

## Generation and capture of methyl(vinyl)silanone

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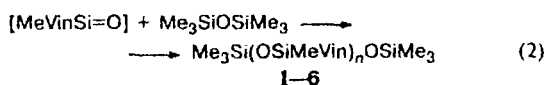
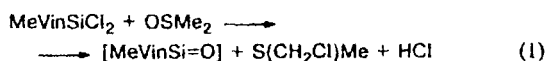
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Methyl(vinyl)dichlorosilane reacts with DMSO in the presence of hexamethyldisiloxane to give the corresponding linear oligosiloxanes of the general formula  $\text{Me}_3\text{Si}(\text{OSiMeVin})_n\text{OSiMe}_3$  ( $n = 1-6$ ) as well as  $\text{MeSi}(\text{OSiMe}_3)_3$  and  $\text{Me}_3\text{Si}(\text{MeOSiVin})_m\text{OSi}(\text{OSiMe}_3)(\text{Me})\text{OSiMe}_3$  ( $m = 1-2$ ). The same reaction in the presence of chlorotrimethylsilane results in oligomers of the general formula  $\text{Me}_3\text{Si}(\text{OSiMeVin})_n\text{Cl}$  ( $n = 1-3$ ). A possible scheme of their formation is discussed.

**Key words:** chloro(organyl)silanes, dimethylsulfoxide, silanones, organysiloxanes.

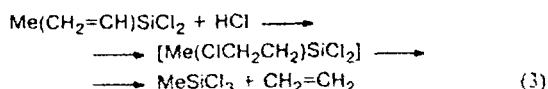
Recently, we were the first to show<sup>1,2</sup> that the reaction of dichlorodiorganylsilanes with DMSO is a convenient method for the generation of diorganylsilanones. Later, these results were confirmed by American scientists.<sup>3</sup> In a continuation of these investigations, we found that methyl(vinyl)dichlorosilane reacts with DMSO in the presence of hexamethyldisiloxane (used as a trap for methyl(vinyl)silanone) at a molar ratio of reagents 1 : 1 : 1 to give compounds of the general formula  $\text{Me}_3\text{Si}(\text{OSiMeVin})_n\text{OSiMe}_3$  ( $n = 1-6$  (1-6)) in overall yield up to 68%, which were identified by GC-MS (Table 1). At a higher concentration of hexamethyldisiloxane in the reaction mixture (molar ratio of reagents 1 : 1 : 3, respectively), the yield of trisiloxane (1) was increased.



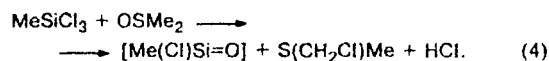
$n = 1$  (1), 2 (2), 3 (3), 4 (4), 5 (5), 6 (6)

Along with oligosiloxanes (1-6), other reaction products, viz.,  $\text{Me}_3\text{Si}[\text{OSi}(\text{OSiMe}_3)\text{Me}]_n\text{OSiMe}_3$  ( $n = 1$  (7), 2 (8), and 3 (9)) (Table 2) were also isolated in overall yield up to 10%.

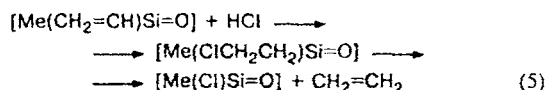
The formation of oligosiloxanes 7-9 can be explained by decomposition of unstable 2-chloroethyl(methyl)dichlorosilane,<sup>4</sup> an addition product of hydrogen chloride evolved during reaction (1), to the original methyl(vinyl)dichlorosilane. This process yields trichloromethylsilane.



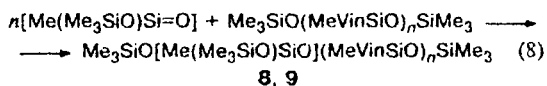
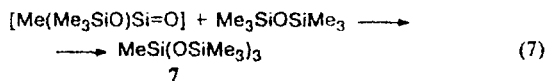
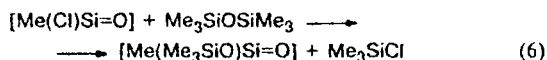
The reaction of  $\text{MeSiCl}_3$  with DMSO leads<sup>5</sup> to chloro(methyl)silanone



Also, it cannot be excluded that chloro(methyl)silanone results from the addition of HCl to methyl(vinyl)silanone.



