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CHEMISTRY

Efficient Method for the Synthesis of Symmetrical α,ω-Dichloro-1,1,3,3-tetraorganyldisiloxanes

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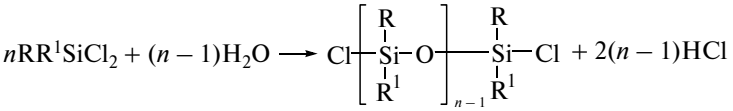
α,ω-Dichloroorganyldisiloxanes (DCSs) are used as precursors in preparing linear and cyclic siloxanes and polysiloxanes showing biological activity; adhesive, hydrophobic, dielectric and properties; durability and ability to operate under extreme conditions (temperature, humidity, etc.). They find a wide application in aerospace, automotive, and chemical industry; electrical engineering, pharmacy, food processing industry, cosmetics, and medicine [1–3].

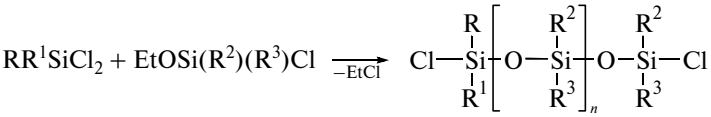
From the 1940s, numerous studies of the synthesis of DCSs have been reported. The main method of their preparation is the controlled hydrolysis of diorganyldichlorosilanes or diorganylchlorosilanes [1, 4–7].



$$n\mathrm{RR^1SiCl_2} + (n-1)\mathrm{H_2O} \longrightarrow \mathrm{Cl}\left[\mathrm{Si}(\mathrm{R})(\mathrm{R^1})\mathrm{O}\right]_{n-1}\mathrm{Si}(\mathrm{R})(\mathrm{R^1})\mathrm{Cl} + 2(n-1)\mathrm{HCl}$$

(R = H, Me, Ph, Cl; R^1 = H, Me, Vin, Ph, α-Np, $C_6H_4SiMe_2Cl$; n = 2–5).

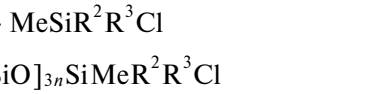
They were detected in the reaction of wet iron(III) oxide with organyldichlorosilanes [8] and on the heterofunctional condensation of the latter with alkoxychlorosilanes [9].



$$\mathrm{RR^1SiCl_2} + \mathrm{EtOSi(R^2)(R^3)Cl} \xrightarrow{-\mathrm{EtCl}} \mathrm{Cl}\left[\mathrm{Si}(\mathrm{R})(\mathrm{R^1})\mathrm{O}\right]_n\mathrm{Si}(\mathrm{R^2})(\mathrm{R^3})\mathrm{O}\mathrm{Si}(\mathrm{R^2})(\mathrm{R^3})\mathrm{Cl}$$

(R = Me, Et; R^1 = H, Me, Et; R^2 = Me, Et; R^3 = H, Me; n = 0–3).

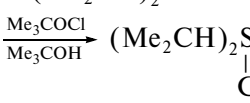
Telomerization of cyclosiloxanes is an ingenious method of DCS synthesis [10].



$$n[\mathrm{RR^1SiO}]_3 + \mathrm{MeSiR^2R^3Cl} \longrightarrow \mathrm{Cl}[\mathrm{RR^1SiO}]_{3n}\mathrm{SiMeR^2R^3Cl}$$

(R = Me, Et; R^1 = Me, Et, Ph; R^2 = H, $ClCH_2$, Me, Vin, Ph; R^3 = Cl, Me; n = 1–10).

