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Reaction of the Dioxane Complex of Dichlorogermylene with Siloxanes

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Abstract—The major organogermanium compounds formed by reactions of the dioxane complex of dichlorogermylene with hexamethyldisiloxane, octamethyltrisiloxane, and hexamethyltricyclotrisiloxane are bis(trimethylsiloxy)dichlorogermane, 3,3-dichloro-1,1,1,5,5,7,7,7-octamethyl-3-germa-2,4,6-trioxa-1,5,7-trisilaheptane, and a cyclic germatetrasiloxane.

In the present work we have studied reactions of the dioxane complex of dichlorogemylene (**I**) with linear (hexamethyldisiloxane and octamethyltrisiloxane) and cyclic (hexamethylcyclotrisiloxane) siloxanes.

No reactions of dichlorogermylenes or their complexes with siloxanes have previously been reported.

The reactions of complex **I** with siloxanes were performed at 85–95°C. The reaction of complex **I** with gexamethyldisiloxane (**II**) gives three types of compounds: (1) compounds containing Si–O–Ge groups [bis(trimethylsiloxy)dichlorogermane (**III**), bis(trimethylsiloxy)chloromethylgermane (**IV**), 3,3-dichloro-1,1,1,5,5,7,7,7-octamethyl-3-germa-2,4,6-trioxa-1,5,7-trisilaheptane (**V**), trichlorotrimethylsiloxygermane (**VI**)]; (2) compounds containing C–Ge bonds [1,1,1-trichloro-3,3,5,5,5-pentamethyl-1-germa-4-oxa-3,5-disilapentane (**VII**), 1,1,1-trichloro-3,3,5,5,7,7,7-heptamethyl-1-germa-4,6-dioxa-3,5,7-trisilaheptane (**VIII**)]; and (3) organosilicon compounds [chlorotrimethylsilane, chloropentamethyldisiloxane (**IX**), and octamethyltrisiloxane (**X**)]. The formation of the latter compound suggests that complex **I** reacts not only with compound **II**, but also with siloxane **X**.

We propose the following schemes of the reactions of complex **I** with compounds **II** and **X**.

$$\underset{\mathbf{I}}{GeCl_2 \cdot C_4H_8O_2}$$

$$+ \underset{\mathbf{II}}{Me_3SiOSiMe_3} \to \underset{\mathbf{VII}}{Me_3SiOSiMe_2CH_2GeCl_3}, \quad (1)$$

$$\to \underset{\mathbf{III}}{Me_3SiOGeCl_2OSiMe_3}, \quad (2)$$

$$\mathbf{I} + \underset{\mathbf{X}}{Me_3SiOSiMe_2OSiMe_3}$$

$$\to \underset{\mathbf{VII}}{Me_3SiOSiMe_2CH_2GeCl_3}, \quad (3)$$

$$\to \underset{\mathbf{V}}{Me_3SiOGeCl_2OSiMe_2OSiMe_3}. \quad (4)$$

Reactions like (1) and (3) we recently considered in [1]. Their mechanism involves insertion of $:GeCl_2$ generated from the dioxane complex of dichlorogermylene into the C–H bond of compounds **II** and **X**, followed by substitution of hydrogen in the $GeCl_2H$ group by chlorine. The conversion of $:GeCl_2$ by this direction is not too high. The yields of compounds **VII** and **VIII** are as low as 3%.

The most important conversion pathways of $:GeCl_2$ are reactions (2) and (4) which give rise to compounds **III** and **V**.

It should be noted that compounds **VII** and **VIII** results from the reactions of compounds **II** and **X** with dichlorogermylenes formed by decomposition of complex **I**, whereas the key role in the synthesis of compounds **III** and **V** belongs not to dichlorogermylenes, but to dichlorogermanones ($O{=}GeCl_2$) which are close structural and chemical analogs of silanones ($O{=}SiR_2$) [2–4].

It is known that germylenes actively react with oxygen. The rate constant of the reaction of $:GeMe_2$ with O_2, $2–10^9$ l mol^{-1} s^{-1} at 22°C, is 100 times higher that the rate constant of the reaction of $:GeMe_2$ with 1,3-butadiene (1.24×10^7 l mol^{-1} s^{-1} [5]). The latter reaction is fairly fast and commonly used for proving germylene formation [6].

