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Unstable Silicon Analogues of Olefins and Ketones

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In contrast to carbon, silicon does not tend to form multiple bonds. Until recently it was believed that compounds with multiple bonds at the silicon atom do not exist, but in recent years results were obtained which permitted a new approach to this interesting and important problem in the chemistry of organosilicon compounds.
The present review considers unsaturated compounds the compositions and properties of which may be described in terms of the hypothesis that the silicon atom forms $(p-p)_\pi$ double bonds.
The bibliography includes 81 references.

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I. INTRODUCTION

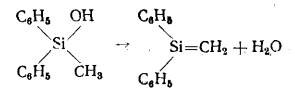
Silicon, the closest analogue of carbon has a similar structure of the outer electron shell: $2s^2 2p^2$ for carbon and $3s^2 3p^2$ for silicon. In most of its compounds silicon is quadrivalent owing to the transition of one $3s$ electron to the $3p_z$ orbital. Like carbon, silicon readily forms compounds with single bonds as a result of the overlapping of the hybridised $3sp^3$ orbitals. On the other hand, it is striking that compounds with multiple bonds of the type $(p-p)_\pi$ are very common in carbon compounds but are completely absent from silicon compounds stable under the usual conditions[1,2]. However, silicon has unfilled $3d$ orbitals which might form bonds of the $(p-d)_\pi$ type with substituents containing lone electron pairs, which would increase the multiplicity of the single bond[2].

The present review deals only with silicon compounds the structure of which can be described in terms of the hypothesis that a multiple bond is formed at the silicon atom. These are the silicon analogues of olefins (R_2Si = = SiR_2; R_2Si = CR_2) and ketones (R_2Si = O). The analogous compounds of bivalent silicon (for example SiO) are not considered, since their properties are largely determined by the presence of the lone electron pair[3].

Until recently it was believed that such unsaturated silicon compounds do not exist. However, the results obtained in recent years give grounds for a modification of this view.

The characteristics of the methods of synthesis of the organosilicon compound belonging to this new class and evidence for their existence are given in the present review and their structures and possible use in syntheses are considered. The employment of the symbol for the double bond, for example, R_2Si = CH_2, in this and in the majority of the studies quoted should be regarded as representing one of the possible structures which explains many of the reactions of these compounds, although the alternative structures $R_2\dot{S}i-\dot{C}H_2$ and $R_2\overset{+}{S}i-\overset{-}{C}H_2$ are also quite possible.

A structure with multiple bonds at the silicon atom was put forward for the first time by Gattermann[4] in 1889 for compounds obtained by treating silicon tetrachloride, trichlorosilane, etc. with ammonia (HN = Si = NH; N = Si = = NH_2). In 1912 Schlenk and Renning[5] reported the synthesis of a stable compound with a silicon–carbon double bond via the mechanism



However, later these results were disproved by Kipping[6], who, having repeated the experiment, showed that Schlenk and Renning[5] did not obtain an individual compound but a mixture of dimethyldiphenylsilane, methyldiphenylsilanol, and biphenyl. In general, towards the end of the 1920s it became clear that the earlier studies[7] where structures with multiple bonds at the silicon atom were attributed to stable compounds must have been erroneous. Moreover, it was shown that the reactions usually employed to form multiple bonds between carbon atoms are unsuitable for the synthesis of the corresponding silicon compounds. Thus the loss of a single water molecule by a tertiary silanol does not occur at all. Disiloxanes are formed instead. Nor are silicon analogues of olefins formed as a result of the dehydrochlorination of silyl chlorides. The latter are extremely stable and can be distilled without decomposition (even in the presence of quinoline). The formation of unsaturated silicon compounds by treating tertiary silyl chlorides with Grignard reagents is also unknown, although many tertiary halogenomethanes do form olefins. Other attempts to prepare stable compounds with a multiple bond at the silicon atom were also unsuccessful[8].

Towards the end of the 1940s and the beginning of the 1950s, the problem of the instability of compounds with multiple bonds at the atoms of elements in the Third and succeeding Periods began to be considered in terms of graphical representations of orbitals and quantum-mechanical calculations (see Section V).

In 1952 Andrianov and Sokolov[9] reported the detection of the dimethylsilanone ion in the mass spectrum of octamethylcyclotetrasiloxane and also the mass spectrometric identification of several dialkylsilanones formed when organopolysiloxanes are heated to 150–200°C and in the gas-phase hydrolysis of dichlorodimethylsilane.

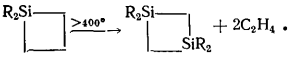
Nevertheless the earlier ideas concerning the possibility of the existence of stable compounds with multiple bonds at the silicon atom were so attractive that even in the 1960s they resulted in the publication of two erroneous communications: concerning the preparation of $Me_3SiCH = SiMe_2$ [10] and of the silicon analogue of benzene[11]. It was soon shown that, instead of the former compound, the authors obtained 1, 1, 3, 3-tetramethyl-1, 3-disilacyclobutane, which was mistaken for an unsaturated compound by virtue of its ability to combine with bromine[12]. The structure of the second compound was not confirmed either[13].

In later studies compounds with double bonds at the silicon atom were regarded only as short-lived species responsible for the formation of particular reaction products. Thus dimethylsilanone was postulated as an intermediate in the cleavage of polysiloxanes by the Iotsich reagent[14]; $MeHSi = CH_2$ was regarded as a product of the carbene–olefin isomerisation of dimethylsilylene[15] and the biradical $Me_2\dot{S}i-\dot{C}H_2$ was introduced into the mechanism of the thermal decomposition of tetramethylsilane to account for the formation of 1, 1, 3, 3-tetramethyl-1, 3-disilacyclobutane[16]; here mention may also be made of the study of Müller and Müller, who considered the dechlorination of chloromethanes in the presence of a silicon–copper alloy[17]. However, all these cases involved complex non-selective processes in which other interpretations of the mechanism are equally probable.

