

## Environmentally Friendly Synthesis of Methylmethoxysilanes

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In 1940, Eugene G. Rochow and Richard Müller independently succeeded in reacting elemental silicon with methyl chloride in the presence of a copper catalyst to form liquid methylchlorosilanes. Due to the war situation, the corresponding patents were not published until later [1-3].

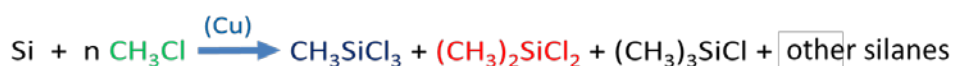


Figure 1: Direct process reaction

With this direct process, the starting materials for the industrial production of silicones became available for the first time on a large scale and in an economically efficient manner, i.e., a bridge was built from quartz sand to silicones, thus creating the prerequisite for the worldwide, tumultuous upswing in silicone production.

Today, industrial synthesis of chloromethyl silanes, the monomeric starting materials of silicones, is almost exclusively carried out by the Müller-Rochow process. In this process, the elemental silicon is made to react with chloromethane in the presence of a copper catalyst and zinc or zinc compounds as 'promoters' at temperatures between 260 and 310 °C in a fluidized bed reactor. The temperature of the process must be closely controlled since the reaction is highly exothermic ( $\Delta H = -3033 \text{ kJ/kg}$ ) and a high yield of the main target product, dichlorodimethylsilane, can only be achieved within a certain temperature corridor.

Commercially most important products of direct synthesis are dimethyldichlorosilane (chain former for polymers), methyltrichlorosilane (crosslinker) and trimethylchlorosilane (end blocker), from which more than 90% of all silicone products are made. In particular, interest is focused on dimethyldichlorosilane as the target product because it is used to prepare the polydimethylsiloxane (PDMS) polymer [4, 5]. Its yield can be increased to just over 90% (see Figure 2).

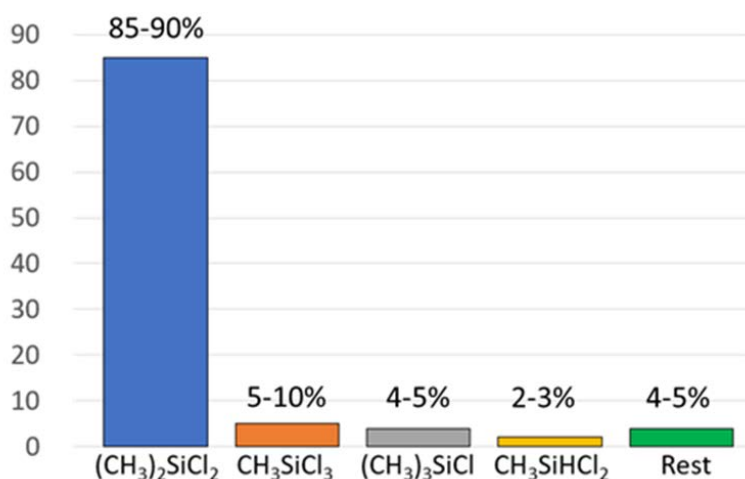


Figure 2: Product distribution in Müller-Rochow process

The  $\text{Me}_2\text{SiCl}_2$  is purified by fractional distillation, while the excess chloromethane is fed back into the direct process again. Since the boiling points of the various chloromethylsilanes are quite similar

(Me<sub>2</sub>SiCl<sub>2</sub>: 70 °C, MeSiCl<sub>3</sub>: 66 °C, Me<sub>3</sub>SiCl: 57 °C, MeHSiCl<sub>2</sub>: 41 °C, Me<sub>2</sub>HSiCl: 35 °C), the distillation utilizes columns with high separating capacities, connected in series. The purity of the products crucially affects the production of siloxane polymers, otherwise chain branching or termination arises. [6]

In recent years, the manufacture of industrial chemicals via the 'green chemistry principles', which are consistent with the overall ecological and sustainable development trend in human society became increasingly important, even for silicones [7]. Therefore, industrial teams started to look at ways of replacing toxic chemicals and reducing the environmental footprint of chemical process.

A team of scientists at Dow Silicones in Midland, Michigan, has now found that the toxic and mutagenic methyl chloride can be replaced by dimethyl carbonate (DMC), a 'green' and relatively unproblematic methylating agent, opening the door to the development of a new industrial approach to silicone production [8]. DMC can also be understood as carbonic acid dimethyl ester and is thus accessible by chemical reaction of CO<sub>2</sub> and methanol in the presence of suitable heterogeneous catalysts [9]. The CO<sub>2</sub> can be extracted from the air (carbon capture).

The team succeeded in the direct synthesis of methylmethoxysilanes from penta-copper silicide, Cu<sub>5</sub>Si, and DMC. The reaction of Cu<sub>5</sub>Si powder (99.5 % purity) with DMC at 350 °C afforded dimethyldimethoxysilane Me<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub> as the major product with a selectivity of > 70 %.

#### Sources:

<https://onlinelibrary.wiley.com/doi/abs/10.1002/ciuz.202000035>

[https://chemiedidaktik.uni-wuppertal.de/fileadmin/Chemie/chemiedidaktik/disido/en/info/m\\_fact/mrochow.htm](https://chemiedidaktik.uni-wuppertal.de/fileadmin/Chemie/chemiedidaktik/disido/en/info/m_fact/mrochow.htm)

[https://en.wikipedia.org/wiki/Direct\\_process](https://en.wikipedia.org/wiki/Direct_process)

#### Literature:

- [1] Rochow, E.G., U.S. Patent No. 2,380, 995, 1945, filed 26 September, 1941.
- [2] Müller, R. East German Patent No. DWP 5348, 1953, filed June 6, 1942.
- [3] Müller, R., J. Chem. Educ., 1965, 42(1), 41-47, <https://doi.org/10.1021/ed042p41>
- [4] Schliebs, R. and Ackermann, J., Chemie in unserer Zeit, 1987, 21, 121–127, <https://doi.org/10.1002/ciuz.19870210404>
- [5] Seyferth, D., Organometallics, 2001, 20(24), 4978–4992, <https://doi.org/10.1021/om0109051>
- [6] Rösch, L.; John, P.; Reitmeier, R. (2003). "Organic Silicon Compounds". Ullmann's Encyclopedia of Industrial Chemistry. Weinheim: Wiley-VCH. doi:10.1002/14356007.a24\_021.
- [7] Pakuła, D., Marciniak, B., and Przekop, R.E., Direct Synthesis of Silicon Compounds—From the Beginning to Green Chemistry Revolution, Applied Chem 2023, 3(1), 89-109; <https://doi.org/10.3390/appliedchem3010007>

- [8] Roberts, J. M., Pushkarev, V. V., Sturm, J. J. and Katsoulis, D. E., *Ind. Eng. Chem. Res.*, 2020, 59(16), 7457–7465, <https://doi.org/10.1021/acs.iecr.0c00505>
- [9] Hofmann, H. J., Brandner, A. und Claus, P., *Chem. Eng. Tech.*, 2012, 35, 2140–2146, <https://doi.org/10.1002/ceat.201200475>

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