

Gas Phase Reaction of Dichlorogermylene with the Chlorine-Substituted Ethylenes

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Abstract—Gas phase reaction of dichlorogermynes formed in the systems $\text{GeCl}_4\text{--Si}_2\text{Cl}_6$ or Ge--GeCl_4 with 1,2-dichloroethylene and trichloroethylene was studied. It is shown that $:\text{GeCl}_2$ inserts into the C–Cl bond of 1,2-dichloroethylene and forms the derivatives with one or two trichlorogermynyl groups. A specific feature of the reaction of $:\text{GeCl}_2$ with trichloroethylene was found. In this reaction the formation of only monosubstituted compounds like 1,1-dichloro-2-trichlorogermylethylene and 1,2-dichloro-1-trichlorogermylethylene takes place. The rule established is valid in general also for the reaction of trichloroethylene with dichlorosilylene, another analog of carbene. Reactions taking place in the course of synthesis of organochlorogermynes are considered.

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In the recent years analogs of carbenes like silylenes, germynes, etc., are widely used for the synthesis of organoelemental compounds [1–4]. Use of these highly reactive species ($:\text{SiMe}_2$, $:\text{SiCl}_2$, $:\text{GeCl}_2$, etc.) permits to perform syntheses by simpler ways, and in some cases to prepare substances which are hardly available by another methods.

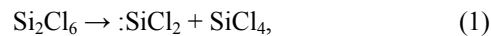
Synthesis of organosilicon compounds with the help of dichlorosilylene is sufficiently well developed, and many studies are considered in the reviews [2, 4]. Reports dealing with the synthesis of organogermanium compounds with the participation of $:\text{GeCl}_2$ are scarce [5–14]. Note that the greater part of this research concerns the synthesis of germanium-containing aromatic compounds via dichlorogermynes [5–9]. Some data on the synthesis of alkylchlorogermynes were reported [10, 11], but the studies concerning the synthesis of alkylchlorogermynes containing ethylene fragments are few [12, 13] though these compounds are extremely valuable. On their basis drugs as well as gas distributing membranes can be synthesized [14].

In the present work we have carried out the study of the gas phase reaction between dichlorogermylene and

1,2-dichloroethylene or trichloroethylene with the purpose of establishing the possibility of obtaining of their trichlorogermynyl derivatives by this way.

For generating dichlorogermylene, the short-living analog of carbene, we have used two methods.

According to the first one for obtaining dichlorogermylene a reaction between GeCl_4 and hexachlorodisilane was used. In the course of this process the following reactions take place [4].



According to the second method the dichlorogermylene was prepared by the reaction of GeCl_4 with germanium treated with the concentrated (56%) hydrofluoric acid for removing the oxide film from its surface [11].



For our experiments we used finely pulverized germanium with the total amount of impurities no more than 0.001% and the particle size 0.3–0.8 mm.

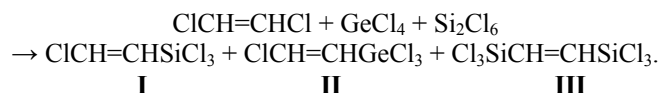
The reaction of 1,2-dichloroethylene with GeCl_2 generated by the reaction with Si_2Cl_6 (first method of

Table 1. Conditions of the reaction of GeCl_4 with 1,2-dichloroethylene ($\text{C}_2\text{H}_2\text{Cl}_2$) in presence of Si_2Cl_6 and yields of the products (reaction time 30–40 s, temperature 500°C)

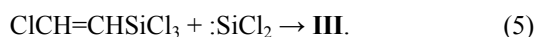
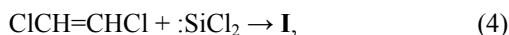
Exp. no.	$\text{C}_2\text{H}_2\text{Cl}_2\text{:GeCl}_4\text{:Si}_2\text{Cl}_6$	Yield, % ^a		
		I	II	III
1	1.1:2:1	7.01	1.01	19.9
2	1.4:2:1	16.1	22.2	7.2
3	2.1:2:1	26.3	21.2	1.1
4	3.2:2:1	28.1	20.4	0.8

^a Calculated on the starting Si_2Cl_6 .

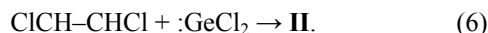
generation of dichlorogermylene) was carried out at 350°C at various ratios of the starting substances. Results of the experiments are listed in Table 1. In the course of the reaction the formation of 1-chloro-2-trichlorosilylethylene **I**, 1-chloro-2-trichlorogermylethylene **II**, and 1,2-bis(trichlorosilyl)ethylene **III** was observed.