In 1965 the present authors discovered the selective thermal decomposition of monosilacyclobutanes[18,19] via the formation of silicon analogues of olefins. The study of this reaction yielded for the first time kinetic and chemical evidence for the existence of an intermediate compound with a silicon-carbon double bond[20–22] and led to methods for their stabilisation. As a result, these species and other compounds with double bonds at the silicon atom again attracted the attention of chemists, as can be judged from the publication of numerous studies on this subject in recent years. The results of this new stage in the development of the chemistry of silicon analogues of unsaturated compounds are discussed below.

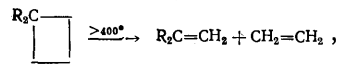
II. MONOSILICON ANALOGUES OF OLEFINS

In a study of the pyrolysis of a number of monosilacyclobutanes we observed the elimination of ethylene and the formation of 1, 3-disilacyclobutanes[18,19].

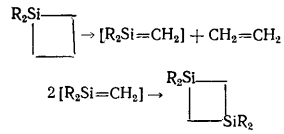


For example, in the pyrolysis of 1, 1-dimethyl-1-silacyclobutane the only reaction products were ethylene and 1, 1, 3, 3-tetramethyl-1, 3-disilacyclobutane. The yield of 1, 3-disilacyclobutane was lower when chlorine atoms were attached to the silicon atom. However, it amounted to 34.8% even for 1, 1-dichloro-1-silacyclobutane, which was of preparative interest for the synthesis of 1, 1, 3, 3-tetrachloro-1, 3-disilacyclobutane which is otherwise difficult to obtain.

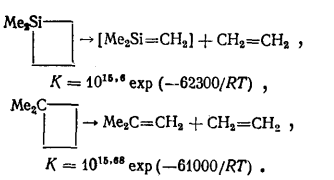
For the analogous thermal decomposition of compounds of the cyclobutane series[23],



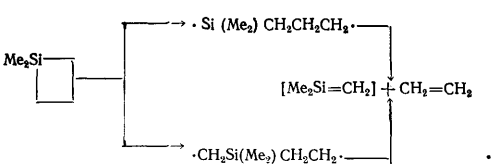
we assumed that the reaction proceeds via an intermediate unstable compound — a silicon analogue of an olefin, which is in fact responsible for the formation of 1, 3-disilacyclobutane[20]:



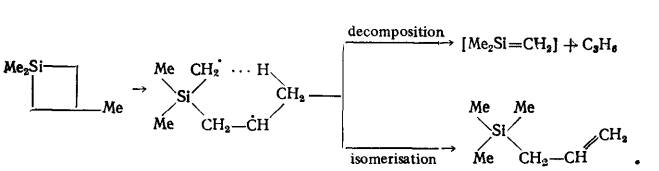
Indeed, kinetic data for the thermal decomposition of 1, 1-dimethyl-1-silacyclobutane proved to agree well with this hypothesis[21,22]. The reaction was of first order with respect to monosilacyclobutane and was homogeneous and the variation of the decomposition rate constant with temperature was very close to the corresponding variation for the thermal decomposition of 1, 1-dimethylcyclobutane[24]:



The closeness of the Arrhenius parameters of these reactions suggests that they have the same mechanism, namely the reaction begins with the dissociation of one bond in the ring (Si–C or C–C) and a consequent formation of a biradical, which decomposes spontaneously to a short-lived compound and ethylene (the biradical mechanism provides a satisfactory explanation of the characteristics of the thermal decomposition of cyclobutanes[25]):



The dissociation of the ring C–C bond is consistent with the isomerisation of 1, 1, 3-trimethyl-1-silacyclobutane[26,27] to allyltrimethylsilane during its thermal decomposition †. Such isomerisation is probably due to the 1, 5-migration of a hydrogen atom in the biradical:



† We may note incidentally that the above reaction is the first instance of the isomerisation of monosilacyclobutanes to silaolefins.

A subsequent investigation established[28] that in the pyrolysis of 1,1-dimethyl-1-silacyclobutane in a flow reactor at low pressures the processes involving the formation and disappearance of the silicon analogue of an olefin can be separated. Thus we found that, when the pyrolysis is carried out at pressures below 1 torr, the region where $Me_2Si = CH_2$ undergoes cyclodimerisation moves to an increasing distance beyond the reactor, as shown by the increase of the ratio $[C_2H_4]/[Me_2SiCH_2)_2]$ by two powers of ten on reducing the pressure to 10^{-3} torr (Fig. 1) owing to the formation by the silicon analogue of isobutene of a polymeric product $(-Me_2SiCH_2-)_x$ on the cold surface.

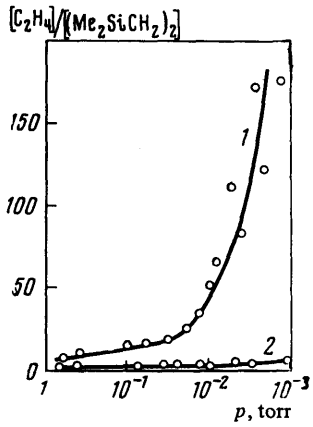
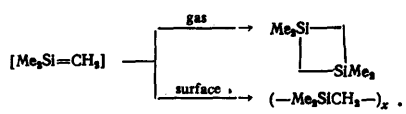


Figure 1. Variation of $[C_2H_4]/[(Me_2SiCH_2)_2]$ with pressure in the pyrolysis of 1,1-dimethyl-1-silacyclobutane in a flow reactor; distance between the pyrolysis and condensation zones: *1*) 30; *2*) 250.

