Reviews

Advances in the gas-phase synthesis of organochloro derivatives of silicon, germanium, and tin *via* dichlorosilylene*

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The results of studies carried out in the past five years on the gas-phase synthesis of organochlorosilanes, pentachlorodisiloxanes, organochlorogermanes, and organochlorostannanes at 400—550 °C in the presence of hexachlorodisilane or 1,1-dichloro-1-silacyclopent-3-ene as sources of dichlorosilylene are summarized.

Key words: alkylchlorosilanes, alkenylchlorosilanes, pentachlorodisiloxanes, alkenylchlorogermanes, arylchlorogermanes, organylchlorostannanes, gas-phase synthesis, hexachlorodisilane; dichlorosilylene, dichlorogermylene, dichlorostannylene.

It has been previously shown[1,2] that hexachlorodisilane is the most promising source of dichlorodisilane in the gas phase. Its thermolysis occurs at 400—550 °C according to the scheme

$$Si_2Cl_6 \longrightarrow :SiCl_2 + SiCl_4. \qquad (1)$$

The mechanism of Si_2Cl_6 decomposition was studied by the matrix isolation technique,[3] and data on the kinetics[4] and thermodynamics[5] of this reaction have been obtained. The reactions of dichlorosilylene with 1,3-dienes and various chloroarenes were studied in detail, and experimental data on the chemistry of $:SiCl_2$ were reviewed.[1,2,6,7]

In this review, we systematized and generalized the results of our recent works devoted to the study of the reactions of $:SiCl_2$ with alkyl chlorides, alkenyl chlorides, and oxo compounds, which practically have not been studied previously. In addition, we attempted to use $:SiCl_2$ for the generation of other carbene analogs ($:GeCl_2$ and $:SnCl_2$). The synthesis of organoelement compounds based on the reactions of $:GeCl_2$ and $:SnCl_2$ is also considered.

Synthesis of organochlorosilanes

Synthesis of alkylchlorosilanes

Alkylchlorosilanes were obtained by the reactions of alkyl chlorides with Si_2Cl_6 in the gas phase at 500 °C.[8,9] Bis(trichlorosilyl)methane (2) and bis(trichlorosilyl)ethane (3) along with alkyltrichlorosilanes (1) are the products of the reaction (Table 1).

$$AlkCl + Si_2Cl_6 \longrightarrow \underset{\mathbf{1}}{AlkSiCl_3} + \underset{\mathbf{2}}{CH_2(SiCl_3)_2} + \underset{\mathbf{3}}{Cl_3SiCH_2CH_2SiCl_3}$$

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* Dedicated to the memory of Academician M. E. Vol'pin timed to his 75th birthday.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1063—1070, June, 1998.

1066-5285/98/4706-1029 $20.00

Table 1. Conditions and products of the reactions of Si_2Cl_6 with alkyl chlorides (500 °C, reaction duration 25—30 s)[8]

RCl	Si_2Cl_6 : RCl*	Yields of products (%)			
		1	2	3	1 + 2 + 3
EtCl	0.7 : 1.0	50	0.04	0.06	50.1
BuCl	2 : 1	32	8.2	2.3	42.5
PrCl	2 : 1	12	16	4.8	32.8
HexCl*	2 : 1	0.5	22	12	34.5

* Molar ratio.

The insertion of $:SiCl_2$ (generated from Si_2Cl_6) into the C—Cl bond of alkyl chloride is the main stage of the process

$$\text{AlkCl} + :SiCl_2 \longrightarrow \text{AlkSiCl}_3$$

Alk = Et, Pr^n, Bu^n, Hex^n (Hex is C_6H_{13})

The reaction is highly exothermic; the thermal effects ($\Delta H°_{298}(g)$) for methyl- and ethyl chlorides are −343 and −312 kJ mol^{-1}, respectively. Vibration-excited molecules of $AlkSiCl_3$ are formed in the reaction.[8]

