Formation and Properties of Unstable Intermediates Containing Multiple p_π–p_π Bonded Group 4B Metals

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I. Introduction

A. General Considerations

The formation of multiple p_π–p_π bonds is a well-known property of the first-row elements, namely, of carbon, nitrogen, and oxygen. A great body of experimental data is available on organic compounds containing isolated, conjugated, and cumulated carbon–carbon double bonds, alkynes, aldehydes, ketones and carboxyl compounds, azomethines, nitriles, azo and diazo compounds, and azides. Multiple bonds are present in such inorganic molecules as nitrogen, oxygen, carbon dioxide, etc. Recently borabenzene π complexes, boraarene anions, and thioborine containing double p_π–p_π bonded boron atom have also been obtained.[1–4]

In contrast to the first-row elements, their heavier congeners are reluctant to form stable molecules involving p_π–p_π bonding. Single compounds of this type were known only for sulfur, tellurium, and arsenic.[5,6] To explain why the p_π–p_π bonds formed by second- and subsequent-row elements are unstable (or

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nonexistent),[5,7-9] one is generally referred to the large size of atoms reducing the sideways overlap of the p orbitals[10-18] or the diffuse nature[19,20] or the high energy[21] of (np) orbitals with $n > 2$.

The low stability of the compounds containing multiple bond between elements of the second and subsequent rows was first considered theoretically by Pitzer,[22] who postulated that the low π-bond strength was due to the repulsion between the bonding p_x orbital of one atom and the filled inner shell of the other atom ("inner-shell repulsion"). It is evident that such a repulsion foɪ molecules with double bonds between first-row elements is not significant, as the inner shell contains only two electrons. The role of repulsion energy in weakening multiple bonds is emphasized in a monograph.[23] Mulliken[24] calculated overlap integrals of atomic orbitals for 2s–2s, $2p_\sigma$–$2p_\sigma$, $2p_\pi$–$2p_\pi$ and 3s–3s, $3p_\sigma$–$3p_\sigma$, and $3p_\pi$–$3p_\pi$ bonds. It was found that the repulsion postulated by Pitzer would not be larger for the second-row elements as compared with elements of the first row. Therefore, the inner-shell repulsion is hardly the reason for absence of multiple p_π–p_π bonds between heavier elements. Moreover the overlap integrals calculated for multiply bonded silicon proved to be higher than for carbon. Mulliken believes that the observed tendency of heavier elements to form single bonds is not the result of the loosening of multiple bonds, but of a lesser tightening of multiple-bonded atoms compared to the single bonded ones; i.e., "the difference between first- and second-row atoms with respect to readiness of formation of multiple bonds . . . are shown to be attributable to strengths of σ bonds in the second row".

Based on the conclusion drawn by Mulliken,[24] Gilman and Dunn[25] assumed that the absence of silicon–carbon double bonds may be explained by the much more favorable ratio of energies of two single bonds and one double bond than in the case of the carbon–carbon double bond. Nevertheless, it is mentioned[25] that, contrary to the prediction of Mulliken, the single Si–Si bond is weaker than the C–C bond.

According to Beattie and Gilson,[26] "a monomer containing a double bond might occur if the efficiency of filling of the d-orbitals were not markedly affected by polymerization". In particular, the unstability of $R_2Si{=}O$ is explained by more effective use of d orbitals in a polymer compared to monomer,[26,27] although the formation of a p_π–p_π bond in the latter apparently also involves d orbitals.[28] Similarly the absence of silicon,[29] tin, and lead[30] multiple p_π–p_π bonded compounds is attributed to the greater stability of the polymer form.

Levin, Syrkin, and Dyatkina[31] believe that the π-bond strength in silicon analogs of ethylene and acetylene is too low to stabilize Si=Si or Si≡Si bonds. They calculated the value of the p_π–p_π interaction for both carbon and silicon atoms from the heats of sublimation of diamond and crystalline silicon. It was found that the value of the resonance integral β ($\beta = SI$, where S is the overlap integral and I is the ionization potential) for silicon was approximately half that of carbon.

The above-mentioned studies later on lead to the formulation of the so-called "classical double bond rule", according to which elements having a principal quantum number greater than 2 should not be able to form a p_π–p_π bond with themselves or with other elements.[1] However, this theoretical prediction was disproved by further experimental studies on unsaturated systems with multiple bonds formed by elements of second and subsequent rows. Such compounds were first obtained for phosphorus[32,33] and thereafter for other elements, i.e., arsenic, antimony, bismuth, selenium, silicon, germanium, etc.[1,34-39] Depending on the nature of heteroatom and molecular structure, they are either stable compounds or short-lived intermediates.

This review is dedicated to the problem of p_π–p_π bonding involving group 4B metals. Intense development of the problem was initiated in 1965 by the discovery of the highly selective reaction of thermal decomposition of monosilacyclobutanes,[40] which proceeds, as it was proved later on, via silicon–carbon p_π–p_π double-bonded intermediates.[41,42] A detailed study of the reaction mechanism made it possible to characterize these intermediates as a new class of organosilicon compounds having distinct properties. At present much attention is being paid to the problem of p_π–p_π bonding involving silicon and other group 4B metals. As a result, a large number of papers have appeared, which relate to generation processes, the study of the nature of double bond and its properties, and the attempts for stabilizing intermediates containing such bonds. Since the publication of previous reviews,[1,5,27,37-39] much new information has become available, which has significantly widened conceptions about p_π–p_π bonding of group 4B elements. The aim of this review is to provide a comprehensive and retrospective consideration of the developments made in this area and to characterize its present state. The discussion is classified by reactions resulting in double-bonded intermediates. The properties of these intermediates will be considered along with the reactions. Indeed, the classification of the reaction mechanism is not always based on unambiguous data, and therefore in some cases it is only a formal description of the processes. All reactions dealing with decomposition of cyclic compounds even implicated by intermediates are classified as "cycloelimination reactions" [43,44] unless they do not correspond to Hoffmann's definition[44] as "the cleavage of carbocycle or heterocycle into two or more, usually independent fragments". Intramolecular cycloaddition and reverse reactions are grouped as "electrocyclic reactions", whereas intramolecular migrations of the σ bond attached to the π-bonded atoms are called "sigmatropic reactions".[45] The following discussion involves the names of multiple p_π–p_π bonded intermediates as group 4B analogs of unsaturated compounds: silaethylene (germaethylene), silanone (germanone), thiosilanone (thiogermanone), silaimine (germaimine), etc., for example:

$Me_2Si{=}CH_2$	1,1-dimethyl-1-silaethylene
$Me_2Ge{=}CH_2$	1,1-dimethyl-1-germaethylene
$Me_2Si{=}SiMe_2$	tetramethyldisilaethylene
$Me_2Si{=}O$	dimethylsilanone

Section I.B is an exception, where the names of the compounds given in original papers have been used.

B. Historical Survey

The structures with multiple bonds at the silicon atom were used almost from the time of the appearance of organosilicon chemistry. Based on the data of the element composition of reaction products of chlorosilanes with such reagents as water, hydrogen sulfide, or ammonia, and having no conception about their possible existence as polymeric or cyclic structures, chemists of the last century believed that silicon was much analogous to carbon in its ability to form stable unsaturated compounds. With regard to the polymeric structure of "unsaturated" compounds of silicon, SiO_2 was first mentioned by Mendeleev[46] in his book "The Principles of Chemistry", published in the Russian language in 1868.

Studying the reaction of hydrogen sulfide with tetrachlorosilane at elevated temperature, Pierre[47] obtained a colorless liquid, which he assigned to "silicon sulphochloride", Cl_2SiS. Nineteen years later Fridel and Ladenburg[48] reinvestigated this reaction and found that the primary product was "silicon sulphohydrate":

$$SiCl_4 + H_2S \rightarrow HCl + SiCl_3SH$$

The latter, as shown by Blix and Wirbelauer,[49] upon prolonged standing transforms into crystalline Cl_2SiS:

$$SiCl_3SH \rightarrow Cl_2SiS + HCl$$

Similarly the aluminum bromide catalyzed reaction of hydrogen sulfide with silicon tetrabromide at 150 °C results in crystalline "silicon sulphobromide".[50]

As "silicon diethyloxid" were characterized both the products obtained by Fridel and Crafts[51] upon oxidation of tetraethylsilane and by Ladenburg[52,53] upon hydrolysis of dimethyldiethoxysilane or dimethyldichlorosilane. The strong tendency of not forming compounds with Si=O, but of groupings, in which two silicon atoms are attached to oxygen, SiOSi, or $(SiO)_x$ (a prediction made by Mendeleev[46]), was first confirmed by Stokes[54] when studying the catalytic action of $AlCl_3$ on ethoxysilanes. Dilthey and Eduardoff[55] obtained "diphenylsilicon", Ph_2SiO, on melting "diphenylsilicol", $Ph_2Si(OH)_2$. A more detailed study of "diphenylsilicon" showed[56] that its structure might be better described as the cyclic trimer.

In 1907 Kipping published his first work[57] on silicones. He obtained "phenylethylsilicon", PhEtSiO, by reacting phenylethyldichlorosilane with water. Similarly "benzylethylsilicon", BeEtSiO, and "dibenzylsilicon", Be_2SiO, were prepared.[58] To decide whether silicones have any analogy with ketones they were subjected to reactions typical for ketones,[58] and it was shown that "benzylethylsilicon" did not react with phenylhydrazine or hydroxyamine, and could not be reduced by sodium in ethanol. As "diphenylsilicons" [56] they appeared to be trimolecular compounds having properties quite different from those of ketones. Therefore, it was suggested "that silicones, as a class, differ from ketones in their ability to readily form comparatively stable molecular aggregates".[58] However, the authors did not have sufficient proof to consider the latter "as composed of loosely associated, or of chemically united, molecules".[58] More specific problems related to the production of silicones were also discussed by Robinson and Kipping.[59,60]

Stock, Somieski, and Wintgen[61] obtained a volatile product by treating dibromosilane with water; this was assigned to the silicon analog of formaldehyde resulting from the intramolecular loss of water by transient dihydroxysilane:

$$H_2Si(OH)_2 \xrightarrow{-H_2O} H_2Si{=}O \rightarrow (H_2SiO)_x$$

Because of the pronounced tendency of "oxomonosilane" to polymerize, which leads, as it was assumed, to the formation of cyclic siloxane structures (x = 2, 3, etc.), this unstable product was termed "prosiloxan". It was also obtained in the hydrolysis of dichlorosilane.[62,63] However, a detailed study of the gas-phase reaction showed[63] that the volatile product was not a monomer but a hexamer, which on standing changed to an insoluble amorphous polymer. Formation of "dimethylsilicon" was also claimed in the alkali hydrolysis of dimethylsilane.[62]

The ammonolysis of halogenosilanes leads to unsaturated products, if they are to be considered as monomer compounds. This reaction was first studied by Persoz in 1830.[64] Thereafter, it was considered by Wohler and Deville,[65] Besson,[66] Gattermann,[67] and Lengfeld.[68] In the beginning of the 20th century Vigoroux and Hugot,[69] Ruff and Albert,[70] Blix and Wirbelauer,[49] and Schwarz and Sexauer[71] also studied this reaction. Thus, Gattermann[67] described with the possible structures **1** or **2**

$$\underset{\textbf{1}}{HN{=}Si{=}NH} \quad \text{or} \quad \underset{\textbf{2}}{N{\equiv}Si{-}NH_2}$$

the product formed on the ammonolysis of tetrachlorosilane; for the ammonolysis product of trichlorosilane, the structure N≡SiH was proposed. Blix and Wirbelauer[49] studied the reaction of liquid ammonia with "silicon sulphochloride" obtained by treating tetrachlorosilane with hydrogen sulfide:

$$Cl_2SiS + 5NH_3 \rightarrow HNSiNH + 2NH_4Cl + NH_4SH$$

3

The imide **3** yielded $Si(NH)_2{\cdot}2HCl$ when treated with liquid hydrogen chloride. Based on this the conclusion was drawn that structure **1** proposed by Gattermann seemed to be more probable than structure **2**. Vigoroux and Hugot[69] assumed that silicon imides were formed in the decomposition of tetraaminosilane, a primary reaction product.

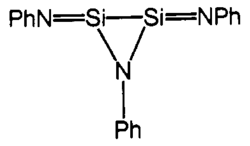
$$Si(NH_2)_4 \rightarrow 2NH_3 + HNSiNH$$

Studying the thermal decomposition of tetraanilinosilane in a hydrogen flow at reduced pressure Reynolds[72] found stepwise cleavage of aniline and formation of crystallizing products "silicotriphenylguanidine" (**4**) and "silicodiphenyldiimide" (**5**) containing, as believed, a double bond between silicon and nitrogen:

$$(PhNH)_4Si \xrightarrow{>137\ °C} \underset{\textbf{4}}{PhN{=}Si(NHPh)_2} + PhNH_2$$

$$\xrightarrow{>137\ °C} \underset{\textbf{5}}{PhN{=}Si{=}NPh} + 2PhNH_2$$

Further heating of **5** in hydrogen flow resulted in a compound described by structure **6**, whereas in ammonia the removal of a phenyl group led to postulated structure **7**.



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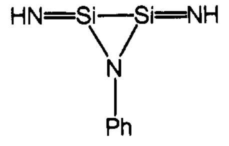

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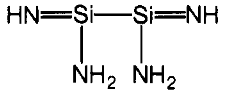
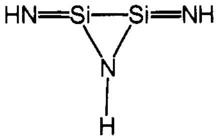
Similar compounds, but containing bromine in aromatic ring, were obtained upon bromination of tetraanilinosilane.[73]

Schwarz and Sexauer[71] did not succeed in isolating individual organosilicon compounds from the reaction of liquid ammonia with hexachlorodisilane. Instead of expected monomers **8** and **9**, nonvolatile polymer substances were obtained. This provides support for the viewpoint that the polymer form is preferred to the monomer one for organosilicon compounds.[46,58,74]



$$HN{=}Si(NH_2){-}Si(NH_2){=}NH$$

8



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The first report on the formation of compounds with silicon-carbon double bonds dates from 1912. On treating silicon tetrachloride with phenylmagnesium bromide and methylmagnesium iodide followed by decomposition of the reaction mixture with water, Schlenk and Renning[75] obtained a liquid, which according to its element composition and molecular weight was assigned structure **10**, formed upon dehydrating diphenylmethylsilanol:

$$MePh_2SiOH \rightarrow \underset{\textbf{10}}{Ph_2Si{=}CH_2} + H_2O$$

However, compound **10** did not react either with bromine or an aqueous solution of permanganate. In 1927 Kipping[76] restudied this reaction and proved that the authors had not obtained the individual compound, but a mixture of diphenyldimethylsilane, diphenylmethylsilanol, and, probably, biphenyl. The obtained diphenylmethylsilanol gradually decomposed upon heating, thereby yielding not **10** but dimethyltetraphenyldisiloxane.

Therefore, unlike tertiary alcohols, intramolecular dehydration is not typical of silanols; instead of intramolecular dehydration, generally intramolecular condensation proceeds with the loss of water and formation of a Si–O–Si bond

$$R_2SiOH(CH_2R) \nrightarrow R_2Si{=}CHR + H_2O \rightarrow R_2(RCH_2)SiOSi(CH_2R)_2 + H_2O$$

Similarly intramolecular dehydrohalogenation is not inherent in $R_2SiCl(CH_2R)$-type silane chlorides. For example, both PhEtPrSiCl and $(PhCH_2)_3SiCl$ can be distilled at relatively high temperatures without significant decomposition (even in the presence of quinoline),[76] whereas similar halogen derivatives of hydrocarbons form olefins even in vacuum distillation.

$$R_2SiCl(CH_2R) \nrightarrow R_2Si{=}CHR + HCl$$

Silicon-carbon double bonds are not formed when Grignard reagents attack tertiary chlorosilanes. The formation of tetrasubstituted silanes is preferred in this reaction, whereas the production of olefins is more characteristic for tertiary halomethanes. In the case of chlorosilanes, however, the formation of high-boiling products was hypothetically attributed to the intermediacy of a silicon-carbon double-bonded compound.[76]

The reaction of sodium with disubstituted chlorosilanes was first described as a reaction resulting in a silicon-silicon double-bonded compound:[77]

$$2PhEtSiCl_2 + 4Na \rightarrow PhEtSi{=}SiEtPh + 4NaCl$$

Kipping and Sands[78,79] isolated a crystalline product from the reaction of diphenyldichlorosilane with sodium in boiling toluene. Since the obtained compound reacted with iodine at room temperature, it was assigned the silicon-silicon double bond structure **11**. But quantitative analysis showed that 1 mol of

$$Ph_2Si{=}SiPh_2$$

11

the obtained compound added 0.5 g-mol of iodine; i.e., the addition product corresponded to $Si_4Ph_8I_2$. Therefore it was concluded[80] that the product is not **11**, but octaphenylcyclotetrasilane, Si_4Ph_8. Detailed studies[78-82] of the products formed in this reaction have shown that "the products obtained upon heating dichlorides, R_2SiCl_2, with sodium do not contain a Si=Si complex, but are either open- or close-chain structures consisting entirely of $-SiR_2SiR_2-$ groups".[83] Similarly, attempts made to obtain unsaturated compounds of silicon by reacting phenyltrichlorosilane with sodium failed. It is shown that "$C_6H_5Si{\equiv}SiC_6H_5$ cannot be obtained under such conditions; instead of this a mixture of very complex products, most of which apparently are saturated compounds, is formed".[83]

Thus, by the end of '20s and the beginning of '30s, it became clear that all attempts to obtain compounds with multiple-bonded silicon did not give satisfactory results. In other words, silicon, the closest analog of carbon, differs significantly from carbon, showing a negative tendency to form stable multiple-bonded compounds. It is this difference in the chemistry of silicon from the chemistry of carbon that, probably, led Kipping[84] to the pessimistic conclusion drawn by him in 1936 at a Bakerian lecture: "Most if not all of the known types of organic derivatives of silicon have now been considered and it may be seen how few they are in comparison with those which are entirely organic; as, moreover, the few which are known are very limited in their reactions, the prospect of any immediate and important advance in this section of organic chemistry does not seem to be very hopeful".

However, the fast development of organosilicon chemistry in the postwar period and thereafter proved a complete failure of this forecast. At the close of the '40s the investigators again directed their attention to the problem of the existence of compounds with multiple-bonded silicon. In particular, quantum chemical methods (see section I.A) were first employed to solve the problem. However, most experimental approaches led either to negative or indefinite, and sometimes to faulty, results. For example, the study of the hydrolysis of dimethyldichlorosilane and decomposition of polydimethylsiloxane[85,86] showed that cyclic siloxane oligomers (trimers and higher), but not dimethylsilanone, $Me_2Si{=}O$, or its cyclic dimer, were formed. In 1952, Andrianov and Sokolov[87] announced the existence of dialkylsilanones as unstable intermediates formed on electron impact fragmentation of cyclosiloxanes, on heating of organopolysiloxanes up to 150–200 °C, and on gas-phase hydrolysis of dimethyldichlorosilane. The intermediates were observed by mass spectrometry. Based on the obtained data they suggested an alternative mechanism for the synthesis of polysiloxanes (Scheme I), which involves the intermediacy and polymerization of silanones.

SCHEME I

$$R_2SiX_2 + 2H_2O \xrightarrow{-2HX} R_2Si(OH)_2 \xrightarrow{-H_2O} [R_2Si{=}O] \rightarrow (R_2SiO)_x$$

$$[R_2Si{=}O] + HOR_2SiOSiR_2OH \rightarrow HOR_2SiOSiR_2OSiR_2OH, \text{ etc.}$$

Later it was shown that the peaks of dialkylsilanone ions were not typical for mass spectra of cyclosiloxanes.[88-90] Hence, "the report on the observation of alkylsilanone type species in the mass spectra of siloxanes . . . should be regarded rather as a prediction of their existence, since the authors using comparatively less effective equipment of that time, evidently, took even-electron fragment ions generally present in such compounds as hypothetical silanones".[91]

Sommer and Tyler[92] studied intramolecular dehydration of di-*tert*-butylsilanediol assuming that steric hindrances due to *tert*-butyl substituents at silicon would restrict the intramolecular process. They did not succeed in obtaining "di-*tert*-butyloxosilane", $t\text{-}Bu_2Si{=}O$.

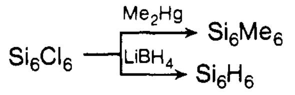
It was assumed that intermediate silanones were formed by subjecting polydimethylsiloxane to ultrasonic vibrations.[93]

$$\sim\!SiMe_2{-}OSiMe_2{-}OSi\!\sim \rightarrow \sim\!MeSi{=}O + Me_3Si{-}OSi\!\sim$$

Based only on the molecular weight data of the reaction product of "sodium triphenylgermanide" with tetrachlorosilane, Milligan and Kraus[94] assigned the formed amorphous product to "tetrakis(triphenylgermanyl)silicoethylene":

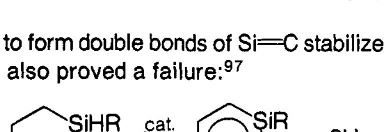
$$(Ph_3Ge)_2Si{=}Si(GePh_3)_2$$

In 1958, at the 133th National Meeting of the American Chemical Society, Urry[95] reported a number of new unsaturated or aromatic silicon compounds, in particular Si_6Cl_6, obtained by passing tetrachlorosilane through a ferrosilicon alloy. Methylation and reduction of the obtained compound yielded Si_6Me_6 and Si_6H_6, respectively.



Later these results were reinterpreted along quite different lines.[96]

Attempts to form double bonds of Si=C stabilized by aromatic conjugation also proved a failure:[97]



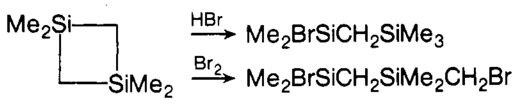
R = H, Me

Dehydration of these silacyclohexenes did not proceed either on platinum or on palladium catalysts at temperatures up to 500 °C. Above this temperature, some thermal cracking to hydrogen and mixed olefins took place. Over a chromia-alumina dehydration catalyst both compounds were rapidly oxidized to siloxanes.

The announcement about the derivation of a stable compound with the silicon-carbon double bond[98] by pyrolysis of tetramethylsilane aroused considerable interest. The latter reacted with hydrogen bromide and hydrogen iodide yielding addition products:

$$\underset{\mathbf{12}}{Me_2Si{=}CHSiMe_3}\quad \begin{array}{l} \xrightarrow{HBr} Me_2BrSiCH_2SiMe_3 \\ \xrightarrow{Br_2} Me_2BrSiCH(Br)SiMe_3 \end{array}$$

A year later it was shown[99] that the compound obtained was not **12**, but its cyclic isomer, 1,1,3,3-tetramethyl-1,3-disilacyclobutane (**13**), which like the unsaturated compound **12** easily adds bromine and hydrogen bromide:



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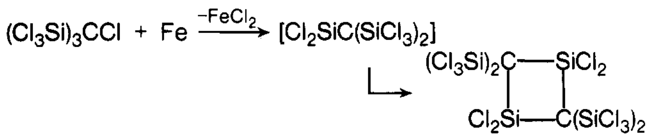
It was suggested[100,101] that dimerization of the diradical $Me_2\dot{S}i\text{-}\dot{C}H_2$ is responsible for the formation of **13**.

The unconfirmed reports on the involvement of the silicon atom in aromatic systems of silacyclopentadienol anion, silabenzene, and silatropylium cation,[102] on participation of monomeric silanone in the reaction of Jozitsh agent with polysiloxanes,[103] on formation of diradical, $Me_2\dot{S}i\text{-}\dot{S}iMe_2$, in the pyrolysis of polydimethylsilane, and on the possibility of isomerization of silylenes into olefins also date back to this period.[104]

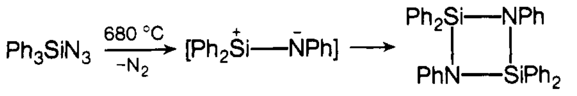
A silicon-carbon double-bonded intermediate is possibly formed upon dechlorination of chloromethyltrichlorosilane and other silicon derivatives of methyl chloride (Scheme II) in the presence of iron, copper, or their alloys.[105]

SCHEME II

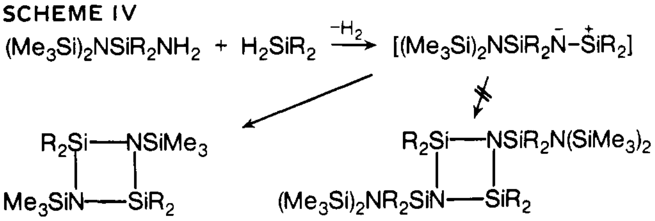


Finally, the formation of the dipolar ion $R_2{}^{\oplus}Si\text{-}N^{\ominus}R$, equivalent to the intermediate $R_2Si{=}NR$, was noted in the thermal decomposition of triphenylsilylazide[106,107] (Scheme III) and in silylation of primary aliphatic and aromatic amines and silaamines (Scheme IV) in the presence of alkali metals or their hydrides as catalysts.[107-109]

SCHEME III



SCHEME IV

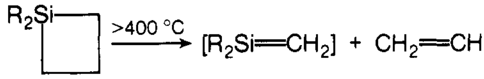


II. [4→2+2] Cycloelimination

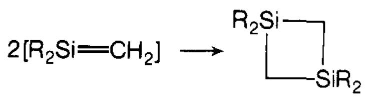
A. Pyrolysis of Monosilacyclobutanes and Monogermacyclobutanes

1. Thermal Transformation of Monosilacyclobutanes into 1,3-Disilacyclobutanes and Reactions of Silaethylene Intermediates with Trapping Agents

The formation of highly reactive silaethylenes was first clearly revealed in the studies of the thermal decomposition of monosilacyclobutanes:[40,110,117,118]

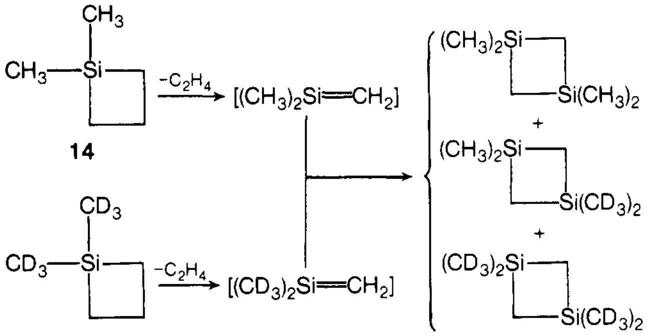


In the absence of trapping agents the reaction competes with cyclodimerization of silaethylene yielding 1,3-disilacyclobutane:



In accordance with this mechanism the only products of decomposition of 1,1-dimethyl-1-silacyclobutane (**14**) were ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Pyrolysis of the mixture of **14** and 1,1-di(deuteriomethyl-d_3)-1-silacyclobutane (Scheme V) resulted in the expected three 1,3-disilacyclobutanes.[111a] A similar course of the reaction was observed upon copyrolysis of **14** and 1-methyl-1-chloro-1-silacyclobutane.[111b]

SCHEME V



Kinetic data showed[41,42,115b] that the reaction is a homogeneous, unimolecular decomposition very similar to thermal decomposition of 1,1-dimethylcyclobutane.

Pyrolysis of 1,1-dimethyl-1-silacyclobutane:

$$k\,(s^{-1}) = 10^{15.6}\exp(-62300/RT)$$

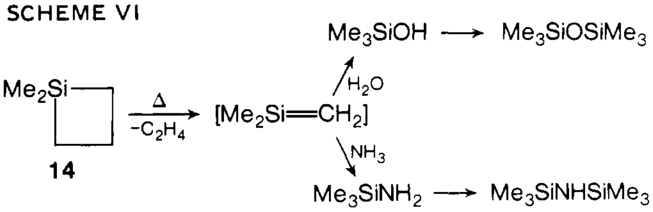
Pyrolysis of 1,1-dimethylcyclobutane[113b]:

$$k\,(s^{-1}) = 10^{15.68}\exp(-61000/RT)$$

The concentration ratio of ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane formed upon very low pressure pyrolysis (VLPP) of 1,1-dimethyl-1-silacyclobutane in a flow system appeared to be dependent on the distance between the heater and the trap cooled by liquid nitrogen.[115a,150b] The smaller the distance, the higher was the concentration ratio (over the stoichiometric). The latter seems to be associated with the formation of polymer by 1,1-dimethyl-1-silaethylene either upon defrosting the trap or upon condensation.

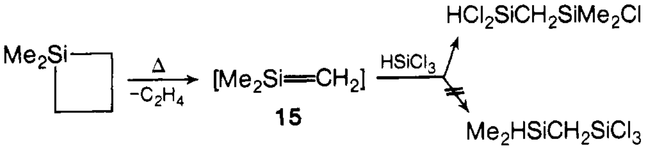
If the pyrolysis of monosilacyclobutanes is carried out in the presence of additives capable of forming with silaethylenes stable adducts under conditions of their generation, then the reactions competitive with cyclodimerization proceed, sometimes, supressing completely the latter. In particular, only the addition products to the silaethylene intermediate are formed upon pyrolysis of **14** in the presence of water vapors or ammonia[41,42,113a] (Scheme VI).

SCHEME VI



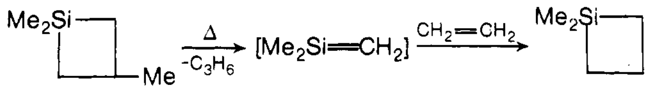
In a similar manner the reaction proceeds in the presence of such trapping agents as alcohols,[114,117] phenols,[114] amines,[114] and nitriles.[116] However, hydrosilylation seems to be not typical for silaethylenes. Thus, upon pyrolysis of **14** in the presence of trichlorosilane (Scheme VII), an adduct with silaethylene is formed as a result of cleavage of the Si-Cl bond (and not of the Si-H bond) in the latter.[119] Halosilylation of 1,1-dimethyl-1-silaethylene (**15**) also takes place in the copyrolysis of **14** with SiF_4, $SiCl_4$, or $MeSiCl_3$.

SCHEME VII



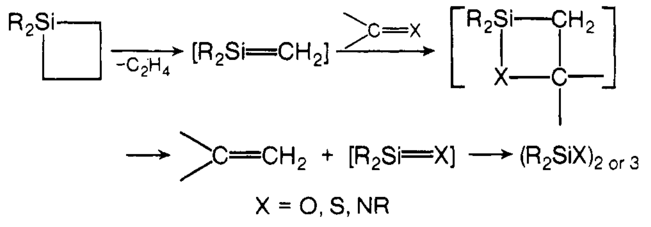
Besides the above-mentioned addition reactions and cyclodimerization, silaalkenes enter into [2+2] and [2+4] cycloaddition reactions. [2+2] cycloaddition to olefins was first postulated in the kinetic study of the thermal decomposition of 1,1-dimethyl-1-silacyclobutane.[41,42] It was found that the [2+2] cycloaddition of silaethylene to ethylene, a reverse reaction of [4→2+2] thermocycloelimination of **14**, in the kinetic scheme was attributed to the observed decrease in the rate constant of 1,1-dimethyl-1-silacyclobutane thermal decomposition.[42] Copyrolysis products of both **14**, in the presence of excess propene[120,121] (or other alkenes),[122] and 1,1,3-trimethyl-1-silacyclobutane with excess ethylene[120,121] provide support for the chemical evidence of [2+2] cycloaddition to silaethylene. In the former, 1,1,3-trimethyl-1-silacyclobutane was formed along with parent compounds. In the latter, 1,1-dimethyl-1-silacyclobutane was formed. Both reactions may be explained by a [2+2] cycloaddition mechanism, for example, by the Scheme VIII.

SCHEME VIII

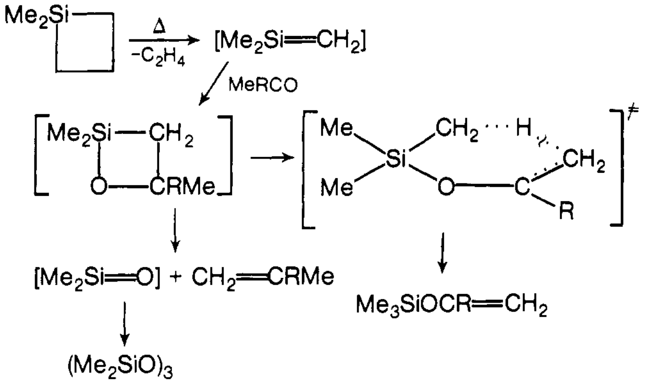


[2+2] cycloaddition of silaethylenes proceeds more readily with compounds containing isolated >C═O, >C═S, or >C═N- double bonds. Pyrolysis of monosilacyclobutanes in the presence of aldehydes and ketones,[114,123-126] thioketones,[127] and imines[128] is generally described as in the Scheme IX. As is seen, this reaction enables silaethylenes formed upon decomposition of monosilacyclobutanes to be transformed into >Si═O, >Si═S, and >Si═N double-bonded intermediates. Since carbonyl, thiocarbonyl, and azomethine compounds get converted into the corresponding unsaturated hydrocarbons, the action of silaethylenes is similar to phosphorus ylides (so-called "pseudo-Wittig reaction"). In the case of carbonyl compounds, alkenyloxysilanes isomeric to intermediate silaoxetanes are formed along with the products of the pseudo-Wittig reaction. The mechanism for the reaction of silaalkenes with carbonyl compounds has been proposed[38] (Scheme X) which involves decomposition and isomerization of intermediate silaoxetane via 1,5-migration of a hydrogen atom.

SCHEME IX

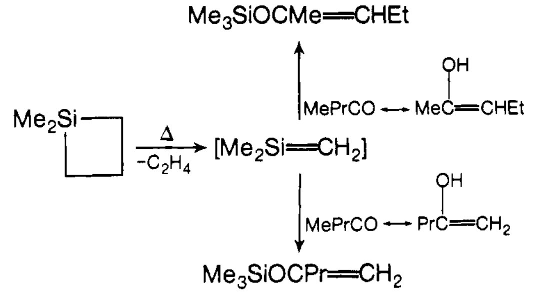


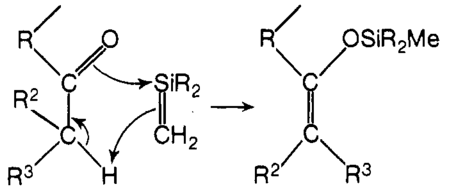
SCHEME X



An alternative mechanism[124] (Scheme XI) involving addition of enol form ketones to silicon-carbon double bond of silaethylenes seems to be less probable. The argument of the nonoccurrence of the reaction with nonenolizing ketones such as $Ph_2C═O$ is not conclusive, since the six-membered cyclic transition state necessary for isomerization via 1,5-migration of hydrogen cannot be realized because of the absence of hydrogen atom at carbon attached to carbonyl group. Actually, the recently suggested mechanism explains isomerization without taking recourse to the concept of enolization of ketones:[125]

SCHEME XI





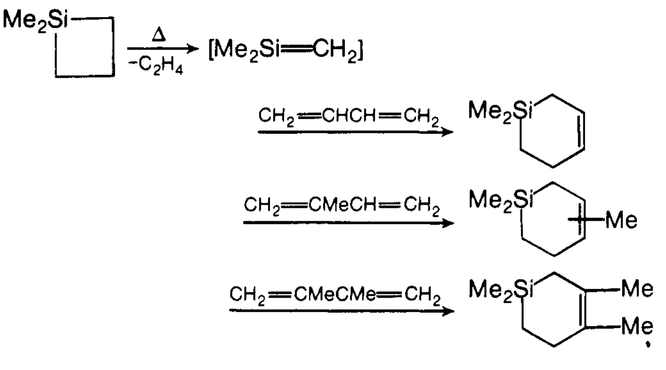
It is seen that reaction proceeds via a six-membered transition state very similar to that suggested by the silaoxetane mechanism. Thus, both transformations, i.e., pseudo-Wittig reaction and formation of alkenyloxysilanes, are better described via decomposition and isomerization of intermediate siloxetane.

Silaethylenes proved to be good dienophiles in Diels-Alder-type reactions.[120,121,296,297] Upon pyrolysis of monosilacyclobutanes in the presence of conjugated dienes the products of [2+4] cycloaddition to silaethylenes are formed. Thus, the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane is completely suppressed and corresponding 1-silacyclohex-3-enes are formed upon carrying out the pyrolysis of 1,1-dimethyl-1-silacyclobutane in the presence of butadiene, isoprene, or 2,3-dimethylbutadiene (Scheme XII).

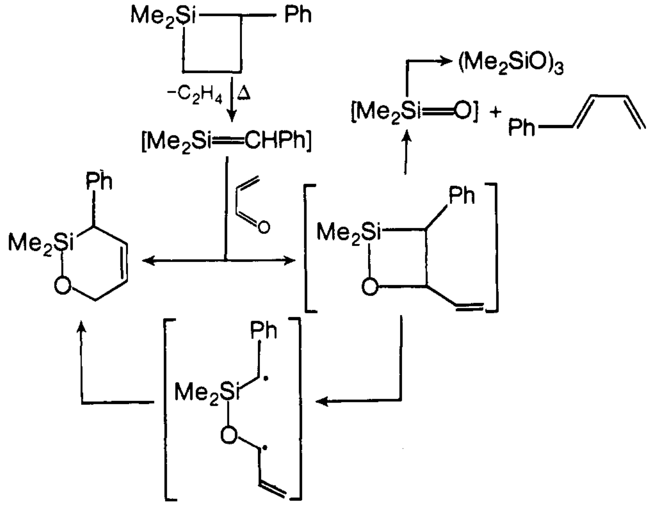
The reaction with acrolein (Scheme XIII) proceeds in a somewhat different manner.[339-341] A higher yield of cyclosiloxanes, compared to silaoxacyclohexene, is observed in this reaction possibly because of facile [2+2] cycloaddition of silaethylene to the carbonyl double bond.

