

# Reaction of Organylchlorosilanes with Dimethyl Sulfoxide in the Presence of Octamethyltrisiloxane

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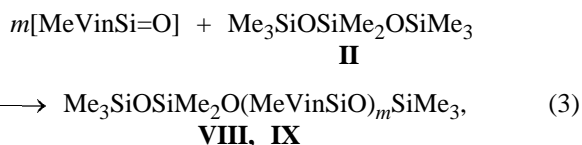
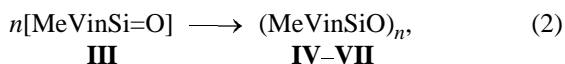
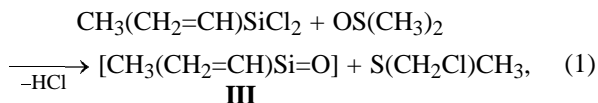
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**Abstract**—Dichloro(methyl)(vinyl)silane reacts with DMSO in the presence of octamethyltrisiloxane to form cyclooligomethyl(vinyl)siloxanes (MeViSiO)<sub>n</sub> (*n* = 3–6). The reaction involves disproportionation of octamethyltrisiloxane into hexamethyldisiloxane and decamethyltetrasiloxane. Along with the latter two products, insertion products of methyl vinyl silanone into both permethyloligosiloxanes were identified. Alkyltrichlorosilanes RSiCl<sub>3</sub> (R = Me, Et) react with DMSO in the presence of octamethyltrisiloxane to form cyclic oligoalkyltrichlorosiloxanes (RCISiO)<sub>m</sub> (*m* = 3–6).

Previously we showed that the reaction of diorganyldichloro- and organyltrichlorosilanes with DMSO in a hexamethyldisiloxane (I) medium is a convenient synthetic route to linear and cyclic organyl-(trimethylsiloxy)siloxanes [1, 2].

The major products of reaction (1) between dichloro(methyl)(vinyl)silane with DMSO in the presence of octamethyltrisiloxane (II) that serves for trapping the intermediate methyl vinyl silanone (III), at 20°C and a 1:1:1 reagent molar ratio are cyclo-methyl(vinyl)siloxanes (MeViSiO)<sub>n</sub> (IV–VII, *n* = 3–6) in a total yield of 75–80%. Therewith, the yield of insertion products of methyl vinyl silanone into trisiloxane II, namely 1,1,1,3,5,5,7,7,7-nonamethyl-3-vinyltetrasiloxane (VIII) and 1,1,1,3,5,7,7,9,9,9-decamethyl-3,5-divinylpentasiloxane (IX), is as low as 3–5%.

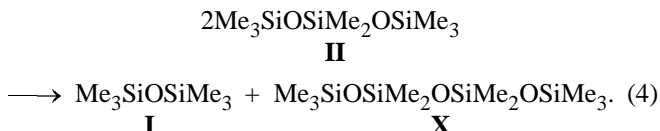


*n* = 3 (IV), 4 (V), 5 (VI), 6 (VII); *m* = 1 (VIII), 2 (IX).

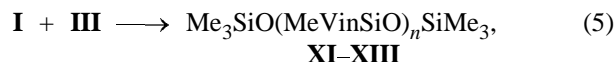
Reaction (2) between MeViSiCl<sub>2</sub> and DMSO can occur in the absence of trisiloxane II [1], and the yield of compounds IV–VII is slightly higher. At higher concentrations of trisiloxane II in the reaction mixture

(1:1:3 reagent molar ratio), the yield of cyclomethyl(vinyl)siloxanes IV–VII is almost the same.

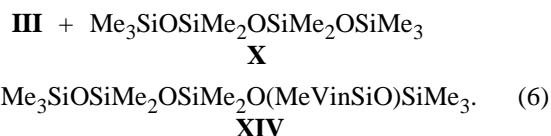
Under the reaction conditions, trisiloxane II undergoes disproportionation into disiloxane I and decamethyltetrasiloxane (X). Neither MeViSiCl<sub>2</sub> nor DMSO taken separately induce disproportionation of compound II.



Siloxanes I and X were isolated and characterized by GC–MS, along with insertion products of silanone III into disiloxane I [1,1,1,3,5,5,5-heptamethyl-3-vinyltrisiloxane (XI), 1,1,1,3,5,7,7,7-octamethyl-3,5-divinyltetrasiloxane (XII), 1,1,1,3,5,7,9,9,9-nona-methyl-3,5,7-trivinylpentasiloxane (XIII)] and into decamethyltetrasiloxane [1,1,1,3,5,5,7,7,9,9,9-undecamethyl-3-vinylpentasiloxane (XIV)].