Further, chloro(methyl)silanone cleaves the molecule of hexamethyldisiloxane to give methyl(trimethylsiloxy)silanone,<sup>5</sup> which is inserted into the molecule of the initial hexamethyldisiloxane to yield oligomer 7, or into the products of reaction (2) (1 and 2) to yield compounds 8 and 9.



$n = 1$  (8), 2 (9)

Methyl(vinyl)silanone, which is an intermediate in reaction (1), is also inserted into the Si-Cl bond of chlorotrimethylsilane. Thus the reaction of methyl(vinyl)dichlorosilane with DMSO in the presence of

Table 1. Data for characteristic peaks in the mass spectra of oligosiloxanes 1–6

Ion	$m/z$ ( $I_{rel}$ (%))					
	1	2	3	4	5	6
[M–Me] <sup>+</sup>	233 (100)	319 (54)	405 (51)	491 (2)	577 (4)	663 (4)
[M–Vin] <sup>+</sup>	221 (15)	307 (2)	393 (3)	—	565 (1)	651 (1)
[M–C <sub>2</sub> H <sub>5</sub> ] <sup>+</sup>	205 (72)	291 (2)	—	—	—	—
[M–OSiMe <sub>2</sub> Vin] <sup>+</sup>	147 (7)	233 (5)	319 (3)	—	—	577 (2)
[M–Me–Me <sub>4</sub> Si] <sup>+</sup>	145 (2)	231 (24)	317 (11)	—	489 (2)	—
[M–OSiMeVin <sub>2</sub> ] <sup>+</sup>	—	221 (13)	307 (17)	—	479 (2)	565 (3)
[M–Vin–Me <sub>4</sub> Si] <sup>+</sup>	133 (12)	219 (100)	305 (87)	391 (4)	—	—
[M–Vin–Me <sub>3</sub> VinSi] <sup>+</sup>	—	207 (73)	293 (93)	379 (13)	465 (8)	551 (4)
[Me <sub>3</sub> SiOSiMeVin] <sup>+</sup>	159 (3)	159 (1)	159 (72)	159 (14)	159 (44)	159 (40)
[Me <sub>3</sub> SiOSiMe <sub>2</sub> ] <sup>+</sup>	147 (7)	147 (2)	147 (28)	147 (8)	147 (23)	147 (19)
[Me <sub>3</sub> SiOSiMeH] <sup>+</sup>	133 (12)	133 (6)	133 (12)	133 (7)	133 (12)	133 (12)
[MeVin <sub>2</sub> Si] <sup>+</sup>	—	97 (26)	97 (32)	97 (25)	97 (52)	97 (67)
[Me <sub>2</sub> VinSi] <sup>+</sup>	85 (30)	85 (83)	85 (77)	85 (69)	85 (91)	85 (100)
[Me <sub>3</sub> Si] <sup>+</sup>	73 (64)	73 (80)	73 (100)	73 (100)	73 (100)	73 (90)
[Me <sub>2</sub> SiH] <sup>+</sup>	59 (18)	59 (27)	59 (42)	59 (31)	59 (37)	59 (32)

Table 2. Data for characteristic peaks in the mass spectra of oligosiloxanes 7–12

