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Gas Phase Reaction of Dichlorogermylene with the Chlorine-Substituted Ethylenes

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Abstract—Gas phase reaction of dichlorogermylenes formed in the systems $GeCl_4$–Si_2Cl_6 or Ge–$GeCl_4$ with 1,2-dichloroethylene and trichloroethylene was studied. It is shown that :$GeCl_2$ inserts into the C–Cl bond of 1,2-dichloroethylene and forms the derivatives with one or two trichlorogermyl groups. A specific feature of the reaction of :$GeCl_2$ 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 organochlorogermanes are considered.

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In the recent years analogs of carbenes like silylenes, germylenes, etc., are widely used for the synthesis of organoelemental compounds [1–4]. Use of these highly reactive species (:$SiMe_2$, :$SiCl_2$, :$GeCl_2$, 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 :$GeCl_2$ are scarce [5–14]. Note that the greater part of this research concerns the synthesis of germanium-containing aromatic compounds via dichlorogermylenes [5–9]. Some data on the synthesis of alkylchlorogermanes were reported [10, 11], but the studies concerning the synthesis of alkylchlorogermanes 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 trichlorogermyl 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].

$$Si_2Cl_6 \rightarrow :SiCl_2 + SiCl_4, \qquad (1)$$

$$GeCl_4 + :SiCl_2 \rightarrow [Cl_3Ge - SiCl_3] \rightarrow SiCl_4 + :GeCl_2. \qquad (2)$$

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].

$$GeGl_4 + Ge \rightarrow 2:GeCl_2. \qquad (3)$$

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-dichloroetylene 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 ($C_2H_2Cl_2$) in presence of Si_2Cl_6 and yields of the products (reaction time 30–40 s, temperature 500°C)

Exp. no.	$C_2H_2Cl_2$:$GeCl_4$:Si_2Cl_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 varios 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.

$$\mathrm{ClCH{=}CHCl + GeCl_4 + Si_2Cl_6}$$
$$\rightarrow \underset{\textbf{I}}{\mathrm{ClCH{=}CHSiCl_3}} + \underset{\textbf{II}}{\mathrm{ClCH{=}CHGeCl_3}} + \underset{\textbf{III}}{\mathrm{Cl_3SiCH{=}CHSiCl_3}}.$$

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**.

$$\mathrm{ClCH{=}CHCl + {:}SiCl_2 \rightarrow \textbf{I}}, \tag{4}$$

$$\mathrm{ClCH{=}CHSiCl_3 + {:}SiCl_2 \rightarrow \textbf{III}}. \tag{5}$$

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

$$\mathrm{ClCH{-}CHCl + {:}GeCl_2 \rightarrow \textbf{II}}. \tag{6}$$

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(trichlorogermyl)ethylene was not found in the reaction products. It is evidently connected with the fact that the yield of dichlorogermylenes in the reaction (2) is small and they first of all react according to the Eq. (6) to form monosubstituted compound **II**.

While using dichlorogermylenes generated in the system $GeCl_4$–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(trichlorogermyl)ethylene **IV**.

$$\mathrm{ClCH{=}CHCl + {:}GeCl_2}$$
$$\rightarrow \underset{\textbf{II}}{\mathrm{ClCH{=}CHGeCl_3}} + \underset{\textbf{IV}}{\mathrm{Cl_3GeCH{=}CHGeCl_3}}.$$

Study of the reaction of 1,2-dichloroethylene with :$GeCl_2$ was carried out in the temperature range 450–500°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 500–550°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 $GeCl_4$–Si_2Cl_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.

$$\mathrm{ClCH{=}CCl_2 + {:}SiCl_2 \rightarrow \underset{\textbf{V}}{Cl_3SiCH{=}CCl_2}}, \tag{7}$$

$$\mathrm{ClCH{=}CCl_2 + {:}SiCl_2 \rightarrow \underset{\textbf{VI}}{ClCH{=}CClSiCl_3}}. \tag{8}$$

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 :$SiCl_2$ 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 :$SiCl_2$, and the yield of organosilicon products decreases. The total yield of these products in the reaction of :$SiCl_2$ 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 :$GeCl_2$ in different C–Cl bonds of trichloroethylene.

$$ClCH{=}CCl_2 + {:}GeCl_2 \rightarrow \underset{\mathbf{VIII}}{Cl_3GeCH{=}CCl_2}, \qquad (9)$$

$$ClCH{=}CCl_2 + {:}GeCl_2 \rightarrow \underset{\mathbf{IX}}{ClCH{=}CClGeCl_3}. \qquad (10)$$

The insertion of :$GeCl_2$ 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 :$SiCl_2$ with trichloroethylene are repeated in the reaction of :$GeCl_2$. 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 leads to a decrease in its reactivity not only in relation to :$SiCl_2$, but to :$GeCl_2$ as well. For example, the total yield of organogermanium compound in the reaction of :$GeCl_2$ 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. :$GeCl_2$ reacts with 1,2-dichloroethylene to form mono- as well as disubstituted compounds, but in the reaction with trichloroethylene no disubstituted compounds are found.

Table 2. Conditions and yields of the reaction products in the reaction of $GeCl_4$ with 1,2-dichloroethylene ($C_2H_2Cl_2$) in presence of germanium (reaction time 30–40 s)

T, °C	Ge:$GeCl_4$:$C_2H_2Cl_2$	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.