The following scheme including the formation of vibration-excited molecules (the excitation energy is 300—340 kJ mol^{-1}) of alkyltrichlorosilanes of type **4** and their subsequent transformations was suggested.[8]

$$RCH_2CH_2Cl + :SiCl_2 \longrightarrow \underset{\mathbf{4}}{RCH_2CH_2SiCl_3^*} \qquad (2)$$

$$\mathbf{4} + Si_2Cl_6 \longrightarrow :SiCl_2 + SiCl_4 + \mathbf{1} \qquad (3)$$

$$\mathbf{4} + Si_2Cl_6 \longrightarrow 2\ {}^{\cdot}SiCl_3 + \mathbf{1} \qquad (4)$$

$$\mathbf{4} \longrightarrow RCH_2{}^{\cdot} + {}^{\cdot}CH_2SiCl_3 \qquad (5)$$

$$\mathbf{4} \longrightarrow R^{\cdot} + {}^{\cdot}CH_2CH_2SiCl_3 \qquad (6)$$

$$\mathbf{4} \longrightarrow RCH_2CH_2{}^{\cdot} + {}^{\cdot}SiCl_3 \qquad (7)$$

$${}^{\cdot}CH_2SiCl_3 + {}^{\cdot}SiCl_3 \longrightarrow \underset{\mathbf{2}}{Cl_3SiCH_2SiCl_3} \qquad (8)$$

$${}^{\cdot}CH_2CH_2SiCl_3 + {}^{\cdot}SiCl_3 \longrightarrow \underset{\mathbf{3}}{Cl_3SiCH_2CH_2SiCl_3} \qquad (9)$$

$$2\ {}^{\cdot}CH_2SiCl_3 \longrightarrow \mathbf{3} \qquad (10)$$

R = H, Me, Et, Bu^n

Alkyltrichlorosilanes can be transformed in two directions. The first direction includes the deactivation of molecule **4** due to collisions with other molecules. Reactions (3) and (4) are evidently the most significant. Colliding with the hexachlorodisilane molecules, the excited molecules of **4** transfer a portion of their excessive energy and favor the decomposition of hexachlorodisilane. The decomposition of a Si_2Cl_6 molecule in reactions (3) and (4) requires 200 and 320 kJ mol^{-1}, respectively.[5]

The second direction is the decomposition of vibration-excited molecules of **4** to free radicals in reactions (5)—(7). It is noteworthy that the energies of the C—C (320—350 kJ mol^{-1})[10] and Si—C (340—355 kJ mol^{-1})[10,11] bond cleavage are close. The ${}^{\cdot}CH_2SiCl_3$ and ${}^{\cdot}CH_2CH_2SiCl_3$ free radicals appearing in reactions (5) and (6) react with the ${}^{\cdot}SiCl_3$ radicals (reactions (8) and (9)) to form chloroalkanes **2** and **3**. Compound **3** can be evidently obtained also due to the recombination of the ${}^{\cdot}CH_2SiCl_3$ radicals (reaction (10)).

Thus, the ratio of compounds **1**—**3** formed is mainly determined by the behavior of the excited molecules of **4**. If they are rapidly deactivated and transit from the excited state to the ground state, the mixture of products predominantly contains alkyltrichlorosilanes. This type of transformations is observed during the synthesis of the lowest trichlorosilanes of the homologous series: $EtSiCl_3$ and $PrSiCl_3$ (see Table 1). If the rate of decomposition of the excited molecules of **4** is higher than the rate of their deactivation, compounds **2** and **3** are the predominant products. This situation is characteristic of the synthesis of the $RSiCl_3$ compounds with bulky radicals, for example, R = Hex (see Table 1). Evidently, the reaction of cyclohexyl chloride with $:SiCl_2$ gives cyclohexyltrichlorosilane only in a small (6—11%) yield due to the same reason.[9]

Reactions of :SiCl$_2$ with chlorosubstituted methane derivatives

The reactions of $:SiCl_2$ with polychloromethanes are interesting.[12,13] The reaction of CH_2Cl_2 with $:SiCl_2$ at 620 °C is known[14] to give only one product, bis(trichlorosilyl)methane (55% yield). The study of this process in detail shows[12] that two consecutive-parallel reactions proceed at 400—520 °C to form chloromethyltrichlorosilane (**5**) and bis(trichlorosilyl)methane (**2**).

$$ClCH_2Cl + :SiCl_2 \xrightarrow{k_{11}} \underset{\mathbf{5}}{ClCH_2SiCl_3} \qquad (11)$$

$$\mathbf{5} + :SiCl_2 \xrightarrow{k_{12}} \underset{\mathbf{2}}{Cl_3SiCH_2SiCl_3} \qquad (12)$$

The ratio between the rate constants of these reactions was determined,[12] and the maximum yield (Y_{max}) of the intermediate compound **5** was calculated at different temperatures:

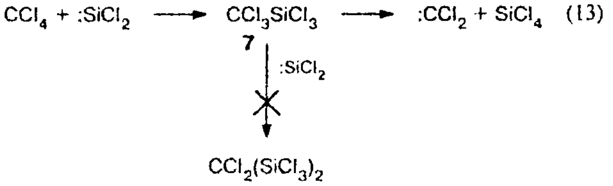
T/°C	404	440	501
k_{12}/k_{11}	1.08	1.18	1.80
$Y_{max}(5)$ (%)	35.4	33.8	26.6

The yield of compound 5 at 400—440 °C (32—34%) is higher than that at 520 °C (26%). In the same work,[12] side reactions of CH_2Cl_2 pyrolysis were considered. The pyrolysis products react with $:SiCl_2$ to give tris(trichlorosilyl)methane **6**.

