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Review

GAS PHASE REACTIONS OF DICHLOROSILYLENE *

E.A. CHERNYSHEV, N.G. KOMALENKOVA and S.A. BASHKIROVA

State Scientific Research Institute of Chemistry and Technology of Organoelement Compounds, Moscow (U.S.S.R.)

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Introduction

In recent years a great deal of attention has been given to the study of the chemistry of unstable compounds of silicon, the silylenes. Especially promising is dichlorosilylene, whose chemistry has served to solve many preparative problems dealing with the production of organosilicon compounds, including heterocyclic compounds containing functional groups at the silicon atom.

Early in 1968, dichlorosilylene was postulated for trichlorosilane pyrolysis as the intermediate species responsible for the formation of previously unknown organosilicon heterocycles such as dichlorosila- and tetrachlorodisila-acenaphthene, tetrachlorodisilaphenalane and others [1–3]. However, later it was found that trichlorosilane, when used as the source of dichlorosilylene, has some important drawbacks [4]. The main interference for the development of dichlorosilylene chemistry on a trichlorosilane base is the fact that due to the large volume of side-reactions, the unsaturated compounds in copyrolysis with trichlorosilane form practically no dichlorosilylene adducts [5].

In 1969–1970 a highly effective method was elaborated to generate dichlorosilylene, consisting of a one-stage process of thermal decomposition of perchloropoly-

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* This review is dedicated, with best wishes, to the reverend Professor M. Kumada, who has made an invaluable contribution to the development of silylene chemistry.

silanes via α-elimination reaction [6]:

$$\mathrm{Cl_3Si(SiCl_2)_{\mathit{n}}SiCl_3} \xrightarrow{500-600\,^\circ\mathrm{C}} \mathrm{SiCl_4} + (n+1):\mathrm{SiCl_2} \qquad (1)$$
$$n \geqslant 0$$

The chemical and kinetic evidence for dichlorosilylene formation was obtained for the first time under the above conditions [7–10]. The results of those experiments were reported in reviews [11,12].

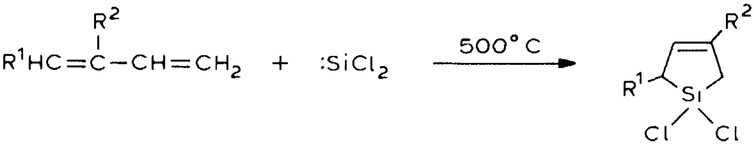
The investigations carried out by us opened up the way for new opportunities for the stabilization of dichlorosilylene [13], as well as for the synthesis and study of the properties of many of the earlier inaccessible organosilicon compounds. This is shown by the large number of papers which have appeared recently [14–23].

We regard the present review as being a generalization of the most interesting results of our investigations of gas-phase dichlorosilylene reactions. At the present time the gas-phase dichlorosilylene reactions which laid the basis for the development of many original methods of producing organosilicon compounds [6,24–26] fall into the following groups: (1) addition to multiple C–C bonds; (2) insertion of dichlorosilylene into ordinary C–H, O–H, O–C bonds without intermediate formation of a free radical state; (3) insertion into C–Hal bonds according to a "elimination-recombination" radical mechanism; (4) the elimination of the halogen with separation of the radicals without direct recombination. Though such a division is, to some extent, arbitrary, it nevertheless allows one to reveal the major features of dichlorosilylene behaviour in reactions with different compounds.

1. Addition reactions of dichlorosilylene to unsaturated C–C bonds

The first group of reactions involves pyrolysis of hexachlorodisilane and higher perchloropolysilanes in the presence of dienes [3–6,8,11,12,27], olefins [4,5,11,12] and acetylenes [3–8,11,12].

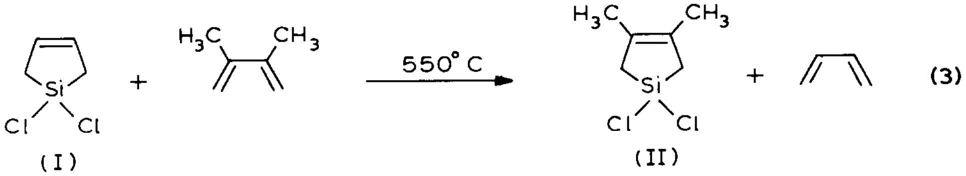
This method afforded an efficient synthetic route to different silacyclopentenes in almost quantitative yields:



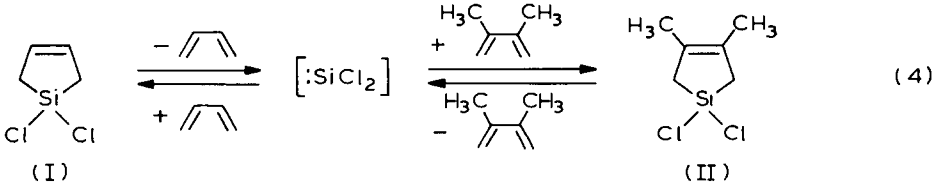
(2)

(R^1 = H, CH_3, R^2 = H, CH_3, Cl, C_6H_5)

The mechanism of this reaction was for a long time obscure. A study of the thermal conversions of 1,1-dichloro-1-silacyclo-3-pentene (I) [28,29] has recently shed light on this problem. This compound was found to be unstable at temperatures above 500 °C and capable of generating dichlorosilylene by the retro-diene decomposition route [29]. Thus, pyrolysis of compound I in the presence of an equimolar quantity of 2,3-dimethyl-1,3-butadiene (dichlorosilylene "trap") leads to the formation of a "trapping" product, i.e. of the corresponding 3,4-dimethyl-substituted silacyclopentene II (in a 50% theoretical yield and an 80% yield based on the converted initial compound):



