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Hetero-π-systems from 2+2 cycloreversions. Part 1. Gusel'nikov–Flowers route to silenes and origination of the chemistry of doubly bonded silicon

Leonid E. Gusel'nikov *

Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky Prospect, 119991 GSP-1 Moscow, Russia

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* Fax: +7-095-230-2224.
E-mail address: guselnikov@ips.ac.ru (L.E. Gusel'nikov).

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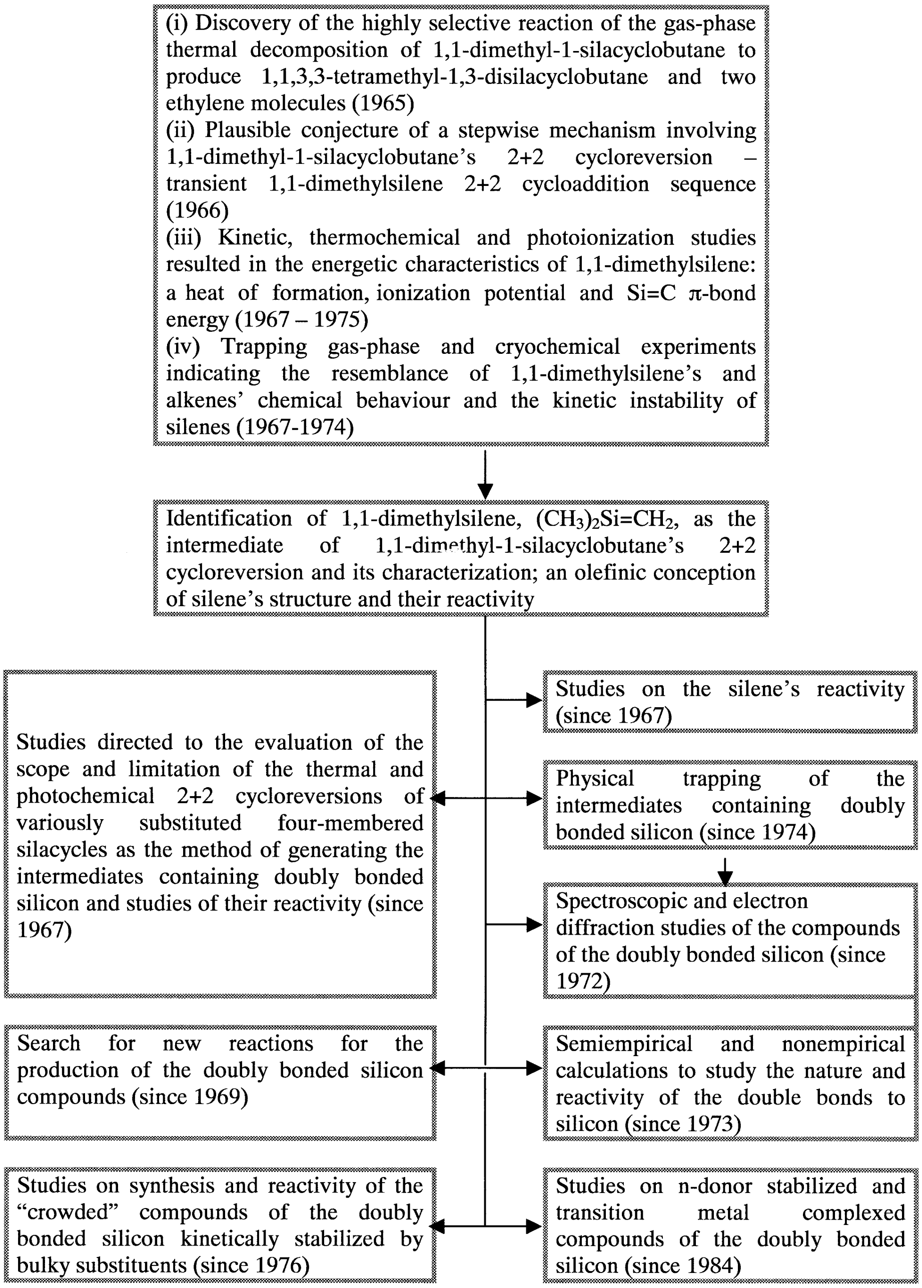
Abstract

The review concerns the production of the unsaturated compounds of a doubly bonded silicon via the four-membered silacycles' 2+2 cycloreversion, a reaction which allowed 35 years ago the evidence of 1,1-dimethylsilene (DMSE), $(CH_3)_2Si{=}CH_2$, the first compound containing the silicon–carbon double bond, and inspired a renewed interest to the chemistry of the multiply bonded silicon compounds at that time believed to be non-existent. Since then a great many of the doubly bonded silicon compounds have been obtained by various methods. Of them sterically non-hindered compounds are kinetically unstable because of their unprecedented reactivity in the bimolecular reactions, whereas those ones kinetically stabilized by the bulky groups, the 'crowded' compounds of the multiply bonded silicon, are relatively stable. Thermal and photochemical 2+2 cycloreversions occurring both in gas and liquid phases are reviewed. A special section is devoted to the gas-phase 2+2 thermocycloreversion of 1,1-dimethyl-1-silacyclobutane as a clean reaction of the transient DMSE production for the study of its chemistry as well as for its characterization by physicochemical and spectroscopic methods. Scope and limitations of 2+2 cycloreversion affected by the numbers and the position of silicon atoms in the four-membered ring, by the presence of Groups 15 and 16 elements, by the substituents and by the reactions conditions are evaluated.

Keywords: Silenes; Silanones; Silanthiones; Silanimines; Phosphasilenes; 2+2 Cycloreversion; Silacyclobutanes; Silaoxacyclobutanes; Silathiacyclobutanes; Silaphosphacyclobutanes; Silaazacyclobutanes; Cyclodisilazanes; Cyclodisiloxanes; Cyclodisilthianes



1. Introduction

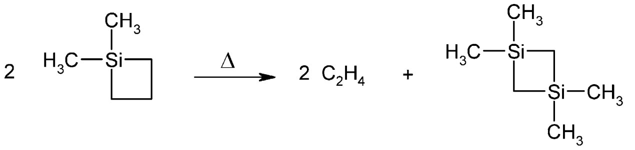
Multiply bonded compounds are common in organic chemistry since the first row elements, i.e., carbon, nitrogen, and oxygen are predisposed to form p_π–p_π bonds in their low coordinate states. In contrast, their heavier congeners are known to be reluctant to form compounds involving p_π–p_π bonding. In 1960s, the first compounds of multiply bonded elements of the second and subsequent rows, namely, phosphorus, arsenic, antimony, bismuth, selenium, silicon, were reported. This review concerns the problem of p_π–p_π bonding involving a silicon atom. Its intense development was initiated in 1965 by the discovery of a highly selective reaction of the gas-phase thermal transformation of monosilacyclobutanes into 1,3-disilacyclobutanes [1], which proceeds, as it was proved later on, via a 2+2 cycloreversion reaction to form silenes, $R_2Si{=}CH_2$, the silicon–carbon double p_π–p_π bonded intermediates [2–4] (see Section 2.1). The historical survey of previously failed attempts to obtain silicon analogs of olefins, ketones, and etc. is given in reviews [5,6]. Thus, a Gusel'nikov–Flowers route to silenes via 2+2 cycloreversion opened up the first approach to the compounds, containing a doubly bonded silicon. Since then this approach was widely explored and resulted in many different findings which are the subject of present review. Furthermore, it appeared to be the starting point for three and half decades of intensive and fruitful research on previously unknown Si=C, Si=N, Si=O, Si=P, Si=S, Si=Si, Si=Ge doubly bonded silicon compounds. Among a variety of such compounds described in literature, those bearing sterically non-hindered substituents are transient intermediates, whereas those containing crowded double bonds are stable ones [5,7–25]. A schematic representation of a set of studies that resulted in the modern chemistry of the doubly bonded silicon is shown in the above chart:

2. Gas-phase thermal cycloreversions

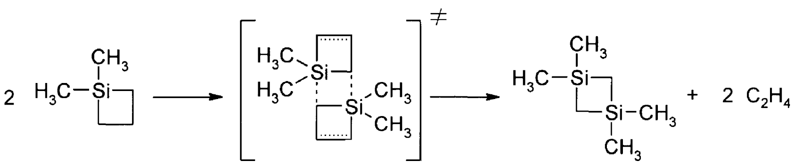
2.1. From 1,1-dimethyl-1-silacyclobutane to 1,1-dimethylsilene

2.1.1. A route to 1,1-dimethylsilene

A clean reaction of the gas-phase thermal transformation of 1,1-dimethyl-1-silacyclobutane (DMSCB) into 1,1,3,3-tetramethyl-1,3-disilacyclobutane [1,26] had at once become a subject of rapt attention not only because it provided a new method for the synthesis of 1,3-disilacyclobutanes, in particular those hardly available by conventional methods, e.g. 1,1,3,3-tetrachloro-1,3-disilacyclobutane, but also (and mainly!) because it turned out to be the starting point for more than three and a half decades of intensive research on previously unknown multiply bonded silicon compounds.

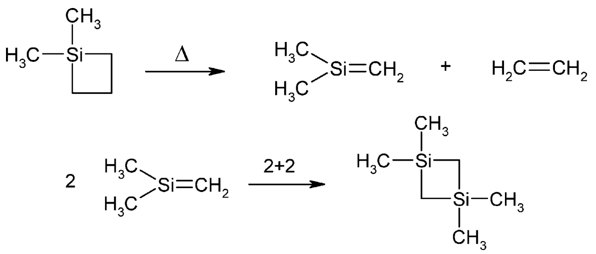


(1)



(4)

Two putative mechanisms were suggested at the very early stage of the study (i) a more preferable one involving a unimolecular 2+2 cycloreversion reaction resulting in ethylene and 1,1-dimethylsilene (DMSE) (Eq. (1)) followed by 'head-to-tail' dimerization of the latter (Eq. (2)) and (ii) a one step bimolecular 'push–pull' mechanism (Eq. (3)) involving no DMSE formation [27] (Eq. (4)).



(2, 3)

A gas kinetic study [2–4] revealed that DMSCB decomposition is of the first order, i.e., occurs in accordance with Eq. (1) resulting in ethylene and DMSE, not by Eq. (4), for which the second reaction order would be expected. Furthermore, the cyclodimerization reaction (Eq. (3)) and the first trapping experiments had undoubtedly demonstrated that a chemical behavior of the transient DMSE was as if it contained a silicon–carbon double bond [2–4,28]. A number of further chemical, kinetic, thermochemical, and spectroscopic studies were published dealing with the dimethysilene generated by the gas-phase 2+2 cycloreversion of DMSCB.[1] They are discussed in Section 2.1.

The following reaction conditions were used for the DMSE generation by the gas-phase 2+2 thermocycloreversion of DMSCB: (i) in the static quartz system (temperature range 394.3–450.7 °C and pressure 1.9–54.5 Torr, within an hour), (ii) in the short residence time flow systems at a very low pressure or under inert gas flow with at a higher temperature (550–700 °C).

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[1] Vapor phase thermal decarbonylation of 1,1-dimethyl-2-silacyclopentanone with Si–C bond formation results in 1,1-dimethyl-1-silacyclobutane that undergoes 2+2 cycloreversion to dimethylsilene [330].

2.1.2. *Kinetics*

An original kinetic study of the thermal decomposition of DMSCB in a static system at 394.3–450.7 °C and pressure 1.9–54.5 Torr showed [2–4] that at up to 50% conversion, the reaction obeys a first-order kinetic equation, the rate constant (k_2) being independent of the DMSCB initial pressure and the ratio of the reactor surface to volume (i.e. the process is homogeneous). Ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane were the only products. The rate equation was given by

$$k_2(\mathrm{s}^{-1}) = 10^{15.63\pm0.3}\ \exp\,(-62300\pm800/RT)$$

The mechanism of the reaction was interpreted in terms of a reversible initial 2+2 cycloreversion giving a transient silene (Eq. (2)) followed by a head-to-tail cyclodimerization of the latter (Eq. (3)).[2] The total process was inhibited by ethylene. The higher the conversion and the accumulation of ethylene in the static reaction system, the greater the contribution of the slow reverse reaction of 2+2 cycloaddition of ethylene to DMSE. Studies of the effects of the ethylene added revealed a good agreement between the results obtained and those calculated for the kinetic scheme including a reversible unimolecular reaction 2. The following Arrhenius relationship was obtained for the rate constants of 2+2 cycloaddition of ethylene to DMSE, k_{-2}, (reverse reaction 2) and DMSE cyclodimerization, k_3, (reaction 3):

$$k_{-2}/k_3^{1/2}(\mathrm{l}^{1/2}\ \mathrm{mol}^{-1/2}\ \mathrm{s}^{-1/2}) = 10^{3.3\pm1.2}\ \exp\,(-14500\pm4000/RT)$$

Eleven years later a kinetic study of 1,1-dimethylsilacyclobutane's pyrolysis was undertaken at a low pressure in a static (1 Pa) and at a very low pressure (5 × 10^{-2} Pa) in a flow system interfaced with a quadrupole mass spectrometer [29]. Pyrolysis in a static system between 537 and 569 °C gave similar results to those obtained originally at a higher pressure [3,4]. In the VLPP experiments the activation energy was 59.0 kcal mol^{-1} (below 777 °C). Above 777 °C the results were consistent with the original [3,4] high-pressure activation energy of 62.6 kcal mol^{-1}.

Twenty-two years later the kinetics of DMSCB pyrolysis in a static system (370–500 °C) was reexamined again [30],[3] yielding the following rate constant expressions:[4]

$$k_2(\mathrm{s}^{-1}) = 10^{15.46\pm0.13}\ \exp\,(-61682\pm433/RT)$$

$$k_{-2}/k_3^{1/2}(\mathrm{l}^{1/2}\ \mathrm{mol}^{-1/2}\ \mathrm{s}^{-1/2}) = 10^{4.73\pm1.8}\ \exp\,(-15598\pm1255/RT)$$

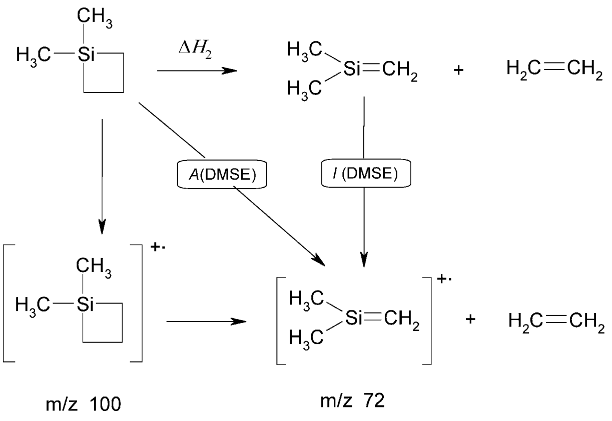
The kinetic data obtained using the pulse pyrolysis gas chromatography design had also become available [31].

$$k_2(\mathrm{s}^{-1}) = 10^{15.3}\ \exp\,(-61600/RT)$$

Investigation of DMSCB pyrolysis kinetics by VLPP/MS [29,32] led to the conclusion that DMSE 2+2 cyclodimerization is a non-activated process, i.e., $E_{(3)}$ is equal to or close to zero.[5] Taking into consideration that $E_{(-2)} - (1/2)E_{(3)} = 14.5 \pm 4$ kcal mol^{-1} and $E_{(3)} = 0$, the activation energy of the ethylene to DMSE 2+2 cycloaddition was estimated to be $E_{(-2)} = 14.5 \pm 4$ kcal mol^{-1} [32].

2.1.3. *Thermochemistry*

The energetic characteristics of DMSE such as the enthalpy of formation and the ionization energy were calculated using (i) DMSCB 2+2 cycloreversion enthalpy (Section 2.1.3.1) derived from the kinetic studies (Section 2.1.2), (ii) the results of thermochemical studies of DMSCB and 1,1,3,3-tetramethyl-1,3-disilacyclobutane [33–35] as well as (iii) the results of DMSCB photoionization study [36]. The following thermochemical cycle was evaluated [10,37] (Eq. (5)).



(5)

2.1.3.1. *Reaction enthalpies.* The reaction enthalpy of 1,1-dimethylsilacyclobutane's 2+2 cycloreversion calculated as the difference between E_1 and E_{-1} (see Section 2.1.2) was found to be equal to $\Delta H_2^\circ = 47.8 \pm 4.8$ kcal mol^{-1} [29,37,38]. The reaction enthalpy of the total process (reaction 1) was calculated from the enthalpies of formation of DMSCB and 1,1,3,3-tetramethyl-1,3-

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[2] Noteworthy, the Arrhenius parameters of the reaction 2 are similar to those found for 2+2 cycloreversion of a number of cyclobutanes.

[3] For some other kinetic study of 1,1-dimethyl-1-silacyclobutane pyrolysis see Refs. [331,332].

[4] In Ref. [29]: k_2 (s^{-1}) = $10^{15.46\pm0.13}$ exp($-31043\pm218/T$); $k_{-2}k_3^{1/2}$ (cm$^{3/2}$ s$^{-1/2}$) = $10^{7.0\pm0.3}$ exp($-7850\pm300/T$).

[5] For zero activation energy of cyclodimerization of dimethylsilene see also [30,79,251].

disilacyclobutane in the gas-phase being equal to -19.8 ± 1.4 kcal mol^{-1} and -53.9 ± 2.4 kcal mol^{-1}, respectively [35].[6] The obtained value of $\Delta H_1^\circ = 10.7$ kcal mol^{-1} together with $\Delta H_2^\circ = 47.8$ kcal mol^{-1} gives $\Delta H_3^\circ = -84.9$ kcal mol^{-1}. Notably that by absolute magnitude the latter is almost equal to the value of 1,1,3,3-tetramethyl-1,3-disilacyclobutane's 2+2 cycloreversion enthalpy (85.6 kcal mol^{-1}) derived from ab initio calculations [39].

2.1.3.2. DMSE enthalpy of formation. DMSE enthalpy of formation is associated with the enthalpy of DMSCB 2+2 cycloreversion (reaction 2) by equation:

$$\Delta H_2^\circ = \Delta H_f^\circ(\text{DMSE}) + \Delta H_f^\circ(\text{C}_2\text{H}_4) - \Delta H_f^\circ(\text{DMSCB})$$

Using $\Delta H_2^\circ = 47.8 \pm 4.8$ kcal mol^{-1}, $\Delta H_f^\circ(\text{C}_2\text{H}_4) = 12.5$ kcal mol^{-1} and $\Delta H_f^\circ(\text{DMSCB}) = -19.8 \pm 1.4$ kcal mol^{-1} (see Section 2.1.3.1) DMSE enthalpy of formation was estimated to be equal to 15.5 ± 6.2 kcal mol^{-1} [37,38]. This early estimate of $\Delta H_f^\circ(\text{DMSE})$ appeared to be in excellent agreement with the late theoretical prediction for DMSE enthalpy of formation being equal to 15 kcal mol^{-1} [40]. Other estimates for DMSE enthalpy of formation are 20.5 kcal mol^{-1} [41],[7] 15.5 ± 5 [29], 0.5 kcal mol^{-1} [42], 14.6 ± 3.2 kcal mol^{-1} [43]. In fact the latter value was obtained when recalculating the previous one, 8.6 ± 1.7 kcal mol^{-1} [30], using a newer value for $\Delta H_f^\circ(\text{DMSCB}) = -20.3$ kcal mol^{-1} [44,45].

2.1.3.3. Ionization potential of DMSE. It may be deduced from the thermochemical cycle given in Section 2.1.3. The ionization potential of DMSE, I(DMSE), is associated with the enthalpy of DMSCB 2+2 cycloreversion, ΔH_2°, and the appearance potential of a DMSE ion, m/z 72, $A(\text{DMSE})^+$, by equation:

$$\Delta H_2^\circ = A(\text{DMSE})^+ - I(\text{DMSE})$$

The appearance potential of a DMSE ion, m/z 72, measured by the photoionization mass spectrometry is 9.61 ± 0.05 eV [36]. Together with $\Delta H_2^\circ = 47.8 \pm 4.8$ kcal mol^{-1} it results in $I(\text{DMSE}) = 7.5 \pm 0.3$ eV. Calculated in 1975 [37] this value is in a fairly good agreement with $I(\text{DMSE}) = 7.7 \pm 0.4$ eV and $I(\text{DMSE}) = 7.71 \pm 0.03$ eV measured when studying DMSCB 2+2 cycloreversion by mass spectrometry [29] and photoelectron spectroscopy [46], respectively.

2.1.3.4. Si=C π-bond energy in DMSE. The following equation was proposed [47] for the calculation of a silicon–carbon π-bond energy in DMSE from the enthalpy of 1,1-dimethyl-1-silacyclobutane's 2+2 cycloreversion (reaction 2):

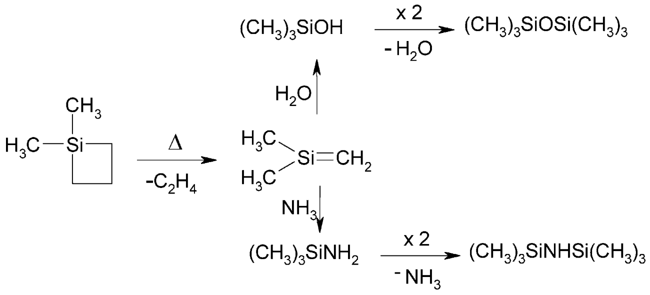
$$D_\pi(\text{Si=C}) = D(\text{Si–C}) + D(\text{C–C}) - D_\pi(\text{C=C}) - E_s - \Delta H_2$$

The analysis of the kinetic data [3,4] resulted in estimation of the lower and the upper limits of D_π(Si=C) to be in the range of $26 < D_\pi(\text{Si=C}) < 46$ (kcal mol^{-1}) [47]. Later, when $\Delta H_2 = 47.8 \pm 4.8$ kcal mol^{-1} was estimated [37,38] similar calculations had given the value of $D_\pi(\text{Si=C}) = 40.2$ kcal mol^{-1} with the $D(\text{Si–C}) = 85$ kcal mol^{-1}, and the strain energy $E_s = 25.9$ kcal mol^{-1} [37]. Further revision of D(Si–C), D_π(C=C) and E_s values, each of which had undergone a change, gave again 40.2 kcal mol^{-1} for the Si=C π-bond energy in DMSE [39].

2.1.4. Chemical and physical trapping experiments

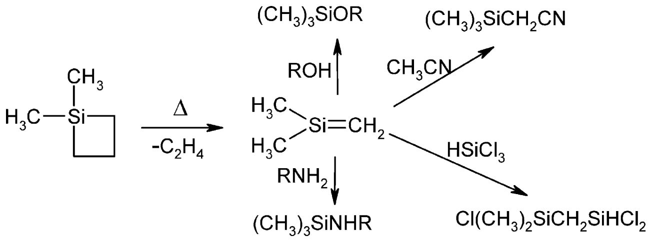
2.1.4.1. Chemical trapping. Besides kinetic and thermochemical evidence for the DMSE formation via 2+2 cycloreversion of DMSCB a number of chemical trapping reactions were reported indicating the chemical behavior of the former as a typical unsaturated compound entering into different reactions of addition across the silicon–carbon p_π–p_π double bond.

The pyrolysis of DMSCB in the presence of water vapors or ammonia gave corresponding adducts with DMSE and/or products of their condensation [2,3] (Eq. (6)):



(6)

Corresponding adducts with silenes were obtained during copyrolysis with alcohols [48,49], amines [48], nitriles [50], and even with silicon halides [51] (Eq. (7)):



(7)

DMSE adds rapidly to hydrogen chloride and to hydrogen bromide in the gas-phase to form the corre-

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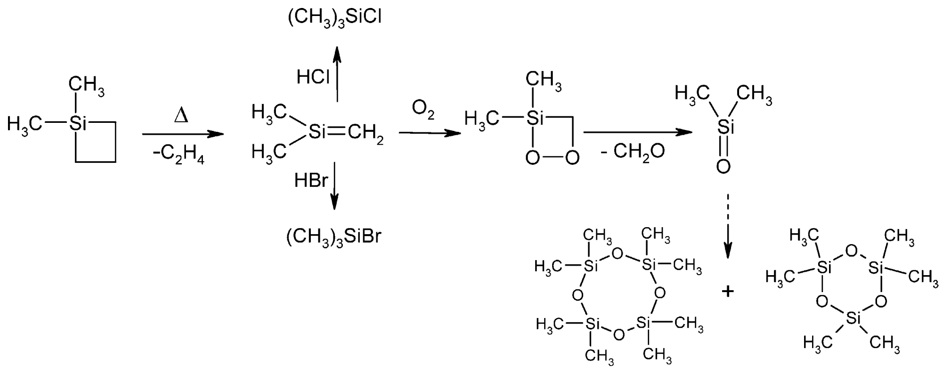
[6] New determination gave a close value of $\Delta H_f^\circ(\text{DMSCB}) = -20.3$ kcal mol^{-1} [44,45].

[7] The more recent value of the heat of formation of 1,1-dimethylsilene is decreased to 13 kcal mol^{-1} [341].

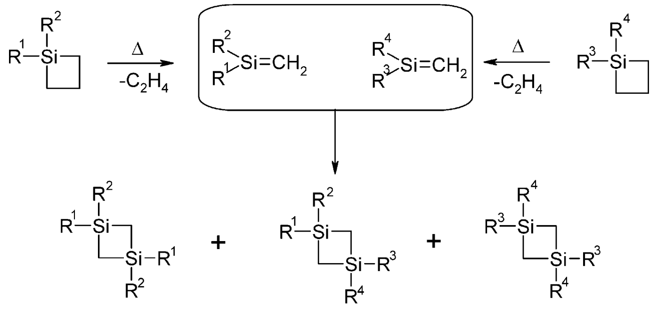


(8)

sponding trimethylsilyl halide, and to molecular oxygen to form dimethylsilanone via a plausible 2+2 cycloreversion of siladioxetane [52] (Eq (8)).

Besides the above addition reactions, insertion reactions into Si–O bonds of alkoxysilanes [53,54] and cyclosiloxanes [55] are characteristic of silenes (Eq. (9)).

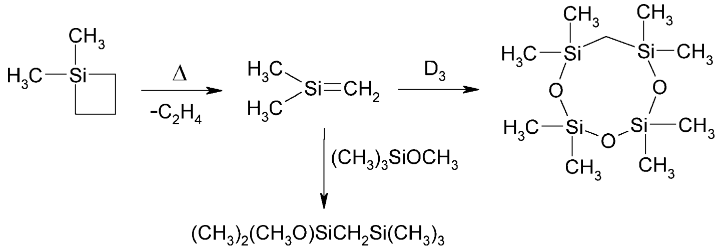
A feature of compounds with a $Si{=}C$ double bond is their ability to react via a 2+2 cycloaddition. Thus, 'head-to-tail' cyclodimerization reaction yielding 1,3-disilacyclobutanes spontaneously occurs in the absence of the traps [3]. A copyrolysis of two different 1,1-disubstituted 1-silacyclobutanes yielded a mixture containing 1,3-disilacyclobutanes arising from the all possible 2+2 cycloreversions of the two silenes in the ratio 1:2:1 [5,56–58] (Eq. (10)).



$R^1 = R^2 = CH_3$; $R^3 = R^4 = CD_3$
$R^1 = R^2 = CH_3$; $R^3 = R^4 = Cl$
$R^1 = R^2 = R^3 = CH_3$; $R^4 = Cl$

(10)

2+2 Cycloaddition of silenes to olefins was first discovered when studying ethylene's additives on the kinetics of thermal decomposition of DMSCB [3]. A copyrolysis of the latter with excess propene [3] and copyrolysis of 1,1,3-trimethyl-l-silacyclobutane with excess ethylene led in the first case to 1,1,3-trimethyl-l-silacyclobutane (the 2+2 cycloaddition product of DMSE to propene), and in the second case to DMSCB [59,60] (Eq. (11)).



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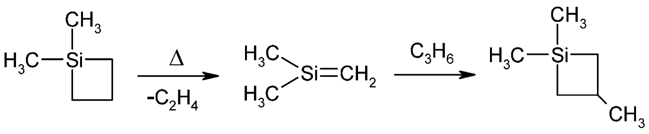
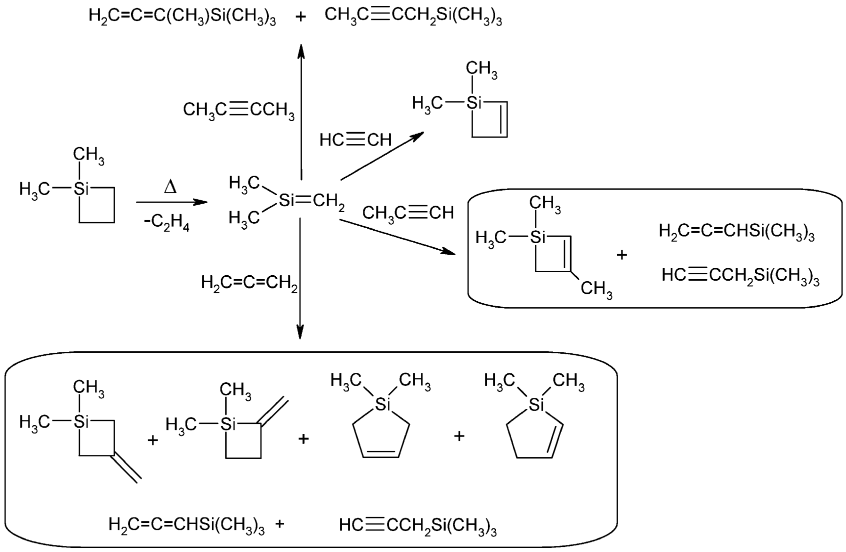


(11)

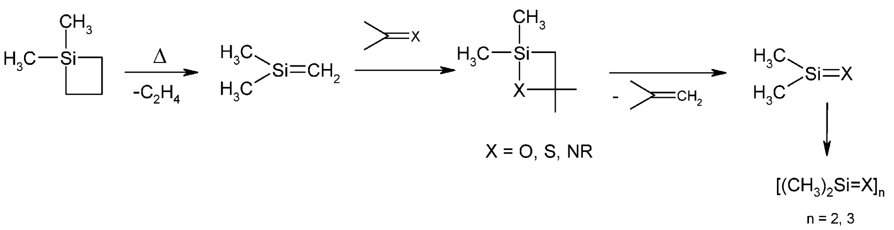
The 2+2 cycloaddition of DMSE to olefins proceeds much slower than the cyclodimerization, since the activation energies of the reactions with ethylene and propene amount up to 14.5 [61] and 8.4 kcal mol^{-1} [42], while the cyclodimerization requires no activation energy.



(12)

Upon copyrolysis of DMSCB with acetylene, methyl- and dimethylacetylene, and also with allene [62,63], which exhibits a dual reactivity to DMSE, products of 2+2 cycloaddition (silacyclobutenes, methylenesilacyclobutanes) and also of 'ene' reactions (trimethylsilylallene and 3-(trimethylsilyl)propyne) are formed (Eq. (12)).

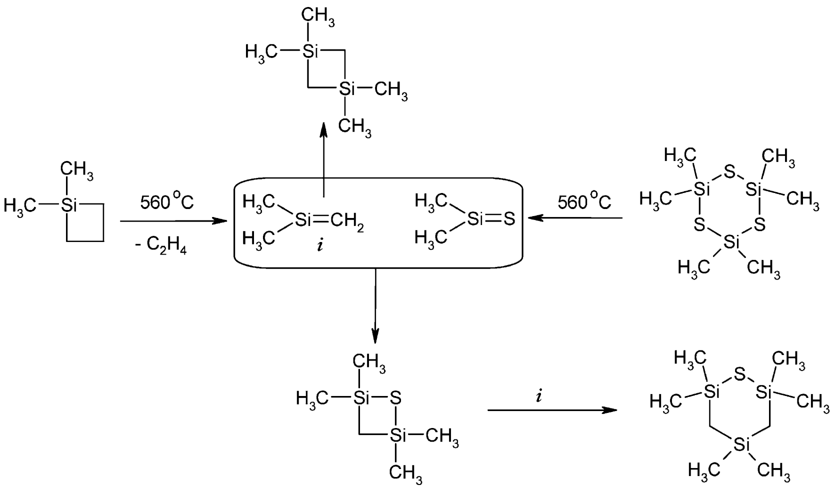
The effective silene interceptors are carbonyl compounds [48,64–68], thiones [69] and also azomethine compounds [68,70], which react with silenes by the mechanism involving 2+2 cycloaddition (Eq. (13)).



(13)

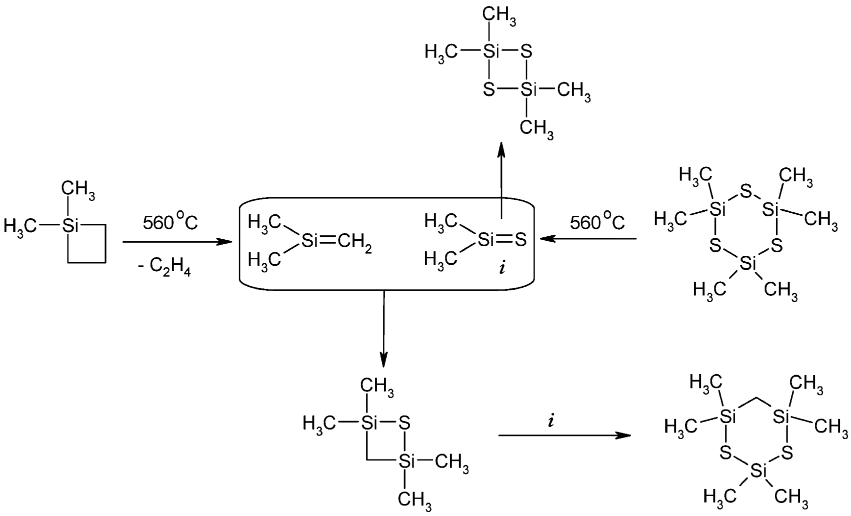
It is assumed that these reactions proceed via thermally unstable four-membered heterocycles: 2-silaoxetane (X = O), 2-silathiethane (X = S), and 2-silaazetidine (X = NR), which 2+2 cycloreversion leads to intermediates with Si=X double bonds. Although ab initio calculations predict that 1,2-silaoxetane should undergo rather bimolecular transformations than the monomolecular decomposition to silanone [71] under the low pressure pyrolysis conditions the former should be suppressed in favor of 1,2-silaoxetane's 2+2 cycloreversion.

Silenes are not known to react with silanones. However, it is not so in case of their reaction with silanthiones. A copyrolysis of hexamethylcyclotrisilthiane, a source of dimethylsilanthione, with the fivefold excess of DMSCB results in 1,1,3,3-tetramethyl-2-thia-1,3-disilacyclobutane, a DMSE to dimethylsilanthione 2+2 cycloaddition product together with a corresponding DMSE cyclodimer and a product of DMSE insertion into the Si–S bond of 1,1,3,3-tetramethyl-2-thia-1,3-disilacyclobutane [72,73] (Eq. (14)):



(14)

When stochiometric amounts of the starting compounds are taken into copyrolysis the products distribution is changed to produce mainly dimethylsilanthione's



(15)

cyclodimer and the product of dimethylsilanthione's insertion into the Si–S bond of 1,1,3,3-tetramethyl-2-thia-1,3-disilacyclobutane [72,73] (Eq. (15)).

In the ratio of 3.7 to 1 a copyrolysis of DMSCB with thietane, a source of thioformaldehyde, leads to 1,1,3,3-tetramethyl-2-thia-1,3-disilacyclobutane, 1,1,3,3-tetramethyl-1,3-disilacyclobutane and 1,1,3,3,5,5-hexamethyl-2-thia-1,3,5-trisilacyclobutane by a somewhat different pathway [72,73] (Eq. (16)).

A copyrolysis of DMSCB and the conjugated dienes results in the products of DMSE to dienes 2+4 cycloaddition [59,60,74,75] (Eq. (17)).

Upon copyrolysis of DMSCB and acrolein [76] DMSE reacted via 2+4 and 2+2 cycloaddition yielding silaoxacyclohexene and cyclosiloxanes. The latter is predominant in the reaction mixture, indicating a greater reactivity of a carbonyl group in the reaction with a silicon–carbon double bond (Eq. (18)).

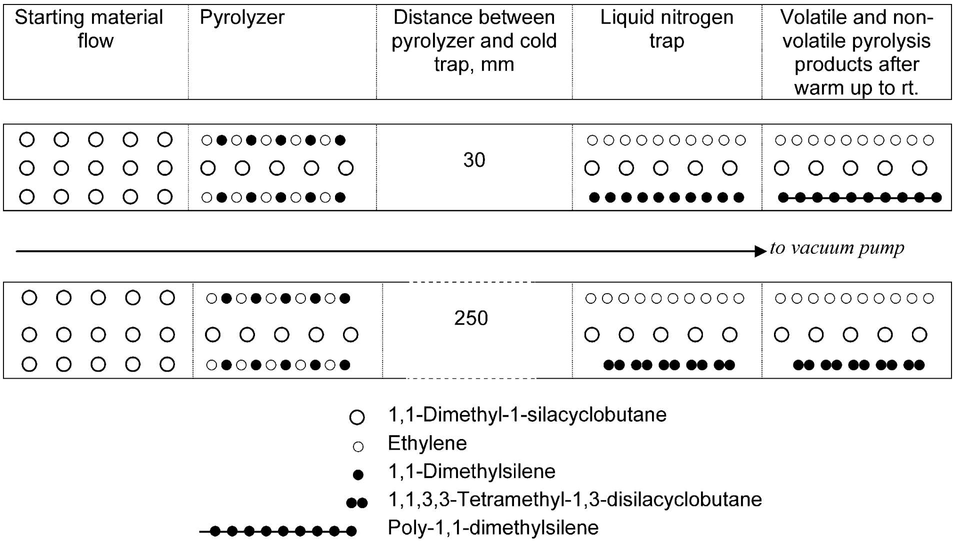
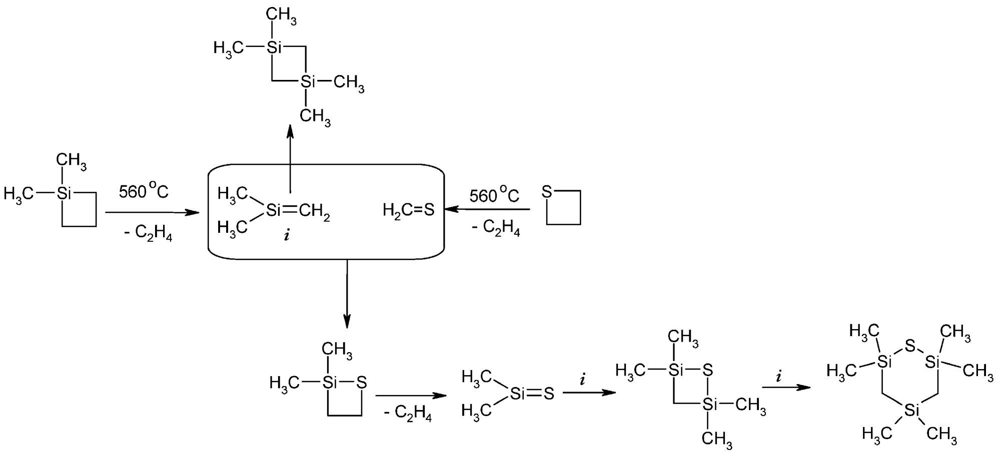


Fig. 1. The idealized presentation of DMSCB very low-pressure pyrolysis in a flow system followed by DMSE low temperature stabilization and polymerization.



(16)

Table 1
Arrhenius parameters of the gas-phase addition reactions involving DMSE

Reagent	log *A* (l mol^{-1} s^{-1})	*E* (kcal mol^{-1})	$k_{(800\ °C)}$ (l mol^{-1} s^{-1})	References
$Me_2Si{=}CH_2$	6.6	0	3.6×10^6	[32]
$Me_2Si{=}CH_2$	-14 [a]	Very low		[79]
$Me_2Si{=}CH_2$		2.7		[80]
$Me_2Si{=}CH_2$	$(3.3 \pm 0.8) \times 10^{-17}$ [a]	0		[30]
C_2H_4	6.2	14.5	1.7×10^3	[32]
$CH_3CH{=}CH_2$	5.2	8.4	8.2×10^2	[81]
Me_3SiOMe	5.3	26.4	7.7×10^4	[54]
H_2O	7.5	2.4	3.6×10^7	[80]
HCl	7.5	2.4	7.0×10^6	[52]
HBr	7.4	8.6	1.1×10^5	[52]
O_2	7.6	3.6	4.2×10^6	[52]
C_4H_6		4.8		[82]
MeOH		1.4		[82]

[a] $cm^3\ s^{-1}$.

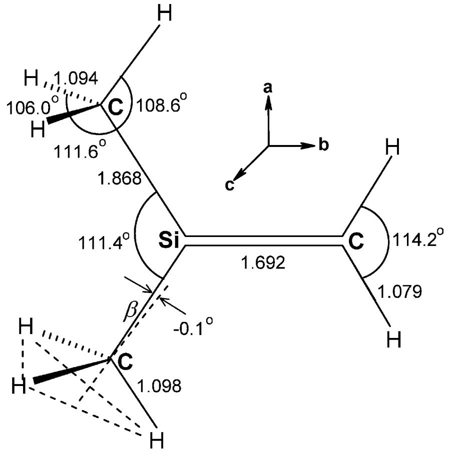
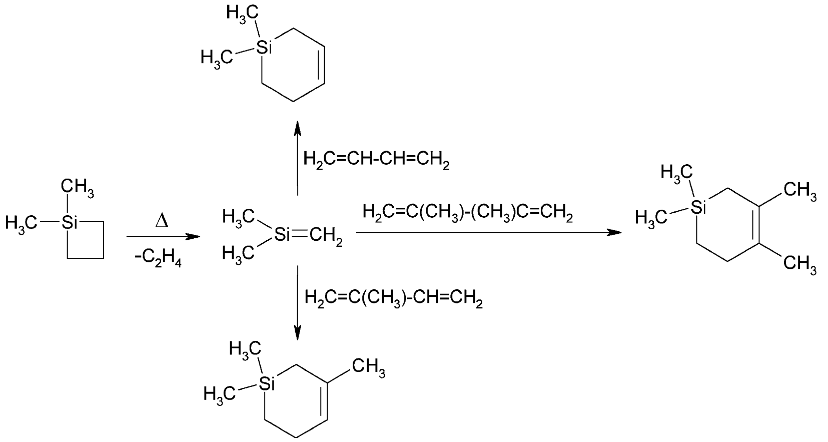


Fig. 2. Effective (r_o) structure determined for the heavy atoms in DMSE.



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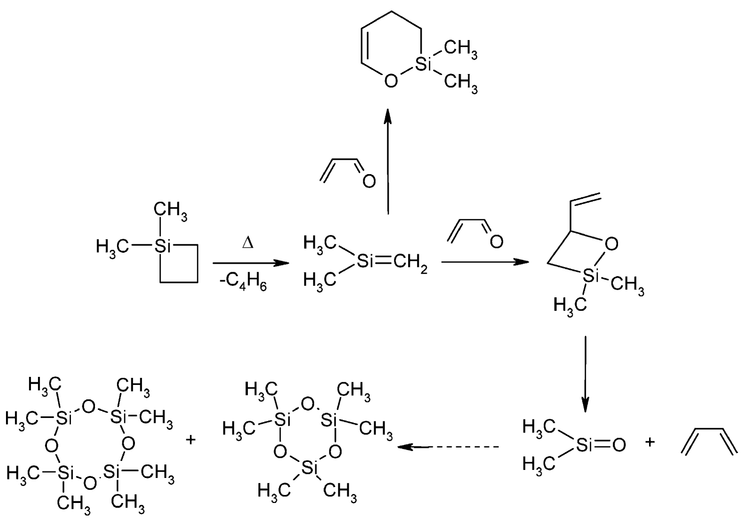
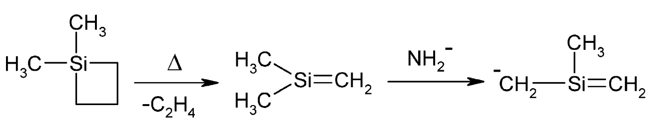


(18)

Ion–molecule chemistry of DMSE in the flowing afterglow (FA) instrument equipped with a pyrolyzer was explored to examine its reactions with anions of various types. Thus, DMSE generated by DMSCB 2+2 cycloreversion was detected in the FA by the reaction with H_2N^- or HO^- resulting in proton abstraction from carbon [77,78] (Eq. (19)).



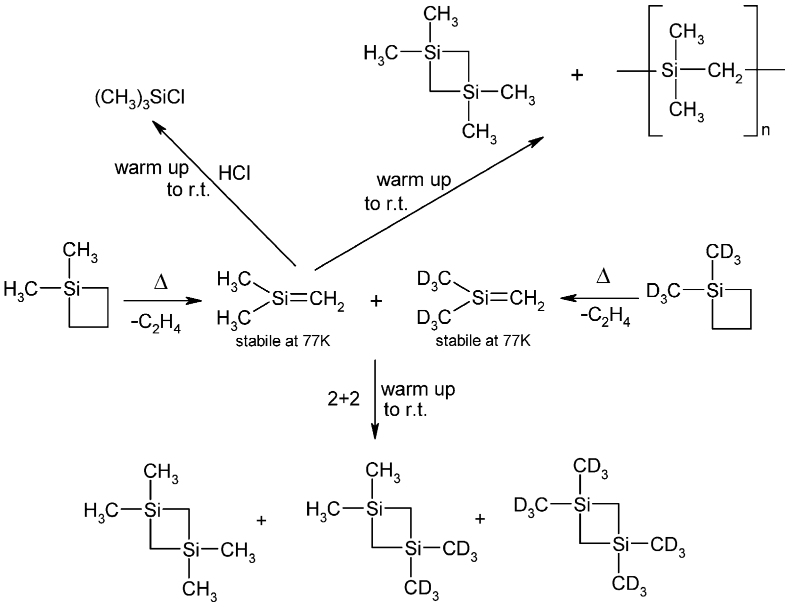
(19)

Silaallyl M^{-1} anion was characterized by its reaction with CO_2, CS_2, and COS. A comparison of the DMSE acidity (~ 377 kcal mol^{-1}) with that of isobutene (390 kcal mol^{-1}) indicates a substantial stabilizing effect by silicon.

2.1.4.2. Arrhenius parameters of addition reactions across Si=C double bond of DMSE.

The Arrhenius parameters and rates of different gas-phase addition reactions across the silicon–carbon double bond of DMSE are given in Table 1.

The ratio of the rate constants of the addition reactions of butadiene to DMSE and its cyclodimerization amounts to 1.1×10^{-4} [82]. The rates of reaction of other DMSE interceptors during the copyrolysis with



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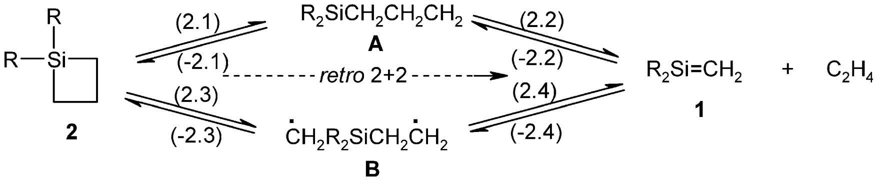

(21)

DMSCB fall in the following order [48,50]: $Ph_2C=O > ROH > ArOH > ClC_6H_4NH_2 > CH_3CN$.

2.1.4.3. Liquid nitrogen cryochemistry of DMSE. Because of DMSE short lifetime the processes of its formation during DMSCB pyrolysis and spontaneous cyclodimerization can not be normally separated in the ordinary flow systems. However, at very low pressures and short residence times, a cyclodimerization zone can be extended beyond the reactor and DMSE can be frozen on a low-temperature target. The shorter distance between the reactor and the target, the higher efficiency of DMSE isolation. With the target cooled by liquid nitrogen the ratio of ethylene to 1,1,3,3-tetramethyl-1,3-disilacyclobutane, the dimer of DMSE, is strongly dependent on the pyrolysis pressure when the distance is 30 mm, i.e. it rises by two orders at 1×10^{-3} Torr as compared with stochiometric ratio (2:1) at 2 Torr [83]. The ratio increase is accompanied by DMSE polymer formation, $-(Me_2SiCH_2)_n-$. No polymer formation was noticed in the very low-pressure pyrolysis with the target placed at 250 mm from the reactor, ethylene to 1,1,3,3-tetramethyl-1,3-disilacyclobutane ratio was nearly stochiometric (Fig. 1). There might be two explanations of the polymer formation on the low-temperature target. The first one consists in DMSE low-temperature stabilization followed by its polymerization when the target is warmed up. The second assumption concludes in the polymer formation in the course of DMSE chemical vapor deposition (CVD). Whatever it is, the phenomenon observed clearly indicates what technique to study thermally generated DMSE outside the pyrolysis zone should be like.[8]

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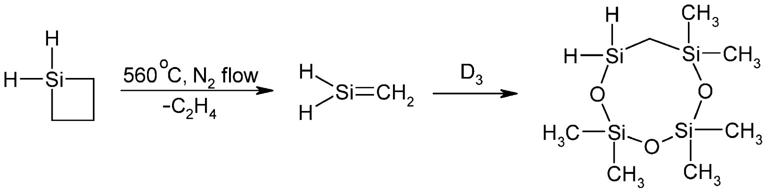
[8] The principle of this technique was used for detecting silenes in the gas phase (see Sections 2.1.5.1, 2.1.5.2, 2.1.5.3, 2.1.5.4 and 2.1.5.8), isolation in matrices (see Sections 2.1.5.5 and 2.1.5.6), and low temperature NMR study (see Section 2.1.5.7).

Moreover, some of the given below cryochemical reactions performed with sandwiches made of the reagents and the successively frozen DMSCB very low pressure pyrolysis pyrolyzate definitely demonstrate that the low-temperature stabilization of DMSE occurs at 77 K. Thus, the latter reacts on warming up with HCl to produce trimethylchlorosilane [84]. Similarly, a successive condensation of silene pairs on a cold surface followed by its warming leads to the formation of their cyclic adducts, co-dimers, and also a DMSE polymer [84] (Eq. (20)).



