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INORGANIC CYCLIC SILICON-CONTAINING COMPOUNDS AND THEIR ORGANIC DERIVATIVES

K. A. Andrianov, I. Haiduc,
and L. M. Khananashvili

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INTRODUCTION

The growth of the chemistry of macromolecular organic derivatives of inorganic elements has been due to their valuable technical properties, which have ensured their wide use in various fields of technology and life. Of particular interest are polymers consisting of inorganic main chains substituted by organic groups; these are structurally intermediate between organic and inorganic compounds. The production of polymers containing inorganic chains has been little studied. It is difficult, and in most cases actually impossible, to adapt or use for the production of polymers containing inorganic chains the usual methods for the production of organic polymers.

The widely used polymerisation of unsaturated organic compounds cannot be used for the production of polymers containing inorganic chains, because there are no corresponding reactive unsaturated monomers. No attempts to polymerise monomers containing the P=O bond have yet been successful.

Polycondensation reactions, which are widely used for the preparation of organic polymers, are of limited application to polymers with inorganic chains, since in most cases they are accompanied by side reactions producing low-molecular-weight cyclic compounds.

The formation of inorganic rings and their conversion to macromolecular compounds are of great significance in the chemistry of organic–inorganic polymers containing inorganic chains[1,2]. The ring-opening polymerisation of octamethylcyclotetrasiloxane has given linear polymers of molecular weight of the order of 10^6. The study of the formation of inorganic silicon-containing rings and their conversion to macromolecular compounds is of exceptional theoretical and practical interest. There have been no general reviews of the production and reactions of inorganic cyclic silicon compounds.

This review deals with various aspects of the chemistry of inorganic silicon rings and includes the most important material published in the first half of 1962. For convenience in dealing with the large volume of experimental material, all inorganic silicon-containing rings have been divided into the following classes[3,4,5]: (1) homocyclic silicon compounds $[R_2Si]_n$; (2) symmetrical heterocyclic silicon compounds $[R_2SiX]_n$, where X = O, N, S, or Se; (3) heterocyclic compounds of mixed type $[R_2SiO]_n$–Q–Y, where Q = Al, B, Ti, P, As, or Sb, and Y = O or N; and (4) polycyclic silicon compounds.

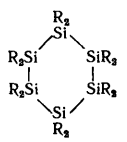
I. HOMOCYCLIC SILICON COMPOUNDS

These homocyclic compounds contain rings formed only from silicon atoms. Derivatives of the following rings have been described:



(I)

Cyclotetrasilanes



(II)

Cyclohexasilanes

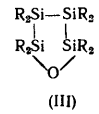
CYCLOTETRASILANES

Only the aryl-substituted cyclotetrasilanes $[R_2Si]_4$, where R = C_6H_5 [6–15] or $CH_3C_6H_4$ [10] have been described. These were obtained by the action of metallic sodium on diaryldichlorosilanes:

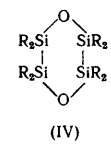
$$4R_2SiCl_2 + 8Na \longrightarrow [R_2Si]_4 + 8NaCl.$$

Two compounds of composition $[(C_6H_5)_2Si]_4$ have been characterised[6–13]. One, the so-called product A, is a chemically unsaturated reactive compound which was therefore originally assigned a linear structure with two "tervalent" silicon atoms. The second compound, product B, was less reactive; Kipping assigned to it structure (I) with R = C_6H_5. However, recent studies have shown that product A is the cyclic tetramer (I) (R = C_6H_5) [14,15], and that product B, to which structure (I) had been incorrectly assigned, is in fact the hexamer (II) (R = C_6H_5).[15–17]

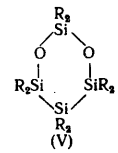
Octaphenylcyclotetrasilane reacts with iodine[6], dichloroethane[6], and mercuric chloride[18], the ring opening to form the diiodo- and dichloro-derivatives of octaphenyltetrasilane respectively, with the structures $Cl[(C_6H_5)_2Si]_4Cl$ and $I[(C_6H_5)_2Si]_4I$; hydrolysis of these gives a compound $(C_6H_5)_8Si_4O$, which has been assigned the cyclic structure (III) (R = C_6H_5).[6,19] Oxidation of octaphenylcyclotetrasilane or compound (III) with nitric acid or moist iodine[6,19] produces a compound of composition $(C_6H_5)Si_4O_2$, which is also formed by dehydration of tetraphenyldisilanediol $HO[(C_6H_5)_2Si]_2OH$,[19] which proves structure (IV) (R = = C_6H_5). Oxidation of octaphenylcyclotetrasilane with nitrobenzene produces another isomeric form of $(C_6H_5)_8.Si_4O_2$, of structure (V) (R = C_6H_5).[6,19]



(III)



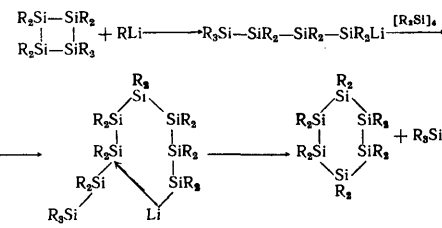
(IV)



(V)

Lithium metal in tetrahydrofuran opens the four-membered ring to form $Li[(C_6H_5)_2Si]_4Li$, in which the lithium can be replaced by methyl groups; this has been used as an indirect proof of the structure of the initial cyclic compound[14,15].

Organometallic compounds also react with $[(C_6H_5)_2Si]_4$; for example phenyllithium gives a mixture of products, from which dodecaphenylcyclohexasilane, a higher cyclosilane, has been isolated[20]:



where R = C_6H_5.

The reaction between octaphenylcyclotetrasilane and triphenylsilyllithium also produces $[(C_6H_5)_2Si]_6$, among other products[20].

Octaphenylcyclotetrasilane is decomposed on heating, giving a very complex mixture of products containing the groups $-(C_6H_5)_2Si-$ and $(C_6H_5)_3Si-$.[21]

Fig. 1 shows the most important reactions of octaphenylcyclotetrasilane.

CYCLOHEXASILANES

Dodecamethyl- [22] and dodecaphenyl-cyclohexasilanes[16,17] have been described.

Dodecamethylcyclohexasilane (II) (R = CH_3) was isolated from the products of the reaction between dimethyldichlorosilane and metallic sodium[22], and its use as an additive for improving the properties of butyl rubber has been patented[23]; it apparently acts as an oxidation inhibitor.

Dodecaphenylcyclohexasilane (II) (R = C_6H_5) was first obtained by Kipping, who erroneously considered it to be the tetramer $[(C_6H_5)_2Si]_4$.[6,8] Gilman and coworkers, who obtained this compound from diphenyldichlorosilane and metallic sodium[16,17], proved that Kipping's product B is not the tetramer, but the cyclic hexamer.

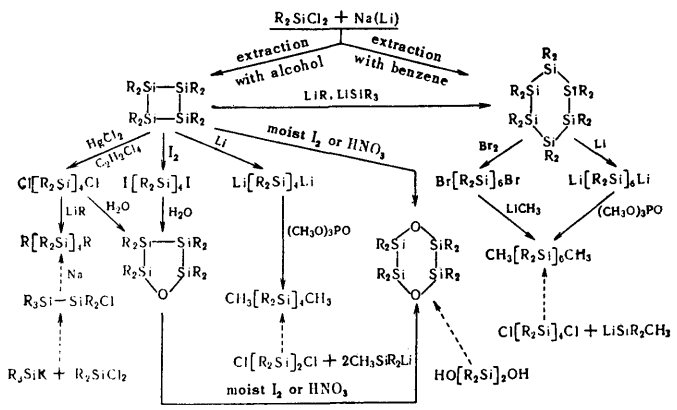


Fig. 1. Reactions of organocyclosilanes (R = C_6H_5).

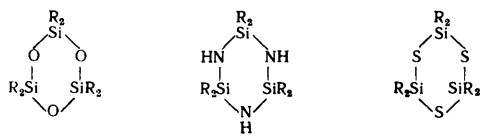
Certain observations have indicated that cyclohexasilanes are more stable than cyclotetrasilanes, since the ring is less strained. Thus unlike the tetramer, the cyclic hexamer does not react with phenyllithium[20] and is not oxidised by nitrobenzene. However, the six-membered ring is opened by lithium in tetrahydrofuran, giving $Li[(C_6H_5)_2Si]_6Li$, and by bromine, giving $Br[(C_6H_5)_2Si]_6Br$.[17]

The reactions and interconversions of cyclosilanes and their derivatives are shown in Fig. 1. The preparation of some of the cyclosilane reaction products by other methods is a proof of their structure.

The production of Si_6H_6 and derivatives thereof has been reported[24], and a cyclic unsaturated structure has been proposed for them, involving conjugated $-Si=Si-$ double bonds in the ring, but this structure requires confirmation, since it is improbable on the basis of existing data.

II. HETEROCYCLIC SILICON COMPOUNDS

Heterocyclic silicon compounds are obtained when some of the silicon atoms in the homocyclic compounds are replaced by other heteroatoms [see formulae (III)–(V)], or when silicon atoms alternate with other elements such as oxygen, nitrogen, sulphur, and selenium around the ring:



These three rings, which are made up of the repeating units SiO, SiN, and SiS, play an important part in the chemistry of inorganic cyclic silicon compounds.

Mixed rings are obtained when some of the silicon atoms in rings made up of identical repeating units are replaced by other elements (for instance phosphorus or boron), or when some of the oxygen in oxygen-containing rings is replaced by nitrogen.

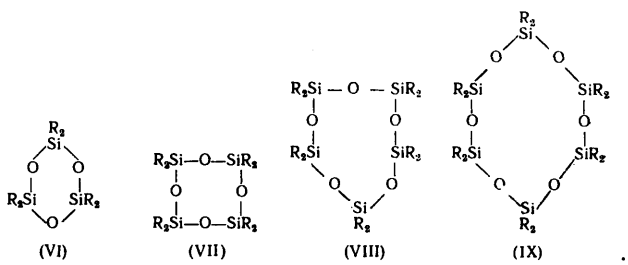
Consequently, three types of inorganic heterocyclic silicon rings are known at present: (a) heterocycles containing the $-Si-Si-$ bond and hetero-atoms; (b) heterocycles with a regular alternation of silicon atoms with atoms of other elements (oxygen, nitrogen, sulphur, or selenium); and (c) mixed heterocycles, containing different structural units.

Heterocyclic compounds of type (a) have been little studied, and what is known of them has been discussed in the preceding section in connection with the reactions of organocyclosilanes. Monomers such as $Cl[R_2Si]_2Cl$ and $Cl[R_2Si]_4Cl$ are known, and it would seem that nitrogen- and sulphur-containing analogues of the oxygen-containing heterocycles already described should be obtainable from these by ammonolysis and thiohydrolysis.

Silicon is an element of low electronegativity, and hence the $-Si-Si-$ bond is sensitive to oxidation, so that rings containing such bonds are relatively unstable. The alternation of silicon atoms with atoms of more electronegative elements in a ring is therefore of great importance, since such rings, containing oxygen, nitrogen, or sulphur in addition to silicon, will be more stable, because the tendency of the silicon towards oxidation will be compensated by the tendency of the electronegative elements towards reduction[5,25]. Another factor is that electronegative elements such as oxygen and nitrogen are electron donors, and their unshared electron pairs may be delocalised in the ring with utilisation of the free *d* orbitals of the silicon atoms, and this will also increase the stability of the ring and will lead to partial aromatic character (see Haiduc's book[5], Chapters XXI and XXII).

1. CYCLOSILOXANES

The structural unit SiO is the basis of a large number of cyclic inorganic and organosilicon compounds, which are known as "cyclosiloxanes". Cyclosiloxanes of the general formula $[R_2SiO]_n$ containing 3–12 SiO groups in the ring have been described:



(VI) (VII) (VIII) (IX)

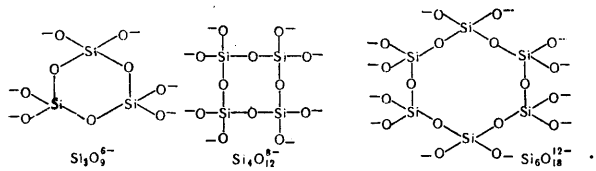
Such rings can contain inorganic groups (R = Cl, Br, OH, or $O^{(-)}$), organic radicals (R = alkyl or aryl), or functional groups (R = alkoxy, aryloxy, alkylamino, arylamino, etc.) as substituents taking up the remaining valencies of the silicon after formation of the ring. Mainly the six- and eight-membered rings have been studied.

Inorganic Derivatives

Several silicates have been shown by X-ray diffraction to contain a cyclic silicate anion; such minerals are usually named cyclosilicates[26]. The six-membered ring Si_3O_3 is contained as the anion $Si_3O_9^{6-}$ in benitoite $BaTi[Si_3O_9]$,[27] wadeite $K_2Zr[Si_3O_9]$,[28] catapleiite $Na_2Zr[Si_3O_9].H_2O$,[29] eudialite $(Na, Ca, Fe)_6Zr[(OH, Cl)(Si_3O_9)_2]$,[30] manganese metasilicate α-$MnSiO_3$,[31] and other minerals[26]. The

eight-membered ring Si_4O_4 is contained as the anion $Si_4O_{12}^{8-}$ in neptunite $Na_2(Fe, Mn)Ti[Si_4O_{12}]$,[32] kainosite $Ca_2(Ce, Y)_2.[(CO_3)(Si_4O_{12})]$,[33] axinite $Ca_2(Fe, Mn)Al_2[(OH)(BO_3)Si_4O_{12}]$,[33] and others. The twelve-membered ring Si_6O_6 is contained as the anion $Si_6O_{18}^{12-}$ in beryl $Be_3Al_2[Si_6O_{18}]$,[34,35] dioptase $Cu_6[Si_6O_{18}].6H_2O$,[35-38] lovozerite $Na_2Zr[Si_6O_{12}(OH)_6]$,[39] and in a number of silicates of the tourmaline group[26].

