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Cyclocarbosiloxanes

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Cyclocarbosiloxanes are a comparatively new class of heterocyclic silicon compounds[1,2] the cyclic skeleton of which consists of alternating siloxane and carbon groups. During the last decade, considerable advances have been made in the chemistry of cyclocarbosiloxanes.
The present review considers the methods of preparative synthesis of cyclocarbosiloxanes and certain reactions leading to the formation of carbosiloxane rings (including reactions in complex polycondensation and polymerisation systems), their physical properties and structure, and also chemical properties. The latter have been divided into reactions involving the cleavage of the heterocyclic skeleton and the reactions of groups and atoms functioning as substituents in the carbosiloxane ring. The polymerisation of cyclocarbosiloxanes, thermal reactions in the gas phase, and dissociations on electron impact have been considered separately.
The bibliography includes 135 references.

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I. INTRODUCTION

Cyclocarbosiloxanes (CCS) are compounds whose cyclic skeleton consists of Si–O, Si–C, and sometimes C–C bonds, i.e. the main structural elements of these compounds are siloxane and carbosilane groups.

Owing to the presence of the cyclic siloxane groups, cyclocarbosiloxanes are capable of polymerisation with ring opening, forming polymers, the main chains of which are made up of siloxane and carbosilane units. According to the data of a number of patents and publications, the characteristic features of these polymers are high thermal[3-11] and chemical[3] stabilities, resistance to a thermal oxidation[9,10,12], resistance to radiation[6], and also improved physicomechanical properties[6,10] compared with polysiloxanes. Carbosiloxane polymers can be used as brake fluids[5,13], moulding materials[13,14], rubbers[13,14], films[8,13,14], oriented fibres[14], and binding resins in the manufacture of fibreglass[15].

In addition, the study of the structure, the nature of the bonds, and the properties of this new class of heterocyclic silicon compounds with a mixed organic–inorganic skeleton is of considerable interest.

The study of the processes involving the formation of cyclocarbosiloxanes makes it possible to estimate in turn the effect of factors such as the number of carbon atoms and silicon functional groups in the initial molecule, their distribution, the inductive and steric effects of the substituents, etc. on the capacity of the molecule for cyclisation. The knowledge of these factors is extremely important in the choice of the optimal monomers for the preparation of polycondensation polymeric materials based on polyfunctional bridge-type silanes, which are of practical value, and makes it possible to assess the structure of the products formed.

The first mention of the synthesis of cyclocarbosiloxanes was made in 1947,[16] but neither the constants of the compounds obtained nor the reaction conditions were quoted. Soon after this an eight-membered heterocycle, 1,1,3,3,5,5,7,7-octamethyl-2,6-dioxa-1,3,5,7-tetrasilacyclo-octane, was obtained; this was the first characterised representative of the class of cyclocarbosiloxanes[3,17].

Among the cyclocarbosiloxanes known at the present time, compounds containing five and more atoms in the heterocycle have been described. The simplest representatives of cyclocarbosiloxanes with the four-membered 2-oxa-1,3-disilacyclobutane ring are probably chemically and thermally unstable, as a result of which all attempts at their synthesis have so far resulted in the formation of cyclic dimers or more rarely polymeric products.

This paper is a first attempt at an exhaustive review and a systematic account of data concerning compounds of the above type published in journal articles or patents.

II. METHODS OF SYNTHESIS

The most common methods for the formation of carbosiloxane rings are based on the hydrolytic and joint hydrolytic condensation of bridge compounds containing hydrolysable silicon functional groups Si–X (X = Cl, F, H, OH, OCH_3, or OC_2H_5), heterofunctional condensation of bridge-type silanes with other silanes or siloxanes, organometallic synthesis based on siloxanes containing halogen–carbon and halogen–silicon bonds, reaction of acetylenic compounds with dihydrodisiloxanes (cycloaddition), synthesis via malonic ester derivatives, and thermal and thermocatalytic rearrangement of linear carbosiloxanes. In addition, a number of reactions of cyclocarbosiloxanes are known, which, although resulting in the formation of new compounds of this class, do not involve the formation or rearrangement of the cyclic skeleton of the molecule. These reactions are considered in Section IV dealing with the chemical properties of cyclocarbosiloxanes.

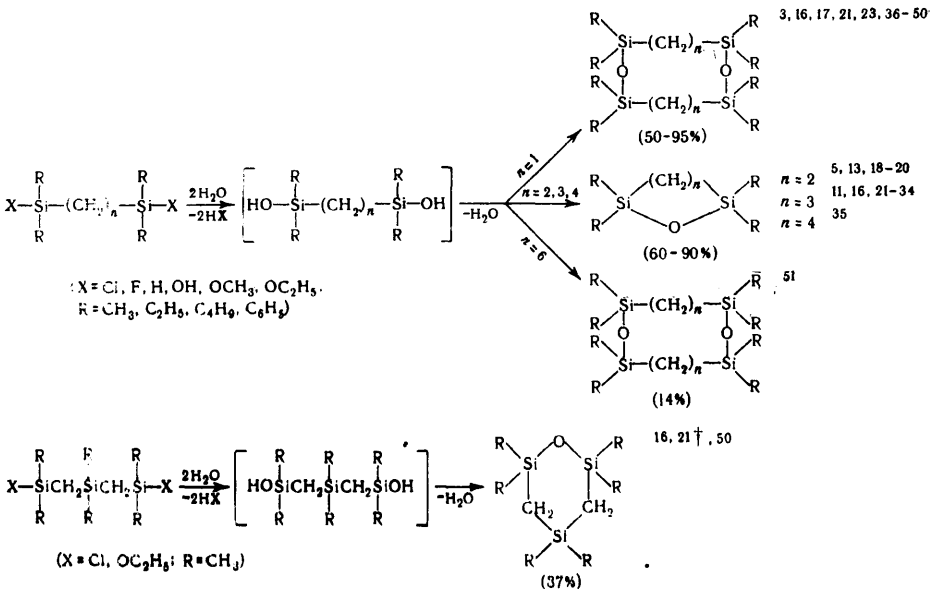
1. HYDROLYTIC CONDENSATION OF POLYFUNCTIONAL ORGANOSILICON COMPOUNDS WITH A CARBON BRIDGE BETWEEN SILICON ATOMS°

The hydrolytic condensation of polyfunctional organosilicon compounds $X_nR_{3-n}Si-A-SiR_{3-n}X_n$ [where A is a

carbon bridge of the type $(CH_2)_n$, $-(\bigcirc\!\!\!\!\bigcirc)$, etc.] has been used to synthesise a large number of five-,[5,13,18-20] six-,[11,16,21-34] seven-,[35] and eight-membered[3,16,17,21,23,36-50] cyclocarbosiloxanes, cyclocarbosiloxanes with a large number of units[51], and polycyclic cyclocarbosiloxanes[11,30-32,45,46,52-55].

a. Difunctional Compounds

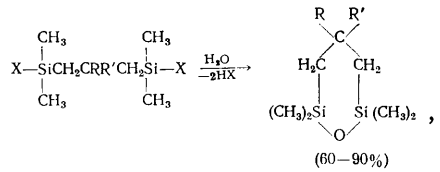
The hydrolysis of difunctional bridge-type di- or trisilanes leads to the formation of cyclocarbosiloxanes according to the following mechanism:



The condensation reaction is carried out at moderate temperatures in the bulk phase of the reactant or in solvents, frequently in the presence of an acceptor of the hydrogen halide evolved; intermolecular condensation of the $\alpha\omega$-silanediol, leading to the formation of linear carbosiloxane oligomers, is a competing reaction.

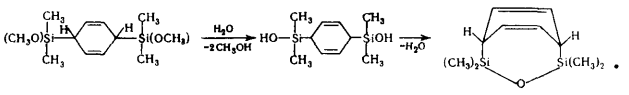
The yield of cyclocarbosiloxane depends on the concentration of the difunctional compound in the reaction mixture: on dilution, intermolecular condensation of the intermediate silanediols is facilitated. For example, the yield of 1,1,3,3-tetramethyl-2-oxa-1,3-disilacycloheptane[35] increases by a factor of two, from 43 to 85%, on dilution of the reaction mixture. In the hydrolysis of 1,3-bis-(chlorodimethylsilyl)propane in ether, the yield of the cyclic product is 60–70%;[11] in similar reactions of 1,2-bis(chlorodimethylsilyl)ethane[18], but in the absence of solvent, the oligomer is mainly formed. The latter may be converted into a cyclocarbosiloxane by thermal catalytic rearrangement (see p. 116).

The hydrolysis of bridge-type compounds with a substituted carbon atom results in the formation of the corresponding C-substituted cyclocarbosiloxanes[24-27]:

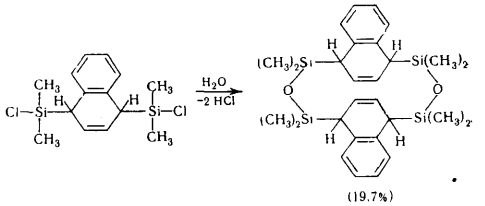


where X = Cl or OC_2H_5, R = CN or H, and R′ = COOH, COOK, $COOCH_3$, or $COOC_2H_5$.

If there is a cyclic group between the silicon atoms, the cyclisation process takes place with greater difficulty—the yield of the products of the intramolecular cyclisation of silanediols diminishes. Thus in the hydrolysis and condensation of 3,6-bis(methoxydimethylsilyl)-hexa-1,4-diene the yield of 2,2,4,4-tetramethyl-3-oxa-2,4-bicyclo-[3,2,2]nona-6,8-diene is only 20%:[56]



When the cyclohexene ring is condensed with an aromatic ring [for example, when the starting material is 1,4-bis(chlorodimethylsilyl)-1,4-dihydronaphthalene], bimolecular condensation products are formed[57]:

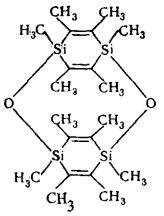


In this case the intramolecular condensation product was not detected.

If the silicon atoms in the difunctional compound are part of a cyclohexadiene ring, cyclocarbosiloxanes with a single siloxane group are not detected even when the reaction is carried out in a highly dilute solution and the corresponding cyclic dimer is formed in a yield of 1–5%.

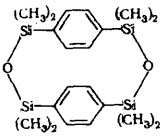
† The formula of a twelve-membered cyclocarbosiloxane $\{[Si(CH_3)_2CH_2]_2Si(CH_3)_2O\}_2$ is attributed to the product, but is probably erroneous since the physical constants of this compound are identical with those of the six-membered heterocycle[50].

Thus, when 1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene is treated with anhydrous hydrazine, a certain amount of a [1,1]paracyclophane analogue is formed together with the polymer[58]:



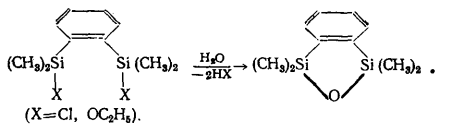
The same compound was synthesised by the reaction of equimolar amounts of 1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene and 1,4-dihydroxyhexamethyl-1,4-disilacyclohexa-2,5-diene.

It has been shown[14,59] that in the hydrolysis of difunctional compounds with a *para*-substituted aromatic bridge, for example 1,4-bis(chlorodimethylsilyl)benzene, cyclic compounds are not formed at all; the main reaction product is the corresponding silanediol which forms a polymer on dehydration. However, McKay[60], who carried out this reaction in the presence of trifluoroacetic acid and in dilute benzene solution, succeeded in isolating a cyclic product of the intermolecular condensation of *p*-phenylenebis(dimethylsilanol):



It is noteworthy that later attempts to obtain this compound[61] by hydrolysing *p*-phenylenebis(dimethylsilane) or by the condensation of *p*-phenylenebis(dimethylsilanol) were unsuccessful even in dilute solution; the main reaction products were linear polymers with a molecular weight of $(2-7)\times 10^3$, the thermal-catalytic rearrangement of which results in the formation of the cyclic dimer mentioned above (see p. 116).

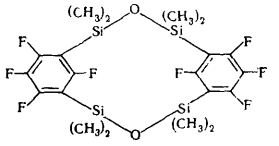
In contrast to *p*-disilyl-substituted benzene, in the hydrolysis of *o*-substituted compounds, for example *o*-bis(chloroethoxydimethylsilyl)benzene[62,63], a certain amount of an intramolecular cyclisation product is formed:



(X=Cl, OC_2H_5).

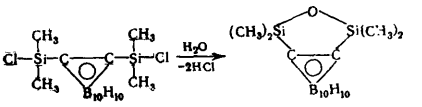
A similar compound with a perfluorophenylene ring was obtained by the hydrolysis of *o*-tetrafluorophenylenebis-(dimethylsilane).[64]

When hydrochloric acid is allowed to react with *m*-tetrafluorophenylenebis(dimethylsilanol), or on hydrolytic condensation of *m*-chlorotetrafluorophenylenedimethylsilane, or on intramolecular condensation of 1,1,3,3-tetramethyl-1,3-bis(tetrafluorophenylenedimethylsilane)disiloxane, a dimeric cyclocarbosiloxane is formed[64,65]:



(1-10%)

A cyclic oxadisilacarborane was also obtained by hydrolytic condensation[66]:

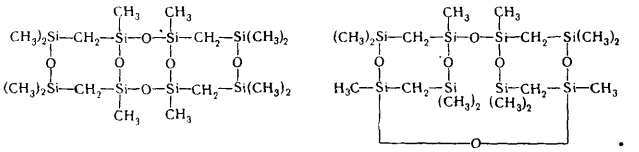


(75%)

When a benzene solution of 1-[*m*-(ethoxydimethylsilyl)-phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane is refluxed[67,68] in 50% of sulphuric acid, a polymer is formed, which can be converted into the corresponding cyclocarbosiloxane (see p. 116).