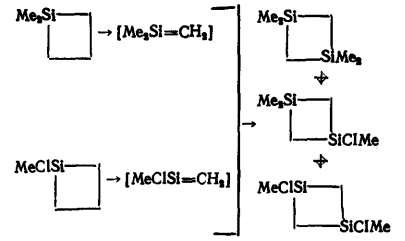
Walsh[29], who employed our kinetic data for the pyrolysis of 1,1-dimethyl-1-silacyclobutane and Davidson and Lambert's data[30] for the pyrolysis of trimethylsilane, found that the π-bond energy in the silicon analogues of olefins is in the range 30–42 kcal mole^{-1} and Barton and McIntosh[31], who investigated the pyrolysis of 1,1-dimethyl-1-silacyclobutane at -196°C by infrared spectroscopy, observed a band at 1407 cm^{-1} which they believe to be due to the presence of $Me_2Si = CH_2$. The methylenediamethylsilane ion is also formed in the dissociative ionisation of 1,1-dimethyl-1-silacyclobutane[32,33] (the peak of this ion is the most intense in the mass spectrum).

Certain reactions of the silicon analogues of olefins, which may be regarded as chemical evidence for the existence of these compounds, are discussed below in relation to $Me_2Si = CH_2$.

It has already been mentioned that, in the absence of trapping agents, cyclodimerisation takes place in the gas phase and polymerisation on the cold surface:

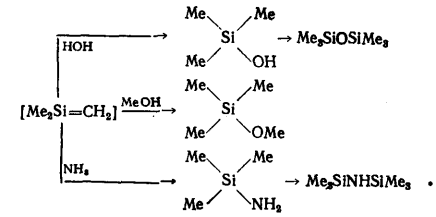


Products of direct and cross cyclodimerisation are formed in the pyrolysis of two different monosilacyclobutanes[20,34]:

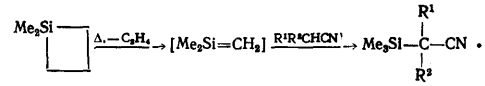


One should note that we never observed among the reaction products dimers of the "head to head" type or cyclic trimers.

Trapping agents form adducts with silicon analogues of olefins. Chemical trapping of $Me_2Si = CH_2$ was first achieved with the aid of water and ammonia in the pyrolysis of 1,1-dimethyl-1-silacyclobutane in their presence[21,22]. The reaction with alcohols occurred similarly:



Quite recently Sommer and coworkers[35] carried out this reaction with acetonitrile and its derivatives:



Another reaction of silicon analogues of olefins is cycloaddition to olefins. However, since the rate constant for this reaction is low compared with the cyclodimerisation rate constant, its contribution can be observed only at olefin concentrations greatly exceeding that of the intermediate. For example, this reaction results in a decrease of the rate constant for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane at conversions in excess of 60%[22]. Kinetic evidence for the cycloaddition of $Me_2Si = CH_2$ to ethylene was obtained in a study of the pyrolysis of 1,1-dimethyl-1-silacyclobutane in the presence of added ethylene[22]. Indeed the apparent first-order reaction rate constant was found to depend on ethylene concentration, in agreement with the kinetic mechanism involving a reversible first stage of the thermal decomposition:

$$A \underset{k_3}{\overset{k_1}{\rightleftharpoons}} B + C$$

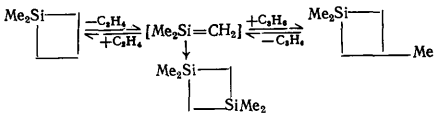
$$2B \xrightarrow{k_2} D$$

$$-\frac{d\ln A}{dt} = k_1\left\{1 - \frac{k_3 C}{(2k_1k_2)^{1/2}A^{1/2}}\left(1 - \frac{k_3 C}{2(2k_1k_2)^{1/2}A^{1/2}}\right)\right\}.$$

where A = 1,1-dimethyl-1-silacyclobutane, B = Me_2Si = $= CH_2$, C = ethylene, and D = 1,1,3,3-tetramethyl-1,3-disilacyclobutane [or the corresponding concentrations (Ed. of Translation)] variation of the apparent first-order reaction rate constant with $(C/A^{1/2})[1-k_2/2(2k_1k_3)^{1/2}-C/A^{1/2}]$ should be linear, which was in fact observed experimentally at different temperatures (Fig. 2). It was also possible to estimate the ratio $k_2/k_3^{1/2}$ and $E_2 - \frac{1}{2}E_3 = 14.5 \pm 4$ kcal mole^{-1}.

The formation of 1,1,3-trimethyl-1-silacyclobutane in the pyrolysis of 1,1-dimethyl-1-silacyclobutane in the

presence of a 15–20-fold excess of propane and the formation of 1,1-dimethyl-1-silacyclobutane in the pyrolysis of 1,1,3-trimethyl-1-silacyclobutane in ethylene constituted chemical evidence for the reversibility of the first stage of the thermal decomposition[36,37]:



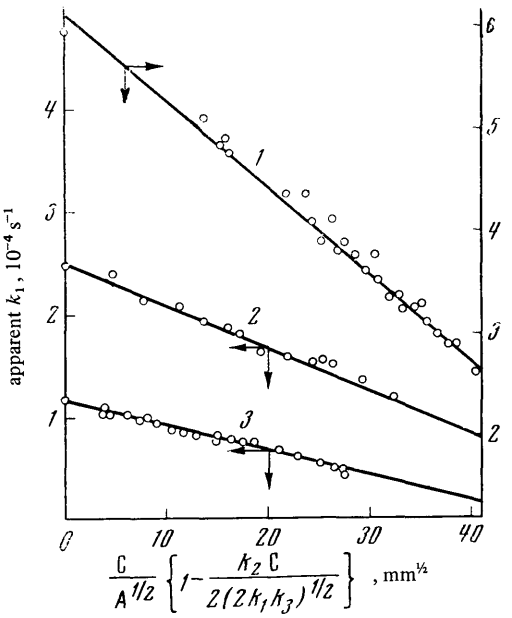
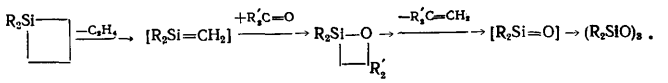


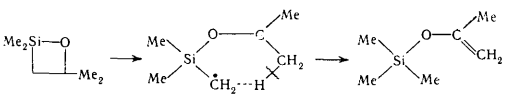
Figure 2. Variation of the apparent rate constant for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane with the concentration of added ethylene (in terms of the coordinates corresponding to the kinetic equation quoted); temperature (°C): *1*) 450.7; *2*) 437.1; *3*) 423.