These cyclic anions have the structures:



The acids corresponding to these anions have not been isolated, because of the great tendency of Si—OH bonds towards condensation, so that polysilicic acids are always obtained as macromolecular compounds. However, the formation of tetrametasilicic acid $Si_4O_4(OH)_8$ (VII) (R = OH) has been observed in the hydrolysis of silicon sulphide[40].

Silicon oxyhalides $[X_2SiO]_n$, where X = Cl or Br and n = 3 or 4, are also cyclic compounds. The oxychloride $Cl_8Si_4O_4$ (octachlorocyclotetrasiloxane) has been obtained by oxidising silicon tetrachloride vapour at an elevated temperature[41-45]. It has recently been shown[46] that this reaction also produces the trimer $Cl_6Si_3O_3$ (VI) (R = Cl) and the pentamer $Cl_{10}Si_5O_5$ (VIII) (R = Cl). The oxidation of silicon tetrabromide at 670°–695° produces the oxybromide $Br_8Si_4O_4$ (octabromocyclotetrasiloxane)[47], together with linear bromosiloxanes of the general formula $Br_{2n+2}Si_nO_{n-1}$.

The hydrocyclosiloxanes $[H_2SiO]_n$, where n = 4, 5, or 6, have been obtained[48]; these (VII, VIII, and IX) (R = H) are the prototypes of the organic derivatives.

Organic Derivatives

This section deals with compounds containing two organic radicals directly attached to each silicon atom, *i.e.* dialkyl-, diaryl-, and alkylaryl-cyclosiloxanes.

In principle, organocyclosiloxanes can be prepared by any reaction in which siloxane bonding is produced. Siloxane bonding is produced by many different types of reaction, which can be classified as follows:

(a) *Reactions of functional derivatives of silicon with substances which can release oxygen.* The oxygen source can be water, metal oxides, ethers, aldehydes, ketones, alcohols, mixtures of alcohols with acids, etc.:

$$2\equiv Si{-}X + H_2O \longrightarrow \equiv Si{-}O{-}Si\equiv + 2HX, \quad (1)$$
$$2\equiv Si{-}X + MeO \longrightarrow \equiv Si{-}O{-}Si\equiv + MeX_2, \quad (2)$$
$$2\equiv Si{-}X + R_2O \longrightarrow \equiv Si{-}O{-}Si\equiv + 2RX, \quad (3)$$
$$2\equiv Si{-}X + RCHO \longrightarrow \equiv Si{-}O{-}Si\equiv + RCHX_2, \quad (4)$$
$$2\equiv Si{-}X + ROH \longrightarrow \equiv Si{-}O{-}Si\equiv + RX + HX, \quad (5)$$
$$2\equiv Si{-}X + ROH + R'COOH \longrightarrow \equiv Si{-}O{-}Si\equiv + R'COOR + 2HX. \quad (6)$$

Of these hydrolysis is the most important reaction.

(b) *Homofunctional condensation reactions.* These usually take place in the presence of catalysts or condensation agents:

$$2\equiv Si{-}OH \longrightarrow \equiv Si{-}O{-}Si\equiv + H_2O, \quad (7)$$
$$2\equiv Si{-}OR \longrightarrow \equiv Si{-}O{-}Si\equiv + ROR, \quad (8)$$
$$2\equiv Si{-}OCOR \longrightarrow \equiv Si{-}O{-}Si\equiv + (RCO)_2O, \quad (9)$$
$$2\equiv Si{-}OR + 2R'COOH \longrightarrow \equiv Si{-}O{-}Si\equiv + 2RCOOR' + H_2O. \quad (10)$$

(c) *Heterofunctional condensation reactions.* These normally occur in the presence of catalysts or on heating:

$$\equiv Si{-}X + RO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + RX, \quad (11)$$
$$\equiv Si{-}X + ROCO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + RCOX, \quad (12)$$
$$\equiv Si{-}X + HO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + HX, \quad (13)$$
$$\equiv Si{-}X + MO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + MX\ (M=Na, K), \quad (14)$$
$$\equiv Si{-}OR + R'OCO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + ROCOR', \quad (15)$$
$$\equiv Si{-}OR + HO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + ROH, \quad (16)$$
$$\equiv Si{-}NH_2 + HO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + NH_3. \quad (17)$$

(d) *Reactions involving rupture of a siloxane–element bond:*

$$2\equiv Si{-}O{-}Q{-} \longrightarrow \equiv Si{-}O{-}Si\equiv + Q{-}O{-}Q. \quad (18)$$

(e) *Reactions involving rupture of an organo-silicon bond,* under the action of sulphuric acid or other reagents:

$$2\equiv Si{-}R \xrightarrow[2.H_2O]{1.H_2SO_4} \equiv Si{-}O{-}Si\equiv + 2RH. \quad (19)$$

The production of organocyclosiloxanes clearly requires only bifunctional compounds. In addition to cyclic compounds there will also be obtained linear polymers retaining terminal functional groups. Not all of the above reactions have been used in the production of organocyclosiloxanes. Some have simply not yet been sufficiently studied, while others have given only linear polymers. The factors which determine the mode of a reaction and the structure of the products are not yet fully understood, and further study is therefore required.

An interesting case of the production of organocyclosiloxanes is the *depolymerisation of macromolecular linear diorganosiloxanes*, by which the products of any of the above reactions can be converted into organocyclosiloxanes, a feature of the reaction being that the total number and nature of the bonds remain unaltered, the starting materials and products differing only in molecular weight. The reaction involves only the rearrangement or redistribution of the siloxane bonds, the macromolecular polymers being converted into low-molecular-weight cyclic compounds[49-54]:

$$[R_2SiO]_x \longrightarrow y\,[R_2SiO]_n, \quad (20)$$

where $ny = x$. This reaction has been widely used, especially for the preparation of hexaorganocyclotrisiloxanes[55-70].

(a) Reactions of functional derivatives of silicon with substances which can release oxygen. The hydrolysis of functional derivatives of silicon is the most important method for the production of cyclosiloxanes. Organocyclosiloxanes $[R_2SiO]_n$ are formed, together with the linear siloxanes $HO[R_2SiO]_xSiR_2OH$, when bifunctional compounds R_2SiX_2, (where X = halogen, $-OR'$, $-OCOCH_3$, etc.), are hydrolysed [reaction (1)]. Despite the relatively simple structure of the starting materials,

the hydrolysis is a complex process involving two competing reactions:

hydrolysis of Si–X bonds

$$\equiv Si-X + H_2O \longrightarrow \equiv Si-OH + HX,$$

and condensation

$$\equiv Si-OH + HO-Si\equiv \longrightarrow \equiv Si-O-Si\equiv + H_2O,$$
$$\equiv Si-OH + X-Si\equiv \longrightarrow \equiv Si-O-Si\equiv + HX.$$

This reaction is more correctly named hydrolytic polycondensation[75].

It should be noted that hydrolysis alone cannot produce cyclic compounds, since the hydrolysis products are dialkyl- (or diaryl-) silanediols. The reaction can be stopped at this stage only if the medium is kept strictly neutral, since traces of acid produce further condensation of the diorganosilanediols with the formation of linear and cyclic organosiloxanes. The formation of rings and linear chains is thus the result of stepwise hydrolytic polycondensation.

The mechanism of formation of organosiloxanes in the hydrolysis reaction has been most studied with diorganodichlorosilanes (and in particular with dimethyldichlorosilane); several intermediates have been isolated. It can be assumed that dialkoxy- and diacetoxy-silanes undergo hydrolysis by an analogous mechanism.

Fig. 2 illustrates the hydrolysis of dialkyldichlorosilanes. Under the influence of protons, the hydrolysis products $R_2SiClOH$ and $R_2Si(OH)_2$ can react with one another and with their reaction products to give various different compounds. Proof of this mechanism is to be found in the hydrolysis of dimethyldichlorosilane under various conditions. Hydrolysis with a deficiency of water (in a homogeneous medium) will produce $\alpha\omega$-dichloroorganosiloxanes (series a_1-a_n); *e.g.* the compounds $Cl[R_2SiO]_{n-1}SiR_2Cl$, where $R = CH_3$ and $n = 1-5$, have been obtained in this way[49,71]. With hydrolysis in a neutral medium (with neutralisation of the hydrogen chloride formed) it is possible to isolate dimethylsilanediol $(CH_3)_2Si(OH)_2$ [72,73] and tetramethyldisiloxanediol $HO(CH_3)_2SiOSi(CH_3)_2OH$.[74] Compounds of series *b*, *i.e.* organochlorosiloxanols, cannot be obtained, because of the impossibility of the simultaneous existence of $\equiv Si-Cl$ and $\equiv Si-OH$ bonds, which immediately condense with the elimination of HCl and the formation of an $\equiv Si-O-Si\equiv$ bond.

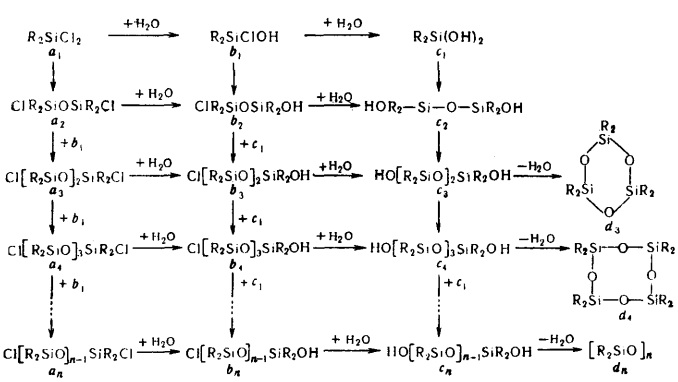


Fig. 2. Hydrolysis of diorganodichlorosilanes.

The chain grows as a result of intermolecular condensation. Cyclisation occurs by intramolecular reactions of this type with chains containing more than three silicon atoms; a proof of this is the condensation of $\alpha\omega$-organosiloxanediols, which gives high yields of cyclic compounds[75]. The monomeric silicone R_2SiO and the cyclic dimer $[R_2SiO]_2$ have not been isolated, although species of mass corresponding to $(CH_3)_2SiO$ and $(C_2H_5)_2SiO$ have been observed by mass spectrometry[76].

The factors which determine the course of hydrolysis have been little studied, but it is known that the composition of the reaction products depends greatly on the nature of the organic radical and the functional groups of the initial monomer, and on the temperature, concentration, and pH of the medium[75].

The organic radicals determine the size of the rings formed: the hydrolysis of dimethyldichlorosilane produces 6-, 8-, 10-, and 12–18-membered rings, the ethyl compound and certain other diorganodichlorosilanes produce 6-, 8-, 10-, and 12-membered rings, while many diorganodichlorosilanes produce only 6- and 8-membered rings. This may be due to the steric effect of the organic radical.

The functional groups of the monomer determine the rate of hydrolysis, since different groups have different reactivities. The following order of reactivity in hydrolysis reactions has been established[75]:

$$-Cl \geqslant -OCOR > -OR,$$

in accordance with the change in electronegativity of these groups.

The composition of the reaction products also depends on the concentration and on the nature of the solvent used. A decrease of concentration increases the formation of cyclic compounds and reduces the yield of linear products. The nature of the solvent also affects the reaction[77]; thus the hydrolysis of diethyldichlorosilane in ether gives 41% of the trimer $[(C_2H_5)_2SiO]_3$ and 31% of the tetramer $[(C_2H_5)_2SiO]_4$,[78] while hydrolysis in methanol produces the cyclic tetramer in 70% yield[70]. In general, water-miscible solvents increase the yield of cyclic compounds.

The acidity of the medium has a large effect on the composition of the hydrolysis products. As already mentioned, diorganosilanediols can be isolated from a netural medium, while an acid medium favours condensation, especially the formation of low-molecular-weight cyclic organosiloxanes. An alkaline medium prevents ring-formation to a considerable extent. It is of interest here that the hydrolysis of diorganodichlorosilanes by aqueous solutions of metal salts also gives large amounts of cyclic siloxanes[80].

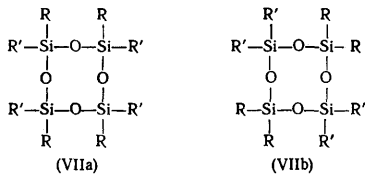
Hydrolysis of the corresponding diorganodichlorosilanes has provided the following cyclosiloxane derivatives of general formula $[R_2SiO]_n$, the substituent radicals being dimethyl ($n = 3-9$)[49,77,81-85], hydrogen and methyl ($n = 4-6$)[86-89], diethyl ($n = 3-5$)[78,90-93], hydrogen and ethyl ($n = 3-5$)[94,95], methyl and ethyl ($n = 3-6$)[96,97], methyl and butyl ($n = 3-5$)[97], methyl and trifluoropropyl ($n = 3$)[98], methyl and trifluorobutyl ($n = 4$)[99], methyl and vinyl ($n = 4$ and 6)[100], ethyl and vinyl ($n = 3$)[101], diphenyl ($n = 3$ and 4)[82,102,103], methyl and phenyl ($n = 3$ and 4)[90,104,105], di-(chlorophenyl) ($n = 3$ and 4)[106], methyl and chlorophenyl ($n = 3$ and 4)[107,108], ethyl and phenyl ($n = 3$ and 4)[82,90], ethyl and benzyl ($n = 3$)[109], spiropentamethylene ($n \leqslant 5$)[110], and others[82,97,111-121].

The hydrolysis of the $\alpha\omega$-dichloroorganosiloxanes $Cl[R_2SiO]_{n-1}SiR_2Cl$ (where R = CH_3 and C_2H_5) has also been studied[122]; this produces cyclic compounds with n, $2n$, $3n$, ... siloxane groups in the ring.

