

Siloxanes | Hot Paper |

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

Felix Neumeyer and Norbert Auner*^[a]

Abstract: The well-established Müller–Rochow Direct Process for the chloromethylsilane synthesis produces a disilane residue (DPR) consisting of compounds $\text{Me}_n\text{Si}_2\text{Cl}_{6-n}$ ($n=1-6$) 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_2O 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 $n \geq 4$. Moreover, the HCl/ Et_2O reagent is also suitable to produce siloxanes from the corresponding monosilanes under comparable conditions.

Production of monosilanes $\text{Me}_n\text{SiCl}_{4-n}$ ($n=0-4$) by the Müller–Rochow Direct Process (DP),^[1] is one of the main pillars in silicon chemistry. The subsequent hydrolysis and condensation of dichlorodimethylsilane (Me_2SiCl_2) yields cyclic or linear siloxanes that are further polymerized to a wide range of polydimethylsiloxanes (PDMS).^[2] The DP produces up to 10 weight percent of a residue (DPR),^[3] mainly comprising a disilane fraction of mixed chloromethylsilanes, $\text{Me}_n\text{Si}_2\text{Cl}_{6-n}$ ($n=1-6$). More specifically, a typical mixture consists of 70–75% $\text{Cl}_2\text{MeSi-SiMe}_2\text{Cl}$ **1**, 15–20% unsymmetrical $\text{Cl}_2\text{MeSi-SiMe}_2\text{Cl}$ **2**, 8–10% of $\text{ClMe}_2\text{Si-SiMe}_2\text{Cl}$ **3**, as well as low amounts of $\text{Me}_3\text{Si-SiMe}_2\text{Cl}$ **4**, and $\text{Me}_3\text{Si-SiMe}_3$ **5**.^[4] A variety of procedures to recover valuable chloromethylsilane monomers by virtue of cleavage, redistribution, or disproportionation reactions were conceived to increase commercial benefit.^[3-5] 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°C ,^[6] thus creating polymeric resins as byproducts. At lower temperatures, disproportionation reactions with catalytic amounts of amines^[3,5,7] and ammonium or phosphonium chlorides^[3,5,8] yields monosilanes, again with

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 bond-cleavage reagent such as hydrogen chloride (HCl) is necessary, but requires harsh reaction conditions;^[9] disilanes **3**, **4**, and **5** react only at $T > 400^\circ\text{C}$ to give the corresponding monosilanes.^[10] Combinations of these processes use amines,^[11] amides,^[12] or ammonium chlorides^[13] as catalysts for the HCl assisted Si–Si bond cleavage. Alternatively, AlCl_3 has also been discussed as catalyst for the HCl^[14] or H_2 ^[15] supported disilane cleavage. Moreover, transition-metal-catalyzed conversions of disilanes^[16] into monosilanes in the presence of H_2 ^[17] and HCl,^[18] in some cases in combination with amines or phosphines^[19] or with allyl chloride, are reported in the literature.^[20] 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.^[5,19b] In light of these findings, AlCl_3 catalyzed methyl-chlorine exchange reactions for disilanes have been developed.^[21] In these, the “non-cleavable” fraction ($\text{Me}_n\text{Si}_2\text{Cl}_{6-n}$, $n \geq 4$) 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).^[22] This approach involves the

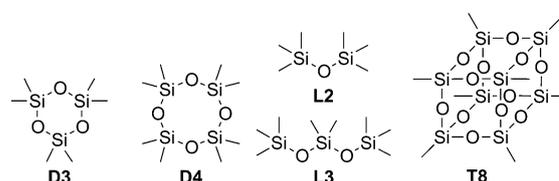


Figure 1. Cyclic, linear, and cage-like methylsiloxanes.

cleavage of disilanes by HCl dissolved in diethyl ether (Et_2O) as the active reagent.^[23]

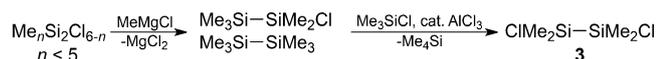
To gain more detailed insight into siloxane formation, model disilanes **1**, **3**, **4**, and **5** for the DPR were subsequently reacted with the HCl/ Et_2O reagent. In initial experiments, disilane

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Supporting information for this article can be found under
<http://dx.doi.org/10.1002/chem.201603842>.