Insertion into the Si-O bond is a typical reaction of double-bonded intermediates of silicon. It was first noticed when studying the gas-phase thermal transformations of cyclosilox-

SCHEME XII

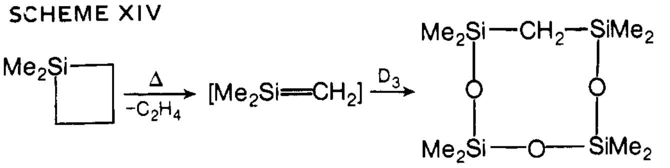


SCHEME XIII



anes.[129-131] Like silanones and thiosilanones,[127] silaethylenes[132] are readily inserted into the siloxane bond of hexamethylcyclotrisiloxane (D_3) (Scheme XIV).

SCHEME XIV



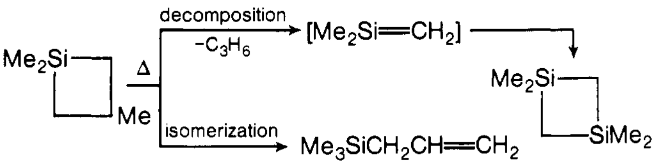
Thus, the above-considered data on the pyrolysis of monosilacyclobutanes with different trapping agents show that the following reactions are typical for silaethylenes: (1) addition (of water, ammonia, alcohols, amines, nitriles, halosilanes), (2) [2+2] cycloaddition (cyclodimerization, to olefins, to ketones and aldehydes, to thiocarbonyl and azomethine compounds), (3) [2+4] cycloaddition, (4) insertion into the Si-O bond, (5) polymerization. Using competitive reactions the following order of reactivity of 1,1-dimethyl-1-silaethylene generated in the pyrolysis of 1,1-dimethyl-1-silacyclobutane was estimated: $Ph_2C{=}O > ROH > ArOH \gg$ *m*-$ClPhNH_2 > CH_3CN$.[114,116b]

2. More Complex Thermal Transformations of Monosilacyclobutanes

It has been shown above that gas-phase thermal transformations of monosilacyclobutanes involve short-lived intermediate silaalkenes, which are responsible for the observed resulting products. In the absence of trapping agents these are 1,3-disilacyclobutanes. However, there are cases when pyrolysis of monosilacyclobutanes even in the absence of trapping agents does not result in 1,3-disilacyclobutanes. This may be due to the following reasons: (1) 1,3-disilacyclobutanes are not formed because of another readily occurring reaction of silaalkene rather than cyclodimerization; (2) silaalkene generated in the pyrolysis of silacyclobutanes reacts with parent compound or with the product of its decomposition; (3) the reaction proceeds without generating silaalkenes.

Thermal isomerization of *C*-methyl substituted monosilacyclobutane into alkenyl silanes, accompanying their thermal decomposition (Scheme XV), is a reaction without the intermediacy of silaalkenes.[133] A kinetic study of decomposition and isomerization of 1,1,3-trimethyl-1-silacyclobutane[134,135] at temperatures of 380–450 °C and pressure of 20 Torr gave the following Arrhenius equations:

SCHEME XV

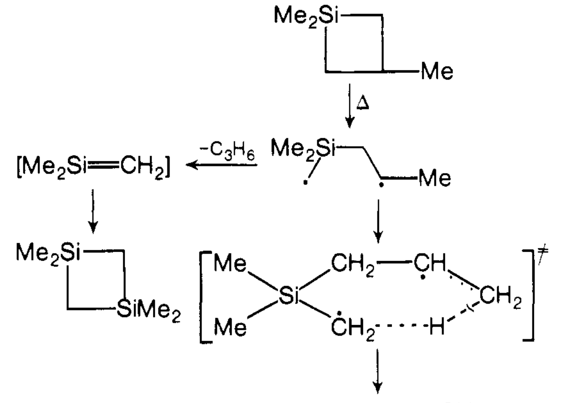


$$K_d\,(s^{-1}) = 16.33 \pm 0.36 - (63600 \pm 1000)/RT$$

$$K_i\,(s^{-1}) = 15.62 \pm 0.26 - (62600 \pm 800)/RT$$

As is seen, the activation energies of decomposition and isomerization are equal within the limits of determination errors. Therefore, the difference in the rates of these processes will be wholly determined by entropy restrictions which seem to be more pronounced in the case of isomerization, because this process involves formation of a rigid six-membered cyclic transition state (Scheme XVI) by primary biradical formed upon opening the monosilacyclobutane ring.

SCHEME XVI

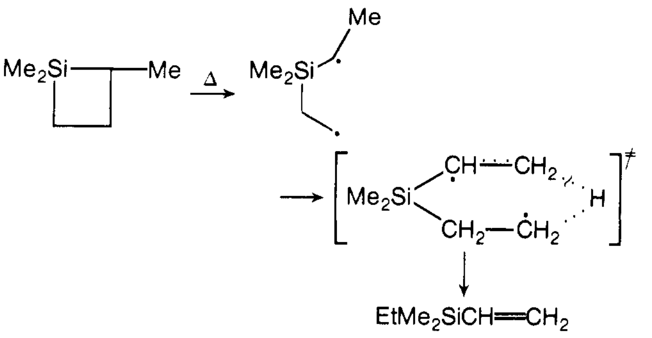


The estimated difference in activation entropies of biradical decomposition and isomerization amounts to 3.1 cal/deg·mol. Thus, both the processes, i.e., decomposition and isomerization of 1,1,3-trimethyl-1-silacyclobutane, are well explained by the mechanism involving formation of biradical due to primary cleavage of the C-2 bond of the monosilacyclobutane ring. This conclusion agrees with the data obtained from the study of the pyrolysis of 1,1,2-trimethyl-1-silacyclobutane[132,136] (Scheme XVII), the decomposition of which is also accompanied by isomerization.[136]

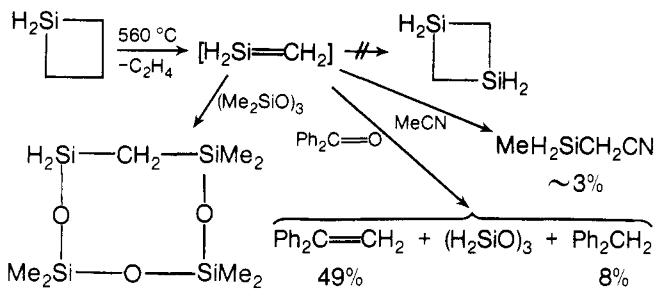
Although the formation of silaethylene was proved by trapping experiments (Scheme XVIII), no 1,3-disilacyclobutane was detected among pyrolysis products of nonsubstituted monosilacyclobutane.[126] The absence of dimer is possibly related to the preferred polymerization of silaethylene. However, nonoccurrence of trimer and tetramer of silanone in the reaction with benzophenone is attributed to the inherent instability of these cyclosiloxanes.

As additional evidence for intermediate $H_2Si{=}O$ are con-

SCHEME XVII

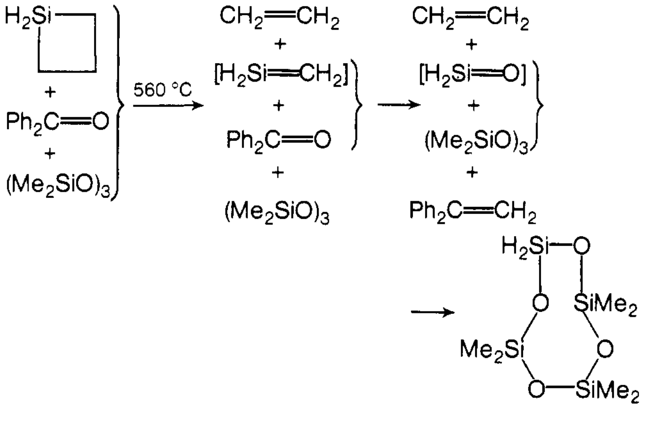


SCHEME XVIII



sidered[126] the data on copyrolysis of silacyclobutane with a mixture of benzophenone and hexamethylcyclotrisiloxane (Scheme XIX).

SCHEME XIX

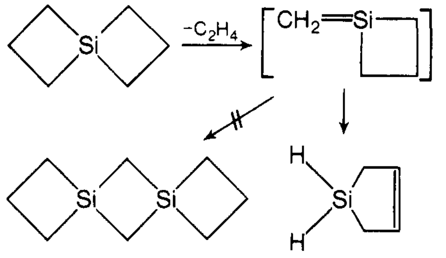


Pyrolysis of silacyclobutane and 1-methyl-1-silacyclobutane has been studied in a pulse system connected with the GC–MS system.[137] Decomposition of silacyclobutane was found to proceed mainly with the elimination of ethylene. Other gaseous products, i.e., hydrogen and propene, were found to the extent of 20 and 18% ethylene. In addition, a complex mixture of reaction products was obtained.

Pyrolysis of 1-methyl-1-silacyclobutane proceeds in a similar manner. Ethylene was found to be the main gaseous decomposition product. Hydrogen (20%), methane (1%), and propene (7%) were also observed. Apparently, upon pyrolysis of hydrosilacyclobutanes the formation of silaethylene still dominates over other decompositions. Therefore, one should elucidate processes suppressing their cyclodimerization.

In the series of 4-silaspiroalkenes, 4-silaspiro[3.3]heptane undergoes abnormal thermal decomposition. Unlike 4-silaspiro[3.4]octane and 4-silaspiro[3.5]nonane,[138,139] it forms a complex reaction mixture consisting of ethylene and 1-silacyclopent-3-ene, hydrogen, acetylene, propylene, allene, butene, butadiene, etc.[140,141] The absence of 1,3-disilacyclobutane compounds is explained by rearrangement of 1-methylene-1-silacyclobutane, a primary decomposition product (Scheme XX).

SCHEME XX



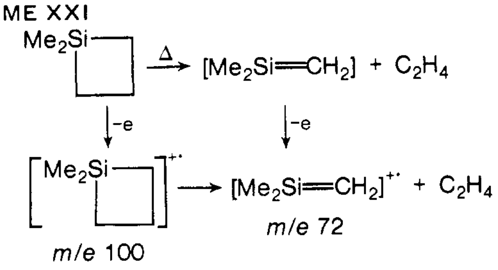
3. Direct Observation of Intermediates by Spectral Methods

The first attempt[142] to detect 1,1-dimethyl-1-silaethylene in the IR spectrum of pyrolysis products of 1,1-dimethyl-1-silacyclobutane frozen from the low-pressure gas phase on the target cooled by liquid nitrogen failed.[143] Later this was done by isolating decomposition products in an argon matrix.[144-147] Absorption bands assigned to 1,1-dimethyl-1-silaethylene were noticed: 642.9 cm^{-1} (stretching vibrations Si–CH_3), 825.1 cm^{-1} (deformation vibration HCSi), 1003.5 cm^{-1} (deformation vibration ρ=CH_2). In Figure 1 are shown the IR spectra of the matrix-isolated pyrolysis products of 1,1-dimethyl-1-silacyclobutane and 1,1,3-trimethyl-1-silacyclobutane.[148] Absorption bands at 644, 696, 817, 824, 932, 992, 1001, 1253 cm^{-1}, which belong neither to parent molecules nor to expected stable products of their thermal decomposition (marked by asterisks), are present in both spectra. The final assignment of the observed absorptions is reserved until the spectra of the pyrolysis products of deutero-substituted monosilacyclobutanes are obtained.

Radical intermediates produced upon pyrolysis of monosilacyclobutanes were detected[149,150] by the spin-trapping technique with phenyl *N-tert*-butyl nitrone or in frozen VLPP products. In Figure 2 is shown the ESR spectrum of the frozen (77 K) products of thermal decomposition of 1,1-dimethyl-1-silacyclobutane, which is not a fully resolved triplet, the hyperfine coupling constant being 22.4 G, with a superimposed singlet in the center. The triplet belongs to the –CH_2• radical, and the singlet apparently, results from unpaired electrons on silicon. The hyperfine splitting constant equal to 128 G strongly supports a silicon-centered radical. No coupling on hydrogen atoms of substituents at silicon may be related to the frozen state. Additional data are necessary to assign spectrum lines to definite structures.

In the gas phase, silaethylenes were observed by mass spectrometry.[151,152] As is seen from Scheme XXI, identification of 1,1-dimethyl-1-silaethylene produced upon pyrolysis of 1,1-dimethyl-1-silacyclobutane as a molecular ion is complicated by the formation of a fragment ion of the same composition.

SCHEME XXI



Molecular and fragment ions of 1,1-dimethyl-1-silaethylene were distinguished in the mass spectra of VLPP products of **14** by varying the ratio $I_{(M-28)}/I_M$, which depends on conversion. By locating the pyrolyzer inside the ion source, the ratio was in-

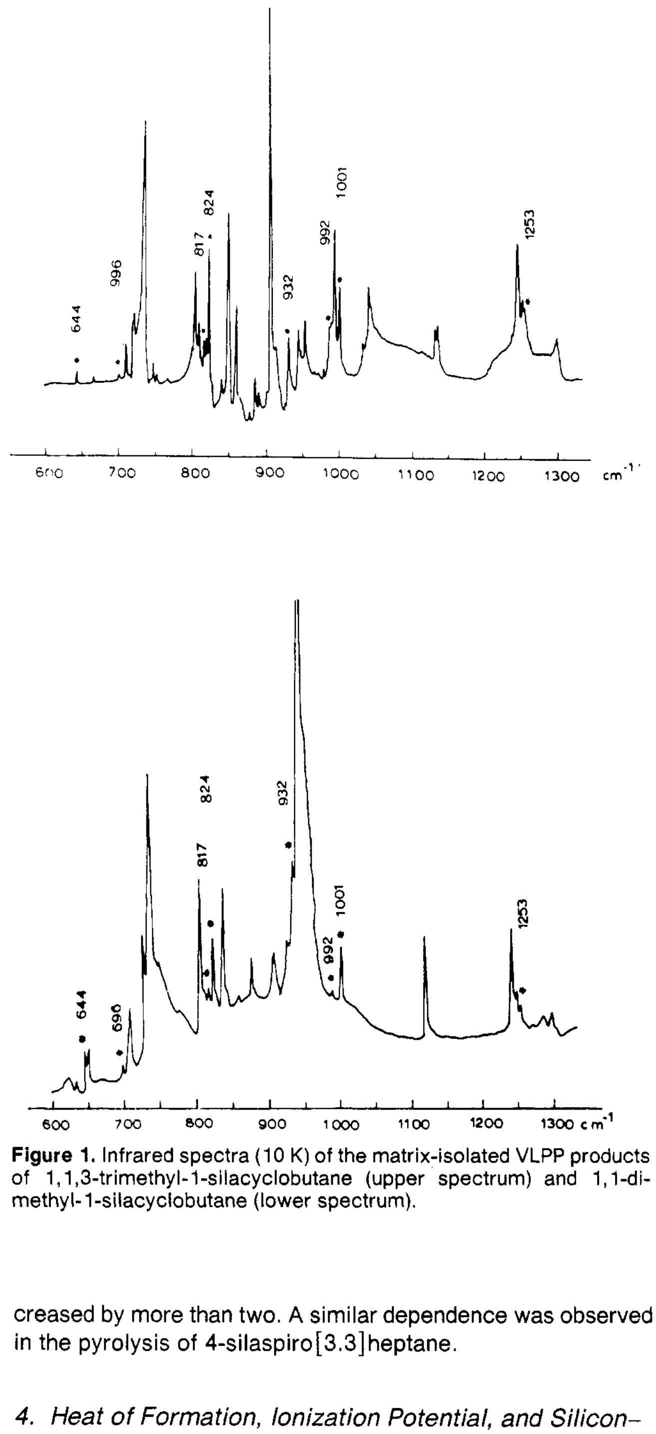


Figure 1. Infrared spectra (10 K) of the matrix-isolated VLPP products of 1,1,3-trimethyl-1-silacyclobutane (upper spectrum) and 1,1-dimethyl-1-silacyclobutane (lower spectrum).

creased by more than two. A similar dependence was observed in the pyrolysis of 4-silaspiro[3.3]heptane.

4. Heat of Formation, Ionization Potential, and Silicon–Carbon π-Bond Energy of 1,1-Dimethyl-1-silaethylene

The heat of formation, $\Delta H_f°(Me_2Si{=}CH_2)$, ionization potential, $I(Me_2Si{=}CH_2)$, and silicon–carbon π-bond energy, $D_\pi(Si{=}C)$, were determined[153] from the data of the kinetic study of the thermal decomposition of 1,1-dimethyl-1-silacyclobutane,[41,42] from the data on kinetics of the cyclodimerization of 1,1-dimethyl-1-silaethylene,[152] from the thermochemical determination of the heat of formation of 1,1-dimethyl-1-silacyclobutane,[154–160] and from the appearance potential of the *m/e* 72 ion, $AP(Me_2Si{=}CH_2)^{+\cdot}$, in its photoionization mass spectrum[162] by using the following equations:

$$\Delta H° = \Delta H_f°(Me_2Si{=}CH_2) + \Delta H_f°(C_2H_4) - \Delta H_f°(\mathbf{14})$$

$$\Delta H_f° = AP(Me_2Si{=}CH_2)^{+\cdot} - I(Me_2Si{=}CH_2)$$

$$\Delta H_f° = D(C\text{-}C) + D(Si\text{-}C) - D_\pi(Si{=}C) - D_\pi(C{=}C) - E_s$$

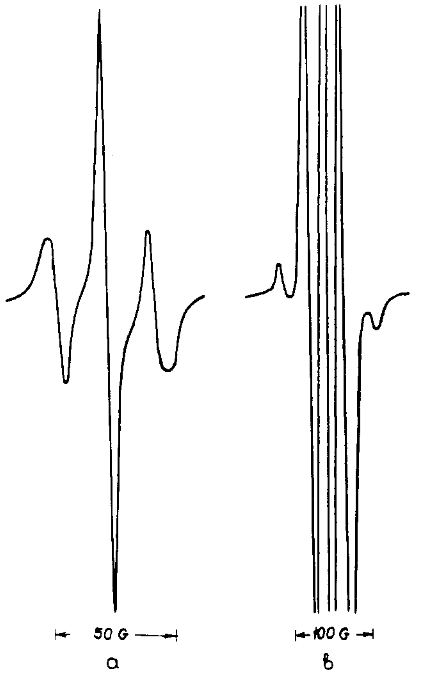


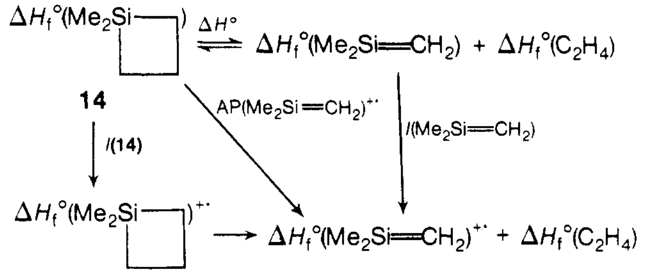
Figure 2. ESR spectra of the VLPP products of 1,1-dimethyl-1-silacyclobutane frozen at 77 K: (a) coupling with the protons of $-CH_2^\cdot$ group and silicon atom; (b) spectrum showing the doublet due to coupling with ^{29}Si.

TABLE I

	Walsh[164]	Dewar et al.[163]	Our data[153]
$\Delta H_f°$ ($Me_2Si{=}CH_2$), kcal/mol	...	−19.9	15.5 ± 6.2
$I(Me_2Si{=}CH_2)$, eV	...	9.0	7.5 ± 0.3
$D_\pi(Si{=}C)$, kcal/mol	26–46	42.3	28.8 ± 8

These equations result from the thermodynamic cycle given in Scheme XXII, where $\Delta H°$ is the enthalpy of thermal decomposition; $\Delta H_f°(C_2H_4)$ and $\Delta H_f°(\mathbf{14})$ are the enthalpies of formation; $D(C\text{-}C)$, $D(Si\text{-}C)$, and $D_\pi(C{=}C)$ are the bond dissociation energies; and E_s is the strain energy of monosilacyclobutane ring.

SCHEME XXII

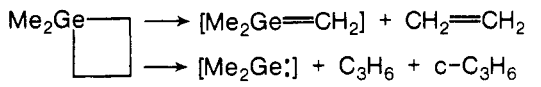


In Table I are given the obtained values[153] of mutually consistent $\Delta H_f°$, I, and $D_\pi(Si{=}C)$ for 1,1-dimethyl-1-silaethylene, which are compared with the MINDO/3 data[163] and silicon–carbon π-bond energy computed by Walsh.[164] The differences in the values are apparently due to the deviations resulting from the use of the semiempirical method MINDO/3 to silaethylenes.[165]

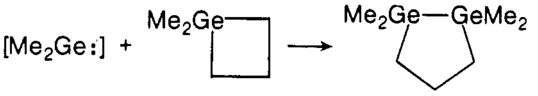
5. Pyrolysis of 1,1-Dimethyl-1-germacyclobutane

Gas-phase pyrolysis of 1,1-dimethyl-1-germacyclobutane[166] results in both olefinic and carbenoid decompositions (Scheme XXIII). The course of the first process may be assumed from the

SCHEME XXIII



elimination of ethylene, since 1,1,3,3-tetramethyl-1,3-digermacyclobutane, a dimer of 1,1-dimethyl-1-germaethylene, was not detected although it is stable under pyrolysis conditions. The second pathway of decomposition explains the formation of 1,1,2,2-tetramethyl-1,2-digermacyclopentane as an insertion product of dimethylgermylene into the cyclic Ge–C bond of the parent compound:



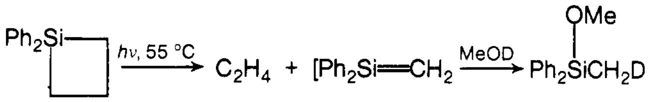
The contribution of olefinic and carbenoid decompositions depends on pyrolysis temperature, it being greater for the former at higher temperatures.

Analogous pathways are observed in the fragmentation of 1,1-dimethyl-1-germacyclobutane upon electron impact.[166,167]

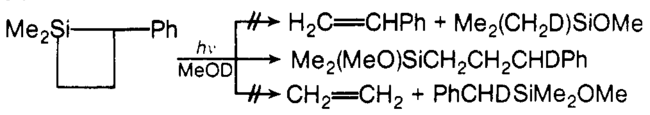
B. Photodecomposition of Monosilacyclobutanes

The photolysis of 1,1-diphenyl-1-silacyclobutane[168] results in a high yield of short-lived 1,1-diphenyl-1-silaethylene trapped by deuteriomethanol (Scheme XXIV). Irradiation of 1,1-dimethyl-2-phenyl-1-silacyclobutane in the presence of methanol-O-d_1 does not result in styrene and trimethyl-d_1-methoxysilane or ethylene and benzyl-d_1-dimethylmethoxysilane[169] (Scheme XXV). The only reaction product is 3-phenyl-3-d_1-propyldimethylmethoxysilane. As is seen, only those reactions which involve formation of intermediate silaethylenes do not take place.

SCHEME XXIV



SCHEME XXV

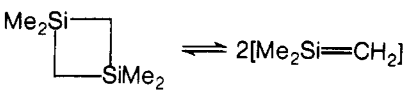


Among the products of the gas-phase photolysis (λ 147 nm) of 1,1-dimethyl-1-silacyclobutane[170] the main one was ethylene. 1,1-Dimethyl-1-silaethylene has not been isolated although its intermediacy is proved by trapping methanol. Minor products are dimethylsilylene, propene, and methyl radical. No explanations are given for the further reactions of 1,1-dimethyl-1-silaethylene.

C. Pyrolysis of Disilacyclobutanes and Digermacyclobutanes

1,3-Disilacyclobutanes are not prone to selective [4→2+2] cycloelimination. A comparative study of the ability to form silaethylenes upon thermolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane and 1,1-dimethyl-1-silacyclobutane has shown[115a,171,172] that the former starts decomposing at temperatures exceeding by 150 °C that of the latter. Unlike monosilacyclobutanes, 1,1,3,3-tetramethyl-1,3-disilacyclobutane yields a complex mixture of pyrolysis products due to the rupture of silicon–carbon bonds of both the four-membered ring and methyl groups.

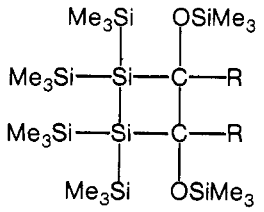
Trapping experiments have shown[115a] that the equilibrium does not occur below the range of nonselective decomposition.



For example, 1,1,3,3-tetramethyl-1,3-disilacyclobutane reacts with methanol at temperatures above 600 °C. Copyrolysis of 1,1,2,3,3-pentamethyl-1,3-disilacyclobutane with benzaldehyde[136] proceeds in the same temperature range.

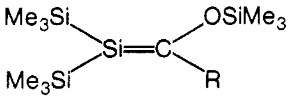
An analogous decrease in the ability to form group 4B analogs of olefins is typical of 1,3-digermacyclobutanes. Thus, 1,1,3,3-tetramethyl-1,3-digermacyclobutane proved to be stable under conditions of decomposition of 1,1-dimethyl-1-germacyclobutane.[166]

1,2-Disilacyclobutanes (A) easily dissociate upon heating and yield silaethylenes[173,174] (B). High yields of adducts with silaethylene were obtained when the former (R = Ph) was boiled in THF with methanol or dimethylbutadiene. The latter, 1,2-disilacyclobutane (R = CMe$_3$), proved to be even less stable, and yielded monomer in a solution of THF at room temperature. The relative stability of the resultant silaethylene made it possible to identify it by spectral methods (see section XIV.B). In the absence of trapping agents a very mobile equilibrium of silaethylene–head-to-head dimer exists.



A

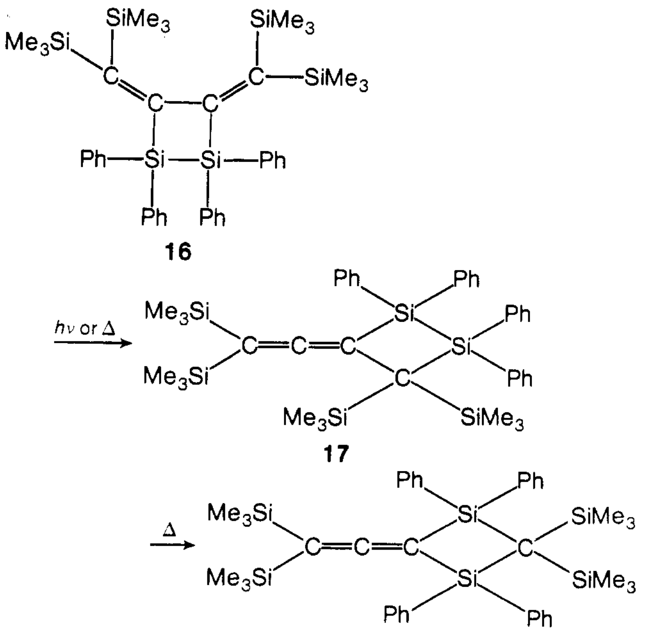
R = Ph or Me$_3$C



B

1,1,2,2-Tetraphenyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane (**16**) undergoes a novel isomerization

SCHEME XXVI

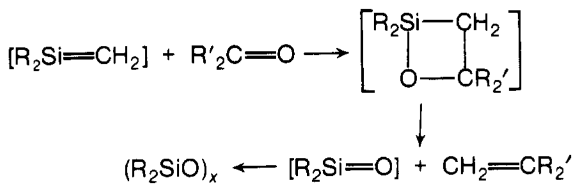


photochemically or thermally[175] producing another type of 1,2-disilacyclobutane, **17**. The latter changes readily to a 1,3-disilacyclobutane system possibly via transiently formed silaethylene (Scheme XXVI)

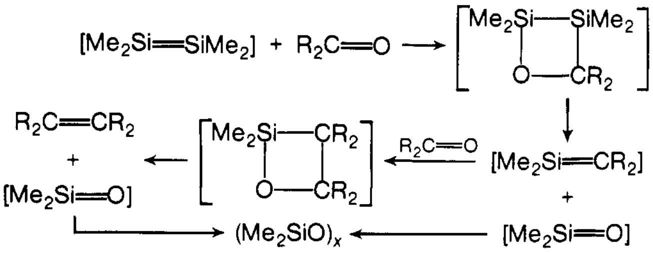
D. Decomposition of Oxetanes, Thietanes, and Azetidines Containing Group 4B Metal in the Ring

The reactions of silaalkenes with carbonyl, thiocarbonyl, and azomethine compounds via a [2+2] cycloaddition–[4→2+2] cycloelimination sequence (see, for example, Scheme XXVII), which involves the title intermediates, have been discussed in section II.A.1. Analogously, the reaction of tetramethyldisilaethylene with benzaldehyde, given in Scheme XVIII, has been explained.[176]

SCHEME XXVII

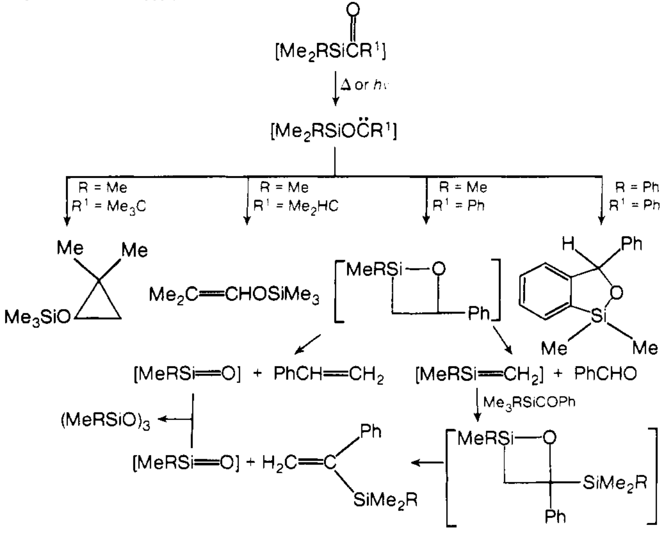


SCHEME XXVIII



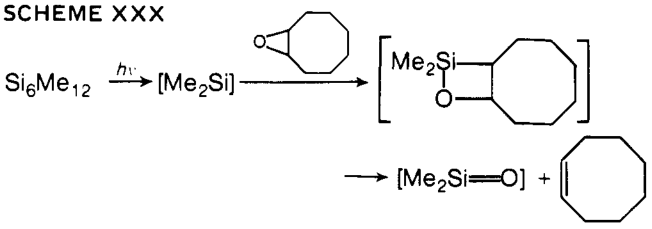
Silaoxetanes are formed apparently as intermediate compounds upon thermolysis[177,178] and photolysis[179] of α-ketosilanes (Scheme XXIX). As is seen, the course of transformation depends upon the nature of substituents R and R^1. An alkyl substituent at carbonyl carbon rearranges carbene to give an olefin or a cyclopropane ring.[180] With a phenyl at the carbonyl carbon, the siloxycarbene formed on thermolysis affects the substituents at the silicon atom.[177,178a] Thus, as a result of the reaction of intramolecular insertion into the C–H bond of the methyl group attached to silicon, an intermediate siloxetane is formed. This immediately decomposes via the [4→2+2] cycloelimination mechanism forming silanone and silaalkene. In this process the rupture of both Si–O, C–C and Si–C, C–C bonds of siloxetane was observed for the first time. Intramolecular insertion products of the carbenic carbon into the C–H bond of the aromatic ring are formed if phenyl is attached to silicon.

SCHEME XXIX

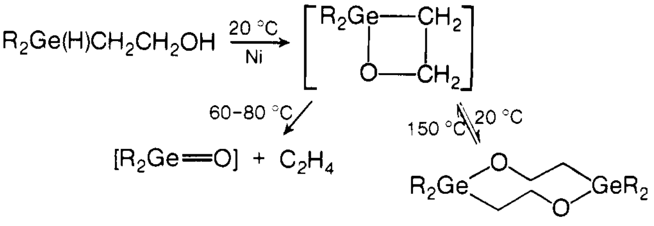


One more method of generating silanones (Scheme XXX) involves formation of a precursor, silaoxetanes, via insertion of dimethylsilylene into the C–O bond of oxiranes.[301] Apparently, germaoxetanes, unstable intermediates formed upon intramolecular dehydrocondensation of β-hydroxyhydrogermanes, decompose in the same way as silaoxetanes[181-184] (Scheme XXXI).

SCHEME XXX

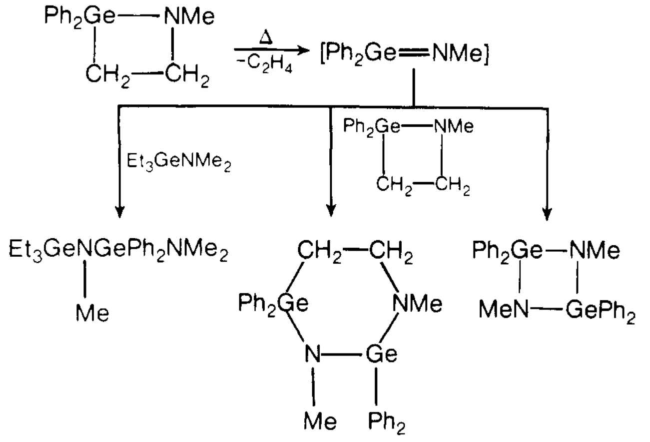


SCHEME XXXI



In a like manner 2,2-diethyl-2-germathietane[185a] and 1-methyl-2,2-diphenyl-2-germaazetidine[186] decompose (Scheme XXXII). The latter is an isolated relatively stable compound.

SCHEME XXXII



1,3-Diphenyl-2-germa-3-oxaazetidine is claimed to decompose forming germanone. Possibly the reaction of β-aminosilanes with butyllithium proceeds via intermediate silaazetidines.[188,189]

E. Scope and Limitations of [4→2+2] Cycloelimination as the Method for Generation of Unstable Intermediates Containing Double p_π-p_π Bonded Heteratoms

It is evident that the above given examples of [4→2+2] cycloelimination are related to the well-known thermal decomposition of cyclobutanes[190-192] resulting in production of two olefinic molecules. Until recently the only process involving the heterocycle was pyrolysis of oxetanes.[161] The first use of the

[4→2+2] cycloelimination for generation of intermediates succeeded in the pyrolysis of monosilacyclobutanes (see section II.A), which is an excellent example of Hoffmann's suggestion that "if one of the fragments is a high-energy reactive intermediate, thermal cycloelimination can still be achieved under relatively mild conditions provided that the other fragment is very stable".[44] To produce silaethylenes silicon must replace one carbon atom of the four-membered ring. A silyl group in the substituent at the cyclobutane ring results in the expected alkenylsilanes.[193] The change of a carbon atom in the cyclobutane ring for germanium still results in olefinic type of decomposition[166] but is accompanied by a cheletropic reaction generating germylenes. A strong tendency toward decomposition into unsaturated intermediates is also observed in the pyrolysis of azetidine[194,195] and thietane.[196]

In contrast to monosilacyclobutanes 1,3-disilacyclobutanes are not capable of selective decomposition into two silaethylene fragments[115a] because of the disfavored energetics of the reaction. Taking into consideration this restriction it is suggested that 1,2-disilacyclobutanes will decompose producing disilaethylenes and olefins rather than two silaethylenes. In fact, their electron-impact fragmentation proceeds in that way (see section XII). However, data obtained with rather complex 1,2-disilacyclobutane do not confirm this suggestion.[173,174,175] The main course of their decomposition is formation of silaethylenes. Recent advances in the synthesis of simple 1,2-disilacyclobutanes[197] will undoubtedly lead to the solution of the problem.

In the monosilacyclobutane series the selectivity of the thermal generation of silaethylenes is high when alkyl or aryl substituents at the silicon atom, or the aryl group, are attached to the carbon atom of the four-membered ring. A decrease in selectivity due to the structure of monosilacyclobutanes is discussed in section II.A.2.

Four-membered rings, containing a group 4B metal attached to a group 5 or group 6 heteratom, decompose thermally generating mainly $R_2M{=}X$ fragments (where M = Si, Ge; X = O, S, or NR), although there is an indication for an alternative course of decomposition into $R_2Si{=}CR_2$ and $R_2C{=}O$ (see section II.D). As in the case of monosilacyclobutanes, here again one must avoid substituents at the ring carbon facilating 1,5-migration of the hydrogen atom in diradicals formed upon cleavage of the four-membered heterocycle.

