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Organosiloxazanes—A New Line of Advance in the Chemistry of Hetero-organic Oligomers and Polymers

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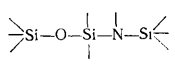
Organosiloxazanes synthesised by the beginning of 1977 have been classified for the first time (according to their structure and molecular weight). For each of the three main groups—(1) cyclic, (2) linear and cyclolinear, and (3) polymeric—the main methods of preparation and the physicochemical characteristics are surveyed. In conclusion several fields of practical application of the new compounds and materials based on them are considered. [A list of 114 references is included.]

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I. INTRODUCTION

The development of the chemistry of organosilazanes, especially during the past 10–15 years, has been accompanied by a considerable growth in the interest taken in organosilicon compounds containing both organosilazane and organosiloxane groups, i.e.



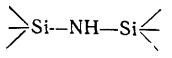
segments. The trend to a systematic study of compounds of this type originated from the wish to combine the characteristic features of organosiloxanes and organosilazanes. The new compounds show greater possibilities than organosiloxanes for the controlled modification of properties, both from the introduction of an additional element (nitrogen) into the molecules and by variation in the nature of the organic radical attached to the nitrogen atoms.

Organosiloxazane compounds that have been obtained to date can be divided into three main groups—(1) cyclic, (2) oligo-organosiloxazanes of linear or cyclolinear molecular structure, and (3) polyorganosiloxazanes varying in the structure of the molecular chains—according to structure and molecular weight. The present Review surveys the preparation, chemical and physical properties, and possible applications of organosiloxazane compounds in preparative chemistry and in industry.

II. ORGANOCYCLOSILOXAZANES

Synthesis of the first individual organocyclosiloxazanes, which initiated the development of the new trend in the chemistry of hetero-organic oligomers and polymers, was accomplished in our country. Investigating the aminolysis of organo-α-ω-dichlorosiloxanes, Sokolov[1] was the first to isolate and identify six- and eight-membered heterocycles containing both silazane and siloxane groups in the molecule.

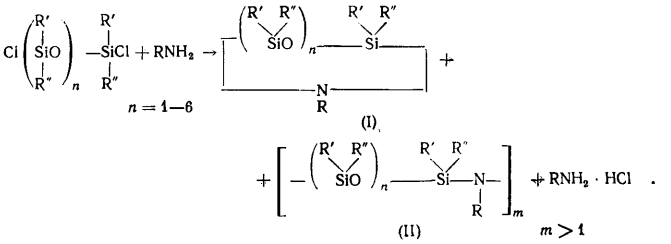
More than 60 six-, eight-, ten-, and twelve-membered heterocycles have now been described, as well as representatives of spiran organocyclosiloxazanes. The homologous series of dimethylsilyl organocyclosiloxazanes is most fully represented in the literature, with reports of all kinds of structural isomers with six and eight atoms in the ring, containing one, two, or three



groups, and several compounds having larger ring skeletons have been synthesised (Tables 1–3).

Methods of Preparation

The most widely used methods for obtaining organocyclosiloxazanes are the ammonolysis[1-11] and the aminolysis[2,5,12,13,15] of individual organo-$\alpha\omega$-dichlorosiloxanes or their mixtures with organodichlorosilanes[14-17]:



Ammonolysis or aminolysis, effected by passing the amine into a solution of the dichlorosiloxane, takes place either by an intramolecular mechanism to give heterocycles (I) containing a single silazane bond or by an intermolecular mechanism giving cyclic compounds (II) comprising two or more siloxazane units. Formation of oligomeric and polymeric as well as cyclic products has been observed in these reactions[7,10,11,13].

In the coammonolysis (coaminolysis) of mixtures of polychloro-organosiloxanes and diorganodichlorosilanes

the desired products are compounds formed by an intermolecular mechanism and containing two or more silazane bonds[14-18]:

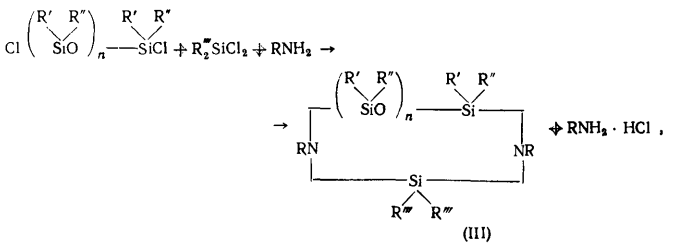
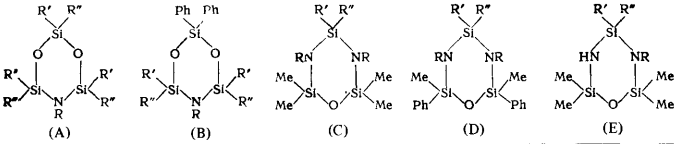


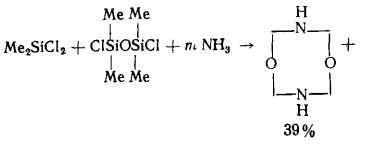
Table 1. Properties of six-membered organocyclosiloxazanes.



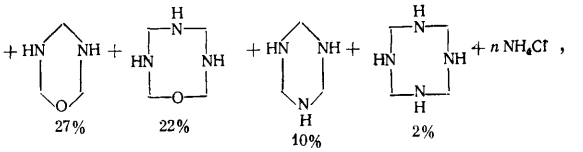
(A) (B) (C) (D) (E)

R	R′	R″	M.p., °C	B.p., °C (*p*, mmHg)	n_D^{20}	d_4^{20}	Ref.
				(A)			
H	Me	Me	9.5—10	151 (760)	1.4088	0.9313	1,2,5—7,9,10
Me	Me	Me	—	163 (760)	1.4100	0.9254	13,20
Et	Me	Me	—	41 (1—2)	1.4153	0.9343	12
n-Bu	Me	Me	—	31 (0.5—1)	1.4244	0.9235	2,5,22
Ph	Me	Me	80	—	—	—	15
C_6F_5	Me	Me	42	66 (0.2)	—	—	21,36
$SiMe_3$	Me	Me	—	135 (44)	1.4488	—	30,41
H	Me	Ph	113—115	169—172 (0.25)	—	—	2,5,19
Me	Me	Ph	111—112	184—189 (10.5)	—	—	13
Et	Ph	Ph	170—171	—	—	1.195	38
Me	Ph	NHMe	—20	196—198 (1)	1.557	1.153	25
Et	Ph	NHEt	—24	223 (1)	1.546	1.129	25
Pr	Ph	NHPr	—45	250—255 (1)	1.534	1.082	25
C_6H_{11}	Ph	NHC_6H_{11}	15	345—347 (1)	1.545	—	25
Ph	Ph	NHPh	84	352—354 (1)	—	—	25
				(B)			
H	Me	Me	99—100	119—135 (0.05)	—	—	2,32,35
Et	Me	Me	—	117—119 (0.07)	—	—	15,32
				(C)			
H	Me	Me	—4÷—5	100 (75)	1.4292	—	17,41
Me	Me	Me	—14	75 (11)	1.4326	0.9244	31,32
Me	Me	Vin	—21	80—81 (0.5)	1.4380	0.9184	27
Me	Cl	Cl	38	89 (10)	—	—	27
Me	Br	Br	45—46	63 (0.2)	—	—	27
Ph	Me	Me	109—110	—	—	—	15
C_6F_5	Me	Me	168—170	—	—	—	36
$SiMe_3$	Me	Me	—	111 (5)	1.4589	—	30,41
$Si(Me_2)OSiMe_3$	Me	Me	—	88 (0.25)	—	—	41
				(D)			
H	Me	Me	63.5	172—174 (6)	—	—	26
H	Cl	Cl	80—82	—	—	—	26
				(E)			
$SiMe_3$	Me	Me	—	81 (5)	1.4330	—	30,41
$Si(Me_2)OSiMe_3$	Me	Me	—	81 (1)	—	—	41

Products of separate amination—organocyclosiloxazanes (I) and organocyclosilazanes—are also formed. Thus chromatography indicates[17] that the composition distribution of products of the simultaneous ammonolysis of dimethyldichlorosilane and tetramethyldichlorodisiloxane is



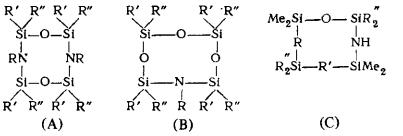
39%



27% 22% 10% 2%

where each corner in a ring represents a dimethylsilylene group.

Table 2. Properties of eight-membered heterocycles.



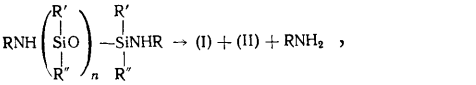
(A) (B) (C)

R	R′	R″	M.p., °C	B.p., °C (*p*, mmHg)	n_D^{20}	d_4^{20}	Ref.
				(A)			
H	Me	Me	37—40	206—208 (760)	—	—	1,2,6—10, 17,32,33
Me	Me	Me	24.5—28	232—234 (760)	1.4321 (30°)	0.9463 (30°)	4,13,20,32, 33
Et	Me	Me	—	95—96 (1—2)	1.4410	0.9470	12
Bu	Me	Me	—	95—98 (0.25)	—	—	2
C_6F_5	Me	Me	107—108	170—175	—	—	21,36
$SiMe_3$	Me	Me	—	126 (5)	1.4571 (22°)	—	24,74
H	Me	Ph	134—136	200—206 (0.1)	—	1.215	2,39
Me	Me	Ph	1) 115—118* 2) 136—137*	228 (0.4)	—	—	13
Me	OMe	OMe	—	173—175 (0.05)	—	—	29
Me	Ph	NHMe	5	257—260 (1)	1.573	1.163	25
Et	Ph	NHEt	10	275—278 (1.5)	1.559	1.151	25
Pr	Ph	NHPr	7	257—260 (1)	1.082	1.550	25
Me	Ph	$OSiEt_3$	—	285 (1)	1.4998	—	90
				(B)			
H	Me	Me	20—20,5	190—191 (760)	1.4151	0.9921 (26°)	2,5—7,10
Me	Me	Me	—	84—85 (8)	1.4202	—	4
H	Ph	Me	—	192—202 (0.15)	—	—	2,5
Me_3Si	Me	Me	—	90 (4.5)	1.4316 (25°)	—	41
				(C)			
NH	O	Et	—	70 (0.5)	1.4308	—	1,8,9
NH	NH	Me	63	—	—	—	16—18
O	NH	Me	46	—	—	—	16

* Isomers.

