Hexa(organylsilsesquioxanes)*

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A method for the synthesis of earlier practically unknown hexa(organylsilsesquioxanes) (RSiO_{1,5})₆ have been developed based on the reaction of organyltrichlorosilanes RSiCl₃ (R = Et, Vin) with DMSO. The reaction proceeded in several steps. The initial stage of the reaction gave poorly available 1,3,5-trichloro-1,3,5-triorganylcyclosiloxanes in 40–80% yield, as well as organyl(chloro)oligohomosilsesquioxanes, which further are converted to the corresponding organyloligosilsesquioxanes. Based on the monitoring of the reaction mixture by GC-MS, a scheme for the formation of the intermediate silsesquioxane structures have been suggested.

Key words: organyltrichlorosilanes, dimethyl sulfoxide, organyl(chloro)silanones, organyl-(chloro)cyclosiloxanes, organylsilsesquioxanes.

Organylsilsesquioxanes of caged structure $(RSiO_{1,5})_n$, especially octa(organylsilsesquioxanes) (n = 8), are the basis for the synthesis of octopus-like molecules,¹ organosilicon dendrimers,² and resins. They are suggested as radiation-sensitive materials for dry vacuum submicron lithography.³ They are traditionally synthesized by hydrolysis of the corresponding organyltrichlorosilanes RSiCl₃ (R = Me, Et, Vin) in organic solvents. These conditions predominantly lead to octa(organylsilsesquioxanes). Hexa(organylsilsesquioxanes) are formed in trace amounts.⁴⁻⁶

Earlier, we have shown that the use of DMSO as oxygenation agent allows one to predominantly effect the synthesis of small cycles.^{7–9} Thus, the reaction of Me₂SiCl₂ with DMSO gives hexamethylcyclotrisiloxane as the main reaction product (48–85%),^{7–10} whereas hydrolysis of Me₂SiCl₂ leads to tetramethylcyclotetra- and pentamethylcyclopentasiloxanes.^{11–12}

The attempts to obtain hexa(vinylsilsesquioxane) by a combination of two methods (the use of the oxygenation reagent (DMSO) and subsequent hydrolysis of the reaction mixture in chloroform) led, according to the authors,¹³ to the formation of a mixture of unidentified products.

We found the condition for the synthesis of hexa-(organylsilsesquioxanes) with ethyl and vinyl substituents at the silicon atom by the reaction of ethyl- and vinyltrichlorosilanes, respectively, with DMSO in organic solvents (CHCl₃, diethyl ether, toluene, *etc.*) under argon in 11-15% yield. The reaction, as we suggest, proceeds

* Based on the materials of the XIII Andrianov Conference "Organosilicon Compounds: Synthesis, Properties, and Application" (June 28–July 1, 2015, Moscow). through the intermediate generation of organyl(chloro)silanones 1 (Scheme 1), with further cyclotrimerization to organyl(chloro)cyclotrisiloxanes 2, which are the basis for the formation of hexasilsesquioxane structure 3.

Scheme 1



Cyclic organylchlorosiloxanes (RClSiO)_n (R = Et, Vin, n = 3) are poorly available compounds. This largely limits their application as synthons in organic and organoelement chemistry. Before our studies,¹⁴ a method for the preparation of (EtClSiO)₃ based on the chlorination of preliminary synthesized ethylcyclotrisiloxane (EtHSiO)₃ has been described.¹⁵

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 4, pp. 1034–1038, April, 2016.

1066-5285/16/6504-1034 © 2016 Springer Science+Business Media, Inc.



Note that the content of 1,3,5-trichloro-1,3,5-trivinylcyclotrisiloxane (**2b**) in the reaction mixture compared to 1,3,5-trimethyl-¹⁴ and 1,3,5-triethyl-substituted cyclotrisiloxanes considerably differs. The yield of cyclosiloxane **2b** in the reaction of VinSiCl₃ with an equimolar amount of DMSO at 0 °C in organic solvents (CHCl₃, diethyl ether, *m*-xylene, toluene) does not exceed 35-40%, whereas in similar reaction with EtSiCl₃, the yield of the cyclic derivatives reaches almost 80%.