(22)

2.1.5. Spectroscopic manifestations and structural studies of DMSE

The route to DMSE via a clean gas-phase DMSCB 2+2 thermocycloreversion was widely used for its observation and characterization by instrumental methods, such as mass spectrometry [29,61,85], photoelectron spectroscopy [46,86], microwave spectroscopy [87,88], electron diffraction [89]. It was subjected to IR [90–98], UV [99,100] NMR [85] and ESR [101] spectroscopic studies at low temperatures and isolated in matrices.

2.1.5.1. Mass spectra. A relationship between the relative peak intensities of DMSE (*m/z* 72) to the molecular (*m/z* 100) ions and the conversion of DMSCB was established using VLPP/MS technique: the higher the conversion, the higher the I_{72}/I_{100} ratio. It was proved to be associated with the direct observation of DMSE thermally generated by DMSCB 2+2 cycloreversion [61]. In the analogous experiment [29] it was shown that at room temperature the appearance potential of the DMSE ion is 0.5 eV higher than that for the 1,1-dimetyl-1-silacyclobutane molecular ion, whereas at 722 °C the energies were reversed. In the latter case, the appearance potential for *m/z* 72 was lower by 1.3 eV than that for *m/z* 100. The estimated ionization potential for DMSE was 7.7±0.4 eV [29]. Mass spectrometry was also used for routine identification of DMSE in the DMSCB pyrolysis stream [85].

2.1.5.2. Photoelectron spectra. Studies of DMSCB 2+2 cycloreversion by VLPP/PES method resulted in the determination of the DMSE ionization potential: VIP 8.3±0.05 eV [86], 7.98±0.01 eV [46]; AIP 8.00±0.05 eV [86], 7.71±0.03 eV [46]. The latter value of the adiabatic ionization potential is in a good agreement with the earlier thermochemical estimate [37,38] (see Section 2.1.3.3).

2.1.5.3. Electron diffraction spectra. The first structural study of the molecule containing a silicon–carbon double bond, i.e. a gas-phase electron diffraction study of DMSE generated by the pyrolysis of DMSCB resulted in the average Si=C and Si–C bond distances being 1.83±0.04 Å and 1.91±0.02 Å, respectively [89]. There was a serious discrepancy between the measured and calculated Si=C bond lengths. So the problem was called to the attention to check by microwave spectroscopy (see Section 2.1.5.4).

2.1.5.4. Microwave spectra. A rather long Si=C distance, 1.83±0.04 Å, being completely outside the range of theoretical predictions resulted from the electron diffraction study of DMSE generated by DMSCB 2+2 cycloreversion [89] (see Section 5.1.2) encouraged the microwave determination of the rotational spectrum of DMSE as the traditional method for determining an accurate structure of a volatile, small, stable, polar molecule [87,88]. Six *b*-dipole rotational transitions were observed between 8 and 9.2 GHz for the transient DMSE produced by the thermal decomposition of DMSCB at ~1000 °C. The assignment of these transitions was unambiguous since they disappeared when the temperature of the furnace was turned down. The Si=C and Si–C bond lengths were in excellent agreement with the theoretical predictions [102]. In comparison with isobutylene, methyl groups are farther apart and have only half as large a barrier to internal rotation to give a tilt of only about −0.1°. The heavy atom effective structure was determined and is shown in Fig. 2.

2.1.5.5. Infrared spectra. The first attempt [103] to detect DMSE in the IR spectrum of DMSCB gas-phase 2+2 thermocycloreversion products frozen on the target cooled by liquid nitrogen had failed [104]. The isolation

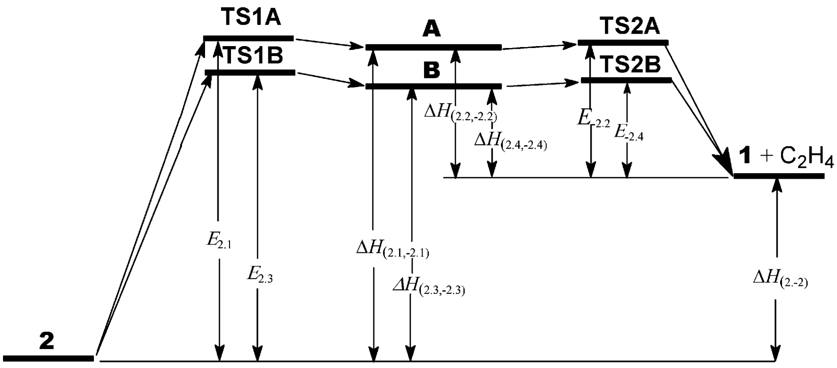


Fig. 3. A schematic energy level diagram for 2+2 cycloreversion of 1-silacyclobutanes.

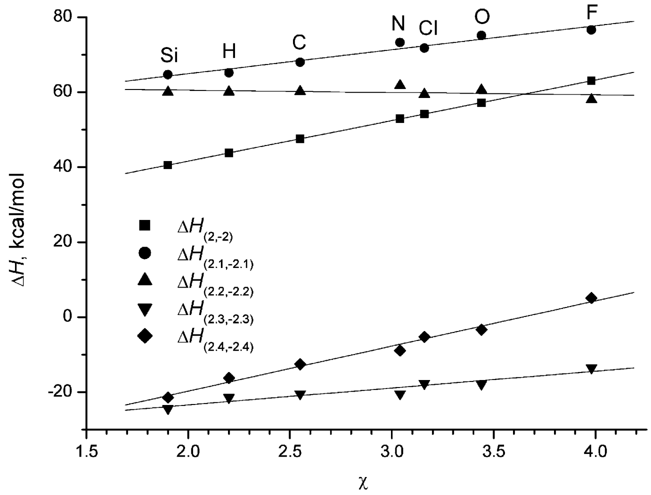


Fig. 4. A view of the contribution of reactions 2.1, 2.2, 2.3 and 2.4 to the enthalpy of 2+2 cycloreversion of 1-silacyclobutanes versus Pauling electronegativity. (Corrected for 1,1-disilyl-1-silacyclobutane's strain energy to be equal 20.4 kcal mol^{-1}.)

of DMSE in an argon matrix had first resulted in observation of three bands, 642.9, 825.1 and 1003.5 cm^{-1}, no assignment of the bands was made [90]. Their disappearance when annealing the sample was accompanied by the emergence of 1,1,3,3-tetramethyl-1,3-disilacyclobutane's bands. Taking into account that (i) DMSCB is a well known source for a clean gas-phase thermal generation of DMSE (reaction 2) [2,3] and that (ii) the latter is known to form a head-to-tail cyclodimer under both the gas-phase and cryochemical conditions (reaction 3) [83] there was no other reason except to conclude that the observed bands are due to DMSE. Shortly thereafter, six bands, 642.9, 817.5, 825.2, 1003.5, 1251 and 1259 cm^{-1}, were found to be due to DMSE on the same ground [91]. Some tentative band assignment with the exception of Si=C stretching were suggested. Thus, at this point (1977) the IR spectroscopic manifestation of the intermediate of DMSCB 2+2 cycloreversion-transient DMSE 2+2 cyclodimerization sequence was demonstrated.

The aim of the further work carried out by two Russian groups was to search for the band of the Si=C double bond stretching vibration in the IR spectrum of DMSE. In 1979 they presented their results at the conference on low-temperature chemistry [92,105]. In particular, eight bands in the matrix IR spectrum of VLLP products of DMSCB, 644, 696, 817, 824, 935, 992, 1001 and 1253 cm^{-1}, to be due to DMSE were observed [92]. Of them the band at 1001 cm^{-1} was assigned to Si=C stretching based on normal coordinate treatment of the olefin like model (C_{2v} symmetry) [92].[9] The otherwise assignment of the band at 1003.5 cm^{-1} to the Si=C stretching was made by the second Russian group. They came to the conclusion that the silicon–carbon double bond in dimethysilene is of ylide character (the force constant and the frequency are close to those in phosphorus ylide, $(CH_3)_3P^+{-}CH_2^-$) [105]. These two different viewpoints were developed by further theoretical and experimental studies [94,95,97,106] and resulted in radically different conclusions concerning the nature of the Si=C double bond in silenes (i) silenes are highly reactive unsaturated organosilicon compounds containing the silicon–carbon double 3p$_\pi$–2p$_\pi$ bond [95] whose chemical behavior resembles olefins [5] and (ii) 'the vibrational frequency and the force constant are practically the same for Si=C bond in $(CH_3)_2Si{=}CH_2$ and the $P^+{-}C^-$ bond in the simple phosphorus ylide molecule $(CH_3)_3P^+{-}CH_2$. Their structural and chemical properties compared to ylides emphasize their clear similarity and allows to consider silaolefins as C-ylides of silicon' [97].[10]

At present, the olefinic conception of silenes is widely accepted. It is very unlike that the ylide-like structure contributes to the structure of silene [107]. In silene π-orbital is localized on C atom and elongated towards silicon. It provides π-bonding between Si and C atoms.

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[9] The assignment of the band at 1156 cm^{-1} to Si=C stretching in the IR spectrum of the pyrolyzate after its trap-to-trap distillation is improper [134].

[10] In fact the olefinic structure was recently recognized by one of the authors [333].

On the contrary, in phosphorane there is no π-bonding on HOMO [108]. The distinction of Si=C bond in $Me_2Si{=}CH_2$ and $P^+{-}C^-$ bond in phosphorane is also evident when comparing the potential energy profiles as a function of internal rotation about Si=C bonds in the silene and $P^+{-}C^-$ bond in $H_3P^+{-}CH_2^-$ as well as the values of their rotational barriers. Unlike silene which potential energy profile has two minima (at $\varphi = 0, 180°$) and two maxima (at $\varphi = 90, 270°$) the potential energy profile of phosphorane consists of three global (at $\varphi = 0, 120, 240°$) and three local minima (at $\varphi = 60, 180, 300°$) as well as of six maxima (at $\varphi = 50, 75, 170, 195, 290, 315°$). Periodicity of the curve for phosphorane is equal to 6 and the rotational barrier is extremely low (1.0 kcal mol^{-1}, cf., 40.0 kcal mol^{-1} for silene) [108]. The facile freedom of rotation about the 'double' bond in the ylide-like silenes should also result in a magnetic equivalence of the groups attached. However, the NMR spectra of the stable Brook's silene indicate that the trimethylsilyl groups attached to silicon are nonequivalent giving no evidence of rotation about the double bond, and no evidence of ylide-like behavior of a silene [107]. Furthermore, if the sp^2-hybridized carbon of silene had a significant carbanionic character, it should have been relatively shielded by the virtue of an acquired negative charge as it is in case of phosphorus ylides. In contrast, the sp^2-hybridized carbon in silene is strongly deshielded to about 214 ppm [107].

2.1.5.6. Ultraviolet spectra. DMSE prepared by the gas-phase 2+2 cycloreversion of DMSCB showed an absorption maximum at 244 nm in argon at 10 K [99].

The gas-phase UV spectroscopic observation of the intermediates of the thermal decomposition of DMSCB (~ 1% in argon) was obtained by millisecond technique of time-resolved measurements under pulse adiabatic compression conditions in a free-piston device [109]. It turned out that the light absorption by the intermediate ($\lambda_{max} = 244$ nm) appeared prior to the ethylene formation, i.e., at the temperature (~ 530 °C) at which 2+2 cycloreversion (reaction 1) does not still occur. The first-order kinetics of the equilibrium reaction between DMSCB and 244 nm intermediate was determined from the intensity of light absorption and is consistent with the chemical composition of the intermediate to be the same as for DMSCB. However, the determined reaction enthalpy (28.5 kcal mol^{-1}) was much lower than that of the ring opening to assign the intermediate to the diradical unless the latter is stabilized by 32.5 kcal mol^{-1}. The formation of ethylene starts at ~ 590 °C and is accompanied by the appearance of the three more light absorption bands at 280, 290 and 605 nm of which 280 nm is presumably due to DMSE.

2.1.5.7. NMR spectra. It is stated that the low-pressure pyrolysis experiments (1.5×10^{-9} mbar, 1000 °C) performed with DMSCB in a special pyrolysis apparatus with a liquid nitrogen trap resulted in a molten glasslike, highly viscous condensate that could be stored at liquid nitrogen temperatures for days without decomposition and then transferred into adjoining NMR tube [85]. Low-temperature NMR spectroscopy of the pyrolyzate after dimethyl ether-d_6 and dichlorodifluoromethane were condensed into the NMR tube showed that the solution of DMSE is stable up to −100 °C. Above this temperature a rapid polymerization occurs as it is indicated by the decreasing intensity of the ^{29}Si-NMR resonance at 16.8 ppm [85].

2.1.5.8. ESR spectra. Radical intermediates produced upon the pyrolysis of DMSCB were detected by a spin-trapping techique with phenyl *N-tert*-butyl nitrone or the frozen at 77 K VLPP products [38,56,101]. In the first case the observation of the ESR spectrum of the benzene solution of the niroxyl radical obtained by passing the gaseous pyrolysis products over the nitrone clearly indicated the presence of the radicals outside the pyrolysis zone. In the second case the ESR spectrum looked like a not completely resolved triplet, with the hyperfine splitting constant being 22.4 G and the singlet in the center. At first the radical quantity linearly grew with the pyrolysis time. Then the curve had become saturated indicating the equilibria between the production and the quenching of the radical. After the end of the pyrolysis the radical had slowly disappeared presumably transforming into 1,1,3,3-tetramethyl-1,3-disilacyclobutane and the polymer (see Section 2.1.4.3). At present we are inclined to assign the observed ESR spectrum to the $^{\cdot}SiCH_2SiCH_2^{\cdot}$ diradical known to be the precursor of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (see Section 2.2.1).

2.2. Silenes from other 1-silacyclobutanes

The other 1-silacyclobutanes also thermocyclorevert to produce silenes. However, when the appropriate substituents are attached to the doubly bonded atoms of silicon or carbon silenes may also react forming self-trapping rearrangement products. In some cases the latter reactions completely suppress silenes' cyclodimerization. In a few cases substituents facilitate side reactions of 1-silacyclobutanes' transformations. The pyrolysis of 1,1-disubstituted silacyclobutanes was examined as a method for the preparation of 1,1,3,3-tetrasubstituted 1,3-disilacyclobutanes [27,100].

2.2.1. Effect of substitution at silicon on 1-silacyclobutanes' strain energies, their ring opening and 2+2 cycloreversion enthalpies, and Si=C π-bond energy in silenes

The effect of geminal substitution at silicon on 1-silacyclobutanes strain energies and their 2+2 cycloreversion enthalpies, and the Si=C π-bond energy in silenes was evaluated by an ab initio MO study of silenes (**1**) and 1-silacyclobutanes (**2**). It was deduced from the structural data and reaction enthalpies (so-called thermochemical approach) obtained from computational experiments using the MP4/TZ(d)//MP2/6-31G(d) level of theory, where TZ is the 6-311G(d) basis for the elements of the second period and hydrogen, the McLean-Chandler (12s,9p)/[6s,5p](d) basis for the third period elements [39].

2.2.1.1. Strain energies, 2+2 cycloreversion, ring opening and 1,4-diradical decomposition enthalpies. There are two apparent diradical routes that may lead to 1-silacyclobutanes' 2+2 cycloreversion products, i.e. ethylene and silene: (i) a two-step process via a Si–C bond cleavage (reactions 2.1 and 2.2) and (ii) a two-step process via a C–C bond cleavage (reactions 2.3 and 2.4) (Eq. (21)).

In the series of R = H, CH_3, SiH_3, CH_3O, NH_2, Cl, F, the growth of the reaction enthalpies is proportional to the substituents electronegativity [39]. The endothermicity of the 2+2 cycloreversion increases by 22.6 kcal mol^{-1}, cf. 2+2 cycloreversion enthalpies, 41.4 kcal mol^{-1} ($R = SiH_3$) and 64 kcal mol^{-1} (R = F). On going from silyls to fluorines the strain energy rises by 4.0 kcal mol^{-1}, i.e. the replacement of hydrogen atoms in the parent 1-silacyclobutane ($E_s = 22.3$ kcal mol^{-1}) with fluorines slightly increases the strain energy, by 2.1 kcal mol^{-1}, whereas the same replacement by silyls slightly decreases the one by 1.9 kcal mol^{-1}.

The schematic energy level diagram for 1-silacyclobutanes 2+2 cycloreversion is shown in Fig. 3. The energy levels of the reactants, the intermediates and the products as well as the ones for the transition states (TS1**A** and TS1**B**) are drawn. The contributions of reactions 2.1 and 2.2 as well as 2.3 and 2.4 to the reaction 2 enthalpy are given in Fig. 4. Except 1,1-disilyl-1-silacyclobutane the energy gap between $\Delta H_{(2.1,-2.1)}$ and $\Delta H_{(2.3,-2.3)}$ expands as more electronegative substituents appear at silicon indicating the ring opening to be more preferable via C–C bond homolysis rather than via Si–C bond homolysis. The C–C bond initial cleavage is suggested to be the most likely route for the parent silacyclobutane [111]. At the same time the decompositions of both 1,4-diradicals, **A** (reaction 2.2) and **B** (reaction 2.4), are exothermic and the exothermicity is getting lesser as substituents' electronegativity rises. The effect is more pronounced for diradical **B** so that its difluoro derivative's decomposition becomes even endothermic by 5.5 kcal mol^{-1}.

2.2.1.2. Si=C π-bond energy in silenes. The parent silene and its Si-substituted derivatives are the 'classical' planar doubly bonded systems, boundary between olefins and heavier Group 14 analogs, in the sense of more electronegative substituents, which like in olefins, do not disturb a planar geometry, shorten the double bond and weaken the π-bond. This is not so in case of germene analogs where fluorine substitution distorts the planarity. C-fluoro substituted silenes and germenes are also *trans*-bent systems with elongated double bonds [108]. The weakening Si=C π-bond in silenes, e.g., 40.4 kcal mol^{-1} in $H_2Si{=}CH_2$, and 30.7 kcal mol^{-1} in $F_2Si{=}CH_2$, and the corresponding decrease of π-population are rationalized in terms of their more strained geometry resulting from the energetic cost for planarizing R_2SiC moiety [39].

Similar potential energy profiles as a function of internal rotation about the double bonds Si=C, C=C, Ge=C, P=C and their definitely high rotational barriers, 40.4, 64.2, 40.0, 46.1 kcal mol^{-1}, indicate a certain resemblance between silene, germene, and phosphene altogether being analogous or isoelectronic to ethylene [108]. In contrast to Si=C bond in silene, $P^+{-}C^-$ bond in phosphorane, $H_3P{=}CH_2$, have a drastically different periodicity and an exceptionally low-rotational barrier, 1.0 kcal mol^{-1} [108]. These observations are not in favor of the earlier (1980) Nefedov's suggestion 'to consider silaolefins as C-ylides of silicon' [97] (see Section 2.1.5.5).

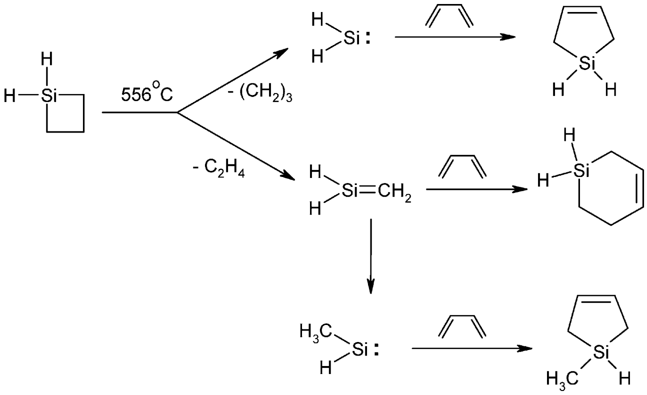
2.2.2. 1-Hydrido-1-silacyclobutanes

The study of silacyclobutane and 1-methyl-1-silacyclobutane's gas-phase pyrolysis has a long historical evolution started in 1975 [68,85,93,99,100,110–125]. The problem arose because unlike DMSCB 2+2 cycloreversion was not the only one channel of the gas-phase thermal decomposition of 1-hydrido-1-silacyclobutanes and unlike DMSE 2+2 cyclodimerization was not the only reaction of hydridosilenes.

2.2.2.1. 1-Silacyclobutane. Early attempt to obtain 1,3-disilacyclobutane via silene's cyclodimerization during the pyrolysis of silacyclobutane in a nitrogen-flow system failed. Only intractable polymer of an unidentified structure was obtained [68]. The pyrolysis in the presence of hexamethylcyclotrisiloxane as a trapping agent gave an eight-membered ring compound resulted from the insertion of silene into one of the Si–O bonds [68]. Trapping with benzophenone yielded diphenylmethane and 1,1-diphenylethylene [68] (Eq. (22)).

Silacyclobutane's pyrolysis study in a helium (nitrogen) flow systems with GC and GC/MS analysis of the injected sample at 507 °C revealed that ethylene was the main gaseous product. Besides, hydrogen and propylene were formed (20 and 18% relative to ethylene, respectively) [56]. No 1,3-disilacyclobutane was detected. Instead, 1,3-disilacyclohexane and 1-methyl-1,2-disilacyclopentane (both the products of formal insertion of silene and methylsilylene into silacyclobutane's Si–C bond, respectively) were identified as the major volatile silicon-containing products. The total quantity of the volatile products did not exceed 15% [56].

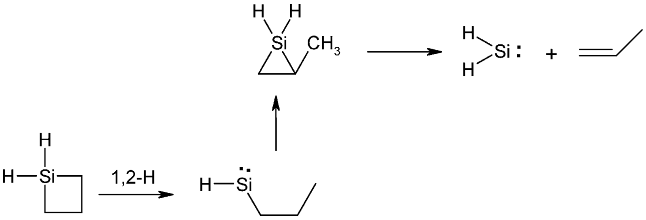
It is stated that the low-pressure silacyclobutane's gas-phase pyrolysis study [112] resulted in silene on a cold surface at the temperature of liquid nitrogen which can be stored for several months and can be transferred by trap-to-trap distillation in a vacuum system.[11] It is assumed that similar silacyclobutane's pyrolysis technique resulted in the obtaining of the silene–dimethyl ether-d_6 donor complex characterized by ^{29}Si-NMR resonance at −25.2 ppm [85]. According to matrix isolation IR [99] and PE [113] spectroscopic studies a very low-pressure pyrolysis of silacyclobutane is not a good way to prepare an unambiguously characterized silene samples due to many by-products. Other attempts in matrix isolation of the parent silene from the pyrolysis of silacyclobutane [93,99,100] failed. Silacyclobutane was also employed as a precursor of silene when studying pyrolysis by millimeter and submillimeter-wave spectroscopy, but it appeared to be a poorer source of silene rather than 5,6-bis(trifluoromethyl)-2-silabicyclo[2.2.2]octa-5,7-diene. Silene's spectrum was only half intense even employing a higher partial pressure and a temperature of the oven as high as 1000 °C [124–126].



(23)

The detailed study of the mechanism of silacyclobutane's low-pressure pyrolysis was undertaken [116,117,121]. Pyrolysis in a high vacuum flow system between 556 and 697 °C with a tenfold excess of 1,3-butadiene revealed the formation of silene, methylsilylene along with silylene and cyclo-propane via their adducts with butadiene, i.e., 1-silacyclopent-3-ene, 1-methyl-1-silacyclopent-3-ene and 1-silacyclohex-3-ene. The ratio of methylsilylene to silene products increased at higher temperatures due to more pronounced thermal isomerization of the silene, yielding methylsilylene [116] (Eq. (23)).[12]

A kinetic study of the thermal decomposition of silacyclobutane by a low-pressure pyrolysis and a stirred flow reactor technique led to the conclusion that methylsilylene and propene arise from an initial rearrangement to propylsilylene [117] rather than by a stepwise sequence of the Si–C bond homolysis [115] (Eq. (24)).



(24)

Further evidence for the latter mechanism was obtained from a detailed study of the pyrolysis of 1,1-dideuterio-1-silacyclobutane. The gaseous pyrolysis products consisted mainly of ethene (86%) and propene (14%). While ethylene was largely undeuteriated, 75% of propene contained at least one deuterium and deuterium was located on all of the carbons. These results are taken as a clear evidence that one path for silacyclobutane's thermal decomposition involves a 1,2-hydrogen shift from silicon to carbon to produce a propylsilylene which decomposes to products via a reversible formation of silacyclopropanes through β-CH insertion [121].

In the low-pressure CVD study ethylene was a primary decomposition product indicating that film growth proceeds by incorporation of silene. Among C_3H_6 production of cyclopropane is unambiguous at lower temperatures, suggesting silylene elimination by either a concerted or stepwise cleavage of two Si–C bonds. It is concluded that silacyclobutane provide the sources of the isomers $HSiCH_3$ and $H_2Si{=}CH_2$, which are considered to be SiC film forming precursors [123].

Recent ab initio study had suggested that the most likely route of silacyclobutane's 2+2 cycloreversion to ethylene and silene is the initial cleavage of a ring C–C bond to form a *trans* diradical, followed by the rupture of the central Si–C bond. Production of propylsilylene should be both thermodynamically and kinetically competitive with 2+2 cycloreversion [111]. When theoretically studying the interaction between ethylene and silene, *trans* and *gauche* forms of the diradical $H_2C{-}H_2Si{-}CH_2{-}CH_2$ were proven to exist, with the *trans*

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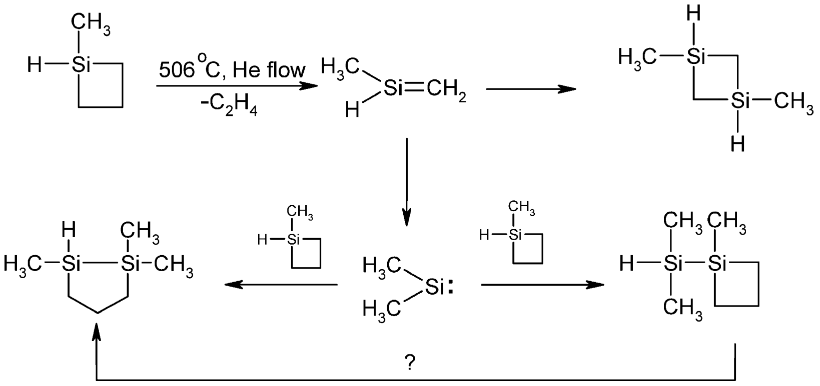
[11] These results contradict with the data [99,100,334] indicating that silene obtained by vacuum flash pyrolysis 5,6-bis(trifluoromethyl)-2-silabicyclo[2.2.2]octa-5,7-diene demonstrated a much higher reactivity upon thawing of the matrices.

[12] This conclusion was doubted later by the observation that above 600 °C hydridosilacyclohexene begins to isomerize to silacyclopentene [117,119].



(25)

form having the energy by 0.9 kcal mol^{-1} lower than that the *gauche* [127]. Fragmentation of the *trans* diradical to ethylene and silene has a very low-energy barrier (0.6 kcal mol^{-1}). The barrier to an interconversion of the *trans* to the *gauche* diradical is estimated to be 2.6 kcal mol^{-1}.

2.2.2.2. 1-Methyl-1-silacyclobutane. A pulse pyrolysis study with GC or and GC/MS analysis of the products revealed that at 506 °C ethylene was the main gaseous product. Besides, hydrogen and propylene were formed (20 and 7% relative to ethylene, respectively) [56]. The main volatile reaction products were 1-methyl-1-dimethylsilyl-1-silacyclobutane and 1,1,2-trimethyl-1,2-disilasycyclopentane, both may be considered as the products of dimethylsilylene insertion into Si–H and Si–C bonds of the starting compound.[13] 1,3-Dimethyl-1,3-disilacyclobutane, a product of methylsilene's cyclodimerization, was observed only in a very small quantity being by the order of magnitude less than the sum of two insertion products [56]. Scheme 25 was suggested for the formation of these pyrolysis products.

At low conversions the selectivity of ethylene's formation was equal to 50 M/100 M.[14] At a higher conversion it grew due to 2+2 cycloreversion of 1-methyl-1-dimethylsilyl-1-silacyclobutane [56].

A radical intermediate produced upon the pyrolysis of 1-methyl-1-silacyclobutane was detected in the frozen VLPP products at 77 K [56]. The ESR spectrum was a quartet, the hyperfine splitting constant was equal to 20.2 G, with the intensity ratio 1:3:3:1 (see Section 2.2.2.1).

A low-pressure pyrolysis of 1-methyl-1-silacyclobutane was used to generate 1-methylsilene for its spectroscopic observation [31,93,100,112]. The infrared absorptions of 1-methylsilene were detected in the pyrolyzate of 1-methyl-1-silacyclobutane isolated in the argon matrix at 10 K [31].[15]

By condensing the pyrolysis products in the cooling trap at −196 °C a molten glasslike, highly viscous condensate was obtained and transferred into an adjoining NMP tube. The methylsilene dimethyl ether-d_6 donor complex ^{29}Si-NMR resonance was measured at −1.8 ppm [85].

The Arrhenius parameters of 1-methyl-1-silacyclobutane total decomposition ($\log A = 13.2$ s^{-1}, $E = 52.4$ kcal mol^{-1}) in the pulse pyrolysis system [31] were close to those ($\log A = 14.0$ s^{-1}, $E = 52.6$ kcal mol^{-1}) obtained in the stirred flow system [117]. In the presence of a tenfold excess 1,3-butadiene the Arrhenius parameters became closer to those expected for 2+2 thermocycloreversion ($\log A = 15.3$ s^{-1}, $E = 60.4$ kcal mol^{-1})[16] and for the formation of ethylene were $\log A = 16.0$ s^{-1}, $E = 63.5$ kcal mol^{-1} [31].[17] The activation energy of the propylene formation reaction was found to be by 15 kcal mol^{-1} higher than that of ethylene [31]. This contradicts the Arrhenius parameters for the propylene formation ($\log A = 14.4$ s^{-1}, $E = 57.8$ kcal mol^{-1}) estimated in the stirred flow system [117].

1-Methylsilene and dimethylsilylene were trapped effectively by 1,3-butadiene resulting in the expected adducts [120] (Eq. (26)).

At higher pyrolysis temperatures 1-methyl-1-silacyclohex-3-ene was not found among the reaction products [114] because of its isomerization into 1,1-dimethyl-1-silacyclopent-3-ene [117,119].

The question of how dimethylsilylene is produced upon 1-methyl-1-silacyclobutane's pyrolysis, by isomerization of 1-methylsilene [114,119,120], or by a multistep

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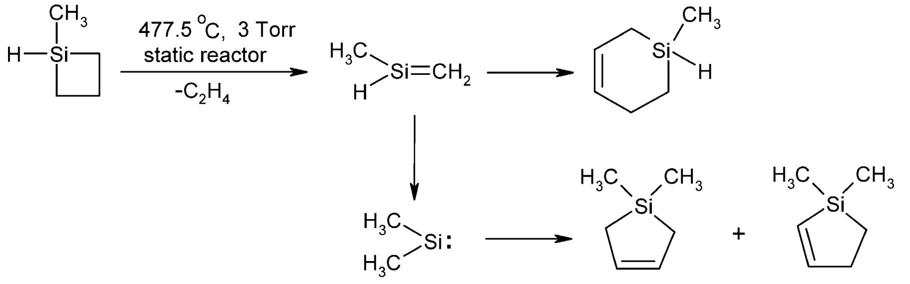
[13] The latter may be also considered as rearrangement product of the former.

[14] Yield in moles per 100 moles of the converted starting compound.

[15] Previous attempts to detect methylsilene in the pyrolyzate of 1-methyl-1-silacyclobutanes by low-temperature matrix IR spectroscopy failed [93,100].

[16] Cf. with $\log A = 14.9$ s^{-1}, $E = 59.1$ kcal mol^{-1} for the gas phase pyrolysis of 1-methyl-1-silacyclobutane (3 Torr) and a fivefold excess of butadiene in a static system [335].

[17] Cf. with $\log A = 16.4^{-1}$, $E = 63.1$ kcal mol^{-1} for the gas phase pyrolysis of 1-methyl-1-silacyclobutane in the stirred flow system [117].



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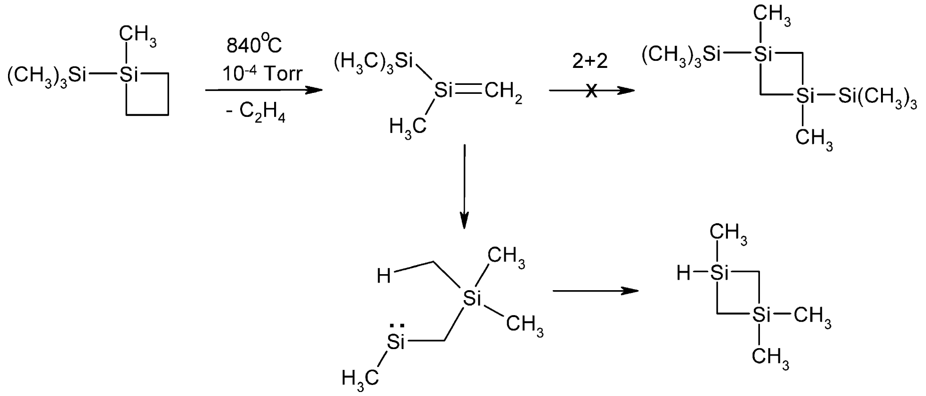

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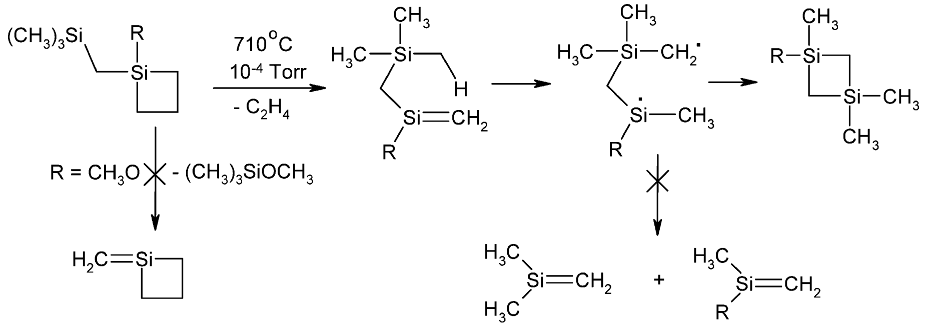

(28)

diradical mechanism [115,117,128], was under discussion but it is beyond the scope of present review.[18] The only thing to point out is that the difference between the heats of formation of 1-methylsilene and dimethylsilylene (28 kcal mol^{-1}) contradicts some experimental and theoretical findings on their nearly equal stability [129].[19]

2.2.3. *1-Methyl-1-(trimethylsilyl)-1-silacyclobutane*

Although 1-methyl-1-(trimethylsilyl)-1-silacyclobutane undergoes the normal gas-phase 2+2 cycloreversion which is indicated by the elimination of ethylene the final product is not the silene's dimer, 1,1,3-trimethyl-1,3-disilacyclobutane was obtained instead [115]. The proposed mechanism consisted of three steps: (i) 2+2 cycloreversion to form methyltrimethylsilene; (ii) rearrangement of the latter, via 1,2-migration of $(CH_3)_3Si$ to β-silylsilylene; and (iii) γ-CH insertion by β-silylsilylene to form 1,1,3-trimethyl-1,3-disilacyclobutane (Eq. (27)).

2.2.4. *1-Methoxy-1-[(trimethylsilyl)methyl]-1-silacyclobutane and 1-methyl-1-[(trimethylsilyl)methyl]-1-silacyclobutane*

The pyrolysis of l-methoxy-l-(trimethylsilyl)silacyclobutane and l-methyl-l-(trimethylsilyl)methylsilacyclobutane [130] occurs not as a β-elimination but as a 2+2 cycloreversion leading to ethylene and the expected silenes' rearrangement product. The rearrangement involves 1,5-H migration to form 1,4-diradical similar to that produced by the ring opening of 1,3-disilacyclobutanes. The latter is reluctant to decompose due to its high endothermicity (see Section 2.4.1) and obviously prefers ring closure rather than decomposition to two silenes (Eq. (28)).

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[18] See also [118,201].

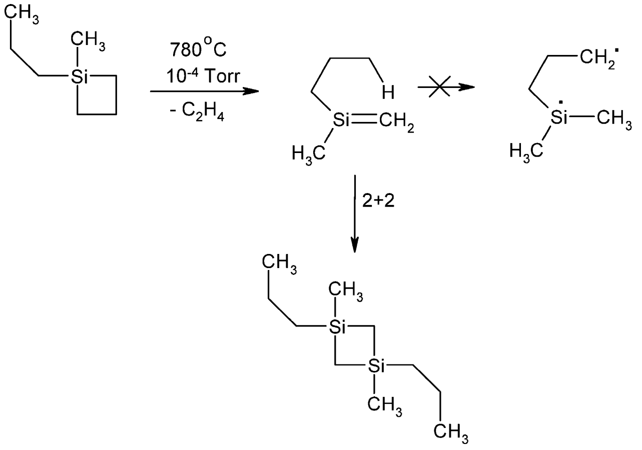
[19] Thermal isomerization of dimethylsilylene into 1-methyl-1-silene but not the reverse reaction was spectroscopically detected [336].

2.2.5. 1-Methyl-1-ethyl-1-silacyclobutane

At 650 °C in a helium-flow 1-methyl-1-ethyl-1-silacyclobutane resulted in a 53% yield of 1,3-dimethyl-1,3-diethyl-1,3-disilacyclobutane, a product of 2+2 cycloreversion-transient 1-methyl-1-ethylsilene's 2+2 cycloaddition sequence [57].

2.2.6. 1-Methyl-1-n-propyl-1-silacyclobutane

The rearrangement similar to that described in Section 2.2.3 does not occur in case of 1-methyl-1-propylsilene obtained by a 2+2 cycloreversion of 1-methyl-1-propyl-1-silacyclobutane [130]. Instead, the expected cyclodimer, the normal product of head-to-tail dimerization, was formed (Eq. (29)).



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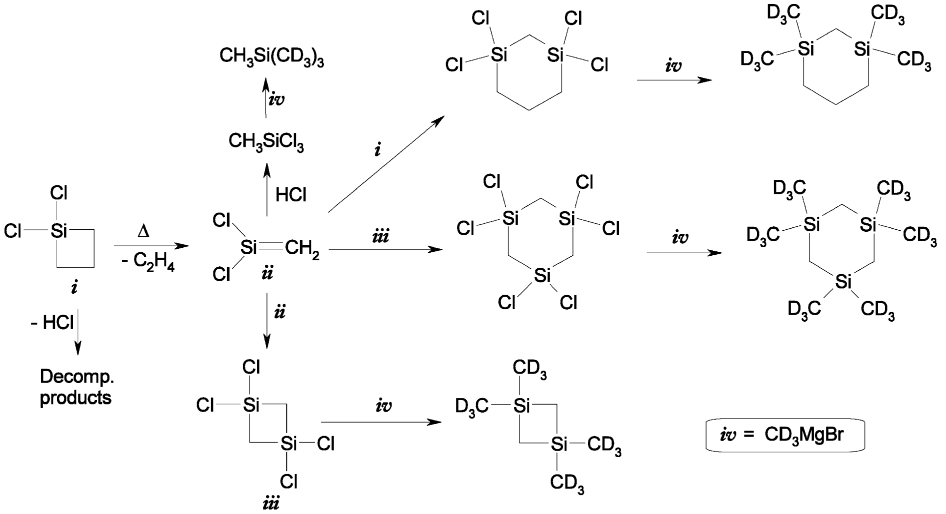
2.2.7. 1,1-Di-tert-butyl-1-silacyclobutane

The gas-phase pyrolysis of 1,1-di-*tert*-butyl-1-silacyclobutane in the temperature range 600–700 °C and the pressure range 10–0.01 mbar results in a very small amount of ethylene and the traces of propane. No silicon-containing volatile product with the exception of the starting compound could be trapped [131]. No cyclodimerization products of 1,1-di-*tert*-butylsilene were detected in the another study of 1,1-di-*tert*-butyl-1-silacyclobutane in a nitrogen-flow reactor [132].

2.2.8. 1-Halo- and 1-amino substituted 1-silacyclobutanes

2.2.8.1. 1,1-Dichloro-1-silacyclobutane. 1,1-Dichloro-1-silacyclobutane's gas-phase thermal decomposition was studied under different reaction conditions (i) in a packed or hollow quartz tube in vacuum [27,57,93,133–135] or in an inert gas flow [132,136], (ii) in a pulse pyrolysis–GC/MS system [136]. The higher thermal stability of 1,1-dichloro-1-silacyclobutane requires more severe conditions for the pyrolysis. The most interesting and under proper conditions the main reaction product was 1,1,3,3-tetrachloro-1,3-disilacyclobutane. In fact the first pure sample of 1,1,3,3-tetrachloro-1,3-disilacyclobutane was obtained and characterized from the pyrolysis of 1,1-dichloro-1-silacyclobutane [27,57]. This synthetic procedure was used later for preparing 1,1,3,3-tetrachloro-1,3-disilacyclobutane aimed at either its reduction to the parent 1,3-disilacyclobutane [133,137] or at CVD study [138]. However, the whole reaction was not as clean as DMSCB pyrolysis (Section 2.1). 2+2 Cycloreversion was accompanied by dehydrochlorination and, therefore, a head-to-tail cyclodimerization of dichlorosilene competed by a hydrogen chloride addition yielding methyltrichlorosilane [110,132,136,139].

Matrix isolation infrared spectroscopy studies of 1,1-dichloro-1-silacyclobutane pyrolysis gave radically con-



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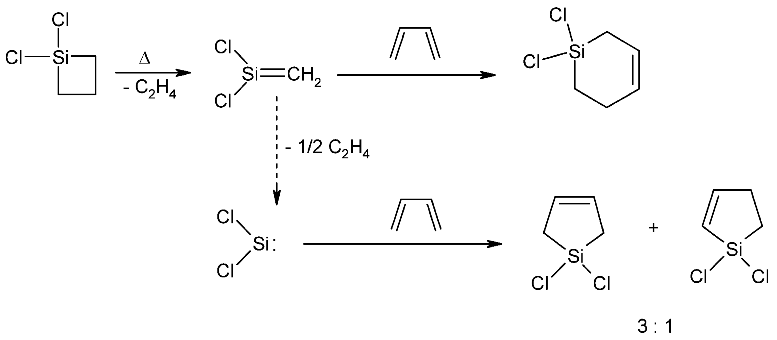


(31)

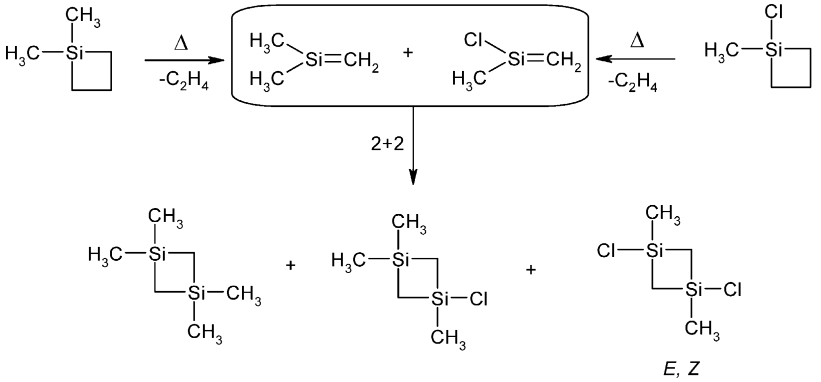
troversial results [3,93,135]. One of them revealed dichlorosilene [135] whereas the other contradicted its involvement in the decomposition suggesting that 1,1,3,3-tetrachloro-1,3-disilacyclobutane's formation is a bimolecular process involving no dichlorosilene [93]. Dichlorosilylene was detected instead [93]. The band at 732 cm^{-1} in the matrix IR spectrum of 1,1-dichloro-1-silacyclobutane's vacuum flash pyrolysis was assigned to dichlorosilene in the third study [100].

To make clear the reaction pathways the reaction was studied in a pulse pyrolysis—GC/MS system [136] in the presence of 1,3-butadiene, an effective trap for both silenes and silylenes. Also the pyrolyzate obtained by conventional pyrolysis in helium-flow system was subjected itself and after the treatment with $(CD_3)_3MgBr$ to GC/MS analysis [136]. It is seen in Scheme 30 that besides cyclodimer's formation and HCl addition, the insertion of dichlorosilene into the Si–C bonds of the starting compound as well as 1,1,3,3-tetrachloro-1,3-disilacyclobutane may be deduced.

In the absence of traps dichlorosilylene appeared itself yielding 1,1,2,2,4,4-hexachloro-1,2,4-trisilacyclopentane, the insertion product into the Si–C bond of the 1,1,3,3-tetrachloro-1,3-disilacyclobutane. In the presence of 1,3-butadiene both the 2+4 adduct with dichlorosilene and 1+4 adduct with dichlorosilylene, 1,1-dichloro-1-silacyclohex-3-ene and isomeric 1,1-dichloro-1-silacyclopentenes, were isolated in the 2.3:1 ratio. The origin of dichlorosilylene is a problem to be solved. However, it is clear that it is not formed in the direct process since only ethylene, no propene, was detected among the gaseous products [136]. Presumably the formation of dichlorosilylene is related to the decomposition of either dichlorosilene or the intermediate diradical which ring closure results in 1,1,3,3-tetrachloro-1,3-disilacyclobutane (Eq. (31)).

2.2.8.2. *1-Methyl-1-chloro-1-silacyclobutane.*

Low-pressure pyrolysis of 1-methyl-1-chloro-1-silacyclobutane at 700 °C in a packed flow reactor yielded ethylene and 31.7% of *E* and *Z* isomers of 1,3-dimethyl-1,3-dichloro-1,3-disilacyclobutane [27,57]. Later, 63% yield of 1,3-dimethyl-1,3-dichloro-1,3-disilacyclobutane was reported [110,139]. In a nitrogen-flow system at 720–750 °C ethylene and 29% 1,3-dimethyl-1,3-dichloro-1,3-disilacyclobutane were formed. Whatever the case, 2+2 cycloreversion competed with HCl elimination just like in the case of 1,1-dichloro-1-silacyclobutane's pyrolysis



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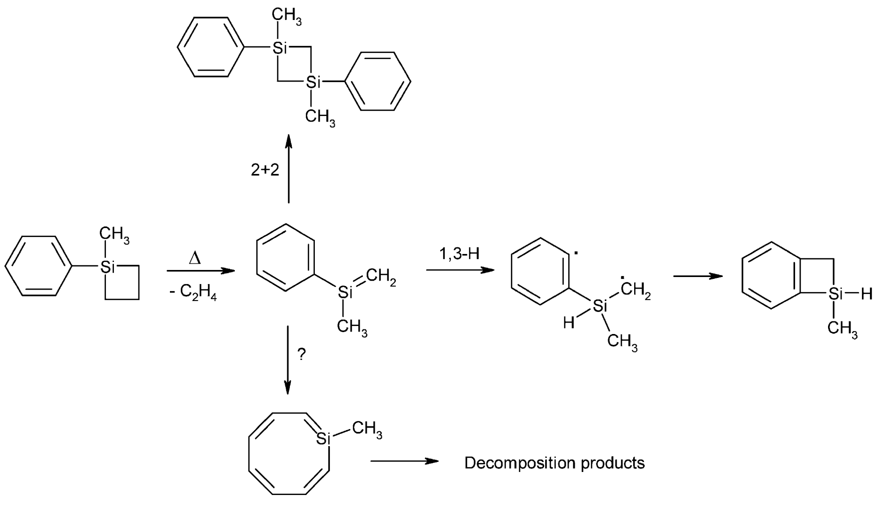


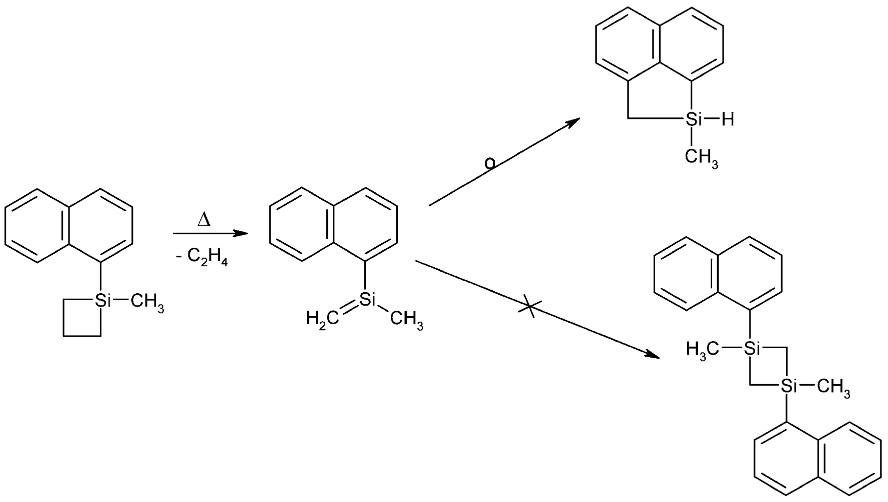
(33)

[132,139]. The expected head-to-tail dimers and the main product of cross-cyclodimerization of methylchlorosilene and DMSE were obtained upon the copyrolysis of 1-methyl-1-chloro-1-silacyclobutane and DMSCB in a helium-flow reactor at 750 °C [57] (Eq. (32)).

2.2.8.3. *1-tert-Butyl-1-chloro-1-silacyclobutane.* Pyrolysis of 1-*tert*-butyl-1-chloro-1-silacyclobutane in a nitrogen-flow reactor at 720 °C yields a very small amount (14%) of *E* and *Z* isomers of 1,3-di-*tert*-butyl-1,3-dichloro-1,3-disilacyclobutane, a dimer of 1-*tert*-butyl-1-chlorosilene [132].

2.2.8.4. *1,1-Difluoro-1-silacyclobutane and 1-methyl-1-fluoro-1-silacyclobutane.* Low-pressure pyrolysis of 1,1-difluoro-1-silacyclobutane in a flow reactor at 850 °C yields 90% ethylene and 63% 1,1,3,3-tetrafluoro-1,3-disilacyclobutane along with the trapping products of difluorosilene with HF, the latter presumably resulted from dehydrohalogenation of the starting compound [139,140]. Similarly, the pyrolysis of 1-methyl-1-fluoro-1-silacyclobutane at 780 °C quantitatively yields ethylene and 75% *E* and *Z* isomers of 1,3-dimethyl-1,3-difluoro-1,3-disilacyclobutane and methylpropyldifluorosilane, the adduct of HF and the starting 1-silacyclobutane. Also 1-methyl-l,3,3-trifluoro-l,3-disilacyclobutane was isolated [139,140].

