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Generation and reactions of silylenes in the gas phase

E A Chernyshev, N G Komalenkova
State Scientific Research Institute for the Chemistry and Technology of Heteroorganic Compounds, Moscow

ABSTRACT. Results of the investigations in recent years on the gas phase thermal reactions of both inorganic and organic silylenes have been correlated. Particular attention has been paid to the sources used for generation of these unstable intermediates and also to methods of obtaining and to the properties of cyclic silylenes.

The bibliography contains 62 references.

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I. Introduction

Much attention has been paid in recent years to the study of the synthetic possibilities of using unstable derivatives of divalent silicon, viz. the silylenes, in gas phase pyrolytic reactions and also to the search for accessible sources of these molecules.[1–16] Recent achievements in the chemistry of gas phase reactions of silylenes, which are most interesting in the authors' view, have been correlated and systematised in the present work.

II. Reactions of silylenes generated from substituted di- and polysilanes

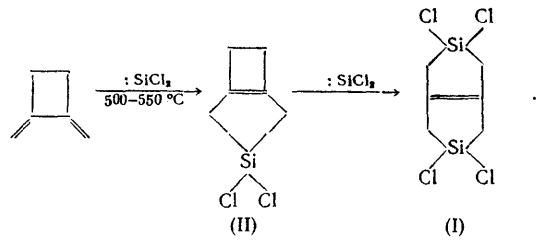
1. Addition of silylenes to multiple bonds

Thermal decomposition of various substituted disilanes in the gas phase is one of the most convenient and sufficiently general methods of generating silylenes. It was shown recently[17,18] that methyl and methylphenyl substituted cyclohexasilanes are also sources of organic silylenes in thermal reactions.

(a) Inorganic silylenes

Spectrometric investigations of gas phase reactions of addition of dichlorosilylene, generated from hexachlorodisilane, to the multiple bonds of acyclic and cyclic dienes have permitted on the one hand a significant broadening of the synthetic possibilities of the gas phase technique of thermal cyclisation and on the other the obtaining of data on the relative reactivity of various classes of compounds towards $:SiCl_2$.

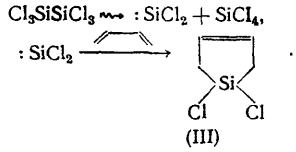
Addition of $:SiCl_2$ to such a specific diene system as 1,2-dimethylenecyclobutane leads to the formation of an unsaturated bicyclic compound with two silicon atoms in the ring, viz. 3,3,7,7-tetrachloro-3,7-disilabicyclo[3.3.0]oct-1,5-ene (I).[19] The sequence of conversions may be represented by the scheme:



(II) (I)

Seemingly the first product of addition of $:SiCl_2$ to the initial diene is the heterocycle (II) which then undergoes further insertion of $:SiCl_2$ into a C–C bond of the strained four-carbon ring. At a reagent ratio of Si_2Cl_6 : diene equal to 2 : 1 the yield of heterocycle (I) was 70%. On reducing the quantity of $:SiCl_2$ in the reaction mixture by half the yield of heterocyclic compounds fell to 25–30%.

A new method of generating dichlorosilylene by decomposing hexachlorodisilane radiochemically has been proposed.[20] 1,3-Butadiene was used as active intercepting agent for dichlorosilylene.



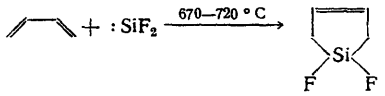
(III)

Under static conditions using an ELV-8 electron accelerator with a 30 kV beam as source of ionising radiation 1,1-dichloro-1-silacyclopent-3-ene (III) was formed at lower temperatures (200 –300 °C) than without irradiation (> 350 °C).

There is significant practical interest in the thermal interaction of perchloropolysilanes containing hydrochloropolysilanes with various acyclic 1,3-butadienes leading to the formation in almost quantitative yield of 1,1-dichloro-1-silacyclopent-3-ene or derivatives of it.[21] This method permits the use of still residues formed in processes of hydrochlorinating silicon as a source of dichlorosilylene in place of hexachlorodisilane.