The hydrolysis of dialkyl(or aryl)dialkoxysilanes has also produced cyclosiloxanes: dimethyl (n = 3–12)[123-129], methyl vinyl (n = 4–6)[130-132], methyl chlorophenyl (n = = 3)[133], ethyl vinyl (n = 3)[101], tetramethylbisferrocenyl[134], and others[135]. The hydrolysis of alkoxysilanes even with a deficiency of water yields cyclic compounds in addition to the linear organodialkoxysiloxanes $RO[R_2SiO]_{n-1}SiR_2OR$.[136]

The hydrolysis of methylhexynyldiacetoxysilane with water has given tetra-(methylhexynyl)cyclotetrasiloxane $[CH_3(CH_2)_3C\equiv C-Si(CH_3)O]_4$.[137]

The organocyclosiloxanes so far described have identical repeating units in the ring. The simultaneous hydrolysis of two (or sometimes more) bifunctional monomers gives cyclic compounds containing different units in the ring (*i.e.* differently substituted units). Simultaneous hydrolysis is thus a method for the production of organocyclosiloxane isomers differing in the positions of the organic radicals around the ring, *e.g.*:



(VIIa)

(VIIb)

A compound (VIIa) is produced by the simple hydrolysis of a monomer $RR'SiX_2$, and a compound (VIIb) by the simultaneous hydrolysis of two monomers R_2SiX_2 and R'_2SiX_2. Dimethyldichlorosilane has been cohydrolysed with H_2SiCl_2,[138] CH_3SiHCl_2,[139,140] $CH_3(CH_2=CH)SiCl_2$,[141-143] $C_2H_5(CH_2=CH)SiCl_2$,[142,143] $(C_6H_5)_2SiCl_2$,[144] $C_6H_5(CH_3)$. $.SiCl_2$,[144,145] $ClC_6H_4(CH_3)SiCl_2$,[144,145] and $C_6H_5(CH_3)Si$. $.(OC_2H_5)_2$;[146] other cohydrolysis reactions have also been described[90,135,140,142,143,147,148].

In the reaction of organodichlorosilanes with metal oxides [reaction (2)] the oxide oxygen is used to form the siloxane bond; for example, the reaction between dibenzyldichlorosilane and mercuric oxide produces the trimer $[R_2SiO]_3$.[149] Oxides of copper, zinc, beryllium, magnesium, silver, cadmium, and lead have been used[150-152]. With a deficiency of metal oxide, acyclic organohalogenosiloxanes are formed[153]. The reaction between dimethyldichlorosilane and ferric oxide also does not produce cyclic compounds, and only 1,3-dichlorotetramethyldisiloxane is formed[154,155].

In general, this interesting type of reaction has been insufficiently studied, and it is still not clear why the mode of the reaction varies with the metal used as the oxide.

Metal salts may be used in place of the oxides[152,156]; thus diethyldichlorosilane with $NaHCO_3$ yields the trimer $[(C_2H_5)_2SiO]_3$.[156]

Organohalogenosilanes react with ethers to form cyclosiloxanes [reaction (3)]. Dimethyldibromosilane and ethyl ether give $[(CH_3)_2SiO]_4$ and ethyl bromide[157]. At 200° and under pressure dimethyldichlorosilane reacts with dimethyl ether in the presence of $AlCl_3$ to give a silicone oil which contains the trimer $[(CH_3)_2SiO]_3$.[158]

The reaction between chlorosilanes and aldehydes [reaction (4)] has been used to prepare silicon oxychlorides[159]. Alkylalkoxysilanes react with aldehydes to form organocyclosiloxanes[160]. Acetone reacts with diphenyldichlorosilane to yield cyclosiloxanes; the reaction mechanism is not clear[161,162]. Dimethylformamide also reacts with organochlorosilanes to give linear and cyclic siloxanes[163,164]. In all these cases the organochlorosilane splits off and combines with the carbonyl oxygen.

The reaction of chlorosilanes with alcohols normally produces alkoxysilanes, but siloxanes are formed in a side-reaction [by reaction (5)], particularly with methyl[165,166] and t-butyl alcohols[167,168]. The yield of cyclic organosiloxanes is very low, since the reaction proceeds effectively the whole time with a deficiency of water, which is produced by the reaction of the alcohol with hydrogen chloride.

Reaction (6) is actually a disguised hydrolysis reaction, since it takes place by virtue of the water liberated; it produces mainly linear polymers. The yield of cyclic organosiloxanes when dimethyldichlorosilane is reacted with a mixture of methanol and acetic acid, is less than 10%.[169]

(b) Homofunctional condensation reactions. The condensation of organosilanols [reaction (7)] is one of the competing reactions in the hydrolysis of bifunctional organosilanes, since in some cases organosilanols can be isolated during the hydrolysis. The condensation of diphenylsilanediol in alcohol or acetic anhydride produces the cyclic trimer $[(C_6H_5)_2SiO]_3$, which was the first organocyclosiloxane to be identified[170]. Other reactions of this type have been described[102,106,111,171-179].

Condensation with ring-formation has been especially studied with siloxanediols $HO[R_2SiO]_nH$, which give mainly cyclic compounds containing $2n$, $3n$ ... R_2SiO groups in the ring when $n \geq 2$ or even when $n \geq 3$.[75]

The condensation of organosilanols is favoured by heat and the catalytic action of acids or bases. It is interesting that the condensation of $(C_6H_5)_2Si(OH)_2$ produces the tetramer $[(C_6H_5)_2SiO]_4$ in the presence of alkalis[180,181], but the trimer in the presence of acids or alcohols[181]. The condensation of organosilanediols by the action of ion-exchange resins has been described: diethylsilanediol yields a mixture of the trimer and the tetramer[182].

The homocondensation of alkoxysilanes to form siloxanes [reaction (8)] is carried out by heating under pressure in the presence of catalysts (AlX_3, BX_3). Diethyldiethoxysilane gives linear alkoxysiloxanes and the cyclic trimer[183].

Organic acids and their anhydrides can be used as condensation agents for alkoxysilanes[184-186] [reaction (10)]: thus dimethyldiethoxysilane reacts readily with acetic anhydride or acetic acid to give linear and cyclic organosiloxanes. The mechanism here is more complex, and includes heterofunctional condensation reactions between alkoxysilanes and acetoxysilanes[187].

The homocondensation of acyloxysilanes, *e.g.* diacetoxydiorganosilanes [reaction (9)], is carried out by heating above 200°, and gives liquid organosiloxanes[188]; the reaction products were not fully investigated.

(c) Heterofunctional condensation reactions. These are reactions between two monomers having different functional groups attached to silicon atoms;

a siloxane bond is formed, with elimination of a secondary reaction product [reactions (11)–(17)].

Organohalogenosilanes react with alkoxysilanes [reaction (11)] on heating in the presence of a Friedel–Crafts catalyst; generally the products are linear organosiloxanes containing the functional groups. With an exactly equimolar mixture of R_2SiCl_2 and $R_2Si(OR)_2$ (R = C_2H_5) and in the presence of $AlCl_3$, the main products are organocyclosiloxanes[183]. Excess of chloro- or alkoxy-silane produces the linear $\alpha\omega$-dichloro- or $\alpha\omega$-dialkoxy-siloxane. When R = CH_3, a polymer is formed[189]. Heating $(CH_3)_2.Si(OCH_3)_2$ at 80° in the presence of $FeCl_3$ yields a mixture of linear and cyclic siloxanes[190].

The reaction of organohalogenosilanes with acyloxysilanes, in particular with acetoxysilanes [reaction (12)] leads predominantly to the formation of linear siloxanes[191].

The reaction between organohalogenosilanes and organosilanols [reaction (13)] is one of the steps in hydrolytic polycondensation, and produces cyclic and linear polymers. The reaction of dimethyldichlorosilane with tetramethyldisiloxane-1,3-diol gives a polydimethylsiloxane[192].

Reaction (14) has been used for the preparation of organocyclosiloxanes containing functional groups, and is dealt with below.

Alkoxysilanes react with acyloxysilanes [reaction (15)] on heating in the presence of alkaline or acid catalysts. The reaction is not of great interest for the production of cyclic compounds, since it gives mainly linear polymers[191,193].

The reaction of alkoxysilanes with organosilanediols [reaction (16)] takes place in the presence of alkaline or acidic catalysts, *e.g.* sodium silanolates, and can be used for the preparation of cyclic compounds. The reaction of $(CH_3)_2.Si(OC_2H_5)_2$ with $(t\text{-}C_4H_9)_2Si(OH)_2$ in the presence of H_2SO_4 produces the cyclotetrasiloxane $(t\text{-}C_4H_9)_4(CH_3)_4Si_4O_4$.[194] The following reactions have also been carried out[194]:

$$(C_6H_5)_2Si(OH)_2+C_2H_5O(CH_3)_2SiOSi(CH_3)_2OC_2H_5 \xrightarrow{-C_2H_5OH} (C_6H_5)_2(CH_3)_4Si_3O_3,$$

$$2(C_6H_5)_2Si(OH)_2+2(CH_3)_2Si(OC_2H_5)_2 \xrightarrow{-C_2H_5OH} (CH_3)_4(C_6H_5)_4Si_4O_4.$$

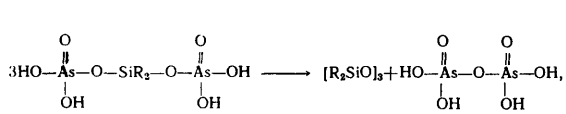
Aminosilanes also react with organosilanols to form the siloxane bond [reaction (17)]. The formation of linear and cyclic organosiloxanes[195] has been demonstrated in the reaction of $(CH_3)_2Si[N(C_2H_5)_2]_2$ with hexamethyltrisiloxane-1,5-diol.

(d) Reactions involving rupture of a siloxane – element bond [reaction (18)] can occur hydrolytically or by disproportionation on heating, and can also produce cyclosiloxanes, *e.g.*[196,197]:

$$(R_2SiClO)_3B \xrightarrow{160°} [R_2SiO]_3+R_2SiCl_2+B_2O_3,$$

where R = CH_3.

The formation of cyclosiloxanes has also been observed in the disproportionation of arsenatosiloxanes[198]:



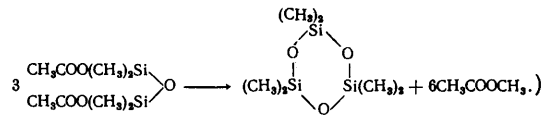
where R = C_6H_5.

The Si–O–Pb, Si–O–Mg, Si–O–Cu, and Si–O–Hg bonds are also readily broken, with the formation of cyclosiloxanes[199].

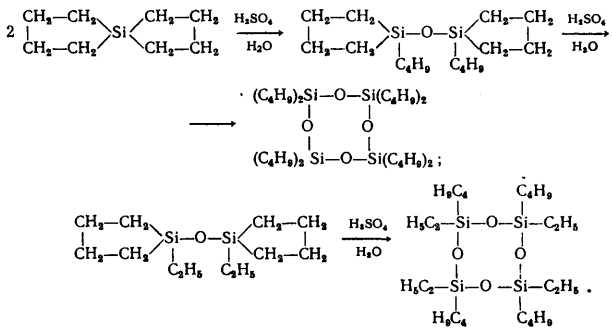
(e) Reactions involving rupture of an organo-silicon bond generally proceed under the action of concentrated sulphuric acid and water, forming the hydrocarbon and a siloxane bond. The first stage of the reaction is the formation of silyl sulphates, which are then hydrolysed by the water. The trimethylsilyl group may thus be converted into the dimethylsiloxane group[200]:

$$(CH_3)_3Si- \xrightarrow[2.H_2O]{1.H_2SO_4} \frac{1}{n}[-(CH_3)_2Si-O-]_n+CH_4.$$

(These elimination reactions are typical of a series of compounds containing functional groups in the organic radical, *e.g.* [201]:



An interesting use of this reaction is the conversion of cyclic silicon-containing hydrocarbons into cyclosiloxanes[202]:



Phenyl groups are more easily removed from silicon atoms than alkyl groups. Di-(cyclohexyl)phenylsilanol gives a cyclic trimer on heating with HCl or HNO_3 in acetic acid[111]:

$$3C_6H_5(C_6H_{11})_2SiOH \longrightarrow [(C_6H_{11})_2SiO]_3+3C_6H_5.$$

Bromine in acetic acid produces a mixture of the same trimer together with the tetramer[111].

Physical Properties of Organocyclosiloxanes

In addition to such physical properties as melting and boiling point, density and refractive index, other physical properties of certain organocyclosiloxanes, in particular the dimethyl derivatives, have been determined. Thus data have been given on viscosity[203–209], compressibility[209–211], surface tension[212], and molecular volume[203]. Thermodynamic characteristics have been evaluated: heats of formation[213–217], equation of state[218], thermal expansion[203], vapour pressure[204,218–220], heats of evaporation[203,218,220], heats of fusion and sublimation and entropy[218,219,221], and cryoscopic constants[218,221–223]. Dielectric constants[224–226], dipole moments[224,227,228], and magnetic properties[229] have been determined. Organocyclosiloxanes have been quite widely studied spectroscopically. Infrared spectra have

been recorded for dimethylcyclosiloxanes[90,230,231], diethylcyclosiloxanes[90], diphenylcyclosiloxanes[90,232,233], other cyclosiloxanes containing organic radicals[90,234-236], and cyclic silicates[237,238]. It has been shown that the absorption band at 1020 cm^{-1} corresponds to the six-membered ring, and the band at 1060–1080 cm^{-1} to the eight-membered ring. The Raman spectra of dimethyl-[230,231,239-241], diethyl-[242], and other cyclo-siloxanes[233,242,243], have been investigated. The ultraviolet[244] and nuclear magnetic resonance spectra[245-248] of certain organocyclosiloxanes have been described.

Structure of the Organocyclosiloxanes

The structure of the dimethylcyclosiloxanes has been investigated by electron diffraction[249-253] and X-ray diffraction[254-258] methods.

The six-membered Si_3O_3 rings in the trimer $[(CH_3)_2SiO]_3$ is planar. The Si–O bond distance of 1.614 Å is considerably less than the sum of the covalent radii of oxygen and silicon, demonstrating delocalisation of the oxygen π electrons because of the 3*d* orbitals of the silicon, with partial aromatisation[5]. The bond angles[256] $\angle$ OSiO = 104° and $\angle$ SiOSi = 136° in the planar ring indicate that the ring is somewhat strained, which is shown in the greater reactivity of the cyclotrisiloxanes as compared with their cyclosiloxane homologues.