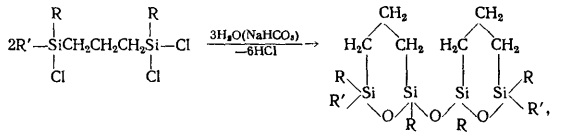
b. Trifunctional Compounds

Hydrolytic condensation of compounds with carbon bridges between silicon atoms and with more than two hydrolysable groups leads as a rule to the formation of polycyclic cyclocarbosiloxanes[11,30-32,45,46,52-55]. Thus hydrolysis of (ethoxydimethylsilyl)(diethoxymethylsilyl)-methane in ethereal solution leads to the formation of a compound in 20% yield, to which the following possible formulae have been ascribed:



According to the authors[45,46], the first structure is more likely.

Hydrolysis of trichlorodisilanes with a trimethylene bridge in ethereal solution results in the formation of bicyclic carbosiloxanes[11,30-32]:

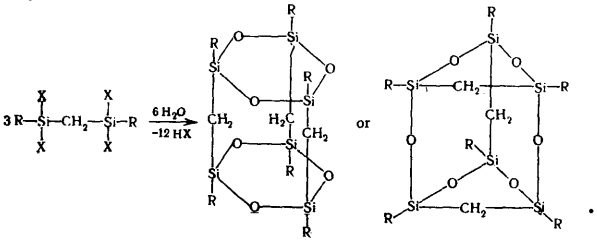


where R = R′ = CH_3 (62.5%) or R = CH_3 and R′ = C_6H_5.

Hydrolysis of an analogous compound with a phenylene bridge—1-chloromethylphenylsilyl-4-dichlorophenylsilylbenzene—in an acid medium does not result in the formation of a bicyclic compound of the above type, an oligomer being formed instead[55].

c. Tetrafunctional Compounds

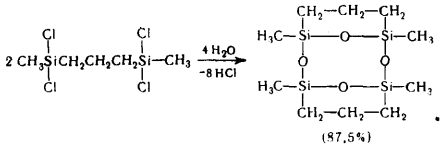
Hydrolytic condensation of symmetrical tetrafunctional disilylmethanes[45,46,52,53,69] yields cyclocarbosiloxanes with a "cage" structure:



Although the authors[45,46,52] give preference to the first structure, the second formula is probably more likely,

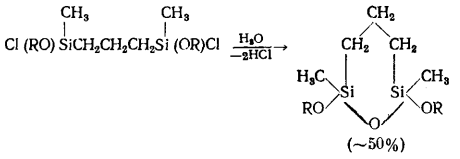
since the ^1H NMR spectra of this compound show two signals due to nonequivalent methylene protons[53,69]: in the first structure all the methylene protons should be equivalent.

A tricyclic cyclocarbosiloxane has been obtained in a high yield by the hydrolytic condensation in a neutral medium of a tetrafunctional disilane with a trimethylene bridge:



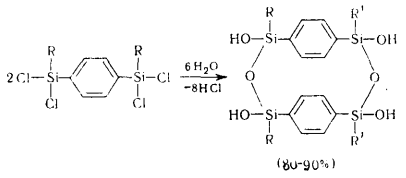
In alkaline and acid media, the yields of this compound were reduced to 60.5 and 45% respectively[11,31,32].

Hydrolysis of 1,3-bis(alkoxychloromethylsilyl)propanes in the presence of a hydrogen chloride acceptor (triethylamine or its mixture with urea) yields 2,6-dialkoxy-2,6-dimethyl-1-oxa-2,6-disilacyclohexanes[11,31,32], i.e. in this case the compound behaves like difunctional disilanes:



In the presence of sodium bicarbonate, the above tricyclic compound is mainly formed.

Hydrolytic condensation of silicon compounds with *p*-phenylene bridges [for example 1,4-bis(dichloromethylsilyl)benzene] leads to an insoluble polymer; individual cyclocarbosiloxanes were not isolated[10]. However, a more detailed study of this process[54,55] showed that the intermediates in the reaction are cyclocarbosiloxanes containing hydroxy-groups:



(R = R′ = CH_3 or C_6H_5; R = CH_3, R′ = C_6H_5), which give rise to di- and poly-cyclic compounds on prolonged standing in solution.

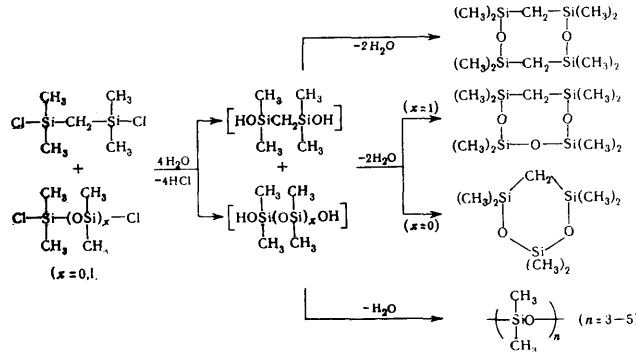
If the hydrolysis of 1,4-bis(dichloromethylsilyl)benzene is carried out in the presence of chlorotrimethylsilane, the halogen is partly replaced by the trimethylsiloxy-group; complete substitution of the chlorine can be achieved by treatment with an excess of hydroxytrimethylsilane in the presence of ammonia[70].

d. Pentafunctional Compounds

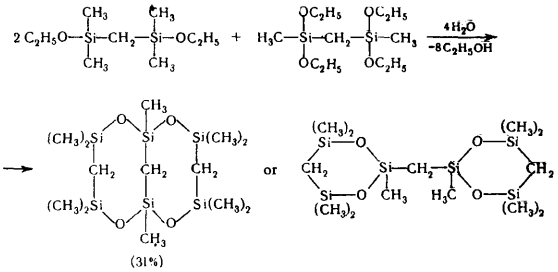
Hydrolysis of (diethoxymethylsilyl)(triethoxysilyl)-methane yielded an infusible and insoluble polymers in a yield of 96%, the structure of which could not be established[45,46]. It has been suggested that it contains cyclocarbosiloxane units of the "cage" type built into a three-dimensional network.

2. JOINT HYDROLYTIC AND HETEROFUNCTIONAL CONDENSATION

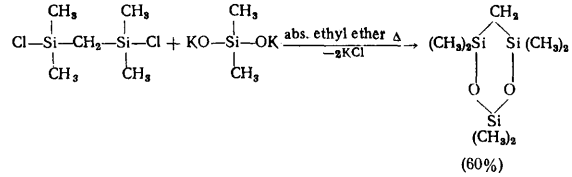
The possibility of obtaining cyclocarbosiloxanes by the joint hydrolytic condensation of bis(chlorodimethylsilyl)-methane with dichlorodimethylsilane or 1,3-dichloro-1,1,3,3-tetramethyldisiloxane had been investigated[50,71]. The composition of the joint hydrolysis product depends on the component ratio and the amount of hydrolysing agent. The optimal conditions for the preparation of 1,1,3,3,5,5-hexamethyl-2,4-dioxa-1,3,5-trisilacyclohexane (yield 64.5%) are equimolar proportions of the dichlorides and an excess of water; the maximum yield of 1,1,3,3,5,5,7,7-oxamethyl-2,4,6-trioxa-1,3,5,7-tetrasilacyclo-octane (about 40%) is also attained for equimolar proportions of the initial compounds and a stoichiometric amount of the hydrolysing agent. The principal reactions occurring on joint hydrolysis are shown below:



The joint hydrolysis of tetrafunctional compounds with di- and tri-functional silicon derivatives has been described. For example, the following possible structures have been attributed to the crystalline products obtained by the joint hydrolytic condensation of bis(ethoxydimethylsilyl)methane with bis(diethoxymethylsilyl)-methane[45,46]:

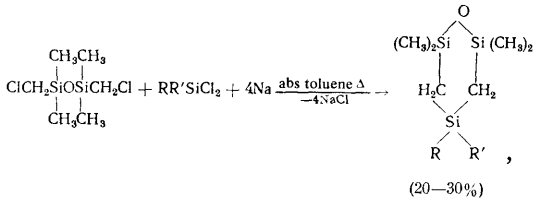


According to the authors[45,46], the first formula is more likely. Heterofunctional condensation has been hardly used for the synthesis of cyclocarbosiloxanes. Only one example of this type of synthesis is known. When bis-(chlorodimethylsilyl)methane was allowed to react with potassium dimethylsilanediolate, the main product was 1,1,3,3,5,5-hexamethyl-2,4-dioxa-1,3,5-trisilacyclo-hexane[50,71]:



3. ORGANOMETALLIC SYNTHESIS

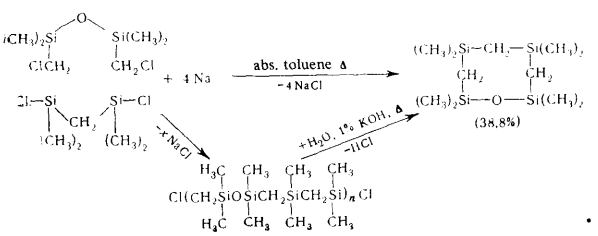
When symmetrical bis(chloromethyl)tetramethyldisiloxane and aryl(alkyl)dichlorosilanes reacted with metallic sodium, a number of six-membered cyclocarbosiloxanes were obtained[72]:



where R = R′ = CH_3 or C_2H_5 and R = CH_3 and R′ = C_6H_5. In addition, considerable amounts of oligomers are formed, which can be converted into six-membered cyclocarbosiloxane by hydrolysis and subsequent thermal catalytic rearrangement of the hydrolysate; in this case the overall yield of cyclocarbosiloxanes may be increased approximately to 70%.[50,73]

A condensation reaction with magnesium similar to that described above yielded a cyclocarbosiloxane (R = R′ = CH_3) in a yield of about 45%.[50]

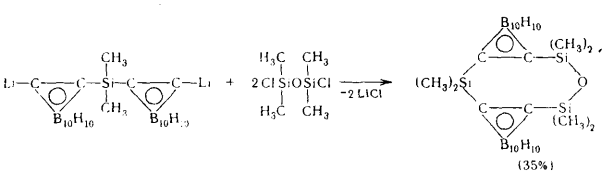
If instead of dichlorodimethylsilane one employs bis(chlorodimethylsilyl)methane, the main reaction product is 1,1,3,5,5,7,7-octamethyl-4-oxa-1,3,5,7-tetrasilacyclooctane[49,50,73]:



On condensation of 1,5-bis(chloromethyl)-1,1,3,3,5,5-hexamethyltrisiloxane and dichlorodimethylsilane in the presence of metallic sodium or magnesium, 1,1,3,3,5,5,7,7-octamethyl-2,4-dioxa-1,3,5,7-tetrasilacyclo-octane is hardly formed[50]. It was found that in both cases the main reaction products are six-membered cyclocarbosiloxanes. Their formation can probably be accounted for by rearrangements of the siloxane bonds under the reaction conditions.

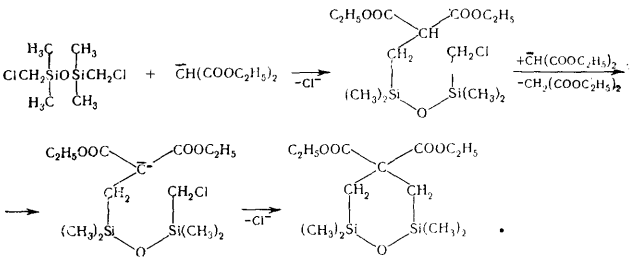
The possibility of the cyclisation of chloromethyldisiloxanes containing a halogen or an alkoxy-group at the silicon atom [$ClCH_2Si(CH_3)_2OSi(CH_3)_2X$; X = Cl or OC_2H_5] with metallic magnesium has been investigated[50]. The formation of an intramolecular cyclisation product of the initial compound—1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclobutane—was not observed. The main reaction products were 6- and 8-membered methylenesiloxane cyclocarbosiloxanes.

A cyclocarbosiloxane with two carborane rings[74] was obtained via a dilithium derivative by the following reaction:

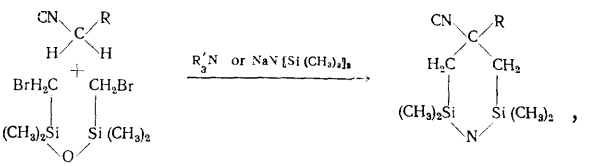


4. SYNTHESIS OF CYCLOCARBOSILOXANES BY THE CONDENSATION OF BIS(HALOGENOMETHYL)DISILOXANES WITH COMPOUNDS CONTAINING ACTIVE HYDROGEN ATOMS

The reaction of *sym*-bis(iodomethyl)tetramethyldisiloxane with sodiomalonic ester yielded a cyclic diester—1,1-diethoxycarbonyl-3,3,5,5-tetramethyl-4-oxa-3,5-disilacyclohexane[75] (yield 61%). The use of the less reactive *sym*-bis(chloromethyl)tetramethyldisiloxane reduced the yield of this heterocycle to 28%. The following reaction mechanism has been proposed:



C-substituted six-membered cyclocarbosiloxanes are formed also on condensation of *sym*-bis(bromomethyl)-tetramethyldisiloxane with cyanoacetic esters[26] (in the presence of tertiary amines) or with nitriles[27] [in the presence of sodium bis(trimethylsilyl)amide]:



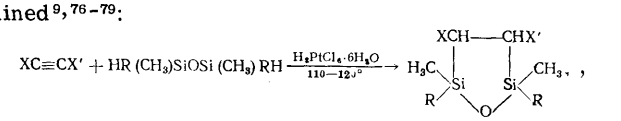
where R = H, CH_3, CN, $COOCH_3$, or $COOC_2H_5$.