The interception reaction of the highly reactive monomeric :SiF_2 in gas phase pyrolysis of hexafluorodisilane in an excess of 1,3-butadiene has recently been effected successfully.[22]

$$Si_2F_6 \rightarrow : SiF_2 + SiF_4,$$

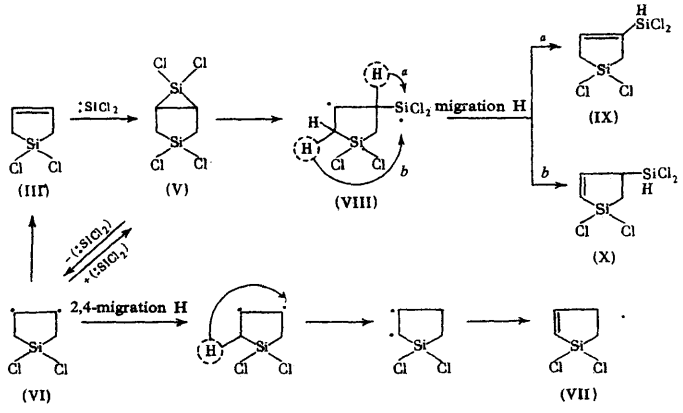


(IV), 56—75% .

The process was carried out in a flow system with a reactant contact time of 0.01—0.02 sec.

Study of the gas phase thermal isomerisation of 1,1-dichloro-1-silacyclopent-3-ene (III) into 1,1-dichloro-1-silacyclopent-2-ene in the presence of added hexachlorodisilane showed the essential role of dichlorosilylene in this process.[23] Thus isomerisation of the heterocycle in the absence of a source of :$SiCl_2$ began only at 480—500 °C but introduction of added hexachlorodisilane (4.86—16.4 mol%) into the reaction zone accelerated the isomerisation of compound (III) and reduced the temperature for the start of reaction to 380—400 °C. With an increase in the quantity of added hexachlorodisilane, and therefore an increase in :$SiCl_2$ concentration in the reaction zone, the extent of isomerisation of heterocycle (III) was increased. To explain the accelerating influence of dichlorosilylene a scheme was proposed for the isomerisation with the initial addition of :$SiCl_2$ to the olefinic bond of 1,1-dichloro-1-silacyclopent-3-ene (III).

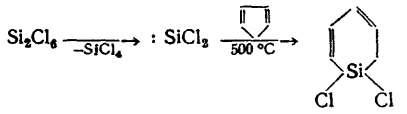
Scheme 1



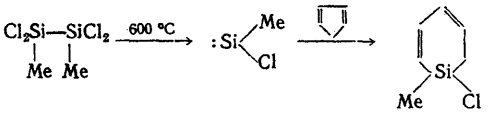
On adding :$SiCl_2$ to the multiple bond of heterocycle (III) the bicyclic compound (V) is formed which has an unstable silacyclopropane ring the decomposition of which at both intracyclic Si—C bonds leads to biradical (VI) which is subsequently converted either to the initial heterocycle (III) or (with 2,4 migration of hydrogen) to heterocycle (VII).

The proposed Scheme 1 is also in good agreement with the formation of dichlorosilyl substituted dichlorosilacyclopentenes in this reaction. Fission of one Si—C bond of the silacyclopropane ring of bicycle (V) leads to biradical (VIII) and then to a mixture of silyl-substituted heterocycles with Si—H bonds (IX) and (X) as a result of intracyclic hydrogen migration.

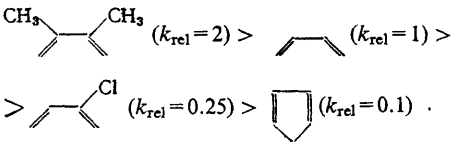
Such cyclic diene systems as cyclopentadiene (or its dimer) proved to be interesting subjects for studying the addition reaction. Reaction of hexachlorodisilane with cyclopentadiene leads to 1,1-dichloro-1-silacyclohexa-2,4-diene in 45—50% yield.



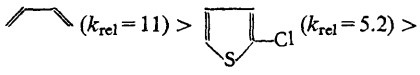
The procedure, published in our studies[2,3,5,6,24] on the thermal synthesis of this previously unavailable monocyclic silicon compound, has been reproduced repeatedly.[25,26] Thus Barton and Banasiak[27] synthesised 1-methyl-1-chloro-1-silacyclohexa-2,4-diene by thermal interaction of tetrachlorodimethyldisilane with cyclopentadiene.



A similar reaction has also been carried out in vacuum (650 °C, 10^{-2} Torr).[28] Communications have appeared recently for the first time on the relative reactivity of various classes of compounds towards :$SiCl_2$ generated thermally from hexachlorodisilane.[19,29,30] The following series of relative activities of various dienes for :$SiCl_2$ adding to multiple bonds has been established using competing reactions (flow reactor, 500 °C).[19,29]



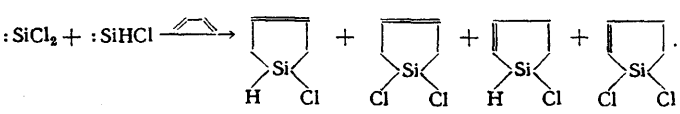
The relative reactivities of 1,3-butadiene, 2-chlorothiophen, chlorobenzene and hydrogen chloride towards :$SiCl_2$ have also been determined (flow reactor, 420—440 °C).[30]



> C_6H_5Cl (k_{rel} = 1) < HCl (k_{rel} = 0.33) .

