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Silicon Analogues of Carbenes

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A systematic account is given of data published up to 1975 on the preparation and chemical properties of silicon analogues of carbenes—short-lived bivalent silicon compounds (silylenes). Methods for their formation with the aid of high temperatures as well as other sources of energy (silent electric discharge, photolysis, and radiolysis) are discussed.
The chemical properties of silylenes have been classified in accordance with three types: (1) polymerisation; (2) insertion in single bonds; (3) addition to multiple bonds.
The possibility of employing silylenes (particularly dichlorosilylene) for preparative purposes is discussed. Attention has been concentrated on experimental data relevant to the gas-phase reactions of silylenes.
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I. INTRODUCTION

The chemistry of bivalent Group IVB elements has been attracting much attention in recent years. The interest aroused by these substances is due to the considerable advances in the theoretical and practical developments of the chemistry of carbenes, which already have a twenty year old history. However, the chemistry of organic derivatives of the elements which are carbene analogues, particularly the chemistry of silylenes, has not so far passed beyond the limits of laboratory tests owing to the complete absence of convenient methods for their synthesis.

Since the publication of the first reviews[1,2] devoted to the most important aspects of the chemistry of silylenes, the number of studies in this field has greatly increased and continues to increase. This is due to the advances in experimental techniques in the last decade—the development of methods for the creation of high temperatures and a high vacuum and also a new technique involving the quenching of the reaction mixture[3], which makes it possible to carry out the reactions of silylenes with a series of reactive organic compounds. Extensive experimental data have now accumulated on the chemistry of inorganic silylenes at low temperatures (−196°C) (the low-temperature condensation method), which has been surveyed in a number of reviews[5-8]; the similarity of the chemical properties of silicon monoxide, which is also of interest for syntheses at low temperatures[9], and those of other silylenes, for example difluorosilylene[7], has been noted. On the other hand, the gas-phase reactions of silylenes have not been described systematically (with the exception of the paper by Schaschel et al.[9]). Interesting communications have been published in which the stabilisation of silylenes by coordination in transition metal complexes is discussed[10-13]. Considerable advances have been made also in research on the physical properties of silylenes[14]. Methods for the generation of bivalent silicon compounds in extremely short time intervals (a millisecond or less), such as flash photolysis, electrical discharge, radioactive nuclear decomposition processes etc., have become common and make it possible not only to detect the presence of unstable species but also to determine their characteristics[15]. The development of methods for the matrix isolation[16-18] of such species greatly supplemented the available information about their nature and properties.

Apart from the purely theoretical interest in silylenes, attempts have been made in recent years to find direct practical applications for such species. From this standpoint, dihalogenosilicon derivatives are particularly promising[19]. Studies demonstrating the great synthetic possibilities of the employment of dichlorosilylene in gas-phase reactions have been published only in the last 3–4 years. Apart from a brief assessment of the present state of chemistry of silylenes, attention is concentrated in the present review of their "high-temperature" gas-phase chemistry, particularly that of dichlorosilylene, and the synthetic aspects of their utilisation.

II. METHODS OF SYNTHESIS

1. METHODS OF SYNTHESIS USING HIGH TEMPERATURES

The commonest methods for the preparation of bivalent silicon compounds involve high-temperature processes. Since pyrolytic methods for the preparation of inorganic and organic silylenes differ somewhat, we believe it to be useful to consider them separately.

A. Inorganic Silylenes

Short-lived silylenes can be isolated in high-temperature processes[3] only when the rate of cooling of these species is much higher than the rate of side reactions. Under the conditions of a high vacuum, it is possible to remove the gaseous species from the hot zone virtually without collisions and then condense them, which enables them to react with one another or with other condensed molecules. The high-temperature processes involving the formation of inorganic silylenes can be divided into processes at atmospheric pressure (1 atm) and low pressure (below 1 mmHg). We shall henceforth adhere to this classification.

1. Processes at atmospheric pressure. High-temperature processes at atmospheric pressure scarcely allow the isolation of silylenes, but they do make it possible to investigate their reactions and to carry out kinetic and thermodynamic studies. The reaction mechanism is then clear only in rare instances and in order to

account for the observed effects it is usually necessary to postulate the intermediate formation of silylenes on the basis of the determination of the composition of the mixture of final products.

Among processes of this type, involving the formation of inorganic silylenes, the reduction of tetrahalogenosilanes by silicon has been known for a long time[20,21]:

$$SiX_4(gas) + Si(solid) \underset{}{\overset{1000-1300^\circ C}{\rightleftarrows}} 2\ddot{S}iX_2(gas). \quad (1)$$

The reviews[1,2] do not make it clear how the efficiency of reaction (1) depends on the nature of the halogen in the SiX_4 series, where X = F, Cl, Br, or I. A detailed study has now been made of the case where X = Cl.[22-35] The formation of $\ddot{S}iCl_2$ has been confirmed by thermodynamic calculations[23,24,26,29-31] and kinetic studies[28]. However, it has been suggested recently that the composition of the gas phase is more complex and that considerable amounts of $\cdot\ddot{S}iCl$ and $\dot{S}iCl_3$ are present together with $SiCl_4$ and $\ddot{S}iCl_2$.[36,37]

Reaction (1) for X = Br has also been investigated in detail[27,31,39] and that for X = I in less detail[27,31,38]. It is is noteworthy that di-iodosilylene can be obtained by this method, since both this species and silicon tetraiodide are appreciably dissociated into silicon and atomic iodine already at temperatures between 900° and 1000°C.[31,39] When X = F, the product is a mixture of gaseous, liquid, and solid subfluorides the composition of which has not yet been established exactly[20,40,41].

The reaction where X = Cl, Br, and I can serve as a source of pure silicon, which is used to coat surfaces with silicon[25,27,32,33,42,43]. In its preparative aspects, it has been used for the synthesis of trichlorosilane[34,44], mixed halogenosilanes[35], and chloromethylsilane[35]. In the absence of acceptors of dihalogenosilylenes, various compounds are formed as a function of reaction conditions—polymers $(-SiX_2-)_n$, linear polysilanes (Si_nCl_{2n+2}),[44] or cyclic polysilanes (Si_nCl_{2n}),[35] but a detailed structural study has not been made. On heating, the polymers are converted into perhalogenosilanes, starting from SiX_4 and extending as far as Si_6X_{14}; the residual subhalides have a molecular weight of approximately 1600.[35,44] It is probable that this entails also the formation of dihalogenosilylenes, the interaction of which with silicon tetrahalides actually leads to the formation of all the perhalogenosilanes.

The intermediate formation of dichlorosilylene also occurs in the reduction of silicon tetrachloride[45-51] or trichlorosilane[49,50,52,53] by hydrogen:

$$SiCl_4 + H_2 \xrightarrow{1000-2000K} \ddot{S}iCl_2 + 2HCl \quad . \quad (2)$$

This reaction is widely used as a method for the preparation of pure silicon film coatings[48,49,51,52]. The formation and the important role of dichlorosilylene in these processes have been confirmed by thermodynamic calculations alone. There is no clear-cut information about other evidence or about the use of $\ddot{S}iCl_2$, formed in this reaction, for synthetic purposes.

The possibility of employing trichlorosilylene in the "direct" synthesis of organochlorosilanes (250-400°C) when organic chlorides interact with silicon has been frequently discussed[54,55]. Andrianov and Golubtsov[56] have shown that it is generated by the reduction of copper(I) chloride by silicon:

$$2CuCl + Si \rightarrow 2Cu + \ddot{S}iCl_2 \quad . \quad (3)$$

Numerous facts confirming this view have now been observed[56,57]. Reliable evidence for the formation of dichlorosilylene in the "direct" synthesis was secured by the mass-spectrometric study of reaction (3).[58-60]

The information available previously[57,61,62] about the formation of dichlorosilylene in the "direct" synthesis of trichlorosilane,

$$2HCl + Si \rightarrow \left(\begin{matrix} | \\ \ddot{S}iCl \\ | \end{matrix}\right) + H_2 \quad , \quad (4)$$

may be supplemented by the following remarks: mass-spectrometric data for the products desorbed from the surface of silicon before and after reaction (4) with the aid of a desorbing gas confirm the probability of the formation on the surface of the $\ddot{S}iCl_2$ species which is capable of both desorption and of reaction with hydrogen chloride[63,64].

Various chlorosilanes can serve as convenient sources of inorganic silylenes in many instances. Thus is has been established recently that dichlorosilylene plays an important role in many pyrolytic processes occurring with participation of chlorosilanes[65-71].

It has been suggested in a paper by Sirtl and Reuschel[49] and then in a review[2] that the pyrolysis of trichlorosilane proceeds via the following mechanism:

$$HSiCl_3 \xrightarrow{>1100^\circ} HCl + \ddot{S}iCl_2 \quad . \quad (5)$$

On the other hand, a detailed study of the products of its pyrolysis showed that, in the temperature range 500-750°C, hydrogen chloride is not formed in appreciable amounts[72]. A reinvestigation of the kinetics of the thermal decomposition of trichlorosilane confirmed these results[73]. It has now been established that the main products of the decomposition of $HSiCl_3$ are silicon tetrachloride, hydrogen, and silicon[72-74]. This suggests the following more probable general mechanism of its pyrolysis with formation of $\ddot{S}iCl_2$:[67,68]

$$2HSiCl_3 \xrightarrow{650-670^\circ} SiCl_4 + H_2 + \ddot{S}iCl_2 \quad . \quad (6)$$

Maksimova's categorical statement[69] that the pyrolysis of trichlorosilane proceeds via the radical mechanism

$$HSiCl_3 \rightleftarrows H + \dot{S}iCl_3 \quad (7)$$

at 600°C and via mechanism (5) at 650°C is therefore puzzling. In this case, it is obviously more correct to postulate the dominant role of one of the two reactions, (6) or (7), in a particular temperature range.

It has been established that, apart from trichlorosilane, certain other organochlorosilanes can also serve as donors of dichlorosilylene and it is of interest that pyrolysis can proceed via two pathways[70]:

$$R\overset{H}{\overset{|}{S}}iCl_2 \xrightarrow{670-690^\circ} R\dot{S}iCl_2 + H \quad ; \quad (8)$$

$$2R\dot{S}iCl_2 \longrightarrow RSiCl_3 + R\ddot{S}iCl \quad ; \quad (9)$$

$$R\overset{H}{\overset{|}{S}}iCl_2 \rightarrow RH + \ddot{S}iCl_2 \quad , \quad (10)$$

where R = α-$C_{10}H_7$, C_6H_5, or CH_3.