In the presence of triethylamine, the condensation with cyanoacetic ester taking place with a yield of about 60%, monoalkylated products being virtually absent from the reaction mixture.

When acetonitrile and sodium bis(trimethylsilyl)amide are employed, the yield of 4-cyano-2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane is 60—70%. It is interesting that a reagent such as sodium bis(trimethylsilyl)amide gives rise to hardly any side reactions (cleavage of the Si—C bond in $Si-CH_2Br$, cleavage of the Si—O bond, substitution of the bromomethyl group with formation of $Si-CH_2-N$, etc.). The acetonitrile monoalkylation product is detected only in a small amount. If other compounds with active C—H bonds are introduced into this reaction, the yield of cyclocarbosiloxane diminishes[27]. For example, in the presence of diethyl malonate and ethyl cyanoacetate, the yield is about 20%. When an acetate ester is employed, only traces of cyclocarbosiloxanes are formed.

5. INTERACTION OF SUBSTITUTED ACETYLENES WITH DIHYDROSILOXANES (CYCLOADDITION)

When substituted acetylenes reacted with dihydrodisiloxanes in the presence of chloroplatinic acid as a catalyst, a number of five-membered cyclocarbosiloxanes with different substituents at the carbon atom were obtained[9,76-79]:

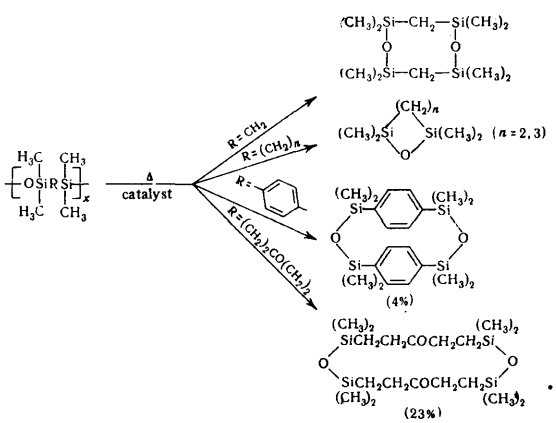


where X = H, C_6H_5, C_4H_9, or α-$C_{10}H_7$, X' = H, CH_3, or C_6H_5, and R = CH_3, C_2H_5, or C_6H_5.

The yield of cyclocarbosiloxanes varies between 5 and 75% depending on the structure of the initial reagents and the reaction conditions. It was established that the tendency towards the formation of a cyclic compound is greatly influenced by the nature of the substituents at the carbon atoms in acetylene and at the silicon atoms in dihydrodisiloxane. The substituents at the carbon atoms in acetylene can be arranged in the following sequence in terms of their effect on the formation of cyclic compounds: aryl > alkyl > hydrogen; the corresponding sequence of substituents at the silicon atoms is ethyl > phenyl > methyl.

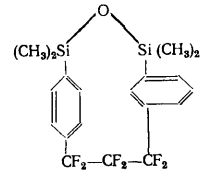
6. THERMAL CATALYTIC AND THERMAL REARRANGEMENT OF LINEAR CARBOXILOXANES

The thermal catalytic rearrangement of oligomeric products containing siloxane and silicon–carbon residues can be employed as a preparative method for the synthesis of many cyclocarbosiloxanes. Such oligomers are usually formed as side products in the synthesis of cyclocarbosiloxanes. They are obtained as the main products, for example, in the reaction involving the polyaddition of $\alpha\omega$-dihydrodisiloxanes to dienes and acetylene[9,76–85], in the copolymerisation of cyclosiloxanes with 1,3-disilacyclobutanes[50], and of course in the polymerisation of cyclocarbosiloxanes. At fairly high temperatures (up to 300°C) in the presence of catalytic amounts of alkalis or acids, the siloxane bond dissociates in linear carbosiloxane oligomers with formation of cyclocarbosiloxanes ("siloxy–siloxy" rearrangement). In particular, this method has proved convenient for the preparation of five-membered[5,13,18–20], six-membered[28,29,50,71,73], eight-membered[48,50,71,73], and sixteen-membered[86] compounds and also cyclocarbosiloxanes with *p*-phenylene bridges[61]:



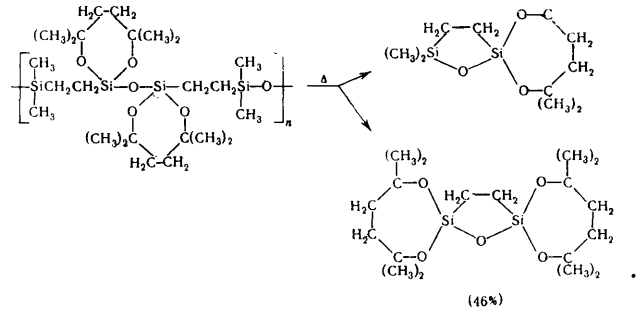
In the thermal decomposition of a polymer with the composition $[-SiCH_2CH_2CH_2SiO-]_n$, the main product was a six-membered heterocycle—1-oxa-2,6-disilacyclohexane[11].

Oxadisila-[3,3]-metaparacyclophane

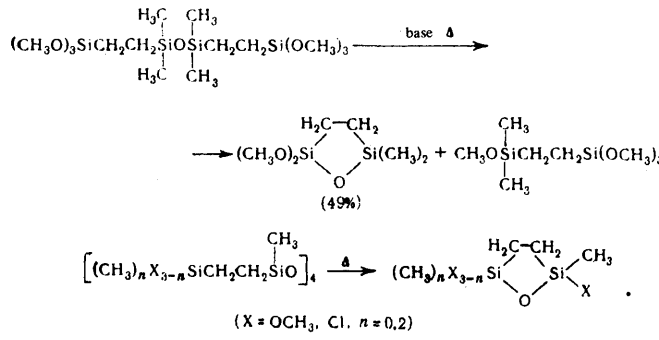


was obtained by heating *in vacuo* a linear polymer with the corresponding structure[67,68].

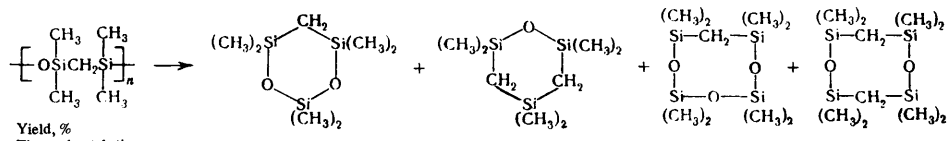
Thermal rearrangement of organosilicon oligomers also yielded oxadisilacyclopentane heterocycles[87]:



Thermal and thermalcatalytic "alkoxy–siloxy" and "chloro–siloxy" rearrangements of the corresponding compounds are varieties of the above method for the preparation of cyclocarbosiloxanes[87]:



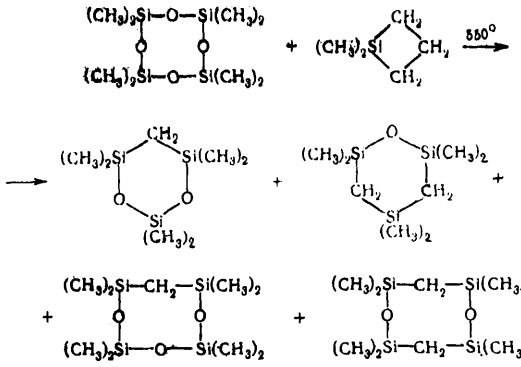
Examples of thermal and thermalcatalytic rearrangements of oligomeric carbosiloxanes involving the dissociation not only of Si–O but also of Si–C bonds in the chain are given below[50]:



Yield, %				
Thermal catalytic rearrangement (1% KOH; <300°)	43.1	32.2	10.6	7.5
Thermal rearrangement (>500°)	48.	24.8	9.6	3.1

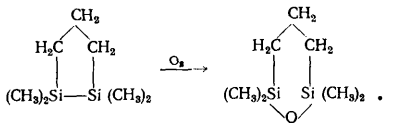
7. OTHER METHODS

Apart from the reactions discussed above, there are others leading to the formation of carbosiloxane rings, but these are without preparative value. Thus it has been shown that cyclocarbosiloxanes can be formed, in principle, on joint pyrolysis of cyclosiloxanes and cyclocarbosilanes[50,88]:

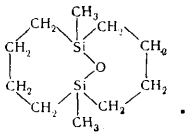


The formation of the same cyclocarbosiloxanes was observed on thermolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane in the presence of water vapour at 550°C.[50,88] However, in both cases the yield of cyclocarbosiloxanes does not exceed several per cent.

Like 1,2-digermacyclopentanes[89], 1,2-disilacyclopentane can be oxidised with formation of the corresponding oxadisilacyclohexanes[135]. Thus 1,1,2,2-tetramethyl-1,2-disilacyclopentane is converted on prolonged standing into 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane:

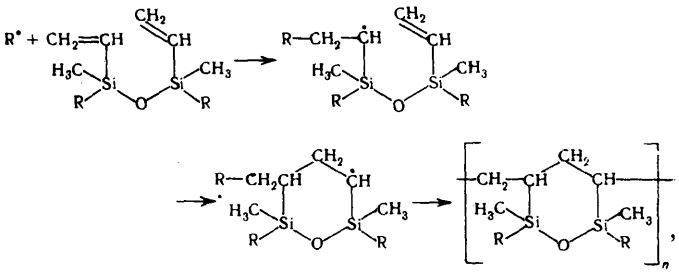


1,2-Disilacyclohexanes (*cis*- and *trans*-) are converted into the corresponding seven-membered *cis*- and *trans*-cyclocarbosiloxanes on interaction with perbenzoic acid. The reaction is distinguished by high stereospecificity[90]. A bicyclic compound with a similar structure is also readily oxidised by perbenzoic acid, yielding 1,6-dimethyl-11-oxa-1,6-disilabicyclo[4,4,1]undecane[91]:



It is interesting to note that, regardless of which (*cis*- or *trans*-) initial isomeric compound was oxidised, the reaction products always had the *cis*-configuration. Construction of molecular models for *cis*- and *trans*-isomers shows that, in contrast to the *cis*-isomer, the *trans*-siloxane isomer has a strained structure giving rise to steric hindrance. Oxidation with trimethylsilyl peroxide proceeds similarly, but the yield of the oxidation product is only 22% in the case of the *trans*-isomer.

The formation of cyclocarbosiloxane structures in the polymer chain has been noted in the free-radical and radiation-induced polymerisation of certain polyfunctional vinylsiloxanes[28,29,92]:



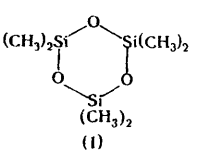
where R = CH_3 or C_6H_5.

Thermal rearrangements of cyclocarbosiloxanes with a change in the skeleton may be of definite interest for the synthesis of other cyclocarbosiloxanes (see p. 125).

III. PHYSICAL PROPERTIES

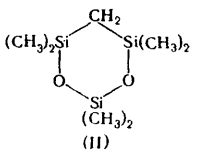
Cyclocarbosiloxanes are liquid or crystalline substances (Tables 1–2). The boiling points, refractive indices, and specific gravities of cyclocarbosiloxanes vary steadily as siloxane oxygen is replaced by methylene groups. Thus in the series of six- and eight-membered heterocycles the boiling points and refractive indices increase linearly and the specific gravity decreases with increase in the number of methylene groups[49,50,73].

Cyclosiloxanes

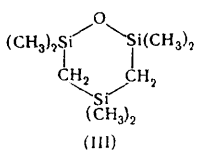


(I)

Cyclocarbosiloxanes

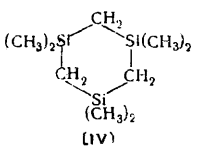


(II)

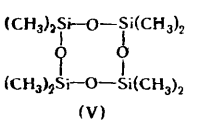


(III)

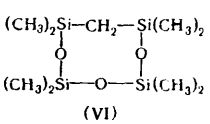
Cyclocarbosilanes



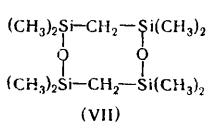
(IV)



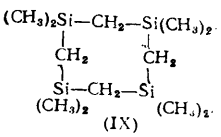
(V)



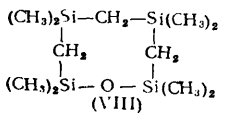
(VI)



(VII)

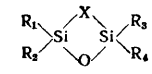


(IX)



(VIII)

Table 1. Physical properties of cyclocarbosiloxanes of the type

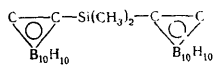
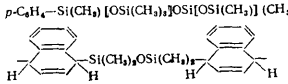
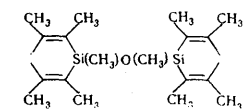