Ion	$m/z$ ( $I_{rel}$ (%))					
	7	8	9	10	11	12
[M–Me] <sup>+</sup>	295 (42)	381 (10)	479 (0.5)	179 (100)	265 (100)	351 (100)
[M–Vin] <sup>+</sup>	—	—	467 (11)	167 (4)	253 (8)	339 (5)
[M–C <sub>2</sub> H <sub>5</sub> ] <sup>+</sup>	—	355 (2)	—	153 (26)	239 (6)	325 (6)
[M–C <sub>2</sub> H <sub>4</sub> ] <sup>+</sup>	—	—	—	151 (7)	237 (11)	323 (3)
[M–OSiMe <sub>2</sub> Vin] <sup>+</sup>	—	295 (4)	—	93 (14)	179 (7)	265 (5)
[M–Me–Me <sub>4</sub> Si] <sup>+</sup>	207 (100)	293 (16)	—	—	—	—
[M–Vin–Me <sub>4</sub> Si] <sup>+</sup>	—	281 (23)	367 (14)	79 (13)	165 (1)	251 (6)
[M–Vin–Me <sub>3</sub> VinSi] <sup>+</sup>	—	—	355 (5)	—	153 (7)	239 (6)
[Me <sub>3</sub> SiOSiMeVin] <sup>+</sup>	—	159 (23)	159 (36)	159 (3)	159 (1)	159 (1)
[Me <sub>3</sub> SiOSiMe <sub>2</sub> ] <sup>+</sup>	147 (3)	147 (33)	147 (34)	147 (7)	147 (4)	147 (13)
[Me <sub>3</sub> SiOSiMeH] <sup>+</sup>	133 (3)	133 (7)	133 (7)	133 (11)	133 (6)	133 (6)
[MeVin <sub>2</sub> Si] <sup>+</sup>	—	—	97 (13)	—	97 (33)	97 (38)
[Me <sub>2</sub> VinSi] <sup>+</sup>	—	85 (27)	85 (55)	85 (8)	85 (25)	85 (48)
[Me <sub>3</sub> Si] <sup>+</sup>	73 (64)	73 (100)	73 (100)	73 (15)	73 (30)	73 (100)
[Me <sub>2</sub> SiH] <sup>+</sup>	59 (6)	59 (23)	59 (19)	59 (9)	59 (17)	59 (23)

\* For the <sup>35</sup>Cl isotope. The intensity ratio of isotope peaks corresponds to the calculated one.

chlorotrimethylsilane (molar ratio 1 : 1 : 1) results in compounds 10–12 in overall yield up to 30% (see Table 2).



$n = 1$  (10), 2 (11), 3 (12)

The presence of linear siloxanes 1–4 (yield up to 40%) along with compounds 10–12 in the reaction products is due to the reaction of chlorotrimethylsilane with DMSO that occurs in parallel to give hexamethyldisiloxane followed by its reaction with methyl(vinyl)silane according to Eq. (2).<sup>1</sup>

## Experimental

GC-MS analysis was carried out on an LKB-2091 GC-MS instrument (ionizing voltage 60 V, capillary column 38 m long, phase SE-54, programmed temperature increase rate 16 deg min<sup>−1</sup> up to 270 °C). Accelerating voltage was 2 kV.

Dimethylsulfoxide was kept over melted KOH, decanted, frozen, and distilled *in vacuo*. Methyl(vinyl)dichlorosilane was purified by distillation.

**Reaction of dimethylsulfoxide with methyl(vinyl)dichlorosilane.** Methyl(vinyl)dichlorosilane (14.1 g, 0.1 mol) and hexamethyldisiloxane (16.2 g, 0.1 mol) were placed in a 50-mL flask equipped with a Vigreux distilling column, and dimethylsulfoxide (7.8 g, 0.1 mol) was added dropwise with cooling to 0 °C. Vigorous evolution of hydrogen chloride was

observed. The reaction mixture was slowly heated to boiling, and chloromethyl(methyl) sulfide (7.3 g, 74%) was distilled off, b.p. 109–110 °C,  $n_D^{20}$  1.4965 (cf. Ref. 6: b.p. 110–112 °C). Found (%): C, 25.25; H, 5.24; Cl, 36.94; S, 32.85.  $C_2H_5ClS$ . Calculated (%): C, 24.87; H, 5.22; Cl, 36.71; S, 33.20. Distillation of the residue *in vacuo* gave a fraction with b.p. 70–200 °C (6 Torr), yield 5.2 g (60%). GC-MS data are given in Tables 1 and 2.

The reaction of  $Me_2SO$  with  $MeVinSiCl_2$  in the presence of  $(Me_3Si)_2O$  (molar ratio 1 : 1 : 3) or  $Me_3SiCl$  (molar ratio 1 : 1 : 1) was carried out analogously.

In the presence of  $(Me_3Si)_2O$ , dimethyl sulfide was a reaction product along with chloromethyl(methyl) sulfide.

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