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,^[31] 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 Me₃SiCl and catalytic amounts of AlCl₃ to give selectively disilane **3** in high yields (Scheme 3).^[21b,32]

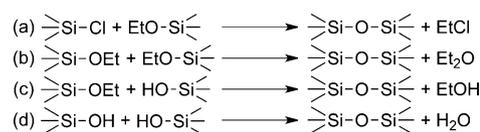


Scheme 3. Methylation and redistribution for the step-wise conversion of DPR to **3**.

In the course of this reaction, Me₄Si 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 Me₃SiCl 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/Et₂O 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/Et₂O 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



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_nSi₂Cl_{6-n}, n < 4) and a noncleavable fraction (n ≥ 4). By reaction with HCl in Et₂O, the DPR is completely transferred into siloxanes, because a 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/Et₂O 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 phosphonium chlorides.^[3] 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 Me₃SiCl to disilane **3** shifts the product composition to mainly linear siloxanes.

Experimental Section

Experiments under elevated temperatures were performed in closed glass ampoules with a length of 125 mm, outer diameter of 26 mm, and a wall thickness of 2 mm (internal volume of ≈ 43 mL). Chlorosilane (100–200 mg) was dissolved in a saturated solution of HCl in Et₂O (5 mL, ≈ 5 M), vacuum-sealed, and heated. Product

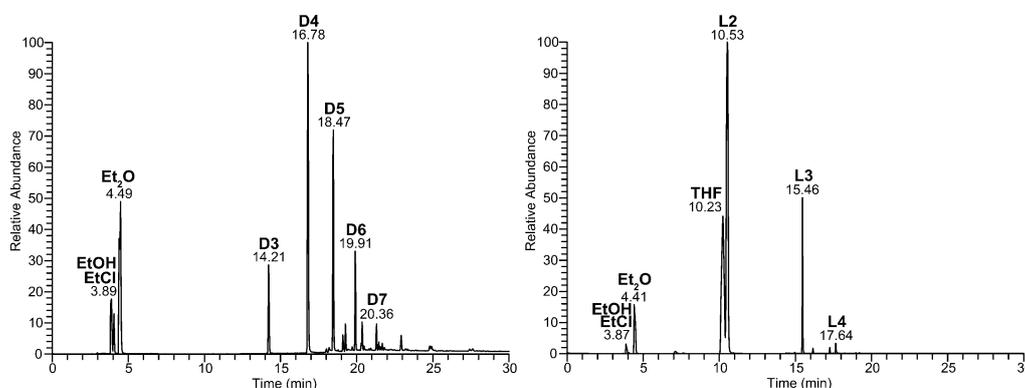


Figure 2. GC of the product mixtures of the reaction of **3** (left) and a mixture of **4** and **5** (right) with HCl in Et₂O.

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.

Acknowledgements

F.N. gratefully acknowledges a PhD scholarship by the Beilstein-Institut (Frankfurt).

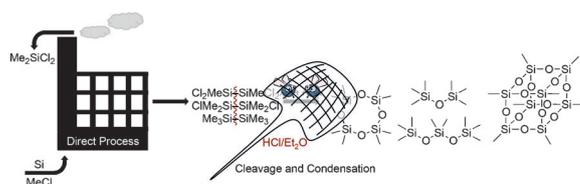
Keywords: Direct Process · Direct Process residue · disilane cleavage · HCl in Et₂O · siloxanes

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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 Me₂Si(OEt)₂ gives Me₂SiCl(OEt) and Me₂SiCl₂ (60/40%) upon reaction with HCl/Et₂O. (EtO)Me₂Si–SiMe₂(OEt) yields the chlorinated disilane **3** under these reaction conditions.
- [29] For an unequivocal proof of the Si–H/Si–Cl exchange, pentamethyldisilane Me₂Si–SiMe₂H was treated with a solution of HCl in Et₂O 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).
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Received: August 11, 2016

Published online on ■■■■■, 0000

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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 Et₂O. 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 the Direct Process Disilane Residue