2.2.8.5. *1-Methyl-1-dimethylamino- and 1,1-bis(dimethylamino)-1-silacyclobutane.* Low-pressure



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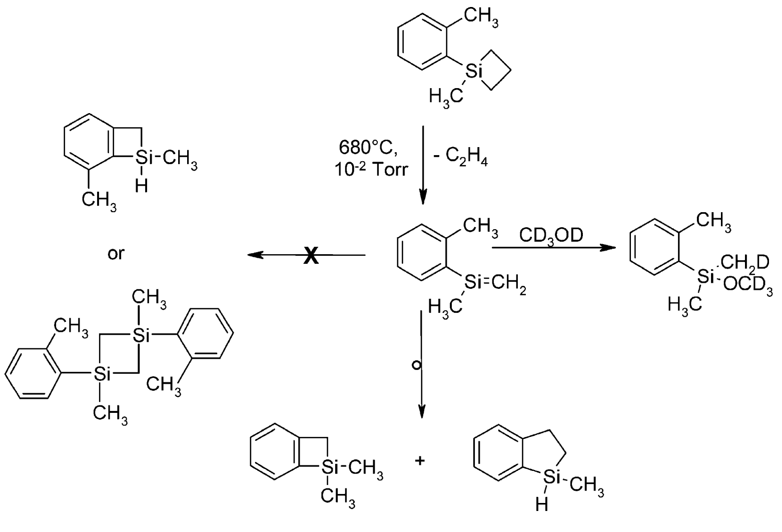

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pyrolysis of the title compounds in a flow reactor at 625 °C yields 83–86% of ethylene and 70–72% of the corresponding 1,3-disilacyclobutanes, the dimers of the transient silenes [110].

2.2.9. 1-Aryl- and 1-benzyl-1-silacyclobutanes cycloreversions and intramolecular rearrangements of silenes

1-Aryl-substituted 1-silacyclobutanes were studied as the sources for a thermal generation of silenes containing a conjugating aryl group attached to the silicon atom. Particularly, of interest were intramolecular rearrangements involving 1,*n*-migration of hydrogen from the aryl and benzyl groups to the silicon–carbon double bond.

2.2.9.1. 1-Methyl-1-phenyl-1-silacyclobutane. Low-pressure pyrolysis of 1-methyl-1-phenyl-1-silacyclobutane (625 °C, 10^{-2} mbar) was studied with the trapping products in the liquid nitrogen trap. The pyrolyzate was fractionated by trap-to-trap distillation and then the fractions were analyzed by NMR and MS. Ninety percent yield of ethylene and 35% yield of the corresponding 1,3-disilacyclobutane indicated a fairly clean 2+2 cycloreversion and a prominent contribution of the reaction which accompanies the head-to-tail cyclodimerization of 1-methyl-1-phenylsilene. Hypothetically the authors suggested that the isomerization of 1-methyl-1-phenylsilene into 1-methyl-1-silacyclooctatetraene followed by its decomposition [141]. Another low-pressure pyrolysis study of 1-methyl-1-phenyl-1-silacyclobutane in a flow system resulted in a fairly clean 2+2 cycloreversion process giving the transient 1-methyl-1-phenylsilene which rearranged into 3,4-benzo-1-methyl-1-sila-3-cyclobutene and dimerized yielding *E* and *Z* isomers of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane. The ratio of the silene's rearrangement to dimerization products depended on the pressure: the lower the pressure, the higher the ratio. The rearrangement was mechanistically explained by 1,3-hydrogen atom migration from an aromatic group to the silicon atom of the silicon–carbon double bond followed by the ring closure of the resulting diradical to form the benzoannelated silacyclobutene [142] (Eq. (33)).

2.2.9.2. 1,1-Diphenyl-1-silacyclobutane. In a nitrogen-flow system at 720 °C 1,1-diphenyl-1-silacyclobutane yields 61% of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane, a cyclic dimer of diphenylsilene [132].

Low-pressure pyrolysis of 1,1-diphenyl-1-silacyclobutane (625 and 700 °C, 10^{-2} mbar) with trapping products in the liquid nitrogen trap yielded 58% of ethylene and 20% of the corresponding 1,3-disilacyclobutane resulted from the 2+2 cycloreversion [110]. The authors explain the prominent amount of benzene by a decomposition of hypothetical 1-phenyl-1-silacyclooctatetraene formed by an isomerization of diphenylsilene (for similar isomerization of 1-methyl-1-phenylsilene into 1-methyl-1-silacyclooctatetraene, see Section 2.2.9.1) [141].

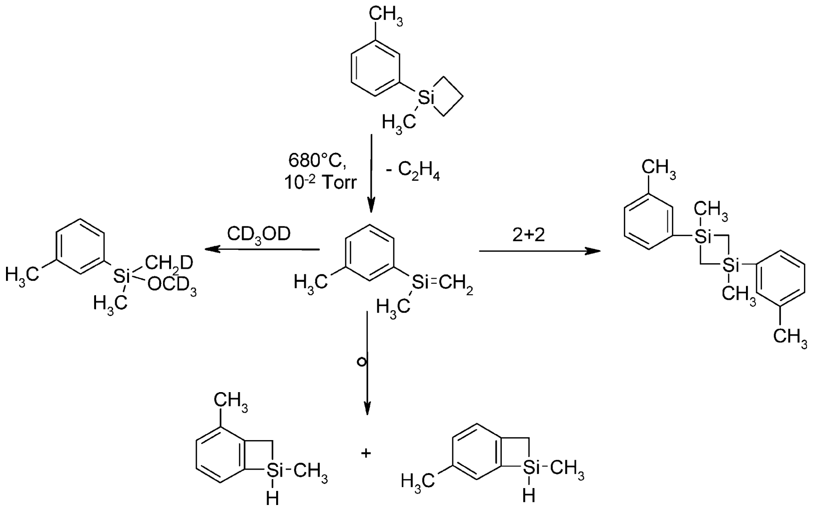
2.2.9.3. 1-tert-Butyl-1-mesityl- and 1,1-dimesityl-1-silacyclobutane. Likewise 1,1-di-*tert*-butyl-1-silacyclobutane, the pyrolyses of 1-*tert*-butyl-1-mesityl- and 1,1-dimesityl-1-silacyclobutane resulted in no cyclodimerization products of the corresponding silenes. Only polymeric products were observed [132].

2.2.9.4. 1-Methyl-1-naphthlyl-1-silacyclobutane. In the temperature range 720–760 °C and the pressure 3 ×

10^{-3} Torr in a flow reactor pyrolysis of 1-methyl-1-naphthyl-1-silacyclobutane a clean 2+2 cycloreversion occurs resulting in ethylene and transient 1-methyl-1-naphthylsilene which does not dimerize but rearranges into 1-methyl-1-silacenaphthene. The rearrangement involves 1,4-H shift from the *peri*-carbon atom of a naphthalene nucleus to a sp^2 silicon of the silicon–carbon double bond [143] (Eq. (34)).

2.2.9.5. 1-Methyl-1-o-tolyl-1-silacyclobutane. The low-pressure pyrolysis of 1-methyl-1-*o*-tolyl-1-silacyclobutane in a flow system occurs as a 2+2 cycloreversion yielding ethylene and transient 1-methyl-1-*o*-tolylsilene, which rearranges into 3,4-benzo-1,1-dimethyl-1-sila-3-cyclobutene. Trapping with methanol-d_4 had proved the intermediacy of the silene. The rearrangement is rationalized as involving 1,5-H atom migration from the sp^3 C (*ortho* methyl attached to an aromatic nucleus) to the carbon atom of the Si=C double bond following by the ring closure. Neither cyclodimerization products, i.e., *E* and *Z* isomers of 1,3-dimethyl-1,3-di-*o*-tolyl-1,3-disilacyclobutane, nor the rearrangement product resulted from 1,3-H migration from the benzene ring to the silicon atom of the Si=C bond were detected. A minor formation of isomeric silaindanes was also observed [144,145] (Eq. (35)).

2.2.9.6. 1-Methyl-1-m-tolyl-1-silacyclobutane. Like in case of 1-methyl-1-*o*-tolyl-1-silacyclobutane the low-pressure pyrolysis of 1-methyl-1-*m*-tolyl-1-silacyclobutane in a flow system occurs as a 2+2 cycloreversion yielding ethylene and a transient 1-methyl-1-*m*-tolylsilene, which, however, further reacts by two ways: (i) cyclodimerization resulting in *E* and *Z* isomers of 1,3-dimethyl-1,3-di-*m*-tolyl-1,3-disilacyclobutane and (ii) rearrangements yielding two isomeric 3,4-benzo-1-methyl-1-sila-3-cyclobutene derivatives distinguished by the position of the methyl group attached to an aromatic nucleus. Trapping with methanol-d_4 proved the intermediacy of the silene. The rearrangements may be



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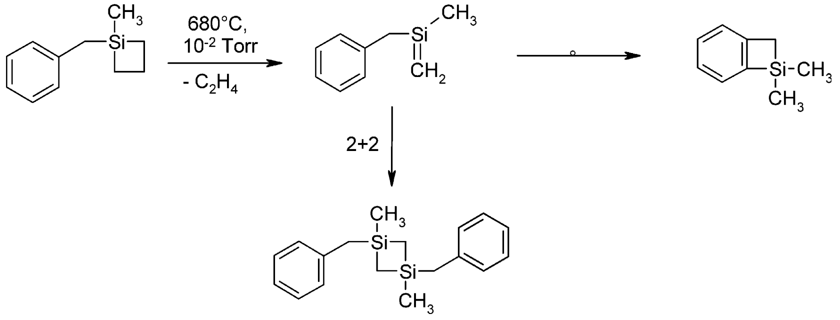

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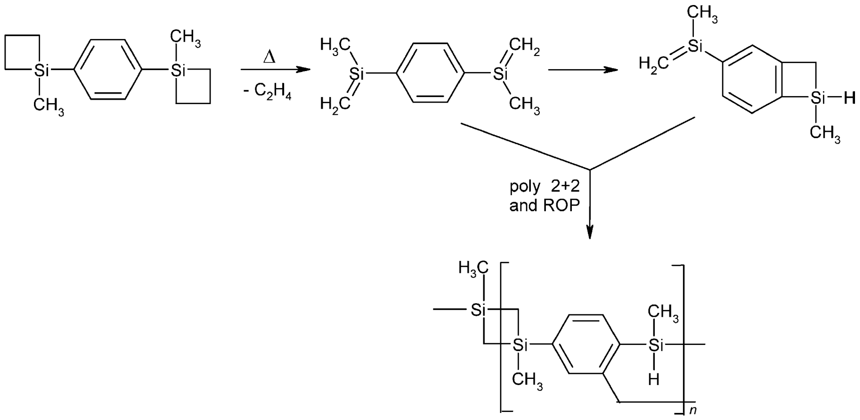

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rationalized as involving 1,3-H atom migration from the *ortho* of the aromatic nucleus to the silicon atom of the Si=C double bond following by the ring closure [145] (Eq. (36)).

2.2.9.7. *1-Methyl-1-benzyl-1-silacyclobutane.* Low-pressure pyrolysis of 1-methyl-1-benzyl-1-silacyclobutane occurs as 2+2 cycloreversion-transient silene 2+2 cyclodimerization sequence. Along with the dimer of 1-methyl-1-benzylsilene, *E* and *Z* isomers of 1,3-dimethyl-1,3-dibenzyl-1,3-disilacyclobutane, the product of intramolecular rearrangement of the silene, 3,4-benzo-1,1-dimethyl-1-sila-3-cyclobutene, was also observed. The rearrangement involves 1,5-H migration from the *ortho* carbon of the aromatic nucleus to the carbon atom of the silicon–carbon double bond. Minor isomeric silaindanes were also formed [144,146] (Eq. (37)).

2.2.9.8. *1,4-Bis(1-methyl-1-silacyclobut-1-yl)benzene.* A pyrolysis of the 1,4-bis(1-methyl-1-silacyclobut-1-yl)benzene under CVD conditions yielded ethylene and an insoluble polymer deposit formed by two processes of the intermediate silenes. These are poly[2+2]cycloaddition and ring opening polymerization (ROP) of the benzosilacyclobutene moiety produced in turn by the rearrangement of the silene moiety involving 1,3-H shift from an aryl carbon to the sp^2 silene silicon atom [142] (Eq. (38)).

MNDO-PM3 study of 1,4-bis(1-methyl-1-silacyclobut-1-yl)benzene as well as its *meta*- and *ortho*-isomers showed that their two FMO pairs mainly belong to the π-electrons of Si=C bonds, while the lower occupied π-MO is responsible for the delocalization of the π-electron system [147]. High polarity and a low-HOMO–LUMO transition energetic gap allow 2+2 cycloaddition, whereas the weakened *ortho*-C–H bonds of the aromatic nucleus may facilitate H-migration to the Si=C bond followed by the formation of the benzosilacyclobutene moiety.

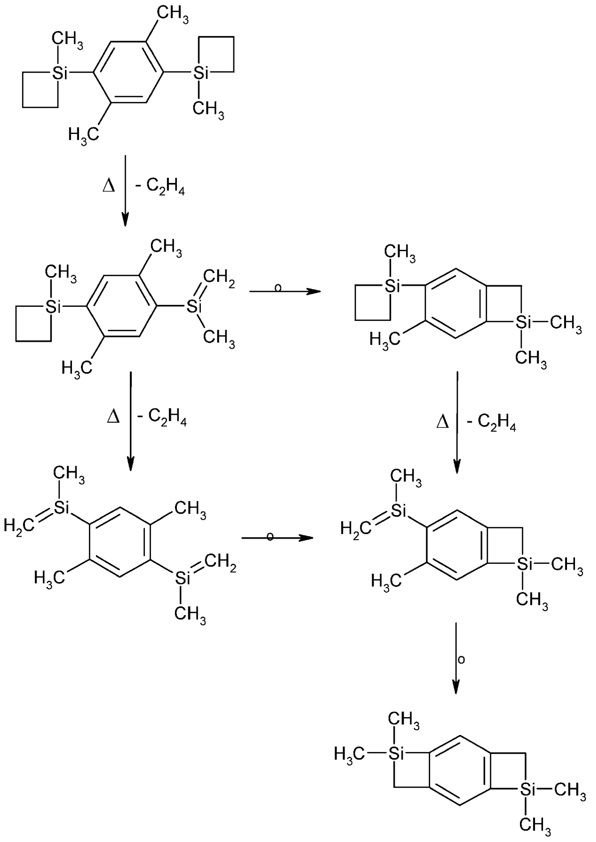
2.2.9.9. *2,5-Bis(1-methyl-1-silacyclobut-1-yl)-p-xylene.* Low-pressure pyrolysis of 2,5-bis(1,1-dimethyl-1-silacyclobut-1-yl)-*p*-xylene occurs as a 2+2 cycloreversion and results in the formation of ethylene and the rearrangement products of the transient silenes, 1,2,4,5-tetrahydro-1,1,4,4-tetramethyl-1,4-disiladicyclobuta-[*a*,*d*]benzene. The rearrangement involves 1,5-H atom migration from the sp^3 C (*ortho* methyl attached to the aromatic nucleus) to the carbon atom of the Si=C double bond [148] (Eq. (39)).

1,2,4,5-Tetrahydro-1,1,4,4-tetramethyl-1,4-disiladicyclobuta-[*a*,*d*]benzene is itself of particular interest as representing the first silacyclobutene diannelated [*a*,*d*]benzene. It was isolated and characterized by NMR, IR and MS methods and its structure was determined by single crystal X-ray diffraction analysis.

2.2.10. *1-Vinyl-1-silacyclobutanes*

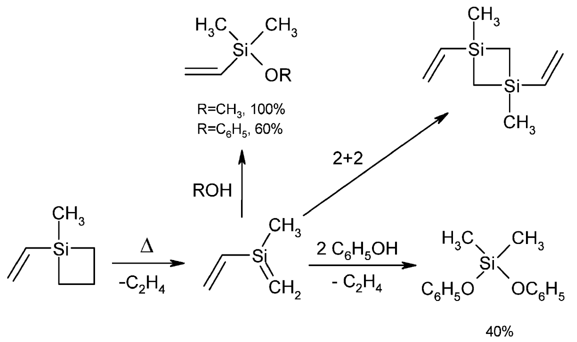
1-Vinylsubstituted 1-silacyclobutanes were studied as the sources for thermal generation of silenes containing a conjugating vinyl group attached to the silicon atom. Particularly, the effect of vinyl groups on the rate of silacyclobutanes' 2+2 cycloreversion and the reactivity of silenes was of interest.

2.2.10.1. *1-Methyl-1-vinyl-1-silacyclobutane.* Pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane in a pulse pyrolysis–gas chromatography system at 575 °C resulted in two products to be due to 2+2 cycloreversion, ethylene and head-to-tail dimer of 2-silaisoprene, i.e., 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane. The latter compound was also isolated from the reaction mixture obtained from the conventional pyrolysis in a helium-flow system [149]. A pyrolysis in the presence of methanol resulted in a complete suppression of the



(39)

silene's dimerization yielding only the adduct, dimethylvinylmethoxysilane, whereas in the presence of phenol the adduct, dimethylvinylmethoxysilane, and the dimethyldiphenoxysilane were formed [150] (Eq. (40)).



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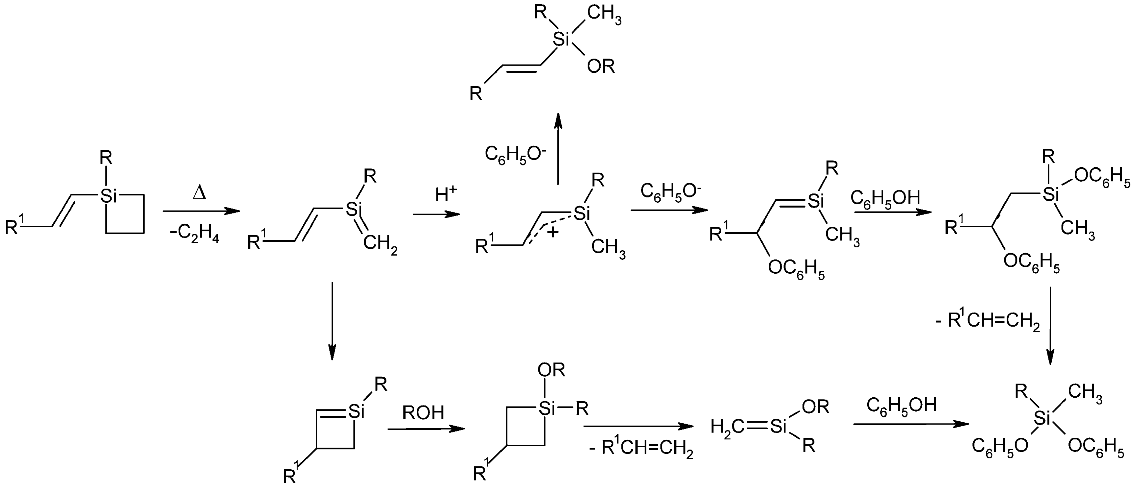
Two mechanisms were suggested to explain the nature of the products obtained with phenol, one involving 1-silacyclobut-1-ene intermediate and the other involving an allylic silicenium cation. In both hypothetical mechanisms, the 2-silaisoprene (scheme 41, $R^1 = H$) behaves as a conjugated system since it leads either to 2+2 cycloaddition or to (1,2)- and (1,4)-electrophilic addition [150,151]:

In the absence of traps the electrocyclic ring closure to give silacyclobutenes should be a reversible non-productive pathway of 2-silabutadienes.

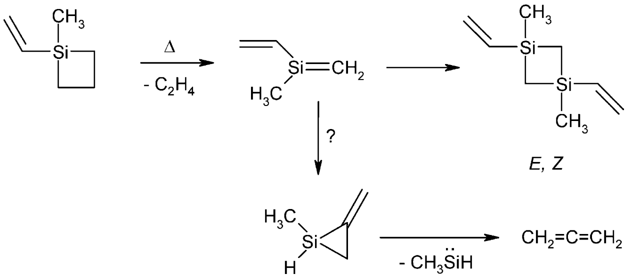
A kinetic study in the special pulse pyrolysis–gas chromatography device gave the Arrhenius parameters ($\log A = 15.3\ s^{-1}$, $E = 61.4$ kcal mol^{-1}) [31]. They were similar to those obtained earlier ($\log A = 15.64\ s^{-1}$, $E = 62.5$ kcal mol^{-1}) when studying the low-pressure copyrolysis of 1-methyl-l-vinyl-1-silacyclobutane and DMSCB [152]. These results were in a striking contrast to the decomposition of cyclobutanes for which vinyl substitution significantly decrease the activation energy. Therefore, unlike vinylcyclobutane the 'allyl' stabilization of the radical formed by the initial cleavage of the Si–C bond is small to influence the activation energy of



(41)

1-methyl-l-vinyl-1-silacyclobutane's 2+2 cycloreversion.

Low-pressure pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane (625–700 °C, 10^{-2} mbar) with the trapping products in the liquid nitrogen trap resulted in the pyrolyzate which was fractionated by trap-to-trap distillation and then fractions were analyzed by IR, NMR and MS. The quantitative yield of ethylene and 75% yield of the corresponding 1,3-disilacyclobutane indicated a clean 2+2 cycloreversion and a main reaction of head-to-tail cyclodimerization of 2-silaisoprene. Absorption at 2120 cm^{-1} (ν Si–H) in the low-temperature infrared spectrum and the peak m/z 84 in the mass spectrum of the condensate were observed. Therefore, it was suggested that 2-silaisoprene can also isomerize into 1-methyl-2-methylene-1-silacyclopropane which further decomposes producing allene [134] (Eq. (42)).



(42)

However, isomerization seems to be a relatively minor reaction judging from the small yields of the C_3H_4 products relative to ethylene [152].

2.2.10.2. 1-n-Butyl-1-vinyl-1-silacyclobutane. Low-pressure pyrolysis of the title compounds in a flow reactor at 625 °C resulted in no products clearly indicating the occurrence of 2+2 cycloreversion. A complex reaction mixture containing mainly butane, ethylene, allene and lesser amount of 1,3-butadiene and propylene were obtained. It seems that the 2+2 cycloreversion hardly competes with other decomposition pathways when the larger substituent are attached to the silicon atom of 1-silacyclobutanes [134].

2.2.10.3. 1,1-Divinyl-1-silacyclobutane. Low-pressure pyrolysis of 1,1-divinyl-1-silacyclobutane in a flow reactor at 625 °C yields ethylene in about 90 and 40% 1,1,3,3-tetravinyl-1,3-disilacyclobutane along with benzene (20%), propene (10%) and 1,3-butadiene (10%). After trap-to-trap distillation of the pyrolyzate absorption at 2124 cm^{-1} (ν Si–H) in the low-temperature infrared spectrum and the peak m/z 96 in the mass spectrum were observed. These spectroscopic manifestations were hypothetically assigned to the isomer of divinylsilene, namely, either 1-vinyl-2-methylene-1-silacyclopropane or 1-vinyl-1-silacyclobut-2-ene [134].

2.2.10.4. 1-Phenyl-1-vinyl-1-silacyclobutane. Low-pressure pyrolysis of 1-phenyl-1-vinyl-1-silacyclobutane in a flow reactor at 625 °C yields ethylene in about 52%, 1,3-dimethyl-1,3-dichloro-1,3-disilacyclobutane (5–10%). Of the other products the main was benzene. Cyclopentadiene, toluene, propylene were formed in a lesser amount [110,141].

In a nitrogen-flow reactor pyrolysis of a benzene solution of 1-phenyl-1-vinyl-1-silacyclobutane in the presence of methanol gave 100% of methylphenylvinylmethoxysilane, the addition product of methanol to phenylvinylsilene. In the presence of phenol methylphenylvinylphenoxysilane and methylphenyldiphenoxysilane were formed (see reaction 41, $R = C_6H_5$) [150].

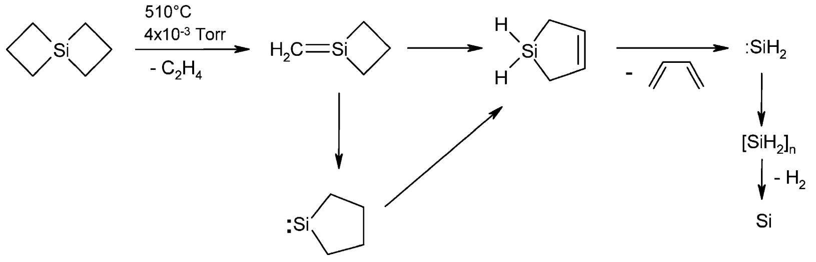
2.2.10.5. 1-Methyl-1-styryl-, and 1-methyl-1-propenyl-1-silacyclobutane. In a nitrogen-flow reactor pyrolysis of benzene solution of 1-methyl-1-styryl-1-silacyclobutane in the presence of methanol gave 100% of methylphenylstyrylmethoxysilane, the addition product of methanol to methylstyrylsilene. In the presence of phenol methylphenylstyrylphenoxysilane and methylphenyldiphenoxysilane were formed (see reaction 41, $R = CH_3$, $R^1 = C_6H_5$) [150]. In case of 1-methyl-1-propenyl-1-silacyclobutane a complex thermal decomposition occurred [150].

2.2.11. 1-Cyclopentadienyl-1-R-1-silacyclobutanes

Pyrolysis of 1-cyclopentadienyl-1-R-1-silacyclobutanes ($R = CH_3$, t-C_4H_9) in a flow reactor at 625 °C and 10^{-2} mbar yielded quantitatively ethylene but no 1,3-disilacyclobutanes. The main decomposition products were benzene, cyclopentadiene, toluene, allene which formation is explained by the different hypothetical isomerization reactions of 1-cyclopentadienyl-1-R-silenes followed by the decomposition of the transient isomers. No silicon-containing volatile products were isolated [153]. In case of 1-cyclopentadienyl-1-chloro-1-silacyclobutane the above decompositions are accompanied by HCl elimination [153].

2.2.12. Spirosilacyclobutanes

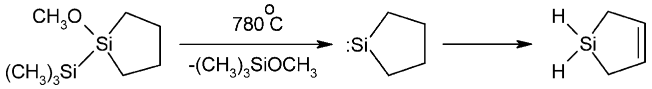
2.2.12.1. 4-Silaspiro[3,3]heptane. Rearrangement of 1-methylene-1-silacyclobutane. A specific reaction pathways of the gas-phase thermal decomposition of 4-silaspiro[3,3]heptane are due to the chemical behavior of 1-methylene-1-silacyclobutane, a primary 2+2 cycloreversion product. A pyrolysis in a flow reactor in a current of inert gas yielded mainly nonvolatile oily products. The main gaseous product was ethylene that presented together with hydrogen, propene and 1,3-butadiene (4.5, 7 and 3.2% from ethylene). Oligomerization was suppressed under the conditions of a very low-pressure pyrolysis. In this case, the only isolated volatile silicon-containing product, 1-silacyclopentene-3, was



(43)

rationalized as arisen from the rearrangement of the primary 1-methylene-1-silacyclobutane [154] presumably via the intermediacy of silacyclopentylidene [130,149,155] (Eq. (43)).[20]

The rearrangement of silacyclopentylidene was proved by the flash vacuum pyrolysis (FVP) study of 1-methoxy-1-trimethylsilyl-1-silacyclopentane which indeed produced trimethylmethoxysilane and the product of silacyclopentylidene rearrangement, i.e., 1-silacyclopentene-3 [130] (Eq. (44)).



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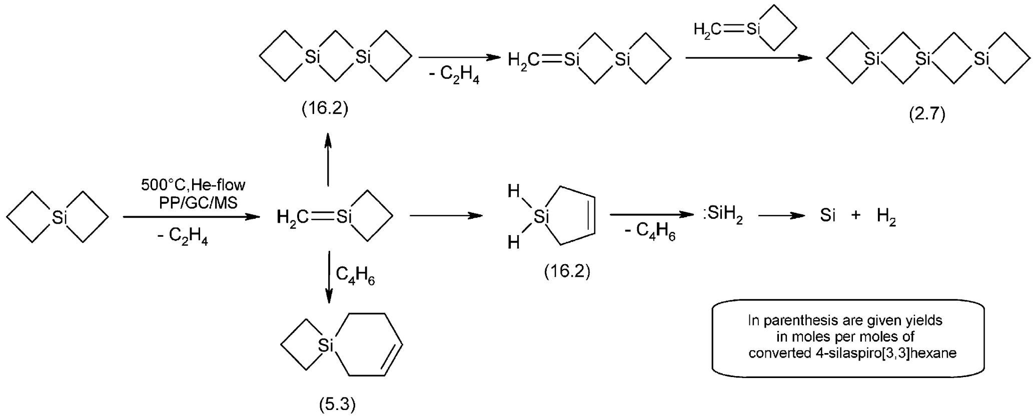
In the pulse pyrolysis GC/MS system some volatile 2+2 cycloaddition products could be identified [56] (Eq. (45)).

Also, silenes trapping products were deduced from GC/MS data for the copyrolysis of 4-silaspiro[3,3]heptane and DMSCB [56]. The rate of the thermal decomposition of the former (log $A = 13.7$ s^{-1}, $E = 52.9$ kcal mol^{-1}) is somewhat higher than that of the latter [31] (Eq. (46)).



In parenthesis are given yields in moles per moles of converted 4-silaspiro[3,3]hexane

(45)

2.2.12.2. *4-Silaspiro[3,4]octane.*

Pyrolysis of 4-silaspiro[3,4]octane in a flow reactor in a current of inert gas yielded ethylene and the dimer of 1-methylene-1-silacyclopentane as the only products at a 60–70% conversion [156]. The Arrhenius parameters of the cycloreversion are log $A = 15.1$ s^{-1}, $E = 60.4$ kcal mol^{-1} [31].

The low-pressure pyrolysis products were found to have composition substantially different from that obtained under conventional pyrolysis conditions. Silacyclohexene and a number of hydrocarbons to the extent of up to 40% of the ethylene yield were also formed. Their production appeared to be the result of silene–silylene rearrangement followed by the decomposition of silacyclohexylidene [31] (Eq. (47)).

2.2.12.3. *4-Silaspiro[3,5]nonane.*

Pyrolysis of 4-silaspiro[3,5]nonane in a flow reactor in a current of inert gas yielded ethylene and the crystals of the dimer of 1-methylene-1-silacyclohexane as the only products at a 60–70% conversion [156] (Eq. (48)).

2.2.12.4. *Spiro[silacyclobutane-1,9′-[9H-9]silafluorene].*

Pyrolysis of spiro[silacyclobutane-1,9′-[9H-9]silafluorene] under the low pressure gave a head-to-tail silene dimer in a 15% yield. Its pyrolysis in the presence of benzophenone (540 °C) gave 1,1-diphenylethylene and siloxane oligomer, the products normally associated

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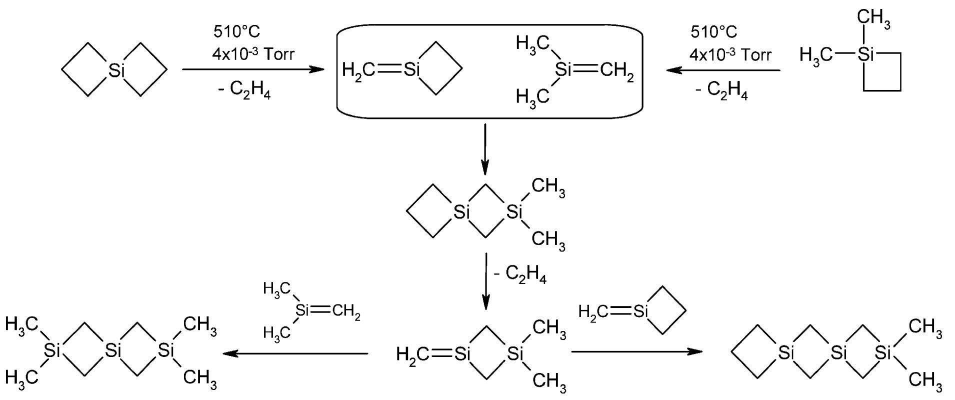
[20] At much higher temperature two isomers were formed [130].



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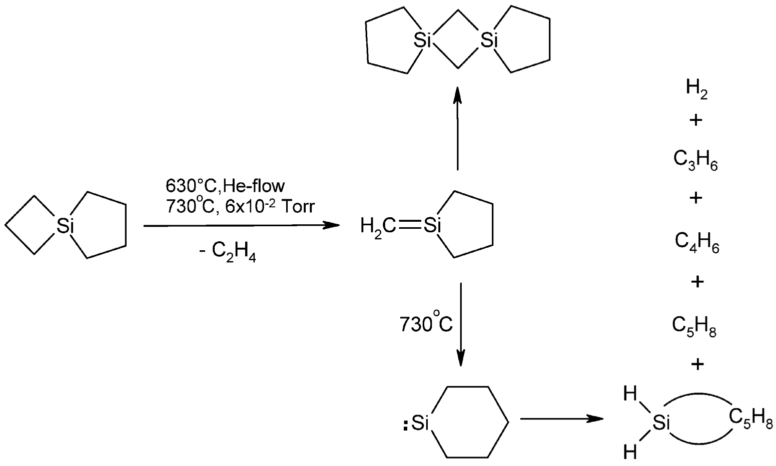

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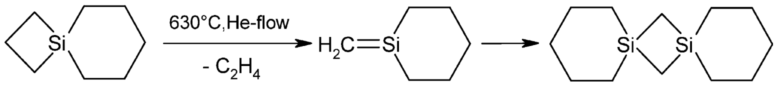


(48)

with the intermediacy of silenes and silanones [157] (Eq. (49)).

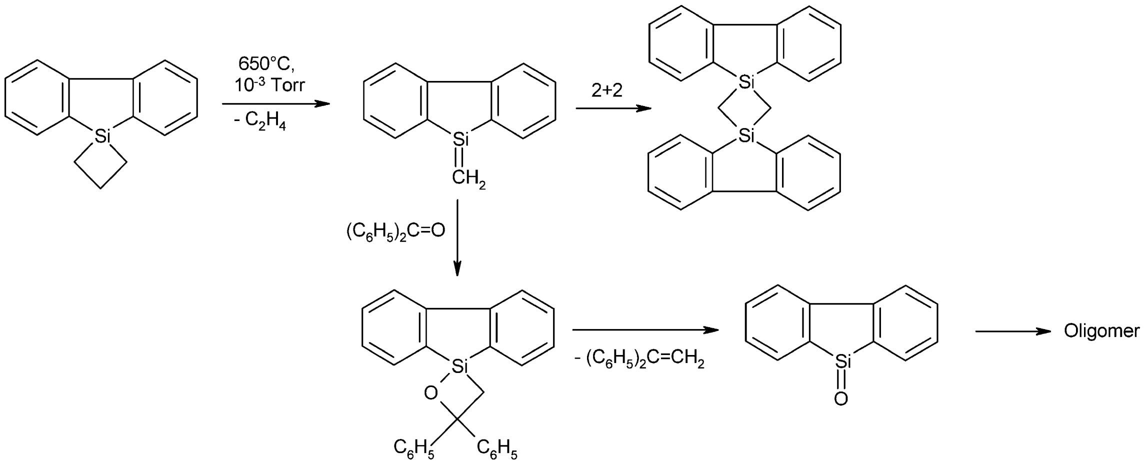
2.2.13. C-substituted 1-silacyclobutanes

2.2.13.1. 1,1,3-Trimethyl-1-silacyclobutane. Unlike pyrolysis of DMSCB for which a 2+2 cycloreversion and dimerization of the transient silene are the only reactions, in the pyrolysis of 1,1,3-trimethyl-1-silacyclobutane 2+2 cycloreversion to propylene and DMSE is accompanied by the isomerization of the starting compound into allyltrimethylsilane [60,158].

Both processes, cycloreversion and isomerization, are characterized by the same activation energy ($E = 63.2$ kcal mol^{-1}), their different rates are defined by the entropy factors of 2+2 cycloreversions ($\log A = 16.3$ s^{-1},) and isomerization ($\log A = 15.6$ s^{-1}) [159]. The identical activation energies for propene and allyltrimethylsilane's formation are best rationalized in terms of the initial cleavage of the ring C–C bond being a limiting stage and yielding 1,4-diradical which either decomposes or isomerizes via a 1,5-H migration in a six-membered cyclic transition state [31,60,159] (Eq. (50)).

The intermediacy of DMSE in the above 2+2 cycloreversion but carried out under conditions of a very low-pressure pyrolysis was confirmed by the low-temperature matrix infrared spectroscopy studies [92,95,97,105,160].

The UV spectroscopic observation of the intermediates of the thermal decomposition of 1,1,3-trimethyl-1-silacyclobutane (~1% in argon) was obtained by a millisecond technique of time-resolved measurements



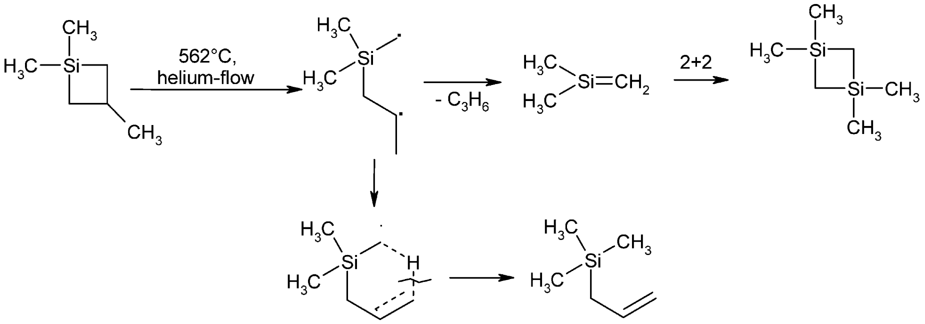
(49)

under pulse adiabatic compression conditions in a free-piston device [109]. It turned out that the light absorption by two intermediates appeared prior to the propene formation, i.e., at the temperatures ~310 °C (λ_{max} = 227.5 nm) and ~450 °C (λ_{max} = 235 nm) at which 2+2 cycloreversion does not still occur. The first-order kinetics of the equilibrium between 1,1,3-trimethyl-1-silacyclobutane and the 227.5 nm transient intermediate as well as between 1,1,3-trimethyl-1-silacyclobutane and the 235 nm transient intermediate determined from the intensity of light absorption indicated that the chemical composition of both intermediate was the same as for 1,1,3-trimethyl-1-silacyclobutane. The reaction enthalpies determined, 12.5 and 20.3 kcal mol^{-1}, respectively, were much lower than that of the ring opening to assign the intermediates to the diradicals. The formation of propene started at ~600 °C and was accompanied by the appearance of the three more light absorption at 280, 290 and 605 nm of which 280 nm is presumably due to DMSE.

The radical intermediate produced upon the pyrolysis of 1,1,3-trimethyl-1-silacyclobutane was detected in the frozen VLPP products at 77 K [56]. The ESR spectrum was a triplet, with the hyperfine splitting constant being equal to 22.2 G, and the intensity ratio being 1:2.5:1 (see Section 2.2.2.1).

2.2.13.2. *1,1,2-Trimethyl-1-silacyclobutane.* The gas-phase 2+2 cycloreversion of 1,1,2-trimethyl-1-silacyclobutane in the nitrogen-flow system occurs with a predominant initial cleavage of the carbon–carbon bond rather than the silicon–carbon bond followed by the further cleavage to afford 1,1,2-trimethylsilene [161]. Products resulting from the initial C–C bond cleavage predominated by factor 3 below 600 °C but at higher temperature the two processes became competitive. At the lower temperature the formation of dimethylethylvinylsilane clearly indicated the initial C–C bond rupture (Eq. (51)).

A copyrolysis of 1,1,2-trimethyl-1-silacyclobutane and different substrates also resulted in the isolation of



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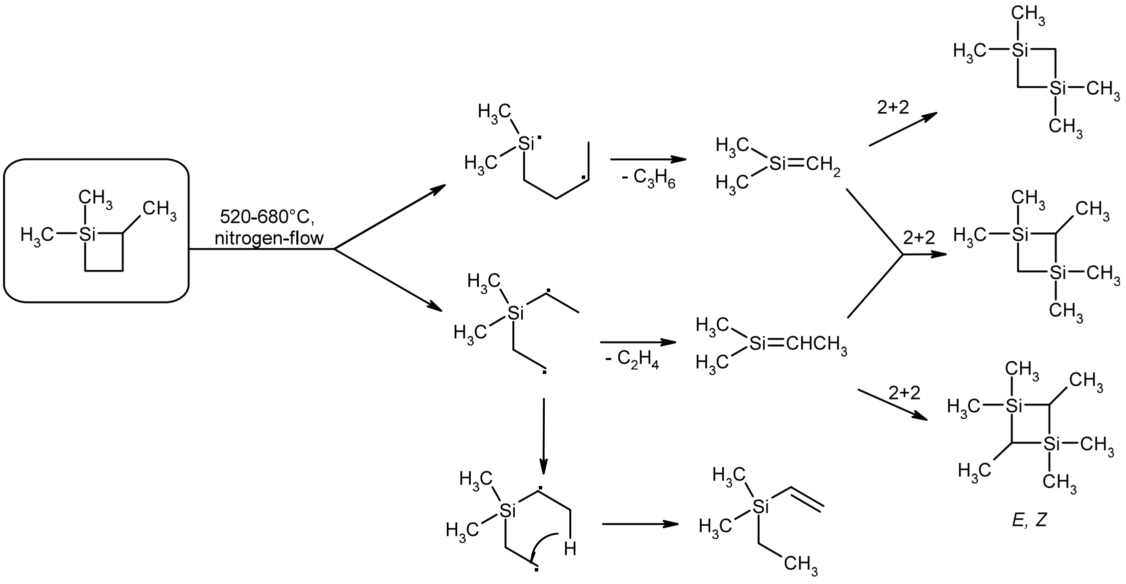


(51)

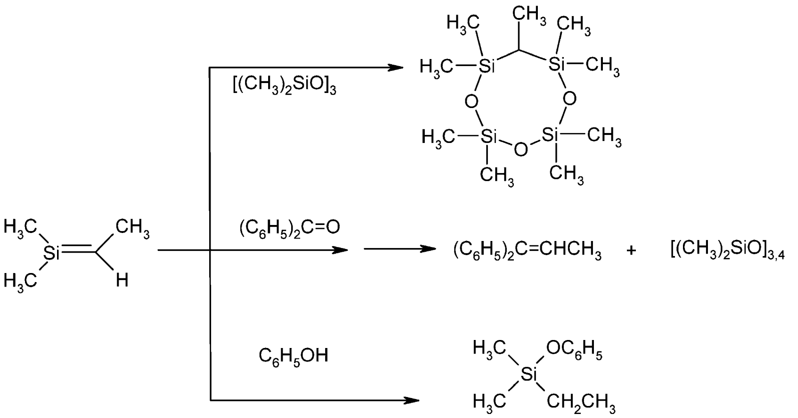
the products indicating that the predominant decomposition product was 1,1,2-trimethylsilene [55]. These results also provide evidence in support of C–C bond scission as the initial step of the thermal silacyclobutane's decomposition (Eq. (52)).

A thermal decomposition kinetic study of 1,1,2-trimethyl-1-silacyclobutane resulted in the Arrhenius parameters of the total process ($\log A = 15.7\ \mathrm{s}^{-1}$, $E = 61.4\ \mathrm{kcal\ mol}^{-1}$) reflecting somewhat lesser thermal stability of 1,1,2-trimethyl-1-silacyclobutane compared to DMSCB. The activation energies of ethylene's and propylene's as well as of vinyldimethylethylsilane's formation were found to be alike. The different rates of alternative 2+2 cycloreversions and isomerization are entirely defined by the entropy factor which for the cycloreversion to propylene and isomerization are correspondingly by 0.7 and 1.4 s^{-1} less than those for the formation of ethylene [31].

The radical intermediate produced upon pyrolysis of 1,1,2-trimethyl-1-silacyclobutane was detected in frozen at 77 K VLPP products [56]. The ESR spectrum was a quintuplet, with the hyperfine splitting constant being equal to 25.2 G, and the intensity ratio being 1:4:6:4:1 (see Section 2.2.2.1).

2.2.13.3. *1,2-Dimethyl-1-[(trimethylsilyl)methyl]-1-silacyclobutane.*

The major product of FVP of 1,2-dimethyl-1-[(trimethylsilyl)methyl]-1-silacyclobutane was 1-ethyl-



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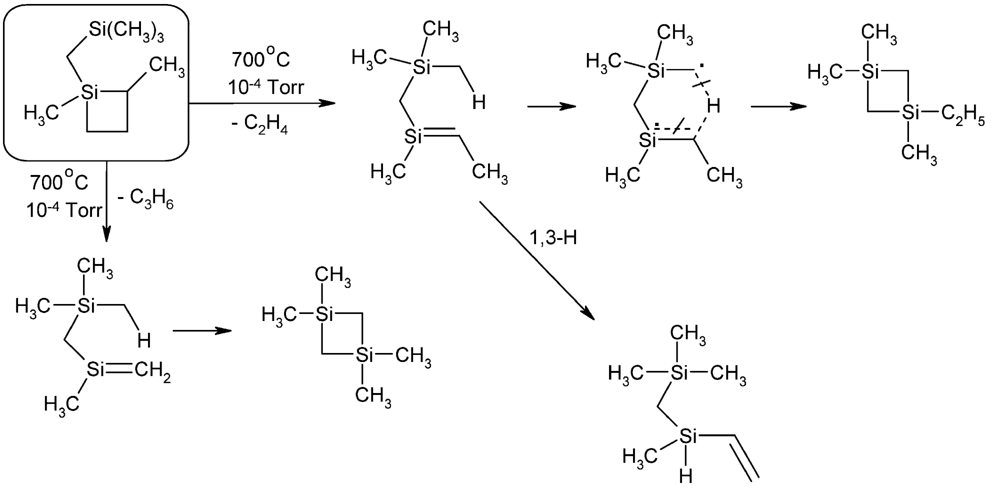

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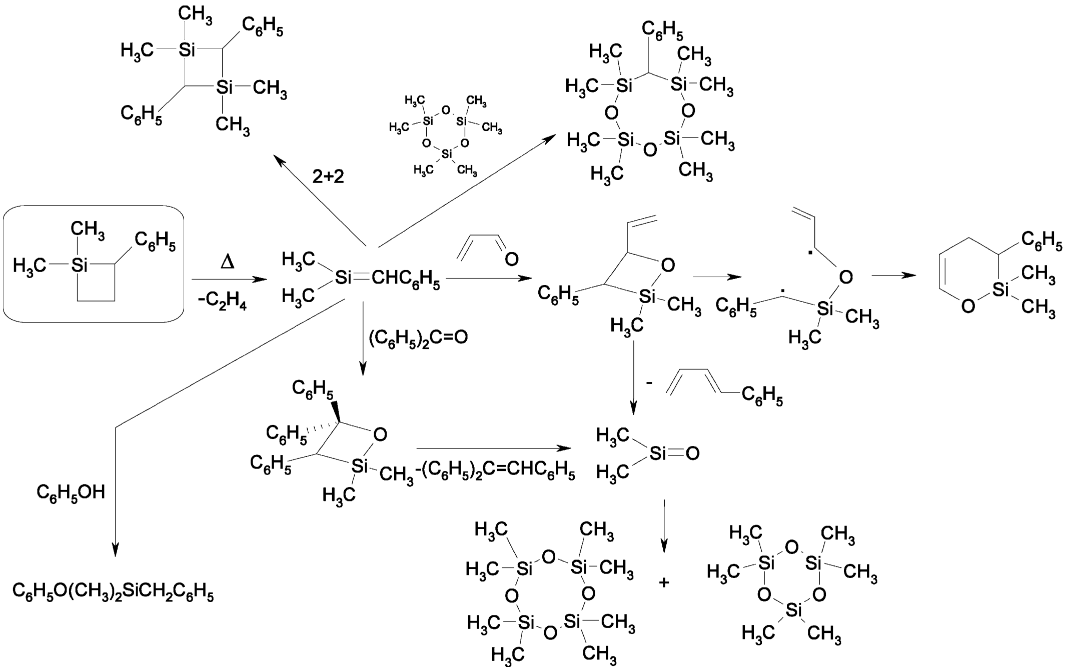
1,3,3-trimethyl-1,3-disilacyclobutane. Its formation is rationalized by silene's rearrangement involving hydrogen shift and a closure of the 1,4-diradical [130]. A minor product, (trimethylsilylmethyl)methylvinylsilane is explained as arising from the isomerization of silene via a 1,3-hydrogen migration. The product from the apparently radical rearrangement of the minor silene resulted from the propene elimination was formed in only a 5% yield (Eq. (53)).

2.2.13.4. *1,1-Dimethyl-2-phenyl-1-silacyclobutane.*

At 500 °C in a nitrogen-flow 1,1-dimethyl-2-phenyl-1-silacyclobutane cycloreverts almost exclusively to yield ethylene and 1,1-dimethyl-2-phenylsilene which dimerizes to a 60:40 mixture of *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane [162]. Copyrolysis with benzophenone [55] and acrolein [163] yielded products expected from the intermediate silaoxetanes. 1,1-Dimethyl-2-phenylsilene reacted with phenol and hexamethylcyclotrisiloxane producing addition and insertion products, respectively [55] (Eq. (54)).

2.2.13.5. *1,1,2-Triphenyl-1-silacyclobutane.*

A pyrolysis of a benzene solution of 1,1,2-triphenyl-1-silacyclobutane in a nitrogen-flow reactor at 720 °C resulted in 11% of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane, a product of cyclodimerization of diphenylsilene, together with styrene and polymeric products. A 2+2 cycloreversion to ethylene and 1,1,2-triphenylsilene is a minor reaction [132].