No.	X	R_1	R_2	R_3	R_4	Empirical formula	Mol. wt.	B.p., °C/mmHg	M.p., °C	n_D^{20}	d_4^{20}	Yield, %	References
1	$(CH_2)_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_6H_{16}O_2$	160.4	124/735	—	1.4142*	0.8550*	68.0	18
								125/734	—	1.4155*	0.8616*	68.0	5, 20, 100
2	$(CH_2)_2$	CH_3	CH_3	CH_3	C_6H_5	$Si_2C_{11}H_{18}O_2$	222.4	146/50	—	1.4962*	0.9740*	87.0	18
								144/50	—	1.4962*	0.9742*	90.8	5, 20
3	$(CH_2)_2$	CH_3	C_6H_5	CH_3	C_6H_5	$Si_2C_{16}H_{20}O_2$	284.5	182/10	—	1.5492*	1.047*	69.0	18
								158—160/3	—	1.5502*	1.0378*	5.0	9
4	$(CH_2)_2$	CH_3	CH_2	C_6H_5	C_6H_4	$Si_2C_{16}H_{20}O_2$	284.5	181/11	—	1.5492	1.044	75.0	18
5	$(CH_2)_2$	CH_3	C_6H_5	C_6H_5	C_6H_5	$Si_2C_{21}H_{22}O_2$	346.6	241/11	—	1.5860	1.092	86.0	18
6	$(CH_2)_2$	C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Si_2C_{31}H_{28}O_2$	408.7	—	80—81	—	—	78.0	5, 18
7	$(CH_2)_2$	CH_3	CH_3	CH_3	C_6H_{11}	$Si_2C_{16}H_{32}O_2$	216.5	—	—	—	—	—	5
8	$(CH_2)_2$	CH_3	CH_3	CH_3	$C_{12}H_{25}$	$Si_2C_{27}H_{56}O_2$	314.7	—	—	—	—	—	5
9	$(CH_2)_2$	CH_3	C_6H_5	CH_3	C_6H_5	$Si_2C_{17}H_{20}O_2$	188.4	27.5—30/1	—	1.4360	0.8797	3.2	9, 79
10	$(CH_2)_2$	CH_3	CH_3	CH_3	OCH_3	$Si_2C_6H_{14}O_2$	176.2	30/5.5	—	—	—	48.0	87
11	$(CH_2)_2$	CH_3	CH_3	OCH_3	OCH_3	$Si_2C_6H_{14}O_3$	192.2	52/15	—	—	—	49.0	87
12	$(CH_2)_2$	CH_3	OCH_3	OCH_3	OCH_3	$Si_2C_6H_{14}O_4$	208.2	61/4.5	—	—	—	36.0	87
13	$(CH_2)_2$	CH_3	CH_3	CH_3	Cl	$Si_2C_5H_{13}O_2Cl_1$	180.7	~120	—	—	—	82.0	87
14	$(CH_2)_2$	CH_3	Cl	Cl	Cl	$Si_2C_5H_7O_2Cl_3$	221.5	50—60/4—5	—	—	—	39.0	87
15	$(CH_2)_2$	OC_4H_9	OC_4H_9	OC_4H_9	OC_4H_9	$Si_2C_{14}H_{40}O_4$	392.3	119/0.01	—	—	—	43.0	87
16	$(CH_2)_2$	CH_3	CH_3	$OC(CH_3)_2(CH_2)_2C(CH_3)_2O$		$Si_2C_{12}H_{22}O_3$	274.3	55/0.2	—	—	—	—	87
17	$(CH_2)_2$	$OC(CH_3)_2(CH_2)_2C(CH_3)_2O$		$OC(CH_3)_2(CH_2)_2C(CH_3)_2O$		$Si_2C_{18}H_{34}O_5$	388.3	97/0.05	78—80	—	—	46.0	87
18	$CH(C_6H_5)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_{12}H_{20}O_1$	236	82—83/3	—	1.5038	0.9680	16.0	9, 77, 79
19	$CH(C_6H_5)CH_2$	CH_3	C_6H_5	CH_3	C_6H_5	$Si_2C_{17}H_{24}O_1$	264	119—120/3	—	1.5050	0.9689	40.5	9, 77, 79
20	$CH(C_6H_5)CH_2$	CH_3	C_6H_5	CH_3	C_6H_5	$Si_2C_{22}H_{24}O_1$	360.5	178—180/3	—	1.5858	1.0784	28.0	9, 79
21	$CH(C_6H_5)CH(CH_3)$	CH_3	C_6H_5	CH_2	C_6H_5	$Si_2C_{17}H_{22}O_1$	278	110/2	—	1.5003	0.9602	10.0	9, 79
22	$CH(C_6H_5)CH_2$	CH_3	C_6H_5	CH_3	C_6H_5	$Si_2C_{18}H_{20}O_1$	244	70/1	—	1.4470	0.8701	14.6	9, 79
23	$CH(\alpha\text{-}C_{10}H_7)CH_2$	CH_3	C_6H_5	CH_3	C_6H_5	$Si_2C_{21}H_{22}O_1$	314	156—159/2	—	1.5580	1.0302	40.0	9, 79
24	$[CH(C_6H_5)]_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_{11}H_{16}O_1$	312.5	133—134/2	76—77	—	—	51.0	9, 79
25	$[CH(C_6H_5)]_2$	CH_3	C_6H_5	CH_2	C_6H_5	$Si_2C_{20}H_{28}O_1$	340.0	154—156/3	~0	1.5668	1.0232	74.5	9, 77, 79
26	$(CH_2)_3$	CH_3	CH_3	CH_3	CH_3	$Si_2C_7H_{18}O_1$	174.4	146/760	—	1.4240	0.8679	—	23, 24
								146/761	—	1.4263	0.8735	79.4	2, 30, 31, 101
27	$(CH_2)_3$	CH_3	CH_3	CH_2	C_2H_5	$Si_4C_7H_{20}O_1$	188.4	48—49/10	—	1.4324	0.8796	37.8	11, 103
28	$(CH_2)_3$	CH_3	CH_3	CH_3	$n\text{-}C_3H_7$	$Si_4C_8H_{22}O_4$	202	61/2	—	1.4368	0.8791	68.0	2, 11, 31
29	$(CH_2)_3$	CH_3	CH_3	CH_3	C_4H_9	$Si_4C_{10}H_{24}O_4$	212	75/2	—	1.4394	0.8776	69.4	2, 11, 31
30	$(CH_2)_3$	CH_3	CH_3	CH_3	C_5H_{11}	$Si_2C_{11}H_{26}O_1$	230.0	116—117/25	—	1.4385	0.8726	28.0	11, 103
31	$(CH_2)_3$	CH_3	CH_3	CH_3	C_6H_5	$Si_2C_{12}H_{20}O_1$	236.4	98/2	—	1.4990	0.9758	—	2, 11, 31
								128—129/25	—	1.4969	0.9747	64.6	28, 29
32	$(CH_2)_3$	CH_3	CH_3	CH_3	C_6H_4Cl	$Si_4C_{19}H_{19}Cl_1O_4$	270.5	115—116/3	—	1.5100	1.0612	57.2	11, 103
33	$(CH_2)_3$	CH_3	CH_3	CH_3	OCH_3	$Si_4C_7H_{14}O_3$	190	49—50/10	—	1.4254	0.9378	66.0	11, 33
34	$(CH_2)_3$	CH_3	CH_3	CH_3	OC_2H_5	$Si_4C_7H_{16}O_3$	204	59—62/10	—	1.4264	0.9295	81.6	11, 33
35	$(CH_2)_3$	CH_3	CH_3	CH_3	$n\text{-}OC_3H_7$	$Si_4C_8H_{18}O_3$	218	71—73/17	—	1.4253	0.9177	56	11, 33
36	$(CH_2)_3$	CH_3	CH_3	CH_3	$iso\text{-}OC_4H_9$	$Si_4C_{10}H_{22}O_3$	232	86—87/10	—	1.4322	0.9178	60.5	11, 33
37	$(CH_2)_3$	CH_3	CH_3	CH_3	$iso\text{-}OC_5H_{11}$	$Si_4C_{11}H_{24}O_3$	242	98—99/7	—	1.4338	0.9125	67.5	11, 33
38	$(CH_2)_3$	CH_3	CH_3	CH_3	OC_6H_5	$Si_4C_{12}H_{20}O_3$	252	115—116/7	—	1.4888	1.0145	60.7	11, 33
								134.5/16		1.4810	1.0071		11
39	$(CH_2)_3$	CH_3	CH_3	CH_3	CH_3COO	$Si_4C_7H_{14}O_3$	218	79—80/14	—	1.4343	0.9922	60.2	11, 33
								74—75/10	—	1.4316	0 9976	91.0	11, 33
40	$(CH_2)_3$	CH_3	CH_3	CH_3	$(C_2H_5)_2N$	$Si_4C_{10}H_{21}O_3N_1$	231	98—100/7	—	1.4438	0.9047	62.0	11, 33
41	$(CH_2)_3$	CH_3	CH_3	CH_3	$C_6H_4CH_3O$	$Si_4C_{13}H_{22}O_3$	266.4	130—132/10	—	1.4848	1.0080	64.5	33
42	$(CH_2)_3$	CH_3	CH_3	CH_3	Cl	$Si_4C_7H_{15}O_3Cl_1$	194.8	50—52/7	—	1.4412	1.014	68.0	2, 11, 38
								50—52/11	—	1.4419	—	74.0	11
								67/25	—	—	—	58.4	30, 31

Table 1 (continued).

No.	X	R_1	R_2	R_3	R_4	Empirical formula	Mol. wt.	B.p., °C/mmHg	M.p., °C	n_D^{20}	d_4^{20}	Yield, %	References
43	$(CH_2)_3$	CH_3	Cl	CH_3	Cl	$Si_2C_6H_{12}O_1Cl_2$	230.0	64—66/7	—	1.4570	1.1655	77.0	11, 33
								90—91/15	—	1.4592	1.1680	27.0	11, 33
44	$(CH_2)_3$	CH_3	OC_6H_5	CH_3	OCH_3	$Si_2C_{19}H_{20}O_2$	252.4	92—95/1	—	1.5130	1.044	16.8	32
45	$(CH_2)_3$	CH_3	C_6H_5	CH_3	C_6H_5	$Si_2C_{17}H_{20}O_1$	298.4	142.5—143/1	—	1.5495	1.0509	31.1	31, 32
								135—137/1	—	1.5545	1.0500	—	11
46	$(CH_2)_3$	CH_3	$C_6H_5CH_2O$	CH_3	OC_3H_7	$Si_2C_{19}H_{28}O_2$	310.4	90—93/1	—	1.4825	1.022	32.0	31, 32
47	$(CH_2)_3$	CH_3	OCH_3	CH_3	OCH_3	$Si_2C_7H_{14}O_2$	206.4	59—61/7	—	1.4250	1.001	57.4	11, 31, 32
48	$(CH_2)_3$	CH_3	OCH_3	CH_3	C_6H_5	$Si_2C_{19}H_{20}O_2$	252.3	94—95/1	—	1.4592	1.168	16.8	11
49	$(CH_2)_3$	CH_3	OC_2H_5	CH_3	OC_2H_5	$Si_2C_9H_{22}O_2$	234.5	32—34/2	—	1.4250	0.9655	51.7	11, 22, 31, 32
50	$(CH_2)_3$	CH_3	iso-OC_3H_7	CH_3	iso-OC_3H_7	$Si_2C_{11}H_{26}O_2$	262.4	53—54/1	—	1.4240	0.9371	39.8	11, 31, 32
51	$(CH_2)_3$	CH_3	iso-OC_4H_7	CH_3	$OC_6H_5CH_2$	$Si_2C_{15}H_{26}O_2$	310.5	90—92/1	—	1.4825	1.022	—	11
52	$(CH_2)_3$	CH_3	n-OC_4H_9	CH_3	n-OC_4H_9	$Si_2C_{13}H_{30}O_2$	290.2	122—123/4	—	1.4345	0.9477	38.6	11, 31, 32
53	$(CH_2)_3$	CH_3	iso-OC_4H_9	CH_3	iso-OC_4H_9	$Si_2C_{13}H_{30}O_3$	290.2	68—69/1	—	1.4300	0.9286	49.5	11, 31, 32
54	$(CH_2)_3$	CH_3	n-OC_5H_{11}	CH_3	n-OC_5H_{11}	$Si_2C_{15}H_{34}O_2$	318.6	91—93/1	—	1.4380	0.9346	38.5	11, 31, 32
								105—107/2	—	1.4378	0.9311	—	11
55	$(CH_2)_3$	CH_3	iso-OC_5H_{11}	CH_3	iso-OC_5H_{11}	$Si_2C_{15}H_{34}O_3$	318.6	97—98/1	—	1.4360	0.9306	43.1	11, 31, 32
56	$(CH_2)_3$	CH_3	OC_6H_5	CH_3	OC_6H_5	$Si_2C_{17}H_{26}O_3$	330	139—140/1	—	1.5285	1.100	42.0	11, 31, 32
57	$(CH_2)_3$	CH_3	$C_6H_5CH_2O$	CH_3	$C_6H_5CH_2O$	$Si_2C_{19}H_{26}O_3$	358.5	173—174/1	—	1.5220	1.083	74.5	11, 31, 32
58	$(CH_2)_3$	CH_3	$OSi(C_2H_5)_3$	CH_3	$OSi(C_2H_5)_3$	$Si_4C_{17}H_{42}O_3$	406.9	137—139/2	—	1.4430	0.9340	70.5	11, 31, 32
								168—173/8	—	1.4433	0.9345	85.0	11, 33
59	$CH_3CH(CH_2OH)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_8H_{20}O_2$	204.4	123—125/1	—	1.4432	0.9292	—	11
								68/0.4	—	1.4516	—	72.0	27
								81—83/2	—	1.4498	—	78.0	27
								70/0.5	—	1.4509	—	73.0	27
60	$CH_3CH(COOH)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_8H_{18}O_3$	218.4	—	142—143	—	—	83.0	26
								—	145	—	—	91.0	73
								—	143—144	—	—	80.0	25
								—	142—144	—	—	79.7	24
61	$CH_3CH(COOC_2H_5)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_{10}H_{22}O_2$	246.5	102/11	—	1.4392	0.9718	96.0	73
								75—77/0.5	—	1.4390	1.043	79.0	24, 27
62	$CH_3CH(CONH_2)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_6H_{16}N_2O_2$	217.4	—	137—140	—	—	90.0	26
63	$CH_3CH(CH_2NH_2)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_6H_{22}N_2O_1$	203.4	87—88/12	—	1.4518	—	75.0	26
								45/0.3	—	1.4521	—	70.0	27
64	$CH_3CH(COOK)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_8H_{17}K_1O_3$	256.5	—	—	—	—	~100	26
65	$CH_3C(CN)HCH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_8H_{17}N_1O_1$	199.4	105/12	55—56	—	—	71.0	26
								105—108/11	—	—	—	68.0	27
66	$CH_3C(CN)(COOH)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_9H_{17}N_1O_2$	243.4	—	131—131.5	—	—	72.0	26
								—	128.5—129.5	—	—	94.7	24, 25
67	$CH_3C(CN)(COOK)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_9H_{17}K_1N_1O_2$	281.5	—	—	—	—	98.0	26
								—	—	—	—	77.0	24
68	$CH_3C(CN)(CH_2OH)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_9H_{19}N_1O_2$	229.4	—	99—101	—	—	83.0	27
								—	100—101	—	—	89.0	27
69	$CH_3C(CN)(CONH_2)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_9H_{18}N_2O_2$	242.4	—	166—167.5	—	—	74.0	26
70	$CH_3C(CN)(CO_2CH_3)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_{10}H_{19}N_1O_2$	257.5	115—117/3	29—30	—	—	—	26
71	$CH_3C(CN)(CO_2C_2H_5)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_{11}H_{21}N_1O_2$	271.5	90/0.3	31—32	—	—	59.0	26
72	$CH_3C(CN)_2CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_8H_{14}N_2O_1$	224.4	—	138—138.5	—	—	27.0	27
73	$CH_3C(CN)(CH_2)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_9H_{15}N_2O_1$	213.4	98—102/13	80—83	—	—	43.0	27
74	$CH_3C(CH_2OH)_2CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_9H_{22}O_3$	234.4	120/0.5	90—92	—	—	20.0	27
								—	93—94	—	—	75.0	27
75	$CH_3C(CH_2NH_2)(CH_2OH)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_8H_{22}N_2O_2$	233.5	—	100—101	—	—	40.0	27
76	$CH_3C(CH_2NH_2)_2CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_9H_{24}N_2O_1$	232.5	112—114/2	—	1.4798	—	65.0	27
77	$CH_3C(COOC_2H_5)_2CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_2C_{13}H_{26}O_4$	318.5	134/6—7	—	1.4485	1.043	61.0	73
								95—97/1.5	—	1.4465	—	21.0	27
78	CH_2COCH_2	CH_3	CH_3	CH_3	CH_3	$Si_2C_7H_{16}O_2$	—	—	—	—	—	—	27
79	$CH_3Si(CH_3)_2CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_3C_8H_{22}O_1$	218.4	90—93/45	—	1.4385	0.8844	25.9	72
								179—180	—13.5	1.4370	0.8760	67.8	50, 73
								179—180	—13.5	1.4370	0.8760	15.0	48, 50
								179—180	—13.5	1.4370	0.8760	87.3	50
								77/27	—	1.4371*	0.8720*	—	21

