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Reaction of Organylchlorosilanes with Dimethyl Sulfoxide in the Presence of Octamethyltrisiloxane

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Abstract—Dichloro(methyl)(vinyl)silane reacts with DMSO in the presence of octamethyltrisiloxane to form cyclooligomethyl(vinyl)siloxanes$(\mathrm{MeViSiO})_n$ (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 $\mathrm{RSiCl_3}$ (R = Me, Et) react with DMSO in the presence of octamethyltrisiloxane to form cyclic oligoalkyltrichlorosiloxanes $(\mathrm{RClSiO})_m$ (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 cyclomethyl(vinyl)siloxanes $(\mathrm{MeViSiO})_n$ (**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%.

$$\mathrm{CH_3(CH_2{=}CH)SiCl_2 + OS(CH_3)_2} \xrightarrow[-\mathrm{HCl}]{} \underset{\mathbf{III}}{\mathrm{[CH_3(CH_2{=}CH)Si{=}O]}} + \mathrm{S(CH_2Cl)CH_3}, \quad (1)$$

$$n\underset{\mathbf{III}}{\mathrm{[MeVinSi{=}O]}} \longrightarrow \underset{\mathbf{IV\text{–}VII}}{(\mathrm{MeVinSiO})_n}, \quad (2)$$

$$m\mathrm{[MeVinSi{=}O]} + \underset{\mathbf{II}}{\mathrm{Me_3SiOSiMe_2OSiMe_3}} \longrightarrow \underset{\mathbf{VIII,\ IX}}{\mathrm{Me_3SiOSiMe_2O(MeVinSiO)_\mathit{m}SiMe_3}}, \quad (3)$$

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

Reaction (2) between $\mathrm{MeVinSiCl_2}$ 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 $\mathrm{MeVinSiCl_2}$ nor DMSO taken separately induce disproportionation of compound **II**.

$$2\underset{\mathbf{II}}{\mathrm{Me_3SiOSiMe_2OSiMe_3}} \longrightarrow \underset{\mathbf{I}}{\mathrm{Me_3SiOSiMe_3}} + \underset{\mathbf{X}}{\mathrm{Me_3SiOSiMe_2OSiMe_2OSiMe_3}}. \quad (4)$$

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-nonamethyl-3,5,7-trivinylpentasiloxane (**XIII**)] and into decamethyltetrasiloxane [1,1,1,3,5,5,7,7,9,9,9-undecamethyl-3-vinylpentasiloxane (**XIV**)].

$$\mathbf{I} + \mathbf{III} \longrightarrow \underset{\mathbf{XI\text{–}XIII}}{\mathrm{Me_3SiO(MeVinSiO)_\mathit{n}SiMe_3}}, \quad (5)$$

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

$$\mathbf{III} + \underset{\mathbf{X}}{\mathrm{Me_3SiOSiMe_2OSiMe_2OSiMe_3}} \longrightarrow \underset{\mathbf{XIV}}{\mathrm{Me_3SiOSiMe_2OSiMe_2O(MeVinSiO)SiMe_3}}. \quad (6)$$

Insertion products **XI**–**XIII** we also identified earlier in the reaction of $\mathrm{MeVinSiCl_2}$ with DMSO and disiloxane **I** [1].