III. Other Cycloelimination Reactions

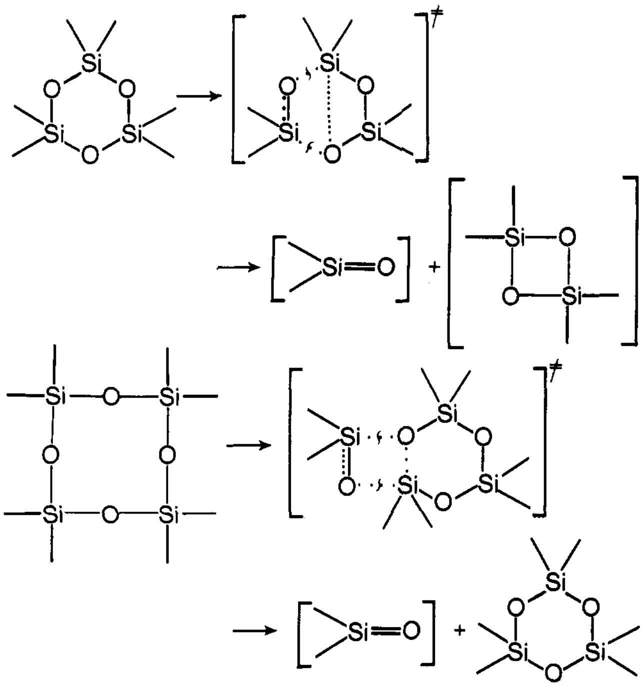
A. Intramolecular Redistribution of Cyclic Systems Containing Group 4B Metals at Alternative Positions

1. Pyrolysis of Cyclosiloxanes and Cyclocarbosiloxanes

Thermal redistribution[198] of cyclosiloxanes, D_n, results in an equilibrium mixture of homologs containing R_2SiO groups in the ring.[129-131,199,200] Two different mechanisms have been proposed for the thermal decomposition of cyclosiloxanes.

The first, the molecular cycloelimination mechanism[129,200] based on the transannular interaction of silicon and oxygen, is in good agreement with the observed higher thermal stability of the cyclic trimer compared with the tetramer, pentamer, and others (Scheme XXXIII). As predicted by the mechanism the loss of dimethylsilanone is more favored energetically for the decomposition of cyclosiloxanes D_4 and D_5 than for D_3, since the latter would form two high-energy reactive intermediates. In the pyrolysis of D_6, D_7, and others preference is given to more advantageous cycloelimination processes resulting in extrusion of D_3,D_4, etc. Further reactions of dimethylsilanone are formation of cyclic products and insertion into the Si–O bond of cyclosiloxanes. For example, formation of cyclosiloxanes D_{n+1} at low conversions of D_n takes place owing to the contribution of the latter reaction. No homologues of the D_{n+2}, D_{n+3} type are observed in significant amount. In general, generation and reactions of silanones upon pyrolysis of cyclosiloxanes may be presented as in Scheme XXXIV.

SCHEME XXXIII



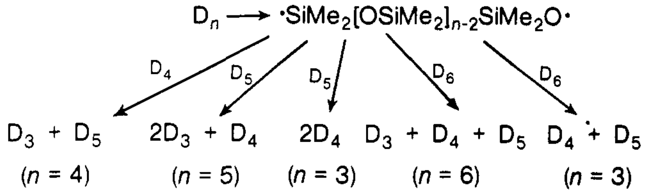
SCHEME XXXIV

$$D_n \longrightarrow [Me_2Si{=}O] + D_{n-1}$$
$$[Me_2Si{=}O] + D_n \longrightarrow D_{n+1}$$
$$3\,[Me_2Si{=}O] \longrightarrow D_3$$

The mechanism is well corroborated by the data.[130,131]

An alternative radical mechanism[201,202] given in Scheme XXXV involves homolytic cleavage of Si–O bonds. However, it does not explain the preferable cleavage of stronger Si–O bonds over weaker Si–C ones as well as the pronounced stability of strained cyclic trimer.

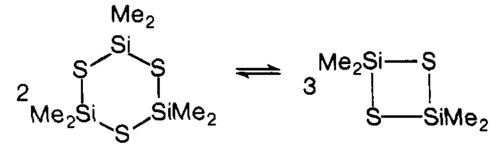
SCHEME XXXV



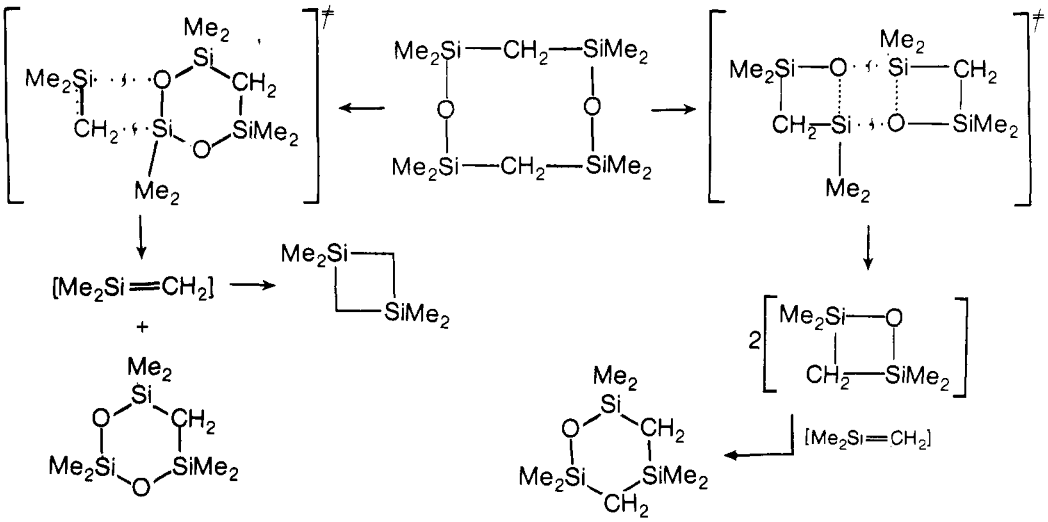
A molecular cycloelimination mechanism also explains the thermal decomposition of a number of eight-membered cyclocarbosiloxanes (Scheme XXXVI) which proceeds via intermediacy of dimethylsilanone and 1,1-dimethyl-1-silaethylene.[199,200,203-205]

2. Pyrolysis of Cyclosilathianes, Cyclogermathianes, and Cyclosilazanes

Redistribution of hexamethylcyclotrisilathiane[206,207] and other

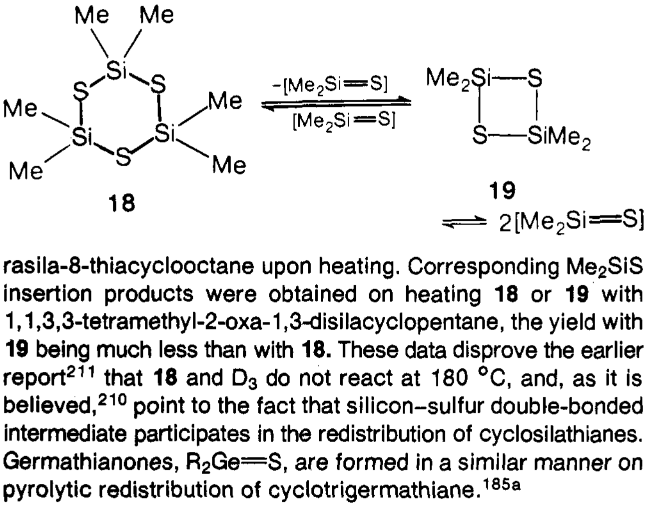


SCHEME XXXVI



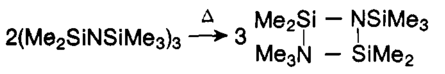
cyclotrisilathianes[208,209] takes place even at room temperature. By using trapping agents the assumption of formation of unstable silathianone in this reaction was verified[210] (Scheme XXXVII). The mixture of **18** and hexamethylcyclotrisiloxane (10:1) yielded at 200 °C 1,1,3,3,5,5,7,7-octamethyl-2,4,6-trioxa-1,3,5,7-tetrasila-8-thiacyclooctane upon heating. Corresponding Me_2SiS insertion products were obtained on heating **18** or **19** with 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane, the yield with **19** being much less than with **18**. These data disprove the earlier report[211] that **18** and D_3 do not react at 180 °C, and, as it is believed,[210] point to the fact that silicon–sulfur double-bonded intermediate participates in the redistribution of cyclosilathianes. Germathianones, $R_2Ge{=}S$, are formed in a similar manner on pyrolytic redistribution of cyclotrigermathiane.[185a]

SCHEME XXXVII



$$(Et_2GeS)_3 \xrightleftharpoons{160\ °C} 3(Et_2Ge{=}S) \xrightarrow{Et_2GeSMe} [Et_3GeSGeEt_2SMe]$$

Redistribution of cyclosilazanes results only in ring contraction. Thus, 1,3,5-tris(trimethyl)silylated cyclotrisilazane, but not 1,3,5-trimethylated cyclotrisilazane, changes into a four-membered cyclotrisilazane at 400–425 °C:[107]



$$2(Me_2SiNSiMe_3)_3 \xrightarrow{\Delta} 3\ \begin{matrix} Me_2Si - NSiMe_3 \\ Me_3N - SiMe_2 \end{matrix}$$

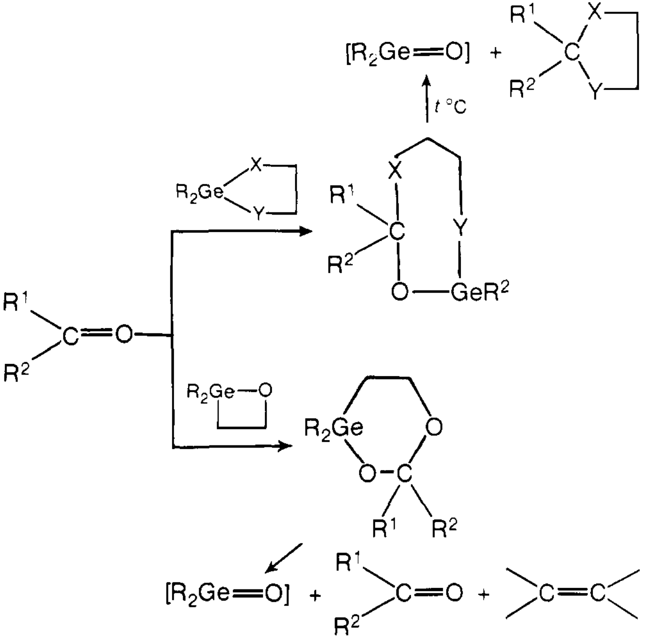
This and other known redistribution reactions[212] possibly also proceed involving double-bonded intermediates $R_2Si{=}NR$.

$$3(Me_2SiNH)_4 \rightarrow 4(Me_2SiNH)_3$$

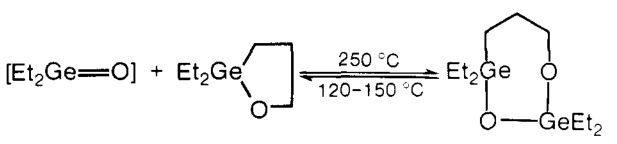
B. [7→2+5] and [6→2+2+2] Cycloeliminations

Thermolysis of heterocycles formed upon insertion of carbonyl compounds into germaoxetanes or dioxalanes or diazolidines (Scheme XXXVIII) was interpreted as a process involving short-lived germanones.[184] Decomposition temperature (t °C) depends on the nature of R^1, R^2, X, and Y. Because of decomposition the insertion product of diethylgermanone into oxagermacyclopentane proved to be less stable:

SCHEME XXXVIII



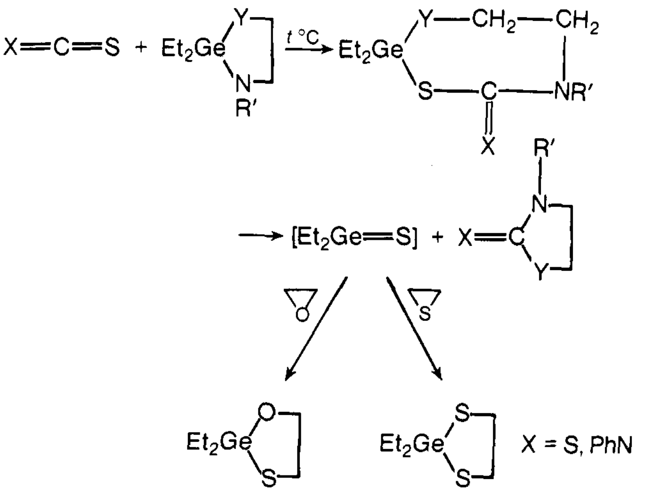
R^1	R^2	X	Y	t, °C
Me	H	O	O	160
Me	H	O	NMe	20
Me	H	NMe	NMe	20
Ph	H	O	O	160
Ph	H	O	NMe	20
Ph	H	NMe	NMe	20
Me	Me	O	O	160
Me	Me	O	NMe	20
Me	Me	NMe	NMe	20
PhN=		O	O	180
PhN=		NMe	NMe	140–150



The germanones thus generated were identified by reactions with trimethoxygermane, ethylene oxide, and other traps.[184]

Transient diethylthiogermanone is formed upon decomposition

SCHEME XXXIX

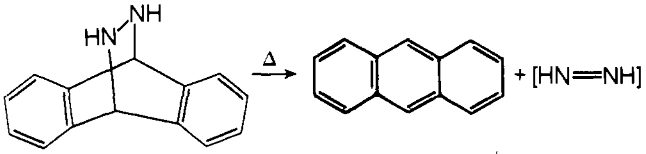


of adducts of both carbon sulfide and phenyl thioisocyanate with germaoxalidines or germadiazolidines[185] (Scheme XXXIX). Here also, the decomposition temperature depends to a large extent on the nature of X, Y, and R′.

All reactions described in this section proceed in the liquid phase, and, therefore, may be interpreted as cycloelimination only if first-order decomposition is proved.

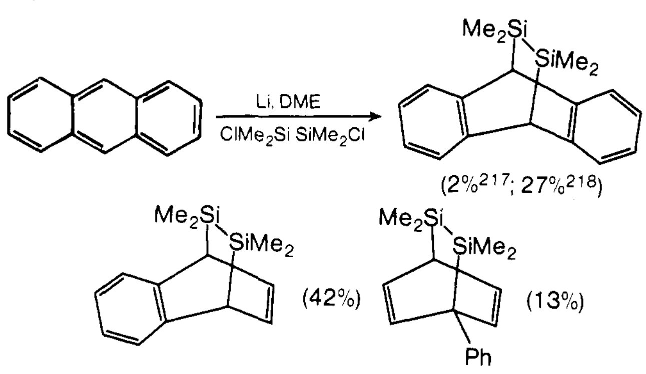
C. [6→4+2] Cycloelimination

The retrodiene thermal process or [6→4+2] cycloelimination from bicyclo[2.2.2]octadi-2,5-enes[213] is a convenient reaction of generation of unstable molecules with element-carbon and element-element double bonds. Transformation of the diene system into an aromatic one is the driving force of the reaction. For example, Corey and Mock[214] succeeded in generating unstable diimide:

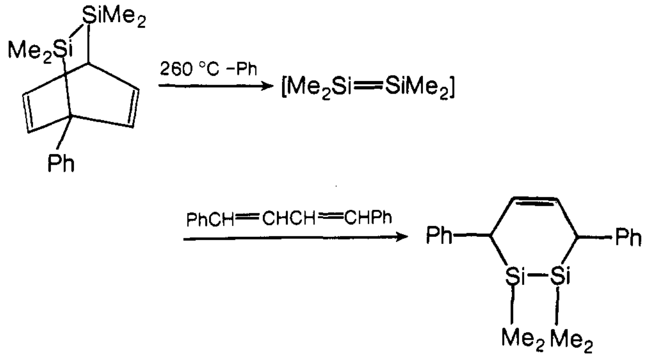


Short-lived intermediates with silicon-carbon,[215] germanium-carbon,[216] and silicon-silicon[176,217-220] were obtained in a similar manner.

Peddle and Roark[217,218] studied the thermal decomposition of disilabicyclo[2.2.2]octadi-2,5-enes obtained in the reaction of 1,2-dichlorotetramethyldisilane with dianions of anthracene, naphthalene, and biphenyl. These compounds on heating in sealed tubes up to 500, 360, and 260 °C, respectively, decomposed yielding aromatic hydrocarbon, traces of trimethylsilane, and a nonvolatile viscous white oil highly soluble in organic solvents. Pyrolysis in the presence of dienes resulting in the formation of adducts indicating the intermediacy of $Me_2Si{=}SiMe_2$ (Scheme XL).



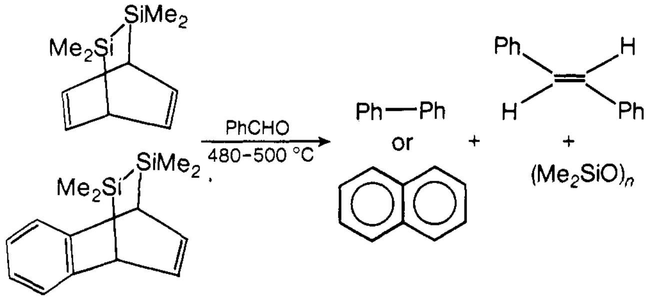
SCHEME XL



Trapping of the intermediate by anthracene, 9-deuterioanthracene, and naphthalene was done in an analogous way. Since $Me_2Si{=}SiMe_2$ forms in a singlet state by a thermally initiated concerted retrodiene reaction, it may be regarded as having a silicon-silicon π bond unless steric repulsion of the vicinal methyl groups is greater than the π-bond energy.[218] Mass spectra of 7,8-disilabicyclo[2.2.2]octadi-2,5-enes are characterized by the most abundant fragment ion m/e 116 assigned to $Me_2Si{=}SiMe_2$.[217,218]

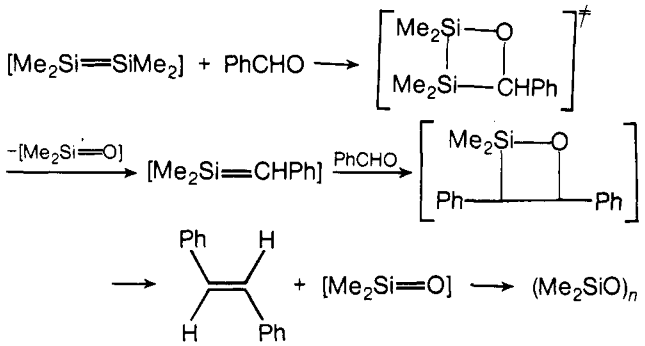
Barton and Kilgour[176] studied the pyrolysis of 7,8-disilabicyclo[2.2.2]octadi-2,5-enes in excess benzaldehyde (Scheme XLI). Concurrent with primary products of decomposition (biphenyl or naphthalene), *trans*-stilbene and cyclic methylsiloxane oligomers (D_3, 16%; D_4, 13.8%) were identified.

SCHEME XLI



The mechanism of formation of these products (Scheme XLII)

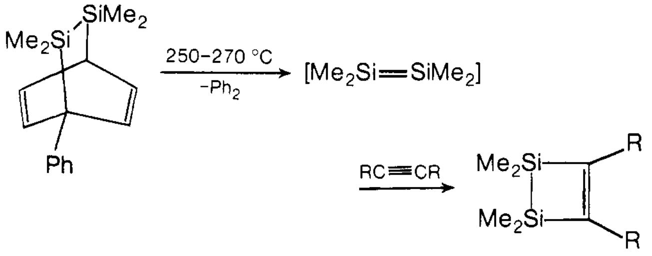
SCHEME XLII



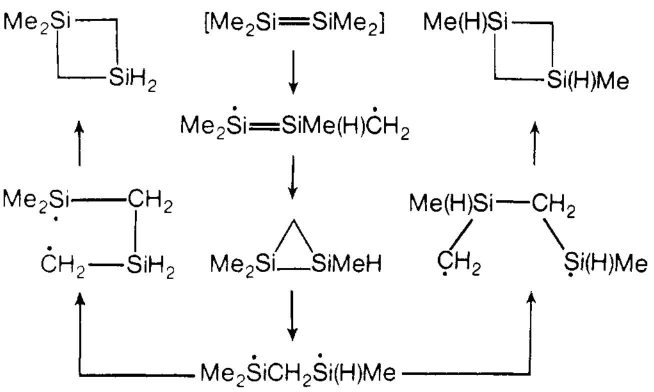
involves [2+2] cycloaddition of the intermediate $Me_2Si{=}SiMe_2$ to the carbonyl double bond, and further decomposition of the unstable disilaoxetane.

Disilaethylene, $Me_2Si{=}SiMe_2$, may also be trapped via a [2+2] cycloaddition reaction with diphenylacetylene (Scheme XLIII) and phenyltrimethylsilylacetylene.[221] In the absence of a trap the following products were formed at low pressures: trimethylsilane (3%), 3,3-dimethyl-1,3-disilacyclobutane (0.5%), 2-methyl-2,4-disilapentane (2%), 1,1-dimethyl-1,3-disilacyclobutane (30%), and 1,3-dimethyl-1,3-disilacyclobutane (10%). A mechanism given in Scheme XLIV[218] has been proposed for explaining the formation of last two compounds.

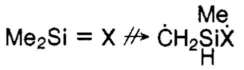
SCHEME XLIII



SCHEME XLIV



Isomerization of disilaethylene into a 1,3-biradical, which proceeds, as is believed, via 1,2-migration of the H atom from the methyl group to the vicinal silicon atom, is the most uncertain point of this mechanism. In fact, similar transformations were noted neither in the case of intermediates $Me_2Si{=}X$ (X = CR_2, NR, O, S)[37-39]



$$Me_2Si = X \not\rightarrow \dot{C}H_2\underset{H}{\overset{Me}{Si}}X$$

nor in organosilyl[222-225]

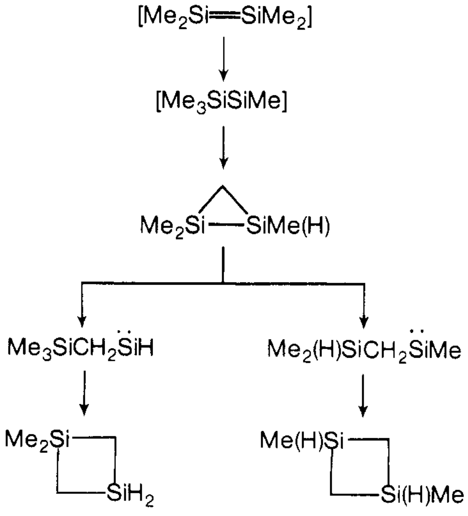
$$Me_3Si\cdot \not\rightarrow Me_2Si(H)\dot{C}H_2$$

nor silylmethyl radicals.[226-228]

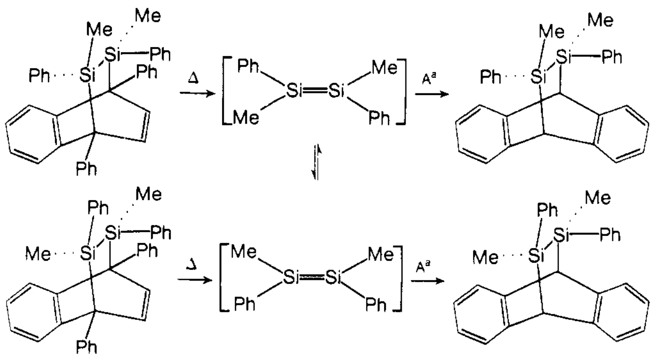
$$R_3SiCH_2^{\cdot} \not\rightarrow R_2\dot{S}iCH_2R$$

Barton et al.[229] proposed and experimentally substantiated another pathway of formation of 1,1,2-trimethyl-1,2-disilacyclopropane, which involves rearrangement of tetramethyldisilaethylene into trimethylsilylsilylene and subsequent insertion of the carbenoid center into the C-H bond. Further development of the process is also related to the reactions of silylenes (Scheme XLV).

SCHEME XLV



SCHEME XLVI

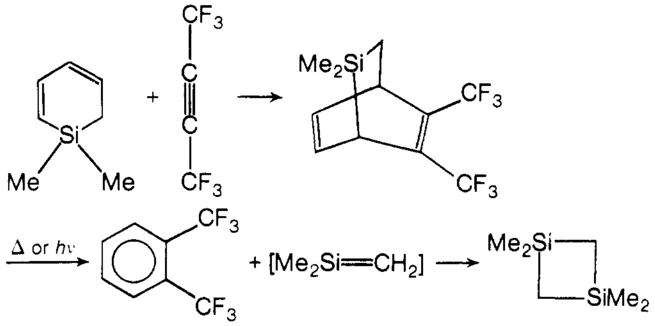


^{a} A = anthracene.

Sakurai, Kobayashi, and Nakadaira[220,230] have recently reported the geometric isomerization of disilaethylenes. Pyrolysis of a mixture (1:1) containing *trans*-2,3-benzo-1,4,7,8-tetraphenyl-7,8-disilabicyclo[2.2.2]octadi-2,5-enes and anthracene led to the formation of mainly trans adduct. Pyrolysis of cis isomer under similar conditions yielded the cis adduct (Scheme XLVI). Somewhat less stereospecifically disilaethylenes reacted with 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene.[230] The stereospecificity of the process indicates that disilaethylenes have a virtual double bond subjected to gradual geometric isomerization.

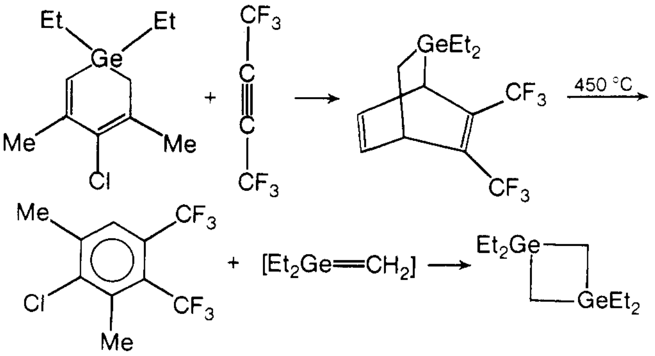
Barton and Kline[215] developed a method for synthesizing 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]octadi-2,5-ene, and showed that retrodiene process proceeded on heating or under photolysis conditions (Scheme XLVII).

SCHEME XLVII

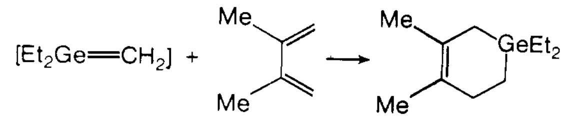


In a similar manner, the retrodiene thermal reaction of germacyclohexadiene adduct and perfluorobut-2-yne occurs[216] (Scheme XLVIII). Formation of intermediate germaethylene in

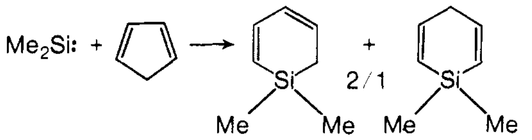
SCHEME XLVIII

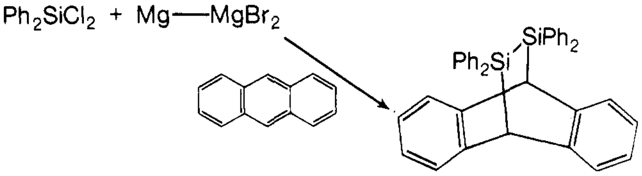


the given process was proved by trapping it with dimethylbutadi-1,3-ene:



It should be pointed out that the applicability of the processes of generation of silaalkenes, considered in this section, is restricted by the difficulty of obtaining starting bicyclooctadi-2,5-enes. In the first case, the limiting factor is the reproducibility of the reaction of dianion with 1,2-dichlordisilane; in the second case, the availability of 1-silacyclohex-2,4-enes. Therefore, the methods of obtaining 1-silacyclohex-2,4-enes by reacting silylenes with cyclopentadienes[231,232] and also the synthesis of 7,8-disilabicyclo[2.2.2]octadi-2,5-enes by the reaction of diphenyldichlorosilane, anthracene, magnesium bromide, and metal magnesium in tetrahydrofuran[219] are of interest. Like the methyl-substituted homolog, this bicyclo[2.2.2]octadiene decomposes with the formation of intermediate disilaethylene (Scheme XLIX). Fragmentation of this compound upon electron impact proceeds in a similar manner. Unfortunately this synthesis does not proceed with dimethyldichlorosilane.





20

SCHEME XLIX

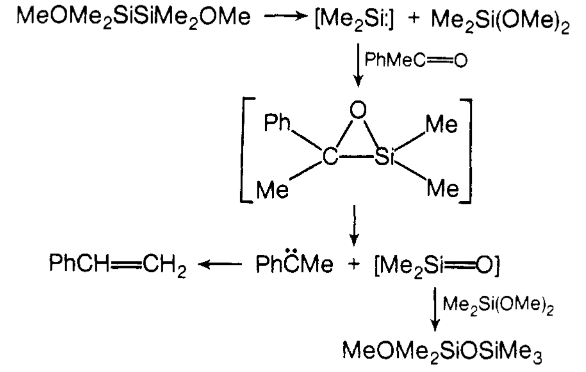
$$\mathbf{20} \xrightarrow{>320\ ^\circ C} C_4H_{10} + [Ph_2Si{=}SiPh_2] \longrightarrow (Ph_2SiSiPh_2)_n$$

By two alternative mechanisms (Scheme L) involving generation of 2-silaallene or 2-silaketene, molecules containing a diagonal silicon atom, the thermal decomposition of 2,8-dimethyl-3,9-dichloro-6-sila[5.5]spiroundecatetra-2,4,8,10-ene is explained.[233] Both of them are formed by a [6→4+2] cycloelimination reaction. Silaphosgene, $Cl_2Si{=}O$, is presumably formed via a [6→4+2] cycloelimination upon gas-phase thermal reaction of substituted furans with trichlorosilane.[234]

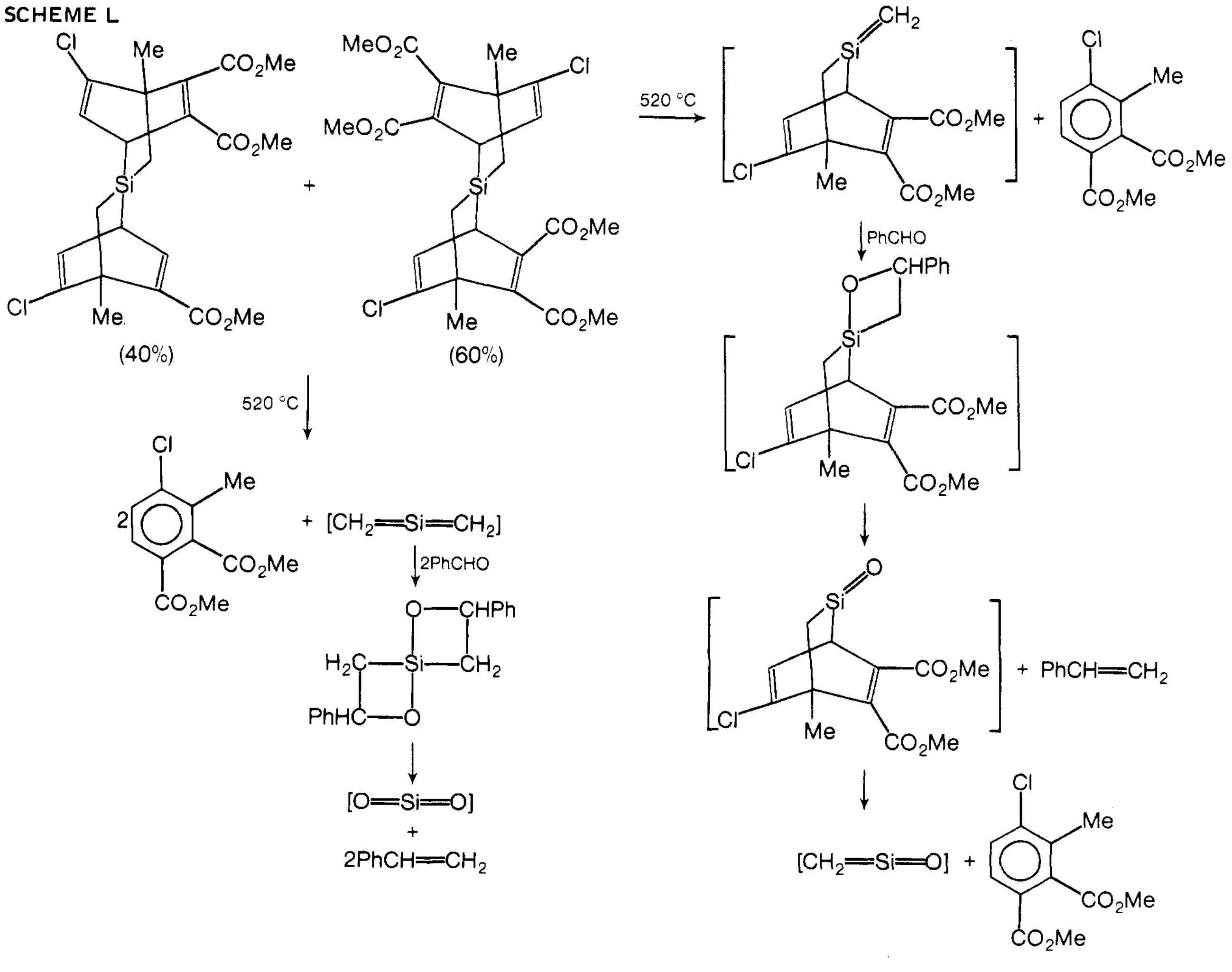
D. [3→2+1] Cycloelimination

Ando et al.[235,236] suggested that dimethylsilylene thermally generated from 1,2-dimethoxy-1,1,2,2-tetramethyldisilane reacted with carbonyl compounds yielding transient oxasilacyclopropane, which was subjected to further decomposition. Thus,

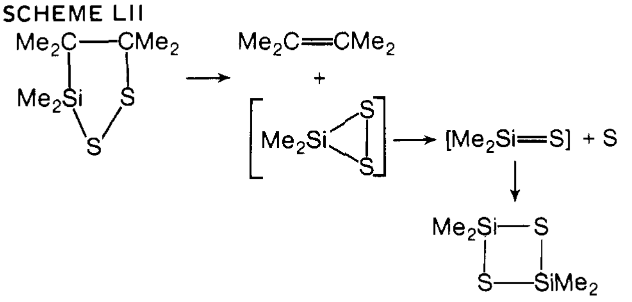
SCHEME LI



SCHEME L



SCHEME LII

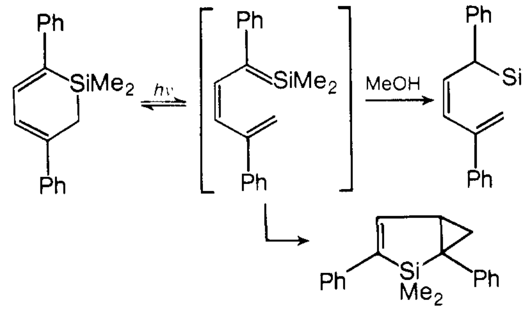


the formation of styrene and tetramethyldimethoxydisiloxane in the reaction with acetophenone is explained (Scheme LI) by the sequence including [3→2+1] cycloelimination from oxasilacyclopropane to give phenylmethylcarbene and dimethylsilanone. However, this interpretation of the reaction mechanism is not confirmed by other data[237-241] related to thermal transformations of intermediate oxasilacyclopropanes, oxagermacyclopropanes, and germaaziridienes. Decomposition of 1,1,4,4,5,5-hexamethyl-2,3-dithia-1-silacyclopentane into tetramethylethylene and tetramethyl-1,3-disilathiane by a plausible mechanism is given in Scheme LII, which also involves a [3→2+1] cycloelimination step.[242]

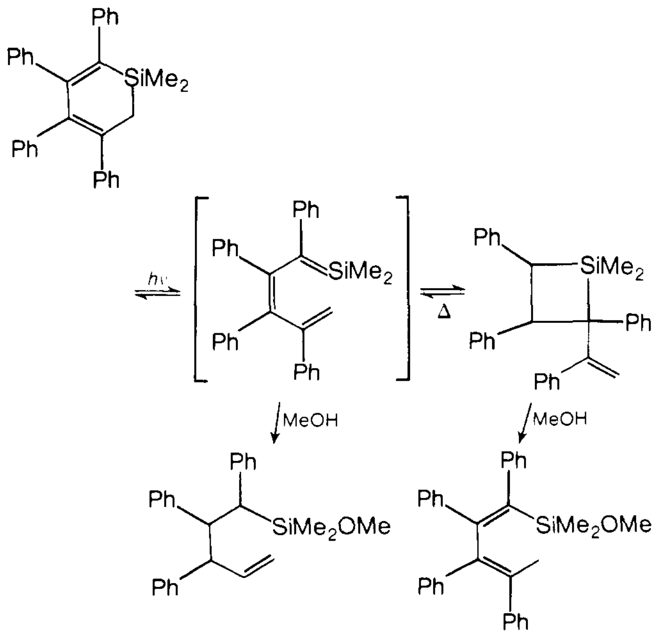
IV. Electrolytic Transformations of Silacycles into Polyenes

Thermal cyclization of hexatrienes into cyclohexadienes and reverse photochemical process are distinctive examples of electrolytic reactions.[45,243] Photoisomerization of 1,1-dimethyl-2,5-diphenyl-1-silacyclohexa-2,4-diene (Scheme LIII) is believed[244] to proceed with the formation of intermediate 1,1-dimethyl-2,5-diphenyl-1-silahexa-1,3,5-triene.