Compound **6** is also formed in the gas-phase reaction of $CHCl_3$ with $:SiCl_2$ at 450—550 °C.[13] The products of this reaction contain bis(trichlorosilyl)methane as well.

$$CHCl_3 + :SiCl_2 \longrightarrow \underset{(25\text{—}34\%)}{\underset{\mathbf{6}}{CH(SiCl_3)_3}} + \underset{(10\text{—}30\%)}{\underset{\mathbf{2}}{Cl_3SiCH_2SiCl_3}}$$

The reaction of $:SiCl_2$ with CCl_4 proceeds in a different way.[13] Evidently, the primary product (**7**) of the insertion of $:SiCl_2$ into the C—Cl bond of the starting compound is thermally unstable and, according to the published data,[15] can decompose *via* α-elimination (Eq. (13)) to form $:CCl_2$. Therefore, no insertion of another $:SiCl_2$ molecule into the C—Cl bond of carbon tetrachloride occurs.

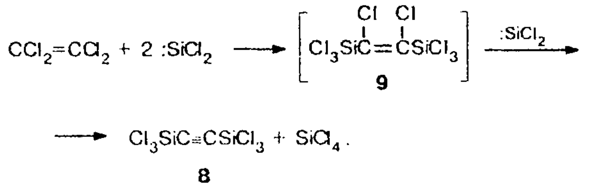


Bis(trichlorosilyl)acetylene (**8**) is the main product of the gas-phase copyrolysis of Si_2Cl_6 with CCl_4. This compound is most likely formed in the reaction of $:SiCl_2$ with tetrachloroethylene observed in the reaction products. The latter can appear due to dimerization of $:CCl_2$, which is obtained in reactions (13) or (14).[16]

$$CCl_4 \longrightarrow :CCl_2 + Cl_2 \qquad (14)$$

$$2\ :CCl_2 \longrightarrow CCl_2{=}CCl_2$$

Compound **8** can probably be formed due to the following transformations:



It follows from this scheme that excess Si_2Cl_6 in the starting mixture is required for preparing acetylene **8**. In fact, at 500 °C and the molar ratio $Si_2Cl_6 : C_2Cl_4 = 4 : 1$, the yield of alkyne **8** is 42%. When the molar ratio of the reagents decreases to 2 : 1, the yield of compound **8** decreases to 26%.[13]

Table 2. Influence of the reagent ratio and the temperature of the reactions of Si_2Cl_6 with alkenyl chlorides on the yields of alkenylchlorosilanes $(RSiCl_3)$[17,18]

RCl	Si_2Cl_6 : RCl[a]	T/°C	Yield of $RSiCl_3$ (%)
AllCl	1 : 2	500	49.0
AllCl	1 : 1	500	64.4
AllCl	2 : 1	500	81.0
VinCl	1 : 1	500	55.7
VinCl	2 : 1	500	63.0
VinCl	1 : 1	550	44.6
C_4H_7Cl[b]	1 : 1	520	31.8
C_4H_7Cl[b]	2 : 1	520	53.4

[a] Molar ratio.

[b] Methallyl chloride $(CH_2{=}C(Me){-}CH_2Cl)$.

Synthesis of alkenylchlorosilanes

Unlike alkyl chlorides, alkenyl chlorides contain not one but two reaction centers (C—Cl and C=C bonds) at which the attack of $:SiCl_2$ can occur. The studies for allyl chloride,[17] vinyl chloride,[17] and methallyl chloride[18] as substrates have shown that $:SiCl_2$ is predominantly inserted into the C—Cl bond.

The yields of alkenylchlorosilnes under different reaction conditions are presented in Table 2. The maximum yield (81%) is achieved when AllCl is used.

Alkenyltrichlorosilanes are obtained in reactions (2)—(4), and the thermal effect for the formation of excited $RSiCl_3{}^*$ molecules (Eq. (15)) virtually does not differ from the thermal effect of reaction (2) (the enthalpy $\Delta H^\circ{}_{298}(g)$ of reaction (15) for AllCl is equal to -313 kJ mol^{-1}).[17]

$$RCl + :SiCl_2 \longrightarrow \underset{\mathbf{10}}{RSiCl_3{}^*} \qquad (15)$$

$$R = CH_2{=}CH,\ CH_2{=}CH{-}CH_2,\ CH_2{=}C(Me){-}CH_2$$

Thus, the reactions of $:SiCl_2$ generated from Si_2Cl_6 with alkenyl chlorides also result in vibration-excited molecules of **10**, which can either be stabilized or decompose.

