atoms. In accordance with the literature,<sup>[31]</sup> methylation of **1** with either two equivalents of MeMgCl or MeLi gives a mixture of **4** and **5**, besides unreacted **1** and traces of **3**. With three to four equivalents of the methylation reagent, mixtures of **4** and **5** or exclusively **5** are obtained. Methylation was adapted for both, the model disilane mixture as well as the authentic industrial DPR (see the Supporting Information). Finally, either **5** or the mixture of **4** and **5** react with Me<sub>3</sub>SiCl and catalytic amounts of AlCl<sub>3</sub> to give selectively disilane **3** in high yields (Scheme 3).<sup>[21b,32]</sup>

Mo Si Cl	MeMgCl	Me <sub>3</sub> Si-SiMe <sub>2</sub> Cl	Me <sub>3</sub> SiCl, cat. AICl <sub>3</sub>	CIMO SI-SIMO CI
NIC <sub>n</sub> O12O16-n	-MaCla	MesSi-SiMes	-Me <sub>4</sub> Si	
n < 5	ing oi2	Megor Onneg	1110401	3

Scheme 3. Methylation and redistribution for the step-wise conversion of DPR to 3.

In the course of this reaction,  $Me_4Si$  distills off as the scavenger of surplus methyl groups in the starting mixture. **3** is then cleaved at 120 °C to selectively give cyclic **D3–D7** (Figure 2, left). As mentioned earlier, by addition of an excess of  $Me_3SiCl$  to disilane **3**, linear siloxanes **L2–L6** are the strongly preferred products. Moreover, from a mixture of pure disilanes **4** and **5** in a molar ratio 1:9, linear siloxanes **L2–L4** are obtained selectively upon treatment with an HCl/Et<sub>2</sub>O solution at 120 °C for 72 h (Figure 2, right). Thus, the selectivity of the siloxane formation is perfectly tuned using clean disilanes **3**, **4**, and **5** or mixtures thereof in different molar ratios (see the Supporting Information).

Our experimental findings are consistent with the HCl/Et<sub>2</sub>O assisted Si–Si bond cleavage forming mono-, di-, and trifunctional chlorinated, ethoxylated, and/or hydroxylated monosilane building blocks. Condensation reactions at elevated temperatures subsequently form the thermodynamically most stable Si–O–Si bond moieties (Scheme 4).

Production of silicones essentially consists of two steps: synthesis of chloromethylsilanes by the DP with subsequent hydrolysis and condensation to Si–O–Si networks. Associated with the organofunctionality at the silicon center, different

(a) ⇒Si-Cl + EtO-Si	─ <b>→</b> ⇒Si-O-Si  + EtCl	
(b) ⇒Si-OEt + EtO-Si	→ ⇒Si-O-Si  + Et <sub>2</sub> C	)
(c) ⇒Si-OEt + HO-Si ⊂	→ ⇒Si-O-Si는 + EtOł	Н
(d) →Si-OH + HO-Si	$\longrightarrow$ $\geq$ Si-O-Si $\leq$ + H <sub>2</sub> O	

Scheme 4. Condensation reactions of chloro-,  $^{[33]}$  ethoxy- $^{[34]}$  and hydroxysilanes  $^{[34a]}$  to siloxanes.

types of siloxanes are formed. While trichlorosilanes possess a threefold capability for siloxane binding, that is, as corners in silsesquioxanes, dichlorosilanes form cyclic siloxanes or act as elongation agents with monochlorosilanes for capping. The DP produces a disilane mixture that is divided into a cleavable  $(Me_nSi_2Cl_{6-n}, n < 4)$  and a noncleavable fraction  $(n \ge 4)$ . By reaction with HCl in Et<sub>2</sub>O, the DPR is completely transferred into siloxanes, because an Si-Si as well as Si-Cl bond cleavage occurs to exclusively yield Si-O-Si bond motifs upon the Si-Cl/Si-OEt/Si-OH condensation reaction. The product composition directly depends on the grade of methylation at the silicon monomers formed. For an increase in economic value of a well-established technology it is proposed to run a reaction sequence consisting of the methylation of the DPR disilanes into 4 and/or 5, followed by the transformation into clean 3. HCl/Et<sub>2</sub>O treatment of **3** gives the cyclic siloxanes D3-D7, while from mixtures of 4 and 5 linear siloxanes are obtained selectively (see the Supporting Information). Alternatively, the cleavable disilane fraction might be transferred into valuable monomers treating the complete DPR with conventional methods, e.g. reactions with amines and phoshonium chlorides.<sup>[3]</sup> The remaining noncleavable species, after a simple distillation step mainly consisting of 3, are then fully converted to the cyclic siloxanes as well. Addition of disilane 5 or of excess Me<sub>3</sub>SiCl to disilane 3 shifts the product composition to mainly linear siloxanes.

#### **Experimental Section**

Experiments under elevated temperatures were performed in closed glass ampules with a length of 125 mm, outer diameter of 26 mm, and a wall thickness of 2 mm (internal volume of  $\approx$  43 mL). Chlorosilane (100–200 mg) was dissolved in a saturated solution of HCl in Et<sub>2</sub>O (5 mL,  $\approx$  5 M), vacuum-sealed, and heated. Product



Figure 2. GC of the product mixtures of the reaction of 3 (left) and a mixture of 4 and 5 (right) with HCl in Et<sub>2</sub>O.

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analyses were done by GC-MS and NMR spectroscopy and compared with authentic samples. The employed mono- and disilanes were commercially available and used as is. A more detailed description of the siloxane-giving reactions and product analyses can be found in the Supporting Information.

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- [28] The results of our cleavage reactions imply the existence of a complex equilibrium mixture especially at elevated temperatures. Already at rt Me<sub>2</sub>Si(OEt)<sub>2</sub> gives Me<sub>2</sub>SiCl(OEt) and Me<sub>2</sub>SiCl<sub>2</sub> (60/40%) upon reaction with HCl/Et<sub>2</sub>O. (EtO)Me<sub>2</sub>Si–SiMe<sub>2</sub>(OEt) yields the chlorinated disilane **3** under these reaction conditions.
- [29] For an unequivocal proof of the Si–H/Si–Cl exchange, pentamethyldisilane Me<sub>3</sub>Si–SiMe<sub>2</sub>H was treated with a solution of HCl in Et<sub>2</sub>O at room temperature. GC-MS and NMR analyses of the reaction mixture confirmed the clean conversion into **4**, strongly supporting a facile Si–H to Si–Cl exchange. Heating to 120 °C (70 h) gave a siloxane mixture as discussed for disilane **4** (see the Supporting Information).
- [30] For Si\_2Me\_{6\prime} a Si–Me cleavage is observed (see the Supporting Information).
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# COMMUNICATION



**Two birds with one stone:** The disilane residue from the Müller–Rochow Direct Process undergoes cleavage and condensation to methylsiloxanes in a single step using HCl in Et<sub>2</sub>O. Variation and optimization of reaction conditions lead to the selective formation of cyclic, linear, or cage-like methylsiloxanes.

## Siloxanes

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One-Step Synthesis of Siloxanes from Sil