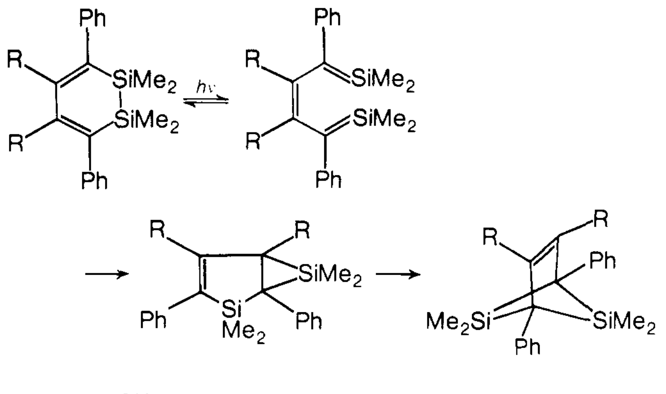
SCHEME LIII



SCHEME LIV



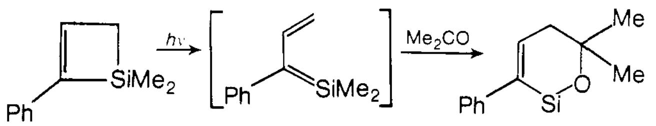
SCHEME LV



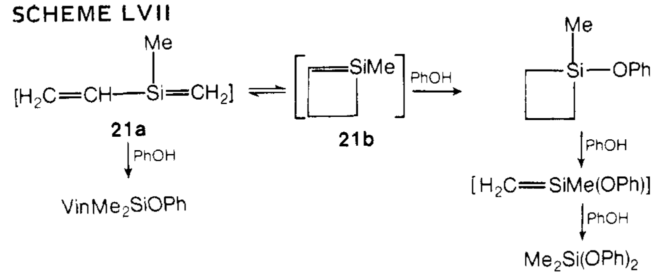
Photolysis of the tetraphenyl derivative (Scheme LIV) yields silacyclobutane which at 550 °C changes qualitatively to starting silacyclohexa-2,4-diene.[244] The mechanism of this reaction also involves participation of silahexatriene. In terms of silahexatriene intermediates are also explained[245,246] by photochemical transformations of 1,2-disilacyclohexadienes (Scheme LV).

The pathway of the photochemical transformation of 1,1-dimethyl-2-phenyl-1-silacyclobutene-2 in acetone solution (Scheme LVI) is undoubtedly defined by the formation of intermediate 1,1-dimethyl-2-phenyl-1-silabutadi-1,3-ene.[247] The reverse process, i.e., electrocyclic cyclization of thermally generated 1-silabutadi-1,3-enes into silacyclobutenes[248] is discussed in section V.D. 2-Silabutadiene **21a** formed upon pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane[37,38,249] possibly undergoes intramolecular cyclization into silacyclobutene **21b** (Scheme LVII), both silicon-carbon double-bonded intermediates, **21a** and **21b**, forming adducts with phenol.[250] Similarly, 1,4-disilabuta-1,3-dienes can be generated thermally[251,252] (Scheme LVIII).

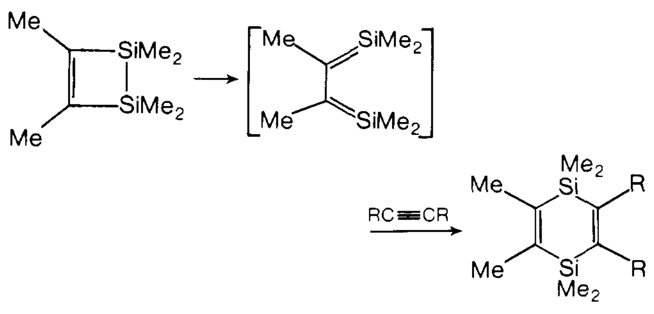
SCHEME LVI



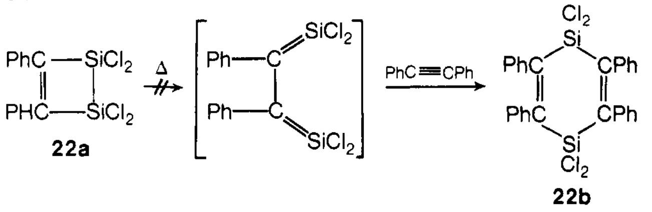
SCHEME LVII



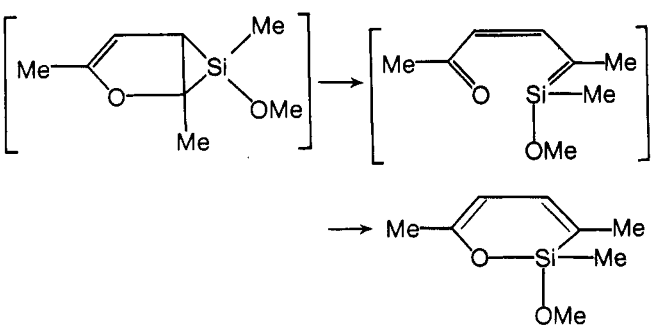
SCHEME LVIII



SCHEME LIX



SCHEME LX



In contrast to Scheme LVIII, the gas-phase reaction of 1,2-disilacyclobutane **22a** with diphenylacetylene[253] did not yield 1,4-disilacyclohexadiene **22b** (Scheme LIX).

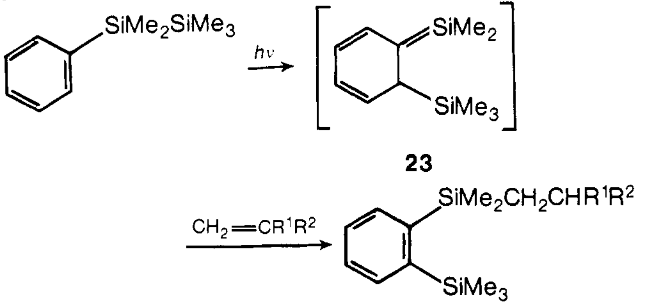
In view of the demonstrated reactivity of methyl-substituted 1,2-disilacyclobutene[251,252] toward acetylenes, this result is rather unexpected. It is also assumed[254] that the isomerization shown in the Scheme LX is a necessary step in the sequence resulting in 2-methoxy-2,3,6-trimethyl-1-oxa-2-silacyclohexa-3,5-diene upon copyrolysis of *sym*-tetramethoxydimethyldisiloxane and 2,5-dimethylfuran. An entirely different mechanism has been suggested for the reaction between dichlorosilane and furan.[232]

V. Sigmatropic Rearrangements

A. 1,3-Migration of Silyl Group from Silicon to Carbon upon Photolysis of Arylmethyl Polysilanes

When a σ-bonded silicon atom is attached to the allylic[255,256] or silaallylic system, sigmatropic rearrangements occur involving 1,3-migration of the silyl group. The latter is illustrated by the addition of arylpentamethyldisilane to olefins and dienes (Scheme LXI), a reaction discovered by Kumada et al.,[257-259]

SCHEME LXI

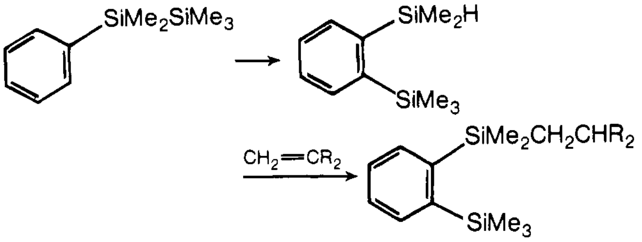


R^1 = Me; R^2 = Me
R^1 = Me; R^2 = Vin

which includes photorearrangement of disilane into a silicon-carbon double-bonded intermediate, **23**.

Although photolysis of organopolysilanes is known to yield silylenes,[260-262] they do not play any significant role in the reaction. The mechanism involving rearrangement of arylpentamethyldisilane into hydrosilane (Scheme LXII) followed by hydrosilylation proved to be also not the controlling process.[257]

SCHEME LXII

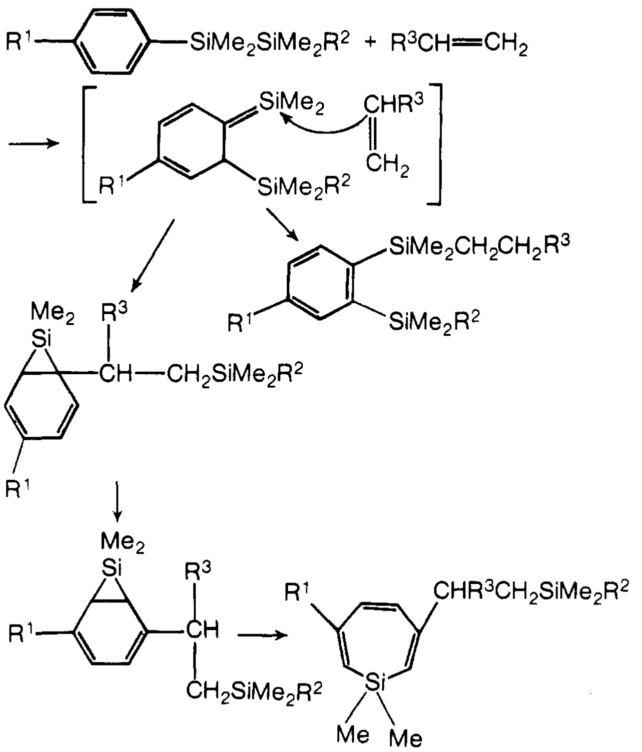


The chemical behavior of the intermediate with these and other trapping agents[263] is different from the one described in previous sections. This is due to the greater tendency of the intermediate to stabilize itself by reducing the aromatic sextet via addition to an unsaturated substrate with a simultaneous hydrogen shift from the ring to the substrate. The presence of a bulky substituent such as Me_3Si adjacent to the silicon-carbon double bond is also responsible for such behavior. Adducts with **23** are formed more readily by terminal olefins than by olefins having internal double bonds. Among internal olefins the cis isomers are more reactive than the trans.[259] The schematic representation of the HOMO-LUMO interaction (see Figure 3) shows that the positive overlap of orbitals favors the formation of an adduct.

Irradiation of arylmethyldisilanes with vinyl silanes or vinyl ether gives together with expected adducts a smaller yield of silepins (Scheme LXIII), which also result from the intermediacy of the silicon-carbon double bond.[259,264]

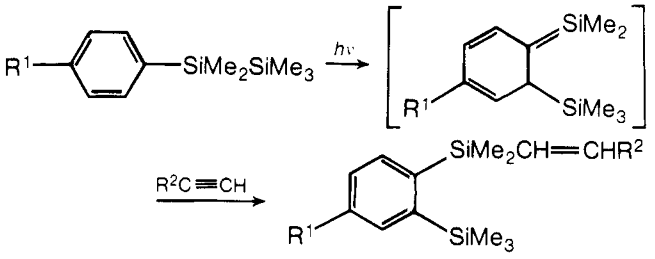
Adducts were not found in the photolysis of arylpentamethyldisilanes in the presence of 2,5-dimethylhexadi-1,4-ene or 1,3-cyclooctadiene.[265] Therefore, the intermediate, **23**, may react only with the terminal double bond of dienes. Addition of **23** to conjugated dienes involves only one double bond, it being

SCHEME LXIII



R^1 = H; R^2 = Me; R^3 = $SiMe_3$
R^1 = H; R^2 = Ph; R^3 = $SiEtMe_2$
R^1 = Me; R^2 = Me; R^3 = $SiHMe_2$
R^1 = H; R^2 = Me; R^3 = OVin

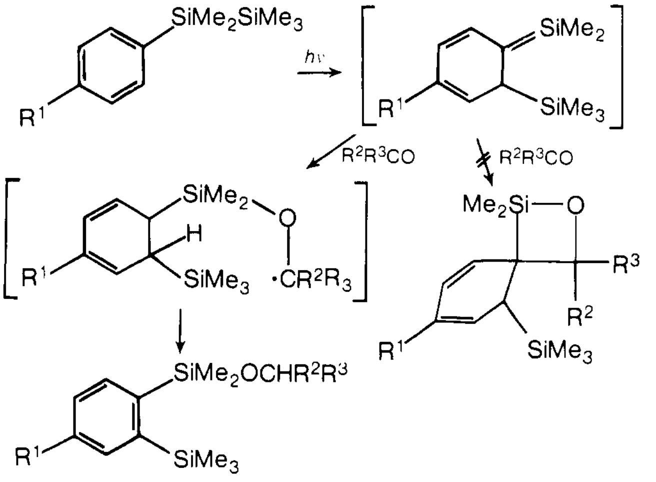
SCHEME LXIV



$R^1 = H; R^2 = n\text{-Bu}$ $R^1 = Me; R^2 = n\text{-Bu}$
$R^1 = H; R^2 = Me_3Si$ $R^1 = H; R^2 = H$

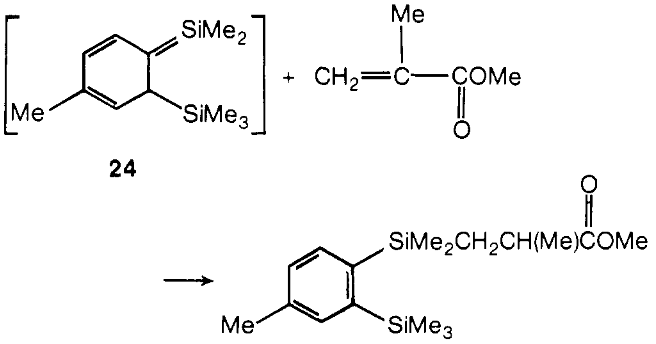
preferably the methyl-substituted double bond. Addition of alkynes to the intermediate resulting from the photolysis of arylpentamethyldisilanes (Scheme LXIV) proceeds in the same manner as to olefins and dienes, but more slowly.[266] The intermediates also react with enolizing and nonenolizing carbonyl compounds yielding 2-trimethylsilyl (alkoxydimethylsilyl)benzenes.[267] The reaction (Scheme LXV) proceeds readily if equal

SCHEME LXV



amounts of the reactants are taken. If the carbonyl compound is taken in excess, disilane does not rearrange itself probably because of the large absorption of energy by the former. No [2+2] cycloaddition products were observed in any of the experiments.

A similar course of the reaction was noted with methyl vinyl ketone and acrolein, but in the case of methyl methacrylate, reaction proceeds involving the carbon-carbon double bond.[267]



With methyl acetate and *N,N*-dimethylacetamide the reaction did not proceed at all; nonvolatile polymerization products of **24** were formed, but not the adduct. A sharp decrease in the yield of adduct was also noticed when photolysis of arylpentamethyldisilane was carried out in the presence of propionaldehyde. Such a change in reactivity is explained by the formation of a 1,4-biradical in the addition stage.[267] Hence, it may be concluded that reaction with intermediates like **23** or **24** is favored by those carbonyl compounds which have substitutents capable of stabilizing the radical center at the neigboring carbon atom.

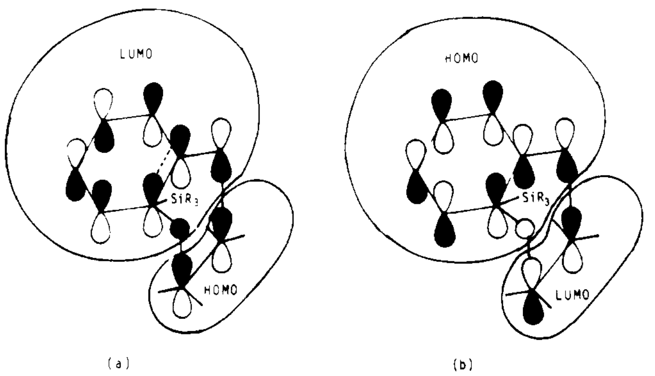
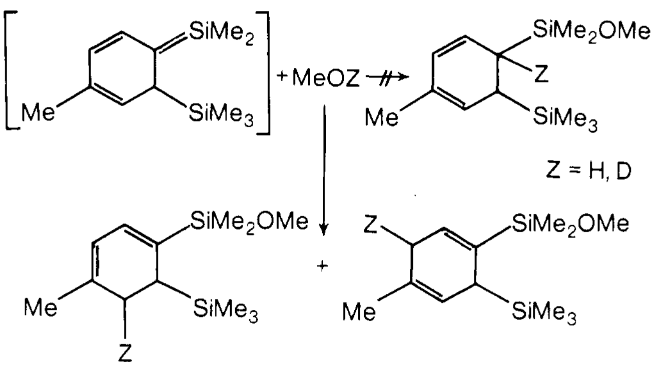


Figure 3. Schematic representation of the orbital interactions: (a) interaction between HOMO of olefin and LUMO of intermediate, (b) interaction between HOMO of intermediate and LUMO of olefin (after Ishikawa, Fuchikami, and Kumada[259]).

The intermediate formed in the photolysis of arylpentamethylsilane reacts with methanol in an unusual manner (Scheme LXVI) forming 1,4- and 1,6-adducts.[268] Thus, these reactions are

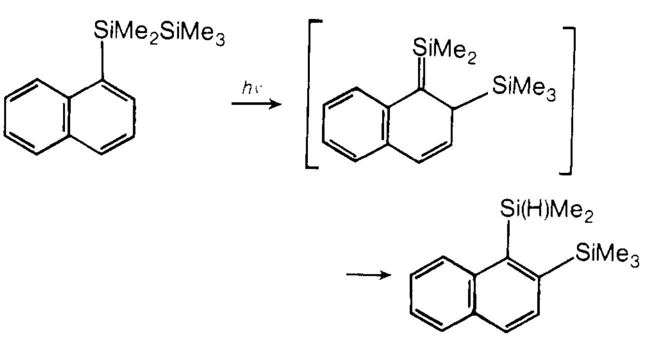
SCHEME LXVI



indicative of specific properties of silicon-carbon double-bonded intermediates formed upon pyrolysis of arylpentamethyldisilane.[269]

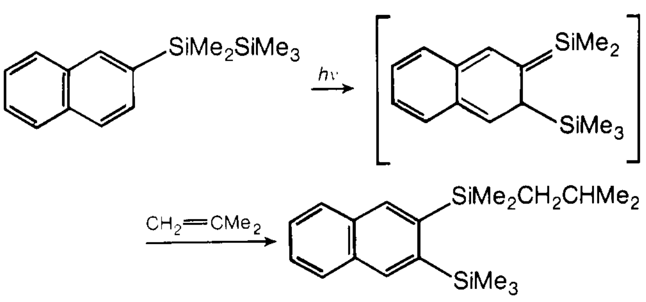
A similar 1,3-migration of the silyl group was also observed during photolysis of disilanes with fused aromatic substituents.[269] Thus, photolysis of 1-pentamethyldisilanylnaphthalene is not affected by trapping agents, but yields 1-dimethylsilyl-2-trimethylsilylnaphthalene (Scheme LXVII). In this case the intermediate readily changes into the resultant product owing to intramolecular migration of the hydrogen atom. In distinction to this, 2-pentamethyldisilanylnaphthalene isomerizes and reacts with olefins in the usual manner (Scheme LXVIII).

SCHEME LXVII



The pathway of photochemical transformation of arylmethyldisilanes depends on the number of aryl groups. A detailed study of this dependence has not been made yet. However, it is known that photolysis of pentaphenylmethyldisilane[270] proceeds via a silicon-carbon p_π-p_π double-bonded intermediate derived

SCHEME LXVIII

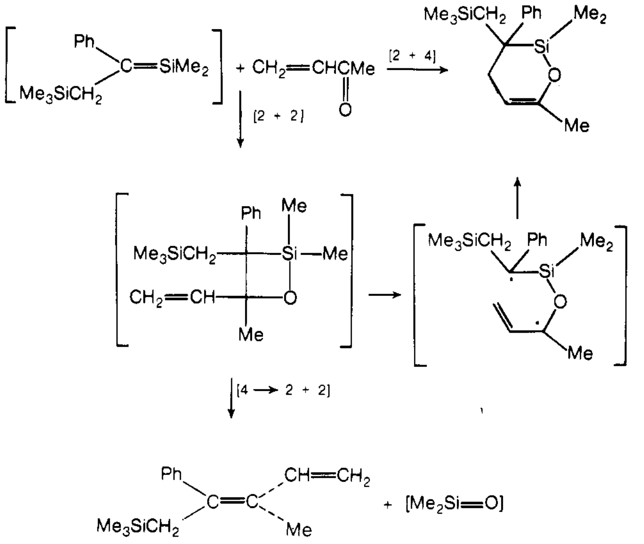


from dehydrosilylation, but not from isomerization. A similar reaction proceeds to a smaller extent upon photolysis of *p*-tolylpentadimethyldisilane.[268] Rearrangement, but not dehydrosilylation, governs the photochemical transformation of disilanes with two aryl substituents.[265]

Among phenylmethylpolysilanes containing more than two silicon atoms photorearrangement is not the main reaction. For example, in 2-phenylheptamethyltrisilane[258,275] and tris(trimethylsilyl)phenylsilane[239] photorearrangement is accompanied by the formation of silylenes,[272-275] which is predominant. Products indicative of 1,3-migration of silyl group to the ortho carbon of the aromatic ring were not found at all upon pyrolysis of arylmethyldisilanes, 2-phenylheptamethyltrisilane, and 2,3-diphenyloctamethyltetrasilane in the presence of dimethyl sulfoxide.[275,276]

B. Migrations of Silyl Group from Silicon to Carbon upon Photolysis and Thermolysis of Alkenyldisilanes

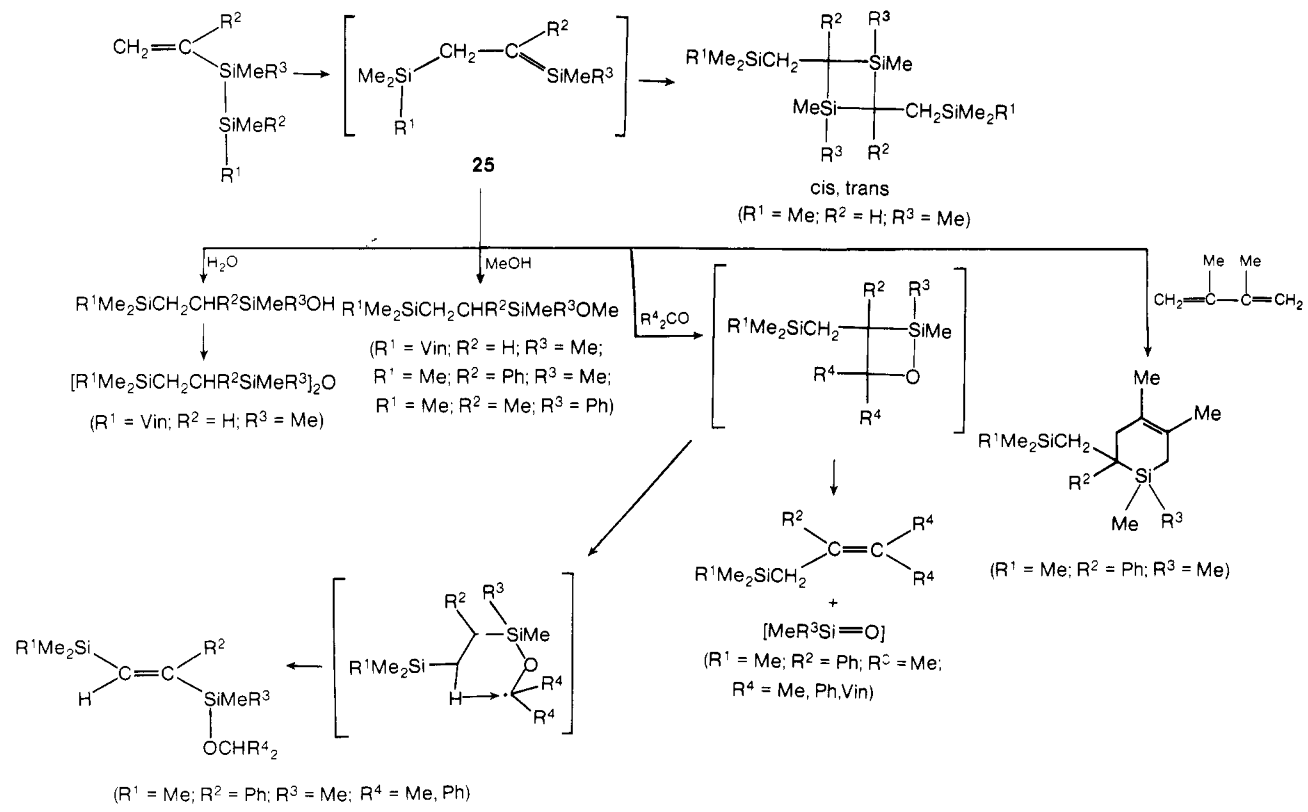
SCHEME LXX



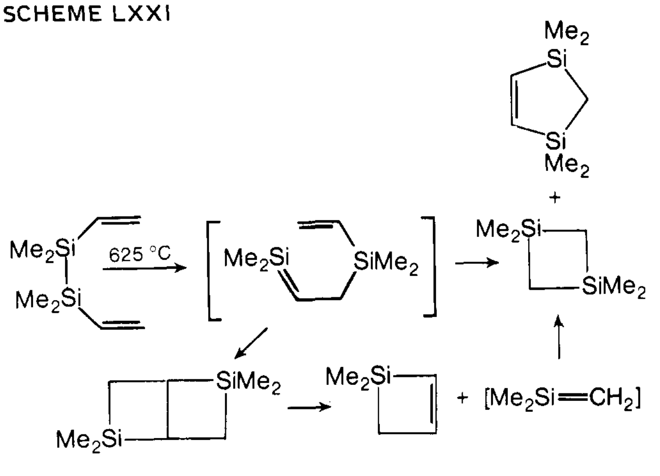
Alkenyldisilanes are photoisomerized by 1,3-migration of the silyl group resulting in intermediate **25**, which has properties similar to other silicon-carbon double-bonded intermediates (Scheme LXIX). It yields adducts with water, methanol, carbonyl compounds, and dienes and dimerizes in the absence of trapping agents.[263,277] For example (Scheme LXX), Me_3SiCH_2C-$Ph{=}SiMe_2$ reacts with methyl vinyl ketone yielding [2+2] and [2+4] cycloaddition products, of which the former undergoes [4→2+2] cyclodecomposition. It is of interest to note that isomerization of transient 1,2-disilaoxetane[263] proceeds only with ring expansion, but not via known 1,5-migration of hydrogen atom in the biradical intermediate.

The phenyl substituent at silicon has no effect on the pyrolysis of alkenyldisilanes; the silyl group first migrates to the alkenyl substituent but not to the phenyl ring. Phenyl attached to the double-bonded carbon atom causes various reactions. It is seen from the Scheme LXIX that all processes except cyclodimerization are typical for disilane, in which R^2 = Ph. Steric hindrances due to phenyl groups also suppress cyclodimerization when R^3 = Ph.

SCHEME LXIX



SCHEME LXXI

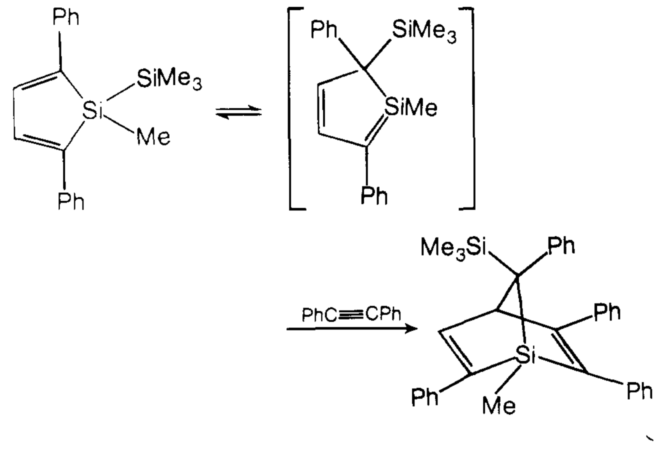


In β-styryldisilanes,[246,263,269] 1,2-migration of the silyl group predominates resulting in derivatives of silacyclopropane and 1-silaindan. Products indicating participation of the silicon–carbon double-bonded intermediates were not observed.[263]

Thermally induced 1,3-migration of the silyl group from silicon to carbon (Scheme LXXI) to produce a silicon–carbon double bond occurs upon pyrolysis of 1,2-divinyl-1,1,2,2-tetramethyldisilane.[278,279] This process involves two types of silicon–carbon double p_π–p_π bonded intermediates.

Finally, 1,5-migration of the silyl group from silicon to carbon in 1-silacyclopentadi-2,4-ene results in 1-silacyclopentadi-1,3-ene, an intermediate with a p_π–p_π bonded silicon[280a] (Scheme LXXII).

SCHEME LXXII



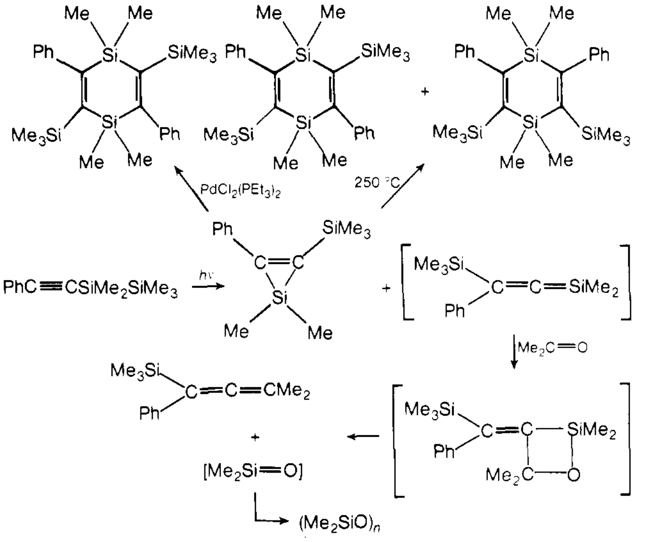
C. Photolysis of Alkynyldisilanes

Upon photolysis of (pentamethyldisilanyl)phenylacetylene (Scheme LXXIII), silicon–carbon p_π–p_π double-bonded intermediates are formed in small yield.[281] This reaction is mainly directed to formation of 1-silacyclopropane,[282] which transforms into a dimer in the presence of a catalyst or on heating by the cyclodimerization mechanism.[283]

Photolysis of 1-silyl- and 1-disilanyl-3-trimethylsilyl-3-phenylpropynes, and 1-silyl- and 1-disilanyl-1,3-bis(trimethylsilyl)-3-phenylpropadienes, is not indicative of the intermediacy of silaethylenes.[284]

The formation of 1,2-disilacyclobutane **27** in the photolysis of trimethylsilyl(1,1-diphenyltrimethyldisilanyl)acetylene is explained.[175] (Scheme LXXIV) is explained in terms of the head-to-head dimerization of the transiently formed silapropadiene **26**.

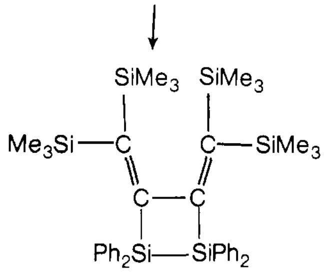
SCHEME LXXIII



SCHEME LXXIV

$Me_3SiC{\equiv}CSi(Ph_2)SiMe_3 \xrightarrow{h\nu} [(Me_3Si)_2C{=}C{=}SiPh_2]$

26



27

D. Photolysis and Thermolysis of Acyl Polysilanes

Brook et al.[173,174,285] showed that polysilanes on photolysis and thermolysis (Scheme LXXV) rearrange into silaethylenes.

SCHEME LXXV

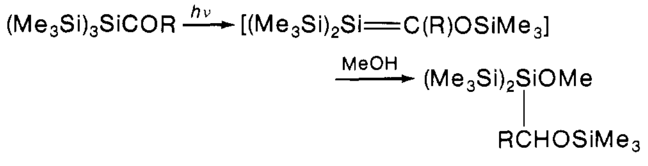
$$R^1{}_3SiSiR^2{}_2COR^3 \xrightarrow{h\nu} [R^2{}_2Si{=}C(R^3)OSiR^1{}_3] \xrightarrow{MeOH} MeO(R^2{}_2)SiCH(R^3)OSiR^1{}_3$$

$R^1 = R^2 = R^3 = Ph$

$R^1 = R^3 = Ph;\ R^2 = Me$

This reaction to a known extent simulates 1,3-migration of substituents observed earlier for α-ketosilanes.[286,287] An increase in the number of silyl groups capable of migrating to the carbonyl carbon makes the process more selective (Scheme LXXVI).

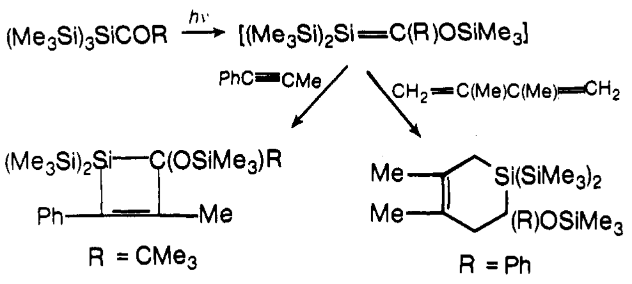
SCHEME LXXVI



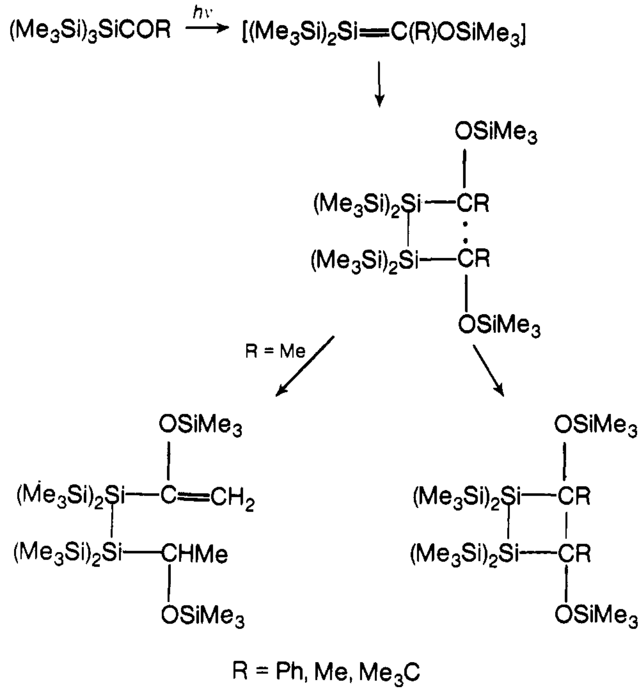
$$(Me_3Si)_3SiCOR \xrightarrow{h\nu} [(Me_3Si)_2Si{=}C(R)OSiMe_3] \xrightarrow{MeOH} \begin{array}{c}(Me_3Si)_2SiOMe\\ |\\ RCHOSiMe_3\end{array}$$

R = Ph, Me, CMe3 >95%

SCHEME LXXVII



SCHEME LXXVIII



It is quite probable that silyl groups at the silicon end of silicon–carbon double bond also exert a significant stabilizing effect on silaethylenes.

The photolysis of acyltrisilanes in the presence of 2,3-dimethylbutadi-1,3-ene or phenylpropene yielded corresponding products of their [2+4] and [2+2] cycloaddition to silaethylene (Scheme LXXVII). In the absence of interceptors, head-to-head cyclic dimer and disproportionation product, preceding cyclization of a biradical, were formed (Scheme LXXVIII). Thus, unlike the well-known head-to-tail cyclodimerization, these silaethylenes dimerize in a different manner yielding 1,2-disilacyclobutanes.

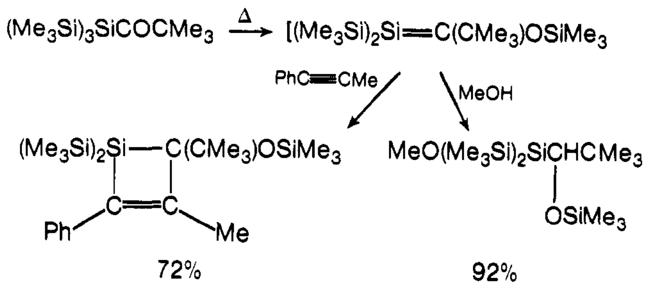
Silaethylene, formed on photolysis of pivaloyltris(trimethylsilyl)silane, is far more stable in the monomeric form than other silicon–carbon double-bonded intermediates. It forms adducts even upon adding interceptors after photolysis is over.[174]

The thermolysis of acylpolysilanes yields a mixture of products. The decomposition mechanism may be judged by the composition of a mixture obtained on copyrolysis of pivaloyltris(trimethylsilyl)silane (at 160–170 °C) with methanol and 1-phenylpropyne (Scheme LXXIX).

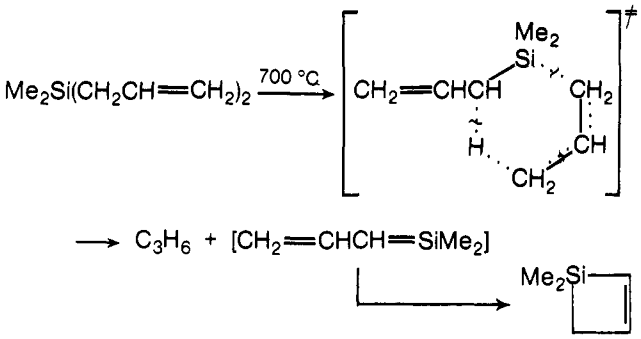
E. The Retroene Generation of Silaalkenes and Siladienes

The retroene reaction proceeding via a six-membered transition state is classified as a sigmatropic rearrangement.[243] Recently detailed studies have been made on the retroene reaction of $(CH_2{=}CHCH_2)_2X$ type molecules, namely, of heptadiene,[288] diallyl sulfide,[289,290] diallyl ether,[291,292] and diallylamine.[293-295] Block and Revelle[248] extended this reaction to diallylsilanes (Scheme LXXX). A number of little known silacyclobutanes were obtained with satisfactory yields under vacuum flash-pyrolysis conditions, the formation of which is explained in terms of cyclization of silabutadiene intermediates formed in the retroene process. The absence of 1,5-hexadiene (derived from combination of allyl radicals) argues against significant contributions from the free-radical mechanism.