Mechanism (10) is satisfactorily confirmed by the formation of the corresponding amounts of naphthalene, benzene, and methane. It is noteworthy that, with increase of the temperature of the reaction zone from 640° to 690°C, pyrolysis proceeds via mechanism (10) to a greater extent. A similar pyrolysis mechanism [reaction (9) and (10)] has been proposed for methylsilane[75]:

$$CH_3SiH_3 \rightleftarrows CH_3\ddot{S}iH + H_2 \quad ; \quad (11)$$

$$CH_3SiH_3 \rightleftarrows \ddot{S}iH_2 + CH_4 \quad . \quad (12)$$

According to other data[76], the decomposition of methylsilane is not accompanied by the formation of $\ddot{S}iH_2$.

Methane has not been detected among the reaction products in the study by Ring et al.[77] Evidently, more detailed studies are required in order to refine the mechanism of the pyrolysis of methylsilane. However, the simultaneous occurrence of a reaction with formation of a silyl radical [reactions of type (7) or (8)] has been noted in all cases. The radical reactions greatly complicate the pyrolytic processes involving silanes and constitute a significant disadvantage of the latter as silylene donors.

There are literature data showing that the intermediate formation of silylenes is observed also in the pyrolysis of tetrahalogenosilanes and silane:

$$SiX_4 \rightarrow \ddot{S}iX_2 + X_2 \quad . \qquad (13)$$

Reaction (13) occurs when X = Cl [24] or I [39] at 900°C and when X = H [78,79] at 400°C.

Despite the fact that the pyrolysis of silane has been investigated in considerable depth for a long time[78], there is at present no unanimous view concerning the mechanism of the initial stage of its decomposition—some workers[78,79] suggest a mechanism involving the formation of silylene [reaction (13)], while others[77] propose a radical-chain mechanism:

$$\begin{aligned} SiH_4 &\rightarrow \dot{S}iH_3 + H \quad ; \\ H + SiH_4 &\rightarrow H_2 + \dot{S}iH_3 \quad ; \\ \dot{S}iH_3 + SiH_4 &\rightarrow Si_2H_6 + H \quad ; \\ 2\dot{S}iH_3 &\rightarrow Si_2H_6 \quad . \end{aligned} \qquad (14)$$

The arguments in support of both points of view depend only on the reliability of the thermochemical information; however, it has been correctly pointed out[79] that the scatter of the available $H-SiH_3$ and $H_3Si-SiH_3$ bond dissociation energies is much greater than the expected differences between the activation energies for reactions (13) and (14). The contradictory nature of the available data on this problem so far precludes a definite conclusion. However, the latest calculations of the absolute entropies of formation of silylene and the silyl radical suggest that preference should be given to reaction (13).[80]

An effective method for the generation of inorganic silylenes proved to be the thermal decomposition of polysilanes and their halogeno-derivatives. The decomposition of hexahalogenodisilanes, which was observed by Friedl and Ladenburg[81] as early as 1880, has not received due attention until the present time:

$$xSi_2X_6 \rightarrow xSiX_4 + (SiX_3)x, \qquad (15)$$

where X = I,[81-83] Cl,[83] or Br.[83]

The hypothesis of the intermediate formation of dihalogenosilylenes in reaction (15) was put forward about 10 years ago[84] and has been frequently quoted[2,76,85], but its mechanism still remains obscure. It was believed previously that hexachlorodisilane is capable of decomposing on pyrolysis via a homolytic mechanism and the formation of dichlorosilylene was explained by the recombination of two trichlorosilyl radicals[84,86]:

$$Cl_3SiSiCl_3 \xrightarrow{\Delta} 2\dot{S}iCl_3 \quad ; \qquad (16)$$

$$\dot{S}iCl_3 + \dot{S}iCl_3 \rightarrow \ddot{S}iCl_2 + SiCl_4 \quad . \qquad (17)$$

An interesting attempt to predict the direction of pyrolysis of disilanes[76], including hexachlorodisilane, was made very recently and it has been suggested that the thermal dissociation of hexachlorodisilane has a carbenoid mechanism:

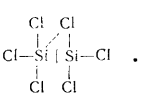
$$Cl_3SiSiCl_3 \rightarrow \ddot{S}iCl_2 + SiCl_4 \quad . \qquad (18)$$

The study of the kinetics of the thermal decomposition of hexachlorodisilane under flow conditions in a quartz reactor in the temperature range 360–420°C established that its decomposition is described satisfactorily by the equation for first-order kinetics with $E_a = 49.6 \pm 1.2$ kcal mole^{-1} and $\lg A\ (s^{-1}) = 13.8 \pm 0.36$. The heats of reactions (16) and (18) are respectively 77 ± 5 and 48 ± 5 kcal mole^{-1}.[87] Using these data, it is possible to show approximately that the preferential occurrence of reaction (18) requires that the activation energy for the reverse reaction

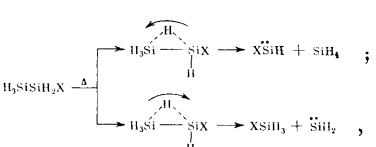
$$\ddot{S}iCl_2 + SiCl_4 \rightarrow Si_2Cl_6 \qquad (19)$$

should not exceed 27–28 kcal mole^{-1}. Although its value has not been determined, it is known that reaction (19) takes place rapidly both in the gas phase and on cocondensation, so that one can assume with a good deal of certainty that reaction (18) is a primary process in the decomposition of hexachlorodisilane.

This is confirmed directly by the results obtained recently in a spectroscopic study of the primary products of the pyrolysis of hexachlorodisilane by the matrix isolation method[88]. The dissociation of Si_2Cl_6 under the conditions described takes place at temperatures in the range 600–650°C. The reaction products are only silicon tetrachloride and dichlorosilylene. These results permit the final conclusion that the pyrolysis of hexachlorodisilane (as well as higher perchloropolysilanes)[89-91] is an example of the α-elimination reaction and involves attack by the chlorine atom linked to one of the silicon atoms on the neighbouring silicon atom with formation of "bridging" chlorine:



The pyrolysis reactions of higher silanes have been investigated comparatively recently and it has never been established reliably that disilane and many substituted disilanes are effective sources of silylene and substituted silylenes. The mode of decomposition of the compounds H_5Si_2X is represented by two pathways involving intramolecular 1,2-transfer of hydrogen:



$$H_3SiSiH_2X \xrightarrow{\Delta} X\ddot{S}iH + SiH_4 \quad ; \qquad (20)$$

$$H_3SiSiH_2X \xrightarrow{\Delta} XSiH_3 + \ddot{S}iH_2 \quad , \qquad (21)$$

where X = H,[93-97] Cl, F,[98] or CH_3.[99]

It is suggested on the basis of the latest kinetic investigations that the pyrolysis of trisilane likewise proceeds in two ways [Eqns. (20) and (21)] woth formation of silylene and silylsilylene ($H\ddot{S}iSiH_3$).[100]

Two similar decomposition pathways have been found for disubstituted disilanes, but the 1,2-transfer of the atom X was not observed:

$$1,1\text{-}X_2Si_2H_4 \rightarrow \ddot{S}iH_2 + X_2SiH_2 \quad ; \qquad (22)$$

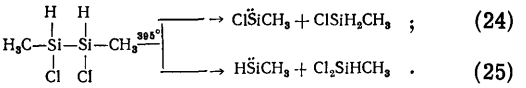
$$1,1\text{-}X_2Si_2H_4 \rightleftarrows \ddot{S}iX_2 + SiH_4 \quad , \qquad (23)$$

where X = Cl [98] or CH_3.[99]

Reaction (23) is less favourable for dihalogenodisilanes and reaction (22) only is observed for 1,1-difluorodisilane[98]

Interesting results have been obtained for the decomposition of *sym*-$Cl_2Si_2H_2(CH_3)_2$ [Eqns. (24) and (25)], suggesting that the 1,2-transfer of the Cl atom is nevertheless

possible in those cases where the latter and the hydrogen atom are in identical environments[98]:



$$H_3C-Si(H)(Cl)-Si(H)(Cl)-CH_3 \xrightarrow{395^\circ} \begin{cases} \rightarrow ClSiCH_3 + ClSiH_2CH_3 ; & (24) \\ \rightarrow HSiCH_3 + Cl_2SiHCH_3 . & (25) \end{cases}$$

The ratio of the contributions of reactions (24) and (25) is 4:1.

2. Processes at a low pressure in the system. The study of such processes in the last 15 years has developed considerably, since they make it possible to obtain at a high temperature unstable and highly reactive gaseous atomic and molecular species. When the processes are carried out at a low pressure, one can reduce to a minimum the number of mutual collisions of the species and their collisions with the walls. Among the latest advances, particular mention should be made of certain processes involving the formation of inorganic silylenes *in vacuo*:

(a) evacuation of metals, for example:

$$Si(solid) \underset{}{\overset{1400^\circ C,\ 10^{-5}\ mmHg}{\rightleftharpoons}} \cdot\ddot{S}i\cdot\ (gas) \qquad (26)$$

followed by the insertion of the atoms in Si–X bond;

(b) reduction methods, for example:

$$Si(solid) + SiO_2(solid) \overset{1200^\circ C,\ 10^{-2}\ mmHg}{\rightleftharpoons} 2\ddot{S}iO\ (gas); \qquad (27)$$

$$Si(solid) + SiX_4(gas) \overset{115^\circ C,\ 1\ mmHg}{\rightleftharpoons} 2\ddot{S}i\,X_2\ (gas); \qquad (28)$$

(c) thermal decomposition of halogenosilanes.

Methods a and b presuppose the possibility of isolating the silylenes by condensation as a result of extensive cooling (down to −196°C) and also the investigation of their chemical properties by cocondensation with other compounds[3-6,9,101],

(a) Evaporation of silicon. In 1967 Skell and Owen published a study devoted to the chemistry of atomic silicon[102]. Almost simultaneously, another report was published about the high reactivity of atomic silicon[3]. Up to that time, only the molecular composition of silicon vapour had been described in the literature[103]. The above investigators[3,102] were able to isolate from the hot zone at a low pressure extremely reactive atoms, which can be obtained under the conditions of reaction (26), or on thermal evaporation of silicon[102,104], or by bombarding silicon with electrons[5,101,104-106]. Under these conditions, the content of polymeric species in gaseous silicon is much smaller than in carbon vapour[107]; at a low pressure, the dominant species are silicon atoms[5].

