Translated from *Uspekhi Khimii*, 49, 2314-2343 (1980) U.D.C. 678.84.765:54.07.09(047)

Advances in the Chemistry of Compounds with the Cyclodisilazane Structure

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Data on the monomeric four-membered cyclic silazane systems are surveyed and arranged systematically. The available methods for the synthesis of these compounds are examined in detail, the results of studies on the mechanism of the formation of organocyclodisilazanes are described, and the mechanisms of individual stages of this process are considered. The review includes an exhaustive bibliography on monomeric organocyclodisilazane compounds up to 1978, comprising 116 references.

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I. INTRODUCTION

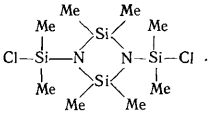
Studies in the field of organosilicon compounds containing a silicon–nitrogen bond have developed particularly vigorously in the last two decades. During this period, it has been shown that such compounds are of great theoretical interest and can be of practical importance as valuable heat-resistant materials capable of being used at high temperatures and exhibiting high thermal and chemical stabilities, great mechanical strength, and effective electrical insulating, semiconducting, and other valuable properties; in addition, they can be hardened at room temperature and exhibit an effective adhesion to various materials.

The principal trend in the development of the chemistry of compounds containing the ≡Si—Ni= bond has been until recently the synthesis of open-chain silazanes and silylamines and the study of their properties. However, nowadays cyclic compounds with the silazane structure, particularly four-membered cyclic silazane systems—cyclodisilazanes and polymers with alternating units comprising such systems—have attracted increasing attention. Studies in recent years on the properties and practical applications of four-membered cyclic silazane systems have shown that such compounds have a striking thermal stability.

Until now, there have been no reviews on monomeric four-membered cyclodisilazane systems. Isolated information about the methods of synthesis and chemical properties of these compounds can be found in a few publications[1-4]. This review surveys the published literature data on the synthesis of monomeric four-membered cyclic silazane systems.

II. FUNDAMENTALS OF THE NOMENCLATURE AND CERTAIN CHARACTERISTICS OF ORGANOCYCLODISILAZANE COMPOUNDS

In the literature there is no clear-cut system of nomenclature for four-membered cyclic silazane systems, but the majority of authors adhere to the following methods for the naming of such substances, which can be illustrated in relation to the compound.



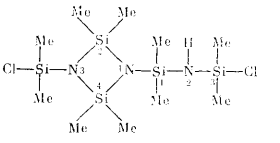
(1) *N,N'*-bis(chlorodimethylsilyl)tetramethylcyclodisilazane;

(2) 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethylcyclodisilazane;

(3) 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethyl-1,3,2,4-diazadisiletidine;

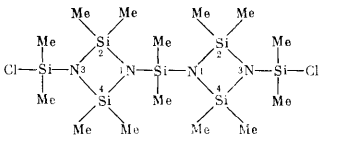
(4) 1,3-bisdimethylchlorosilyl-1,3-diaza-2,2,4,4-tetramethylcyclodisilazane.

Nomenclatures (1) and (2) are most widely used. From our point of view, the second system is most convenient as regards simplicity and yields the maximum information about the structure of the compound and will in fact be used in this review. An advantage of this system is its universality and rationality. The names of compounds containing a single cyclodisilazane ring are derived from the name of this ring; for example,



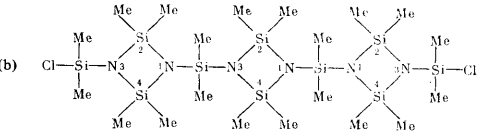
is 1-(1,1,3,3-tetramethyl-3-chlorodisilazanyl)-2,2,4,4-tetramethyl-3-dimethylchlorosilylcyclodisilazane.

The names of cyclodisilazane oligomers containing repeating cyclodisilazane fragments are constructed on the basis of the "central symmetry" rule; for example, in case (a) the dimethylsilyl unit is central and two similar cyclodisilazane fragments are located symmetrically relative to it, so that this unit is adopted as the basis for the name:

(a) 

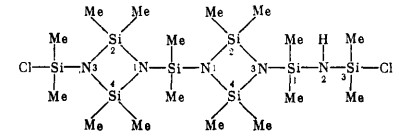
is dimethylbis(2,2,4,4-tetramethyl-3-dimethylchlorosilyl-1-cyclodisilazanyl)silane.

In case (b) the name is based on the cyclodisilazane ring, which is the centre of the oligomer molecule:

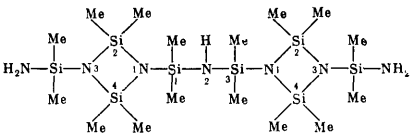
(b) 

is 1,3-bis[dimethyl(2,2,4,4-tetramethyl-3-dimethylchlorosilylcyclodisilazanyl)silyl]-2,2,4,4-tetramethylcyclodisilazane.

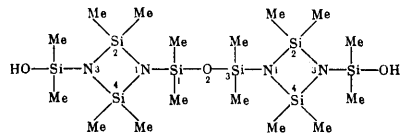
In all the remaining cases the molecular fragment most convenient for the construction of the name is adopted as central—the dimethylsilyl unit for (c), the disilazane unit for (d), and the disiloxane unit for (e):

(c) 

is dimethyl(2,2,4,4-tetramethyl-3-dimethylchlorosilyl-1-cyclodisilazanyl)-[2,2,4,4-tetramethyl-3-(1,1,3,3-tetramethyl-3-chlorodisilazanyl)-1-cyclodisilazanyl]silane.

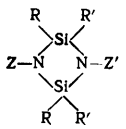
(d) 

is 1,1,3,3-tetramethyl-1,3-bis(2,2,4,4-tetramethyl-3-aminodimethylsilyl-1-cyclodisilazanyl)disilazane.

(e) 

is 1,1,3,3-tetramethyl-1,3-bis(2,2,4,4-tetramethyl-3-hydroxydimethylsilyl-1-cyclodisilazanyl)disiloxane.

All the known monomeric four-membered cyclic silazane systems can be divided into three groups:

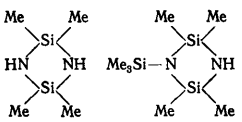


(1) Symmetrical or asymmetric 1,3-bis(organo)-substituted cyclodisilazanes (Z and Z′ are organic groups of H);

(2) symmetrical or asymmetric 1,3-bis(silyl)-substituted cyclodisilazanes (Z and Z′ = SiR''_3 or SiR''_nHal_{3-n}, where R″ is an organic group or H and Hal is a halogen atom);

(3) asymmetric 1,3-substituted cyclodisilazanes (one of the substituents is an organic group and the other is a triorganosilyl, diorganohalogenosilyl, organodihalogenosilyl, or trihalogenosilyl group).

2,2,4,4-Tetramethylcyclodisilazane[5] and 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane[6] can be quoted as the simplest representatives of the series of organocyclodisilazanes containing hydrogen atoms at the endocyclic nitrogen atoms and methyl groups at the silicon atoms:



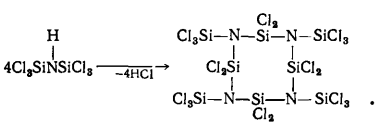
1,3-Bis(silyl)-substituted organocyclodisilazanes are thermally and hydrolytically stable; these compounds are fairly reactive via their functional groups, which makes it possible to obtain oligomeric and polymeric products based on them.

The high thermal and hydrolytic stability of 1,3-bis(silyl)-substituted organocyclodisilazanes can be accounted for by a number of factors. An increase of the electronegativity of the substituents at the nitrogen or silicon atoms (H, Me, $SiMe_3$, Ph) causes a corresponding decrease of electron density at this atom and an increase of the hydrolytic stability of the endocyclic silicon–nitrogen bond[1,7]. The p_π–d_π interaction of the exocyclic organosilyl groups with an endocyclic nitrogen atom reduces the electron density at the nitrogen atom with a simultaneous increase of electron density at the exocyclic silicon atoms, which leads to an increase of the thermal and hydrolytic stability of 1,3-bis(silyl)-substituted organocyclodisilazanes[8,9].

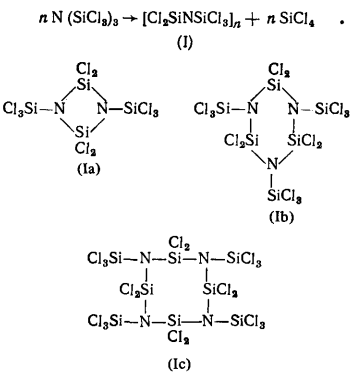
The high degree of hyperconjugation in the ring, which is characteristic of four-membered cyclic silazane systems and leads to a change in bond lengths, a deformation of angles[1,10], and a decrease of the basicity of the endocyclic nitrogen[6], determines to a significant extent the reactivity and physical properties of organocyclodisilazanes[11]. Thus, the high degree of conjugation in the 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane ring leads to an increase of the acidity of the protons at the nitrogen atoms and to a corresponding increase of the reactivity of this compound[6]. On the other hand, the electronic nature of the substituents at the nitrogen atom also affects the properties of the compounds. Thus the temperature range of the decomposition is 450–500 °C for cyclodisilazanes with organosilyl groups at a nitrogen atom, 400–450 °C for cyclodisilazanes with organic substituents, and 320–360 °C for hexaorganocyclotrisilazanes[11,12].