Silicon analogues of olefins readily undergo cycloaddition to the double bond of the carbonyl group. Cyclosiloxanes (mainly the cyclic trimer), ethylene, and new olefin are formed in the pyrolysis of 1,1-dimethyl-1-silacyclobutane in the presence of isobutyl methyl betone[38] and in the pyrolysis of 1,1-diphenyl-1-silacyclobutane in the presence of 2-pentanone, 2-heptanone, and benzophenone[39]:

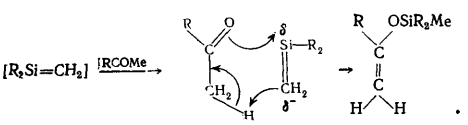


The cycloaddition product (silaoxetan) was not isolated, although Barton and Kline[38] reported its mass-spectrometric identification. We isolated a compound with the corresponding composition in the pyrolysis of 1,1-dimethyl-1-silacyclobutane in the presence of acetone (*m/e* 130), but its spectrum showed bands due to a double bond and the band due to the Si–O bond was in the usual region (1050 cm^{-1}) (in strained rings, this band should undergo a pronounced bathochromic shift — 100 cm^{-1} and more). This made it possible to assign the isomeric structure $Me_3SiOC(Me)=CH_2$ to the product.

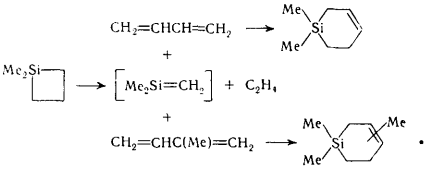
The formation of isopropenyloxytrimethylsilane can be readily represented as a result of the isomerisation of the silaoxetan, which is unstable under the reaction conditions, via the 1,5-migration of the hydrogen atom in the biradical formed on dissociation of the C–C bond of the four-membered ring:



The mechanism of the formation of analogous products based on the addition of the enolised form of the ketone of the silicon–carbon double bond[39] appears more likely. The argument based on the fact that the reaction does not occur in the presence of benzophenone is not convincing, since the 1,5-migration of hydrogen in the biradical is also impossible in this case. In his latest investigations[35,40] Sommer proposes an essentially new mechanism, which includes a six-centre transition state, but, in contrast to our mechanism, no account is taken of the formation of the intermediate silaoxetan:



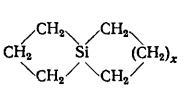
Silicon analogues of olefins are effective dienophiles; they readily enter into the diene synthesis reaction. Thus the corresponding Diels–Alder adducts are formed in the pyrolysis of 1,1-dimethyl-1-silacyclobutane in the presence of butadiene[37], isoprene[37], or 2,3-dimethylbutadiene[41]:



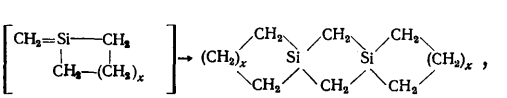
The formation of a single adduct with butadiene and of two adducts with isoprene suggests that the reaction proceeds via a single-state 1,4-cycloaddition mechanism.

Thus there are many reactions demonstrating the existence of short-lived silicon analogues of olefins. The pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane[26] and 1,1-diphenyl-1-cyclobutane[39] proceeds similarly.

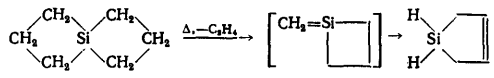
We observed an interesting feature in a study of the thermal decomposition and dissociative ionisation of silaspiroalkanes[43] containing the monosilacyclobutane ring:


(where x = 1, 2, or 3).

Whereas 4-silaspiro[3,4]octane (x = 2) and 4-silaspiro[3,5]nonane (x = 3) form the corresponding 1,3-disilacyclobutanes,



4-silaspiro[3,3]heptane ($x = 1$) behaves anomalously in the pyrolysis[23,43]. Oily products with the composition corresponding to that of the initial compound after the elimination of an ethylene molecule are mainly formed in a flow system in an atmosphere of helium. On the other hand, *in vacuo* this compound decomposes into hydrogen, ethylene, propene, butadiene, and 1-silacyclopent-3-ene, the relative contents of which depend on temperature (Fig. 3). It is significant that compounds with 1,3-disilacyclobutane rings were not formed and the precipitation of elemental silicon on the reactor walls was noted. We believe that these characteristics of the thermal decomposition are in many ways determined by the specific features of the behaviour of the methylenecyclobutane analogue formed from this silaspiroheptane, which is capable of isomerising, in contrast to other compounds of this type:



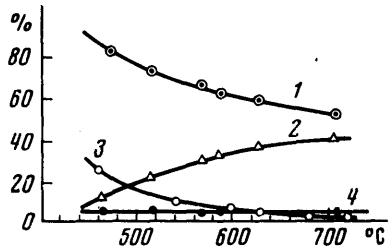
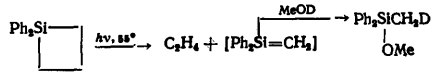


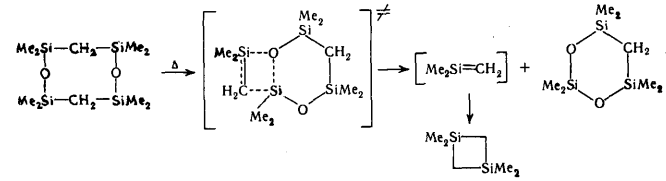
Figure 3. Temperature variation of the relative contents (%) of the decomposition products in the pyrolysis of 4-silaspiro[3,3]heptane: *1*) ethylene; *2*) butadiene; *3*) 1-silacyclopent-3-ene; *4*) propene.