It was found that the silacyclopentene decomposition reaction is reversible. This is shown by the formation of compound II by pyrolysis of I in the presence of 2,3-dimethyl-1.3-butadiene, or of compound I by pyrolysis of the dimethyl-substituted silacyclopentene II in an excess of 1,3-butadiene:



From the data presented we see that the pyrolysis of 1,1-dichloro-1-silacyclo-3-pentenes (I, II and obviously any others) at 550 °C in the presence of the chemical "traps" is a highly-selective process leading to the formation of only a "trapping" product and the initial compound.

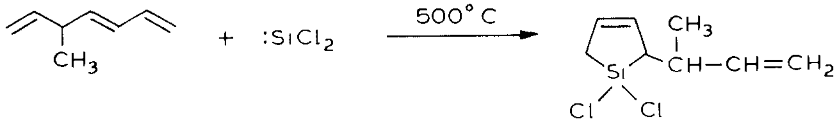
A study of the influence of 1,3-butadiene and silacyclopentenes (I or II) concentration in an inert diluent ($SiCl_4$) has shown that a decrease in the concentration does not affect the yield of the corresponding "trapping" products (II or I). Apparently, the silylene reaction mechanism operates in this case, and the thermal decomposition of dichlorosilacyclo-3-pentenes is unimolecular.

The data available on the behaviour of dichlorosilacyclo-3-pentenes (I,II) under electron impact [30] have also shown that they afford an intense (100%) peak with $m/e = 54$ or 82 corresponding to a diene fragment. The spectra of the compounds reveal metastable peaks indicating a one-act elimination of $:SiCl_2$ from the molecular ions. The peaks with $m/e = 54$ or 82 are also maximal in the low voltage (15 V) mass spectra of compounds I and II.

Thus the one type of process taking place under the action of electron impact, and as a result of the thermal initiation, shows that the decomposition of silacyclopentenes (I and II) is concerted and, in our opinion, that it corresponds formally to the retro-Diels–Alder reaction.

The results obtained also indicate a formal correspondence of the gas-phase interaction of the singlet dichlorosilylene with *S-cis*-1,3-butadienes (eq. 2) to the Diels–Alder reaction and consequently that it proceeds, as distinct from carbenes, via a concerted 1,4-cycloaddition.

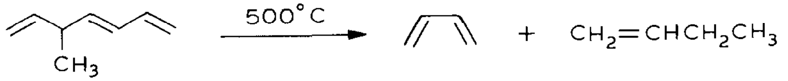
Apparently, dichlorosilylene should also have reacted with a conjugated diene such as 5-methyl-1,3,6-heptatriene. However, the experiments performed have shown that the yield of the corresponding adduct (III) does not exceed 8–10%:



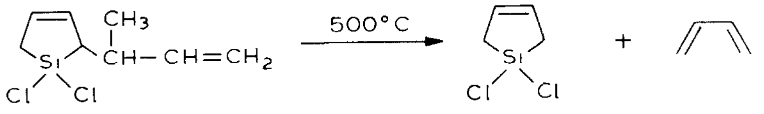
(III)

(5)

This result is likely associated, on the one hand, with the fact that the necessity of carrying out the synthesis (because of the nature of the :SiCl$_2$ source) under severe conditions leads to by-reactions, thus reducing the yield of the main adduct (III). Thus, pyrolysis of the methylheptatriene at 500 °C was found to lead to the formation of 1,3-butadiene and 1-butene (eq. 6), as well as to that of *o*- and *p*-xylenes, whereas compound III, under the same conditions, dissociated via elimination of the alkenyl chain, in the form of a diene (eq. 7):



(6)



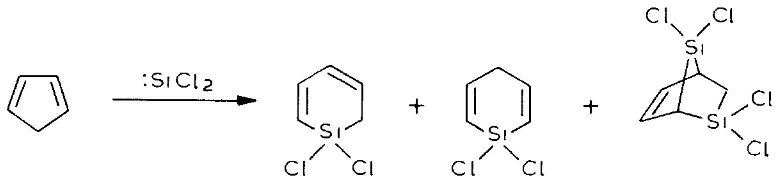
(III)

(7)

On the other hand, the low yield of III may imply that the formation of a *cis*-conformation of the methylheptatriene is hindered under our conditions.

The addition reactions of dichlorosilylene to cyclic dienes (cyclopentadiene, furan) reported earlier [3,4–8,11,12] may at present be regarded from the point of view of their feasible course according to the diene synthesis route. However, beyond all expectations and in spite of the fact that these compounds have a fixed *cis*-conformation, no trace of a single-typed course for their reactions with dichlorosilylene was detected.

