Generation and capture of methyl(vinyl)silanone

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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 $Me_3Si(OSiMeVin)_nOSiMe_3$ (n = 1—6) as well as $MeSi(OSiMe_3)_3$ and $Me_3Si(MeOSiVin)_mOSi(OSiMe_3)(Me)OSiMe_3$ (m = 1—2). The same reaction in the presence of chlorotrimethylsilane results in oligomers of the general formula $Me_3Si(OSiMeVin)_nCl$ (n = 1—3). A possible scheme of their formation is discussed.

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

Recently, we were the first to show[1,2] that the reaction of dichlorodiorganylsilanes with DMSO is a convenient method for the generation of diorganylsilanones. Later, these results were confirmed by American scientists.[3] 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 $Me_3Si(OSiMeVin)_nOSiMe_3$ (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.

$$\begin{aligned}&MeVinSiCl_2 + OSMe_2 \longrightarrow\\&\quad\longrightarrow [MeVinSi{=}O] + S(CH_2Cl)Me + HCl \qquad (1)\end{aligned}$$

$$\begin{aligned}&[MeVinSi{=}O] + Me_3SiOSiMe_3 \longrightarrow\\&\quad\longrightarrow \underset{\mathbf{1-6}}{Me_3Si(OSiMeVin)_nOSiMe_3} \qquad (2)\end{aligned}$$

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

Along with oligosiloxanes (**1—6**), other reaction products, *viz.*, $Me_3Si[OSi(OSiMe_3)Me]_nOSiMe_3$ (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,[4] an addition product of hydrogen chloride evolved during reaction (1), to the original methyl(vinyl)dichlorosilane. This process yields trichloromethylsilane.

$$\begin{aligned}&Me(CH_2{=}CH)SiCl_2 + HCl \longrightarrow\\&\quad\longrightarrow [Me(ClCH_2CH_2)SiCl_2] \longrightarrow\\&\quad\longrightarrow MeSiCl_3 + CH_2{=}CH_2 \qquad (3)\end{aligned}$$

The reaction of $MeSiCl_3$ with DMSO leads[5] to chloro(methyl)silanone

$$\begin{aligned}&MeSiCl_3 + OSMe_2 \longrightarrow\\&\quad\longrightarrow [Me(Cl)Si{=}O] + S(CH_2Cl)Me + HCl. \qquad (4)\end{aligned}$$

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

$$\begin{aligned}&[Me(CH_2{=}CH)Si{=}O] + HCl \longrightarrow\\&\quad\longrightarrow [Me(ClCH_2CH_2)Si{=}O] \longrightarrow\\&\quad\longrightarrow [Me(Cl)Si{=}O] + CH_2{=}CH_2 \qquad (5)\end{aligned}$$

Further, chloro(methyl)silanone cleaves the molecule of hexamethyldisiloxane to give methyl(trimethylsiloxy)silanone,[5] 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**.

$$\begin{aligned}&[Me(Cl)Si{=}O] + Me_3SiOSiMe_3 \longrightarrow\\&\quad\longrightarrow [Me(Me_3SiO)Si{=}O] + Me_3SiCl \qquad (6)\end{aligned}$$

$$\begin{aligned}&[Me(Me_3SiO)Si{=}O] + Me_3SiOSiMe_3 \longrightarrow\\&\quad\longrightarrow \underset{\mathbf{7}}{MeSi(OSiMe_3)_3} \qquad (7)\end{aligned}$$

$$\begin{aligned}&n[Me(Me_3SiO)Si{=}O] + Me_3SiO(MeVinSiO)_nSiMe_3 \longrightarrow\\&\quad\longrightarrow \underset{\mathbf{8,\,9}}{Me_3SiO[Me(Me_3SiO)SiO](MeVinSiO)_nSiMe_3} \qquad (8)\end{aligned}$$

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

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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**
$[M-Me]^+$	233 (100)	319 (54)	405 (51)	491 (2)	577 (4)	663 (4)
$[M-Vin]^+$	221 (15)	307 (2)	393 (3)	—	565 (1)	651 (1)
$[M-C_2H_4]^+$	205 (72)	291 (2)	—	—	—	—
$[M-OSiMe_2Vin]^+$	147 (7)	233 (5)	319 (3)	—	—	577 (2)
$[M-Me-Me_4Si]^+$	145 (2)	231 (24)	317 (11)	—	489 (2)	—
$[M-OSiMeVin_2]^+$	—	221 (13)	307 (17)	—	479 (2)	565 (3)
$[M-Vin-Me_4Si]^+$	133 (12)	219 (100)	305 (87)	391 (4)	—	—
$[M-Vin-Me_3VinSi]^+$	—	207 (73)	293 (93)	379 (13)	465 (8)	551 (4)
$[Me_3SiOSiMeVin]^+$	159 (3)	159 (1)	159 (72)	159 (14)	159 (44)	159 (40)
$[Me_3SiOSiMe_2]^+$	147 (7)	147 (2)	147 (28)	147 (8)	147 (23)	147 (19)
$[Me_3SiOSiMeH]^+$	133 (12)	133 (6)	133 (12)	133 (7)	133 (12)	133 (12)
$[MeVin_2Si]^+$	—	97 (26)	97 (32)	97 (25)	97 (52)	97 (67)
$[Me_2VinSi]^+$	85 (30)	85 (83)	85 (77)	85 (69)	85 (91)	85 (100)
$[Me_3Si]^+$	73 (64)	73 (80)	73 (100)	73 (100)	73 (100)	73 (90)
$[Me_2SiH]^+$	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**
$[M-Me]^+$	295 (42)	381 (10)	479 (0.5)	179 (100)	265 (100)	351 (100)
$[M-Vin]^+$	—	—	467 (11)	167 (4)	253 (8)	339 (5)
$[M-C_2H_2]^+$	—	355 (2)	—	153 (26)	239 (6)	325 (6)
$[M-C_2H_4]^+$	—	—	—	151 (7)	237 (11)	323 (3)
$[M-OSiMe_2Vin]^+$	—	295 (4)	—	93 (14)	179 (7)	265 (5)
$[M-Me-Me_4Si]^+$	207 (100)	293 (16)	—	—	—	—
$[M-Vin-Me_4Si]^+$	—	281 (23)	367 (14)	79 (13)	165 (1)	251 (6)
$[M-Vin-Me_3VinSi]^+$	—	—	355 (5)	—	153 (7)	239 (6)
$[Me_3SiOSiMeVin]^+$	—	159 (23)	159 (36)	159 (3)	159 (1)	159 (1)
$[Me_3SiOSiMe_2]^+$	147 (3)	147 (33)	147 (34)	147 (7)	147 (4)	147 (13)
$[Me_3SiOSiMeH]^+$	133 (3)	133 (7)	133 (7)	133 (11)	133 (6)	133 (6)
$[MeVin_2Si]^+$	—	—	97 (13)	—	97 (33)	97 (38)
$[Me_2VinSi]^+$	—	85 (27)	85 (55)	85 (8)	85 (25)	85 (48)
$[Me_3Si]^+$	73 (64)	73 (100)	73 (100)	73 (15)	73 (30)	73 (100)
$[Me_2SiH]^+$	59 (6)	59 (23)	59 (19)	59 (9)	59 (17)	59 (23)

* For the ^{35}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).

$$Me_3SiCl + n[O{=}SiMeVin] \longrightarrow \underset{\mathbf{10-12}}{Me_3Si(OSiMeVin)_nCl} \quad (9)$$

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)silanone according to Eq. (2).[1]

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^{-1} 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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