It follows from the obtained data that aromatic chlorides are poorer acceptors of :$SiCl_2$ than 1,3-butadiene. The least effective acceptor of dichlorosilylene proved to be HCl. Its reactivity was 30 times lower than that of 1,3-butadiene.

Hexachlorodisilane and its mono- and dihydro derivatives were formed on pyrolysis of trichlorosilane in the presence of added chloroform (quartz flow reactor, 450—600 °C, 1 mol% $CHCl_3$ relative to $HSiCl_3$).[31,32] Thus at 350 °C the content of tetrachloro-, pentachloro- and hexachlorodisilanes in the pyrolysate was ~15%, and of $SiCl_4$ 25%. It is possible that the decomposition products of chloroform are capable of forming these compounds. Interaction of dichloro- and chlorosilylenes generated from the disilanes indicated above with 1,3-butadiene yields a mixture of mono- and dichlorosilacyclopentenes.[32] The maximum overall yield of chloro-substituted silacyclopentenes (21% on initial trichlorosilane) was observed at 550 °C.



It should be mentioned that monochlorosilacyclopentenes (11%) are formed at a lower temperature (510 °C).

(b) Organic silylenes

Investigations carried out recently on the study of gas phase addition reactions of organic silylenes generated from various di-, poly- and cyclohexasilanes with organic substituents on the silicon atom encompass processes both at atmospheric pressure and at high vacuum. Mainly alkynes and conjugated dienes were used as active 'interceptors' of silylenes. The principal directions of the work were as follows. At the theoretical level kinetic data were obtained on gas phase reactions of the pyrolytic formation of silylenes and the mechanisms of the reactions involving them were studied. At the synthetic level new sources for generating organic silylenes have been sought.

Among the kinetic investigations which should be mentioned is the determination of rate constants and activation parameters for gas phase reactions for the pyrolytic formation of silylenes from 1,2-dimethoxytetramethyldisilane, methoxypentamethyldisilane, 1-methoxy-1-propyltetramethyldisilane and 1,2-dimethyldisilane (pyrolysis in a nitrogen stream, 304–450 °C, ~1000 Torr).[33] The reactions studied were first order with respect to disilane. The majority of experiments with disilanes were carried out in an excess of 1,3-butadiene as a trap for silylenes to suppress secondary reactions.

There are interesting data on the reaction mechanism for the addition of $:SiH_2$ generated on pyrolysis of disilane to ethylene.[34] The obtained results made it possible to consider the interaction of $:SiH_2$ with ethylene in the gas phase as a sequential stepwise process comprising the initial formation of a silacyclopropane intermediate and subsequent conversion of it either into the starting materials or into ethylsilylene and vinylsilylene.

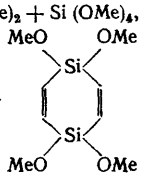
$$H_3SiSiH_3 \longrightarrow :SiH_2 + SiH_4,$$

$$:SiH_2 + CH_2{=}CH_2 \rightleftharpoons \begin{array}{l} H_2C \\ | \\ H_2C \end{array}\!\!>SiH_2 \longrightarrow \begin{cases} C_2H_5\ddot{S}iH \\ CH_2{=}CHSiH_3 \end{cases}.$$

Hexamethoxydisilane is a good source of dimethoxysilylene in the gas phase.[35] Copyrolysis of this disilane with acetylene leads to 1,1,4,4-tetramethoxy-1,4-disilacyclohexa-2,5-diene in 56% yield.

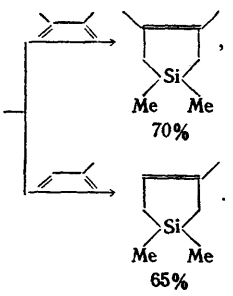
$$(MeO)_3SiSi(OMe)_3 \xrightarrow{\Delta} :Si(OMe)_2 + Si(OMe)_4,$$

$$:Si(OMe)_2 + CH{\equiv}CH \xrightarrow{370\ ^\circ C}$$

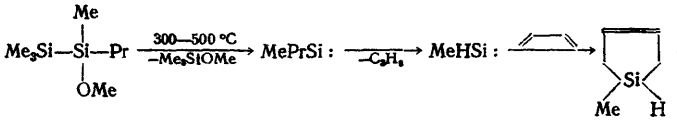


The addition of dimethylsilylene, generated thermally from 1,2-dimethoxytetramethyldisilane, to acyclic 1,3-dienes both at atmospheric pressure[36] and in vacuum[37] has been described.