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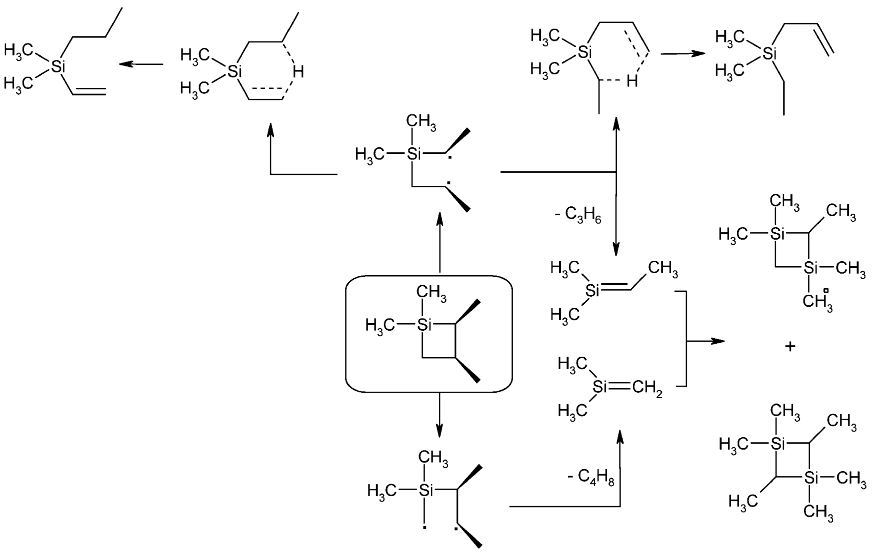

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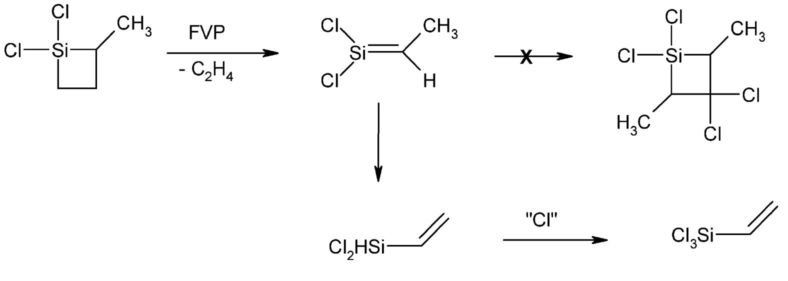
2.2.13.6. 1,1,2,3-Tetramethyl-1-silacyclobutane. A pyrolysis of either isomer of (*E*)- and (*Z*)-l,l,2,3-tetramethylsilacyclobutanes in a static reactor at 398 °C provides the same decomposition and structural isomerization products [164]. An initial cleavage of the most highly substituted C–C bond is preferred: cycloreversion is dominated by the propene formation, whereas 2-butene is a minor product. The stereoorientation of 2-butene is high in both cases (fivefold preference for retention in the 2-butene fragment) indicating that the second bond breaking (Si–C bond) in the diradical competes effectively with a bond rotation. A migration of hydrogen from an exocyclic methyl groups on a carbon to an α- or β-ring carbon produces allylethyldimethylsilane and dimethylpropylvinylsilane (major isomer). The formation of propene with the accompanying trimethylsilene and 2-butene with DMSE is indicated by the near statistical distribution of silene dimers, i.e., 1,3-disilacyclobutanes: (Eq. (55)).

2.2.13.7. 1,1-Dichloro-2-methyl-1-silacyclobutane. FVP of 1,1-dichloro-2-methyl-1-silacyclobutane did not result in the expected dimer of silene but in 46% yield of vinyltrichlorosilane. It is suggested that the latter arose from the rearrangement of the anticipated 1,1-dichloropropene into dichlorovinylsilane via a [1,3]-hydrogen shift followed a facile H/Cl redistribution on silicon [165] (Eq. (56)).

2.2.13.8. 1,1-Dimethyl-2-((vinyldimethylsilyl)methyl)-3-vinyl-1-silacyclobutane. A low-pressure flow pyrolysis of (*E*)- and (*Z*)-1,1-dimethyl-2-((vinyldimethylsilyl)methyl)-3-vinyl-1-silacyclobutanes at 450 °C provides a relatively mild thermal source of silene in the gas phase which forms two intramolecular rearrangement products [166] (Eq. (57)).

2.2.13.9. 2-Methylene-1,1-dimethyl-1-silacyclobutane. A pyrolysis of 2-methylene-1,1-dimethyl-1-silacyclobutane at 421 °C produced isomeric 1,1-dimethyl-1-silacyclopentenes in a nearly quantitative yield, no 2+2 cycloreversions occurred. It was suggested that Si–C bond migration to the methylene substituent places the carbene center β to the Si atom [63]. A kinetic investigation of the thermal isomerization [167] resulted in the Arrhenius parameters, $\log A = 11.3\ \mathrm{s}^{-1}$, $E = 47.5$ kcal mol^{-1} which were in accord with a concerted process although the activation energy is close to what one might have expect for the strength of the C–C bond. However, the negative value of the activation entropy demanded a constrained transition state as opposed to a homolytic cleavage. Interestingly, a non-productive homolysis of 2-methylene-1,1-dimethyl-1-silacyclobutane involving a reversible ring opening to a 1,4-diradical had also occurred at temperatures below those required to ring expansion via a carbene transition state. Although its activation energy is greater than that of the



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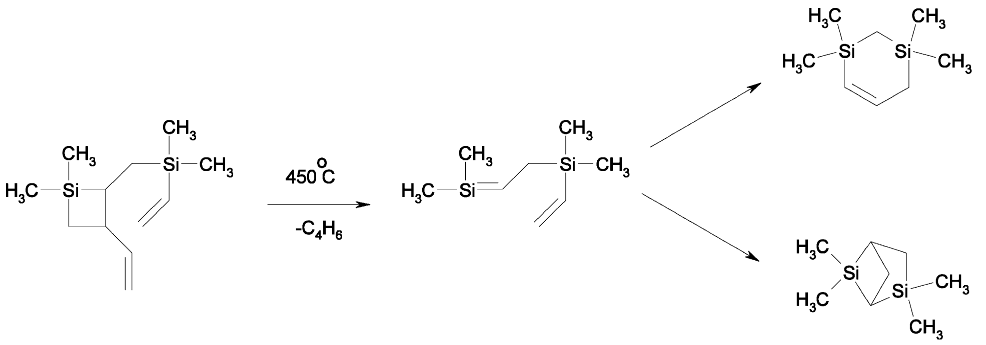

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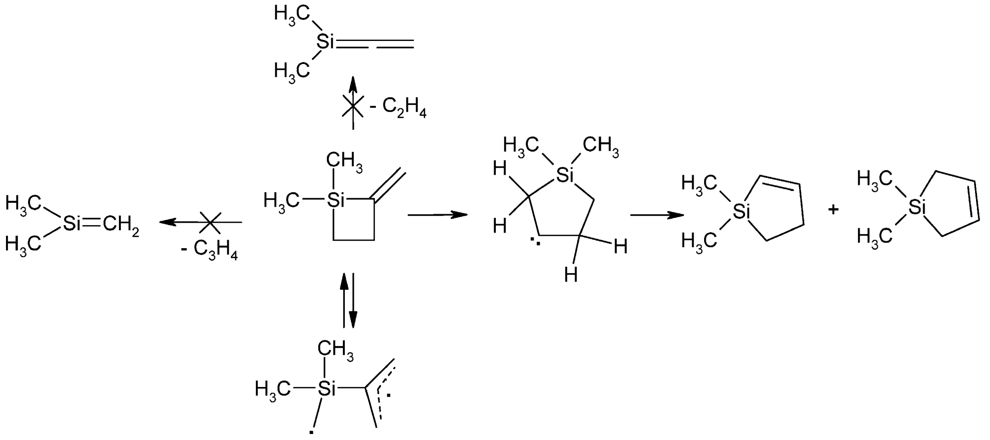


(58)

carbene's formation, the former reaction occurs at lower temperatures due to the more favorable entropy factor (Eq. (58)).

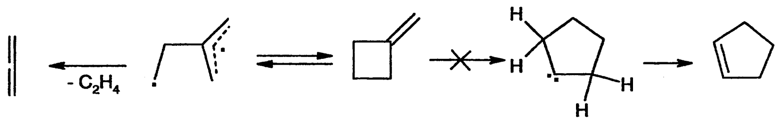
Unlike 2-methylene-1,1-dimethyl-1-silacyclobutane a thermal isomerization does not occur in case of methylenecyclobutane which cycloreverts to ethylene and allene ($E = 61.5$ kcal mol^{-1}) [168] (Eq. (59)).

2.3. 1-Sila-2(3)-elementacyclobutanes

2.3.1. Silaazetidines

2.3.1.1. 1-Isopropyl-2,2,3-trimethyl-1-aza-2-silacyclobutane. The first step of pyrolysis in the temperature range 750–950 °C is interpreted as a 2+2 cycloreversion yielding 1,1-dimethyl-2-*i*-propylsilanimine which rapidly dimerizes into its cyclic dimer. At higher temperatures the equilibrium between the dimer and silanimine is displaced from the dimer to silanimine. The *N*-isopropylated silanimine was observed by PES with two energetically close ionization potentials at 7.8 eV, associated with the n_N^- and $\pi_{Si=N}$ orbitals. A decomposition with formation of propene and the dimer of silanimine, $(CH_3)_2Si{=}NH$, also occurs. Above 950 °C further decomposition with the formation of ethylene and acetylene was observed [23,169] (Eq. (60)).

2.3.1.2. 1-tert-Butyl-2,2,3-trimethyl-1-aza-2-silacyclobutane. At 700 °C FVT of the title azasilacyclobutane gave propene and the cyclic dimer of 1,1-dimethyl-2-*tert*-butylsilanimine. In addition, at higher temperatures the loss of isobutene and a formation of tetramethyldisilazane were observed, showing that dimethylsilanimine had been formed. Its intermediacy was proved by a reaction with *tert*-butyl alcohol [170]. The 7.4 eV band in the photoelectron spectrum was assigned to the ejection of electrons from the n_N^- and $\pi_{Si=N}$ orbitals of 1,1-dimethyl-2-*tert*-butylsilanimine [23,169] (Eq. (61)).



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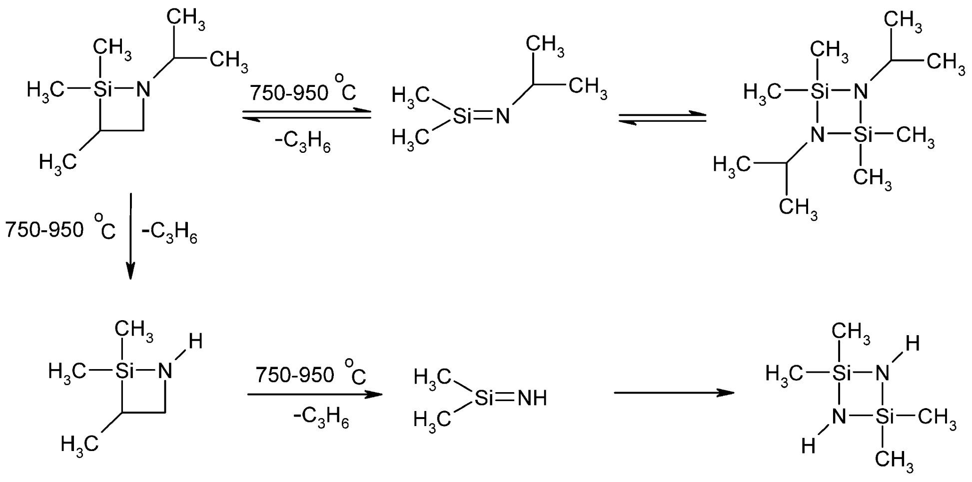
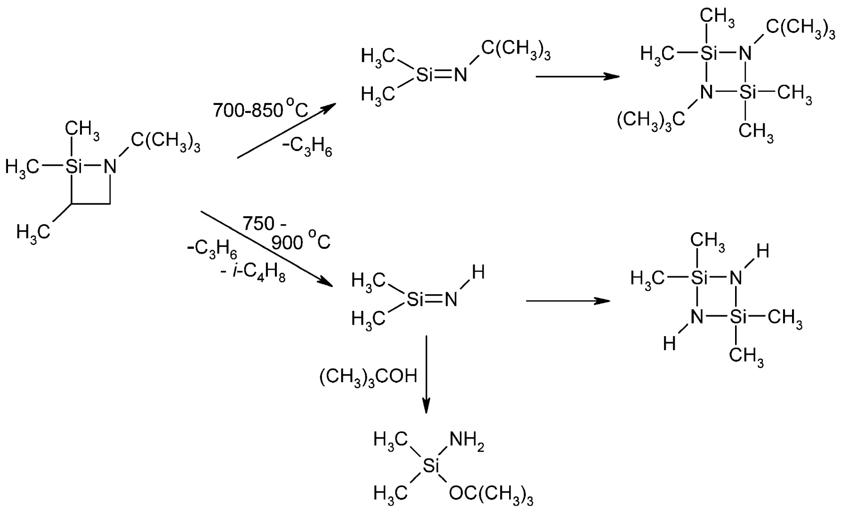
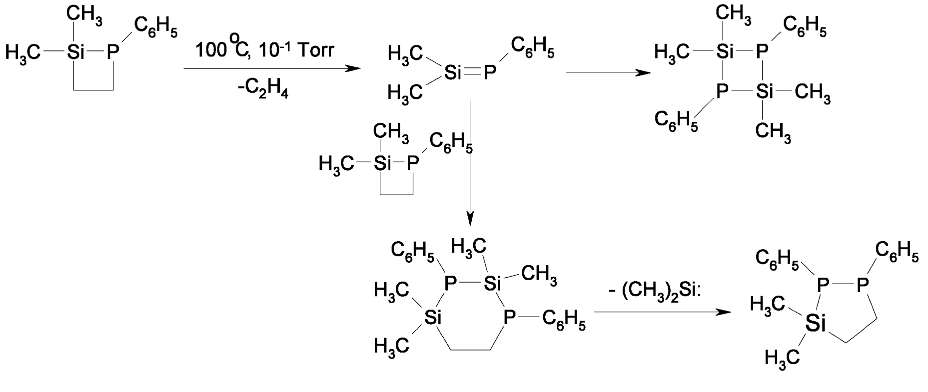

750-950 °C
-C3H6
750-950 °C
-C3H6
750-950 °C
-C3H6

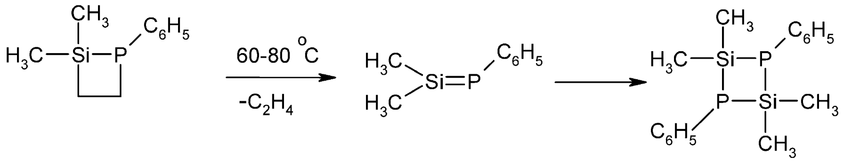
(60)


700-850 °C
-C3H6
750 - 900 °C
-C3H6
- i-C4H8
(CH3)3COH

(61)


100 °C, 10-1 Torr
-C2H4
- (CH3)2Si:

(62)



(63)

2.3.2. Silaphosphetanes

2.3.2.1. 1,1-Dimethyl-2-phenyl-1-sila-2-phosphacyclobutane. The first evidence for phosphasilenes was obtained by a 2+2 thermocycloreversion of 1,1-dimethyl-2-phenyl-2-phospha-1-silacyclobutane [171]. The latter generated transient 1,1-dimethyl-2-phenyl-1,2-phosphasilene upon vacuum distillation at 100 °C yielding a mixture of products resulting from its head-to-tail 2+2 cyclodimerization, as well as insertion into the Si–P bond of the starting compound (Eq. (62)):

A FVT/PES study of 1,1-dimethyl-2-phenyl-2-phospha-1-silacyclobutane allowed to measure the first vertical ionization potential of phosphasilene, $(CH_3)_2Si{=}PC_6H_5$, to be 8.3 eV. The only stable product of the reaction was the dimer, 1,1,3,3-tetramethyl-2,4-diphenyl-2,4-diphospha-1,3-disilacyclobutane [172] (Eq. (63)).

2.3.3. Silaoxetanes

Although both stable 1,2-silaoxetanes [173–176], and 1,3-silaoxetanes [177,178] were synthesized and characterized their gas-phase thermal or photochemical reactions were not studied yet presumably because of their low volatility.[21]

2.3.3.1. 1,2-Silaoxetanes. 1,2-Silaoxetanes are postulated to be intermediates in the gas-phase reactions of transient silenes with aldehydes and ketones (for intermediate 1,2-disilaoxetanes in the copyrolysis of 1-silacyclobutanes and carbonyl compounds see Section 2.1.4.1).[22, 23] According to ab initio calculations a 2+2 cycloreversion of 1,2-silaoxetane to silanone and ethylene as well as to silene and formaldehyde are endothermic by 50 and 30 kcal mol^{-1}, respectively, in contrast to the exothermic reaction of silanone to form dimer (25 kcal mol^{-1} below 1,2-silaoxetane). This led to the prediction that 1,2-silaoxetane should be isolable and in the liquid phase they should undergo rather bimolecular transformations than the monomolecular decomposition to silanone [71].[24, 25] However, under the low-pressure pyrolysis conditions the bimolecular reactions should be suppressed in favor of 1,2-silaoxetane's 2+2 cycloreversion. A pyrolysis of trimethylsilyl and phenyldimethylsilyl phenyl ketones results in an unstable silaoxetane intermediate which silicon–carbon and silicon–oxygen bonds cleavaged producing Si=O and Si=C bonded intermediates. The latter is involved in a Wittig-type reaction with the starting silyl phenyl ketone or benzophenone [65,179] (Eq. (64)).

The formation of transient 2-silaketene was proposed via a 2+2 cycloreversion of the 2-silaallene's and benzaldehyde's adduct [180].

A generation of 2,2-dimethyl-2-silaoxetane by an alkali metal vapor dehalogenation of 2-chloroethoxydimethylchlorosilane results in its 2+2 cycloreversion yielding the trimer and tetramer of dimethylsilanone and ethylene [181] (Eq. (65)).

Thermal behavior of 6-oxa-3-silabicyclo[3.1.0]hexanes is characterized by a transannular reaction leading to transient silaoxetanes which cyclorevert to silanones [182]. Arrhenius parameters of the butadiene's elimination are in accord with the radical mechanism involving the formation and 2+2 cycloreversion of 2,2-dimethyl-4-vinyl-2-silaoxetane resulting in dimethylsilanone [183] (Eq. (66)).

2.3.4. Silathietanes

Thermolysis of the only known stable 1,2-silathietane [184] was studied in a liquid-phase (Section 5.2.1). Of several 1,3-silathietanes, which are stable compounds [177,178,185,186] the gas-phase thermal decomposition studies were performed for 1,1-dimethyl-1-sila-3-thiacyclobutane (Section 2.3.4.2) and 1,1-diethyl-2,4-dimethyl-1-sila-3-thiacyclobutane (Section 2.3.4.3).

2.3.4.1. 1,2-Silathietanes. Transient 1,2-silathietanes' 2+2 cycloreversion is commonly postulated when considering mechanisms involving the reactions of silenes

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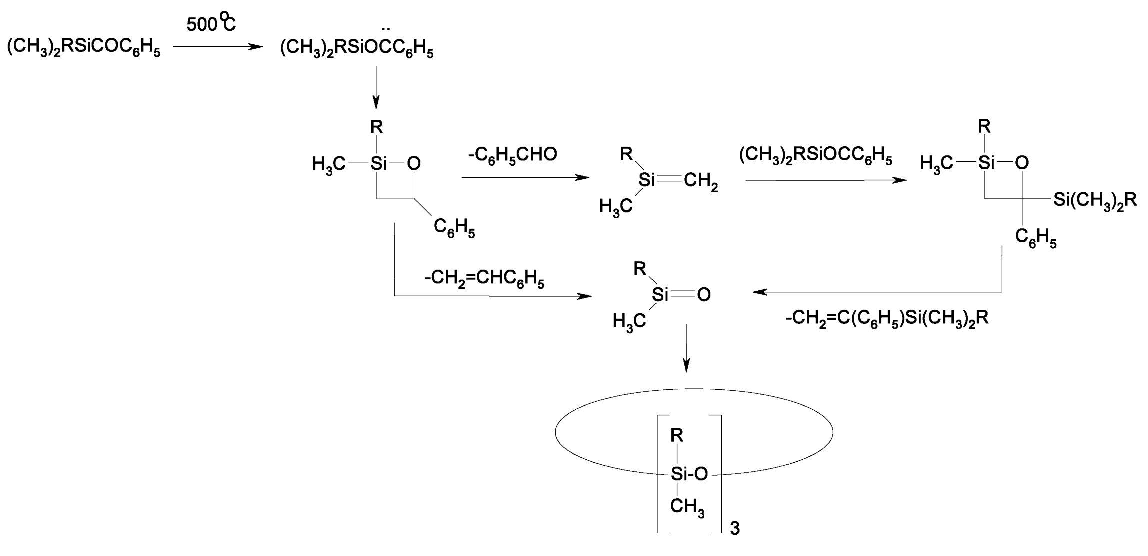
[21] For liquid-phase reactions of 1,2-silaoxetanes see Section 5.1.1.

[22] For more examples of 2+2 cycloreversion of 1,2-silaoxetane intermediates see [337].

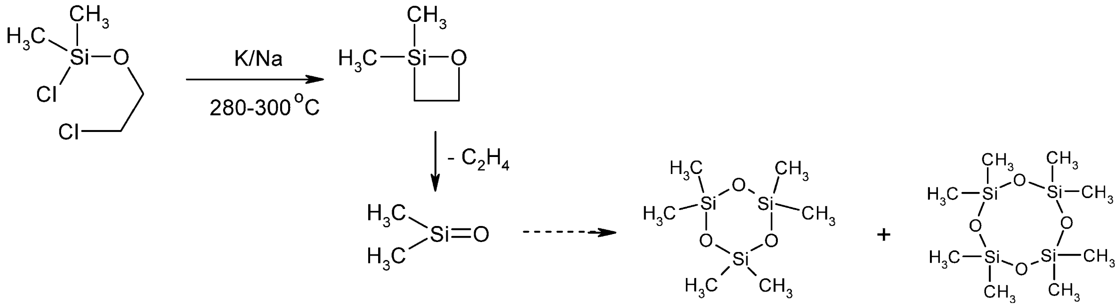
[23] In an argon matrix silenes reacts with carbonyl compounds having an α-H atom, in particular formaldehyde, to produce the van der Waals complex which further results in no silaoxetane but siloxycarbene [340].

[24] More recent calculations of the silene reaction with formaldehyde leading to 1,2-oxetane resulted in its exothermicity by 67 kcal mol^{-1} and the overall reaction, including 2+2 cycloreversion to ethylene and silanone, to be still exothermic by 30 kcal mol^{-1} [340].

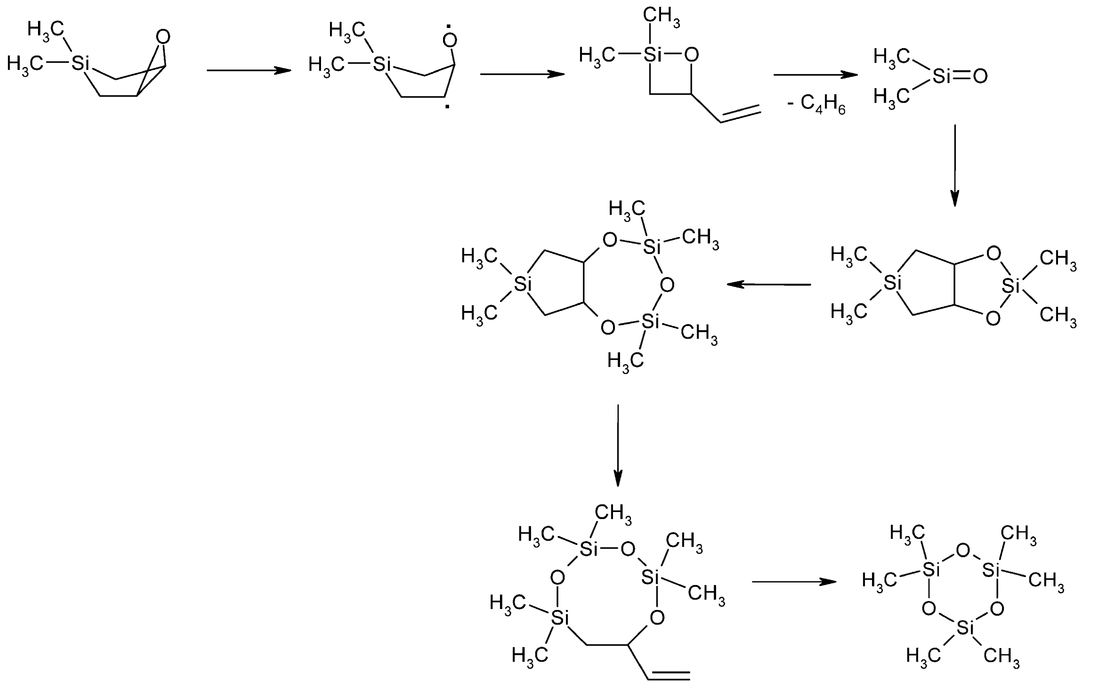
[25] For moderately stable silaoxetane see [174]. The earlier report on obtaining isolable 2-silaoxetane [342] was later subjected to an alternative view [343].


500°C
(CH3)2RSiCOC6H5
(CH3)2RSiOCC6H5
-C6H5CHO
(CH3)2RSiOCC6H5
Si(CH3)2R
-CH2=CHC6H5
-CH2=C(C6H5)Si(CH3)2R
3

(64)


K/Na
280-300 °C
- C2H4

(65)


- C4H6

(66)

with thiocarbonyl compounds (see Sections 2.1.4.1, 2.3.4.2 and 2.3.4.3).

2.3.4.2. 1,1-Dimethyl-1-sila-3-thiacyclobutane. In a flow system (He, residence time 4 s) the conversion of 3,3-dimethyl-3-silathietane started at 470 °C and accomplished 95% at 580 °C [187]. The only gaseous product was ethylene. The main products were tetramethylcyclodisilthiane and 1,1,3,3-tetramethyl-2-thia-1,3-disilacyclobutane. The presence of sulfur atom in the 3-position of the silacyclobutane makes the rate of 3,3-dimethyl-3-silathiethane's 2+2 cycloreversion (log $A = 15.1\ s^{-1}$, $E = 58.9$ kcal mol^{-1}) higher than that of DMSCB [122].

A copyrolysis with 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane (1:9) gave products of DMSE and dimethylsilanthione insertion into the Si–O bond. Scheme 67 was suggested for the process [187]:

A copyrolysis of 3,3-dimethyl-3-silathietane with 1,1-bis(trideutriomethyl)-1-silacyclobutane (580 °C, residence time 4.1 s, molar ratio 1:7.7, conversion 94.8 and 55.3%, respectively), resulted in trapping of the intermediate DMSE, thioformaldehyde, dimethylsilanthione and 2,2-dimethyl-2-silathietane by bis(trideutriomethyl)silene [187] (Eq. (68)).

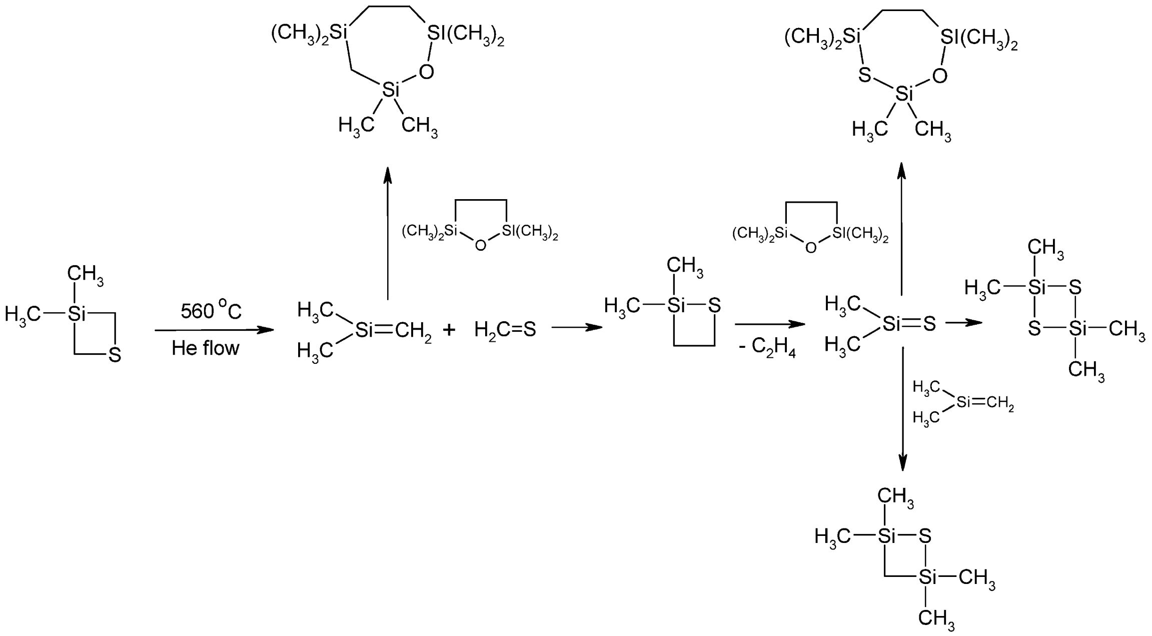
The IR spectroscopic study of 3,3-dimethyl-3-silathietane VLPP products isolated in Ar matrices resulted in the observation of the absorption bands of two intermediates, i.e., DMSE and thioformaldehyde [187–189]. No dimethylsilanthione but its cyclic dimer, tetramethylcyclodisilthiane, as well as ethylene could be detected (Eq. (69)).

A perturbation molecular orbital study of 2+2 cycloaddition reactions involving DMSE, dimethylsilanthione, and thioformaldehyde showed that the former reacts more readily with the two others than it cyclodimerizes. Dimerization of dimethylsilanthione is the most prominent process [72,190].

2.3.4.3. 1,1-Diethyl-2,4-dimethyl-1-sila-3-thiacyclobutane. The gas-phase pyrolysis of 1,1-diethyl-2,4-dimethyl-1-sila-3-thiacyclobutane was studied by a pulse pyrolysis–GC/MS method. The decomposition was a complex process proceeding with the elimination of ethane, ethylene, propene, *cis*- and *trans*-but-2-ene, and also with the loss of the atomic sulfur. The isomerization into the sulfur-containing unsaturated compounds is the main process. The intermediacy of 1,1-diethyl-2-methyl-1-silene and diethylsilanthione was suggested [191] (Eq. (70)).

2.3.5. Siladioxetanes

DMSE adds rapidly to molecular oxygen to form dimethylsilanone by the 2+2 cycloreversion of the intermediate siladioxetane [52] (see Section 2.1.4.1, reaction 8). A methylsilicone deposit formation upon the laser photolysis of 1,3-disilacyclobutane–O_2 mixture is judged to involve oxidation of silene and thermal 2+2



(67)

cycloreversion of the intermediary siladioxetane [192] (Eq. (71)).

2.3.6. *Silaoxathietanes*

2.3.6.1. 1,1-Dimethyl-3-methylene-2-oxa-4-thia-1-silacyclobutane. A cycloadduct of dimethylsilanthione and ketene, oxathiasiletane, is a stable product. Its FVT at a higher temperature results in thioketene and dimethylsilanone cyclic trimer [193] (Eq. (72)):

2.4. *1,3-Disilacyclobutanes*

2.4.1. *Effect of substitution at silicon on 1,3-disilacyclobutanes' strain energies, their ring opening and 2+2 cycloreversion enthalpies*

In terms of a diradical mechanism a 2+2 cycloreversion of 1,3-disilacyclobutanes may be drawn as follows (Eq. (73)):

It implies that the ring opening (3.1)–diradical decomposition (3.2) sequence and the reverse reactions of silenes cyclodimerization (−3.2) should be considered taking into account the principle of microscopic reversibility, i.e. as ones occurring via the diradicals ring closure (−3.1). The effect of geminal substitution at silicon on 1,3-disilacyclobutanes' strain energies and their 2+2 cycloreversion enthalpies was evaluated by an ab initio MO study of silenes (**1**) and 1,3-disilacyclobutanes (**3**) using the basis set noted as MP4/TZ(d)//MP2/6-31G(d) (TZ denotes 6-311G(d) basis set for elements of the second period and hydrogen, and the McLean–Chandler (12s,9p)/[6s,5p](d) basis set for the third period elements) [39]. In the series of R = H, CH_3, SiH_3, CH_3O, NH_2, Cl, F the growth of the reaction enthalpies and the strain energies is proportional to the substituents electronegativity. In particular, on going from silyls to fluorines the strain energy rises by 11.9 kcal mol^{-1}. Despite the growth of the strain energy the endothermicity of the 2+2 cycloreversion also increases by 41.5 kcal mol^{-1}, cf., 72.7 kcal mol^{-1} (R = SiH_3) and 114.2 kcal mol^{-1} (R = F). More importantly, of this value only the growth by 12.0 kcal mol^{-1} is due to the ring-opening reaction 3.1, cf., 67.4 kcal mol^{-1} (R = SiH_3) and 79.4 kcal mol^{-1} (R = F), whereas 1,4-diradical decomposition reaction 3.2 mainly contributes to the 2+2 cycloreversion enthalpy. Indeed, apart from the disilyl derivative the decomposition of 1,4-diradical is the *endothermic* process which enthalpy varies from 10.6 to 40.4 kcal mol^{-1}.

Therefore, the pronounced difference in the enthalpies of a 2+2 cycloreversion of 1-silacyclobutanes (see Section 2.1) and 1,3-disilacyclobutanes is mainly due to the difference in their diradicals' decomposition reaction being the *exothermic* process for the former and the *endothermic* one for the latter.

The schematic energy level diagram for 1,3-disilacyclobutanes' 2+2 cycloreversion and the contribution of the reactions 3.1 and 3.2 to the enthalpy of the 2+2 cycloreversion versus Pauling electronegativity are shown in Figs. 5 and 6.

The energy level for the transition state TS1 of the ring opening should lie above the enthalpy of 1,3-disilacyclobutanes' ring opening on a rather small quantity of the 'Benson barrier'. The energy level for the transition state TS2 of the 1,4-diradical's decomposition should be close to the enthalpy of 2+2 cycloreversion, since the reverse reaction, the silenes' 2+2 cycloaddition, is a nonactivated process. The concerted TS3 should lie close to TS2 and a little above the energy level for the two silene molecules because the

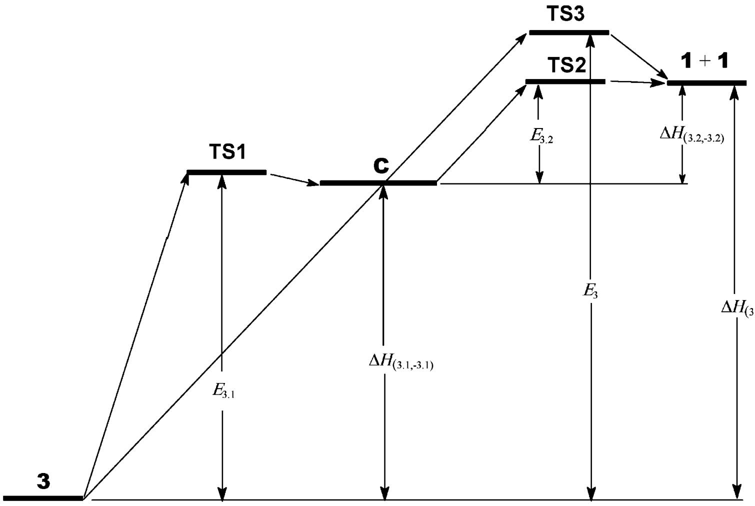


Fig. 5. A schematic energy level diagram for 2+2 cycloreversion of 1,3-disilacyclobutanes.

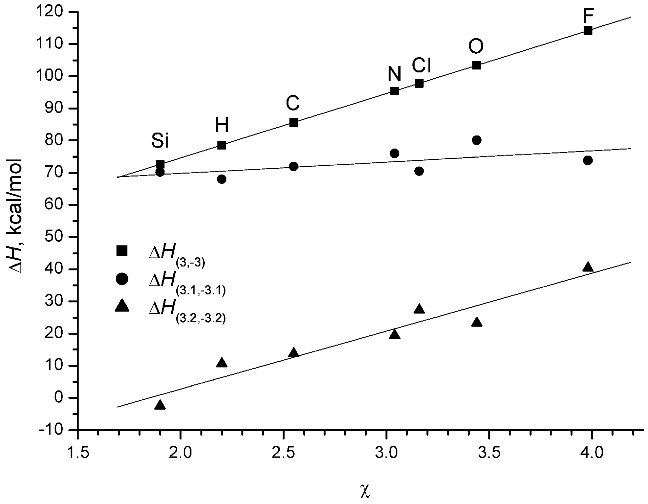


Fig. 6. A view of the contribution of reactions 3.1 and 3.2 to the enthalpy of 2+2 cycloreversion of 1,3-disilacyclobutanes versus Pauling electronegativity. (Corrected for 1,1,3,3-tetrasilyl-1,3-disilacyclobutane's strain energy to be equal 14.9 kcal mol^{-1}.)

theoretically predicted barrier height for the concerted silene's head-to-tail dimerization is only 3.8 kcal mol^{-1} [194]. Such a high energy level can be hardly realized in the one-step concerted process, simply because the first step of the stepwise diradical process, a cleavage of a Si–C bond, requires so much less energy in comparison with the synchronous decomposition to two molecules of silene [39]. Therefore, of the two alternative mechanisms of 1,3-disilacyclobutanes' 2+2 cycloreversion, the diradical (via TS1 and TS2) and the concerted (via TS3), the first one involves a low-lying transition state TS1 which predetermines the preference of the diradical route. In terms of the 'principle of microscopic reversibility' the reverse reaction, a head-to-tail 2+2 cyclodimerization of silenes, should also be a diradical process [195–197], but not a concerted [194] one.

2.4.2. *1,1,3,3-Tetramethyl-1,3-disilacyclobutane*

The gas phase decomposition of 1,1,3,3-tetramethyl-1,3-disilacyclobutane occurs by the cleavage of Si–CH_3 and Si–CH_2 bonds resulting in methane, ethane, 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane, 1,3,5,7-tetrasilaadamantane, and oligomers. An attempted trapping of DMSE with water gave a very complex mixture of the products, some of which could arise from DMSE intermediacy [198,199]. The pyrolysis onset of 1,1,3,3-tetramethyl-1,3-disilacyclobutane in a helium-flow pulse system was observed at 600 °C likewise the pyrolysis onset of its non-strained homolog, 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane. In fact the pyrolysis onset of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was observed 150 °C above the onset of DMSCB 2+2 cycloreversion. DMSE was not trapped below 600 °C indicating that the thermal stability of 1,1,3,3-tetramethyl-1,3-disilacyclobutane is not attributable to its equilibrium with DMSE. The latter was trapped with methanol above 600 °C, but the overall process was a complex one because of the contribution of the chain reactions initiated by the methyl radical formed by the homolysis of the Si–CH_3 groups[26, 27] [49]. Similarly, a copyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane and benzoaldehyde in a nitrogen-flow system failed to trap DMSE at 500 and 600 °C. Only at 700 °C it was accomplished by the isolation of cyclosiloxanes and styrene indicating the DMSE intermediacy [161]. The extreme temperatures make this method of no synthetic value [49,134,161]. Since the Si–C bond energy in the four-membered ring is lower than the energy of the Si–CH_3 bond homolysis by the value of the strain energy (18 kcal mol^{-1} [39]) it was suggested that the observed thermal stability in the temperature range above 450–600 °C is apparent because of a non-productive equilibrium between 1,1,3,3-tetramethyl-1,3-disilacyclobutane and 1,4-diradical formed by the cleavage of the Si–C bond of the four-membered ring [56].

2.4.3. *1,1,2,3,3-Pentamethyl-1,3-disilacyclobutane and 1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes*

A pyrolysis of 1,1,2,3,3-pentamethyl-1,3-disilacyclobutane at 630 °C yielded 1,1,3,3-tetramethyl-1,3-disilacyclopent-4-ene as the only detectable product along with the starting material. It involved a homolytic opening, a hydrogen atom expulsion and an intramolecular attack by a silyl radical on the generated π-bond and a hydrogen loss by the resulting radical [161] (Eq. (74)):

Similarly, *cis*- and *trans*-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes yielded 1,1,2,3,3-pentamethyl-1,3-disilacyclopent-4-ene [161].

2.4.4. *1,3-Dimethyl-1,3-disilacyclobutane*

A pyrolysis of 1,3-dimethyl-1,3-disilacyclobutane does not proceed as a 2+2 cycloreversion resulting in the production of methylsilene. Its decomposition relative rate constant is 50 times greater than that for 1,1,3,3-tetramethyl-1,3-disilacyclobutane. The 1,2-hy-

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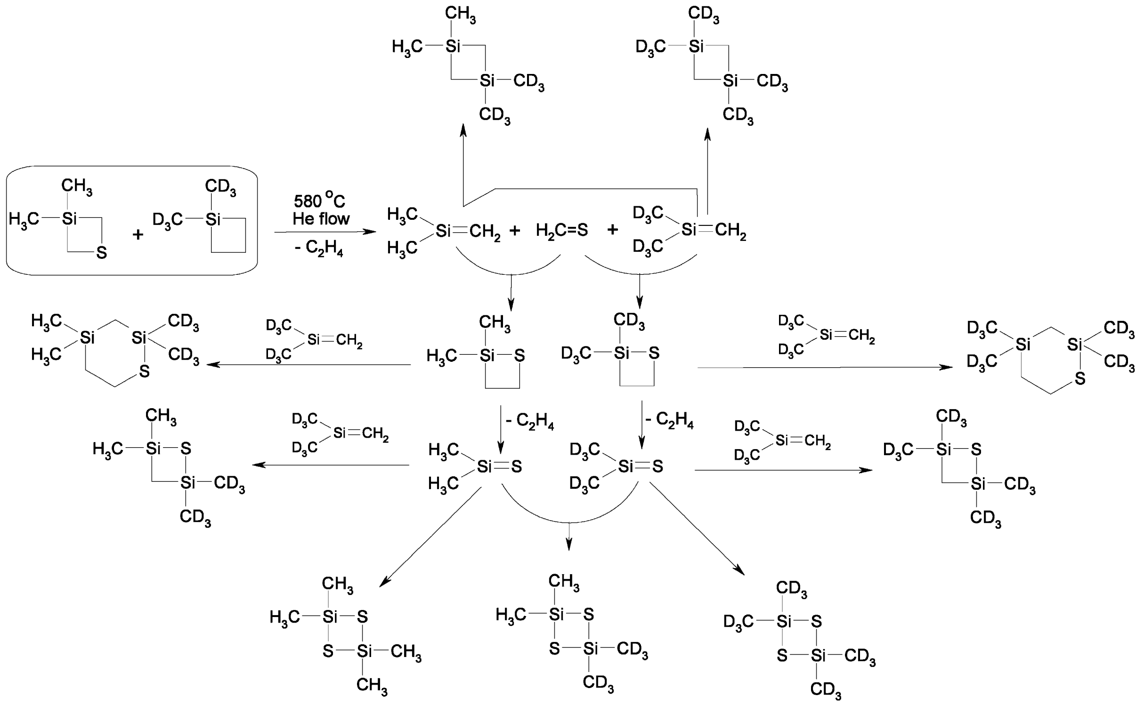
[26] Arrhenius parameters for the decomposition of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, $\log A = 14.4$, $E = 70.7$ kcal mol^{-1} are somewhat similar to those for the pyrolysis of tetramethylsilane, $\log A = 14.3$, $E = 67.6$ kcal mol^{-1} [200].

[27] In the plasma chemical vapor deposition of 1,1,3,3-tetramethyl-1,3-disilacyclobutane the ring opening dominates over Si–CH_3 cleavage [338].



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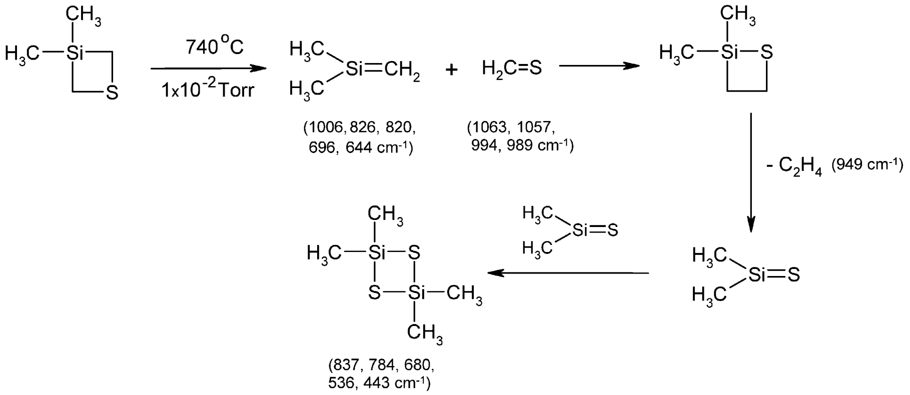
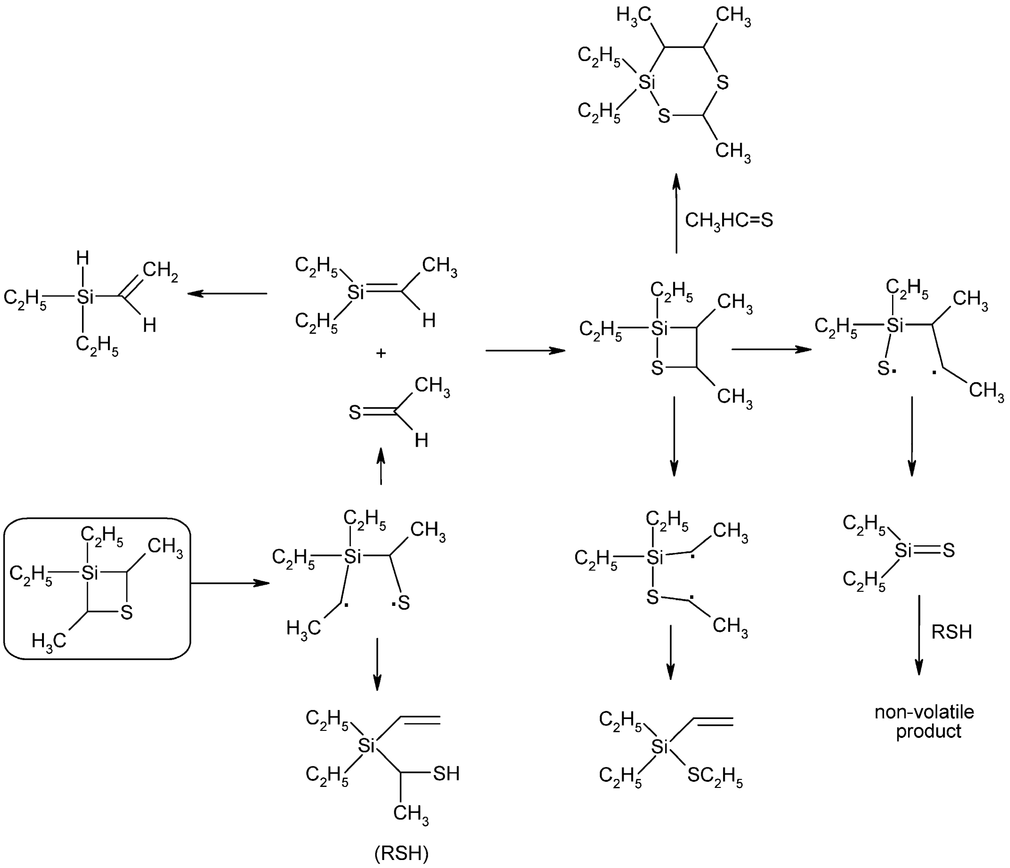


(69)

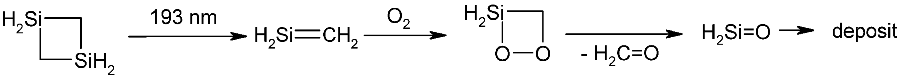
drogen shift from silicon to carbon to yield silylene is the primary step of the reaction [200]. The Arrhenius parameters of the 1,2-hydrogen shift are: $\log A = 14.13$, $E = 61.0$ kcal mol^{-1} [201] (Eq. (75)).