The monitoring of the reaction of VinSiCl₃ with DMSO (molar ratio 1:1, 0 °C) in organic solvents (CHCl₃, diethyl ether) by GC-MS was carried out immediately after mixing the reagents and then every 6-24 h. It was identified about a dozen reaction products, including those formed in insignificant amounts (2-5%). Thus, the formation of linear and cyclic siloxanes is observed in the initial stage of the reaction. In the case of trichlorovinyl-silane these products mainly are 1,1,3,3-tetrachloro-1,3-divinyldisiloxane and 1,3,5-trichloro-1,3,5-trivinylcyclo-trisiloxane. The presence of 1,1,3,5,5-pentachloro-1,3,5-trivinyltrisiloxane in the reaction mixture is observed for a long time, until the formation of the silsesquioxane structure is completed, however, its yield in any of the steps did not exceed 7–11%.

Apart from that, already in the initial stage of the reaction, the formation of chloro(vinyl)oligohomosilsesquioxanes 4b-9b is observed together with the linear and cyclic chlorovinylsiloxanes (Schemes 2-4), whereas the target hexa(vinylsilsesquioxane) 3b is formed after standing of the reaction mixture during 48-96 h. Even when DMSO is taken in less than equimolar amount, the cyclization process for trichlorovinylsilane does not stop in the step of the formation of chlorocyclosiloxane 2b, rather it continues to form $(VinSiO_{1,5})_6$ and a number of unfinished (chloro(vinyl)oligohomosilsesquioxane) structures. In the reaction of EtSiCl₃ with DMSO (molar ratio 1 : 1, 0 °C) the formation of such structures is observed when the reaction mixture is allowed to stand for a longer time (2–3 weeks) and accelerates only upon addition of DMSO to the reaction mixture.

No intermediate formation of structures with hydroxy groups was observed in the course of monitoring. The main terminal elements of condensed structures in all the stages of our observation (together with a vinyl group) were chlorine atoms.

In contrast to the hydrolytic methods for the synthesis of silsesquioxanes, no processes of cleavage and rearrangement with the formation of complex and





Ion	$m/z^*(I_{\rm rel}(\%))$						
	4b	5b	6b	7b	8b	9b	11b
M ^{+.}	582 (2)	528 (8)	476 (12)	422(1)	580 (9)	686 (17)	738 (75)
$[M - Vin]^+$	555 (17)	501 (100)	449 (82)	395 (100)	553 (100)	659 (100)	711 (100)
M - Cl] ⁺	547 (15)	493 (11)	441 (24)	387 (6)	545 (3)	651 (9)	_ `
$[M - Vin - CH_2]^+$	541 (15)	487 (54)	435 (100)	_	539 (2)	645 (19)	597 (23)
$[M - Vin - C_2 H_2]^+$	527 (40)	475 (44)	423 (62)	369(7)	527 (13)	_	685 (41)
$[M - Vin - C_2H_2 - CH_2]^+$	515 (16)	461 (9)	409 (21)	_	513 (2)	619 (13)	_
$[M - Vin - 2C_2H_2]^+$	503 (27)	449 (19)	397 (30)	343 (13)	501 (16)	607 (32)	_
$[M - Vin - 2C_2H_2 - CH_2]^+$	489 (30)	_	383 (19)	_	487 (1)	_	_
$[M - Vin - 3C_2H_2]^+$	477 (15)	423 (10)	371 (17)	317 (8)	475 (2)	581 (10)	_
$[M - Vin - 3C_2H_2 - CH_2]^+$	463 (19)	_	_	_	461 (1)		619 (24)
$[M - Vin - 4C_2H_2]^+$	451 (8)	397 (19)	345 (12)	291 (2)	449 (1)	555 (24)	
$[M - Vin - 4C_2H_2 - CH_2]^+$	437 (9)	_	_	_	_	541 (6)	_
Vin ₂ SiCl	117 (100)	_	117 (23)	_	117(1)	117 (5)	_
VinHSiCl	91 (42)	91 (1)	91 (7)	91 (1)	91 (1)	91 (5)	91 (57)

Table 1. The mass spectrometry data for intermediate chloro(vinyl)oligohomosilsesquioxanes

* Calculated on isotope ³⁵Cl. The ratio of intensities of isotope peaks corresponds to the calculations.

more strained cyclosiloxane molecules were observed in our case.

Based on the data obtained (Table 1), the following scheme for the synthesis of hexa(organylsilsesquioxanes) can be suggested, which consists in the sequential condensation of cyclic molecules involving DMSO (Scheme 2).

