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The thermal gas-phase synthesis of heterocyclic compounds with one or several silicon atoms in the ring

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ABSTRACT. The results of studies on the synthesis of organosilicon heterocyclic compounds under the influence of high temperatures in a flow system at atmospheric pressure and in a high vacuum are surveyed. The preparative possibilities of the gas-phase thermal method for the synthesis of new or previously difficult to obtain mono-, bi-, and poly-cyclic compounds with one or several silicon atoms in the ring are examined. The principal aspects of the thermal heterocyclisation processes are described.

Attention is concentrated on the synthesis of heterocycles with functional group substituents at the silicon atom as well as high-temperature reactions with participation of unstable intermediates: silylenes, sila-alkenes, and siladienes.

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I. Introduction

The chemistry of heterocyclic compounds of silicon constitutes at the present time an independent branch of organosilicon chemistry. The number of publications devoted to the method of synthesis and the study of the structure and properties of organosilicon heterocyclic compounds has been steadily increasing. The interest in these compounds is associated both with their practical applications (biological activity, thermal stability, etc.) and with theoretical aspects due to the appearance of new properties in the compounds after the introduction of a silicon atom into the carbon ring and their different behaviour in chemical reactions compared with acyclic organosilicon compounds.

One of the simplest and most effective methods of synthesis of many classes of organosilicon heterocyclic systems, previously impossible to obtain, is the gas-phase thermal method, which consists in the interaction of various silicon-containing and organic compounds at temperatures in the range 300–700 °C in a flow system (the reactor consists of a hollow quartz or metallic tube). It is simple as regards apparatus and in most cases is distinguished by a high selectivity.

The present review is devoted to the discussion of the synthetic possibilities of this method and includes studies published up to the middle of 1987.

Extensive experimental data have now accumulated, which makes it possible to discover the principal fundamental aspects of the high-temperature synthesis of silicon heterocycles. These are primarily the intramolecular thermal cyclisation of organosilicon compounds containing structural fragments necessary for cyclisation in the presence of thermally labile bonds as well as bonds exhibiting an increased reactivity as a consequence of steric interaction with bulky substituents in the α-position in naphthalene and in the *o*-position in benzene or biphenyl. Another aspect vigorously developing recently has been the thermal synthesis of silicon heterocycles with participation of unstable species and compounds: silylenes, sila-alkenes, and siladienes. The sources from which these highly reactive intermediates can be generated in the gas phase as well as acceptors—systems capable of trapping them with formation of thermally stable compounds—have been found. The use of hexachlorodisilane and higher perchloropolysilanes as sources of dichlorosilylene have made it possible to extend greatly the preparative possibilities of the pyrolytic cyclisation method. The high reactivity of the thermally generated dichlorosilylene and the appreciable selectivity of its interaction with specific chemical bonds have made it possible to synthesise specifically various classes of heterocycles with one or several silicon atoms in the ring, whose preparation by other methods was difficult or impossible.

Interesting communications concerning the thermal method for the generation of unstable silicon intermediates in extremely short time intervals (vacuum flash pyrolysis) have appeared comparatively recently. The latest review of these studies was published in 1985.[1] The detection of these species and the study of their properties are mainly of theoretical interest. Nevertheless, despite the increased complexity of the apparatus required for their synthesis, in many cases, the high-temperature reactions of these intermediates can be considered also on the preparative scale—for the synthesis of silicon-containing heterocyclic systems.

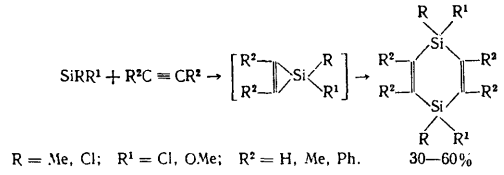
II. Monocyclic compounds

1. Synthesis with participation of silylenes

(a) The addition of silylenes to multiple bonds

The interactions of silylenes with unsaturated compounds must be regarded as some of their most characteristic reactions. Such reactions are of great preparative interest for the synthesis of silicon-containing heterocyclic systems. The most active silylene "trapping agents" are alkynes and conjugated dienes. The most convenient and fairly general method of synthesis of silylenes is the thermolysis of various disilanes. Thus the gas-phase reaction of

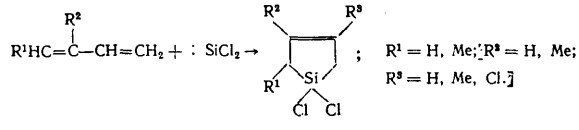
tetrachlorodimethyl-, tetramethoxydimethyl-, and hexachlorodisilanes with acetylene and its derivatives is widely used for the synthesis of disilacyclohexa-2,5-dienes with functional group substituents at the silicon atom:[2–8]



$R = Me, Cl;\ R^1 = Cl, OMe;\ R^2 = H, Me, Ph.$ 30—60%

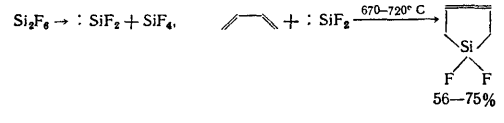
A report of the synthesis of 1,1,4,4-tetramethoxy-1,4-disilacyclohexa-2,5-diene in the copyrolysis of hexamethoxydisilane with acetylene (temperature 370 °C, yield of heterocycle 56%) appeared in 1985.[9] An excellent source from which dimethoxysilylene can be generated, namely hexamethoxydisilane, was proposed in that study. Evidently, the primary step in the thermal interaction is the addition of the corresponding silylene to the triple bond of the alkyne with formation of a silacyclopropene derivative and its subsequent reaction.[2,3,8,10,11]

The thermal generation of $:SiCl_2$ from hexachlorodisilane has led to effective ways of synthesising the simplest unsaturated organosilicon heterocycles—derivatives of silacyclopent-3-ene—from conjugated dienes:[2,3,7,8,12–14]



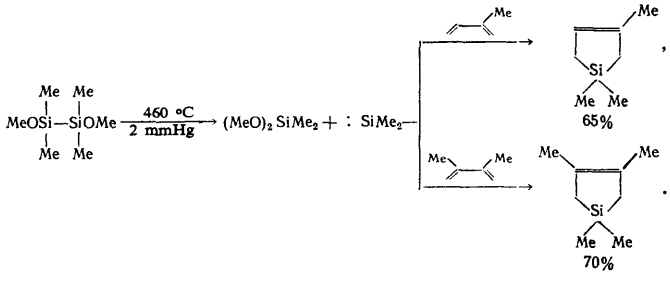
$R^1 = H, Me; R^2 = H, Me; R^3 = H, Me, Cl.$

The yields of the heterocycles are almost quantitative (90–95%). A report has recently appeared[15] of the synthesis of 1,1-difluoro-1-silacyclopent-3-ene by the gas-phase pyrolysis of hexafluorodisilane in an excess of buta-1,3-diene:



56—75%

By carrying out the process in a flow system with a reactant contact time of 0.01–0.2 s, it has been possible to capture the highly reactive monomeric $:SiF_2$. The reactions involving the addition of dimethylsilylene, generated thermally from 1,2-dimethoxytetramethyldisilane, to acyclic 1,3-dienes both at atmospheric pressure[10,16] and *in vacuo*[17] also take place readily in the gas phase, for example:



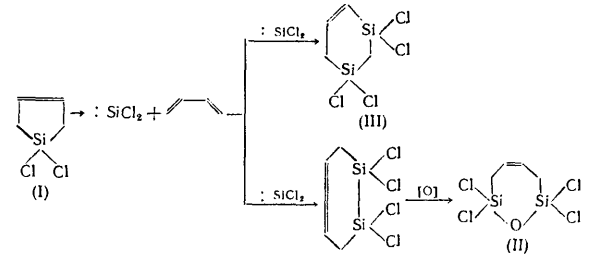
65%

70%

The authors[17] suggest the concerted 1,2-addition of dimethylsilylene to substituted buta-1,3-dienes with subsequent opening of the vinylsilacyclopropane ring.

On the other hand, the evidence obtained[2,8,18–20] for the retrodiene thermal decomposition of 1,1-dichloro-1-silacyclopent-3-ene justifies the assumption that the gas-phase interaction of $:SiCl_2$ with buta-1,3-dienes formally corresponds to the Diels–Alder reaction and therefore proceeds via the concerted 1,4-cycloaddition mechanisms.

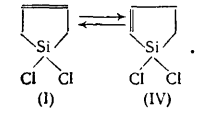
The ability of 1,1-dichloro-1-silacyclopenta-3-ene (I) to generate $:SiCl_2$ has been used for the preparative high-temperature synthesis of new heterocycles with two silicon atoms in the ring: 1,1,3,3-tetrachloro-1,3-disila-2-oxacycloheptene-5-ene (II) and 1,1,3,3-tetrachloro-1,3-disilacyclohex-4-ene (III):[2,8,21]



(I) (III) (II)

In the pyrolysis of the heterocycle (I) (680 °C), the yields of compounds (II) and (III) and 25 and 45% respectively. When the temperature is reduced, the yields of these compounds diminish and amount to only 7 and 3% at 500 °C. The heterocycle with the Si—Si bond is evidently unstable and is converted into compound (II) under the conditions of the pyrolysis.