These compounds were also obtained by chlorination, for example with *tert*-butyl hypochlorite, of the corresponding tetraorganylsiloxanes [10, 11].



$$(\mathrm{Me_2CH})_2\mathrm{HSi{-}O{-}SiH(CHMe_2)_2} \xrightarrow[\mathrm{Me_3COH}]{\mathrm{Me_3COCl}} (\mathrm{Me_2CH})_2\underset{\mathrm{Cl}}{\mathrm{Si}}{-}\mathrm{O}{-}\underset{\mathrm{Cl}}{\mathrm{Si}}(\mathrm{CHMe_2})_2.$$

A disadvantage of the majority of the known methods of DCS synthesis is reaction nonselectivity resulting in a mixture of different linear and cyclic siloxanes containing two or more silicon atoms in a molecule. Almost all these methods require high energy consumption, while the yields of target products do not exceed 43%, except the yields of DCSs obtained by chlorination (60–88%), but this method requires preliminary preparation of initial organyldisiloxanes with Si–H bonds.

We have found a new efficient method for synthesis of symmetrical α,ω-dichloro-1,1,3,3-tetraorganyldisiloxanes ClRR'Si–O–SiRR'Cl (R = H, Me; R' = $ClCH_2$,

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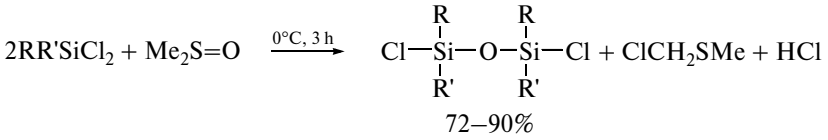
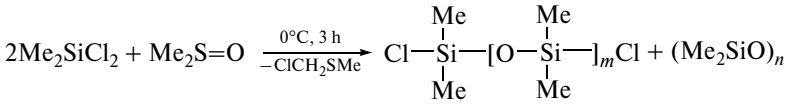
Me, Et, Vin, Ph) in 70–90% yield. The method is based on the reaction of a 3–4-fold excess of the corresponding diorganyldichlorosilane $RR'SiCl_2$ with dimethyl sulfoxide (DMSO). The reaction proceeds at 0°C (the best yield of methyl(chloromethyl)dichlorosilane was obtained at –40°C) for 3 h.



72–90%

[R = R' = Me (**I**); R = H, R' = Et (**II**); R = Me, R' = $ClCH_2$ (**III**); R = Me, R' = Vin (**IV**); R = Me, R' = Ph (**V**)].

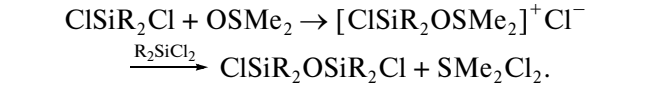
The yield of the target products is strongly affected by the ratio of the initial reactants. Thus, at the molar ratio $RR'SiCl_2$: DMSO = 1 : 1, the major reaction products are perorganylcyclosiloxanes. In the case of dichlorodimethylsilane,the reaction leads to permethylcyclosiloxanes (D_3–D_5) in yield 77, 16, and 7%, respectively. 1,3-Dichlorotetramethyldisiloxane forms only in trace amounts. At the molar ratio Me_2SiCl_2 : DMSO = 2 : 1 in the absence of solvent, the reaction leads to up to 10–17% of α,ω-dichloropermethyldisiloxanes $ClMe_2Si(OSiMe_2)_mCl$ (m = 1–3) along with permethylcyclosiloxanes.



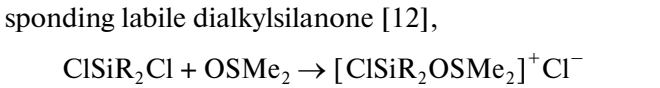
(m = 1–3, n = 3–6).

The use of solvents (diethyl ether, methylene chloride, hexane, etc.) substantially alters the reaction product composition. In particular, in a methylene chloride medium at the molar ratio Me_2SiCl_2 : DMSO = 2 : 1 DCSs form in yields 49 (m = 1), 28 (m = 2), 12 (m = 3), and 5% (m = 4), respectively, along with 6% of octamethylcyclotetrasiloxane. At the molar ratio Me_2SiCl_2 : DMSO = 3 : 1 in the absence of a solvent, the yield of DCS is 73 (m = 1), 19 (m = 2), and 8% (m = 3), respectively, while at the molar ratio 4 : 1, the yield is roughly constant: 78 (m = 1), 16 (m = 2), and 6% (m = 3), respectively. The excess of diorganyldichlorosilane suppresses the cyclosiloxane formation; therefore, organylcyclosiloxanes $(RR'SiO)_n$ form in trace amounts.