Several studies on the synthesis of organocyclosiloxazanes have examined the variation of the yield of products with temperature[4], nature of solvent[5,15], proportions and mode of introduction of reactants[4,12,19,20], catalysts[5,20], etc.[13] Thus the aminolysis by aniline of $\alpha\omega$-dichlorohexamethyltrisiloxane[15] yields in most solvents merely linear diamino-derivatives. Nor could cyclic organosiloxazanes be obtained by the reaction of $\alpha\omega$-dichlorodimethylsiloxanes with pentafluorophenylaniline[21]. Only the use of dimethylformamide enables the reaction to be directed towards formation of *N*-phenylated six-membered rings[15].

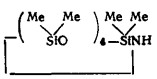
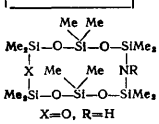
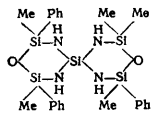
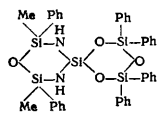
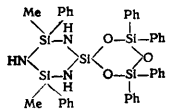
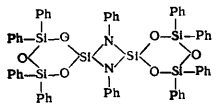
Owing to the formation of linear organosiloxanes having terminal amino-groups[3,12,19,22,23] the homocondensation of amino-derivatives has acquired greater importance in the synthesis of cyclic organosiloxazanes:



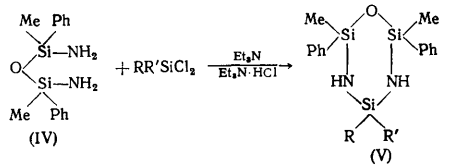
where R = H or Alk. Not only heterocycles of types (I) and (II) but also polymeric products have been obtained by homocondensation[19,10]. In the absence of a catalyst

$\alpha\omega$-diamino-derivatives of organosiloxanes readily undergo homocondensation only when the terminal amino-groups are primary[25]. When they are secondary, such reactions either do not take place or give only a low degree of conversion[4,6,7,10,13,19,22]. Ammonium chloride, copper(I) chloride, and certain other catalysts have been used in these reactions[2,4,13,20,22].

Table 3. Properties of organocyclosiloxazanes.

Compound	M.p., °C	B.p., °C (*p*, mmHg)	n_D^{20}	d_4^{20}	Ref.
	—	115—119 (13)	1.4125	0 9683	2, 3, 5
 X=O, R=H	—	58—60 (1)	1.4122	0.9690	2, 3, 5
X=NH, R=H	—12	148—150 (2)	1.4269	0.9756	2, 5, 9
X=NH, R=SiMe$_3$	—	94 (0.5)	—	—	41
X=NSiMe$_3$, R=SiMe$_3$	57—58	106 (0.5)	—	—	41
X=NC$_6$F$_5$, R=C$_6$F$_5$	117—118	—	—	—	21, 36
	134—136	212—230 (0.02)	—	—	26
	134—135	265—270 (0.02)	—	—	26
	170	299—301 (0.02)	—	—	26
 (XI)	261	—	—	—	58
	230—231	—	—	—	58

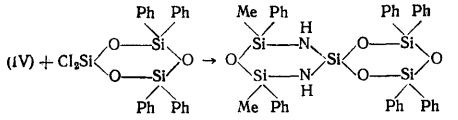
Heterofunctional condensation of organo-$\alpha\omega$-diaminosiloxanes with diorganodihalogenosilanes and tetrachlorosilane yields heterocycles of type (III). Thus the corresponding six-membered organosiloxazanes have been obtained[26,27] by treating tetraorganodisiloxane-1,3-diamines with dimethyldichlorosilane, methylvinyldichlorosilane, and tetrachlorosilane in the presence of triethylamine:



(IV) (V)

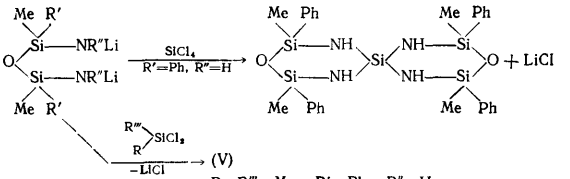
R=R′=Me; R=R′=Cl; R=Me, R′=Vin.

Use of an organodichlorocyclosiloxane instead of a dialkyldichlorosilane in such a reaction yielded a spirosiloxazane[26]:



Replacement of (IV) by dimethyldiphenyldisilazane-1,3-diamine led to the formation of a spiro-compound comprising a silazane ring and a siloxane ring[26].

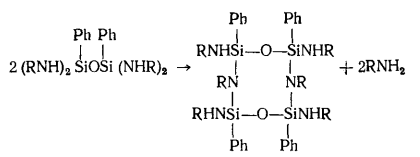
Rings of type (V) have been obtained from dilithium derivatives of (IV) with dimethyl- or methylvinyl-dichlorosilane without the use of a tertiary amine as acceptor of hydrogen chloride, but condensation with tetrachlorosilane gives a symmetrical bicyclic methylphenylspirosiloxazane[26]:



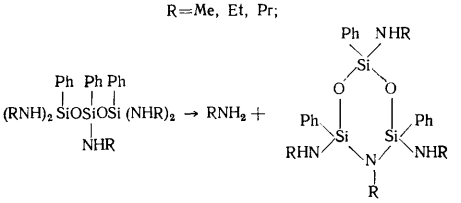
(V)

R=R‴=Me, R′=Ph, R″=H;
R=Me, R‴=Vin, R′=R″=Me.

Six- and eight-membered organocyclosiloxazanes containing one amino-group on every silicon atom[25] are the chief products of the homocondensation of organosiloxane-tetra(and penta) amines[19,28]:

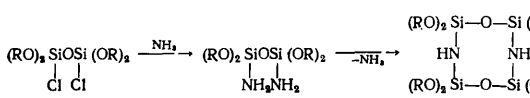


R=Me, Et, Pr;

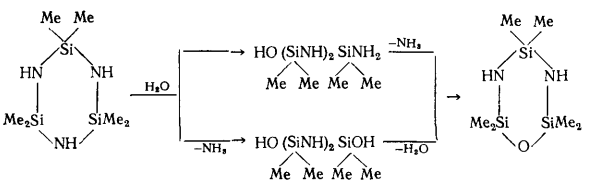


R=Me, Et, Pr, Ph, C_6H_{11}.

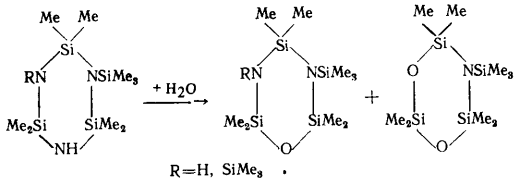
Cyclisation predominates in the condensation of such compounds, as evidenced both by the high yields of individual cyclic compounds and by the absence from the reaction mixture of insoluble polymers having a three-dimensional macromolecular structure. An eight-membered organosiloxazane containing two alkoxy-groups on every silicon atom was first obtained in 1963, from a tetra-alkoxy-1,3-dichlorodisiloxane[29]:



Organocyclosiloxazanes have been obtained also by hydrolysing hexamethylcyclotrisilazane[17]:

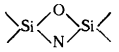


Partial hydrolytic condensation of organocyclosiloxanes in diglyme gave *N*-silylated six-membered organosiloxazanes[30]. This method enabled two of the three silazane groups in the ring to be replaced by oxygen:

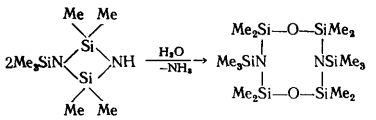


R=H, $SiMe_3$.

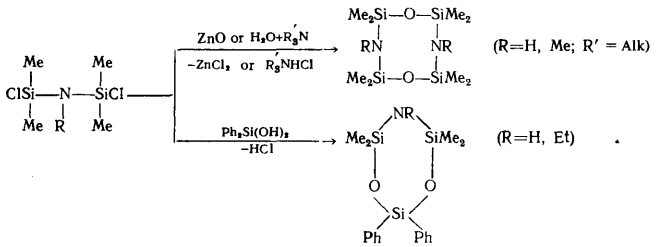
In contrast to the above reactions the partial hydrolysis of a tetramethyldisilazane ring results in the formation not of a four-membered ring



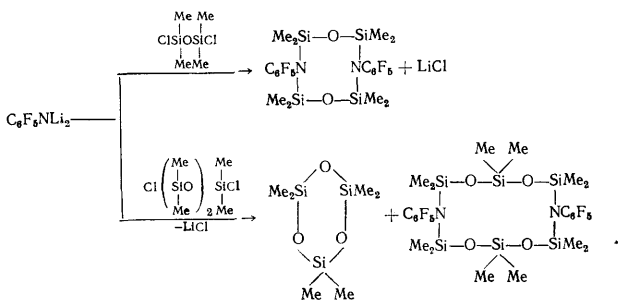
but of the symmetrical eight-membered 1,1,3,3,5,5,7,7-octamethyl-4,8-bistrimethylsilylcyclo-1,3,5,7-tetrasil-2,6-dioxa-4,8-diazane[24,74]:



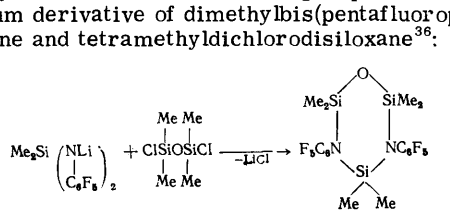
When linear organosilazanes containing halogen attached to the silicon atoms are used to obtain cyclosiloxazanes, the silazane bonds are unaffected, and siloxane units result from the action of water[31-33], zinc oxide[34], or a disubstituted silanediol[35] on the terminal halogen atoms:



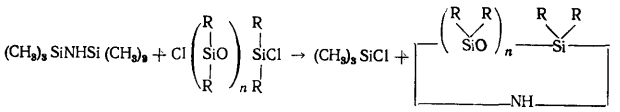
Six-, eight-, and twelve-membered organocyclosiloxazanes have been obtained[21,36] by cyclising $\alpha\omega$-dihalogenated organosiloxanes by the action of *NN*-dilithium derivatives of amines·



A six-membered organocyclosiloxazane having two perfluorophenyl radicals in the silazane groups is formed from the dilithium derivative of dimethylbis(pentafluorophenylamino)silane and tetramethyldichlorodisiloxane[36]:

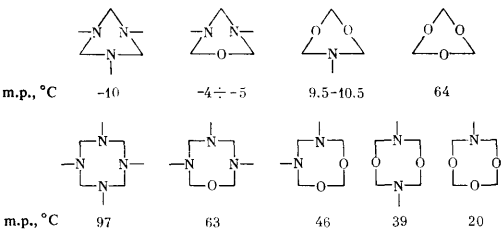


It has been claimed also[37] that linear $\alpha\omega$-dihalogenated organosiloxanes can be converted into cyclic siloxazanes by exchange between the chlorosilyl group and hexamethyldisilazane[37]:



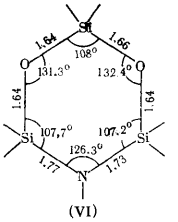
Physicochemical Properties

Melting points. Tables 1–3 list several physical properties of monocyclic organosiloxazanes. In structural analogues such properties depend on the ratio of the total numbers of Si–O–Si and Si–N–Si bonds in the molecules. This is typified by the variation in melting point in the two homologous series of dimethylsilylene six- and eight-membered ring compounds (with one hydrogen atom attached to every nitrogen atom):



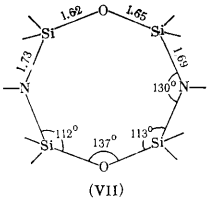
In the first series hexamethylcyclotrisilazane melts 74 deg below hexamethylcyclotrisiloxane, but in the second series the melting point of the dimethylsilylene eight-membered cyclosilazane is lower than that of the corresponding siloxane by 80 deg. The overwhelming majority of heterocycles are readily soluble in aromatic solvents but less soluble in alkanes.

Structure. Among crystalline organocyclosiloxazanes one six-membered ring[38] and one eight-membered ring[39] have been subjected to structural analysis: *N*-ethylhexaphenylcyclo-1,3,5-trisil-2,4-dioxa-6-azane (VI) and 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclo-1,3,5,7-tetrasil-2,6-dioxa-4,8-diazane (VII) have the structures



(VI)

Monoclinic, space group $P2_1/a$; $a = 17.412$; $b = 16.287$; $c = 13.752$ Å; $\beta = 116°31'$;



(VII)

Orthorhombic, space group $Pbca$, $a = 11.652$; $b = 19.798$; $c = 12.833$ Å; $V = 2960.5$ Å^3.

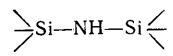
The cyclic skeleton of (VI) departs slightly though definitely from planar and gravitates towards the "boat" form in structure. Compound (VII) has the "chair" conformation. The mean silicon–nitrogen bond length is rather shorter in the eight-membered than in the six-membered ring (1.71 and 1.747 Å). No less interesting is the difference in silicon–carbon bond lengths, obviously due to p_π–d_π interaction of electrons of exocyclic substituents with vacant *d* orbitals of silicon and to hyperconjugation in the

siloxazane ring (Table 4). The position of the phenyl group in (VII) with respect to the siloxazane ring (perpendicular) is regarded[39] as optimal in terms of maximum overlap of the π-electron systems of the phenyl rings with $3d_{z^2}$ orbitals of silicon, so that the remaining $3d$ orbitals of the silicon atom may be involved in delocalisation of the electron cloud of the siloxazane ring.

Table 4.

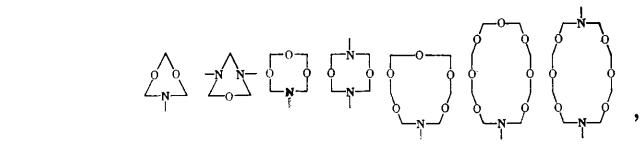
Compound	Si–C bond length, Å	
	Ar	Alk
(VI)	1.875	–
(VII)	1.85 (2)	1.91 (1)
Arylsilanes	1.843	–
Alkylsilanes	–	1.875

Infrared spectra. The infrared absorption band corresponding to asymmetric siloxane-stretching vibrations is sensitive to variation in the dimensions of the ring. As example, the homologous series of dimethylsilylated cyclosiloxazanes containing one silazane bond



with respectively 2–5 siloxane bonds exhibits a shift in ν_{as}(Si.O.Si) from 983–1023 to 1067–1090 cm^{-1} on passing from six- to eight-, ten-, and twelve-membered heterocycles[2,10,40]. Analogous shifts are exhibited by other six- and eight-membered organocyclosiloxazanes[25,41]. A shift in this band towards higher frequencies occurs with increase in ring size effected not only by additional siloxane groups but also by the introduction of a new silazane bond[2,10,25,40,41].

The series of *SiSi*-dimethylated cyclosiloxazanes suggests that the ν_{as}(Si.N.Si) band is extremely sensitive both to change in the ring size and to the number of cyclic silazane bonds. A regular displacement of this band to higher frequencies is observed either when the number of silazane bonds is increased at the expense of a diminished number of siloxane bonds in a ring of unchanged size or when the ring is expanded while the number of silazane groups remains constant. This is demonstrated by the homologous series



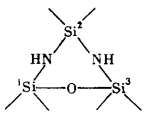
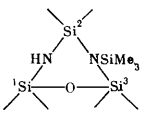
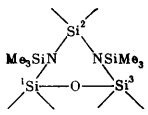
where the corners represent dimethylsilylene groups, and one hydrogen atom is attached to each nitrogen atom.

In contrast to an *Si*-substituent, whose effect on the position of the Si.O.Si vibrational band is little apparent in the infrared spectra of most of the organocyclosiloxazanes studied, radicals attached to the nitrogen atom of a silazane group cause characteristic and considerable shifts in the ν_{as}(Si.N.Si) band. In the homologous series of hexamethylcyclo-1,3,5-trisil-2,oxa-4,6-diazanes having the structural formula



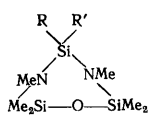
variation in the inductive effect of one or two substituents—in the sequence R = H, $Si(CH_3)_3$, $Si(CH_3)_2OSi(CH_3)_3$—led to a shift in the ν_{as}(Si.N.Si) absorption band from 930 to 979 cm^{-1}.[41] Similar changes had been observed previously in the spectra of four-membered organodisilazane compounds[42], as well as for other *N*-alkylated (or *N*-arylated) organocyclosiloxazanes[25]. Radicals having a negative inductive effect, such as phenyl, lower the ν_{as}(Si.N.Si) frequency to 907–910 cm^{-1} when attached to the nitrogen atom[15,25].

Nuclear magnetic resonance spectra. The structure of the ^{1}H n.m.r. spectra of cyclic organosiloxazanes is more complicated than with cyclosiloxanes and silazanes. As the spectra became more complex, however, the information potential also became greater, revealing finer structural features. Thus the effect of a trimethylsilyl group on the hydrogen atoms of the dimethylsilylene groups gradually decayed with distance[41]. The following data

(τ, ppm)			
Me_2Si^1	9.92	9.92	9.82
Me_2Si^2	9.93	9.83	9.67
Me_2Si^3	9.92	9.83	9.87

show that replacement of a hydrogen atom in an SiNHSi group by trimethylsilyl has different effects on the signals of neighbouring and more remote dimethylsilylene groups. Introduction of a second trimethylsilyl group has the strongest effect on a methyl group attached to $Si_{(2)}$, lying between the two added radicals. Substitution of phenyl for the hydrogen atoms of both silazane groups shifted the signal only of methyl groups located at $Si_{(2)}$ (to τ = 9.82), while the position of the second signal in the spectrum remained unchanged (τ = 9.94).[15] An analogous effect was observed furthermore when silazane hydrogen in six-membered rings was replaced by methyl or pentamethyldisiloxanyl substituents, as well as in the case of eight-membered homologues[41].

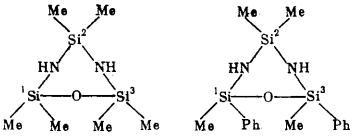
Radicals attached to the silicon atoms have an appreciably more marked effect on the proton magnetic resonance than on the infrared spectra. Thus the spectra of a series of *NN'*-dimethylcyclotrisiloxazanes of general formula



reveal a tendency for the signal to move down field with decrease in the $+I$ effect of the substituents R and R':

R, R'	Me, Me	Br, Br	Cl, Cl	Vin, Me
τ, ppm	9.93	9.85	9.83	9.73

The signal of the methyl hydrogen atoms in methylphenylsilyl derivatives is usually displaced down field in comparison with the dimethylsilyl analogues. This is characteristic also of cyclic organosiloxazanes[26,41]:



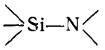
$Me(Si^1)$	9,92	9,66
$Me(Si^2)$	9,93	9,93
$Me(Si^3)$	9,92	9,66

These values of τ (ppm) show that, when two dimethylsilylene groups are replaced by methylphenylsilylene radicals, the position of the signal corresponding to the hydrogen atoms of the dimethylsilylene group remains unchanged, whereas the signal of the methyl hydrogen atoms in a methylphenylsilylene group is displaced by >0.2 ppm. Nuclear magnetic resonance data have been published also for several other organocyclosiloxazanes[4,10,12,17,31,35].