*n* = 1 (XI), 2 (XII), 3 (XIII).

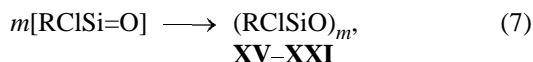


Insertion products XI–XIII we also identified earlier in the reaction of MeViSiCl<sub>2</sub> with DMSO and disiloxane I [1].

Mass spectra of  $\text{Me}_3\text{Si}(\text{OSiMeVin})_n(\text{OSiMe}_2)_m\text{OSiMe}_3$  (**VIII**, **IX**, **XI–XIV**) [ $n = 1$ ,  $m = 1$  (**VIII**);  $n = 2$ ,  $m = 1$  (**IX**);  $n = 1$ ,  $m = 0$  (**XI**);  $n = 2$ ,  $m = 0$  (**XII**);  $n = 3$ ,  $m = 0$  (**XIII**);  $n = 1$ ,  $m = 2$  (**XIV**)]

Ion	$m/z$ ( $I_{\text{rel}}$ , %)					
	<b>VIII</b>	<b>IX</b>	<b>XI</b>	<b>XII</b>	<b>XIII</b>	<b>XIV</b>
$[\text{M} - \text{Me}]^+$	307 (60)	393 (33)	233 (100)	319 (52)	405 (47)	381 (12)
$[\text{M} - \text{OSiMe}_2\text{Vin}]^+$	221 (42)	307 (3)	147 (8)	233 (7)	319 (7)	295 (9)
$[\text{M} - \text{Me} - \text{Me}_4\text{Si}]^+$	219 (80)	305 (36)	145 (4)	231 (25)	317 (19)	293 (86)
$[\text{M} - \text{Vin} - \text{Me}_4\text{Si}]^+$	207 (100)	293 (100)	133 (17)	219 (100)	305 (85)	281 (100)
$[\text{Me}_3\text{SiOSiMeVin}]^+$	—	159 (55)	159 (3)	159 (1)	159 (77)	—
$[\text{Me}_3\text{SiOSiMe}_2]^+$	147 (2)	147 (41)	147 (7)	147 (2)	147 (29)	147 (12)
$[\text{Me}_3\text{SiOSiMeH}]^+$	133 (2)	—	133 (10)	133 (5)	133 (10)	—
$[\text{Me}_2\text{VinSi}]^+$	85 (32)	85 (36)	85 (30)	85 (85)	85 (80)	—
$[\text{Me}_3\text{Si}]^+$	73 (62)	73 (59)	73 (68)	73 (80)	73 (100)	73 (9)
$[\text{Me}_2\text{SiH}]^+$	59 (7)	59 (12)	59 (10)	59 (23)	59 (32)	—

The reaction of organyltrichlorosilanes  $\text{RSiCl}_3$  ( $\text{R} = \text{Me}, \text{Et}$ ) with DMSO in the presence of trisiloxane **II** (1:1:1 molar ratio) at 20°C gives no cycloorganyl-(trimethylsiloxy)siloxanes  $[\text{R}(\text{Me}_3\text{SiO})\text{SiO}]_n$  that form in a high yield in the disiloxane **I** medium. The major products of the former reaction are cyclic oligoalkylchlorosiloxanes  $(\text{RClSiO})_m$  (**XV–XXI**,  $m = 3–6$ ) whose yields reach 80%. Their formation can be explained in terms of cyclization of the intermediate alkyl chlorosilanones.



$\text{R} = \text{Me}$ ,  $m = 3$  (**XV**), 4 (**XVI**), 5 (**XVII**);  $\text{R} = \text{Et}$ ,  $m = 3$  (**XVIII**), 4 (**XIX**), 5 (**XX**), 6 (**XXI**).

## EXPERIMENTAL

Gas chromatography–mass spectrometry was performed on an LKB-2091 GC–MS system at an ionizing voltage of 60 V, using an SE-54 capillary column, length 38 m. The oven temperature was raised at a rate of 16 deg/min to 270°C. Accelerating voltage 2 kV. The  $m/z$  values for chlorine-containing ions relate to  $^{35}\text{Cl}$ . The intensity ratio for isotope peaks is consistent with calculation.

Dimethyl sulfoxide was kept over melted KOH, decanted, frozen, and distilled in a vacuum. Dichloro(methyl)(vinyl)silane was purified by column rectification.