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 2000×3 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 180–200°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 trough 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 48–89°C containing 4.21 g of compound **I** [*m/e* 194 $(M)^+$, 159 $(M - Cl)^+$, 133 $(SiCl_3)^+$], 4.17 g of compound **II** [*m/e* 240 $(M)^+$, 205 $(M - Cl)^+$, 179 $(GeCl_3)^+$], and 0.27 g of compound **III** [*m/e* 292 $(M)^+$, 257 $(M - Cl)^+$, 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 tetrachlorogermane 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 67–139°C, yield 18.1 g. It contained 17.45 g of compound **II** [*m/e* 240 $(M)^+$, 205 $(M - Cl)^+$, 179 $(GeCl_3)^+$] and 0.64 g of compound **IV** [*m/e* 384 $(M)^+$, 349 $(M - Cl)^+$, 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 hexachlorodisilane. 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 58–135°C. It contained 12.29 g of compound **V** [*m/e* 228 $(M)^+$, 193 $(M - Cl)^+$, 133 $(SiCl_3)^+$, ^1H NMR spectrum, d, ppm (J, Hz): 6.10 s (1H, C–$CHSiCl_3$)], 1.71 g of compound **VI** [*m/e* 228 $(M)^+$, 193 $(M - Cl)^+$, 133 $(SiCl3)^+$, 60 $(M - SiCl_4)^+$, ^1H NMR spectrum, d, ppm(J,Hz): 7.16 s (1H, C=CHCl)], and 0.09 g of compound **VII** [*m/e* 326 $(M)^+$, 291 $(M - Cl)^+$, 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 tetrachlorogermane 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 84–92°C was collected. It contained 5.61 g of compound **VIII** [*m/e* 274 $(M)^+$, 239 $(M - Cl)^+$, 179 $(GeCl_3)^+$] and 0.85 g of compound **IX** [*m/e* 274$(M)^+$, 239 $(M - Cl)^+$, 179 $(GeCl_3)^+$, 60 $(M - GeCl_3)^+$]. 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.

REFERENCES

1. Nefedov, O.M., Ioffe, A.I., and Menchikov, L.S., *Khimiya karbenov* (Carbene Chemistry), Moscow: Khimiya, 1990.
2. Chernyshev, E.A. and Komalenkova, N.G., *Usp. Khim.*, 1990, vol. 59, no. 6, p. 918.
3. Gaspar, P.P., *React. Intermed.*, vol. 2, New York: Plenum Press, 1981.
4. Chernyshev, E.A., Komalenkova, N.G., and Bykovchenko, V.D., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, no. 6, p. 1063.
5. Chernyshev, E.A., Komalenkova, N.G., and Yakovleva, G.N., *Dokl. Ross. Akad. Nauk*, 1994, vol. 336, no. 1, p. 69.
6. Chernyshev, E.A., Komalenkova, N.G., Yakovleva, G.N., and Bykovchenko, V.G., *Zh. Obshch. Khim.*, 1995, vol. 65, no. 11, p. 1869.
7. Okamoto, M., Asano, T., and Suzuki, E., *Organometallics*, 2001, vol. 20, no. 26, p. 5583.
8. Chernyshev, E.A., Komalenkova, N.G., Yakovleva, G.N., Bykovchenko, V.G., Dubikhina, M.A., and Lakhtin, V.G., *Zh. Obshch. Khim.*, 2997, vol. 77, no. 8, p. 1251.
9. Chernyshev, E.A., Komalenkova, N.G., Yakovleva, G.N., Bykovchenko, V.G., and Lakhtin, V.G., *Vestnik MITKhT*, 2007, vol. 2, no. 2, p. 59.
10. Chernyshev, E.A., Komalenkova, N.G., Yakovleva, G.N., Bykovchenko, V.G., Khromykh, N.N., and Bochkarev, V.N., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 3, p. 433.
11. Okamoto, M., Asano, T., and Suzuki, T., *Dalton Trans.*, 2004, p. 2372.

12. Chernyshev, E.A., Komalenkova, N.G., Yakovleva, G.N., Bykovchenko, V.G., Khromykh, N.N., and Bochkarev, V.N., *Zh. Obshch. Khim*., 1997, vol. 67, no. 6, p. 955.
13. Chernyshev, E.A., Komalenkova, N.G., Yakovleva, G.N., Bykovchenko, V.G., Khromykh, N.N., Bochkarev, V.N., and Shcherbinin, V.V., *Zh. Obshch. Khim*., 1997, vol. 67, no. 11, p. 1835.
14. Lakhtin, V.G., Komalenkova, N.G., Bykovchenko, V.G., Yakovleva, G.N., and Chernyshev, E.A., *Vse materially. Entsyklopedicheskii spravochnik* (All Materials, Encyclopedic Handbook), 2010, no. 12, p. 34.
15. Chernyshev, E.A., Komalenkova, N.G., Kapitova, I.A., and Bykovchenko, V.G., *Zh. Obshch. Khim*., 1996, vol. 66, no. 7, p. 1141.
16. Bochkarev, V.N., Khromykh, N.N., Bykovchenko, V.G., Komalenkova, N.G., Shcherbinin, V.V., and Chernyshev, E.A., *Zh. Obshch. Khim*., 2000, vol. 60, no. 6, p. 962.