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Mass spectra of $Me_3Si(OSiMeVin)_n(OSiMe_2)_mOSiMe_3$ (**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_{rel}, %)					
	VIII	**IX**	**XI**	**XII**	**XIII**	**XIV**
$[M - \mathrm{Me}]^+$	307 (60)	393 (33)	233 (100)	319 (52)	405 (47)	381 (12)
$[M - \mathrm{OSiMe_2Vin}]^+$	221 (42)	307 (3)	147 (8)	233 (7)	319 (7)	295 (9)
$[M - \mathrm{Me} - \mathrm{Me_4Si}]^+$	219 (80)	305 (36)	145 (4)	231 (25)	317 (19)	293 (86)
$[M - \mathrm{Vin} - \mathrm{Me_4Si}]^+$	207 (100)	293 (100)	133 (17)	219 (100)	305 (85)	281 (100)
$[\mathrm{Me_3SiOSiMeVin}]^+$	–	159 (55)	159 (3)	159 (1)	159 (77)	–
$[\mathrm{Me_3SiOSiMe_2}]^+$	147 (2)	147 (41)	147 (7)	147 (2)	147 (29)	147 (12)
$[\mathrm{Me_3SiOSiMeH}]^+$	133 (2)	–	133 (10)	133 (5)	133 (10)	–
$[\mathrm{Me_2VinSi}]^+$	85 (32)	85 (36)	85 (30)	85 (85)	85 (80)	–
$[\mathrm{Me_3Si}]^+$	73 (62)	73 (59)	73 (68)	73 (80)	73 (100)	73 (9)
$[\mathrm{Me_2SiH}]^+$	59 (7)	59 (12)	59 (10)	59 (23)	59 (32)	–

The reaction of organyltrichlorosilanes $RSiCl_3$ (R = Me, Et) with DMSO in the presence of trisiloxane **II** (1 : 1 : 1 molar ratio) at 20°C gives no cycloorganyl(trimethylsiloxy)siloxanes $[R(Me_3SiO)SiO]_n$ that form in a high yield in the disiloxane **I** medium. The major products of the former reaction are cyclic oligoalkylchlorosiloxanes $(RClSiO)_m$ (**XV**–**XXI**, m = 3–6) whose yields reach 80%. Their formation can be explained in terms of cyclization of the intermediate alkyl chlorosilanones.

$$m[\mathrm{RClSi{=}O}] \longrightarrow \underset{\textbf{XV–XXI}}{(\mathrm{RClSiO})_m}, \tag{7}$$

R = Me, m = 3 (**XV**), 4 (**XVI**), 5 (**XVII**); R = 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}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 dichloro(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. C_2H_5ClS. 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 $(MeVinSiO)_n$ (n = 3–6) have been reported in [4].

The reactions of Me_2SO with $MeVinSiCl_2$ in the presence of trisiloxane **II** (1 : 1 : 3 molar ratio) and with RSiCl3 were performed in a similar way. In the latter case, compounds **XV**–**XXI** were obtained.

Compound XV. Mass spectrum, m/z (I_{rel}, %): 267 (100) $[M - \mathrm{Me}]^+$, 247 (11) $[M - \mathrm{Cl}]^+$, 173 (10) $[M - \mathrm{Me} - \mathrm{Me(Cl)SiO}]^+$, 113 (16) $[\mathrm{MeSiCl_2}]^+$, 93 (4) $[\mathrm{Me_2SiCl}]^+$, 79 (12) $[M - \mathrm{Me} - 2\,\mathrm{Me(Cl)SiO}]^+$.

Compound XVI. Mass spectrum, m/z (I_{rel}, %): 361 (100) $[M - \mathrm{Me}]^+$, 341 (11) $[M - \mathrm{Cl}]^+$, 267 (13) $[M - \mathrm{Me} - \mathrm{Me(Cl)SiO}]^+$, 173 (8) $[M - \mathrm{Me} - 2\mathrm{Me(Cl)SiO}]^+$, 113 (15) $[\mathrm{MeSiCl_2}]^+$, 93 (24) $[\mathrm{Me_2SiCl}]^+$.

Compound XVII. Mass spectrum, m/z (I_{rel}, %): 455 (65) $[M - \mathrm{Me}]^+$, 435 (21) $[M - \mathrm{Cl}]^+$, 361 (17) $[M - \mathrm{Me} - \mathrm{Me(Cl)SiO}]^+$, 267 (100) $[M - \mathrm{Me} - 2\mathrm{Me(Cl)SiO}]^+$, 113 (25) $[\mathrm{MeSiCl_2}]^+$, 93 (74) $[\mathrm{Me_2SiCl}]^+$.

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

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