Free radicals are generated in the decomposition of highly excited molecules of $AllSiCl_3$, $VinSiCl_3$, and (2-methylprop-2-enyl)trichlorosilane. Their subsequent interactions with each other, $^{\cdot}SiCl_3$ radicals, and $:SiCl_2$ lead to various organosilicon compounds.[17,18]

For example, an additional five compounds are formed in yields from 0.3 to 10.4% during the synthesis of vinyltrichlorosilane:[17] 1,1-dichloro-1-silacyclopent-3-ene (**11**) and its trichlorosilyl derivatives (**12**), bis(trichlorosilyl)ethylene, trichlorophenylsilane, and 1,1,3,3-tetrachloro-1,3-disilacyclohex-4-ene (**13**).

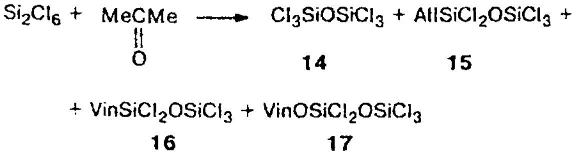
The reaction of allyl chloride[17] with Si_2Cl_6 gives six secondary products in 0.6—4.6% yields: bis(trichlorosilyl)-

methane, allyldichlorosilyl(trichlorosilyl)methane, trichlorophenylsilane, and heterocyclic compounds **11**—**13**.

Several secondary products are formed in yields from 1.2 to 13% in the reaction of methallyl chloride[18] with Si_2Cl_6, along with the main product chloro(2-methylprop-2-enyl)silane (see Table 2) and its isomer, trichloroisocrotylsilane (5—9% yield). Bis(trichlorosilyl)methane, 1,1,1,5,5,5-hexachloro-1,5-disila-3-methylpent-2-ene, and bis(trichlorosilyl)benzene are the most interesting compounds among the secondary products.

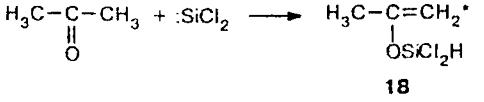
Reaction of :SiCl₂ with acetone

We studied the reaction of Si_2Cl_6 with acetone in the gas phase within the 520—560 °C temperature range at different ratios of the reagents.[19] The main reaction products were found to be hexachlorodisiloxane (**14**), 1-allyl-1,1,3,3,3-pentachlorodisiloxane (**15**), 1,1,3,3,3-pentachloro-1-vinyldisiloxane (**16**), and 1,1,3,3,3-pentachloro-1-vinyloxydisiloxane (**17**).



$$Si_2Cl_6 + \underset{\underset{O}{\|}}{MeCMe} \longrightarrow \underset{\mathbf{14}}{Cl_3SiOSiCl_3} + \underset{\mathbf{15}}{AllSiCl_2OSiCl_3} + \underset{\mathbf{16}}{VinSiCl_2OSiCl_3} + \underset{\mathbf{17}}{VinOSiCl_2OSiCl_3}$$

The influence of the reagent ratio was studied[19] at 520 °C and the molar ratio $Si_2Cl_6 : Me_2CO = 1 : 2$. Under these conditions, the maximum yield (33.5%) is observed for compound **15**. When the reagents are taken in an equimolar ratio, the yields of compounds **15** and **16** are close (19.8 and 18.9%, respectively). Further increase in the content of Si_2Cl_6 results in an increase in the yield of $(Cl_3Si)_2O$ only (to 7.5%) and in a decrease in the yields of the other compounds. An increase in the reaction temperature up to 560 °C has a slight effect on the yields of the products.