One could suppose that DCS formation is a result of consecutive reactions

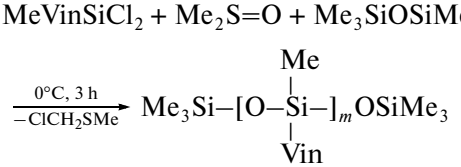


However, it must be admitted that the major intermediate product of the studied reaction is the corresponding labile dialkylsilanone [12],



which further undergoes insertion into diorganyldichlorosilane at the Si–Cl bond

The reaction of methyl(vinyl)dichlorosilane with dimethyl sulfoxide (at the molar ratio 4 : 1) in a hexamethyldisiloxane medium provides the direct evidence of this assumption. The major reaction products are 3-vinylheptamethyltrisiloxane, 3,5-divinyloctamethyltetrasiloxane, and 3,5,7-trivinylnonamethylpentasiloxane in 71, 23, and 6% yield, respectively. α,ω-Dichloromethyl(vinyl)siloxanes and methyl(vinyl)cyclosiloxanes were detected only in trace amounts.



(m = 1–3).

Methyl chloromethyl sulfide and dimethyl sulfide (its formation is observed in the presence of solvents and with an increase in the molar amount of diorganyldichlorosilane in mixture) were removed with excess diorganyldichlorosilane by vacuum distillation.

EXPERIMENTAL

Dimethyl sulfoxide was kept over KOH pellets, decanted, frozen, and distilled in a vacuum. Initial diorganyldichlorosilane and hexamethyldisiloxane were purified by rectification on a column.

The mass spectra of previously described $(Me_2SiO)_n$ (n = 3–6), $(MeVinSiO)_n$ (n = 3–6), $(MePhSiO)_n$ (n = 3, 4), $[Me(ClCH_2)SiO]_n$ (n = 3–6) [13], $ClMe_2Si(OSiMe_2)_nCl$ (n = 1–3) [14], $ClMeVinSi(OSiMeVin)_nCl$ (n = 1–3), and $Me_3Si(OSiMeVin)_nOSiMe_3$ (n = 1–3) [15] are not given.

The ^1H, ^{13}C, and ^{29}Si NMR data for the obtained α,ω-dichloro-1,1,3,3-tetraorganyldisiloxanes ClRR'Si–O–SiRR'Cl (R = H, Me; R' = Me, Et, $ClCH_2$, Vin, Ph) are presented in the table.

^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DRX-400 spectrometer (operating at 400.13, 100.61, and 79.5 MHz, respectively) in $CDCl_3$ using TMS as an internal reference. Mass spectra were recorded on a Shimadzu GCMS-QP5050A chromatograph–mass spectrometer, injector temperature of 200–250°C, helium as a carrier gas, detector temperature of 200°C, quadrupole mass analyzer, and electron ionization at an ionizing voltage of 70 eV. IR spectra were recorded as thin films on a Specord IR-75 spectrophotometer in the range 400–4000 cm^{-1}.

1,3-Dichloro-1,1,3,3-tetramethyldisiloxane (I). Dimethyl sulfoxide (4.84 g, 0.06 mol) was added dropwise to 32 g (0.25 mol) of cooled dichlorodimethylsilane (0°C) in 60 min. The reaction mixture was magnetically stirred at ambient temperature until complete dissolution of a colorless precipitate for 2 h. Vacuum distillation afforded 9.8 g (78%) of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane with bp 35–37°C (20 mmHg) (lit. [9]: bp 135.3°C (738 mmHg)).

For $C_4H_{12}Cl_2OSi_2$ anal. calcd. (%): C, 23.64; H, 5.95; Cl, 34.89; Si, 27.64.

Found (%): C, 23.34; H, 5.70; Cl, 35.24; Si, 27.29.

1,5-Dichlorohexamethyltrisiloxane (2.5 g, 15%) was also isolated, bp 60–63°C (20 mmHg) (lit. [9]: bp 178°C (738 mmHg)).