**Reaction of dimethyl sulfoxide with dichloro(methyl)(vinyl)silane in the presence of octamethyltrisiloxane (II).** Dimethyl sulfoxide, 7.8 g, was added dropwise with cooling (0°C) to 14.1 g of di-

chloro(methyl)(vinyl)silane and 23.6 g of octamethyltrisiloxane, placed in a 50-ml flask equipped with a long Vigreux column. The mixture was heated to the boil. Therewith, 4.3 g (44%) of chloromethyl methyl sulfide distilled, bp 109–110°C,  $n_D^{20}$  1.4965 (bp 110–112°C [3]). Found, %: C 25.25; H 5.24; Cl 36.94; S 32.85.  $\text{C}_2\text{H}_5\text{ClS}$ . Calculated, %: C 24.87; H 5.22; Cl 36.71; S 33.20. Along with chloromethyl methyl sulfide, dimethyl sulfide formed. Vacuum distillation of the residue gave a fraction [8.2 g (95%)] with bp 70–200°C (6 mm). It was subjected to GC–MS analysis. The resulting data are presented in the table. The mass spectra of  $(\text{MeVinSiO})_n$  ( $n = 3–6$ ) have been reported in [4].

The reactions of  $\text{Me}_2\text{SO}$  with  $\text{MeVinSiCl}_2$  in the presence of trisiloxane **II** (1:1:3 molar ratio) and with  $\text{RSiCl}_3$  were performed in a similar way. In the latter case, compounds **XV–XXI** were obtained.

**Compound XV.** Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 267 (100)  $[\text{M} - \text{Me}]^+$ , 247 (11)  $[\text{M} - \text{Cl}]^+$ , 173 (10)  $[\text{M} - \text{Me} - \text{Me}(\text{Cl})\text{SiO}]^+$ , 113 (16)  $[\text{MeSiCl}_2]^+$ , 93 (4)  $[\text{Me}_2\text{SiCl}]^+$ , 79 (12)  $[\text{M} - \text{Me} - 2 \text{Me}(\text{Cl})\text{SiO}]^+$ .

**Compound XVI.** Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 361 (100)  $[\text{M} - \text{Me}]^+$ , 341 (11)  $[\text{M} - \text{Cl}]^+$ , 267 (13)  $[\text{M} - \text{Me} - \text{Me}(\text{Cl})\text{SiO}]^+$ , 173 (8)  $[\text{M} - \text{Me} - 2\text{Me}(\text{Cl})\text{SiO}]^+$ , 113 (15)  $[\text{MeSiCl}_2]^+$ , 93 (24)  $[\text{Me}_2\text{SiCl}]^+$ .

**Compound XVII.** Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 455 (65)  $[\text{M} - \text{Me}]^+$ , 435 (21)  $[\text{M} - \text{Cl}]^+$ , 361 (17)  $[\text{M} - \text{Me} - \text{Me}(\text{Cl})\text{SiO}]^+$ , 267 (100)  $[\text{M} - \text{Me} - 2\text{Me}(\text{Cl})\text{SiO}]^+$ , 113 (25)  $[\text{MeSiCl}_2]^+$ , 93 (74)  $[\text{Me}_2\text{SiCl}]^+$ .

**Compound XVIII.** Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 295 (100)  $[\text{M} - \text{Et}]^+$ , 267 (34)  $[\text{M} - 2\text{Et} + \text{H}]^+$ , 187 (1)

$[M - Et - Et(Cl)SiO]^+$ , 127 (2)  $[EtSiCl_2]^+$ , 121 (4)  $[Et_2SiCl]^+$ .

**Compound XIX.** Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 403 (100)  $[M - Et]^+$ , 375 (34)  $[M - 2Et + H]^+$ , 295 (31)  $[M - Et - Et(Cl)SiO]^+$ , 187 (4)  $[M - Et - 2Et(Cl)SiO]^+$ , 127 (12)  $[EtSiCl_2]^+$ , 121 (14)  $[Et_2SiCl]^+$ .

**Compound XX.** Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 511 (100)  $[M - Et]^+$ , 483 (14)  $[M - 2Et + H]^+$ , 403 (11)  $[M - Et - Et(Cl)SiO]^+$ , 295 (4)  $[M - Et - 2Et(Cl)SiO]^+$ , 127 (11)  $[EtSiCl_2]^+$ , 121 (34)  $[Et_2SiCl]^+$ .

**Compound XXI.** Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 619 (60)  $[M - Et]^+$ , 591 (14)  $[M - 2Et + H]^+$ , 511 (61)  $[M - Et - Et(Cl)SiO]^+$ , 403 (100)  $[M - Et -$

$2Et(Cl)SiO]^+$ , 295 (75)  $[M - Et - 3Et(Cl)SiO]^+$ , 127 (11)  $[EtSiCl_2]^+$ , 121 (33)  $[Et_2SiCl]^+$ .

## REFERENCES

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