III. SYNTHESIS OF ORGANOCYCLODISILAZANES

For a long time the existence of four-membered cyclic silazane compounds with alternating silicon–nitrogen bonds gave rise to doubts. Thus in 1953 a new compound was obtained by the condensation of hexachlorodisilazane, for which the authors suggested the cyclotetrasilazane structure[13]:



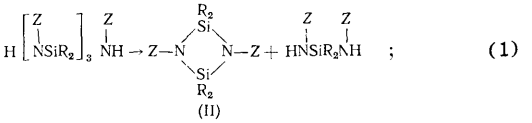
Somewhat later an analogous cyclic perchlorosilazane was obtained by a different procedure[14]—the condensation of tris(trichlorosilyl)amine (isolated from the product of the pyrolysis of the $SiCl_4/N_2$ mixture), for which the authors proposed structures (Ia), (Ib), and (Ic):



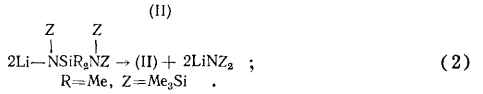
But the authors[14] gave preference to the cyclotetrasilazane structure (Ic) for their compound, having excluded the four-membered system (Ia) in view of the expected high ring strain. However, in 1958 it was demonstrated for the first time that the compound had in fact the cyclodisilazane structure[15].

1. N-Alkyl-, N-Trialkylsilyl, and N-Aryl-substituted Organocyclodisilazanes

1,3-Bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (II) was obtained by the thermolysis of long-chain or metallated silazanes[16,17] via reactions (1) and (2):



(1)

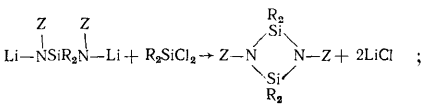


(2)

Compound (II) can also be obtained by the thermolysis of *N*-trimethylsilylated cyclotri- and cyclotetra-silazanes; compound (III, R = Z = Me), having an analogous structure, is obtained by the thermolysis of permethylated cyclosilazanes[18,19].

The structure of four-membered silazane systems was established by X-ray diffraction[10] and by specific synthesis[1].

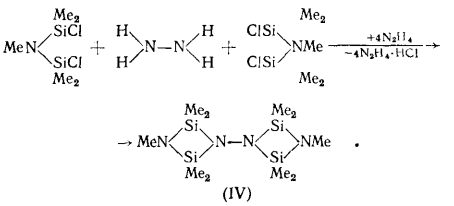
1,3-Bis(trimethylsilylated) organocyclodisilazanes can be obtained in high yields by the reaction of doubly metallated octamethyltrisilazane with organodichloro- and organotrichloro-silanes or with silicon tetrachloride[16,18]. Cyclodisilazanes (II) and (III) with methyl substituents at a nitrogen atom were obtained similarly from the doubly metallated bis(methylamino)dimethylsilane[20,21]:



(II): R = Me, Z = Me_3Si;

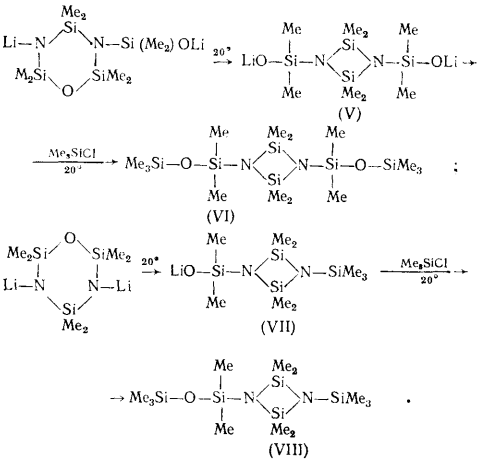
(III): R = Z = Me .

The interesting *N*-methyl-substituted biscyclodisilazane (IV) was obtained by the reaction of 1,3-dichloropentamethyldisilazane with hydrazine[22]:



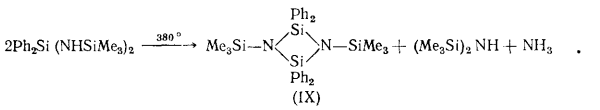
(IV)

Symmetrical and asymmetric *O*-lithiocyclodisilazanes (V) and (VII) have been isolated after condensing six-membered *N*-lithio-organocyclosiloxazanes at room temperature and their subsequent treatment with trimethylchlorosilane yielded *N*-substituted organocyclodisilazanes (VI) and (VIII):[23,24]



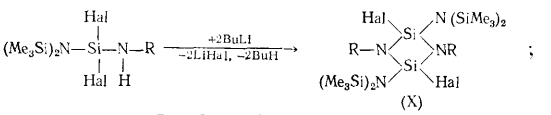
(V), (VI), (VII), (VIII)

Organoaminosilanes containing phenyl groups linked to the silicon atom cyclise on thermal condensation to form 1,3-bis-(trimethylsilyl)phenylcyclodisilazanes. Thermal condensation of *N,N'*-bis(trimethylsilylamino)diphenylsilane leads to the formation of 1,3-bis(trimethylsilyl)-2,2,4,4-tetraphenylcyclodisilazane (IX):[25,26]



(IX)

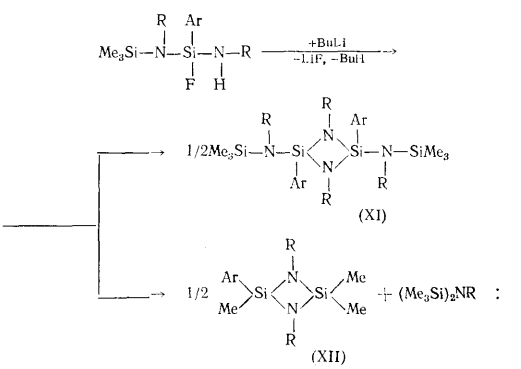
Symmetrical organocyclodisilazanes containing fluorine or chlorine atoms or amino-groups attached to a silicon atom have been obtained[27,28]:



(X)

R = t-Bu; Hal = F or Cl.

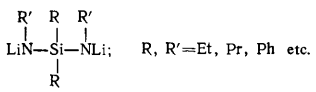
This reaction proceeds fairly smoothly when alkylaminobis(trimethylsilyl)aminodifluorosilane is used but, when one fluorine atom at a silicon atom is replaced by an aryl residue and the trimethylsilyl group is replaced by the t-butyl group, the symmetric cyclodisilazane (XII) is formed instead of the symmetrical compound (XI);[27] as a result of steric hindrance, a 1,3-rearrangement of the Me anions at the silicon atoms with subsequent cyclisation takes place instead of the expected cyclodimerisation:



(XI), (XII)

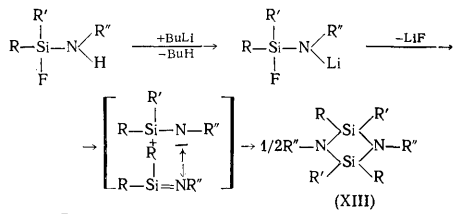
R = t-Bu .

Other *N*-alkylated and *N*-arylated cyclodisilazanes (see Table 1 below) have been obtained analogously from dilithio-derivatives of the corresponding silylamines[29–34]:



R, R′=Et, Pr, Ph etc.

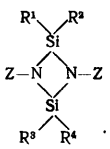
or by the reaction of aminofluorosilanes with butyl-lithium[35]:



(XIII)