(b) The reduction reactions. This method is most convenient for the preparation of a highly reactive silylene—silicon monoxide (ŠiO). Like silicon atoms, it can be isolated only at a very low pressure.

The formation of gaseous ŠiO as an intermediate in the reduction of silicon dioxide has been known for a long time[108-118]. It has been found that reducing agents may be arranged in the following sequence in terms of decreasing activity[116,117]:

$$Si(gas) > C(solid) > Si(liq.) > Si(solid) > FeSi(liq.) > FeSi(solid) > SiC.$$

It has been reported that silicon monoxide is also formed in the reduction of silicon dioxide by hydrogen[119,121]. Silicon monoxide is likewise formed when silicon is treated with an oxidising agent[122,123] such as a metal oxide, for example by the reaction

$$2Si + Al_2O_3 \overset{1800^\circ}{\rightleftharpoons} Al_2O_3\ (gas) + 2\ddot{S}iO\ (gas) \qquad (29)$$

and also on heating silicon dioxide alone above 1600 K.[124-127] However, the best preparative method is the reduction of pure SiO_2 (99.7%) by pure silicon (99.8%) via reaction (27).[9,118,125,127-129] It is of interest that gaseous silicon monoxide can be obtained for preparative purposes by heating "solid SiO" *in vacuo*[9,130,131], the content of the dimer being only 0.1% under these conditions.

Owing to the technical difficulty of maintaining a sufficiently low pressure in the high-temperature system, the gaseous ŠiO molecule, which has been known for a long time, has not been used in further reactions until recently[9,130,131]. The formation of silicon monosulphide is also a reaction of the same type[132-134]:

$$SiS_2(solid) + Si(solid) \overset{900-1150^\circ,\ <0.1\ mmHg}{\rightleftharpoons} 2\ddot{S}iS\ (gas). \qquad (30)$$

It is much easier to synthesise and isolate dihalogenosilylenes under the conditions described[3]. All the dihalogenosilylenes have been obtained under the conditions of reaction (28), but $\ddot{S}iBr_2$,[135-137] $\ddot{S}iI_2$,[136,138] and $\ddot{S}iCl_2$,[136,139] are less stable than $\ddot{S}iF_2$.[136] It has been shown that di-iodosilylene cannot be synthesised efficiently by this procedure[138]. Its polymer has been obtained in approximately 1% yield at 800–900°C. The synthesis of difluorosilylene reported previously in fact also involved the formation of the polymer $(-SiF_2-)_n$.[136,140]

Since Timms devised recently a suitable apparatus[3,6,101], which provides for the rapid transfer of dihalogenosilylenes by suction into the region at a pressure of the order of 10^{-5} mmHg, it has been possible to avoid the gas-phase polymerisation of dichloro- and dibromo-silylenes, to prevent their reaction with the corresponding silicon tetrahalides, and hence to obtain them in high yields (95 and 80% respectively)[101,141-143]. Owing to its higher stability, difluorosilylene can be obtained in simpler apparatus than that of Timms[3,144] in fairly high yields (up to 65%) at a residual pressure of 0.1–0.2 mmHg.[145-147]

(c) Thermal decomposition of halogenosilanes. The thermal methods for the synthesis of inorganic silylenes *in vacuo* have not been developed quite so effectively as the analogous methods at atmospheric pressure (see above); nevertheless, it has been stated that the thermal decomposition of hexafluorodisilane[148] [reaction (15)] in a high vacuum is the best method for the generation of difluorosilylene. According to the authors, this procedure makes it possible to obtain $\ddot{S}iF_2$ completely free of oxygen.

The pyrolysis *in vacuo* of the tetrahalogenosilanes $SiBr_4$[149] and SiI_4,[138,149] which is treated merely as a method for the preparation of the polymers $(-SiX_2-)_x$, has been little studied. From the standpoint of the generation of silylenes on a preparative scale, these reactions evidently have no importance.

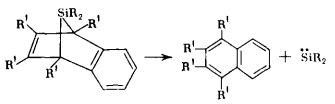
B. Organic Silylenes

Owing to the lack of a suitable method for the preparation of silylenes with organic substituents, these substances have been little studied until recently. There has been a considerable development of the chemistry of organosilylenes during the last ten years and there are now several methods for their synthesis.

1. Reduction of dialkyldichlorosilanes by metals. Analysis of studies of the reactions of dialkyldichlorosilanes with metals has shown that the available information about the possible formation of silylenes in this reaction is fairly contradictory. Skell and Goldstein[150,151] obtained convincing proof of the formation of dimethylsilylene when dichlorodimethylsilane reacts with potassium in the gas phase (t = 260–280°C), having trapped $\ddot{S}i(CH_3)_2$ by trimethylsilane.

However, the analogous formation of silylene in the condensed phase has not been established[152,153]. Despite the fact that the reaction of dichlorodimethylsilane with lithium[154] is also consistent with the hypothesis of the intermediate formation of $\ddot{S}i(CH_3)_2$,[2] convincing evidence for this has not been obtained so far. Since the yields of reaction products are very low (2–10%) when the above source of silylenes is used and more convenient methods for the generation of organic silylenes are available at the present time, the reaction of alkali metals with dialkyldichlorosilanes in solvents has not assumed practical importance in the investigation of silylenes.

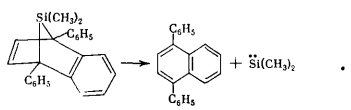
2. Thermolysis of 7-silanorbornadienes. This method, proposed in 1964 by Gilman et al.[155,156], is widely used for the preparative synthesis of dimethyl- and diphenyl-silylenes:



(33)

where R′ = C_6H_5 and R = CH_3 or C_6H_5.

The conversion of disubstituted 7-silanorbornadiene, which yields $\ddot{S}i(CH_3)_2$ at low temperatures, also merits attention[157]:



(34)

This method combines the utilisation of mild process conditions with the formation of the least reactive side products.

Attempts have been made to use the adduct of 1,1,-dimethyl-2,5-diphenyl-1-silacyclopentadiene with tolane for the same purposes[157]. However, the adduct not only eliminates dimethylsilylene but also dissociates simultaneously.

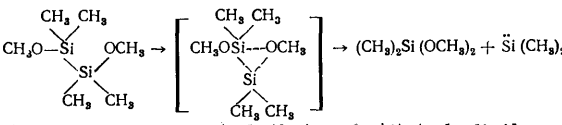
3. Thermal decomposition of polysilanes. The studies by Atwell and coworkers have shown that the most convenient and the most general source of organic silylenes is the thermolysis of alkoxymethylpolysilanes[2,158–162], for example:

$$(CH_3O)_6Si_2 \xrightarrow{175^\circ} (CH_3O)_4Si + \ddot{S}i(OCH_3)_2 ; \quad (35)$$

$$CH_3(CH_3O)_2SiSi(OCH_3)_2CH_3 \xrightarrow{200^\circ} CH_3Si(OCH_3)_3 + \ddot{S}i(OCH_3)CH_3 . \quad (36)$$

It was noted that, with increase of the number of alkoxy-groups, the thermolysis takes place at lower temperatures. These reactions can also be carried out in the gas phase. Following the development of this procedure, organic silylenes became readily available and have been the object of numerous interesting investigations.

The thermolysis of alkoxypolysilanes is a typical example of α-elimination:



(37)

It has been reported that substituted disilanes $(CH_3)_3SiSi(CH_3)_2X$, where X = Cl, OC_6H_5, or C_6H_5, undergo similar reactions[163] and it is of interest that pentamethyldisilane is also apparently an effective donor of $\ddot{S}i(CH_3)_2$. Presumably, all the methyldisilanes $(CH_3)_{6-x}Si_2H_x$, where $x = 1 - 6$, and naturally also the similar alkylpolysilanes undergo thermal decomposition into silylene and silane[76] by the intermolecular transfer of a hydrogen atom discussed above.

The pyrolysis of cyclic and linear polymers having the general formula $[Si(CH_3)_2]_n$, where $n > 3$, also leads to the formation of dimethylsilylene[153,164]. However, the yield of its adducts with various trapping agents is low (1–6%).[1,164]

2. OTHER ENERGY SOURCES IN THE SYNTHESES OF SILYLENES

A. The Silent Electric Discharge

The silent electric discharge in the vapours of silane and some of its derivatives has been found[165–173] to result in the formation of silylenes, the mechanism of which is believed to be described by equations similar to those discussed above:

$$SiX_4 \rightarrow \ddot{S}iX_2 + X_2 , \quad (14)$$

where X = Cl,[167–169] F,[170,171] or H[165,166,172] and

$$CH_3SiH_3 \xrightarrow{[173]} CH_3\ddot{S}iH + H_2 ; \quad (11)$$

$$\rightarrow \ddot{S}iH_2 + CH_4 . \quad (12)$$

At the same time decomposition under the influence of the electric discharge is a more complex process than pyrolysis, since it is accompanied by the formation of various charged and neutral species.

This method has not assumed preparative importance and it has been used for spectroscopic studies only.

B. Photolysis

The photochemical method for the generation of silylenes has developed considerably in recent years. The search for convenient sources of silylenes for both spectroscopic investigations and for preparative purposes has continued. Among the compounds investigated, various silanes, whose Si–H bonds are readily photodissociated, have found extensive applications. Flash photolysis of halogenosilanes has proved a very promising procedure for recording highly resolved absorption spectra of halogenosilylenes Their formation is evidently due to the following reaction:

$$H_3SiX \xrightarrow{h\nu} H\ddot{S}iX + H_2 \quad (38)$$

where X = Cl, Br,[174] or I.[175]

$\ddot{S}iH_2$, obtained in the photochemical decomposition of silane, has been identified similarly[176–178]. The vacuum ultraviolet photolysis[178] of silanes leads to the formation of silyl radicals and silicon atoms in addition to silylene.

The mercury-sensitised photochemical decomposition of silane evidently involves initial processes in which silyl radicals and silicon atoms are formed together with silylene via the reaction[179-182]:

$$Hg(^3P_1) + SiH_4 \rightarrow \ddot{S}iH_2 + 2H + Hg(^1S_0) \quad . \qquad (39)$$

However, it is interesting to note that all the methylsilanes are capable of decomposing under these conditions via a radical pathway involving the dissociation of a single Si–H bond[181,182], while silyl radicals disproportionate with formation of silylenes only to a slight extent.