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The rate constant of the reaction of $:GeCl_2$ with O_2, lacking in the literature, can be estimated the assumption that it is close to the known rate constant of the reaction of $:GeMe_2$ with O_2. This assumption relies on the fact that varying substituents in silylenes, the closest analogs of germylenes, produces no radical changes in the rate constant. Thus, the rate constants of the reactions of $:SiCl_2$, $:SiMePh$, and $:SiH_2$ with O_2 are 3.4×10^9 [7], 3.0×10^8 [8], and 7.2×10^9 $l\,mol^{-1}\,s^{-1}$ [9], respectively.

Thus, the reaction of $:GeCl_2$ with oxygen to form $O{=}GeCl_2$ should occur sufficiently fast, since the rate constant of this reaction should be close to 10^9 $l\,mol^{-1}\,s^{-1}$. However, the reaction rate will be limited by the rate of feeding oxygen to the reaction system. To check this assumption, we reacted complex **I** with hexamethyldisiloxane under two different conditions of contacting the reaction mixture with air oxygen.

The synthesis at a poor contact of the reaction mixture with air oxygen (in air, without barboting air through the reaction mixture) was slow, up to 80–90 h (determined by the time of complete decomposition of complex **I**). Therewith, the yields of germasiloxanes **III** and **V** were low (5 and 1%, respectively). Because of the low yields of germasiloxanes, we did not perform detailed analysis of the reaction products.

To improve the conditions for formation of dichlorogermanones and the yield of germasiloxanes, we barboted air through the reaction mixture throughout the synthesis. In this case, the synthesis occurred 2.5–3 times faster (32 h), and the yields of germasiloxanes **III** and **V** improved to 37 and 9%.

Thus, we propose that germasiloxanes **III** and **V** are formed by the following reactions.

$$\mathbf{II} + O{=}GeCl_2 \longrightarrow \mathbf{III}, \qquad (5)$$

$$\mathbf{X} + O{=}GeCl_2 \longrightarrow \mathbf{V}. \qquad (6)$$

Reactions (5) and (6) are likely to be rather fast, since similar reactions with the closest analogs of germanones, silanones, are highly exothermic and rather fast in the liquid phase [10, 11]. Thus, for instance, we estimated the enthalpy [ΔH^0_{298}(g.)] of $O{=}SiMe_2$ insertion into hexamethyldisiloxane [reaction (7)] at –372 kJ/mol.

$$Me_3SiOSiMe_3 + O{=}SiMe_2 \longrightarrow Me_3SiOSiMe_2OSiMe_3. \qquad (7)$$

For estimating the enthalpy of reaction (7) we took the enthalpies of formation [$\Delta H^0_{f,298}$(g.), kJ/mol] of $Me_3SiOSiMe_3$ (–795 [12]), $Me_3SiOSiMe_2OSiMe_3$ (–1389 [12]), and $O{=}SiMe_2$ (–222 [13]).

Germasiloxanes **III** and **V** formed by reactions (5) and (6) can further react with methylsiloxanes by way of substitution of chlorine atoms at germanium by siloxane methyl groups.

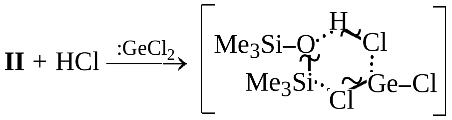
$$\mathbf{II} + \mathbf{III} \longrightarrow \underset{\mathbf{IV}}{Me_3SiOGeCl(Me)OSiMe_3} + \underset{\mathbf{IX}}{Me_3SiOSiMe_2Cl}. \qquad (8)$$

Compounds **IV** and **IX** were found among products of the reaction of complex **I** with compound **II**.

Germasiloxanes $Me_3SiOGeMe_2(OSiMe_2)_2OSiMe_3$ (**XI**) and $Me_3SiOGeMe_2(OSiMe_2)_3OSiMe_3$ (**XII**) formed by substitution of both chlorine atoms at germanium by methyl groups were found among products of the reaction of octamethyltrisiloxane with complex **I**.