In conclusion of the discussion of the thermal decomposition reactions of monosilacyclobutanes as a method for the generation of silicon analogues of olefins, we may mention that in the series of compounds  (where E = C, Si, or Ge) the selectivity of the olefin decomposition process is maintained only for the first two members of the series. The reaction of the germanium compound is significantly complicated by a carbenoid decomposition[44], which precludes its employment for the selective generation of germanium analogues of olefins.

Monosilacyclobutanes are also effective sources of silicon analogues of olefins in the liquid-phase photochemical decomposition reaction[45], as can be seen from the formation of an adduct with deuteriomethanol (yield 80%):

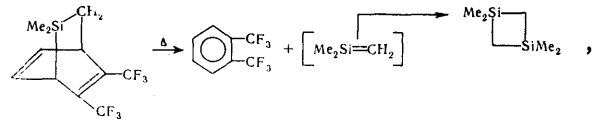


We noted the formation of a silicon analogue of isobutene in the pyrolysis of eight-membered cyclocarbasiloxanes containing siloxane and silmethylene groups[46,47], for example:



However, an alternative decomposition with formation of dimethylsilanone also takes place in this case (see Section IV).

Bicyclo[2,2,2]octa-2,5-dienes proved to be extremely promising for the generation of silicon analogues of olefins. Barton and Kline[48] found that the pyrolysis of 7,7-dimethyl-2,3-bis(trifluoromethyl)-7-silabicyclo[2,2,2]octa-2,5-diene takes place at 400°C in the gas phase with formation of *o*-bis(trifluoromethyl)benzene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane via the mechanism



and the photolysis of this compound at 77° and 28°K resulted in the formation of a large amount of the first product and only of traces of the second. The latter is probably due to the polymerisation of $Me_2Si = CH_2$ in the condensed phase. $Et_2Ge = CH_2$, formed as a result of the pyrolysis, gives rise to 1,3-digermacyclobutane and in the presence of 2,3-dimethylbuta-1,3-diene the product is 1,1,3,4-tetramethyl-1-germacyclohexene.

* * *

The formation of silicon analogues of olefins was also postulated in a number of gas-phase thermal decomposition reactions of cyclic organosilicon compounds. However, in contrast to the majority of the cases which have been discussed, these reactions are not selective and the yield of products due to the formation of unstable species with a multiple bond at the silicon atom is usually low. The thermal decomposition of tetramethylsilane[18], where the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane and 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane was attributed to the cyclodimerisation and cyclotrimerisation of the silicon analogue of isobutene, was mentioned above:

$$Me_4Si \rightarrow Me_3Si\cdot + Me\cdot ,$$
$$Me\cdot + Me_4Si \rightarrow Me_3SiCH_2^{\cdot} + MeH ,$$
$$Me_3SiCH_2^{\cdot} \rightarrow [Me_2Si{=}CH_2] + Me^{\cdot} .$$

The authors[16] suggest that the intermediate is formed as a biradical species in the decomposition of the trimethylsilylmethyl radical. However, Davidson and Lambert[30,50], who investigated the thermal decomposition of trimethylsilane, showed that the disproportionation of the radicals is more important under these conditions:

$$HMe_2Si^{\cdot} + \dot{C}H_2SiMe_2H \rightarrow Me_2SiH + [CH_2{=}SiMeH] ,$$
$$Me_3Si^{\cdot} + \dot{C}H_2SiMe_2H \rightarrow Me_3SiH + [CH_2 = SiMe_2] ,$$
$$2\,\dot{C}H_2SiMe_2H \rightarrow Me_2SiH + [CH_2{=}SiMe_2] .$$

The competing radical recombination reaction proceeds less vigorously at elevated temperatures owing to the low

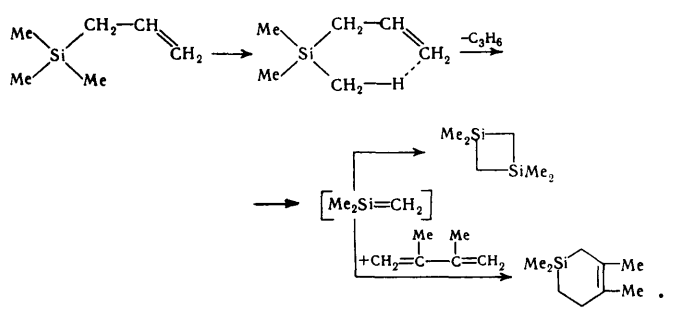
stability of disilanes. The cyclodimerisation of the above olefin analogues leads to the formation of the corresponding three 1,3-disilacyclobutanes. It is important to note that the formation of a cyclic trimer was not observed in this case either.

Moreover, a recent study of the kinetics of the thermal decomposition of tetramethylsilane[51] showed that the disproportionation of silyl radicals

$$2\,Me_3Si^{\bullet} \rightarrow Me_3SiH + [Me_2Si=CH_2]\ ,$$

plays an important role among the reactions involving the formation of $Me_2Si = CH_2$. In particular, whereas at 900°K the ratio of the disproportionation and recombination rate constants for trimethylsilyl radicals is 1.2,[51] at 300°K it is less than 10^{-3}.[52] This corresponds to a disproportionation activation energy of 6–7 kcal mole^{-1}.

According to Bailey and Kaufmann[41], $Me_2Si = CH_2$ is an intermediate in the pyrolysis of allyltrimethylsilane. Together with other products, 1,1,3,3-tetramethyl-1,3-disilacyclobutane is formed in the process and pyrolysis in the presence of 2,3-dimethylbuta-1,3-diene gives 1,1,3,4-tetramethyl-1-silacyclohexene:



However, Sakurai et al.[53] found that the thermal decomposition of allyltrimethylsilane occurs at a temperature as low as 500°C. Under these conditions, the main reaction is α-elimination of methylene:

$$Me_3SiCH_2CH{=}CH_2 \xrightarrow{\Delta} Me_3Si\cdots CH{=}CH_2 \rightarrow Me_3SiCH{=}CH_2 + CH_2:\ .$$

Comparison of the results of these studies suggests that the formation of $Me_2Si = CH_2$ in the first case is more likely to be associated with the decomposition to the trimethylsilyl radical and its disproportionation:

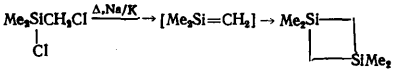
$$Me_3SiCH_2CH{=}CH_2 \xrightarrow{\Delta} Me_3Si^{\bullet} + CH_2{=}CH{=}CH_2\ ,$$
$$2\,Me_3Si^{\bullet} \longrightarrow Me_3SiH + [Me_2Si=CH_2]\ .$$

This is consistent with the non-selectivity of the reaction noted by Bailey and Kaufmann[41].