The eight-membered Si_4O_4 ring in the tetramer $[(CH_3)_2.SiO]_4$ is not planar, and has the "chair" configuration. The Si–O distance of 1.65 Å [257] also indicates delocalisation of π electrons with $d_\pi - p_\pi$ conjugation[5,259]. The bond angles are $\angle$ SiOSi = 142.5° and $\angle$ OSiO = 109°.

Chemical Properties of Organocyclosiloxanes

The cyclosiloxane derivatives are very reactive. They can react with retention of the ring (substitution reactions), breakdown of the ring (production of monomers), or opening of the ring (production of oligomers, telomers, and polymers). Cyclosiloxanes are not very reactive in homolytic reactions, and are very stable from this point of view, but, because of the polarity of the Si–O bonds in the rings, they can undergo many diverse heterolytic reactions, and their reactions with electrophilic and nucleophilic reagents are very widely used for the preparation of various types of silicon compounds.

The composition of the reaction products of cyclosiloxanes with various reagents depends on the relative proportions of reactants used. The same reagent, *e.g.* NaOH, can produce monomers or oligomers or can lead to polymerisation of the cyclosiloxane. The reaction mechanism is the same, but the products will differ, depending on the relative quantities of NaOH and cyclosiloxane used and on the reaction conditions.

Reactions involving breakdown of the ring. If sufficient reactant is taken to react with all the Si–O bonds of the cyclosiloxane, the products will be monomers, *i.e.* compounds containing only one silicon atom per molecule. Thus the reaction between NaOH and a cyclosiloxane taken in the molar ratio NaOH : $[R_2SiO]_n$ = $= 2n : 1$ (where n is the number of SiO groups in the ring) produces the monomers $R_2Si(ONa)_2$. Acids, for instance HCl and HF, also decompose the siloxane ring; thus HF converts $[(C_2H_5)_2SiO]_3$ into $(C_2H_5)_2SiF_2$.[260] Lithium aluminium hydride reduces organocyclosiloxanes to diorganosilanes[261]:

$$2\,[R_2SiO]_n + n\,LiAlH_4 \longrightarrow 2n\,R_2SiH_2 + n\,LiAlO_2,$$

where R = CH_3.

Organomagnesium compounds produce triorganosilanols after hydrolysis of the intermediates[262,263]:

$$1/n\,[R_2SiO]_n + RMgI \longrightarrow R_3SiOMgI \xrightarrow{H_2O} R_3SiOH + MgIOH.$$

Boron halides react with organocyclosiloxanes to form compounds containing the Si–O–B bond; these disproportionate to the diorganodihalogenosilane and B_2O_3.[196,197] The stereochemical influence of the organic radicals and the size of the ring have been studied: the larger the organic radical and the greater the number of SiO units in the ring, the more hindered is the reaction, because of the difficulty of approach of the reactant to the ring oxygen atoms.

Aluminium halides also break down the ring, but only half the silicon appears as a chloro-derivative; the remainder forms aluminosiloxanes[264]; $[(C_6H_5)_2SiO]_3$ produces $SiCl_4$.[265]

Organocyclosiloxanes are also converted into dialkyldichlorosilanes by the action of $SiCl_4$ at 250° under pressure; *e.g.* with sufficient $SiCl_4$ $[(CH_3)_2SiO]_4$ gives $(CH_3)_2.SiCl_2$.[266]

Under certain conditions alkylhalogenosilanes also decompose cyclosiloxanes in the presence of ferric chloride; *e.g.* alkylbromo- and alkyliodo-silanes react at the boiling point[267]:

$$[(CH_3)_2SiO]_4 + 8\,(C_2H_5)_3SiBr \xrightarrow{FeCl_3} 4\,(CH_3)_2SiBr_2 + 4\,(C_2H_5)_3SiOSi(C_2H_5)_3.$$

Alkylchlorosilanes decompose cyclosiloxanes only under pressure.

An interesting reaction is the decomposition of organocyclosiloxanes by alcohols or phenols in the presence of 1–10 mole % of sodium hydroxide, alkoxide, or silanolate[268-273]:

$$1/n\,[R_2SiO]_n + 2R'OH \overset{\text{catalyst}}{\rightleftharpoons} R_2Si(OR')_2 + H_2O,$$

where n = 3, 4, or 5, and R = alkyl or aryl. The water formed must be removed by azeotropic distillation, or, preferably, by using a dehydrating agent such as $Si(OC_2H_5)_4$.

A special case of this reaction is the decomposition of cyclosiloxanes by alkoxysilanes[269,270,271] in the presence of KOH:

$$2\,[R_2SiO]_n + n\,Si(OC_2H_5)_4 \xrightarrow{KOH} 2n\,R_2Si(OC_2H_5)_2 + n\,SiO_2 \quad (n \geqslant 3),$$

$$1/n\,[R_2SiO]_n + 2R_3''SiOR' \xrightarrow{KOH} R_2Si(OR')_2 + R_3''SiOSiR_3''.$$

The ease of catalytic decomposition of organocyclosiloxanes by alkoxysilanes decreases in the series[272]:

$$[R_2SiO]_3 > [R_2SiO]_4 > [R_2SiO]_{n+3} > R_3Si[OSiR_2]_nR \quad (n \geqslant 2).$$

A similar reaction is the disproportionation of alkoxycyclosiloxanes in the presence of KOH:[269,270,272]

$$2\,[(RO)_2SiO]_n \xrightarrow{KOH} n\,Si(OR)_4 + n\,SiO_2.$$

Organocyclosiloxanes react with butyl titanate[274] to form dialkoxysilanes and a polymer containing the Si–O–Ti linkage:

$$[R_2SiO]_4 + Ti(OC_4H_9)_4 \xrightarrow{180°} R_2Si(OC_2H_5)_2 + C_4H_9OSiR_2OSiOSiR_2OC_4H_9 + \text{polymer}.$$

Ring opening with the formation of oligomers. Particular interest attaches to the cleavage of only one siloxane bond of cyclosiloxanes, which produces linear oligomers; thus the action of sodium or potassium hydroxide on organocyclosiloxanes converts them into oligomers containing the same number of silicon atoms[275]:

$$[(C_6H_5)_2SiO]_{3,4} \xrightarrow{+NaOH,3\%} NaO[(C_6H_5)_2SiO]_{3,4}Na \xrightarrow{CH_3COOH} HO[(C_6H_5)_2SiO]_{3,4}H.$$

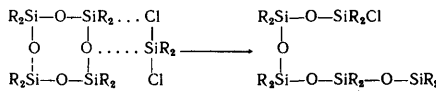
Certain organometallic compounds react similarly[276]:

$$[R_2SiO]_4 + AlR'_3 \longrightarrow R'[R_2SiO]_4AlR'_2.$$

At a high temperature and under pressure diorganodihalogenosilanes also give oligomers[277]:

$$[R_2SiO]_n + R_2SiCl_2 \xrightarrow{380^\circ-400^\circ} Cl[R_2SiO]_nSiR_2Cl \quad (n = 3-6).$$

Ring opening with the formation of telomers. An interesting case of siloxane ring opening with increase of the siloxane chain length is telomerisation; thus at a high temperature (250°–300°) and under pressure organocyclosiloxanes react with dialkyldichlorosilanes to give a series of $\alpha\omega$-dichlorosiloxanes containing $an + 1$ silicon atoms, where n is the number of silicon atoms in the initial ring, and $a = 1, 2, 3 \ldots$. The reaction can be considered to proceed as follows. The first stage is the opening of the ring with the formation of an $\alpha\omega$-dichlorosiloxane containing $n + 1$ silicon atoms[278]:



Under the reaction conditions the $\alpha\omega$-dichlorosiloxane reacts with a second cyclosiloxane molecule, and the chain increases in length by n SiO units. This method has been used to obtain $\alpha\omega$-dichlorosiloxanes $Cl[R_2SiO]_nSiR_2Cl$ with $n = 3$, 6, and 9, and R = CH_3 and C_2H_5 by ring opening of $[R_2SiO]_3$,[279] and $Cl[R_2SiO]_nSiR_2Cl$ with $n = 4$, 8, 12 ... and R = CH_3, C_2H_5, etc. by ring opening of $[R_2SiO]_4$.[278,280] Ring opening of cyclosiloxanes with trialkylchlorosilanes yields oligomers containing the R_3Si group at one end of the chain[281].

A similar telomerisation reaction is that between titanium tetrachloride and organocyclosiloxanes[282], to produce compounds $Cl[R_2SiO]_nTiCl_3$, where $n = 4$, 8, etc.

According to patent data, dimethylsiloxane-$\alpha\omega$-diols $HO[(CH_3)_2SiO]_nH$ (where n has average values of 5.5, 10.4, and 18.1) are produced by the action of water under pressure on hexamethylcyclotrisiloxane[283].

Rearrangement reactions. Mixtures of organocyclosiloxanes with organodisiloxanes react in the presence of alkali metal hydroxides, acids, silanolates, or other compounds (quaternary ammonium and phosphonium bases, etc.) as catalysts, with rearrangement of the siloxane bonds and formation of linear organosiloxanes with terminal R_3SiO groups[49,284-291]:

$$n[R_2SiO]_4 + R_3SiOSiR_3 \xrightarrow{catalyst} R_3SiO[SiR_2O]_{4n}SiR_3.$$

The reaction of an organocyclosiloxane with an organodisiloxane produces linear polymers $R_3SiO[R_2SiO]_{an}SiR_3$, where n is the number of SiO groups in the initial ring, and a is 1, 2, or 3.[285] This reaction is widely used for the production of liquid organosiloxanes. Many examples of this catalytic rearrangement have been described, *e.g.* the reaction of $[(CH_3)_2SiO]_4$ with $(CH_3)_3SiOSi(CH_3)_3$,[49,284-291] $[(C_6H_5)_2(CH_2=CH)Si]_2O$,[292] $[(C_6H_5)(CH_3)_2Si]_2O$,[293] and $[(CH_3)_2SiO]_2SO_4$,[294] the reaction of $[(CH_3)_2SiO]_3$ with $[ClCH_2(CH_3)_2Si]_2O$,[295,296] of $[(CH_3)_2SiO]_4$ with $[(C_2H_5)_3Si]_2O$,[297] and others[138,298].

Kinetic studies have shown[286] that the ability of organosiloxanes to rearrange in the presence of acid catalysts decreases in the series:

$$[R_2SiO]_3 > R_3SiOSiR_3 > R_3Si[OSiR_2]OSiR_3 > R_3Si[OSiR_2]_2OSiR_3 > [R_2SiO]_4.$$

With alkaline catalysts the order changes:

$$[R_2SiO]_3 > [R_2SiO]_4 > R_3Si[OSiR_2]_2OSiR_3 > R_3Si[OSiR_2]OSiR_3 > R_3SiOSiR_3.$$

The rearrangement reaction is of particular interest for the production of linear siloxane oligomers containing substituted hydrocarbon end-groups: organocyclosiloxanes and a symmetrical disiloxane are used:

$$a[R_2SiO]_n + ZR_2SiOSiR_2Z \xrightarrow{catalyst} \Phi R_2Si[OSiR_2]_{an}OSiR_2Z,$$

where Z is a substituted hydrocarbon group, $a = 1$, 2, 3 ..., and n is the number of SiO groups in the initial ring. This method has given siloxane oligomers having the following terminal groups:

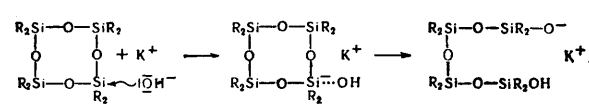
$C_2H_5OCOCH_2CH_2(CH_3)_2SiO$,[299,300]
$HOOC(CH_2)_4OCOCH_2(CH_3)_2SiO$,[301]
$2\text{-}C_5H_4NCH_2CH_2(CH_3)_2SiO$,[302]
$2\text{-}C_5H_5NCH_2CH_2(CH_3)_2SiO$,[303]
$Cl_2C_6H_3OCOCH_2(CH_3)_2SiO$,[304]
$Cl_5C_6OCH_2(CH_3)_2SiO$,[305]
$Cl_5C_6SCH_2(CH_3)_2SiO$,[306]
$Cl_2C_6H_3OCH_2OCOCH_2(CH_3)_2SiO$,[307]
$HOC_6H_4OCOCH_2(CH_3)_2SiO$,[308]
$CH_3OCO(CH_2)_3(CH_3)_2SiO$,[309]
$CH_3OCO(CH_2)_4(CH_3)_2SiO$,[309,310]

and others[311-315].

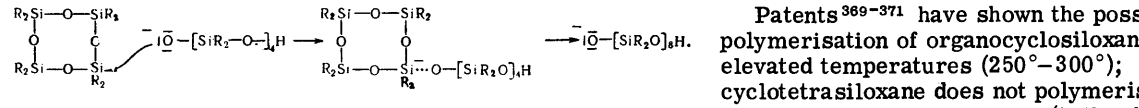
Ring opening with the formation of polymers. Attention is directed to the following features of some of the reactions described above: (*a*) agents such as alkalis and acids can open the siloxane ring; and (*b*) the initial products of ring opening can themselves open further siloxane rings, with growth of the chain. The mechanism of polymerisation of organocyclosiloxanes under the catalytic action of alkalis, acids, or other agents can thus be understood. The mechanism is general for a number of types of reaction, but the nature of the final product depends on the amount of ring-opening agent used. Catalytic amounts cause polymerisation by continuous chain growth as the result of reaction between the active end-groups and cyclic molecules before equilibrium is reached.

Organocyclosiloxanes can be polymerised by nucleophilic reagents (alkalis, alkoxides, etc.) or by electrophilic reagents (acids, boron halides, aluminium halides, etc.).