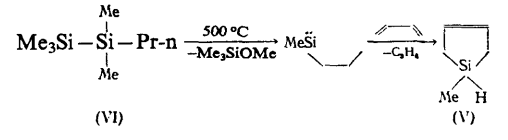
A detailed study of the thermal reactions of the heterocycle (I) showed that it is also capable of isomerising to 1,1-dichloro-1-silacyclopent-2-ene (IV) and that this reaction is reversible:[12,22,23]



(I) (IV)

A method has been proposed for the synthesis of compound (IV) by passing its more readily available isomer (I) repeatedly (5–6 times) through a quartz flow reactor at 540 °C.[22]

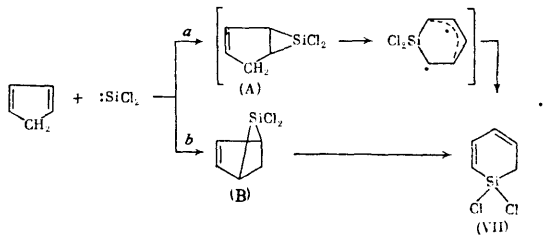
The generation of dimethylsilylene by the vacuum flash pyrolysis (750 °C, 1 mmHg) of 1,1-dimethyl-1-silacyclopent-3-ene has been reported.[24,25] The isomeric 1-silacyclopent-2-ene is also formed under these conditions. The same workers proposed a new source of $:SiMe_2$ in pyrolytic cyclisation reactions—dimethyl(*cis*-prop-1-enyl)-vinylsilane.[25] The synthesis of the 1-silacyclopent-3-ene hydride derivative (V) via methylpropylsilylene, generated from the disilane (VI), merits special attention:[26]



(VI) (V)

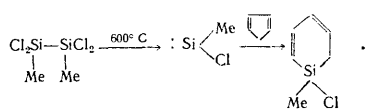
A new aspect of the chemistry of silylenes is the study of their reactions involving addition to cyclic conjugated systems with formation of previously inaccessible monocyclic silicon compounds. Such a reaction was carried out in the thermal interaction of hexachlorodisilane with cyclopentadiene.[2,3,7,13,14,27] The copyrolysis of hexachlorodisilane with cyclopentadiene or its dimer at 500 °C led

to the formation of 1,1-dichloro-1-silacyclohexa-2,4-diene as the main product (yield up to 50%):

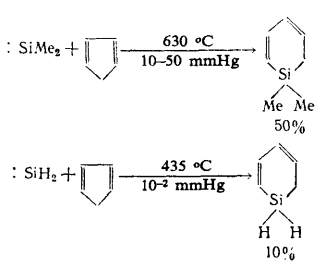


It is notable that the preparation of this compound by other methods is difficult, since these are multistage syntheses leading to low yields of compound (VII) with an admixture of isomers which are difficult to separate.[28] It is possible to put forward two alternative schemes for the expansion of the ring in the five-membered cyclic diene: by adding to it dichlorosilylene in the 1,2-positions (pathway *a*) or in the 1,4-positions (pathway *b*). The first version provides for the formation of the silacyclopropane intermediate (A), which then rearranges to the final reaction product via a biradical. A similar biradical mechanism has been proposed for the thermal rearrangement of the hydrocarbon analogue[29] and also in the study of the gas-phase interaction of dimethylsilylene with cyclopentadiene.[30] However, one cannot rule out also the possibility of the 1,4-cycloaddition of $:SiCl_2$ to cyclopentadiene, which has a fixed cisoid conformation. A fairly pronounced strain in the four-membered ring of the intermediate bicyclic compound (B) is created, as a result of which it can rearrange to the final product—1,1-dichlorosilacyclohexa-2,4-diene. The possibility of the thermal generation of dichlorosilylene in the pyrolysis of compound (VII), demonstrated by the method of "chemical trapping agents",[31] and also the mass-spectrometric study of the pathways leading to the decomposition of this compound[32] confirm to some extent the pathway *b*.

The method described in a number of studies[2,3,7,13,14,27] has been frequently reproduced.[30,33] The preparative possibilities of the method proposed have been greatly expanded by employing both a series of different sources of silylenes as well as certain other organic cyclic compounds with a diene group. 1-Chloro-1-methyl-1-silacyclohexa-2,4-diene has been synthesised in this way:

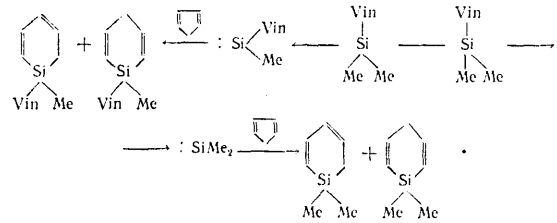


A similar reaction has also been carried out *in vacuo* (650 °C, 10^{-2} mmHg).[35] The interaction of dimethylsilylene and the unsubstituted silylene, generated from the corresponding disilanes, with cyclopentadiene led to the formation of silacyclohexadienes with methyl or hydride substituents at the silicon atom:[30]

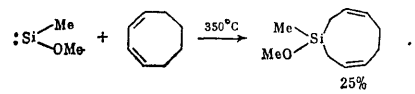


In all cases, except the last, the formation of small amounts of the corresponding derivatives of silacyclohexa-2,5-diene has been noted.

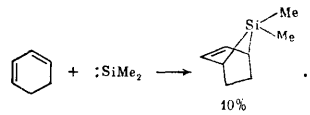
The copyrolysis of 1,1,2,2-tetramethyl-1,2-divinyldisilane $(Me_2VinSi)_2$ with cyclopentadiene has been investigated[35] (650 °C, 10^{-2} mmHg). Four cyclic compounds in approximately equal amounts were detected in the reaction products; non-selective decomposition of the organic disilane via two schemes has been proposed:



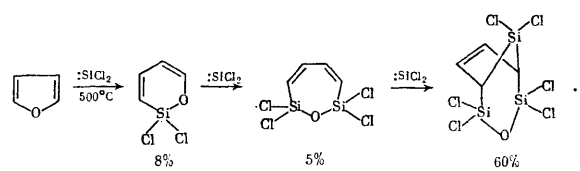
Methoxymethylsilylene adds to cycloocta-1,3-diene with formation of a non-conjugated cyclic diene:[36]



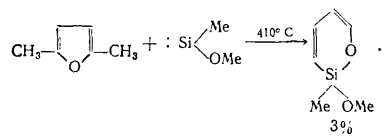
On the other hand, the expansion of the ring of the organic diene is not observed in the interaction of dimethylsilylene with cyclohexa-1,3-diene; only a bicyclic compound is formed in a low yield:[30]



The interaction of dichlorosilylene with furan takes place in a more complex manner. An oxygen-containing analogue of silacyclohexa-2,4-diene, namely 1,1-dichloro-2-oxa-1-silacyclohexa-3,5-diene, was isolated from the reaction mixture in a very low yield.[2,3,7,13,14] The principal product of this reaction is a bicyclic compound with three dichlorosilylene fragments:

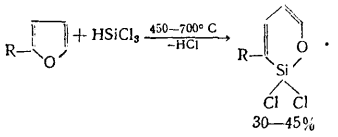


The pyrolytic interaction of methoxymethylsilylene with 2,5-dimethylfuran also does not lead to the specific formation of the six-membered diene system with the Si—O fragment. The yield of the heterocycle does not exceed 3%:[37]



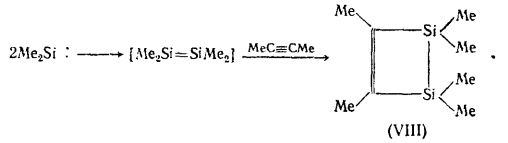
Heterocycles of a similar type are formed in much higher yields in the pyrolytic interaction of furan and its α-substituted derivatives with trichlorosilane. The method proposed makes it possible to obtain derivatives of 2-oxa-1-silacyclohexa-3,5-diene with functional

group substituents at the silicon atom from readily available reactants:[8,38–40]

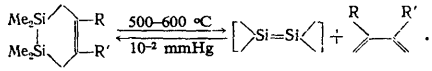


(b) Disilenes. The isomerisation of disilenes to silylsilylenes

In a study of the gas-phase reaction of dimethylsilylene, generated from dimethoxy-tetramethyldisilane, with dimethylacetylene in 1973, a new heterocyclic compound was isolated—permethyldisilacyclobutene (VIII):[41]

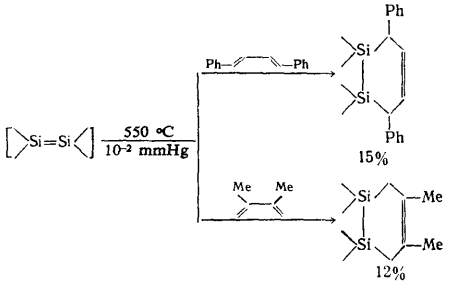


Several schemes for the formation of compound (VIII) have been proposed; one of them involves a stage in which :$SiMe_2$ dimerises to disilene—an unstable intermediate with π-bonded silicon atoms.[10,11] Reaction involving the [6 → 4 + 2]cyclo-elimination of tetramethyldisilene in the extensive gas-phase vacuum pyrolysis of 1,2-disilacyclohex-4-ene has been proposed recently:[42]

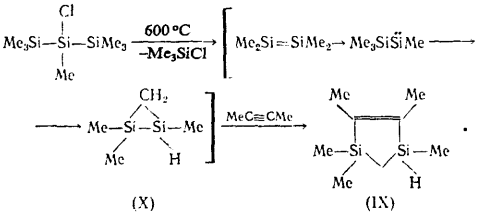


R, R′ = H, Me.