Table 1 (continued).

No.	X	R_1	R_2	R_3	R_4	Empirical formula	Mol. wt.	B.p., °C/mmHg	M.p., °C	n_D^{20}	d_4^{20}	Yield, %	References
80	$CH_2Si(C_6H_5)_2CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_3C_{16}H_{22}O_1$	246.0	97—100/15	—	1.4524	0.8930	29.9	70
81	$CH_2Si(CH_3)(C_6H_5)CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_3C_{12}H_{24}O_1$	280.6	134—138/8	—	1.5112	0.9607	10.5	70
82	$CH_2Si(CH_3)_2O$	CH_3	CH_3	CH_3	CH_3	$Si_3C_7H_{20}O_2$	220.4	156—157 156—157	—28.0	1.4113 1.4113	0.9040 0.9040	66.0 45.0	50, 71, 73 48, 50
83	$(CH_2)_4$	CH_3	CH_3	CH_3	CH_3	$Si_2C_6H_{20}O_1$	188.4	169/730	—	1.4340	0.8794	85.0	35
84	$(CH_2)_4$	CH_3	C_6H_5	CH_3	C_6H_5	$Si_2C_{18}H_{24}O_1$ *cis*	312.5	158—160/3	—	1.5473	—	—	90, 133
85	$(CH_2)_4$	CH_3	C_6H_5	CH_3	C_6H_5	$Si_2C_{18}H_{24}O_1$ *trans*	312.5	160—164/3	—	1.5479	—	—	90, 133
86	$(CH_2)_4$	CH_3	F	CH_3	F	$Si_2C_6H_{14}F_2O_1$ *cis*	196.2	55/15	—	1.4035	—	68.0	133
87	$(CH_2)_4$	CH_3	F	CH_3	F	$Si_2C_6H_{14}F_2O_1$ *trans*	196.2	—	—	1.4020	—	50.0	133
88	$CH_2Si(CH_2)_2OSi(CH_3)_2CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_4C_{10}H_{24}O_2$	292.7	213—213.5 213—214/768 103—104/20 208—209 213—214 213—214	30.0 28.6—29.0 28—29 30.0 27.4 —	1.4341 1.4328* 1.4345 1.4345 1.4328*	0.9039 0.9035* 0.9048 0.9048 0.9042*	— 95.0 50.0 70.6 60.0 78.0	17, 36 45, 46 3, 44 41—43 48, 50, 71, 73 21
89	$CH_2Si(C_6H_5)_2OSi(C_6H_5)_2CH_2$	C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Si_4C_{41}H_{44}O_2$	404.6	154—155/2 165/3	—84	1.4683 1.4662	0.9361 0.9330	74.3 —	40—43 40—43
90	$CH_2Si(C_4H_9)_2OSi(C_4H_9)_2CH_2$	C_4H_9	C_4H_9	C_4H_9	C_4H_9	$Si_4C_{34}H_{74}O_2$	629.2	214—216/1	—64	1.4649	0.8907	63.5	41—43
91	$OSi(CH_3)_2CH_2Si(CH_3)_2O$	CH_3	CH_3	CH_3	CH_3	$Si_4C_8H_{22}O_3$	294.7	192—193	—22.3	1.4182	0.9354	39.4	50, 71, 73
92	$CH_2Si(CH_3)_2CH_2Si(CH_3)_2CH_2$	CH_3	CH_3	CH_3	CH_3	$Si_4C_{11}H_{30}O_1$	290.7	235—236	37.0	1.4533**	0.8825**	38.8	50, 73
93	$[CH_2CH_2COCH_2CH_2Si(CH_3)_2]_2O$	CH_3	CH_3	CH_3	CH_3	$Si_4C_{18}H_{40}O_4$	432.9	—	129—130	—	—	23.0	86, 93
94	$[(CH_3)_2Si(CH_2)_3]_2O$	CH_3	CH_3	CH_3	CH_3	$Si_4C_{18}H_{42}O_2$	433.0	—	47.5—48.4	—	—	14.0	51
95	*o*-C_6H_4	CH_3	CH_3	CH_3	CH_3	$Si_2C_{10}H_{16}O_1$	208.4	91—94/20 117/53	33.0 38.5	1.4950 1.4892*	0.9727 0.960*	7.5	63 62
96	*o*-C_6F_4	CH_3	CH_3	CH_3	CH_3	$Si_2C_{10}H_{12}F_4O_1$	280.3	—	49—51			5.2	64
97	*m*-$C_6H_4(CF_2)_3$-*p*-C_6H_4	CH_3	CH_3	CH_3	CH_3	$Si_2C_{19}H_{20}F_6O_1$	434.5	—	80—81.5	—	—	12.0	67, 68
98		CH_3	CH_3	CH_3	CH_3	$Si_2C_{10}H_{16}O_1$	210.4	—	71—72	—	—	20.0	56
99		CH_3	CH_3	CH_3	CH_3	$Si_4C_6H_{22}B_{10}O_1$	274.5	—	—	—	—	75.0	66
100		CH_3	CH_3	CH_3	CH_3	$Si_3C_{10}H_{32}B_{20}O_1$	474.9	—	207—208	—	—	35.0	74
101	*m*-C_6F_4—$Si(CH_3)_2OSi(CH_3)_2$—*m*-C_6F_4	CH_3	CH_3	CH_3	CH_3	$Si_4C_{20}H_{24}F_8O_2$	560.6	— —	136—137 136.3—137	— —	— —	1.5 10.0	64 65
102	*p*-C_6H_4—$Si(CH_3)_2OSi(CH_3)_2$—*p*-C_6H_4	CH_3	CH_3	CH_3	CH_3	$Si_4C_{20}H_{32}O_2$	416.8	— —	207—208 208	— —	— —	10.0 4.0	60 61
103	*p*-C_6H_4—$Si(CH_3)_2OSi(CH_3)_2$—*p*-C_6H_4—$Si(CH_3)_2OSi(CH_3)_2$—*p*-C_6H_4	CH_3	CH_3	CH_3	CH_3	$Si_6C_{30}H_{46}O_3$	625.2	—	—	—	—	—	61
104	*p*-C_6H_4—$Si(CH_3)(OH)OSi(OH)(CH_3)$—*p*-$C_6H_4$	CH_3	OH	OH	CH_3	$Si_4C_{16}H_{34}O_6$	424.7	—	—	—	—	82.7	54
105	*p*-C_6H_4—$Si(C_6H_5)(OH)OSi(OH)(C_6H_5)$—*p*-$C_6H_4$	CH_3	OH	OH	CH_3	$Si_4C_{36}H_{34}O_6$	548.8	—	—	—	—	89.3	54
106	*p*-C_6H_4—$Si(C_6H_5)(OH)OSi(OH)(C_6H_5)$—*p*-$C_6H_4$	C_6H_5	OH	OH	C_6H_5	$Si_4C_{56}H_{34}O_6$	673	—	93—104	—	—	83.5	55
107	*p*-C_6H_4—$Si(CH_3)[OSi(CH_3)_3]OSi[OSi(CH_3)_3](CH_3)$—*p*-$C_6H_4$	CH_3	OH	OH	CH_3	$Si_6C_{22}H_{60}O_6$	569.1	—	—	—	—	83.5	70
108	*p*-C_6H_4—$Si(CH_3)[OSi(CH_3)_3]OSi[OSi(CH_3)](CH_3)$—*p*-$C_6H_4$	CH_3	$OSi(CH_3)_3$	$OSi(CH_3)_3$	CH_3	$Si_6C_{25}H_{56}O_6$	713.4	217—220/2	—	1.4610	0.9680	7.0	70
109		CH_3	CH_3	CH_3	CH_3	$Si_4C_{32}H_{46}O_2$	520	—	glass temp. 80—82°	—	—	19.7	57
110		CH_3	—	—	CH_3	$Si_4C_{26}H_{56}O_2$	420.2	—	subl. temp. 268	—	—	5.0	58, 132

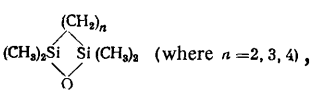
*At 25°C.
**At 40°C.

Table 2. Physical properties of polycyclic cyclocarbosiloxanes.

No.	Cyclocarbosiloxane	Empirical formula	Mol. wt.	B.p., °C/mmHg	M.p., °C	n_D^{20}	d_4^{20}	Yield, %	References
1	$[OSi(CH_3)(CH_2)_3Si(CH_3)O]_2$	$Si_4C_{10}H_{24}O_4$	320.4	138—140/30	101—102	—	—	87.5	11, 31, 32
2	$[OSi(CH_3)(R)(CH_2)_3Si(CH_3)]_2O$, R=$CH_3$	$Si_4C_{12}H_{30}O_3$	334.7	142/21	—	1.4429	0.9710	62.5	2, 11, 30, 31
3	R=C_6H_5	$Si_4C_{22}H_{34}O_3$	458.0	225—226/2	—	1.5222	1.070	—	11, 31, 32
4	$[CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CHCO]_2O$	$Si_4C_{15}H_{34}O_5$	418.8	160/0.8	—	1.4638	—	84.0	27
5	$\left[\begin{array}{c}(O)_{1/2}\quad (CH_2)_{1/2}\quad (O)_{1/2}\\ OSi(R)\ CH_2Si(R)\ OSi(R)\end{array}\right]_2$, R=$CH_3$	$Si_6C_9H_{24}O_6$	396.7	—	199—202	—	—	92.4	45, 46, 53, 69
6	R=C_6H_5	$Si_6C_{39}H_{36}O_6$	769.2	—	312—314	—	—	23.0	53, 69
7	$[OSi(CH_3)CH_2Si(CH_3)_2OSi(CH_3)_2CH_2Si(CH_3)O]_2$	$Si_8C_{16}H_{44}O_8$	557.2	125—126/2.5	—	1.4509	1.0350	20.0	45
8	$OSi(CH_3)_2CH_2Si(CH_3)_2OSi(CH_3)CH_2Si(CH_3)OSi(CH_3)_2CH_2Si(CH_3)_2O$	$Si_6C_{13}H_{36}O_4$	425.0	120—121/8	54.2—54.8	—	—	31.0	45,46
9	$[CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH—CH_2NBH]_3$	$Si_6C_{24}H_{60}B_3N_3O_3$	639.8		122—124 124—125	— —	— —	98.0 69.0	26 27
10	$\left[CH_2Si(CH_3)_2OSi(CH_3)_2CH_2C\begin{array}{l}CH_2—O\\ \diagdown\\ \diagup\\ CH_2—N\end{array}B\right]_3$	$Si_6C_{27}H_{66}B_3N_3O_6$	723.7	230—240/1	157	—	—	70.0	27
11	$—OSi(CH_3)[OSi(CH_3)_2]—p\text{-}C_6H_4—Si(CH_3)(OH)OSi(CH_3)\text{-}p\text{-}C_6H_4—Si(CH_3)—$ $—O(HO)(CH_3)Si—p\text{-}C_6H_4—[(CH_3)_2SiO]_2(CH_3)SiO—$	$Si_8C_{30}H_{50}O_8$	763.5	—	—	—	—	88.6	70
12	$[OSi(OH)(C_6H_5)—p\text{-}C_6H_4—Si(C_6H_5)(OH)OSi(C_6H_5)(OH)—p\text{-}C_6H_4—Si(C_6H_5)]_2O$	$Si_{14}C_{72}H_{62}O_{11}$	1328.0	—	—	—	—		55
13	$—O—Si(CH_3)(CH_2)_4Si(CH_3)(CH_2)_4—$ (*cis*-)	$Si_2C_{10}H_{22}O_1$	210.0	—	—	—	—	~100	91

The thermal conductivities of the compounds in the gaseous state also decrease linearly with the number of methylene groups[50], except for cyclosiloxanes, the thermal conductivities of which are lower than those of the corresponding cyclocarbosiloxanes with a single methylene group.