A relatively stable structure **7b** observed in an insignificant amount practically all the time of reaction monitoring, probably, is an unfinished pyramid formed according to Scheme 3. Octa(vinylsilsesquioxane) (10b) is also observed among the reaction product, however, its yield did not exceed 4-5%. The detection in the mass spectra of the intermediate chloro(vinyl)oligohomosilsesquioxane structures (8b and 9b), the formation of which can be explained by a sequential incorporation of chloro(vinyl)silanone, involving, as we assume, in the processes of the formation of silsesquioxane structures, allows us to suggest Scheme 4 for the formation of (VinSiO_{1,5})₈.

The initial step of further transformation of $(VinSiO_{1,5})_8$ was also identified (Scheme 5).



Scheme 4





Hexa(organylsilsesquioxanes) were isolated from the reaction precipitate by sublimation *in vacuo* ($10^{-1}-10^{-2}$ Torr) at 100–150 °C. Sublimation of octa(organylsilsesquioxanes) was observed at the temperatures of 150–200 °C.

The GC-MS analysis data showed some details of the disintegration of hexa(organylsilsesquioxanes).

The mass spectrum of $(\text{EtSiO}_{1,5})_6$ (**3a**) somewhat differs from the spectrum of $(\text{EtSiO}_{1,5})_8$. First of all, by the presence of the molecular ion M⁺ with m/z 486, the second in intensity after the $[M - \text{Et}]^+$ ion with m/z 457. It should be also noted a low intensity of the doubly charged ion $[M - 2 \text{ Et}]^{2+}$ with m/z 214, as well as the presence of relatively strong ions formed by a sequential elimination of neutral fragments C_2H_4 and C_2H_6 against the background of weak (0.1–1%) linear ions formed, apparently, by the loss of CH₂ and CH₄ groups from the ethyl substituents.

The molecular ion M^+ with m/z 474 in the mass spectrum of $(VinSiO_{1,5})_6$ (**2b**) is the strongest in contrast to the spectrum of $(VinSiO_{1,5})_8$, in which it has the fourth intensity. The spectrum also exhibits the $[M - Vin - C_2H_2 - -CH_2 - OSiCH_2]^+$ ion with m/z 349, which for $(VinSiO_{1,5})_8$ indicates the disintegration of the siloxane framework, ¹⁶ however, its intensity is lower.

In conclusion, we have developed a new method for the synthesis of actually earlier unknown hexa(organylsilsesquioxanes) and used GC-MS monitoring of the reaction mixtures to suggest a scheme of their formation.

Experimental

¹H, ¹³C, and ²⁹Si NMR spectra were recorded on a Bruker DPX 400 spectrometer (400, 100.13, 79.49 MHz, respectively) in CDCl₃, using SiMe₄ as an internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer, injector temperature 200–250 °C, carrier gas helium, detector temperature 200 °C, a quadrupole mass analyzer, EI ionization (70 eV). Elemental analysis (C, H) was carried out on a FLASH EA 1112 Series analyzer. The content of chlorine and silicon was analyzed using the Gel man procedure.¹⁷

Trichloroethylsilane and trichlorovinylsilane are industrial products purified by distillation. Dimethyl sulfoxide was stored over melted KOH, after decantation it was frozen out and distilled *in vacuo*. Their physical constants agreed with the literature data.

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Reaction of trichlorovinylsilane with DMSO. A solution of DMSO (7.8 g, 0.1 mol) in chloroform was slowly (over 1 h) added to a solution of trichlorovinylsilane (16.0 g, 0.1 mol) at 0 °C in chloroform under argon. The mixture was stirred for 6 h and distilled *in vacuo*. The following products were isolated: 1,3-tetrachloro-1,3-divinyldisiloxane, 1,1,3,5,5-pentachloro-1,3,5-trivinyltrisiloxane, compounds **2b** and **3b**.

1,3-Tetrachloro-1,3-divinyldisiloxane. The yield was 1.8 g (14%), b.p. $51-52 \circ C$ (2 Torr). Found (%): C, 17.57; H, 2.19; Cl, 52.49; Si, 21.18. C₄H₆Cl₄OSi₂. Calculated (%): C, 17.92; H, 2.26; Cl, 52.90; Si, 20.95. ¹H NMR, δ : 6.10 (dd, 2 H, SiCH=CH₂, ³J_{cis} = 14.5 Hz, ³J_{trans} = 20.3 Hz); 6.35 (dd, 2 H, ²J_{gem} = 5.2 Hz, ³J_{trans} = 14.3 Hz), 6.28 (dd, 2 H, SiCH=CH₂, ³J_{erans} = 20.3 Hz). ¹³C NMR, δ : 135.75, 135.97, 136.11, 136.54, 136. 79, 137.60. ²⁹Si NMR, δ : -30.85. MS, m/z (I_{rel} (%)): 266(1) [M]⁺, 239 (28) [M - Vin]⁺, 231 (100) [M - Cl]⁺, 213 (39) [M - Vin - C₂H₂]⁺, 203 (33) [M - Vin - HCl]⁺, 179 (46) [HCl₂SiOSiClH]⁺, 115 (17) [HCl₂SiO]⁺, 99 (4) [HCl₂Si]⁺.