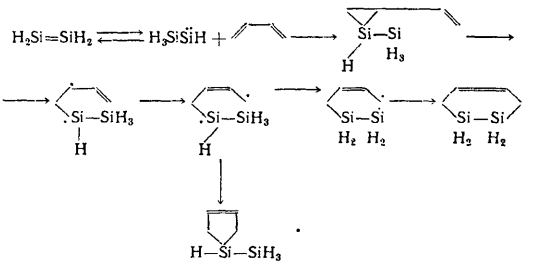
The pyrolysis of this compound in the presence of "trapping agents" made it possible to extend the set of heterocycles with the structure indicated above:



A novel method of synthesis of unsaturated heterocyclic systems with one or two silicon atoms in the ring involving disilenes has been described.[10,11,43,44] The proposed schemes for the preparation of these heterocycles reflect a specific property of disilenes—their ability to isomerise to silylsilylenes during pyrolysis. Thus 1,1,2,3,4-pentamethyl-1,3-disilacyclopentene (IX) has been synthesied by the cothermolysis of various sources of tetramethyldisilene, namely 7,7,8,8-tetramethyl-1-phenyl-2,3-benzo-7,8-disilabicyclo[2.2.2]octa-2,5-diene[10,11] and 2-chloroheptamethyltrisilane,[43] in the presence of dimethylacetylene in 25–28% yield. The authors regard the heterocycle (IX) as the formal product of the insertion of an alkyne in the Si–Si bond of the intermediate disilacyclopropane (X). The isomerisation of tetramethyldisilene to methyl(trimethylsilyl)silylene is postulated under these conditions:[43]

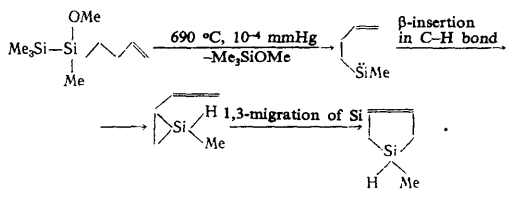


Heterocyclic compounds with endocyclic and exocyclic Si–Si bonds have been obtained in proportions of 1 : 1 by the thermal interaction of butadiene with trisilane, which is apparently capable of generating during pyrolysis not only :SiH_2 but also the product of its recombination with subsequent isomerisation to silylsilylene:[44]



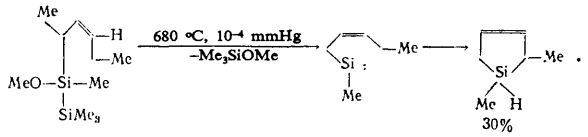
(c) Intramolecular reactions of silylenes

A new apsect of the high-temperature chemistry of organic silylenes, associated with the study of their intramolecular reactions, has begun to develop in the last few years. A method has been proposed for the intramolecular trapping of silylenes, the idea of which consists in the fact that the role of the chemical trapping agent is assumed by the very source from which the silylene is generated. In order to limit the contribution of intermolecular reactions and secondary processes in the generation of such silylenes, they are investigated in a high vacuum. Some of the reactions of this kind can be regarded as methods of synthesis of unsaturated silicon-containing heterocyclic structures. Thus it has been established[45] that 3-butenylmethylsilylene, thermally generated from 1-(3-butenyl)-1-methoxytetramethyldisilane, cyclises to 1-methyl-1-silacyclopent-3-ene in 56% yield:

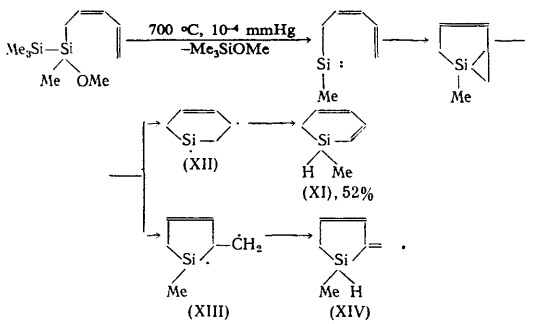


The same heterocycle has been obtained in a satisfactory yield also from another source of 3-butenylmethylsilylene—butenyldichloromethylsilane in its interaction with alkali metal atoms (K/Na) in the gas phase (flow system, temperature 300–340 °C, pressure

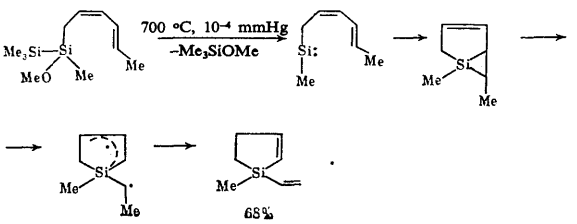
10^{-1} mmHg, K/Na = 7/1).[46] The intramolecular reaction of another alkenylsilane, namely methyl-4-(2-pentenyl)silylene, leads to the formation of 1,2-dimethyl-1-silacyclopent-3-ene:[45]



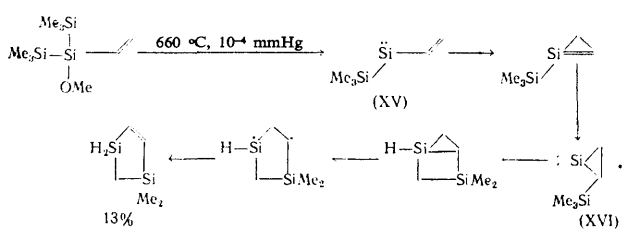
A six-membered heterocycle with a diene group—1-methyl-1-silacyclohexa-2,4-diene (XI)—is the main product of the intramolecular reactions of methyl-5-(penta-1,3-dienyl)silylene.[45] The latter undergoes intramolecular π-addition to the terminal double bond with the subsequent formation of the biradicals (XII) and (XIII), whose further reactions lead to the final products (XI) and (XIV). 2-Methylene-1-methylsilacyclopentene (XIV) has been isolated in 13% yield:



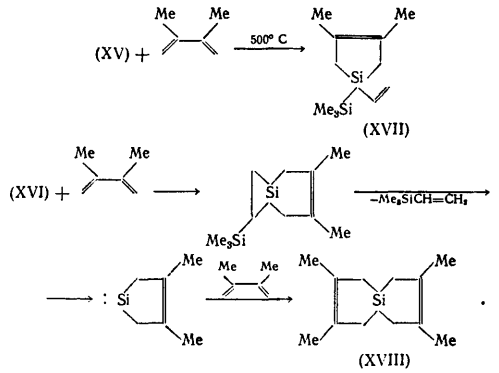
The pyrolysis of the methyl-substituted hexadienyldisilane can be regarded as a thermal method of synthesis of 1-methyl-1-vinyl-1-silacyclopent-2-ene:[45]



A very interesting vinylsilylene intramolecular rearrangement has been observed in the vacuum pyrolysis of 2-methoxy-2-vinylhexamethyltrisilane.[47] The hypothesis of the possible existence of silacyclopropanylidene as an intermediate was proposed for the first time and a scheme for the preparation of 1,1-dimethyl-1,3-disilacyclopent-4-ene with its participation was put forward:

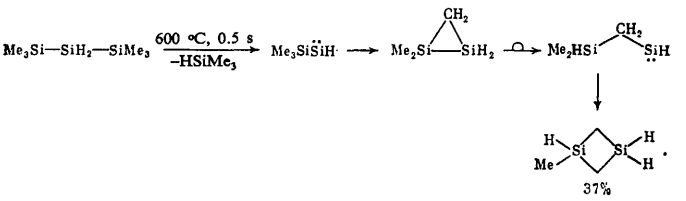


The existence of the intermediates (XV) and (XVI) has been confirmed by the reaction of the initial trisilane with dimethylbutadiene, whereupon also the new heterocyclic systems (XVII) and (XVIII) were obtained:



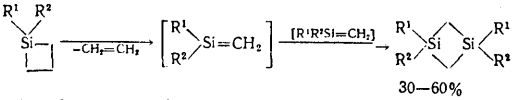
With increase in the excess of dimethylbutadiene, the yield of the spiro-product (XVIII) also increases. It amounts to 20 and 44% for the diene:trisilane ratios of 3:1 and 8:1 respectively. The yield of the heterocycle (XVII) does not exceed 8% in both cases.

An interesting new intramolecular thermal rearrangement of α-silylsilylenes, discovered recently[48] in the pyrolysis of 1,1,1,3,3,3-hexamethyltrisilane, can be regarded as a method of synthesis of 1-methyl-1,3-disilacyclobutane:



2. Synthesis with participation of silaalkenes

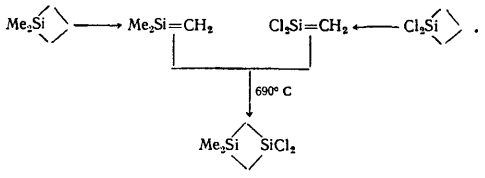
Systematic study of the processes involved in the pyrolysis of monosilacyclobutanes with various substituents at the silicon atom has led to the discovery of an interesting highly selective thermal [4 → 2 + 2]cycloelimination reaction, which proceeds with formation of disilacyclobutanes.[49–51] A unimolecular mechanism of the decomposition of the initial cyclic sila-compounds to ethylene and an unstable intermediate with an unsaturated bond at the silicon atom—silaalkene (silene)—was established. Stabilisation of the silaalkene by cyclodimerisation leads to the formation of disilacyclobutanes:[51–53]



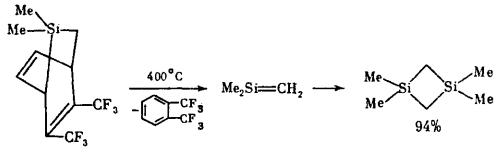
$R^1 = R^2$ = Me, Cl; R^1 = Me, R^2 = Cl; R^1 = Me, R^2 = CH=CH$_2$.

The reaction takes place in an inert gas atmosphere or at reduced pressure in flow reactors (a hollow tube or a tube filled with a heat exchanger) or in static reactors (quartz bulb). In the general case, the pyrolysis of monosilacyclobutanes is a relatively simple and convenient method of synthesis of 1,3-disilacyclobutanes, especially those whose synthesis by other methods is difficult. In the chemistry of organosilicon compounds, this method has been frequently used for preparative purposes, for example, for the synthesis of tetrachloro-1,3-disilacyclobutanes[50,51] and also its

derivatives with mixed substituents at the silicon atom,[54] which are difficult to obtain:

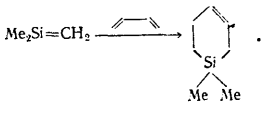


Another highly selective method for the synthesis of tetramethyl-1,3-disilacyclobutane, in which dimethylsilene is generated by the pyrolysis of 7,7-dimethyl-2,3-bis(trifluoromethyl)-7-silabicyclo-[2.2.2]octa-2,5-diene, has been proposed:[55]

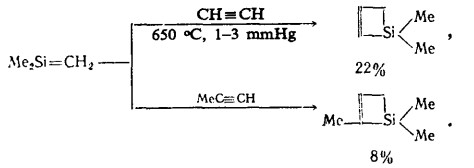


A high yield of the target product was obtained only on thermolysis of the initial compound in a stream of cyclohexane. In the absence of the carrier gas, the yield of the heterocycle was only 4%.