The photolysis of alkylsilanes under the influence of vacuum ultraviolet proceeds via the molecular elimination mechanism and thus constitutes a convenient source of silylenes, which are generated via reactions analogous to reactions (11) and (12):[183-185]

$$CH_3SiH_3 \xrightarrow{1470\text{Å}} \begin{cases} \rightarrow CH_3\ddot{S}iH + H_2 \ ; \\ \rightarrow H_2\ddot{S}i + CH_4 \ . \end{cases}$$

The photochemical decomposition of dimethyl- and trimethyl-silanes proceeds similarly, although less efficiently[186].

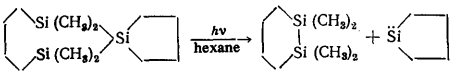
A satisfactory method for the synthesis of dichloro-[187] and difluoro-silylenes[188] to be used in spectroscopic studies is the vacuum ultraviolet photolysis of dichloro- and difluoro-silanes. It is suggested that the $\ddot{S}iF_2$ obtained by this procedure is purer than the product synthesised by Timms' method[145].

The photochemical method can be used to synthesise silylenes with organic substituents. Interesting possibilities in the synthesis of such silylenes arise on photolysis of substituted cyclic[189-191] or linear[191-195] polysilanes, for example:

$$[(CH_3)_2Si]_5 \xrightarrow{h\nu} \ddot{S}i(CH_3)_2 + [(CH_3)_2Si]_5 \ ; \qquad (40)$$

$$(CH_3)_3Si(\overset{CH_3}{\underset{C_6H_5}{Si}})_2Si(CH_3)_3 \xrightarrow{h\nu} 2\ddot{S}i(CH_3)C_6H_5 + (CH_3)_3SiSi(CH_3)_3 \ . \qquad (41)$$

A very promising method for the preparation of silylenes with various substituents involves modification of the substituent at the central silicon atom in 1,2,3-trisilacycloheptane[195], which makes it possible to obtain new, unusual silylenes, for example a cyclic silylene from spirotrisilane:



(42)

C. Nuclear Reactions

Together with the methods indicated above, the recently developed method for the synthesis of silylenes with the radioactive ^{31}Si isotope has assumed considerable importance. The ^{31}Si atoms ($\tau_{1/2}$ = 2.62 h) generated by the nuclear reaction $^{31}P(n, p)^{31}Si$ (on bombarding a phosphorus compound with fast neutrons) acquire energies corresponding to their chemical reactions as neutral species and their interaction with phosphine[196-202] or silane[196-198,200] apparently result in the formation of silylenes:

$$^{31}\dot{S}i\cdot \xrightarrow{PH_3} {}^{31}\ddot{S}iH_2 \ , \qquad (43)$$

$$^{31}\dot{S}i\cdot \xrightarrow{SiH_4} H{}^{31}\ddot{S}iSiH_3 \ . \qquad (44)$$

^{31}Si atoms can interact similarly with phosphorus trifluoride, forming difluorosilylene[203]:

$$^{31}\dot{S}i\cdot + PF_3 \rightarrow {}^{31}\ddot{S}iF_2 \quad . \qquad (45)$$

Quite recently this method made it possible to show that $^{31}\ddot{S}iH_2$ exists in the triplet state to the extent of 80%.[199,202]

III. CHEMICAL PROPERTIES OF SILYLENES

Before discussing the chemical properties of silylenes, the large number of experimental data concerning their physical properties should be noted. Investigators in this field have devoted most attention in the last five years to the examination of the molecular parameters of the species, the knowledge of which is necessary for the prediction of their chemical properties. The results of such studies have been reflected in recently published reviews[14,204] and papers[205-208].

We shall examine the chemistry of silylenes in accordance with their three characteristic intermolecular reactions—polymerisation, insertion in single bonds, and addition to multiple bonds. One should note immediately that, since data for the mechanism of the insertion of silylenes into single bonds are lacking, inferences about the nature of the insertion reaction are drawn mainly on the basis of the structure of the final products and are therefore frequently arbitrary.

The intermolecular reactions of the majority of silylenes can occur at elevated temperatures (in both gas and liquid phases) and at low temperatures on cocondensation with trapping agents. The majority of the reactions of difluorosilylene have little in common with those of other silylenes. The higher stability of $\ddot{S}iF_2$ in the gas phase compared with other silylenes[145,146,209-211] made it a convenient object of study. It is known, that with rare exceptions[140,144,209], difluorosilylene is inert in the gas phase[4,146,209]. Because of this and because its chemistry has been frequently discussed[4,6,8,9,212], less attention is devoted to it in the present review.

1. POLYMERISATION

In the absence of active trapping agents, silylenes are polymerised with formation of polysilanes:

$$n\,R_2Si\ddot{S}iH \rightarrow \left(\begin{array}{c} SiR_2 \\ | \\ -Si- \\ | \\ H \end{array}\right)_n \quad R=CH_3 \ ; \qquad (46)$$

$$n\,\ddot{S}iX_2 \rightarrow (SiX_2)_n \quad . \qquad (47)$$

This property is characteristic of any silylene, i.e. when X = Cl,[22,44,83,139,141,142,149,167] Br,[83,135,137,149] H,[79,93,95,166] I,[27,81,82,138,149,213] CH_3,[150,154,155,162,164,190], etc.

Difluorosilylene does not form polymers in the gas phase. Its reactivity increases greatly on cocondensation with other reagents at the temperature of liquid nitrogen (−196°C).[4,146,209,212,214-221] This unusual effect may be due to the stepwise polymerisation of difluorosilylene. $\ddot{S}iX_2$ polymerises in the condensed phase with formation of biradicals of the type $\ddot{S}iF_2-(SiF_2)_n-\dot{S}iF_2$ (where $n = 0, 1, 2, \ldots$) and these are in fact the reactive species[4,146,222-230]. Experiments in an argon matrix showed that polymerisation begins at approximately 35 K.[146,224]

Silicon monoxide, a very reactive silylene, polymerises rapidly even at 30 K,[130,233] forming dimers and oligomers with a bridging oxygen atom[9,130]. Owing to the

causes indicated above and in contrast to other silylenes, the reactions of $\ddot{S}iF_2$ and $\ddot{S}iO$ with acceptors are investigated exclusively by the cocondensation method.

2. REACTIONS INVOLVING INSERTIONS IN SINGLE BONDS

Until recently, the ability of silylenes to form products of insertion in Si–H, E–X (E = Si, P, B, or C and X = halogen), Si–O, and Si–N bonds only were believed to be reliably established[2,76,229]. The research on insertion reactions has recently developed on a large scale, which has tended to extend current ideas about the synthetic possibilities of silylenes. Together with a description of the familiar general reactions of silylenes, we have therefore devoted much attention in the present section to new data on their properties.

The Insertion of Silylenes in Si–X Bonds (X = Halogen or OCH_3)

The formation of perhalogenopolysilanes as products of the thermal interaction of tetrahalogenosilanes with silicon [reaction (1)] involving the formation of dihalogenosilylenes which is evidently followed by their insertion in the Si–X (X = halogen) bond, has been known for a long time:

$$(n-1)\ddot{S}iX_2 + SiX_4 \rightarrow Si_nX_{2n+2} \quad . \qquad (48)$$

These reactions occur in gas[25,35,44] and liquid[5,6] phases and have been thoroughly investigated; a number of perhalogenopolysilanes with $n = 2$–6 for X = Cl [136,139] and $n = 2$–5 for X = Br [136] have been obtained on their basis. The reactions of organosilylenes with alkoxypolysilanes have also been thoroughly investigated[2,158,160]. The formation of products of the $CH_3O[Si(CH_3)_2]_nOCH_3$ series in the thermolysis of *sym*-dimethoxytetramethyldisilane can be accounted for by the insertion of dimethylsilylene in the Si–O bond and not the Si–Si bond[3,161,162]. The dimethylsilylene obtained by photolysis is likewise not inserted in the Si–Si bond of 1,2-diethyltetramethyldisilane[193].

Although the possibility of the insertion of $\ddot{S}iH_2$ in the Si–Si bond has been postulated in certain recently published studies[95,100,198], nevertheless convincing confirmation of such behaviour has not been obtained for other silylenes. It is interesting that the insertion of organic silylenes (obtained by the thermolysis of alkoxypolysilanes) in the Si–O bond of an alkoxymonosilane does not compete with the analogous insertion into an alkoxypolysilane[161]. However, the absence of alkoxypolysilanes, the reaction of photolytically generated $\ddot{S}i(CH_3)_2$ with dimethyldimethoxysilane[190] proceeds with formation (in a high yield) of products resulting from insertion in the Si–O bond:

$$\ddot{S}i(CH_3)_2 + (CH_3O)_2Si(CH_3)_2 \rightarrow CH_3O\,{}^{\prime}Si(CH_3)_2]_nOCH_3 \quad ; \qquad (49)$$
$$n = 2.3 \quad .$$

Insertion in the Si–O bond has also been postulated in the cocondensation of difluorosilylene with trimethylmethoxysilane, but the initial reaction product $(CH_3)_3Si\ddot{S}iF_2OCH_3$ was not isolated, apparently owing to its further transformations[228].

Thus, although insertion in the Si–X bond (X = halogen or O) is a fairly general reaction for all silylenes, usually accompanying their formation, its further investigation is required in order to explain the different reactivities of such bonds.

Insertion in E–X Bonds (E = B, P, or C and X = F or Cl)

One of the first reactions of silylenes investigated, the interaction of SiF_2 with boron trifluoride[209,222,224,231], belongs to this type. It was established that the reaction does not occur in the gas phase, while in the condensed phase (with consecutive condensation initially of boron trifluoride and then of difluorosilylene) a number of compounds $SiF_3(SiF_2)_nBF_2$ ($n = 1$–4) are formed with an overall yield of 10–20%. The simplest member with $n = 1$ was not detected for a long time among the perfluoroborosilanes formed. Difluoro(trifluorosilyl)borane was isolated quite recently with simultaneous condensation of the reactants[232]:

$$\ddot{S}iF_2 + BF_3 \xrightarrow{\text{cocondensation}} SiF_3BF_2 \qquad (50)$$

the yield being higher when $\ddot{S}iF_2$ is obtained by passing SiF_4 over silicon carbide at 1850°C. It is suggested that short-lived species (possibly an excited form of $\ddot{S}iF_2$) are formed together with the long-lived $\ddot{S}iF_2$ species.