R = Me or Ph; R′=Me, *s*-Bu, or Ph; R″ = iso-Pr, t-Bu, -Bu, 2, 4, 6-$Me_3C_6H_2$

Table 1. Symmetrical *N*-substituted organocyclodisilazanes



Z	R^1	R^2	R^3	R^4	B.p., °C/mmHg	M.p., °C	n_D^{20}	d_4^{20}	References*
Cl_3Si	Cl	Cl	Cl	Cl	83–85/0.01	66	—	—	14,15,106,108
Me_3Si	Me	Me	Me	Me	85/7	39	1.4237 (45°)	0.998	16,18,19,66,76
Me_3Si	Et	Me	Et	Me	74/0.9	—	1.4502	—	16
Me_3Si	Et	Et	Et	Et	80—82/0.9	—		—	16
Me_3Si	Me	Me	Ph	H	147/5	—	1.4794	—	116
Me_3Si	Me	Me	Ph	Ph	120/0.03	52	—	—	51
Me_3Si	Ph	Ph	Ph	Ph	—	256—257	—	—	25
Me_3Si	Me	Me	Cl	Cl	118/21	28	1.4360 (45°)	—	16
Me_3Si	Me	Me	EtO	EtO	79.5/1.5	—	1.4312	—	16
$n\text{-}Bu_3Si$	Ph	Ph	Ph	Ph	240—242/0.04	111	—	—	51
$ClMe_2Si$	Me	Me	Me	Me	64/0.08	68—69	—	—	21,76,77,79,80, 82,84,99,111,112
$ClMe_2Si$	Me	Me	Ph	Cl	170/12	—	1.5046	—	26
Cl_2PhSi	Me	Me	Me	Me	225/12	102	—	—	26
$EtOMe_2Si$	Me	Me	Me	Me	115—116/18	—	1.4332	—	76
$(MeO)_3Si$	MeO	MeO	MeO	MeO	127—129/2	—41	1.4187	1.1721	108
$(EtO)_3Si$	EtO	EtO	EtO	EtO	142/2	21	1.4180	1.0388	108
$(MeNH)_3Si$	MeNH	MeNH	MeNH	MeNH	70/0.01 (subl.)	83	—	—	108
$(Me_2N)_3Si$	Me_2N	Me_2N	Me_2N	Cl	185—195/0.1	103—106	—	—	108
$Cl(Et_2N)_2Si$	Et_2N	Cl	Et_2N	Cl	215—220/0.1		1.4961	1.1263	108
$Me_3SiO(Me_2)Si$	Me	Me	Me	Me	80/0.25	—	—	—	23
H	Me	Ph	Ph	Ph	—	65	—	—	72,73
H	Ph	Ph	Ph	Ph	—	206	—	—	72,73
H	Me_3SiO	Me_3SiO	Me_3SiO	Me_3SiO	180—183/4	103—104	—	—	74,75
H	Et_3SiO	Et_3SiO	Et_3SiO	Et_3SiO	—	186	—	—	75
H	Me_3SiNH	Me_3SiNH	Me_3SiNH	n-BuNH	153—155/1.5	—	—	—	25
Me	Me	Me	Me	Me	52/51	17	1.4210	0.8403 (23°)	20,21
Me	Me	Me	Me	Ph	69—71/3	—	1.4932	—	20,21
Me	Me	Me	Ph	Ph	144/4	—	1.5460	1.0234 (24°)	20,21
Me	Et	Et	Et	Et	115—120/0.01	95	—	—	31
Me	Ph	Ph	Ph	Ph	262	95	—	—	44
Et	Me	Me	Me	Me	98—98.5/82	—	1.4250	—	29
Et	Ph	Ph	Ph	Ph	—	195—196	—	—	29
Et	CH_2=CH	Et	CH_2=CH	Et	54/0.05	—	1.4638	—	51
Et	CH_2=$CHCH_2$	CH_2=$CHCH_2$	CH_2=$CHCH_2$	CH_2=$CHCH_2$	90/0.02	—	1.4877	—	51
Et	CH_2=CH	CH_2=CH	CH_2=CH	CH_2=CH	100/12	—	1.4745	—	44
iso-Pr	Me	Ph	Me	Ph	—	23—25	—	—	35
iso-Pr	Ph	Ph	Ph	Ph	—	181—184	—	—	35
n-Bu	Me	Me	Me	Me	89/6	—	1.4367	—	51
n-Bu	Me	Ph	Me	Ph	220—225/2	—	1.5460	1.0280	57
n-Bu	n-BuNH	n-BuNH	n-BuNH	n-BuNH	190/1	—	1.4640	—	48
t-Bu	Me	Me	Me	Me	100/12	35	1.4450	—	51
t-Bu	Me	s-Bu	Me	s-Bu	91/0.01	—	—	—	35
t-Bu	Me	Ph	Me	Me	—	57	—	—	27
t-Bu	F	$(Me_3Si)_2N$	F	$(Me_3Si)_2N$	—	204	—	—	27
t-Bu	Cl	Me	Cl	Me	—	68	—	—	28
CH_2=$CHCH_2$	Me	Me	Me	Me	74/11	—	—	—	51
CH_2=$CHCH_2$	Ph	Ph	Ph	Ph	—	167	—	—	51
$n\text{-}C_7H_{15}$	Me	Me	Me	Me	123/0.01	105	—	—	29
$n\text{-}C_{12}H_{25}$	Ph	Ph	Ph	Ph	300/0.05	—	—	—	51
Ph	Me	Me	Cl	Cl	210/720 (subl.)	210—215	—	—	29
Ph	Me	Me	Me	Cl	—	243—245	—	—	29,30
Ph	Me	H	Me	H	193/0.05	91	—	—	1
Ph	Me	Me	Me	Me	—	252.5	—	—	29
Ph	Me	Me	Ph	Ph	—	180—181	—	—	29,30
Ph	Me	Ph	Ph	Me	—	251—252	—	—	37
Ph	Ph	Ph	Ph	Ph	—	355.5	—	—	29
Ph	Me	PhNH	Me	PhNH	—	229—230	—	—	49
Ph	Me	PhNH	Me	$(PhNH)_2Si(Me)N(Ph)$	—	186—187	—	—	49
Ph	Ph	PhNH	Ph	PhNH	—	285—286	—	—	49
Ph	PhNH	PhNH	PhNH	PhNH	—	204—207	—	—	48
Ph	Ph_2SiO	Me	Ph_2SiO	Me	—	259—261	—	—	49
Ph	Ph_2SiO	Ph	Ph_2SiO	Ph	—	288	—	—	49
Ph	4-$PhOC_6H_4$	4-$PhOC_6H_4$	4-$PhOC_6H_4$	4-$PhOC_6H_4$	—	322	—	—	44
Ph	—$(CH_2)_4$—		—$(CH_2)_4$—		—	227	—	—	44
Ph	$Si_2O_3Ph_4$		$Si_2O_3Ph_4$		—	261	—	—	47
α-Naphthyl	Me	Me	Me	Me	—	252—253	—	—	29

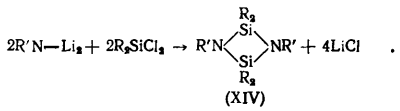
Table 1 (contd.)

Z	R^1	R^2	R^3	R^4	B.p., °C/mmHg	M.p., °C	n_D^{20}	d_4^{20}	References*
β-Naphthyl	Me	Me	Me	Me	—	237	—	—	29
β-Naphthyl	Ph	Ph	Ph	Ph	—	319,5	—	—	29
$3\text{-}FC_6H_4$	Ph	Ph	Ph	Ph	—	311—312	—	—	29
$4\text{-}FC_6H_4$	Ph	Ph	Ph	Ph	—	322—323	—	—	29
$2.5\text{-}F_2C_6H_3$	Ph	Ph	Ph	Ph	—	326	—	—	44
$2.4\text{-}F_2C_6H_3$	Ph	Ph	Ph	Ph	—	338	—	—	44
$3\text{-}CF_3C_6H_4$	Me	Me	Me	Me	—	153—154	—	—	29,44,45
$3\text{-}CF_3C_6H_4$	Ph	Ph	Ph	Ph	—	183—185	—	—	29
$3.5\text{-}(CF_3)_2C_6H_3$	Ph	Ph	Ph	Ph	—	364	—	—	44
$3\text{-}ClC_6H_4$	Ph	Ph	Ph	Ph	—	261—262	—	—	29
$3\text{-}BrC_6H_4$	Ph	Ph	Ph	P t	—	272	—	—	44
$3\text{-}MeOC_6H_4$	Me	Me	Me	Me	—	171	—	—	44
$4\text{-}MeC_6H_4$	Me	Me	Me	Me	—	196—197	—	—	58
$2.4,6\text{-}Me_3C_6H_2$	Me	Me	Me	Me	—	73	—	—	44
$2.4,6\text{-}Me_3C_6H_2$	Me	Ph	Me	Ph	—	228	—	—	35
$2\text{-}Me_2C_6H_3$	Me	Me	Me	Me	—	188	—	—	44
$4\text{-}Me_2C_6H_3$	Me	Me	Me	Me	—	273—276	—	—	44
$4\text{-}MeOC_6H_4CO$	Ph	Ph	Ph	Ph	—	241	—	—	44
Me_3SiCH_2	Me	Me	Me	Me	—	63—64	—	—	44
$3\text{-}PhOC_6H_4$	Ph	Ph	Ph	Ph	470/728	169—172	—	—	44
$4\text{-}PhOC_6H_4$	$3\text{-}PhOC_6H_4$	$3\text{-}PhOC_6H_4$	$3\text{-}PhOC_6H_4$	$3\text{-}PhOC_6H_4$	425—435/721	—	—	—	44
$2.6\text{-}(PhO)_2C_6H_3$	Me	Me	Me	Me	315—319/728	—	—	—	44
$3'\text{-}PhO\text{-}3\text{-}C_6H_4OC_6H_4$	Me	Me	Me	Me	—	212	—	—	44
C_6F_5	Me	Me	Me	Me	—	305—306	—	—	38
C_6F_5	Ph	Ph	Ph	Ph	—	296	—	—	38
$3,5\text{-}Me_2C_6H_3CH_2$	Me	Me	Me	Me	—	248—250	—	—	45
$4\text{-}Me_2NC_6H_4$	Me	Me	Me	Me	—	233—236	—	—	44
$3\text{-}MeOC_6H_4$	Me	Me	Me	Me	—	169—171	—	—	44,45
Me_2NSO_2	Me	Me	Me	Me	—	185—187 (decomp.)	—	—	62
Me_2NSO_2	Ph	Ph	Ph	Ph	—	231—233	—	—	62
$O(CH_2CH_2)_2NSO_2$	Me	Me	Me	Me	—	185 (decomp.)	—	—	62

*Only the references to the main literature are given.

