Synthesis of Heterocyclic Organosilicon Di- and Polyfunctional Compounds

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INTRODUCTION

The present state of the synthesis of cyclic organosiloxanes and organocarbosiloxanes with assigned disposition of various functional groups is reviewed.

Organosilicon monomers containing functional groups at silicon atoms are extremely inclined to various reactions of transformation, which produce $\equiv$Si—O—Si$\equiv$ bonds.[1] At the present time, the most practically significant organosilicon polymers are industrially produced from organochlorosilanes of various functionalities.[2] To carry out directed synthesis of oligomers and block-copolymers with cyclic and polycyclic fragments in the macromolecular backbone, methods of linear di- and polyfunctional oligochlororganosiloxanes synthesis have been developed,[3,4] on the basis of which organocyclosiloxanes with the given disposition of chlorine atoms and other functional groups at atoms of silicon may be derived.

ORGANOCYCLOSILOXANES WITH GIVEN DISPOSITION OF FUNCTIONAL GROUPS AT ATOMS OF SILICON

Synthesis of organocyclosiloxanes with different disposition of functional groups at atoms of silicon is mainly reduced to two methods: hydrolytic condensation of chlorine-containing organosilanes and alkoxyorganosilanes and heterofunctional condensation reaction (HFC) of silanes with siloxanes containing functional chlorine-, alkoxy-, amino, and hydroxyl groups or to modification of previously prepared organocyclosiloxanes.

Hydrolytic condensation of dibutoxydichlorosilane in the presence of hydrogen chloride acceptor (tertiary amine) was used for synthesizing organocyclosiloxanes with butoxyl groups.[5,6] Similarly, hydrolytic condensation of diethoxydichlorosilane proceeds in the presence of pyridine.[7] Partial hydrolytic condensation of tetraethoxysilane and hexaethoxydisiloxane[8,9] induces the formation of organocyclosiloxanes with ethoxy groups at silicon atoms.

Hydrolytic condensation of alkylalkoxydichlorosilanes in the presence of pyridine also produces organocyclosiloxanes containing, besides alkoxy groups, alkyl ones at silicon atoms.[10,11]

Joint reactions of $SiCl_4$ etherification and hydrolytic condensation with isopropyl alcohol produce organocyclosiloxanes with isopropyloxy groups at silicon atoms.[12]

Joint hydrolytic condensation between dimethyldichlorosilane and methylalkoxydichlorosilanes in the presence of pyridine has produced organocyclosiloxanes with two alkoxy groups at different silicon atoms (Scheme 1).[13]

Hydrolytic cocondensation between diphenyldichlorosilane and phenyltrichlorosilane at 1 : 4 molar ratios of the initial components produces hydroxypentaphenylcyclotrisiloxane and 1,5-dihydroxyhexaphenylcyclotetrasiloxane (Scheme 2).[14]

However, it should be noted that the yield of individual phenylcyclosiloxanes is negligible.
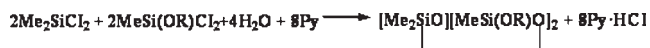
Joint hydrolysis of dimethyldichlorosilane and methylvinyldichlorosilane produced divinylhexamethylcyclotetrasiloxane.[15] Despite the application of efficient rectification towers as well as analytical chromatograph with preparative attachment, the authors have not managed to separate isomeric 1,3- and 1,5-divinylhexamethylcyclotetrasiloxanes, which may be produced by joint hydrolysis. The reaction proceeds in accordance with Scheme 3.

In accordance with the scheme as follows,[16] 1-hydride-3-vinylhexamethylcyclotetrasiloxane was synthesized in cohydrolysis reaction between 1,3-dichlorotetramethyldisiloxane and 1,3-dichloro-1-hydro-3-vinyldimethyldisiloxane (Scheme 4).
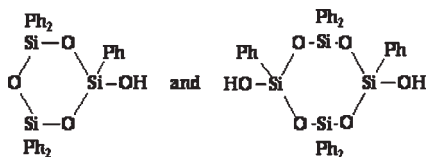
Hydrolytic condensation of phenyltrichlorosilane in aqueous solution of acetone, in acidic medium has

$$2Me_2SiCl_2 + 2MeSi(OR)Cl_2 + 4H_2O + 8Py \longrightarrow [Me_2SiO][MeSi(OR)O]_2 + 8Py \cdot HCl$$

Scheme 1 Hydrolytic condensation between dimethyldichlorosilane and methylalkoxy-dichlorosilanes in the presence of pyridine.

Scheme 2 Structure of obtained products during hydrolytic cocondensation between diphenyl-dichlorosilane and phenyltrichlorosilane at 1:4 molar ratios of the initial components.
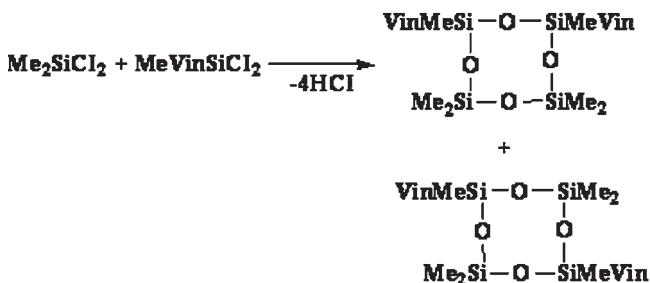
Scheme 3 Joint cohydrolysis of dimethyldichlorosilane and methylvinyldichlorosilane.

synthesized cis-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenyl-cyclotetrasiloxane (tetrole) with high yield.[17] Scheme 5 shows how the reaction proceeds.

Later on, mutual configurative transformations of four stereoisomers of tetrole were detected. These stereoisomers are shown in Scheme 6.

It has been shown[18] that isomerization of tetrasiloxane ring may proceed both with reversal of silicon atoms configuration and without it.

Tetrole-like compounds were also synthesized by hydrolytic condensation of (b-phenyl)phenethyltrichlorosilane, stilbene trichlorosilane, and (α-phenyl)phenethyltrichlorosilane.[19]

At 20–50°C in acetone, partial hydrolytic condensation of 1,1,3,3-tetrachloro-1,3-diphenyldisiloxane[20] proceeds with 20% yield of cyclotetraandcyclohexasiloxane products, [PhClSiO]₄ and [PhClSiO]₆. Low yield
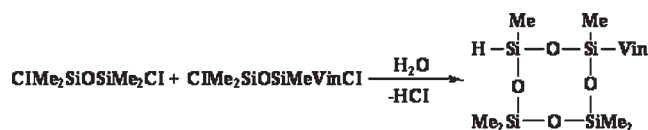
Scheme 4 Cohydrolysis reaction between 1,3-dichlorotetramethyldisiloxane and 1-chloro-3-chloro-3-vinyltetramethyldisiloxane.
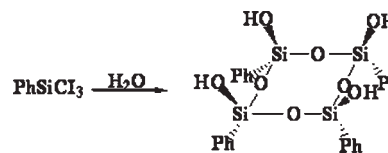
Scheme 5 Hydrolytic condensation of phenyltrichlorosilane in aqueous solution of acetone, in acidic medium.
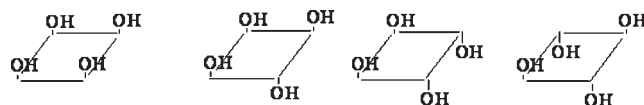
Scheme 6 Mutual configurative transformations of four stereoisomers of tetrole.

of cyclic products is explained by formation of a significant quantity of linear products.

Besides 1,5-dimethyl-1,5-divinyl-3,3,7,7-tetraphenylcyclotetrasiloxane, the interaction between equimolar amounts of diphenylsilanediol and methylvinyldichlorosilane also synthesizes 1,3-dimethyl-1,3-divinyl-5,5-diphenylcyclotrisiloxane, 1-methyl-1-vinyl-3,3,5,5-tetraphenyltrisiloxane, and high-molecular products in accordance with Scheme 7.[21]

HFC reaction is more suitable for synthesizing organocyclosiloxanes with functional groups at silicon atoms. High yields of organocyclosiloxanes with a single functional group are produced in double replacement reaction of disodium salts of dimethylsiloxanes with ethylbutoxydichlorosilane,[14] methylbutoxydichlorosilane,[22] and methyltrichlorosilane.[23]