In the course of the synthesis organosilicon compounds are formed in slightly larger amount than organogermanium ones. It evidently is due to the fact that the dichlorosilylenes generated in the reaction (1) to mostly participate in the reactions (4), (5), but not in the reaction (2) thus forming organosilicon compounds **II**, **III**.



Dichlorogermynes generated via reaction (2) react according to Eq. (6) to form compound **II**.

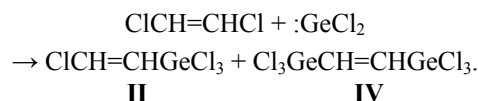


Yields of compounds **I** and **III** significantly depend on the molar ratio of reagents. It especially concerns the disubstituted compound **III**. If the amount of starting 1,2-dichloroethylene is small (exp. 1, Table 1) the yield of compound **III** reaches 20%. At the increase in the amount of 1,2-dichloroethylene in the reaction zone the yields of the product **III** decrease to 1–7% (exp. 2–4, Table 1).

Note that disubstituted germanium compound, 1,2-bis(trichlorogermylethylene) was not found in the reaction products. It is evidently connected with the fact that the yield of dichlorogermynes in the

reaction (2) is small and they first of all react according to the Eq. (6) to form monosubstituted compound **II**.

While using dichlorogermynes generated in the system $\text{GeCl}_4\text{--Ge}$ (the second method of obtaining GeCl_2) in the reaction with 1,2-dichloroethylene two organogermanium compounds are mainly formed, that is, 1-chloro-2-trichlorogermylethylene **II** and bis(trichlorogermylethylene) **IV**.

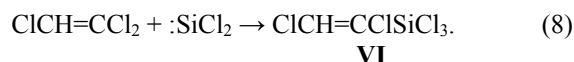
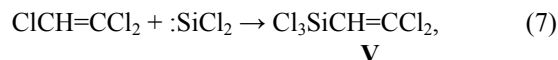


Study of the reaction of 1,2-dichloroethylene with :GeCl_2 was carried out in the temperature range $450\text{--}500^\circ\text{C}$ at different ratios of the starting substances (Table 2). From the data of this table it follows that the highest yield (37.4%) of monosubstituted substance **II** is observed at 450°C , and the yield of disubstituted product **IV** is small (0.87%). At the increase in the reaction temperature to $500\text{--}550^\circ\text{C}$ the yield of monosubstituted substance **II** decreases, while the yield of disubstituted product **IV** increases to 14%. Total yield of compounds **II** and **IV** weakly depends on the reaction temperature (Table 2).

Hence, from the comparison of data of Tables 1 and 2 it follows that for preparation of compounds **II** and **IV** it is expedient to use dichlorogermylene generated by the second method. In this case compound **IV** is formed in contrast to the case of using dichlorogermylene generated in the system $\text{GeCl}_4\text{--Si}_2\text{Cl}_6$. Increase in the yield of compound **II** is also observed.

Reaction of trichloroethylene with the analogs of carbenes (:GeCl_2 , :SiCl_2) was not studied previously. For revealing the general rules we have studied the reaction of trichloroethylene with dichlorosilylene.

Experiments were carried out at 500°C and equimolar ratio of reagents. It was established that under these conditions two monosubstituted organosilicon compounds, 2,2-dichloro-1-trichlorosilylethylene **V** and 1,2-dichloro-2-trichlorosilylethylene **VI** are mainly formed.



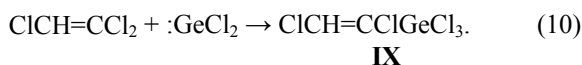
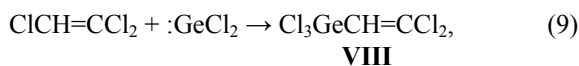
Insertion of :SiCl_2 proceeds mainly according the Eq. (7) into the C–Cl bond contained in the CHCl

group, and to a small degree, according the Eq. (8). The insertion of $:\text{SiCl}_2$ according to Eq. (8) into the C–Cl bond belonging to CCl_2 group is complicated evidently by the sterical hindrances connected with the presence of two sufficiently bulky chlorine atoms in this fragment.

Yield of organosilicon compounds **V** and **VI** at 500°C and the reaction time 30 s is 38.1% and 5.3% respectively. Note that disubstituted organosilicon substance, 1-chloro-1,2-bis(trichlorosilyl)ethylene **VII**, is formed in a very small amount. Its yield does not exceed 0.2–0.3%.