The interaction of $\ddot{S}iCl_2$, obtained by the reaction of silicon and silicon tetrachloride [reaction (28)], with E–Cl bonds (E = B, P, or C) [141,142] has been suggested as a general method for the synthesis of compounds with an E–SiCl linkage[234–236], for example:

$$\ddot{S}iCl_2 + BCl_3 \xrightarrow{\text{cocondensation}} Cl_3SiBCl_2 \quad . \qquad (51)$$

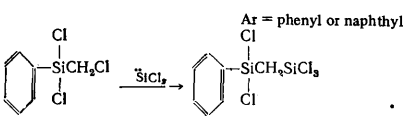
In all the experiments of this kind, the yield has been fairly low (approximately 10%). The analogous interaction of $\ddot{S}iBr_2$ with BF_3 is complicated by the exchange of halogens[2].

The gas-phase reactions of dichlorosilylene with the C–Cl bond of organic halides are of considerable preparative interest:

$$\ddot{S}iCl_2 + CH_3Cl \rightarrow CH_3SiCl_3 \quad ; \qquad (52)$$

$$ArCH_2Cl \xrightarrow{\ddot{S}iCl_2} ArCH_2SiCl_3 \quad (30–35\%) \quad , \qquad (53)$$

Ar = phenyl or naphthyl



$$(\sim 30\%) \qquad (54)$$

At first sight the interaction of $\ddot{S}iF_2$ with trifluoroiodomethane[237–239] also leads to the product resulting from insertion in the C–F bond (the main product is the compound with $n = 1$):

$$CF_3I + \ddot{S}iF_2 \xrightarrow{\text{cocondensation}} CF_3(SiF_2)_nI \quad . \qquad (55)$$

However the additional formation of further two types of compounds suggests a more complex mechanism with formation in the first stage of the radical $\dot{S}iF_2I$ and its subsequent reactions.

The results of a study of the reaction of silicon monoxide with 1-bromo- or 1-chloro-butane and bromo- or chlorobenzene suggested that the main reaction involves insertion in the C–halogen bond[9]:

$$C_4H_9Cl \xrightarrow{\ddot{S}iO} C_4H_9(SiO)_6Cl \quad . \qquad (56)$$

However, the product of the reaction of monomeric silicon monoxide was not detected. The possibility of the occurrence of the above reaction for difluorosilylene may be demonstrated by the interaction with fluoro-derivatives of benzene[216] and alkenes[217,218]:

$$\ddot{S}iF_2 + C_6F_6 \xrightarrow{\text{cocondensation}} C_6F_5SiF_3 + C_6F_4(SiF_3)_2, \qquad (57)$$

$$\ddot{S}iF_2 + n\text{-}C_6H_4F_2 \xrightarrow{\text{cocondensation}} n\text{-}FC_6H_4SiF_3 \qquad (58)$$

$$\ddot{S}iF_2 + H_2C{=}CF(CH_3) \xrightarrow{\text{cocondensation}} H_2C{=}C(CH_3)SiF_3 + H_2C{=}C(CH_3)Si_2F_5 \quad (59)$$

It is suggested that the attacking species is monomeric difluorosilylene. Thus, when the compounds contain the C–F bond, the latter is evidently attacked more readily than the C=C bond by monomeric $\ddot{S}iF_2$ with formation of the SiF_3 group.

Insertion in Halogen, Hydrogen Chloride, and Hydrogen Molecules

Silylenes are easily inserted in halogen–halogen bonds[76]:

$$\ddot{S}iCl_2 + X_2 \xrightarrow{\Delta} X_2SiCl_2, \quad (60)$$

where X = I, Br,[35] or Cl.[24];

$$\ddot{S}iF_2 + X_2 \xrightarrow{\Delta} F_2SiX_2 \text{ (yield up to 70\%)}, \quad (61)$$

where X = Br, Cl,[144] or I.[144,240] It must be emphasised that the reaction with halogens [reaction (61)] is so far the only example of a gas-phase reaction of difluorosilylene, which is apparently involved in the monomeric form.

Insertion in the H–Cl bond was postulated as early as 1953 [44] and was subsequently confirmed[34,46]:

$$\ddot{S}iCl_2 + HCl \rightarrow HSiCl_3 \quad . \quad (62)$$

The reaction of photolytically generated dimethylsilylene is typical[191]:

$$\ddot{S}i(Me_2) + HCl \xrightarrow{h\nu} (CH_3)_2SiHCl \text{ (yield 72\%).} \quad . \quad (63)$$

The intermediate $\ddot{S}iCl_2$ may be inserted in the H–H bond[44]:

$$\ddot{S}iCl_2 + H_2 \xrightarrow{\Delta} H_2SiCl_2 \quad . \quad (64)$$

Insertion in E–H Bonds (E = Si, Ge, O, N, or S)

The insertion of silylenes in the Si–H bond, first observed by Skell and Goldstein[150,151],

$$\ddot{S}i(CH_3)_2 + (CH_3)_3SiH \xrightarrow{260^\circ} \underset{(\sim 30\%)}{(CH_3)_3SiSi(CH_3)_2H} \quad , \quad (65)$$

has been widely used both to demonstrate the intermediate formation of various silylenes and to obtain new compounds with the Si–Si bond[8,75,79,94–100,241], for example:

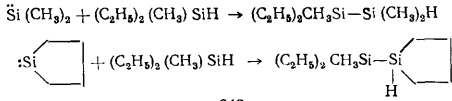
$$CH_3\ddot{S}iH + CH_3SiH_3 \xrightarrow{\Delta} CH_3SiH_2SiH_2CH_3 \quad ; \quad (66)$$

$$\ddot{S}iH_2 + Si_3H_8 \xrightarrow{\Delta} \text{n- and iso-}Si_4H_{10}; \quad (67)$$

$$H\ddot{S}iSiH_3 + Si_3H_8 \xrightarrow{\Delta} \text{n- and iso-}Si_5H_{12}. \quad (68)$$

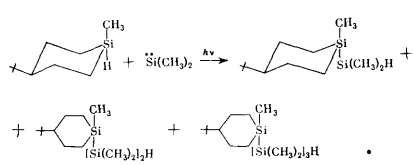
Organic silylenes obtained photochemically are also readily inserted in the Si–H bond[183–186,189,190,192–194]:

$$\ddot{S}i(CH_3)_2 + (C_2H_5)_2(CH_3)SiH \rightarrow (C_2H_5)_2CH_3Si{-}Si(CH_3)_2H \quad ; \quad (69)$$



$$+ (C_2H_5)_2(CH_3)SiH \rightarrow (C_2H_5)_2CH_3Si{-}\text{(Si-ring)}{-}H \quad . \quad (70)$$

It has been shown by NMR [242] that the insertion of dimethylsilylene in the Si–H bond of *cis*- or *trans*-4-t-butyl-1-methyl-1-silacyclohexane proceeds *cis*-stereospecifically, as for dichlorocarbene[243]:



$$+ \ddot{S}i(CH_3)_2 \xrightarrow{h\nu} \text{(Si-ring)}{-}Si(CH_3)_2H + \text{(Si-ring)}{-}Si(CH_3)_2I_3H + \text{(Si-ring)}{-}Si(CH_3)_2I_3H \quad . \quad (71)$$

The observed conservation of configuration in the insertion reaction (71) is undoubtedly associated with a three-centre mechanism involving direct electrophilic attack by dimethylsilylene on the Si–H bond.

The silicon atoms obtained by thermal evaporation [see reaction (26)] are inserted in the Si–H bond with formation of silylenes[102,104–106]:

$$\cdot\dot{S}i\cdot + \cdot R_3SiH \rightarrow R_3Si{-}\ddot{S}iH \quad , \quad (72)$$

which involves a further insertion in its turn:

$$R_3Si{-}\ddot{S}iH + R_3SiH \rightarrow R_3SiSiH_2SiR_3 \quad . \quad (73)$$

Similarly ^{31}Si Atoms [see reaction (43)] form silylenes which are subsequently involved in a secondary process with formation of radioactive disilane[196,197] and trisilane[198]:

$$^{31}\ddot{S}iH_2 + SiH_4 \rightarrow H_3{}^{31}Si{-}SiH_3 \quad ; \quad (74)$$

$$^{31}\ddot{S}iH_2 + H_3SiSiH_3 \rightarrow H_3{}^{31}SiSiH_2SiH_3 \quad . \quad (75)$$

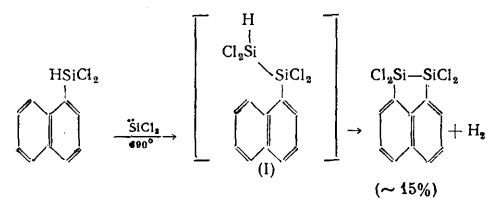
The ratio of trisilane and disilane occurring in this process enabled the authors to postulate the competing insertion of silylene in the Si–Si bond[198]. A similar hypothesis has been put forward also in studies of the pyrolysis of disilane[25] and trisilane[100]. The available data concerning the different bond strengths in disilane and silane[244] suggest the need for further research in order to account for the observation.

The reactions involving the insertion of silylene $\ddot{S}iH_2$ in the Si–H bond have been most fully investigated. Thus experiments on the joint pyrolysis of disilane and all methylsilanes have shown that $\ddot{S}iH_2$ is undoubtedly inserted exclusively in the Si–H bond of the reactant[95]. Measurements of the relative rates of insertion of $\ddot{S}iH_2$ in the E–H bonds (E = Si, Ge, or P) at 350°C have shown that the reactivity per E–H bond decreases in the following sequence[100]:

$$(CH_3)_3SiH > Si_2H_6 > (CH_3)_2SiH_2 > CH_3SiH_3 > SiH_4 > CH_3GeH_3 \quad .$$

The differences between the rates of insertion can be explained from the standpoint of the hydride nature of the E–H bond (i.e. they are correlated with the negative charge on the attacking hydrogen atom). This is particularly evident in the reaction with methylphosphine, where the hydrogen atom has a positive charge and the insertion of silylene is not observed[100,241].