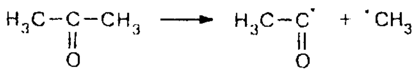
$$H_3C-\underset{\underset{O}{\|}}{C}-CH_3 + :SiCl_2 \longrightarrow \underset{\mathbf{18}}{H_3C-\underset{OSiCl_2H}{\overset{}{C}}=CH_2{}^*} \quad (16)$$

$$\mathbf{18} \longrightarrow H_3C-CH=CH_2 + O=SiCl_2 \quad (17)$$

$$O=SiCl_2 + SiCl_4 \longrightarrow \underset{\mathbf{14}}{Cl_3SiOSiCl_3} \quad (18)$$

$$Cl_3SiOSiCl_3 + :SiCl_2 \longrightarrow \underset{\mathbf{19}}{Cl_3SiOSiCl_2SiCl_3{}^*} \quad (19)$$

$$\mathbf{19} \longrightarrow \underset{\mathbf{20}}{Cl_3SiO\dot{S}iCl_2} + {}^{\cdot}SiCl_3 \quad (20)$$

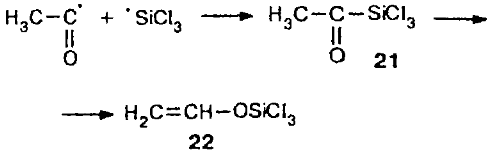


$$H_3C-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow H_3C-\underset{\underset{O}{\|}}{\dot{C}} + {}^{\cdot}CH_3 \quad (21)$$

$$CH_2=CH-CH_3 + {}^{\cdot}CH_3 \longrightarrow CH_2=CH-\dot{C}H_2 + CH_4 \quad (22)$$

$$CH_2=CH-\dot{C}H_2 + \mathbf{20} \longrightarrow \underset{\mathbf{15}}{CH_2=CH-CH_2SiCl_2OSiCl_3} \quad (23)$$

$$\mathbf{15} \longrightarrow \underset{\mathbf{16}}{CH_2=CHSiCl_2OSiCl_3} + :CH_2 \quad (24)$$

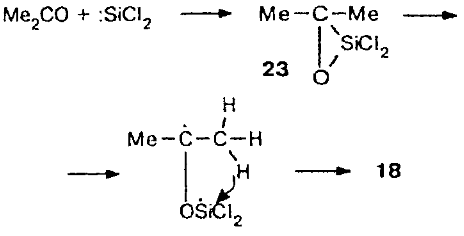


$$H_3C-\underset{\underset{O}{\|}}{\dot{C}} + {}^{\cdot}SiCl_3 \longrightarrow \underset{\mathbf{21}}{H_3C-\underset{\underset{O}{\|}}{C}-SiCl_3} \longrightarrow \underset{\mathbf{22}}{H_2C=CH-OSiCl_3} \quad (25)$$

$$\mathbf{22} + O=SiCl_2 \longrightarrow \underset{\mathbf{17}}{CH_2=CHOSiCl_2OSiCl_3} \quad (26)$$

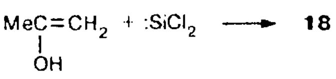
(Molecules of **18** and **19** formed in the vibration-excited state are marked by asterisks.)

The mechanism of the reaction of $:SiCl_2$ with acetone was not studied. It is assumed[19] to be similar to that of the addition of $:SiCl_2$ to the double C=C bond and to include the formation of oxasilacyclopropane (**23**). The cleavage of the endocyclic Si—C bond accompanied by the migration of the H atom from carbon to silicon and the appearance of the C=C bond results in the formation of compound **18**.



It is noteworthy that a product of type **18** is formed in the reaction of Mes_2Si: with acetone,[20] whereas a compound of type **23** with the oxasilacyclopropane structure was obtained in the reaction of Mes_2Si: with 1,1,3,3-tetramethylindan-2-one.[21]

It is most likely that compound **18** can also be formed due to the insertion of $:SiCl_2$ into the O—H bond of the enol form of acetone.



$$Me\underset{\underset{OH}{|}}{C}=CH_2 + :SiCl_2 \longrightarrow \mathbf{18}.$$

Compound **18** is evidently formed in the excited state, which usually appears when thermally generated dichlorosilylene is inserted into other bonds[8] and, hence, decomposes to propylene and dichlorosilanone (reaction (17)). The latter, as known,[22] is easily inserted into the Si—Cl bonds of tetrachlorosilane to give hexachlorodisiloxane (**14**) (reaction (18)). The insertion of $:SiCl_2$ into the Si—Cl bond of siloxane **14** results in the excited product **19**, whose decomposition gives free radicals **20** and $^{\cdot}SiCl_3$ (reactions (19) and (20)). It is known[5] that insertion of $:SiCl_2$ into the Si—Cl bond is accompanied by a heat liberation of ~200 kJ mol^{-1}.

Free radicals also appear in the thermal decomposition of acetone[23] (reaction (21)). Methyl radicals that formed in this reaction react with propylene according to Eq. (22) to give allyl radicals. It is noteworthy that the addition of methyl radicals to the double bond of propylene occurs considerably more slowly than the elimination of hydrogen according to Eq. (22), which is related to the difference in activation energies of these reactions (38.1 and 18.8 kJ mol^{-1}, respectively).[24]

The recombination of allyl radicals with radicals **20** in reaction (23) results in compound **15**. It is known[25] that during their thermal decomposition, allylsilanes of type **15** easily eliminate methylene and are transformed into vinylsilyl compounds (reaction (24)).

