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Spirocyclic compounds of the siloxane series

M A Sipyagina (deceased), E A Stepanova, N M Buzyreva, T V Vasetchenkova, E A Chernyshev

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Abstract. Monomeric and oligomeric spirocyclic compounds of the siloxane series, the methods of their synthesis, some of their physicochemical properties, and the reactions leading to their conversion into polymers of different structure are examined. The bibliography includes 69 references.

I. Introduction

The term spirocyclic is given to compounds whose molecules consist of two or several cyclic fragments linked to one another via a common atom, which enters simultaneously into the compositions of two neighbouring rings.[1]

In spirocyclic compounds of the siloxane series, either a silicon atom or the atom of any other element whose valence is four may be found in the spiro-position. The silicon atoms at the spiro-nodes of organospirocyclosiloxanes are involved in a fairly rigid tetrahedral coordination.[2] According to X-ray diffraction data, the Si–O bonds in the spiran group are somewhat shortened compared with the Si–O bonds in the cyclic fragment of the molecule, which is usually attributed to the more complete involvement of the central silicon atom in $p_\pi - d_\pi$ conjugation with the four oxygen atoms surrounding it.[2] The cyclic fragments in the molecules of organospirocyclosiloxanes can differ also in their strain. The most strained cyclic fragments play the role of chemically active centres responsible for the conversion of the spirocyclic compounds into oligomers and polymers.

By creating spirocyclic molecules of different composition and by altering the size of the cyclic fragments and their strain, it is possible to obtain three-dimensionally cross-linked polymers with a controllable network density and with different properties.

The fundamental principles of the synthesis of such compounds have already been described.[3] Individual communications concerning the distinctive features of polymeric materials based on spirocyclic oligomers and polymers can also be encountered.[4]

The aim of the present review is the examination of the methods of synthesis of spirocyclic monomers and oligomers and the procedures for their conversion into polymers of different structure.

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II. Synthesis of organospirocyclosiloxanes

The complexity of the synthesis of organospirocyclosiloxanes consists in the fact that many of them may polymerise during synthesis and isolation owing to the opening of the strained cyclic fragments, forming polymers with three-dimensional structures.

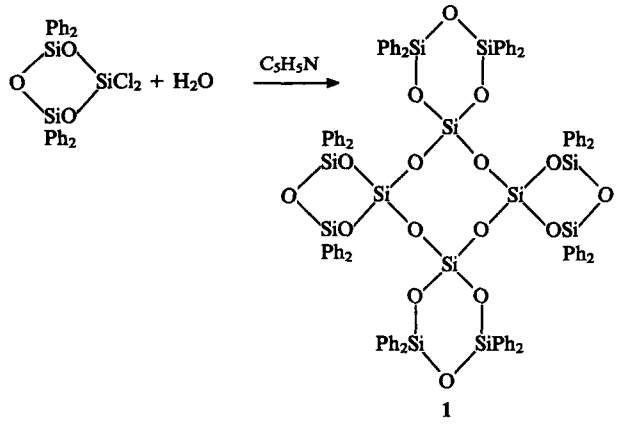
The majority of the traditional methods of synthesis of organosilicon compounds have been tried in order to obtain spirosiloxanes but not all of them proved to be suitable.

1. Hydrolytic polycondensation

The simplest spirocyclic compounds of the siloxane series (together with other polysiloxanes) were first obtained in very low yields by hydrolytic polycondensation (HPC). Thus octamethylspiro[5.5]pentasiloxane was isolated in 1% yield from a complex mixture produced by the thermal rearrangement of the products of the cohydrolysis of dichlorodimethylsilane and silicon tetrachloride.[5] Subsequently a series of cyclic compounds were isolated in 3%–7% yield from the products of the cohydrolysis of the same monomers and a spirocyclic structure was assigned to them on the basis of elemental analysis and their molecular weights.[6] The authors do not present more rigorous proof of the structures of the compounds synthesised. After the appearance of these studies, the literature contained for a long time no publications devoted to the synthesis of organospiropolysiloxanes by the hydrolytic polycondensation method. This can evidently be explained by the fact that the hydrolytic polycondensation of monomers with different functional groups is very difficult to control. Furthermore, the appreciable difference between the rates of hydrolysis and subsequent condensation of the initial monomers leads in the given instance to a sharp decrease in the yield of the target products and hinders their isolation.[5]

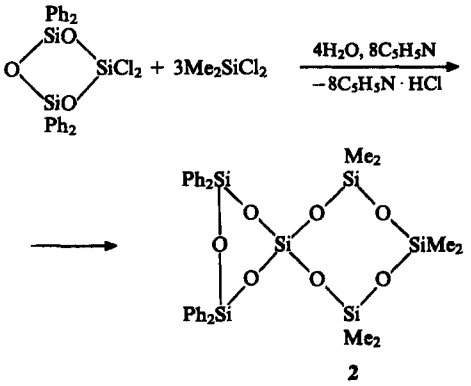
Studies dealing in fair detail with the hydrolytic polycondensation of chlorine-containing organocylcosiloxanes and their copolycondensation with organochlorosilanes have appeared in recent years.[7, 8] It has been established that the products of the hydrolytic polycondensation of these monomers are a mixture of cyclic compounds which cannot always be fully separated.

However, by selecting reaction conditions for each specific case, the authors were able to isolate a series of individual spirocyclic compounds (albeit in low yields) from the complex range of products, whose structure was confirmed by X-ray diffraction and IR and ^{1}H NMR spectroscopy. Thus the spiropentacyclic compound **1** was isolated in a yield reaching 30% from the products of the hydrolytic polycondensation of 2,2-dichlorotetraphenyl-cyclotrisiloxane in ether in the presence of a hydrogen chloride acceptor and a less than stoichiometric amount of water.[8]



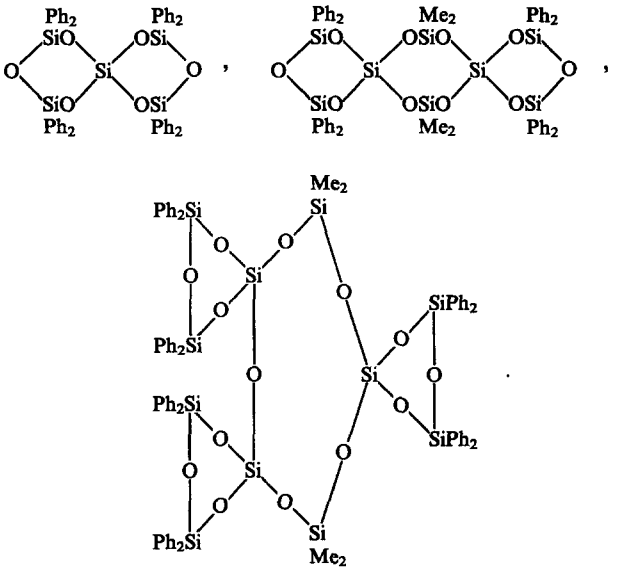
1

In the hydrolytic cocondensation of 2,2-dichlorotetraphenyl-cyclotrisiloxane with dichlorodimethylsilane, the formation of a mixture of bicyclic, tricyclic, and tetracyclic organospirosiloxanes, containing simultaneously tetraphenylcyclotrisiloxane and dimethyl-siloxane units, is formed only when the cohydrolysis is carried out with an equimolar amount of water in the presence of a hydrogen chloride acceptor.[8] The composition of the mixture formed then depends only slightly on the ratio of the initial reactants. For example, the hydrolytic polycondensation of 2,2-dichlorotetra-phenylcyclotrisiloxane and dichlorodimethylsilane in proportions of 1 : 3 with an equimolar amount of water in the presence of pyridine leads to a mixture of spirocyclic compounds which can be vacuum distilled. The main reaction product[8] is 8,8,10,10,12,12-hexamethyl-2,2,4,4-tetraphenylspiro[5.7]hexasiloxane **2**, which was isolated in 21.4% yield.