1,3,5-Trichloro-1,3,5-trivinylcyclotrisiloxane (2b). The yield was 4.2 g (40%), b.p. 129–131 °C (2 Torr). Found (%): C, 22.34; H, 2.77; Cl, 32.91; Si, 26.17. $C_6H_9Cl_3O_3Si_3$. Calculated (%): C, 22.54; H, 2.82; Cl, 33.33; Si, 26.29. ¹H NMR, δ : 6.10–6.35 (m, 18 H, CH=CH₂). ¹³C NMR, δ : 135.75–137.60 (CH=CH₂). ²⁹Si NMR, δ : -45.06. MS, m/z (I_{rel} (%)): 318 (6) [M]⁺, 291 (68) [M – Vin]⁺, 283 (100) [M – Cl]⁺, 277 (23) [M – Vin – CH₂]⁺, 265 (53) [M – Vin – C₂H₂]⁺, 257 (74) [M – Cl – C₂H₂]⁺, 239 (52) [M – Vin – 2 C₂H₂]⁺, 229 (47), 219 (7), 205 (31) [M – Cl – 3 C₂H₂]⁺, 194 (12), 167 (6), 159 (5), 134 (2), 123 (3) [VinClSiO(OH)]⁺, 107 (2) [VinClSiOH]⁺, 80 (35) [HClSiO]⁺, 66 (19), 54 (17), 49 (3).

1,1,3,5,5-Pentachloro-1,3,5-trivinyltrisiloxane. The yield was 1.3 g (10%), b.p. 101–102 °C (2 Torr). Found (%): C, 19.56; H, 2.29; Cl, 47.19; Si, 22.28. $C_6H_9Cl_5O_2Si_3$. Calculated (%): C, 19.33; H, 2.42; Cl, 47.65; Si, 22.55. ²⁹Si NMR, δ : -31.97 (VinCl₂SiO), -55.17 (OVinClSiO). MS, *m/z* (I_{rel} (%)): 372 (1) [M]⁺, 345 (8) [M – Vin]⁺, 337 (100) [M – Cl]⁺, 319 (10) [M – Vin – C_2H_2]⁺, 309 (22) [M – Vin – HCl]⁺, 283 (8) [M – Vin – HCl – C_2H_2]⁺, 247 (2) [M – Vin – 2 HCl – C_2H_2]⁺, 179 (2) [HCl₂SiOSiClH]⁺, 145 (2) [H₂ClSiOSiClH]⁺, 115 (15) [HCl₂SiO]⁺, 99 (2) [HCl₂Si]⁺, 80 (14) [HClSiO]⁺.

Chloromethyl methyl sulfide 8.7 g (89%) was collected in the cooled trap, which after distillation under atmospheric pressure had the following constants: b.p. 109–110 °C (*cf.* data Ref. 18: b.p. 110–112 °C), n_D^{20} 1.4955.

Hexa(vinylsilsesquioxane) (3b) was isolated from the reaction precipitate by sublimation *in vacuo* $(10^{-1}-10^{-2}$ Torr) at 100–140 °C. The yield was 1.2 g (15%). Found (%): C, 29.99; H, 3.69; Si, 35.21. C₁₂H₁₈O₉Si₆. Calculated (%): C, 30.35; H, 3.79; Si, 35.51. ²⁹Si NMR, δ : -71.40. MS (VinSiO_{1,5})₆: 474 (100) [M]⁺, 447 (80) [M – Vin]⁺, 433 (3) [M – Vin – CH₂]⁺, 421 (18) [M – Vin – C₂H₂]⁺, 419 (11) [M – Vin – C₂H₄]⁺, 409 (9), 403 (1) [M – VinSiO]⁺, 393 (3) [M – Vin – C₂H₄]⁺, 409 (9), 403 (1) [M – VinSiO]⁺, 393 (3) [M – Vin – C₂H₄]⁺, 409 (2) [M – VinSiO – C₂H₄]⁺, 351 (3) [M – VinSiO – 2 C₂H₂]⁺, 349 (2) [M – VinSiO – C₂H₄ – C₂H₂]⁺, 351 (3) [M – VinSiO – C₂H₄]⁺, 297 (2) [M – VinSiO – C₂H₄ – 3 C₂H₂]⁺, 295 (2) [M – VinSiO – - 2 C₂H₄ – 2 C₂H₂]⁺, 278 (1), 271 (1) [M – VinSiO – C₂H₄ – 2