The HFC reaction between 1,1,3,3-tetrachlorodiphenyldisiloxane and dihydroxydiorganosilanes in the presence of hydrogen chloride acceptor causes the formation of 1,3-dichlorotetraorganocyclotrisiloxanes[24] in accordance with Scheme 8.
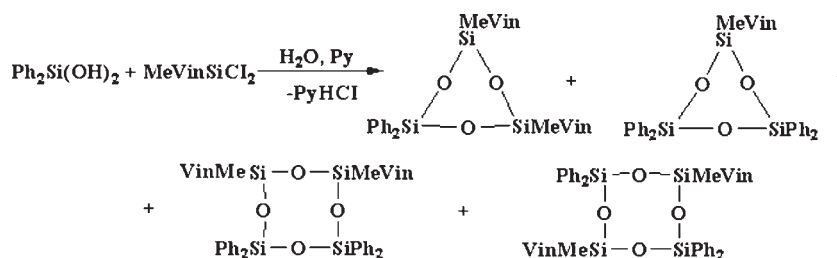
Scheme 7 HFC of equimolar amounts of diphenylsilanediol and methylvinyldichlorosilane.
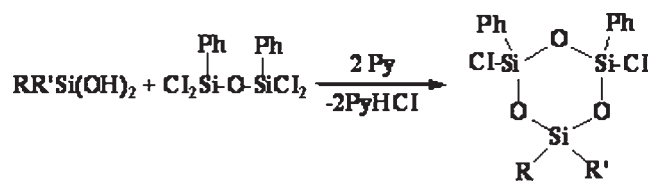
Scheme 8 HFC reaction between 1,1,3,3-tetrachlorodiphenyldisiloxane and dihydroxydiorganosilanes in the presence of pyridine. R = R' = Ph, p-CH₃C₆H₅; R ≠ R'; R = Ph, R' = Me.
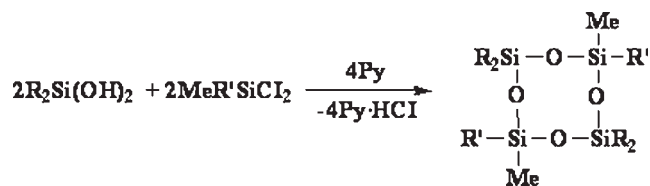
Scheme 9 Condensation reactions of dihydroxydiphenylsilane or dihydroxydimethylsilane with methylvinyldichlorosilane and methyldichlorosilane. R = Me, Ph, Et; R' = Vin, H.
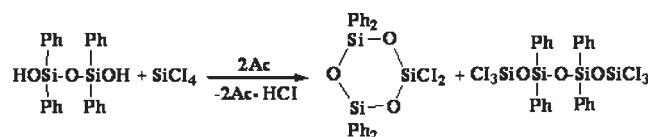
Scheme 10 HFC reaction of 1,3-dihydroxytetraphenylsiloxane with silicon tetrachloride.

Hydrolysis of synthesized 1,3-dichlorotetraorganocyclotrisiloxanes has produced appropriate dihydroxy derivatives.

Condensation reactions of dihydroxydiphenylsilane or dihydroxydimethylsilane with methylvinyldichlorosilane and methyldichlorosilane[25,26] in the presence of pyridine (1 : 1 molar ratio of the initial components) have given high yields of organocyclotetrasiloxanes with 1,5-disposition of functional groups at silicon atoms. The reaction proceeds as shown in Scheme 9.

The study of HFC reaction of 1,3-dihydroxytetraphenylsiloxane with silicon tetrachloride at equimolar ratio of the initial components has indicated[27] that besides organocyclosiloxanes, linear polyfunctional organosiloxane are also produced in accordance with Scheme 10.

The yield of linear products is increased with the quantity of silicon tetrachloride. In a similar manner, equimolar HFC reaction of silicon tetrachloride with 1,3-dihydroxy-1,3-divinyl-1,3-diphenyldisiloxane has been studied.[27]

The HFC reaction of 1,3-dihydroxytetraphenyldisiloxane or 1,5-dihydroxyhexaphenyltrisiloxane with organochlorosilanes at 1 : 3 ratio of initial components in anhydrous toluene solution at −5°C in the presence of pyridine under the above-mentioned conditions

proceeds ambiguously, and besides linear organochlorosiloxanes, the yield of which equals 70–87%, organocyclotrisiloxanes and organocyclotetrasiloxane are also produced in low amounts (4–6%). As a consequence, the reaction proceeds in accordance with the Scheme 11.[28,29]

The HFC reaction between methyldichlorosilane, dihydroxydimethylsilane and dihydroxytetra(hexa)methyldi(tri)siloxane at 1 : 1 molar ratio of initial components in the presence of acceptor (amine) mainly proceeds with formation of linear tetrachlororganosiloxanes[30] (Scheme 12).

The same investigators[31] have also obtained linear tetrachloroethylsiloxanes and cyclic ethylsiloxanes by the HFC reaction of ethyltrichlorosilane with dihydroxydiethylsilane or 1,3-dihydroxytetraethyldisiloxane in chlorosilane excess.

The HFC reaction of dihydroxydiorganosilanes disodium salts with organochlorosilanes causes the formation of linear, cyclic, and star-shaped siloxanes.[32–35]

Investigation of the HFC reaction between 1,3-dihydroxy-1,3-dimethyl-1,3-diphenyldisiloxane and 1,5-disodiumoxyhexamethyltrisiloxane and silicon tetrachloride, methyl- and phenyltrichlorosilanes has displayed that with regard to the ratio of initial components both linear and cyclic compounds may be produced. The yield of linear reaction products is increased with excess of chlorosilanes in the primary
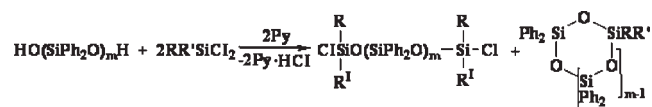

Scheme 11 HFC reaction of 1,3-dihydroxytetraphenyldisiloxane and 1,5-dihydroxyhexaphenyltrisiloxane with organochlorosilanes at 1 : 3 ratio of initial components. m = 2, 3; R = Ph, Me, Vin, Cl; R' = Cl, H, Vin.
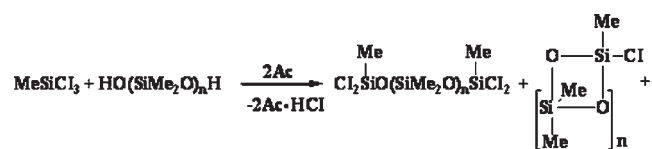

Scheme 12 HFC reaction between methyldichlorosilane, dihydroxydimethylsilane and dihydroxytetra(hexa)methyldi(tri)siloxane. n = 1, 2, 3.
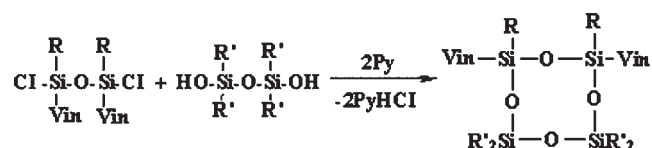
Scheme 13 HFC reaction of 1,3-dihydroxyorganodisiloxanes with 1,3-dichlororganodisiloxanes in the presence of pyridine. R = R' = Me, Ph; R ≠ R'.
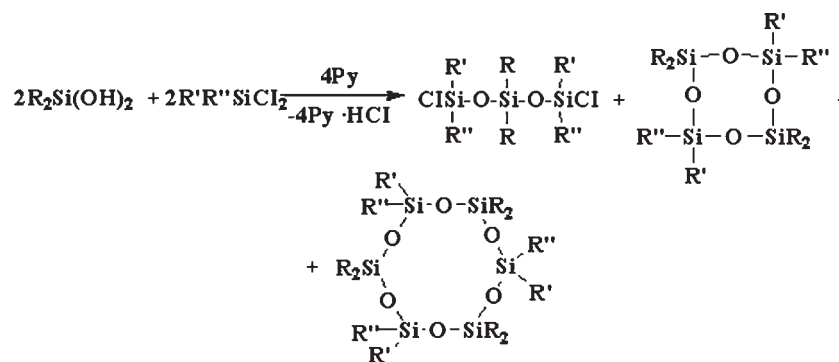
Scheme 14 HFC reaction of dihydroxydiphenylsilane with organochlorosilanes. R = Me, Ph, Et; R′ = Me, Ph, Et, CI, Vin; R″ = CI, H, Vin.
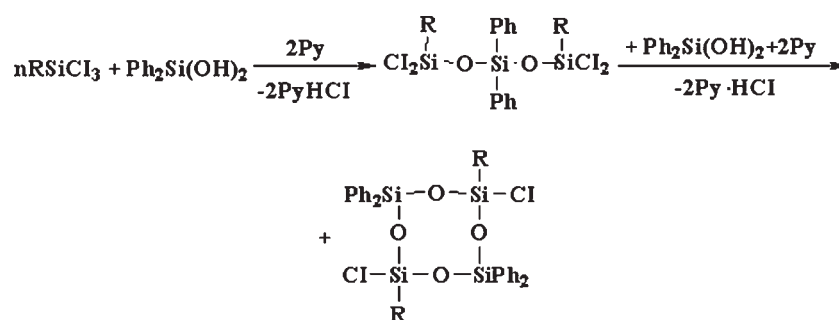
Scheme 15 Synthesis of organocyclosiloxanes by two stage HFC reaction. R = Me, Ph, CI.

reaction mixture, and the yield of cyclic compounds is decreased.

Divinyl- and dihydride-containing organocyclosiloxanes with different disposition of functional groups at silicon atoms were synthesized by the HFC reaction of 1,3-dihydroxyorganodisiloxanes with 1,3-dichlororganodisiloxanes in the presence of pyridine in accordance with Scheme 13.[25,36]

By analogy, heterofunctional condensation of dihydroxydiphenylsilane with methyltrichlorosilane,[36,37] silicon tetrachloride,[38] and phenyltrichlorosilane,[39,40] as well as between diethyldihydroxysilane and ethylvinyldichlorosilane and ethyldichlorosilane, proceeds at equimolar (1 : 1) ratio of the initial components, in the presence of pyridine. The yield of target products with 1,5-disposition of chlorine atoms at silicon ones is varied from 41 to 55% (Scheme 14).