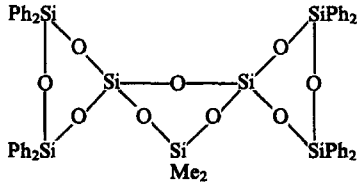


2

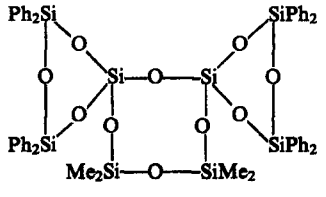
The following compounds are also isolated from the products of this reaction in much lower yield, not exceeding 3%:



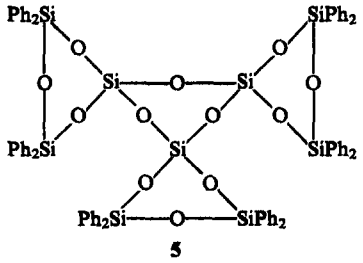
The spirotricyclic and spirotetracyclic compounds **3**–**5** were isolated in 3.5%–9% yield from the mixture of products formed and identified after the cocondensation of 2,2-dichlorotetra-phenylcyclotrisiloxane with dichlorodimethylsiloxane (2 : 1 reactant ratio) and with 1,3-dichlorotetramethyldisiloxane.[8]



3

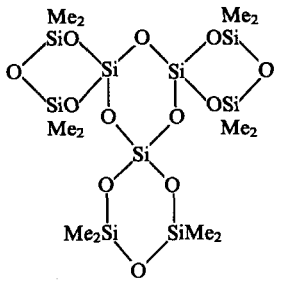


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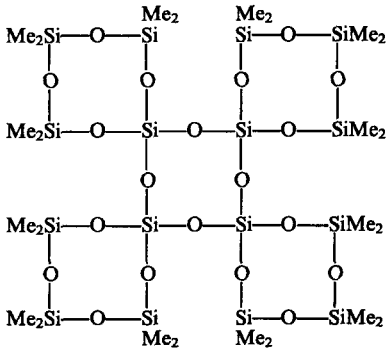
5

The hydrolytic polycondensation of chlorine-containing cyclosiloxanes with methyl groups attached to the silicon atom is no less complex. Thus the hydrolytic polycondensation of 2,2-dichlorotetramethylcyclotrisiloxane with the stoichiometric amount of water in the presence of a hydrogen chloride acceptor leads to a mixture of spirocyclic compounds,[7] from which only one compound, namely the spirotetracyclic compound **6**, was isolated in 22% yield.



6

The spiropentacyclic compound **7**, whose structure was determined by X-ray diffraction, was isolated from the products of the hydrolytic polycondensation of 2,2-dichlorohexamethylcyclotetrasiloxane under conditions similar to those described above.[7, 9]



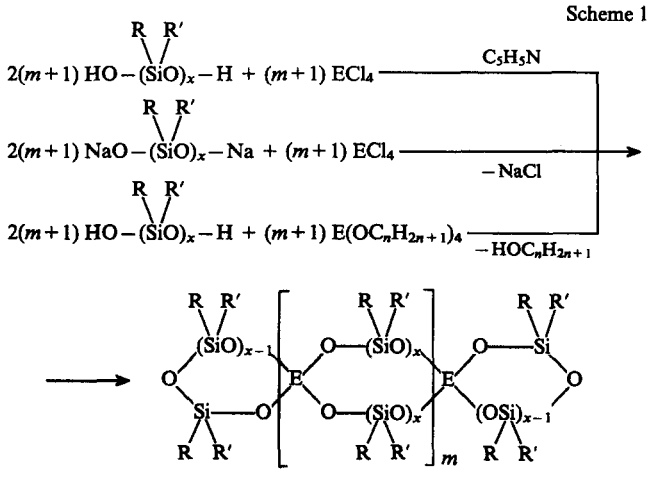
7

Thus the hydrolytic polycondensation of organochlorosiloxanes and organochlorocyclosiloxanes proceeds in a complex manner and leads under the conditions indicated to a mixture of spirocyclic compounds which are difficult to separate and whose yield in each specific case is determined both by the composition and structure of the initial polymers and by the reaction conditions. By virtue of the causes discussed above, it is difficult to obtain by this method organospirocyclosiloxane with a specified disposition and ratio of siloxane units.

2. Heterofunctional condensation

The method most widely used for the synthesis of organospirocyclosiloxanes is based on the heterofunctional condensation (HFC) reaction of di- and tetra-functional organosilicon compounds. In contrast to hydrolytic polycondensation, this method has been used for the specific synthesis of both the simplest spirobicyclic compounds[10–15] and for the synthesis of polyspirocyclic systems.[7, 16–21] The yield of organospirocyclosiloxanes in these reactions depends on the ratio of the initial reactants, their composition and structure, and the reaction conditions. The heterofunctional condensation of bifunctional organosilanes and linear organosiloxanes with tetrafunctional monomers of the type EX_4 (where E = Si or Ti and X = Cl or OC_nH_{2n+1}) is frequently used for the synthesis of organospirosilosiloxanes.[3, 16–19, 22–24] In this case, the initial reactants are taken in proportions of 2 : 1. α, ω-Dihydroxy- or α, ω-disodio-oxyorganosiloxanes are used as the bifunctional component. In the general case, the reaction can be represented by Scheme 1.

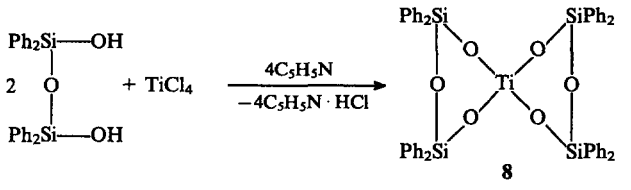
Scheme 1



E = Si, Ti; R = Me; R′ = Ph; $x = 1-8$.