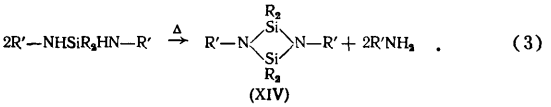
The mechanism of the latter reaction was demonstrated by mass spectrometry and NMR.[35]

The direct reaction of dilithio-derivatives of primary, preferentially aromatic, amines [or compounds described by the formula $R''R_2SiNSi(R_2)NSiR_2R''$] with diorganodichlorosilanes can also be used to synthesise the corresponding organocyclodisilazanes (XIV):[29,30,33,36–38]



(XIV)

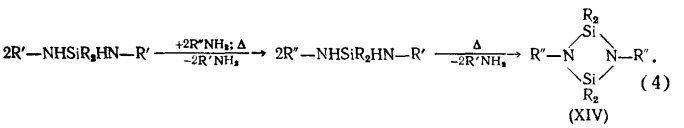
The pyrolysis of diaminodiorganosilanes at 200–450 °C is used particularly widely for the synthesis of *N*-alkylated and *N*-arylated cyclodisilazanes[29–31,39]:



(XIV) (3)

It has been suggested[40–43] that cyclodisilazanes of type (XIV) be synthesised by heating the diaminosilanes $R'-NHSiR_2HN-R'$ (R = substituted alkyl, alkenyl, cycloalkyl, aryl, arylalkyl, or alkoxy-group; R′ = organic group) or the asymmetric disilylamines $XR_2Si-NR'-SiR_2R''$ (R, R′, R″ = organic groups; X = halogen).

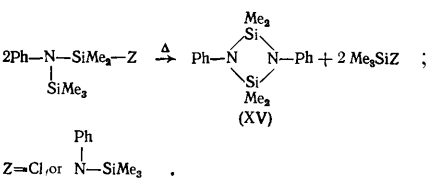
Reaction (3) (particularly for R′ = aryl) is as a rule used only for compounds whose decomposition temperature is much above the boiling point. If the removal of the high-boiling amine formed as a result of the reaction is difficult, the initial diaminosilane is sometimes subjected to a preliminary transamination with subsequent formation of cyclodisilazanes[29,31,32,44,45]:



(XIV) (4)

Reaction (4) takes place only when the boiling point of $R''NH_2$ is higher than that of $R'NH_2$.

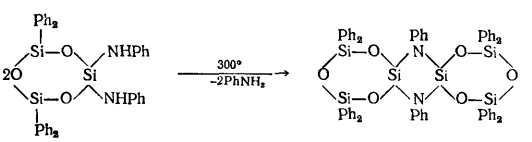
The synthesis of *N*-phenylated tetramethylcyclodisilazanes (XV) is based on the pyrolysis of *N*-phenyl-substituted di- and tri-silazanes[29] in accordance with the mechanism



(XV)

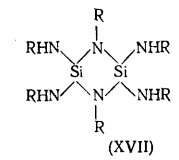
Cyclodisilazanes (XV) are also formed[46] on thermal condensation of tetra-aminosilane with dimethyldianilinosilane at 360–400 °C.

Thermal condensation of 2,2-dianilinotetraphenylcyclotrisiloxane, which takes place with the liberation of aniline only above 300 °C, led to the isolation of an *N*-phenylated four-membered silazane ring having the complex structure (XVI):[47]



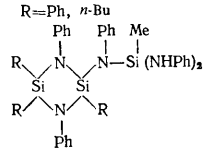
(XVI)

At low degrees of conversion the polycondensation of tetra(arylamino)- and tetra(alkylamino)-silanes proceeds with formation of the corresponding *N*-substituted cyclodisilazanes (XVII).[48] Asymmetric *N*-phenylated cyclodisilazanes (XVIII) have been obtained by the pyrolysis of methyltris(anilino)silane at 400 °C:[49]



(XVII)

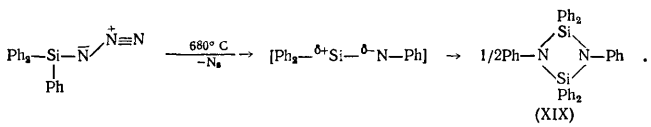
R=Ph, *n*-Bu



(XVIII)

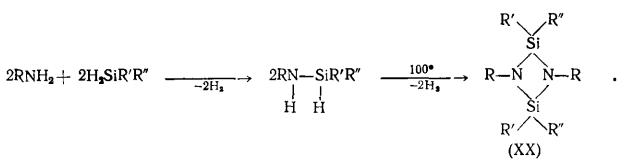
R = Me or NHPh.

Hexaphenylcyclodisilazane (XIX) is formed in the pyrolysis of triphenylsilyl azide at 680 °C:[50]



(XIX)

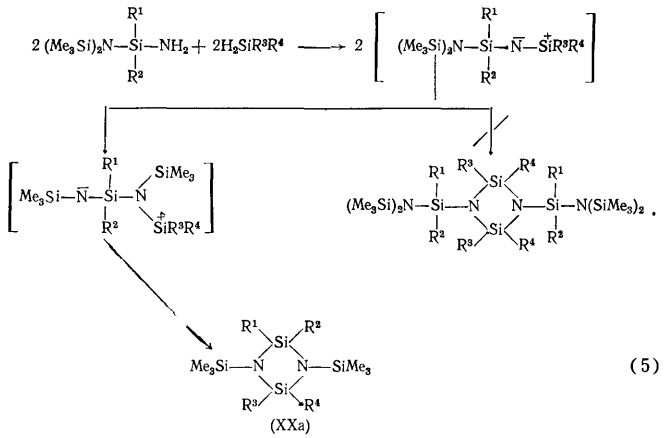
Organocyclodisilazanes can be synthesised by silylating primary aliphatic and aromatic amines or organosilylamines by diorganosilanes in the presence of alkali metals or their hydrides[51–58]:



(XX)

This results in the formation of the cyclodisilazanes (XX), where R′ and R″ are unsubstituted or substituted alkyl, alkenyl, cycloalkyl, arylalkyl, aryl, or polymethylene chains, while R is a lower alkyl, phenyl, benzyl, tolyl, xylyl, quinolinyl, etc. This reaction, which proceeds at a higher rate and with a quantitative field of organocyclodisilazanes, can be carried out in both polar (tetrahydrofuran, 1,2-dimethoxyethane, diethyl ether) and non-polar (benzene and hexane) solvents or altogether without a solvent.

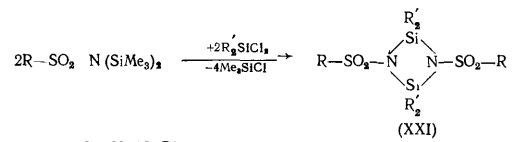
Compound (XXa) with different organic groups at the silicon atom in the ring and with trimethylsilyl groups at the nitrogen atoms can be obtained by reaction (5) via an unstable intermediate. It has been shown[51] that the intermediate does not dimerise but rearranges with migration of the trimethylsilyl group and subsequent formation of the cyclodisilazane:



(XXa) (5)

Organocyclodisilazanes containing halogen atoms or aminogroups in the substituent linked to a nitrogen atom can be obtained by heating the organodisilazanes $X_{3-n}R_nSi-NZ-SiR_nX_{3-n}$ (R is an organic substituent, X a halogen, $n = 0–3$, and Z is a halogenoaryl, halogenoalkylaryl, alkylaminoaryl, cyclohexylamino-, or phenylamino-group) in the absence of oxygen[59–61].

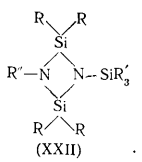
Disilylated sulphamide reacts with the dimethyl- or diphenyl-dichlorosilane to form the corresponding cyclodisilazanes (XXI):[62]



(XXI)

R=OC_4H_8N or Me_2N; R′= Me or Ph.

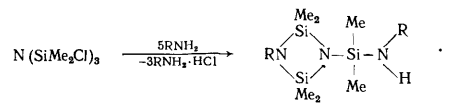
Asymmetric organocyclodisilazanes (XXII) with one triorganosilyl group (R and R′ are different or identical alkyl substituents containing between one and five carbon atoms or aryl, vinyl, and allyl groups; R″ = H, Me, Et, or Pr) have been obtained by the reaction of ammonia or amines $R''-NH_2$ with tris(organosilyl)amines $(XR_2Si)_2NSiR'_3$, where X = H, Cl, Br, or I, in an inert solvent at 18–20 °C:[63–65]



(XXII)

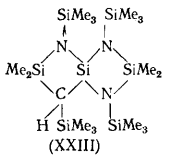
Analogous *N*-alkyl-, *N*-aryl-, or *N′*-triorganosilyl-cyclodisilazanes have been synthesised by the reaction of an asymmetric trisilylamine, for example, bis(chlorodimethylsilyl)(trimethylsilyl)amine or bis(chlorodimethylsilyl)(dimethylphenylsilyl)amine with primary amines at low temperatures (between −20° and −60 °C).[66–67] The reaction of tris(dimethylchlorosilyl)amine with primary amines at room temperature yielded asymmetric organocyclodisilazanes containing an amino-group in one of the substituents linked to an endocyclic nitrogen

atom[68]:



R = Me, Ef, or *iso*-Pr

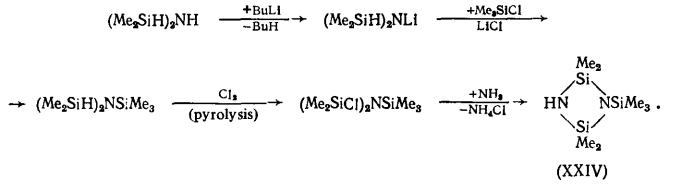
The cyclodisilazane (XXIII), asymmetric relative to the endocyclic silicon atoms and containing a cyclic system as a substituent at one of them, has been obtained by the interaction of $SiCl_4$ with $NaN(SiMe_3)_2$ at 200 °C:[69]



(XXIII)

Its structure was established by ^{1}H NMR [69] and X-ray diffraction[70].