SCHEME LXXIX

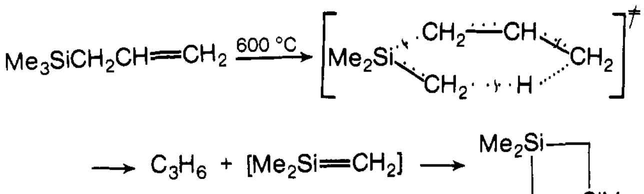


SCHEME LXXX

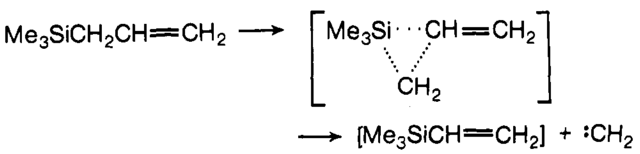


Earlier a retroene mechanism of allyltrimethylsilane pyrolysis was suggested[296,297] (Scheme LXXXI). This, however, is inconsistent with the data[298] on decomposition of allyltrimethylsilane at 500 °C with the formation of methylene and vinyltrimethylsilane classified as α-elimination (Scheme LXXXII).

SCHEME LXXXI



SCHEME LXXXII

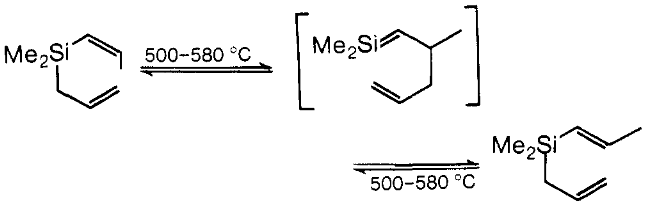


1,2- and 1,3-sigmatropic migration of the silyl group[255,299,300] also proceeds under reaction conditions. Therefore, it is proposed[38] that formation of 1,1-dimethyl-1-silaethylene in the pyrolysis of allyltrimethylsilane[296,297] may proceed in the free-radical process by disproportionation or by decomposition of trimethylsilyl radicals. In light of the obtained results[248] it would also be desirable to reexamine the pyrolysis of allyltrimethylsilane, a reaction whose mechanism has been the subject of controversy.

F. Cope [3,3]-Sigmatropic Rearrangement

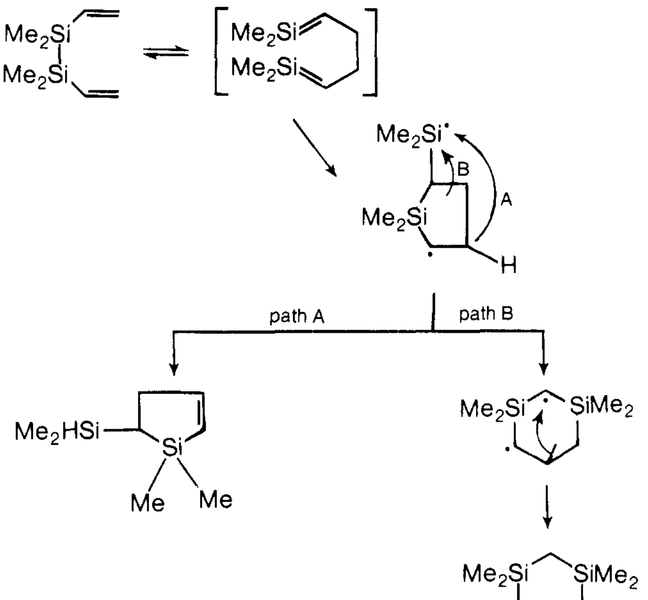
Slutsky and Kwart[256] attributed the [3,3]-sigmatropic rearrangement, which proceeds via a silicon-carbon double-bonded intermediate, to the geometric isomerization of *cis-* and *trans-*propenylallyldimethylsilane (Scheme LXXXIII). Arrhenius parameters prove to be very close to those for the similar rearrangement of heptadienes. Somewhat amazing appears to be a low increase of activation energy (only by 3 kcal/mol) which does not reflect the difference in C=C and Si=C bond energies. This effect is believed[256] to be compensated by the distinctive ability of silicon to get involved in a pericyclic transition state.

SCHEME LXXXIII



Cope rearrangement upon thermolysis of 1,2-divinyl-1,1,2,2-tetramethyldisilane is not the most economical mechanistic rationalization for all of the products.[279] However, some of them (Scheme LXXXIV) may be explained as originating from an initial Cope rearrangement followed by radical closure and either hydrogen migration (path A) or ring migration (path B).

SCHEME LXXXIV



VI. *Photoinduced Molecular Elimination of Silaethylenes from Silane, Disilane, and Disiloxane Derivatives*

Triplet silaethylene, $CH_2{=}SiD_2$, is believed to be formed with the 1470-Å radiation of methylsilane-d_3.[302] With the 1236-Å radiation[302,303] further decomposition of the intermediate proceeds with the loss of HD:

$$\begin{tikzcd}
CH_3SiD_3 \arrow[r, "1470\ \text{Å}"] & CH_2SiD_2 + HD \\
CH_3SiD_3 \arrow[r, "1236\ \text{Å}"] & CH_2SiD_2 + HD \arrow[d] \\
HD + CSi & CHSiD + HD \arrow[l]
\end{tikzcd}$$

Polymerization seems to be the main way of quenching the $CH_2{=}SiD_2$ intermediate. In the photolysis of dimethylsilane[304] up to 25% of primary reaction products are silaethylenes:

$$Me_2SiD_2 \xrightarrow{h\nu} CH_2SiD_2 + MeH$$

$$\rightarrow CH_2SiMeD + HD$$

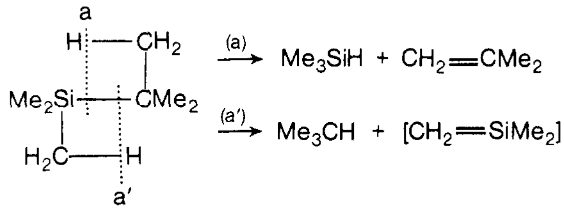
Molecular elimination of 1,1-dimethyl-1-silaethylene was noted in studies of the photolysis of tetramethylsilane:[305]

$$Me_4Si \rightarrow CH_4 + [Me_2Si{=}CH_2]$$

Free-radical oligomerization of silaethylene readily occurs under these conditions.

Two pathways of molecular decomposition were noted in the 1407-Å photolysis of *tert*-butyltrimethylsilane[306] (Scheme LXXXV). As the yield of isobutane proved to be twice as much as that of trimethylsilane, it was concluded that decomposition a′ was preferred to decomposition a.

SCHEME LXXXV

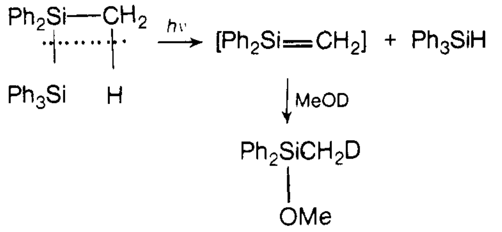


Under similar conditions hexamethyldisilane[306] decomposes to trimethylsilane and 1,1-dimethyl-1-silaethylene:

$$Me_3SiSiMe_3 \xrightarrow{h\nu} Me_3SiH + [Me_2Si{=}CH_2]$$

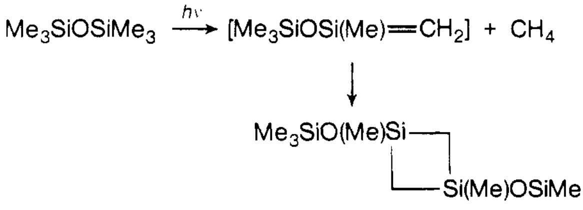
This process is reminiscent of the earlier observed photochemical dehydrosilylation of pentaphenylmethyldisilane[270] (Scheme LXXXVI).

SCHEME LXXXVI



Liquid-phase photolysis of hexamethyldisilane (185 nm) results in products, a large part of which is also obtained by molecular decomposition[307] (Scheme LXXXVII).

SCHEME LXXXVII



Trapping experiments with methanol have proved the formation of silaethylene. With no interceptor it disappears in reactions with free radicals to which the Si=C bond is more reactive than C=C.[307] To some extent decomposition to 1,1-dimethyl-1-silaethylene also proceeds:

$$Me_3SiOSiMe_3 \xrightarrow{h\nu} Me_3SiOH + [CH_2{=}SiMe_2]$$

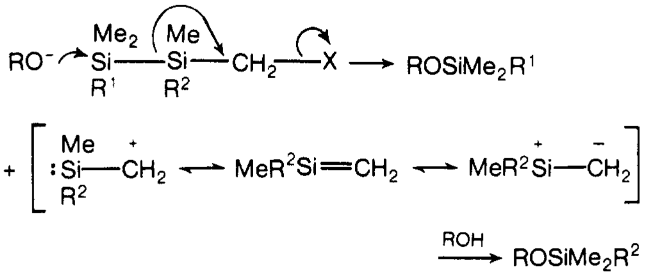
Molecular elimination of disilaethylene occurs upon decomposing chemically activated tetrasilane formed in disilane-sensitized photolysis:[308]

$$Si_4H_{10}^{\ddagger} \rightarrow Si_2H_4 + Si_2H_6$$

VII. Cleavage Involving β-Elimination

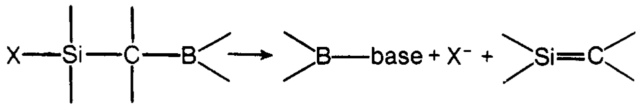
Cleavage of halomethyldisilanes by sodium ethoxide in ethanol was first explained as concerted β-elimination of unstable silaethylene followed by ethanol addition[309] (Scheme LXXXVIII).

SCHEME LXXXVIII

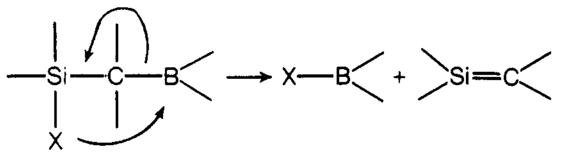


Later,[310] preference was given to the mechanism which does not involve a silaethylene intermediate.

Hopper and Fine[311] verified the possibility of generating silaethylenes by the well-known reaction[316] of β-elimination of alkenes from organoboron compounds:



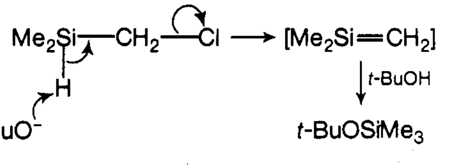
or



Base-catalyzed cleavage of $(RMe_2SiOSiMe_2CH_2)_3B$ with ethanol seems to prove silaalkene β-elimination predicted by the first scheme.

No dehydrohalogenation of trimethylsilyl iodine was observed after prolonged heating at 500 °C.[314] However, an elimination–addition mechanism is discussed[312] to account for the formation of observed products in reactions of solid alkoxide bases with chloromethyldialkylsilanes (Scheme LXXXIX) and

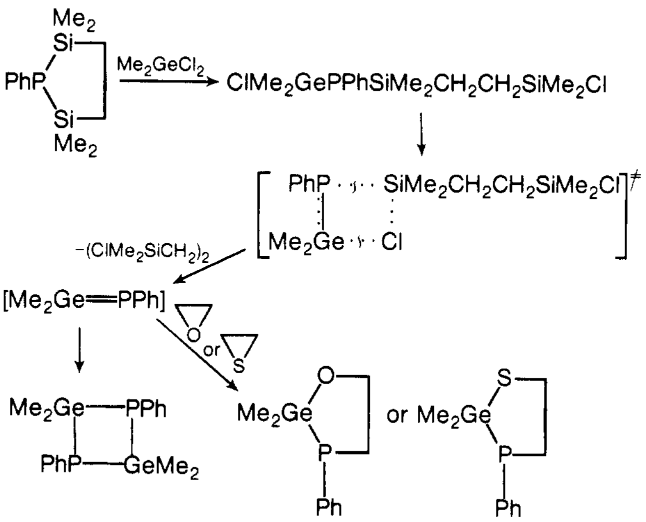
SCHEME LXXXIX



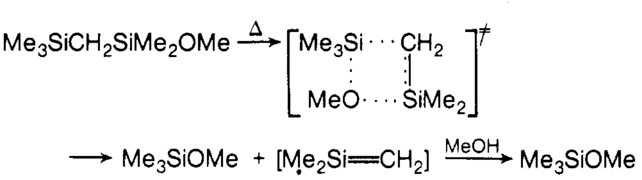
in the decomposition of α-dimethylsilylbenzylphenyl selenoxide.[313]

The exchange reaction between 2,5-bis(dimethylsila)-1-phenylphospholane and dimethyldichlorosilane[315] may possibly be represented as addition and subsequent intramolecular loss of the germaphasphoimine intermediate, $Me_2Ge{=}PPh$ (Scheme XC).

SCHEME XC



SCHEME XCI



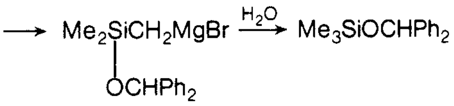
Thermal elimination of silaethylenes,[115a] germathionones,[185] and germanones[184] from structures $Me_3SiCH_2SiMe_2OMe$, $(Et_2GeSMe)_2S$, and $(Et_2GeOMe)_2O$ apparently occurs via a four-center transition state as given in Scheme XCI. Presumably the formation of 1,1,3,3-tetrachloro-1,3-disilacyclobutane upon pyrolysis of hexachlorodisilamethylene is also due to generating 1,1-dichloro-1-silaethylene from the unimolecular decomposition involving β-elimination.[317]

The unusual behavior of benzophenone in the reaction with dimethylmagnesium bromide (Scheme XCII) is possibly also related to the formation of an intermediate silaalkene.[318] This is supported by the known hydrogen transfer from the C–H bond to the metallic center resulting in the production of alkenes.[318] If 1,1-dimethyl-1-silaethylene is actually formed, then most probably it is due to the rearrangement of the benzophenone complex with Grignard reagent.[319]

SCHEME XCII

$$Ph_2C{=}O + Me_2Si(H)CH_2MgBr \longrightarrow Ph_2CHOMgBr + [Me_2Si{=}CH_2]$$

$$Ph_2CHOMgBr + [Me_2Si{=}CH_2]$$



$$\longrightarrow Me_2Si(OCHPh_2)CH_2MgBr \xrightarrow{H_2O} Me_3SiOCHPh_2$$

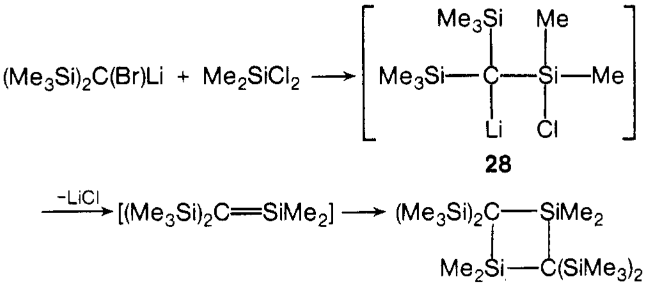
$$[Me_2Si{=}CH_2] + Me_2Si(H)CH_2MgBr \xrightarrow{H_2O} HMe_2SiCH_2SiMe_3$$

Recently Seyferth and Lefferts[320,321] have demonstrated that the reaction of bis(trimethylsilyl)bromomethyllithium with dimethyldihalo derivatives of silicon, germanium, and tin in each case gave the respective 1,3-dimetallocyclobutane. Formation of intermediate 1,1-dimethyl-2,2-bis(trimethylsilyl)-1-silaethylene via lithium chloride elimination from **28** is suggested as a possible step for the reaction mechanism (Scheme XCIII).

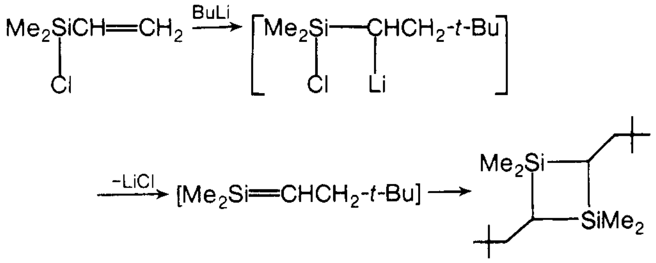
Jones and Lim[322] studied the addition of *tert*-butyllithium to vinylchlorosilanes at low temperatures and found that 1,3-disilacyclobutanes were formed in hydrocarbon solvents with a yield of 80%. To explain this unusual transformation the mechanism given in Scheme XCIV was proposed.

Attempts to trap intermediate α-lithiochlorosilane by trimethylchlorsilane were not successful. The reaction, carried out in the presence of butadi-1,3-ene, resulted in [2+2] and [2+4] cycloaddition products of the silaethylene intermediate

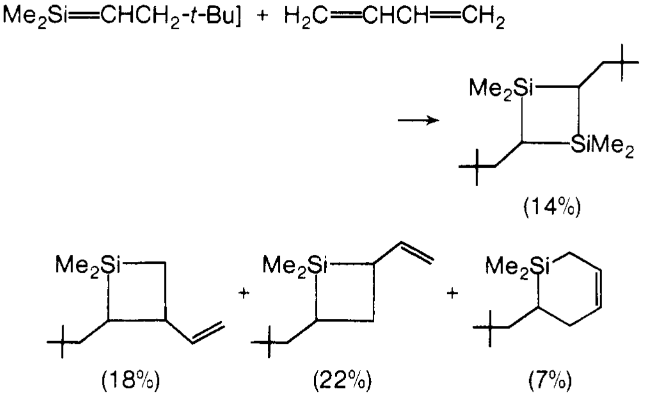
SCHEME XCIII



SCHEME XCIV



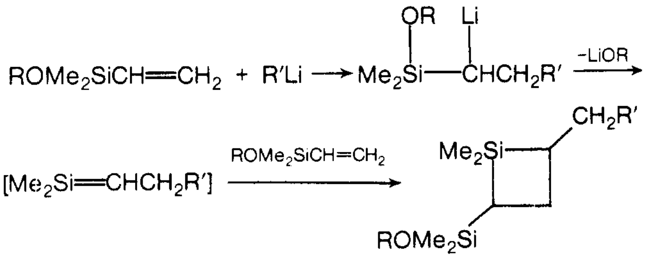
SCHEME XCV



to dienes (Scheme XCV) observed in a ratio proportional to the amount of syn-cis and syn-trans conformers.[323,324] Replacement of hydrocarbon solvent by ether or tetrahydrofuran increased the rate of combination of chlorosilane with organolithium compounds, thereby making it competitive with the lithium chloride elimination reaction.

When alkoxysilanes react with *tert*-butyllithium[323,325] monosilacyclobutanes become the main products. This was first explained[323] as given in Scheme XCVI. A more detailed study

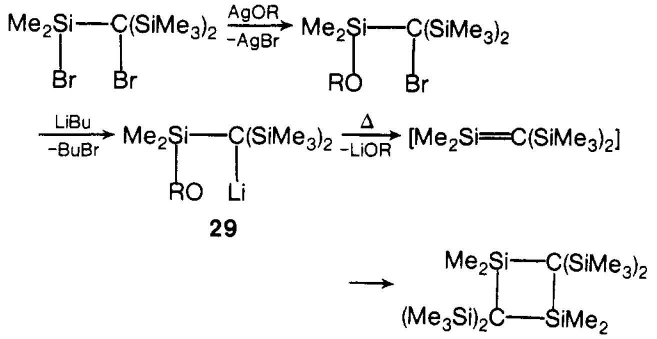
SCHEME XCVI



of the reaction proves the alternative mechanism which does not involve transient silaethylenes.[325]

Wiberg and Preiner[326,327] generated 1,1-dimethyl-2,2-bis(trimethylsilyl)-1-silaethylene from α-lithioalkoxysilanes and α-lithiosilyl phosphates, phosphites, or tosylates (Scheme XCVII). The decomposition temperature of 29 is dependent upon the nature of substituent R.

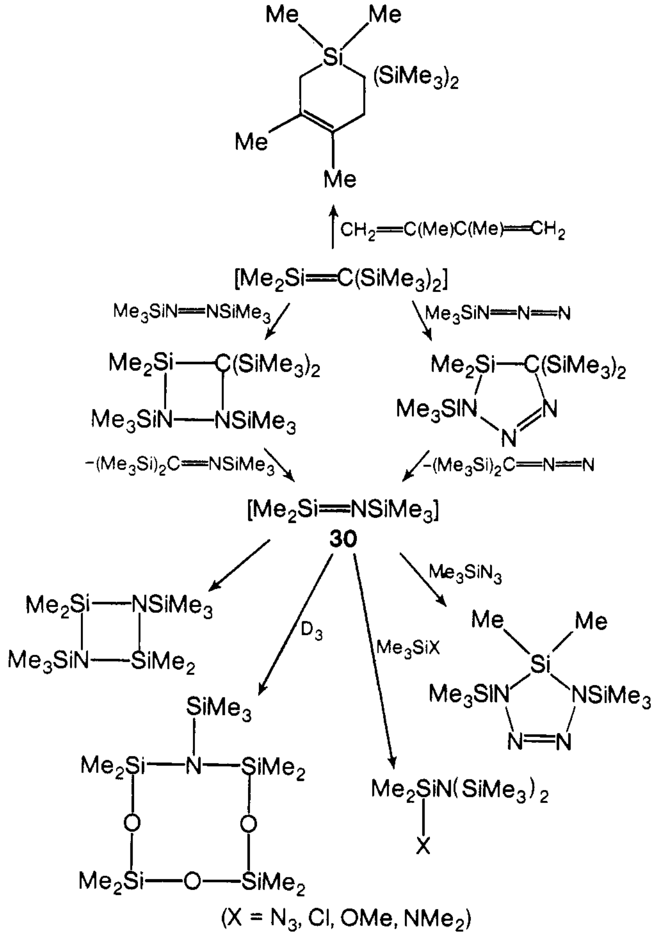
SCHEME XCVII



R	Decomp temp of **29**, °C
Me	220
Ph	220
Ph_2PO	90
(PhO)PhPO	12
$(PhO)_2PO$	-15
Tos	-50

As may be seen, α-lithiosilyl compounds in some cases are quite stable. The more electronegative is the substituent R, the easier is its decomposition. Gas-phase, low-pressure thermolysis enables silaethylene to be observed by mass spectroscopy. Given in Scheme XCVIII is chemical evidence for silaethylene intermediacy including reactions with trapping agents,[326-328] of which the reactions with bis(trimethylsilyl)diazene and trimethylsilyl azide result in silicon-nitrogen double-bonded intermediate **30**.

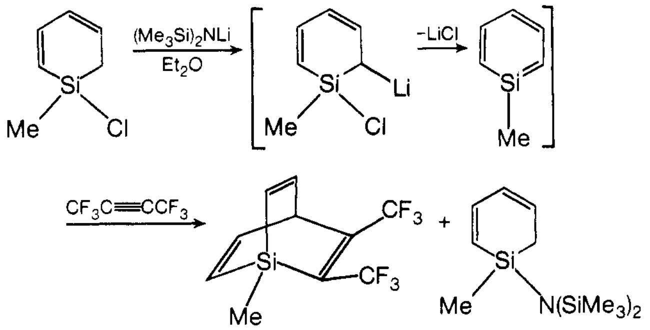
SCHEME XCVIII



($X = N_3$, Cl, OMe, NMe_2)

Lithium chloride elimination appeared to be a useful reaction for generating silabenzene,[329] as is shown in Scheme XCIX. It

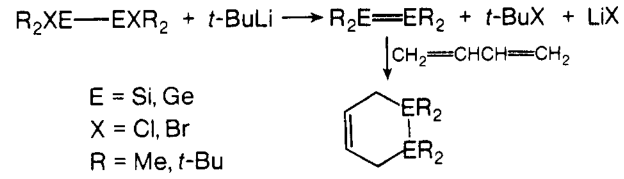
SCHEME XCIX



is seen that silabenzene readily yields [2+2] cycloaddition product with perfluorobut-2-yne, but not 1,3-disilacyclobutane. The negative tendency toward cyclodimerization is in line with predictions.[163]

The behavior of dihalodisilanes and -digermanes with various alkyllithium reagents has been investigated[587] in order to produce alkene analogs (see Scheme C). *tert*-Butyllithium, *n*-butyllithium, its tetramethylenediamine complex, and methyllithium failed to react with (t-Bu)$_2$BrSiSiBr(t-Bu)$_2$. No reaction was observed with lithium, sodium, or magnesium amalgams in THF. With molten potassium a viscous polymer was formed. Results were essentially unchanged with 1,3-dienes, e.g., cyclohexadi-1,3-ene, or *trans,trans*-2,4-hexadiene was initially present. The production of large quantities of polygermanes in the reaction of Me$_2$ClGeGeClMe$_2$ with t-BuLi may indicate the formation of Me$_2$Ge=GeMe$_2$ which immediately polymerizes even in the presence of a trapping agent, but other mechanisms can also account for the polymer.

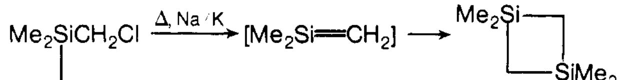
SCHEME C



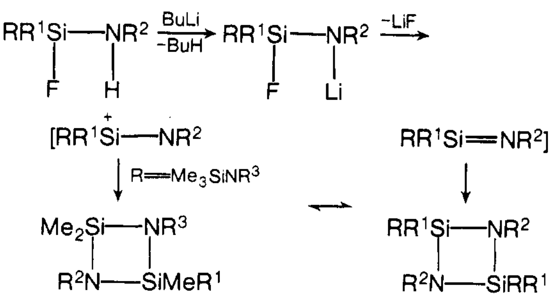
E = Si, Ge
X = Cl, Br
R = Me, t-Bu

However, 1,1-dimethyl-1-silaethylene is possibly formed upon gas-phase dechlorination of chloromethyldimethylchlorosilane with sodium–potassium vapors[330] (Scheme CI).

SCHEME CI



SCHEME CII



R^1 = Me; R^2 = R^3 = CMe$_3$
R^1 = Vin; R^2 = R^3 = CMe$_3$
R^1 = Ph; R^2 = R^3 = CMe$_3$
R^1 = Ph; R^2 = SiMe$_3$; R^3 = CMe$_3$

R = Me$_3$SiNCMe$_3$; R^2 = CMe$_3$
R = Me$_3$SiNCMe$_3$; R^1 = Me; R^2 = CMe$_3$
R = (Me$_3$Si)$_2$N; R^1 = Ph; R^2 = i-Pr
R = R^2 = CMe$_3$; R^1 = Ph

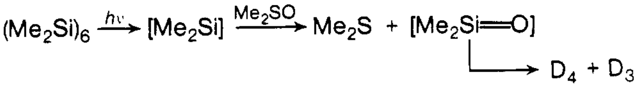
Klingebiel[331-338] established that the reaction pathway of butyllithium with aminofluorosilanes depends on the steric effect of substituents. The greater is the size of substituents, the easier are dimerization, cyclization, and other reactions; some of them proceed via intermediate ylide[332,336] formally equivalent to silaimine's silicon–nitrogen double bond[338] (Scheme CII). This has been confirmed by the experiments with trapping agents.[344] A similar mechanism, apparently, governs the reaction between lithium and hexachlorodisilazane[345] or 1,1,1-trichloro-3,3,3-trimethyldisilazane,[346] and also the dehydrocondensation of amines with triorganosilanes in the presence of lithium.[347]

VIII. *Formation of Silanones in Reactions of Polysilanes, Siliranes, and Silirenes with Dimethyl Sulfoxide*

A. Photolysis of Polysilanes in the Presence of Dimethyl Sulfoxide

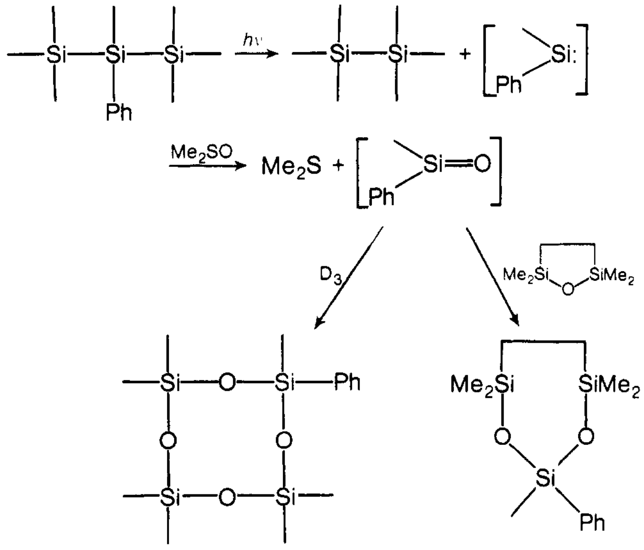
Photolysis of dodecamethylcyclohexasilane in the presence of dimethyl sulfoxide results in the formation of dimethyl sulfide and cyclic siloxanes D$_3$ and D$_4$.[348] The reaction (Scheme CIII) is explained in terms of generation of dimethylsilylene, its oxidation by dimethyl sulfoxide, and subsequent oligomerization of intermediate dimethylsilanones.

SCHEME CIII



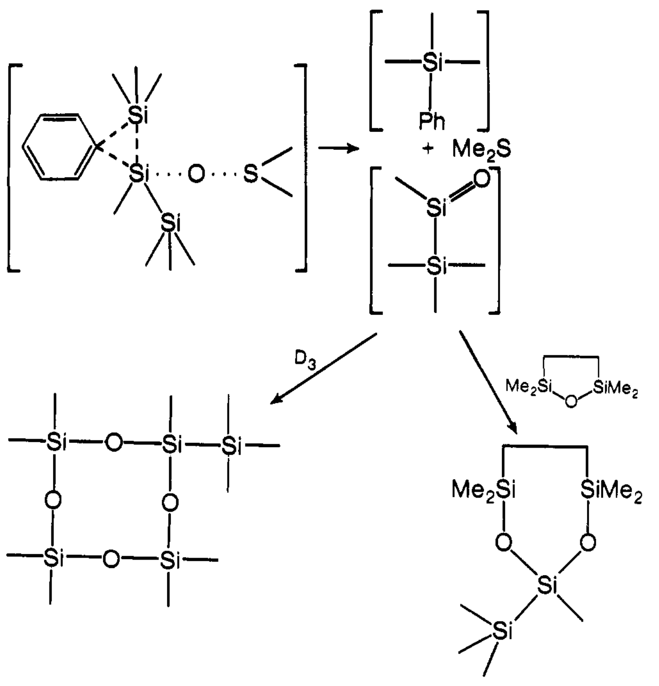
At least two pathways are typical for photolysis of heptamethyl-2-phenyltrisilane and octamethyl-2,3-diphenyltetrasilane in the presence of dimethyl sulfoxide.[275,349] The first given in the Scheme CIV involves generation and subsequent oxidation of methylphenylsilylene. The second pathway (Scheme CV) involves nucleophilic attack of oxygen of Me$_2$SO on the phenyl-substituted silicon atom, which leads to the formation of silanone via migration of the phenyl group to the neighboring silicon atom.

SCHEME CIV

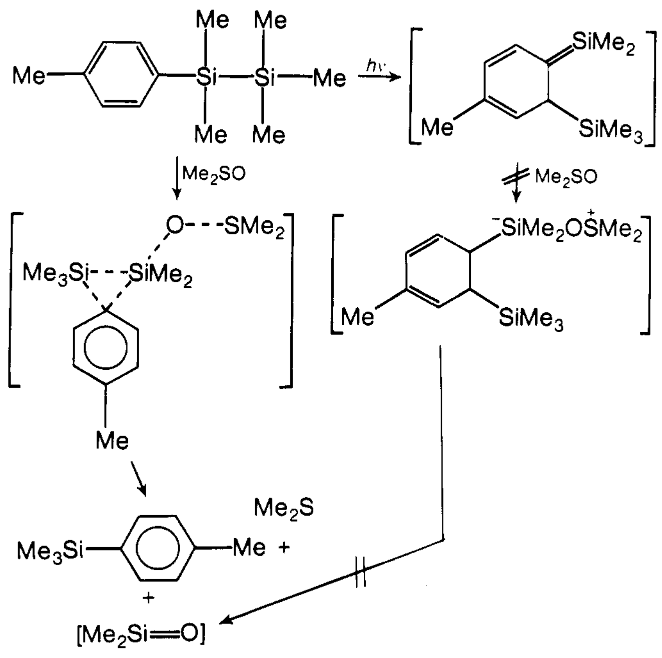


Photolysis of aryl-substituted disilanes in the presence of dimethyl sulfoxide[276] results in silanones only in accordance with the latter reaction (Scheme CVI) which does not involve the Kumada intermediate (see section V.A).

SCHEME CV



SCHEME CVI

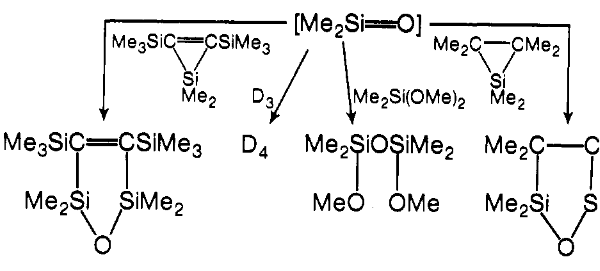


B. Reaction of Dimethyl Sulfoxide with Silirenes and Siliranes

Dimethyl sulfoxide as well as *N*-oxides of pyridine or triethylamine reacts with silirenes forming compounds due to the intermediacy of silanone[350,351] (Scheme CVII).

Generated dimethylsilanone readily reacts with silirenes and siliranes, D_3, and dimethyldimethoxysilane (Scheme CVIII). As

SCHEME CVIII



shown by competitive reactions, silirenes react more readily with dimethyl sulfoxide than siliranes. The difference in reactivity of these three-membered heterocycles decreases with respect to dimethylsilanone. The mechanism involving formation and oxidation of dimethylsilylene seems not to be controlling silanone generation in this case.[350]

IX. Decomposition and Disproportionation of Silyl and Silylmethyl Radicals

The views prevailing until recently that elements of the second and higher periods are unable to form multiple bonds did not induce researchers to elucidate production of group 4B olefin analogs by decomposition and disproportionation of radicals,[222,223] although these reactions were long known in the chemistry of carbon radicals.[352] For example, pyrolysis of tetramethylsilane,[353] methyldiethylsilane, tri-*n*-propylsilane, and tri(*tert*-butyl)silane, triethylsilane,[354] tetramethylgermane and tetramethyltin,[355,356] and tetramethyllead[357] was explained without involving any group 4B multiple-bonded intermediate. Decomposition of trimethylsilylmethyl radical (reaction 4) was first postulated to explain the formation of cyclic carbosilanes, $(Me_2SiCH_2)_n$, where $n = 2, 3$ (reactions 5 and 6), in tetramethylsilane pyrolysis.[100,101,358] But the complexity of the reaction

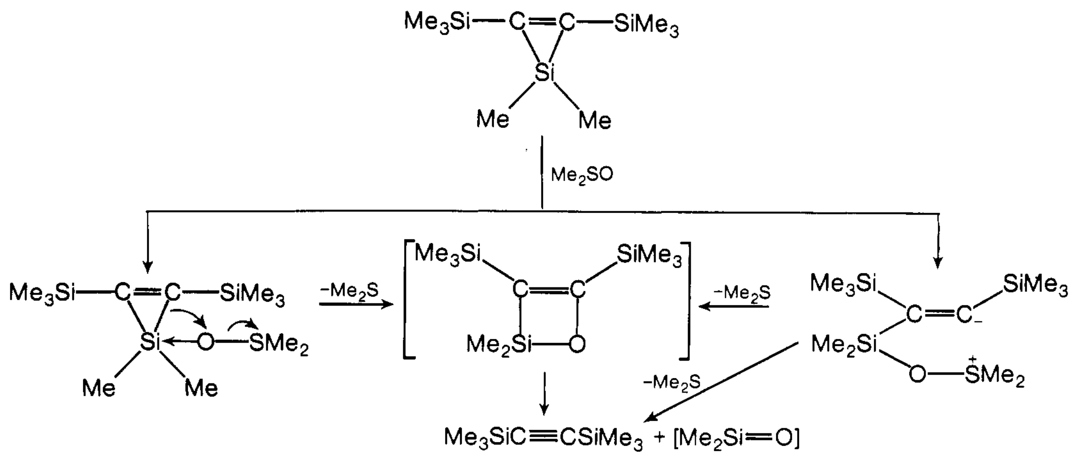
$$Me_4Si \longrightarrow Me_3Si\cdot + Me\cdot \tag{1}$$

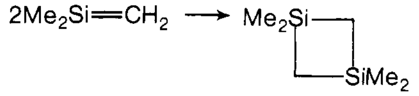
$$Me_4Si \longrightarrow Me_3SiCH_2\cdot + H\cdot \tag{2}$$

$$Me\cdot + Me_4Si \longrightarrow Me_3SiCH_2\cdot + MeH \tag{3}$$

$$Me_3SiCH_2\cdot \longrightarrow Me_2Si{=}CH_2 + Me\cdot \tag{4}$$

SCHEME CVII





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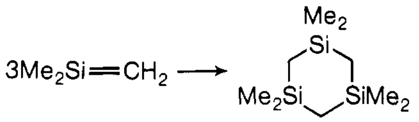


(6)

mixture and the absence of kinetic data did not exclude other mechanistic rationalizations of the formation of these cyclocarbosilanes.