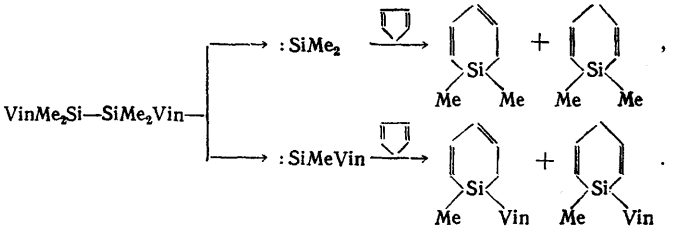
$$(MeO)\,Me_2Si{-}SiMe_2\,(OMe) \xrightarrow[-(MeO)_2SiMe_2]{450\ ^\circ C/2\ Torr} Me_2Si:$$



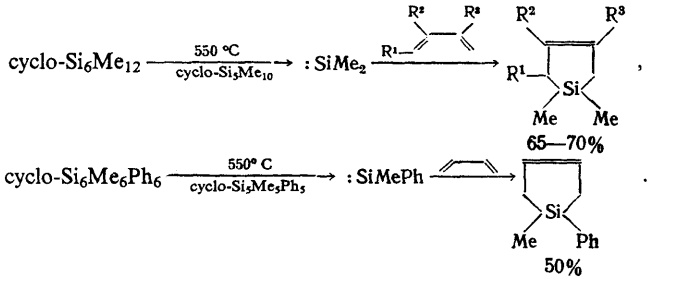
On pyrolysis 1-methoxy-1-propyltetramethyldisilane first forms PrMeSi: which is rapidly decomposed into MeHSi: and propene.[33,38]



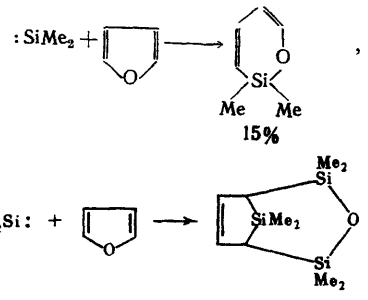
Thermal decomposition of 1,2-divinyltetramethyldisilane occurs non-selectively with the formation of dimethyl- and methylvinylsilylenes. Thus on copyrolysis of 1,2-divinyltetramethyldisilane with cyclopentadiene (650 °C, 10^{-2} Torr) substituted silacyclohexadienes are formed which are products of addition of both organic silylenes in approximately equal amounts.[39]



Studies on the thermal generation of dimethyl- and methylphenylsilylenes from dodecamethylhexaphenylcyclohexasilanes deserve special attention. These compounds were known to date only as photochemical sources of silylenes and were regarded, evidently due to their low volatility, as unsuitable for thermal reactions.[17,18] It has been shown that these cyclohexasilanes were capable of decomposing in the gas phase to the corresponding cyclopentasilanes and silylenes (flow reactor, 500–550 °C, contact time 40–60 sec).[17]

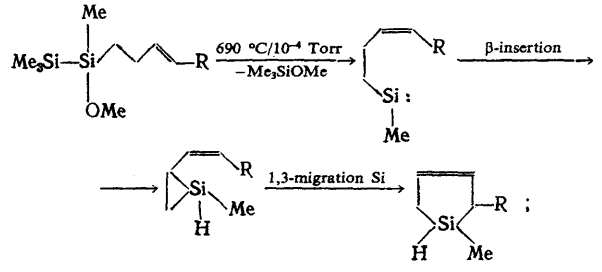


The formation of silylenes in these reactions was confirmed by the formation of silacyclopent-3-enes in the presence of 1,3-butadienes. The reaction of intercepting $:SiMe_2$, generated by pyrolysis of dodecamethylcyclohexasilanes, by furan (flow system, 500 °C) at atmospheric pressure has been studied for the first time.[18] Among the main reaction products 2,2-dimethyl-2-sila-1-oxacyclohexa-3,5-diene and the product of addition of three molecules of dimethylsilylene to furan were detected.