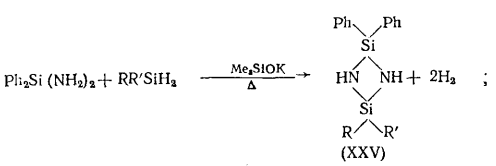
As already mentioned above, *N*-substituted (particularly *N*-triorganosilylsubstituted) organocyclodisilazanes are stable. However, since the cyclodisilazane ring is a highly strained system, the replacement of one of the substituents at a nitrogen atom by hydrogen leads to chemically fairly reactive compounds[6,71], for example, the cyclodisilazane (XXIV):



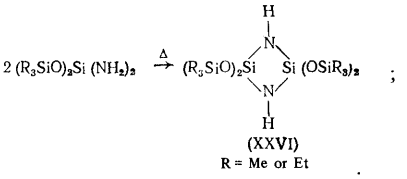
(XXIV)

In the spectra of these compounds there is an anomalous distribution of the absorption bands associated with stretching vibrations. Thus in the spectrum of compound (XXIV) the "upper" band due to the NH bond is displaced to 3510 cm^{-1}, which indicates an increased acidity of the proton at the nitrogen atom, and the corresponding shift of the "lower" band to 1000 cm^{-1}. The absorption band of the $\equiv Si-N-Si\equiv$ group, corresponding to anti-symmetric stretching vibrations, which probably also characterises the cyclodisilazane ring[21], is located[6] in the region of 870 cm^{-1}.

Andrianov and coworkers obtained organocyclodisilazanes containing hydrogen at both endocyclic nitrogen atoms by heating diphenyldiaminosilane with diphenylsilane or methylphenylsilane in molar proportions of 1 : 1 in the presence of potassium trimethylsilanoxide[72,73] or by prolonged heating of bis(triorganosiloxy)diaminosilanes[74,75] (at 212–304 °C for R = Me and 280–340 °C for R = Et):



R=R′=Ph; R=Me, R¹=Ph .

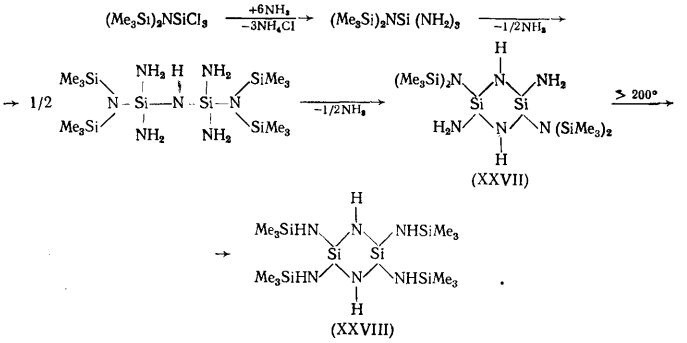


(XXVI)

R = Me or Et

Compounds (XXVI) having an analogous structure were isolated in the ammonolysis of the corresponding bis(triorganosiloxy)dichlorosilanes at elevated temperatures (55 °C for R = Me and 75 °C for R = Et).[75]

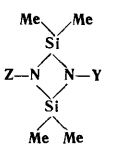
The ammonolysis of hexamethyldisilylaminotrichlorosilane with gaseous ammonia in benzene leads to the formation of products with the cyclodisilazane structure, which contain hydrogen at the endocyclic nitrogen atoms and amino-groups at the silicon atoms[25]:



(XXVII)

(XXVIII)

Table 2. Asymmetric *N*-substituted organocyclodisilazanes.

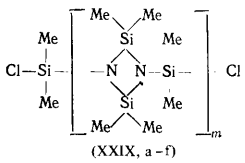


Z	Y	B.p., °C/mmHg	M.p., °C	n_D^{20}	References
H	$SiMe_3$	—	—	—	6
Me	$SiMe_3$	52—53/7	—	1.4273	66
Me	$SiMe_2Ph$	86—87/0.65		1.4863	66
Me	$Si(Me_2)NHMe$	72/10	—	1.4387	68
Et	$SiMe_3$	61—62/7	—	1.4301	66
Et	$Si(Me_2)NHEt$	91.5/8	—	1.4390	68
iso-Pr	$Si(Me_2)NHPr$-iso	98.5/5	—	1.4407	68
Ph	$SiMe_3$	—	95	—	66
Me_3Si	$SiMe_2Cl$	103/12	52	—	79,80,111,113
Me_3Si	$SiMe_2(OH)$	—	56	—	75,111
Me_3Si	$SiMe_2(NH_2)$	—	36	—	114,115
Me_3Si	$Si(Me_2)OSiMe_3$	—	—	—	23
Me_3Si	$SiMePh_2$	124/0.005	—	1.5210	26,67
$PhMe_2Si$	$SiMe_2Cl$	104/0.05	—	1.4892	79,80
$PhMe_2Si$	$SiMe_2(NH_2)$	87/0.005	—	1.4880	79
Cl_2PhSi	$SiMe_2Cl$	132/0.005	—	1.5485	26
$ClMe_2Si$	$SiMe_2(C_6H_4C_6H_5$-4)	49	—	—	79,80

The properties of symmetrical organocyclodisilazanes are listed in Table 1 and those of the asymmetric compounds are in Table 2.

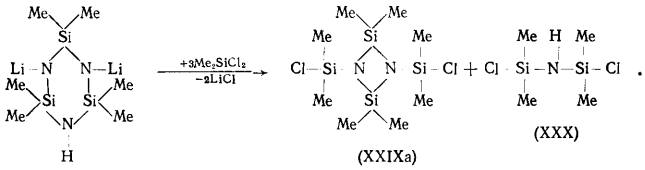
2. α,ω-Bis(diorganohalogenosilyl)-Substituted Cyclodisilazanes

Reports[2,76–93] of the synthesis of α,ω-bis(dimethylchlorosilyl)-substituted monomeric and oligomeric cyclodisilazane (XXIX, a–f) with chlorodimethylsilyl groups at a nitrogen atom, which can be used for the synthesis of linear polymers with cyclodisilazane chain units, are appearing at an increasing frequency at the present time; in compounds (XXIX, a–f) *m* varies from 1 to 6 respectively.



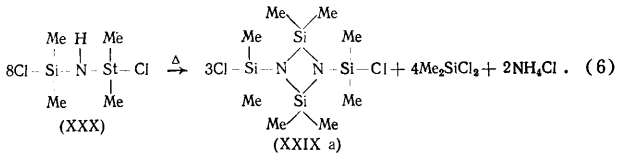
(XXIX, a–f)

When doubly or triply metallated hexamethylcyclotrisilazane (or octamethylcyclotetrasilazane) is treated with an excess of dimethyldichlorosilane, the corresponding dimethyldichlorosilyl derivative is not formed; the reaction yielded 1,3-dichlorotetramethyldisilazane (XXX) and 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXIXa).[77,79] The readily crystallisable compound (XXIXa) can be isolated in a yield of 75% or higher:



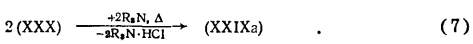
(XXIXa) (XXX)

1,3-Dichlorotetramethyldisilazane (XXX) can also be converted into compound (XXIXa) by prolonged refluxing. The temperature of the reaction mass then increases from 143 °C [the boiling point of compound (XXX)] to 235 °C [the boiling point of compound (XXIXa)]. According to the authors' hypothesis[79], the reaction proceeds via the formation of 1,5-dichlorohexamethyltrisilazane. The yield of the cyclodisilazane (XXIXa) is 70–75% of theoretical:



(XXX) (XXIX a)

In the presence of a tertiary amine, for example, triethylamine, compound (XXX) is also converted into compound (XXIXa):[79]

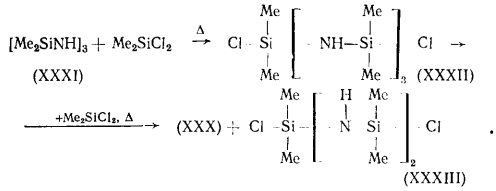


(7)

The optimum yield of compound (XXIXa) is obtained when the reaction is carried out under a low pressure at a temperature somewhat above 150 °C. Partly and fully phenylated substituted 1,3-dichlorotetraorganodisilazanes can be converted into the corresponding organocyclodisilazanes[79]. 1-Chloropentaorganodisilazane can be converted into 1,3-bis(triorganosilyl)-substituted cyclodisilazanes[79].