2.4.5. 1,3-Disilacyclobutane

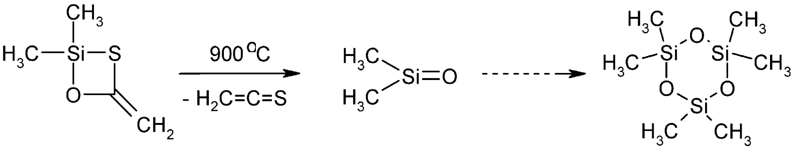
A pyrolysis of 1,3-disilacyclobutane is also a complex process involving no silene resulting from a 2+2 cycloreversion. Its decomposition relative rate constant


CH3HC=S
RSH
non-volatile product
(RSH)

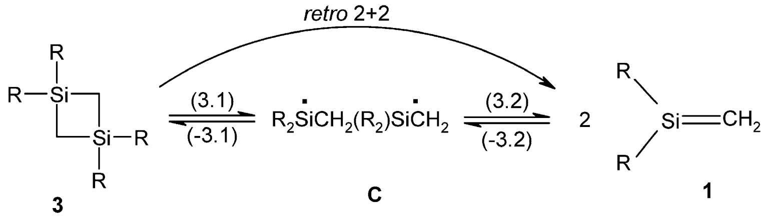
(70)


193 nm
O2
- H2C=O
deposit

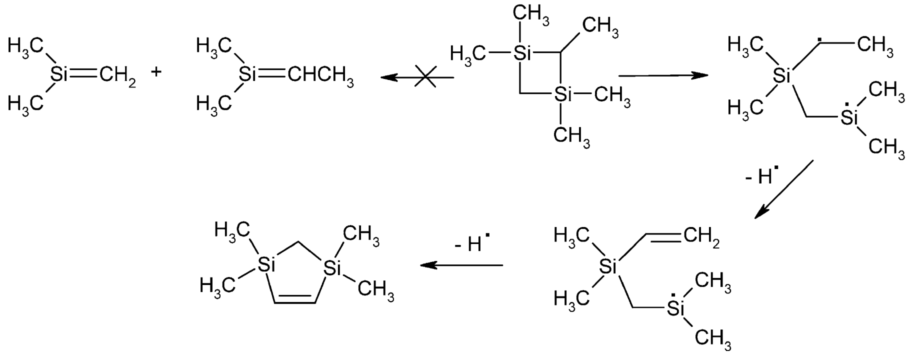
(71)


900 °C
- H2C=C=S

(72)



(73)



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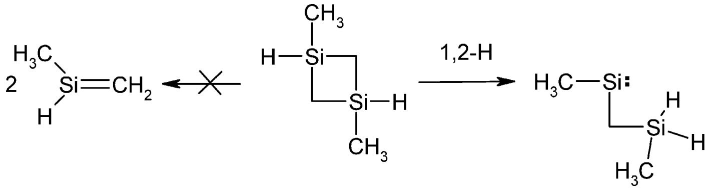
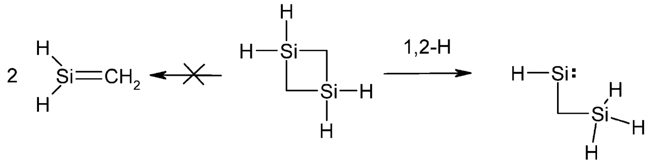


(75)

is 1220 times greater than that for 1,1,3,3-tetramethyl-1,3-disilacyclobutane. The basic reason for its lower thermal stability is the prominent 1,2-hydrogen shift from silicon to carbon with a concomitant formation of silylene [138,200] (Eq. (76)).[28]



(76)

2.4.6. 2,4-Dimethylene-1,1,3,3-tetramethyl-1,3-disilacyclobutane

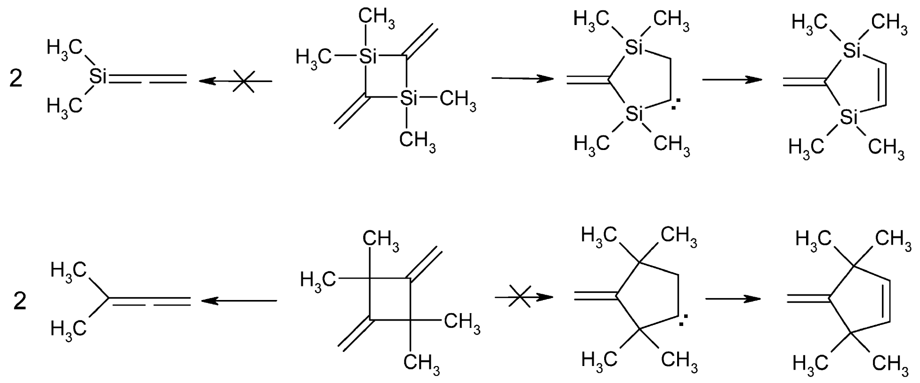
A pyrolysis of 2,4-dimethylene-1,1,3,3-tetramethyl-1,3-disilacyclobutane in a vertical nitrogen-flow system at 600 °C produced 2-methylene-1,1,3,3-tetramethyl-1,3-disilacyclopentene via the intermediacy of carbene resulting from the olefin-to-carbene rearrangement,[29] no 2+2 cycloreversion occurred. On the contrary, its all-carbon analog began to decompose at 550 °C, resulting in no isomerization into the corresponding methylenecyclopentene [167] (Eq. (77)):[30]

---

[28] For rather ambiguous earlier works see [112,134].

[29] The measured first order Arrhenius parameters for the rearrangement were: log $A = 12.48$, $E = 54.09$ kcal mol^{-1} [167].

[30] Ab initio calculations revealed that this was opposite to any predictions which would be made from the ring strain considerations. The calculations showed that for silyl migration the transition state was late and was actually the carbene, while for carbon migration it was early and considerably higher in energy than the resulting carbene [167].



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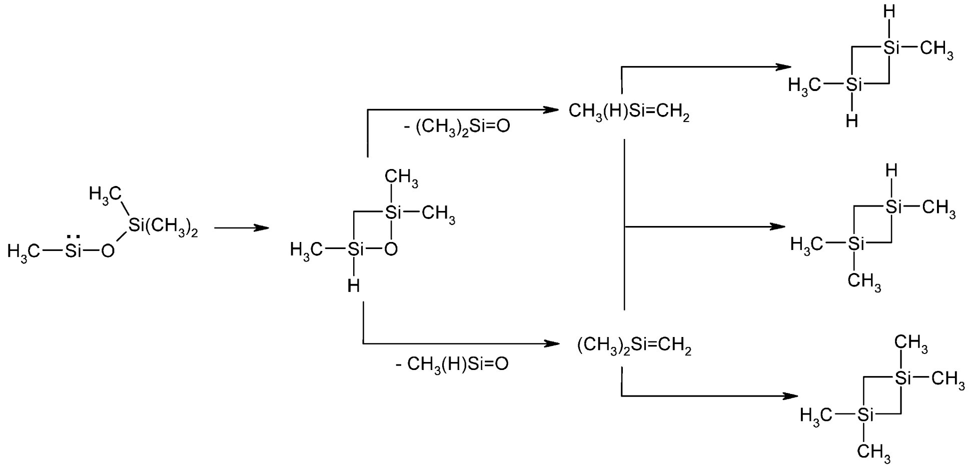


(78)

2.4.7. 1,3-Dimethyl-1,3-diphenyl-1,3-disilacyclobutane

A non-clean decomposition occurs at the low-pressure pyrolysis of the title compound at 700 °C. None the less the authors postulate the existence of the equlibrium between 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane and 1-methyl-1-phenylsilene [141].

2.5. 1,3-Disila-2-oxacyclobutanes

2.5.1. 1,1,3-Trimethyl-2-oxa-1,3-disilacyclobutane

2+2 Cycloreversion of the 1,1,3-trimethyl-2-oxa-1,3-disilacyclobutane intermediate resulting from the cyclization of the corresponding siloxysilylene was postulated to explain the formation of the three 1,3-disilacyclobutanes [202] (Eq. (78)).

However, it seems that such 2+2 cycloreversion is hardly feasible because of its very high endothermicity. Indeed, for the parent 1,3-disila-2-oxacyclobutane the reaction enthalpy is equal to 89.3 kcal mol^{-1} [203].

2.6. 1,3-Disila-2-thiacyclobutanes

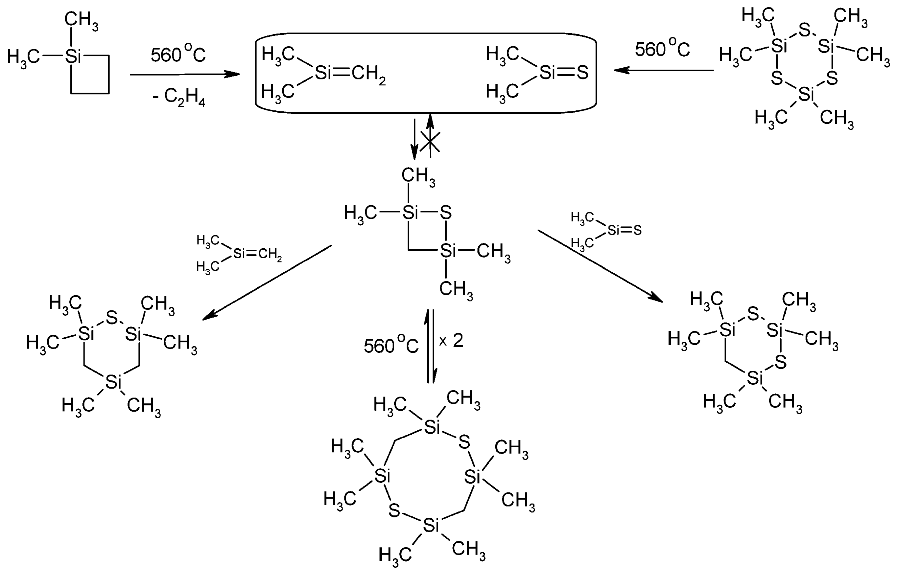
2.6.1. 2,2,4,4-Tetramethyl-2-thia-1,3-disilacyclobutane

The title compound was formed in the pyrolysis of 3,3-dimethyl-3-silathietane (Section 2.3.4.1) and also upon the copyrolysis of DMSCB and tetramethyldisilthiane (Section 2.10.1) or hexamethyltrisilthiane. It did not cyclorevert but rather dimerized. It was also consumed by the insertion of either DMSE or dimethylsilanthione [72,73,188,189] (Eq. (79)).

Such a thermal behavior of 2-thia-1,3-disilacyclobutane systems could be expected since the enthalpy of 2+2 cycloreversion for the parent molecule is 76.0 kcal mol^{-1} [203].

2.7. Cyclodisilazanes

FVT/PES study of a few cyclodisilazane 2+2 cycloreversions resulted in the characterization of a highly

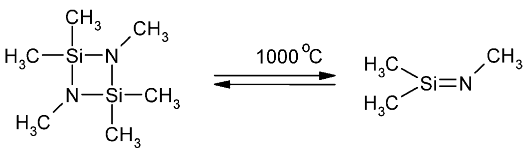


(79)

reactive *N*-alkylated silanimines [169]. The first ionization energy of silanimines originates from the ejection of an electron from the nitrogen lone pair orbital, whereas the second ionization potential arises from the $\pi_{Si=N}$ orbital. In comparison to the homologous imines the important destabilization of the ionization energy associated with $\pi_{Si=N}$ orbital (about 2 eV) relative to $\pi_{C=N}$ ionization originates from the diffuse character of $\pi_{Si=N}$ bond and explains their strong trend to react via a 2+2 cycloaddition [169].

2.7.1. Hexamethylcyclodisilazanes

According to a FVT/PES study hexamethylcyclodisilazane is thermally stable up to 900 °C. Above this temperature the ionizations at 7.9 and 8.3 eV were assigned to trimethylsilanimine, $(CH_3)_2Si{=}NCH_3$. They arise from the ejection of an electron from the nitrogen lone pair orbital and from $\pi_{Si=N}$ orbital of trimethylsilanimine [169] (Eq. (80)).



(80)

However, the extremely high reaction enthalpy of the parent compound's 2+2 cycloreversion, 102.7 kcal mol^{-1}, [203] makes the reaction hardly feasible. In fact, 2+2 cycloreversion is not the only process occurring upon the pyrolysis of hexamethylcyclodisilazane. A decomposition yielding ethylene and acetylene accompanies the 2+2 cycloreversion [23,169].

2.7.2. *N,N'*-Diisopropyl-1,3-disila-2,4-diazane

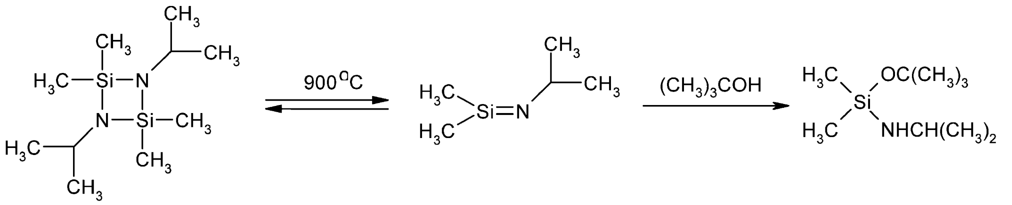
It is stated [23] that upon FVT in the conjunction with PES *N,N'*-diisopropyl-1,3-disila-2,4-diazane is an excellent precursor for silanimine, $(CH_3)_2Si{=}N{-}i{-}C_3H_7$. However, no PES data have been published yet to make a conclusion whether the reaction is really as clean as it is shown in scheme 81. Trapping *N*-isopropyl-1,1-dimethylsilanimine with *tert*-butanol is favored by 2+2 cycloreversion of the title compound [92].

2.7.3. *N,N'*-Di-*tert*-butyl-1,3-disila-2,4-diazane

As it was deduced from a FVT/PES study *N,N'*-di-*tert*-butyl-1,3-disila-2,4-diazane is a good precursor for silanimine, $(CH_3)_2Si{=}NC(CH_3)_3$ in the temperature range 850–930 °C. The 7.4 eV band was assigned to the energetically close ionizations $\pi_{Si=N}$ and $n_{\bar{N}}$. The formation of isobutene at the temperatures above 930 °C might have indicated the formation of silanimine $(CH_3)_2Si{=}NH$ but it was not detected by PES. On the other hand ethylene and acetylene were present in the spectra. In addition, it is stressed that the main decomposition pathway at 900 °C is the loss of methane from the *tert*-butyl groups, leading to the unsaturated cyclodisilazanes [23,92,169] (Eq. (82)).

2.8. 1,3-Diphospha-2,4-disilacyclobutanes

2,4-Diisopropyl-, 2,4-di-*tert*-butyl-, 2,4-dicyclohexyl-, and 2,4-diphenyl-1,1,3,3-tetramethyl-2,4-diphospha-1,3-disilacyclobutanes were subjected to the FVP/HRMS and FVP/PES studies. Only one of them approved itself as a source of phosphasilene [172]. A thermodynamic and kinetic stability of phosphasilenes is reduced



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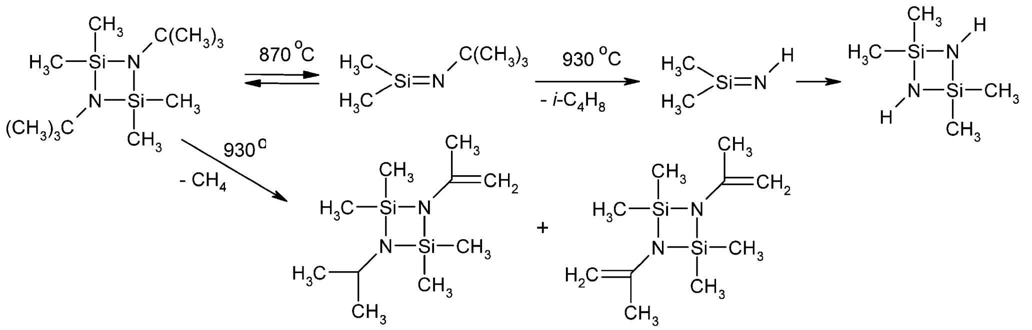

(82)

compared to the corresponding silanimines and is due to the diffuse character of the $3p_{\pi}$–$3p_{\pi}$ overlap (cf. ionizations observed at 7.0 eV for $(CH_3)_2Si{=}P$–*tert*-C_4H_9 and 7.4 eV for $(CH_3)_2Si{=}N$–*tert*-C_4H_9). The ionization of the phosphorus lone pair is stabilized by 0.8 eV, when compared to that of the silanimine's nitrogen. This leads to the conclusion that the compounds containing Si=P bond are rather silaphosphaalkenes than silaphosphaimines [172].

2.8.1. 1,1,3,3-Tetramethyl-2,4-diisopropyl-2,4-diphospha-1,3-disilacyclobutane

The FVP/HRMS study of the title compound revealed no change in the photoelectron spectrum between the room temperature and 1000 °C. However, owing to the distance between the FTP oven and the ionization chamber (ca. 20 cm), the authors could not exclude a 2+2 cycloreversion–2+2 cycloaddition sequence involving the corresponding phosphasilene [172].

2.8.2. 1,1,3,3-Tetramethyl-2,4-di-*tert*-butyl-2,4-diphospha-1,3-disilacyclobutane

The FVP/HRMS study of the title compound showed the presence of the monomeric phosphasilene, $(CH_3)_2Si{=}P$–*tert*-C_4H_9, at the temperatures above 500 °C. In the FVP/PES study the new bands observed at 7.0 and 8.2 eV were associated with the phosphasilene. The formation of isobutene and P-unsubstituted cyclodiphosphasiletane was also detected above 550 °C [172]. The latter is obtained through the intermediacy of the new phosphasilene by the elimination of isobutene and by the dimerization[31] [23] (Eq. (83)).

The endothermicity of such 2+2 cycloreversion for a parent cyclodiphosphasiletane is 61.0 kcal mol^{-1} [203].

2.9. Cyclodisiloxanes

The unhindered cyclodisiloxanes are the unstable molecules whose intermediacy was postulated in a number of gas-phase reactions [204,205].[32] The enthalpy of a 2+2 cycloreversion of the parent disiloxane is very high and equals to 98.0 kcal mol^{-1} [203]. Therefore, one cannot expect a 2+2 cycloreversion for the cyclodisiloxane series. More likely they should dimerize to tetrasiloxanes and be good acceptors for the insertion of the transient silenes, silanones, and other transient intermediates of the doubly bonded silicon.

2.10. Cyclodisilthianes

It was pointed out that due to the strong thermodynamic stability the cyclodisilthiane ring does not cyclorevert to two silanthiones at a high temperature [206]. However, ab initio calculations predict its 2+2 cycloreversion enthalpy to be equal to 68.0 kcal mol^{-1}, i.e. much less of that for cyclodisilazane (102.7 kcal

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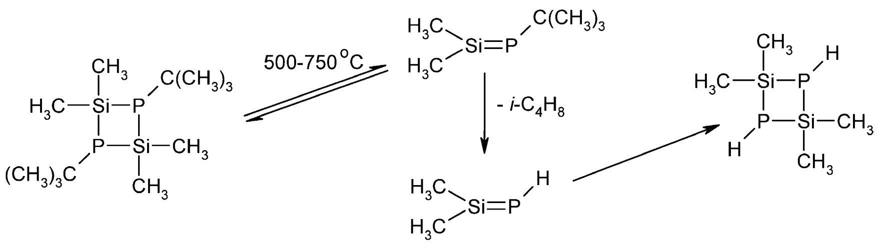
[31] In the original paper [172] a direct loss of isobutene from 1,1,3,3-tetramethyl-2,4-di-*tert*-butyl-2,4-diphospha-1,3-disilacyclobutane is suggested.

[32] Cyclodisiloxanes with bulky substituents are the stable but rather unusual compounds [301].



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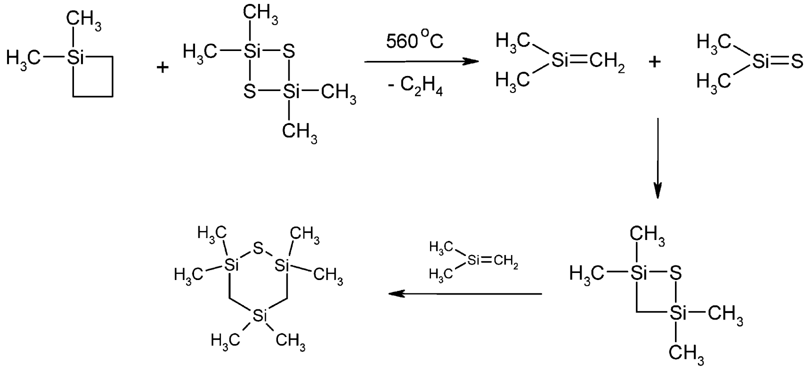

(84)

mol^{-1}) and only a bit higher than that of cyclodiphosphadisiletane (61.0 kcal mol^{-1}) [203]. Taking these reaction enthalpies into consideration one should expect the strongest thermodynamic stability of cyclodisilazane with cyclodisilthiane being less stable and at last cyclodiphosphadisiletane being the most unstable in the series.

2.10.1. Tetramethylcyclodisilthiane

The infrared spectra of tetramethylcyclodisilthiane VLPP products obtained at 730 °C and isolated in argon matrix exhibit mainly the bands of the starting compound [207]. No expected bands for dimethylsilanthione were detected [188,189]. There might be two explanations for this observation: (1) tetramethylcyclodisilthiane does not undergo a 2+2 cycloreversion[33] or (2) cycloreversion occurs, but dimethylsilanthione dimerizes before it reaches the target. The results of the copyrolysis study of tetramethylcyclodisilthiane with a fivefold excess of DMSCB indicate in favor of the latter conclusion. No starting cyclodisilthiane was present among the products owing to the suppression of dimethylsilanthione's cyclodimerization by its 2+2 cycloaddition to DMSE yielding 1,1,3,3-tetramethyl-2-thia-1,3-disilacyclobutane (main reaction product) and a subsequent DMSE insertion into the adduct [72,73] (Eq. (84)).

Furthermore, because of a complete decomposition to yield dimethylsilanthione no tetramethylcyclodisilthiane remains available for DMSE insertion into its Si–S bond (Eq. (85)):

For a liquid-phase 2+2 cycloreversion of tetramethylcyclodisilthiane see Section 5.5.

2.10.2. Tetrakis(*tert*-butoxy)cyclodisilthiane

According to FVT/IR and FVT/MS experiments a 2+2 cycloreversion of tetrakis(*tert*-butoxy)1,3-dithia-2,4-disilacyclobutane is accompanied by a subsequent β-elimination [206,208] (Eq. (86)):

2.10.3. Tetrafluorocyclodisilthiane

An attempt to examine a 2+2 cycloreversion of tetrafluorocyclodisilthiane had failed [47] because the literature procedures for the synthesis of the target compound led the authors to hexafluorodisiloxane and hexafluorodisilthiane.

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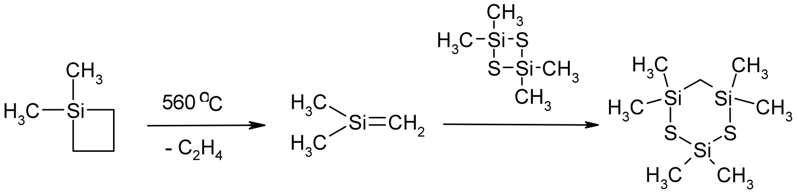
[33] It is pointed out that the thermodynamic stability of the cyclodisilthiane ring is higher than that of cyclodisilazane and cyclodisilaphosphane [339]. It contradicts the 2+2 cycloreversion enthalpies of the parent four-membered rings (see Section 2.10).



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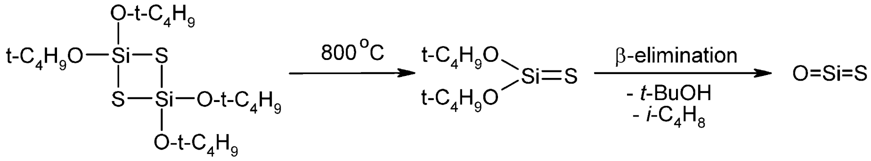

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2.11. 1,2-Disilacyclobutanes

2.11.1. 1,1,2,2-Tetramethyl-1,2-disilacyclobutane

A low-pressure pyrolysis of the title compound at 700 °C in a flow system resulted in ethylene and a complex mixture of the liquid products of which dimethyl-1,3-disilacyclobutanes were the rearrangement products of the transient tetramethyldisilene. However, the main product, 1,1,3-trimethyl-1,3-disilacyclopentane, arose from the rearrangement of 1,1,3,3-tetramethyl-1,2-disilacyclobutane. A 2+2 cycloreversion to two transient DMSE occurred to a lesser extent at the temperatures above 750 °C [209–211] (Eq. (87)).

2.11.2. Octamethyl-1,2-disilacyclobutane

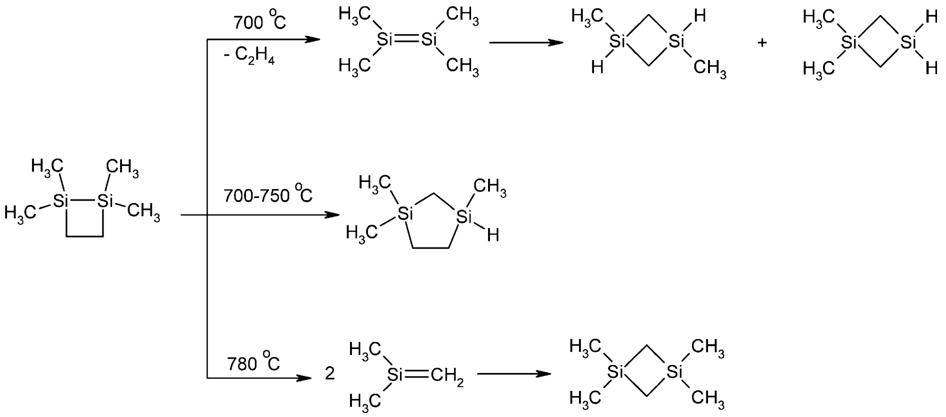
A 2+2 cycloreversion of octamethyl-l,2-disilacyclobutane is not typical at all. Upon pyrolysis [212] the ring scission proceeds by an initial C–C cleavage followed by an intramolecular hydrogen abstraction (Eq. (88)).

2.11.3. 1,1,2,2-Tetrakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane]

A low-pressure gas-phase 2+2 thermocycloreversion of the title 1,2-disilacyclobutane at 597 °C allowed to obtain a photoelectron spectrum of the transient silene and to measure its first ionization potential to be equal to 6.9 eV [213] (for the liquid phase cycloreversions see Section 4.2.3.2) (Eq. (89)).

2.12. 1,2-Disila-3-oxacyclobutanes

Thermal 2+2 cycloreversion of 2,3-disilaoxetane produced by the addition of benzaldehyde to tetramethyldisilene was considered but not proved as one of



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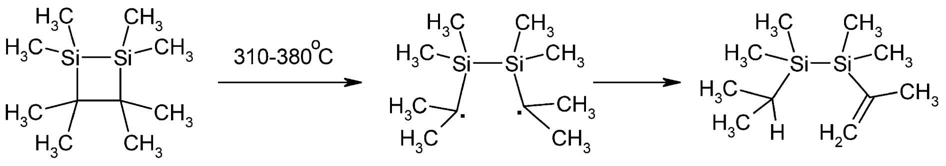

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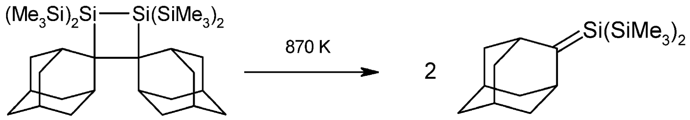


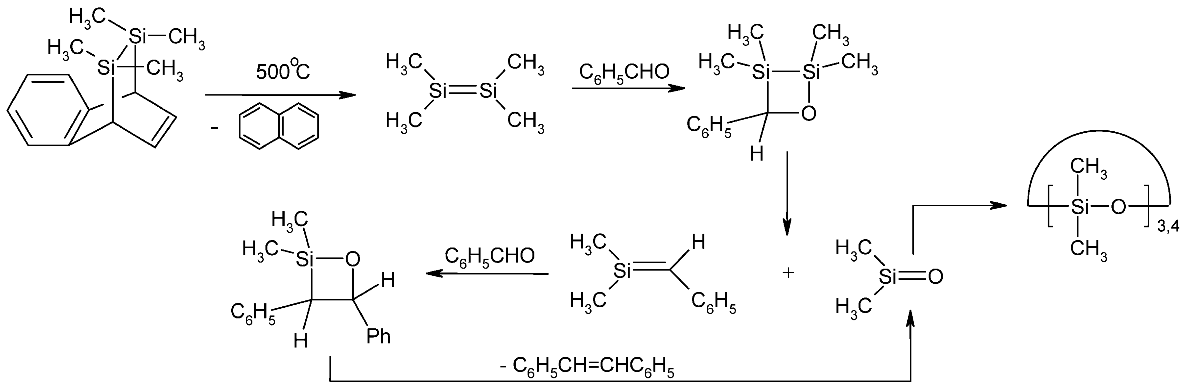
(89)

the several mechanistic possibilities to explain the formation of *trans*-stilbene, hexamethylcyclotrisiloxane, and octamethyltetracyclosiloxane upon the copyrolysis of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes with the excess benzaldehyde [214] (Eq. (90)).

Similarly, the gas phase copyrolysis of 1,1,2,2,4,5-hexamethyl-1,2-disilacyclohex-4-ene and benzaldehyde at 600 °C gave cyclosiloxanes and *trans*-stilbene. Their formation was rationalized by the 2+2 cycloreversion of the transient disilaoxetane followed by the 2+2 cycloaddition of the second benzaldehyde to silene and 2+2 cycloreversion of the resultant silaoxetane [215].

3. Gas phase infrared laser multiphoton and photosensitized thermocycloreversions

The infrared multiphoton excitation and decomposition (IRMPD) of the absorbing silacyclobutanes are in some instances similar to the conventional pyrolysis [216–218]. In the laser-powered homogeneous pyrolysis (LPHP) a thermal decomposition of CO_2 laser-radiation of the non-absorbing silacyclobutanes is induced through the collisions between silacyclobutane and photosensitizing (the energy rich but chemically inert) sulfur hexafluoride, SF_6. A major route of these decompositions is the elimination of ethene and the transient silene formation. The latter polymerizes very efficiently in the gas phase and produces solid materials deposited on a substrate of choice. The progress of the precursor's decomposition and that of the polymer's formation is enhanced at the higher laser outputs and the pressures which cause an increase in the effective temperature from 600 to 1000 K. The formation of the polymers is ascribed to the elimination of the surface effects and the presence of a small hot zone, wherein the temperature gradients and the high concentrations of silenes favor polymerization [219]. Both IRMD and LPHP of silacyclobutanes are the thermal processes. They take place from the vibrationally excited ground states which make them different from the UV laser-induced photochemical decomposition (see Section 4)



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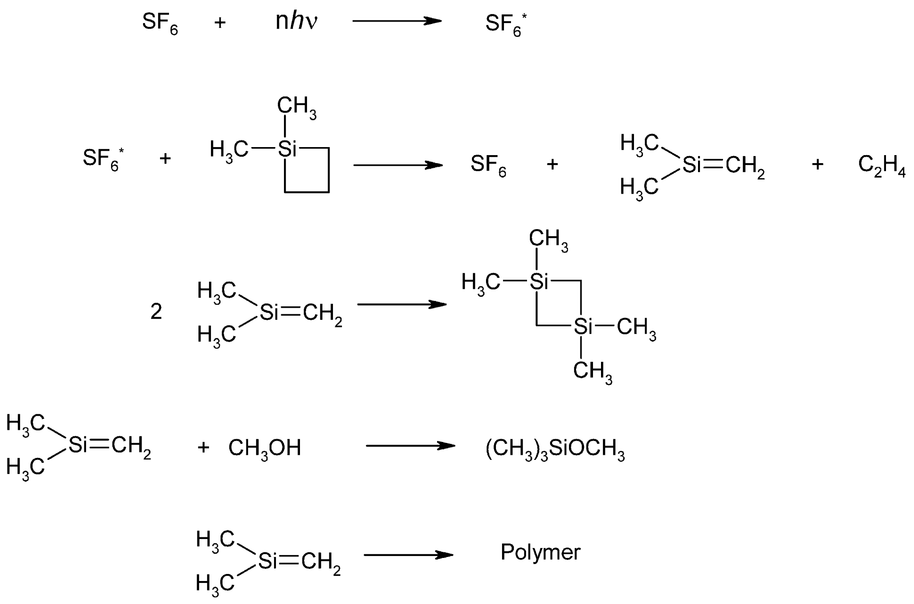


(91)

which in its turn occurs from the electronically excited states [218].

3.1. 1-Silacyclobutanes

3.1.1. 1,1-Dimethyl-1-silacyclobutane

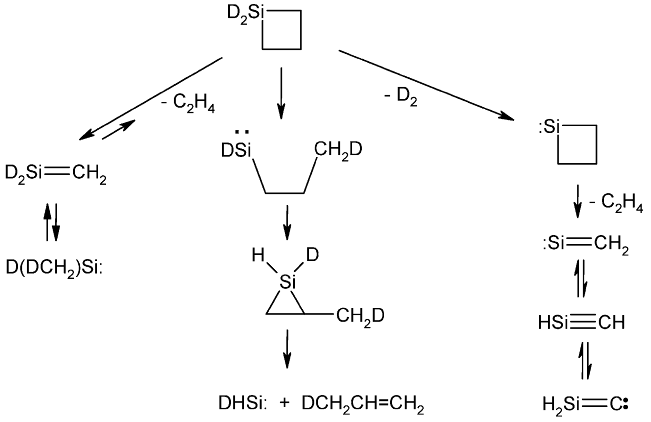
LPHP of 5–15 Torr of DMSCB and 2–3 Torr of SF_6 yielded ethene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane so that 80% of the transient DMSE was recovered and the remaining 20% of DMSE resulted in the polymer formation. Experiments with the added methanol showed that the ratio of the adduct, $(CH_3)_3SiOCH_3$, to 1,1,3,3-tetramethyl-1,3-disilacyclobutane is increased monotonically with the CH_3OH pressure growth. DMSE was also trapped with 1,3-butadiene [82]. The results can be described by the following reactions (Eq. (91)):

The same reaction was induced by irradiating the sample with P(50) [00^01–10^00] laser emission line at 914.42 cm^{-1} which overlaps the ring stretching vibrations of DMSCB. It was found that the longer irradiation or the higher power densities could drive the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane to a completion [220]. The reaction with the added hidrogen chloride is indicative of the intermediacy of transient DMSE.

An IR laser-induced SF_6 photosensitized decomposition of DMSCB in the presence of some common monomers, i.e. vinyl acetate, allyl methyl ether, acrolein, methyl vinyl ether, methyl acrylate, methyl methacrylate was studied at a mean effective temperature range 427–527 °C [221]. An intermediate DMSE was trapped by these monomers or by the products of their thermal decomposition to yield both volatile and viscous or solid organosilicon compounds. DMSE was suggested to react with unsaturated methyl ethers to yield methoxytrimethylsilane and to undergo a copolymerization with methyl acrylate [221].

3.1.2. 1-Silacyclobutane

An IR laser-induced SF_6 photosensitized decomposition of 1-silacyclobutane results in the elimination of ethylene and propylene (3–4% of ethylene) and the formation of a transparent deposit due to a polymerization of methylsilene and 1,1-dimethylsilylene [222]. A direct excitation by a pulsed CO_2 laser radiation causes infrared multiphoton decomposition (IRMPD) of 1-silacyclobutane resulting in a very efficient deposition of Si/C/H and Si/C materials via formation of the transient silene and its rearrangement to methylsilylene [223]. A time-resolved study performed using a grating tuned pulsed TEA CO_2 laser resulted in the identification of the transient silene as the major primary product, which was identified by its optical absorption spectrum with $\lambda_{max} \approx 260$ nm. An observed broadening of the spectrum suggests a further absorption of CO_2 photons by the nascent silene leading to the formation of the 'hot' molecules [224]. The mechanism of silacyclobutane's decomposition was refined when studying the laser induced homogeneous SF_6-photosensitized decomposition of 1,1-dideuterio-1-silacyclobutane [225]. It was stated that the identified volatile products and the hydrogen and deuterium content in them are in accord with 1,2-H(D)-shift in the intermediate silene and with the radical reactions (Eq. (92)).



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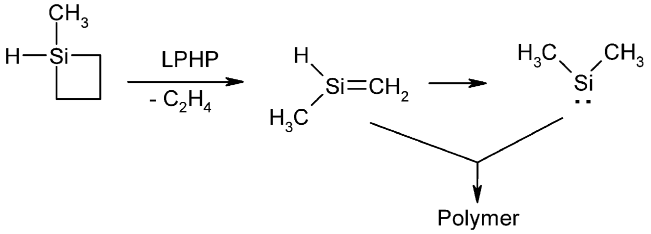
3.1.3. 1-Methyl-1-silacyclobutane

A laser induced thermolysis of 1-methyl-1-silacyclobutane is a highly selective method for the gas phase polymer deposition via the intermediacy of 1-methylsilene and its rearrangement product, dimethylsilylene [225] (Eq. (93)).



(93)

3.1.4. 1-Methyl-1-vinyl-1-silacyclobutane

A continuos-wave, CO_2 laser-induced 2+2 cycloreversion of 1-methyl-1-vinylsilacyclobutane can be conducted as a non-explosive or explosive gas-phase reaction depending on its ratio to SF_6. The former shows the first-order kinetics with Arrhenius parameters ($\log A$ (s^{-1}) = 16.0, $E = 59.7$ kcal mol^{-1}) that are very close to those obtained for its conventional thermal decomposition (see Section 2.2.10.1). Trapping with hexafluoroacetone and tetrafluoroethene confirms the intermediacy of silaisoprene [226,227]. Transient 2-methyl-2-silabuta-1,3-diene (silaisoprene) polymerizes by the participation of the both Si=C and C=C double bonds producing polysilaisoprene. Such polymerization contrasts with the carbon analog (isoprene) which yields polymer containing half of the double bonds to be retained. It is assumed that silaisoprene disappears through a sequence of the 1,4- and 1,2-polymerizations in which the first step gives a reactive polymer with Si=C double bonds driving the reaction to a completion [226] (Eq. (94)).

3.1.5. 1,1-Diethynyl-1-silacyclobutane

A continuos-wave, CO_2 laser-induced 2+2 cycloreversion of 1,1-diethynyl-1-silacyclobutane in the gas-phase involves a clean elimination of ethene to give a transient highly unsaturated diethynylsilene which undergoes a very efficient polymerization to yield a saturated cross-linked polymer via a separate 1,2-polymerization (path A) or via a 1,4-polymerization (path B) [228] (Eq. (95)).

3.1.6. 4-Silaspiro[3,3]heptane

A continuos-wave, CO_2 laser-induced 2+2 cycloreversion of 4-silaspiro[3,3]heptane in the gas-phase involves a clean elimination of ethene with the minor amounts of 1,3-butadiene and silacyclopentene and a deposition of a transparent material on the cold reactor surface. The material balance was indicative of a twofold elimination of ethene yielding 2-silaallene which readily polymerizes. The transient occurrence of 2-silaallene was demonstrated by the scavenging experiments with alcohols. No transparent deposit but volatile dimethyl(dialkoxy)silanes were formed in this case [229] (Eq. (96)):

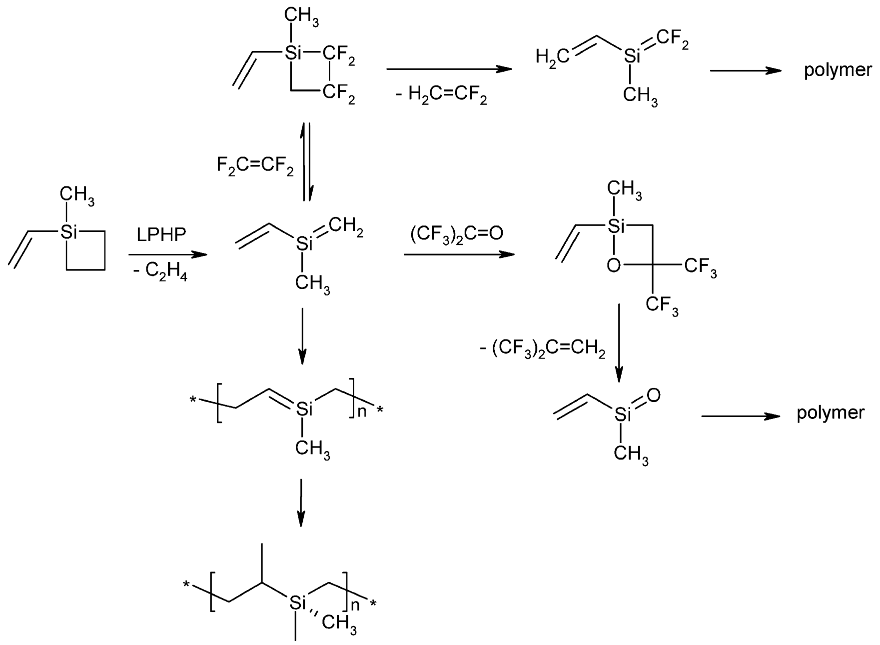
3.1.7. 4-Silaspiro[3,4]octane

4-Silaspiro[3,4]octane cycloreverts under a continuos-wave, CO_2 laser-induced gas-phase pyrolysis to yield ethene and a polymer of a transient 1-methylene-1-silacyclopentane. Along with ethene small amounts of gaseous hydrocarbons are also formed (11 wt.%) together with a very minor liquid portion (about 5 wt.% of 4-silaspiro[3,4]octane reacted) containing in particular bis-1,3-(cyclopentylidene)-1,3-disilacyclobutane [230]: (Eq. (97)).

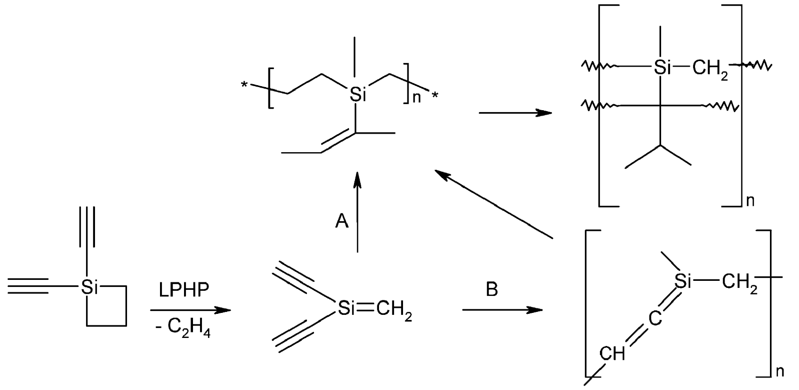
3.1.8. 1,1-Dichloro-1-silacyclobutane

A continuos-wave, CO_2 laser-induced decomposition of 1,1-dichloro-1-silacyclobutane in the gas-phase leads to ethene, methyltrichlorosilane, 1,1,3,3-tetrachloro-1,3-disilacyclobutane and a solid material. The reaction is assumed to occur by a competitive 2+2 cycloreversion and dehydrochlorination. The amount of the starting silacyclobutane decomposed is roughly equal to that of the ethene produced. The following reaction scheme 98 is supported by the experiments carried out with the excess of DCl [231]:

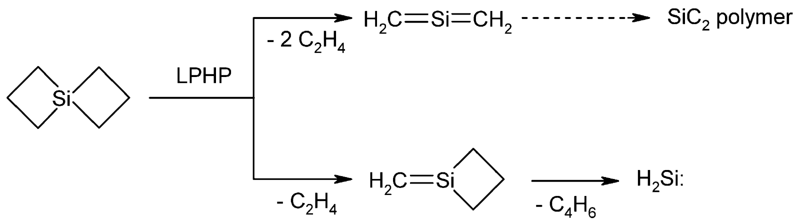
A detection of methyltrichlorosilane-d_2 is considered as an indirect evidence for the intermediacy of silyne, ClSi≡CH [231].


LPHP
- C_2H_4
$F_2C=CF_2$
- $H_2C=CF_2$
polymer
$(CF_3)_2C=O$
- $(CF_3)_2C=CH_2$
polymer

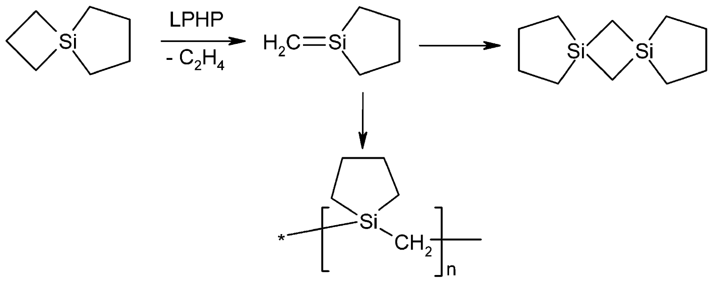
(94)


LPHP
- C_2H_4
A
B

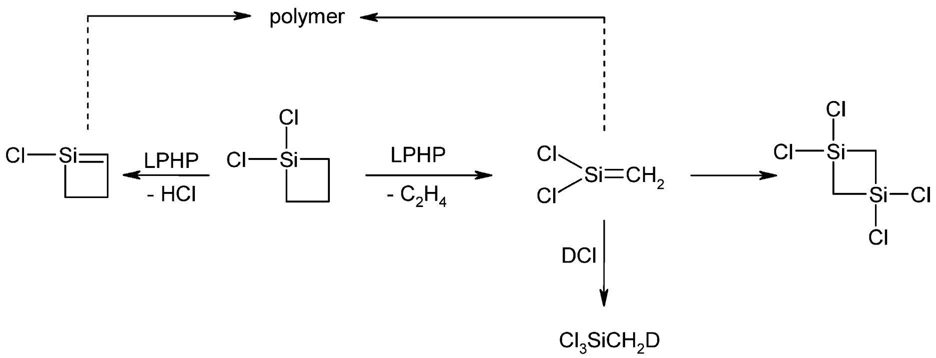
(95)


LPHP
- 2 C_2H_4
$H_2C=Si=CH_2$
SiC_2 polymer
- C_2H_4
- C_4H_6
H_2Si:

(96)



(97)



(98)

3.2. 1,3-Disilacyclobutanes

3.2.1. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane

1,1,3,3-Tetramethyl-1,3-disilacyclobutane was found to absorb a P24 line of the 10.4 μm CO_2 band. An extensive decomposition resulted in a large number of hydrocarbons, the most prominent of which was C_2H_4 as well as a whitish yellow polymer. The high yield of hydrocarbons implies that the other processes of decomposition apart from 2+2 cycloreversion are occurring. In the experiments with added methanol and ammonia [82] and hydrogen chloride [220] the adducts formed indicated the transient presence of DMSE.

3.2.2. 1,3-Disilacyclobutane

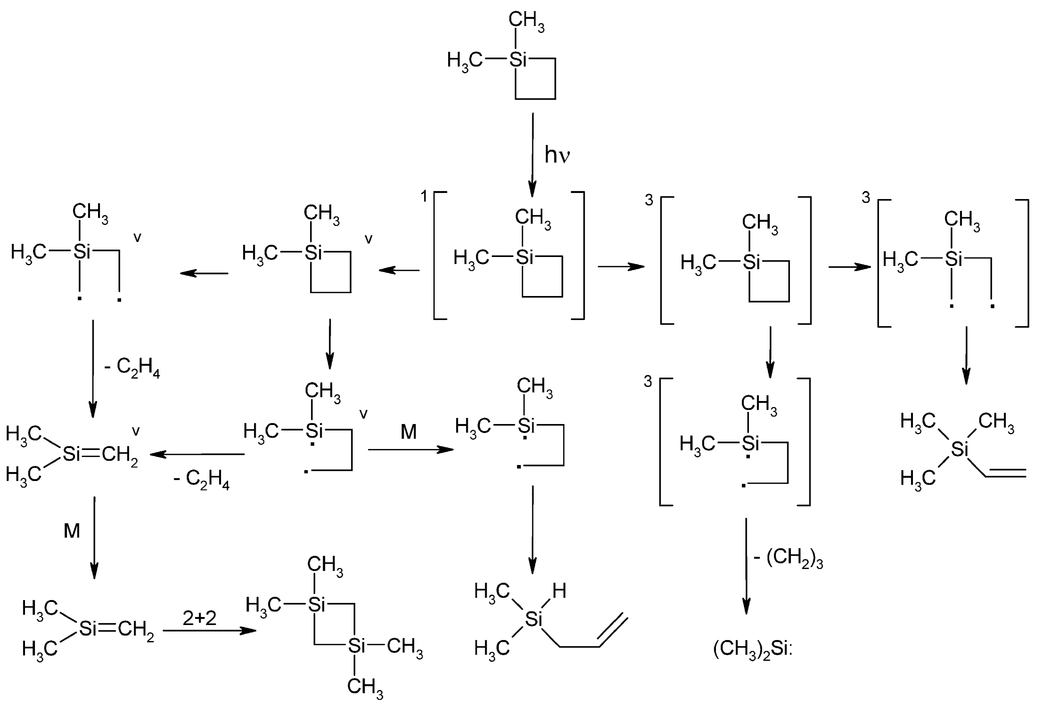
An IRMPD of 1,3-disilacyclobutane results in a very efficient deposition of Si/C/H and Si/C materials via the formation of a transient silene and its rearrangement to methylsilylene [223]. A time-resolved study performed using a grating tuned pulsed TEA CO_2 laser resulted in a transient silene, $\lambda_{max} \approx 260$ nm. At a high fluence the transient absorption signals become very complex owing to the onset of a number of the reactions and the formation of several species which appear to have strong absorption in 250–650 nm region [224].

4. Photochemical 2+2 cycloreversion

A photochemical silene formation proceeds with useful efficiencies from silacyclobutanes containing alkyl, vinyl, ethynyl, silyl, and phenyl substituents at silicon, and possesses a UV absorption maxima between 190 and 250 nm [232]. Also 2+2 photocycloreversion occurs for silacyclobutanes containing a ring Si–Si bond. (see Sections 4.2.3.1, 4.2.3.2, 4.2.4, 4.2.4.1, 4.2.5, 4.2.5.1, 4.2.6 and 4.2.6.1)

For 1,1-dialkyl-substituted 1-silacyclobutanes that absorb below ~230 nm the reaction is initiated from the lowest (σ,σ*) excited singlet state by the cleavage of one of the ring Si–C bonds to form a biradicaloid intermediate that cleaves to silene and alkene, recloses to the starting material, and undergoes an intramolecular disproportionation if an alkyl substituent is present at C2 [233]. The one-bond and two-bond cleavage processes of monosilacyclobutanes reflect a strong preference for scission of a Si–C bond in the excited state, whereas in the ground state a weaker C–C bond is initially broken [234].

The situation becomes different in case of a phenyl substituent being the primary chromophore. 1,1-Diphenyl-1-silacyclobutane produces 1,1-diphenylsilene with a reasonable efficiency, and time-resolved experiments



(99)

showed that silene's formation occurs on the nanosecond time scale [232]. The reactive excited state is most likely the lowest excited singlet state of predominantly benzenoid π,π* character. For efficient cleavage to occur the ring Si–C bonds must be weakened. So the lowest benzenoid excited singlet state is presumably a mixed with σ,σ*, σ,π*, or π,σ* configuration that activates the ring toward the cleavage [232].

4.1. Gas phase photocycloreversion

4.1.1. 1-Silacyclobutanes

4.1.1.1. 1,1-Dimethyl-1-silacyclobutane. The gas phase photolysis of DMSCB was studied at 147 nm light. The major products of the photodissociation were ethylene and the inferred coproduct, DMSE, which is produced with some excess internal energy. Besides, the presence of an uncharacterized reaction of DMSE is estimated [235].

The gas phase photolysis of DMSCB was studied at $185 < \lambda < 210$ nm. The major products of the photodissociation were ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Under these conditions DMSE oligomerization was established in addition to its homogeneous cyclodimerization [236].