The formation of a heterocyclic compound with an Si–Si bond, namely 1,1,2,2-tetrachloro-1,2-disila-acenaphthene, by the pyrolysis of trichlorosilane or hexachlorodisilane with dichloro-α-naphthylsilane, probably proceeds via a mechanism involving intramolecular dehydrocyclisation of compound (I)—the primary product of the insertion of dichlorosilylene in the Si–H bond[63]:



$$\xrightarrow[690^\circ]{\ddot{S}iCl_2} \text{[H, } Cl_2Si, SiCl_2\text{]} \rightarrow Cl_2Si{-}SiCl_2 + H_2 \quad (76)$$

(I)

(~ 15%)

The interaction of difluorosilylene with germane led to the formation of products of the type $GeH_3(SiF_2)_nH$, where $n = 1–3$.[215] The main product with $n = 1$ may be regarded as the product of the insertion of monomeric $\ddot{S}iF_2$ in the Ge–H bond:

$$\ddot{S}iF_2 + GeH_4 \xrightarrow{\text{cocondensation}} GeH_3SiF_2H \quad . \quad (77)$$

At the same time, it was suggested that germane attacks the silylene chains in $\ddot{S}iF_2(SiF_2)_nSiF_2$, abstracting fragments containing 1, 2, and 3 silicon atoms.

The reactions of silylenes with E–H bonds, where E = O, N, or S, have been less thoroughly investigated. Several investigations have dealt with the interaction of silylenes with alcohols[9,161,245] and water[9].

$$\ddot{S}i(OCH_3)_2 + CH_3OH \xrightarrow{\Delta} HSi(OCH_3)_3 \quad ; \tag{78}$$

$$4\ddot{S}iO + C_2H_5OH \xrightarrow{\text{cocondensation}} (C_2H_5O)H(SiO)_4 \quad . \tag{79}$$

The reaction of difluorosilylene with methanol proceeds in a much more complex manner[245]. It is suggested that it involves monomeric $\ddot{S}iF_2$, which is inserted in the O–H bond, but the product formed reacts further with the excess of alcohol, forming difluorodimethoxysilane. The most likely pathway of the reaction with water appears to be insertion of monomeric $\ddot{S}iF_2$ with subsequent condensation of the product:

$$\ddot{S}iF_2 + H_2O \xrightarrow{\text{cocondensation}} HF_2SiOH \quad ; \tag{80}$$

$$2HF_2SiOH \rightarrow HF_2SiOSiF_2H + H_2O \quad . \tag{81}$$

As in the reaction of $\ddot{S}iF_2$ with oxygen[4,222,246], polymeric oxides are not formed in this case and the biradicals are not therefore involved in the reaction mechanism.

The interaction of silicon monoxide with ammonia[9] led to the formation of a new compound having the approximate composition $NH_3(SiO)_4$.

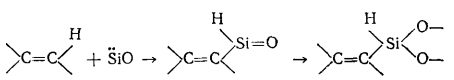
The insertion of $\ddot{S}iF_2$ in the S–H bond of hydrogen sulphide was reported earlier[2]:

$$\ddot{S}iF_2 + H_2S \xrightarrow{\text{cocondensation}} HF_2SiSH \quad . \tag{82}$$

Later detailed studies[219,238] showed that the process does not proceed in a single stage and evidence concerning the validity of the exclusion of the dimerisation stage was not obtained.

New Silylene Insertion Reactions

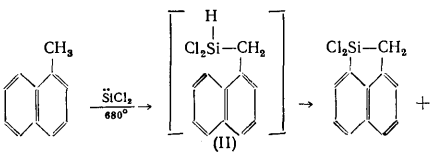
The results of studies demonstrating the ability of dichlorosilylene[68,90,92,247–249] and silicon monoxide[9,130] to interact with a wide variety of carbon–hydrogen bonds are perhaps the most interesting. It should be noted that these processes, which are the most characteristic reactions of carbenes, were completely unknown for silylenes until recently. Alkanes, anthracene, and benzene have been used in the reactions with silicon monoxide. The structure of the compounds obtained corresponds in all cases to the products resulting from insertion in the C–H bond. Furthermore, it was found that, apart from adding to multiple bonds, silicon monoxide is also "inserted" in the C–H bonds of alkenes and alkynes:



(83)

The products contain 2–3 moles of silicon monoxide per mole of alkene. Thus polymerisation evidently competes with the reaction involving the alkene, as in other cases.

The study of the gas-phase reaction of dichlorosilylene with C–H bonds[68,90,92] elucidated several important factors. After the first investigations indicating the ability of $\ddot{S}iCl_2$ to form products resulting from insertion in the C_{alk}–H bond of α-methylnaphthalene[65],



(84)

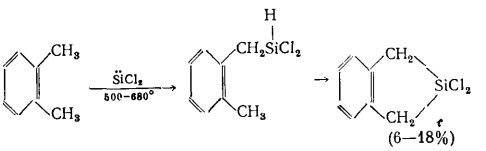
it was found that this reaction is common to all methylsubstituted aromatic hydrocarbons and heterocycles[91,92,247–249]

$$ArCH_3 + \ddot{S}iCl_2 \xrightarrow{450\text{–}500^\circ} \underset{\text{(II)}}{ArCH_2SiHCl_2} \quad , \tag{85}$$

where Ar = phenyl, *o*- and *p*-tolyl, *p*-biphenylyl, α- and β-naphthyl, 2- and 3-thienyl, etc.

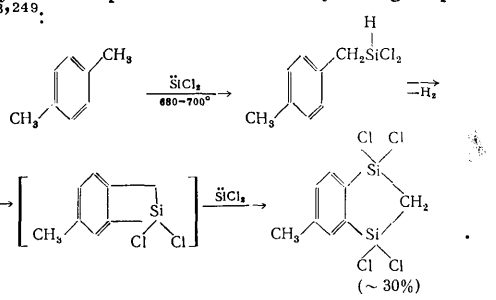
The absence of primary $\ddot{S}iCl_2$ insertion products [compounds of type (II)] in the experiments carried out at 680°C and the low yield under the conditions of reaction (85) are due to the increased tendency of these compounds to undergo radical reactions[92].

In the presence of the given substituent in the *ortho*-positions of the initial compounds, the interaction of dichlorosilylene with the C–H bond may be accompanied by subsequent intramolecular cyclisation[91,92]:



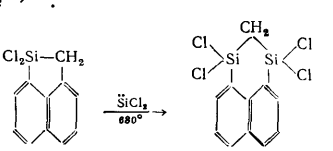
(86)

Another feature of dichlorosilylene observed in these reactions, which is of great preparative importance, is its ability to be "inserted" in the C_{ar}–C_{alk} bond of strained rings[90,92], i.e. the reaction on which the synthesis of heterocyclic compounds with two silylene groups is based[248,249]:



(87)

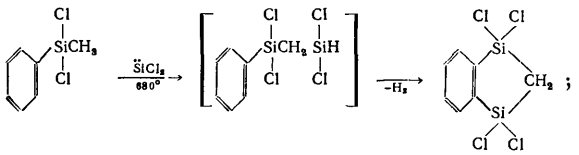
The available literature data concerning the unusual strength of the Si–C bond in pyrolytic syntheses serves as a basis for this mechanism[250]. Furthermore, pyrolysis of the primary insertion products [of the type of compound (II)] in the presence of a dichlorosilylene donor leads to the same heterocycles[92]. It is noteworthy that a reaction of this type, expansion of a five-membered ring to a six-membered ring as a result of the formal insertion of $SiCl_2$ in the C_{ar}–C_{alk} bond, has been observed also in another instance[68,92]:



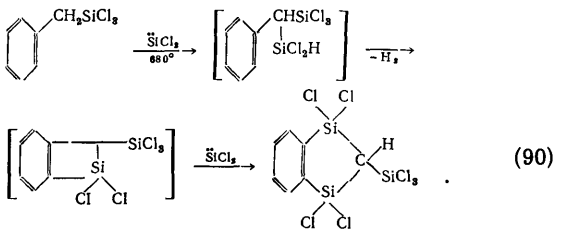
(88)

Studies on the interactions of dichlorosilylenes with other C–H bonds are only just beginning. In particular, the ability of $\ddot{S}iCl_2$ to be "inserted" in the C–H bond

involving the α-carbon atom attached to the silicon atom has been confirmed by the formation of the corresponding heterocycle as a result of gas-phase reactions[92,249]:

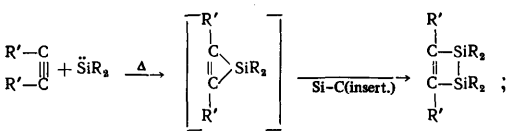


(89)



(90)

Among the latest communications, those presenting data suggesting the insertion of dimethylsilylene[251] and dichlorosilylene[92] in the Si–C bond of a silicon-containing heterocycle are of greatest interest. This hypothesis was put forward on the basis of a study of the products of the reactions of silylenes with substituted acetylenes. One of the possible mechanisms of the formation of the observed four-membered heterocycle with an Si–Si bond, put forward by analogy with dichlorocarbene[252,253], is the insertion of $\ddot{S}i(CH_3)_2$ and $\ddot{S}iCl_2$ in the Si–C bond of silacyclopropene formed as an intermediate in the first stage of the reaction (see below):



(91)

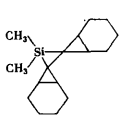
(a) R=R′=CH_3[251];

(b) R=Cl, R′=C_6H_5[92].

Summarising the foregoing findings, one may conclude that the insertion reactions investigated are at present at the stage of rapid development. In this sense, the gas-phase method must be regarded as one of the most promising procedures, the wide-scale employment of which will lead to the discovery of hitherto unknown properties of silylenes.