Hexamethylcyclotri- and octamethylcyclotetra-silazanes are cleaved by dimethyldichlorosilane with formation of compound (XXX) in 70–80% yield[2,78,86,94–97]:

The cleavage of hexamethylcyclotrisilazane (XXXI) by dimethyldichlorosilane has been investigated by quantitative gas chromatography[84,98]. It was established that hexamethylcyclotrisilazane (XXXI) is initially cleaved by dimethyldichlorosilane at a temperature below 100 °C with formation of 1,7-dichloro-octamethyltetrasilazane (XXXII); the latter reacts further with dimethyldichlorosilane to form 1,3-dichlorotetramethyldisilazane (XXX) and 1,5-dichlorohexamethyltrisilazane (XXXIII):



(XXXI) (XXXII) (XXXIII)

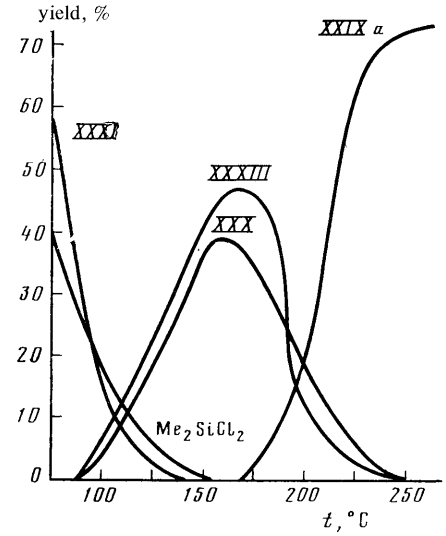


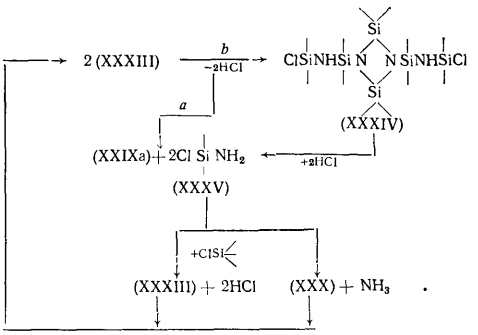
Figure 1. The interaction of hexamethylcyclotrisilazane with dimethyldichlorosilane (in proportions of 1 : 2); the yield with respect to silicon is indicated.

The content of compounds (XXX) and (XXXIII) in the mixture increases up to 160–170 °C, while at a higher temperature it falls and the formation of compound (XXIXa) begins at the same time (Fig.1).[79]

In a study of the pyrolysis of compound (XXX) it was found that dimethyldichlorosilane is evolved in the range 150–170 °C and compound (XXXIII) is formed (Fig.2). Compound (XXIXa) is not formed under these conditions, but even at 170–180 °C the content of compound (XXXIII) in the mixture diminishes and compound (XXIXa) appears[79].

Compound (XXIXa) can be formed from compound (XXXIII) via two pathways: (*a*) via intermolecular migration of hydrogen; (*b*) via the elimination of hydrogen chloride with formation of the intermediate (XXXIV), which subsequently

interacts with hydrogen chloride:



(8)

In both cases the same desired product is obtained. The unstable compound (XXXV), formed via both reaction *a* and *b*, can evolve ammonia to form compound (XXX) or can react with dimethyldichlorosilane to form compound (XXXIII) and then compound (XXIXa).[79]

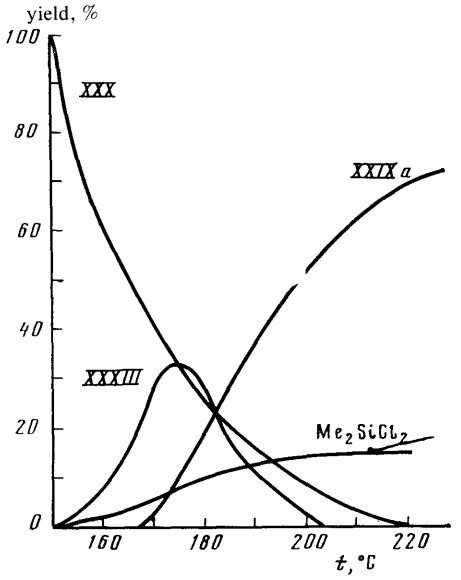
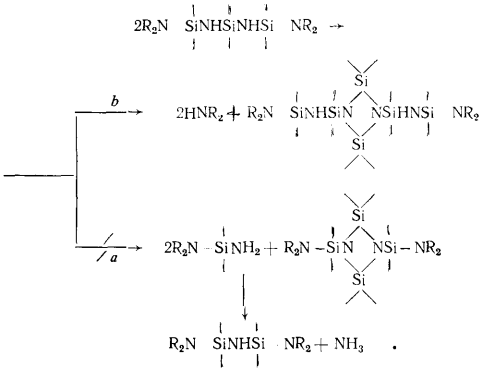


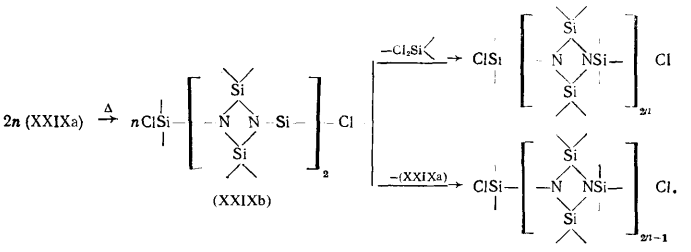
Figure 2. The pyrolysis of 1,3-dichlorotetramethyldisilazane; the yield with respect to silicon is indicated.

The probability of mechanism *b* is confirmed by the results of the pyrolysis of 1,5-bis(diethylamino)hexamethyltrisilazane [Eqn.(9)]. Diethylamine is then formed in amounts corresponding to the formation of hydrogen chloride by reaction (8) (mechanism *b*); ammonia, which can be formed via mechanism *a*, is not evolved[79]:



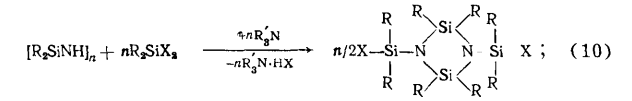
(9)

The final stage of the interaction of hexamethylcyclotrisilazane (XXXI) with dimethyldichlorosilane is the condensation of compound (XXIXa) to (XXIXb) [at the boiling point of compound (XXIXa)] and the subsequent formation of the oligomers (XXIXc)–(XXIXf) takes place fairly slowly at temperatures of the order of 300 °C with evolution of dimethyldichlorosilane and the possible elimination of compound (XXIXa):[79]



The author[79] notes that the mechanism of the formation of compound (XXIXa) and oligomers with a small number of cyclodisilazane units [compounds (XXIXb)–(XXIXf)] is not yet entirely clear.

Since compound (XXX) reacts subsequently with formation of compound (XXIXa), the simplest and most rational method for the synthesis of the cyclodisilazane (XXIXa) is direct interaction of six- and eight-membered methylcyclosilane respectively[2,76,78,79,86,87,93,97,99–101]. This reaction can be carried out between cyclic silazanes having substituents at a nitrogen atom and dimethyldichlorosilane[79,84,98], between cyclic silazanes $(R_2SiNH)_n$ and dihalogenodiorganosilanes R_2SiX_2, where R = hydrogen, fluorine, or a substituted or unsubstituted hydrocarbon, heterocyclic, or triorganosilyl group, while X = chlorine, bromine, or iodine[81,83,86], and also in the presence of the corresponding amount of a tertiary amine under an excess pressure[82], whereupon there is a sharp reduction of the reaction time, an increase of the yield of the desired product, and some decrease of the reaction temperature:



(10)

n=3 or 4.

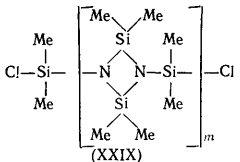
A study of the reaction of 1,3-dichlorotetramethyldisilazane (XXX) with a tertiary amine [Eqn.(7)] or of the interaction

of hexamethylcyclotrisilazane (XXXI) with dimethyldichlorosilane in an excess of a tertiary amine [Eqn.(10)] showed that even at elevated temperatures they are not fully converted into compound (XXIXa).[79] It was established that the optimum yields (89%) are reached when the reaction is carried out in the temperature range 170–190 °C.[79] At higher temperatures the yield of compound (XXIXa) decreases appreciably, since the rate of the reverse reaction increases and the equilibrium shifts towards the initial compound. On the other hand, when the reaction is carried out under an excess pressure (23–28 atm), the yield of compound (XXIXa) increases to 93–97%.[83]

If the reaction between hexamethylcyclotrisilazane (XXXI) and dimethyldichlorosilane is carried out in the absence of a tertiary amine, the maximum yield of compound (XXIXa) is reached for the ratio (XXXI) : dimethyldichlorosilane = 1 : 3 and the amount of oligomers formed is minimal.

On decrease of the amount of dimethyldichlorosilane by 1–2 moles, the yield of compound (XXIXa) falls and increasing amounts of α,ω-bis(dimethylchlorosilyl)-substituted cyclodisilazane oligomers are formed. For example, when compound (XXXI) is heated with dimethyldichlorosilane in proportions of 1 : 3 at 175 °C for 48–77 h, compound (XXIXa) is formed in 60–85% yield[76,85,87]; when the proportions are 1 : 2 (the reaction temperature increases), the yield of compound (XXIXa) falls somewhat and compound (XXIXb) [2,76–79,81–87]—the first member of the series of α,ω-bis(dimethylchlorosilyl)-substituted oligomeric cyclodisilazanes—is isolated on repeated fractionation from the oily material remaining after the removal of ammonium chloride and compound (XXIXa) (Table 3).