The kinetic and chemical evidence of the formation of 1,1-dimethyl-1-silaethylene in the pyrolysis of 1,1-dimethyl-1-silacyclobutane[41,42] (see section II.A) urged two teams of researchers to study the kinetics of thermal decomposition of tetramethylsilane[359-361] and trimethylsilane,[361,362] so as to ascertain the role of decomposition and disproportionation reactions of silyl or silylmethyl radicals in the pyrolysis of organosilicon compounds. Clifford, Gowenlock, Johnson, and Stevenson[359] have found that pyrolysis of tetramethylsilane proceeds with the formation of products generated by the reactions of free radicals or 1,1-dimethyl-1-silaethylene. The estimated activation energy of the total process, 67.6 kcal/mol, appears to be lower than the Si-C bond dissociation energy by 15-20 kcal/mol. The proposed mechanism of decomposition differs from the one given above in the elimination of primary fission of the C-H bond (reaction 2) and in the introduction of new propagation (7-9) and termination (10, 11) reactions.

$$Me_3Si\cdot \rightarrow Me_2Si{=}CH_2 + H\cdot \qquad (7)$$

$$Me_3SiCH_2\cdot \rightarrow Me_2Si{=}CH_2 + Me\cdot \qquad (8)$$

$$H\cdot + Me_4Si \rightarrow Me_3Si{-}CH_2^{\cdot} + H_2 \qquad (9)$$

$$2Me_3Si\cdot \rightarrow Me_2Si{=}CH_2 + Me_3SiH \qquad (10)$$

$$Me\cdot + Me_3Si\cdot \rightarrow Me_2Si{=}CH_2 + MeH \qquad (11)$$

Reaction 7 in particular explains production of hydrogen. However, among decomposition reactions (7 and 8) reaction 8 is preferrable, because it proceeds with the rupture of the weaker Si-C bond. It is reaction 8 which is responsible for the chain mechanism of decomposition of tetramethylsilane. Disproportionation reactions (10, 11) are believed[359,363] to be more important for trimethylsilyl radicals, although they proceed much more slowly than the disproportionation reaction of the *tert*-butyl radical.

The contribution of disproportionation reactions increases with temperature. For example, at 900 K the ratio of disproportionation and recombination rate constants for tetramethylsilyl radicals is 1.2,[359] whereas at 300 K it is 0.001.[364] (The upper limit of the ratio, according to kinetic data obtained for vacuum photolysis of tetramethylsilane, is as high as 0.5;[305] the value 0.046 is also suggested[365]). Baldwin, Davidson, and Reed[361] established two mechanisms of decomposition of tetramethylsilane, the contribution of which depends upon temperature.

682-782 °C:

$$\log K(\mathrm{s}^{-1}) = (17.6 \pm 0.3) - (84920 \pm 1500)/2.303RT$$

567-677 °C:

$$\log K(\mathrm{s}^{-1}) = (11.2 \pm 0.1) - (57190 \pm 359)/2.303RT$$

The activation energy of the first process is practically equal to the dissociation energy of the Si-methyl bond in tetramethylsilane (85.1 kcal/mol).[366] For this reason decomposition of tetramethylsilane at elevated temperatures is related to a nonchain process, whose rate is determined by cleavage of the Si-methyl bond.

The short-chain process involving reactions 3, 8, and 12 apparently proceeds at lower temperatures.

$$Me_3Si\cdot + Me_4Si \rightarrow Me_3SiH + Me_3SiCH_2^{\cdot} \qquad (12)$$

Chain termination is believed to occur owing to radical combination only.[361] It is interesting to note that formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, a dimeric 1,1-dimethyl-1-silaethylene, was not observed at temperatures below 597 °C. Although this is explained by the activation barrier of cyclodimerization of 1,1-dimethyl-1-silaethylene,[361] a more probable reason seems to be the suppression of reaction 4, the activation energy of which is as high as 45-50 kcal/mol. The formation of 1,3-disilacyclobutanes in the pyrolysis of $MeSiCl_3$, $MeCl_2SiCH_2SiCl_3$, or a mixture of $SiMe_4$ and $SiMe_3H$ evidently also confirms the intermediacy of silaethylenes.[317]

A comparative study of the pyrolysis of the tetramethyl derivatives of silicon, germanium, and tin using a wall-less reactor[367] showed that the reactions

$$CH_3\cdot + Me_4M \longrightarrow CH_4 + Me_3MCH_2\cdot$$

$$Me_3MCH_2\cdot \longrightarrow 3CH_3\cdot + M{=}CH_2 \longrightarrow \text{polymer}$$

were important only at very low conversions of Me_4M. No 1,3-disilacyclobutanes or other 1,3-dimetallacyclobutanes were observed.

The estimated contribution of chain mechanism to pyrolysis of tetramethylsilane cast doubts[224] on the earlier interpretation of a pyrolysis mechanism for trimethylsilane[362,368] and hexamethyldisilane[369] (pyrolysis of the latter is also discussed in refs 370-374). Thus, the formation of all 1,3-disilacyclobutanes in the pyrolysis of trimethylsilane[361,375] may be attributed to generation of silaethylenes resulting from decomposition of silylmethyl and silyl radicals (13, 14, and 7).

$$\cdot CH_2SiMe_2H \rightarrow HMeSi{=}CH_2 + Me\cdot \qquad (13)$$

$$\cdot CH_2SiMe_2H \rightarrow Me_2Si{=}CH_2 + H\cdot \qquad (14)$$

Therefore, there is no need now to account for disproportionation of dimethylsilylmethyl and silyl radicals postulated earlier[223,362,368] in the thermolysis mechanism for trimethylsilane. The mechanism of thermal decomposition and isomerization of hexamethyldisilane,[224,376-378] with allowance made for the contribution of chain process (chain length being 2.5-4.5), involves the following reactions:

$$Me_3SiSiMe_3 \rightarrow 2Me_3Si\cdot \qquad (15)$$

$$Me_3Si\cdot + Me_3SiSiMe_3 \rightarrow Me_3SiH + Me_3SiSiMe_2CH_2^{\cdot} \qquad (16)$$

$$Me_3SiSiMe_2CH_2^{\cdot} \rightarrow Me_3SiCH_2\dot{S}iMe_2 \qquad (17)$$

$$Me_3SiCH_2\dot{S}iMe_2 \rightarrow Me_3Si\cdot + Me_2Si{=}CH_2 \qquad (18)$$

$$Me_3SiCH_2\dot{S}iMe_2 + Me_3SiSiMe_3 \rightarrow Me_3SiCH_2SiMe_2H + {} + Me_3SiSiMe_2CH_2^{\cdot} \qquad (19)$$

Contrary to this the formation of silaalkenes was not elucidated in the pyrolysis of disilanes: $Me_3SiSiMe_2H$,[379,380] Me_3SiSiH_3,[381] $Me_2HSiSiH_2Me$,[380] MeH_2SiSiH_2Me,[382] MeH_2SiSiH_3,[382,383] MeH_2SiSiD_2H,[384] H_3SiSiH_3,[385-387] D_3SiSiD_3,[384] $(MeO)Me_2SiSiMe_2(OMe)$,[388-390] F_3SiSiF_3,[391,392] FH_2SiSiH_3,[392] $F_2HSiSiH_3$,[392] $Me_3SiSiMe_2Cl$,[393] $Cl_2MeSiSiMe_2Cl$,[393] $Cl_2MeSiSiMeCl_2$,[393] $MeClHSiSiHClMe$,[392] ClH_2SiSiH_3,[392] $Cl_3SiSiCl_3$,[394] and digermane H_3GeGeH_3.[384] These compounds decompose forming mainly silylenes (germylene), that is, in agreement with theoretical predictions.[395]

A unique mechanism of disproportionation of disilyl radicals, which consists of the combination and unimolecular decomposition of resultant chemically activated radicals of tetrasilane, was suggested for the sensitized photolysis of disilane.[308]

$$\mathrm{Si_2\dot{H}_5 + Si_2\dot{H}_5 \rightarrow Si_4H_{10}^{\ddagger}} \quad (20)$$

$$\mathrm{Si_4H_{10}^{\ddagger} \rightarrow Si_2H_4 + Si_2H_6} \quad (21)$$

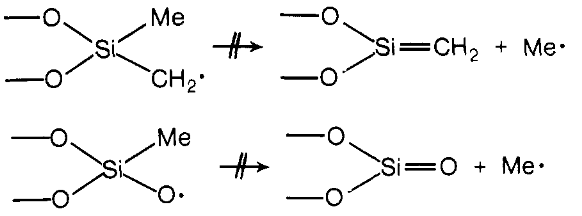
Thus, disproportionation of disilyl radicals is appreciably different from that of ethyl radicals proceeding via a head-to-tail collision transition complex.[396]

Disproportionation of siloxy silyl radicals was noticed in the liquid-phase photolysis of hexamethyldisiloxane:

$$\mathrm{2Me_3SiO\dot{S}iMe_2 \rightarrow Me_3SiOSiMe_2H + Me_3SiOSi(Me){=}CH_2} \quad (22)$$

No decomposition or disproportionation was observed for radicals formed upon oxidation of octamethylcyclotrisiloxane[397] (Scheme CIX). However, reaction 23 was postulated[398] in the pyrolysis of methylphenylsiloxane oligomers.

SCHEME CIX

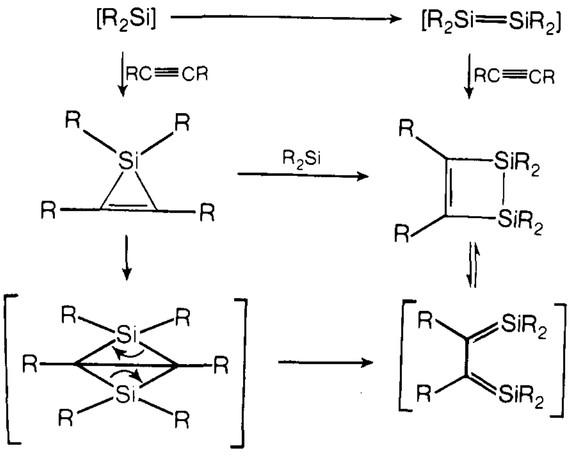


$$\mathrm{MePh_2SiO\cdot \rightarrow MePhSi{=}O + Ph\cdot} \quad (23)$$

X. Combination and Insertion Reactions of Group 4B Analogs of Carbenes

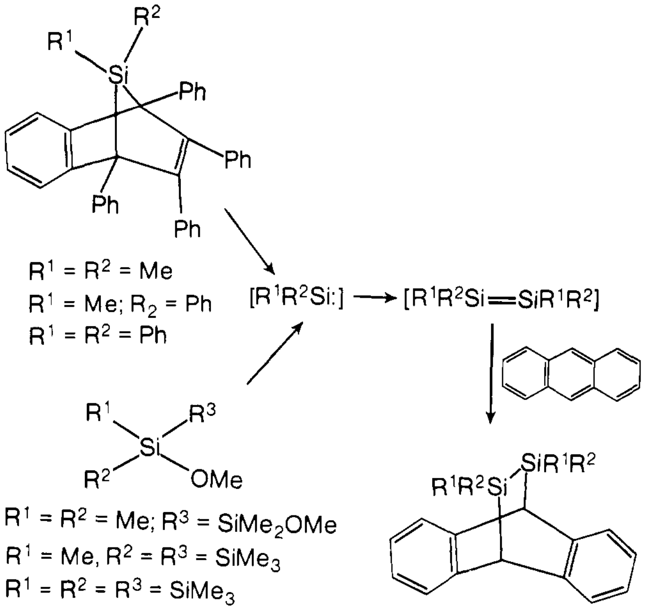
Recently it has been shown[399] that copyrolysis of *sym*-tetramethyldimethyldisilane and dimethylacetylene in a flow system results in 1,1,2,2,3,4-hexamethyl-1,2-disilacyclobutane, whereas 1,4-disilacyclohexadiene is formed in a static system.[388] The mechanisms shown in Scheme CX were suggested[251,252,399] to explain the reaction. One of them[251,252] involves cycloaddition of tetramethyldisilaethylene formed by combination of dimethylsilylene to the acetylene compound.[221]

SCHEME CX



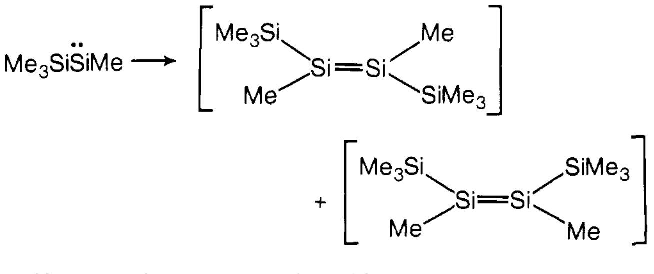
The formation of disilaethylene was confirmed in the studies of the low-pressure flow pyrolysis of net *sym*-tetramethyldimethoxydisilane,[400] and it was found that 1,1-dimethyl-1,3-disilacyclobutane, 1,3-dimethyl-1,3-disilacyclobutane, and 1,1,3-trimethyl-1,3-disilacyclobutane, all rearrangement products of tetramethyldisilaethylene[218] (see section III.C), had a high yield (28%). Data on the pyrolysis of *sym*-tetramethyldimethoxydisilane in the presence of carbonyl compounds[235] also support the concept of dimethylsilylene dimerization.

SCHEME CXI



Recently the formation of disilaethylenes via dimerization of silylenes was observed[401,402] in the pyrolysis of 7,7-disubstituted 2,3-benzo-1,4,5,6-tetraphenyl-7-silanorbornadienes or methoxysilanes (Scheme CXI).

As is seen from the formation of two isomers of 7,8-disilabicyclo[2.2.2]octadi-2,5-ene, methyl(trimethylsilyl)silylene dimerizes stereoselectively to the disilaethylene in favor of one isomer (3:1) which was assigned to be trans:[402]

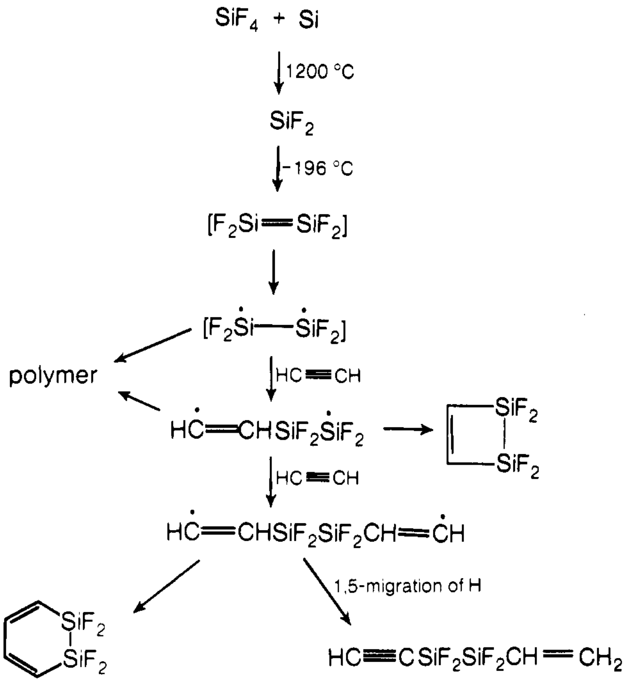


However, these data are the subject of controversy to Wulff, Goure, and Barton whose results[229] consist of isomerization of methyl(trimethylsilyl)silylene into 1,1,2-trimethyl-1,3-disilacyclobutane. In other gas-phase reactions concerning its generation of silylenes[342,389,390,403,404] in the presence of such acceptors as alkenes,[405,406] conjugate dienes,[231,261,402,407-411] allene,[436] hydrosilanes,[412] and others, the formation of adducts with silylenes rather than with their dimers is preferred.

It is thought that dihalosilylenes do not dimerize.[413] Among them difluorosilylene[231] has a low activity in the gas phase[267,414] (an exception being its generation in the recoil reaction,[411,415-417] and also in reactions with iodine[418] and oxygen[419]). However, its reactivity is greatly increased when condensed with organic or inorganic substrates at the surface cooled by liquid nitrogen.[9,342,414,419-424]

It is of particular interest that in many transformations difluorosilylene reacts as dimer, F_2SiSiF_2, along with trimer, tetramer, and other intermediates.[425] The processes occurring upon condensation of difluorosilylene were studied by IR spectrometry[414,426-428] and electron paramagnetic resonance methods,[414,429] and were interpreted in terms of formation of radicals $\cdot(SiF_2)_x\cdot$, where $x = 2, 3, \ldots$.[414] This explains[430] the reactions of difluorosilylene with olefins,[431-434] conjugated dienes,[435] acetylene,[437] other alkynes,[432,438] cyclopropanes,[430] benzene,[440] and boron trifluoride.[441] Unlike these, the reactions with methoxytrimethylsilane,[442] methanol,[443] iodotrifluoromethane,[444] water,[445] hydrogen sulfide,[446] iodine,[418] ger-

SCHEME CXII



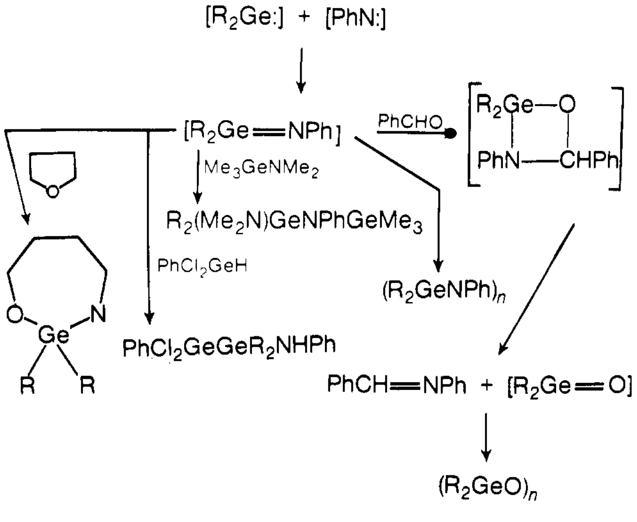
mane,[447] and other inorganic substrates[414,419,420] proceed rather with monomeric difluorosilylene than with dimer.

Margrave and Perry[448] recently reconsidered the reaction of difluorosilylene with acetylene and its derivatives to decide whether singlet difluorosilylene dimerization results in a diamagnetic intermediate with the silicon-silicon double bond (Scheme CXII). However, as before, preference was given to reactions of diradicals. The mechanism of reactions of difluorosilylene with unsaturated substrates will apparently be reconsidered in the light of recent data reported by Seyferth and Duncan,[449] who obtained similar adducts in the liquid-phase reaction of 1,1-difluoro-2,2,3,3-tetramethyl-1-silirane with ethylene, acetylene, etc. Their interpretation of the reaction is based on monomeric difluorosilylene.

Unlike difluorosilylene, dichlorosilylene behaves like other carbenes forming adducts[419] with acceptors. For this silylene the tendency to dimerize was not noted.[419,450,451] Of greater interest is the recent investigation into the possibility of the formation of tetrachlorodisilaethylene in the gas-phase reaction of dichlorosilylene generation.[253]

No data are available on the formation of 1-silaethylene due to combination of silylenes with carbenes. The reaction of difluorosilylene with BF, which proceeds upon condensation, is the only indication of interaction of silylenes with other carbene analogs.[419]

SCHEME CXIII



Formation of germaimines (Scheme CXIII) was observed in the reaction of the complex R_2Ge–THF with phenyl azide.[187] It is interesting to note that the intermediate $Cl_2Sn{=}CH_2$ might form upon reacting tin dichloride with diazomethane.[452]

The role of combination reaction in the chemistry of stannylenes is discussed in a review.[453] It is, however, clear that on going from carbenes to their group 4B analogs, the dimerization of carbene analogs becomes less favorable when compared with that of carbenes.[454]

Silanones are formed when silicon monoxide is inserted into C—H or C=C bonds of organic compounds.[455] The reaction occurs at −196 °C, intermediate resultant products undergoing uncontrolled polymerization.

XI. 1,2-Migration from Group 4B Metal to Carbene or Carbenoid Center

A. Photolysis and Pyrolysis of Diazomethane Derivatives

Intramolecular 1,2-migration of hydrogen atoms, and alkyl or phenyl substitutents resulting in olefins is a well-known reaction of carbene chemistry:[456,457]

$$Me_3CC(N_2)R \xrightarrow{h\nu} [Me_3\ddot{C}CR] \rightarrow Me_2C{=}CRMe$$

However, such a rearrangement is not always inherent in α-silylcarbenes.[458-473] Although this process is believed to be favorable energetically,[308] ab initio calculations predict that silylcarbene is thermodynamically more stable than silaethylene.[474,475] Nevertheless, the course of the reaction

$$[H_3Si{-}\ddot{C}H] \rightarrow [H_2Si{=}CH_2]$$

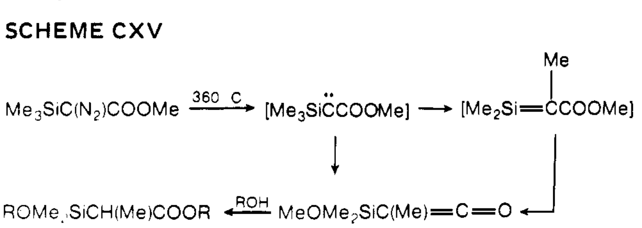
is deduced from the absence of insertion products of silylmethylene in the Si-H bond of methylsilane under conditions of its vacuum photolysis.[302,303,308] An analogous rearrangement of trimethylsilylcarbethoxycarbene into the corresponding silaethylene is involved to explain the photolysis of ethyl trimethylsilyldiazoacetate in the presence of alcohols[476] (Scheme CXIV).

SCHEME CXIV

$$Me_3SiC(N_2)COOEt \xrightarrow{h\nu} [Me_3Si\ddot{C}COOEt] \rightarrow [Me_2Si{=}C(Me)COOEt] \xrightarrow{ROH} ROMe_2SiCH(Me)COOEt$$

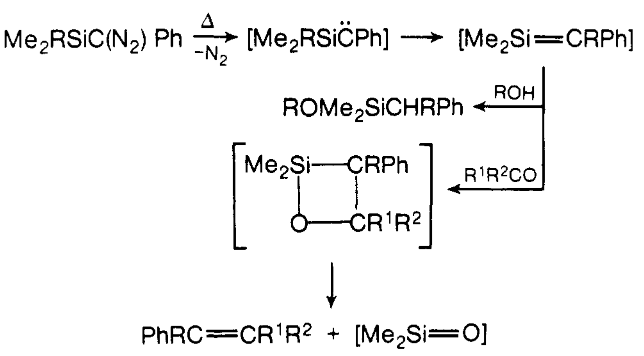
However, this assumption does not explain the formation of adducts with the two same alkoxy groups upon trapping pyrolysis products of methyl trimethylsilyldiazoacetate by alcohols other than methanol.[477] This is possibly due to isomerization of silaethylene into ketene[478] (see Scheme CXV).

SCHEME CXV



Formation of net pyrolysis products of phenyl(trimethylsilyl)diazomethane may be explained without involving any silaalkene intermediates.[465,466] But this is not the case when silylated phenyl diazomethanes are copyrolyzed with 2,3-dimethylbu-

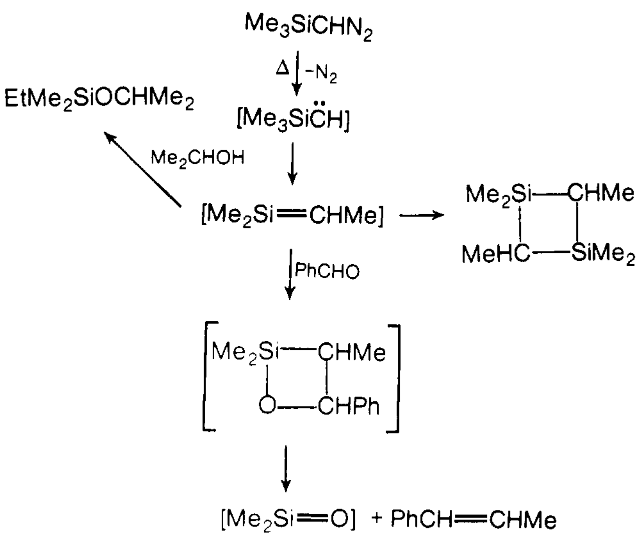
SCHEME CXVI



tadi-1,3-ene,[479,480] or with carbonyl compounds[479,480] or alcohols[478,480] (Scheme CXVI). Products generally associated with the formation of silalkene intermediates were observed. Migration of the substituent from silicon to the carbene center is accompanied by intramolecular and intermolecular reactions of phenylsilylcarbene, the contribution of which decreases at higher temperatures.

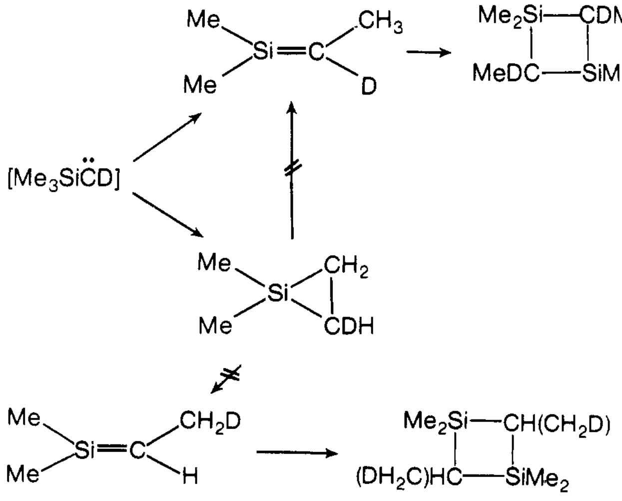
The pyrolysis of trimethylsilyldiazomethane[481] was also rationalized in terms of a silaethylene intermediacy (Scheme CXVII).

SCHEME CXVII

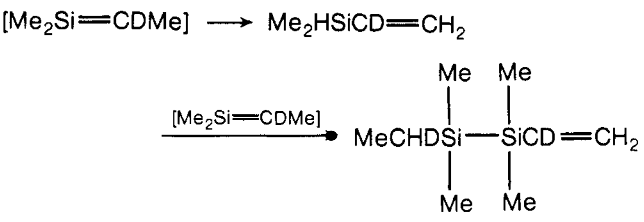


By conducting experiments with α-deuteriotrimethylsilyldiazomethane (Scheme CXVIII), it was shown[481] that silaethylene was formed owing to 1,2-migration of methyl group from silicon to carbene carbon, and not because of isomerization of intermediate silacyclopropane, which might appear in small quantities during pyrolysis of silyldiazomethanes.[480,482] Formation of vinyldimethylsilane was also explained without the steps involving silacyclopropane (Scheme CXIX).

SCHEME CXVIII



SCHEME CXIX



The suggested hydrosilylation of 1,1,2-trimethyl-1-silaethylene is of particular interest, because the data[119] are indicative of the inability of silaalkenes to participate in this reaction. The trimethylsilyldiazomethane pyrolysis mechanism is claimed to be[146,147] a subject of study for the matrix isolation technique.

1,1,2-Trimethyl-1-silaethylene is also formed in the photolysis of trimethylsilyldiazomethane;[143,478,481,482] corresponding adducts with silaethylene were obtained in the presence of alcohols[478,481] and amines.[481] Chapman et al.[143] irradiated with light of wavelength greater than 355 nm trimethylsilyldiazomethane in an argon matrix at 8 K. 1,1,2-Trimethyl-1-silaethylene absorption bands at 3020 cm^{-1} (olefinic C–H stretch) and 795 and 646 cm^{-1} (the deformation modes) were observed. Since no data on labeling compounds are available, it is not possible to assign a silicon-carbon double bond stretching vibration. However, the similarities of the obtained spectra with the spectrum of trimethylethylene have led to the conclusion that 1,1,2-trimethyl-1-silaethylene is a planar molecule. The disappearance of absorption bands of 1,1,2-trimethyl-1-silaethylene above 45 K is concurrent with the appearance of bands of the dimers (*cis*- and *trans*-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes).

As observed by Chedekel et al.,[482] irradiation of trimethylsilyldiazomethane in an argon matrix with light of wavelength greater than 3600 Å results in the formation of triplet trimethylsilylcarbene, which is stable in the range from 4 to 40 K and changes into *trans*-1,2-bis(trimethylsilyl)ethylene upon warming up the matrix to room temperature. It is not the case when the matrix is irradiated with light of wavelength shorter than 3000 Å which results in at least one set of new bands assignable to 1,1,2-trimethyl-1-silaethylene. The strong bond at 641 cm^{-1} is shifted to 510 cm^{-1} in the spectrum of 1,1,2-trimethyl-2-deuterio-1-silaethylene, and is thus assigned to the out-of-plane deformation for the lone hydrogen atom attached to the silicon-carbon double bond. No band was assigned to the stretch of the silicon-carbon double bond.

Recently a report[280a] has appeared on selective rearrangement of bis(trimethylsilyl)carbene into 1,1,2-trimethyl-2-trimethylsilyl-1-silaethylene:

$$[\mathrm{Me_3Si\ddot{C}SiMe_3}] \rightarrow [\mathrm{Me_2Si{=}C(Me)SiMe_3}]$$

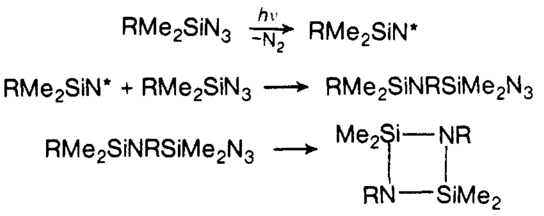
No reports are available on the 1,2-rearrangement for α-germylcarbenes[470,483,484] and α-stannylcarbenes.[463,485]

A failed attempt to obtain silabenzene via 1,1-dimethyl-1-silacyclohexadienylidene–silabenzene rearrangement was undertaken by means of pyrolysis of 4-diazo-1,1-dimethyl-1-silacyclohexadi-2,5-ene.[486]

B. Photolysis and Pyrolysis and Silyl Azides

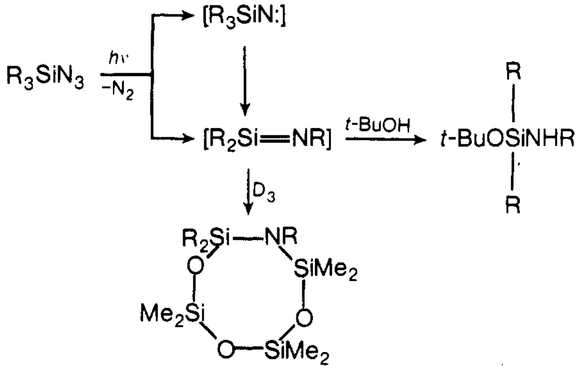
Migration of a substituent to an adjacent nitrene center[487] apparently takes place upon photolysis and pyrolysis of silyl azides.[106,107,488-494] Photolysis of trialkylsilyl azides in benzene solution results in silazane azide which in turn transforms into cyclodisilazane and high-molecular products.[488] These data were interpreted by Scheme CXX that involves nitrene or a photoexcited azide intermediate.

SCHEME CXX



However, the results of silyl azide photolysis in the presence of trapping agents (*tert*-butyl alcohol, hexamethylcyclotrisiloxane) may be best presented assuming participation of unstable silaimine intermediates[489] (Scheme CXXI).

SCHEME CXXI



Photolysis of silyl azides having different substituents at silicon yields a mixture of silaimines:[489]

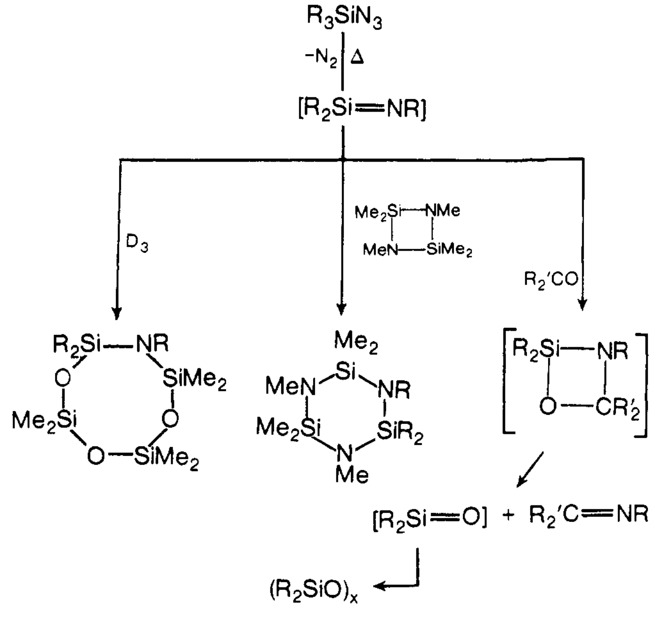
$$R_2R'SiN_3 \xrightarrow[-N_2]{h\nu} [R_2Si{=}NR'] + [RR'Si{=}NR]$$

The attempt to detect with infrared spectroscopy silaimines formed upon trimethylsilyl azide photolysis in Ar, N_2, or CO matrices at 10 K failed. Not silaimines, but the secondary photolysis product assigned to one of the following structures:

$$Me_2Si(H)N{=}CH_2 \text{ or } Me_2Si(H)CH{=}NH$$

was observed.[495] Secondary processes leading in particular to HNSi were also noticed upon matrix photolysis of silyl azide, H_3SiN_3.[496]

SCHEME CXXII



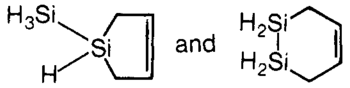
Pyrolysis of triphenylsilyl azide results in hexaphenylcyclosilazane[106,107,490] formed possibly by cyclodimerization of triphenylsilaimine, $Ph_2Si{=}NPh$. Meanwhile, it was not possible to ascertain participation of silaimine intermediate from the complex mixture of products formed upon pyrolysis of trimethylsilyl azide.[106] However, formation of silaimines was clearly demonstrated in studies of pyrolysis of silyl azides with traps[492] (Scheme CXXII).

C. Isomerization of Alkyl and Silyl Silylenes

The ability of hydrogen atom 1,2-migration in alkyl silylenes is less pronounced[104] compared with alkylcarbenes and silylcarbenes. Such a process is believed[302,303,405] to be uneconomical with the reverse reaction, which, however, under conditions of pyrolysis also does not proceed.[126,362,368] Nevertheless, the contribution of dimethylsilylene isomerization is accounted for when studying the pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane at low pressure[400] or in the presence of ketones.[235]

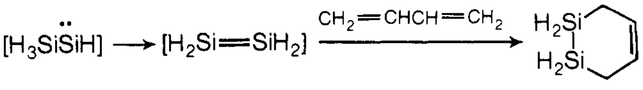
$$CH_3\ddot{S}iCH_3 \rightarrow CH_3(H)Si{=}CH_2$$

Pyrolysis of trisilane[383,409,497] results in silylenes $:SiH_2$ and $H_3Si\ddot{S}i$-H. The latter reacts with butadiene yielding adducts



in the ratio 1:1.[409] One of the possible mechanistic rationalizations involves an efficient stage of isomerization of $H_3Si\ddot{S}iH$ into disilaethylene (Scheme CXXIII). On the contrary, isomerization into disilaethylene is not regarded as a possible pathway of the process in the reaction of trimethylsilylsilylene, $Me_3Si\ddot{S}iH$, with trimethylsilane.[498] However, the reverse reaction is believed to be faster than any bimolecular reaction of disilaethylene.[497]

SCHEME CXXIII



Trimethylsilylsilylene also does not rearrange itself into tetramethyldisilaethylene.[229] The reverse reaction is rather typical for such intermediates.[229,280a]

$$Me_2Si{=}SiMe_2 \rightarrow Me_3Si\ddot{S}iMe$$

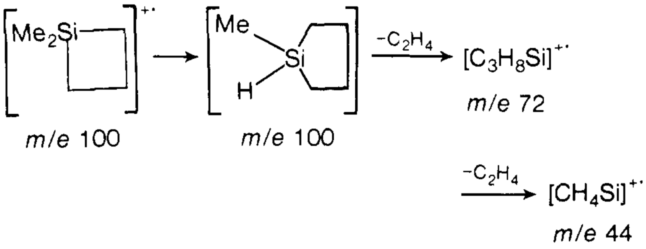
In conclusion, the rearrangement of silylenes via 1,2-migration of hydrogen or substituent to the carbene or carbenoid center seems to be hardly probable. This is supported by the recent theoretical optimization of closed-shell states of methylsilylene showing that processes resulting in the formation of singlet methylsilylene do not lead to silaethylenes.[474,475]

XII. Formation of Ions and Neutral Fragments with p_π-p_π Bonded Group 4B Metal in Dissociative Ionization Processes

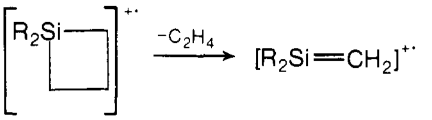
In dissociative ionization processes structures are formed with p_π-p_π bonded group 4B metals either as fragment ions or as neutral molecules leaving the charged portion of decomposing ion precursor. The search for such processes is interesting because an analogy is observed between decomposition of ions in mass spectrometry (electrolysis) and pyrolysis or photolysis.[91,499,500] For example, there exists an analogy between retrodiene,[501-504] retroene[505-507] (McLafferty rearrangement), and other reactions induced by electron impact or thermally. Although there are principal differences between the mechanisms of thermolysis and dissociative ionization processes due to the methods employed for exciting molecules, it has been shown theoretically[508] that an analogy may be observed at least for those reactions which are confirmed by metastable peaks and have high probability.