A stepwise scheme for the formation of compound **17** was suggested.[19] The scheme included the recombination of the acetyl and $^{\cdot}SiCl_3$ radicals and the appearance of an unstable compound **21**, which isomerizes to trichlorovinyloxysilane (**22**). Then reaction (26) occurs to give compound **17** (2—6% yield).

Synthesis of organochlorogermanes

It has been shown[26] that dichlorosilylene can be used for the generation of dichlorogermylene according to the following scheme:

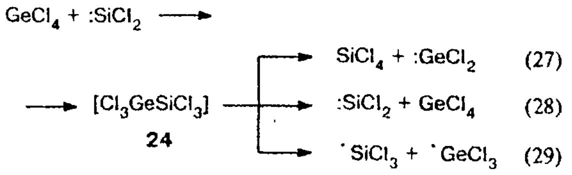
$$GeCl_4 + :SiCl_2 \longrightarrow [Cl_3GeSiCl_3] \longrightarrow SiCl_4 + :GeCl_2.$$

The dichlorogermylene thus obtained was used in the syntheses of aromatic and unsaturated organogermanium compounds.

Synthesis of arylchlorogermanes

The gas-phase methods for the synthesis of phenyltrichlorogermane (~40% yield) and thienyltrichlorogermane (~70% yield) by the reactions of $GeCl_4$ with chlorobenzene and chlorothiophene, respectively, in the presence of Si_2Cl_6 at 550 °C have been described.[26] The authors of Ref. 26 found that Si_2Cl_6 initiates this reaction; in the absence of Si_2Cl_6, PhCl does not react with $GeCl_4$. Further studies showed[27] that the reaction can also occur at a lower temperature (460—500 °C, Table 3). The following scheme for the synthesis of $PhGeCl_3$ was suggested:[26,27]

$$Si_2Cl_6 \longrightarrow :SiCl_2 + SiCl_4$$

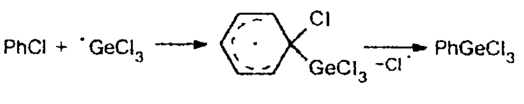


$$GeCl_4 + :SiCl_2 \longrightarrow [Cl_3GeSiCl_3]\ (\mathbf{24}) \longrightarrow SiCl_4 + :GeCl_2 \quad (27)$$

$$[Cl_3GeSiCl_3] \longrightarrow :SiCl_2 + GeCl_4 \quad (28)$$

$$[Cl_3GeSiCl_3] \longrightarrow {}^{\cdot}SiCl_3 + {}^{\cdot}GeCl_3 \quad (29)$$

$$PhCl + :GeCl_2 \longrightarrow PhGeCl_3 \quad (30)$$



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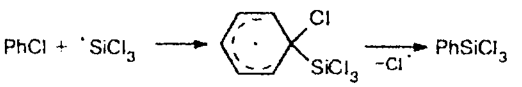

(32)

$$PhCl + :SiCl_2 \longrightarrow PhSiCl_3 \quad (33)$$

The decomposition of Si_2Cl_6 (see reaction (1)) starts at 380—400 °C.[4] The insertion of $:SiCl_2$ into the Ge—Cl bond of germanium tetrachloride results in the formation of compound **24**,[26] which is very labile and decomposes rapidly in reactions (27)—(29).

Reaction (27) is shown[27] to be exothermic ($\Delta H^{\circ}_{298}(g) = -174$ kJ mol^{-1}), and reaction (29) is endothermic ($\Delta H^{\circ}_{298}(g) = 8.9$ kJ mol^{-1}). The Polanyi—Semenov equation[28] is evidently appropriate for reactions (27)—(29) occurring *via* the free-radical or concerted mechanism. It follows from this equation that the activation energy for the exothermic reaction is lower than that for the endothermic or thermoneutral reac-

Table 3. Synthesis of $PhGeCl_3$ by the reaction of $GeCl_4$ with PhCl in the presence of Si_2Cl_6 (the reaction duration is 30—35 s)[27]