According to the latest results[54,55], the pyrolysis of hexamethyldisilane in a flow system at a low pressure proceeds with formation of trimethylsilane, $Me_3SiCH_2Si(H)Me_2$, and 1,1,3,3-tetramethyl-1,3-disilacyclobutane via $Me_2Si = CH_2$:

$$R^{\bullet} + Me_3SiSiMe_3 \rightarrow RH + Me_2SiSiMe_2CH_2^{\bullet}\ ,$$
$$Me_2SiSiMe_2CH_2^{\bullet} \rightarrow Me_2SiCH_2\dot{S}iMe_2\ ,$$
$$Me_2SiCH_2\dot{S}iMe_2 \rightarrow Me_2Si^{\bullet} + [Me_2Si=CH_2]\ .$$

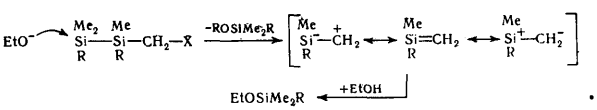
Among other ways of generating intermediates with a double bond at the silicon atom, mention may be made of the gas-phase dechlorination of chloromethyldimethylchlorosilane by sodium and potassium vapours[56]:



and of the photolysis of methylsilane[57,58] by vacuum ultraviolet radiation.

* * *

The hypothesis of the formation of silicon analogues of olefins was also used in the treatment of the mechanisms of certain liquid-phase reactions. Thus Kumada et al.[59] suggested that, when sodium ethoxide is allowed to react with 1-chloromethylpentamethyldisilane and other halogenomethyldisilanes in ethanol solution, there is a synchronous β-elimination of $Me_2Si = CH_2$, which is trapped by ethanol:

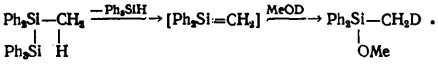


and Jarvie and Rowley[60] introduced this intermediate into the mechanism of the anomalous reaction between dimethylsilylmethylmagnesium bromide and benzophenone:

$$Ph_2C{=}O + Me_2Si(H)CH_2MgBr \rightarrow Ph_2CHOMgBr + [Me_2Si=CH_2]\ ,$$
$$[Me_2Si=CH_2] + Ph_2CHOMgBr \rightarrow Me_2SiCH_2MgBr \xrightarrow{+H_2O} Me_2SiOCHPh_2\ ,$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OCHPh_2$$
$$[Me_2Si=CH_2] + Me_2Si(H)CH_2MgBr \xrightarrow{+H_2O} HMe_2SiCH_2SiMe_3\ .$$

However, one should note that in both cases there are alternative reaction mechanisms[60,61] which do not involve the formation of species with a double bond at the silicon atom.

From our point of view, the most convincing studies demonstrating the generation of silicon analogues of olefins in liquid-phase reactions are the investigation of the photolysis of 1,1-diphenyl-1-silacyclobutane already discussed[47] and a study of the photochemical dehydrosilylation of methylpentaphenyldisilane[62], where it was shown that the photolysis of this compound in methanol-d_1 leads to the formation of triphenylsilane and $Ph_2(CH_2D)SiOMe$ in 60% yield. The formation of these products is indeed consistent with the dehydrosilylation mechanism in which the intermediate compound is trapped by deuteriomethanol:

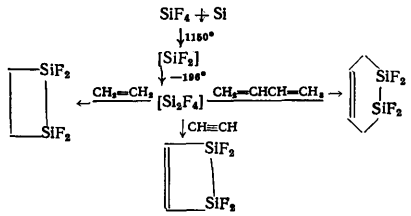


Likewise photolysis of $Ph_2(CD_3)SiSiPh_3$ in methanol yields $Ph_2(CD_2H)SiOMe$ and triphenyldeuteriosilane.

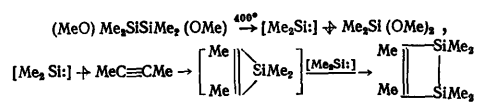
III. DISILICON ANALOGUES OF OLEFINS

After considering data on the joint condensation of difluorosilylene with unsaturated compounds and also the

low-temperature infrared and ESR spectra of difluorosilylene, Margrave and Wilson[63] suggested the formation of the biradical Si_2F_4 at -196°C:



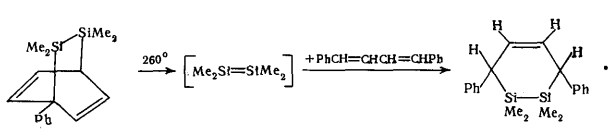
A similar conclusion was reached in a study of the reactions of difluorosilylene with BF_3, benzene, methylacetylene, and dimethylacetylene. However, the reactions of difluorosilylene with methanol, water, hydrogen sulphide, iodine, and germane could not be accounted for by the involvement of the dimeric biradical. It is therefore interesting to note a recent investigation[64] in which a reaction analogous to that described above was also explained without postulating the involvement of Si_2F_4:



Moreover, the observation of the ESR spectrum of singlet difluorosilylene condensed on a cold surface probably cannot be regarded as evidence for the triplet structure of Si_2F_4. This spectrum may be due to the polymeric species $\cdot SiF_2(SiF_2)_xSiF_2\cdot$, where $x = 1, 2, 3\ldots$, and not to Si_2F_4.