For $C_6H_{18}Cl_2O_2Si_3$ anal. calcd. (%): C, 25.98; H, 6.54; Cl, 25.56.

Found (%): C, 26.33; H, 6.16; Cl, 25.84.

1,3-Dichloro-1,3-diethyldisiloxane (II) (76%) was obtained in a similar manner, bp 38–39°C (5 mmHg) (lit. [6]: bp 81–82°C (70 mmHg)).

For $C_4H_{12}Cl_2OSi_2$ anal. calcd. (%): C, 23.64; H, 5.95; Cl, 34.89; Si, 27.64.

Found (%): C, 23.87; H, 6.18; Cl, 35.16; Si, 27.44.

NMR parameters of α,ω-dichloroorganyldisiloxanes ClRR'Si–O–SiRR'Cl (R = Me, R' = Me (**I**); R = H, R' = Et (**II**); R = Me, R' = $ClCH_2$ (**III**); R = Me, R' = Vin (**IV**); R = Me, R' = Ph (**V**))

Compound	δ, ppm		
	^1H	^{13}C	^{29}Si
I	0.49 (s, 12H, CH_3)	3.83 (CH_3)	7.25
II	0.90–0.99 (CH_2) 1.04–1.11 (CH_3) 5.16 (s, Si–H)	10.79 (CH_2) 12.74 (CH_3)	–8.99
III	0.66 (s, 6H, CH_3) 2.90–3.01 (q, 4H, $ClCH_2$)	0.06 (CH_3) 29.44 ($ClCH_2$)	–3.31
IV	0.56; 0.57 (6H, CH_3) 5.98–6.13 (m, 6H, $CH=CH_2$)	3.21 (CH_3) 135.14–136.57 ($CH=CH_2$)	–7.56
V	0.70; 0.74 (6H, CH_3) 7.29–7.59 (m, 10H, C_6H_5)	2.74 (CH_3) 127.80; 130.55; 132.85; 134.26 (C_6H_5)	–5.95

MS (m/z (I_{rel}, %)): 201(8) $[M - H]^+$, 173(100) $[M - C_2H_5]^+$, 145(84) $[M - 2C_2H_5 + H]^+$, 109(22) $Cl(C_2H_5)HSiO^+$.

1,3-Dichloro-1,3-bis(chloromethyl)-1,3-dimethyldisiloxane (III) (72%) was obtained at –40°C, bp 98–100°C (7 mmHg).

For $C_4H_{10}Cl_4OSi_2$ anal. calcd. (%): C, 17.65; H, 3.70; Cl, 52.12; Si, 20.64.

Found (%): C, 17.85; H, 3.95; Cl, 51.72; Si, 20.52.

1,3-Dichloro-1,3-dimethyl-1,3-divinyldisiloxane (IV) (74%), bp 64–65°C (7 mmHg) (lit. [6]: bp 61–63°C (0.9 mmHg)).

For $C_6H_{12}Cl_2OSi_2$ anal. calcd. (%): C, 31.72; H, 5.32; Cl, 31.20; Si, 24.72.

Found (%): C, 31.92; H, 5.03; Cl, 31.60; Si, 24.55.

1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisiloxane (V) (91%) bp 201–205°C (20 mmHg) (literature data [5]: bp 154°C (4 mmHg)).

For $C_{14}H_{16}Cl_2OSi_2$ anal. calcd. (%): C, 51.37; H, 4.93; Cl, 21.66; Si, 17.16.

Found (%): C, 51.56; H, 5.05; Cl, 21.32; Si, 17.06.

MS (m/z (I_{rel}, %)): 326(49) $[M]^+$, 311(100) $[M - Me]^+$, 291(4) $[M - Cl]^+$, 275(57), 249(3) $[M - C_6H_5]^+$, 233(40), 215(13) $[M - Ph - Cl + H]^+$, 195(17), 175(9), 155(9), $PhMeSiCl^+$, 137(6), 130(11), 113(3), 91(16) $C_6H_5CH_2^+$, 77(6) $C_6H_5^+$.

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