The yields of germasiloxanes **XI** and **XII** are 5 and 1.5%, respectively. The major reaction product is compound **V** (yield 23%) which is probably formed by reaction (6).

The reaction of compounds **I** and **II** also involves conversions of the starting siloxane into other siloxanes. The most intricate stage of such conversions is siloxane bond cleavage. The mechanism of such cleavage in the presence of metal chlorides MCl_n and HCl has been proposed in the monograph [14]. According to this mechanism, the Si–O–Si bond reacts with MCl_n (in our case, $GeCl_2$) and HCl to form a six-membered cyclic transition complex which then decomposes with cleavage of the Si–O, Ge–Cl, and H–Cl bonds. Such transformation of compound **II** gives rise to trimethylsilanol and chlorotrimethylsilane.



$$\longrightarrow Me_3SiCl + Me_3SiOH + :GeCl_2. \qquad (9)$$

Note that chlorotrimethylsilane was found among products of the reaction of complex **I** with siloxane **II**.

Further reaction of trimethylsilanol with chlorosilanes present in the reaction mixture is rather fast and yields new siloxanes. Thus, for instance, Me_3SiOH reacts with compound **IX** formed by reaction (8) to give octamethyltrisiloxane.

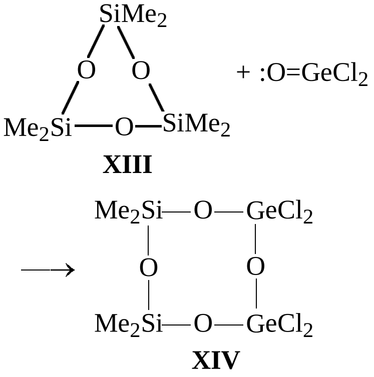
$$Me_3SiOH + \mathbf{IX} \xrightarrow[-HCl]{} Me_3SiOSiMe_2OSiMe_3. \qquad (10)$$

It should be noted that chlorosiloxanes may be formed not only by reaction (8), but also by direct reaction of methylsiloxanes with $:GeCl_2$.

$$\mathbf{II} + :GeCl_2 \longrightarrow \mathbf{IX} + :GeClMe. \qquad (11)$$

Reactions of the dioxane complex of dichlorogermylene with cyclosiloxanes we studied on an example of its reaction with gexamethylcyclotrisiloxane (**XIII**). In this synthesis, like in the synthesis with linear siloxanes, complex **I** generates dichlorogermylene which then in the presence of air oxygen converts into dichlorogermanone.

Further dichlorogermanone by a reaction similar to reactions (5) and (6) inserts into the Si–O bond of cyclosiloxane **XIII** to form germatetrasiloxane **XIV**.



The yield of compound **XIV** in the reaction of complex **I** with compound **XIII** (32 h, 85–95°C) was 13%. It should be noted that this reaction also gives various cyclosiloxanes, such as octamethylcyclotetrasiloxane (**XV**), decamethylcyclopentasiloxane (**XVI**), and dodecamethylcyclohexasiloxane (**XVII**) (34, 16, and 6%, respectively). These by-products are probably formed by reactions like (9)–(11) which are induced by $:GeCl_2$ and HCl, generated in the course of the synthesis, and lead to Si–O–Si bond redistribution in the starting compound **XIII**.

EXPERIMENTAL

Reaction products were analyzed by GC–MS. The mass spectra were obtained on a Hewlett–Packard HP-5971 system at an ionizing voltage of 70 V. Separation was performed on a DB-5 capillary column (0.032×2500 cm, film thickness 25 μm). The oven temperature was programmed from 50 to 280°C at a rate of 7 deg/min; carrier gas helium (0.8 ml/min). The *m/e* values are given for the ^{28}Si, ^{35}Cl, and ^{74}Ge isotopes. The mass spectra were assigned with account for the mass spectral data for compounds **III**, **V**, and other germasiloxanes, reported in [15]. According to that work, (1) electron impact induces complete randomization (intramolecular disproportionation) of substituents and (2) the mass spectra of compounds with a central $GeCl_2$ group contain a strong $GeMe_3^+$ ion peak. The dioxane complex of dichlorogermylene was prepared as described in [16].