- 4 C₂H₂]^{+,} 237 (3), 224 (5), 211 (4), 210 (2) [M - 2 Vin]²⁺, 197 (6), 170 (4), 158 (2).

Octa(vinylsilsesquioxane) was sublimated at $10^{-1}-10^{-2}$ Torr and temperature 150–200 °C in 4% yield (0.3 g). Its mass spectrum agrees with that published earlier.¹⁹

Reaction of trichloroethylsilane with DMSO was carried out similarly to obtain the following products: 1,3-tetrachloro-1,3-diethyldisiloxane, compounds **2a** and **3a**.

1,3-Tetrachloro-1,3-diethyldisiloxane. The yield was 12%, b.p. 41–42 °C (2 Torr) (*cf.* Ref. 20: 186–187 °C (757 Torr)). ¹H NMR, δ : 1.11 (CH₂); 1.02 (CH₃). ¹³C NMR, δ : 13.33 (CH₂); 5.92 (CH₃). ²⁹Si NMR, δ : -15.20.

1,3,5-Trichloro-1,3,5-triethylcyclotrisiloxane (2a). The yield was 74%, b.p. $121-122 \,^{\circ}C (2 \,^{\circ}Torr), n_D^{20} 1.2585 (cf. Ref. 15: b.p. 126-127 \,^{\circ}C (2 \,^{\circ}Torr), n_D^{20} 1.2591)$. Found (%): C, 21.87; H, 4.19; Cl, 32.49; Si, 26.16. C₆H₁₅Cl₃O₃Si₃. Calculated (%): C, 22.12; H, 4.61; Cl, 32.72; Si, 25.81. ²⁹Si NMR, δ : -30.59.

The mass spectrometric data data of synthesized 1,3-tetrachloro-1,3-diethyldisiloxane and 1,3,5-trichloro-1,3,5-triethylcyclotrisiloxane (**2a**) agree with those published earlier.¹⁴

Hexa(ethylsilsesquioxane) (3a) was isolated from the reaction precipitate by sublimation *in vacuo* at $10^{-1}-10^{-2}$ Torr and 100-150 °C. The yield was 1.0 g (12%). Found (%): C, 29.87; H, 6.19; Si, 35.03. C₁₂H₃₀O₉Si₆. Calculated (%): C, 29.60; H, 6.17; Si, 34.64. ²⁹Si NMR, δ : -56.93. MS (EtSiO_{1,5})₆: 486 (24) [M]⁺, 457 (100) [M - Et]⁺, 429 (10) [M - Et - C₂H₄]⁺, 401 (3) [M - Et - 2 C₂H₄]⁺, 385 (2) [M - Et - C₂H₄ - C₂H₆ - CH₂]⁺, 373 (2) [M - Et - 3 C₂H₄]⁺, 372 (3) [M - 3 C₂H₄ - C₂H₆]⁺, 357 (2) [M - Et - 2 C₂H₄]⁺, 372 (3) [M - 3 C₂H₄ - C₂H₆]⁺, 357 (2) [M - Et - 2 C₂H₄ - C₂H₆ - CH₂]⁺, 345 (2) [M - Et - 2 C₂H₄]⁺, 344 (5) [M - 4 C₂H₄ - C₂H₆]⁺, 330 (6) [M - 4 C₂H₄ - CH₂]⁺, 316 (5) [M - 5 C₂H₄ - C₂H₆]⁺, 299 (2), 285 (1), 271 (1), 234 (2), 215 (2), 214 (<1), 200 (5), 186 (3), 172 (3), 157 (2).

This work was financially supported by the President of the Russian Federation Council for Grants (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh 3649.2014.3). The principal results were obtained using material and technical facilities of Baikal Analytical Multi-access Center of the Siberian Branch of the Russian Academy of Sciences.

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Received June 29, 2015; in revised form December 21, 2015