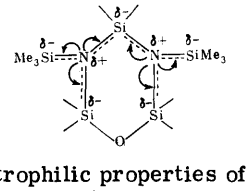
Mass spectra. Among other physical methods, mass spectrometry has also been used to analyse organocyclosiloxazanes[43].

Interpretation of physicochemical properties and reactivity. The approach to interpreting e.g. the ability to polymerise under the influence of nucleophiles is usually more cautious with organocyclosiloxazanes than with cyclic organosiloxanes and organosilazanes, most probably because of the additional effects arising from the combination of siloxane and silazane groups. Despite the comparatively few data that have accumulated, we can distinguish some of the most important factors governing such properties of cyclosiloxazanes as thermal and hydrolytic stability, ability to rearrange or polymerise.

Firstly may be mentioned the inductive and mesomeric effects of substituents attached to the silazane nitrogen. For the series of substituents—hydrogen, methyl, trimethylsilyl, phenyl—the inductive effect changes sign from positive to negative, corresponding to diminished electron density on the nitrogen and enhanced resistance of the

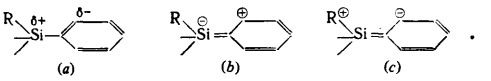


bond to hydrolysis, which usually involves protonation of the nitrogen[44]. Since moreover the negative mesomeric effect of the trimethylsilyl group (p_π–d_π interaction of exocyclic groups with nitrogen) lowers the electron density on the nitrogen and increases it on the silicon atoms, we can explain the high hydrolytic and thermal stability of trimethylsilylated heterocycles. The scheme



shows that the electrophilic properties of silicon are weakened by the above negative mesomeric effect with simultaneous decrease in the basic strength of the nitrogen. Basic properties are completely absent from tris-trimethylsilylamine $((CH_3)_3Si)_3N$.[45]

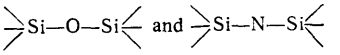
Another important factor—the influence of groups attached to the silicon atoms—can also be considered in terms of mesomeric and inductive effects. In the case of an *Si*-phenyl substituent, for example, the inductive effect guides electrons from the silicon orbitals to the phenyl ring (*a*), whereas the mesomeric effect resulting from interaction of π electrons of the phenyl ring with vacant (*b*) orbitals of the silicon atom has the opposite direction (*b*) or transmits electric charge to the *ortho*- and *para*-positions by hyperconjugation (*c*) and thus strengthens the inductive effect[46]:



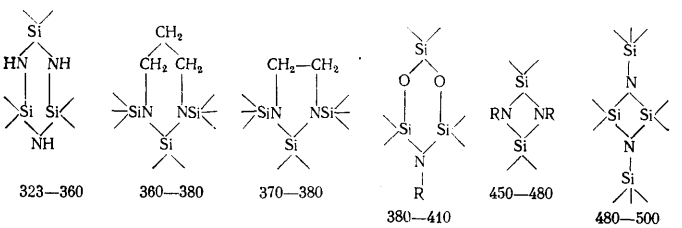
(*a*) (*b*) (*c*)

Depending on the steric disposition of the phenyl group, p_π–d_π conjugation may be either strengthened or weakened[39].

A no less important factor determining the reactivity and the physical properties of organocyclosiloxazanes is hyperconjugation (pseudoaromatisation) within the siloxazane ring, which depends on the size of the ring, its conformation, the regularity of alternation of

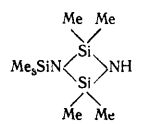


units, etc. Study of this problem is not yet sufficient to permit unambiguous interpretation of many regular changes in properties on passing from cyclic organosiloxanes to organocyclosilazanes or organocyclosiloxazanes. Judging from the variation in bond lengths and angles[38,39] and also the diminished basicity of the silazane nitrogen[24] due to its involvement in delocalisation of the electron cloud within the ring, however, hyperconjugation interactions have a considerable influence on the stability and other properties of the compounds. Indeed, in the series of organosilicon heterocycles[47]



323—360 360—380 370—380 380—410 450—480 480—500

(the temperature ranges of decomposition (°C) are indicated below the formulae) four-membered cyclodisilazanes are the most thermostable. Thus in 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane

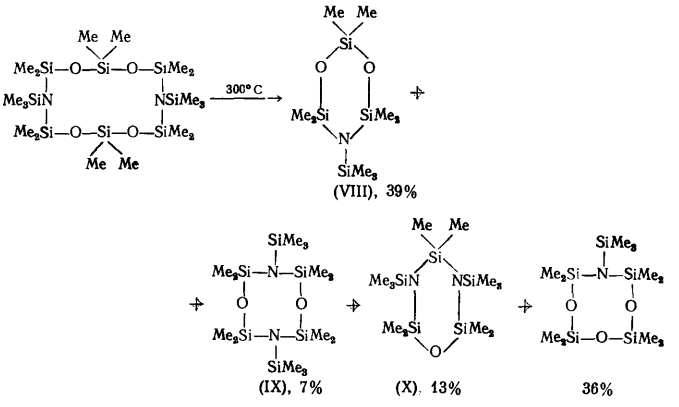


the proton attached to the second nitrogen atom exhibits enhanced acidity (and the nitrogen atom is correspondingly less basic), which indicates a considerable contribution to conjugation within the ring by the nitrogen electrons, including those bonding the hydrogen atom with the nitrogen[24].

Thermal stability. Study of organocyclosiloxazanes as a novel type of heterocycles showed[44,48,49] that the thermal stability of organocyclotetrasildioxadiazanes exceeded those of cyclic organosilazanes and organosiloxanes. Perfluorophenylated derivatives of six- and

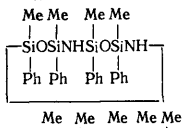
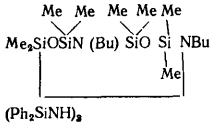
eight-membered heterocycles begin to decompose[21] over the temperature range 400–450°C. The start of the decomposition of hexaphenylcyclotrisiloxazane also lies above 410°C.[50]

Comparison of the thermal stability of *N*-silylated *SiSi*-dimethylated twelve-, eight-, and six-membered cyclosiloxazanes has revealed[41] the extraordinary stability of the six-membered 2,2,4,4,6,6-hexamethyl-5-trimethylsilylcyclotrisil-1,3-dioxa-5-azane (VIII) to isothermal heating at 300°C: whereas the *N*-trimethylsilylated twelve-membered heterocycle underwent the rearrangement



after being heated in a sealed ampoule at 300°C for only 13 h, compound (VIII) remained unchanged after 260 h at the same temperature. Heating (IX) under the same conditions for 120 h led to the formation of approximately equal quantities of (VIII) and (X) (totalling ~90%). The heterocycle (X) suffered only slight losses after the same treatment.

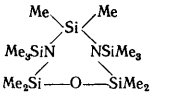
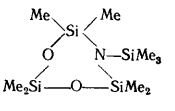
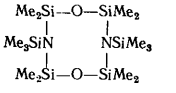
Table 5.

Compound	ν_{as}(Si.N.Si), cm^{-1}	Rate of disappearance of band at 25°C
$(Me_2SiNH)_3$	925	1 h
$(Me_2SiNH)_4$	941	1 h
$Ph_2SiOSiMe_2OSiMe_2NH$	898	1 h
$Me_2SiOSiMe_2N(H)SiMe_2OSiMe_2NH$	947	slight changes after 13 h
	941	no change after 25 h, slight changes after 7 days
	904	no change after 7 days
$(Ph_2SiNH)_2$	952	no change after 7 days

Hydrolytic stability. The resistance of organocyclosiloxazanes to hydrolysis is governed mainly by the nature of the silazane bond, being considerably affected by the substituent on the nitrogen atom. This factor was noted in one of the first preparations of the heterocycles[2]. Table 5 gives relative rates of hydrolytic cleavage of the silazane bond in cyclic organosilazanes and siloxazanes determined from the disappearance of the ν_{as}(Si.N.Si) band from the infrared spectra of 0.25 M solutions of the heterocycles in dimethylformamide containing 5% of water.

Later work has established the great hydrolytic stability of cyclosiloxazanes containing an *N*-phenyl[15] or an *N*-perfluorophenyl[21] group. The accompanying data show that the nature and the bulk of substituents attached to the silicon atoms may also have a considerable influence on the rate of hydrolysis.

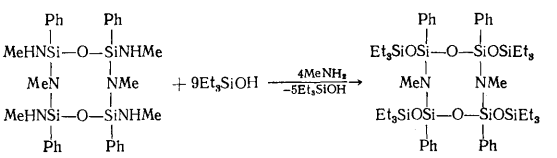
Table 6.

Compound	Time of hydrolytic cleavage of ring, h		Rate constant, k, h^{-1}
	50%	95%	
	—	20	—
	132	400	$5.2\cdot10^{-3}$
	66	200	$1.2\cdot10^{-2}$

N-Trimethylsilylated compounds are among the hydrolytically most stable organosiloxazanes. Parallel tests of the hydrolytic stability of organosilazanes and organosiloxazane heterocycles, made under homogeneous conditions in a boiling solvent (dimethoxyethane) containing excess of water (relative to the silazane bonds), demonstrated rapid breakdown of the cyclosilazanes, whereas the cleavage of *N*-trimethylsilylated organosiloxazane rings occurs considerably more slowly[41] (Table 6).

The resistance of organocyclosiloxazanes and also of cyclic organosilazanes is greater in neutral and alkaline than in acid media[8]. The main hydrolytic condensation products are oligomeric and cyclic organosiloxanes[10].

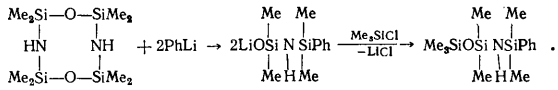
Triethylsilanol acts on organocyclosiloxazanes containing *Si*-amino-groups at temperatures up to 130°C predominantly at these groups[51]:



The cleavage of heterocycles at the silazane bond under the influence of organic primary amines[12] can be regarded as displacement to the left of the equilibrium formation of cyclic organosiloxazanes from organosiloxane-$\alpha\omega$-diamines.