As shown in the earlier scheme, besides isomeric organocyclosiloxanes, linear tetrachlororganotrisiloxanes are also synthesized with the yield of 15–20%. For methyl-containing organocyclotetrasiloxanes, two singlet signals with almost equal peak ratio (53–47%) at 0.38 and 0.42 ppm have been detected in ^{1}H-NMR spectra. These ranges are typical of cis- and transforms of methyl groups. Shift for methyl protons to a weak field testifies about the electron acceptor type of functional groups at the same silicon atom, where methyl groups are disposed. To increase the yield of

organocyclosiloxanes with 1,5-disposition of chlorine atoms at silicon ones, the two-stage synthesis method was suggested.[41,38,40] At the first stage, HFC of dihydroxydiphenylsilane with excess of organotrichlorosilane is carried out. At the second stage, HFC of obtained tetrachloroorganotrisiloxanes with dihydroxydiphenylsilane proceeds (Scheme 15).

It is shown[42] that depending on the ratio of initial reagents, diorganodiaminosilanes mixed with diorganodichlorosilanes interact with diphenylsilanediol giving cyclic or linear siloxanes. The yield of mixed cyclotetrasiloxanes is quantitative and almost independent of the type of framing at silicon atoms in amino- and chlorosilanes. Trisiloxane is synthesized
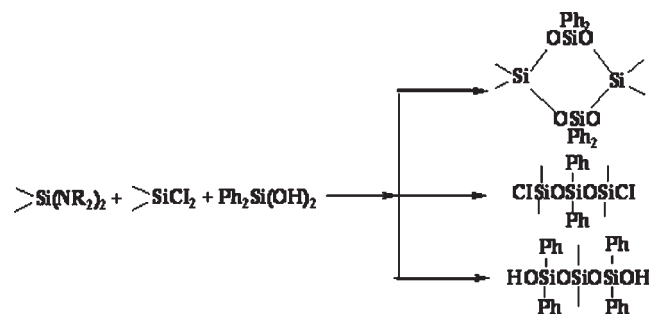

Scheme 16 HFC reaction of diorganodiaminosilanes mixed with diorganodichlorosilanes with diphenylsilanediol.
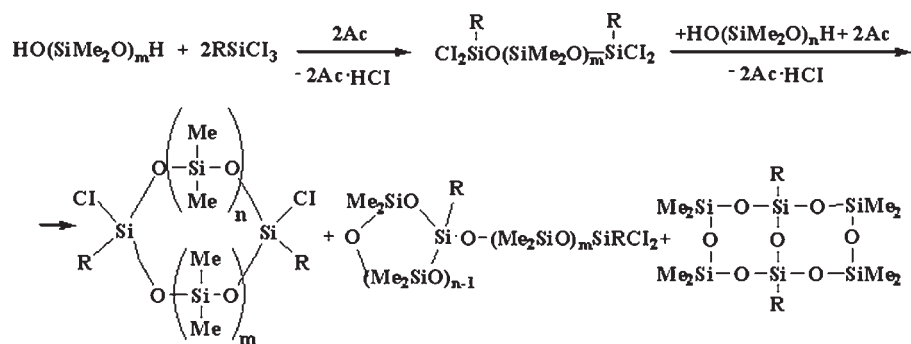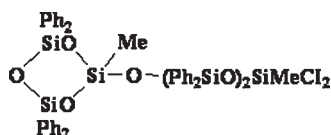
Scheme 17 Synthesis of methylcyclosiloxanes with given disposition of functional groups at silicon atoms, by two-stage HFC reaction. $m = n = 1, 2, 3$; $m \neq n$; R = Me, Ph.
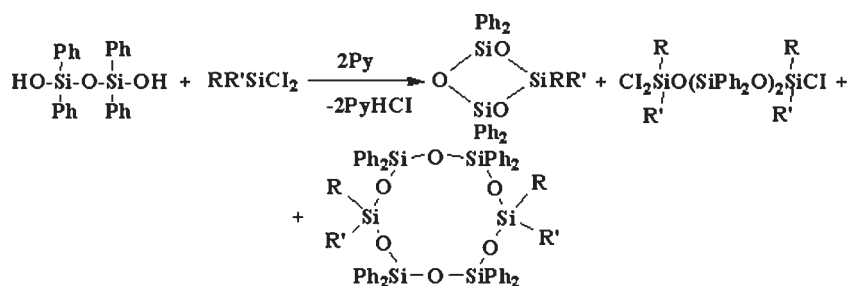
Scheme 18 HFC reaction of organodichlorosilanes or organotrichlorosilane with 1,3-dihydroxytetraphenyldisiloxane. R = Me, Ph, Cl; R' = Cl, Vin, H.
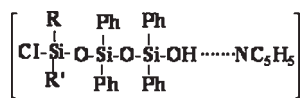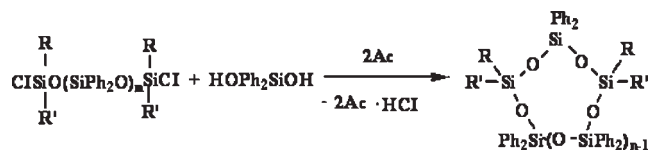

Scheme 19 Transient complex with pyridine.

Scheme 20 Structural isomer of 1,7-dichloro-1,7-dimethyloctapenylcyclohexasiloxane.

Scheme 21 HFC reaction of tetrachloro- or dichlororganotetrasiloxanes with dihydroxydiphenylsilane or 1,3-dihydroxytetraphenyldisiloxane. $n = 1, 2$; R = Me, Ph; R' = Cl, H, Vin.

Scheme 22 HFC reaction of hexa(tetra, di)chlororganotetra(penta)siloxanes with dihydroxydiphenylsilane. $n = 2, 3$; R = Me, Ph, Cl; R' = Cl, H, Vin.

with lower yield (~70%) due to a noticeable formation of secondary products, which are long-chain α,ω-dichlorosiloxanes.
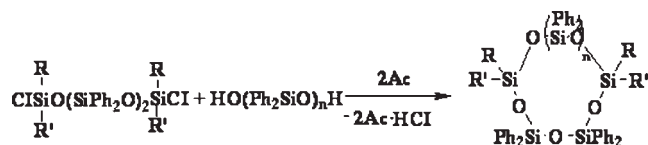
Formation of long-chain siloxanes is much more typical of the condensation reaction proceeding with dihydroxydiphenylsilane excess. In this case, the yield of trisiloxane does not exceed 50%. The reaction proceeds as shown in Scheme 16.

For obtaining high yields of synthesized methylcyclosiloxanes with given disposition of functional groups at silicon atoms, the two-stage synthesis was suggested[31,43,44] in accordance with Scheme 17.

Two-stage reaction proceeding resulted in the yield of organocyclotetra(penta, hexa)siloxanes equal 28–51%. The ratio of dichlorocyclosiloxane isomers was

monitored by NMR and mass-spectrometry methods. Basically, dichlororganocyclosiloxanes of 96.0–99.5% purity were produced. Separation of dichlororganocyclotetra(penta, hexa)siloxanes to stereoisomers was made and majority dichlororganocyclotetra(hexa)siloxanes are separated to cis- and trans-isomers. All attempts to separate stereoisomers of dichloroctaorganocyclopentasiloxane and dichlorododecaorganocycloheptasiloxane to cis- and trans-isomers have failed. Hydrolysis and aminolysis of dichloromethylcyclote-
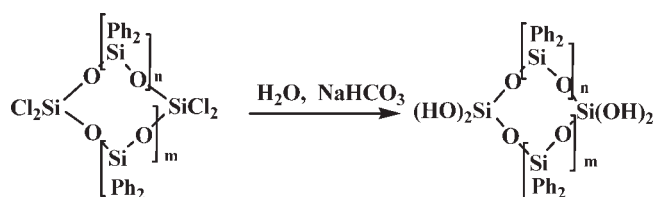
Scheme 23 Hydrolysis reactions of tetrachlororganocyclotetra(penta, hexa)siloxanes.
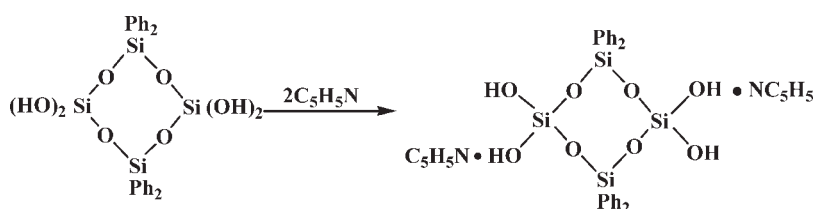
Scheme 24 Complex of 1,1,5,5-tetrahydroxytetraphenylcyclotetrasiloxane with pyridine.

tra- (penta, hexa, hepta, octa)siloxanes proceeding in the presence of hydrogen chloride acceptors have produced corresponded dihydroxy- and diaminomethylcyclosiloxanes. Inversion of isomers configuration during hydrolysis was separation methylcyclosiloxane dihydroxy-derivatives to cis- and trans-isomers was performed for 1,5-dihydroxyhexamethylcyclotetrasiloxane and 1,7-dihydroxydecamethylcyclohexasiloxane by recrystallization from heptane; under similar conditions, the rest hydroxy derivatives cannot be separated. X-ray diffraction studies of the crystalline structure of 1,5-dihydroxydecamethylcyclohexasiloxane cis- and trans-isomers show that $\equiv$Si—O—Si$\equiv$ bond angle in cis-isomers displays two values: 145.7°–150.2° and 173.6°–174.1°. The ring is tub-shaped with silicon atoms in the hydroxyl group distant from the middle atom plane by 0.96–0.98 Å. This allows OH-groups in cis-isomers forming intra- and intermolecular hydrogen bonds.[45]

In the range of 3200–3800 cm^{-1} typical of valence oscillations of OH groups, IR spectra of dihydroxymethylcyclo(tetra, hexa)siloxanes, mold with KBr and in CCl$_4$ solutions of various concentration display the absence of a broad absorption band at 3300–3500 cm^{-1}, which is present in spectra of all dihydroxymethylcyclosiloxanes mold with KBr, and the presence of a narrow band at 3700 cm^{-1} typical of hydroxyl group with intermolecular hydrogen bonds, which confirms separation of pure trans-isomer of dihydroxymethylcyclosiloxanes. For cis-isomers, IR spectra of diluted solution possess two bands: a broad one in the range of 3300–3500 cm^{-1} typical of intramolecular hydrogen bond and a narrow one at 3700 cm^{-1}.