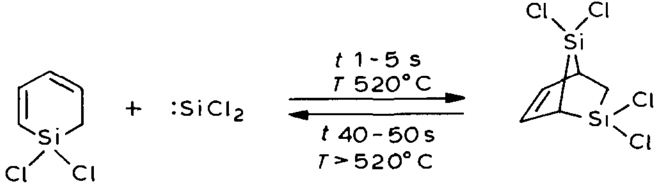
A comprehensive investigation of the :SiCl$_2$ interaction with cyclopentadiene has revealed the formation of the following compounds (IV–VI) [31]:



(IV, 45%) (V, 15%) (VI, 25%)

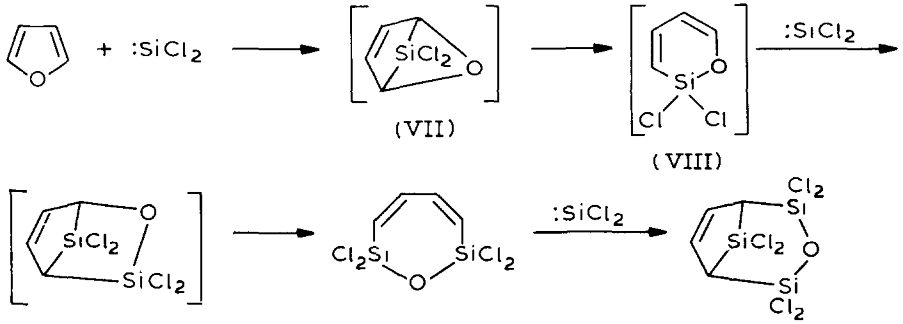
(8)

The percentage yields shown are optimal under the conditions of the target formation of each of the heterocycles (IV–VI). Thus, for instance, under the conditions of maximal formation of the silacyclo-2,4-hexadiene (IV) (initial reagents ratio 1 : 1, contact time 40 s, temperature 520 °C), compound VI is formed in a small yield, which is a result of its definite instability. It is for this reason that it was not detected by us in previous investigations. The ratio of the structural isomers IV and V depends mainly on the initial reagents ratio and is practically unchanged with temperature. This fact may indicate that, in the course of the reaction, one and the same intermediate compound is formed which is capable of being stabilized by two different routes, giving compounds IV and V. By virtue of this fact, the two compounds cannot as yet be unambiguously regarded as adducts of diene condensation. Such an adduct is apparently the bicyclic VI, an hitherto unknown product of the 1,4-cycloaddition of $:SiCl_2$ to the cyclic diene IV, which occurs at the first stage of the reaction 8 [31]:



(IV) (VI) (9)

We found this reaction to be reversible; the forming adduct VI, under more severe conditions (contact time being 40–50 s, temperature > 520 °C) in comparison with the optimal (contact time being 1–5 s, temperature 520 °C), is capable of dissociating into the initial components. The results obtained afford the explanation for the difference in the routes of reaction 8 and the previously-studied interaction between dichlorosilylene and furane [4,8,11]:

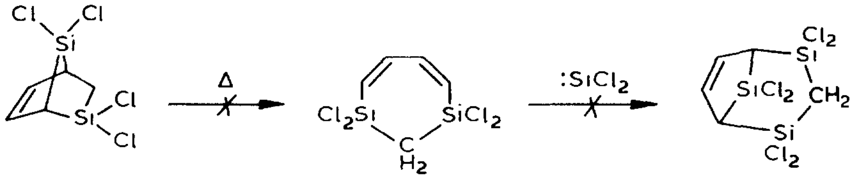


(VII) (VIII)

(IX) (X) (XI) (56%) (10)

The absence of isomers of a similar structure to compound VIII among the reaction products allows one to consider this course of interaction from the point of view of general regularities of diene synthesis. The adduct of furan with $:SiCl_2$ must be the bicyclic VII, however in such a cyclic system a rather large stress appears, as a result of which there apparently takes place a rearrangement into the ring-expansion product (VIII) which may enter into reaction with another $:SiCl_2$ molecule to form a secondary product, the bicycloheptene IX. Apparently, the latter, also due to its instability, is converted irreversibly into the cycloheptadiene X, which in its turn is capable of entering rapidly into reaction with dichlorosilylene to form the stable bicyclooctene XI in high yield. Such a reaction route is, in all appearance, due to the energetic advantage of Si–O–(Si) bond formation, and to the higher activity of the forming dienes VIII and X with respect to dichlorosilylene.

By comparing the dichlorosilylene reaction products with furan (eq. 10) and the products of its reaction with cyclopentadiene (eq. 8), we may note that the bicycloheptene VI is more stable under the formation conditions than its oxygen-containing analogue IX. So far there is no confirmation as to the possible rearrangement of the bicyclic VI into the corresponding diene XII and, consequently, its further reaction with :$SiCl_2$ to form compound XIII:



(11)

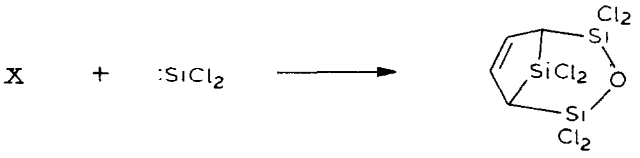
(VI) (XII) (XIII)

Under our conditions, compound VI is more capable of decomposing in a reverse reaction, (eq. 9), than of being rearranged into compound XII. For this reason it does not react with free dichlorosilylene.

In the case of furan the suggested scheme was confirmed experimentally:

(12)

(VIII) (X)

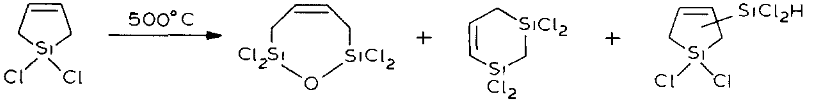


(13)

(XI)

Also, it appears that the cycloheptadiene X enters into the reaction with :$SiCl_2$ faster than does the cyclohexadiene VIII, which hinders the preparation of compound X in a pure form.