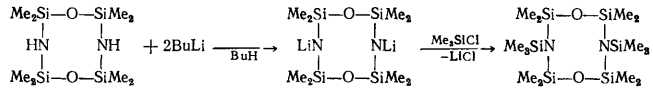
Several investigations have been made on the metallation of organocyclosiloxazanes at the secondary amino-group by means of metal aryls or alkyls[10,41,52–54]. Treatment of symmetrical octamethylcyclotetrasildioxadiazane with phenyl-lithium in ethereal solution at room temperature led to fission of the siloxane bond[10], but

subsequent reaction of the lithium silanolate with trimethylchlorosilane gave the corresponding trimethylsilyl derivative:

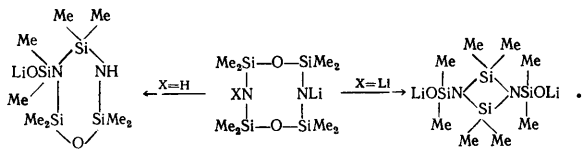


A cyclosiloxazane undergoes a similar reaction with sodamide.

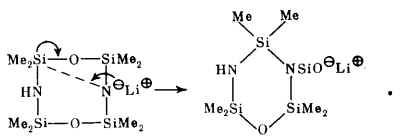
The action of butyl-lithium on the same organocyclosiloxazane has been examined in greater detail[41,53,54]. At low temperatures cleavage of siloxane bonds is not effected, and at −60°C metallation occurs smoothly, to yield mono- or di-*N*-trimethylsilylated products after treatment of the *N*-lithium derivatives with trimethylchlorosilane:



If, however, the di- or mono-lithium derivative is left at a higher temperature (from −30 to +20°C) for some time, it undergoes rearrangement with contraction of the ring, when the dilithium compound passes into a cyclodisilazane, and the monolithium compound into a six-membered organocyclosiloxazane:



The mechanism of the rearrangement most probably involves nucleophilic attack by N^- on silicon, leading to cleavage of the siloxane bond and formation of a new silazane bond:



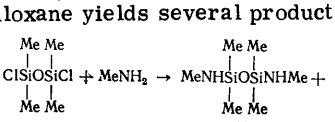
Rearrangements of this type are transannular interactions, and occur rapidly in 1,2-dimethoxyethane and oxolan; they are far slower in ether and in hexane[53].

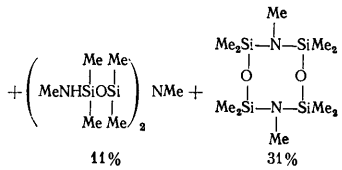
The preparation and certain properties of cyclic organosiloxazanes have been discussed also in several other references[55-57].

III. OLIGO-ORGANOSILOXAZANES—LINEAR, CYCLO-LINEAR, AND SPIROCYCLIC

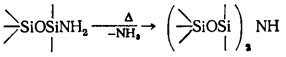
Methods of Preparation

The methods used are more diverse than for organocyclosiloxazanes. The ammonolysis and aminolysis of organochlorosiloxanes, as well as the homocondensation of organosiloxanes containing *Si*-amino-groups, are common to the two classes of products[6,7,13,58,59]. Thus the introduction of methylamine into a solution of 1,3-dichlorotetramethyldisiloxane yields several products[13]:



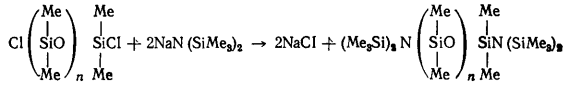


The tendency for heterocycles or linear products to be formed in such reactions depends on the structure of the initial compounds and on the experimental conditions. Homocondensation processes for obtaining such linear oligo-organosiloxazanes take place according to the general scheme[6,7,59,60]



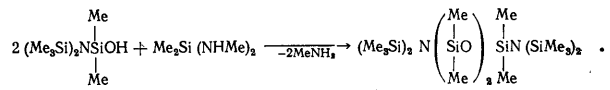
Certain properties of the resulting oligomers are listed in Table 7.

Linear oligo-organosiloxazanes having terminal bistrimethylsilylamino-groups have been synthesised by the action of bistrimethylsilylsodamide on organo-$\alpha\omega$-dichlorosiloxanes[59,61]:

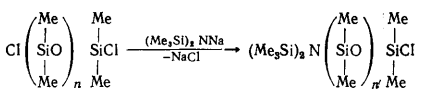


$n = 3, 5, 7, 13.$

In this reaction both halogen atoms are smoothly replaced by bistrimethylsilylamino-groups only in halogenated siloxanes containing four or more siloxane units[59]. The oligomer of this homologous series having three siloxane units has been obtained by condensing dimethylbismethylaminosilane with bistrimethylsilylaminodimethylsilanol[62]:



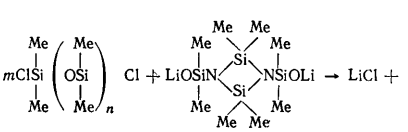
When the proportion of bistrimethylsilylsodamide is lowered to equimolecular relative to the organodichlorosiloxane, monosubstituted compounds are formed in yields up to 70%:[6,7,59,61]



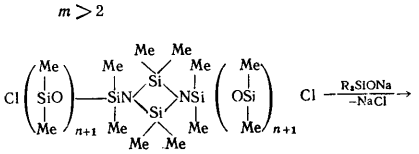
$n = 1, 2, 3, 6.$

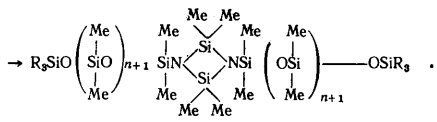
Various derivatives—hydroxysilyl, aminosilyl, etc.—have been obtained from α-bistrimethylsilylamino-ω-chlorodimethylsiloxanes.

Exchange of mono- or di-lithium derivatives of cyclodisilazanediols with dimethyldichlorosilane or organo-$\alpha\omega$-dichlorosiloxanes has been used to obtain a series of oligomers containing organodisilazane rings in the molecular chains[63-65]; the terminal halogenosilyl groups in the resulting oligomers were then blocked by means of alkylated (or arylated) silanolates[63]:

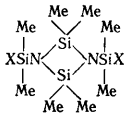


$m > 2$



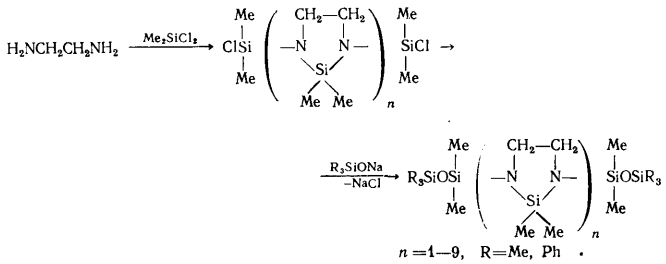


Other methods of heterofunctional condensation used to prepare analogous products include the reactions of organocyclodisilazane derivatives

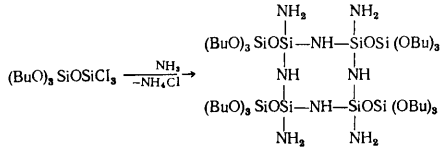


(X = NR_2 or Cl) with alkyl(aryl) silanols or the corresponding silanolates[66,67].

The same processes based on exchange reactions underlay the method of obtaining "mixed" oligomers of cyclocarbosiloxazane type. Diazasila-alkane rings and polycyclolinear products formed by the action of ethylene-1,2-diamine on dimethyldichlorosilane were used as starting materials[68,69]; treatment of the bischlorosilyl derivatives with trimethylsilanol or triphenylsilanol hence gave cyclolinear carbosiloxazanes having terminal triorganosiloxy-groups:

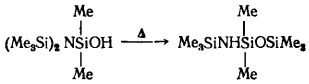


Among oligomers containing eight-membered silazane rings with siloxane units in exocyclic groups the tetrafunctional 1,3,5,7-tetrakistributoxysiloxycyclo-1,3,5,7-tetrasilazane-1,3,5,7-tetramine has been synthesised[70]:

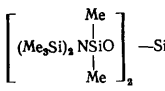


Besides the above condensation methods, oligo-organosiloxazanes can be obtained by cleaving the siloxane bonds in organocyclosiloxazanes by the action of phenyl-lithium or sodamide and then treating the resulting lithium or sodium silanolates with alkylchlorosilanes[10] (see fourth last equation in Section II).

An interesting laboratory preparation of a linear organosiloxazane involved rearrangement[71]: contrary to expectation, when bistrimethylsilylaminodimethylsilanol was heated to 200°C, neither heterofunctional condensation of hydroxysilyl and aminosilyl groups nor homocondensation of hydroxy-groups was observed, but the isomerisation

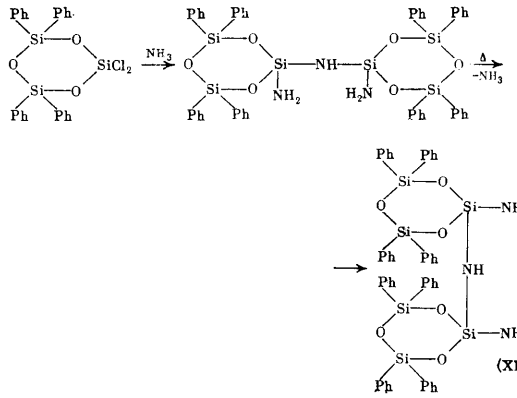


Yet with dimethylbismethylaminosilane the same reactant gave a 57% yield of the expected linear siloxazane[62]



The above type of rearrangement goes smoothly in the presence of basic catalysts; catalytic additions of sulphuric acid gave bistrimethylsilylaminopentamethyldisiloxane.