Based on ^{1}H-NMR spectra, chemical shifts and multiplicity of methyl protons of chloro(hydroxy)-substituted methylcyclotetra(penta, hexa)siloxanes were studied.[46]

By similar two-stage HFC method, difunctional methyl (ethyl)cyclotetra(penta, hexa)siloxanes with defined disposition of chlorine, hydride, or vinyl groups at silicon atoms were produced.[47,48]
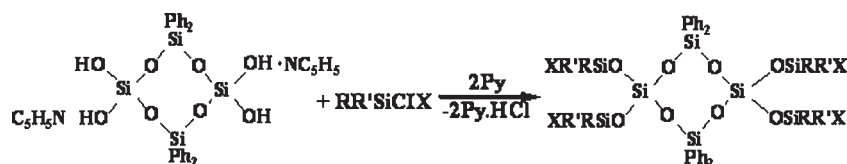
HFC reaction of organodichlorosilanes or organotrichlorosilane with 1,3-dihydroxytetraphenyldisiloxane under usual conditions (equimolar (1 : 1) ration of initial reagents, presence of hydrogen chloride acceptor—pyridine, diluted toluene solution, 0–5°C temperature range) mainly produces both linear organochlorosiloxanes and cyclic compounds. The presence of linear organochlorosiloxanes, the content of which in the reaction mixture did not exceed 6%, was confirmed by GLC analysis. The reaction proceeds as shown in Scheme 18.[49,50]

To the authors' point of view, similar to the case described in Ref. 51, the reaction proceeds with the formation of a transient formation (Scheme 19), which is then subject to intramolecular condensation, producing a hexatomic rings and intermolecular condensation with further cyclization of condensation products. The latter leads to the formation of dodecatomic rings and higher boiling products. The study of NMR spectrum of 1,7-dichloro-1,7-dimethyloctapenylcyclohexasiloxane has indicated that HFC reaction of 1,3-dihydroxytetraphenyldisiloxane produces cyclohexasiloxane and its structural isomer (Scheme 20).

A singlet at 0.27 ppm is corresponded to methyl group of methyldichlorosiloxy-fragment; for methyl protons in silsesquioxane unit, a singlet at 0.46 ppm is
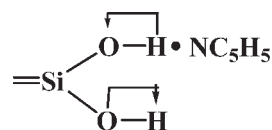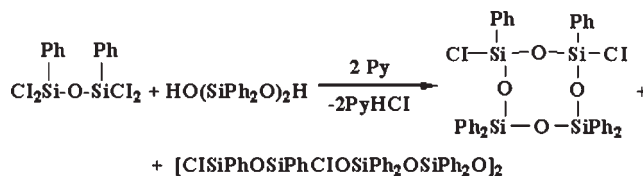

**Scheme 25** Redistribution of electron density in the complex.

Scheme 26 HFC reaction of dipyridine-1,1,5,5-tetrahydroxytetraphenylcyclotetrasiloxane with diorganodichlorosilanes or diorganoethoxychlorosilanes. R = Me, R' = Me, Ph; X = Cl, OEt.
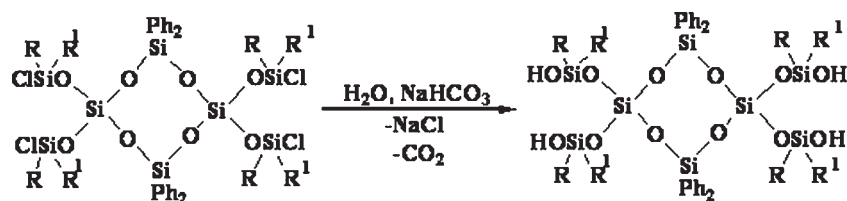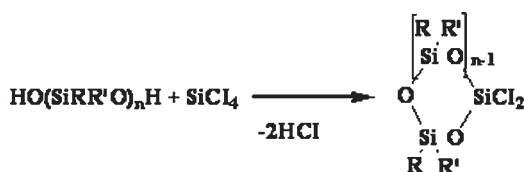

Scheme 27 Hydrolysis of tetrachlorine-containing branched cyclic compounds. R = R_1 = Me, Ph; R ≠ R_1.


Scheme 28 HFC reaction of 1,1,3,3-tetrachlorodiphenyldisiloxane with 1,3-dihydroxy-tetraphenyldisiloxane at 1 : 1 molar ratio of initial components.
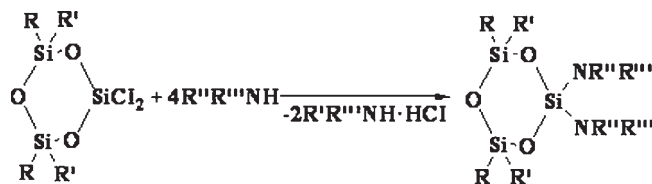
Scheme 30 Aminolysis reaction of 1,1-dichlorotetraorganocyclotrisiloxanes. R = Me, Et; R″ = R‴ = H, Me, Et; R″ ≠ R‴.

Scheme 29 HFC reactions of 1,3-dihydroxytetraorganodi- and xytetraorganodi- and 1,5-dihydroxyhexaorganotrisiloxanes with silicon tetrachloride in the presence of amine. n = 1, 2; R = R' = Me, Ph; R ≠ R'.
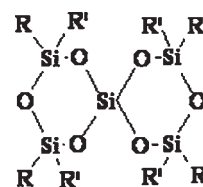
Scheme 31 Structure of spirocyclosiloxanes. R = R' = Me, Ph; R ≠ R'.

also observed. Two singlets at 0.38 and 0.41 ppm, corresponded to two methyl groups of cis- and transforms, respectively, are observed in spectra. After recrystallization from toluene–heptane mixture, organocyclohexasiloxane product was purified from isomeric admixtures. The ratio of cis- and trans-isomers equaled 54% and 46%, respectively. Accordingly, after fractionation, HFC reaction products of organotrichlorosilanes and silicon tetrachloride with 1,3-dihydroxytetraphenyldisiloxane were recrystallized from the toluene–heptane mixture. HFC reaction of dichlorodiorganosiloxanes with 1,3-dihydroxytetraphenyldisiloxane did not produce isomeric products. At the single-stage synthesis, the yield of organocyclohexasiloxanes equaled 26–43%. HFC reaction of tetrachloro- or dichlororganotetrasiloxanes with dihydroxyophenylsilane or 1,3-dihydroxytetraphenyldisiloxane under usual conditions (at equimolar ratio of initial components, in the presence of pyridine, in diluted anhydrous toluene solution) produced organocyclopenta- and organocyclohexasiloxanes with 1,5- and 1,7-disposition of chlorine atoms at silicon (Scheme 21).[52–55]

By HFC reaction of hexa(tetra, di)chlororganotetra(penta)siloxanes with dihydroxydiphenylsilane under usual conditions (in the presence of pyridine, at equimolar ratio of initial reagents, in diluted anhydrous toluene solution, in −5 to −0°C temperature range), high yields of difunctional organocyclopentasiloxanes and organocyclohexasiloxanes with 1,5-disposition of functional groups were obtained. Therefore, the yield of organocyclopenta(hexa)siloxanes is increased to 61–70% (Scheme 22).[53,56,57]

Hydrolysis of tetrachlororganocyclotetra(penta, hexa)siloxane proceeding in the presence of hydrogen chlo-