T /°C	$GeCl_4 : PhCl : Si_2Cl_6$ *	Conversion of $GeCl_4$ (%)	Yield of $PhGeCl_3$ per starting $GeCl_4$	Yield of $PhGeCl_3$ per reacted $GeCl_4$	$PhGeCl_3 : PhSiCl_3$ *
460	1.0 : 1.0 : 0.5	57	6.54	11.5	16.2 : 1.0
500	1.0 : 1.0 : 0.5	60	7.65	12.8	11.3 : 1.0
550	1.0 : 1.0 : 0.5	62	16.4	26.4	9.8 : 1.0
550	1.0 : 1.0 : 1.0	71	41.1	57.9	4.7 : 1.0

* Molar ratio.

tion. When the values of the pre-exponential factors of the one-type processes (27)—(29) are close, this results in a situation in which the exothermic reaction (27) occurs with maximum rate. The rates of the thermoneutral (28) and endothermic (29) reactions are substantially lower. The $:GeCl_2$ that formed in reaction (27) reacts with PhCl *via* Eq. (30) to yield $PhGeCl_3$.

The $^{\cdot}SiCl_3$ and $^{\cdot}GeCl_3$ radicals generated in lesser amounts (reaction (29)) react with PhCl according to Eqs. (31) and (32). Trichlorophenylsilane can also be formed due to the insertion of $:SiCl_2$ into the PhCl molecule (reaction (33)). However, reactions (32) and (33) occur to a lesser extent, since the yield of $PhSiCl_3$ is 5—16-fold lower than that of $PhGeCl_3$ (see Table 3). The reactions of types (31) and (32) have been studied previously.[29—31]

Dichlorosilylene obtained by the pyrolysis of 1,1-dichloro-1-silacyclopent-3-ene[32] (25) can be used for the generation of $:GeCl_2$.

25

$$\rightleftharpoons CH_2{=}CH{-}CH{=}CH_2 + :SiCl_2 \qquad (34)$$

Reaction (34) has previously been studied in detail.[33] The reaction of $GeCl_4$ with PhCl in the presence of silacyclopentene **25** at 550 °C affords $PhGeCl_3$ and $PhSiCl_3$ in 45.9 and 4.6% yields, respectively.[32]

Synthesis of alkenylchlorogermanes

It has been shown[34,35] that $:GeCl_2$ generated in reaction (27) can also be used in the synthesis of alkenyltrichlorogermanes if alkenyl chlorides (allyl chloride,[34] methallyl chloride,[34] and vinyl chloride[35]) are used as reagents (Table 4).

The yields of alkenyltrichlorogermanes obtained at 500 °C range within 22—31%. However, alkenyltrichlorosilanes are also formed during the reaction, and their yields are insignificant in the case of vinyl chloride, but increase substantially in the reactions with allyl chloride or methallyl chloride (see Table 4).

Table 4. Synthesis of alkenyltrichlorogermanes in the reactions of $GeCl_4$ with alkenyl chlorides (RCl) in the presence of Si_2Cl_6 (500 °C)[a]

RCl	Yield (%)		$RGeCl_3 : RSiCl_3$[b]	Reference
	$RGeCl_3$	$RSiCl_3$		
VinCl	30.9	4.8	6.44 : 1.0	35
AllCl	23.5	21.6	1.09 : 1.0	34
C_4H_7Cl[c]	22.4	25.5	0.87 : 1.0	34

[a] Molar ratio of the starting reagents $GeCl_4 : RCl : Si_2Cl_6 = (1.5-2) : 1 : 1$.

[b] Molar ratio.

[c] Methallyl chloride.

The following scheme for the formation of alkenyltrichlorogermanes and alkenyltrichlorosilanes was suggested[34] (it is similar to that presented above for the reactions with chlorobenzene):

$$Si_2Cl_6 \longrightarrow :SiCl_2 + SiCl_4$$

$$\begin{tikzcd}
GeCl_4 + :SiCl_2 \arrow[r] & {} & \\
{} \arrow[r] & {[Cl_3GeSiCl_3]} \arrow[r] \arrow[dr] & SiCl_4 + :GeCl_2 \\
& & {^{\cdot}SiCl_3 + {^{\cdot}GeCl_3}}
\end{tikzcd}$$

$$RCl + :GeCl_2 \longrightarrow RGeCl_3 \qquad (35)$$

$$RCl + :SiCl_2 \longrightarrow RSiCl_3 \qquad (36)$$

$R = CH_2{=}CH, CH_2{=}CH{-}CH_2, CH_2{=}C(Me){-}CH_2$

Three additional products are formed during the synthesis of $VinGeCl_3$: trichlorochloroethylgermane (**26**), trichlorochloroethylsilane (**27**), and bis(trichlorosilyl)ethane **3** (0.3—4.1% yields).[35] The following scheme for the formation of compounds **3**, **26**, and **27** was suggested in the same work:[35]