Being directly photolyzed DMSCB decomposes at 254 nm[34] predominantely to ethene and DMSE arising from a singlet state. In the presence of benzene it decomposes to cyclopropane and dimethylsilylene being the result of sensitization by triplet benzene [237]. A study of DMSCB photolysis at 147–214 nm showed that of the four primary processes identified the predominant mode of decomposition is to ethylene and DMSE [30]. An evidence from the experiments in the presence of SF_6 suggests that DMSE is initially formed in a vibrationally excited state. Taking earlier results into consideration [237] the following tentative mechanism was suggested [30] (Eq. (99)):

Laser pulsed photolysis experiments at 193 nm were carried out to measure the absorption spectrum of $Me_2Si{=}CH_2$, its absorption cross-section, and the rate constant for $Me_2Si{=}CH_2$ combination. The values obtained are σ (240 nm, base e) $= (1.0 \pm 0.3) \times 10^{-17}$ cm^2 and $k = (3.3 \pm 0.8) \times 10^{-11}$ $cm^3\ s^{-1}$ [30].

4.1.1.2. 1-Silacyclobutane. A laser photolysis of 1-silacyclobutane in the gas-phase using an ArF laser operating at 193.3 nm is dominated by 2+2 cyclorever-

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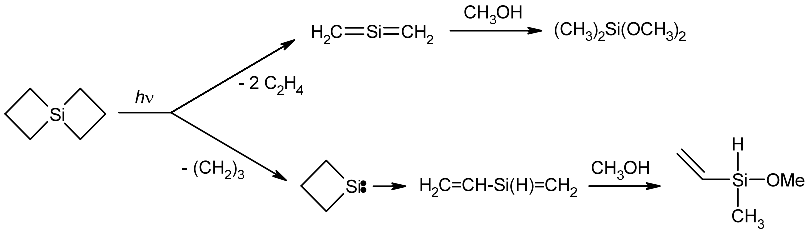
[34] The molar extinction coefficient of 1,1-dimethyl-1-silacyclobutane at 254 nm is $\cong 0.2\ M^{-1}\ cm^{-1}$.



(100)

sion and results in the deposition of polycarbosilanes formed by the polymerization of the transient silene. The energy delivered by the photons corresponded to 148 kcal mol^{-1} which was twice and a half higher than the activation energy of silacyclobutanes' 2+2 cycloreversion [137]. A 193 nm (ArF) laser flash photolysis yields the transient absorption spectrum with $\lambda_{max} \approx 260$ nm which is narrower compared to that obtained by IRMPD. A striking similarity between the results of IRMPD and those of 193 nm photolysis suggests that the initial transient species in either case are the same, i.e. the r_o-vibrationally excited silene [224].

4.1.1.3. 1-Methyl-1-silacyclobutane. A laser photolysis of 1-methyl-1-silacyclobutane in the gas-phase (ArF laser operating at 193.3 nm) is also dominated by a 2+2 cycloreversion and a deposition of polycarbosilanes formed by a polymerization of transient 1-methylsilene [137]. A 193 nm photolysis of gaseous 1-methyl-1-silacyclobutane with a laser fluence of 50 mJ cm^{-2} yields 1-methylsilene which decays exclusively by a dimerization to form 1,3-dimethyl-1,3-disilacyclobutane as a stable product with an estimated rate constant $(2.4\pm0.5)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [238].

4.1.1.4. 1,1,3-Trimethyl-1-silacyclobutane. A direct photolysis of 1,1,3-trimethyl-1-silacyclobutane (5 Torr) at 147 nm produces mainly propene, a product of its 2+2 cycloreversion. The significant yield of ethene (19% of propene) is suggested to arise from ethylidene's expulsion. At 254 nm a direct photolysis produces no hydrocarbons which exceed 8% of the propene yield. In the oxygen scavenged photolysis at 254 nm propene accounts for 88% of all the observed hydrocarbons. Adding benzene until it constituents 90% of the sample mixture decreases the propene yield to 63% of the hydrocarbon production and increases the relative yield of isobutene by more than a factor of six. Further modification of the reaction mixture by the addition of xenon results in significant amounts of isobutene and methylcyclopropane. Thus, benzene's photosensitization may serve to select dissociation products of 1,1,3-trimethyl-1-silacyclobutane. Increasing the population of the benzene triplet state using a heavy atom, xenon, has the effect of enhancing dimethylsilylene elimination from the ring [239].

4.1.1.5. 4-Silaspiro[3,3]heptane. A direct photolysis of 4-silaspiro[3,3]heptane at 147 nm yields ethylene, propene, and cyclopropane among other less important products. An addition of methanol results in the production of methoxymethylvinylsilane and dimethoxydimethylsilane being both dependent on the methanol concentrations. A tentative explanation for these observations is as follows [240] (Eq. (100)):

4.1.2. 1,3-Disilacyclobutanes

4.1.2.1. 1,3-Disilacyclobutane. A laser photolysis of 1,3-disilacyclobutane using an ArF laser operating at 193.3 nm resulted in the gas-phase polymerization of the transient silene, $H_2Si=CH_2$ [137]. The latter was identified by its UV spectrum ($\lambda_{max}\sim260$ nm). Under the low-laser fluence conditions this species have two decay channels (i) a unimolecular process ($k=2.3\pm0.7\times10^4$ s^{-1}) and (ii) a reaction with the parent compound ($k=3.0\pm0.5\times10^{-13}$ cm^3 M^{-1} s^{-1}). The rate constants for these decay processes were also measured [224].

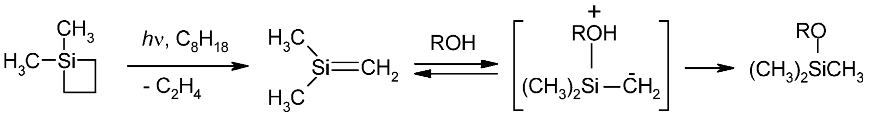
4.2. Liquid phase photocycloreversions

The kinetics and mechanism of a number of characteristic reactions of Si=C double bond was studied in solution using a laser flash photolysis of 1-silacyclobutanes for the generation of transient silenes under the conditions where they may be detected directly [241].

4.2.1. 1-Silacyclobutanes

4.2.1.1. 1,1-Dimethyl-1-silacyclobutane. The far-UV (193 nm) laser flash photolysis of the nitrogen-saturated isooctane solutions of 1,1-dimethylsilacyclobutane (1,1-dimethylsiletane) allowed a direct detection of transient DMSE which (at low-laser intensities) decays with pseudo-first-order kinetics ($\tau\sim10$ s) and exhibits a UV absorption spectrum with $\lambda_{max}\sim255$ nm [242].

DMSE reacts at nearly the diffusion-controlled rate with MeOH in isooctane. A characteristic rapid quenching is observed for the silene with methanol ($k_{MeOH}=(4.9\pm0.2)\times10^9$ M^{-1} s^{-1}), *tert*-butanol ($k_{BuOH}=(1.8\pm0.1)\times10^9$ M^{-1} s^{-1}) and oxygen ($k_{O_2}=(2.0\pm0.5)\times10^8$ M^{-1} s^{-1}). The Arrhenius activation parameters for the reaction with methanol were determined to be $E=-2.6\pm0.6$ kcal mol^{-1} and $\log A=7.7\pm0.3$. The reaction


(101)

of silenes with alcohols is thought to proceed by a mechanism involving a reversible nucleophilic attack at silicon to form an alcohol–silene complex in a fast pre-equilibrium step, followed by its collapse to the products by a proton transfer by means of a competing unimolecular and bimolecular mechanisms [242] (Eq. (101)).

4.2.1.2. 1-Methyl-1-R-1-silacyclobutanes [R = H, C_2H_5, t-Bu, $CH_2Si(CH_3)_3$, CH=CH_2, C≡CH, $Si(CH_3)_3$, OCH_3, $OSi(CH_3)_3$]. Photocycloreversion of 1-methyl-1-R-1-silacyclobutanes (where R = H, ethyl, *t*-butyl, vinyl, ethynyl, trimethylsilyl, and trimethylsilylmethyl) proceeds cleanly yielding ethylene and the corresponding silene. The latter can be trapped as the alkoxysilane, $RSiMe_2OR'$, cleanly upon 193- or 214-nm photolysis in solution in the presence of aliphatic alcohols. 1,1-Alkoxymethyl-1-silacyclobutanes (R = OMe_3, $OSiMe_3$) appear to be inert to photolysis with 193–214 nm light [243].

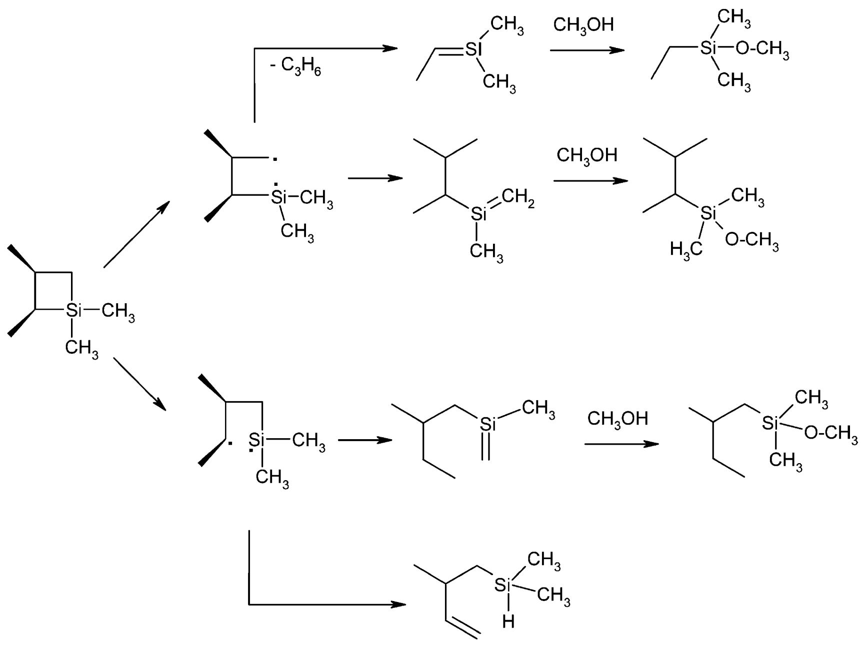
Cycloreversion is thought to involve the lowest excited singlet state in which the ring Si–C bonds are weakened through the population of a σ* molecular orbital. The absolute rate constants for the reaction of aliphatic alcohols with the corresponding silenes in a hexane solution vary by about 2 order of magnitude depending on the alcohol reacting with 1-ethynyl-1-methylsilene the fastest and with 1-methyl-1-trimethylsilylsilene the slowest. The rate constants for the reaction of substituted silenes with methanol and ethanol vary regularly as a function of the single variable substituent at silicon increasing in the order $SiMe_3 \ll CH{=}CH_2$, $CH_2SiMe_3 < Ph < H$, Me, Et, *t*-Bu < C≡CH [243].

Methanol addition proceeds with a negative Arrhenius activation energy and exhibits a small primary deuterium kinetic isotope effect in all cases but that of the ethynyl-substituted derivative. These characteristics indicate silenes to react by a common mechanism involving a reversible formation of a silene–alcohol complex which collapses to alkoxysilane by a rate-limiting, entropy-controlled proton transfer from the oxygen to carbon. The rate constants for the reaction of the nine silenes of the type $R(Me)Si{=}CH_2$ with methanol, ethanol, and *t*-butanol correlate with a three parameter function incorporating resonance, inductive, and steric substituent parameters. The signs and magnitudes of the coefficients indicate that the resonance and the inductive effects act in opposite but roughly equal fashions on the kinetic stability of the transient 1-methylsilenes towards their addition. Silene's reactivity is reduced by π-electron acceptor and/or σ-electron donor substituents at silicon most likely through an effect on the degree of electrophilicity at silicon which affects the complexation step and the degree of nucleophilicity at carbon which at its turn effects the proton-transfer step. Steric effects can act to reinforce, cancel, or even reverse the electronic effects of substituents at silicon on the intrinsic kinetic stability of the Si=C bond [243].

4.2.1.3. 1,1,2,3-Tetramethyl-1-silacyclobutane. Upon 185 nm photolysis of *(E)*- and (*Z*)-1,1,2,3-tetramethylsilacyclobutanes in 0.5 M methanol in pentane [233,234] 3-butenylsilane and methanol adducts were the sole products of Si–C one bond cleavage. In the excited state the cleavage to isomeric 2-butenes is by factor 2–3 over the cleavage to propene. Both (*E*)- and (*Z*)-butenes are formed stereospecifically. A different set of products from 1,4-diradical's disproportionation is obtained in the gas pyrolysis of 1,1,2,3-tetramethylsilacyclobutanes (see Section 2.2.13.6) (Eq. (102)).

4.2.1.4. 1,1-Dialkyl-2-phenyl-1-silacyclobutanes. An irradiation of 1,1-dimethyl-2-phenyl-1-silacyclobutane in a degassed methanol-*O*-d_1 at 0 °C with a 450-W Hanovia medium pressure mercury lamp did not lead to a formation of 2+2 cycloreversion products. Neither styrene and trimethyl-d_1-methoxysilane (an adduct of methanol to DMSE), nor ethylene and benzyl-d_1-dimethylmethoxysilane (an adduct of methanol to 1,1-dimethyl-2-phenylsilene), but rather an adduct of methanol to starting compound, 3-phenyl-3-d_1-propyldimethylmethoxysilane was formed in a quantitative yield [162]. Similarly, the photolysis of 1,1-di-*tert*-butyl-2-phenyl-1-silacyclobutane in methanol leads to ring opening and addition of methanol to produce di-*tert*-butylmethoxy(3-phenylpropyl)silane. It was stated that alkyls at silicon atom facilitate methanol addition, whereas aryls assist ethylene elimination [132] (Eq. (103)).

Nevertheless, it was found later that the photolysis of 1,1-dimethyl-2-phenyl-1-silacyclobutane yields, indeed, styrene and DMSE evidenced by the formation of methyldiphenylmethoxysilane [244]. But the formation



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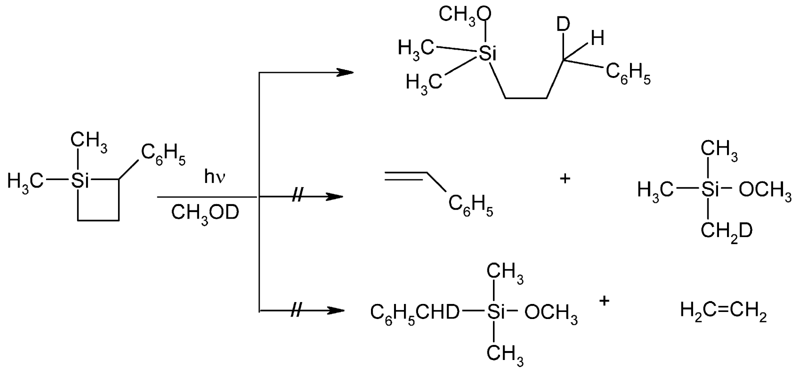


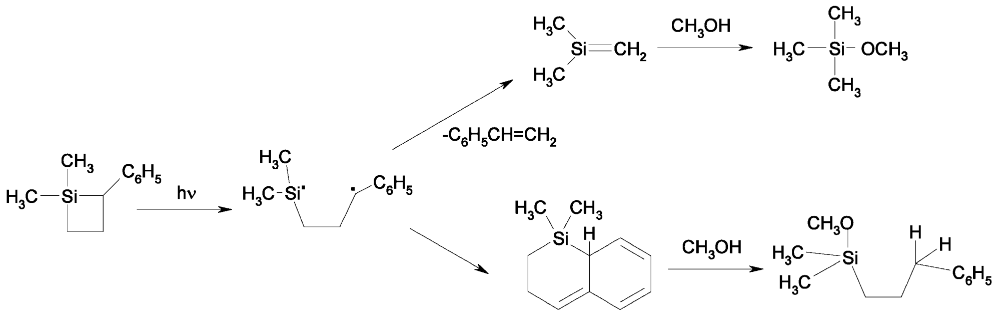
(103)

of 3-phenyl-3-propyldimethylmethoxysilane was supposed to be not due to a nucleophilic trapping of the 1,4-biradical/zwitterion formed by a cleavage of a single silicon–carbon bond in the silacyclobutane's excited state as it was ascribed earlier [132,162]. It was proved that the formation of the latter methoxysilane is due to the reaction of methanol with the isotoluene derivative resulted from the photochemical [1,3]-rearrangement of 1,1-dimethyl-2-phenyl-1-silacyclobutane, a so-called 'masked' benzylsilane (see Sections 4.2.1.8 and 4.2.1.9) [244] (Eq. (104)):

4.2.1.5. 1-Phenyl-1-silacyclobutane. 1-Alkyl-1-phenyl-, 1-methyl-1-(2-phenylethynyl)-, and 1-methyl-1-(4′-biphenylyl)-1-silacyclobutanes. A direct photolysis (254 nm) of the title 1-phenyl-1-silacyclobutanes leads to the formation of ethylene and the corresponding 1-phenylsilenes which can be trapped by water, alcohols, methyltrimethoxysilane, triethoxysilane, and etc. [232,245–247] (Eq. (105)).

The reaction of 1-methyl-1-phenyl-1-silene with acetone affords silyl enol ether and proceeds much faster in hydrocarbon solvents rather than in acetonitrile [248].

The quantum yield for silene's formation from 1-methyl-1-phenyl-1-silacyclobutane is up to ~8 times lower than those for 1-methyl-1-(2-phenylethynyl)-1-silacyclobutane and 1-methyl-1-(4′-biphenylyl)-1-silacyclobutane [232]. 1-Methyl-1-phenyl-1-silacyclobutane



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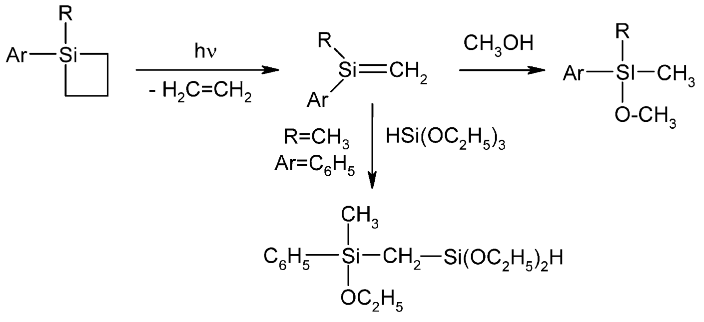

R	Ar
H	C_6H_5
CH_3	C_6H_5
CH_3	$C{\equiv}CC_6H_5$
CH_3	4-C_6H_4-C_6H_5
C_2H_5	C_6H_5
$C(CH_3)_3$	C_6H_5

(105)

undergoes 2+2 cycloreversion from its lowest excited singlet state with a rate constant 10–80 times lower than those of the other two derivatives [232].[35] Silenes were detected by a laser flash photolysis: they have lifetimes of several microseconds, exhibit a UV absorption maxima ranging from 315 to 330 nm, and react with methanol with the rate constants on the order of (2–5) $\times 10^9$ M^{-1} s^{-1} in hexane [232]. A comparison of the singlet lifetimes of the three 1-aryl-1-methyl-1-silacyclobutanes and the corresponding aryltrimethylsilane suggests that the cycloreversion proceeds by a cleavage of the one of the ring Si–C bonds to yield a 1,4-biradicaloid. The relative rates of the cleavage and coupling in the putative 1,4-biradicaloid intermediate are very sensitive to substitution at silicon center; the coupling predominates in the biradical originated from 1-methyl-1-phenyl-1-silacyclobutane, while the cleavage predominates in that from 1,1-diphenyl-1-silacyclobutane [232].

A photolysis of 1-phenyl-1-ethyl-1-silacyclobutane and 1-phenyl-1-*tert*-butyl-1-silacyclobutane in a benzene solution resulted in prochiral silenes that react with a chiral alcohol to give unequal amounts of diastereometric pairs of alkoxysilanes. However, only a sterically hindered isoborneol had gave a good asymmetric induction [246,247].

4.2.1.6. 1,1-Diphenyl-1-silacyclobutane and its para-substituted derivatives. In the absence of the trapping reagent, a laser (248 nm) flash photolysis of continuously flowing, air saturated solutions of 1,1-diphenylsilacyclobutane in dry acetonitrile allows a ready detection of the characteristic UV absorption spectrum of 1,1-diphenylsilene ($\lambda_{max} = 325$ nm, $\tau = 3$ s) which decays with the mixed first- and second-order kinetics [249] and with the production of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane. Arrhenius parameters for the head-to-tail dimerization of diphenylsilene in a hexane solution were determined ($A = 10^9$ M^{-1} s^{-1}, $E = 0$ kcal mol^{-1}) [250,251]. A photolysis of 1,1-diphenyl-1-silacyclobutane in cyclohexane–methanol-d_1 solution at 253.7 nm and 55 °C produces a high yield of diphenylsilene which adds MeOD resulting in diphenylmethoxymethyl-d_1-silane [252]. Trapping diphenylsilene by triethoxysilane in a benzene solution occurs rather as an EtO^- nucleophilic attack on silicon than a free-radical attack resulting in the abstraction of H. The latter leads to a

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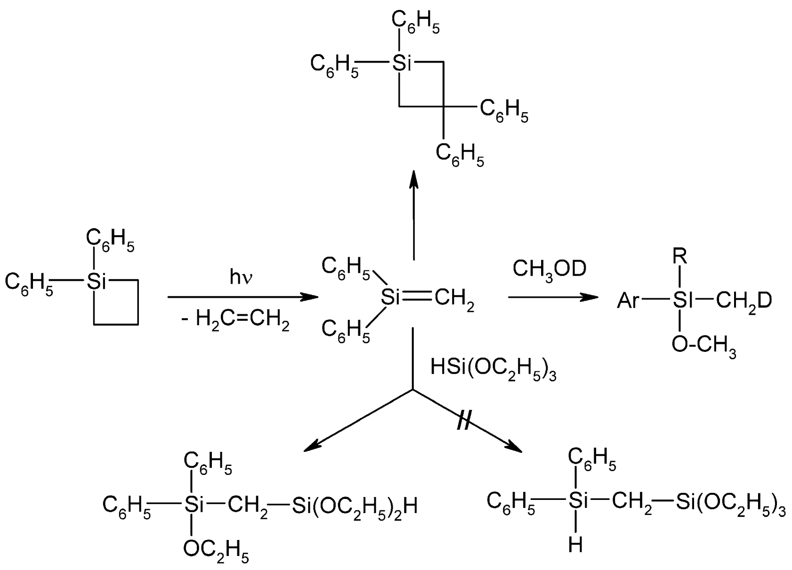
[35] In case of 1-(2-phenylethynyl)-, and 1-(4′-biphenylyl)-1-methyl-1-silacyclobutanes triplet states were easily detectable by laser flash photolysis (the triplet lifetimes are ~14 and 12 μs) and were shown not to be involved in the silene formation [232].



(106)

conclusion that a highly reactive silicon–carbon double bond has a considerable dipolar character [245] (Eq. (106)):

The kinetics of water, methanol, ethanol, 2-propanol, *tert*-butyl alcohol, and acetic acids addition to 1,1-diphenylsilene generated by a steady state and nanosecond laser flash photolysis of 1,1-diphenyl-1-silacyclobutane showed that silene's quenching follows in all cases a linear dependence on a quencher's concentration and proceeds with the rate constants which vary over a range of 4.1×10^8–1.6×10^9 M^{-1} s^{-1} [253]. An addition of methanol, *tert*-butyl alcohol, or acetic acid results in the expected shortening of the lifetime of a silene and a change to clean psuedo-first-order decay kinetics due to the reaction of silene to form the corresponding alkoxysilane [249]. A two step mechanism involving an initial, reversible formation of a silene–alcohol complex, followed by a rate-determining proton transfer to yield the corresponding alkoxysilane was suggested. The addition of both methanol and *tert*-butyl alcohol to 1,1-diphenylsilene are characterized by negative Arrhenius activation energies and strongly negative entropies of activation [249].

The following absolute rate constants were determined for the reaction of diphenylsilene with nucleophiles in a hexane solution at 23 °C (10^8 M^{-1} s^{-1}): 97 ± 4 (n-$C_4H_9NH_2$), 19 ± 2 (CH_3OH), 4.0 ± 0.7 (t-C_4H_9OH), 31 ± 3 (CH_3COOH), 3.8 ± 0.2 ($(CH_3)_2C{=}O$), 2.9 ± 0.3 (t-C_4H_9CHO)[36] [241].

The effects of the solvent, substituents, and temperature on the absolute rate constants for the addition of methoxytrimethylsilane to 1,1-diphenylsilene and four ring-substituted derivatives, $H_2C{=}Si(C_6H_4X)_2$ (X = H, Me, F, Cl, and CF_3) generated by a laser flash photolysis of the corresponding 1,1-diarylsilacyclobutanes were measured [254]. The absolute rate constant for the addition of methoxytrimethylsilane to silenes in a hexane solution are roughly 10–20 times lower than those for the ene-addition of acetone [248], and are roughly 100 times lower than those for the addition of methanol or acetic acid [255]. The data are consistent with a two-step mechanism involving a preassociation of silene and the alkoxysilane to form a Lewis-acid complex which collapses to a product by an intramolecular transfer of trimethylsilyl from the oxygen to the silenic carbon [254] (Eq. (107)).

Lewis-base solvents complex readily with silenes to the extent that depends on the basicity of the solvent, the electrophilicity of the silene, and the temperature. In hydrocarbon or acetonitrile solvents the silene, $(CF_3C_6H_4)_2Si{=}CH_2$, is significantly more reactive than $(C_6H_5)_2Si{=}CH_2$ towards the above reagents and in most cases the Arrhenius activation energies for the reactions are negative. In contrast, the reactivities of the both silenes are reduced in a THF solution, their relative reactivities are reversed, and the positive Arrhenius activation energies for the reactions were obtained in both cases. Therefore, the reaction of a free silene is substantially faster than that of the complexed one and the latter generally acts as a spectator supplying the free silene for the reaction via a rapid pre-equilibrium step. The effect increases with the Lewis basicity of the

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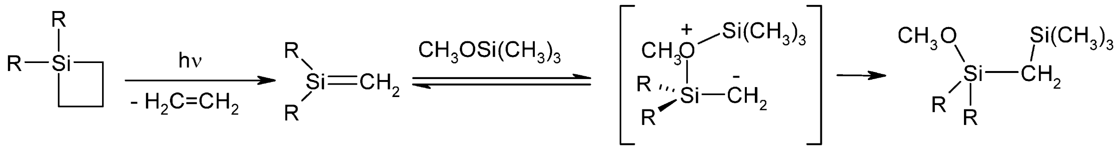
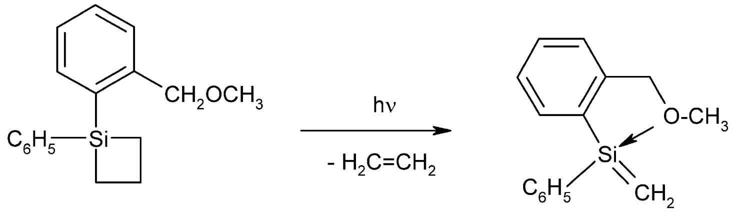
[36] For comparison: diphenylgermene is significantly less reactive than diphenylsilene towards these nucleophiles [241].



(107)

R = p-C_6H_4X, where X = H, CH_3, F, Cl, CF_3



(108)

solvent and with the intrinsic electrophilicity of the silene [256].

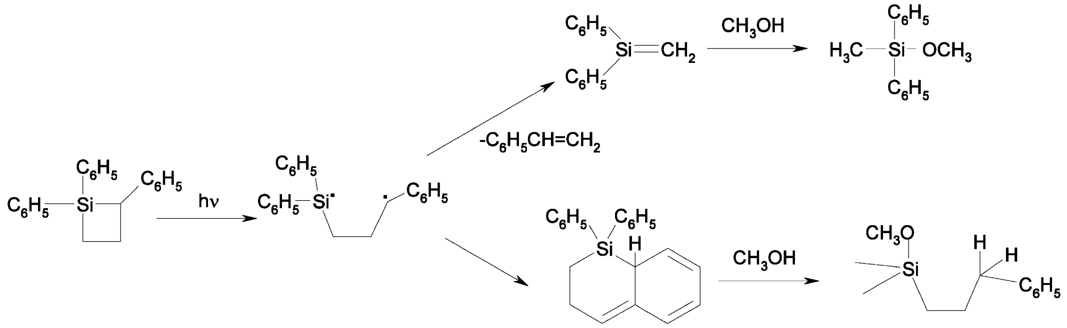
4.2.1.7. *1-Phenyl-1-(ortho-methoxymethylphenyl)-1-silacyclobutane.*

A 2+2 photocycloreversion of 1-phenyl-1-(*ortho*-methoxymethylphenyl)-1-silacyclobutane leads to the formation of a transient silene and three isomers resulting from the migration of the benzylic methoxy substituent coupled with the rearrangement of the carbon skeleton. The UV spectrum and bimolecular reactivity of the silene with various nucleophiles was studied using a flash photolysis technique, endeavoring to quantify the effects of an intramolecular complexation of the ether substituent on the reactivity of the silicon–carbon double bond [257] (Eq. (108)).

4.2.1.8. *1,1-Diphenyl-2-methyl-, and 1,1,2-triphenyl-1-silacyclobutane.*

A photolysis of 1,1-diphenyl-2-methyl-1-silacyclobutane in methanol gave methyldiphenylmethoxysilane. The latter is the addition product of methanol to 1,1-diphenylsilene. It was also formed upon the photolysis of 1,1,2-triphenylsilacyclobutane in a methanol solution [132]. The steady-state photolysis was carried out immediately after the addition of methanol to diminish the dark reaction between 1,1,2-triphenylsilacyclobutane and methanol resulting in the corresponding adduct [258].

A nanosecond laser flash photolysis in dried acetonitrile gave rise to a readily detectable 'short lived' transient absorption of 1,1-diphenylsilene ($\lambda_{max} = 325$ nm). Its lifetime was shortened in the presence of silene traps such as methanol, acetone, or dienes, but was unaffected by saturation of the solution with oxygen. The introduction of carbonyl compounds leads to the formation of the corresponding silyl enol ether accounted for > 80% of the consumed 1,1-diphenylsilene after 10–50% of conversion. No evidence for the formation of siloxetanes (by a formal 2+2-cycloaddition) was obtained [258]. A photolysis of hexane or cyclohexane-d_{12} solution of 1,1,2-triphenyl-1-silacyclobutane in the absence of the added methanol revealed also the species which are stable over the timescale of the experiment and exhibit $\lambda_{max} \sim 335$ nm and ^{1}H-NMR spectrum consistent with isotoluene [244]. It reacted



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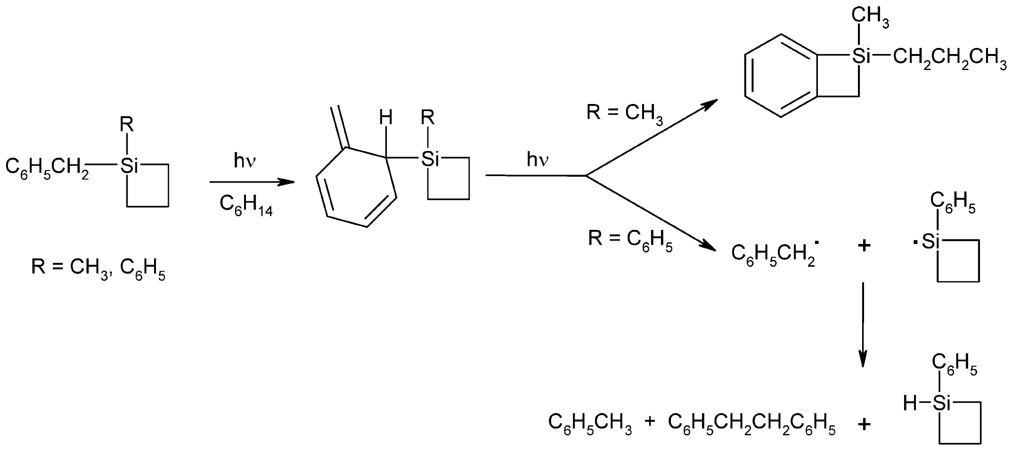


(110)

within 5 s upon the dissolution in methanol to yield methyldiphenylmethoxysilane (Eq. (109)).

4.2.1.9. 1-Benzyl-1-R-1-silacyclobutanes (R = methyl, phenyl). A direct photolysis of 1-benzyl-1-methyl-1-silacyclobutane in a methanolic hexane solution results in no 2+2 cycloreversion [244]. It produces 1-propyl-1-methyl-2,3-benzosilacyclobutene in a quantitative yield by a sequential two-photon process involving the photoactive isotoluene derivative, 1-methylene-6-(1-methylsilacyclobutyl)-2,4-cyclohexadiene, which was identified by ^{1}H-NMR and UV absorption spectra. In contrast, a direct irradiation of 1-benzyl-1-phenyl-1-silacyclobutane under similar conditions results in the formation of a complex mixture of products consistent with the competing formation of 1-benzyl-1-phenylsilene and benzyl- and 1-phenyl-1-silacyclobut-1-yl radicals (Eq. (110)).

The silene is a transient, which was detected directly by a laser flash photolysis of 1-benzyl-1-phenylsilacyclobutane ($\lambda_{max} = 315$ nm, $\tau \sim 4.5$ s). A free radical formation was shown to be due to the secondary photolysis of a second primary product, 1-methylene-6-(1-phenylsilacyclobutyl)-2,4-cyclohexadiene, which had also been detected and identified by a static UV absorption ($\lambda_{max} = 335$ nm) and ^{1}H-NMR spectroscopy [244].

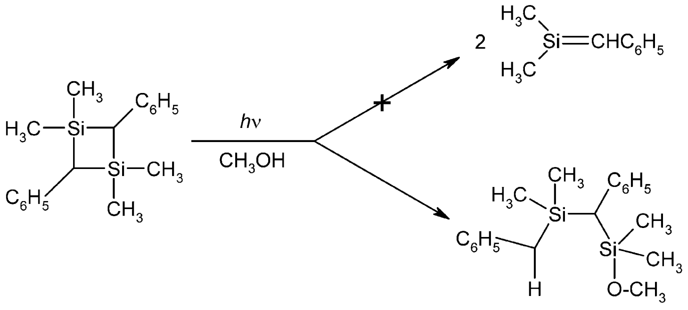
4.2.1.10. 1-tert-Butyl-1-mesityl-, and 1,1-dimesityl-1-silacyclobutane. Photolyses of 1-*tert*-butyl-1-mesityl-1-silacyclobutane and 1,1-dimesityl-1-silacyclobutane in methanol led to the corresponding alkoxysilanes, which are the addition products of methanol to the transient silenes [132].

4.2.1.11. 1-α-Naphthyl-, and 1-phenyl-1-α-naphthyl-1-silacyclobutane. 1-Phenyl-1-α-naphthyl-1-*R*-silacyclobutane and 1-α-naphthyl-1-silacyclobutane were irradiated for 24 h ($\lambda = 254$ nm) in a benzene solution in the presence of a stoichiometric amount of a chiral alcohol (borneol, isoborneol, and methanol). Both derivatives gave no reaction with alcohols, probably owing to the absorption of the α-naphthyl group [246,247].

4.2.1.12. 1-tert-Butyl-1-vinyl-, and 1-phenyl-1-vinyl-1-silacyclobutanes. 1-*tert*-Butyl-1-vinyl-, and 1-phenyl-1-vinyl-1-silacyclobutanes were irradiated for 24 h ($\lambda =$ 254 nm) in a benzene solution in the presence of a stoichiometric amount of a chiral alcohol (borneol, isoborneol, and methanol). Both reactions studied gave almost quantitative yields of alkoxysilanes [246,247].

4.2.2. 1,3-Disilacyclobutanes

4.2.2.1. 1,1,3,3-Tetramethyl-2,4-diphenyl-1,3-disilacyclobutanes. The photolysis of a mixture of *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane in methanol gave only the addition product, 2-methoxy-



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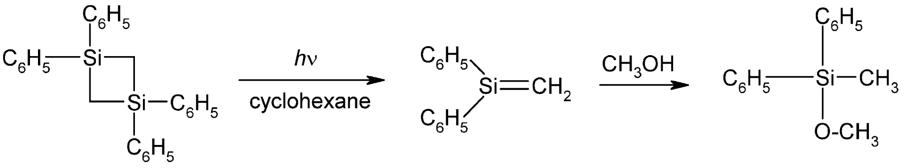

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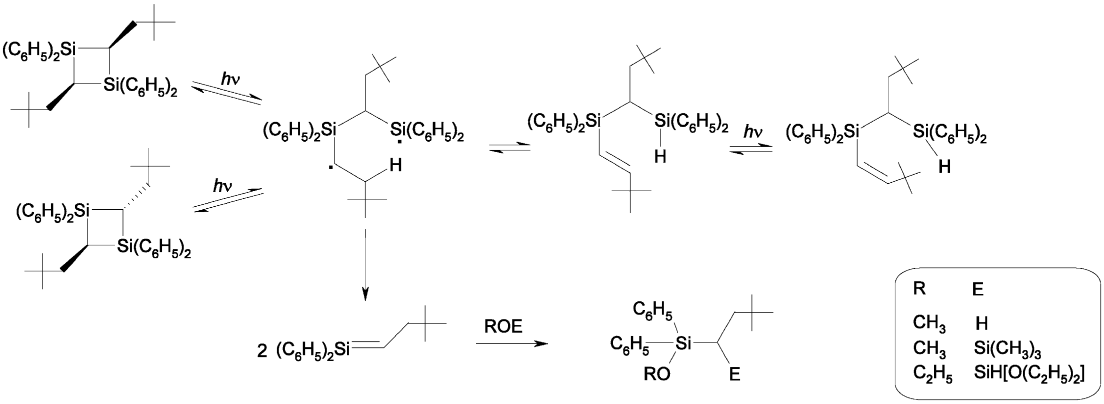


(113)

2,4,4-trimethyl-3,5-diphenyl-2,4-disilapentane. No 1,1-dimethyl-2-phenylsilene trapping was observed [132] (Eq. (111)).

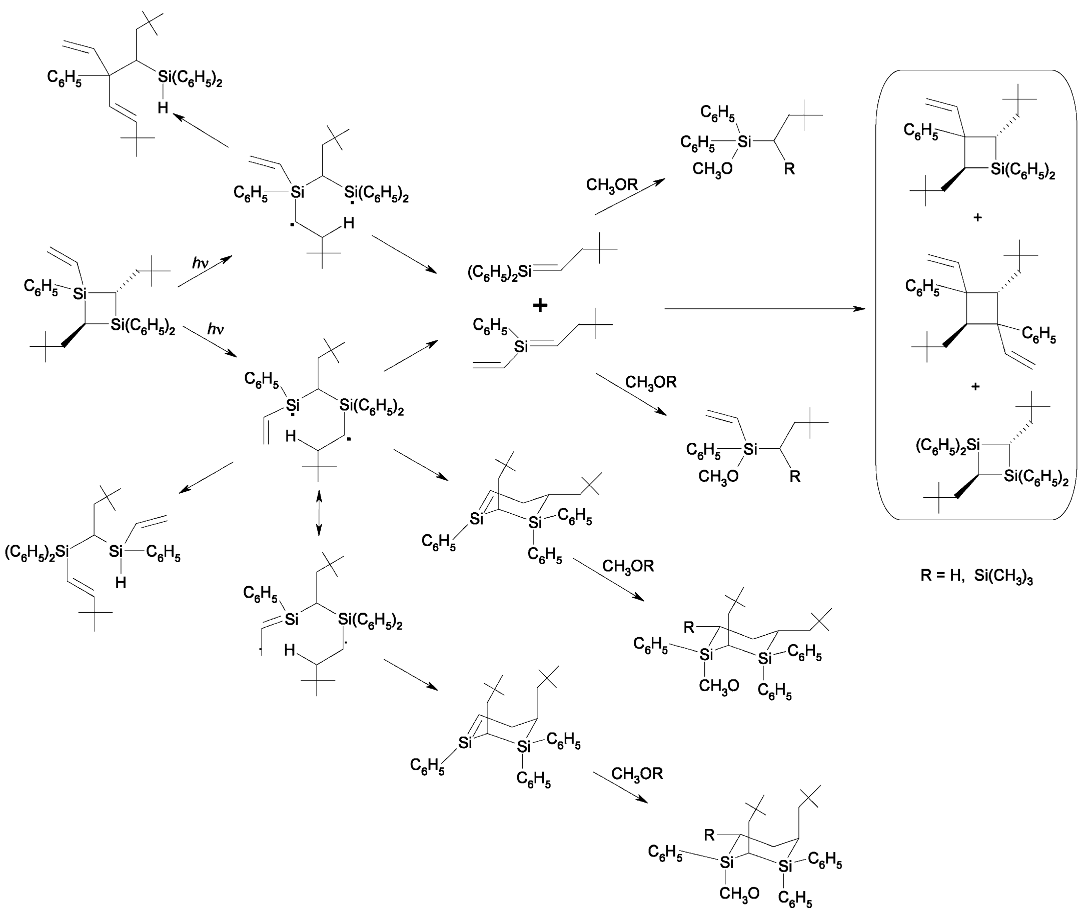
4.2.2.2. 1,1,3,3-Tetraphenyl-1,3-disilacyclobutane. Earlier study of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane's photolysis did not show any reaction [132]. It was found later that upon the photolysis of 1,1,3,3-tetraphenyl-1,3-disilacyclobutane in a solution in the presence of methanol 2+2 cycloreversion to diphenylsilene undergoes inefficiently. The quantum yield of the photocycloreversion product is 4–5 times lower than that of the homologous 1-sila-3-germacyclobutane's and about 15 times lower than that of 1,1,3,3-tetraphenyl-1,3-digermacyclobutane's one [251] (Eq. (112)).

The reactions of 1,3-disilacyclobutanes' 2+2 cycloreversion most likely proceed via the excited-state Si–C bond cleavage to yield the $^{\bullet}$Si–C–Si–C$^{\bullet}$ biradical, which undergoes a competing reclosure and fragmentation to silene [251]. Proceeding the reverse reaction of diphenylsilene's dimerization nonconcertedly, it must involve the intermediacy of the corresponding 1,3-disila-1,4-butanediyl biradical [250].

4.2.2.3. 1,1,3,3-Tetraphenyl-2,4-dineopentyl-1,3-disilacyclobutanes. The photolysis (254 nm) of a benzene or cyclohexane solution of either pure *cis*- or *trans*-1,1,3,3-tetraphenyl-2,4-dineopentyl-1,3-disilacyclobutanes gives a rapid isomerization to a 70/30 equilibrium mixture of the isomers and a less rapid formation of the ring-opened vinylsilane isomers. In the presence of traps the expected adducts to 1,1-diphenyl-2-neopentylsilene are also observed. The results are consistent with the intermediacy of a singlet ring-opened 1,4-biradical which recloses rapidly to the starting material or goes on to the products shown in Eq. (113) below [259]:

The fact that the ring closure is, apparently, the most rapid of these processes provides an explanation for the lack of observation of silene products in Jutzi's tetraphenyldisilacyclobutane photolysis [132] providing that the fragmentation to form silene is not competitive with the ring closure in that system [259].

4.2.2.4. 1,1,3-Triphenyl-3-vinyl-2,4-dineopentyl-1,3-disilacyclobutane. A photolysis of 2,4-dineopentyl-1,1,3-triphenyl-3-vinyl-1,3-disilacyclobutane in the presence of methanol and methoxytrimethylsilane gives three major products: ring-opened alkenylsilanes, trapping products of silenes, and six-membered-ring products. The results are consistent with the initial formation of 1,4-biradicals, which undergo three competing reactions: an intramolecular hydrogen abstraction leading to alkenylsilanes, a fragmentation to silenes, and a ring closure to six-membered-ring silenes [260] (Eq. (114)).



R = H, $Si(CH_3)_3$

(114)

4.2.3. 1,2-Disilacyclobutanes

4.2.3.1. Octamethyl-1,2-disilacyclobutane. A reasonable suggestion for a fragmentation of octamethyl-1,2-disilacyclobutane to tetramethyldisilene and 2,3-dimethylbut-2-ene was made from a mass spectrometric analysis of the reaction mixture obtained after the photolysis at the room temperature with an unfiltered medium pressure mercury arc [212] (Eq. (115)).

4.2.3.2. 1,1,2,2-Tetrakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane]. A continuous photolysis of 1,1,2,2-tetrakis(trimethylsilyl)dispiro-[3,3′,4,4′-biadamantane-1,2-disilacyclobutane] at 254 nm in hexane at −78 °C in the presence of 1,3-butadiene leads to 2,2′-biadamantylidene and a 2:1 mixture of 1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacycolhex-4-ene (the trapping product of tetrakis(trimethylsilyl)disilene) and of 1,1-bis(trimethylsilyl)-1-silacyclopent-3-ene (the trapping product of bis(trimethylsilyl)silylene). In the absence of 1,3-butadiene the solution becomes violet and its spectrum shows a very broad maximum at 538 nm assigned to silylene. The photolysis at −196 °C in methylcyclohexane produces a green glass whose spectrum showing the maximum at 415 nm and the weaker band at 346 nm to be due to tetrakis(trimethylsilyl)disilene. A nanosecond flash photolysis using a KrF eximer laser (248 nm) was also applied to measure the kinetic behavior of the intermediates. A conclusion was made that the photolysis yields disilene, $(Me_3Si)_2Si{=}Si(SiMe_3)_2$, which undergoes a subsequent photodissociation to produce the silylene, $(Me_3Si)_2Si$ [261,262] (Eq. (116)):

4.2.4. 1,2-Disila-3-oxetanes

4.2.4.1. 1,1,2,2-Tetramesityl-4,4-dimethyl(diethyl, diphenyl)-1,2-disila-3-oxetanes. The title compounds were photolyzed at 254 nm (−60 °C, 2 h, pentane solution). They cyclorevert yielding dimesitylsilanone and the corresponding dimesitylsilene[37] which may be

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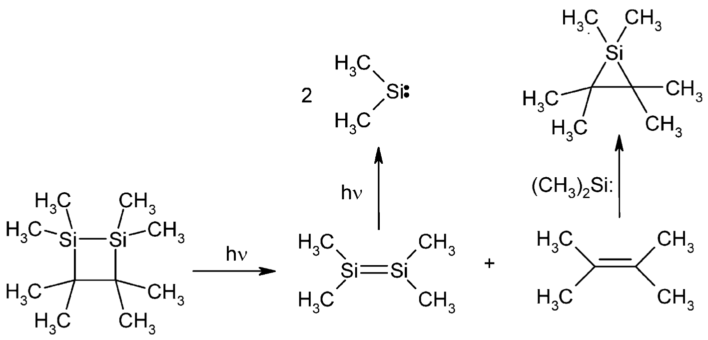
[37] 2+2 Cycloreversion enthalpy of cyclo-$(H_2SiSiH_2OCH_2)$ is moderately endothermic, 40.9 kcal mol^{-1} [203].



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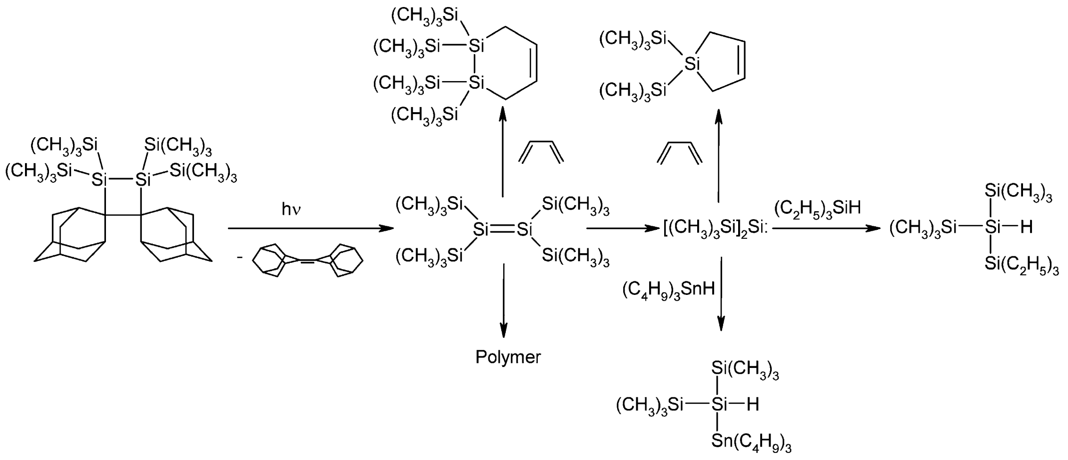

(116)

trapped with ethanol. In the absence of ethanol the latter partly undergoes a rearrangement involving a 1,3-hydrogen shift and partly undergoes a 2+2 cycloaddition followed by the ring opening of the intermediate 1,3-disilaoxetane [263,264] (Eq. (117)):

4.2.5. *1,2-Disila-3-thietanes*

4.2.5.1. 1,1,2,2-Tetramesityl-4,4-diphenyl-1,2-disila-3-thietane. The photolysis of the title compound at −60 °C in pentane with excess ethanol quantitatively yields ethanol adducts of 1,1-dimesityl-2,2-diphenylsilene and dimesitylsilanethione.[38] A photolysis in the absence of ethanol resulted in a 33% yield the yellow 1,1-dimesityl-2,2-diphenylsilene (identified by ^{1}H-NMR) which isolation, however, ended up in a failure [265] (Eq. (118)).

4.2.6. *Trisilacyclobutanes*

4.2.6.1. 1,1,2,2,3,3-Hexakis(trimethylsilyl)spiro[(4,4′-adamantane)-trisilacyclobutane]. A 2+2 photocycloreversion of 1,1,2,2,3,3-hexakis(trimethylsilyl)spiro[(4,4′-adamantane)-trisilacyclobutane] (254 nm, hexane, −78 °C, 1.5 h) in the presence of 1,3-butadiene leads to the production of bis(trimethylsilyl)adamantylidenesilene and tetrakis(trimethylsilyl)disilene which were trapped to give the expected 4+2 cycloaddition products [266] (Eq. (119)).