TABLE I
Physical and Chemical Parameters of Difunctional Organophenylcyclotri(tetra, penta, hexa)siloxanes
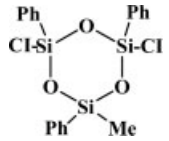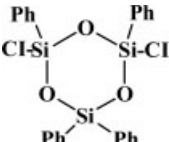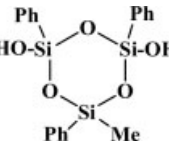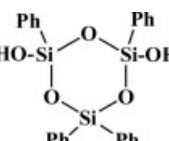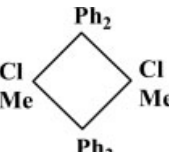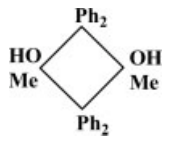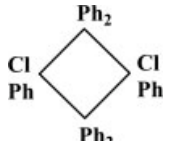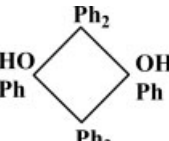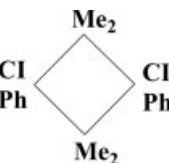
No	Compound	Yield (%)	T_{boil} (°C) (P, mmHg)	T_{melt} (°C)	[1]H(Me) chemical shift		Reference
					cis	trans	
1	Ph, Ph, Cl-Si, Si-Cl, O, O, O, Si, Ph, Me	26	136–137 (0.1)	–	–	–	[24]
2	Ph, Ph, Cl-Si, Si-Cl, O, O, O, Si, Ph, Ph	29	200–203 (0.001)	–	–	–	[24]
3	Ph, Ph, HO-Si, Si-OH, O, O, O, Si, Ph, Me	46	–	–	–	–	24
4	Ph, Ph, HO-Si, Si-OH, O, O, O, Si, Ph, Ph	47	–	–	–	–	24
5	Ph$_2$, Cl, Me, Cl, Me, Ph$_2$	20 (66)*	247–250 (0.02)	–	0.38	0.42	[36,37]
6	Ph$_2$, HO, Me, OH, Me, Ph$_2$	70	–	trans 141–142, cis 147–150	0.16	0.09	[37]
7	Ph$_2$, Cl, Ph, Cl, Ph, Ph$_2$	34.0 (65)	305–310 (0.02)	–	–	–	[37,65]
8	Ph$_2$, HO, Ph, OH, Ph, Ph$_2$	77	–	(mixture)	–	–	[37]
9	Me$_2$, Cl, Ph, Cl, Ph, Me$_2$	60	147–148 (0.5)	trans 116–117	0.42	0.29, 0.16	[44]

TABLE I *Continued*

No	Compound	Yield (%)	T_{boil} (°C) (P, mmHg)	T_{melt} (°C)	[1H(Me) chemical shift] cis	[1H(Me) chemical shift] trans	Reference
10	Me₂ / HO OH / Ph Ph / Me₂	70	–	*trans* 126–127	–	0.12	[44]
11	Ph₂ / Cl Cl / Me Me / Ph₂ Ph₂	48 (79)	222–224 (760)	(mixture)	0.51	0.55	[50,53]
12	Ph₂ / HO OH / Me Me / Ph₂ Ph₂	68	–	(mixture) 67–70	–	–	[50,53]
13	Ph₂ / Cl Cl / Ph Ph / Ph₂ Ph₂	62	310–320 (0.04)	–	–	–	[50,53]
14	Ph₂ / HO OH / Ph Ph / Ph₂ Ph₂	73	–	(mixture) 84–85	–	–	[50,53]
15	Ph₂ Ph₂ / Cl Cl / Me Me / Ph₂ Ph₂	43 (61)	325–330 (0.01)	(mixture) 59–61	0.38	0.41	[49,50,52]
16	Ph₂ Ph₂ / HO OH / Me Me / Ph₂ Ph₂	74	–	(mixture) 209–210	–	–	[49,50,52]
17	Ph₂ Ph₂ / Cl Cl / Ph Ph / Ph₂ Ph₂	29 (65)	337–340 (0.01)	(mixture) 62–64	–	–	[49,50,52]
18	Ph₂ Ph₂ / HO OH / Ph Ph / Ph₂ Ph₂	77	–	(mixture) 161–162	–	–	[49,50,52]

TABLE I *Continued*

No	Compound	Yield (%)	T$_{boil}$ (°C) (P, mmHg)	T$_{melt}$ (°C)	^{1}H(Me) chemical shift cis	trans	Reference
19		62 (65)	346–352 (0.01)	(mixture) 96–97	–	–	[28,29,50]
20		73	–	(mixture) 142–143	–	–	[28,29,50]
21		60 (65)	312–315 (0.01)	–	0.34	0.39	[28,29,50]
22		68	–	(mixture) 101–102	–	–	[28,29,50]

*Shown in parenthesis are yields obtained for the two-stage method.

ride acceptor is described in the literature.[41,29,58–61] It is found that hydrolysis proceeding at room temperature produces polyfunctional oligomers, which are transformed into structured products. However, as the reaction temperature was decreased to 0−5°C, in the presence of sodium bicarbonate, tetrahydroxy-derivatives were synthesized as shown in Scheme 23.

It is also found that 1,1,5,5-tetrahydroxytetraphenyl-cyclotetrasiloxane forms a stable structure with pyridine[59] (Scheme 24).

This was not observed for its isomer, *cis*-1,3,5,7-tetrahydroxytetraphenylcyclotetrasiloxane(tetrole).

It is assumed[62] that the structure formation is associated with increased acidity of hydrogen in hydroxyl groups, caused by interaction of *p*-electrons of oxygen atoms with silicon. Inertness of the second hydroxyl group to pyridine is explained by decrease of its acidity as a consequence of redistribution of electron density in the group (Scheme 25).

Dipyridine-1,1,5,5-tetrahydroxytetraphenylcyclotetrasiloxane structure enters HFC reaction with diorganodichlorosilanes or diorganoethoxychlorosilanes and forms corresponded tetrafunctional compounds (Scheme 26).

The above-mentioned reaction produces quite pure products and, consequently, their production does not require repeated fractionation, which is necessary for the case of HFC of tetrahydroxytetraphenyl-cyclotetrasiloxane with diorganodichloro- or diorganoethoxychlorosilanes.[62]

Hydrolysis of tetrachlorine-containing branched cyclic compounds with methyl and phenyl substituting agents at silicon atoms produced corresponded tetrahydroxy-derivatives[62,63] (Scheme 27).

Hydrolysis proceeds with the water excess at cooling, in the presence of hydrogen chloride acceptor (R = Me) or at room temperature without it (R = Ph).

HFC reaction of 1,1,3,3-tetrachlorodiphenyldisiloxane with 1,3-dihydroxytetraphenyldisiloxane at 1 : 1 molar ratio of initial components in the presence of pyridine synthesizes organocyclotetrasiloxane with 1,3-disposition of chlorine atoms at silicon with ∼50% yield, as well as a mixture of extended isomeric-structured rings. The reaction mainly proceeds in accordance with the Scheme 28.[37,64]

TABLE II
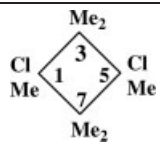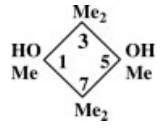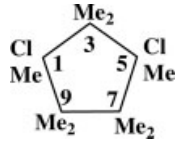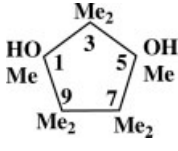**Physical and Chemical Parameters of Difunctional Ethylcyclosiloxanes**
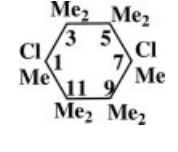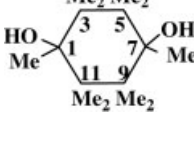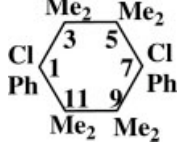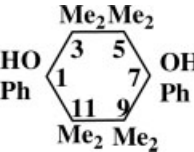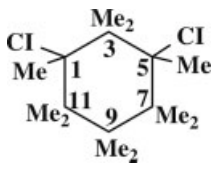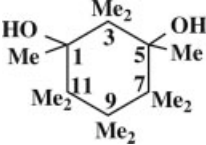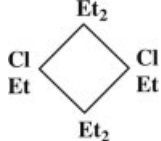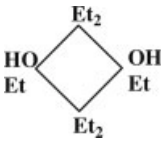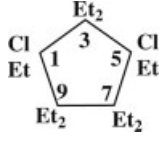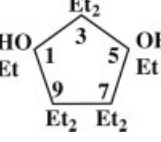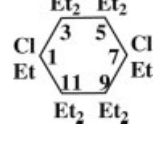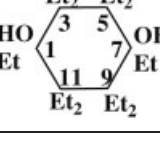
No.	Compound	Yield (%)	T_{boil} (°C) (P, mmHg)	T_{melt} (°C)	^{1}H(CH$_3$) chemical shift Number of Si atoms	cis	trans	Reference
1	Me$_2$ / Cl–Me, Cl–Me / Me$_2$ (positions 3,5,1,7)	50	201–203 (760)	–	1.5	0.461	0.449	[30]
					3.7a	0.170		
					0.296		0.230	
2	Me$_2$ / HO–Me, OH–Me / Me$_2$ (positions 3,5,1,7)	89	115–120 (4–5)	trans 119–121	1.5	0.065	0.067	[30]
							0.084	
					3.7a,b	0.119	0.099	
3	Me$_2$ / Cl–Me, Cl–Me / Me$_2$ Me$_2$ (positions 3,5,1,9,7)	48	222–224 (760)	–	1.5	0.428	0.433	[30]
					3a	0.161	0.213	
					3b	0.279		
					7.9a	0.124	0.140	
					7.9b	0.199	0.175	
4	Me$_2$ / HO–Me, OH–Me / Me$_2$ Me$_2$ (positions 3,5,1,9,7)	76	89–91 (3–4)	–	1.5	0.065	0.072	[30]
					3a	0.091	0.100	
					3b	0.127	0.100	
					7.9a	0.082	0.084	
					7.9b	0.110	0.108	
5	Me$_2$ Me$_2$ / Cl–Me, Cl–Me / Me$_2$ Me$_2$ (positions 3,5,1,7,11,9)	24	55–57 (1–2)	–6 to 8	1.7	0.422	0.428	[30]
					3.5a	0.129	0.140	
					9.11b	0.192	0.174	
6	Me$_2$ Me$_2$ / HO–Me, OH–Me / Me$_2$ Me$_2$ (positions 3,5,1,7,11,9)	93	–	trans 96–99 cis 36–38	1.7	0.065	0.083	[30]
					3.5,9.11a	0.096	0.090	
					3.5,9.11b	0.111	0.120	
7	Me$_2$ Me$_2$ / Cl–Ph, Cl–Ph / Me$_2$ Me$_2$ (positions 3,5,1,7,11,9)	cis 13 trans 15	175–177 (1–1.5)	– trans 90–92	3.5	0.267	0.192	[44]
						0.069	0.134	
8	Me$_2$ Me$_2$ / HO–Ph, OH–Ph / Me$_2$ Me$_2$ (positions 3,5,1,7,11,9)	cis 89 trans 90	– –	cis 87–88 trans 72–73	3.5	0.078	0.110	[88]
						0.115	0.130	
9	Me$_2$ / Cl–Me, Cl–Me / Me$_2$ Me$_2$ / Me$_2$ (positions 3,1,5,11,9,7)	25	82–84 (1–2)	–	3a	0.170		[30]
					3b	0.274	0.214	
					1.5	0.426	0.436	
					9a	0.085		
					9a	0.113	0.098	
					7.11a	0.123	0.130	
					7.11b	0.181	0.170	