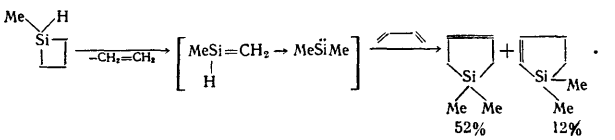
The application of the chemical trapping agent method made it possible to use the properties of silaalkenes as excellent dienophiles for the synthesis of silicon-containing unsaturated heterocycles. The pyrolysis of dimethylsilacyclobutane in the presence of a threefold excess of butadiene afforded 1,1-dimethyl-1-silacyclohex-3-ene in 65% yield. Under these reaction conditions, the formation of tetramethyldisilacyclobutane was fully suppressed:[51]



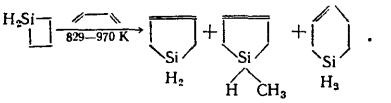
When the same source was used to generate the dimethylsilaalkene, the derivatives of silacyclobutene were isolated in the reaction with alkynes:[56]



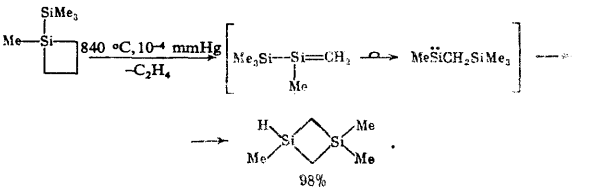
Yet another reaction of silaalkenes, namely their thermally induced isomerisation to silylenes, proved extremely useful as regards synthesis. Thus a study of the copyrolysis of 1-methyl-1-silacyclobutane with butadiene established that the main reaction product is 1,1-dimethylsilacyclopentene (a mixture of isomers), which enabled the authors to propose a scheme for their formation via the isomerisation of intermediates:[57,58]



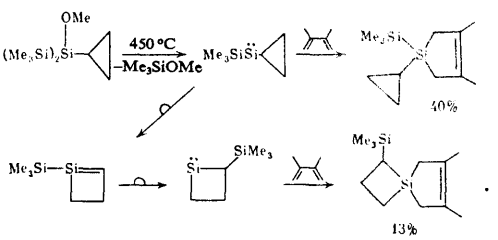
In a study of the pyrolysis of silacyclobutane in the presence of a chemical "trapping agent" for the intermediates in a high vacuum flow system, three heterocyclic compounds were identified—the products of the reactions of silylene, methylsilylene, and silaalkene with butadiene:[59]



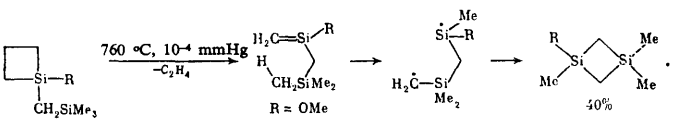
The quantitative formation of 1,1,3-trimethyl-1,3-disilacyclobutane from 1-methyl-1-(trimethylsilyl)-1-silacyclobutane under the conditions of vacuum pulse pyrolysis can also be treated as a process proceeding via the silene–silylene rearrangement:[60]



It is striking that the copyrolysis of 2-cyclopropyl-2-methoxyhexamethyltrisilane in the presence of a sixfold excess of 2,3-dimethylbutadiene led to the main reaction product (a substituted silacyclopentene) via the usual "silylene" scheme. On the other hand, the authors attribute the formation of the spiro-product to a complex silylene–silene–silylene rearrangement illustrated schematically below:[61]



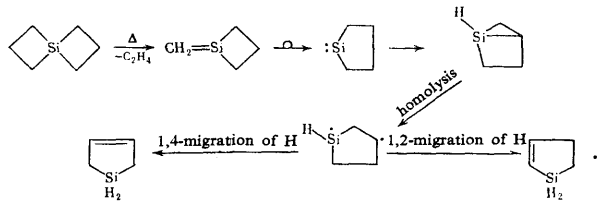
Yet another new rearrangement of silene has been recently proposed[62] in relation to the thermal reactions of certain silyl derivatives of silacyclobutane.[62] Methyl-substituted 1,3-disilacyclobutanes with the methoxy-group at the silicon atom have been obtained on the basis of this rearrangement:



The process is concluded by the ejection of ethylene from the initial compound with formation of an intermediate silene, the subsequent 1,5-shift of a hydrogen atom in it, and subsequent recombination of the 1,4-radical.

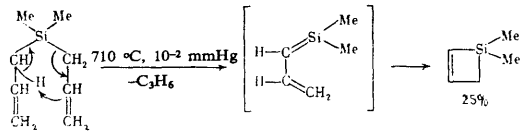
The thermal decomposition *in vacuo* of silaspiro[3,3]heptane is also of theoretical interest.[62,63] The principal products of this reaction are 1-silacyclopentenes. It may be that the primary stage of the process is the formation of a silacyclic silene with its

subsequent rearrangement to a silylene, whose further reactions are presented in the scheme below:

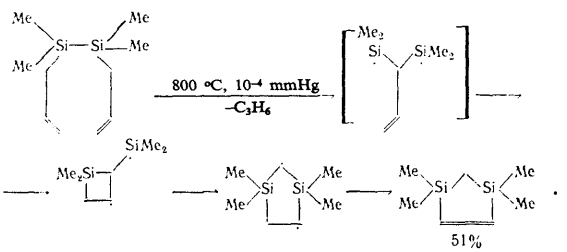


3. Synthesis with participation of siladienes

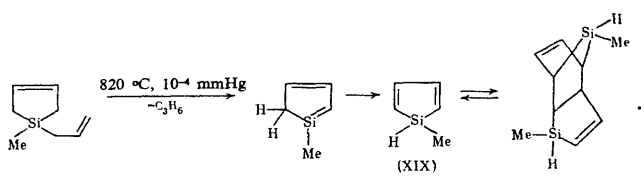
A simple single-stage method of synthesis of 1,1-dimethyl-1-silacyclobutene under the conditions of the vacuum pyrolysis of diallyldimethylsilane was proposed in 1978.[64] The authors put forward a novel scheme for the formation of the heterocycle involving the generation of an unstable compound with an unsaturated bond involving the silicon atom and a diene group (1-silabuta-1,3-diene) in the retroene elimination of propene from the initial compound with subsequent cyclisation of the intermediate:



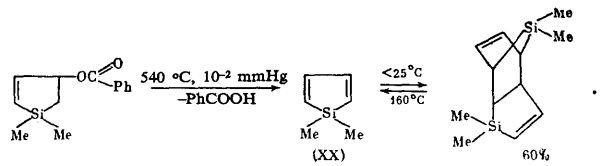
Later a similar scheme was widely used[65–69] in novel syntheses of silicon-containing heterocycles, including monocyclic compounds.[65–67] Thus the pyrolysis of 1,2-diallyl-1,1,2,2-tetramethyl-1,2-disilane yielded 1,1,3,3-tetramethyl-1,3-disilacyclopentene:[65]



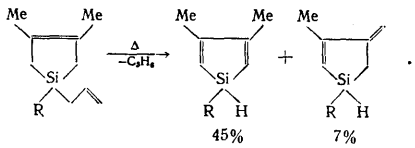
A pathway leading to the synthesis of methyl-1-silacyclopenta-2,4-diene (XIX) in the vacuum pyrolysis of 1-allyl-1-methyl-1-silacyclopent-3-ene has been put forward:[66,67]



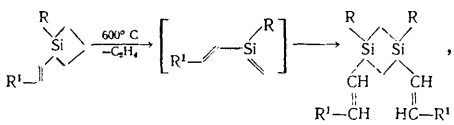
The heterocycle (XIX) was not isolated in a pure form, but its dimer was obtained in 74% yield. The thermolysis of the dimer at 150 °C leads to the formation of compound (XIX), which produces an adduct with maleic anhydride. 1,1-Dimethyl-1-silacyclopentadiene (XX) was synthesised by the vacuum pyrolysis of 4-benzoyloxy-1,1-dimethyl-1-silacyclopent-2-ene:[70]



In the absence of a trapping agent, compound (XX) dimerises at room temperature but can be regenerated on thermolysis of the dimer. In 1986 a group of French investigators[71] succeeded in obtaining the first stable *C*-methyl-substituted 1-silacyclopentadiene containing a Si–H bond:

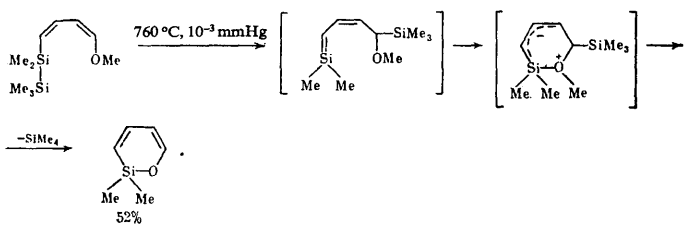


Examples of the thermal transformations of certain silacyclobutanes vinyl-substituted at the silicon atom, proceeding via a hetero-1,3-diene with formation of divinyldisilacyclobutanes, are also known:[72]

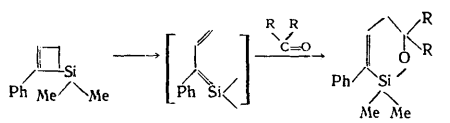


R = Me, R¹ = H; R = Me, R¹ = Ph; R = R¹ = Me; R = Ph, R¹ = H.