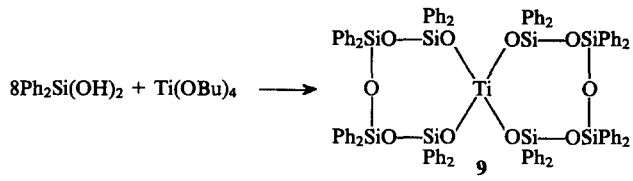
Methylphenylspirocyclosiloxanes, the properties of which have been described,[15, 25, 26] were obtained by means of these reactions. All the compounds synthesised were isolated in 42% to 62% yields and were identified by IR spectroscopy and X-ray diffraction. It is also essential to note that, in the case of the reaction of α, ω-dihydroxyorganosiloxanes with tetrafunctional monomers of the type ECl_4, the reaction proceeds in the direction indicated only in the presence of an acceptor which binds the hydrogen chloride evolved. In the absence of the latter, chlorine-containing cyclosiloxanes, in the molecules of which two chlorine atoms are linked to the silicon atom, are formed preferentially.[14]

Spirobicyclic and polyspirocyclic siloxanes containing titanium as the spiran atom have been obtained by the heterofunctional condensation of linear α, ω-dihydroxyorganosiloxanes with titanium tetrachloride or tetrabutoxytitanium and were identified.[12, 27, 28]



8

The reactions of α,ω-dihydroxyorganosiloxanes with titanium tetrachloride as well as silicon tetrachloride are carried out in the presence of a hydrogen chloride acceptor in anhydrous organic solvents. Under the conditions indicated,[12] the reaction of 1,3-dihydroxytetraphenyldisiloxane with titanium tetrachloride leads to the formation of octaphenyltetrasiloxyspiro[5.5]titanate **8**, which was isolated from the reaction products in a yield of about 14%. The analogous compound **9** with bulky cyclic fragments have been obtained by the reaction of dihydroxydiphenylsilane with tetrabutoxytitanium.[27]

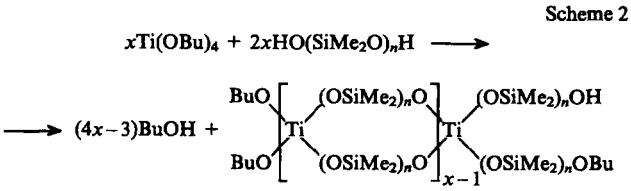


9

Both compounds were characterised by IR spectroscopy and elemental analysis.

Condensation of tetrabutoxytitanium with α,ω-dihydroxypolydimethylsiloxanes[28] having the general formula $HO(SiMe_2O)_nH$, where n is 2, 3, or 4, takes place in conformity with Scheme 2.

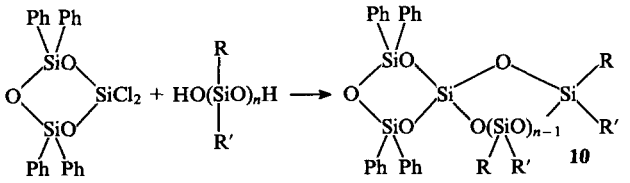
Scheme 2



It has been shown by ^{1}H NMR spectroscopy that the main reaction pathway involves the interaction of the butoxy-groups of tetrabutoxytitanium with the hydroxy-groups of the siloxane. In vacuum at an elevated temperature, the reaction takes place readily with formation of butyl alcohol, the degree of its completion reaching 90%.

One of the versions of the heterofunctional condensation reaction, leading to the formation of organospirocyclosiloxanes, involves the interaction of the bifunctional organosilanes already mentioned and linear organosiloxanes with cyclic di- and tetrafunctional monomers.[7, 10, 11, 29, 30] A series of organodichlorotricyclosiloxanes, organotetrachlorotricyclosiloxanes, and organotetrachlorotetracyclosiloxanes, containing methyl, phenyl, and vinyl substituents at the silicon atom, have now been obtained.[12, 14, 29–31] The study of nucleophilic substitution reactions in organochlorocyclosiloxanes showed that they take place without the cleavage of the siloxane bonds in the rings.[31, 32] This makes it possible to use them as cyclic synthons for the preparation of mixed organospirocyclosiloxanes containing simultaneously different organic substituents in neighbouring rings.[10, 11]

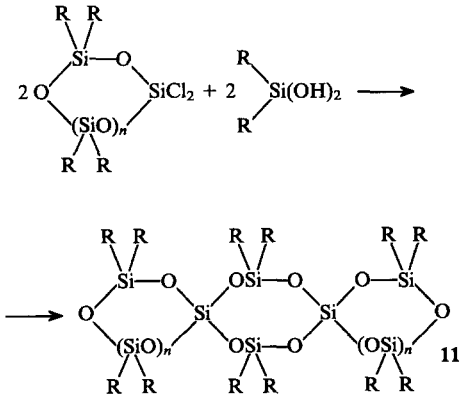
The reactions of organochlorocyclosiloxanes with diorganodihydroxysilanes and α,ω-dihydroxyorganosiloxanes proceed in a complex manner. The yield of organospirocyclosiloxanes depends in this instance to a large extent on the reaction conditions and the organic substituents at the silicon atom. For the equimolar ratio of the initial reactants in the presence of a hydrogen chloride acceptor,[10, 11, 29] the main reaction products are the spirobicyclosiloxanes **10** and spirotricyclosiloxanes **11** having both identical and different sizes of the cyclic fragments in the molecule.[7]



10

for n = 1:	R = R′ = Me	R = Me	R = Me,
for n = 2:	R = R′ = Me	R′ = Ph	R′ = Bu^i

The yield of organospirocyclosiloxanes in these reactions varies from 20% to 48%, the yield of spirobicyclosiloxanes increasing on replacement of the methyl surrounding groups in the diorganodihydroxysiloxane molecule by more bulky substituents, which probably diminish the tendency of diorganodihydroxysiloxanes to enter into homocondensation reactions. The structure of the spirosiloxane thus obtained was confirmed by IR and ^{1}H NMR spectroscopy.

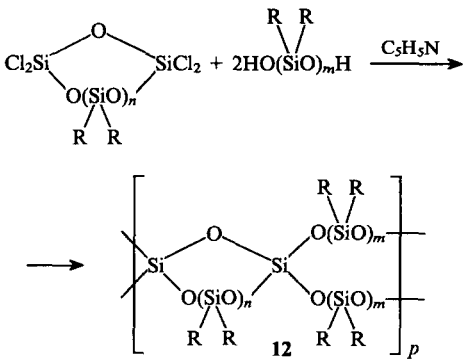


11

R = Me; n = 1, 2.

In contrast to α,ω-dihydroxymethylphenylsiloxanes, the condensation of α,ω-dihydroxyphenylvinylsiloxanes does not lead to the formation of spirocyclic compounds.[12] This is apparently associated with the considerable tendency of compounds in which the silicon atom is surrounded by aliphatic groups to undergo homocondensation.

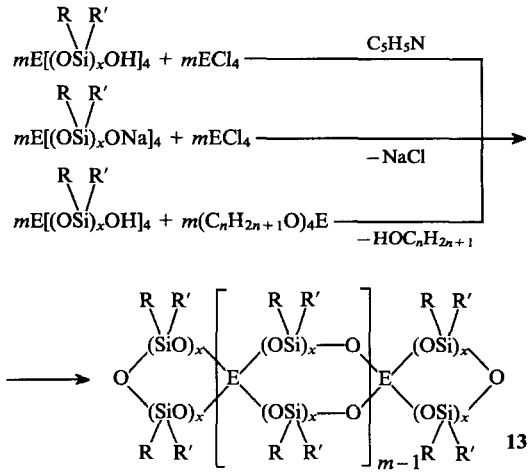
Under conditions analogous to those described above,[30] the oligoorganospirocyclosiloxanes **12** were obtained by the condensation of tetrachlorotetraphenylcyclotetrasiloxane and tetrachlorooctaphenylcyclohexasiloxane with dihydroxydiphenylsilane and 1,3-dihydroxytetraphenyldisiloxane.