TABLE II *Continued*

No.	Compound	Yield (%)	T_boil (°C) (P, mmHg)	T_melt (°C)	Number of Si atoms	cis	trans	Reference
						¹H(CH₃) chemical shift		
10		74	102–104 (0.03)	–	3a	0.106		[30]
					3b	0.136	0.110	
					1.5	0.074	0.086	
					7.11a	0.089	0.091	
					7.11b	0.125	0.119	
					9a	below the reflex	0.100	
					96	0.095		

The ¹H(CH₃) chemical shift header spans the cis and trans columns.

a and b indicate detected signals of nonequivalent methyl groups at silicon atoms.

TABLE III
Physical and Chemical Parameters of Difunctional Ethylcyclosiloxanes

No	Compound	Yield (%)	T_boil, °C (mmHg) T_melt °C	n_D^{20}	M⁺-C₂H₅ molecular mass	Si¹	Si²	Si³	Reference
						²⁹Si NMR spectrum (δ, ppm)			
1		63	113–115 (1–1.5)	1.4355	391 421.6	cis −43,14 trans −42,87	cis −15,45 trans −15,03	– –	[31]
2		80	32	–	– 384.7	cis 54,44 trans −55,53	cis −17,70 trans −18,60	– –	[31]
3		39	128–130 (1–2)	1.4385	493 5238	cis −45,78 trans −45,68	cis −17,71 trans −17,51	cis −19,25 trans −19,33	[31]
4		66	120–122 (0.02)	1.4400	– 486.9	cis −l56,46 trans −55,34	cis −18,42 trans −20,11	cis −21,08 trans −20,59	[31]
5		39	170–172 (1–2)	1.4425	595 626	cis −46,85 trans −46,90	cis −19,72 trans −19,81	– –	[31]
6		46	160–163 (0.02)	1.4420	– 589.1	–	–	–	[31]

*Slashed values indicate calculated values/recorded ones.

TABLE IV
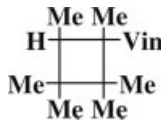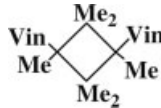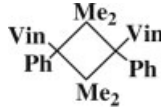**Physical and Chemical Parameters of Vinyl-Containing Organocyclosiloxanes**
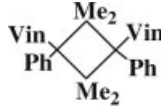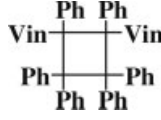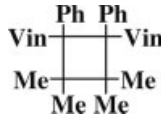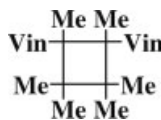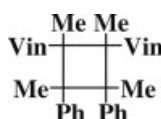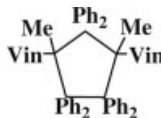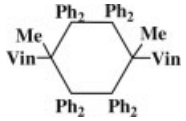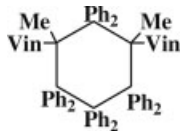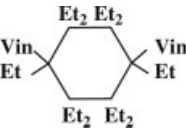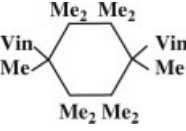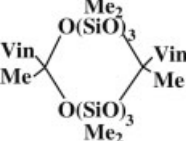
No.	Structural formula	Yield (%)	T_{boil} (°C) P (mmHg) T_{melt}, °C	n_D^{20}	d_4^{20}	MR_D^{**}	[1]H (ppm) (R) RXSi(O)(O~)	References
1	Me Me / H—Vin / Me—Me / Me Me	63	58–60 (8)	1.4017	0.9703	74.35 32.65	–	[16]
2	Vin, Me2, Vin / Me, Me / Me2	35	70–71 (11)	1.4166	0.9704	83.01 82.88	cis −0.146 trans-0.133 0.106 (Me2)	[25]
3	Ph Me / Vin Vin / Me Me / Ph Me	29	150–153 (1–2)	1.5000	1.0779	121.36 122.52	–	[25]
4	Me2 / Vin Vin / Ph Ph / Me2	35	137–138 (2)	1.5024	1.0700	122.75 122.52	–	[25]
5	Me2 / Vin Vin / Ph Ph / Me2	50	242–243 (1–2) 88–89	–	–	–	–	[25]
6	Ph Ph / Vin—Vin / Ph—Ph / Ph Ph	75	255–265 (2) 80–81	–	–	–	–	[26]
7	Ph Ph / Vin—Vin / Me—Me / Me Me	45	130–131 (2)	1.5017	1.0670	122.95 122.52	cis-0.15	[26]
8	Me Me / Vin—Vin / Me—Me / Me Me	66	87–88 (10)	1.4171	0.9719	82.96 82.88	cis-0.156 trans-0.141 0.09*(Me2)	[26]
9	Me Me / Vin—Vin / Me—Me / Ph Ph	29	150–153 (1–2)	1.5000	1.0970	–	–	[25]
10	Me Ph2 Me / Vin—Vin / Ph2 Ph2	50	255–260 (0.02) 152+153	–	–	–	cis 0.20 trans 0.22	[41,53,55]

TABLE IV *Continued*

No.	Structural formula	Yield (%)	T_{boil} (°C) P (mmHg) T_{melt}, °C	n_D^{20}	d_4^{20}	MR_D^{**}	^{1}H (ppm) (R) RXSi O/ O~	References
11		23 (62)	300–305 (0.02) 62–65	–	–	–	*cis* 0.20 *trans* 0.23	[53,56]
12		68	290–294 (0.02) 152+154	–	–	–	*cis* 0.17 *trans* 0.19	[29,57]
13		49	180–182 (1)	1.4443	–	–	0.45 q 0.85 t	[47]
14		64	83–85 (1–2)	1.4128	–	–	*cis* 0.157 *trans* 0.150	[47]
15		31	119–122 (2)	1.4139	–	–	*cis* 0.23 *trans* 0.25	[47]

* Slashed values indicate values/recorded ones.

Hydrolysis of 1,3-dichlorohexaphenylcyclotetrasiloxane has synthesized an appropriate dihydroxy-derivative.

HFC reactions of 1,3-dihydroxytetraorganodi- and 1,5-dihydroxyhexaorganotrisiloxanes with silicon tetrachloride in the presence of amine or hydrogen chloride blowing off the reaction mixture have synthesized 1,1-dichlorotetraorganocyclotri- and 1,1-dichlorohexaorganocyclotetrasiloxanes in accordance with the Scheme 29.[65,66]

The yield of cyclotrisiloxanes is decreased with the size of framing groups at silicon atoms in the initial disiloxane. Application of an acceptor gives better results compared with hydrogen chloride blowing, because in this case, the secondary reactions are noticeably eliminated and the yield of target cyclosiloxanes is increased. It has been shown that affinity of 1,3-dihydroxytetraorganodisiloxanes to homocondensation in HFC reactions increases with the decrease of the framing group size at silicon atoms, which results in reduction of the yield of
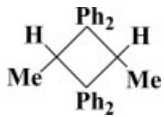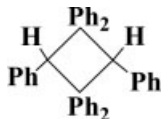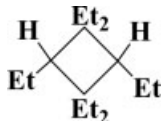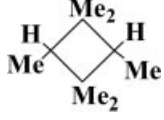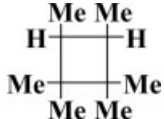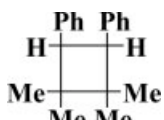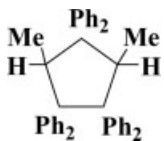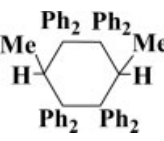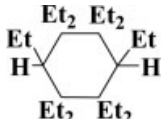
hex atomic organochlorocyclosiloxanes. For example, if at R = R′ = Ph the yield of 1,1-dichlorotetraphenylcyclotrisiloxane equals 62%, then at R = Me and R′ = Ph the yield of the appropriate cycle does not exceed 10%.