In concluding the section devoted to addition reactions of dichlorosilylene to conjugated dienes, we believe it appropriate to report here some of the results obtained in studying the thermal conversions of 1,1-dichloro-1-silacyclo-3-pentene (I) in the absence of "trapping" compounds [28]. It is supposed that the dichlorosilylene, formed by the retro-diene decomposition of the compound I, will interact with the initial olefin (I). However, so far we have failed to detect in the reaction products the intermediate bicycle with a silacyclopropane ring. Thus, the pyrolysis of dichlorosilacyclopentene (I) at 500 °C affords a mixture of compounds of the following structures:



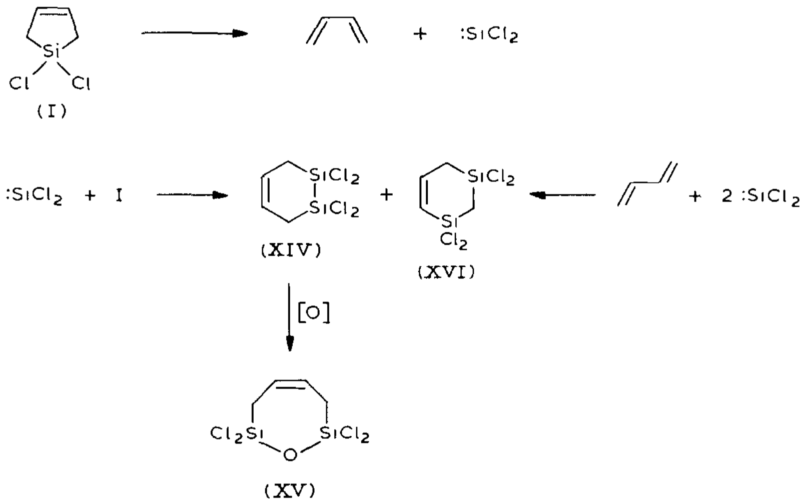
(14)

(I) (XV, 3-4%) (XVI, 7%) (XVII, 3%)

Conducting pyrolysis of I with an excess of :$SiCl_2$ (i.e. in the presence of Si_2Cl_6) leads to the same composition of the reaction end-products, only the amount of the dichlorosilyl-derivatives of silacyclopentene XVII increases, to as high as 20%. A possible scheme for their formation will be considered below.

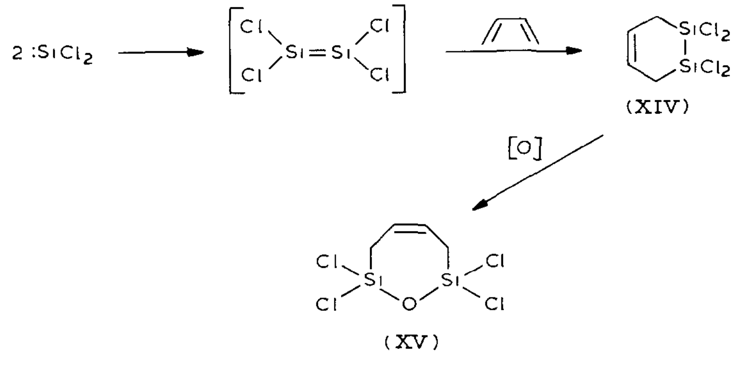
Under more severe conditions, at 680 °C, compounds XV and XVI, in yields of 15 and 45%, respectively, prevail in the pyrolysis products of the silacyclopentene (I) [28], which is of interest for the synthesis of these inaccessible compounds.

The composition of the reaction mixtures are well explained by the multi-step scheme (eq. 15) involving the formation of :$SiCl_2$, according to the retro-diene reaction, which further interacts, either with the initial silacyclopentene (I), or with the forming 1,3-butadiene:



(15)

The increase in yields of compounds XV and XVI with a rise in the pyrolysis temperature may serve as an indication of their formation according to the given scheme. In this case it is also impossible to rule out the alternative mechanism for the formation of the heterocycle XIV via 1,4-addition of the 1,3-butadiene of the disilene species $Cl_2Si{=}SiCl_2$, which may perhaps exist in small amounts in the gas phase:

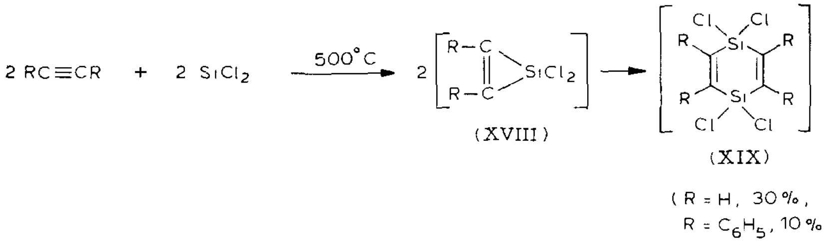


(16)

Compound XIV, with the Si_2Cl_4 fragment, is apparently unstable and under the pyrolysis conditions is converted into 1,3-disila-2-oxacyclo-5-heptene (XV).