The loss of ethylene from dimethylsilacyclobutane ion was earlier interpreted as a process proceeding mainly via rearrangement of molecular ion into silacyclopentane[509] (Scheme CXXIV). This did not correlate well with thermal decomposition of monosilacyclobutanes resulting in olefin and silaalkene (see section II.A).

SCHEME CXXIV



Thereafter, it was shown that loss of olefin due to the decomposition of four-membered ring "in half" was a pronounced property of monosilacyclobutanes (Tables II and III); it does not touch carbon of substitutents at silicon:



Peaks corresponding to metastable ions[167,509,510] in the mass spectra confirm the above process. The ease of decomposition is due to the small difference between the appearance potential of the $[P - 28]^{+\cdot}$ ion (AP) and ionization potential of monosilacyclobutane (IP). Thus, for 1,1-dimethyl-1-silacyclobutane[162] it equals

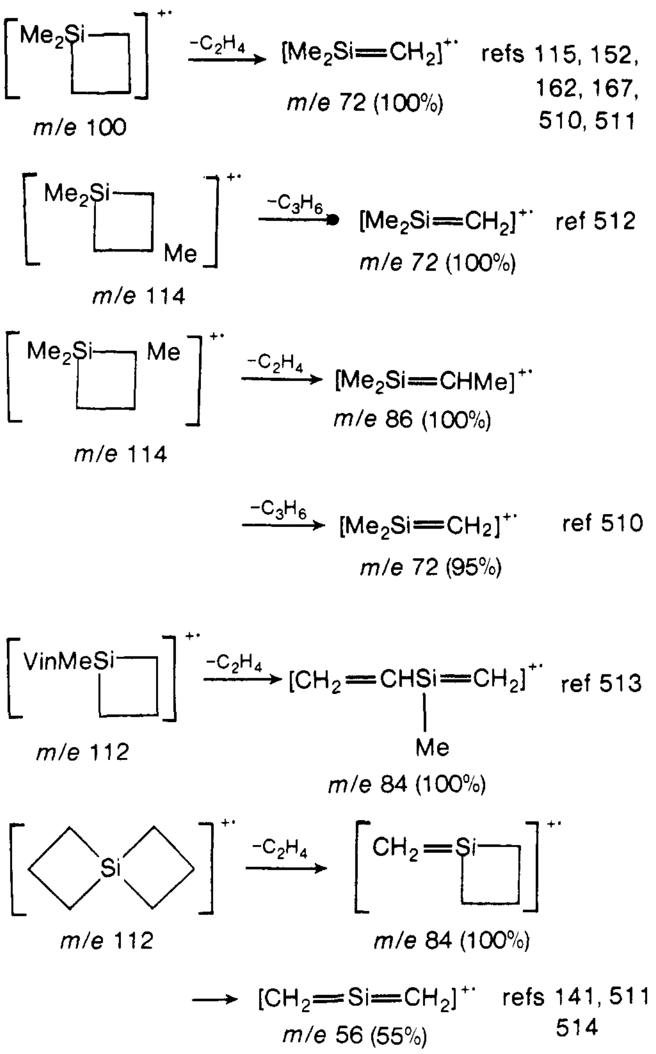
$$AP - IP = 9.61 - 8.97 = 0.64 \text{ eV}$$

In Scheme CXXV are given the fragmentations of molecular ions of monosilacyclobutanes, which correlate with studied thermal decomposition of these heterocycles (see section II.A).

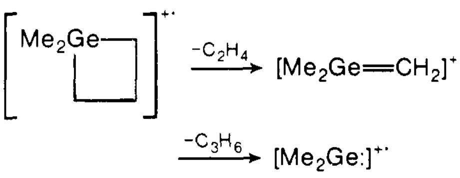
As is seen from the data tabulated in Tables II and III, the behavior of monosilacyclobutanes upon electron impact is also affected by the substituents at silicon and carbon. Thus, fragmentation of 1-alkyl-1-methyl-1-silacyclobutanes (C_2H_5, i-C_3H_7, n- and i-C_4H_9) is related to the consequent loss of two molecules of ethylene. The second process involving the alkyl substituent possibly proceeds via isomerization of silaalkene ion into the cyclic one.[510,512]

Unlike the molecular ion ($P^{+\cdot}$), ions $[P - C_2H_4]^{+\cdot}$ and $[P - 2C_2H_4]^{+\cdot}$ easily lose the methyl radical. Not only the $[P - C_3H_6]^{+\cdot}$ ion, but also the $[P - C_3H_5]^{+}$ and $[P - C_2H_4]^{+\cdot}$ ions are characteristic of the mass spectra of 3-methyl-1-silacyclobutanes.[512] The abundance of the latter ions increases at low ionization energy. The peak of the $[P - C_2H_4]^{+\cdot}$ ion is believed to be caused by ring expansion of the molecular ion up to the silacyclopentane ring which dissociates primarily with the loss of ethylene.[512] This is well illustrated in Scheme CXXVI by the fragmentation upon electron impact of 1,1-dideuteriomethyl-1-silacyclobutane and 1,1-dideuteriomethyl-3-methyl-1-silacyclobutane.[513]

SCHEME CXXV

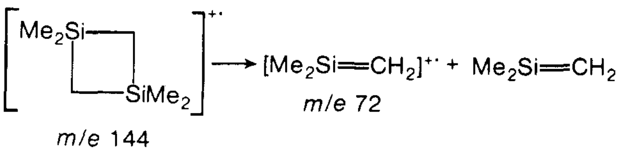


An analogy between thermal dissociation and dissociative ionization was also observed for 1,1-dimethyl-1-germacyclobutane.[166,167]



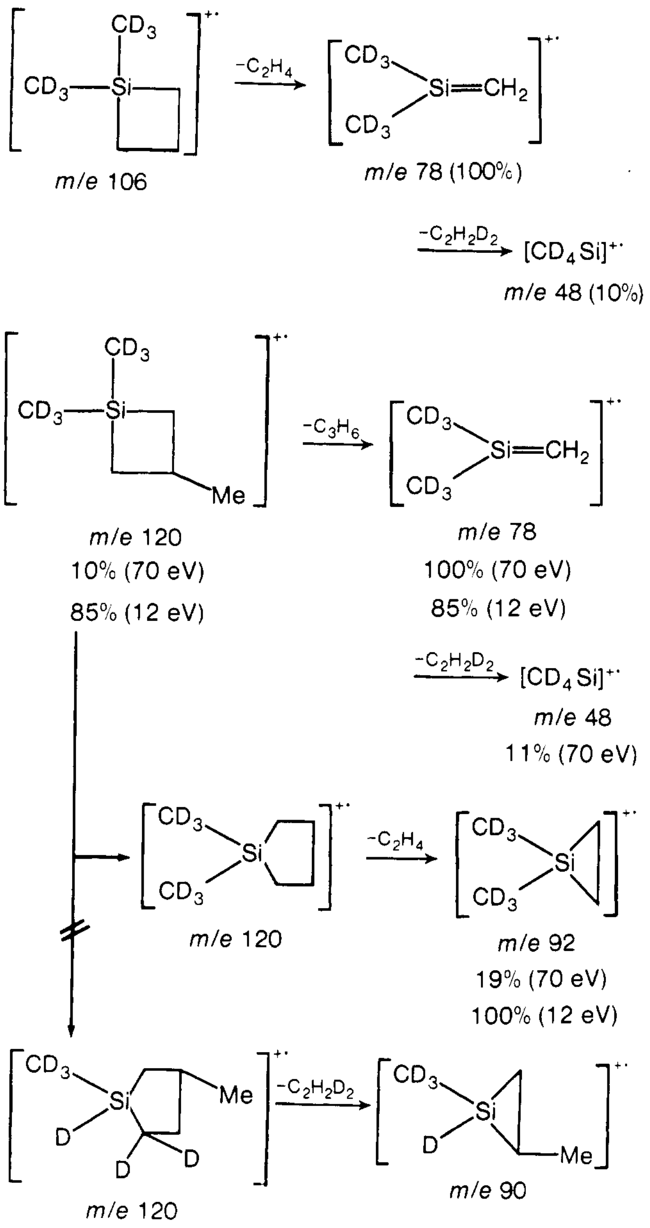
Olefinic and carbenoid decomposition of molecular ions are characteristic of other germacyclobutanes also, i.e., for 1,1-dibutyl-1-germacyclobutane,[515] 1,1-dibutyl-3-methyl-1-germacyclobutane,[515] and 4-germaspiro[3.4]octane.[514,515]

1,3-Disilacyclobutane[317,516] and its methyl[115a,162,400] and other derivatives[317] do not decompose "in half" upon electron impact. The difference between appearance potential of ion m/e 72 in the process:

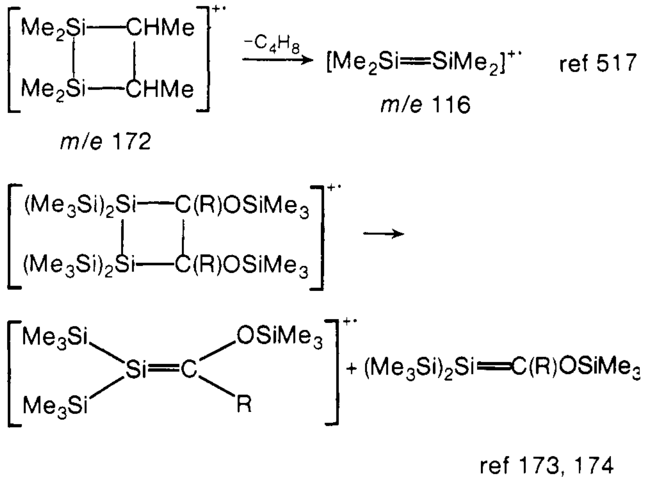


and ionization potential of 1,1,3,3-tetramethyl-1,3-disilacyclobutane amounts to 2.59 eV. This exceeds four times the given

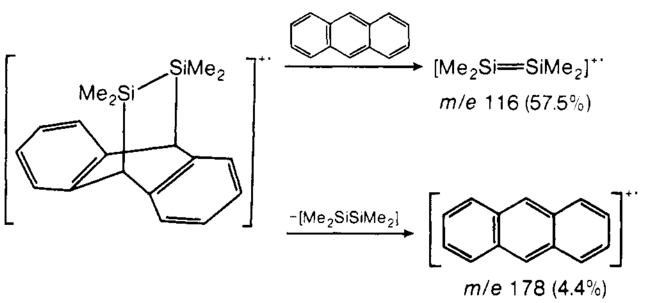
SCHEME CXXVI



SCHEME CXXVII



SCHEME CXXVIII

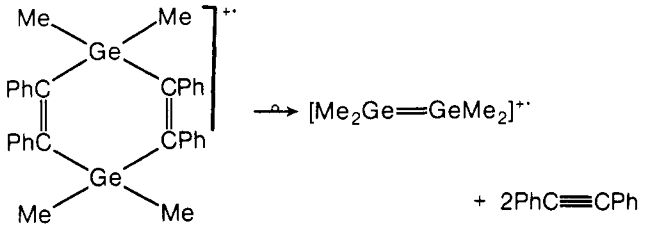


value for 1,1-dimethyl-1-silacyclobutane, and suggests that this decomposition is energetically disfavored. Unlike this, dissociative ionization of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-disilacyclobutane and its 1,3-digerma and 1,3-distanna analogs is characterized by the presence of intense (100, 68, and 15%, respectively) peaks of P/2 ions.[320,321]

Mass spectral fragmentation of 1,2-disilacyclobutanes (Scheme CXXVII) results in disilaethylene ions, whereas those containing bulky substituents decompose upon electron impact "in half" producing silaethylene ions. The latter correlates well with thermolysis.[173,174] The formation of $Me_2Si{=}SiMe_2$ and $Me_2Ge{=}GeMe_2$ in the fragmentation of 1,1,2,2-tetramethyl-1,2-disilacyclopentane and its germanium analog ions is supported by metastable transitions and, to a known extent, is consistent with thermolysis of these compounds.[167]

Tetramethyldisilaethylene ions are also produced during dissociative ionization of 7,8-disilabicyclo[2.2.2]octadi-2,5-enes, a process analogous to thermal retrodiene reaction[217,218] (Scheme CXXVIII).

Elimination of ethylene resulting in formation of the ion Me_4Si_2 was observed upon electron impact fragmentation of vinyltetramethyldisilane.[518] Ions of the $[R_2Ge{=}GeR_2]^{+\cdot}$ type are abundant in the mass spectra of 1,4-digermacyclohexadienes,[519,520] for example:



The earlier report[87] on the observation of dialkylsilanone ions in the mass spectra of siloxanes was not confirmed.[88-90] Apparently, the even-electron fragment ions characteristic of spectra of these compounds were taken as silanones[91] (see section I.B). The formation of silanone as uncharged fragments, for example, Me_2SiO, is more typical of siloxanes, it being known that their elimination takes place only in those cases when the formation of cyclic oligomers is not possible. The latter correlates well with the behavior of cyclosiloxanes upon pyrolysis (see section III.A.1). Correspondingly, extrusion of neutral fragments, $Me_2Si{=}O$ and $Me_2Si{=}CH_2$, is typical of six- and eight-membered cyclocarbosiloxanes.[521] The former is also eliminated upon electron impact fragmentation of both 1,1,3,3-tetramethyl-1,3-disila-2,6-dioxacyclooctane and its cyclic dimer.[522] The loss of silanones was deduced upon fragmentation of 10,10-dimethylphenoxaline,[523] 10,10-dimethyl-10-sila-9-oxarophenanthrene, and 10,10-dichloro-10-sila-9-oxarophenanthrene.[524] Unusual fragmentation was noticed for the $[P - 15]^+$ ion of hexamethyldigermoxane:[525]

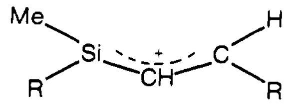
$$Me_3GeOGe^+Me_2 \rightarrow Me_3Ge^+ + Me_2Ge{=}O$$

Also of interest is the loss of the SiO group observed in the mass spectra of cyclosiloxanes[88] and cyclocarbosiloxanes.[521]

Ions **31** and **32** of the silaallyl type were found in the spectra of trimethylsilylmethanes.[526]

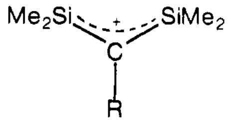
TABLE II. Relative Percentage Abundance of Parent Molecular ($P^{+\cdot}$) and $R^1R^2Si{=}CH_2^{+\cdot}$ Peak Ions in the Mass Spectra of Monosilacyclobutanes: R^1R^2Si

R^1	R^2	$P^{+\cdot}$	$[R^1R^2Si{=}CH_2]^{+\cdot}$	ionization energy, eV	Ref
H	H	90.4	100	70	566
		53.2	100	70	510
		48.4	100	70	513
		51.0	100	50	513
		59.2	100	25	513
H	Me	18.5	100	75	513
		18.7	100	50	513
Cl	Cl	12.1	100	70	510
		14.0	70	70	511
Me	Me	16.9	100	70	167, 509
		30.1	100	70	510
CD_3	CD_3	10.0	100	70	513
		84.6	84.6	12	513
Me	Et	18.0	77.0	70	567
Me	*n*-Pr	32.0	50.0	70	567, 568
Me	*n*-Pr	51.0	83.0	70	567, 568
Me	*n*-Bu	17.0	35.0	70	567
Me	*i*-Bu	27.0	40.0	70	567
i-Pr	*i*-Pr	41.0	50.0	70	567, 568
Me	Be	45.0	100	70	567
Me	CH_2SiMe_3	72	3.0	70	567, 568
Cl	MeS	0.7	1.3	70	569
MeS	MeS	14.2	3.5	70	569
t-Bu	*t*-Bu	10	6.0	70	569
t-Bu	Cl	50	29.2	70	569
Mes	*t*-Bu	7.5	—	70	569
Ph	Ph	9.1	61.9	70	569
Cl	Ph	1.7	2.0	70	569
$CH_2CH_2CH_2$		33	100	70	141, 514
		48	100		511
$CH_2CH_2CH_2CH_2$		23	100	70	141, 514
Vin	Me	10.5	100	70	513
		29.2	100	12	513
Me	Ph	16.7	100	70	568, 570
		36.4	100	15	568, 570
		100	97.0	12	568, 570
Me	*n*-C_6H_4Me	17.5	100	70	568, 570
		55.5	100	15	568, 570
		100	69	12	568, 570
Me	*m*-C_6H_4Me	22.5	100	70	568, 570
		57.0	100	15	568, 570
		100	63	12	568, 570
Me	*n*-C_6H_4Cl	14.6	100	70	568
		39.0	100	15	568
		100	61.5	12	568
Me	*n*-C_6H_4F	13.2	100	70	568
		29.4	100	15	568
		100	82.0	12	568
Me	*n*-$C_6H_4NMe_2$	100	100	70	568
		100	29.4	15	568
		100	3.1	12	568
Me	*m*-$CF_3C_6H_4$	17.5	100	70	570
		38.0	100	70	570
		100	77	12	570
Me	*n*-Me_3SiCH_2	33	100	70	570
		96.0	100	15	570
		100	20.0	12	570



31

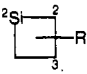
R = Me, R^1 = H, *m/e*85
R = R^1 = Me, *m/e* 99
R = Me, R^1 = Pr, *m/e* 127
R = Cl, R^1 = H, *m/e* 105, 103



32

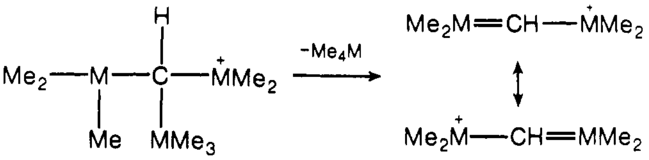
R = H, *m/e* 129
R = Me_3Si, *m/e* 201
R = Cl, *m/e* 163, 161

TABLE III. Relative Percentage Abundance of Parent Molecular ($P^{+\cdot}$), $[R^1R^2Si{=}CHR^3]^{+\cdot}$ and $[R^1R^2Si{=}CH_2]^{+\cdot}$ Peak Ions in the Mass Spectra of Monosilacyclobutanes: R^1R^2Si

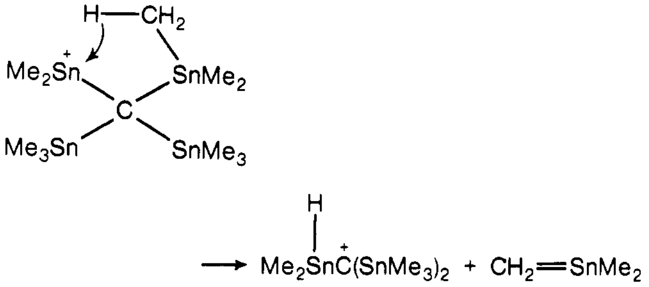


R^1	R^2	R^3	$P^{+\cdot}$	$[R^1R^2Si{=}CHR^3]^{+\cdot}$	$[R^1R^2Si{=}CH_2]^{+\cdot}$	ionization energy, eV	refs
			2-Substituted Monosilacyclobutanes				
Me	Me	Me	22.2	100	95	70	510
Ph	Cl	Me	2.6	6.6	36.8	70	571
Ph	Ph	Me	1.6	6.4	13.1	70	571
t-Bu	Cl	Me	25.9	37.9		70	571
t-Bu	*t*-Bu	Me	15.0	6.6		70	571
Cl	Cl	Ph	13.1	38.5		70	571
Me	Cl	Ph	27.1	100		70	571
t-Bu	Cl	Ph	7.7	11.8		70	571
t-Bu	*t*-Bu	Ph	9.1	0.9		70	571
Me	Me	Ph	5.7	27.3	22.7	70	169
Me	Me	Ph	15.4	36.9	31.4	20	169
Me	*sec*-BuSiO	Me	1	3.0		70	538
			3-Substituted Monosilacyclobutanes				
Me	Me	Me	5		100	70	567
Me	Me	Me	51		82	12	567
CD_3	CD_3	Me	10		100	70	513
CD_3	CD_3	Me	84.6		84.6	12	513
Me	Cl	Me	6		100	70	567
Me	Cl	Me	32		46	12	567
Cl	Cl	Me	9		100	70	567
Cl	Cl	Me	33		27	12	567

Fragmentation of trimethylstannylmethanes proceeds in the same way.[527] The formation of ions with group 4B metals involved an allylic system may be presented as follows:



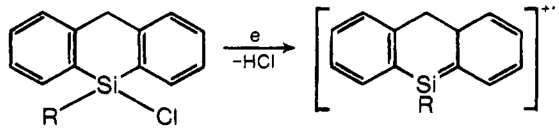
But the loss of stannaalkene apparently occurs in the process:



A relatively intense peak *m/e* 177, the structure of which is possibly stabilized by π-resonance, is noticed in the mass spectra of bis(trimethylstannyl)halomethanes:[527]

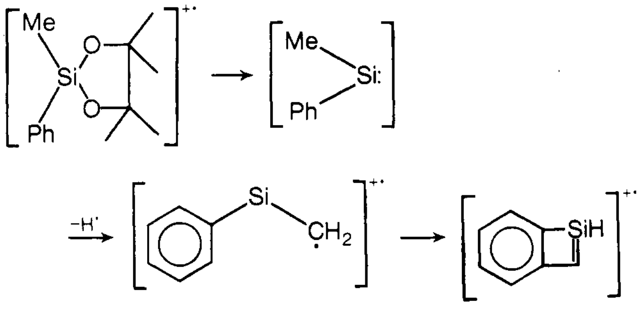
$$\overset{+}{C}H_2CH{=}SnMe_2 \leftrightarrow CH_2{=}CH\overset{+}{S}nMe_2$$

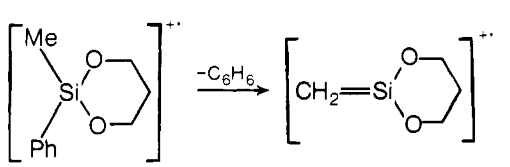
Formation of ions with silicon involved in an aromatic structure was observed in the mass spectra of halogen-substituted 9,10-dihydro-9-silaanthracenes:[528–530]



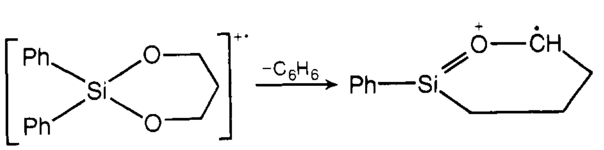
$C_5H_5SiMe_2$ and $C_5D_5Si(CD_3)$ ions were observed in the mass spectra of bis(trimethylsilyl)cyclopentadiene and its deuterosubstituted derivative.[531,532] These ions are believed to have the structure of dimethylsilafulvene. An arylmethyl-substituted 1,3-dioxasilolane decomposes upon electron impact producing benzosilacyclobutadiene ion[533] (Scheme CXXIX). Unlike this, fragmentation of 2-methyl-2-phenyl-1,3-dioxa-2-silacyclohexane results in an *m/e* $[P - 78]^{+\cdot}$ ion.[534] This process was believed to proceed as follows:

SCHEME CXXIX



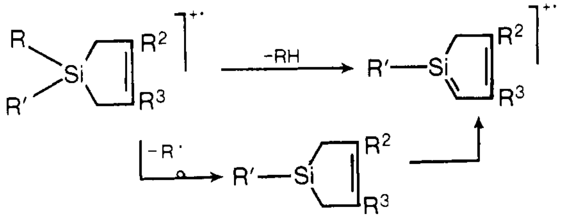


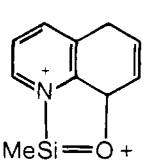
But a detailed study of the dissociative ionization of other related compounds has shown that the hydrogen atom migrates from the ring:[534]



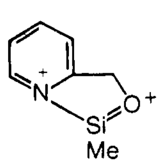
Migration of the hydrogen atom is also characteristic of fragmentation of both silacyclopentane[535] (Scheme CXXX) and germacyclopentane ions.[536]

SCHEME CXXX



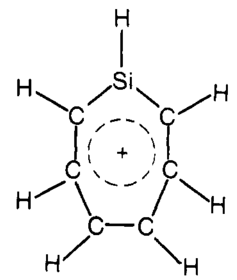


33



34

π-Resonance stabilized ions have been reported.[537-539] In particular, intense peaks of doubly charged $[P - 30]^{2+}$ ions **33** and **34** were observed in mass spectra of trimethylsiloxyquinolines and trimethylsiloxypyridines.[540] Their structure is considered to be a fully delocalized heteroaromatic ion. The structure of the $SiC_6H_7^+$ ion formed upon the ion-molecule reactions in monosilane-benzene mixtures[541] is analogous to that of the tropylium ion, i.e.,



Its formation better corresponds to benzyl-type structure, $C_6H_5SiH_2^+$.

XIII. Theoretical Studies of Multiple Bonds of Group 4B Metals

In section I.A mention has been made of certain theoretical approaches that explain the reluctance of group 4B metals to form multiple bonds. Since 1973, a number of semiempirical and nonempirical calculations have been made by EHMO,[542] CNDO,[542] CNDO/2,[532,543] MINDO/3,[163] FSGO,[544,545] and ab initio[165,365,474,475,546-553] methods to study the nature and reactivity of silaethylenes and related intermediates (see Tables IV and V).

Optimization of the geometry of silaethylene, $H_2Si{=}CH_2$, as a rule, results in shortened length of the silicon-carbon double bond compared with the ordinary one (1.89 Å). Bond angles are generally consistent with a planar configuration, or are close to it. Exceptions are the FSGO data,[544] indicating that the silicon center tends to retain tetrahedral configuration, whereas the carbon center easily forms the trigonal angle. Replacement of hydrogen in silaethylene by fluorine transfers silicon or carbon atom bound with it from trigonal hybridization to tetragonal hybridization, and bonding of carbon atom with fluorine lengthens the Si=C double bond.[543] For fluorinated germaethylenes similar lengthening of the multiple bond also takes place, but this is much less marked than the corresponding change for silaethylenes.[554]

Below are given the overlap integrals (S) of p and d orbitals for elements of the first and second rows (after Curtis[542]):

	S		*S*
$2p_\pi$-$2p_\pi$	0.270	$3p_\pi$-$3p_\pi$	0.228
$2p_\pi$-$3p_\pi$	0.182	$3p_\pi$-$3d_\pi$	0.448
$2p_\pi$-$3d_\pi$	0.362	$3d_\pi$-$3d_\pi$	0.303

Using EHMO data as a basis for a Mulliken population analysis, Curtis[542] found that π-bond overlap in silaethylene was smaller than in C_2H_4 and Si_2H_4. Electron distribution in silaethylene was found to be exceedingly asymmetrical, it being localized primarily in the p orbitals of the carbon atom. As a result the Si=C bond is exceedingly polar, and energy mismatching of carbon and silicon p orbitals to a large extent is responsible for the weakening of the π bond. This results in the Si=C double bond approximating a carbanion-siliconium ion pair, $H_2C^-{-}Si^+H_2$, rather than a biradical. On the contrary, the electron density is higher at the metal atom in germaethylene.[554] Thus, the Si=C and Ge=C bonds have opposite polarities. Replacement of hydrogen atoms bound with carbon by fluorine atoms changes the dipole moment of silaethylenes in accordance with the expected effect of this electronegative substituent. An anomalous tendency resulting in an increase of the dipole moment of the molecule is observed in germaethylenes. A CNDO/2 localized orbital study[555] was applied to seek an explanation for this anomaly, which appeared to be associated with the situation where donation of electrons via the π bond to the germanium atom outweighs the accumulation of charge arround the fluorine atoms attached to the carbon.

A significant contribution of d orbitals to the formation of Si=C and Si=Si bonds was noticed by several au-

TABLE IV. Calculated Properties of the Ground State of Silaethylene, $H_2Si{=}CH_2$

						ab initio			
properties	EHMO, ref 542	CNDO, ref 542	CNDO/2, ref 543	MINDO/3 ref 163	FSGO,[a] ref 544	STO-3G, ref 546	STO-4G, ref 365	extended basis set and electron correlation, ref 548	DZ basis and electron correlation, ref 550
bond lengths, Å									
Si–H	1.46	1.46	1.60	1.468	1.457 (1.455)	1.479	1.429	1.48	1.474
C–H	1.10	1.10	1.12	1.112	1.116 (1.112)	1.074	1.0797	1.08	1.075
Si–C	1.90	1.90	1.75	1.630	1.638 (1.666)	1.693	1.846	1.69	1.715
bond angles, deg									
HSiH	120	120	120		109.5 (109.4)			115	115.1
HCH	120	120	120		122.3 (122.3)			112	115
HSiC				122.1		122.9	109.06		
HCSi				128.3		122.7	123.0		
charge distribution									
Si	(1.6)	0.422	0.40				0.6	0.5	
C	−1.1	−0.308	−0.31				−0.38	−0.4	
H(Si)		−0.118	−0.12				−0.18	−0.01	
H(C)		0.061	0.07				0.04	0.05	
dipole moment $^+Si{-}C^-$, D		2.99		−0.8[b]	1.37 (2.39) 2.91[d]	1.1		1.05[c]	
heat of formation, kcal/mol				17.6	69.5				
ionization potential, eV	9.11	6.62		9.6					
singlet–triplet separation, $E_{S\to T}$, kcal/mol							−1.4 16.1–22.6[e]	27.9	>34.7
π-bond energy, $D_\pi(Si{=}C)$, kcal/mol	2.63 (9.54)	9.0			22.3			46	

[a] Values obtained with d_π contribution are given in parentheses. [b] MINDO/3.[165] [c] Ab initio,[165] using extended basis and electron correlation. [d] Bond dipole moment. [e] Ab initio,[549] using extended basis and electron correlation.

thors.[542,543,554] However, the involvement of d orbitals in the FSGO calculations[544] produced only minor structural changes. According to ab initio calculations[548] d orbitals are not of particular importance and play about the same role as for carbon.

Determination of the π-bond strength as a barrier to rotating one end of the molecule by 90° with respect to another gives values which depend much on the computation method and parametrization. As a rule the π bond Si=Si proved to be more stable than the π bond Si=C. From FSGO data,[544] $D_\pi(Si{=}Si)$ and $D_\pi(Si{=}C)$ amount to one-half and one-third of $D_\pi(C{=}C)$.

By MINDO/3 calculations,[163] Dewar, Lo, and Ramsden investigated a number of molecules of multiple-bonded silicon. The values of heat of formation obtained were used to determine π-bond strengths of multiple bonds containing silicon (kcal/mol):

C=C, 60.3; C=Si 42.3; Si=Si 20.2
C=C, 51.1; C=Si 44.3; Si=Si 23.0

Like other semiempirical methods MINDO/3 is extremely sensitive to parametrization. Its application to molecules with quite different bonds may lead to unreliable results. This is the case with certain hydrocarbons,[556] compounds containing heteroatoms, and, in particular, compounds having unusual bonds.[165,557,558] One must be wary of bonding conclusions based on these calculations.[559]

Unlike silaethylenes, germaethylenes have a relatively weak σ bond and much stronger π bond.[554]

In view of the large interest shown in compounds with multiple-bonded silicon atoms, the simplest of them have been calculated by the ab initio[165,365,546-551] method. Schlegel, Wolfe, and Mislow[546] confirmed that the $H_2Si{=}CH_2$ molecule is planar with a partial positive charge on silicon and a partial negative charge on carbon. The infrared spectra of $H_2Si{=}CH_2$ and $H_2Si{=}CD_2$ predicted by theoretical calculations are given in Table VI.

Four geometrically different structures of silaethylene were optimized with the ab initio method using s and p Gaussian-type functions contracted to a minimal (STO-4G) basis.[365] The absolute minimum was found at the skew position in the pyramidal triplet state lying about 1.4 kcal/mol below the minimum in the planar singlet state. An analogous conclusion about the triplet ground state of silaethylene was achieved by the other theoretical calculation.[560] Using a much larger s,p basis and electron correlation,[549] a value of the singlet–triplet separation energy for silaethylene in the range of 16.1 to 22.6 kcal/mol was estimated. Here, the singlet is the ground state of molecules and the triplet is the excited state.

A similar nonempirical calculation of a molecule of silaethylene predicted that its planar π-bonded singlet ground state is about 28 kcal/mol below the lowest triplet which has perpendicular structure with the SiH_2 flap angle of 45°.[548] Below are given predicted equilibrium geometries for triplet and singlet silaethylene, after Hood and Shaefer.[550] The value of the singlet–triplet separation energy amounts to 34.7 kcal/mol.

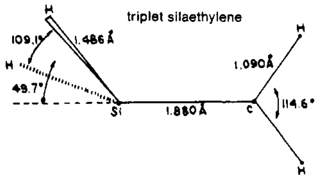
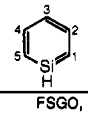
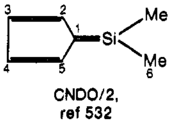


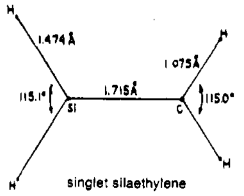
TABLE V. Theoretically Optimized Geometries, Heats of Formation, and Ionization Potentials of Compounds Containing Multiple p_π–p_π Bonded Silicon

properties	molecule and method of calculation							
	$^2Me_2Si{=}^1CH_2$ MINDO/3, ref 163	$CH_2{=}Si{=}CH_2$ MINDO/3, ref 163	$H_2{}^3C{=}^2CH\text{-}SiH{=}^1CH_2$ MINDO/3, ref 163					
				ab initio, ref 545	FSGO, ref 545	MINDO/3, ref 163	CNDO/2, ref 532	
bond length, Å	C_1Si: 1.671 C_2Si: 1.859 C_1H: 1.108 C_2H: 1.117	SiC: 1.631 CH: 1.111	C_2Si: 1.818 CC: 1.330	C_1Si: 1.722 C_1C_2: 1.381 C_2C_3: 1.395 SiH: 1.419 C_1H: 1.079 C_2H: 1.086 C_3H: 1.080	1.819 1.409 1.420 1.446 1.097 1.088 1.099	1.753 1.405 1.409 1.461 1.112 1.111 1.080	C_1Si: 1.962 C_6Si: 2.10 C_1C_2: 1.475 C_2C_3: 1.347 C_3C_4: 1.462 (CH): 1.111	SiSi: 2.20[a,b] 1.988[e] 2.023[f] 2.15[j] 2.1575[j] SiH: 1.46[a,b] 1.451[e] 1.466[f]
bond angle, deg	C_1SiC_2: 121.0 HC_1Si: 128.0 HC_2Si: 115.5	HCSi: 127.7	CSiC: 127.8 SiCC: 134.6	C_1SiC_5: 110.3 SiC_1C_2: 117.4 $C_1C_2C_3$: 125.1 $C_2C_3C_4$: 124.6 C_2C_1H: 118.2 C_1C_2H: 118.4 SiC_1H:	102.7 122.5 122.7 126.9 120.4 123.0		C_6SiC_5: 120 $C_5C_1C_2$: 120	1.4798[j] HSiSiH: 11195[e] 120 HSiSi: 124.5[f]
heats of formation, kcal/mol	−19.9	31.3	16.8			13.7		48.9[e] 49.2[f]
ionization potential, eV	9.0	9.17	8.8			8.6		6.56[a] 6.68[b] 8.8[f]
π-bond energy, kcal/mol					6.9		19.8	17.64[a,c] 50.01[a,d] 34.0[b] 33.4[e] 30.0[j]

[a] EHMO.[542] [b] CNDO.[542] [c] Values obtained with d_π contribution. [d] Values obtained without d_π contribution. [e] FSGO.[544] [f] MINDO/3.[163] [g] Triple bond

TABLE VI. In-Plane Vibration for Silaethylene (after Schlegel, Wolfe, and Mislow[546])

description	$H_2Si{=}CH_2$	$H_2Si{=}CD_2$
asym CH(CD) str	3160 (9)	2341 (1)
asym CH(CD) str	3096 (18)	2260 (13)
asym SiH str	2483 (80)	2484 (80)
sym SiH str	2479 (46)	2480 (46)
CH_2 bend; Si=C str	1490 (19)	1238 (23)
Si=C str; SiH_2 bend; CH_2 bend	1140 (14)	954 (11)
SiH_2 bend	993 (55)	1002 (50)
CH_2 rock; SiH_2 rock	777 (68)	700 (65)
SiH_2 rock; CH_2 rock	317 (10)	266 (5)



singlet silaethylene

The effect of polarity on the p_π–p_π bond in silaethylene amounts to the fact that accumulation of electronic charge at the carbon end leads to increased screening of nuclear charge and, hence, to an extension of $|2p_\pi\ C\rangle$ as compared to the isolated 2p AO. The reverse effect takes place for the corresponding silicon AO. Therefore, to form the π-bond an adjustment of the size of atomic orbitals forming the π-bond and the release of "mismatching" of the corresponding AO's on C and Si[542] is necessary. An increase of the $2p_\pi$–$3p_\pi$ overlap is estimated[548] from $S = 0.18$ (for unperturbed AO's[542]) to $S = \langle 2p_\pi\ C|3p_\pi\ Si\rangle = 0.33$ (without d AO's) and $S = 0.38$ (with allowance made for the contribution of d orbitals). The diagram of the π MO in silaethylene is given in Figure 4.