12

R = Ph; n = 2, 4; m = 1, 2.

Organospirocyclosiloxanes can also be obtained as a result of the heterofunctional condensation of two tetrafunctional compounds. In this case, a tetrafunctional monomer of the type EX_4 (where E = Si or Ti and X = Cl or OC_nH_{2n+1}) is taken as one of the reactants, while the other is a tetrafunctional compound with a branched or cyclic structure.[3, 16–19, 33–35] Thus the condensation of tetrafunctional compounds having a branched cross-shaped structure with the tetrafunctional monomers indicated above, in proportions of 1 : 1,[3, 16–19] leads to the organospirocylcosiloxanes **13**.

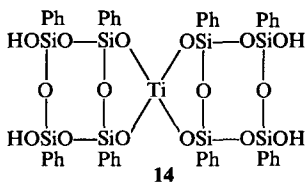


13

E = Si, Ti; R = Me; R′ = Ph; x = 3, 4.

It is noteworthy that the condensation of tetrafunctional monomers with cross-shaped compounds containing a branching titanium atom proceeds readily. The yield of the polycondensation products reaches 63–65% in this case. On passing to compounds with a branching silicon atom, the reaction is retarded and the yield of the reaction product falls to 10%. This mode of reaction is probably due to differences in the steric structure of the above compounds and the influence of the central atom. Nor can one rule out the catalytic action of the titanium atom, which exists in such compounds in a coordinatively unsaturated state.

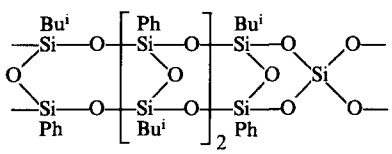
The condensation of tetrafunctional monomers with tetrafunctional cyclic compounds results in the formation of compounds with a spiroladder structure, in contrast to the reaction with tetrafunctional branched organosiloxanes.[33-35] For example, compound **14** was obtained and isolated by the reaction of tetrahydroxytetraphenylcyclotetrasiloxane with tetrabutoxytitanium in proportions of 2 : 1.[34, 35]



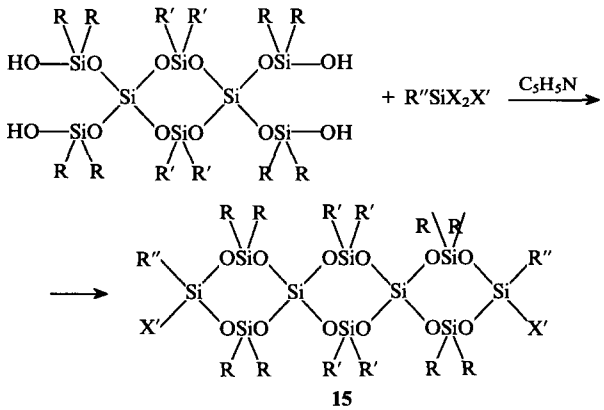
14

Further condensation of this compound leads to a titanophenylsiloxane oligomer containing spirocyclic fragments.[34]

Polyphenylisobutylsiloxane with a spiroladder molecular structure was obtained by the heterofunctional condensation of tetrafunctional polycyclic compounds with carbon tetrachloride. Its elementary unit has the following structure:[33]



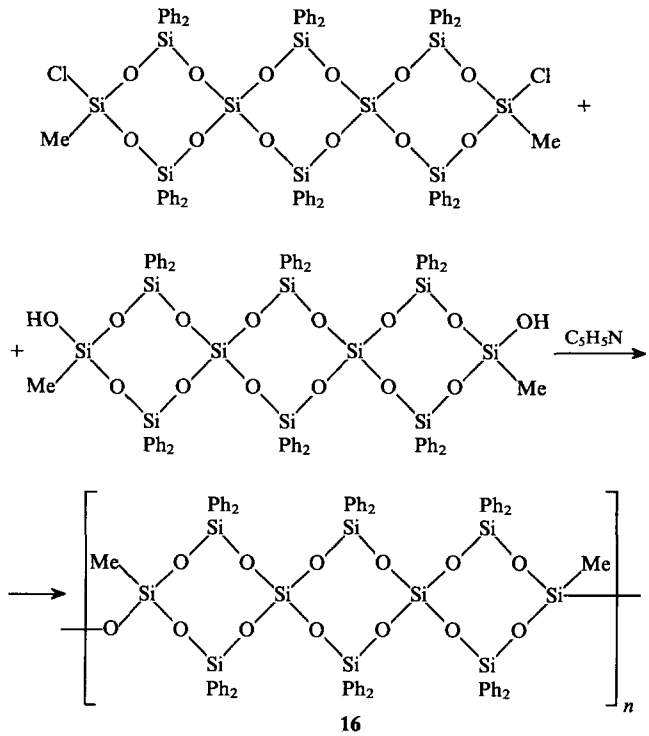
In those cases where the groups surrounding the siloxane chain comprise only phenyl substituents, polymers similar structure are not formed, which is probably due to steric hindrance.[33] Communications describing the synthesis of organospirotricyclic compounds **15** and polymers based on them by the heterofunctional condensation of tetrafunctional branched organocyclosiloxanes and bifunctional organospirocyclosiloxanes with di- and tri-functional organosilicon compounds have been published in recent years.[20, 21, 36-38]



15

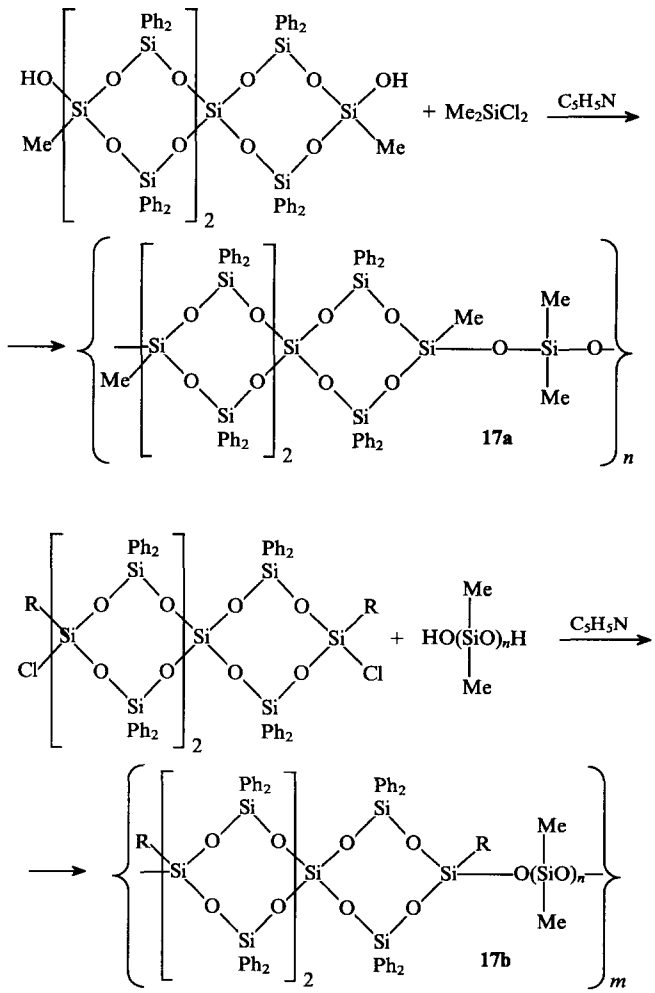
R = R′ = Ph; R″ = Me, Ph; X = Cl; X′ = Cl, OEt, CH=CH$_2$;
R = Et; R′ = R″ = Ph; X = Cl; X′ = Ph;
R = Et; R′ = R″ = Ph; X = X′ = Cl;
R = R″ = Me; R′ = Ph; X = X′ = Cl;
R = Me; R′ = R″ = Ph; X = X′ = Cl.