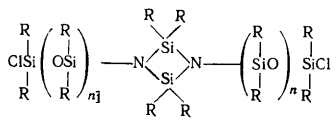
The ammonolysis of organopolychlorosiloxanes followed by homocondensation of the amino-derivatives has recently been used[58,72] to synthesise polycyclic systems consisting of fused organosiloxane and organosilazane rings:



Physicochemical Properties

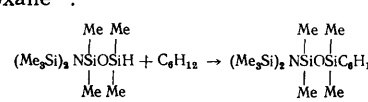
Table 7 shows that most of the oligo-organosiloxanes are liquids that can be distilled in a vacuum. Their viscosity increases with increase both in molecular weight and in the number of cyclic units and phenyl groups in the molecule. All known oligomers containing triphenylsilyl radicals are crystalline compounds melting in the range 100–200°C. The solubility of oligo-organosiloxazanes in polar and non-polar solvents depends on the content of aliphatic and aromatic radicals in the molecule, as well as on the structure and composition of the cyclic segements.

Controlled hydrolysis of oligomers of general formula $((CH_3)_3Si)_2N.[SiR_2.O]_n.SiR_2Cl$ in the presence of acceptors of hydrogen chloride enables the corresponding hydroxy-derivatives to be isolated[6,7,59]. The ammonolysis of oligomers containing an α-chlorine atom and an ω-bistrimethylsilylamino-group gives silylated amines with chloro in the above formula replaced by amino, which can be selectively hydrolysed only at one of the silicon–nitrogen bonds[73]. Hydrolysis of oligomers of the series



has enabled the corresponding organosiloxazane-$\alpha\omega$-diols to be obtained[63,65,75] as oily liquids.

The hydride addition of an *SiSi*-dimethylated siloxazane containing a free hydrogen atom to hex-1-ene proceeds smoothly in the presence of chloroplatinic acid to give the expected product—1-bistrimethylsilylamino-3-hexyltetramethyldisiloxane[62]:



The most specific feature of the infrared spectra of oligo-organosiloxazanes is the absorption band corresponding to asymmetric stretching vibrations of the silazane bond. Its spectral position permits reliable identification

Table 7. Properties of oligo-organosiloxazanes.

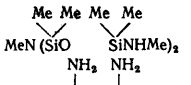
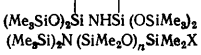
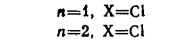
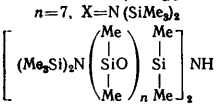
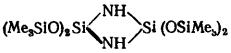
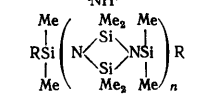
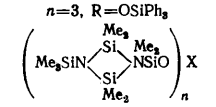
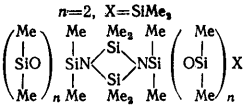
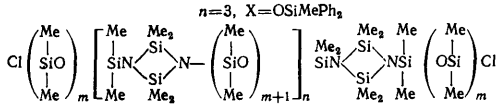
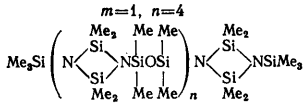
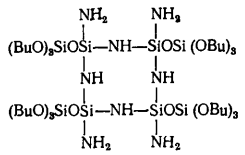
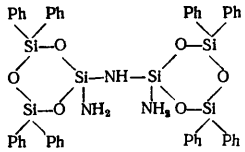
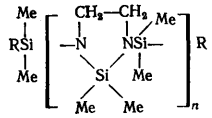
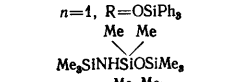
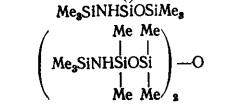
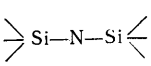
Compound	M.p., °C	B.p., °C (*p*, mmHg)	n_D^{20}	d_4^{20}	Ref.
	—	90—94 (0.8)	1.4280 (24°)	—	13
	—	117—119 (3)	1.4119	0.9338	60
					
n=1, X=Cl	—	109,5—110,5 (10)	1.4440	0.9446 (25°)	59
n=2, X=Cl	—	106—107 (2.5)	1.4365	—	59
n=3, X=Cl	—	123—124 (2)	1.4333	0.9493	6,7,59,61
n=6, X=Cl	—	208—210 (2)	1.4179	0.9684	61
n=1, X=NH_2	—	75—76 (2)	1.4409	0.9122 (25°)	59
n=2, X=NH_2	—	91—92 (1.5)	1.4346	0.9123 (27°)	59
n=3, X=NH_2	—	98—99 (1)	1.4297	0.9237 (26°)	6,7,59
n=2, X=OH	—	102—104 (2)	1.4370	0.9346 (25°)	59
n=3, X=OH	—	103—104 (1.5)	1.4288	—	6,7,59
n=1, X=H	—	73 (3)	1.4340 (25°)	—	62
n=1, X=Me	—	71 (2)	—	—	62
n=1, X=C_6H_{13}	—	118 (1.5)	—	—	62
n=2, X=N($SiMe_3$)$_2$	—	138 (1)	—	—	62
n=3, X=N($SiMe_3$)$_2$	—	159—161 (1)	1.4453	0.9362	59,61
n=13, X=N($SiMe_3$)$_2$	—	290 (2.5)	—	—	61
n=5, X=N($SiMe_3$)$_2$	—	213 (2)	1.4361	0.9415	61,59
n=7, X=N($SiMe_3$)$_2$	—	218 (1.5)	1.4262	0.9449	6,7,59,61
					
n=2	—	196—198 (1.6)	1.4417	—	59
n=3	—	196—198 (1)	1.4437	—	6,7,59
	103	180—183 (4)	—	—	60
					
n=1, R=$OSiMe_3$	—	105 (1)	1.4247	—	41,67
n=1, R=$OSiMe_2Ph$	—	178—180 (0.02)	1.4869	—	66
n=1, R=$OSiMePhI_2$	—	225 (0.01)	1.5338	—	67
n=1, R=$OSiPh_3$	189—191	—	—	—	67
n=2, R=$OSiMe_3$	3	146 (0.05)	1.4425	—	67
n=3, R=$OSiMe_3$	18	205 (0.01)	1.4581	—	67
n=2, R=$OSiMePh_2$	39	274 (0.001)	1.5219	—	67
n=2, R=$OSiPh_3$	95	320—330 (0.002)	—	—	67
n=3, R=$OSiPh_3$	106	—	—	—	67
					
n=1, X=$SiMe_3Cl$	—	132 (14)	1.435	—	64
n=2, X=$SiMe_3$	—	125 (0.04)	1.4462	—	64
					
n=1, X=Cl	—	82 (0,001)	1.4355	—	63
n=2, X=Cl	—	104 (0.005)	1.4281	—	63
n=3, X=Cl	—	146 (0.005)	1.4235	—	63
n=2, X=OH	—	—	—	—	63,75
n=3, X=OH	—	—	—	—	63 75
n=1, X=NEt_2	—	133 (0.005)	1.4413	—	63
n=2, X=NEt_2	—	162 (0.005)	1.4328	—	63
n=1, X=$OSiMePh_2$	26	230 (0.005)	1.5091	—	63
n=2, X=$OSiMePh_2$	1—3	246 (0.005)	1.4925	—	63
n=3, X=$OSiMePh_2$	—	257 (0.005)	1.4808	—	63
					
m=0, *n*=2	—	207 (0.005)	1.4538	—	63
m=0, *n*=4	—	280 (0.005)	1.4525	—	63
m=1, *n*=2	—	198—201 (0.001)	1.4415	—	63
m=1, *n*=4	—	291—305 (0.001)	1.4404	—	63
					
n=1	15—16	125 (0.04)	1.4462	—	63
n=2	25—27	193—195 (0.005)	1.4485	—	63,65

Table 7 (continued).

Compound	M.p., °C	B.p., °C (*p*, mmHg)	n_D^{20}	d_4^{20}	Ref.
	—	220—222 (0.5)	1.4250	—	70
	128—130 (decomp.)	—	—	—	58
					
n=1, R=OSiMe$_3$	—	80 (0.03)	1.4295	—	69
n=2, R=OSiMe$_3$	—	153 (0.02)	1.4505	—	68,69
n=3, R=OSiMe$_3$	—	205—206 (0.02)	1.4622	—	68,69
n=4, R=OSiMe$_3$	—	255 (0.01)	1.4697	—	68,69
n=5, R=OSiMe$_3$	—	280—300 (0.02)	—	—	68,69
n=1, R=OSiMePh$_2$	—	226 (0.02)	1.5420	—	68,69
n=2, R=OSiMePh$_2$	—	275 (0.02)	1.5325	—	68,69
n=1, R=OSiPh$_3$	132—133	—	—	—	68
	—	56—57 (8)	1.4085	—	71
	—	126—127 (0.5)	—	—	73

of the structure of the silazane segments[59,66]. Thus linear oligomers containing silazane bonds in terminal bistrimethylsilylamino-groups are characterised by a doublet in the range 940–920 cm^{-1}; [59] in the infrared spectra of oligoorganosiloxazanes in which the



units forms a disilazane ring the ν_{as}(Si.N.Si) band is observed in the range 895–870 cm^{-1}.

The size and composition of the cyclic segment has an appreciable influence on the position of signals of protons in cyclic dimethylsilylene groups in the ^{1}H n.m.r. spectra of the cyclolinear organosiloxazanes studied (~20 compounds). Thus the shift of the peak corresponding to a dimethylsilylene group forming part of a disilazane ring is τ = 9.70–9.76 ppm.[63] The analogous shift of the peak corresponding to the dimethylsilylene group in a diazasilacyclopentane segement was τ = 9.86 ppm.[69] No perceptible effect of exocyclic siloxazane or other groups on the position of this signal has been observed.

IV. POLYORGANOSILOXAZANES

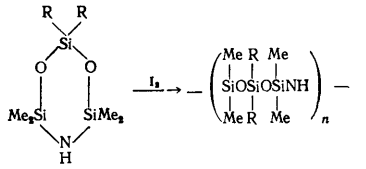
Polyorganosiloxazanes have been synthesised with various molecular structures—(1) linear macrochains having an irregular distribution of siloxane and silazane bonds, and also monochain polymers with cyclic segments, (2) branched and three-dimensional macromolecules, and (3) ladderlike or partly ladderlike.