The thermal synthesis of certain oxygen-containing silicon heterocycles with participation of siladienes also proved to be possible. An interesting version of the synthesis of 2,2-dimethyl-1-oxa-2-silacyclohexadiene has been described.[73] The scheme for the vacuum pyrolysis of the pentamethyldisilane derivative of buta-1,3-diene includes the generation of a sildadiene intermediate with subsequent elimination of tetramethylsilane:



The copyrolysis of 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene with acetone or formaldehyde in the gas phase also leads to the formation of heterocycles with the Si–O fragment.[74] The authors suggest the intermediate formation of the siladiene intermediate (XXI):

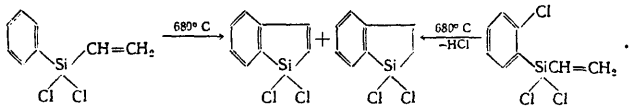


R = Me, 38%; R = H, 35%.

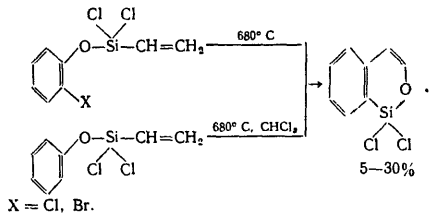
III. Bicyclic compounds

1. Bicyclic compounds with one silicon atom in the ring

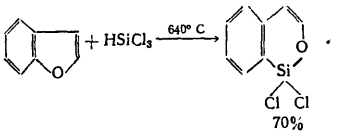
The thermal method proved to be extremely fruitful in the synthesis of bicyclic heterocyclic systems with silicon atoms in the ring. 1,1-Dichloro-1-silaindene was synthesised in a low yield for the first time, simultaneously with 1,1-dichloro-1-silaindan, by the intramolecular thermal cyclisation of dichlorophenylvinylsilane:[8,14,75]



The formation of heterocycles can be explained by the successive occurrence of two stages: the intramolecular thermal alkylation of the initial compound to a saturated heterocycle—1,1-dichloro-1-silaindan—and its subsequent thermal dehydrogenation. The intramolecular dihydrochlorination of dichloro(*o*-chlorophenyl)-vinylsilane also proceeds similarly.[8,75] The pyrolysis of dichlorophenylvinylsilane in the presence of halogenohydrocarbons (chloroform, methylene chloride, chloroethylenes, and hexachloroethane) resulted in an increase in the yield of 1,1-dichloro-1-silaindene to 30% and there was an appreciable rise in the process selectivity—the saturated analogue was not detected and in addition the temperature of the reaction zone was reduced to 520–550 °C.[8,76] The copyrolysis of dichloro(*o*-chlorophenyl)vinylsilane in the presence of another initiator, namely hexachlorodisilane, led to a similar positive result.[8] Using the same principle of pyrolytic synthesis as in the preparation of 1,1-dichloro-1-silaindene, it is possible to cyclise also a series of organosilicon compounds containing the Si–O fragment:

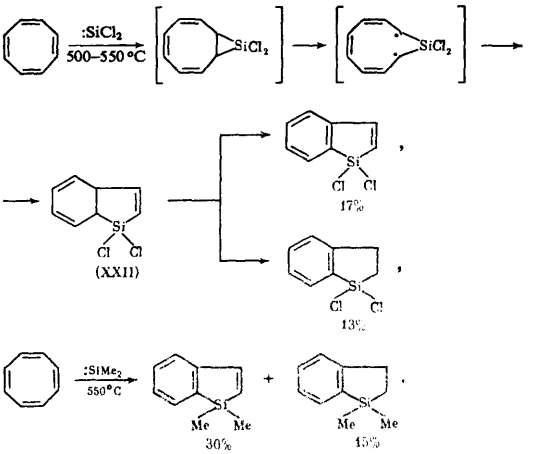


1,1-Dichloro-2-oxa-1-sila-1,2-dihydronaphthalene can be obtained also by the thermal expansion of the benzofuran ring in the presence of trichlorosilane:[8,38–40]

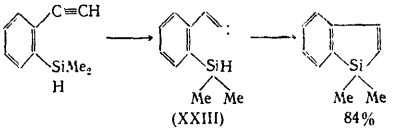


The high yield of the target compound and the ready availability of the starting material make it possible to regard this reaction as a preparative method of synthesis of oxasiladihydronaphthalene.

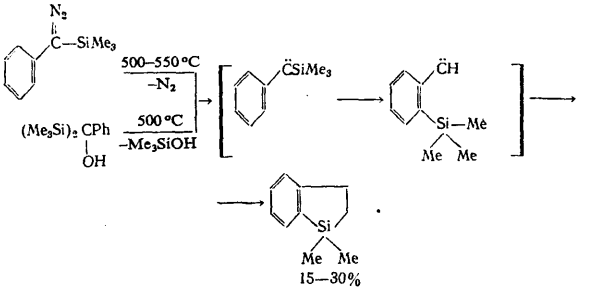
Another method of synthesis of the heterocyclic 1-silaindene and 1-silaindan structures involves the pyrolytic interaction of cyclooctatetraene with hexachlorodisilane[2,8,14,78] and 1,2-dimethoxy-1,1,2,2-tetramethyldisilane,[79] which are sources of dichloro- and dimethyl-silylenes in the gas phase. Tentatively, the 1,2-adduct isomerises to the heterocycle (XXII), which undergoes aromatisation at high temperatures:



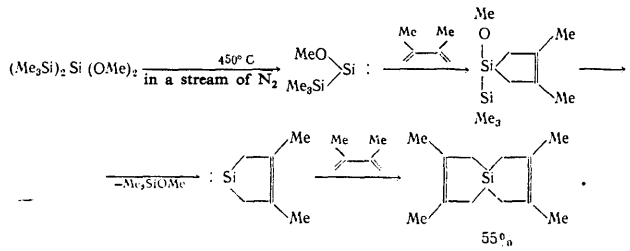
Finally, the specific properties of certain phenylsilylcarbenes, formed in the pyrolytic process from a series of phenyl-substituted organosilicon compounds, have also been used[80–83] for the synthesis of 1,1-dimethyl derivatives of silaindene and silaindan. The recently described study[80] of the vacuum pyrolysis of *o*-dimethylsilylphenylacetylene is novel in this sense. The scheme for the synthesis of 1,1-dimethyl-1-silaindene in this reaction, put forward by the authors, includes the thermally induced acetylene–vinylidene rearrangement of the initial compound to the carbene (XXIII) with the subsequent insertion of the resulting intermediate in a Si–H bond. The high yield of the heterocycle merits special attention:



Well argued evidence for the formation of 1,1-dimethyl-1-silaindan via the intramolecular reactions of phenyltrimethylsilylcarbene has been published in a series of communications.[81–83] The sources from which this α-silylcarbene was generated are phenyltrimethylsilyldiazomethane[81,82] and phenyl-1,1-bis(trimethylsilyl)methanol:[83]



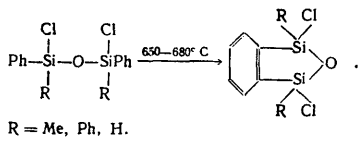
The copyrolysis of 2,2-dimethoxyhexamethyltrisilane in the presence of an excess of dimethylbuta-1,3-diene in accordance with the scheme[84]



may serve as a preparative method of synthesis of 5-silaspiro[4,4]nona-2,7-diene.[84]

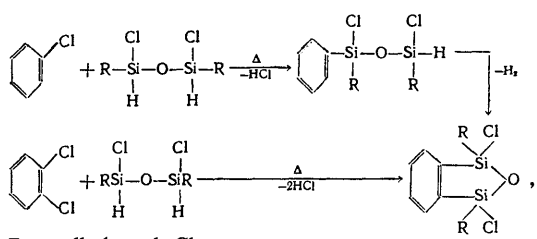
2. Bicyclic compounds with two silicon atoms in the ring

The study of the pyrolytic reactions of various 1,3-diphenyldisiloxanes substituted at a silicon atom has led to the discovery of a new intramolecular cyclisation reaction with elimination of a benzene molecule:[85–87]



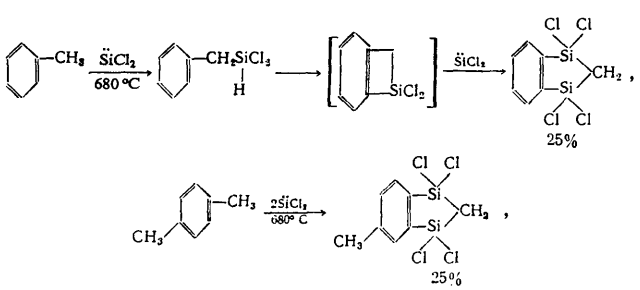
R = Me, Ph, H.

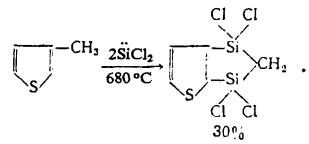
Representatives of a new class of silicon heterocycles—derivatives of 2-oxa-1,3-disilaindan—have been obtained in this reaction in 20% yield. The recovery of the initial disiloxanes amounts to 50%. Heterocycles of a similar kind are also formed via a two-stage scheme—the gas-phase cocondensation of chlorobenzene or *o*-dichlorobenzene with organodihydrodisiloxanes and the subsequent intramolecular cyclisation of the hydrodisiloxane formed:[87,88]



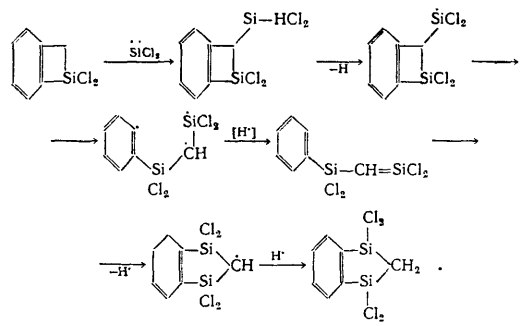
R = alkyl, aryl, Cl.