Hydrolysis of synthesized dichlororganocyclosiloxanes produces appropriate dihydroxy-derivatives. However, it has been found that hydrolysis of dichlororganocyclosiloxanes is not limited by the formation of dihydroxyorganocyclosiloxanes, because besides the main reaction, intermolecular condensation of the target product with formation of more complex cyclic structures does also proceed.[67]

It has been shown[68,69] that 1,1-dichlorotetraorganocyclotrisiloxanes easily enter reactions of chlorine substitution by alkylamino groups (Scheme 30).
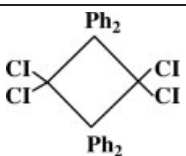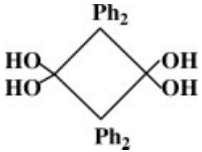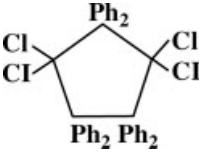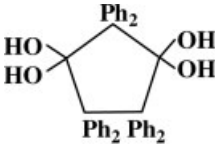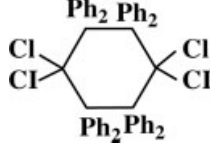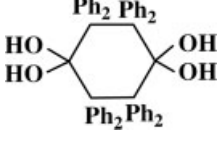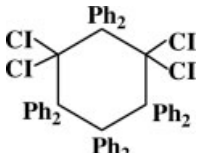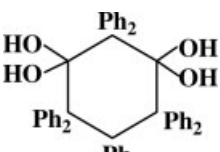
The HFC reaction of 1,1-dichloorganocyclosiloxanes with 1,3-dihydroxytetraorganosiloxane at 1 : 1 ratio of initial components in the presence of pyridine has synthesized spirocyclosiloxanes of the structure[70,71] (Scheme 31).

No.	Structural formula	Yield (%)	T_{boil} (°C) P(mmHg) T_{melt} (°C)	n_D^{20}	d_4^{20}	MR_D^{**}	^1H (ppm)	Reference
1	Ph₂ / H, H / Me, Me / Ph₂	79	245–250 (3–4) 87–88	–	–	–	(mixture)	[25]
2	Ph₂ / H, H / Ph, Ph / Ph₂	35	270–280 (3) 60–61	–	–	–	(mixture)	[26]
3	Et₂ / H, H / Et, Et / Et₂	34	95–98 (2)	1.42 30	–	–	(mixture) 0.62 κ 1.07 T	[47]
4	Me₂ / H, H / Me, Me / Me₂	21	57–58 (18) −40	1.39 30	0.9680	65.88 65.82	–	[72]
5	Ph, Me / H, H / Me, Me / Ph, Me	27	140–145	1.49 14	1.0907	–	(mixture)	[25]
6	Me Me / H, H / Me, Me / Me Me	18	154–155	1.39 27	0.9709	–	(mixture)	[73]
7	Ph Ph / H, H / Me, Me / Me Me	14	137–139 (1–2)	1.48 76	1.0698	–	(mixture)	[74]
8	Ph₂ / Me, Me / H, H / Ph₂ Ph₂	67	235–242 (0.02)	–	–	–	(mixture) cis-0.25 trans-0.28	[49,52]
9	Ph₂ Ph₂ / Me, Me / H, H / Ph₂ Ph₂	23 (67)	263–267 (0.01) 162–163	–	–	–	(mixture) cis-0.26 trans-0.30	[47]
10	Me₂Me₂ / Me, Me / H, H / Me₂Me₂	59	66–68 (1)	1.39 71	–	–	(mixture) cis-0.14 trans-0,15	[46]
11	Et₂ Et₂ / Et, Et / H, H / Et₂ Et₂	53	175–178 (1)	1.43 41	–	–	(mixture) 0.6 q 1.0 t	[46]

* Slashed values indicated calculated values/recored ones.

TABLE VI
Physical and Chemical Parameters of Tetrafunctional Organophenylcyclosiloxanes

No.	Compound	Yield (%)	T_{boil} (°C) (P mmHg)	T_{melt} (°C)	Reference
1		53	206–210 (0.002)	–	[41,58,75]
2		64	–	157–158	[41,58]
3		52 (70)	255–260 (0.02)	–	[41,50]
4		73	–	191–192	[41,50]
5		26	325–330 (0.06)	83–87	[49,50,54]
6		75	–	251–252	[50,54]
7		67	307–311 (0.01)	71–73	[29,50]
8		64	–	161–162	[29,50]

Further on, synthesized spirocyclosiloxanes were used for synthesizing cyclolinear polymers. Some physical and chemical parameters of synthesized organocyclotri(tetra, penta, hexa)siloxanes with different framing and functional groups are shown in Tables I–VI. Where hereinafter, cyclotetra-, cyclopenta-, and cyclohexasiloxane fragments are denoted as shown in Scheme 32.

ORGANOCYCLOCARBOSILOXANES WITH FUNCTIONAL GROUPS AT SILICON ATOMS

For the purpose of synthesizing organocyclocarbosiloxanes with defined disposition of functional groups at silicon atoms, HFC reaction of 1,2-methylchlorosilyl-substituted ethane with dihydroxydiphenylsilane and 1,3-dihydroxytetraphenyldisiloxane in diluted anhydrous toluene solution in the presence of pyridine at 1 : 1 molar ratio of the initial components was studied (Scheme 33).[30,76]

The yield of organocyclocarbosiloxanes is seriously dependent on the reaction temperature. It is found that if the process proceeds at 20–25°C, total yield of cyclocarbosiloxanes does not exceed 70%, the yield of dichlorocarbosiloxanes being equal 55%. Reduction of the reaction temperature to −5 to −10°C allows increase of total yield of cyclocarbosiloxanes up to 85% and dichlorocarbosiloxanes up to 68%. The yield of tetrachlorocyclocarbosiloxane equals 44%. Hydrolysis of di(tetra) chlorocyclocarbosiloxanes has synthesized corresponded di- and tetrahydroxyderivatives in accordance with Schemes 34 and 35).

HFC reaction of 1,3-bis(dichloromethylsilyl)ethane and 1,3-bis(dichloromethylsilyl) propane with dihydroxydimethylsilane proceeded in diluted anhydrous ether solution, in the presence of pyridine at −5°C. However, the yields of produced methylcyclocarbosiloxanes are low, giving 10–22%.

The reaction is shown in[77] Scheme 36.

Extended dichloromethylcyclocarbosiloxane was synthesized by condensation of 1,1,7,7-tetrachloro-1,3,3,5,5,7-hexamethylcarbotetrasilocane with 1,3-dihydroxytetramethyl-disiloxane under similar conditions in accordance with Scheme 37.[77]

The yield of the above-mentioned dichloromethylcyclocarbosiloxane equals ∼40%. Dihydroxy-derivatives were synthesized by the hydrolysis of dichloromethylcyclocarbosiloxanes.

Physical and chemical parameters of di- and tetrafunctional organocyclosiloxanes and organocarbocyclosiloxanes are shown in Table VII.

Difunctional organosilicon heterocyclic compounds were successfully synthesized by pyrolytic ring formation of symmetrical disiloxanes with phenyl radicals. Pyrolysis in the gas phase in the temperature range of 680–690°C proceeds with benzene extraction, which leads to the synthesis of representatives of a new class of heterocyclic compounds, which are organochlorine derivatives of 1,3-disila-2-oxaindane. This reaction proceeds as shown in Scheme 38.[78,79]