The mechanism of polymerisation by alkaline catalysts can be represented as follows. In the first step a hydroxy-group coordinates with a silicon atom by virtue of its free 3*d* orbital, and this produces a redistribution of electron density and opening of the ring:



The anionic end of the linear organosiloxane chain then attaches itself to a silicon atom of another cyclic molecule, and this produces redistribution of electron density and ring opening as before, with growth of the chain[316-321]:

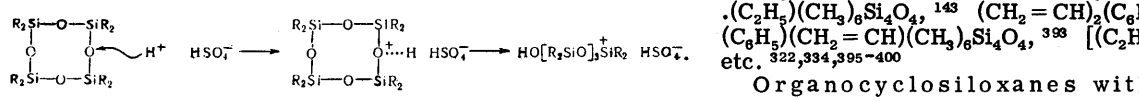


The process continues in this way until equilibrium is reached. The equilibrium mixture obtained in the polymerisation of $[(CH_3)_2SiO]_4$ by the action of potassium hydroxide contains ~ 94% of macromolecular polymer and 6% of unreacted cyclosiloxane[317]. This reaction is the basis of the production of dimethylsilicone rubbers, and many examples of the reaction have been investigated[361].

Kinetic studies have shown[316] that the catalytic activity of aqueous alkali metal hydroxides falls in the series CsOH > KOH > NaOH > LiOH, and of alcoholic hydroxides in the series RbOH > CsOH > $(CH_3)_4NOCH_3$ > KOH. In addition to alkali metal hydroxides[141,316-335], sodium or potassium silanolates[143,323,325,330,336-339], quaternary ammonium or phosphonium bases[330,337,340-344], potassamide[345], or alkali metal alcoholates[346] can be used as catalysts.

The ability of organocyclosiloxanes to undergo polymerisation depends on the number of siloxane groups in the ring and on the organic radicals present. Six-membered rings are the most easily polymerised; the tendency towards polymerisation decreases with increase of the number of SiO groups in the ring[75,347] and with increase in the size of the organic radical.

Electrophilic reagents react differently from nucleophilic reagents, *e.g.*[145]:



There is thus stepwise polymerisation. It has been considered[49,348,349] that a later step is the heterofunctional condensation between ≡Si—OH and ≡Si—OSO_3H groups under the action of protons. It is easy to see that polycondensation can hardly produce polymers of molecular weight as high as 10^6 in short reaction times. The reactivity of the rings depends on the number of SiO groups present: six-membered rings polymerise more readily than eight-membered rings. Increase in the size of the organic radical and the presence of electronegative groups also decrease the ability of the compound to polymerise[141,145,335].

The polymerisation of $[(CH_3)_2SiO]_4$ under the action of H_2SO_4 is a second-order reaction with respect to the cyclosiloxane[348]; the velocity constant is proportional to the acid concentration, and the energy of activation is 12.7 kcal mole^{-1}.

Various acids have been used for the polymerisation: sulphuric[49,326,327,334,348,350,351], nitric[348], hydrochloric[348], phosphoric[348,351], pyrophosphoric[348,352], and redox systems[353-357]. Acid-activated clays also show catalytic activity[358-360]. Organic acids, even those as strong as oxalic, trichloroacetic, and perfluorobutyric, do not polymerise $[(CH_3)_2SiO]_4$.[348] Since the first step in the opening of the cyclosiloxane ring is the coordination of the acceptor (a proton in the case of protic acids) at the siloxane oxygen, other electron acceptors (Lewis acids) can be used as catalysts: $SnCl_4$,[362] $FeCl_3$,[351,363] $AlCl_3 + Fe_2O_3$,[364] BF_3,[365] $ZnCl_2$,[365] and $Al_2(SO_4)_3 \cdot 2H_2O$.[351,366-368]

Patents[369-371] have shown the possibility of thermal polymerisation of organocyclosiloxanes under pressure at elevated temperatures (250°–300°); however, octamethylcyclotetrasiloxane does not polymerise at a pressure of 6000 atm in quartz ampoules (in the absence of catalysts)[348]. The simultaneous use of pressure and alkaline or acid catalysts decreases the time required for polymerisation[372,373].

Other methods of polymerisation are the elimination of organic radicals from the silicon atoms, *e.g.* the polymerisation of $[(C_2H_5)(C_6H_5)SiO]_3$ under the action of acids with elimination of C_6H_6 and formation of a polycyclic linear monomer[374-376], or the thermal oxidation of the organic radicals, *e.g.* the polymerisation of $[(C_2H_5)(C_6H_5)SiO]_3$[377] or $[(CH_3)_2SiO]_3$[82] by treatment with a stream of oxygen at elevated temperatures.

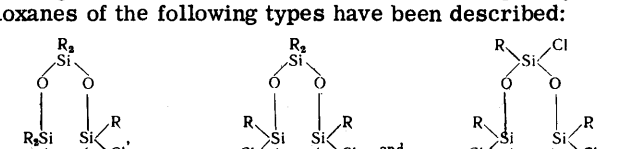
Irradiation also causes polymerisation of organocyclosiloxanes, apparently with retention of the ring and formation of $-CH_2CH_2-$ or $-CH_2-$ bridges between the silicon atoms of different rings[378-383].

Attention is directed to the very much more rapid polymerisation of $[(CH_3)_2SiO]_3$ near its melting point than at higher or lower temperatures[384-386].

Copolymerisation of rings in the presence of electrophilic or nucleophilic catalysts is used to improve the properties of siloxane polymers by the introduction of different radicals. $[(CH_3)_2SiO]_4$ has been copolymerised with the cyclosiloxanes $[H_2SiO]_3$,[48] $[(C_6H_5)_2SiO]_4$,[330,387-389] $[CH_3(CH_2=CH)SiO]_{4.5}$,[130,132,330,390] $[RR'SiO]_n$ (where $n \geq 3$ and R and R′ = CH_3, C_2H_5, or C_6H_5)[341], $[(C_2H_5)_2SiO]_3$,[391] $[(C_2H_5)_2SiO]_4$,[392] $(CH_2=CH)_2(C_2H_5)_4Si_3O_3$,[143] $(CH_2=CH)\cdot(C_2H_5)(CH_3)_6Si_4O_4$,[143] $(CH_2=CH)_2(C_6H_5)_2(CH_3)_4Si_4O_4$,[147] $(C_6H_5)(CH_2=CH)(CH_3)_6Si_4O_4$,[393] $[(C_2H_5)(CH_2=CH)SiO]_3$,[394] etc.[322,334,395-400]

Organocyclosiloxanes with functional groups on the silicon atoms. The preceding section has described the preparation of compounds in which all the silicon valencies (other than those forming the ring) are occupied by alkyl or aryl radicals. There have recently been a number of reports on the preparation and properties of organocyclosiloxanes containing functional groups (Cl, OH, OR, NHR, etc.) on silicon atoms, in addition to the organic radicals. We shall now consider the preparation of such organocyclosiloxane derivatives.

Halogen-substituted tri- and tetra-meric organocyclosiloxanes of the following types have been described:



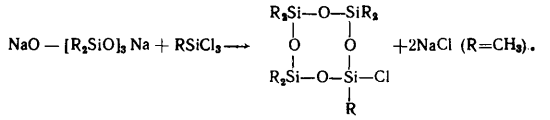
The tetramers have analogous structures.

An interesting method for the preparation of organochlorocyclosiloxanes is the chlorination of hydrogen-containing organocyclosiloxanes[75,87,95,139]:

$$[RHSiO]_n + n\,Cl_2 \longrightarrow [RClSiO]_n + n\,HCl \quad (R=CH_3, C_2H_5;\ n=3-7).$$

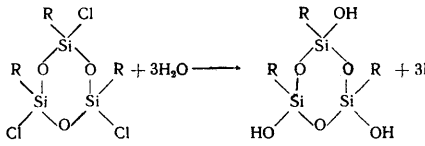
Another method is based on the exchange reaction between sodium silanolates and halogenosilanes; in particular,

this method has been used to prepare monochlorocyclotetrasiloxanes[401,402]:



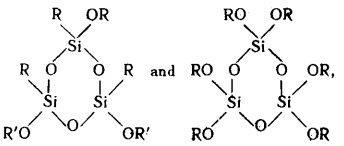
Since the chlorine atom attached to the silicon is readily replaced by other groups, these compounds are of evident interest for the production of other derivatives of organocyclosiloxanes and linear and cyclolinear oligomers and polymers.

Organohydroxycyclosiloxanes are obtained by hydrolysis of the chlorine atoms[75,95]:

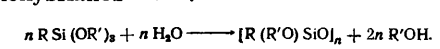


Such compounds are weak alkyl(aryl)cyclosilicic acids, as is shown by the recent isolation of the sodium triphenylcyclosilanolate $(C_6H_5)_3Si_3O_3(ONa)_3.10H_2O$ (prepared by the action of 6 *N* NaOH on the phenylsiloxane polymer[403]).

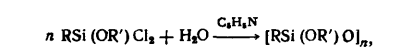
Partially and fully substituted alkoxycyclosiloxanes have been described:



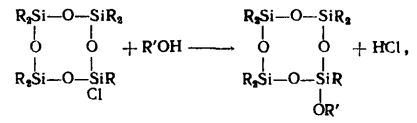
and also the corresponding cyclotetrasiloxanes. Alkylalkoxycyclosiloxanes are obtained by partial hydrolysis of alkyltrialkoxysilanes[404,405]:



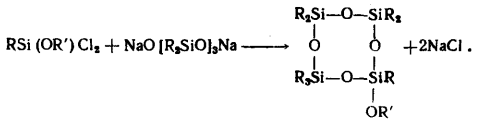
Thus partial hydrolysis of methyltrimethoxysilane has produced the methylmethoxycyclosiloxanes $[CH_3(CH_3O)SiO]_n$, where n = 3, 5, and 6. Hydrolysis of an alkylalkoxydichlorosilane in pyridine gives alkoxy-substituted alkylcyclo-tri- and -tetra-siloxanes[406-408]:



where R = CH_3, C_2H_5; R′ = CH_3, C_2H_5, iso-C_3H_7; n = 3 or 4. Compounds of similar type can also be obtained by reacting chlorocyclosiloxanes with alcohols or phenols, *e.g.*[401]:

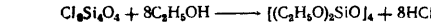


where R = CH_3 and R′ = C_2H_5 or C_4H_9; and by the exchange reaction between alkylalkoxydichlorosilanes and the disodium salts of organosiloxanes[402,409]:

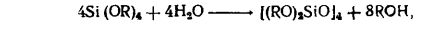


This last method has been used to prepare alkoxyalkylcyclotetrasiloxanes with R = CH_3 and R′ = C_2H_5 or n-C_4H_9; these are transparent liquids.

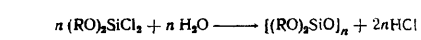
Dialkoxycyclosiloxanes are obtained either by replacing the chlorine atoms in inorganic chlorocyclosiloxanes by alkoxy-groups[410]:



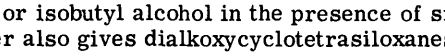
or by partial hydrolysis of tetraalkoxysilanes[411-414]:



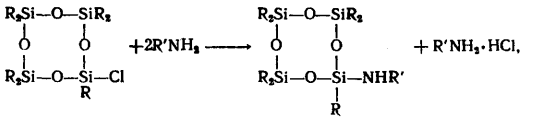
or by hydrolysis of dialkoxydichlorosilanes[415-418] or $[(RO)_3Si]_2O$:[419]



The reaction between silicon tetrachloride and isopropyl or isobutyl alcohol in the presence of small amounts of water also gives dialkoxycyclotetrasiloxanes[420]:

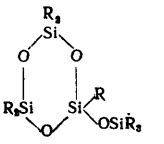


Organoaminocyclosiloxanes have been obtained by replacing the chlorine in organochlorocyclosiloxanes by reaction with ammonia or amines[401]:



where R = CH_3 and R′ = H or C_6H_5.

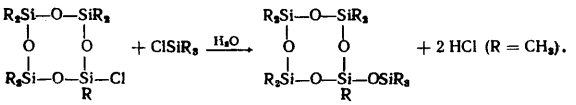
Trialkylsiloxy-substituted organocyclosiloxanes are of interest from the point of view of isomerism of the inorganic rings: thus alkyl(trialkylsiloxy)cyclotrisiloxanes (VII) and dialkylcyclotetrasiloxanes (X):



(X)

are isomers, having the same composition but different ring sizes.

Compounds of type (X) were first prepared by the simultaneous hydrolysis of heptamethylchlorocyclotetrasiloxane and trimethylchlorosilane[75]:



The resulting trimethylsiloxyheptamethylcyclotetrasiloxane is an isomer of the previously known decamethylcyclopentasiloxane. Triethylsiloxy-substituted cyclotri- and cyclotetra-siloxanes have also been described[421].

Organocyclosiloxanes containing functional groups in the organic radical have been described; these are of theoretical and practical interest because of the possibility of their polymerisation. The substituents may be chloroalkyl or chloroaryl RCl, cyano CN, ester COOR, hydroxyl OH, amino NH_2, thiol SH, etc.

The chemistry of silicon derivatives, including organocyclosiloxanes, containing substituted hydrocarbon groups

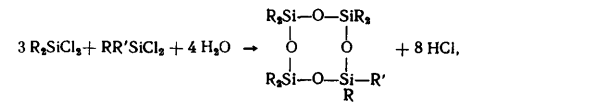
has been reviewed by George *et al.*[422] and discussed in the book by Petrov and coauthors[423].

The methods for the production of silicon derivatives containing substituted hydrocarbon groups fall into two classes: (1) methods involving formation of a siloxane ring, and (2) methods involving conversion of organic radicals present as substituents in cyclosiloxanes.

The normal methods of hydrolysis and cohydrolysis used for unsubstituted organocyclosiloxanes can be employed for organocyclosiloxanes containing substituted organic radicals, provided that the substituents themselves are not hydrolysed. Thus chloroalkyl- and chloroaryl--cyclosiloxanes are obtained by hydrolysis of the corresponding di-(chloroalkyl)- and di-(chloroaryl)dichlorosilanes, *e.g.*[106]:

$$n(ClC_6H_4)_2SiCl_2 + H_2O \rightarrow [(ClC_6H_4)_2SiO]_n + 2HCl \quad (n = 3, 4).$$

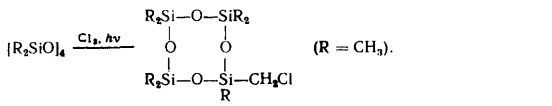
The cyanoalkyl derivatives may also be hydrolysed[424-426]. The simultaneous hydrolysis of dimethyldichlorosilane with α- or β-cyanoethyl(methyl)dichlorosilane produces heptamethyl-α- or heptamethyl-β-cyanoethylcyclotetrasiloxane[427]:



where R = CH_3 and R′ = $CH(CN)CH_3$ or CH_2CH_2CN.