The formation of heterocyclic structures with the disilmethylene group proved possible in the thermal interaction of a series of methyl-substituted aromatic hydrocarbons with a source of dichlorosilylene such as hexachlorodisilane:[2,3,8,14,89–91]



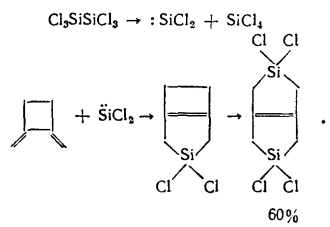


Compounds with a Si—Si bond have not been detected. It may be that conditions for the cyclisation of the primary product of the insertion of $:SiCl_2$ into benzosilacyclobutene are achieved in the first place in this reaction. The next stage represents formally the insertion of $:SiCl_2$ in the $C_{ar}-C_{alk}$ bond of the strained four-membered ring. Bearing in mind the available literature data concerning the insertion of carbenes in the benzyl carbon—hydrogen bond,[92] presumably here too the same type of insertion of the carbene analogue takes place with subsequent elimination of the silyl hydrogen atom. Subsequently, the weakened $C_{ar}-C_{alk}$ bond in the molecule of the strained silacyclobutene is ruptured and the resulting structure undergoes intramolecular addition to the double bond:



The formation of 1,1,3,3-tetrachloro-1,3-disilaindan in the reaction of benzyldichlorosilane with hexachlorodisilane under the conditions investigated has been confirmed experimentally.[91]

Yet another pathway leading to the formation of heterocyclic structures with two silicon atoms has been described.[93,94] The use of 1,2-dimethylenecyclobutane as a dichlorosilylene acceptor has made it possible to synthesise a new unsaturated heterocycle—3,3,7,7-tetrachloro-3,7-disilabicyclo[3.3.0]oct-1(5)-ene:

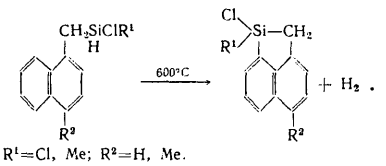


High selectivity of the reaction suggests that yet another carbenoid species is inserted immediately in the $C_{alk}-C_{alk}$ bond of the strained cyclobutene ring of the intermediate heterocycle—the primary product of the addition of $:SiCl_2$ to the conjugated system of double bonds of the initial compound.

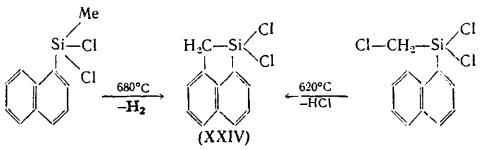
IV. Tricyclic and polycyclic silicon compounds

1. Homolytic *peri*-cyclisation reactions of naphthalene derivatives

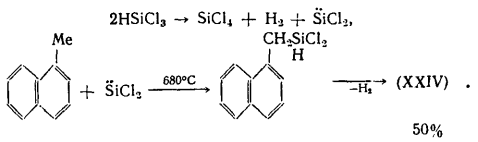
The increased reactivity of the *peri*-hydrogen atom in α-substituted naphthalenes containing the structural fragment necessary for cyclisation, which is induced by its steric interaction with the bulky substituents in the α-position, has made it possible to achieve the specific synthesis of many new classes of tricyclic and polycyclic systems with one or two silicon atoms in the ring, in which there are functional group substituents at the silicon atoms. This principle was first used to obtain a new tricyclic structure—1,1-dichloro-1-silaacenaphthene (XXIV) and its derivatives:[8,14,95-99]



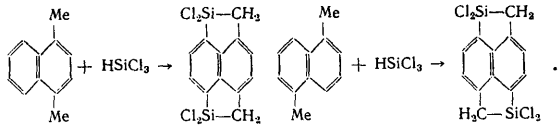
It has been established in a series of studies[8,14,97] that intramolecular cyclisation with formation of 1,1-dichloro-1-silaacenaphthene can take place not only at a Si—H bond but also at C—H and C—Cl bonds but with a lower yield of the heterocyclic compound:



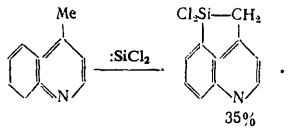
An unusual thermal cyclisation reaction was discovered in 1963 [100] when α-methylnaphthalene was allowed to interact with trichlorosilane, which also led to the synthesis of 1,1-dichloro-1-silaacenaphthene. It was established that this reaction proceeds via the insertion of $:SiCl_2$, formed in the pyrolysis of trichlorosilane,[2,101] in a C—H bond of the methyl substituent with subsequent intramolecular dehydrocyclisation of α-dichlorosilylmethylnaphthalene:[2,8,96,101]



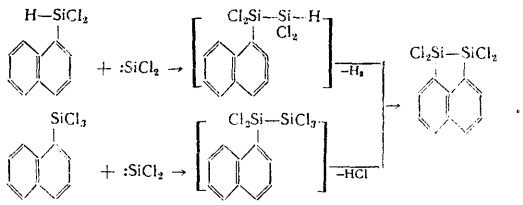
The appreciable selectivity of this interaction, the high yield of compound (XXIV), and the availability of the initial reactants stimulated the development of the method involving the high-temperature *peri*-cyclisation of naphthalene derivatives in the presence of trichlorosilane. The extension of this reaction to 1,4- and 1,5-dimethylnaphthalenes has made it possible to synthesise tetracyclic compounds with two silicon-containing bridges—the corresponding tetrachlorodisilapyracenes:[14,96,98]



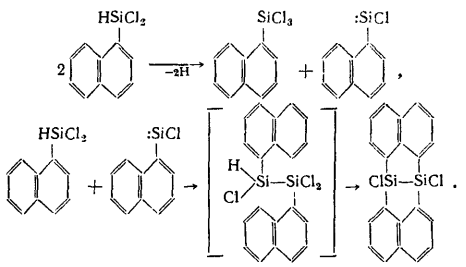
The thermal interaction of 4-methylquinoline with trichlorosilane led to the synthesis of a heterocycle containing silicon and nitrogen atoms in the cyclic system—1,1-dichloro-1-sila-5-azaacenaphthene:[102,103]



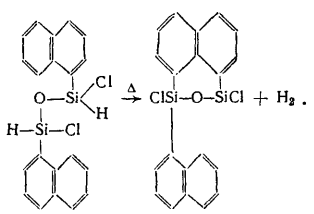
The preparation of the tricyclic 1,1,2,2-tetrachloro-1,2-disila-acenaphthene system, with an extremely stable endocyclic Si—Si bond, is synthetically extremely interesting. This compound was synthesised by the gas-phase copyrolysis of dichloro-α-naphthylsilane or trichloro-α-naphthylsilane in a mixture with trichlorosilane.[9,14,95,101] In this case, the reaction proceeds via the insertion of dichlorosilylene in a Si—H bond and even a Si—Cl bond in the corresponding chloro-α-naphthylsilanes:



The gas-phase pyrolysis of dichloro-α-naphthylsilane in the absence of trichlorosilane led to the formation of yet another heterocyclic system with an endocyclic Si—Si bond, which has no hydrocarbon analogues, namely dichlorobis(1,8-naphthylene)disilane.[2,14,104,105] The "silylene" mechanism of the formation of this heterocycle, postulating the insertion of the intermediate chloro-α-naphthylsilylene in a Si—H bond of the initial compound, is the most probable:

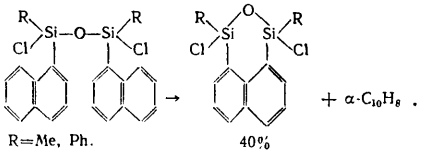


The possibility of the *peri*-cyclisation of the intermediate insertion product has been confirmed by the synthesis of 1,3-dichlorobis-(1,8-naphthylene)disiloxane by the intramolecular dehydrogenation of the corresponding symmetrical disiloxane:[2,14,87,106]

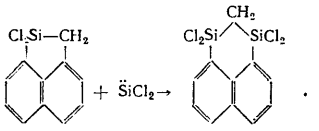


Other thermal reactions of symmetrical disiloxanes with α-naphthyl groups are also of preparative interest. The gas-phase pyrolysis of these compounds eliminates naphthalene and leads to the formation

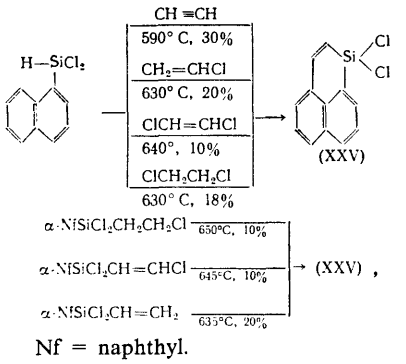
of representatives of a new class of silicon heterocycles—the organochloro-derivatives of 2-oxa-1,3-disilaphenalan:[2,14,87,107]



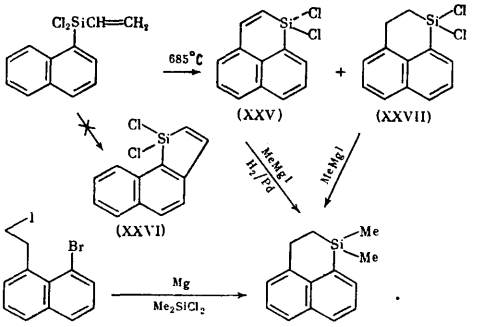
Similar disilaphenalan structures, where the silicon atoms are linked up to form a six-membered heterocycle via a methylene bridge, have been obtained by the thermal interaction of 1,1-dichloro-1-sila-acenaphthene with trichlorosilane. Formally, the formation of 1,1,3,3-tetrachloro-1,3-disilaphenalan can be represented as the insertion of :$SiCl_2$ in the $C_{ar}-C$ bond:[2,14,101]



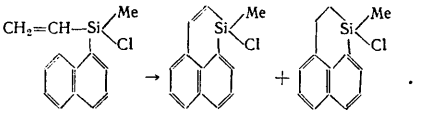
The mobility of the hydrogen atom in the *peri*-position in α-substituted naphthalenes has made it possible to achieve also a series of other thermal reactions designed to obtain a new tricyclic 1,1-dichloro-1-silaphenalene system (XXV), where the silicon atom is incorporated in an unsaturated six-membered ring.[95,108,109] The common features of these reactions are the presence in the initial reactants of, on the one hand, the dichloro-α-naphthylsilyl group and, on the other, of a two carbon atom fragment necessary for the formation of a bridge between the silicon atoms and the C(8) carbon atom of naphthalene:



A detailed study of the pyrolysis products of dichloro(α-naphthyl)-vinylsilane was undertaken somewhat later.[110] The authors doubted the validity of the postulated structure of compound (XXIV) as a *peri*-cyclisation product. On the basis of literature and their own data indicating the impossibility of obtaining a stable hydrocarbon analogue—the α-halogenophenalene—it was suggested that 1,1-dichloro-1-silaphenalene is thermally unstable and that its structural isomer—the heterocycle (XXVI)—is therefore formed in the pyrolytic reaction investigated. However, two heterocycles, (XXV) and (XXVII), were isolated in the pyrolysis of dichloro-(α-naphthyl)vinylsilane. Their structures were confirmed by the specific synthesis of 1,1-dimethylsilaphenalan:

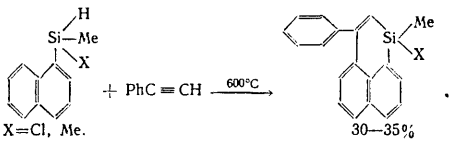


Having thus recognised that the pyrolysis of dichloro(α-naphthyl)-vinylsilane is the best method of synthesis of the heterocycle (XXV), the authors synthesised by this method also 1-chloro-1-methyl-1-silaphenalene mixed with its saturated analogue:

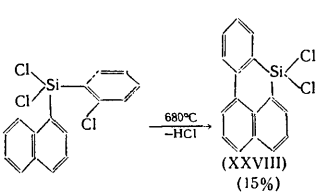


The overall yield of the heterocycles was 25%.

1-Chloro-1-methyl- and 1,1-dimethyl-1-silaphenalenes have been obtained by the thermal interaction of acetylene with chloromethyl-(α-naphthyl)silane and dimethyl(α-naphthyl)silane respectively.[111] Phenylacetylene enters into an analogous *peri*-cyclisation reaction:

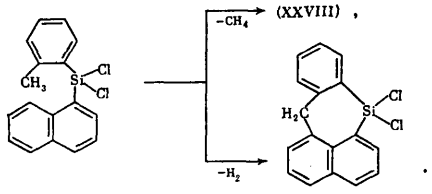


The position of the phenyl substituent in the 1-silaphenalene derivative synthesised has been confirmed by X-ray diffraction data.[111] A more selective method has been proposed[2,14,112] for the synthesis of 1,1-dichloro-1-silaphenalene—by the thermal cyclisation of dichloro(α-naphthyl)vinylsilane in the presence of process initiators (halogenohydrocarbons); the temperature of the reaction zone is then also appreciably reduced (to 520–550 °C). For example, the pyrolysis of dichloro(α-naphthyl)vinylsilane in the presence of hexachloroethane or tichloroethylene leads to the formation of the heterocycle (XXV) in a yield up to 50–60%. The method of the pyrolytic *peri*-cyclisation of naphthalene derivatives has been used successfully also for the synthesis of a new tetracyclic structure—1,1-dichloro-1-sila-2,3-benzophenalene (XXVIII).[2,14,113,114] The latter was synthesised by the intramolecular cyclisation of dichloro(*o*-chlorophenyl)(α-naphthyl)silane:



Compound (XXVIII) is formed also from another *ortho*-derivative—dichloro(α-naphthyl)(*o*-tolyl)silane. However, in this case the

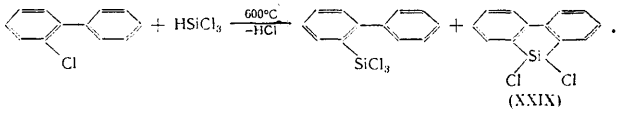
thermal reactions are not so selective and proceed via two mechanisms with ejection of H_2 or CH_4:



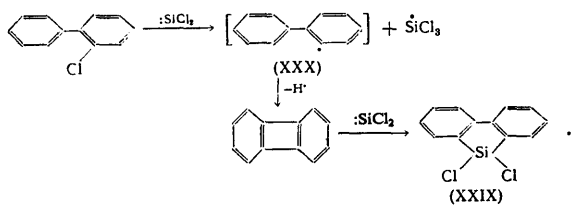
The reaction in which methane is ejected can be accounted for by the tendency to cyclise to a more stable six-membered heterocyclic structure.

2. Thermal cyclisation of *ortho*-substituted biphenyls

The successful use of the mobility of the hydrogen atom in the *peri*-position in α-naphthalene derivatives in order to build up silicon-containing rings aroused interest in the similar cyclisation of *ortho*-substituted biphenyls, which are also a classical example of the manifestation of steric interactions in the aromatic series. The mobility of the *ortho*-hydrogen atoms of *o*-silylbiphenyls has made it possible to devise novel high-temperature methods for the synthesis of new tricyclic silicon-containing structures—the analogues of fluorene and phenanthrene. It was shown[2,115,116] that the interaction of *o*-chlorobiphenyl with trichlorosilane at 600 °C results in the formation of *o*-trichlorosilylbiphenyl, while the subsequent intramolecular cyclisation at higher temperatures (680–700 °C) leads to 9,9-dichloro-9-silafluorene (XXIX) in 45% yield:

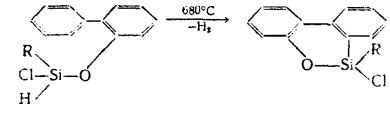


This reaction was the first example of homolytic silylation involving such a high yield with participation of the Si–Cl and C–Ar–H bonds, for which reactions of this type are uncharacteristic. Evidently, the presence of appreciable steric hindrance in the *o*-trichlorosilylbiphenyl molecule and the impossibility of overcoming it without the rupture of the bonds indicated as well as the high temperature of the reaction zone led to the cleavage of the Si–Cl and C_{ar}–H bonds. A new more effective method of synthesis of the heterocycle (XXIX), by the thermal interaction of *o*-chlorobiphenyl with hexachlorodisilane, has been proposed recently;[117] the heterocycle (XXIX) is formed under milder conditions (500–550 °C) and in a higher yield (up to 80%). The principal side product is biphenyl. It is extremely remarkable that *o*-trichlorosilylbiphenyl, which can be regarded in this reaction as the product of the insertion of $:SiCl_2$ and the C_{Ar}–Cl bond of *o*-chlorobiphenyl, is formed in an insignificant yield (up to 5%). The hypothesis of its possible instability under the reaction conditions in the presence of hexachlorodisilane was not confirmed. These factors made it possible to put forward a reaction mechanism via biphenylenes:



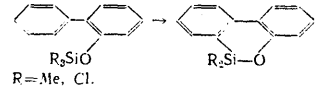
Evidently, the selective abstraction of a chlorine atom from the initial compound by dichlorosilylene leads to the appearance of the radical (XXX), capable of intramolecular cyclisation to biphenylene. On the other hand, the formation of the heterocycle (XXIX) can be regarded as a result of the insertion of $:SiCl_2$ in the strained biphenylene ring. An increase in the $:SiCl_2$ concentration in the reaction mixture increases the yield of the heterocycle, which agrees fully with the proposed reaction mechanism.

The thermal method for the synthesis of silicon-containing heterocycles by the pyrolysis of siloxybiphenyls proved to be extremely fruitful. In contrast to *o*-trichlorosilylbiphenyl, in the latter compounds the relative positions of the atoms seemingly give rise to a much smaller probability of the interaction of the Si–H bonds with the *ortho*-hydrogen atom of the biphenyl group. However, in this case intramolecular cyclisation takes place successfully—the main reaction products are new cyclic compounds with two heteroatoms containing functional group substituents at the silicon atom—derivatives of 9-oxa-10-sila-9,10-dihydrophenanthrene:[2,40,118,119]

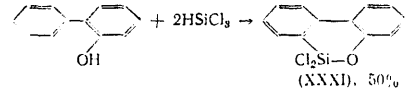


The yield of the heterocycle is ~60% for R = Cl and 30–35% for R = Me or Ph.

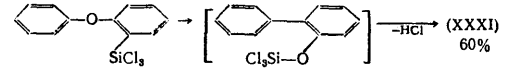
The cyclisation of *o*-siloxybiphenyls can proceed not only at a Si–H bond but also at other bonds involving the silicon atom. However, the yield of the heterocycles is then appreciably lower:[39]



The version of the pyrolytic synthesis of 10,10-dichloro-9-oxa-10-sila-9,10-dihydrophenanthrene (XXXI) from *o*-hydroxybiphenyl, which does not include the stage involving the specific synthesis of *o*-dichlorosiloxybiphenyl, is of great preparative value:[40,120]



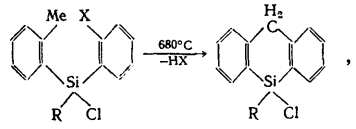
The pyrolysis of phenyl *o*-trichlorosilylbiphenyl ether also leads to the formation of the heterocycle (XXXI). In this case, the cyclisation is accompanied by a rearrangement with formation of the Si–O fragment:[40]



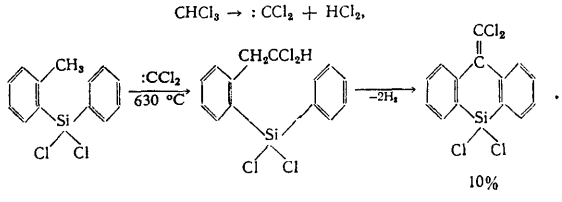
3. Thermal cyclisation of *o*-silylbenzenes

The high-temperature method for the cyclisation of various *o*-substituted benzenes, in which one of the substituents is the silyl group, has opened up extensive possibilities for the synthesis of silicon-containing tricyclic systems. Thus 9-sila-9,10-dihydroanthracenes with the chloro-substituent at the silicon atom have