The products of this reaction, carried out in dilute solutions in the presence of pyridine, are bifunctional spirotricyclosiloxanes (yield from 50% to 75%), whose structure has been confirmed by X-ray diffraction and IR and NMR spectroscopy. The bifunctional organospirocyclosiloxanes obtained by this reaction are capable of interacting with various bifunctional organosilicon compounds and with one another, which leads to the formation of spirocyclolinear polyorganosiloxanes **16** and **17**, whose macromolecules contain rigid fragments with a spiran structure joined together either by an oxygen atom[20, 37] or by dimethylsiloxane units.[20, 37]



16

As in the previous case, the polycondensation reaction is carried out in organic solvents in the presence of pyridine at 50–150 °C.



R = Me, n = 8;
R = Ph, n = 70, 242;
m = 20–60.

For the equimolar ratio of the initial reactants, the yield of the polymers under the conditions indicated reaches 86–92%.

In conclusion, one should note the extensive synthetic possibilities of the heterofunctional condensation method. Spirocyclic compounds with various organic groups surrounding the silicon atom and with different bulk of the cyclic fragments can be obtained by this method in fairly high yields. Both monomeric and oligomeric and polymeric forms of organospirocyclosiloxanes have been obtained by this method and identified.

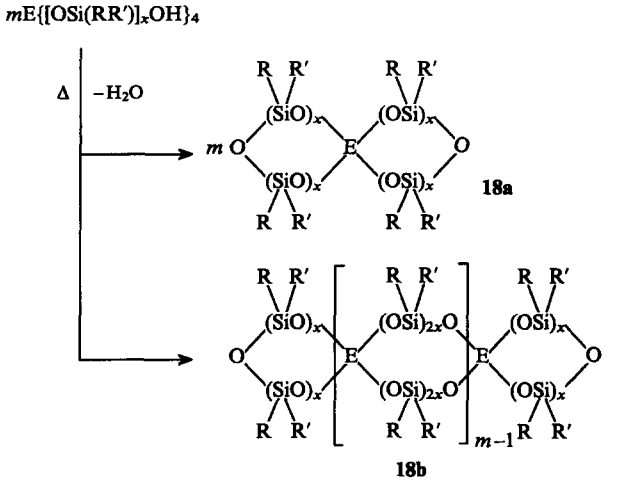
3. Polycondensation of tetrafunctional compounds

The polycondensation of tetrafunctional compounds has been investigated at the present time only for oligomers. The synthesis of organospirocyclosiloxanes by the polycondensation of tetrafunctional cross-shaped oligomers having the general formula

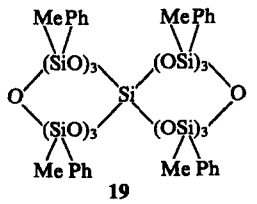
$$E\{[OSi(RR')]_xOH\}_4,$$

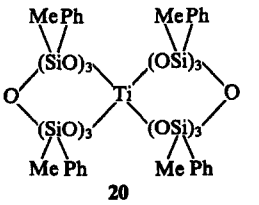
where E = Si, Ti; R = CH_3; R' = C_6H_5, $x = 2-4$, has been described.[3, 15, 16–19]

The block polycondensation of such compounds[15, 39, 40] at 150 °C takes place both intermolecularly and intramolecularly and leads in both cases to the spirocyclic compounds **18**.



The overall yield of the polycondensation products then reaches 70–75%.[15, 40] The spirocyclic structure of the products obtained by this method was demonstrated by isolating the individual compounds and by identifying them by IR spectroscopy and X-ray diffraction. For example, the spirocyclic compounds **19** and **20** were isolated (and identified[15]) in 15 and 10% yields respectively from the products of the polycondensation of tetrakis(3,5,7-trimethyl-3,5,7-triphenylsiloxano-7-hydroxy)silane and tetrakis(3,5,7-trimethyl-3,5,7-triphenylsiloxano-7-hydroxy)-titanium.



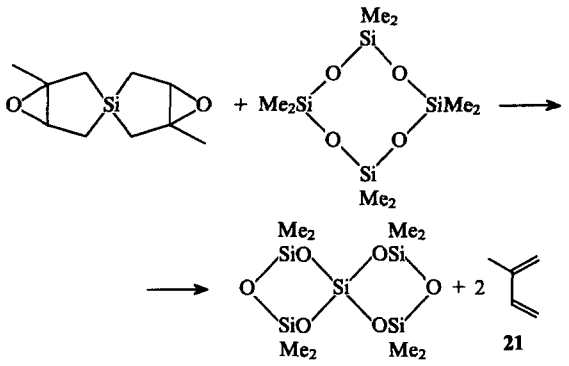


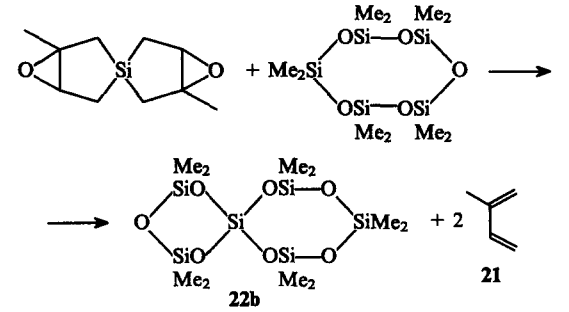
It is also noteworthy that the formation of spirocyclic compounds is observed only in the condensation of oligomers with low values of x.

The above method of synthesis of organospirocyclosiloxanes was not developed further because of its laborious nature.

4. Instantaneous vacuum pyrolysis

Communications describing the synthesis of organospirocyclosiloxanes by the "instantaneous" vacuum pyrolysis of dialkyldiepoxysilaspiroalkanes with organocyclosiloxanes have appeared in the literature in recent years.[41–43] The reaction proceeds in a complex manner via a series of intermediate stages accompanied by the formation of the monomeric silicon dioxide O = Si = O and the so called silanones — reactive intermediates containing silicon–oxygen bonds (silanone intermediates). The final reaction products are[41] isoprene **21** and the corresponding spirosiloxane **22**.