Reaction of the dioxane complex of dichlorogermylene (I) with hexamethyldisiloxane (II). A flat-bottomed flask equipped with a magnetic stirrer and a reflux condenser was charged with 46.3 g of compound **I**, 32.4 g of compound **II**, and 19 g of dioxane. The mixture was stirred for 29 h at 85–95°C with continuous barbotage of air (1–2 ml/min). The postreaction mixture contained a liquid (81.5 g) and a solid (10.9 g) phases. The liquid phase was distilled at atmospheric pressure to isolate 0.6 g of chlorotrimethylsilane, 36.6 g of dioxane, and 3 g of compound **II**. The subsequent vacuum distillation gave 38.5 g of a fraction containing 24 g of compound **III** [mass spectrum, *m/e* (I_{rel}, %): 307(5) $(M - Me)^+$, 219(7) $(M - Me - SiMe_4)^+$, 139(9) $(Me_2ClGe)^+$, 119 (100) $(Me_3Ge)^+$, 73 (8) $(Me_3Si)^+$], 0.5 g of compound **IV** [mass spectrum, *m/e* (I_{rel}, %): 287 (11) $(M - Me)^+$, 139 (8) $(Me_2ClGe)^+$, 119 (100) $(Me_3Ge)^+$, 73 (13) $(Me_3Si)^+$], 7.1 g of compound **V** [mass spectrum, *m/e* (I_{rel}, %): 381 (12) $(M - Me)^+$, 293 (4) $(M - Me - SiMe_4)^+$, 207 (100) $(Me_5Si_3O_3)^+$, 193 (15) $(Me_3GeO \cdot SiMe_2)^+$, 139 (12) $(Me_2ClGe)^+$, 119 (79) $(Me_3Ge)^+$, 73 (12) $(Me_3Si)^+$], 0.7 g of compound **VI**, 2.1 g of compound **VII** [mass spectrum, *m/e* (I_{rel}, %): 325 (100) $(M - Me)^+$, 179 (9) $(GeCl_3)^+$, 139 (26) $(GeMe_2Cl)^+$, 73 (19) $(Me_3Si)^+$], 1.7 g of compound **VIII** [mass spectrum, *m/e* (I_{rel}, %): 399 (32) $(M - Me)^+$, 291 (53) $(M - Me - MeSiCl)^+$, 205 (33) $(M - Me - MeGeCl_3)^+$, 119 (100) $(Me_3Ge)^+$, 73 (42) $(Me_3Si)^+$], 0.9 g of compound **IX**, and 1.5 g of compound **X**. The solid phase contained mostly polymeric germanium subchlorides $(GeCl_x)_n$, where $x = 1.4–1.5$. The yields of compounds **III**, **V**, **VII**, and **VIII** (per the starting compound **I**) were 37, 9, 3, and 2%.

Reaction of the dioxane complex of dichlorogermylene (I) with hexamethylcyclotrisiloxane (XIII). A flat-bottomed flask equipped with a magnetic stirrer and a reflux condenser was charged with 11.6 g of compound **I**, 10.3 g of compound **XIII**, and 20 g of dioxane. The mixture was stirred for 32 h at 85–95°C with continuous barbotage of air (1–2 ml/min). The postreaction mixture contained a liquid (37.1 g) and a solid (3.3 g) phases. According to GC–MS, the liquid phase contained 24 g of dioxane, 0.22 g of Me_3SiCl, 0.28 g of $Cl_3SiOSiMe_3$, 2.56 g of compound **XIV** [mass spectrum, *m/e* (I_{rel}, %): 367 (21) $(M - Me)^+$, 193 (76) $(M - Me - GeCl_2Me_2)^+$, 139 (10) $(Me_2ClGe)^+$, 119 (100) $(Me_3Ge)^+$, 73 (15) $(Me_3Si)^+$], 5.05 g of compound **XV**, 3.1 g of compound **XVI**, and 1.42 g of compound **XVII**. The solid phase contained mostly polymeric germanium subchlorides $(GeCl_x)_n$, where $x = 1.4–1.5$. The yield of compound **XIV** (per the starting compound **XIII**) was 13.4%.

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