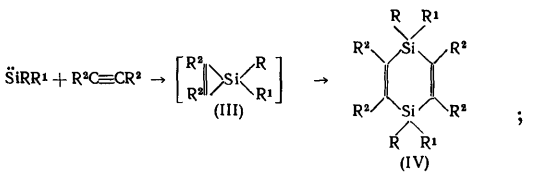
3. THE ADDITION OF SILYLENES TO MULTIPLE BONDS

The interaction with unsaturated compounds is one of the most characteristic reactions of silylenes. Unsaturated compounds are of particular interest as trapping agents for silylenes, since they make it possible to approach the synthesis of hitherto unknown silacyclopropanes and silacyclopropenes. All the attempts to isolate three-membered heterocycles with a silicon atom in the ring, which are evidently extremely labile, have been unsuccessful[154,164,254]. Such cyclic systems can probably be stabilised by increasing the degree of substitution at the ring carbon atoms. This is confirmed satisfactorily by the synthesis of the first relatively stable silacyclopropanes by the organometallic method[255], for example:



Interaction with Alkynes

Among the large number of unsaturated "trapping agents" for silylenes which have been investigated, alkynes are the most effective. The formation of silacyclopropene in the reaction of dimethylsilylene with diphenylacetylene was reported in 1961.[152,153] Subsequent studies on this reaction[256–260] showed that the product has a dimeric structure and is tetraphenyldisilacyclohexa-2,5-diene (IVa). Since then research on the reactions of a wide variety of silylenes with alkynes has developed on a wide scale and the reaction is now used to obtain chemical proof of the formation of silylenes:



(92)

(a) R=R¹=CH_3, R²=C_6H_5[1,152,153,155,158–160];

(b) R=CH_3, R¹=OCH_3, R²=C_6H_5[160,261];

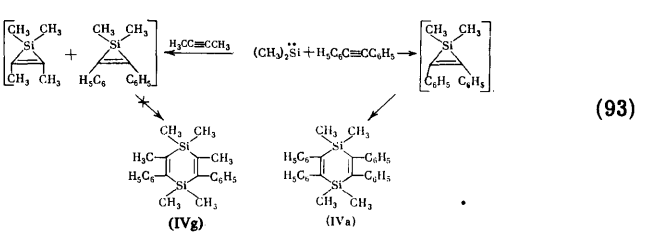
(c) R=CH_3, R¹=OCH_3, R²=CH_3[2,261];

(d) R=CH_3, R¹=OCH_3, R²=H[2,261,262];

(e) R=R¹=Cl, R²=H[89–92,263,288];

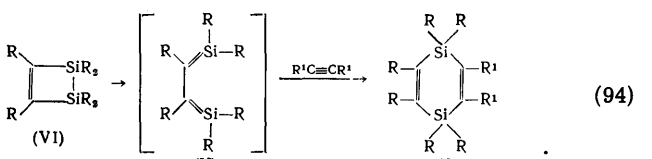
(f) R=R¹=Cl, R²=C_6H_5[89–92,263,288].

The mechanism of this reaction is still obscure. Existing views can be summarised as follows. The majority of investigators believe that the primary step is the addition of silylene to the triple bond of the alkyne with formation of compound (III), but its subsequent fate is represented in different ways. The studies by Atwell and Weyenberg[159] of the reaction of dimethylsilylene with a mixture of diphenylacetylene and but-2-yne, which did not yield 3,5-diphenyldisilacyclohexadiene (IVg), made it possible to exclude from further consideration the previously proposed mechanism involving the π-dimerisation of compound (III). We examined the possibility of the mechanism involving a kind of dimerisation of silacyclopropene (III) with dissociation of the Si–C bond:



(93)

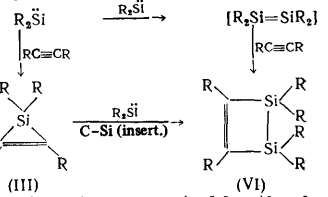
A mechanism for the formation of disilacyclohexadienes, including compound (VII), via the Diels-Alder addition of acetylene to 1,4-disilabuta-1,3-diene (V) has been proposed recently[264]:



(94)

It is suggested that the diene (V) is formed from 1,2-disilacyclobutene (VI) and the authors believe that in the case where R ≠ R¹ this explains the absence of the isomer (IVg) in the experiment with mixed actylenes. Compound (VI) can be formed in several ways: (1) by the insertion of silylene, discussed above, in the Si–C bond of the

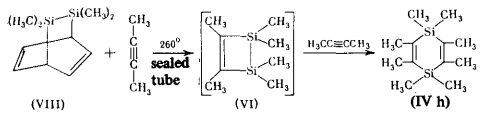
intermediate silacyclopropene; (2) by the dimerisation of silylene accompanied by the addition of the resulting disilylene to acetylene:



(95)

(III) (VI)

The latter mechanism is supported by the formation of disilacyclohexadiene (IVh) in 20% yield in the reaction between the donor $[(CH_3)_2Si{=}Si(CH_3)_2]$ [265] (VIII) and but-2-yne:

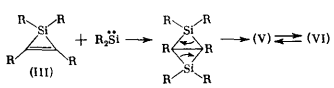


(96)

(VIII) (VI) (IV h)

If, however, the reaction of compound (VIII) with but-2-yne in the gas phase does not lead to the formation of disilyacyclohexadiene (IVh), which may indicate different contributions of this mechanism to the reaction of silylenes with alkynes depending on its conditions. At any rate, the thermolysis of compound (VI) in the presence of but-2-yne (sealed tube, 225°C, 18 h) does indeed lead to compound (IVh) in 31% yield.

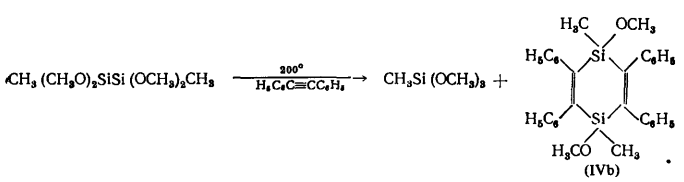
Finally Barton and Kilgour[264] also believe that the addition of silylene to the double bond of silacyclopropene with subsequent thermal rearrangement of the molecule to compound (V) is likely:



(97)

(III)

Among the studies of the above reaction, one must distinguish those which have led to the formation of disilacyclohexadienes with functional groups at the silicon atom[89-92,160,261-263]. The first example is the synthesis of the tetraphenyl-substituted 1,4-dimethoxy-1,4-dimethyl-1,4-disilacyclohexa-2,5-diene (IVb) in 50% yield[160,261]:



(98)

(IVb)

However, the corresponding tetramethoxy-derivatives could not be obtained by a similar procedure from diphenylacetylene and hexamethoxydisilane[159,160].

The most promising procedure involves carrying out the above reactions in the gas phase[89-92,261-263]. The yield of methoxymethyldisilacyclohexadiene (IVd) under the conditions of reaction (92) at 400°C was 60%.[261-262] The use of hexachlorodisilane and octachlorotrisilane in the reaction with alkynes (at 500–550°C) made it possible to obtain tetrachlorodisilacyclohexadiene (IVe) in yields up to 30% and its tetraphenyl derivative (IVf) in a yield of approximately 10%, which is of preparative interest for the synthesis of the previously inaccessible tetrafunctional derivatives of disilacyclohexa-2,5-diene. The stability of all the heterocycles (IV) synthesised on heating to the melting point is noteworthy. Furthermore, tetrachlorodisilacyclohexadiene (IVe) undergoes various reactions characteristic of the Si–Cl bond: methylation, and substitution of chlorine atoms by hydrogen and fluorine atoms with retention of the cyclic skeleton of the molecule. Timms' data[5] concerning the instability above 0°C of tetrachlorodisilacyclohexadiene, which he obtained by the reaction of dichlorosilylene with acetylene by the cocondensation method, must therefore be regarded as unreliable.

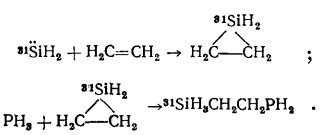
A low yield of tetrachlorotetraphenyldisilacyclohexadiene (IVf) may be associated with the insertion of $\ddot{S}iCl_2$ in the Si–C bond of the intermediate diphenylsilacyclopropene (III) (see subsection 2 of Section III). It is interesting to note that, in the analogous reactions of acetylene and its derivatives with difluorosilylene, the formation of silacyclopropene derivatives has not been observed and the reactive species with respect to alkynes are the diradicals $^{\bullet}(SiF_2)^{\bullet}_2$.[266-272]

A study of the interaction of silicon monoxide with alkynes[9] demonstrated the competition between two reactions: addition to the triple bond and insertion of $\ddot{S}iO$ in the C–H bond. The approximate composition of the solid product formed by the reaction with acetylene is $C_2H_2(SiO)_3$. The reaction with diphenylacetylene evidently results in the formation of the expected compounds $C_{14}H_{10}(SiO)_2$ having the disilacyclohexadiene structure.

Interaction with Alkenes

Various mixtures of products formed in the interaction of silylenes with ethylene in the gas or condensed phases have been reported in a number of studies[2,154,164,254]. The addition of dimethylsilylene to ethylene accompanied by the formation of dimethylvinylsilane has been achieved in the gas phase[254].

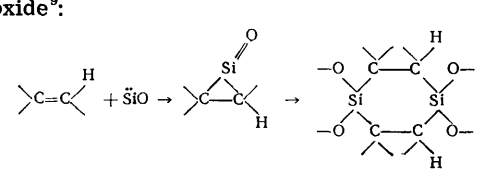
The addition of silylene ($^{31}\ddot{S}iH_2$), obtained by the reaction of ^{31}Si atoms with phosphine, to silylene has been described[197] (see subsection 2 of Section II):



(99)

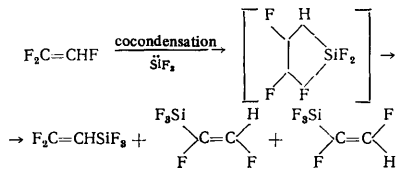
(100)

These results of the interaction of dimethylsilylene with ethylene in the liquid phase are interpreted in different ways. According to Atwell and Weyenberg[2], dimethylsilylene, obtained by the thermolysis of 7-silanorbornadiene [see reaction (33)], reacts with ethylene, forming cyclic and polymeric products in addition to dimethylvinylsilane. However, dimethylvinylsilane is not formed in the analogous reactions of dimethylsilylene formed by the reduction of dichlorodimethylsilane with lithium[154] or by the pyrolysis of the polymers $[Si(CH_3)_2]_n$ [164] see above). The possibility of error is associated with the low yield of volatile products in this reaction (overall yield less than 10%). The formation of cyclic products was postulated in the analogous experiments with silicon monoxide[9]:



(101)

In contrast to the reaction of difluorosilylene with ethylene, the cyclic products of which indicate the involvement of the polymeric species $^{*}(SiF_2)_n^{\cdot}$, the reactions with fluorinated derivatives of ethylene yield monosilanes[217,218], the formation of which is explained either by the insertion of $\ddot{S}iF_2$ in the C–F bond (see subsection 2 of Section III) or by the isomerisation of the intermediate silacyclopropane[4,218]:

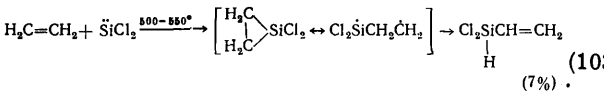


(102)

It has been reported recently[5,6] that the cocondensation of dichlorosilylene with propene (at −196°C) leads to the formation of the corresponding disilacyclohexane derivatives; the authors claim that, owing to the ease of insertion of $\ddot{S}iCl_2$ in the Si–Cl bond, it is difficult to avoid the formation of 1-trichlorosilyl-1,2-disilacyclohexane. However, attempts to demonstrate unambiguously the structure of the compounds obtained were not made.