Polymers containing organosiloxazane segments in the macromolecular chains are obtained by the catalytic polymerisation of cyclic compounds, by the condensation of $\alpha\omega$-diamino- or polyamino-organosiloxanes or cyclo-organosiloxazanes containing functional groups attached to silicon atoms, or by hydride migration.

Attempts to apply to cyclo-organosiloxazanes well known methods of polymerisation using potassium hydroxide as catalyst unexpectedly did not yield polymers of high molecular weight[76]. In the action of this alkali on *SiSi*-dimethylated six-, eight, and ten-membered cyclosiloxazanes (5% of alkali on the weight of the heterocycle) at temperatures above 100°C the increase in viscosity of the reaction products was accompanied by the evolution of ammonia and methane[78]. The formation of these gases indicated the simultaneous occurrence of degradation and polycondensation processes at Si–Ni–Si and Si–C bonds. Subsequent heating of the reaction mixture entailed a fall in viscosity, obviously owing to breakdown of oligomeric chains. In contrast to the above processes the use of caustic potash as catalyst in combination with solvating additives such as dimethyl sulphoxide facilitated the synthesis of polymers of high molecular mass[76].

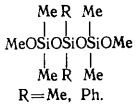
Tetramethylammonium hydroxide, iodine[76,77,79], and ammonium chloride[10] have also proved effective catalysts for the polymerisation of organocyclosiloxazanes. Study of the mechanism of polymerisation in the presence of

catalytic quantities of iodine showed that the process was highly specific involving cleavage only of silazane bonds:



R=Me, Ph

The intrinsic viscosity of the resulting polymers was $[\eta] = 1.25$.[76,77] Evidence of this course of polymerisation was the formation of a single product—a hexasubstituted 1,5-dimethoxytrisiloxane

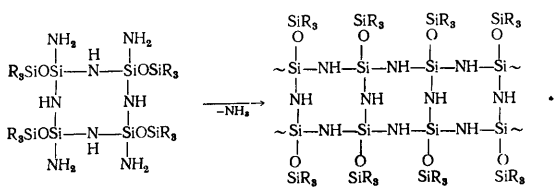


R=Me, Ph.

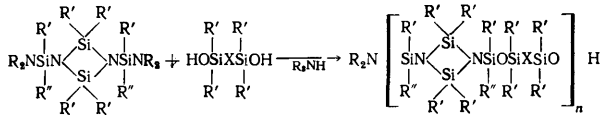
as a result of complete methanolysis of the silazane bonds in the resulting polymer. Chromatographic analysis of analogous methanolysis products from the polymer obtained from hexamethylcyclotrisildioxazane in the presence of tetramethylammonium hydroxide as catalyst indicated also the formation of dimethoxydimethylsilane, 1,3-dimethoxytetramethyldisiloxane, and higher homologues $CH_3O[Si(CH_3)_2O]_nCH_3$ (n = 3–5). The presence of these products was regarded[76] as evidence of the statistical development of polymerisation involving both silazane and siloxane bonds. Individual studies revealed that, among six-membered cyclo-organosiloxazanes, rings in which methyl and phenyl groups were attached to the silicon atoms were least active with respect to polymerisation in the presence of iodine as catalyst[77].

Elastomers of high molecular weight with various contents of silazane groups have been obtained also by the copolymerisation of two eight-membered rings—octamethylcyclotetrasiloxane and octamethylcyclotetrasiltrioxazane—with tetramethylammonium hydroxide as catalyst[80].

The homocondensation of $\alpha\omega$-diamino-, $\alpha\omega$-bismethylamino-, and $\alpha\omega$-bisethylamino-diorganosiloxanes[3,19,23] and of polyamino-organosiloxanes[81] yields polymers in the absence of catalysts. However, no data have appeared on the use of this method to obtain products of high molecular weight. Eight-membered organosilazane rings containing exocyclic siloxane units and a primary amino-group on every silicon atom in the ring are considerably more reactive. When redistilled, they evolve ammonia and form a polymeric organosiloxazane, to which a ladder structure was assigned[70]:



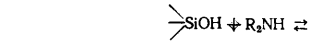
Rather more publications have appeared on the synthesis of cyclolinear organosiloxazanes by heterofunctional condensation. This has most often involved the reaction of cyclodisilazane compounds containing aminosilyl groups with $\alpha\omega$-diol derivatives:



R=H, Me, Et; R′=Me, Ph; R″=Me, Vin, Ph.

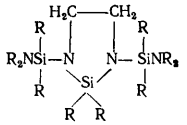
Compounds containing an *SiSi*-dimethylated[47,82–86] or *SiSi*-diphenylated[47,84,86,87] disilazane ring and amino-, dimethylamino-, or diethylamino-silyl groups have been used as cyclic component. The $\alpha\omega$-diols were dimethyl- or diphenyl-siloxane oligomers of various chain lengths[82,84,85], p-bishydroxydiorganosilylated benzenes[47,83,86,87], or analogous derivatives of diphenyl ether[86]. The viscosity of the final polymers obtained by the above reaction scheme depended on the reaction conditions and on the nature of the reactants[82]. However, prolonged heating or raising the temperature of the reaction mixture might result in gelation of the polymers.

The probability of the formation of polyorganosiloxazanes having three-dimensional macromolecules is regarded[82] as directly proportional to the probability of cleavage of the disilazane ring (and also the appearance of additional functional groups) under the influence of nucleophilic species formed according to the scheme



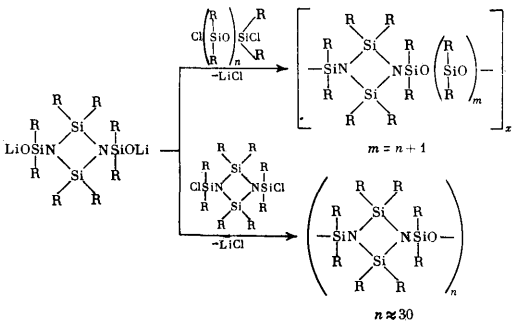
The probability of the appearance of such nucleophilic species should increase with the basicity of the amine, accelerating gel formation by the macromolecules. In the reactions studied a corresponding increase in rate of formation of insoluble polymers has actually been observed according to the nature of R in the sequence $v_H < v_{CH_3} < v_{C_2H_5}$. Reaction between analogous disilazane rings and p-bisdiphenylhydroxysilylbenzene in diglyme or xylene goes practically to completion and is not accompanied by fission of cyclic silazane bonds[47].

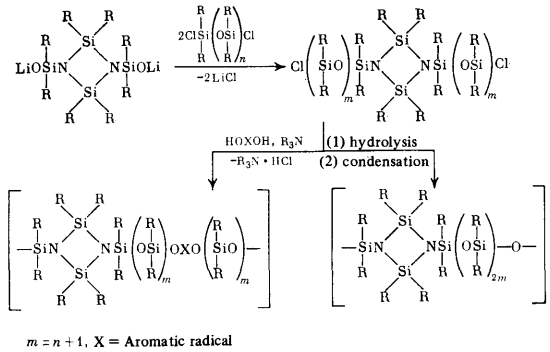
Polymers have been synthesised by a similar procedure from azasilacycloalkanes of general formula



and disubstituted silanediols[88], tetraphenyldisiloxane-1,3-diol, or p-bisdiphenylhydroxysilylbenzene[89].

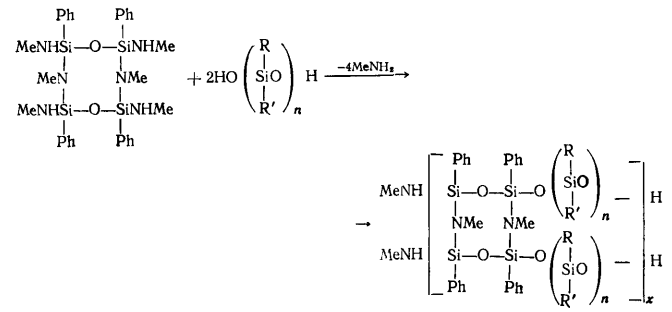
Cyclolinear polymers have been obtained not only by the silanediamine–silanediol type of heterocondensation but also by exchange reactions of cyclic lithium silanediolates with *SiSi′*-dichlorinated cyclodisilazanes or organo-$\alpha\omega$-dichlorosiloxanes[47,65]:





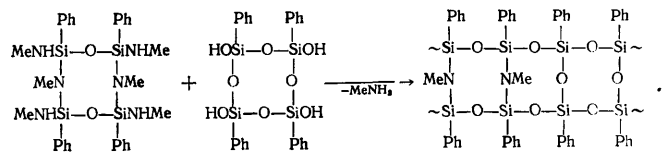
$m = n + 1$, X = Aromatic radical

The use as initial compounds of cyclo-organosiloxazanes of higher functionality ($f = 4$) enables polymers to be synthesised with branched macromolecules or ladderlike siloxazane segments[51]:



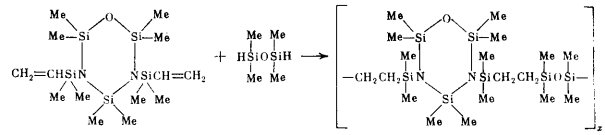
The hydroxylated monomers and oligomers used in these reactions were diphenylsilanediol, tetraphenyldisiloxane-1,3-diol, 1,3-dimethyl-1,3-diphenylsiloxanediol, tetramethyldisiloxane-1,3-diol, decamethylpentasiloxane-1,9-diol, and dimethyl(methylphenyl)siloxane-$\alpha\omega$-diols in which the number average of siloxane units in the molecules was ~100. The nature of the siloxane-$\alpha\omega$-diol—primarily the length and the rigidity of the chain—determined both the course of polycondensation and the structure of the macromolecules. Short and rigid molecules, such as those of diphenylsilanediol and tetraphenyldisiloxane-1,3-diol, caused polycondensation without formation of insoluble polymers having a three-dimensional structure. The use of organosiloxanediols having a very flexible siloxane chain for condensation with cyclic 4,8-dimethyl-1,3,5,7-tetrakismethylamino-1,3,5,7-tetraphenylsil-2,6-dioxa-4,8-diazane, because of the greater mobility of the branches, facilitated long-range intermolecular interaction leading to gel formation. Soluble polymers obtained by this method had molecular weights in the range $(25-30) \times 10^3$.