Hence, the introduction of the third chlorine atom in ethylene molecule leads to a decrease in its reactivity in relation to $:\text{SiCl}_2$, and the yield of organosilicon products decreases. The total yield of these products in the reaction of $:\text{SiCl}_2$ with trichloroethylene along equations (7) and (8) is 40%, while the total yield in the reaction of dichlorosilylene with the less chlorinated 1,2-dichloroethylene is 70–80% [15].

The reaction of trichloroethylene with another carbene analog, dichlorogermylene, generated according to the second method, was carried out at 500°C and equimolar reagents ratio. It was found that in the course of this process the formation of two organogermane substances, 2,2-dichloro-1-trichlorogermylethylene **VIII** and 1,2-dichloro-2-trichlorogermylethylene **IX** takes place. These monosubstituted compounds are formed by insertion of $:\text{GeCl}_2$ in different C–Cl bonds of trichloroethylene.



The insertion of $:\text{GeCl}_2$ proceeds mainly by the reaction (9) in C–Cl bond of the CHCl group, and to lesser extent, by reaction (10).

Hence, general rules, established for the reaction of $:\text{SiCl}_2$ with trichloroethylene are repeated in the reaction of $:\text{GeCl}_2$. In this case the insertion of dichlorogermylene according to Eq. (10) in the C=Cl bond of CCl_2 group is also more difficult. Yields of organogermanium compounds **VIII**, **IX** at 500°C and the contact time 30 s are 15.5 and 2.3% respectively.

From the presented data it follows that introduction of the third chlorine atom in the ethylene molecule

Table 2. Conditions and yields of the reaction products in the reaction of GeCl_4 with 1,2-dichloroethylene ($\text{C}_2\text{H}_2\text{Cl}_2$) in presence of germanium (reaction time 30–40 s)

$T, ^\circ\text{C}$	$\text{Ge}:\text{GeCl}_4:\text{C}_2\text{H}_2\text{Cl}_2$	Yield, % ^a		
		II	IV	II + IV
450	1:1.5:1.5	37.4	0.9	38.3
500	1:1:1	26.2	6.3	32.5
530	1:1:1	24.1	9.4	33.4
550	1:2:1	23.2	13.6	36.8

^a Calculated on the starting 1,2-dichloroethylene.

leads to a decrease in its reactivity not only in relation to $:\text{SiCl}_2$, but to $:\text{GeCl}_2$ as well. For example, the total yield of organogermanium compound in the reaction of $:\text{GeCl}_2$ with 1,2-dichloroethylene is 32–38% (Table 2), but at the increase in the amount of chlorine atoms in ethylene [reactions (9) and (10)] the total yield of products decreases to 17–18%. Another difference also exists in these reactions. $:\text{GeCl}_2$ reacts with 1,2-dichloroethylene to form mono- as well as disubstituted compounds, but in the reaction with trichloroethylene no disubstituted compounds are found.

EXPERIMENTAL

Starting substances and the reaction products were analyzed by GLC on LKhM-80 chromatograph equipped with katharometer, helium carrier gas (30 ml min^{-1}). Stainless steel columns $2000 \times 3 \text{ mm}$ were filled with Chromaton N-AW-DMCS (0.25–0.31 mm) with 5 wt % of silicon elastomer SE-30. Analysis was carried out with temperature programming of oven from 30 to 250°C at a rate 12°C/min . Compounds were identified by means of mass spectrometry and in some cases by NMR spectroscopy. Mass spectra were obtained on an Agilent 5989 mass spectrometer with the direct injection in the ion source at ionizing electrons energy 70 eV at $180\text{--}200^\circ\text{C}$. In the interpretation of the mass spectra data on the mechanism of fragmentation of organogermanium and organosilicon compounds under the electron impact was taken into account [16]. Values of molecular mass are presented for the isotopes ^{28}Si , ^{35}Cl , and ^{74}Ge . ^1H NMR spectra of compounds **V** and **VI** were taken on a Fourier spectrometer Bruker AM-360 (360 MHz) Liquid samples were analyzed as 15–30% solutions in CDCl_3 against internal TMS.