The infrared spectra have been widely employed by many investigators[9,11,18,24,35,48-58,60,62-69,71,79,87,92-99] to study the structures of various cyclocarbosiloxanes. In the spectra of compounds of this class the bands due to the stretching vibrations of the siloxane bonds are the most characteristic; in many cases useful information about the structure of cyclocarbosiloxanes may be obtained by analysing bands due to the carbon bridge. Comparison of the position of the band associated with the Si—O—Si bond in the compounds

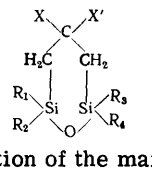


(where n = 2, 3, 4),

showed that, with decrease of ring size, the band is displaced from 1018 cm^{-1} in the seven-membered ring[35] to 990 and 930 cm^{-1} in the six-membered[2,25-33] and five-membered[18,76-79,97,98] rings respectively. In the spectra of acyclic compounds the band due to the Si—O—Si group is observed in the region 1050—1100 cm^{-1}.[9,48,89,96,103-105] This shift is due to the fact that, with decrease of n, the Si—O—Si angle diminishes; it has been estimated[98,99] as 125° (for n = 4), 120° (n = 3), and 105° (n = 2). As a result, the strain in the above cyclocarbosiloxanes increases as n diminishes. For example the strain energy in five-membered cyclocarbosiloxanes is 8—12 kcal $mole^{-1}$.[18]

The Si—O—Si band in the spectrum of 1,1,3,3-tetramethyl-2-oxa-1,3-disilaindane has also been observed[63,97-99] in the region of 930 cm^{-1}.

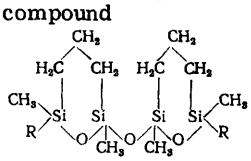
In six-membered cyclocarbosiloxanes of the type



X=H, CN;
X′=H, $COOCH_3$, $COOC_2H_5$, COOH, COOK, $CONH_2$, CH_2NH_2
R_1, R_2, R_3, R_4 = alkyl, aryl, alkoxy-group.

the position of the maximum of the Si—O—Si band is almost independent of the nature of the substituents at the carbon or silicon atom[11,26-33,102] and is in the region 990 to 1000 cm^{-1}, which corresponds to an SiOSi angle of about 110—120°.[25,26,95] The 992 cm^{-1} absorption by the Si—O—Si group has also been observed in the infrared spectrum of the bicyclic compound *cis*-1,6-dimethyl-11-oxa-1,6-disilabicyclo[4,4,1]undecane[91].

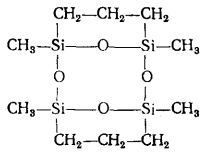
If the cyclocarbosiloxane molecule contains cyclic and acyclic siloxane bonds, the two corresponding bands are observed in the infrared spectrum as expected, the first being at a longer wavelength. Thus in the infrared spectrum of the compound



(R=CH_3, C_6H_5)

there are Si–O–Si absorption bands at 990 and 1080 cm^{-1} characterising the linear and cyclic structures respectively[2,11,30].

In the infrared spectrum of the compound



two Si–O–Si bands are also observed—at 1006 cm^{-1} (for the six-membered carbosiloxane ring) and at 1067 cm^{-1} (for the eight-membered siloxane ring).[11,32,97-99]

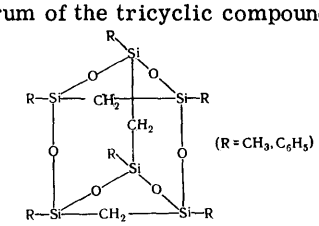
In the spectra of many six-membered compounds (I–IV) the band due to the asymmetric vibration of the Si–O bond[48-50,103-105] is in the region 1020–1030 cm^{-1}, while the CH_2 deformation vibration band is displaced from 980 to 1050 cm^{-1} [in the infrared spectra of compounds (II) to (IV)]. Thus the band due to the deformation vibrations of the ring CH_2 groups in the infrared spectra of compounds (II)–(IV) is more sensitive to changes in the skeleton of the cyclic structure than the siloxane band.

Calculation of the integral intensities of the bands associated with the asymmetric stretching vibrations of the Si–O bonds and the deformation vibrations of the endocyclic CH_2 groups in the infrared spectra of compounds (I), (II), and (IV) [for the spectrum of compound (III), such calculation is difficult owing to the impossibility of resolving the bands] shows that the integral intensity of the Si–O band remains constant, but the intensity of the CH_2 deformation vibration band is variable. The latter finding may be due to the effect of the conformational isomers on these vibrations.

Proton Magnetic Resonance Spectra

The ^1H NMR spectra of six- and eight-membered siloxanylmethylenecyclocarbosiloxanes (II), (III), and (VI)–(VIII) have two or more signals due to the non-equivalent methyl and methylene protons, the latter occurring in stronger fields[50,73]. With increase of ring size, the spin–spin coupling constant $J(^{13}CH_2)$ decreases, probably owing to an increase of the *p*-character of the carbon in the C–H bonds; there is a corresponding increase of $J(^{29}SiCH_2)$, which may be due to an increase of the *s*-character of the Si–C bond. On the basis of these results, it has been concluded that in the cyclocarbosiloxanes investigated the silicon atoms in the Si–C bonds in the ring have less *s*-character than in the Si–C bond directed to the methyl groups.

In the spectrum of the tricyclic compound

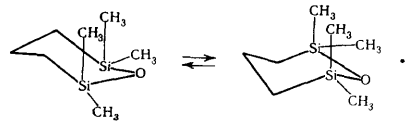


(R = CH_3, C_6H_5)

there are two signals of methylene protons, occurring at higher field (τ = 9.90 and 9.93 p.p.m.) than the signals of the methyl group protons (τ = 9.61 and 9.67 p.p.m.).[53,69]

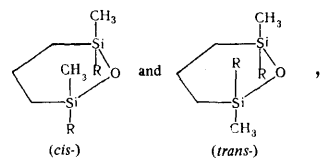
Analysis of the ^1H NMR spectra of a number of derivatives of oxadisilacyclohexane (see p. 121) led to the conclusion that such heterocycles have the "chair" conformation[26,106].

The ^1H NMR spectrum of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane[106] consists of a singlet due to methyl protons (δ = 0.07 p.p.m.), a multiplet due to α-methylene protons (δ = 0.45–0.72 p.p.m.), and a multiplet due to β-methylene protons (δ = 1.65–2.1 p.p.m.). Owing to the rapid "chair–chair" inversion, the axial and equitorial methyl groups are equivalent:



The activation energy for the conformational transitions of this compound has been estimated as about 3.5 kcal $mole^{-1}$, which is much lower than the corresponding value for 1,1,4,4-tetramethylcyclohexane (11 kcal $mole^{-1}$)[107,108] and approaches the activation energies for the "chair–chair" inversion in 1,1-dimethyl-1-silacyclohexane (5.5 kcal $mole^{-1}$)[109] and 1,1,4,4-tetramethyl-1,4-disilacyclohexane (6 kcal $mole^{-1}$).[110]

The *cis*- and *trans*-isomers of oxadisilacyclohexane,



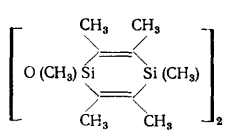
(*cis*-) (*trans*-)

where R = OAlk or C_6H_5, have characteristic ^1H NMR spectra[106]. The signal due to the protons of the methyl group located on the same side of the ring as the alkoxy-substituents is displaced towards lower field compared with the signal of a similar methyl group located in the *cis*-position with respect to a methyl or another alkyl group. In the spectra of methylphenyloxadisilacyclohexanes[106], the signal due to the methyl group in the *cis*-position is displaced towards higher field, while the signal of the *trans*-methyl group is displaced towards lower field.

The ^1H NMR method has also been used to analyse five-membered[9,18,78,79] and other cyclocarbosiloxanes[27,58,64,68,69].

Electron Spin Resonance

The application of the ESR method in studies of the radical-anions obtained from



by reduction with potassium in 1,2-dimethoxyethane solutions at −80°C, has been described[58]. The resulting radical-anion was stable for several hours at −80°C, disappearing rapidly on heating to room temperature. Analysis of the spectrum showed that the unpaired electron is fully delocalised owing to a transannular interaction, the delocalisation over the Si–O–Si bond being insignificant.

Mass Spectra

The application of mass spectroscopy to determine the molecular weight[11,58,97,111] and the mode of dissociation of

cyclocarbosiloxanes on electron impact[11,58,111] has been described. The latter is discussed in greater detail in Section IV.

IV. CHEMICAL PROPERTIES

The characteristic chemical properties of cyclocarbosiloxanes are determined primarily by the reactivity of the bonds forming the heterocycle. In the reactions investigated the Si–O bonds show the highest activity and the Si–C the lowest; the C–C bonds of the carbon bridge are as a rule stable in chemical reactions of cyclocarbosiloxanes. On the other hand, the reactions of cyclocarbosiloxanes can also involve functional groups linked to silicon and carbon atoms.

1. REACTIONS WITH CLEAVAGE OF THE HETEROCYCLE SKELETON

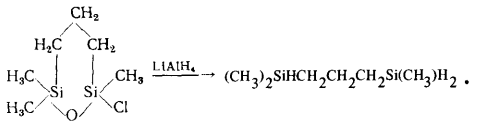
a. Heterolytic Cleavage of Si–C Bonds

The opening of the carbosiloxane rings in the presence of electrophilic or nucleophilic agents takes place as a rule with cleavage of the siloxane bond. Like cyclosiloxanes, five-membered cyclocarbosiloxanes can be titrated with tetra-n-butylammonium hydroxide in pyridine[112]:

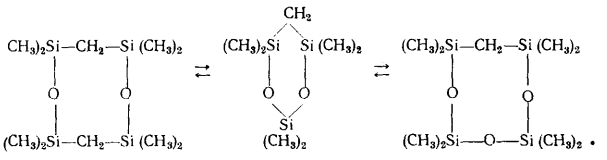


where R = CH_3 or C_6H_5.

When 6-chloro-2,2,6-trimethyl-1-oxa-2,6-disilacyclohexane is hydrogenated with lithium aluminium hydride in ether, not only the chlorine at the silicon atom is reduced but also the Si–O–Si bond, which results in the formation of a compound with a linear structure[11,33]:



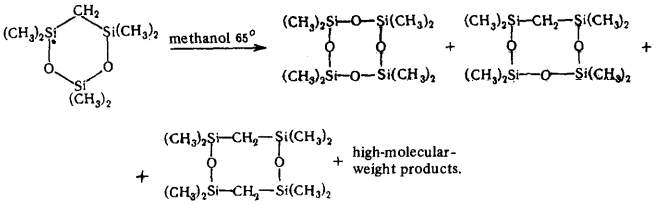
In pyridine solutions containing catalytic amounts of tetramethylammonium hydroxide, six- and eight-membered cyclocarbosiloxanes undergo a rearrangement with ring expansion or contraction even at 60°C:[50,113,114]



The rate of cleavage of heterocycles of the above type decreases with increase in the number of methylene groups in the molecule. Together with cyclic products, the rearrangement here gives rise also to high-boiling oligomers. It has been established that reactions of this kind are also accompanied by dissociation of the ring Si–C bond, as shown by the formation of six-membered heterocycles from eight-membered heterocycles (the cleavage of the Si–C bond of these cyclocarbosiloxanes by nucleophilic agents is described on p. 125).

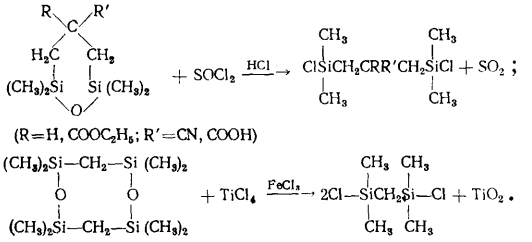
At the same time it is interesting to note that in the presence of an alcoholic solution of NaOH, KOH, and also H_2SO_4 (70%) and $H_2SO_4.SO_3$, 1,1,3,3,5,5,7,7-octamethyl-2,6-dioxa-1,3,5,7-tetrasilacyclo-octane is not cleaved[45,46,115].

In methanol solution, 1,1,3,3,5,5-hexamethyl-2,4-dioxa-1,3,5-trisilacyclohexane gives rise to rearrangement products[50,114]:



A compound having a similar structure and two methyl groups—1,1,3,3,5,5-hexamethyl-2-oxa-1,3,5-trisilacyclohexane—does not undergo any change under identical conditions. Probably the mechanism of this reaction is similar to that of the rearrangements of six-membered cyclosiloxanes in methanol[106,116–118].