The copyrolysis of 2,3 : 7,8-diepoxy-2,7-dimethyl-5-silaspiro-[4.4]nonane with hexamethylcyclotrisiloxane has been studied in greatest detail. According to the authors,[42] it proceeds stepwise in accordance with Scheme 3.

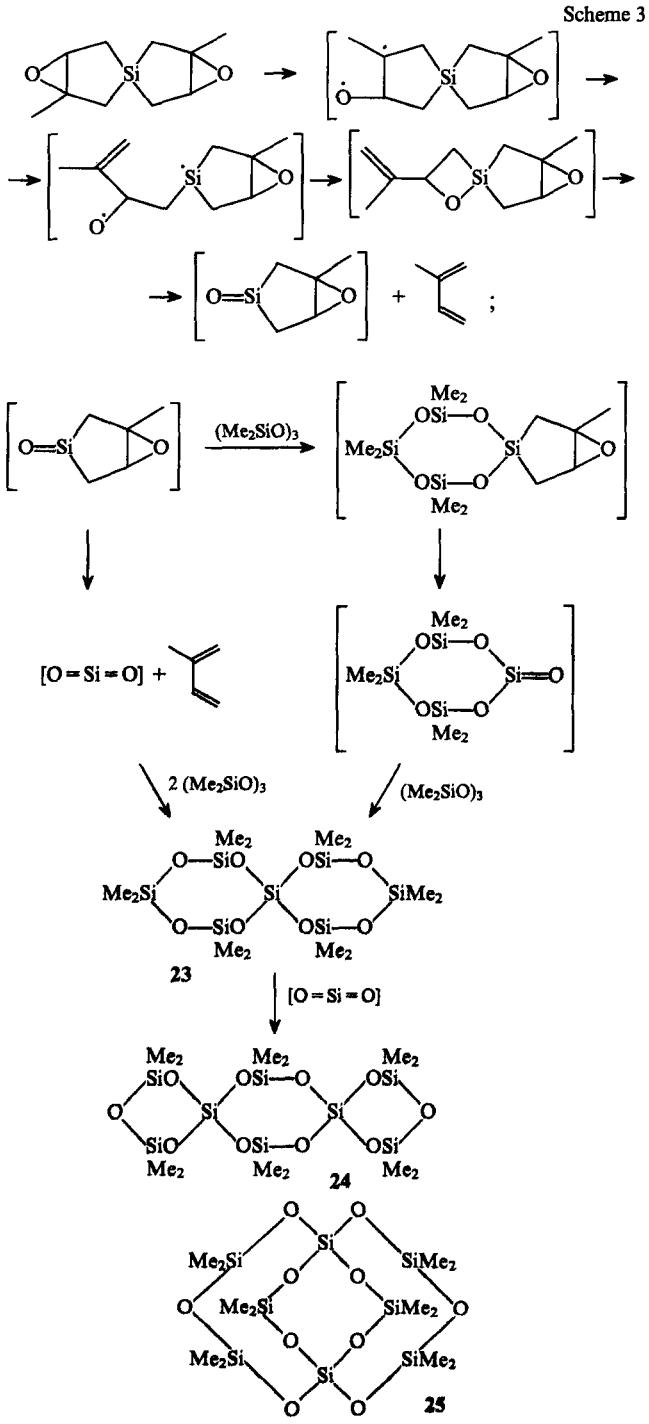
It has been suggested that the reaction begins with the dissociation of the C–O single bond of the bicycle epoxide and with formation of a biradical. The subsequent reactions with its participation lead to silanone intermediates, which are inserted in the Si–O single bonds of the cylcosiloxane and this entails a rearrangement of the siloxane skeleton and ultimately leads to the formation of the corresponding spirosiloxane and isoprene. However, the authors claim[42] that the reaction does not stop at this point and that, together with isoprene and the corresponding spirobicyclosiloxane **23**, a compound with a higher molecular weight is formed. According to X-ray diffraction data, this compound is the spirotricyclosiloxane **24**, which is a product of the interaction of the spirobicyclosiloxane with a second molecule of [O = Si = O]. The interaction of the spirobicyclosiloxane **23** with [O = Si = O] can also lead to the spirotricyclosiloxane **25** according to the results of another study.[43]

The pyrolysis of the above compounds is carried out *in vacuo* at 520 °C. Despite the short residence time of the reactants in the reaction zone, the spirosiloxanes formed under these conditions can probably undergo further reactions. This can be inferred from the low yield of the target products. Thus in most cases of the copyrolysis of 2,3 : 7,8-diepoxy-2,7-dimethyl-5-silaspiro[4.4]-nonane with substituted cyclotrisiloxanes and cyclotetrasiloxanes

(hexaethylcyclotrisiloxane, trimethyltrivinylcyclotrisiloxane, heptamethylcyclotetrasiloxane, heptamethylvinylcyclotetrasiloxane, heptamethylphenylcyclotetrasiloxane, and chloromethylheptamethylcyclotetrasiloxane) the yield of the organospirocyclosiloxanes does not exceed 9%–12%.[41, 42] The structures of all the compounds obtained by this method were confirmed by X-ray diffraction and by ^{29}Si NMR spectroscopy.

Thus, despite the fact that the mechanism of the copyrolysis of dialkyldiepoxysilaspiroalkanes with organocyclosiloxanes has not been elucidated completely and the yield of the target products is low, the method considered is in our view preparative in relation to the synthesis of organospirocyclosiloxanes, is fairly novel, and requires further development.

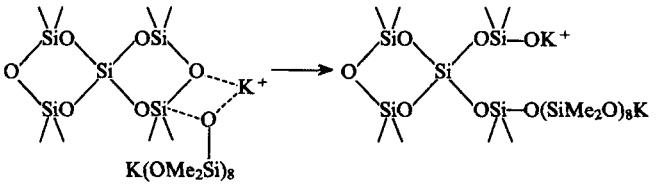
Scheme 3



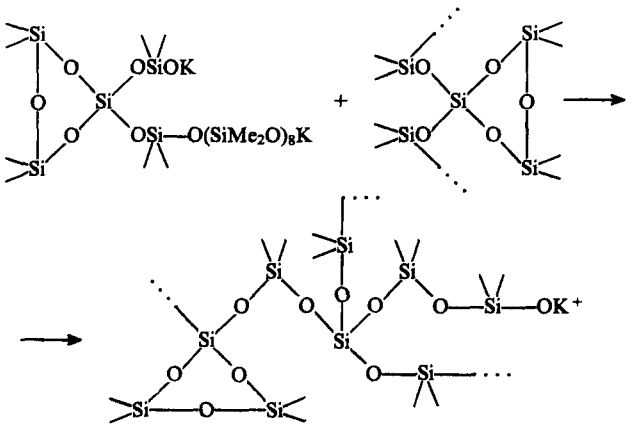
III. Conversion reactions of organospirocyclosiloxanes

The principal reactions involving the conversion of organospirocyclosiloxanes into polymers of different structure are their polymerisation and copolymerisation with organocyclosiloxanes. According to modern ideas, organospirocyclosiloxanes exhibit a functionality of two and four in polymerisation reactions and can form both linear polycyclic polymers and polymers with a three-dimensional structure.[11, 44–49] The catalytic polymerisation of organospirocyclosiloxanes has been little investigated and, in contrast to the polymerisation of organocyclosiloxanes, has a more complex mechanism. In the polymerisation of a spirocyclic compound, the growing polymer chain can enter into two competing reactions. There is then a possibility of either the addition to it of another monomer unit, leading to branching, or the formation of a ring.[11, 45]