Silene and disilene were also directly detected in the flash-laser photolysis of 1,1,2,2,3,3-hexakis(trimethylsilyl)spiro[(4,4′-adamantane)-trisilacyclobutane] [267]. The above 2+2 cycloreversion seems to be the first demonstration of the simultaneous generation of silene and disilene from the single precursor. Such a photoreaction is rather unusual because cyclic as well as linear polysilanes with three adjacent Si atoms are known to extrude silylene under irradiation [266].

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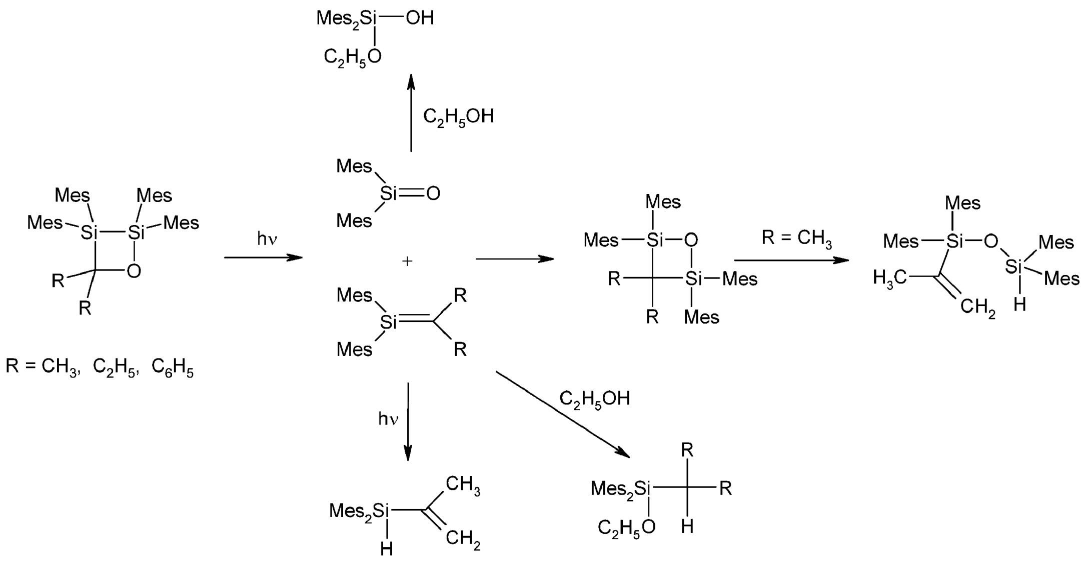
[38] The endothermicity of 2+2 cycloreversion of cyclo-($H_2SiSiH_2SCH_2$) is equal to 46.2 kcal mol^{-1} [203].


Mes
Si
O
R
R = CH3, C2H5, C6H5
hν
C2H5OH
Mes2Si—OH
C2H5O
Si=O
+
R = CH3
H3C
CH2
H
CH3
Mes2Si
R

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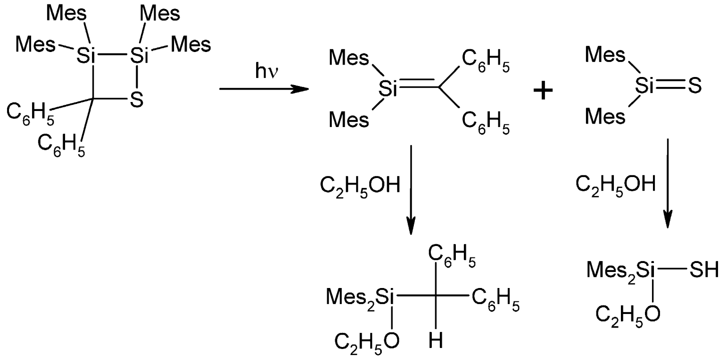
Mes
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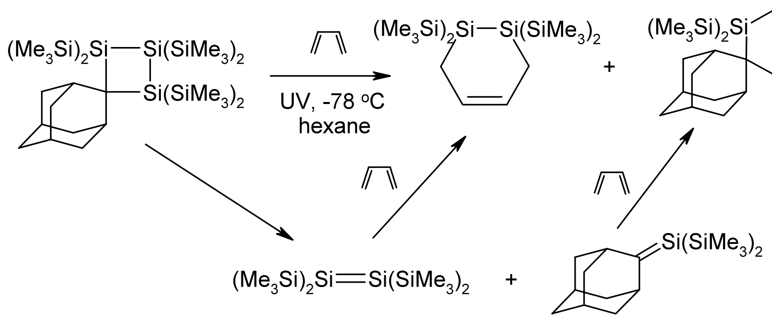
(Me3Si)2Si—Si(SiMe3)2
Si(SiMe3)2
UV, -78 °C
hexane
(Me3Si)2Si—Si(SiMe3)2
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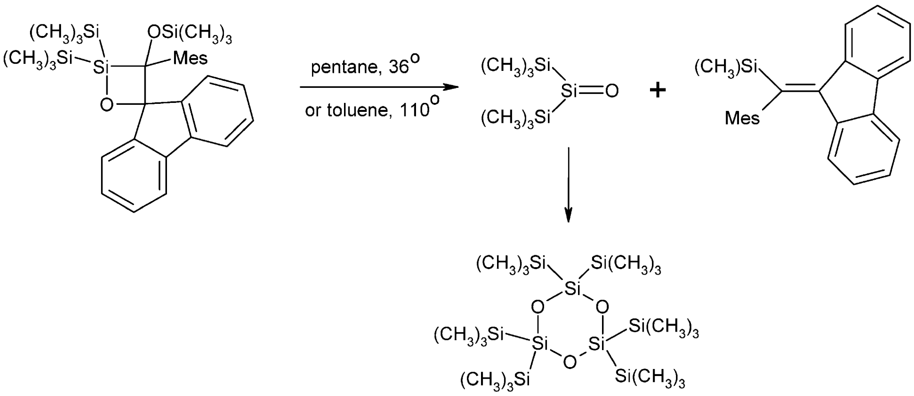
(Me3Si)2Si
(Me3Si)2Si=Si(SiMe3)2
+
Si(SiMe3)2

(119)



(120)

5. Liquid and solid phase spontaneous and thermal cycloreversions

5.1. Silaoxetanes

5.1.1. 1,2-Silaoxetanes

Formation of several 1,2-silaoxetanes by the liquid-phase thermolysis of the head-to-head dimers of silenes, $[(CH_3)_3Si]_2Si{=}C[OSi(CH_3)_3]R$ ($R = C_6H_5$, t-C_4H_9), in the presence of a variety of nonenolizable carbonyl compounds was postulated. They underwent rearrangements, not 2+2 cycloreversion [173]. Of a large number of moderately stable 1,2-silaoxetanes obtained by reacting relatively stable silenes with nonenolizable aldehydes and ketones [174–176] only one underwent 2+2 cycloreversion to silanone and alkene upon thermolysis (reaction 120). All the other silaoxetanes underwent an intramolecular rearrangement involving siloxy and aryl groups migrations [174].

The 2+2 cycloadduct of silene, $(CH_3)_2Si{=}C[Si(CH_3)_3]_2$, with benzophenone at the temperature above 100 °C yielded 1,1-diphenyl-2,2-bis(trimethylsilyl)ethylene and a polymeric product containing $[(CH_3)_2SiO]$ groups [268] (Eq. (121)).

A silene, $(CH_3)_2Si{=}C[Si(CH_3)_3]\{Si(CH_3)[C(CH_3)_3]_2\}$, reacted with benzophenone to give the 2+4 and 2+2 cycloadducts. The equilibrium shown below was postulated to explain this low-temperature reaction [269–271]. Here a 2+2 cycloreversion of 1,2-silaoxetane results in no silanone but silene which can be trapped [269] (Eq. (122)):

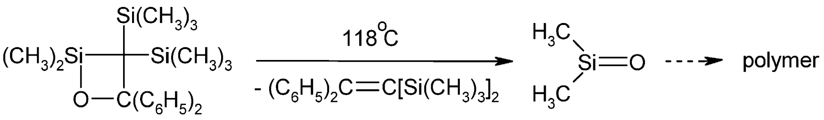
In the presence of alcohols, azo-compounds, azides, or 2,3-dimethylbutadiene the adducts of transient silene may be trapped [269] (Eq. (123)).

Reaction of several aldehydes with silene, $Cl_2Si{=}CHCH_2C(CH_3)_3$, is believed to occur via 1,2-silaoxetane adducts which undergo 2+2 cycloreversion yielding the anticipated alkene and the elimination of $Cl_2Si{=}O$ [272].

A complex reaction mixture with the nonidentified components was obtained upon 70 °C thermolysis of stable 1,2-silaoxetane prepared by the irradiation of 1,1-dimethyl-1-*tert*-butyl-2,2,2-triphenyldisilane in 2-methylbutane containing acetone at −78 °C [273].

5.1.2. Siladioxetanes

When exposed to air a stable solid 1,1-bis(trimethylsilyl)-2-(trimehylsiloxy)-2-(1-adamantyl)-1-silene had immediately and vigorously formed a white smoke with melting and evaporation [107]. In the presence of a dilute dry oxygen under the controlled conditions, the major products were the cyclic trimer of bis(trimethylsi-



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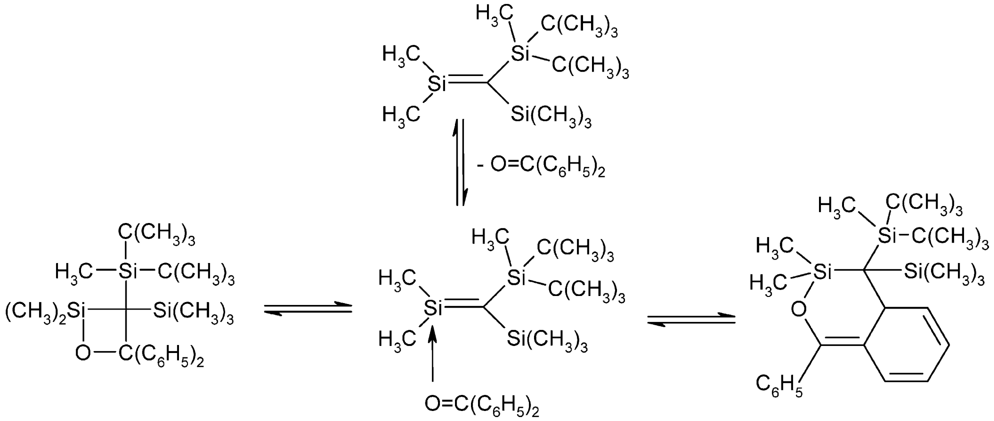

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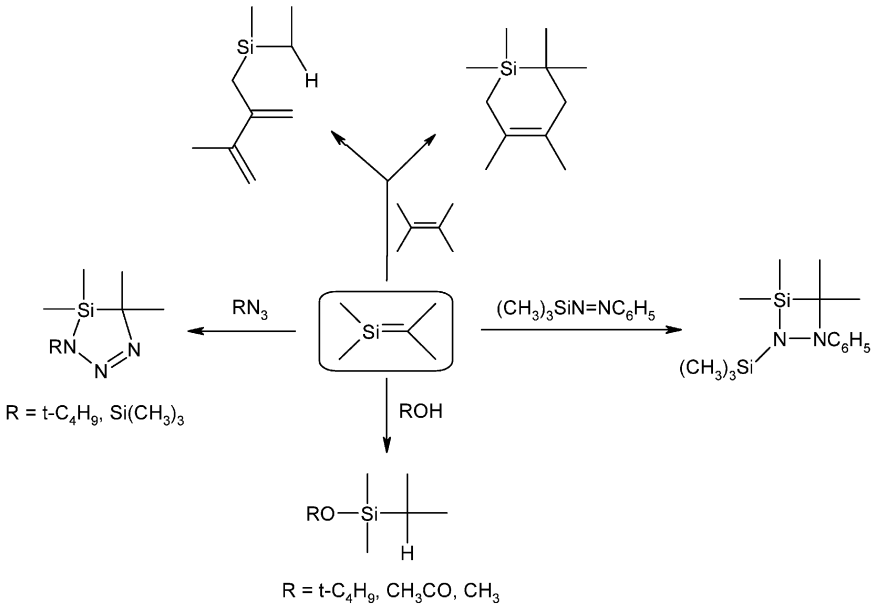
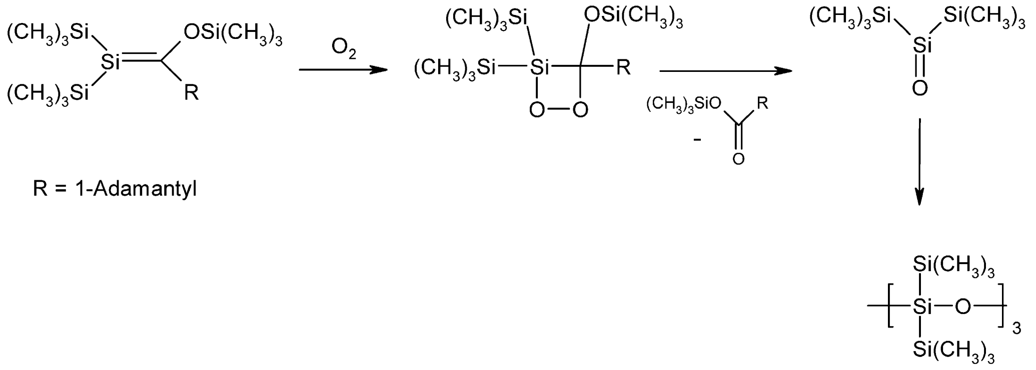


(123)

lyl)silanone and the trimethylsilyl ester of adamantane-1-carboxylic acid which was suggested to arise from the 2+2 cycloreversion of an intermediate siladioxetane (Eq. (124)).

Siladioxetanes produced by the photooxidation of silenes in O_2-doped argon matrices are thermally labile even in the low-temperature matrices and their 2+2 cycloreversion leads to the formation of a silanone and an aldehyde in the same matrix cage which produces formylsilanol after the reorientation of their complex. These results lead to a conclusion that siladioxetanes as well as silanone–aldehyde complexes play a key role in the oxidation of silenes [274] (Eq. (125)).

A careful oxidation of 1,1-bis(trimethylsilyl)-2-trimethylsiloxy-2-adamantylsilene at −70 °C resulted in siladioxetane which had originally been proposed to cyclorevert via the consecutive reactions involving the radicals [275]. Later it was suggested to explain this reaction as occurring via a complex between silanone and an ester [21] (Eq. (126)).



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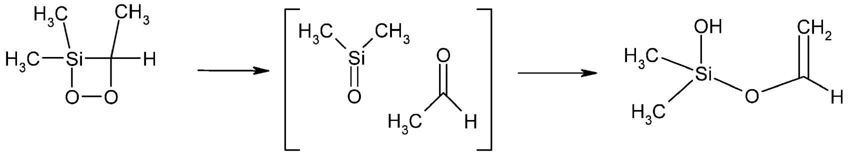

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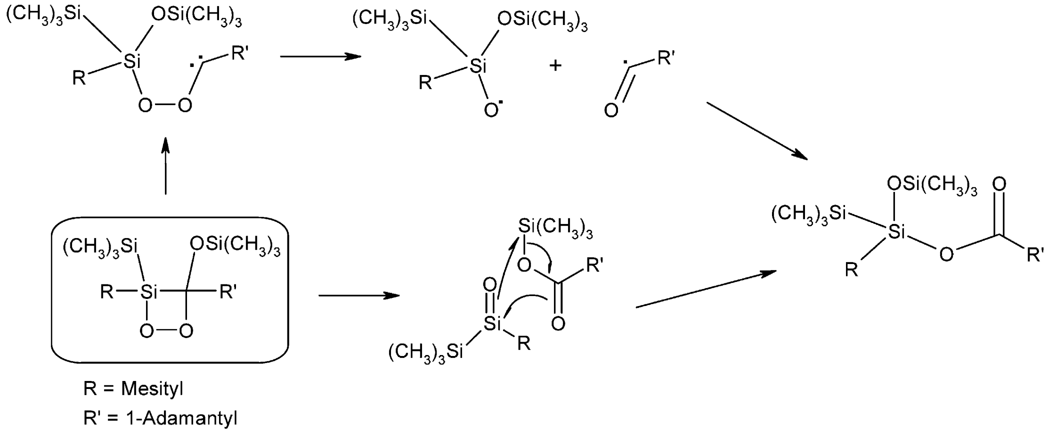


(126)

5.2. Silathietanes

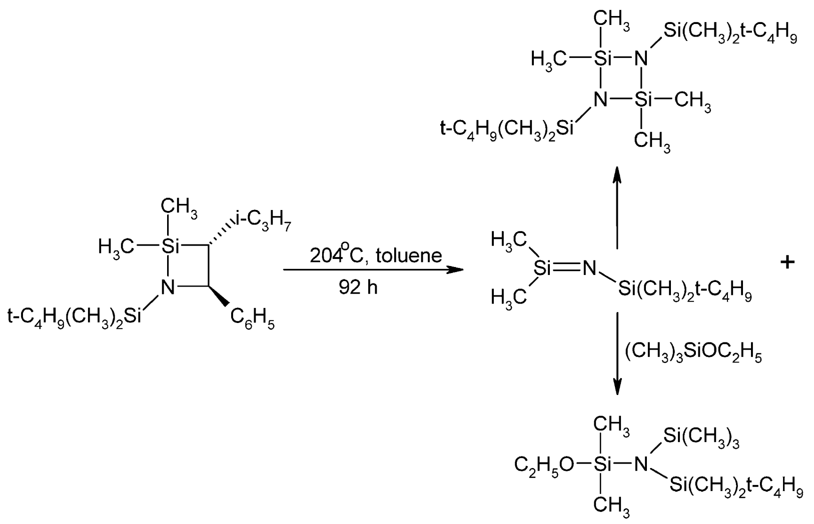
5.2.1. 1,1-Di-tert-butyl-3,4-dimethyl-1,2-silathietane

A pyrolysis of 1,1-di-*tert*-butyl-3,4-dimethyl-1,2-silathietane in benzene at 200 °C resulted in 1,1,3,3-tetra-*tert*-butyl-2,4-dithiadisilacyclobutane that is formally the dimer of the transient di-*tert*-butylsilanthione, $(t\text{-}C_4H_9)_2Si{=}S$. In the presence of hexamethylcyclotrisiloxane the product of silanthione insertion into the Si–O bond was formed [184].

5.3. Silaazetidines

5.3.1. 1-Aza-2-silacyclobutanes

5.3.1.1. trans-1-(tert-Butyldimethylsilyl)-2,2-dimethyl-3-isopropyl-4-phenyl-1-aza-2-silacyclo-butane and related 1-aza-2-silacyclobutane's substrates. Azasilacyclobutanes afford silanimines by a thermal 2+2 cycloreversion. The title 1-aza-2-silacyclobutane undergoes a thermal decomposition at 200 °C in toluene to form silanimine species and olefin. The formation of silani-



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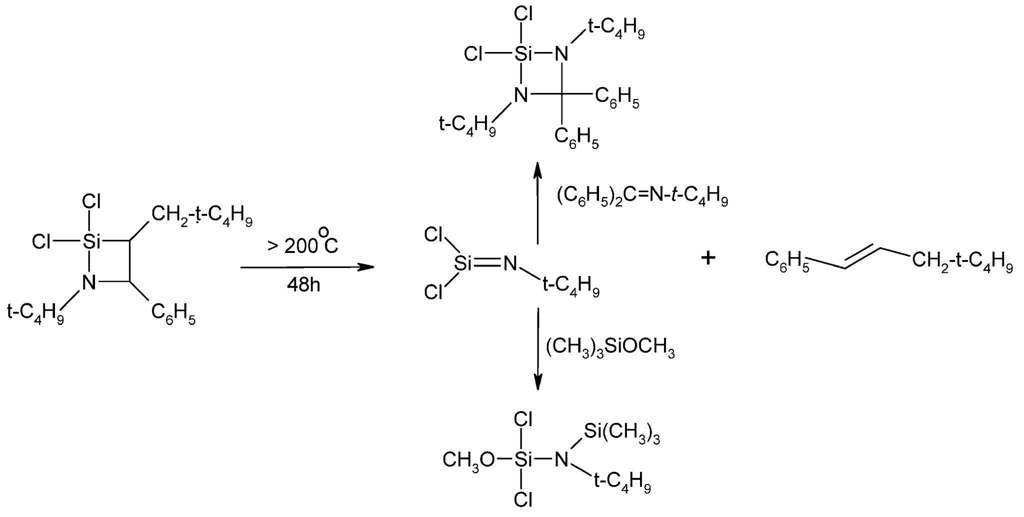


(128)

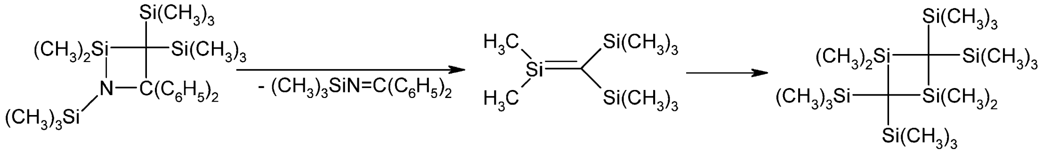
mine was confirmed by the quantitative formation of the dimer and a 1:1 adduct with trimethylethoxysilane in the copyrolysis [276] (Eq. (127)).

Other substrates containing a $H(CH_3)_2Si$ group on the nitrogen had also underwent similar thermal decomposition to form the corresponding olefin together with the complex mixture of oligomers arising from silanimine, owing to the presence of the reactive hydrosilane moiety [276]. The following observations were taken as the evidence in favor of the unimolecular decomposition mechanism: (i) the first-order kinetics, (ii) the activation parameters $\Delta H^{\ddagger} = 41.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 2.3$ eu, (iii) the decomposition rates dependence on the stereochemistry and a number of substituents on the ring carbon atoms.

1,1-Dichloro-2-*tert*-butylsilanimine, resulted from the 2+2 thermocycloreversion shown below, can be trapped by trimethylmethoxysilane or imine to give the addition or the 2+2 cycloaddition products [277,278] (Eq. (128)):

5.3.1.2. *3,3-bis(Trimethylsilyl)-1-aza-2-silacyclobutanes.*

N-Trimethylsilyl-benzophenoneimine is able to 'store'



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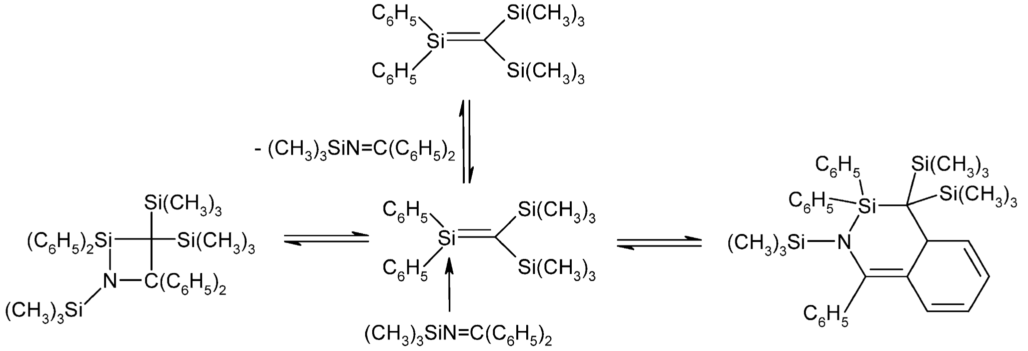

(130)

the silene, $(CH_3)_2Si{=}C[Si(CH_3)_3]_2$, forming a 2+2 cycloadduct. The latter cyclorevert upon heating regenerating silene which can be trapped [279,280]. Heating 1,3,3-tris(trimethylsilyl)-2,2-dimethyl-4,4-diphenyl-1-aza-2-silacyclobutane in the absence of trapping reagents results in a dimer of 1,1-dimethyl-2,2-bis(trimethylsilyl)silene [268] (Eq. (129)).

Silene $(C_6H_5)_2Si{=}C[Si(CH_3)_3)]_2$ reacts with the imino derivatives to give a donor adduct which is then transformed to the 2+2 and 2+4 cycloadducts [281,282]. Upon heating these cycloadducts 1,1-diphenyl-2,2-bis(trimethylsilyl)silene is liberated which in its turn can be trapped: (Eq. (130)).

The following order of relative reactivity of the trapping agents was found: $(C_6H_5)_2C{=}O > (t\text{-}C_4H_9)_2CH_3SiN_3 >$ butadiene $>$ 2,3-dimethylbutadiene $> (C_6H_5)_2C{=}NSi(CH_3)_3 > (t\text{-}C_4H_9)_3SiN_3 >$ anthracene [281].

5.3.2. *1-Oxa-3-aza-2-silacyclobutanes*

Silanimine, $(CH_3)_2Si{=}NSi(t\text{-}C_4H_9)_3$, reacts with benzophenone to give the title 2+2 cycloadduct which at its turn undergoes a fast 2+2 cycloreversion followed by a 2+2 cycloaddition of the resultant dimethylsilanone to the starting silanimine [283] (Eq. (131)):

A more stable oxaazasilacyclobutane was obtained by reacting a metastable silanimine, $(t\text{-}C_4H_9)_2Si{=}NSi\ (t\text{-}C_4H_9)_3$, with benzoaldehyde in pentane at −125 °C [284].

5.3.3. *1,2-Diaza-3-silacyclobutanes*

A thermolysis of the 2+2 cycloadduct, 1,1-dimethyl-2,3-bis(trimethylsilyl)-4-bis(trimethylsilyl)-1-sila-2,3-diazacyclobutane, which is accessible from 1,1-dimethyl-2,2-trimethylsilylsilene and bis(trimethylsilyl)diazene, results in a 2+2 cycloreversion to yield 1,1-dimethyl-2-trimethylsilyl-1-silanimine, $[(CH_3)_3Si]_2C{=}NSi(CH_3)_3$, which forms both the dimer and the product of its insertion into the Si–N bond of the imine, an another product of the cycloreversion [285]. The thermolysis in the presence of a tenfold excess trimethylsilylazide results in the insertion and the 2+3 cycloaddition products [286] (Eq. (132)).

5.3.4. *3+1 Cycloadduct of di-tert-butylsilylene and tri-tert-butylazide*

A reaction of the photochemically generated di-*tert*-butyllsilylene with a sterically hindered azide, $(t\text{-}C_4H_9)_3Si{-}N{=}N{=}N$, results in the intermediate 3+1 cycloadduct which cycloreverts to yield silanimine [287] (Eq. (133)).

5.4. *1,3-Disilacyclobutanes*

The silenes, $(C_6H_5)_2Si{=}C[Si(CH_3)_3)_2]$[39], reversibly isomerize fast by methyl migration, then a bit slower by phenyl migration, and finally fast by methyl migration into the thermodynamically more stable silene '**a**',

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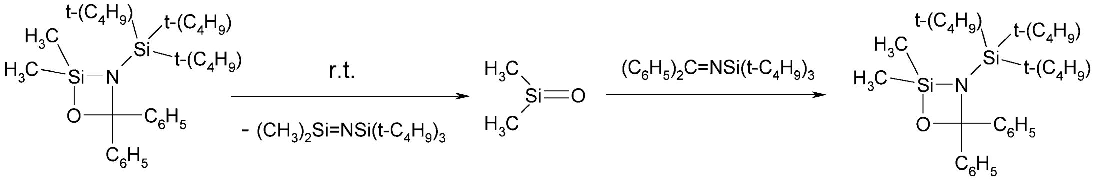
[39] Generated from $(C_6H_5)_2SiBr{-}CLi[Si(CH_3)_2]$ in diethyl ether.



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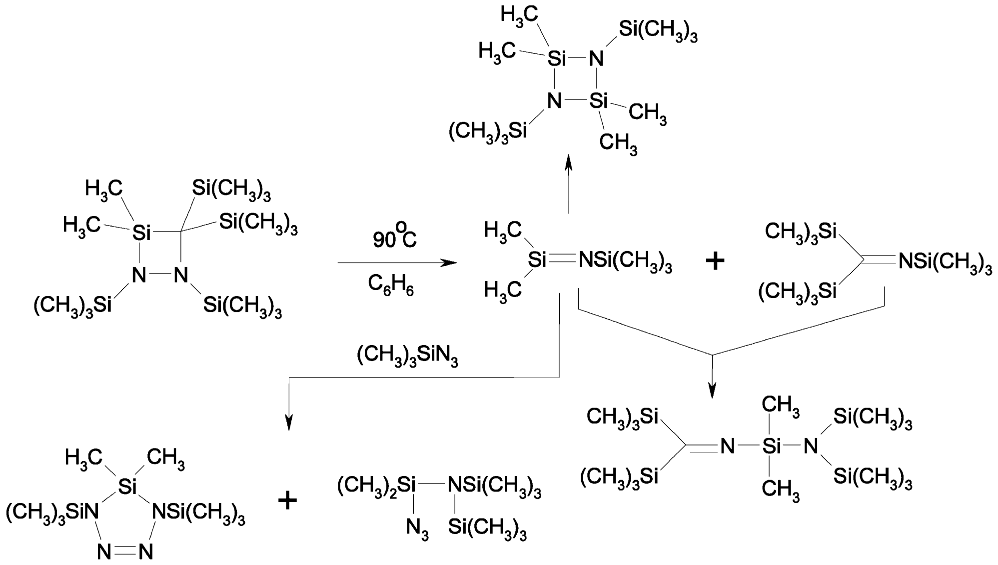


(132)

then into the medium stable silene '**b**', and finally into the most stable silene '**c**'. Simultaneously with isomerization a reversible 2+2 cycloreversion occurs. 2+2 Thermocycloreversion of 1,3-disilacyclobutanes (shown in scheme 134 below) at 340 °C leads to the formation of an equilibrium mixture of silenes which irreversibly isomerize into disilaindanes [282].

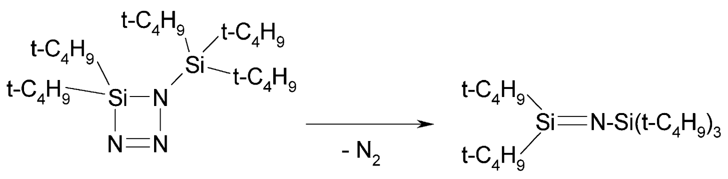
5.5. *Tetramethylcyclodisilthiane*

Heating a 1/5 mixture of tetramethylcyclodisilthiane and 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane at 200 °C resulted in a polymeric residue and 8.5% of 1,1,3,3,5,5-hexamethyl-2-oxa-1,3,5-trisila-4-thiacycloheptane. The latter is believed to be a dimethylsilantione's insertion product into the Si–O bond of 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane [288] (Eq. (135)).

5.6. *1,2-Disilacyclobutanes*

5.6.1. *1,1,2,2-Tetraphenyl-3-[bis(trimethylsilyl)ethenylidene]-4,4-bis(trimethylsilyl)-1,2-disilacyclobutane*

Heating of the title 1,2-disilacyclobutane in a sealed glass tube (250 °C, 3 h) in the presence of anthracene resulted in the anthracene adduct of silabutatriene intermediate. A thermolysis in presence of methanol gave three methoxysilanes indicating the intermediacy of the two silicon–carbon double bonded intermediates. In the absence of any trapping agent the silene intermediate isomerizes through the sequence shown below to form 1,3-disilacyclobutane by the 2+2 cycloaddition to a 1-silabutatriene intermediate [289–291] Eq. (136).



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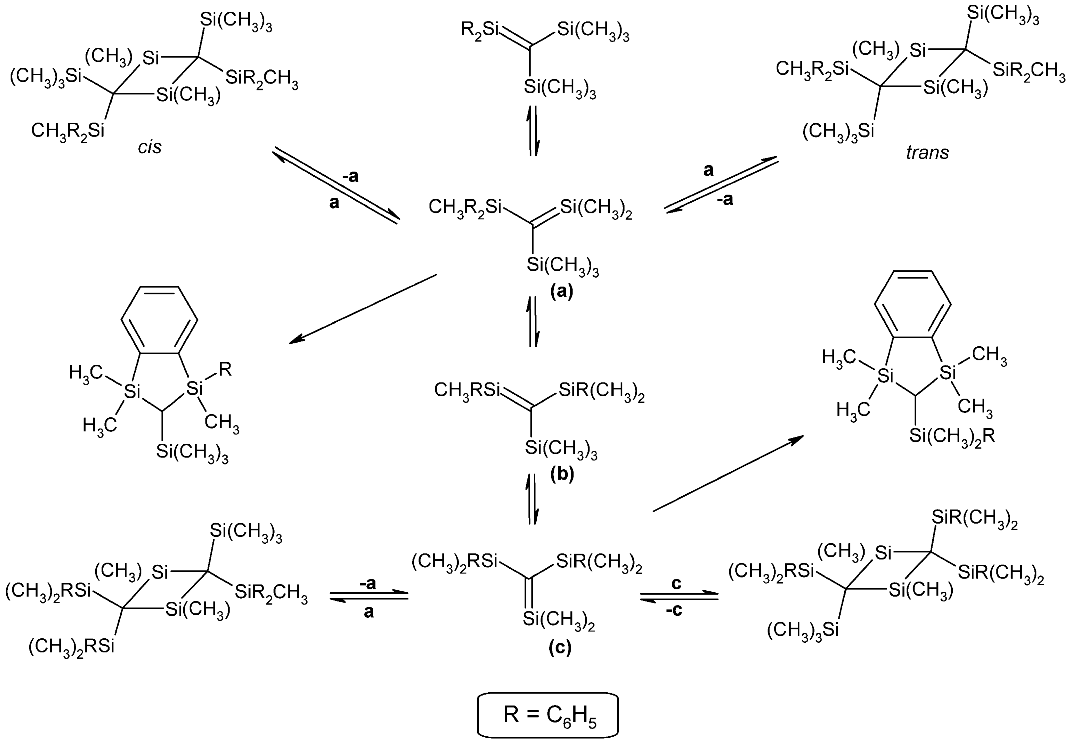

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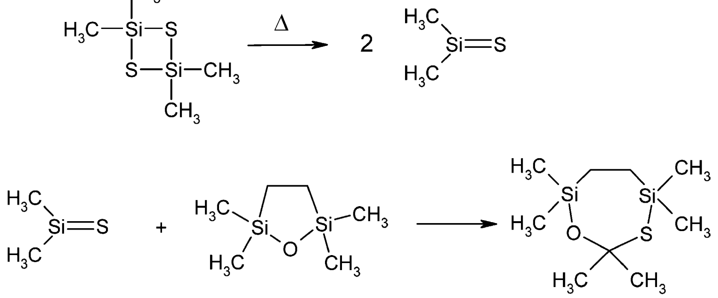

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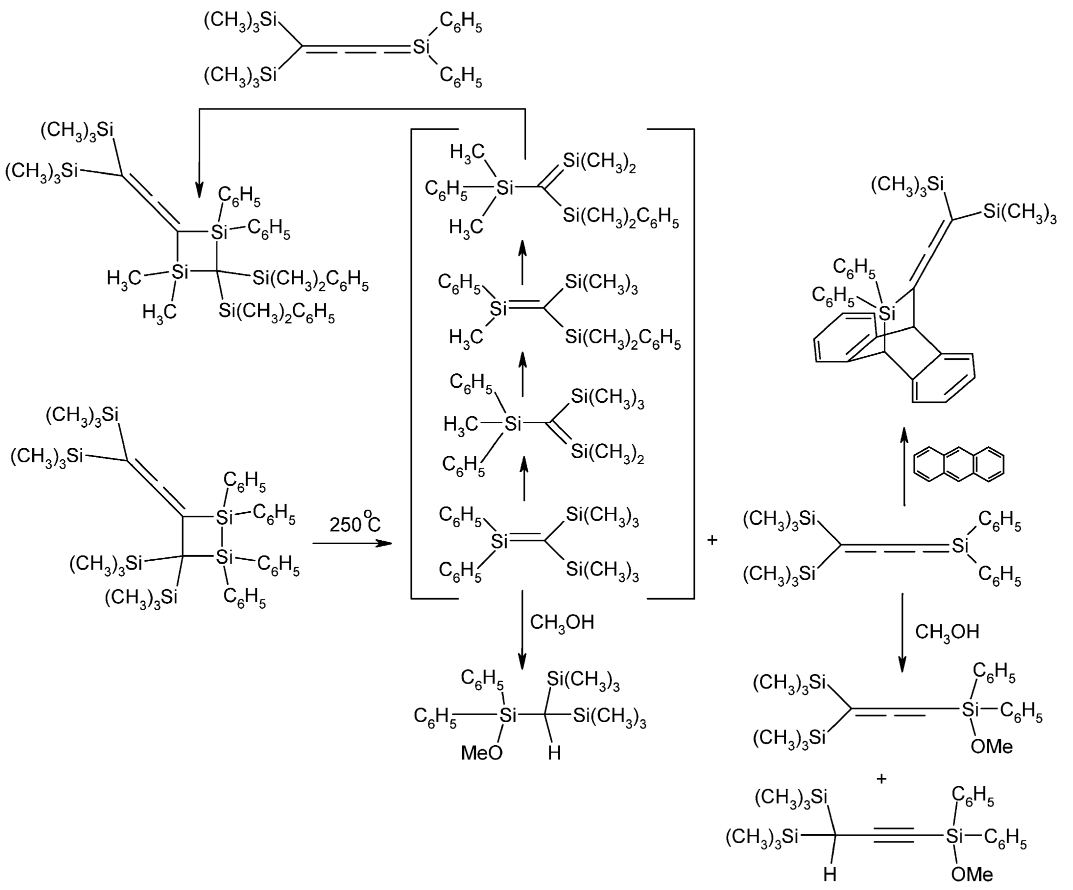

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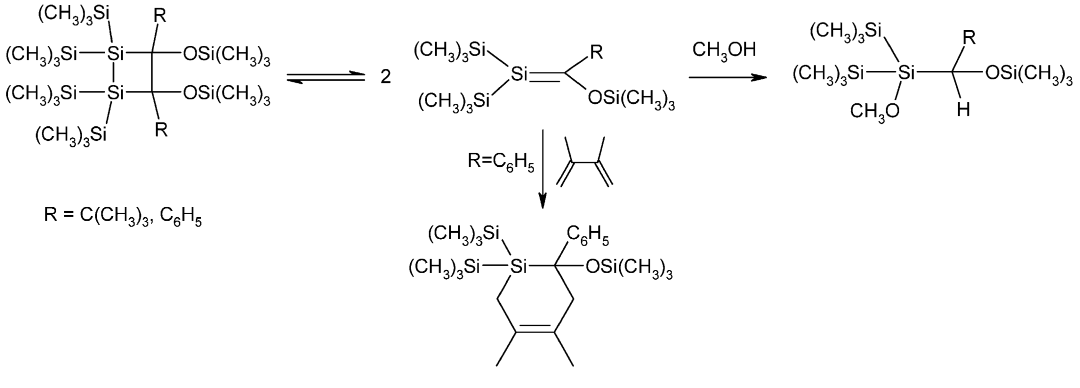
5.6.2. 1,1,2,2-Tetrakis(trimethylsilyl)-3,4-bis(trimethylsiloxy)-3,4-R_2-1,2-disilacyclobutanes

NMR spectra and trapping experiments indicate that 1,1,2,2-tetrakis(trimethylsilyl)-3,4-bis(trimethylsiloxy)-3,4-bis(*t*-butyl)-1,2-disilacyclobutane readily dissociates to silene when dissolving in an inert solvent resulting in a mobile dimer-monomer equilibrium. A mere dissolution at a room temperature in a THF–methanol



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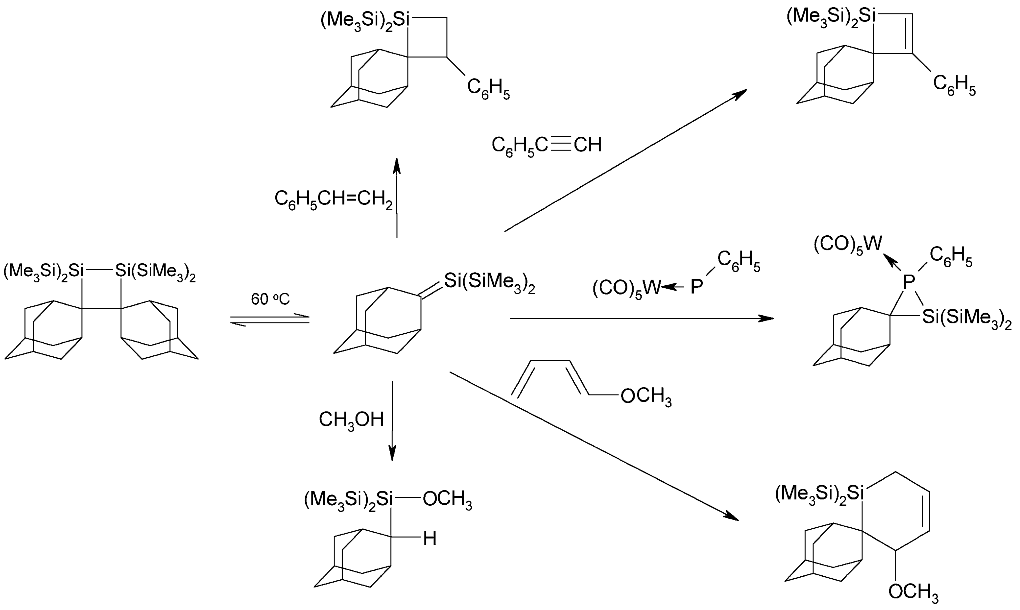

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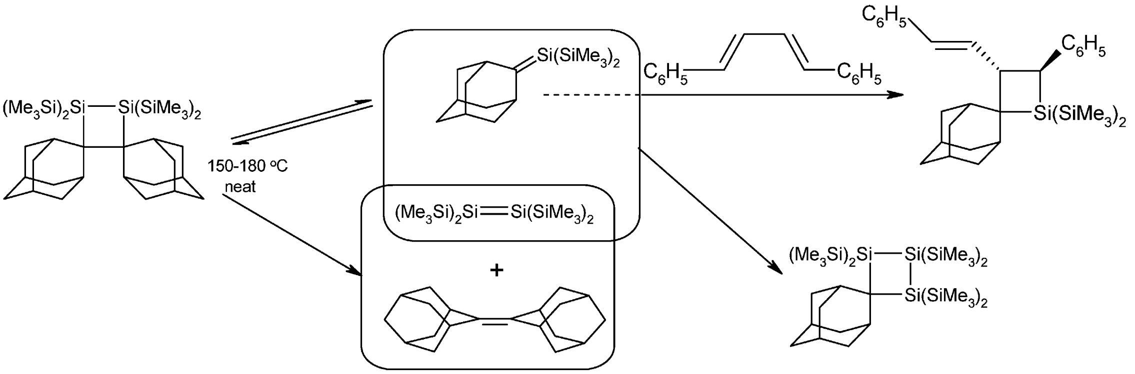


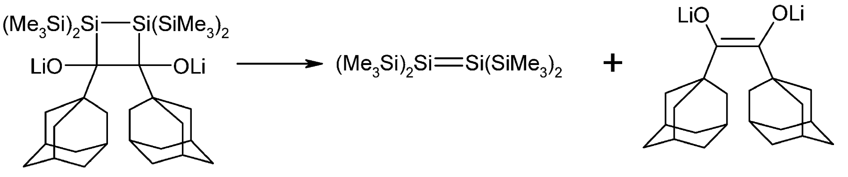
(139)

solution gave an expected silene adduct [292–294]. 1,1,2,2-Tetrakis(trimethylsilyl)-3,4-bis(trimethylsiloxy)-3,4-diphenyl-1,2-disila-cyclobutane dissociates at a higher temperature. The adduct of the silene and methanol was obtained in a good yield when refluxing in THF. Similarly, the silene adduct to 2,3-dimethyl-buta-1,3-diene was obtained [292,293] (Eq. (137)).

It was suggested that the dissociation probably proceeds by a homolytic fission of the carbon–carbon bond to give the corresponding diradical [292]. An ESR signal was observed when 1,1,2,2-tetrakis(trimethylsilyl)-3,4-bis(trimethylsiloxy)-3,4-diphenyl-1,2-disilacyclobutane was heated in pentane in a sealed tube at 90 °C for 10 min and then placed in the ESR spectrometer [293]. No silene–1,2-disilacyclobutane equilibrium was found for the stable silenes containing bulkier groups: R = $C(C_2H_5)_3$ or 1-adamantyl ($C_{10}H_{15}$) prepared by the photolysis of acylpolysilanes [107].

5.6.3. 1,1,2,2-Tetrakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane]

Heating of the title 1,2-disilacyclobutane in hexane at 60 °C for 24 h in the presence of silene traps resulted in the expected trapping products. These reactions were highly regioselective [261]. In the presence of the in situ generated complexed phosphinidene the phosphasilirane was isolated [295]. Since no trapping products of the disilene, $[(CH_3)_3]_2Si{=}Si[(CH_3)_3]_2$, and silylene, $[(CH_3)_3]_2Si$:, were detected the conclusion was made that the thermal 2+2 cycloreversion leads exclusively to two molecules of the silene, $[(CH_3)_3]_2Si{=}CAd$ (Eq. (138)):



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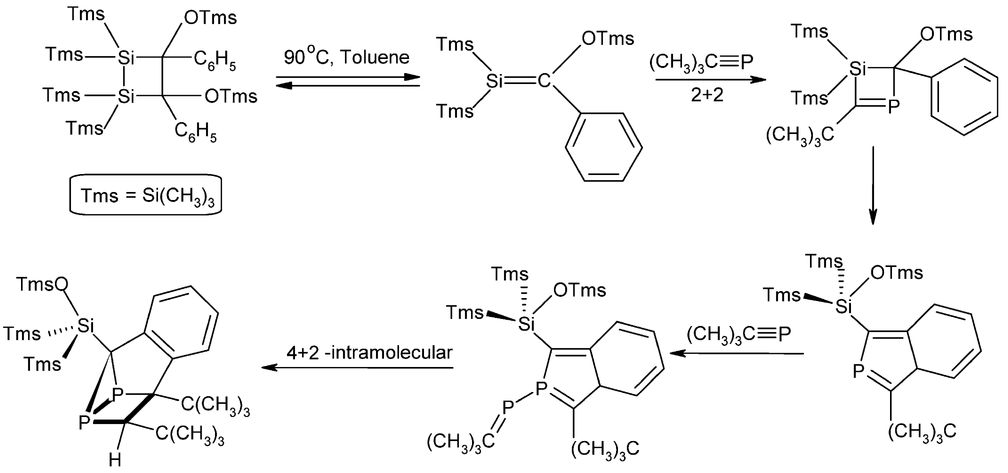


(141)

Therefore, in benzene at 60 °C 1,2-disilacyclobutane exists in an equilibrium with silene. Similar thermal equilibrium with the corresponding silenes is known for other 1,2-disilacyclobutanes with bulky substituents [292–294].

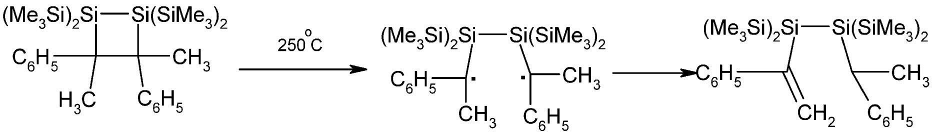
Solvent free thermolysis of the above 1,2-disilacyclobutane at 150–180° leads to a 75% yield of the novel trisilacyclobutane along with diadamantylidene and a polymer (thermolysis in hydrocarbon solutions leads to a significantly lower yield of the trisilacyclobutane). Thermolysis in the presence of *trans,trans*-1,4-diphenyl-1,3-butadiene results in the corresponding 2+2 cycloadduct of the silene $[(CH_3)_3]_2Si{=}CAd$. It is suggested that at a higher temperature there exist two competing routes: (i) a cleavage of the Si–Si and C–C bonds, which produces silene, and (ii) a cleavage of the C–Si bonds, leading to the formation of disilene and diadamantylidene. Therefore, the trisilacyclobutane ring can be formed by the cycloaddition reaction between a silene and a disilene [213,266,296] (Eq. (139)).

5.6.4. *1,1,2,2-Tetrakis(trimethylsilyl)-3,4-diadamantyl-3,4-dilithiolate-1,2-disilacyclobutane*

The reaction of Brook's acylsilane, $[(CH_3)_3Si]_3SiC(=O)Ad$ with a twofold excess $(C_2H_5)_3GeLi$ in THF gives a mixture of 1,1,2,2-tetrakis(trimethylsilyl)-3-trimethylsilyl-3-triethylgermoxy-4-(1-adamantyl)-1,2,3-trisilacyclobutane and adamantoyladamantylcarbinol. It is suggested that the trisilacyclobutane skeleton is formed by a 'head-to-head' cyclodimerization of the primary product, silaenolate, followed by a 2+2 cycloreversion of the adduct to yield the disilene that in turn is captured by the starting silene [297] (Eq. (140)).

5.6.5. *1,1,2,2-Tetrakis(trimethylsilyl)-3,4-diphenyl-3,4-bis(trimethylsiloxy)-1,2-disilacyclobutane*

1-Bis(trimethylsilyl)-2-trimethylsiloxy-2-phenylsilene can be thermally generated from the corresponding 1,2-disilacyclobutane by a 2+2 cycloreversion and trapped by the reaction with two equivalents of phosphaalkyne



(142)

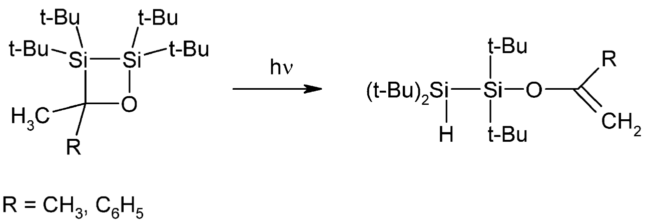
to produce diphosphatricyclobenzoheptane [298]: (Eq. (141)).

5.6.6. (*E*)-1,1,2,2-Tetrakis(trimethylsilyl)-3,4-dimethyl-3,4-diphenyl-1,2-disilacyclobutane

Heating of the title compound at 250 °C in a sealed glass tube results in no 2+2 cycloreversion products. Instead, this 1,2-disilacyclobutane isomerizes [299] similarly as octamethyl-1,2-disilacyclobutane (see Section 2.11.2) (Eq. (142)).