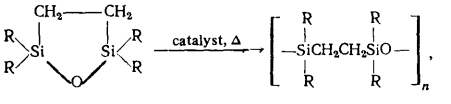
On treatment with chlorinating agents ($TiCl_4$, $SOCl_2$) in the presence of catalysts (HCl,[27] $FeCl_3$,[47] etc.) the siloxane bond of cyclocarbosiloxanes is cleaved and the corresponding linear dichlorides are formed in high yields (80–95%):



b. Polymerisation of Cyclocarbosiloxanes

This section deals with reactions involving the cleavage of the Si–O bond and leading to the formation of linear carbosiloxane polymers. Owing to the presence of the siloxane bond in the ring, cyclocarbosiloxanes can polymerise with ring opening in the presence of the usual catalysts for the polymerisation of cyclosiloxanes. Polymers whose main chain consists of alternating siloxane and carbosilane units have been obtained in this way. However, the polymerisation activity of cyclocarbosiloxane is as a rule lower than that of cyclosiloxanes with similar structures.

As already mentioned, five-membered cyclocarbosiloxanes are the most strained compounds of this class[18], as a result of which they readily polymerise in the presence of anionic [NaOH, KOH, LiOH, $(CH_3)_4NOH$, $(CH_3)_3SiONa$, $(CH_3)_3SiOK$] and cationic (H_2SO_4, CF_3COOH) catalysts[13,18]:



where R = CH_3 or C_6H_5.

The polymers obtained in the presence of anionic catalysts have a high molecular weight (up to about 10^6).

The ease of cleavage of the siloxane bond in these heterocycles depends on the nature of the substituents at the silicon and carbon atoms. Phenyl substituents at the silicon atoms increase the activity of five-membered

cyclocarbosiloxanes in anionic polymerisation[119]. Thus, 2,2,5,5-tetraphenyl-1-oxa-2,5-disilacyclopentane polymerises approximately 18 times faster than the corresponding tetramethyl-substituted cyclocarbosiloxane (Table 3).

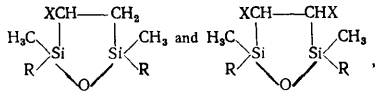
Table 3. Relative reactivities of five-membered cyclocarbosiloxanes and six-membered cyclocarbosiloxanes in base-catalysed polymerisation at 25°C.[119]

No. of cpd.	Monomer	Relative reactivity							
		I	II	III	IV	V	VI	VII	VIII
I	$^1/_3$ $[(CH_3)_2SiO]_3$*	1.00	0.12	0.07	0.04	0.02	0.02	0.01	0.006
II	$(CH_3)_2SiCH_2CH_2(CH_3)_2SiO$	8.10	1.00	0.56	0.32	0.18	0.18	0.097	0.05
III	$(CH_3)_2SiCH_2CH_2(C_6H_5)(CH_3)SiO$	14.5	1.79	1.00	0.58	0.33	0.32	0.17	0.09
IV	$^1/_3$ $[(C_6H_5)_2SiO]_3$	24.9	3.08	1.72	1.00	0.57	0.55	0.29	0.15
V	$(C_6H_5)(CH_3)SiCH_2CH_2(C_6H_5)(CH_3)SiO$	44.0	5.44	3.03	1.76	1.00	0.98	0.52	0.27
VI	$(CH_3)_2SiCH_2CH_2(C_6H_5)_2SiO$	45.0	5.56	3.11	1.82	1.02	1.00	0.53	0.28
VII	$(CH_3)(C_6H_5)SiCH_2CH_2(C_6H_5)_2SiO$	84.3	10.4	5.81	3.45	1.91	1.87	1.00	0.53
VIII	$(C_6H_5)_2SiCH_2CH_2(C_6H_5)_2SiO$	150.0	19.8	11.0	6.67	3.64	3.56	1.90	1.00

*Data obtained at 40°C in copolymerisation with compound (II).

On the other hand, the reactivity of five-membered cyclocarbosiloxanes under the conditions of cationic polymerisation increases when methyl substituents at the silicon atom are replaced by ethyl or phenyl groups.

In the series of C-substituted five-membered cyclocarbosiloxanes[9,76-79]

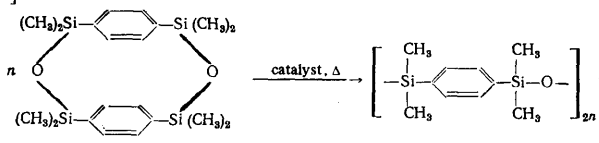


where R = CH_3, C_2H_5, C_6H_5, and X = C_4H_9, α-$C_{10}H_7$, or C_6H_5, the monosubstituted compounds show a greater tendency towards polymerisation. When they are polymerised in the presence of H_2SO_4, KOH, NaOH, and alkali metal silanolates, oily products with molecular weights in the range $(1.5-18)\times10^3$ are formed. Thermal polymerisation of the C-phenyl-substituted compound with R = CH_3 (molecular weight of the polymer up to 2×10^4) and its catalytic polymerisation in the presence of $AlCl_3$, BF_3, and $ZnCl_2$ + chloromethyl ether have been noted. In contrast to the monosubstituted derivatives, cyclocarbosiloxanes disubstituted at carbon atoms are not converted into polymers under the action of acids or bases.

In the copolymerisation of the cyclocarbosiloxanes $R_2SiCH_2CH_2SiR_2$ (R = CH_3 or C_6H_5) with six-membered cyclosiloxanes [hexamethyl(phenyl)cyclotrisiloxane] in the presence of basic catalysts, copolymers of different structures and molecular weights were obtained. The copolymerisation constants found were used to calculate the relative reactivities of the cyclocarbosiloxanes (Table 3).[119] Copolymers of the above type are suitable for conversion into rubbers and can also be used as moulding and casting resins, filling oils, and protective coatings[119,120].

Cyclocarbosiloxanes containing phenylene groups in the ring can also be polymerised in the presence of bases. Thus five-membered heterocycles with an *ortho*-phenylene bridge form at 100–140°C in the presence of 1% KOH low-molecular-weight polymers[11,62,63], while in the presence of H_2SO_4 the Si–C bonds in the ring are cleaved (see p. 125).

Cyclic carbosiloxane dimers and trimers with a *para*-phenylene bridge are converted in the presence of 0.01% potassium dimethylsilanolate at 180°C into high-molecular-weight soluble polymers [molecular weight $(0.7-4)\times10^5$]:[61]



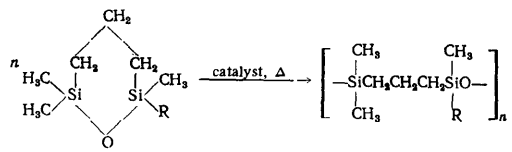
These polymers are thermally stable up to 350°C and are resistant to oxidation.

When 1,2-(1′,1′,3′,3′)-tetramethyldisiloxanyl-(1′,3′)-carborane is treated with bases, the Si–C bonds are dissociated and a siloxane polymer is formed[74] (see p. 125).

In the series of six-membered cyclocarbosiloxanes containing alternating siloxane and silmethylene groups, the polymerisation activity falls as oxygen atoms are replaced by methylene groups[50,113,114]. While the cyclocarbosiloxanes formed by replacing one oxygen atom in hexamethylcyclotrisiloxane by a methylene group polymerise more slowly in the presence of an anionic catalyst than their cyclosiloxane analogue and form a polymer with a molecular weight of 2×10^5, under analogous condition the corresponding compound in which two oxygen atoms have been replaced by methylene groups does not polymerise at all. It can be polymerised under more severe conditions (1.4% KOH, 120°C, 33 h) with formation of a low-molecular-weight oily product in a yield of 19%.[72] The formation of a condensation product of this compound has also been observed in the presence of 6 wt.% $AlCl_3$.

As in the case of five-membered cyclocarbosiloxanes[119], the replacement of a methyl group at a silicon atom by a phenyl group increases the reactivity of six-membered heterocycles in anionic polymerisation[72]. Six-membered heterocycles (oxadisilacyclohexanes) are also polymerised with greater difficulty[11,27,75,101] than hexamethylcyclotrisiloxane; they are less reactive than five-membered cyclocarbosiloxanes.

The anionic and cationic polymerisation of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane and certain other derivatives of this heterocycle has been investigated[11,102,109,121,122].



where R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_5, or C_6H_4Cl.

Under optimal polymerisation conditions (0.6% KOH, 110°C, 640 min), the yield of the polymer (with R = CH_3) was 93% and the molecular weight was 3×10^3. In the presence of sulphuric acid or polydimethylsiloxysulphonic acid, a polymer with a molecular weight of about 10^4 was formed.

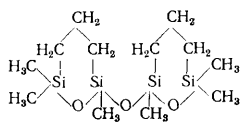
The rate of polymerisation of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane in the presence of KOH and H_2SO_4 is lower by two powers of 10 than the rate of polymerisation of hexamethylcyclotrisiloxane and the activation energies are respectively 21 kcal mole^{-1} for anionic

polymerisation and 7 kcal mole^{-1} for cationic polymerisation[11,101,121,122]. The intrinsic viscosity (molecular weight) of the polymers increases linearly with the degree of conversion. On this basis, the authors conclude that the polymerisation has a stepwise mechanism. In the initial stages the reaction is of first order with respect to the monomer; at higher conversions, the reaction order becomes fractional.

The effect of the substituent at the silicon atom on the rate of polymerisation of oxadisilacyclohexanes in the presence of cationic and anionic catalysts has been investigated[11,102]. Replacement of the methyl group by ethyl and higher alkyl groups lowers the rate of polymerisation in the presence of KOH approximately by a factor of 10. The introduction of electron-accepting substituents (phenyl, chlorophenyl) increases somewhat the rate of reaction. As was to be expected, in the case of cationic polymerisation aryl substituents lower the rate. It is interesting to note that electron-donating substituents also lower the rate of cationic polymerisation of oxadisilacyclohexanes, which has been explained by the swamping of the inductive effect by the steric effect.

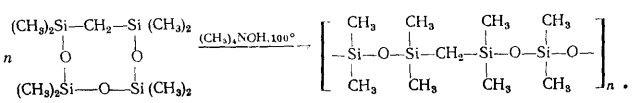
The linear relation between the logarithm of the relative rate of polymerisation of oxadisilacyclohexanes with phenyl substituents and the σ^* constant in the Hammett–Taft equation is evidence of a correlation between the rate of polymerisation and the inductive effect of substituents.

The polymerisation of the bicyclic compound



in the presence of KOH and polydimethylsiloxysulphonic acid takes place with formation of insoluble polymers[11,102].

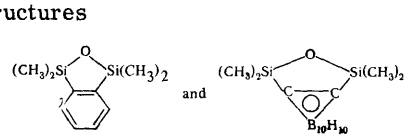
In the series of eight-membered methylenesiloxane heterocycles, only 1,1,3,3,5,5,7,7-octamethyl-2,4,6-trioxa-1,3,5,7-tetrasilacyclo-octane could be polymerised in the presence of anionic catalysts[50,113,114]:



A polymer with a molecular weight of 7.5×10^4 was obtained. The corresponding cyclocarbosiloxanes with two and three methylene groups are not polymerised under these conditions, i.e. in this case the polymerisation activity decreases with the number of methylene groups, probably owing to their positive inductive effect (relative to oxygen), which leads to an increase of electron density at the silicon atoms as a result, nucleophilic attack on the latter is hindered.

c. Heterocyclic Cleavage of Si–C Bonds

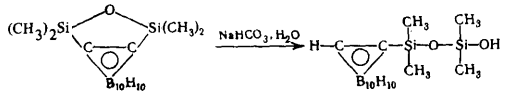
When cyclocarbosiloxanes with a carbon bridge having marked electron-accepting properties are treated with alkalis or acids, the ring Si–C bonds are cleaved. For example, in an attempt to polymerise compounds with the strained structures



(X) (XI)

in the presence of acids [compound (X)] or bases [compound (XI)], the formation of a polydimethylsiloxane and the removal of a phenyl or a carborane group respectively was observed[11,62,63,74].

At room temperature an aqueous solution of sodium bicarbonate also causes the dissociation of the Si–C bond[74]:

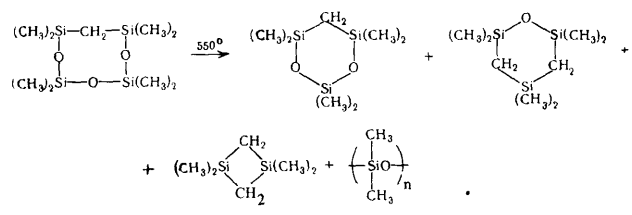


The cleavage of endocyclic Si–C bonds has likewise been observed when certain eight-membered cyclocarbosiloxanes were treated with nucleophilic agents[50,113,114]. In pyridine solutions containing catalytic amounts of $(CH_3)_4NOH$, 1,1,3,3,5,5,7,7-octamethyl-2,6-dioxa-1,3,5,7-tetrasilacyclo-octane gave rise to 1,1,3,3,5,5,7,7-octamethyl-2,4,6-trioxa-1,3,5,7-tetrasilacyclo-octane and 1,1,3,3,5,5,-hexamethyl-2,4-dioxa-1,3,5-trisilacyclohexane together with other products at a temperature as low as 60°C (see the scheme on p. 123). The formation of these heterocycles indicates the dissociation of Si–C bonds in the carbosiloxane ring. The weakening of endocyclic Si–C bonds in cyclocarbosiloxanes is probably due to the effect of the adjacent oxygen atom of the siloxane bond.

d. Thermal Reactions of Cyclocarbosiloxanes in the Gas Phase

At 500–600°C in the gas phase cyclocarbosiloxanes undergo rearrangements accompanied by the dissociation of endocyclic Si–O and Si–C bonds. In the first place this applies to cyclocarbosiloxanes consisting of alternating siloxane and silmethylene groups (p. 117).[48,50,88].