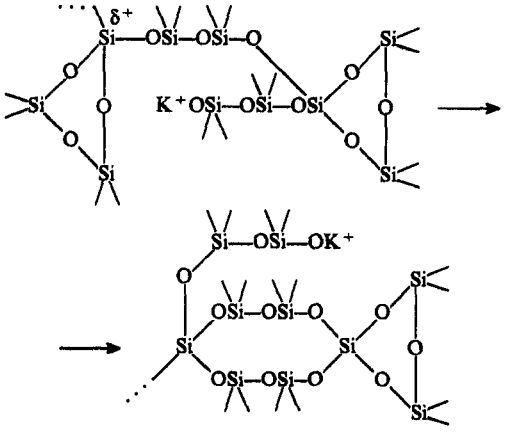
Initiation:



Interchain interaction:

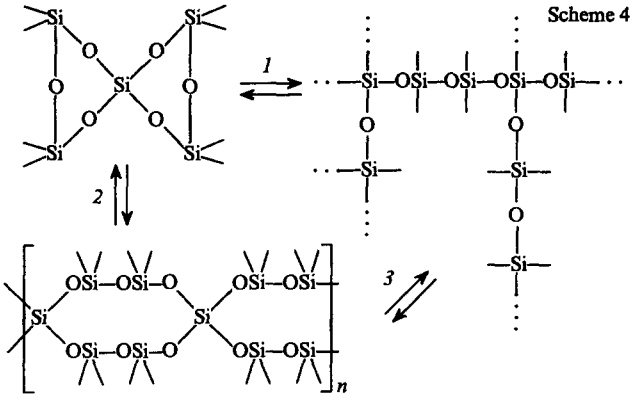


Intrachain cyclisation:



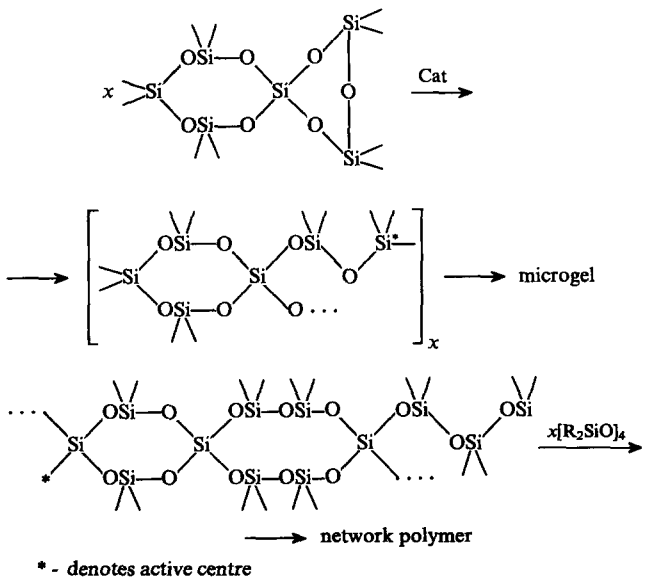
In a general form, the polymerisation of organospirocyclosiloxanes can be represented by Scheme 4, from which it is seen that the polymerisation of organospirocyclosiloxanes develops in the given instance in two directions (reactions *1* and *2* in

Scheme 4). The existence of equilibrium between the soluble and three-dimensionally cross-linked polymers (reaction *3*) has also been established.

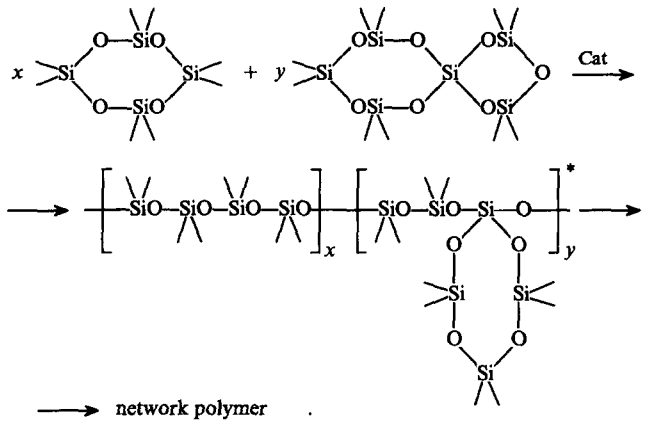


The preferential occurrence of the process via a particular pathway depends mainly on the composition and structure of the initial monomers and also on the reaction conditions. For example, in the case of the anionic polymerisation of spirobicyclic compounds containing only methyl groups at the silicon atom, polymers with a three-dimensional structure are formed.[11, 13] The replacement of some of the methyl groups by phenyl groups leads to a decrease in the equilibrium yield of the gel fraction and, after the complete replacement of methyl groups by phenyl groups or tolyl groups, fully soluble polymers are formed.[14, 44, 46] Consequently pathway *1* predominates for spirosiloxanes with methyl substituents, while pathway *2* is the main one for spirocyclosiloxanes surrounded by phenyl groups. Both pathways operate for spirosiloxanes containing simultaneously both methyl and phenyl groups. It has also been established that there is a definite gel-formation temperature for the process under consideration, above which the formation of a three-dimensional polymer is thermodynamically impossible.[11, 45]

The joint catalytic polymerisation of organospirocyclosiloxanes with organocyclosiloxanes takes place in an even more complex manner and also leads to polymers with a three-dimensional structure.[13, 50–53] In this case, the linear sections of the polymer macromolecules are formed as a result of the polymerisation of the organocyclosiloxane, while the organospirosiloxane, plays the role of a branching agent.[50] A network polymer is formed in this case either as a result of the



homopolymerisation of the spirosiloxane and the formation of microgel particles with subsequent polymerisation of the organocyclosiloxane on the resulting active centres[50] or as a result of the formation in the first stage of the process of a linear polymer containing cyclic fragments, which subsequently passes to an insoluble state as a result of the opening of these fragments by catalytically active centres.[50, 52] The predominance of a particular process is determined by the reactant ratio:

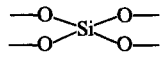


An example of a process leading to three-dimensional polymers may also be provided by the copolymerisation reactions of organospirocyclosiloxanes with linear dihydroxypolydimethylsiloxanes.[54] As in the previous cases, the spirosiloxane plays the role of a branching agent and the polymer chains are cross-linked as a result of the opening of the siloxane rings by the silanolate anions located at the ends of the polymer chains or arising as a result of the exchange between the proton of a hydroxy-group of the dihydroxypolydimethylsiloxane and the cation of the silanolate group of the initiator (Scheme 5).[55]

The subsequent attack by the cyclic fragments of the polymer chain leads to cross-linking. It has been shown that the introduction of α,ω-dihydroxypolydimethylsiloxanes (n = 24–270) into the polymerisation-exchange process makes it possible to obtain three-dimensionally cross-linked polymers with a regular distribution of branching nodes in the network.[56]