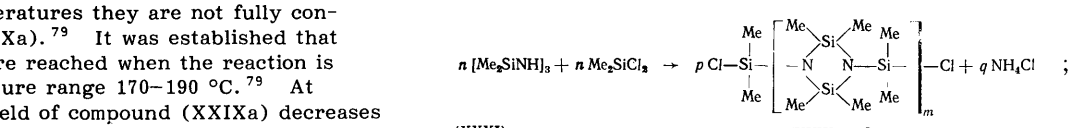
Table 3. The properties of α,ω-bis(dimethylchlorosilyl)-substituted cyclodisilazanes (XXIX) [79]



(XXIX)

Compound	m	B.p., °C/mmHg	M.p., °C
(XXIXa)	1	64/0.08	68–69
(XXIXb)	2	118/0.05	43.5
(XXIXc)	3	186/0.01	109–110
(XXIXd)	4	248/0.01	93
(XXIXe)	5	287/0.005	149–152
(XXIXf)	6	315/0.005	147

When a mixture of hexamethylcyclotrisilazane (XXXI) and dimethyldichlorosilane in proportions of 1 : 1 is heated, its temperature rapidly reaches 280 °C and then increases slowly to 330–340 °C. The resulting reaction mixture contains only 10–15% of compound (XXIXa) and 75–85% of oligomeric cyclodisilazanes in terms of the silicon introduced into the reaction; the oligomers (XXIXb)–(XXIXf) can be isolated in a pure form from this mixture[79]. It is of interest that the melting points or softening temperatures of the oligomers with an odd number of cyclodisilazane units in the chain are significantly higher than the corresponding temperatures of the compounds with an even number of units (Table 3):



(XXXI) (XXIX, a–f)

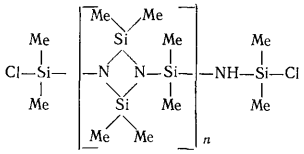
$m = 1–6$.

The yield of oligomers (XXIX, b–f) depends on the reaction time and temperature (Table 4).[79] The isolation of individual compounds from the mixture by repeated fractionation is difficult.

Table 4. Dependence of the yield of oligomeric α,ω-bis-(dimethylchlorosilyl)-substituted cyclodisilazanes on temperature[79] .

Reaction time, h	Final temp., °C	Amount of NH4Cl, g	Yield, %					
			(XXIXa)	(XXIXb)	(XXIXc)	(XXIXd)	(XXIXe)	(XXIXf)
6	285	32.8	32.5	35.3	10.8	12.6	5.7	1.5
11	292	36.9	29.0	34.5	12.7	12.4	7.3	2.1
18	314	39.3	16.2	29.4	17.0	14.3	12.7	6.5
45	334	42.5	10.9	18.3	17.8	16.1	13.3	8.5

Table 5. The properties of the cyclodisilazanes (XXXVI) [79]

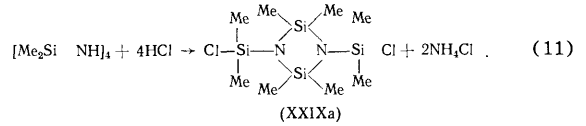


(XXXVI)

Compound	n	B.p., °C/mmHg	M.p., °C	n_D^{20}
(XXXVIa)	1	93/0.04	–	1.4598
(XXXVIb)	2	144/0.01	46	–
(XXXVIc)	3	209/0.005	–	–

Apart from compounds (XXIX, a–f), the oligomers (XXVI), containing NH groups in the side chain, are formed as side (or intermediate) products whatever the ratio of the initial reactants. The content of compounds of type (XXXVI) in the reaction mixture depends on the ratio of the initial reactants and on the reaction temperature; although these compounds are in most cases present only in insignificant amounts, they hinder to a large extent the isolation and purification of individual compounds of type (XXIX, a–f). If the reaction terminates at 200–240 °C, the main products are compounds of type (XXIXa) and (XXXVI).[79] Compound (XXXVIa) is formed in an amount of ~12% at a reaction temperature below 170 °C. The oligomers (XXXVI, a–c) are colourless compounds, which are very sensitive to moisture. The physical constants of compounds (XXXVI) are listed in Table 5.

One of the ways of obtaining compound (XXIXa) involves the interaction of hexamethylcyclotrisilazane or octamethylcyclotetrasilazane with hydrogen chloride[2,86,95,96,99,102]:

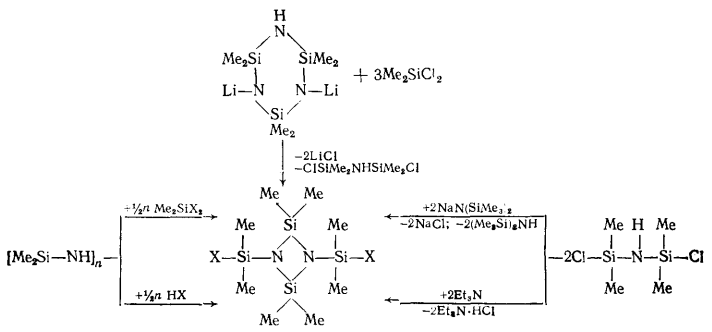


(XXIXa)

Compound (XXIXa) is also obtained in a high yield (70%) by the interaction of compound (XXX) with sodium bis(trimethylsilyl)amide in petroleum ether[78].

Other *N,N'*bis(dimethylhalogenosilyl)-substituted cyclodisilazanes—1,3-bis(dimethylbromosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXXVII) and 1,3-bis(dimethyliodosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXXVIII)—are obtained analogously by reactions of types (6) and (11).[86,96,102]
The methods for the synthesis of 1,3-bis(dimethylhalogenosilyl)-2,2,4,4-tetramethylcyclodisilazanes can be represented by Scheme 1 below:

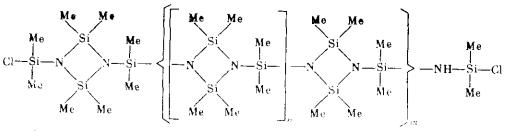
Scheme 1



n=3 or 4; X=Cl, Br, or I.

Tables 6 and 7. For compounds (XXXVII) and (XXXVIII), the spectra were recorded in 5% solution in cyclohexane[86]. For compound (XXXVII), the chemical shifts of the signals due to the protons in the exocyclic fragment XMe_2SiN and the cyclic fragment Me_2SiN_2 are respectively 9.41 and 9.57 p.p.m.; for compound (XXXVIII), $\tau = 9.32$ and 9.57 p.p.m. respectively. The study of the infrared spectra of α,ω-bis(dimethylhalogenosilyl)-substituted cyclodisilazanes showed that the absorption bands characteristic of the stretching vibrations of the cyclodisilazane fragment are in the ranges 880–890 and 1010–1040 cm^{-1}.[76,86,87,103,104] Table 8 presents the ν_1–ν_6 stretching vibrations characteristic of the Si_4N_2 fragment[86].

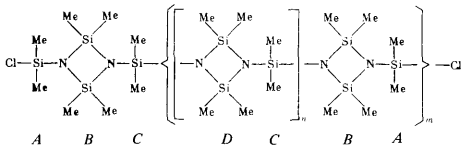
Table 7. The chemical shifts (τ, p.p.m.) in the ^1H NMR spectra of the cyclodisilazanes (XXXVI) [79]



A B C D E B C A

Compound	*m*	*n*	*A*	*B*	*C*	*D*	*E*
(XXXVIa)	0	0	9.69 9.68	9.67	9.86	—	
(XXXVIb)	1	0	9.65	9.63	9.85	—	
(XXXVIc)	1	1	9.65	9.62	9.83	9.61	9.89

Table 6. The chemical shifts (τ, p.p.m.) in the ^1H NMR spectra of the cyclodisilazanes (XXIX) [79]



A B C D C B A

Compound	*m*	*n*	*A*	*B*	*C*	*D*
(XXIXa)	0	0	9.72	9.67	9.67	—
(XXIXb)	1	0	9.66	9.64	9.94	9.64
(XXIXc)	1	1	9.64	9.60	9.90	9.63
(XXIXd)	1	2	9.64	9.59	9.87	9.59
(XXIXe)	1	3	9.64	5.59	9.88	9.58
(XXIXf)	1	4	9.64	9.59	9.88	9.59

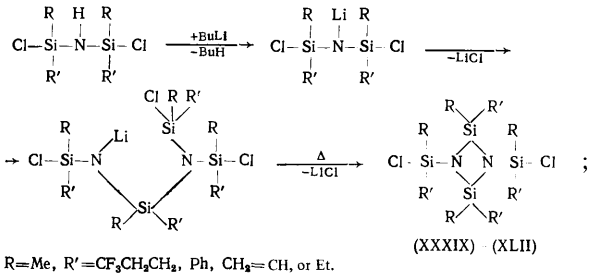
In order to confirm the structure of compounds (XXIX, a–f) and (XXXVI, a–c), ^1H NMR spectra, recorded in benzene as the solvent (only minimal differences between the chemical shifts τ for different types of protons are observed in CCl_4 or $CDCl_3$), were mainly used with tetramethylsilane as the internal standard[79]. The ^1H NMR spectra are presented in

Table 8. Vibrations (cm^{-1}) characteristic of the Si_4N_2 fragment in the cyclodisilazanes (XXIXa), (XXXVIa), (XXXVII), and (XXXVIII).