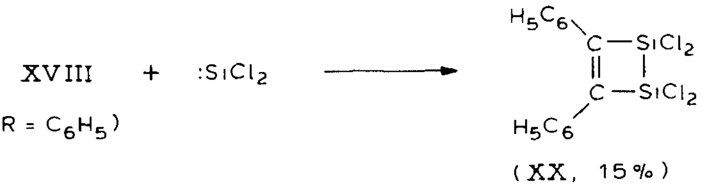
The reactions of dichlorosilylene with acetylene in the gas phase are of great interest for the preparative synthesis of hitherto inaccessible tetrachloro-substituted-

1,4-disilacyclo-2,5-hexadienes [3–8,11,12]:



(17)

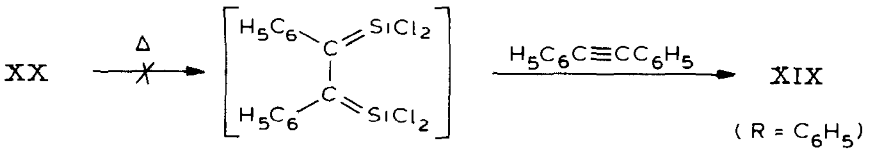
The mechanism of these reactions is currently a topical problem. Apparently, the primary act is the addition of dichlorosilylene to the acetylenic bond to form silacyclopropene XVIII which has, however not been identified. Most promising for the solution of the problem concerning its further conversions is the study of the reaction of :$SiCl_2$ with diphenylacetylene, for through this reaction an interesting compound XX was obtained, which may be regarded as a product of dichlorosilylene insertion into the silacyclopropene ring * [4,5]:



(18)

The formation of compound XIX may be represented either as a σ-dimerization of the silacyclopropene (XVIII, R = C_6H_5) or as the Diels–Alder addition of diphenylacetylene to the intermediate 1,4-disila-1,3-butadiene XXI, formed by opening the ring of the compound XX, as was proposed in ref. 32 for dimethyl- and diphenylsilylenes.

However, the detailed study of the interaction of diphenylacetylene with compound XX in the temperature range 500–600 °C carried out by us, has demonstrated the stability of the latter compound, and consequently, has shown that such a reaction route is not realized under our conditions:



(19)

Therefore, the conclusion on the dominant contribution of the σ-dimerization mechanism to the formation of disilacyclohexadiene XIX (R = C_6H_5) remains as yet the most acceptable one.

Thus, the investigations of the addition reactions of dichlorosilylene carried out in recent years has proved to be very fruitful. The problem concerning its reactions with aliphatic dienes, proceeding by a concerted 1,4-cycloaddition mechanism, has been clarified.

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* As for determining the possible participation of the $Cl_2Si{=}SiCl_2$ species in the process of formation of XX, the corresponding investigations have only just been started.

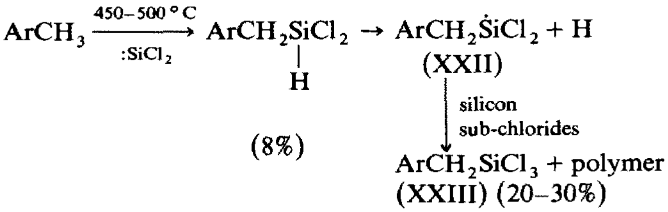
The retro-diene decomposition of the derivatives of 1-silacyclo-3-pentene, as a technique for generating silylenes with different substituents, may be of great significance in organosilicon chemistry.

2. Insertion of dichlorosilylene into C–H, O–H, O–C bonds

The ideas expressed below on the character of insertion reactions of dichlorosilylene into ordinary bonds are based largely on analogies with the behaviour of singlet carbenes, because of the absence of data on the details on its interaction mechanism.

The gas-phase interaction of dichlorosilylene with C–H, O–H and O–C bonds leads to the formation both of the products of the formal insertion of :$SiCl_2$ and of those of their further conversions. On the basis of these reactions, it appeared possible to produce acyclic and heterocyclic organosilicon compounds in satisfactory yields [11,24,33].

The interaction of dichlorosilylene with C–H bonds is the most completely studied [34,36]. We succeeded in revealing general regularities in the routes of these reactions. The structure of the compounds obtained is determined, to a significant extent, by the temperature factor. Under comparatively mild conditions (t being less than 500 °C) we may observe the formation of primary products of :$SiCl_2$ insertion, that is acyclic compounds with Si–H bonds, which tend to undergo a free-radical conversion, especially in the more severe synthetic conditions (680 °C) [34,36].

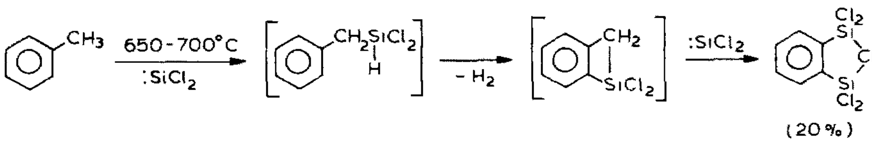


$$\begin{array}{llll} ArCH_3 \xrightarrow[:SiCl_2]{450-500\,^\circ C} & \underset{\displaystyle H}{\underset{|}{ArCH_2SiCl_2}} & \rightarrow & ArCH_2\dot{Si}Cl_2 + H \\ & & & (XXII) \\ & (8\%) & & \Big\downarrow \text{silicon sub-chlorides} \\ & & & ArCH_2SiCl_3 + \text{polymer} \\ & & & (XXIII)\ (20\text{–}30\%) \end{array}$$

(Ar = phenyl, *o*- and *p*-tolyl, *p*-diphenylyl, α- and β-naphthyl, 2- and 3-thienyl)