By studying hydrolysis of disilaoxaindanes, the authors of the work[80] have detected high reactivity of ≡Si—CI bonds, which is explained by the decrease of ≡Si—O—Si≡ valence angle in 1,3-disila-2-oxaindane. Lower reactivity of silaindane fragment with
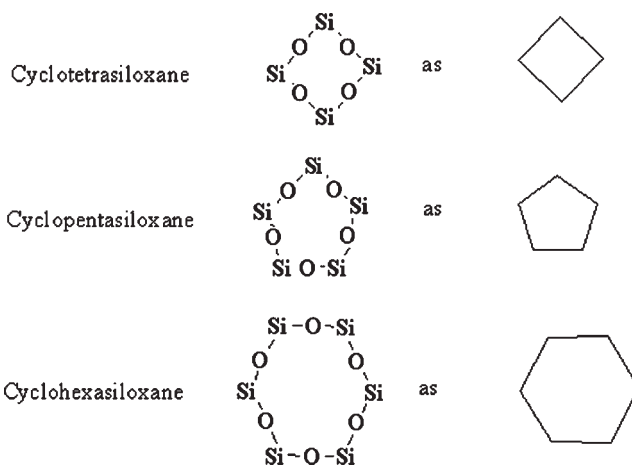
Scheme 32 Denotation of cyclotetra-, cyclopenta- and cyclohexasiloxane structure.
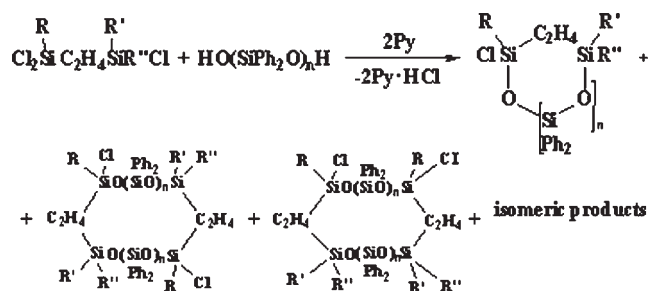
Scheme 33 HFC reaction of 1,2-methylchlorosilyl-substituted ethane with dihydroxydiphenylsilane and 1,3-dihydroxytetraphenyldisiloxane. $n = 1, 2$; R = R′ = Me; R = CI, R′ = R″ = Me; R = R′ = R″ = CI.
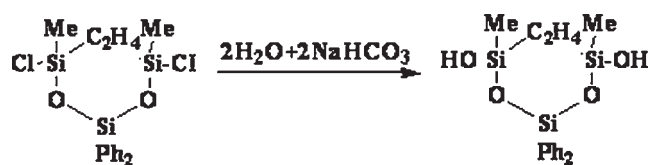
Scheme 34 Hydrolysis of dichlorocyclocarbosiloxanes.
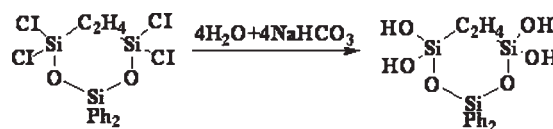
Scheme 35 Hydrolysis of tetrachlorocyclocarbosiloxanes.
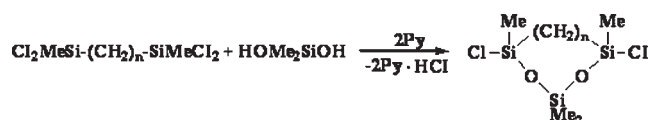
Scheme 36 HFC reaction of 1,3-bis(dichloromethylsilyl)-ethane and 1,3-bis(dichloromethylsilyl) propane with dihydroxydimethylsilane. $n = 2, 3$.
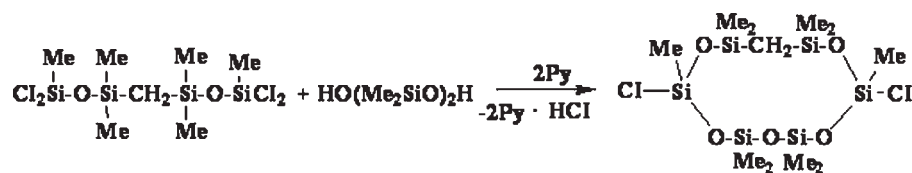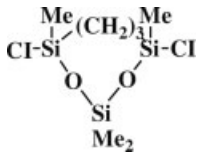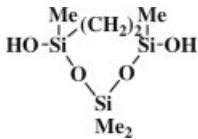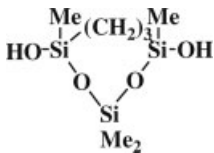
Scheme 37 HFC reaction of 1,1,7,7-tetrachloro-1,3,3,5,5,7-hexamethylcarbotetrasilocane with 1,3-dihydroxytetramethyldisiloxane.

TABLE VII
Physical and Chemical Parameters of Difunctional Organocyclocarbosiloxanes

No.	Compound	Yield (%)	T_{boil} (°C) (mmHg)	T_{meld} (°C)	$^1H(CH_3)$ chemical shift *cis trans*	References
1		67.9	187–193 (0.01)	77–78	(mixture) *cis*–0.47 *trans*–0.52	[29,47]
2		59.4	218–221 (0.02)	110–111	(mixture) *cis*–0.41 *trans*–0.49	[29,47]
3		56	150–155 (0.01)	159–161	–	[47]
4		68	149–520 (0.01)	–	0.45 s	[29,47]
5		71	–	120–122		[29,47]
6		69	–	169–170	–	[29,47]
7		22	61–65 (5)	–	*cis* 0.88 *trans* 1.23	[77]

TABLE VII *Continued*

No.	Compound	Yield (%)	T_{boil} (°C) (mmHg)	T_{meld} (°C)	$^1H(CH_3)$ chemical shift *cis trans*	References
8		10	66–73 (4–5)	–	*cis* 0.38 *trans* 0.40	[76]
9		40	99–110	–	MeSiCI* 45.50	[76]
10		71	80–100 (4–5)	–	0.05	[76]
11		40	130–134	–	0.04	[76]
12		71	–	–	MeSi(OH)* 63.02	[76]

Note: *[29] S1 spectrum.

phenyl framing at silicon atoms is explained by both steric and inductive effects of the framing groups.

However, hydrolysis of 1,3-dichloro-1,3-disila-1,3-diphenyl-2-oxaindane under soft conditions in the temperature range of −5 to −10°C in the presence of both sodium bicarbonate and aniline has synthesized not appropriate dihydroxy-derivatives, but oligomeric α,ω-dihydroxy-1,3-disila-1,3-diphenyl-2-oxaindane. The reaction proceeds in accordance with the Scheme 39.[81]

Homocondensation of oligomeric dihydroxy-derivatives, boiled in toluene, has synthesized oligomers with higher transformation degree.

It is shown[82] that the gas-phase pyrolysis of *ortho*-dichlorosiloxydiphenyl easily synthesizes pentatomic silicon-containing heterocycle of 10,10-dichloro-10-sila-9-oxarophenanthrene with the yield of about 60%, which is caused by high reactivity of hydrogen *ortho*-atom.

However, insignificant ring formation with simultaneous synthesis of dibenzofuran did also proceed. The general reaction is shown in Scheme 40.

Contrary to silaoxaindane, 10,10-dihydroxy-10-silaoxarophenanthrene and oligomeric dihydroxy derivatives have been synthesized in hydrolysis of 10,10-dichloro-10-sila-9-oxarophenanthrene proceeded in

Scheme 38 Gas-phase pyrolysis of 1,3-dichloro-1,3-diphenyl-1,3-diorganodisiloxane.
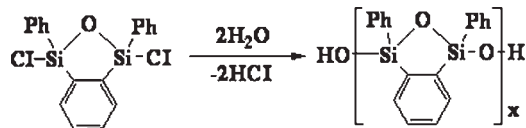
Scheme 39 Hydrolysis reaction of 1,3-dichloro-1,3-disila-1,3-diphenyl-2-oxaindane. $x = 4$.
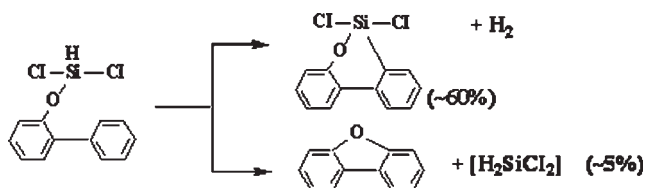
Scheme 40 Gas-phase pyrolysis of *orhto*dichlorosiloxydiphenyl.

Scheme 41 Hydrolysis reaction of 10,10-dichloro-10-sila-9-oxarophenanthrene.

the neutral medium in the presence of aniline. The process is shown in Scheme 41.[83]

It is found that dichlorosilaoxarophenanthrene is not destroyed during boiling with aqueous or alcoholic alkaline, as well as with concentrated hydrochloric acid. At the same time, it is well-known that usual Si—O—C bond is easily degraded by alkali and acids, and Si—C bond is extremely sensitive to the action of

acids.[84] Quantitatively without destruction of $\equiv$Si—O—bond, dichlorosilaoxarophenanthrene is alkylated and arylated by Grignard reagents, restored by lithium aluminum hydride; when treated by hydrofluoric acid, it is transformed to difluorosilaoxarophenanthrene. According to the authors' point of view, the high chemical stability of silaoxarophenanthrene indicates a definite fragrance of this compound.[85] Some physical and chemical parameters of heterocyclic compounds with functional groups are shown in Table VIII.

TABLE VIII
Physical and Chemical Parameters of Heterocyclic Organosiloxanes

No	Compound	Yield (%)	T_{melt} (°C) (P, mmHg)	d_4^{20}	n_D^{20}	References
1		16	86–88 (4)	1.2220	1.5152	[78,79]
2		20	220–222 (3)	1.2521	1.6071	[78,79]
3		56	160–161 (1) 82–83	–	–	[82]
4		97	48–54	–	–	[80,81]
6		86	236–239	–	–	[83]
7		13	120–126	–	–	[83]

CONCLUSIONS

Thus, in the given review basically are considered synthesis of such organocyclosiloxanes and organo-carbocyclosiloxanes with various volumes of cyclic fragments and with various functional groups which further have been used by different authors for obtaining of copolymers with cyclolinear structures of macromolecules. It is shown that joint hydrolytic condensation di- and trifunctional organosilanes was not always possible to receive with high yields organocyclosiloxane with given disposition of functional. For the synthesis organocyclosiloxanes and organocarbo-cyclosiloxanes, more acceptable method is reactions of heterofunctional condensation; therefore, it is possible to synthesize cyclic compounds with the given arrangement of functional groups at silicon. For obtaining dichlorocyclotetra(penta, hexa, hepta, octa)-siloxanes with high yields, it is desirable to carry out reactions to two stages. At attempt of division dichloro-cyclotetra(penta, hexa, hepta, octa)siloxanes on stereo-isomers appeared, that most of dichloroorganocyclo-tetra(hexa)siloxanes are divided shared on cis- and a trans-isomers. All attempts to divide into stereoiso-mers the dichlorooctaorganocyclopentasiloxanes and dichlorododecaorganocyclohexasikloxanes on cis- and the trans- isomers appeared without result. By hydrolysis and aminolyzis of dichloroorganocyclosi-loxanes in the presence of acceptors of hydrogen chloride, corresponding dihydroxyl- and diaminoorgano-cyclosiloxanes are obtained.

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