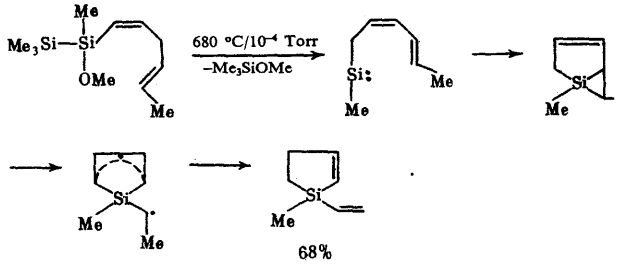


The reactions indicated above were carried out with dimethylsilylene generated by reaction of dimethyldichlorosilane with Na or K vapour at 400–500 °C.[18]

A new direction in the 'high temperature' chemistry of organic silylenes was the investigation of their intramolecular conversions. A method has been proposed for the intramolecular interception of silylenes generated from a series of methoxytetramethyldisilanes containing butenyl or pentadienyl groupings.[39] Reactions were carried out under high vacuum when generating such silylenes with a view to limiting the contribution of intermolecular reactions and secondary processes.

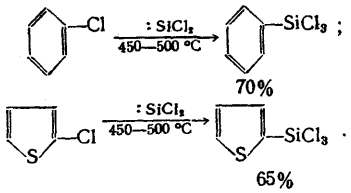


R = H, 56%; R = Me, 30%.

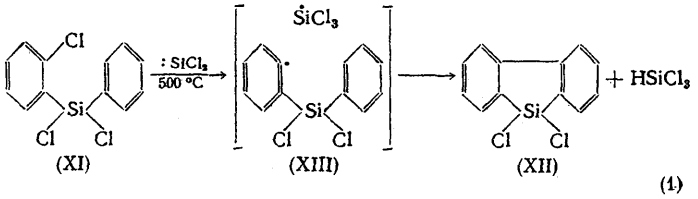


2. Gas phase thermal cyclisation reactions involving :$SiCl_2$

It was recorded previously that processes introducing dichlorosilylene, generated on pyrolysis of hexachlorodisilane, into a $C_{Ar}-Cl$ bond differ widely in selectivity.[2,4–6] They seemingly occur through a fission-recombination stage as in the reaction of singlet carbenes with the C–Cl bond.[40] Singlet :$SiCl_2$ removes a chlorine atom from the starting material with the formation of a pair of radicals. Recombination of the radicals with one another leads to the corresponding aryltrichlorosilane (separation of the radical pair is atypical for this interaction).



On studying the gas phase interaction of (*o*-chlorophenyl)phenyldichlorosilane (XI) with hexachlorodisilane (500 °C, reactant ratio 1:1) it was established unexpectedly that the main reaction product was 9,9-dichloro-9-silafluorene (XII) (90% yield).[41,42] The formation of a product of insertion of :$SiCl_2$ into a $C_{Ar}-Cl$ bond of the starting material did not occur in this case. It is interesting that compound (XI) in the absence of a source of dichlorosilylene was not subject to intramolecular dehydrochlorination with the formation of heterocycle (XII) in the range 400–550 °C and at 680 °C the yield of the latter did not exceed 18%.[43] The suggestion was made that the role of dichlorosilylene in the reaction studied is reduced merely to fission of a chlorine atom from the initial (XI) which permits intramolecular cyclisation, :$SiCl_2$ itself does not enter into the composition of the resulting reaction products.[3,5,6,43]



(1)

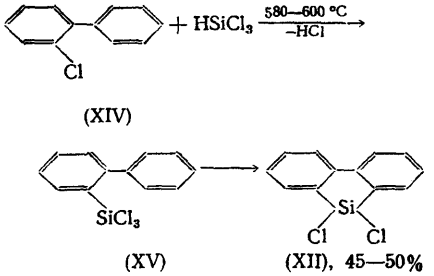
Evidently recombination of the radical pair did not occur in this case because of the increased tendency of radical (XIII) towards intramolecular cyclisation. It is extremely informative that the intermediate formation of a free radical with an unpaired electron solely at the ortho carbon atom, when the radical centre and the aromatic system are sterically close together, leads to an intramolecular cyclisation.

The interaction of (*p*-chlorophenyl)phenyldichlorosilane with hexachlorodisilane under the conditions studied leads only to the formation of (*p*-trichlorosilylphenyl)phenyldichlorosilane (30% yield).[42] *o*-(Trichlorosilylphenyl)phenyldichlorosilane, the product of inserting :$SiCl_2$ into the $C_{Ar}-Cl$ bond of compound (XI), was obtained by a different reaction;[43] up to 500–550 °C it did not undergo thermal conversions and at 680 °C cyclised by a different scheme with the formation of 9,9,10,10-tetrachloro-9,10-disila-9,10-dihydroanthracene (30% yield).