Ab initio calculations on disilaethylene molecules, Si_2H_4, have been made.[553] π-Bond energy is estimated at 30 kcal/mol. The singlet ground state is 7.1 kcal below the lowest triplet. The optimized Si–Si bond distance for singlet, 2.1575 Å, is equal to the value obtained in another ab initio computation[552] of Si_2H_4 (2.15 Å). Ab initio calculations on silabenzene, C_5SiH_6, show only a small (compared with benzene) change of bond angles and lengths for the singlet state of the molecule.[551] Unlike silaethylene,[365,548-550] where the triplet undergoes a large conformational change, triplet silabenzene remains planar. The π-electron distribution is also benzene-like and delocalized over the entire heavy-atom framework. The Mulliken population analysis of the π-electron distribution shows that it is reasonably uniform, with silicon having a somewhat smaller electron density than the carbons. The π bond of Si–C shows a more distinct polarization than does the π-electron system. This suggests that silabenzene may have considerable ylide character. The calculated resonance energy of silabenzene is two-thirds that of benzene.

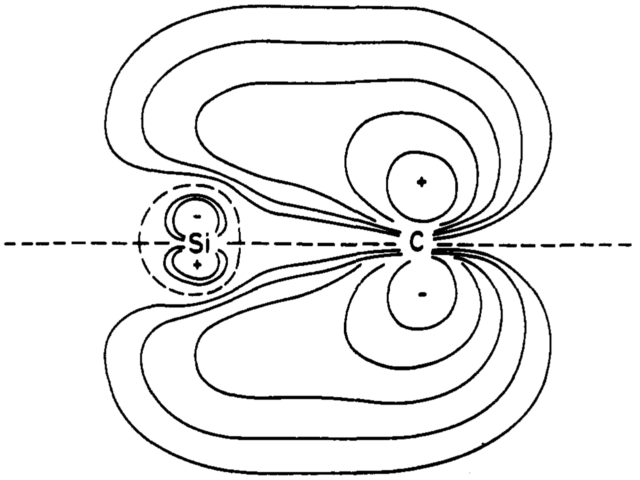


Figure 4. Diagram of the π MO in $H_2Si{=}CH_2$ (after Ahlrichs and Heinzmann[548]).

However, FSGO data[545] indicate that the Si–C bond order in silabenzene is only just above one. π-Bond energy is estimated at 29 kJ/mol (~7 kcal/mol). The high polarity of the Si–C bond implies that the molecule is open to nucleophilic and electrophilic attacks.

molecule and method of calculation								
MeH^{1}Si =^{2}SiH$_2$	Me$_2$Si =SiMe$_2$	Si$_6$H$_6$	HSi$\equiv$CH			MeSi $\equiv$CH	HSi$\equiv$SiH	
MINDO/3, ref 163	MINDO/3, ref 163	MINDO/3, ref 163	FSGO, ref 544	ab initio, ref 547	MINDO/3, ref 163	MINDO/3, ref 163	FSGO, ref 544	MINDO/3, ref 163
SiSi: 2.049 Si$_1$H: 1.472 Si$_2$H: 1.467 CSi: 1.832 CH: 1.119	SiSi: 2.102 CSi: 1.857 CH: 1.116	SiSi: 2.148 SiH: 1.48	CSi: 1.503 1.501[c] SiH: 1.444 1.443[c] CH: 1.085 1.087[c]	1.587 1.453 1.060		C$_1$Si: 1.503 C$_2$Si: 1.796 C$_1$H: 1.095 C$_2$H: 1.121	SiSi: 1.778 SiH: 1.440	1.829 1.440
CSiSi: 129.0 HSi$_1$Si$_2$: 118.5 HSi$_2$Si$_1$: 124.3	CSiSi: 123.0 HCSi: 115.9							
28.6		117.1 108.7[h]	132.4		45.0		84.4	76.6
8.5		8.17 8.0			10.1		9.2	
			77.4[g]				85.8[g]	

ɜnergy. [h] Equilibrium geometry with equal SiSi bond lengths. [i] Ab initio.[552] [j] Ab initio.[553]

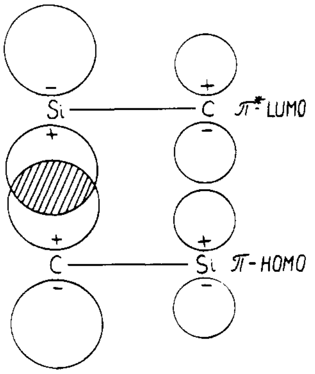


Figure 5. Orientation of HOMO and LUMO in head-to-tail dimerization of $H_2Si{=}CH_2$ (after Curtis[542]).

Little is known about the nature of p_π–p_π bonding divalent silicon compounds. Ab initio calculations[547,561,562] on compounds of divalent silicon, HN=Si (a molecule detected by infrared spectroscopy when silyl azide is photolyzed in a matrix[496]) and $H_2C{=}Si$, and tetravalent silicon, HSi≡N (a set of bands is assigned to the molecule in interstellar spectrum;[563] these, however, are not confirmed by the calculated microwave spectrum[562]) and HSi≡CH, showed that the former were more stable. The reverse relationship is observed in carbon analogs, where HC≡N is stable than HN=C by 14.5 kcal/mol.[564]

Theoretical predictions of the reactivity of silaalkenes first of all concern the discussion on cyclodimerization of silaethylene,[165,542,543,548] its fluorine derivatives,[543] and silabenzene,[163,545] and also cycloaddition of tetrafluorosilane to alkynes and dienes.[430]

In the absence of trapping agents cycloaddition is most typical for silaethylenes $R_2Si{=}CH_2$ and $R_2Si{=}CHR$. But, however strange it is, cyclodimerization was not observed for unsubstituted silaethylene, $H_2Si{=}CH_2$.[126] According to Curtis[542] a schematic orientation of LUMO and HOMO in the head-to-tail cyclodimerization of silaethylene is shown in Figure 5. The relative sizes of the atomic orbitals represent the contribution of those atomic orbitals to the MO's. As is seen, in the π bond the electrons are strongly localized on carbon, whereas in the π* LUMO the reverse is true.

The net positive overlap between the HOMO and LUMO lowers the orbital symmetry restrictions to dimerization. The greater the extent of electronic distortion introduced by the heteroatom, the lower are these restrictions. The inclusion of d orbitals also mitigates the symmetry barriers to reaction due to the decrease in the π–π* separation.[542] The rather low-lying π* MO (as measured by the rather small vertical $\Delta E_{S\rightarrow T}$ of 61 kcal/mol which is only ~60% of the corresponding value in ethylene)[529] indicates a considerable reactivity of Si=C despite the relative strength of the π bond. As a result cyclodimerization of silaethylene is a highly exothermic process ($\Delta E = -76$ kcal/mol). The calculated activated energy is less than 14 kcal/mol;[548] this greatly differs from the value, 64 kcal/mol, calculated by MINDO/3.[165] The correct barrier is even smaller, because all the factors affecting the result were not accounted for in the calculation (data[152] indicate that cyclodimerization of $Me_2Si{=}CH_2$ is a nonactivated process).

Damrauer and Williams[543] proposed that electrostatic interactions control the reactivity of $H_2Si{=}CH_2$, $F_2Si{=}CH_2$, and $H_2Si{=}CF_2$ molecules toward cyclodimerization. The absence of any strong attractive interactions in $F_2Si{=}CF_2$ shows that it should be either unreactive, seek some alternate reaction pathway, or give a head-to-head dimerization product.

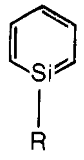
The methylsilylene–silaethylene–silylcarbene rearrangement studied by the ab initio method[474,475] predicts that both carbenoid species be thermodynamically more stable than silaethylene in their triplet state.

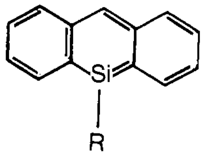
In conclusion, a viewpoint[38,565] about destabilization of silaethylenes due to the tendency of silicon atom to have nonplanar hybridization seems to be a rationalization for explaining the decreased capability of silicon and other group 4B metals to form stable multiple p_π–p_π bonds.

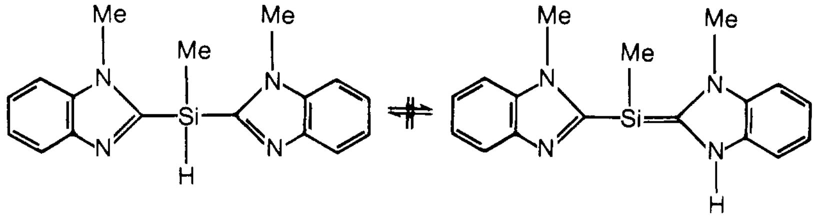
XIV. Attempts to Stabilize the Intermediates Containing Multiple p_π-p_π Bonded Group 4B Metals

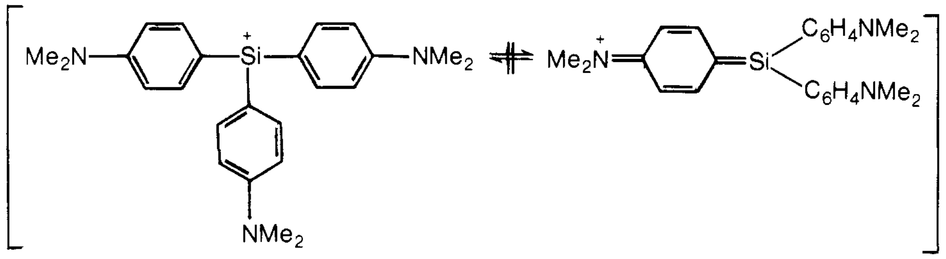
A. Synthesis of Structures Similar to Resonance-Stabilized π Systems

Recently remarkable progress has been achieved in synthesizing compounds containing p_π–p_π bonds between carbon and other elements, which were earlier recognized as nonexistent.[1] In particular, p_π–p_π bonds P=C, As=C, Sb=C, and Bi=C were obtained in such resonance-stabilized systems as dyes of cyanine or the triphenylmethane type, and in arenes analogous to benzene, naphthalene, and anthracene. However, all attempts to obtain similar resonance-stabilized π systems involving silicon or other group 4B metals failed:



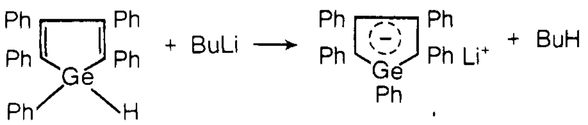




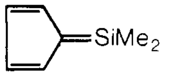


Thus, silabenzene and silaanthracene cannot be obtained by dehydrochlorination of the corresponding Si-chloro-substituted compounds, and also silaanthracene by elimination of LiCl after their prior metalation,[529,572–577] although ions of the desired silaarenes are produced upon electron-impact fragmentation.[528–530] Similar negative results were obtained with the corresponding germanium derivatives.[572] Experiments showing formation of short-lived Si-methyl-substituted silabenzene[280,329] also cast doubt on the assumption of the possible stability of silabenzene derivatives.[163]

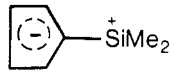
The less pronounced tendency of silicon to form multiple bonds apparently is the reason why silicon compounds analogous to the dyes of the cyanine[578] and triphenylmethane[579] type have no color. In the former, proton migration leading to a resonance stabilized Si=C bond failed to occur. In the latter, p_π–d_π interaction has such a pronounced stabilizing effect that no ionization of silicon is possible. A high acidity hydrodigermacyclopentadiene is due to the anion[583,595] charge delocalization. It forms cherry-red solution when treated with butyllithium in THF:



Two conformations of dimethylsilafulvene **35** and **36** were calculated via a CNDO/2 procedure:[532]

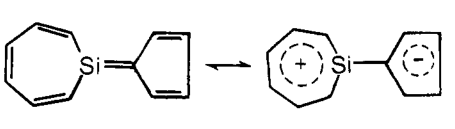


35



36

One of them, **35**, is planar while in the other, **36**, the CH_3–Si–CH_3 plane is perpendicular to the cyclopentadienyl ring plane. The energy difference appeared to be 19.8 kcal/mol indicating that the p_π–p_π Si=C bonding in the former is rather significant. The



37

additional stabilization due to the ylide structure allows the possibility that stable compounds of the type **35** may be synthesized after appropriate substituents have been found. It is also suggested[595] that simultaneous delocalization of the positive charge might confer sufficient stability to allow isolation of structure **37**.

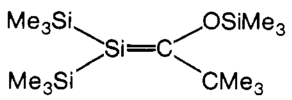
Some even less obvious indications on possible resonance stabilization due to the contribution of p_π–p_π bonding are also mentioned.[102,581–584] At last silylene phosphorane, R_3P^+–$^-SiMe_2$ is reported to be not a stable compound but an intermediate in reactions of hexamethylsilane with carbonyl compounds in the presence of tertiary phosphines.[237]

B. Synthesis of Compounds Containing Multiple p_π–p_π Bonded Group 4B Metals Stabilized by Sterically Hindered Bulky Substituents

Since the very short lifetime of silaethylenes is not the result of unimolecular decomposition, but is due to the ease of bimolecular cyclodimerization, there appears to be no intrinsic but merely thermodynamic instability of such intermediates. This conclusion is also supported by theoretical studies.[585]

Curtis[542] suggested that molecule tetra-*tert*-butyldisilaethylene might be amenable to isolation provided a low-temperature synthesis could be devised. However, attempts to form double bonds Si=Si and Ge=Ge by reaction of (*t*-Bu)BrSiSiBr(*t*-Bu) with a number of dehalogenating reagents (see section VII) failed.[587]

The compound



$(Me_3Si)_2Si{=}C(OSiMe_3)CMe_3$

proved to be relatively stable at room temperature. It is formed upon photolysis of pivaloyltris(trimethylsilyl)silane or upon thermolysis of the corresponding 1,2-disilacyclobutane[174] (see sections II.C and V.D). Of particular interest is the observation of a NMR ^{13}C singlet at 112.7 ppm below Me_4Si in the normal range of a sp^2-hybridized carbon assigned to the unsaturated carbon of silaethylene and the NMR ^{29}Si signal observed at 41.2 ppm downfield from Me_4Si assigned to the sp^2-hybridized silicon[589] of the silicon-carbon double bond. Intense ultraviolet absorption at 339 nm and the average intensity infrared band at 8.8 μ were also assigned to silaethylene. It is evident that enhanced stability of this silaethylene can be attributed to steric factors, which probably also play some role in dictating the mode of dimerization and affect the stability of 1,2-disilacyclobutane dimers.[174] The presence of two weakly electron-donating trimethylsilyl groups should reduce the electron deficiency on silicon. Additionally, an electron-withdrawing trimethylsiloxy group may reduce the electron excess on carbon atom lowering the polarity of the Si=C bond. Therefore, it seems possible to obtain stable and isolable silaethylenes at room temperature using other substituents.

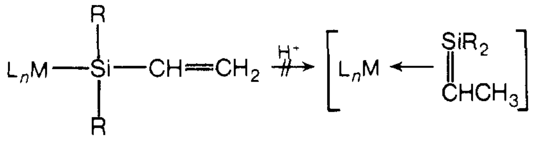
Less stable silaethylenes are probably formed when Me_3Si groups are attached to carbon. Thus, the molecule $Me_2Si{=}C(SiMe_3)_2$ was detected with the mass spectrometer when it was generated in the low-pressure gas phase.[326]

It is suggested[585] that such substituents as $(Me_3Si)_2CH$ will produce stable silaethylenes, disilaethylenes, and silanones.

C. π Complexes of Ligands Containing Group 4B Multiple p_π-p_π Bonded Metal

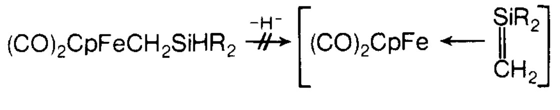
Stabilization of group 4B metal multiple p_π-p_π bonded intermediates in transition metal π complexes seems to be a hopeful approach since a number of short-lived molecules was stabilized in this way.[588,590,591] Attempts to obtain π complexes with ligands donating two, three, four, five, and six electrons which involve π-bonded group 4B metals have been undertaken.

Unlike σ-allylic complexes, transition metal complexes containing vinylsilyl ligands are not transformed into silaalkene π complexes upon protonation.[592]



$$L_nM{-}SiR_2{-}CH{=}CH_2 \xrightarrow[]{H^+}\!\!\!\!\!\!/\;\; \left[L_nM \leftarrow \begin{array}{c} SiR_2 \\ \| \\ CHCH_3 \end{array}\right]$$

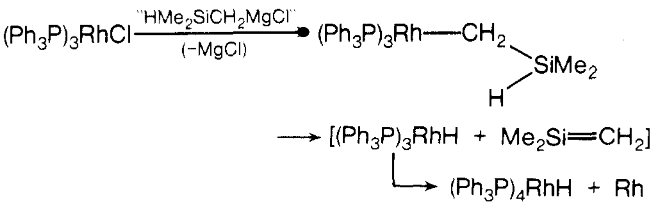
An attempt[594a] to obtain a π complex with the silaethylene ligand by analogy with the known[593] hydride elimination from σ-alkyl complexes failed:



$$(CO)_2CpFeCH_2SiHR_2 \xrightarrow[]{-H^-}\!\!\!\!\!\!/\;\; \left[(CO)_2CpFe \leftarrow \begin{array}{c} SiR_2 \\ \| \\ CH_2 \end{array}\right]$$

Upon treating tris(triphenylphosphine)rhodium chloride with dimethylsilylmagnesium chloride the obtained products are explained[594b] in terms of a silaethylene intermediate (Scheme CXXXI).

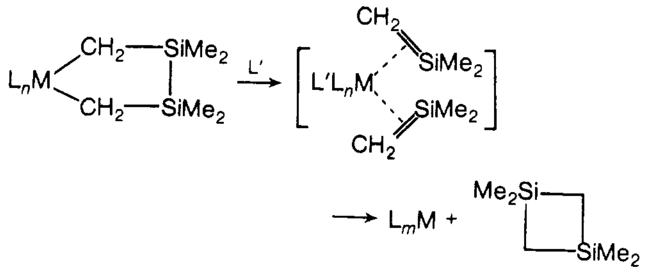
SCHEME CXXXI



A more recent failed approach to a coordinated Si=Si bond consisted of reactions of disilanes $R_2SiH{-}SiHR_2$ (R = *t*-Bu, Me) with low-valent metal complexes.[595]

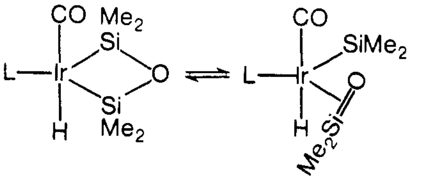
A stepwise mechanism of decomposition of 1-metalla-3,4-disilacyclopentane ring systems via possible formation of complexes containing 1,1-dimethyl-1-silaethylene ligands is suggested[580] to explain the formation of 1,3-disilacyclobutanes (see Scheme CXXXII).

SCHEME CXXXII



L = PPh_3; M = Ni, Pt

Cyclometalladisiloxanes of platinum, palladium, and iridium[596-599] act as catalysts for the disproportionation of 1,1,3,3-tetramethyldisiloxane into dimethylsilane and linear polysiloxanes. The postulated mechanism consists of the cleavage of the cyclometallodisiloxane ring to form an intermediate with coordinated dimethylsilylene and dimethylsilanone:



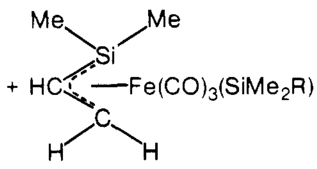
With dimeric rhodium catalyst D_3 and D_4 are formed in addition to linear oligomers. It is believed[598] that two dimethylsilanones coordinated on adjacent metal centers couple to form the highly reactive dimer D_2. The latter can interact with dimethylsilanone to give D_3 or it can dimerize to give D_4.

Transformations of hexamethyldisiloxane and hexamethylcyclotrisiloxane by the action of palladium and platinum compounds are also attributed to the formation of coordinated silanone.[600]

Sakurai, Kamiyama, and Nakadaira[601] were the first who succeeded in preparing the silicon analog of π-allyl complexes. On reacting nonacarbonyldiiron with vinylpentamethyldisilane or 1,2-divinyltetramethyldisilane in benzene oily complexes were obtained (Scheme CXXXIII).

SCHEME CXXXIII

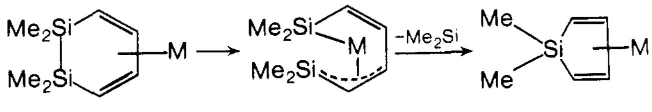
$$RMe_2SiSiMe_2CH{=}CH_2 + Fe_2(CO)_9 \longrightarrow Fe(CO)_5 + CO$$



R = Me, Vin

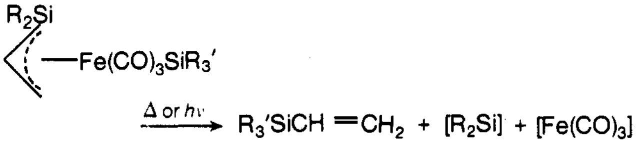
1,2-Disilacyclohexadienes react with penta- and nonacarbonyldiiron yielding diene tricarbonyl complexes which upon heating up to 160 °C transform into silacyclopentadiene complexes[602] (see Scheme CXXXIV). The mechanism of the reaction involves transient silaallyl complexes.

SCHEME CXXXIV



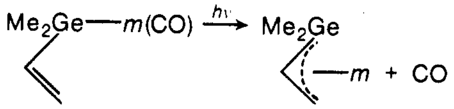
M = $Fe(CO)_3$

Similarly, loss of silylene was observed upon heating or irradiation of the η^3-1-silapropenyl complex[603,604]



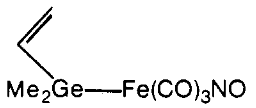
$\xrightarrow{\Delta \text{ or } h\nu} R_3'SiCH{=}CH_2 + [R_2Si] + [Fe(CO)_3]$

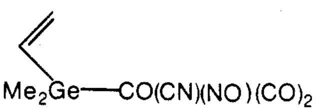
Attempts to prepare the π-germaallyl complex from the vinylgermylmetal complex



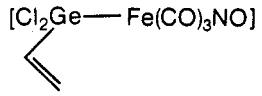
m(CO) = (a) $CpFe(CO_2)$, (b) $CpMO(CO)_3$, (c) $Mn(CO)_5$ (d) $Co(CO)_4$, (e) $Co(CN)(NO)(CO)_2$, (f) $Fe(NO)(CO)_3$

unexpectedly led to transition metal dimers or rearrangement complexes, indicating the homolytic scissions of the metal-germanium bond, which was predominant.[595] With the hope to rearrange the σ-allylic complex into the π-allylic one, the following compounds were prepared:





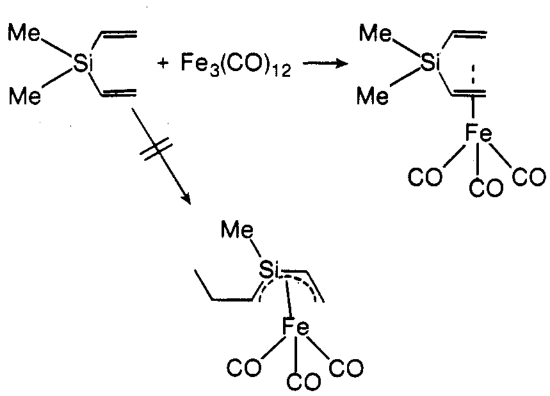
They appeared to be exceedingly unstable, decomposing below room temperature. Dichloro derivative **38** spontaneously lost carbon monoxide, but the vinyl group in the resulting product was uncomplexed.[595]



38

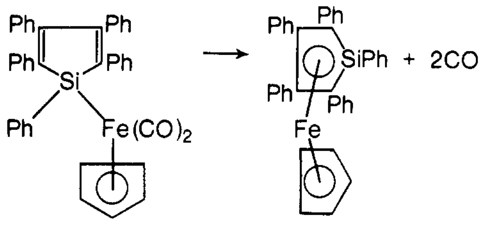
It is well known that nonconjugated dienes yield conjugated diene complexes when treated with transition metal carbonyls.[605,606] However, this is not the case where double bonds are separated by a dimethylsilyl group. When dimethyldivinylsilane is treated with molybdenum, tungsten,[607] or iron[608] carbonyls, π complexes with isolated double bonds of the ligand are observed (Scheme CXXXV).

SCHEME CXXXV



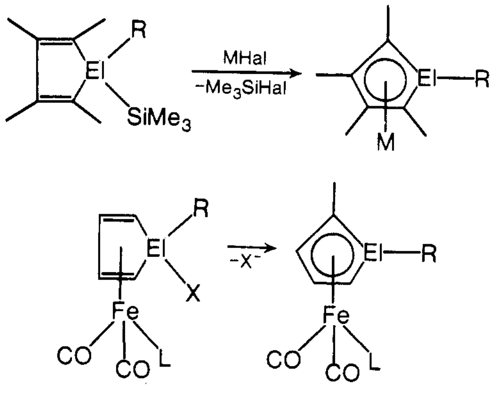
In an attempt to prepare an analog of ferrocene the germyllithium derivative of pentaphenylgermole was allowed to react with iron(II) chloride. The only organogermane isolated was pentaphenylgermole.[583]

By analogy with the known rearrangements of the mixed π and σ complexes[609] attempts were undertaken to rearrange σ-bonded derivatives of silacyclopentadiene and germacyclopentadiene into π-bonded "sandwich" structures.[583,595] However, neither pyrolysis nor photolysis led to the formation of the desired π complex.

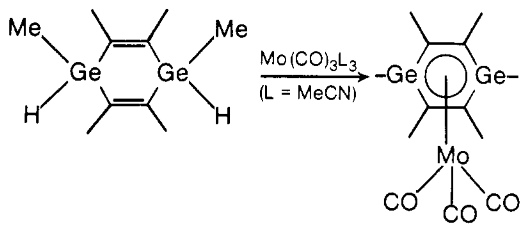


Attempts to synthesize sila(germa)cyclopentadiene complexes (Scheme CXXXVI) are also reported.[610] The only known but failed attempt concerns the preparation of the digermabenzene complex.[595]

SCHEME CXXXVI



El = Si, Ge; L = CO, $P(CH_3)_3$



D. Matrix Isolation

The matrix isolation technique was applied to study a number of unstable intermediates containing multiply bonded group 4B metals. Data obtained with infrared spectroscopy of isolated (in an argon matrix) silaethylenes have been discussed in sections II.A.3, X, XI.A, and XI.B. Using this method silicon monoxide, SiO, was studied.[611-613] This technologically important[9] molecule, usually existing at extremely high or low temperatures,[8,611,612,614] was produced by heating mixtures of Si and SiO_2, or by evaporation of SiO_2.[9,615] In 1971, SiO was discovered in interstellar space.[616] Other inorganic intermediates, such as GeO,[617] SnO,[618] PbO,[621] SiO_2,[613] SiCO,[619] SiN_2,[619] $Si(CO)_2$,[619] F_2SiO,[620] and Si_2F_4,[425,427,448] were also studied by the matrix isolation technique.

XV. Addendum

Since the submission of the original manuscript a number of new works have been done in this rapidly progressing field of chemistry. This section provides a brief account of the new works and a few of those which by mistake were not included in the original manuscript. The material refers to the sections to be supplemented.

Section I.B. Of historic interest is the work[271] on the pyrolysis of alkoxysilanes, in which the formation of $(C_4H_{10}O)_2Si{=}O$ was indicated.

Section II.A.2. In addition to the spectra shown in Figure 1, analogous spectra of matrix-isolated VLPP products of both 1,1-dideuteriomethyl-3-methyl-1-silacyclobutane and 1,1-di(deuteriomethyl)-1-silacyclobutane were also obtained.[148] The absorption bands (543, 580, 683, 718, 722, 768, 891, 929, 985, and 1012 cm^{-1}) assigned to 1,1-di(deuteriomethyl)-1-silaethylene were found to be present in both spectra. Based on both predicted by normal coordinate treatment the weak shift of the frequency of the vibration when deuterating methyl groups and the calculated dependence of the frequency on the force constant $f_{Si{=}C}$, the band at 1001 cm^{-1} (1012 cm^{-1} in the spectra of deuterio analogs) was preliminarily assigned to the Si=C stretching vibration. However, silaethylenes were not observed in the spectra of matrix-isolated products obtained from the pyrolysis of silacyclobutane and 1,1-dichloro-1-silacyclobutane under very low pressure.[652] In this case the anomaly may probably be related to the increased contribution of heterogeneous decomposition on the reactor wall surface.

Section II.A.4. The heat of formation, 20.5 ± 4 kcal/mol,[622] for 1,1-dimethyl-1-silaethylene was estimated from data of ion cyclotron resonance spectroscopy. Within the calculation error this value is close to the data.[153]

Section II.B. Trapping of silaethylenes generated photochemically from 1-methyl-1-phenyl- and 1,1-diphenyl-1-silacyclobutanes by triethoxysilane or trimethoxysilane results in the addition of RO to the silicon and $Si(H)(OR)_2$ to the carbon portion of a highly reactive unsaturated silicon–carbon linkage.[623] This argues against the triplet diradical nature of the intermediate which would involve addition of the silicon–hydrogen bond.

Section II.D. [4→2+2] cycloelimination reaction resulting in the generation of $R_2M{=}Y$ intermediates (M = Ge, Y = O, S, N; M = Si; Y = PR) is extended to several new heterocycles containing both germanium and silicon.[624,625] Platinum-catalyzed hydrosilylation of vinyldimethylcarbinoxydimethylsilane proceeds via an exclusively intramolecular path yielding not only five-membered heterocycles, but also the isomeric and highly unstable four-membered silaoxetane.[626] The latter under mild conditions (50–150 °C) decomposes generating dimethylsilanone.

Section III.B. [6→2+2+2] cycloelimination is postulated[627] for the pyrolysis of 1,1,2,2-tetramethyl-1,2-disila-3,6-dithiacyclohexane.

Section III.C. 2,2-Dimethyl-1-oxa-2-silacyclohexadi-3,5-ene reacts with perfluorobut-2-ene at room temperature yielding *o*-bis(trifluoromethyl)benzene.[628] Presumably, the reaction path involves initially the formation of the Diels–Alder adduct which decomposes through extrusion of dimethylsilanone.

Section V.A. Recent results concerning the generation and reactions of silicon–carbon double-bonded intermediates have been presented in a report[629] on the photolysis of organopolysilanes. The photolysis of tris(trimethylsilyl)phenylsilane in the presence of olefins and dienes results mainly in corresponding silacyclopropanes. However, in the photolysis with 2,3-dimethylbutadiene and with 1,3-cyclooctadiene the adducts of silicon–carbon double-bonded intermediates were also obtained.[630] Photolysis of the disilanyl-substituted naphthalene system was studied to examine the possibility of the formation of silicon–carbon double-bonded intermediates. The chemical behavior of the intermediates which do form was found to differ in many respects from those generated in the pyrolysis of benzoid aryldisilanes.[631] The silicon–carbon double-bonded intermediate generated photochemically from phenylpentamethyldisilane reacts with both methyllithium and methylmagnesium bromide to give a mixture of 1,2- and 1,3-bis(trimethylsilyl)benzene.[632]

Section V.B. A similar reaction proceeds with 1-phenyl-1,2-bis(trimethylsilyl)ethene.[632] More evidence has been presented[633] for silicon–carbon double-bonded intermediates produced via 1,5-sigmatropic migration of the trimethylsilyl group from silicon to carbon.

Section V.C. 1-Sila-1,2-propadienes, $R^2R^3Si{=}C{=}C(Ph)SiMe_2R^1$ (a: $R^1 = R^2 = R^3 = Me$; b: $R^1 = R^2 = Me$, $R^3 = SiMe_3$; c: $R^1 = SiMe_3$, $R^2 = R^3 = Me$; d: $R^1 = Me$, $R^2 = R^3 = SiMe_3$), formed in the photochemical reaction of corresponding phenylethylpolysilanes are evident by trapping experiments.[634]

Section V.E. A concerted six-center reaction which is visualized as involving an unsaturated silicon–carbon double-bonded intermediate has been suggested in the pyrolysis of carbomethoxyketene methyl trimethylsilyl acetal and diphenylketene bis(trimethylsilyl) acetal.[439] A useful precursor for a thermolytic generation of the dimethylsilanone proved to be vinyldimethylcarbinoxydimethylsilane.[653]

Section V.F. Thermolysis of vinyl aryloxy dimethylsilanes is interpreted as a Claisen-type sigmatropic reaction involving a silicon–carbon double-bonded intermediate trapped intramolecularly by an oxygenated group.[635]

Section VII. Thermal decomposition of silyl peroxides proceeds at 140–180 °C producing highly reactive organosilanones.[636] Insertion of silanones into Si–H and Si–O bonds has been observed.

Section VIII. Direct oxidation (O_2, Me_2SO, C_5H_5NO, *p*-$NO_2C_6H_4COOOH$) and sulfuration (S_8) of germylenes lead to the intermediates $>Ge{=}Y$ (Y = O, S).[624] The photolysis of aryl-substituted disilanes in the presence of dimethyl sulfoxide has been restudied.[637]

Section IX. A comparative study on the pyrolysis of both Me_3SiH and Me_3GeH was conducted in an effort to examine the formation of double-bonded germanium–carbon intermediates.[586] Since double-bonded intermediates are presumed to arise from the $Me_2HMCH_2\cdot$ radical, the absence of 1,3-digermacyclobutanes indicating noninvolvement of both $Me_2Ge{=}CH_2$ and $MeHGe{=}CH_2$ is explained in terms of the lack of a proton abstraction from the methyl group in comparison with abstraction of the germyl proton.

Section X. In the interpretation of the reaction between difluorosilylene and vinyl chloride at −196 °C, the authors feel reluctant to consider the intermediate silirane.[638] The proposed mechanism involves diradical species $\cdot(SiF_2)_n\cdot$. The results supporting Seyfert's postulate[449] concerning involvement of monomeric SiF_2 in the reaction of SiF_2 with olefins have been reported.[639]

Section XI.A. Photolysis of silyldiazomethanes in alcohols results in alkoxysilanes. Isomerization of silylcarbene proceeds via Si=C double-bonded intermediates. The migrating ability of the groups attached to silicon atoms decreases in the following manner: methyl > phenyl ≈ benzyl group.[511]

Section XI.B. The facile reaction of a silaimine intermediate which does not involve a Si–H bond is found to proceed with triarylalkoxysilanes.[623]

Section XI.C. Isomerization of silylsilylene into disilaethylene is suggested in the $Hg(^3P_1)$-photosensitized decomposition of Si_2H_6[308] and the 147-nm photolysis of monosilane.[640]

Section XII. Of interest in the mass spectrum of trimethylsilyl phenyl ketone is the origin of the *m/e* 147 ion.[641] Since stepwise loss of a methyl radical and atomic oxygen is unlikely, the elimination of a methoxy radical probably results in the $Me_2Si{=}C^+Ph$ ion.[641] Odd-electron ions derived from isomerized cyclic forms of molecular ions are characteristic of the mass spectra of vinylsilanes.[642] For example, the loss of ethylene molecule by methylvinyldichlorosilane is interpreted as "in half" fragmentation of 1,1-dichloro-1-silacyclobutane ion resulting in $[Cl_2Si{=}CH_2]^{+\cdot}$. Silabenzene ions are observed in the mass spectra of both 4R-silacyclohexa-2,4-dienes and 4R-silacyclohexa-2,5-dienes. In some cases these are the most abundant ions.[643]

Section XIII. CNDO/2 calculations were carried out to understand the photochemical generation of silicon–carbon double-bonded intermediates from disilanylbenzene and disilanylnaphthalene systems.[631] Experimental and ab initio studies were undertaken to resolve the problem of conjugation of 2-silabutadiene systems through the silicon atom.[644] Ab initio SCF calculations for $H_2Si{=}O$ were also carried out.[645] In the SCF calculations of some C_2SiH_4 isomers,[646] the silacyclopropyldiene ring is predicted to be more stable than the 2-silaallene. The lifetime of the latter might be very short, especially with regard to possible cyclization to the much more stable silapropylidene structure. The structure of the Si_2H_4 ground state is calculated to be a singlet silylsilylene.[647] A theoretical study of the photoelectron spectra of GeS, GeSe, and GeFe has been undertaken.[648]

Sections XIV.A. and XIV.B. An attempt to synthesize a silaethylene stabilized both electronically and by extreme steric bulk was undertaken but without any success.[649]

Section XIV.C. A σ-bonded five-membered ring, but not the expected diene π complex, was obtained in the reaction of molybdenum and iron carbonyls with 1,2-disilacyclobutenes.[650] Attempts to obtain a silaolefin–metal complex in the reaction of $(\pi\text{-}C_5H_5)Mn(CO)_3$ with 1,1-diphenyl-1-silaethylene generated photochemically from both 1,1-diphenyl-1-silacyclobutane and methylpentaphenyldisilane failed.[651]

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