Vibration	(XXIXa)	(XXXVIa)	(XXXVII)	(XXXVIII)
ν_1	1045	1038	1037	1028
ν_2	884	883	882	887
ν_3	780	778		
ν'_4	720	722	695	695
ν_4	525	513	505	497
ν_5	440	440		
ν_6	423		428	421

The characteristics of the mass-spectrometric fragmentation of cyclodisilazanes have been found[105] and used to determine the structure of the hydrolysis products—derivatives of compound (XXIXa).

Organocyclodisilazanes (XXXIX)–(XLII) (Table 9) with different organic groups can be obtained either by reactions (6) and (11) or by the reaction of 1,3-dichloro-1,1,3,3-tetraorganodisilazane with butyl-lithium:

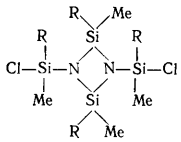


(XXXIX) (XLII)

R=Me, R′=$CF_3CH_2CH_2$, Ph, CH_2=CH, or Et.

Cooling is used in the treatment with butyl-lithium, while the condensation stage is carried out at elevated temperatures[100]. The principal conditions of the synthesis and the yields of organocyclodisilazanes (XXXIX)–(XLII) are presented in Table 10.

Table 9. The structure, properties, and infrared and ^1H NMR spectroscopic data for the organocyclodisilazanes (XXXIX)–(XLII) [100]



Compound	R	B.p., °C/mmHg	M.p., °C	τ for Me protons, p.p.m.	ν, cm^{-1}	
					Si_2N	Si_4N_2
(XXXIX)	$CF_3CH_2CH_2$	130–132/0.2	60–73	9.56 and 9.59	868	1022
(XL)	Ph	220–221/0.2	—	9.27–9.54 and 9.65–9.73*	850	1019
(XLI)	CH_2=CH	120/2	—	9.56 and 9.59	860	1038
(XLII)	Et	114/0.2	—	9.68	855	1032

* Multiplets.

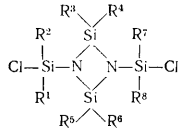
Table 10. The principal conditions of the synthesis and yields of the organocyclodisilazanes (XXXIX)–(XLII).[100]

Compound	Reaction (6)			Reaction (11)		
	t, °C	time, h	yield, %	t, °C	time, h	yield, %
(XXXIX)	230	6	56	270–300	1.5	81
(XXXIX)	290	3	56			
(XL)	295	4	45	285	1	72
(XLI)	175	48	42	—	—	—
(XLII)	140	16	34	175	1	41
(XLII)	180	10	34			

Treatment of 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXIXa) with diphenyldichlorosilane using different proportions of the initial reactants makes it possible to replace one, two, three, or all the dimethylsilyl groups, whereupon the dimethylchlorosilyl (exocyclic) and dimethylsilyl (endocyclic) groups are substituted almost equally readily by the diphenylchlorosilyl and diphenylsilyl groups respectively. It is noteworthy that the complete substitution of the dimethylsilyl groups requires comparatively high temperatures (~400 °C).[26] The compounds isolated as a result of these reactions are listed in Table 11.

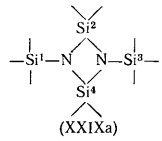
Trans-silylation of compound (XXIXa) with diphenyldichlorosilane (1 : 1 ratio) yields two isomers (XLIIIa) and (XLIIIb) (with endocyclic and exocyclic diphenylsilyl groups) in proportions of 1 : 1 and with an overall yield of 80%.

Table 11. Organocyclodisilazanes obtained by the trans-silylation of 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXIXa) with diphenyldichlorosilane or phenyltrichlorosilane[26]



Compound	R¹	R²	R³	R⁴	R⁵	R⁶	R⁷	R⁸	B.p., °C/mmHg	M.p., °C	n_D^{20}
(XLIIIa)	Me	Me	Ph	Ph	Me	Me	Me	Me	134/0.005	73	—
(XLIIIb)	Ph	Ph	Me	Me	Me	Me	Me	Me	144/0.005	41	—
(XLIVa)	Ph	Ph	Ph	Ph	Me	Me	Me	Me	218/0.05	—	1.5863
(XLIVb)	Ph	Ph	Me	Me	Me	Me	Ph	Ph	218/0.05	139	—
(XLVa)	Ph	Ph	Ph	Ph	Me	Me	Ph	Ph	282/0.05	106	—
(XLVb)	Ph	Ph	Ph	Ph	Ph	Ph	Me	Me	282/0.05	283	—
(XLVI)	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	260	—
(XLVII)	Me	Me	Ph	Cl	Me	Me	Me	Me	170/12	—	1.5046
(XLVIII)	Ph	Cl	Me	Me	Me	Me	Ph	Cl	225/12	102	—
(XLIX)	Ph	Cl	Ph	Cl	Me	Me	Me	Me	132/0.005	—	1.5485

Table 12. The chemical shifts (τ, p.p.m.) of the Me groups in the ^1H NMR spectra of the isomers obtained by the trans-silylation of the cyclodisilazane (XXIXa)



(XXIXa)

Si atom linked to Me group	(XLIIIa)	(XLIIIb)	(XLIVa)	(XLIVb)	(XLVa)	(XLVb)
Si^1	9.81	—	—	—	—	9.99
Si^2	—	9.77	—	9.92	—	—
Si^3	9.81	9.63	9.61	—	—	—
Si^4	9.45	9.77	9.83	9.92	9.78	—

When 2 moles of diphenyldichlorosilane per mole of compound (XXIXa) are used, there is a possibility of three isomeric products (XLIV)[(XLIVa) involving the substitution of one exocyclic and one endocyclic group, (XLIVb) involving the substitution of both exocyclic groups, and (XLIVc) involving the substitution of both endocyclic groups], but only two isomers, namely (XLIVa) and (XLIVb), were isolated. The high and approximately equal yields of the two isomers (86% overall) suggest that the third isomer is either not formed or is formed in a very small amount.

When the ratio of the initial components is 1 : 3, two isomers (XLV), having the same boiling point, are obtained. Isomers (XLVa) and (XLVb) are isolated by recrystallisation from petroleum ether.

Trans-silylation of compound (XXIXa) by treatment with 4 moles of diphenyldichlorosilane takes place very slowly (particularly the last stage). Compound (XLVI) is recrystallised from n-octane or from a mixture of hexane and benzene.

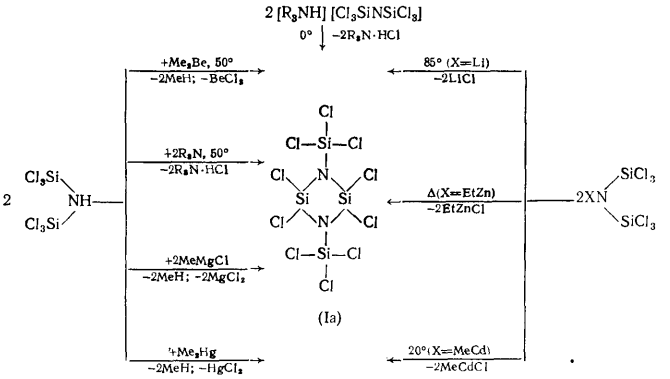
^{1}H NMR data (obtained in $CDCl_3$), confirming the structure of the isomers (XLIII)–(XLVI) obtained, are presented in Table 12.[26]

Other chlorosilanes behave similarly to diphenyldichlorosilanes; for example, phenyltrichlorosilane reacts with formation of compounds (XLVII)–(XLIX) [26] (Table 11).

As already stated, perchlorocyclodisilazanes were obtained as early as 1957 by the pyrolysis of a mixture of $SiCl_4$ and N_2,[14,15] but this synthesis was very complex and the yield of the desired product was extremely low. A new method of synthesis of 1,3-bis(trichlorosilyl)-2,2,4,4-tetrachlorocyclodisilazane (Ia) was proposed in 1967. It involves the interaction of hexachlorodisilazane with methyl-lithium in diethyl ether or with butyl-lithium in petroleum ether; the reaction takes place with cooling to −78 °C and subsequent condensation at 85 °C.[106]

A new more novel method of synthesis of compound (Ia), from lithium bis(trichlorosilyl)amide in the presence of $SiCl_4$, $SiBr_4$, $SiICl_3$, or $GeCl_4$ at 20 °C or by the condensation of tris(trichlorosilyl)amine at 50 °C, was proposed later[107].

The remaining methods of synthesis of perchlorocyclodisilazanes[107–110] are largely preparative and involve the use of organometallic derivatives. A clear idea about the syntheses of compound (Ia) is provided by the following scheme:



Numerous new studies of the formation of organocyclodisilazanes are being published nowadays, the attention of investigators being attracted to an increasing extent by the structure of these compounds, their reactivity, physical properties, and methods of analysis. The data obtained lead to the possibility of a wider practical employment of different types of organocyclodisilazanes, which can find the same applications in many branches of industry as siloxanes and it may be that they will be actually more effective.

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