In the light of these data, the results of studies on the gas-phase reactions of dichlorosilylene are of considerable interest. The joint pyrolysis of perchloropolysilanes and ethylene, which does not lead to the formation of cyclic compounds, is typical[92]. However, silicon-containing products are formed in an overall yield of approximately 70% in this case also.

As in the instances described above, the mechanism involving the addition of dichlorosilylene to ethylene with formation of a labile adduct, the structural isomerism of which leads to dichlorovinylsilane, appears to be most likely:

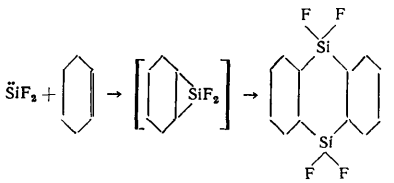


(103)

(7%).

The remaining organosilicon compounds [$Cl_3SiCH{=}CH_2$ (18%), $Cl_3SiC_2H_5$ (16%), $(H_2C{=}CH)Cl_2SiC_2H_5$ (20%), and $(C_2H_5)_2SiCl_2$ (10%)] are most probably the products of secondary reactions of the adduct of $\ddot{S}iCl_2$ and ethylene.

The addition of monomeric $\ddot{S}iF_2$ to cyclohexene[2] with subsequent dimerisation of silacyclopropane has been reported in a preliminary communication, but is not quoted in later reviews on the chemistry of difluorosilylene:



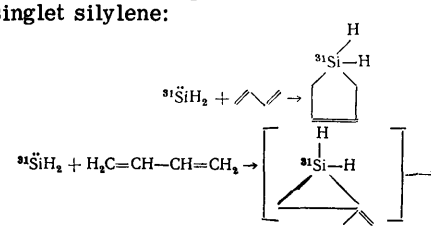
(104)

Reactions with Dienes and Polyenes

Conjugated dienes are the most reactive "trapping agents" for silylenes. Furthermore, the information in the review of Atwell and Weyenberg[2] about the addition of organic silylenes, generated by the thermolysis of alkoxydisilanes, to 2,3-dimethylbuta-1,3-diene can now be supplemented by the following new findings. These reactions proceed quite well also in the gas phase[161], where side reactions involving the dimerisation of the diene proceed to a negligible extent, and the yield of the main products is very high (approximately 60%).

It has been stated that monomeric [^{31}Si] difluorosilylene, obtained by a nuclear reaction (see above), also reacts with butadiene to form 1,1-difluoro-1-[^{31}Si]silacyclopent-3-ene[203].

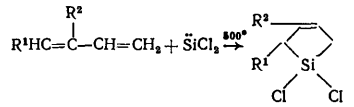
The first study on the addition of the silylene $^{31}\ddot{S}iH_2$ to buta-1,3-diene[199] showed that 80% of the silylene obtained by the nuclear reaction (43) is in the triplet state and 20% is in the singlet state[202]. The proposed mechanism for the formation of [^{31}Si]silacyclopent-3-ene presupposes the 1,4-addition of the triplet silylene and the 1,2-addition of the singlet silylene:



(105)

(106)

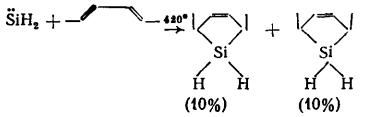
The syntheses of various mono- and bi-functional silacyclopentenes via intermediate silylenes such as $\ddot{S}i(CH_3)Cl$, $\ddot{S}i(CH_3)F$, and $\ddot{S}iCl_2$ have been described in the patent literature[274]. The method of synthesis of dichlorosilylene, based on the pyrolysis of hexachlorodisilane or octachlorotrisilane, opened effective pathways to the synthesis of a wide variety of cyclopentenes in almost quantitative yield (relative to the initial perchloropolysilane)[89–92,263]:



(107)

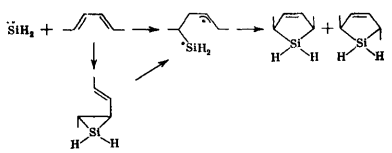
where R^1 = H or CH_3 and R^2 = H, CH_3, or Cl. It is noteworthy that the insertion of the dichlorosilylene in the C–Cl, C–H, and Si–Cl bond is observed in this case.

The silacyclopentenes obtained by reaction (107) are formally products of the 1,4-addition of dichlorosilylene, but one cannot rule out the possibility that dichlorosilylene initially attacks one of the double bonds of the diene with subsequent isomerisation of the intermediate vinylsilacyclopropane. The formation of isomeric 2,5-dimethylsilacyclopent-3-enes in equal amounts,



(108)

makes it possible to rule out the concerted 1,4-addition of silylene ($\ddot{S}iH_2$) to *trans*-2-*trans*-4-hexadiene[233], which should have led to the *cis*-product exclusively. This factor served as basis for the hypothesis of a biradical mechanism. The biradical can be obtained both as the primary adduct or as a result of the opening of the vinylsilacyclopropane ring[2,8]:

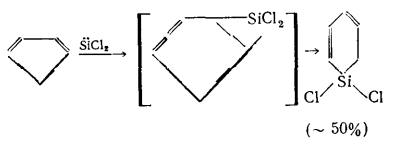


(109)

Reactions via the mechanism discussed above are evidently impossible for difluorosilylene[275] and silicon monoxide[9], the interaction of which with dienes in the

condensed phase is accompanied by the formation of cyclic compounds containing Si_2F_4 and $(SiC)_2$ units. It is believed that the latter are the products of the 1,4-addition of dimeric biradicals.

An interesting version of the reaction involves the addition of $\ddot{S}iCl_2$ to a cyclic diene (cyclopentadiene)[89-92,263]. This reaction probably proceeds via the addition of $\ddot{S}iCl_2$ to the double bond, the resulting intermediate adduct undergoing rearrangement in the next stage:

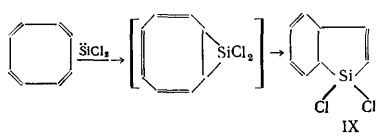


(110)

(~ 50%)

It is noteworthy that the synthesis of 1,1-dichloro-1-silacyclohexa-2,4-diene by other procedures is difficult, since these are mainly multistage syntheses with low yields producing an admixture of isomers which are difficult to separate[276].

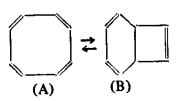
A non-conjugated cyclic polyene system such as cyclo-octatetraene is an interesting object of investigation[92]. The interaction of hexachlorodisilane with this compound at 500–550°C led to the formation of the heterocyclic compounds (IX)–(XI) with an overall yield of about 45%. The addition of dichlorosilylene tentatively proceeds via the following mechanism:



(111)

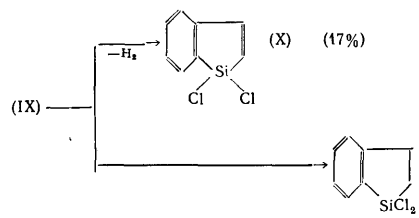
IX

The isomerisation of the cyclo-octatetraene skeleton to the conjugated form (B) prior to the addition step is equally possible:



(A) (B)

1,1-Dichloro-8,9-dihydro-1-silaindene (IX) is fairly unstable at high temperatures and is dehydrogenated with formation of 1,1-dichloro-1-silaindene (X). The isomerisation of compound (IX) with formation of 1,1-dichloro-1-silaindan (XI) also proceeds to some extent:



(112)

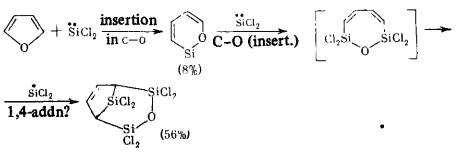
(X) (17%)

(XI) (13%)

Benzene and its derivatives are known to be unreactive as trapping agents in relation to organic silylenes[2] and they should probably also exhibit a low reactivity in relation to other silylenes in the singlet state. Nevertheless one should note that biradical difluorosilylene polymers[216] as well as the less thoroughly investigated silicon monoxide react with aromatic hydrocarbons, forming cyclohexa-1,4-dienes[5,9]. The product of the reaction of silicon monoxide with benzene exhibits a high thermal stability[6].

Reactions with Furan and Its Derivatives

The products of the gas-phase reaction of dichlorosilylenes with furan were unexpected[89-92]. The sequence of reaction steps can be represented in this instance by the following mechanism:

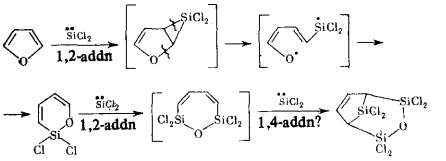


(113)

(8%)

(56%)

However, one cannot rule out another mechanism of the reaction, for example the addition of dichlorosilylene to the double bond of furan combined with a complex intramolecular rearrangement of the intermediate adduct:



(114)

The reaction with sylvan proceeds in the same way. The study of the interaction of perchloropolysilanes with this compound at 500–570°C showed that dichlorosilylene does not attack the methyl group; all the products detected were analogous to those isolated in the reaction with furan, the yield of the methyl-substituted bicyclic compound also being high (50%).

The examples discussed above demonstrate the enormous synthetic possibilities of the silicon analogues of carbenes (silylenes), the chemistry of which has been used in the solution of practical problems as a result of the efforts of many investigators. Summarising the foregoing, one may conclude that the chemistry of silylenes is in a state of vigorous development. This is demonstrated by the recent publications on the mechanism of the addition of phenylmethylsilylene to cyclohexene[277,278] and 2,3-dimethylbuta-1,3-diene[279] and of the addition of dimethylsilylene to cyclohexa-1,2-diene[280], which has provided evidence for the formation of intermediate silacyclopropanes. Methods for the generation of silylenes are also being improved, in particular the existing methods have been supplemented by a new procedure whereby dimethylsilylene is obtained under the mild conditions of the thermolysis of hexamethylsiliran, which until recently was completely inaccessible[281]. The above trends have been reflected also in certain recent publications[282-299], which appeared during the preparation of the review for the press. All these factors give rise to the hope for a rapid improvement of the existing methods for the synthesis and investigation of silylenes, which will undoubtedly help to predict, in a broad outline, the mode of reactions in systems which have not so far been investigated.

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† Potter's earlier studies are apparently to be found in the Patent literature.

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