It should be noted that this gas phase reaction also occurs on using other sources of :$SiCl_2$, such as trichlorosilane and 1,1-dichloro-1-silacyclopent-3-ene in place of hexachlorodisilane.[42]

The observed gas phase reaction of dichlorosilylene has possibly no analogy in carbene chemistry and is the basis of a new general method of forming a series of silicon-containing heterocyclic systems.[3,5,6,44]

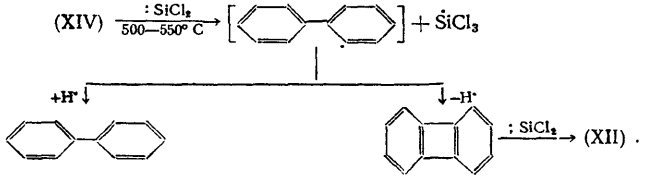
Recently this reaction was extended to ortho substituted aromatic hydrocarbons, particularly to *o*-chlorodiphenyl.[45] Formerly the high temperature synthesis of the heterocycle (XII) from *o*-chlorodiphenyl (XIV) was carried out in the presence of trichlorosilane.[46,47] It was shown that the initial step of the reaction was homolytic silylation of *o*-chlorodiphenyl (XIV) with subsequent intramolecular cyclisation of the resulting *o*-trichlorosilyldiphenyl (XV).



The significant role of temperature was noted. Heterocycle (XII) was formed only at 680–700 °C, at lower temperatures (580–600 °C) only the silylation product (XV) was detected.

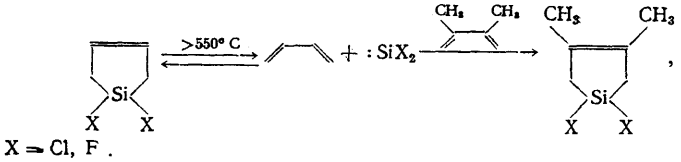
On thermal interaction of compound (XIV) with hexachlorodisilane heterocycle (XII) was formed under milder conditions and its yield was 75–80%. Diphenyl was the main byproduct. Compound (XV), which may be regarded as the product of inserting

$:SiCl_2$ into the $C_{Ar}-Cl$ bond of the initial *o*-chlorodiphenyl (XIV), was also isolated in insignificant yield (5–7%). A suggestion as to the possible cyclisation of compound (XV) at lower temperatures (500–550 °C) in the presence of hexachlorodisilane was not confirmed experimentally. These circumstances made it possible to propose another scheme for forming heterocycle (XII) through biphenylene in the reaction in question.



III. Generation of dihalosilylenes on thermal decomposition of 1,1-dichloro(difluoro)silacyclopent-3-enes and 1,1-dichloro(difluoro)silacyclohexa-2,4-dienes

The retrodiene decomposition of 1,1-dichloro- and 1,1-difluoro-1-silacyclopent-3-enes under high temperature conditions has been reported previously.[5,6,48]



X = Cl, F .

The use of the method of 'chemical trapping agents' has made it possible to obtain proof of the intermediate formation of dihalosilylenes in this reaction.

The formation of dichlorosilylene on pyrolysis of 1,1-dichloro-1-silacyclopent-3-ene (800–1400 K, pressure 10^{-1} to 10^{-2} Torr) was shown with the aid of IR spectroscopy in a solid argon matrix.[49] The direct mass spectrometric detection of primary products of vacuum pyrolysis of 1,1-dichloro- and 1,1-difluoro-1-silacyclopent-3-enes, viz. 1,3-butadiene and dihalosilanes was also effected with the aid of vacuum pyrolytic mass spectrometry.[50]

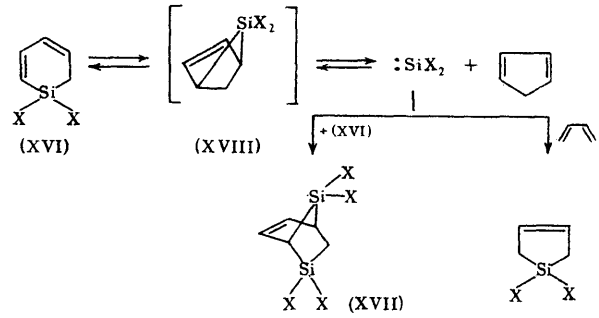
The formation of 1,1-dichloro-1-silacyclopent-3-ene in the gas phase from $:SiCl_2$ and 1,3-butadiene is thermodynamically favoured in the temperature range 300 to 1000 K.[51]

The successful demonstration of the thermal retrodiene decomposition of 1,1-dichloro-1-silacyclopent-3-ene forms a basis for the hypothesis that the gas phase interaction of $:SiCl_2$ with *symm-cis*-1,3-butadiene corresponds formally with the Diels–Alder reaction and therefore proceeds by a concerted 1,4-cycloaddition mechanism.