Since functional groups are very often reactive, the production of cyclosiloxanes with hydrocarbon radicals containing such groups is difficult by ordinary methods, and they are generally prepared by various substitution reactions occurring in the organic radical attached to a ring silicon atom.

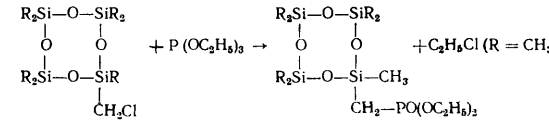
Chemical reactions in the organic radical. An interesting reaction is the chlorination with elemental chlorine of methyl groups attached to silicon in organocyclosiloxanes, to produce the chloromethyl derivatives; thus photochlorination of octamethylcyclotetrasiloxane gives heptamethyl(chloromethyl)cyclotetrasiloxane in 70% yield[428-430]:



The pentamer is chlorinated analogously[431].

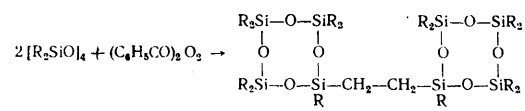
The importance of the chlorinated methylcyclosiloxanes is that they can be polymerised to chlorinated oils, rubbers, and solid polymers having high low-temperature resistivity, good thermal stability, and good adhesion and low swelling capacity in solvents[430]. A feature of the chloromethyl groups is their ability to undergo substitution reactions without attack on the siloxane ring. They react with metallic magnesium to form Grignard reagents which can then be converted into carboxymethylcyclotetrasiloxanes[432,433], hydroxyalkylcyclotetrasiloxanes[434,435], or cyanoalkylcyclotetrasiloxanes[436]. The chloromethyl groups of cyclosiloxanes react fairly readily with potassium iodide[437,438], salts of organic acids[301,439,400], compounds containing *N*-alkyl or *N*-aryl groups[441-443], and metal mercaptides[444,445]. An interesting fact is that aminoalkyl--substituted organocyclosiloxanes polymerise readily at room temperature[441].

Chloromethylcyclosiloxanes undergo the Arbuzov rearrangement[446]:



The reaction between sulphuryl chloride and $[(CH_3)_2SiO]_4$ produces $(CH_3)_7(CH_2SO_3Cl)Si_4O_4$.[447,448]

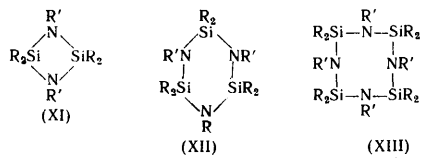
With benzoyl peroxide octamethylcyclotetrasiloxane yields bis-(heptamethylcyclotetrasiloxanyl)ethane[337,449]:



The same reaction occurs on irradiation. These reactions are models for the vulcanisation of polydimethylsiloxane rubber. The two-ring compounds polymerise with ring opening; they are used as partial cross-linking agents in the polymerisation of cyclosiloxanes.

2. CYCLOSILAZANES

Compounds containing Si–N bonds in a ring are known as cyclosilazanes. Rings containing two, three, and four SiN groups are known:



In known compounds R is alkyl, aryl, alkoxy, or amino, and R′ is hydrogen, a hydrocarbon group, or an alkylsilyl radical. The first inorganic compounds containing the Si–N bond were obtained by ammonolysis of chlorosilanes. Monocyclic compounds are produced from bifunctional monomers; thus ammonolysis of dichlorosilane gives solid products or oils, depending on the reaction conditions, of general formula $[H_2SiNH]_n$, where $n = 7-8$.[451,452] The cryoscopic determination of the degree of polymerisation in this case gave approximate results only.

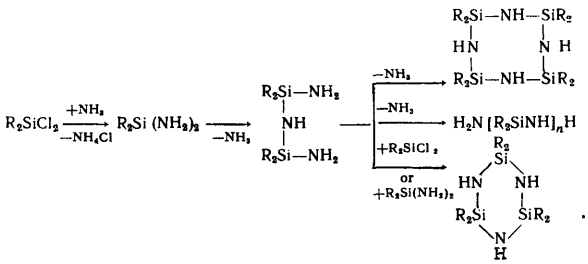
The reaction between gaseous silicon tetrachloride and ammonia at a high temperature (825°)[453] produces the low--molecular-weight linear compound $Cl_3SiNHSiCl_3$ and the cyclic tetramer $Si_8N_4Cl_{20}$ of structure (XIII) (R = Cl, R′ = $= SiCl_3$). The reaction of silicon tetrachloride with nitrogen in a glow discharge produces a range of products[454,455], including the cyclic trimer (XII) (R = Cl, R′ = $SiCl_3$) and tetramer (XIII) (R = Cl, R′ = $SiCl_3$).

The first organocyclosilazanes were obtained in 1948 by ammonolysis of dimethyldichlorosilane[91,457,458]:

$$(CH_3)_2SiCl_2 + 3NH_3 \longrightarrow 1/n\,[(CH_3)_2SiNH]_n + 2NH_4Cl \quad (n = 3, 4).$$

The liquid trimer $[(CH_3)_2SiNH]_3$ and crystalline tetramer $[(CH_3)_2SiNH]_4$ are readily separated from the reaction mixture. Ammonolysis has since been used to prepare the organocyclosilazanes $[(C_2H_5)_2SiNH]_n$ (n = 3 or 4)[91], $[CH_3(C_2H_5)SiNH]_3$,[459] $[CH_3(C_6H_5)SiNH]_3$,[459] $[(n\text{-}C_4H_9)_2$. $.SiNH]_3$,[461] $[CH_3SiHNH]_4$,[462] and $[C_2H_5SiHNH]_n$ (n = 3 or 4)[462].

The mechanism of ammonolysis of organodichlorosilanes is not fully clear. The isolation of certain organosilane diamines $R_2Si(NH_2)_2$ when the organic radical is a cause of steric hindrance to further condensation, *e.g.* $(t\text{-}C_4H_9)_2Si(NH_2)_2$, and the production of linear organodiaminodisilazanes $H_2N-SiR_2-NH-SiR_2-NH_2$,[460,463] would suggest that the formation of organocyclosilazanes proceeds simultaneously with the formation of linear organosilazanes as follows:



The conditions which determine the mode of the reaction have been little studied; the particular organic radical, the solvent used, the reaction temperature, the concentration of reactants, etc., affect the mode of the reaction.

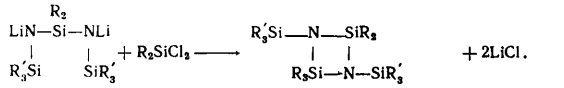
Organocyclosilazanes with functional groups on the silicon can be obtained by analogous reactions; thus ammonolysis of the corresponding dialkoxy- or diaryloxy-dichlorosilanes has given $[(CH_3O)_2SiNH]_n$,[464] $[(C_2H_5O)_2SiNH]_n$,[464] $[(iso\text{-}C_3H_7O)_2SiNH]_{3,4}$,[465,466] $[(t\text{-}C_4H_9O)_2SiNH]_3$,[467] and $[(C_6H_5O)_2SiNH_3]$.[465] As with alkylhalogenosilanes, the ammonolysis of higher alkoxy- and aryloxy-halogenosilanes to produce cyclic products is difficult, apparently because of steric hindrance. The main products are dialkoxysilanediamines $(RO)_2Si(NH_2)_2$ and tetraalkoxydisilazanediamines $(RO)_2(NH_2)SiNHSi(NH_2)(OR)_2$, which are converted into cyclosilazanes only on prolonged heating[465].

Dialkyl- and diaryl-dichlorosilanes react with primary amines, usually forming dialkyldi-(alkylamino)silanes $R_2Si(NHR')_2$,[450] but cyclosilazanes can also be obtained; thus the reaction between dimethyldichlorosilane and aniline produces the *N*-phenylcyclotrisilazane $[(CH_3)_2SiNC_6H_5]_3$ as well as $(CH_3)_2Si(NHC_6H_5)_2$.[456]

Alkylamino-substituted organocyclosilazanes obtained by the thermal decomposition of alkyl(trialkylamino)silanes $RSi(NHR')_3$ have recently been described[468]:

$$3RSi(NHR')_3 \xrightarrow{-R'NH_2} [RSi(NHR')NR']_3.$$

The methods so far discussed have given only cyclic trimers and tetramers. The dimers (XI) are obtained by ammonolysis of bis-(trialkylsiloxy)dichlorosilanes $(R_3SiO)_2.SiCl_2$,[469] by the thermal decomposition of *N*-trialkylsilylcyclosilazanes $[R_2SiNSiR'_3]_n$,[470] or by the exchange reaction[470]:



All organic derivatives of cyclosilazanes are colourless liquids or crystalline solids readily soluble in organic solvents. The physical properties and structure of various organocyclosilazanes have been studied, by infrared spectroscopy[471-473], Raman spectroscopy[472], and nuclear magnetic resonance spectroscopy[474]. Spectroscopic data have shown[472,475] that the unshared pair of electrons from the nitrogen are partially delocalised through the 3*d* silicon orbitals, so that the Si–NH–Si bond has partial double-bond character (the bond order is 1.18) and cyclosilazanes have partial aromatic character[5]. The Si–NH–Si bonds in cyclosilazanes are characterised by absorption bands at 928–932 cm^{-1} and 1169 cm^{-1} in the trimer and 939 cm^{-1} and 1183 cm^{-1} in the tetramer[473].

The following bond lengths and valence angles have been determined in dimethylcyclosilazanes by electron diffraction[251,252]: Si–N 1.78 ± 0.03 Å, ∠ NSiN = 111° ± 5°, ∠ SiNSi = 117° ± 4° (in the trimer) and 123° ± 4° (in the tetramer). Further study is necessary to establish the true structure of organocyclosilazanes, since spectroscopic data indicate that the six-membered ring Si_3N_3 is planar (of symmetry D_{3h})[472], and electron diffraction indicates it to be non-planar[251]. The eight-membered ring Si_4N_4 is non-planar.

Organocyclosilazanes withstand heating to high temperatures. They are less stable towards hydrolysis, and are decomposed by water to ammonia and the diorganosilanediol or organosiloxane. The pH of the medium has a large effect on the hydrolysis: in acid medium organocyclosilazanes are readily hydrolysed, producing the ammonium salt, but they are completely stable to hydrolysis in alkaline medium[476]. Hydrogen chloride decomposes organocyclosilazanes to form the corresponding diorganodichlorosilane and ammonium chloride[471]:

$$[R_2SiNH]_3 + 9\,HCl \rightarrow 3\,R_2SiCl_2 + 3\,NH_4Cl \quad (R = C_6H_5).$$

Interesting data have recently appeared on the transamination of organocyclosilazanes by amines: primary amines in excess open silazane rings, forming diorganodi-(alkylamino)silanes[460]:

$$[R_2SiNH]_3 + 6\,R'NH_2 = 3\,R_2Si(NHR')_2 + 3NH_3.$$

The use of an equivalent quantity of aniline, however, has given the *N*-substituted cyclosilazane[477]:

$$[R_2SiNH]_3 + 3\,R'NH_2 \rightarrow [R_2SiNR']_3 + 3\,NH_3$$

($R = CH_3$, $R' = C_6H_5$). This reaction always produces *N*-substituted cyclotrisilazanes, whether the starting compound is a cyclotrisilazane or a cyclotetrasilazane[477].

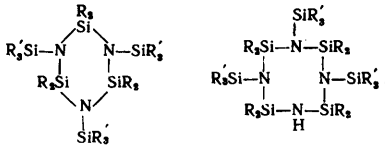
Another interesting reaction is the replacement of the hydrogen of the NH groups in organocyclosilazanes by lithium; the reaction of the cyclosilazanes with butyllithium in n-hexane produces the *N*-lithioorganocyclosilazanes as crystalline solids stable in an atmosphere of nitrogen[478]:

$$[R_2SiNH]_3 + 3\,LiC_4H_9 \rightarrow [R_2SiNLi]_3 + 3\,C_4H_{10}.$$

The hydrogen atoms of 1, 2, or 3 NH groups of the cyclosilazanes can be replaced by lithium by reaction with butyllithium. The *N*-lithio-derivatives of cyclosilazanes react readily with organochlorosilanes to form *N*-silylcyclosilazanes[478]:

$$[R_2SiNLi]_3 + 3\,R'_3SiCl \rightarrow [R_2SiNSiR'_3]_3 + 3\,LiCl.$$

Trimers and a tetramer of analogous structure have been obtained:



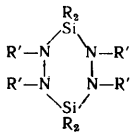
When hexamethyldisilazane was heated with hexamethylcyclotrisilazane at 300°–325° and 350°–410°, the linear

octamethyltrisilazane was isolated from the reaction mixture, indicating rupture of the ring[91].

Cyclosilazanes are starting materials for the production of polymers. The polymerisation of hexaphenylcyclotrisilazane has been described[479], and silazane–siloxane copolymers have been prepared[480]. Polymers with the Si–N bond are considered to have great potential as heat-resistant materials[481]. The use of cyclosilazanes as water-repellents[457,482-484], corrosion inhibitors[466,480,485], modifiers for melamine–formaldehyde resins[479], and hardening agents for epoxy-resins[486], has also been described.

3. DISILATETRAZINES

An interesting class of cyclic compounds are the organocyclodisilatetrazines:



(XIV)

These are obtained by reacting diorganodichlorosilanes with hydrazine[487,488]:

$$2\,R_2SiCl_2 + 6\,H_2N{-}NH_2 \rightarrow [R_2Si{-}NH{-}NH]_2 + 4\,N_2H_5Cl.$$

The methyl compound produces only macromolecular linear polyhydrazinosilanes $[(CH_3)_2SiNHNH]_n$ which are oily or vitreous[488,489], but the phenyl compound gives the cyclic compound (XIV) (R = C_6H_5, R′ = H). Phenylhydrazine also gives cyclic products[488]:

$$2\,R_2SiCl_2 + 6\,C_6H_5NH_2NH_2 \rightarrow [R_2SiN(C_6H_5)NH]_2 + 4\,C_6H_5NHN_2{\cdot}HCl$$

(R = CH_3 or C_6H_5).