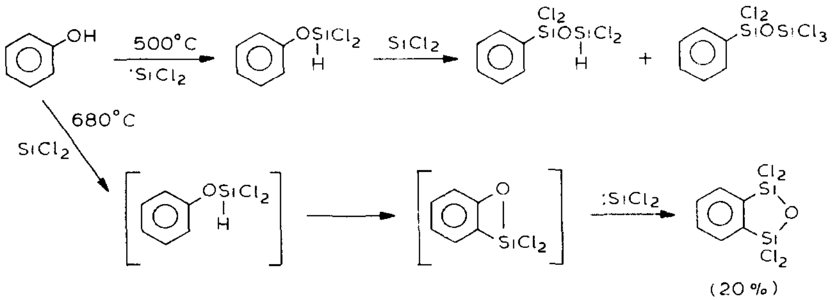
The main compound, aryltrichlorosilylmethane (XXIII), is apparently the product of a secondary reaction in which the radical (XXII) extracts a chlorine from the silicon sub-chlorides present in the reaction zone. An increase in the temperature, up to 680 °C, leads to an increase in the yield of compound XXIII, up to 30%, and a decrease in the $ArCH_2SiHCl_2$ yield.

Another regularity which was revealed in these reactions is the formation of heterocyclic compounds at elevated temperatures (650–700 °C), most likely through a type of intramolecular cyclization of the primary products of insertion, followed by their stabilization via the insertion of a second dichlorosilylene molecule [33,35,36], for instance:



(21)

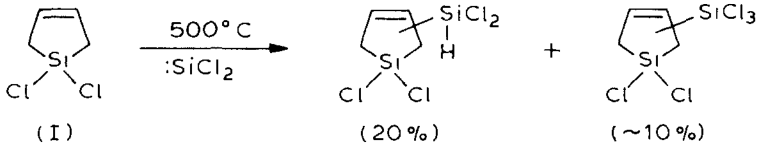
These regularities also determine the general insertion route of :$SiCl_2$ into other ordinary bonds, such as O–H and O–C [36,37], for instance:



(22)

(23)

In the reactions of $:SiCl_2$ with 1,1-dichloro-1-silacyclo-3-pentene (I) (see Section 1) a mixture of isomeric dichloro- and trichloro-silyl-derivatives is formed [28], whose composition is not defined exactly as yet:



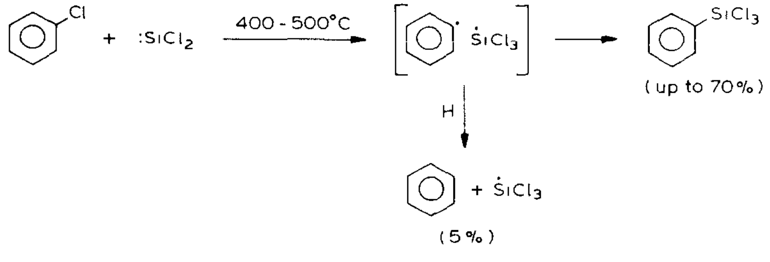
(24)

The low selectivity of insertion, and the structure of the resulting compounds, corresponds to the conceptions about the direct insertion of $:SiCl_2$ into the C–H bonds.

Finally, it should be especially emphasized that the ability of interaction of other silylenes with a variety of carbon–hydrogen bonds has been little studied, i.e. it is quite possible that the behaviour of thermally-generating dichlorosilylene is exceptional. Although the terminal product yields are moderate (20–30%) the reactions considered in this section are nevertheless of preparative value.

3. Insertion of dichlorosilylene into C–Hal bonds

The process of insertion of dichlorosilylene into C–Hal bonds, which apparently occurs through elimination-recombination steps may be applied to the third group of dichlorosilylene reactions. The interaction of singlet carbenes with C–Cl bonds proceeds by such a mechanism [38]. The composition of the products of the dichlorosilylene reaction with different aromatic chlorohydrocarbons indicates its high selectivity in the reaction of insertion into C_{ar}–Cl bonds. We may believe that the singlet $:SiCl_2$ extracts the Cl-atom from the original compound to form a pair of radicals. The recombination of the radicals affords the corresponding organotrichlorosilanes in high yield, whereas the separation of the radical pair is not typical of this interaction [25,34,36,39,40]:



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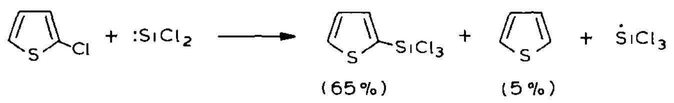

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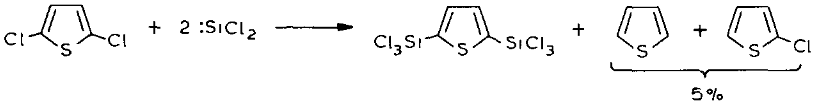

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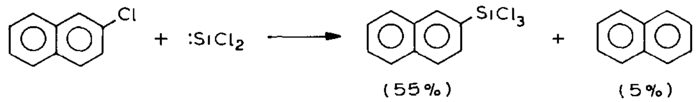
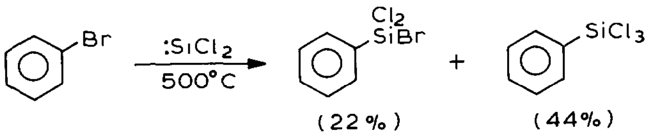