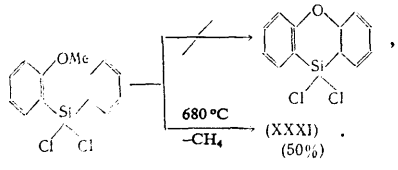
been obtained by the thermal intramolecular cyclisation of dichloro(phenyl)(*o*-tolyl)silane or dichlorobis(*o*-tolyl)silane with ejection of hydrogen or methane:[2,14,95,121,122]



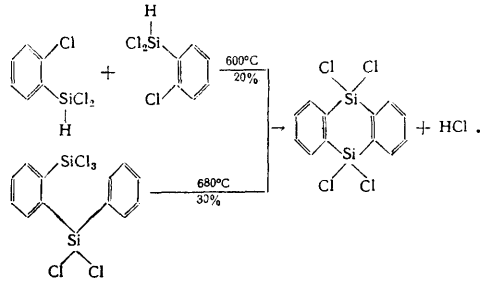
The reactions are distinguished by a high specificity and lead to heterocycles having only the 9-sila-9,10-dihydroanthracene skeleton. 9,9-Dichloro-10-dichloromethylene-9-sila-9,10-dihydroanthracene has been isolated in the cylisation of dichloro(phenyl)(*o*-tolyl)silane in the presence of chloroform or carbon tetrachloride.[2,14,123] Evidently this heterocyclic compound is formed with participation of dichlorocarbene and insertion of the latter in a $C_{alk}-H$ bonds of the initial reactant:



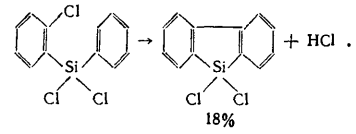
When an attempt was made to synthesise 10,10-dichloro-9-oxa-10-sila-9,10-dihydroanthracene by the pyrolysis of *o*-anisyldichloro(phenyl)silane, 10,10-dichloro-9-oxa-10-siladihydrophenanthrene was isolated instead of the expected heterocycle:[40,124]



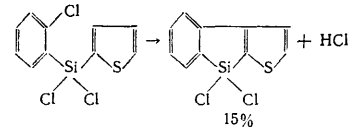
It may be that the first stage of this process is also the ejection of methane from the initial compound, but subsequently the silicon atom migrates to the oxygen atom, which is accompanied by cyclisation to the silaphenanthrene structure. The observed rearrangement with formation of the Si–O fragment is undoubtedly of theoretical interest. The heterocyclic system with two silicon atoms in the central ring—9,9,10,10-tetrachloro-9,10-disila-9,10-dihydroanthracene—was obtained by the pyrolysis of dichloro(*o*-chlorophenyl)silane.[95,124,125] The intramolecular cyclisation of dichloro(phenyl)(*o*-trichlorosilylphenyl)silane leads to the same result but with a higher yield:[2,126]



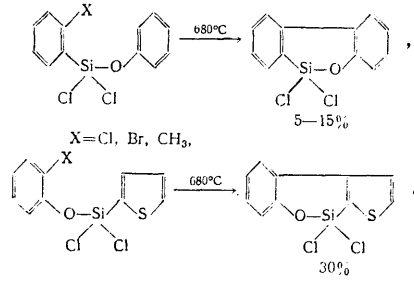
The introduction of a chlorine atom in the *o*-position in dichlorodiphenylsilane promotes the formation of another tricyclic structure—9,9-dichloro-9-silafluorene:[2,85,126]



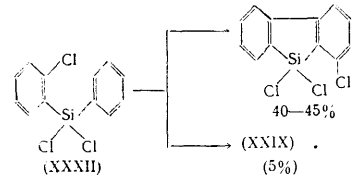
The cyclisation of another *o*-chloro-substituted derivative—dichloro(*o*-chlorophenyl)thienylsilane—takes place with ejection of hydrogen chloride:[2,85,127]



Using the same principle of the pyrolytic synthesis of silicon-containing heterocycles, it is possible to cyclise a series of organosilicon compounds in which two benzene rings are separated by the Si–O fragment instead of the silicon atom alone:[2,40]



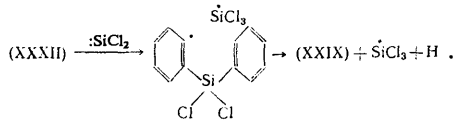
It is extremely remarkable that the copyrolysis of dichloro(*o*-chlorophenyl)phenylsilane (XXXII) with chloroform at 620 °C and with trichloroethylene at 560 °C leads to the virtually selective formation of 1,9,9-trichloro-9-silafluorene; 9,9-dichloro-9-silafluorene (XXIX), unsubstituted in the aromatic ring, was isolated from the reaction mixture in a low yield:[8,14,123]



Thus the cyclisation process takes place in this instance with a high degree of selectivity with respect to the $C_{ar}-H$ bond and not the $C_{ar}-Cl$ bond of the initial compound.

Very interesting results have been achieved in the study of the thermal interaction of a series of organosilicon *o*-chloro-compounds, for example, dichloro(*o*-chlorophenyl)phenylsilane or dichloro(*o*-chlorophenyl)thienylsilane in the presence of sources of dichlorosilylene such as hexachlorodisilane and trichlorosilane. A new gas-phase reaction, involving the formation of silicon-containing heterocycles and having no analogies in the chemistry of carbenes and other intermediates, was discovered in the course of this study. It consists in the selective abstraction of a chlorine atom from the above *o*-chloro-compounds by dichlorosilylene, which promotes the intramolecular cyclisation of these compounds, but the :$SiCl_2$

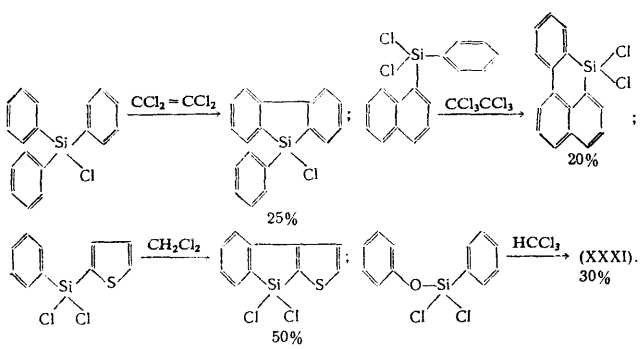
itself does not enter into the composition of the heterocycle formed.[2,14,128,129] Thus the interaction of compound (XXXII) with hexachlorodisilane at 500 °C affords 9,9-dichloro-9-silafluorene in an almost quantitative yield:



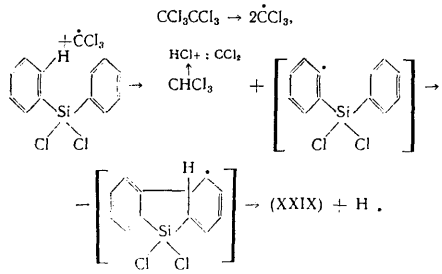
It is extremely instructive that the intermediate formation of a free radical with an unpaired electron at the *o*-carbon atom only, when the radical centre and the aromatic system are close to one another in space, leads to intramolecular cyclisation. The interaction of dichloro(*p*-chlorophenyl)phenylsilane with hexachlorodisilane under the same conditions does not lead to a cyclisation product. Dichloro(phenyl)(*p*-trichlorosilylphenyl)silane—the product of the insertion of $:SiCl_2$ in a $C_{ar}-Cl$ bond of the initial compound—was obtained in this case (yield 30%). The leading role of $:SiCl_2$ in the cyclisation process is also confirmed by the experimental data obtained in the copyrolysis of compound (XXXII) with hexachlorodisilane at the same reaction temperature but at a lower $:SiCl_2$ concentration in the reaction zone. For the reactant ratio (XXXII):HCDS = 1.0–0.5 [HCDS = hexachlorodisilane], the yield of dichlorosilafluorene falls to 40%. This factor may be associated with the fact that the trichlorosilyl radicals formed in the reaction do not participate in the cyclisation process.

4. Cyclisation of unsubstituted chloroarylsilanes

The study of the pyrolysis of unsubstituted aromatic chlorosilanes, for example, such as dichlorodiphenylsilane, dichloro(phenyl)-thienylsilane, chlorotriphenylsilane, and dichloro(α-naphthyl)-phenylsilane, at temperatures up to 700 °C showed that they do not give rise to cyclisation products. The new reaction involving the thermal cyclisation of these compounds in the presence of halogeno-derivatives of methane and ethylene as well as hexachloroethane, which we have proposed, makes it possible to obtain silicon heterocycles with fragments of aromatic systems from more readily available raw material.[8,14,123,130] For example, the pyrolysis of dichlorodiphenylsilane in the presence of $CHCl_3$, CH_2Cl_2, CH_2F_2, and CCl_4 at temperatures in the range 650–680 °C leads to the heterocycle (XXIX) in 30–40% yield. The use of di-, tri-, and tetrachloroethylenes and hexachloroethane in this reaction permits the synthesis of the same heterocycle in a yield up to 60% at a lower temperature of the reaction zone (520–580 °C).[8,14,122,130] Other aromatic organosilicon heterocycles have also been obtained similarly:



The observed thermal interaction, which evidently proceeds via a stage involving the formation of a free radical with the unpaired electron at the *ortho*-carbon atom, is most probably homolytic in character. It may be that unstable species—radicals and carbenes whose formation presupposes the thermal decomposition of the above halogenohydrocarbons—make a significant contribution to this process. The role of these intermediates apparently reduces to creating conditions for intramolecular arylation, for example, in the cyclisation of dichlorodiphenylsilane:



The preparative possibilities of the thermal cyclisation reaction discovered are far from exhausted. It can evidently serve as a basis for the synthesis of various new silicon-containing heterocyclic systems.

Thus inspection of the data presented shows that the thermal gas-phase synthesis is one of the most promising methods of synthesis of organosilicon heterocyclic compounds. The wide-scale employment of this method will undoubtedly lead to the discovery of new highly selective processes for their synthesis.

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