Pyrolysis of dihalo substituted silacyclopent-3-enes is an efficient means of generating not only dichloro- but also difluorosilylene. The preparation of monomeric $:SiF_2$ by other methods is very difficult.

1,1-Dichloro(1,1-difluoro)-1-silacyclohexa-2,4-dienes (XVI) are also capable of decomposing on pyrolysis (500–650 °C, flow system) by a retrodiene scheme with the formation of cyclopentadiene and dichloro(difluoro)silylene. The thermal decomposition of the difluoroderivative requires higher temperatures (600–650 °C).[29,52] The primary content of the pyrolysis products of these heterocycles has been studied by vacuum pyrolytic mass spectrometry.[50] Chemical proof has been obtained of the formation of dihalosilylenes on pyrolysis of these heterocycles. Thus copyrolysis of dienes (XVI) with 1,3-butadiene leads to the formation of the corresponding 1,1-dihalo-1-silacyclopent-3-enes. Pyrolysis of individual compounds (XVI) alone leads to the formation of cyclopentadiene and the 1,4-cyclo adduct (XVII) of $:SiX_2$ with the initial heterocycles probably by the following Scheme (Scheme 2).

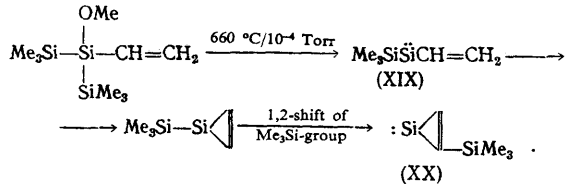
Scheme 2



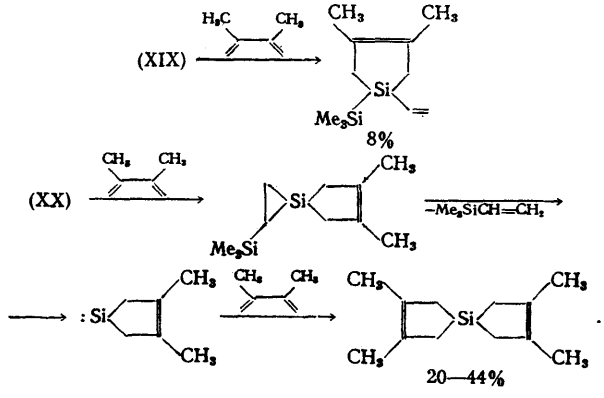
Mass spectrometric investigation of the decomposition routes of heterocycle (XVI) under electron impact also confirmed the possibility of forming the bicycle (XVIII) under these conditions.[53] The results obtained testify in favour of a 1,4-addition mechanism of $:SiCl_2$ to cyclopentadiene, however further study is required.

IV. Methods of preparation and reactions of cyclic silylenes

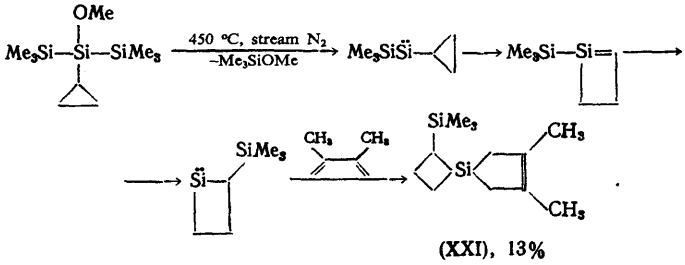
Two main routes for obtaining cyclic silylenes have been contemplated up to the present time: 1) thermal decomposition (at atmospheric pressure in a nitrogen stream or at high vacuum) of difficultly available organosilicon compounds undergoing complex intramolecular rearrangements[54–59] and 2) the use of gas phase dehalogenation of available dichloro substituted silacycloalkanes and silacycloalkenes with alkali metal vapour.[60–62] An interesting vinylsilylene intramolecular rearrangement was discovered on studying the pyrolysis of 2-methoxy-2-vinylhexamethyltrisilane.[54]



The existence of intermediates (XIX) and (XX) was confirmed by reaction of the initial trisilane with 2,3-dimethyl-1,3-butadiene.