(28)

The singlet dichlorosilylene also selectively extracts the bromine, fluorine and iodine atoms from the corresponding halohydrocarbons, although the reactions are complicated by halogen exchange [36]:



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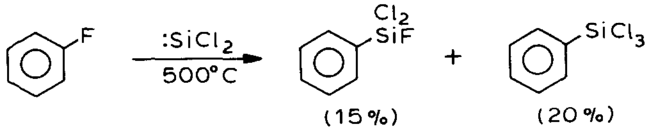
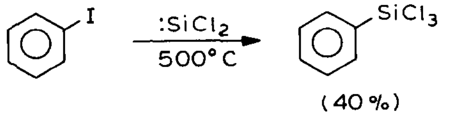
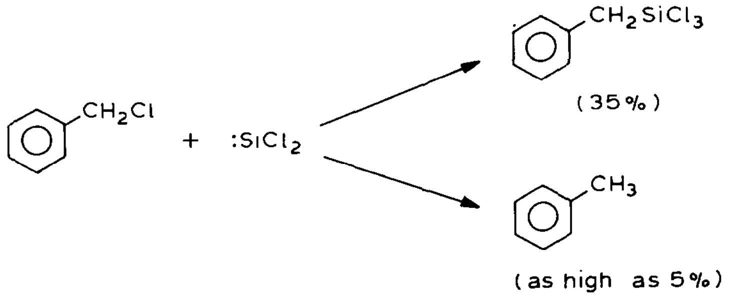


(30)

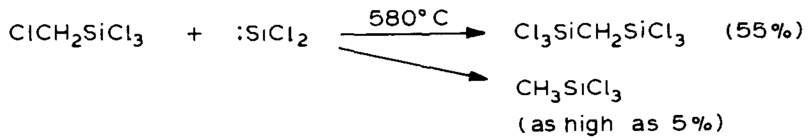


(31)

The dichlorosilylene insertion reaction into the C_{alk}–Cl bond proceed also with sufficient selectivity [24,34,36]:



(32)

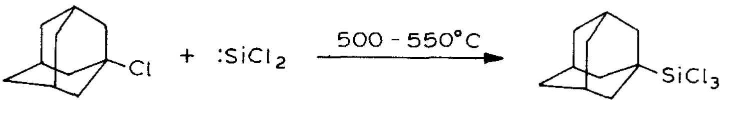


(33)

Bis(trichlorosilyl)methane may also be prepared in the same yield (55%) by the interaction of dichlorosilylene with methylene chloride (reagent ratio 2 : 1) [36]:

$$Cl_2CH_2 + 2\ {:}SiCl_2 \xrightarrow{620\,°C} Cl_3SiCH_2SiCl_3 \tag{34}$$

The same type of introduction of the dichlorosilyl group into 1-chloroadamantane, to form 1-trichlorosilyladamantane as the main product, has aroused great interest [25,40]:



(35)

(XXIV, 60%)

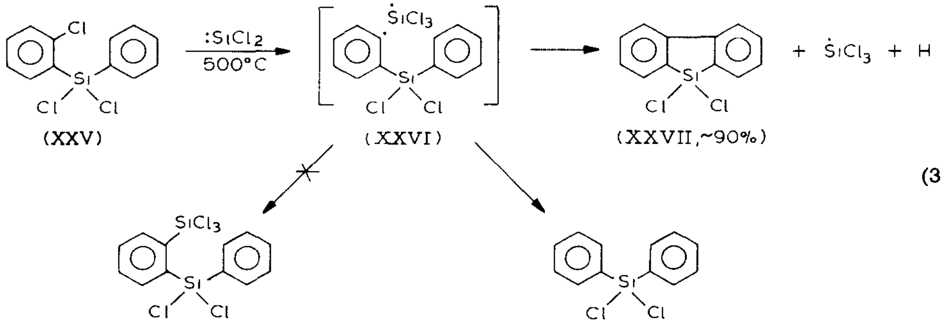
The above reaction (eq. 35) is so far the only preparative method for compound XXIV.

Here it would be appropriate to note that the formation of trichlorosilyl-derivatives when trichlorosilane reacts with organo halides is possible only in those cases when the halogen is bound to a carbon in an sp^2-hybridization state, i.e. with the participation of C_{aryl}–Cl or $C_{alkenyl}$–Cl bonds [41].

4. Elimination of chlorine atoms

The last section of this review is devoted to a comparatively recently detected novel gas-phase reaction of organosilicon heterocyclic compounds with the participation of $:SiCl_2$. In contrast to the reactions described above, dichlorosilylene reacts with certain *o*-chloro-substituted organosilicon compounds only to eliminate the chlorine atom, and while promoting the intramolecular cyclization it does not enter into the composition of the forming products [12,26,42].