Cyclic disilatetrazines can be obtained from diorganodichlorosilanes and the lithium derivative of phenylhydrazine[488]:

$$2\,R_2SiCl_2 + 2\,C_6H_5NLiNLiH \rightarrow [R_2SiN(C_6H_5)NH]_2 + 4\,LiCl\ (R = C_6H_5).$$

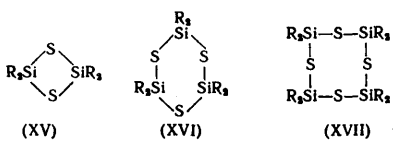
Hexaphenylcyclodisilatetrazine can also be obtained by using the dilithium derivative of azobenzene[490]:

$$(C_6H_5)_2SiCl_2 + C_6H_5NLiNLiC_6H_5 \rightarrow [(C_6H_5)_2SiNC_6H_5NC_6H_5]_2 + 4\,LiCl.$$

The chemical properties of the cyclic disilatetrazines depend on the degree of substitution at the nitrogen atoms. Tetraphenylcyclodisilatetrazine $[(C_6H_5)_2SiNHNH]_2$ is very sensitive to hydrolysis, hexaphenylcyclodisilatetrazine $[(C_6H_5)_2SiNC_6H_5NH]_2$ is not hydrolysed by water or dilute acids, and octaphenylcyclodisilatetrazine $[(C_6H_5)_2SiNC_6H_5NC_6H_5]_2$ is completely stable in air and in the presence of water.

4. CYCLOSILTHIANES

A number of inorganic and organic derivatives of the four-, six-, and eight-membered rings containing 2, 3, and 4 SiS units respectively have been described:



(XV) (XVI) (XVII)

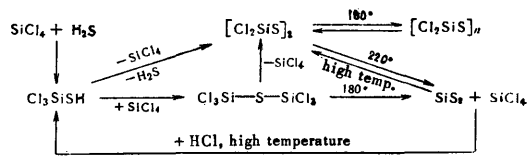
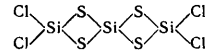


Fig. 3.

In the known inorganic compounds the silthiane rings are substituted by halogen atoms. The first representative of this type of compound, silicon thiochloride Cl_2SiS, was obtained, together with Cl_3SiSH, from silicon tetrachloride and hydrogen sulphide[494,495]. In the presence of pyridine, silicon tetrachloride reacts with hydrogen sulphide to form the cyclic dimer $[Cl_2SiS]_2$.[496] In the gaseous state $SiCl_4$ reacts with hydrogen sulphide only above 500° (optimum temperature 650°) to give Cl_3SiSH, $Cl_3SiSSiCl_3$, and $[Cl_2SiS]_4$ (XVII) (R = Cl).[497] The complex nature of this reaction was elucidated by studying it at 700°–1000°; it was shown[498] that the reaction products depend on the temperature (Fig. 3).

The compound $Si_3S_4Cl_4$ has also been isolated, and has been given structure (XVIII):



(XVIII)

On heating at 180° the crystalline dimer $[Cl_2SiS]_2$ is converted into a liquid polymer of molecular weight near that of the tetramer $[Cl_2SiS]_4$, but the tetramer could not be isolated in the pure state. Its Raman spectrum has confirmed the cyclic structure of the dimer $[Cl_2SiS]_2$, with a planar Si_2S_2 ring[499].

Organocyclosilthianes were first described in 1952.[500] The passage of hydrogen sulphide through a solution of $(C_2H_5)_2SiCl_2$ in petroleum ether in the presence of pyridine gives the cyclic dimer $[(C_2H_5)_2SiS]_2$ (XV) (R = C_2H_5). This reaction,

$$R_2SiCl_2 + H_2S + 2\,C_5H_5N \rightarrow 1/n\,[R_2SiS]_n + 2\,C_5H_5N{\cdot}HCl,$$

has since been used to prepare cyclosilthianes substituted by methyl[501-503], ethyl[500,504], n-propyl[501,504], and phenyl[505] groups.

This thiohydrolysis of dimethylchlorosilane at normal temperatures produces the cyclic trimer $[(CH_3)_2SiS]_3$,[502,503] which on heating in a stream of hydrogen sulphide[503] undergoes an interesting change in the silthiane ring, with formation of the dimer $[(CH_3)_2SiS]_2$. The conversion of the trimer to the dimer on heating has also been observed with the ethyl- and propyl-derivatives; the reverse change of dimer to trimer is also possible[504].

Tetraethyldisilthiane[501] and tetramethyldisilthiane[506] have also been obtained from the dialkyldiiodosilane and silver sulphide:

$$2\,R_2SiI_2 + 2\,Ag_2S \rightarrow [R_2SiS]_2 + 4\,AgI.$$

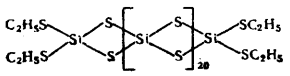
Cyclosilthianes can be obtained by the thermal decomposition of mercaptosilanes; thus heating $(C_2H_5)_2Si(SC_2H_5)_2$ at 350° gives tetraethylcyclodisilthiane[507]:

$$2\,(C_2H_5)_2Si(SC_2H_5)_2 \xrightarrow{350°} (C_2H_5)_2Si\langle S \rangle Si(C_2H_5)_2 + 2S(C_2H_5)_2.$$

and heating tetra-(ethylmercapto)silane yields another substituted cyclodisilthiane[507]:

$$2\,Si(SC_2H_5)_4 \rightarrow (C_2H_5S)_2Si\langle S\rangle Si(SC_2H_5)_2 + 2\,S(C_2H_5)_2,$$

as well as a product of composition $Si_{22}S_{42}(SC_2H_5)_4$:



which is an intermediate in the production of silicon sulphide $[SiS_2]_x$ by the decomposition of mercaptosilanes.

Organocyclosilthianes are colourless liquid or crystalline substances, which in the presence of water (or even atmospheric moisture) are readily hydrolysed to the corresponding organosilanols or organosiloxanes and hydrogen sulphide.

Various physical methods have been used to investigate the structure of the organocyclosilthianes. The dipole moments of the methyl compounds have been determined[228] as $\mu = 0.0$ D for $[(CH_3)_2SiS]_2$ and $\mu = 1.03$ D for $[(CH_3)_2SiS]_3$; consequently the four-membered Si_2S_2 ring is planar and the six-membered Si_3S_3 ring is non-planar. Electron diffraction has confirmed the cyclic structure of the dimer and trimer, and has given the following interatomic distances and bond angles: Si–S 2.18 ± 0.03 Å (dimer) and 2.15 + ± 0.03 Å (trimer), ∠ SSiS 105° (dimer) and 115° (trimer), and ∠ SiSSi 75° (dimer) and 110° (trimer)†.

The infrared spectra of the methylcyclosilthiane dimer and trimer[502] and the Raman spectrum of the dimer[499] $[(CH_3)_2SiS]_2$ have also confirmed their cyclic structure. The "boat" conformation has been suggested for the six-membered Si_3S_3 ring[502].

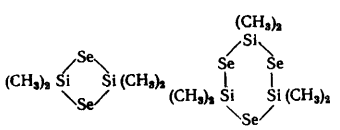
The possible utility of organosilthianes is limited, because of their low resistance to hydrolysis. However, the patent literature indicates the possibility of using them as additives for organosiloxane and hydrocarbon oils and as insecticides and fungicides[505].

5. CYCLOSILSELENANES

Only methyl derivatives of ring compounds containing silicon and selenium have been obtained[509], by the reaction of dimethyldichlorosilane with sodium selenide:

$$(CH_3)_2SiCl_2 + Na_2Se \rightarrow 1/n\,[(CH_3)_2SiSe]_n + 2\,NaCl.$$

Two products were isolated, the dimer and trimer:



The dimer is a crystalline solid, and the trimer is a liquid of unpleasant smell. Both have low stability to hydrolysis.

† These data are contained in a paper by M. Yokoi, T. Nomura, and K. Yamasaki, J. Amer. Chem. Soc., 77, 4484 (1955) (Ed. of Translation).

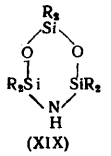
III. MIXED CYCLIC SILICON COMPOUNDS

The structure and properties of organocyclosiloxanes show them to be prototypes of inorganic silicon rings, partial replacement of silicon and oxygen atoms in these rings by other elements producing rings containing aluminium, boron, phosphorus, titanium, nitrogen, or other elements, in addition to silicon. Thus oxygen may be partially replaced by nitrogen or sulphur to obtain cyclosilazoxanes or cyclosilthioxanes respectively, and silicon may be partially replaced by boron, aluminium, phosphorus, arsenic, antimony, or titanium to form the corresponding organocyclo("elemento")siloxanes. These mixed heterocycles are transitional between organocyclosiloxanes and other inorganic rings.

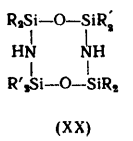
Organocyclosilazoxanes were obtained by the low-temperature ammonolysis of $\alpha\omega$-dichlorosiloxanes[75,122,510]:

$$Cl[R_2SiO]_{n-1}SiR_2Cl + 3\,NH_3 \rightarrow \left[\begin{array}{c}-R_2SiO-_{n-1}SiR_2-\\ \diagdown\!\!\diagup\ NH\ \diagdown\!\!\diagup\end{array}\right] + 2\,NH_4Cl.$$

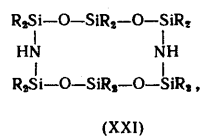
The reaction had previously been described in a patent[511], but the pure cyclic compounds had not been isolated. The organocyclosilazoxanes



(XIX)



(XX)



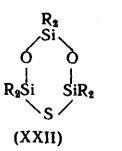
(XXI)

where R = CH_3 and R′ = C_2H_5 or CH_3, have been described[75,510]. These compounds are colourless, except for octamethylcyclotetrasiladiazadioxane; this forms prismatic or acicular crystals melting at 40°. They are all readily soluble in the usual organic solvents.

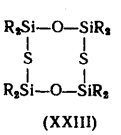
Organocyclosilthioxanes were obtained by the thiohydrolysis of $\alpha\omega$-dichlorosiloxanes in the presence of pyridine[512]:

$$Cl[R_2SiO]_{n-1}SiR_2Cl + H_2S \xrightarrow{C_5H_5N} \left[\begin{array}{c}-[R_2SiO]_{n-1}SiR_2-\\ \diagdown\!\!\diagup\ S\ \diagdown\!\!\diagup\end{array}\right] + 2\,C_5H_5N\cdot HCl.$$

The compounds



(XXII)

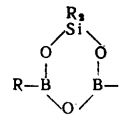


(XXIII)

where R = CH_3, have been prepared. Hexamethylcyclotrisilthiadioxane is a transparent colourless liquid boiling at 172.5°; octamethylcyclotetrasildithiadioxane is a crystalline solid melting at 38°–42°. Both dissolve well in various organic solvents.

Cyclodiborasiltrioxanes of structure (XXIV) have been prepared by heating 2–3 moles of an aryl or cycloalkyl boric acid with a diarylsilanediol in the presence of an acid catalyst[513]. It is interesting that, if the reactants are taken in proportions to give Si : B = 1 : 1, no

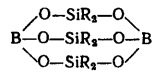
rings containing these elements in this proportion are obtained, but only the cyclodiborasiltrioxane, part of the diarylsilanediol remaining unreacted.



(XXIV)

The organocycloborasiloxanes produced are said to be of use as additives to polymers to render them incombustible and neutron-absorbing, and as scintillators, active components of fungicidal, bactericidal, and insecticidal compositions, heat-exchange media, lubricant additives, etc.[513]; these claims are probably exaggerated.

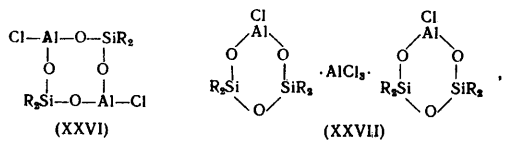
There is a report[198] of the preparation[514] of the bicyclic borasiloxane (XXV)



(XXV)

but the method of preparation and properties were not described.

Cycloaluminosiloxanes. The first reports on the preparation of cycloaluminosiloxanes appeared in the patent literature[264], where it was stated that the reaction of aluminium trichloride with organocyclotetrasiloxanes produces cyclic aluminosiloxanes of structure (XXVI):



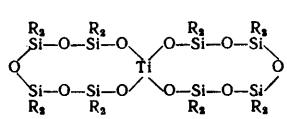
(XXVI) (XXVII)

where R = CH_3 or C_2H_5.

Others have said[515] that $AlCl_3$ reacts with cyclotetrasiloxanes to form the 1,3-dichloro(tetraalkyl)disiloxane and a complex compound of structure (XXVII).

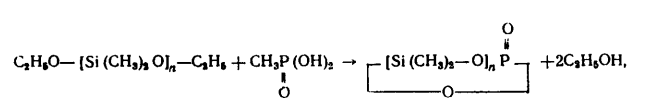
Rings made up of aluminium, silicon, and oxygen atoms, but not containing organic substituents, are found in certain natural silicates. The monocyclic anion $[AlSi_5O_{18}]^{13-}$, obtained by replacing one silicon atom in the ring of $[Si_6O_{18}]^{12-}$ by aluminium, has been found in cordierite α-$Mg_2Al_3 \cdot [AlSi_5O_{18}]$ [516] and indialite γ-$Mg_2Al_3[AlSi_5O_{18}]$. [517]

Cyclotitanosiloxanes. Although several titanosiloxane compounds have been described, there has been only one report[518] of the preparation of an organocyclotitanosiloxane: tetrabutoxytitanium reacts with diphenylsilanediol to give the compound of structure (XXVIII):

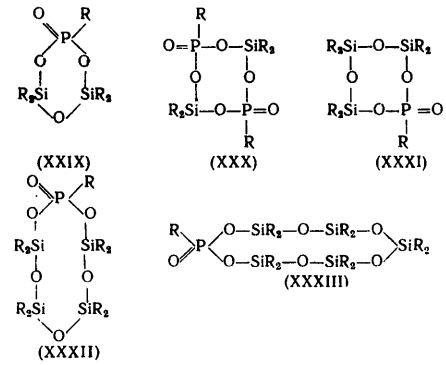


(XXVIII)

The reaction between $\alpha\omega$-diethoxydimethylsiloxanes and methylphosphonic acid has given a number of cyclophosphorosiloxanes[519]:



where $n = 1-5$. The following types of compounds in this new class of inorganic rings with organic substituents have been isolated[519]:



(XXIX) (XXX) (XXXI)

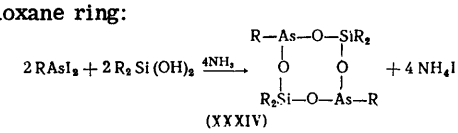
(XXXII) (XXXIII)

These compounds are very readily hydrolysed by water to form methylphosphonic acid and polydimethylsiloxanes.