$$CH_2{=}CHCl + {^{\cdot}GeCl_3} \longrightarrow \underset{\mathbf{28}}{Cl_3GeCH_2\dot{C}HCl} \qquad (37)$$

$$\mathbf{28} + RH \longrightarrow \underset{\mathbf{26}}{Cl_3GeCH_2CH_2Cl} + R^{\cdot} \qquad (38)$$

$$CH_2{=}CHCl + {^{\cdot}SiCl_3} \longrightarrow \underset{\mathbf{29}}{Cl_3SiCH_2\dot{C}HCl} \qquad (39)$$

$$\mathbf{29} + RH \longrightarrow \underset{\mathbf{27}}{Cl_3SiCH_2CH_2Cl} + R^{\cdot} \qquad (40)$$

$$\mathbf{27} + :SiCl_2 \longrightarrow \underset{\mathbf{3}}{Cl_3SiCH_2CH_2SiCl_3} \qquad (41)$$

$RH = ClCHCH_2$, *etc.*

It is known[37,38] that Si- and Ge-centered radicals readily add to double bonds affording radicals of types **28** and **29**, which can abstract an H atom from other molecules to form compounds **26** and **27** (reactions (37)—(40)).

It is noteworthy that $^{\cdot}GeCl_3$ and $^{\cdot}SiCl_3$ radicals add to vinyl chloride at the methylene group (reactions (37) and (39)) contrary to Markovnikov's rule.

Dichlorosilylene is inserted into the C—Cl bond of chlorosilane **27** to form compound **3**. The reactions of type (41) have previously been considered in detail.[8]

The molar ratios of the $RGeCl_3$ and $RSiCl_3$ products formed in the reactions of $GeCl_4$ with AllCl, VinCl, and PhCl in the presence of Si_2Cl_6 are presented in Tables 3 and 4. It is of interest that this ratio depends on the stability of the C—Cl bond in the RCl used: the stronger this bond, the greater the $RGeCl_3/RSiCl_3$ ratio (1.09, 6.44, and 11.3 for AllCl, VinCl, and PhCl, respectively).

RCl	E_b /kJ mol^{-1}
AllCl	263.6 [36]
VinCl	338.9 [36]
PhCl	392.4 [10]

This behavior agrees well with the kinetic analysis of the reactions of types (1), (27), (29), (35), and (36), which has been performed[34] for the reaction of $GeCl_4$ with allyl chloride in the presence of Si_2Cl_6.

The results presented demonstrate the considerable potentialities of the new method for syntheses of organogermanium compounds.

Synthesis of organochlorostannanes

We have shown the principal possibility of the thermal method for syntheses of other organoelement compounds as well, in particular, organylchlorostannanes, by insertion of $:SiCl_2$ into the Sn—Cl bond. It has been found[39] that when $SnCl_4$ is used in reaction (27) instead of $GeCl_4$, dichlorostannylenes can be obtained.

$$SnCl_4 + :SiCl_2 \longrightarrow [Cl_3Si{-}SnCl_3] \longrightarrow SiCl_4 + :SnCl_2 \quad (42)$$

The thermodynamic calculation shows that reaction (42) is exothermic ($\Delta H^{\circ}_{298}(g) = -220$ kJ mol^{-1}).

Dichlorostannylenes formed in reaction (42) can be trapped by different reagents; for example, chloromethyldimethylchlorosilane was used[39] as the trapping reagent:

$$ClMe_2SiCH_2Cl + SnCl_2 \xrightarrow{450-550\ ^{\circ}C} ClMe_2SiCH_2SnCl_3.$$

It should be mentioned that the pyrolysis of the $SnCl_4$ itself does not result in the formation of $SnCl_2$.

* * *

In conclusion one should note that the results presented in this review demonstrate the wide possibilities for using dichlorosilylene in the syntheses of organochloroderivatives of silicon, germanium, and tin. We succeeded in the use of the reactions of $:SiCl_2$ with alkyl and alkenyl chlorides for the synthesis of organosilicon compounds. It has also been established that the introduction of $:SiCl_2$ along with $GeCl_4$ or $SnCl_4$ into the reaction results in $:GeCl_2$ or $SnCl_2$ generation, which can be easily trapped by different reagents to form organogermanium or organotin compounds. Subsequent extension of the limits of using dichlorosilylene for the syntheses of heteroorganic compounds may be possible using halides of other elements along with $GeCl_4$ or $SnCl_4$ in the reactions.

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Received October 10, 1997;
in revised form January 16, 1998