A polyphenylsiloxazane polymer having a high content of ladderlike segments in the macromolecular chains is formed by the polycondensation of two tetrafunctional cyclic compounds[51]:

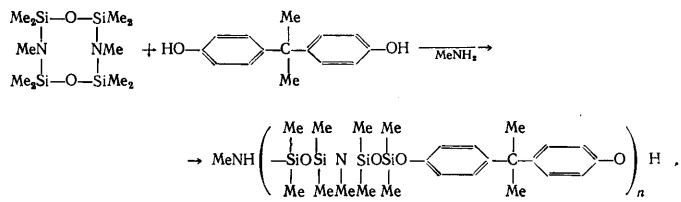


The reaction goes almost to completion. Despite the high functionality of the initial monomers, the resulting polymer is a powder readily soluble in aromatic solvents. Light scattering indicates that its molecular weight is $(100-200) \times 10^3$. The use of various organocyclosiloxazanes having functional amino-groups and diphenylpropane-*pp'*-diol has been claimed[90] for obtaining polyphenylated carbosiloxazane polymers by a similar method.

Processes for obtaining polymeric organosiloxazanes by hydride addition have been claimed in the patent literature. In one case this involved reaction of cyclosiloxanes containing vinylsilyl groups with linear or cyclic organosilazanes containing free hydrogen atoms in the presence of chloroplatinic acid[91]. In another process linear organosiloxanes containing terminal hydrogen atoms were heated with vinylsilylated cyclosiloxazanes or cyclo-organosilazanes in the presence of the same catalyst[52]:

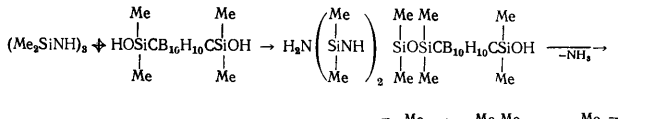


Organosiloxazanes of high molecular weight have been synthesised by splitting some of the silazane bonds in an eight-membered cyclo-organosiloxazane by means of a phenolic hydroxyl[13]:



The elastomeric polycarbosiloxazane obtained had an intrinsic viscosity of 2.7. Polymeric carbosiloxazanes have been synthesised similarly using as hydroxylated compounds fused aromatic diols, bisnitrophenyl sulphone derivatives, and tetraphenylcyclotetrasiloxane-1,3,5,7-tetraol, but polycyclic silazanes were employed together with cyclo-organosiloxazanes[92]. The reduced viscosity of the polymers of this series (0.5% solutions in toluene) lay in the range 0.1–0.95.

The same principle of the partial utilisation of silazane bonds in heterocycles to build up polymer chains underlay the preparation of carborane–siloxazane polymers[108,109]. The reactions of 1,7-bisdimethylhydroxysilylcarborane studied with various heterocycles—hexamethylcyclotrisilazane, octamethylcyclotetrasilazane, hexamethylcyclotrisil-2-oxa-4,6-diazane, octamethylcyclotetrasil-2,6,-dioxa-4,8-diazane, octamethylcyclotetrasil-2,4,6-trioxa-8-azane, and dodecamethylcyclohexasil-2,4,8,10-tetraoxa-6,12-diazane—involved ring cleavage followed by condensation of the linear aminosiloxazanol. With cyclotrisilazane as example the reaction can be written



The rate of cleavage of the heterocycles by the hydroxysilylcarborane is significantly affected by the strain in the ring and its content of silazane bonds: the reactivity of the molecule diminished with increase in size of the cyclo-organosiloxazane and decrease in the number of silazane bonds. The specific viscosity of the resulting polymers (1% solutions in benzene) was 0.2–0.3.

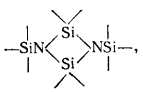
The segmental mobility and the elasticity of linear siloxazane macromolecules in which one silazane unit alternated with two siloxane units were closely similar to those for polyorganosiloxanes. Nuclear magnetic resonance data indicated that segmental mobility in a polymer containing the $Si(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2NH$ unit began around −100°C, but in polydimethylsiloxane it began at about −130°C. The energies of viscous flow for these polymers were respectively 4.3 and 3.4 kcal.[79]

The molecular structure of branched cyclic, ladderlike, and three-dimensional polyorganosiloxazanes has been studied by X-ray diffraction, enabling the rigidity of the polymer chain to be assessed[51] from the interplanar spacing d_1. The largest spacing $d_1 = 12.0$Å is characteristic of a molecular chain comprising only cyclic tetrasiloxazane and siloxane units (see fourth last equation and polymer formula above). Replacement of the siloxane ring in this reaction by linear organosiloxane-$\alpha\omega$-diols produced a gradual decrease in d_1 to 7.5Å with increase in the length and flexibility of the chain of linear organosiloxanes.

Investigation of the stabilising influence of silazane bonds on the thermo-oxidative degradation of organosilicon polymers[93] revealed that the Si–NH–Si group has a significant stabilising effect on the main chains of siloxazane molecules, with considerably less effect on the rate of degradation of organic groups surrounding the main chains. Such a unit serves as a barrier to depolymerisation of the main chain; in its presence, furthermore, fairly intense oxidation of methyl groups attached to silicon atoms has been observed, leading to branching, three-dimensional cross-linking of the polymer, and thus an additional thermostabilising effect.

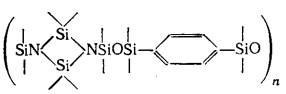
However, a silazane unit containing a secondary nitrogen atom is less stable than Si–NR–Si (R = Alk or Ar) and $Si–N(SiAlk_3)–Si$ groups not only to hydrolytic cleavage but also in the thermo-oxidative degradation of polyorganosiloxazanes. The presence of organosilazane groups having a secondary nitrogen atom is evidently one reason for the relatively low thermal stability in air of several polycarbosiloxazanes[92].

Cyclodisilazane groupings of the type



when introduced into siloxane chains, not only prevent the development of degradative processes involving stepwise cyclisation but also are "suppressors" of hydroxy-groups appearing during thermo-oxidative reactions. Interaction of one hydroxysilyl group with a cyclodisilazane segment does not entail breakdown of the main molecular chains. In a series of polymers whose macromolecules consist of dimethylsiloxane chains separated by tetramethyldisilazane rings thermo-oxidative degradation begins over the temperature range 400–450°C.[82]

Perphenylated polymers having a minimal content of linear chains remain as yet the most stable polyorganosiloxazanes to both thermal and thermo-oxidative treatment. Examples are cyclodisilazane polymers[47] of general formula



and polymers whose macromolecules have predominantly a ladder structure (see fourth last equation above)[51]. Thermal degradation of the former polymers (in nitrogen at 2.8 deg min^{-1}) and thermo-oxidative degradation of the latter (in air at 2.7 deg min^{-1}) began in the region of 500°C.

V. PROSPECTS FOR PRACTICAL APPLICATION

Polyorganosiloxazanes have been tested as protective coatings in the electronics industry[94] and on solar energy installations[95]. The stability of the optical properties of organosiloxazane varnishes on prolonged exposure to light and weathering, combined with good adhesion, moisture resistance, and durability, has permitted these coatings to be recommended for protecting the working surfaces of photocells and concentrators in solar energy technology[95]. Polymers containing organocyclodisilazane segments are among the most thermostable types of binders for paint technology.

Organosiloxazane varnishes and coatings are promising protective materials, exhibiting not only high thermal stability but also the ability to harden under normal conditions by interaction with atmospheric moisture[95,96]. The increasing density of three-dimensional cross-linking of macromolecules during hardening is an obstacle to complete disappearance of silazane groups from the polymeric binder. Several features of film formation by the replacement of some of the silazane bonds by siloxane bonds have been investigated[97]. The drying times in air of coatings used in solar energy technology[95] and recommended for the protection of semiconductor materials and instruments[96] are 0.5–5 h. The adhesion of varnishes to steel and copper surfaces reaches 47 kg cm^{-2} after the coatings have been kept at room temperature for 5 days. The adhesion parameters of the materials can be somewhat improved by heat-treatment. Both Soviet[98–100] and foreign[87,89,101–103] patents indicate not only individual characteristics of the coatings but also fields of application—electrical engineering, electronics, the paper, textile, and leather industries, the protection of glass and silicate surfaces, etc.

Organosiloxazane elastomers are less well represented in the literature. Elastomeric copolymers containing Si–NH–Si units are considerably more thermostable than siloxane rubbers with similar radicals attached to the silicon atoms, but are inferior to the latter in resistance to hydrolytic cleavage[80]. Replacement of secondary-nitrogen silazane bonds in the elastomers by tertiary-nitrogen or especially trisilylamine bonds should improve considerably the resistance of such materials to moisture and to water. Filled organosiloxazane elastomers whose macromolecules contain also carborane and trifluoropropylsilyl groups are distinguished by long fatigue life over the temperature range 300–350°C.[104] Methods for obtaining elastomeric siloxazane materials and for their vulcanisation have been given in patents[5,83,86].

It has been proposed to introduce compounds of boron, phosphorus, titanium, iron, and certain others into organosiloxazane binders to enhance the heat resistance and improve the physicomechanical characteristics[105,106]. On the other hand, additions of methylphenylsiloxazane polymers to stabilising mixtures in the manufacture of polyamides tend to increase the resistance of articles to heat and light[107].

The advisability of using organosiloxazane compounds, primarily organocyclosiloxazanes, to obtain polymeric

organosiloxanes has been noted repeatedly both in the periodical and in the patent literature. In most cases the synthesis is accomplished by the heterocondensation of silazane groups with dihydric phenolic derivatives[110-114].

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