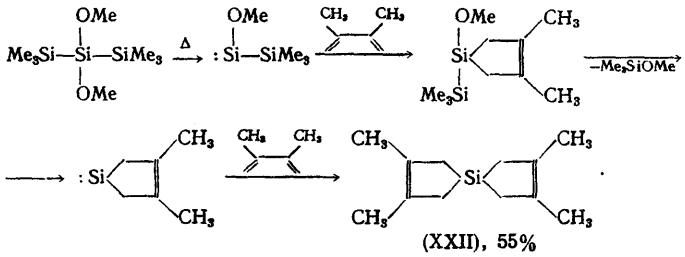


The formation of spiro compound (XXI) on copyrolysis of 2-cyclopropyl-2-methoxyhexamethyltrisilane with an excess of 2,3-dimethyl-1,3-butadiene was explained by the occurrence of a complex silylene–silene–silylene rearrangement including the formation of silacyclobutanylidene.[55]



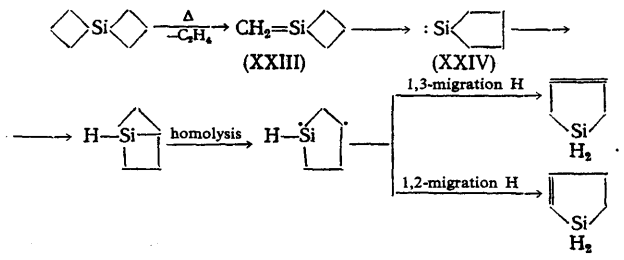
(XXI), 13%

Pyrolysis of 2,2-dimethoxyhexamethyltrisilane (450 °C, nitrogen stream) may be considered a convenient method of generating 3,4-dimethyl-1-silacyclopent-3-en-1-ylidene. Conducting the reaction in the presence of the trapping agent 1,3-dimethyl-1,3-butadiene leads to the formation of spiro compound (XXII).[56]

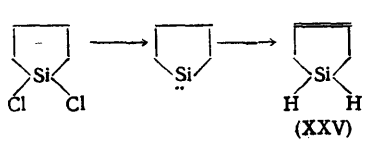


(XXII), 55%

Interesting results were obtained when studying the vacuum thermal decomposition of 3,3-silaspirocycloheptane.[57–59] It was assumed that the first stage of this process was the formation of silene (XXIII) which underwent rearrangement into silylene (XXIV) and subsequent intramolecular conversion as a result of which 1-silacyclopent-2-ene or 1-silacyclopent-3-ene were formed.

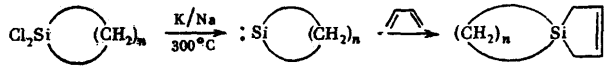


A gas phase method of generating silacycloalkanylidenes by reaction of dichlorosilacycloalkanes with alkali metal vapour (K/Na, 280–300 °C, 10^{-1} to 1.0 Torr) has been described,[60,61] for example:



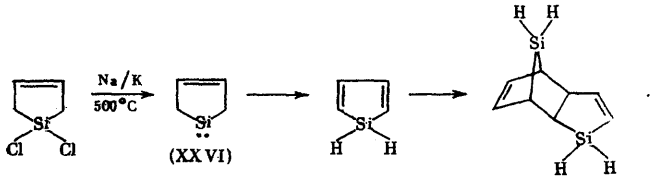
(XXV)

The formation of (XXV) is explained by intramolecular insertion of the initially formed unstable silacyclopentanylidene into the β C–H bond and subsequent conversion of the bicyclic intermediate. The cyclic silylenes obtained by dehalogenation are able to participate in [1 + 4] cycloaddition reaction with dienes such as 1,3-butadiene.

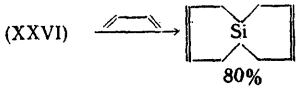


$n = 3 - 5$

The availability of the initial reactants makes the dehalogenation of organochlorosilanes by K/Na vapour a convenient method of generating cyclic silylenes and synthesising various spirane compounds with a central silicon atom.[62] For example reaction of 1,1-dichloro-1-silacyclopent-3-ene (500 °C, atmospheric pressure, argon atmosphere) with an excess of sodium or potassium leads to the formation of 1-silacyclopent-3-en-1-ylidene (XXVI).



The formation of (XXVI) was proved by trapping it with 1,3-butadiene.



80%

Investigation of the gas phase reactions of silylenes is developing intensively at the present time. In this project the thermal method must be considered as one of the most promising and hopeful, the wide use of which will lead to the discovery of both still unknown properties of silylenes and of sources for their generation.

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