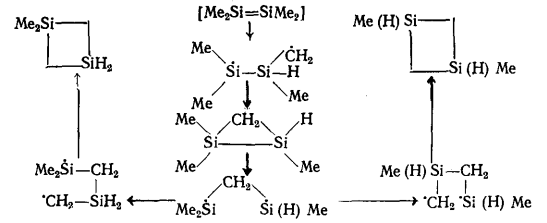
Thus, although there is no doubt about the possibility of the formation of olefin analogues by the dimerisation of silylenes and the structures of the products of the cocondensation of difluorosilylene with alkenes, alkynes, and butadienes can be described in terms of the Woodward–Hoffmann rule as a result of the cycloaddition of tetrafluorodiselene[65], the involvement of the latter as well as its biradical in the above reactions requires additional evidence.

More convincing data concerning the existence of disilicon analogues of olefins were obtained in a study of the thermal decomposition of 7,8-disilabicyclo(2,2,2]octa-2,5-dienes. Peddle, Roark, and coworkers[66,67] found that the pyrolysis of 7,8-disilabicyclo[2,2,2]octa-2,5-dienes leads to the formation of the intermediate $Me_2Si = SiMe_2$, which may be captured by anthracene, naphthalene, and *trans*, *trans*-1,4-diphenylbuta-1,3-diene to form adducts, for example:



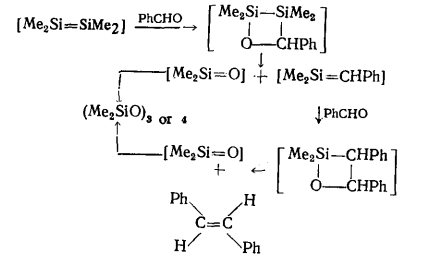
The $Me_4Si_2^+$ ion is the main species also in the mass spectra of these compounds.

In the absence of trapping agents, 1,1-dimethyl-1,3-disilacyclobutane (30%), 1,3-dimethyl-1,3-disilacyclobutane (10%), and a polymer were formed[67]. The mechanism of the formation of 1,3-disilacyclobutanes proposed by the authors is given below:



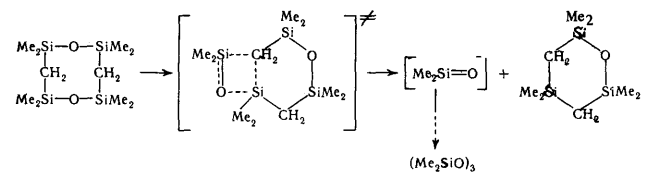
Since the short-lived compound is formed in a thermally activated concerted retrodiene synthesis reaction, it should be in the singlet form, provided that the repulsion of the vicinal methyl groups does not exceed the π-bond energy.

Barton and Kilgour[68] found that the joint pyrolysis of 7,7,8,8-tetramethyl-1-phenyl-7,8-disilabicyclo[2,2,2]octa-2,5-diene or 7,7,8,8-tetramethyl-5,6-benzo-7,8-disilabicyclo[2,2,2]octa-2,5-diene with an excess of benzaldehyde leads to the formation of *trans*-stilbene and cyclosiloxanes together with biphenyl or naphthalene. The following mechanism involving the formation and reactions of $Me_2Si = SiMe_2$ was proposed:



IV. SILICON ANALOGUES OF KETONES

In a systematic study of the pyrolysis of organosilicon compounds, we found that eight-membered cyclocarbosiloxane decompose with formation of products resulting from the elimination of monomeric units[46,47,69]. In particular, it was shown that one of the decomposition pathways involves the scission of dimethylsilanone:



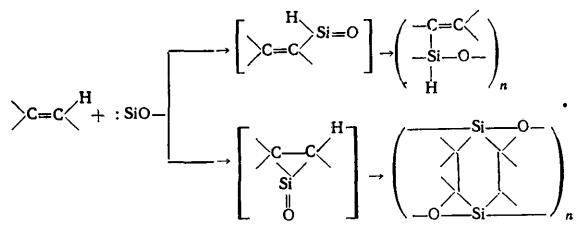
We obtained similar results also in a study of the mechanism of the thermal decomposition of cyclosiloxanes $D_n (n = 3-7)$[70,71]. It was found that in the initial stages of the reaction the main monomolecular decomposition products are compounds of the type D_{n-1} and that virtually the only example of products of the type D_{n+m} is D_{n+1}. This is consistent with the scission of dimethylsilanone, which either forms a cyclic trimer or is inserted in the Si–O bond of the initial compound, yielding D_{n+1}:

$$D_n \rightarrow [Me_2Si=O] + D_{n-1},$$
$$[Me_2Si=O] + D_n \rightarrow D_{n+1},$$
$$3[Me_2Si=O] \rightarrow (Me_2SiO)_3.$$

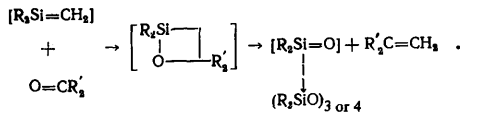
While the scission of dimethylsilanone is characteristic of the cyclic tetramer and pentamer, for higher cyclosiloxanes direct decomposition into D_3 or D_4 is energetically more favourable.

Similar results were obtained by Davidson and Tomson[72], who later investigated the pyrolysis of octamethylcyclosiloxane. The main reaction products D_3 and D_5 were detected in proportions of 1.3 : 1, which is consistent with the above mechanism. As was to be expected, their activation energy for the decomposition reaction (71.9 kcal $mole^{-1}$) was higher than for the cyclic pentamer (61 kcal $mole^{-1}$)[70,71]; they estimated the lower limit of the π-bond energy in dimethylsilanone as 38 kcal $mole^{-1}$).