5.7. 1,2-Disila-3-oxetanes and 1,2-disiladioxetanes

The 2+2 photocycloaddition of tetramesityldisilene to ketones and aldehydes results in solid 1,2-disila-3-oxetanes which are stable in air and do not cyclorevert in a refluxing benzene (for their 2+2 photocycloreversion see Section 4.2.4.1) [264]. 1,1,2,2-Tetra-*tert*-butyl-3,3-dimethyl-1,2-disiladioxetane and 1,1,2,2-tetra-*tert*-butyl-3-methyl-3-phenyl-1,2-disiladioxetane do not cyclorevert either, but readily rearrange to yield disilyl enol ethers [300] (Eq. (143)).



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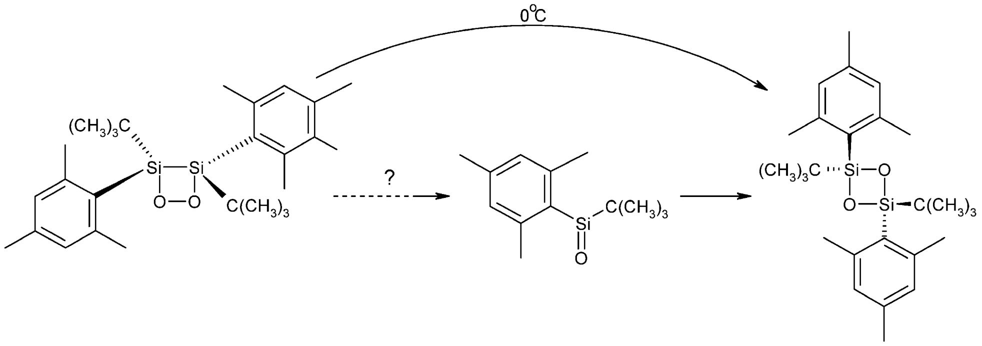
Thermally unstable 1,2-di-*tert*-butyl-1,2-dimesityl-1,2-disiladioxetane is a major oxidation product of the stable 1,2-di-*tert*-butyl-1,2-dimesitylsilene at −78 °C. At 0 °C it rearranges to 1,3-di-*tert*-butyl-1,3-dimesityldisiloxane [301] whose structure was determined by the X-ray diffraction studies [302,303]. Whether this rearrangement involves the intermediacy of (*tert*-butyl)mesitylsilanone remains under question[40] (Eq. (144)).

5.8. Iron carbonyl complexes with phosphaethylsilacyclobutane ligands

An attempt to stabilize silenes in the coordination sphere of the Group 19 transition metals failed. No complexes containing phosphanoethylsilene as a σ/π chelating ligand were produced by the thermolysis or the photolysis of the iron carbonyl complexes of the type



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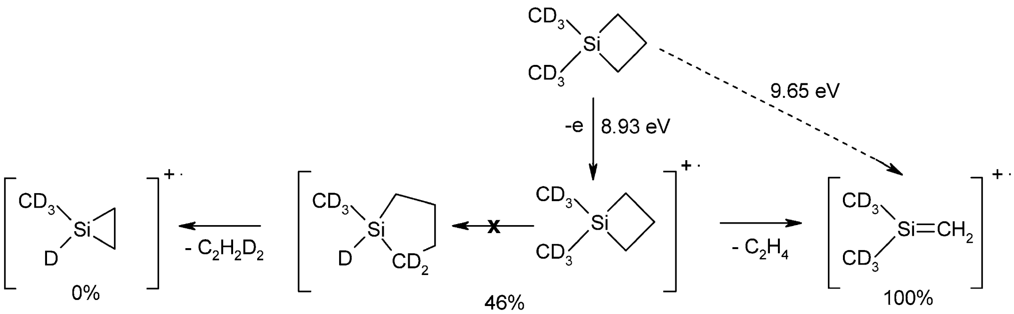

Ionization and ion's appearance energies are given for the patterns containing no deuterium
(at ionizing electron energy 12 eV)

(145)

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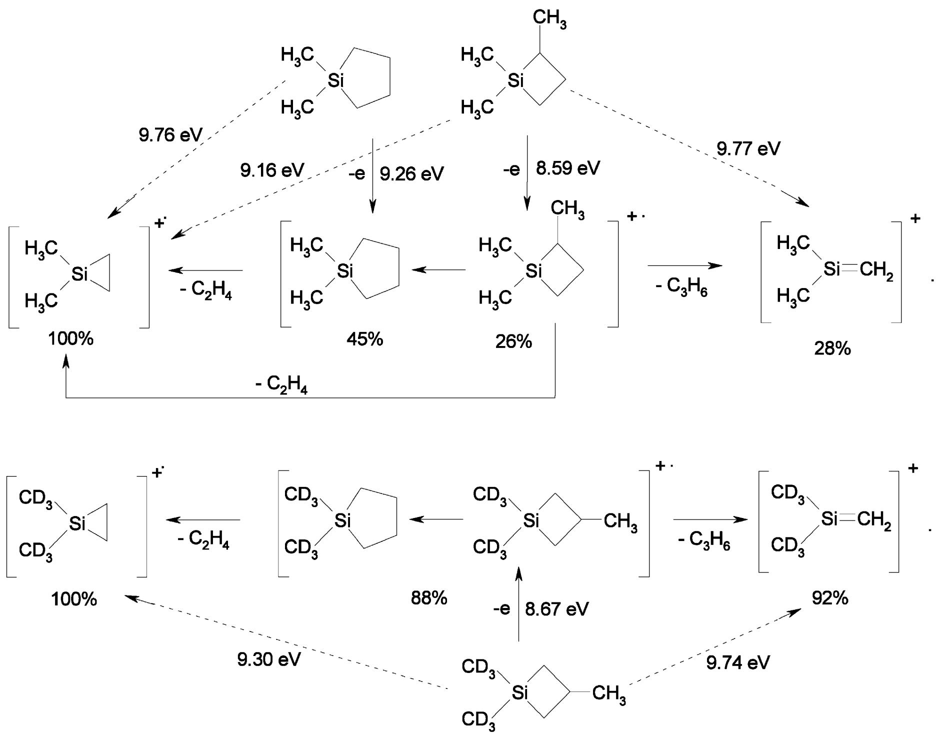
[40] Oxidation in the solid state also results in cyclodisiloxanes [263].



Ionisation and ions' appearance energies are given for patterns containing no deuterium (at ionizing electron energy 12 eV)

(146)

$Fe(CO)_4L$ with phosphanoethylsilacyclobutane ligands, $R^1_2PCH_2CH_2(R)Si(CH_2)_3$, ($R^1 = CH_3$, CF_3; $R = CH_3$, $CH_2{=}CH$, C_6H_5, C_5H_5, $CH_2CH_2PR^1_2$) [304,305].

6. Four-membered ring ions gas-phase 2+2 cycloreversion

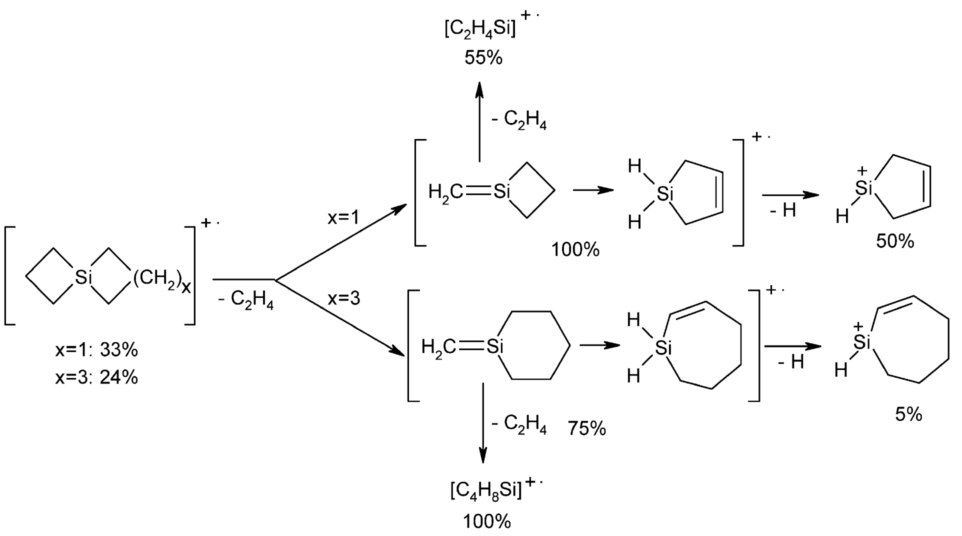
6.1. Positive ions fragmentation

A 2+2 cycloreversion type fragmentation is a characteristic feature of the four-membered silacycle's dissociative ionization processes leading to the doubly bonded silicon fragmentions. The search for such processes is of great interest because an analogy is observed between the decomposition of the ions in mass spectrometry and the pyrolysis or photolysis [162,306–315]. Many of them are reviewed [5].

A dissociative ionization of DMSCB, 1,1-bis(trideuteriomethyl)-1-silacyclobutane, 1,1,3-trimethyl-1-silacyclobutane, 1,1-bis(trideuteriomethyl)-3-methyl-1-silacyclobutane and 1,1,2-trimethyl-1-silacyclobutane was studied [316] in order to distinguish between the fragmentation paths to be due to the 2+2 cycloreversion and the rearrangement of the molecular ions. No fragment ion indicating the rearrangement of DMSCB molecular ion into the rearranged 1-methyl-1-silacyclopentane ion [306] was detected in the mass spectra of 1,1-bis(trideuteriomethyl)-1-silacyclobutane Eq. (145).

The rearrangement and 2+2 cycloreversion are characteristic of the both 1,1,3-trimethyl-1-silacyclobutane and 1,1,2-trimethyl-1-silacyclobutane molecular ions. In particular, a low-energy electron impact fragmentation of 1,1-bis(trideuteriomethyl)-3-methyl-1-silacyclobutane mainly results in the loss of ethene with the involvement of the C-methyl group from the rearranged molecular ion. Mass spectra of 1,1,3-trimethyl-1-silacyclobutane and 1,1-dimethyl-1-silacyclopentane are similar in terms of elimination of ethene molecules from the molecular ion. In the case of 1,1,3-trimethyl-1-silacyclobutane propene is lost directly from the molecular ion, whereas in 1,1-dimethyl-1-silacyclopentane such a process is not observed under the electron impact. The ionization energies for the molecules studied and also the appearance energies for the $[M-28]^{+\cdot}$ and $[M-42]^{+\cdot}$ ions were measured (see Eq. (146)) by the photoionization mass spectrometry and the heats of formation of these ions were calculated [316].

A correlation was noticed between the thermal decomposition and the electron impact fragmentation of 4-silaspiro[3,3]heptane. The most abundant ions in the mass spectra were $[M-28]^{+\bullet}$ and $[M-56]^{+\bullet}$ corre-



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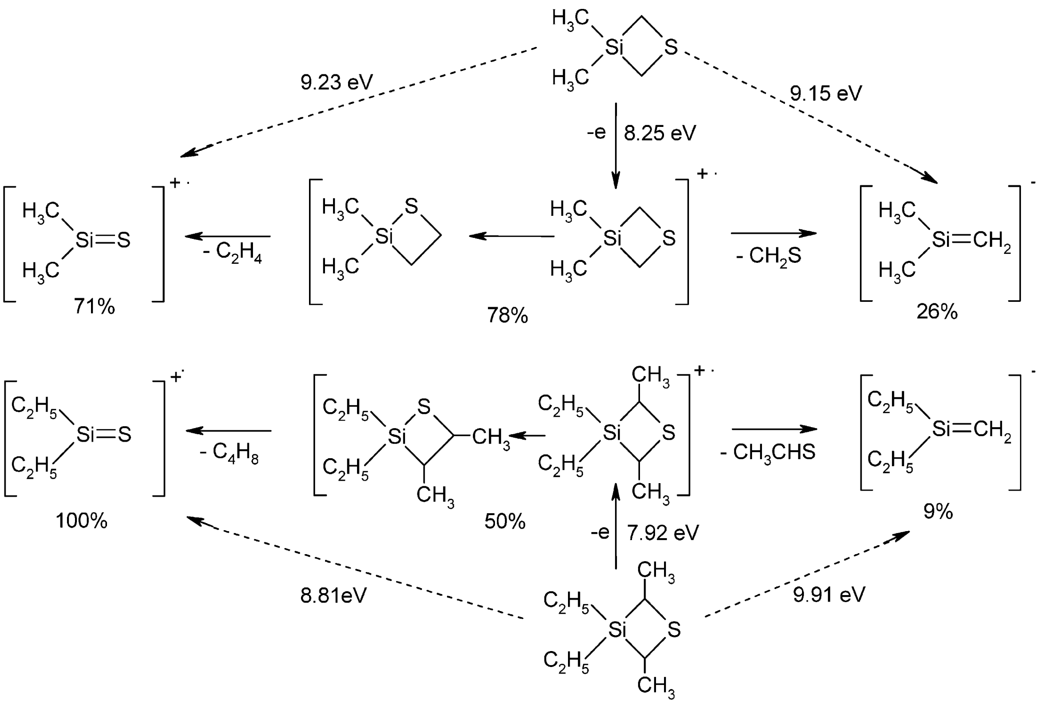
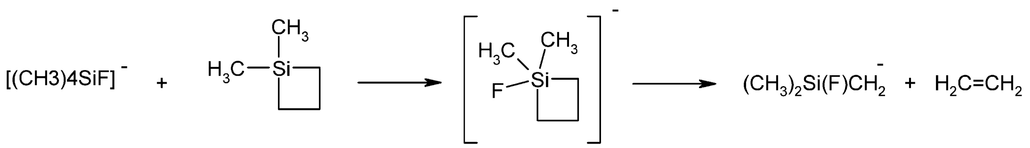


(at ionizing electron energy 12 eV)

(148)

sponding to the loss of the one or two molecules of ethylene. A prominent ion possessing silacyclopentene's structure was formed by the loss of hydrogen from the rearranged $[M-28]^{+\bullet}$ ion (for the analogous thermal rearrangement see Section 2.2.12.1). Such a rearrangement is not characteristic of the $[M-28]^{+\bullet}$ ion in the mass spectrum of 4-silaspiro[3,5]nonane since the peak of $[M-29]^{+}$ ion is only 5% of the intensity. It is similar to the pyrolysis of 4-silaspiro[3,5]nonane yielding transient methylenesilacyclohexane which does not rearrange either (see Section 2.2.12.3) [156] (Eq. (147)).



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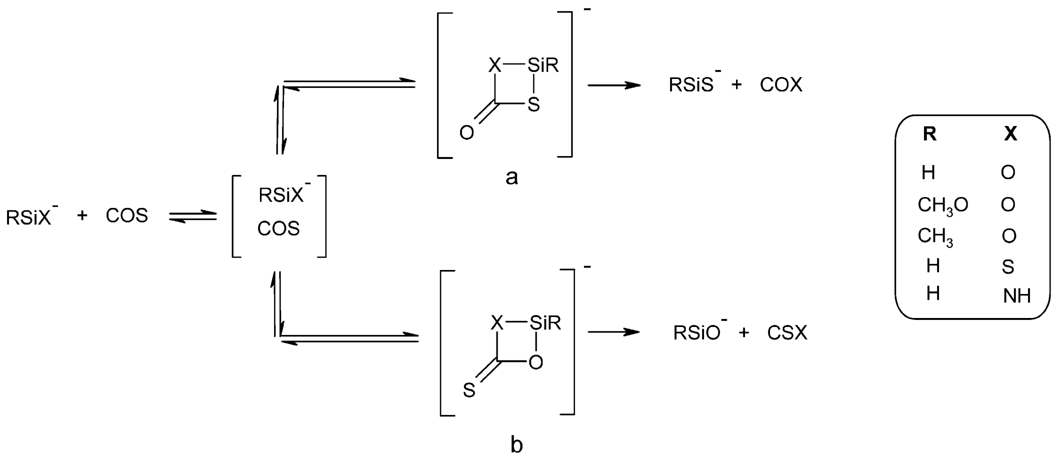

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The loss of silanthione's ions is the main 2+2 cycloreversion fragmentation of the presumably rearranged molecular ions upon the dissociative ionization of both 3,3-dimethyl-3-silathietane and 3,3-diethyl-2,4-dimethyl-3-silathietane. A less prominent 2+2 cycloreversion to yield silene's ions is characteristic of the molecular ions. The ionization energies for the molecules and the appearance energies for the silanthione and silene ions (shown in Eq. (148)) were measured by the photoionzation mass spectrometry. The heats of formation of the parent compounds and of the characteristic ions were also calculated [317].

6.2. Negative ions scission

A reaction of DMSCB and fluoride was carried out using a tandem flowing afterglow instrumentation yielding *m/z* 119 anion with the intact nature of the silacyclobutane ring. The *m/z* 119 anion was isolated and submitted to the increasingly energetic collisions with an argon collision gas. The only anion obtained, $(CH_3)_2Si(F)CH_2^-$ ($m/z = 91$), corresponded to the loss of ethylene [318] (Eq. (149)).

An addition of the silicon-containing anions of $[HSiX]^-$, X = C, O, S, NH, (O)NH, type as well as $[CH_3OSiO]^-$, $[CH_3SiO]^-$ to CO_2, COS, and CS_2 leaded to the four-membered ring negative ions which could react by the ring scission (the equivalent of a 2+2 cycloreversion) [319–323]. It is illustrated for the reaction between $[RSiX]^-$ and COS by Eq. (150):

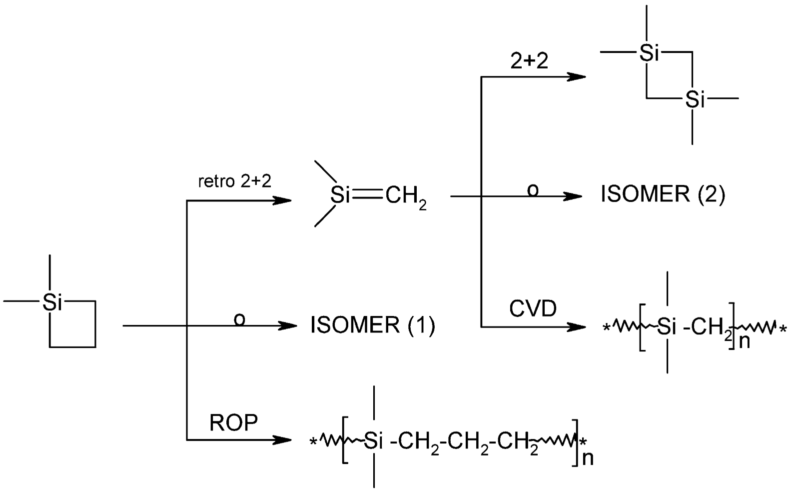
The intermediate 'a' is strongly favored for both X = O and NH, while both 'a' (30%) and 'b' (70%) are formed when X = S. The ring scission dominates the ring extrusion, an alternative decomposition process, by the factor greater than 4 for 'a' when X = NH and O. In 'b', which only forms in significant amounts when X = S, the ring extrusion is exclusive [322].

7. Scope and limitation of 2+2 cycloreversion

7.1. Four-membered rings containing one silicon atom

7.1.1. 1-Silacyclobutanes

2+2 Thermocycloreversion to silene and alkene is the most common reaction of 1-silacyclobutanes in the gas-phase (Sections 2.1, 2.2 and 3.1). In some cases it may be accompanied by the isomerization and rarely by some other side reactions. In the liquid phase the thermal ROP [324] and some other reactions of 1-silacyclobutanes [325,326] can occur. 2+2 Photocycloreversion occurs both in the gas and liquid phases (Sections 4.1 and 4.2).



(151)

Head-to-tail 2+2 cyclodimerization is a typical reaction of silenes in the absence of the trapping agents. When the appropriate substituents are attached to either silicon or carbon atoms of the Si=C bond the intramolecular rearrangements of silene can occur. Under specific conditions facilitating the CVD silenes polymerize.

Scheme 151 illustrates the scope of unimolecular reactions of 1-silacyclobutanes:

7.1.1.1. 2+2 Cycloreversion and accompanying reactions. The gas-phase thermal decomposition of 1-silacyclobutanes in most cases is a clean 2+2 cycloreversion to silene and ethylene occurring at the temperatures above ~400 °C (Sections 2.1, 2.2 and 3.1).

Minor isomerization reactions can accompany the gas-phase 2+2 thermocycloreversion of C-methyl substituted 1-silacyclobutanes (via 1,5-H migration, Section 2.2.13), 1-hydrido-1-silacyclobutanes (via 1,2-H shift, Section 2.2.2), 1-methylene-1-silacyclobutanes (via ring expansion, Section 2.2.12.1).

Other side reactions occuring to the rather considerable extent such as (i) a geometric isomerization, (ii) a ring expansion to silacyclohex-3-ene, and (iii) a homodienyl 1,5-hydrogen shift to 3,3,6,6-tetramethyl-3,6-disiladeca-1,4,8-triene are characteristic of the (*E*)- and (*Z*)-1,1-dimethyl-2-((vinyldimethyl)methyl)-3-vinyl-1-silacyclobutanes' gas-phase 2+2 thermocycloreversion (Section 2.2.13.8).

No 2+2 thermocycloreversion occurs in case of 1,1-dimethyl-2-methylene-1-silacyclobutane, which undergoes the gas-phase ring expansion (Section 2.2.13.9).

Some sterically hindered substituents at silicon, e.g. *tert*-butyl (Section 2.2.7), fail 1-silacyclobutane's ring to cyclorevert.

Like a gas-phase pyrolysis, a gas-phase photolysis of DMSCB results in ethylene and DMSE which, however, are produced with some excess internal energy (Section 4.1.1.1). Also, laser photolysis of hydridosilacyclobutanes in the gas-phase is dominated by a 2+2 cycloreversion (Sections 4.1.1.2 and 4.1.1.3). In the liquid phase the photolysis occurs as a clean 2+2 cycloreversion to silenes (Section 4.2.1).

A direct photolysis of 1-benzyl-1-methyl-1-silacyclobutane results in no 2+2 cycloreversion. It produces 1-propyl-1-methyl-2,3-benzosilacyclobutene in a quantitative yield by a sequential two-photon process involving the photoactive isotoluene derivative (Section 4.2.1.9).

Electronegative substituents at silicon increase the enthalpy of 1-silacyclobutanes' 2+2 cycloreversion and its components, i.e. ring-opening and 1,4-diradical decomposition enthalpies. In particular, the electronegative substituents at silicon strongly decrease the exothermicity of the diradical's decomposition (Section 2.2.1.1).

The gas-phase thermal 2+2 cycloreversion of 1-chloro- and 1-fluoro-1-silacyclobutanes are complicated by the side reaction of dehydrohalogenation (Section 2.2.8).

7.1.1.2. Silenes' reactivity. The reactivity of silenes generated by 1-silacyclobutanes' 2+2 cycloreversion in the absence of chemical traps depends on the substituents some of which can be responsible for occurrence of reactions that compete with 2+2 cyclodimerization.

When generated under the conditions of a conventional or a low-pressure pyrolysis of DMSCB, DMSE spontaneously undergoes a clean head-to-tail cyclodimerization resulting in 1,1,3,3-tetramethyl-1,3-disilacyclobutane (Section 2.1). The thermal isomerizations and rearrangements of transient silenes occur when appropriate substituents are attached to the doubly bonded atoms. The following of them may be mentioned: (i) the isomerization of hydrosilenes into silylenes (Section 2.2.2); (ii) the rearrangements of 1-methyl-1-trimethylsilylsilene (Section 2.2.3) and (trimethylsilylmethyl)silenes (Sections 2.2.4 and 2.2.13.3) into 1,3-disilacyclobutanes; (iii) the ring expansion of 1-methylenesilacyclobutane into 1-silacyclopentenes (Section 2.2.12.1); (iv) transformations of 1,1-dichloro-2-methylsilene into vinyldichlorosilane (Section 2.2.13.7) and 1,2-dimethyl-1-(trimethylsilylmethyl)silene into vinyl(trimethylsilyl)methylsilane (Section 2.2.13.3); (v) aryl- and benzylsilenes rearrangements yielding benzoannelated silacyclobutenes (Section 2.2.9).

Transient silenes generated by a gas-phase infrared multiphoton excitation and a decomposition or by a laser-powered homogeneous pyrolysis of 1-silacyclobutanes polymerize very efficiently in the gas phase producing solid materials. The formation of the polymers is ascribed to the elimination of the surface effects and the presence of a small hot zone, wherein temperature gradients and high concentrations of silenes favor the polymerization (Section 3.1).

For DMSE generated by the gas-phase photolysis of DMSCB oligomerization was established in addition to a homogeneous cyclodimerization (Section 4.1.1.1). Similarly transients silene generated by the gas-phase photolysis of hydridosilacyclobutanes were deposited forming polycarbosilanes (Sections 4.1.1.2 and 4.1.1.3).

7.1.2. 1-Silaelementa(N,P,O,S)cyclobutanes

1,2-Silaazetidines (1-sila-2-azacyclobutanes) are the intermediates in the gas-phase reactions of thermal generated silenes with azomethine compounds (Section 2.1.4.1). The first step of the FVP of stable 1-sila-2-azacyclobutanes (above 700 °C) is a 2+2 cycloreversion yielding silanimines which rapidly dimerize into their cyclic dimers. The *N*-isopropylated silanimine was observed by PES with two energetically close ionization potentials at 7.8 eV, associated with the n_N^- and $\pi_{Si=N}$ orbitals (Section 2.3.1.1). Correspondingly, the 7.4 eV band in the photoelectron spectrum was assigned to the ejection of electrons from the n_N^- and $\pi_{Si=N}$ orbitals of the 1,1-dimethyl-2-*tert*-butylsilanimine (Section 2.3.1.2). A side decomposition to propene (isobutene) and the dimer of silanimine, $(CH_3)_2Si{=}NH$, also occurs. In the liquid phase 2+2 thermocycloreversion of azasilacyclobutanes affording silanimines proceeds at much lower temperatures (200 °C) (Sections 5.3.1.1 and 5.3.1.2).

Upon vacuum the distillation at 100 °C 1,1-dimethyl-2-phenyl-2-phospha-1-silacyclobutane cycloreverts to yield a mixture of products resulting from transient 1,1-dimethyl-2-phenyl-1,2-phosphasilene's head-to-tail 2+2 cyclodimerization, as well as an insertion into the Si–P bond of the starting compound. A FVT/PES study at 60–80 °C allowed to measure the first vertical ionization potential of phosphasilene, $(CH_3)_2Si{=}PC_6H_5$, to be equal to 8.3 eV. The only stable product of the reaction was the dimer, 1,1,3,3-tetramethyl-2,4-diphenyl-2,4-diphospha-1,3-disilacyclobutane (Section 2.3.2.1).

1,2-Silaoxetanes are postulated to be the intermediates in the gas-phase reactions of transient silenes with aldehydes and ketones (Section 2.1.4.1). A 2+2 cycloreversion of the parent 1,2-silaoxetane to silanone and ethylene as well as to silene and formaldehyde is endothermic by 50 and 30 kcal mol^{-1}, respectively (Section 2.3.3.1). 2+2 Cycloreversion is not the preferred pathway for highly substituted silaoxetanes. A large number of moderately stable 1,2-silaoxetanes was obtained by the reaction of the relatively stable silenes with nonenolizable aldehydes and ketones. Only one of them formed from 1,1-bis(trimethylsilyl)-2-mesityl-2-trimethylsiloxysilene and fluorene underwent a 2+2 cycloreversion to silanone and alkene on boiling in pentane or toluene. All the other silaoxetanes underwent an intramolecular rearrangement involving siloxy and aryl group migrations (Section 5.1.1). Silene, $(CH_3)_2Si{=}C[Si(CH_3)_3][Si(CH_3)C(CH_3)_2]$, reacted with benzophenone to give the 2+2 cycloadduct which 2+2 cycloreversion at low-temperature results in no silanone but the silene (Section 5.1.1).

1,2-Silathietanes are the intermediates in the gas-phase reactions of transient silenes with thiones (Section 2.1.4.1). The liquid-phase pyrolysis of 1,1-di-*tert*-butyl-3,4-dimethyl-1,2-silathietane in benzene at 200 °C resulted in 1,1,3,3-tetra-*tert*-butyl-2,4-dithiadisilacyclobutane that is formally the dimer of the transient di-*tert*-butylsilanthione, $(t\text{-}C_4H_9)_2Si{=}S$. In the presence of hexamethylcyclotrisiloxane the product of insertion of the silanthione into a Si–O bond was formed (Section 5.2.1).

An IR spectroscopic study of 3,3-dimethyl-3-silathietane VLPP products isolated in Ar matrices resulted in observation of two expected 2+2 cycloreversion products, i.e., DMSE and thioformaldehyde. Under the conditions of the conventional pyrolysis (470–580 °C) their 2+2 cycloaddition gave 2,2-dimethyl-2-silathietane which in turn underwent 2+2 cycloreversion to ethylene and dimethylsilanthione. The latter dimerized and formed 2+2 cycloadduct to DMSE. (Section 2.3.4.2) The gas-phase pyrolysis of 1,1-diethyl-2,4-dimethyl-1-sila-3-thiacyclobutane decomposition is a complex process. A 2+2 cycloreversion was accompanied by a pronounced isomerization into the sulfur-containing unsaturated compounds (Section 2.3.4.3).

DMSE adds rapidly to molecular oxygen to form the intermediate siladioxetane (Section 2.1.4.1). With a dilute dry oxygen under the controlled conditions the major oxidation products of the stable solid 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-2-(1-adamantyl)silene were the cyclic trimer of bis(trimethylsilyl)silanone and the trimethylsilyl ester of adamantane-1-carboxylic acid which is suggested to arise from 2+2 cycloreversion of an intermediate siladioxetane. Siladioxetanes produced by the photooxidation of silenes in O_2-doped argon matrices are thermally labile and their fragmentation leads to the formation of silanone and aldehyde in the same matrix cage (Section 5.1.2).

Oxaazasilacyclobutane, the product of silanimine $(CH_3)_2Si{=}NSi(t\text{-}C_4H_9)_3$ with benzophenone reaction, undergoes a fast 2+2 cycloreversion (> 100 °C) followed by a 2+2 cycloaddition of the resultant dimethylsilanone to the starting silanimine (Section 5.3.2).

A cycloadduct of dimethylsilanthione and ketene, 1,1-dimethyl-3-methylene-2-oxa-4-thia-1-silacyclobutane, is a stable product. Its FVT at 900 °C results in thioketene and dimethylsilanone's cyclic trimer (Section 2.3.6.1).

A thermolysis of 1,1-dimethyl-2,3-bis(trimethylsilyl)-4-bis(trimethylsilyl)-1-sila-2,3-diazacyclobutane (90 °C) results in 2+2 cycloreversion to yield 1,1-dimethyl-2-trimethylsilyl-1-silanimine, $[(CH_3)_3Si]_2C{=}NSi(CH_3)_3$, which forms both the dimer and the product of its insertion into the Si–N bond of imine, the another product of the cycloreversion (Section 5.3.3).

A reaction of a photochemically generated di-*tert*-butylsilylene with a sterically hindered azide $t\text{-}(C_4H_9)_3Si{-}N{=}N{=}N$ resulted in the intermediate 3+1 cycloadduct which cycloreverted to yield silanimine (Section 5.3.4).

7.2. Four-membered rings containing two silicon atoms

7.2.1. 1,2-Disilacyclobutanes

There are two possible routes of 1,2-disilacyclobutanes' 2+2 cycloreversion: (i) to two silenes and (ii) to disilene and alkene. Low-pressure pyrolysis of 1,1,2,2-tetramethyl-1,2-disilacyclobutane at 700 °C resulted in ethylene and a complex mixture of the liquid products of which dimethyl-1,3-disilacyclobutanes were the rearrangement products of the transient tetramethyldisilene. However, the main product, 1,1,3-trimethyl-1,3-disilacyclopentane, arose from the rearrangement of 1,1,2,2-tetramethyl-1,2-disilacyclobutane. A 2+2 cycloreversion to two transient DMSE occurred to a lesser extent at the temperatures above 750 °C (Section 2.11.1). The 2+2 cycloreversion is not at all typical for octamethyl-l,2-disilacyclobutane's pyrolysis (310–380 °C). Instead, ring scission by an initial C–C cleavage followed by an intramolecular hydrogen abstraction proceeds and results in the isomer (Section 2.11.2). A low-pressure gas-phase 2+2 thermocycloreversion of tetrakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane] at 597 °C to the transient silene allowed to measure its first ionization potential to be equal to 6.9 eV (Section 2.11.3).

Heating 1,1,2,2-tetraphenyl-3-[bis(trimethylsilyl)ethenylidene]-4,4-bis(trimethylsilyl)-1,2-disilacyclobutane in a sealed glass tube (250 °C) in the presence of anthracene resulted in the anthracene adduct of silabutatriene intermediate. A thermolysis in presence of methanol gave three methoxysilanes indicating the intermediacy of two silicon–carbon double bonded intermediates. In the absence of any trapping agent the silene intermediate isomerized to form 1,3-disilacyclobutane by a 2+2 cycloaddition to the 1-silabutatriene intermediate (Section 5.6.1).

1,1,2,2-Tetrakis(trimethylsilyl)-3,4-bis(trimethylsiloxy)-3,4-bis(*t*-butyl)-1,2-disilacyclobutane readily dissociates to silene when dissolved in an inert solvent resulting in a mobile dimer–monomer equilibrium. 1,1,2,2-tetrakis(trimethylsilyl)-3,4-bis(trimethylsiloxy)-3,4-diphenyl-1,2-disilacyclobutane dissociates at a higher temperature. It was suggested that the dissociation probably proceeds through a homolytic fission of the carbon–carbon bond to give the corresponding diradical. An ESR signal was observed when 1,1,2,2-tetrakis(trimethylsilyl)-3,4-bis(trimethylsiloxy)-3,4-diphenyl-1,2-disilacyclobutane was heated in pentane in a sealed tube at 90 °C for 10 min and then placed in the ESR spectrometer. No equilibrium between silene and 1,2-disilacyclobutane was found for stable silenes containing the bulkier groups: $R = C(C_2H_5)_3$ or 1-adamantyl $(C_{10}H_{15})$ prepared by the photolysis of acylpolysilanes (Section 5.6.2).

The thermal 2+2 cycloreversion of 1,1,2,2-tetrakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane in hexane at 60 °C leads to the equilibrium with two molecules of the silene $[(CH_3)_3]_2Si{=}CAd$. Solvent free thermolysis at a higher temperature occurs by the two competing routes: (i) a cleavage of the Si–Si and C–C bonds producing silene, and (ii) a cleavage of the C–Si bonds leading to the formation of disilene and diadamantylidene (Section 5.6.3).

1-bis(Trimethylsilyl)-2-trimethylsiloxy-2-phenylsilene can be generated at 90 °C from 1,1,2,2-tetrakis(trimethylsilyl)-3,4-diphenyl-3,4-bis(trimethylsiloxy)-1,2-disilacyclobutane by 2+2 cycloreversion and trapped by the reaction with two equivalents of phosphaalkyne to produce diphosphatricyclobenzoheptane (Section 5.6.5).

Heating (*E*)-1,1,2,2-tetrakis(trimethylsilyl)-3,4-dimethyl-3,4-diphenyl-1,2-disilacyclobutane at 250 °C in a sealed glass tube results in no 2+2 cycloreversion products. Instead, this 1,2-disilacyclobutane completely isomerizes similarly to the isomerization of octamethyl-1,2-disilacyclobutane (Section 5.6.6).

The photolysis of 1,1,2,2-tetrakis(trimethylsilyl) dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane] at 254 nm in hexane at −78 °C in the presence of 1,3-butadiene leads to a 2:1 mixture of 1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclohex-4-ene (the trapping product of tetrakis(trimethylsilyl)disilene) and of 1,1-bis(trimethylsilyl)-1-silacyclopent-3-ene (the trapping product of bis(trimethylsilyl)silylene). The conclusion was made that the disilene, $(Me_3Si)_2Si{=}Si(SiMe_3)_2$, undergoes a subsequent photodissociation to produce the silylene, $(Me_3Si)_2Si$ (Section 4.2.3.2).

7.2.2. *1,2-Disilaelementa(O,S)cyclobutanes*

A thermal 2+2 cycloreversion of a 2,3-disilaoxetane produced by the addition of benzaldehyde to tetramethyldisilene was considered as one of the mechanistic possibilities to explain the formation of *trans*-stilbene and cyclotrisiloxanes upon the copyrolysis of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes (500 °C) or 1,1,2,2,4,5-hexamethyl-1,2-disilacyclohex-4-ene (600 °C) with excess benzaldehyde (Section 2.12).

Stable in air 1,2-disila-3-oxetanes obtained by the 2+2 photocycloaddition of tetramesityldisilene to ketones and aldehydes do not cyclorevert in the refluxing benzene (Section 5.7). However, 1,1,2,2-tetramesityl-4,4-dimethyl (diethyl, diphenyl)-1,2-disila-3-oxetanes photocyclorevert at 254 nm (−60 °C, pentane solution) yielding dimesitylsilanone and the corresponding 1-1 dimesitulsilene. The latter partly undergoes photochemical rearrangement involving 1,3-hydrogen shift and partly undergoes a 2+2 cycloaddition followed by ring opening the intermediate 1,3-disilaoxetane (Section 4.2.4.1). Neither 1,1,2,2-tetra-*tert*-butyl-3,3-dimethyl-1,2-disiladioxetane nor 1,1,2,2-tetra-*tert*-butyl-3-methyl-3-phenyl-1,2-disiladioxetane do not cyclorevert, but rearrange yielding disilyl enol ethers (Section 5.7).

The 1,1,2,2-tetramesityl-4,4-diphenyl-1,2-disila-3-thietane's photolysis at −60 °C in pentane with excess ethanol quantitatively yielded ethanol adducts of 1,1-dimesityl-2,2-diphenylsilene and dimesitylsilanethione. Photolysis in the absence of ethanol resulted in a 33% yield of the yellow 1,1-dimesityl-2,2-diphenylsilene (proved by ^{1}H-NMR) which isolation, however, failed (Section 4.2.5.1).

Thermally unstable 1,2-di-*tert*-butyl-1,2-dimesityl-1,2-disiladioxetane is a major oxidation product of the stable 1,2-di-*tert*-butyl-1,2-dimesitylsilene at −78 °C. At 0 °C it rearranges to 1,3-di-*tert*-butyl-1,3-dimesityl-disiladioxetane. Whether this rearrangement involves the intermediacy of (*tert*-butyl)mesitylsilanone remains under question (Section 5.7).

7.2.3. *1,3-Disilacyclobutanes*

The endothermicity of 1,1,3,3-tetrasubstituted 1,3-disilacyclobutanes' 2+2 cycloreversion is high and increases from 72.7 kcal mol^{-1} ($R = SiH_3$) to 114.2 kcal mol^{-1} ($R = F$), i.e. by 41.5 kcal mol^{-1}. Of this value the ring-opening enthalpy contributes only by 12.0 kcal mol^{-1}, whereas the contribution of 1,4-diradical's decomposition enthalpy varies by ~30 kcal mol^{-1}. Therefore, the occurrence of the two endothermic steps makes 1,3-disilacyclobutanes' 2+2 cycloreversion a highly uneconomic process (Section 2.4.1). That is why 1,1,3,3-tetramethyl-1,3-disilacyclobutane is so much more stable to 2+2 cycloreversion than DMSCB and its thermal decomposition is a very complex process. The onset of 1,1,3,3-tetramethyl-1,3-disilacyclobutane's decomposition was observed by 150 °C above the onset of DMSCB 2+2 cycloreversion. DMSE was not trapped below 600 °C indicating that the thermal stability of 1,1,3,3-tetramethyl-1,3-disilacyclobutane is not attributable to its equilibrium with DMSE (Section 2.4.1).

The pyrolysis of 1,1,2,3,3-pentamethyl-1,3-disilacyclobutane occurs at 630 °C yielding 1,1,3,3-tetramethyl-1,3-disilacyclopent-4-ene as the only detectable product. It involves homolytic ring opening, hydrogen atom expulsion, and intramolecular attack by silyl radical on the generated π-bond and hydrogen loss by the resulting radical, but no 2+2 cycloreversion. Similarly *cis*- and *trans*-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes yielded 1,1,2,3,3-pentamethyl-1,3-disilacyclopent-4-ene (Section 2.4.3).

Hydrido-1,3-disilacyclobutanes are less thermally stable compounds. The relative rate constants of 1,3-dimethyl-1,3-disilacyclobutane's and 1,3-disilacyclobutane's gas phase thermal decomposition are 50 and 1220 times greater than those for 1,1,3,3-tetramethyl-1,3-disilacyclobutane. A 1,2-hydrogen shift from silicon to carbon ($\log A = 14.1$, $E = 61.0$ kcal mol^{-1}) facilitates their decomposition (Sections 2.4.4 and 2.4.5). An infrared multiphoton thermal decomposition of 1,3-disilacyclobutane resulted in the very efficient deposition of Si/C/H and Si/C materials by silene and its rearrangement product, methylsilylene. A time-resolved study performed using a grating tuned pulsed TEA CO_2 laser even allowed detecting the transient silene, $\lambda_{max} \approx 260$ nm (Section 3.2.2). Laser photolysis of 1,3-disilacyclobutane using ArF laser operating at 193.3 nm resulted in the gas-phase polymerization of the transient silene, $H_2Si{=}CH_2$, which was identified by its UV spectrum with $\lambda_{max} \approx 260$ nm (Section 4.1.2.1).

A pyrolysis of 2,4-dimethylene-1,1,3,3-tetramethyl-1,3-disilacyclobutane produces 2-methylene-1,1,3,3-tetramethyl-1,3-disilacyclopentane via the intermediacy of carbene resulted from an olefin-to-carbene rearrangement, no 2+2 cycloreversion takes place (Section 2.4.6).

A non-clean decomposition occurs at the low-pressure pyrolysis of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane at 700 °C. The existence of the equlibrium between 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane and 1-methyl-1-phenylsilene is postulated (Section 2.4.7).

Rather a special case is the reversible liquid-phase 2+2 thermocycloreversion of the octasubstituted (*E*)- and (*Z*)-1,3-disilacyclobutanes. It occurs at 340 °C resulting in an equilibrium mixture of silenes which irreversibly isomerize into disilaindanes (Section 5.4).

7.2.4. 1,3-Disilaelementa(N,P,O,S)cyclobutanes

FVT/PES study of a few cyclodisilazane's 2+2 cycloreversions resulted in the characterization of highly reactive *N*-alkylated silanimines (Section 2.7). Hexamethylcyclodisilazane is thermally stable up to 900 °C. Above this temperature ionizations at 7.9 and 8.3 eV were assigned to trimethylsilanimine, $(CH_3)_2Si{=}NCH_3$. The first ionization energy of silanimines originates from the ejection of an electron from the nitrogen lone pair orbital, whereas the second ionization potential arises from the $\pi_{Si=N}$ orbital (Section 2.7.1). It is stated that *N*,*N*′-di-*tert*-butyl-1,3-disila-2,4-diazane is a good precursor for silanimine, $(CH_3)_2Si{=}NC(CH_3)_3$, in the temperatures range 850–930 °C (Section 2.7.3). The 7.4 eV band was assigned to the energetically close ionizations $\pi_{Si=N}$ and $n_{\bar{N}}$. Both cycloreversions are not clean. A high 2+2 cycloreversion enthalpy of the parent cyclodisilazane (102.7 kcal mol^{-1}) predicts the reactions to be hardly feasible. A decomposition yielding ethylene and acetylene as well as the loss of methane and *iso*-butene from *tert*-butyl groups occur.

Of a number of 2,4-disubstituted 2,4-diphenyl-1,1,3,3-tetramethyl-2,4-diphospha-1,3-disilacyclobutanes studied by FVP/PES only 1,1,3,3-tetramethyl-2,4-di-*tert*-butyl-2,4-diphospha-1,3-disilacyclobutane was approved to be a source of phosphasilene, $(CH_3)_2Si{=}P{-}t{-}C_4H_9$, with ionizations at 7.0 and 8.2 eV. Thermodynamic and kinetic stability of phosphasilenes is lower than silanimines. Ionization of the phosphorus lone pair is stabilized by 0.8 eV, when compared to that of the silanimine nitrogen. This led to conclusion that the compounds containing Si=P bond are rather silaphosphaalkenes than silaphosphaimines (Section 2.8).

2+2 Cycloreversion of the intermediate 1,1,3-trimethyl-2-oxa-1,3-disilacyclobutane to silanones and silenes postulated to explain the formation of the three different 1,3-disilacyclobutanes seems hardly feasible because of its high endothermicity (89.3 kcal mol^{-1} for the parent 1,3-disila-2-oxacyclobutane) (Section 2.5.1).

Unhindered cyclodisiloxanes are unstable molecules whose intermediacy was postulated in a number of gas-phase reactions. The enthalpy of parent cyclodisiloxane's 2+2 cycloreversion is 98.0 kcal mol^{-1}. Therefore, one cannot expect 2+2 cycloreversion for the cyclodisiloxane series. More likely they should dimerize to tetracyclosiloxanes (Section 2.9).

The intermediate 2,2,4,4-tetramethyl-2-thia-1,3-disilacyclobutane does not cyclorevert but rather dimerizes (Section 2.6.1). Although it is stated (Section 2.10) that the cyclodisilthiane ring does not cyclorevert to two silanthiones at high temperatures because of its strong thermodynamic stability ab initio calculations predict its 2+2 cycloreversion enthalpy to be equal to 68.0 kcal mol^{-1}, i.e. much less of that for cyclodisilazane (102.7 kcal mol^{-1}) and only a bit higher than that of cyclodiphosphadisiletane (61.0 kcal mol^{-1}) (Section 2.10). Infrared spectra of tetramethylcyclodisilthiane VLPP products obtained at 730 °C isolated in argon matrix exhibit no bands expected for dimethylsilanthione. There might be two explanation for this observation: (i) tetramethylcyclodisilthiane does not undergo 2+2 cycloreversion or (ii) the cycloreversion occurs but dimethylsilanthione dimerizes before it reaches the target. Results of the copyrolysis study of tetramethylcyclodisilthiane with the excess of DMSCB are in favor of the latter conclusion. No starting cyclodisilthiane was present among the products owing to the suppression of dimethylsilanthione's cyclodimerization by its 2+2 cycloaddition to DMSE yielding 1,1,3,3-tetramethyl-2-thia-1,3-disilacyclobutane (main reaction product) and the subsequent DMSE insertion into the Si-S bond of the adduct (Section 2.10.1). In the view of the data above the liquid-phase production of dimethylsilantione upon heating tetramethylcyclodisilthiane at 200 °C is rather surprising (Section 5.5).

7.3. Four-membered rings containing three silicon atoms

2+2 Photocycloreversion of 1,1,2,2,3,3-hexakis(trimethylsilyl)spiro[(4,4′-adamantane)-trisilacyclobutane] (254 nm, hexane, −78 °C, 1.5 h) leads to the production of bis(trimethylsilyl)adamantylidenesilene and tetrakis(trimethylsilyl)disilene which were trapped by 1,3-butadiene to give the expected 4+2 cycloaddition products and also were directly detected in a flash-laser photolysis. Such a photoreaction is rather unusual because cyclic as well as linear polysilanes with three adjacent Si atoms are known to extrude silylene under irradiation (Section 4.2.6.1).

8. Conclusion

The chemistry of multiply bonded silicon is an area of great interest since 1967, when the evidence for the first compound containing the silicon–carbon double bond (DMSE, $Me_2Si{=}CH_2$) was published by Gusel'nikov and Flowers [2,3] who discovered that the gas phase pyrolysis of DMSCB occurs as a clean 2+2 cycloreversion—transient DMSE 2+2 cycloaddition sequence. Since then a great many of silenes were described among which those bearing sterically non-hindered substituents appeared to be kinetically unstable transient intermediates.

Like a carbon–carbon double bond in alkenes is formed by the $2p_\pi$–$2p_\pi$ bonding between the sp^2 hybridized carbon atoms, the silicon–carbon double bond in silenes, $R_2Si{=}CH_2$, is formed by the $3p_\pi$–$2p_\pi$

bonding between the sp^2 hybridized atoms of silicon and carbon. However, the result of such bonding is the π-bond which energy does not exceed two thirds of that in olefins, though a planar geometry is not disturbed. The chemistry of silenes is mostly similar to that of alkenes. Indeed, silenes are readily involved in the reactions typical for alkenes, such as addition, cycloaddition, polymerization, and etc. But their rates are so much greater than those for alkenes that most of the reactions occur spontaneously when generating silenes. The two factors are considered to be the driving forces of silene outstanding reactivity: (1) a high polarity of the silicon–carbon double bond and (2) their lower Si=C π-bond energy. In the absence of traps silenes dimerize spontaneously (cyclodimerization is a zero activation energy process). Some of silenes bearing the appropriate substituents at the double-bonded silicon (H, $SiMe_3$, $CH_2CH_2CH_2$, *o*-Tolyl, Phenyl, Naphthyl, etc.) may rearrange to produce silylenes, silacycles, but their intramolecular rearrangements require thermal or photochemical activation. To achieve the kinetic stabilization of silenes one should either (1) create the appropriate physical conditions preventing their cyclodimerization (low-pressure experiments in a flow system, matrix isolation) or (2) attach the bulky groups to the double-bonded atoms (crowded silenes) together with substituents reducing the natural polarity of the Si=C bond. Thermodynamic stabilization may be achieved by the coordination of a donor (Lewis base) on the silicon center or by the complexation with a transition metal. A number of kinetically stabilized 'crowded' compounds of the multiply bonded silicon were prepared using these principles (see reviews [9,11–13,15–20,25]) since 1981 when the first solid relatively stable silenes (Brook [107,327], Wiberg [328]) and disilenes (West [329]) were published.

Finally, the non-hindered compounds of the doubly bonded silicon are intrinsically unstable because of their unprecedented reactivity in the bimolecular reaction taking place in the gas and liquid phases. That is why they appear as transient intermediates in various thermal and photochemical reactions of organosilicon compounds. To suppress the spontaneous bimolecular reactions one should apply physical trapping or deal with highly substituted doubly bonded silicon compounds bearing bulky groups at the mild reaction conditions.

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