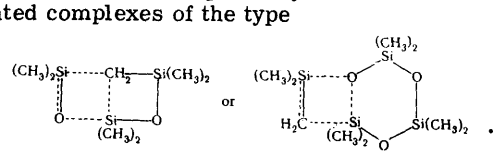
The principal effect of the rearrangements is ring contraction. Thus eight-membered cyclocarbosiloxanes form mainly six-membered compounds; in addition 1,3-disilacyclobutane and cyclosiloxanes are formed, for example:



$(n = 3,4)$

The characteristics of the thermal decomposition of cyclocarbosiloxanes are very similar to those of the thermal decomposition of cyclosiloxanes: the latter is a monomolecular process involving a four-centre mechanism[50,123,124].

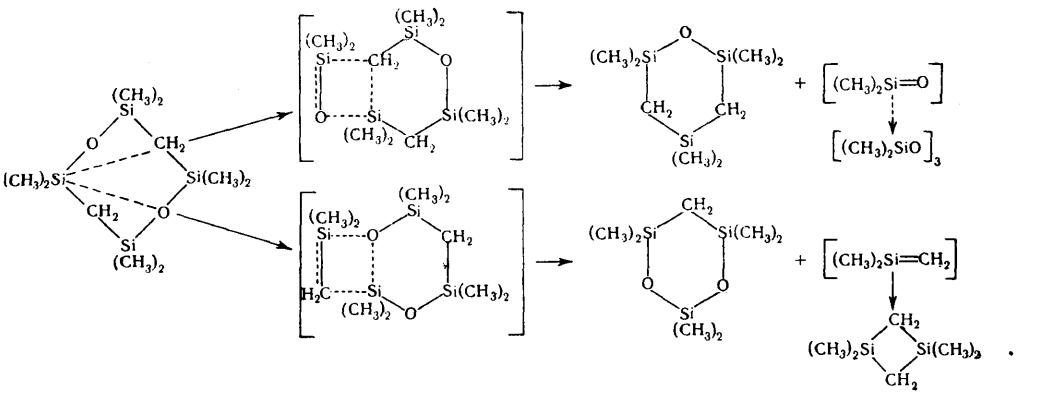
It has been suggested that the thermal rearrangement of cyclocarbosiloxanes has a similar molecular mechanism involving transannular interactions between the oxygen or carbon atoms on the one hand and silicon atoms on the other[50,88,124]. The latter probably lead to the formation of activated complexes of the type



A qualitative assessment of these activated complexes shows[125–127] that the activation energy for the dissociation

of the first is higher than for the second which is consistent with the higher thermal stability of six-membered cyclocarbosiloxanes noted in some investigations[50,88] compared with the eight-membered compounds. The proposed activation mechanism also accounts for the preferential dissociation of endocyclic bonds.

The structures of activated cyclocarbosiloxane complexes presented below show that their dissociation should lead to the formation of unstable intermediates: methylenedimethylsilane or dimethylsilanone, which are probably in fact responsible for the formation of 1,3-disilacyclobutane and cyclosiloxanes:



Oxadisilacyclohexanes behave differently in gas-phase thermolysis. Thus it has been noted[11,128] that the decomposition of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane begins with the removal of methylene groups, after which the siloxane bond is cleaved.

e. Dissociation of Cyclocarbosiloxanes on Electron Impact

The primary process occurring in the dissociative ionisation of cyclocarbosiloxanes (as for many other acyclic and heterocyclic organosilicon compounds) is the removal of a methyl group from the molecular ion (M^+):[11,58,67,111]

$$M^+ \xrightarrow{-CH_3} [M-15]^+.$$

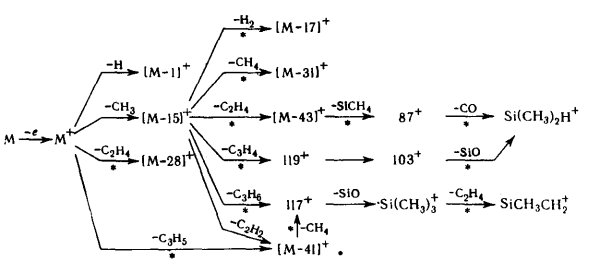
The resulting ion $[M-15]^+$ is more stable than the molecular ion; the formation of all other fragment ions can be as a rule explained by its decomposition and rearrangement. As in the case of cyclosiloxanes[129], the heaviest of the cyclocarbosiloxane fragment ions (II), (III), (VI)–(VIII) (see p. 117) are formed as a result of the loss of neutral fragments originating from the surrounding methyl group, but the cyclic skeleton of the molecule persists. With increase of the number of methylene groups in the ring, the intensity of the fragmentation of compounds (I)–(IV), due to the decomposition or rearrangement of the cyclic skeleton of the molecule, increases.

An interesting feature of the dissociative ionisation of these cyclocarbosiloxanes is the formation of metastable ions due to the loss of the neutral fragments $(CH_3)_2SiO$ and $(CH_3)_2SiCH_2$, which are structural elements of cyclocarbosiloxanes.

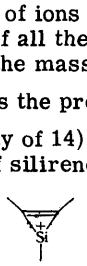
The mass spectra of the above six- and eight-membered cyclocarbosiloxanes contain a group of ions with the general formula $(CH_3)_3Si_2O_2{-}_n(CH_2)_n$ (n = 0, 1, or 2): the cyclosiloxane ion with m/e = 133, the cyclocarbosiloxane ion with m/e = 131, and the cyclocarbosilane ion with m/e = 129. The liberation of a considerable amount of kinetic energy on formation of the first ion[129] and the detection of an ion with a high intensity (m/e = 129) in the mass spectrum of 1,1,3,3-tetramethyl-1,3-disilacyclobutane[130] suggest that ions of this group have a cyclic structure.

Together with the above ions, doubly charged fragment ions formed by the successive removal of hydrocarbon groups from the $[M-2CH_3]^{2+}$ ions were observed in the mass spectrum. However, on passing from cyclosiloxanes to cyclocarbosilanes, the intensity of the doubly charged $[M-2CH_3]^{2+}$ ions falls. In addition, $[M-CH_3]^{2+}$ doubly charged ions were found in the mass spectra of six-membered cyclocarbosiloxanes [compounds (II) and (III)].[111] This is evidence of a particularly high resistance of the six-membered ring to dissociation on electron impact.

In the case of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane[11,128], the formation of the principal fragment ions is due to the decomposition of the $[M-15]^+$ ion and is associated with the removal from it of propene, ethylene, acetylene, and other fragments:



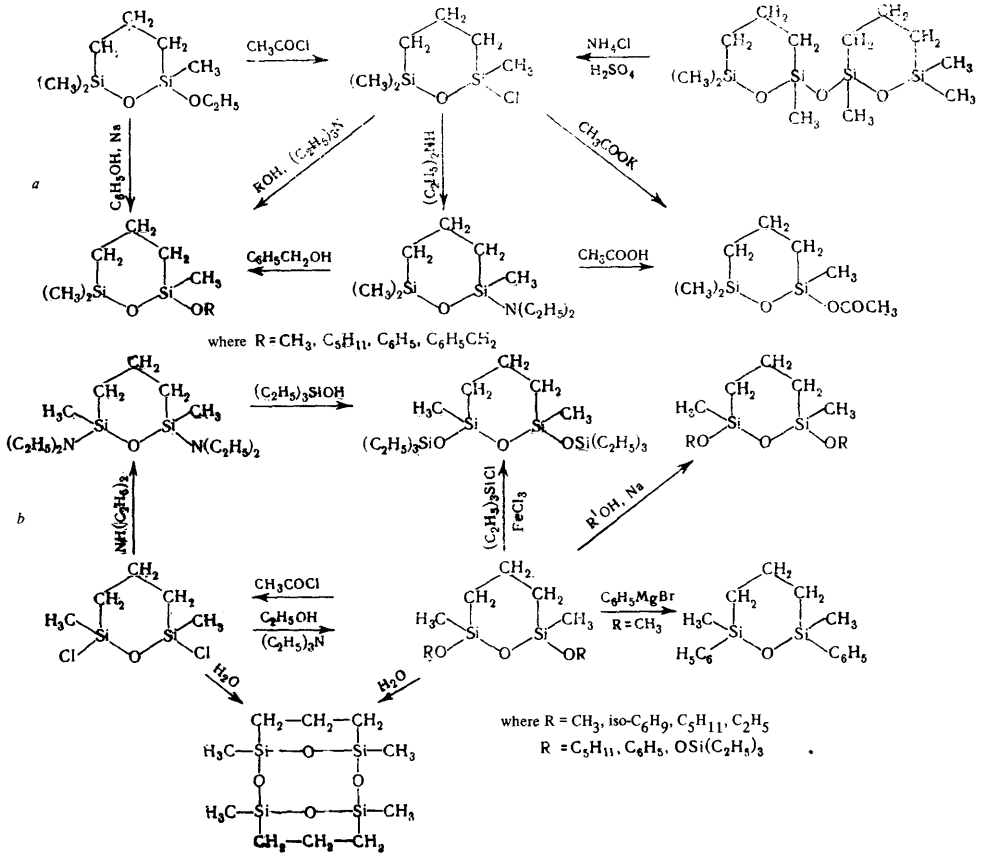
The stability of the siloxane skeleton in this compound has been noted. The number of ions containing the SiOSi group reached up to 85% of all the ions in the spectrum. An interesting feature of the mass spectrum of $[O(CH_3)Si\langle\equiv\rangle Si(CH_3)]_2$ is the presence of a fragment ion with m/e = 97 (an intensity of 14) to which the authors attributed the structure of silirene[58]:



2. REACTIONS INVOLVING THE RETENTION OF THE HETEROCYCLIC SKELETON

a. Reactions Involving Exocyclic Bonds at the Silicon Atom

As for acyclic compounds with functional groups at Si, a number of reactions of cyclocarbosiloxanes involving substitution at the silicon atom have been described; the majority of them can occur without the cleavage of the ring Si–O bonds. Thus reactions involving the substitution of halogen, alkoxy-, and amino-groups in six-membered oxadisilacyclohexanes have been described[11,31–33,54,55,70]: hydrolysis, alcoholysis, transesterification, amination, acetoxylation, alkylation with a Grignard reagent, heterofunctional condensation, and others, for example:

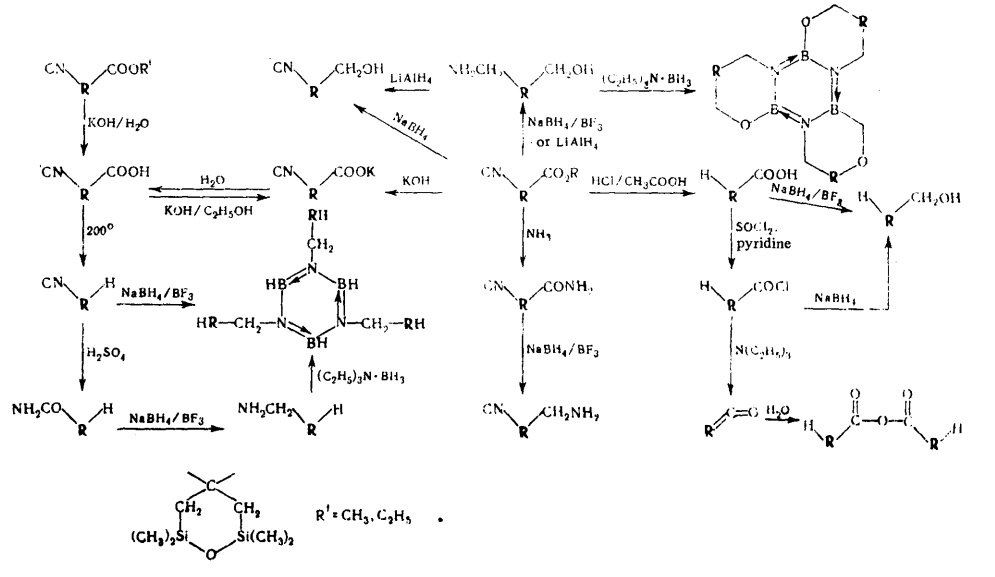


where R = CH_3, C_5H_{11}, C_6H_5, $C_6H_5CH_2$

where R = CH_3, iso-C_6H_9, C_5H_{11}, C_2H_5
R = C_5H_{11}, C_6H_5, $OSi(C_2H_5)_3$

b. Reactions of Groups and Atoms Linked to Carbon

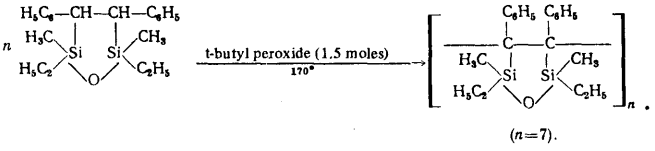
Numerous reactions of oxadisilacyclohexanes containing functional groups at the β-carbon atom of the ring have been investigated[24–27,75,131]:



$R' = CH_3, C_2H_5$

Despite the fact that many of these reactions take place under comparatively severe conditions, the carbosiloxane ring is not cleaved. In particular, it is interesting to note that, in contrast to cyclocarbosiloxanes with functional groups linked to silicon atoms[11,33], compounds with functional groups linked to carbon atoms can be reduced by $LiAlH_4$ without the cleavage of the ring siloxane bond.

When the hydrogen atoms of the methine groups of five-membered C-phenyl-substituted cyclocarbosiloxanes are attacked by free radicals, relatively unreactive cyclocarbosiloxane radicals of the benzyl type are formed and recombine, giving rise to condensation products[9,79]:



(n=7).

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During the preparation of the manuscript for the press, new studies on the synthesis and properties of cyclocarbosiloxanes were published[132-135].

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