Unlike dimethylcyclosiloxanes, dimethylcyclophosphorosiloxanes have been shown to polymerise very poorly in the presence of an acid or alkali as catalyst[520]; however, they copolymerise smoothly with octamethylcyclotetrasiloxane to give a dimethylsiloxane polymer containing phosphorus in the chain. Rubbers obtained from such polymers containing 0.02–0.03% of phosphorus in the polymer chain have a higher resistance to rupture and a larger relative elongation than dimethylsiloxane rubber.

The reaction between $\alpha\omega$-diethoxydimethylsiloxanes and methylphosphonic acid was also studied by Orlov and Voronkov[521], who obtained viscous or rubber-like polymers of high molecular weight. Different products were obtained because of the different reaction temperatures used.

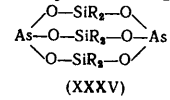
Cyclic compounds containing arsenic have been described[198,522]. Phenyldiiodoarsine and diphenylsilanediol react to produce a compound having an eight-membered arsinosiloxane ring:



(XXXIV)

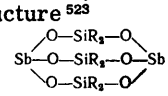
This is a crystalline product, melting at 145°.

The reaction between arsenic trichloride and diphenylsilanediol has given the bicyclic compound



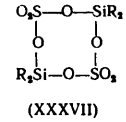
(XXXV)

The only antimony-containing compound of this type described in the literature is the product obtained from triethoxyantimony and dimethyldiacetoxysilane, which has been assigned the structure[523]



(XXXVI)

The reaction of dimethyldichlorosilane with 100% sulphuric acid yields a compound which by composition and molecular weight corresponds to the cyclic structure[524-526]



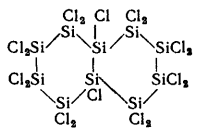
(XXXVII)

Tetramethylcyclodisulphatodisiloxane is a crystalline substance melting at 103°–120°. Above 150° it decomposes to polydimethylsiloxane and SO_3. Compounds of this class are very sensitive to hydrolysis; water destroys the cyclic structure, giving sulphuric acid and polysiloxanes.

IV. POLYCYCLIC SILICON COMPOUNDS

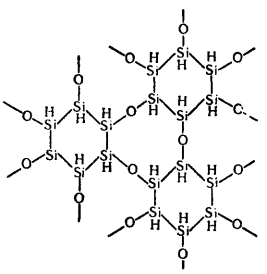
Polycyclic silicon compounds can also be divided into homocyclic and heterocyclic compounds[2-5].

Homopolycyclic compounds contain rings made up of silicon atoms only; few such compounds are known at present. An example is persilicochlorodecalin $Si_{10}Cl_{18}$, obtained by heating $Si_{10}Cl_{20}H_2$:[527]



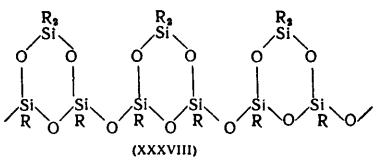
Substances of formulae $[SiCl]_x$ and $[SiH]_x$ are known, which are polycyclic compounds of high molecular weight containing condensed six-membered rings.

Many more heteropolycyclic compounds, containing rings made up of silicon atoms alternating with atoms of other elements, such as oxygen, nitrogen, and sulphur, are known, as well as polycyclic structures containing both homocyclic and heterocyclic rings, *e.g.* the siloxene $[Si_6O_3H_6]_n$ and its derivatives[528-535], which are made up of six-membered Si_6H_6 rings joined by oxygen bridges:



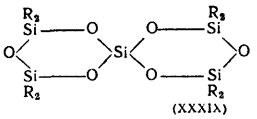
The known polycyclic silicon structures can be classified thus[3-5]:

(a) linear or cyclic chain polycyclic compounds:

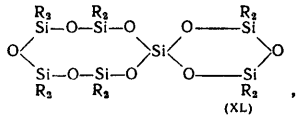


(XXXVIII)

(b) spirane compounds, in which the rings have one common atom:



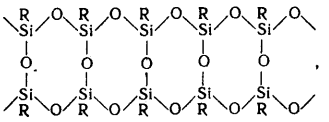
(XXXIX)



(XL)

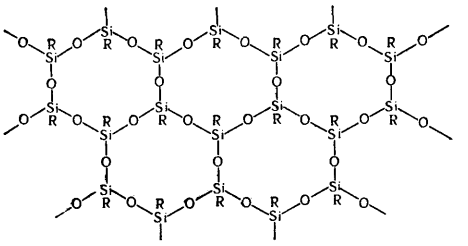
(c) condensed polycyclic compounds, in which the rings have two or more common atoms.

The rings may condense in a single direction, producing ribbon (cyclolinear) polycyclic polymers:



(XLI)

or in two directions (in a plane), producing reticular structures:



(XLII)

or in three dimensions, producing complex cross-linked three-dimensional structures.

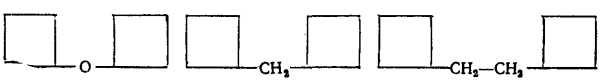
All these types of polycyclic compounds are found in natural silicates[26] and in the synthetic organic siloxane derivatives. We have not the space to discuss the polycyclic silicates here.

Polycyclic compounds of low and high molecular weight are known; most of the former are based on a silicon–oxygen skeleton. Polycyclosiloxanes give all the above types of polycyclic structure.

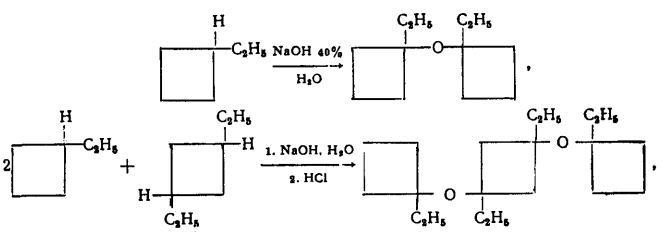
Compounds in which the rings are joined by bridges are obtained by condensation[536]:



where □ = $(CH_3)_7Si_4O_4$, or by the action of high-energy particles (irradiation) on octamethylcyclotetrasiloxane, which gives products in which the rings are joined by oxygen, methylene, or ethylene bridges:



Polycyclosiloxanes have been obtained by alkaline hydrolysis of hydrocyclosiloxanes and condensation of the resulting hydroxycyclosiloxanes[537]:

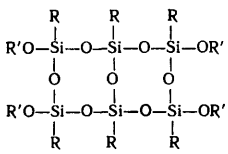


where □ is the methyl-substituted Si_4O_4 ring.

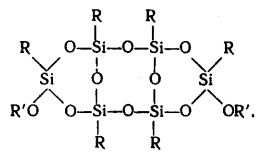
The simultaneous hydrolysis of $(CH_3)_2SiCl_2$ with RCH_3SiCl_2 (where R = CH_2CH_2CN)[427] yields monocyclic products and also a polycyclic compound which analysis and infrared spectroscopy indicated to be tricyclic.

Spirocyclosiloxanes (XXXIX) and (XL) have been obtained in the thermal decomposition of the product of simultaneous hydrolysis of dimethyldichlorosilane with silicon tetrachloride [538,539]. The structure of octamethylspirocyclopentasiloxane has been confirmed by X-ray diffraction [540,541], which gave Si–O = 1.64 ± 0.03 Å.

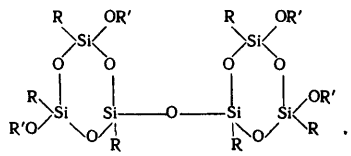
Hydrolysis of methyl- and ethyl-triethoxysilane [542,543] has yielded compounds corresponding to (XLIII) and (XLIV). The bridged structure (XLV) is also possible:



(XLIII)

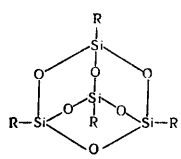


(XLIV)



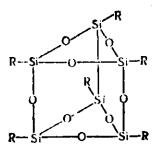
(XLV)

The hydrolysis of trisubstituted derivatives produces various types of polycyclic organosiloxanes. Compounds with the hexamethylenetetramine type of structure have been described — (XLVI) (R = iso-C_3H_7, t-C_4H_9) [544,545]:

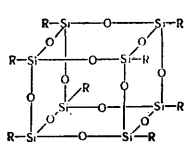


(XLVI)

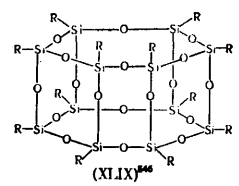
The interesting three-dimensional polycyclic compounds (XLVII), (XLVIII), and (XLIX) were obtained by the thermal degradation of the hydrolysis products of $RSiX_3$: [542–548]



(XLVII) [542,546]



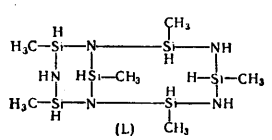
(XLVIII) [542,543,546–548]



(XLIX) [546]

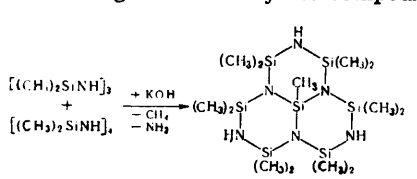
Polycyclic compounds containing Si–N and Si–S bonds have also been described.

Ammonolysis of CH_3SiHCl_2 has produced compound (L): [462]

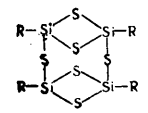


(L)

Catalytic rearrangement of a mixture of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane in the presence of KOH has given the tricyclic compound [549]



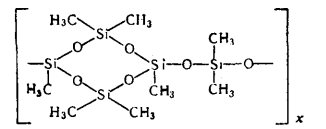
The reaction of alkyltrichlorosilanes with hydrogen sulphide produces the polycyclic compounds (LI): [550,551]



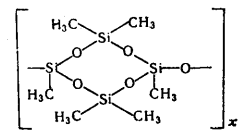
(LI)

Cyclolinear macromolecular compounds (XXXVIII) are obtained by simultaneous hydrolysis of organotrichlorosilanes and a diorganodichlorosilane [552–555], by oxidation of the ethyl groups in $[(C_6H_5)(C_2H_5)SiO]_3$, or by splitting-off of phenyl groups from the same compound by the action of sulphuric acid [374–377].

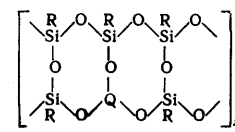
Simultaneous hydrolysis of hexamethyl-1,5-dichlorocyclotetrasiloxane and dimethyldichlorosilane [556] produces polymers of the following structure:



Simple hydrolysis of hexamethyl-1,5-dichlorocyclotetrasiloxane gives the linear polymer

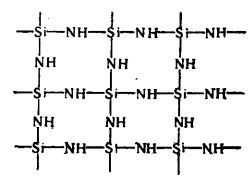


Cyclolinear condensed polysiloxanes of structure (XLI) are obtained by hydrolysis of organotrichlorosilanes $RSiCl_3$ (where R = H, alkyl, or aryl). The inorganic prototypes of this class are known [557], as well as organic derivatives. The phenyl-substituted polysiloxanes $[C_6H_5SiO_{1.5}]_x$ are said to have a stereoregular structure [558,559] (*cis*-syndiotactic). The polyorganosiloxanes obtained by simultaneous hydrolysis of organotrichlorosilanes with aluminium, titanium, or tin halides have the same polycyclic structure [1,2,560]:



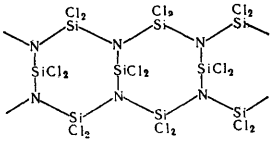
where Q = Al, Ti, or Sn. Thermogravimetric data show that these polymers are highly thermostable.

Polycyclosilazanes are produced by ammonolysis of the silicon polychlorides $HSiCl_3$ or $SiCl_4$; the latter gives "silicodiimide" $[Si(NH_2]_x$, which has the polycyclic structure (LII) [561–563], and it can be assumed that trichlorosilanes also yield a polycyclic product.



(LII)

The reaction between silicon tetrachloride and nitrogen under the action of an electric discharge produces monocyclic and linear products, and also complex polycyclic polymers[454,455]:



The inorganic cyclic silicon compounds and their organic derivatives form a large group of substances, which fall into various classes of inorganic and organic–inorganic compounds. The inorganic rings which form the basis of their molecules impart to them a range of specific properties which are greatly different from those of cyclic organic compounds. The high reactivity towards nucleophilic and electrophilic reagents shown by inorganic rings containing silicon is a characteristic of all inorganic cyclic compounds known at present; this is not shown by organic carbocyclic compounds, and opens up great possibilities in respect of their use in the preparation of organic–inorganic and inorganic compounds, particularly polymers, by various methods.

Inorganic cyclic compounds containing silicon are of special significance for the production of polymers whose main chains are composed of inorganic atoms. Furthermore, the study of the structure, properties, and reactivity of inorganic cyclic silicon compounds and their organic derivatives may help in solving many theoretical problems in organic–inorganic and inorganic chemistry.

Not all the preparative methods possible in this interesting branch of chemistry have yet been applied; very little has been done, but there are great prospects for the future. These compounds lie on the boundary between organic and inorganic chemistry, and further studies may exert a fruitful influence on the development of this little-studied branch of chemistry.

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