Silanones are probably also formed in the joint condensation of silicon monoxide with organic compounds at 196°C.[3] However, in contrast to the compound discussed above, they undergo uncontrollable polymerisation:



As already mentioned above, the thermal decomposition of silaoxetans (see Section II), formed in the reaction of $R_2Si = CH_2$ with ketones and aldehydes, is a very effective reaction for the generation of silicon analogues of ketones:



The reaction with aromatic carbonyl compounds follows a more specific pathway[40]. In the case of aliphatic ketones and aldehydes the decomposition of the silaoxetan is accompanied by its isomerisation to the corresponding alkenyloxysilane. A similar reaction was observed in the decomposition of the adduct of $Me_2Si = SiMe_2$ with benzaldehyde[68] (see Section III).

V. THE STABILITY OF SILICON ANALOGUES OF UNSATURATED COMPOUNDS

As can be seen from the studies discussed above, there are numerous data in agreement with the hypothesis of the existence of silicon analogues of olefins and ketones as short-lived species. Their number increases still further if mass-spectrometric data are included. Only some of these were mentioned in the present review, while others can be found in Orlov's review[73].

In contrast to unsaturated carbon compounds, their silicon analogues exhibit an enhanced reactivity in bimolecular reactions, which hinders their isolation in a monomeric form. The latter can be stabilised only at low temperatures.

On the other hand, compounds of this type are extremely resistant to monomolecular decomposition. Among the examples discussed above, the only exception was methylenesilacyclobutane, formed in the pyrolysis of 4-silaspiro[3, 3]heptane; it undergoes a more profound decomposition or isomerises as a result of its specific structure.

A number of attempts have been made to explain the low stability of the π-bond in double-bonded compounds of elements in the Third and subsequent Periods. On the basis of a graphical representation of orbitals, Pitzer[74] postulated that the low stability of the multiple bonds in such molecules is due to the appreciable repulsion between the bonding orbitals and the filled inner shells of these atoms (*inner shell repulsion*). However, Mulliken[75,76] demonstrated by calculations of overlap integrals that this repulsion is no greater for elements of the Third Period than for elements of the Second Period and therefore it cannot be the cause of the absence of π-bonds in compounds of heavy elements. According to Mulliken, a possible explanation of this phenomenon is that the formation of two σ bonds is more favourable than the formation of a double bond, i.e. there should be a greater tendency towards the formation of a polymeric form than towards the formation of a monomeric form.

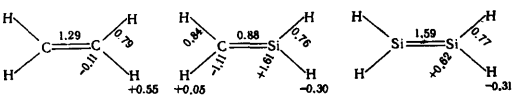
On the basis of the structure of the energy bands in diamond and crystalline silicon, Levin et al.[77] estimated the extent of $(p-p)_\pi$ interaction between carbon and silicon atoms and showed that the corresponding resonance integral for silicon is smaller by a factor of approximately two than for carbon. The authors regard this finding as a possible cause of the absence of silicon compounds with multiple bonds.

Quite recently Curtis[78] carried out calculations on the $H_2Si = CH_2$ and $H_2Si = SiH_2$ molecules using the extended Hückel molecular orbital method and found that 3*d* orbitals contribute significantly to the π-overlap population. Moreover the contribution of the $(p-d)_\pi$ bond actually exceeds that of the $(p-p)_\pi$ bond:

π-Overlap populations

	$(p-p)_\pi$	$(p-d)_\pi$	$(d-d)_\pi$	Σ
$CH_2=SiH_2$	0.130	0.197	—	0.327
$H_2Si=SiH_2$	0.277	0.348	0.038	0.663

The π-overlap populations and atomic charges in ethylene and its silicon analogues are quoted below (after Curtis)[78]:



Evidently the silicon–carbon double bond is extremely polar. The high polarity of this bond also follows from a CNDO calculation on $H_2C = SiH_2$ [79]; the dipole moment of this molecule has been estimated as 2.99 D. The barrier to rotation about the π-bond (and hence the π-bond energy) increases in the following sequence: C = Si < Si = Si < C = = C, and the low stability of the C = Si bond is explained by the energy discrepancy between the carbon and silicon *p* orbitals. Damrauer and Williams[80] carried out CNDO calculations on the $H_2Si = CH_2$, $F_2Si = CH_2$, $H_2Si = CF_2$, and $F_2Si = CF_2$ molecules in order to determine the influence of the positions of the fluorine atoms on the strength of the π-bond. Their high π-bond orders and the small lengths of the silicon-carbon bonds (1.75 Å in $H_2C = SiH_2$ and $H_2C = = SiF_2$; 1.80 Å in $F_2C = SiF_2$ and $F_2C = SiH_2$) indicate the olefinic character of these compounds. The FSiF and FCF angles are 110° and ∠ HSiH and ∠ HCH are 120°. Calculation showed that, in contrast to $H_2Si = CH_2$ and $F_2Si = = CH_2$, the $H_2Si = CF_2$ and $F_2Si = CF_2$ molecules have less polar π-bonds. It is interesting to note that analysis of the reactivities of the above compounds by electrostatic methods led to the conclusion that the formation of 1, 2-disilacyclobutane from $H_2Si = CF_2$ should be more favourable than the formation of 1, 3-disilacyclobutane.

In conclusion of this section, we should note that the stability of the silicon analogues of olefins is in general correlated with the lack of tendency of the silicon atom towards sp^2 hybridisation noted in recent publications[81] on the structure of silyl radicals. It was found that, in contrast to the methyl radical, the silyl radical is non-planar and has a pyramidal configuration. The substitution of a hydrogen atom by methyl group has only a slight influence on the geometry of the radical.

Nevertheless the nature of the bonds in silicon analogous of unsaturated compounds still remains one of the unsolved problems of chemistry. The advances achieved in the stabilisation of compounds of this class, which made possible spectroscopic and other physical studies on these compounds, are promising in this connection.

* * *

The results discussed above have shown that monosilacyclobutanes still remain some of the most effective and most readily available sources of silicon analogues of olefins. Mono- and di-silabicyclo[2, 2, 2]octa-2, 5-dienes are particularly convenient for this purpose. There is no doubt that the discovery of new selective and simple methods for the synthesis of silicon analogues of unsaturated compounds will permit a wider employment of the interesting synthetic possibilities of this new class of organosilicon compounds.

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