Thus, in studying the thermal interaction of *o*-chlorophenylphenyldichlorosilane XXV with hexachlorodisilane, it was found that at 500 °C 1,1-dichloro-1-silafluorene XXVII was formed in a 90% yield:

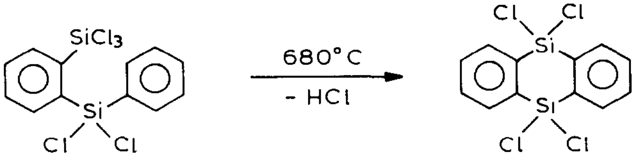


(36)

Although the reaction starts with a selective extraction of the Cl-atom with dichlorosilylene, no formation of the product of its insertion into the C_{ar}–Cl bond (XXIX), as a result of recombination of the radical pair, takes place, obviously, because of the heightened tendency of the phenyldichlorosilylphenyl radical XXVI toward intramolecular cyclization. The observed fact of selective extraction of the Cl-atom confirms the correctness of attributing the insertion reactions of dichlorosilylene into C–Cl bonds to the radical conversions proceeding according to the elimination-recombination mechanism. The formation of diphenyldichlorosilane

XXVIII (5% in reaction 36) as a result of the separation of the radical pair (XXVI) also fits into the above-indicated scheme. We observed similar so-called "reduction products" in all the cases of $:SiCl_2$ interaction with any of the chlorohydrocarbons in reactions 25–28,32,33.

The suggestion that the possible instability of the forming product of $:SiCl_2$ insertion into the C_{ar}–Cl bond (XXIX) leads to its consequent conversion into the silafluorene (XXVII), the product of the reaction, was not confirmed. Compound XXIX, obtained by means of an alternative synthesis, at high temperatures, is cyclized by another route (eq. 37) to form compound XXX [43]:



(XXIX) (XXX, 30%) (37)

Under the investigated conditions, the compound XXV in the absence of the $:SiCl_2$ source undergoes practically no intramolecular dehydrochlorination, to form the dichlorosilafluoren XXVII [43]. In the presence of the new dichlorosilylene source, that of 1,1-dichloro-1-silacyclo-3-pentene (I) (see Section 1), the yield of the cyclization product XXVII amounts to 30%, which is also evidence in favour of the silylene mechanism of the reaction (eq. 36). Probably, the thermal cyclization of the *o*-chlorophenylphenyldichlorosilane XXV in the presence of trichlorosilane also proceeds significantly through the participation of dichlorosilylene generated from trichlorosilane, according to the reaction 38 [2] rather than by the homolytic scheme

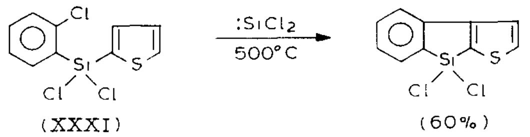
$$2HSiCl_3 \rightarrow :SiCl_2 + SiCl_4 + H_2 \qquad (38)$$

for the reduction reaction suggested earlier [43]. Thus, a comprehensive investigation of the impact of the temperature factor on the yield of compound XXVII when using $HSiCl_3$ in the above-indicated reaction (eq. 36) has shown that the cyclization product yield drops appreciably with a decrease in temperature: at 680 °C it amounts to 50%; at 580–600 °C (the most favourable conditions for the thermal interaction of aryl halides with trichlorosilane) to 30%; at 500 °C it drops to 5%.

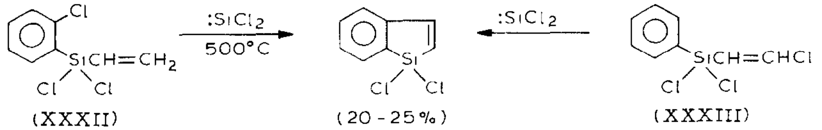
The above experimental findings are in good agreement with the thermodynamic calculations of the product composition of the trichlorosilane decomposition. The data show that with an increase in temperature, in the range 500–700 °C, dichlorosilylene can be prepared in quantities exceeding those of the trichlorosilyl radical [2].

Thus, the experimental data obtained enable us to regard reaction 36 as an extraction by dichlorosilylene of a Cl-atom in a molecule having a structural fragment necessary for cyclization, and as a result of this, the reaction proceeds in this case without a recombination of the radical pair.

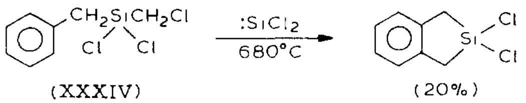
The investigation of the dichlorosilylene interaction with other *o*-chloro-substituted organosilicon compounds XXXI–XXXV has shown the common character of the cyclization reaction; however the compounds under investigation with C_{ar}–Cl (XXXI, XXXII), $C_{alkenyl}$–Cl (XXXIII), C_{alk}–Cl (XXXIV) and Si–Cl (XXXV) bonds do not afford a quantitative yield of the cyclization product. Obviously, this is due to the presence of other reaction centres in the initial molecules, and to the courses of the competitive reactions [12,42].



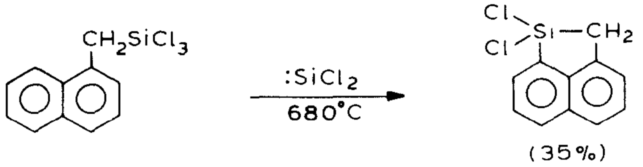
(XXXI) (60%) (39)



(XXXII) (20 - 25%) (XXXIII) (40)



(XXXIV) (20%) (41)



(35%) (42)

The absence of insertion products in almost all the reactions under study is evidence that we are dealing with a unique case when the cyclization, after abstraction of the chlorine atom with dichlorosilylene, is much more beneficial than all the other possible interaction variants.

In conclusion, it should be noted that the regularities which have been found in dichlorosilylene interaction with different bonds allow one purposefully to synthesize many earlier inaccessible organosilicon compounds by means of selecting partner-compounds with corresponding structural fragments. Therefore the gas-phase technique should, in this respect, be regarded as a very promising method, whose broad application will lead to revealing hitherto unknown properties of silylene.

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