IV. Certain physicochemical properties of organospirocyclosiloxanes

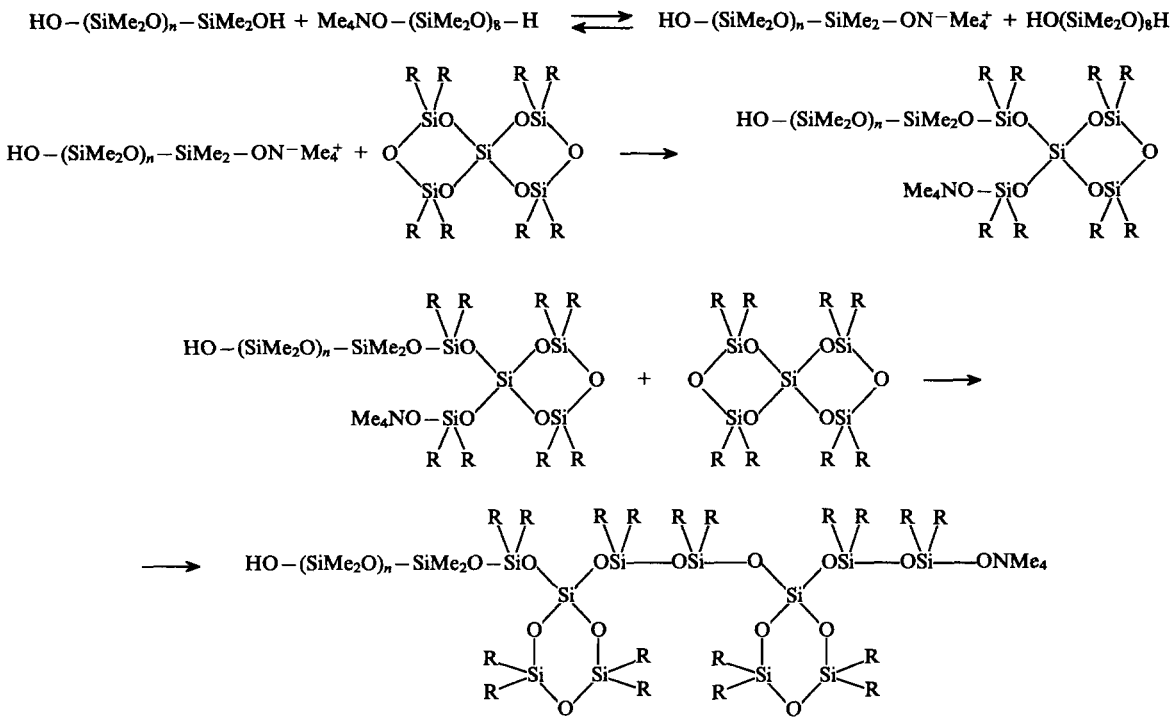
A specific feature of organospirocyclosiloxanes, which distinguishes them from simple organocyclosiloxanes, is the presence of the group



which can be detected with the greatest reliability by means of NMR spectroscopic data. The study of the ^{29}Si NMR spectra of a series of organospirocyclosiloxanes with different surrounding organic groups and different ring sizes showed that signals in the range 6–30 ppm, referring to the silicon atoms of the siloxane rings, and signals in the range 95–105 ppm, corresponding to the silicon atom in the spiro-position, are characteristic of these compounds.[21, 41, 42]

The ring conformations and the geometrical features of the spiro-nodes of organospirocyclosiloxanes[2, 9, 42, 57–62] and organospirocyclosilazoxanes[63, 64] have been determined by X-ray diffraction. It has been shown that the silicon atoms at the spiro-nodes have a fairly rigid tetrahedral coordination; this structural feature is retained also on substitution of the oxygen atoms in the spiro-environment by nitrogen atoms.[64] As already mentioned above, the Si–O bonds at the spiro-nodes of siloxanes are usually somewhat shortened compared with the Si–O bonds of the cyclic

Scheme 5



fragments. On substitution of some of the oxygen atoms in the spiro-environment by nitrogen atoms in the molecules of organospirocyclosilaxanes, the shortening of the Si–O bond lengths becomes extremely insignificant or is altogether absent, which has been attributed to the lower electronegativity of nitrogen compared with oxygen.[62–64]

The trisiloxane rings forming part of spirocyclosiloxanes have an almost planar structure close to that of the molecules of organocyclotrisiloxanes.[58] Analysis of the conformations of the tetrasiloxane rings in the molecules of spirotricyclosiloxanes and spiropentacyclosiloxanes showed that the central rings in these compounds are appreciably flattened compared with the spiro-linked rings surrounding them, which in the authors view[9, 61] is due to steric factors.

The manifestation of the skeletal vibrations of the Si–O bonds of organospirocyclosiloxanes in the IR spectra is also of interest. As a result of the differences between the Si–O bonds of the spiro-node and the siloxane side fragments noted above, one may expect that the characteristic features of the structure of organospirocyclosiloxanes will be manifested in the IR spectra of these compounds.

The most intense absorption in the IR spectra of organo-spirocyclosiloxanes is observed in the range 1020–1100 cm^{-1}. It is characteristic of antisymmetrical stretching vibrations of the Si–O–Si bridge bonds. It has been shown in a number of studies that the Si–O bond vibrations in spirosiloxanes are manifested by a characteristic split ν_{as}(SiOSi) band with two maxima.[3, 8, 10, 15, 29, 31] The positions of these maxima depend on the number of silicon atoms in the ring. On passing from spirocyclic compounds with a smaller number of silicon atoms in the cyclic fragment to compounds with a larger number of such atoms, the ν_{as}(SiOSi) band undergoes a hypsochromic shift. At the same time, the symmetrical stretching vibration frequency ν_s(SiOSi) in the spectra of organospirocyclosiloxanes increases compared with the corresponding vibration in simple organocyclosiloxanes.[3, 15] The observed features of the IR spectra of the spirocyclic compounds of the siloxane series have been attributed[3, 15] to the presence of a branching centre and have been assigned to the vibrations of the Si–O–Si groups adjoining the central spiro-atom and constituting together with the latter a single structural nucleus. However, hitherto there is no unanimous view in the interpretation of the characteristics of the IR spectra of the above compounds. A number of investigators believe that a similar splitting of the ν_{as}(SiOSi) band is characteristic also of the spectra of linear and cyclic compounds containing more than four siloxane units.[2, 65–67]

In the case of spirocyclic compounds containing titanium as the spiro-atom,[3, 12, 15, 27, 28, 68, 69] the IR spectra show, apart from the splitting of the ν_{as}(SiOSi) band into two maxima mentioned above, an intense absorption in the range 910–930 cm^{-1} due to the vibrations of the TiOSi fragment.

In comparing the methods of synthesis of organospiro-cyclosiloxanes examined in this review, one should note that the heterofunctional condensation method is at present the most thoroughly developed and preparatively and technologically most convenient, ensuring a fairly high yield of the target products. Spirocyclic oligomers, on the basis of which a series of composite materials with unique properties have been developed, have now been obtained by this method. These materials are used successfully in various branches of modern engineering.

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