Reaction of 1,2-dichloroethylene with tetrachlorogermane in the presence of hexachloro-

disilane. A mixture of 16.5 g of 1,2-dichloroethylene, 34.8 g of GeCl_4 , and 21.8 g of Si_2Cl_6 was passed through a quartz tube at 500°C and the contact time 30 s. The condensate, 60.5 g, was distilled to give 16.76 g of SiCl_4 , 3.01 g of 1,2-dichloroethylene, and 29.68 g of GeCl_4 . The residue was distilled in a vacuum (30 mm Hg) to give 8.62 g of the fraction with bp $48\text{--}89^\circ\text{C}$ containing 4.21 g of compound **I** [m/e 194 (M)⁺, 159 ($M - \text{Cl}$)⁺, 133 (SiCl_3)⁺], 4.17 g of compound **II** [m/e 240 (M)⁺, 205 ($M - \text{Cl}$)⁺, 179 (GeCl_3)⁺], and 0.27 g of compound **III** [m/e 292 (M)⁺, 257 ($M - \text{Cl}$)⁺, 133 (SiCl_3)⁺]. The still contained 2.4 g of polymeric residue. Yields of compounds **I**, **II**, and **III** with respect to the starting substance Si_2Cl_6 were 26.3%, 21.2%, and 1.1% respectively. Experiments with the other molar ratios of starting substances were carried out analogously. Their results are presented in Table 1.

Reaction of 1,2-dichloroethylene with tetrachloro-germane in presence of germanium. A mixture of 18.6 g of 1,2-dichloroethylene and 41.2 g of GeCl_4 was passed through a quartz tube filled with 10 g of germanium powder at 450°C and the contact time 30 s. The obtained condensate, 57.1 g, was distilled to give 9.6 g of 1,2-dichloroethylene and 26.7 g of GeCl_4 . The residue was distilled in a vacuum (28 mm Hg) collecting the fraction with bp $67\text{--}139^\circ\text{C}$, yield 18.1 g. It contained 17.45 g of compound **II** [m/e 240 (M)⁺, 205 ($M - \text{Cl}$)⁺, 179 (GeCl_3)⁺] and 0.64 g of compound **IV** [m/e 384 (M)⁺, 349 ($M - \text{Cl}$)⁺, 179 (GeCl_3)⁺]. The still contained 2.6 g of polymer. Yields of compounds **II** and **IV** calculated on the starting 1,2-dichloroethylene are 37.4 and 0.87% respectively. Experiments at other temperatures were carried out analogously. Their results are listed in Table 2.

Reaction of trichloroethylene with hexachloro-disilane. A mixture of 18.4 g of trichloroethylene and 37.8 g of Si_2Cl_6 was passed through a quartz tube at 500°C and the contact time 30 s to give 52.1 g of condensate. While its distillation 27.7 g of SiCl_4 and 6.21 g of trichloroethylene were collected. The residue was distilled in a vacuum (25 mm Hg) to give 14.1 g of the fraction with bp $58\text{--}135^\circ\text{C}$. It contained 12.29 g of compound **V** [m/e 228 (M)⁺, 193 ($M - \text{Cl}$)⁺, 133 (SiCl_3)⁺, ^1H NMR spectrum, δ , ppm (J, Hz): 6.10 s (1H, C- CHSiCl_3)], 1.71 g of compound **VI** [m/e 228 (M)⁺, 193 ($M - \text{Cl}$)⁺, 133 (SiCl_3)⁺, 60 ($M - \text{SiCl}_4$)⁺, ^1H NMR spectrum, δ , ppm (J, Hz): 7.16 s (1H, C=CHCl)], and 0.09 g of compound **VII** [m/e 326 (M)⁺, 291 ($M - \text{Cl}$)⁺, 133 (SiCl_3)⁺]. The still contained 4.0 g of polymer residue. Yield of compounds **V**, **VI**, and **VII**

calculated on the starting trichloroethylene was 38.1, 5.3, and 0.2% respectively.

Reaction of trichloroethylene with tetrachloro-germane in presence of germanium. A mixture of 17.3 g of trichloroethylene and 29.8 g of GeCl_4 was passed through a quartz tube filled with 10 g of germanium powder at 500°C and the contact time 30 s to give 46.1 g of condensate. While its distillation 12.3 g of trichloroethylene and 23.8 g of GeCl_4 was isolated. The residue was distilled in a vacuum (24 mm Hg), and 6.46 g of the fraction with bp $84\text{--}92^\circ\text{C}$ was collected. It contained 5.61 g of compound **VIII** [m/e 274 (M)⁺, 239 ($M - \text{Cl}$)⁺, 179 (GeCl_3)⁺] and 0.85 g of compound **IX** [m/e 274 (M)⁺, 239 ($M - \text{Cl}$)⁺, 179 (GeCl_3)⁺, 60 ($M - \text{GeCl}_3$)⁺]. The still consisted of 3.5 g of polymer. Yields of compounds **VIII** and **IX** calculated on the starting trichloroethylene are 15.5 and 2.3% respectively.

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