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Reaction of a Dioxane Dichlorogermylene Complex with Compounds Containing C–H Bonds

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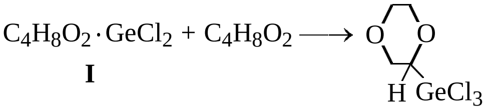
Abstract—The dioxane complex $C_4H_8O_2 \cdot GeCl_2$ reacts with compounds containing C–H bonds (C_6H_{14}, $Me_3SiSiMe_3$, $C_4H_8O_2$) with preferential formation of their trichlorogermyl derivatives.

At present no reactions of dichlorogermylenes or their complexes with compounds containing C–H bonds have been reported [1–3]. We found that prolonged (60 h) heating of dioxanedichlorogermylene complex **I** in dioxane at 60–70°C to give trichlorogermylene dioxane derivative **II** in an yield of 15–20%.



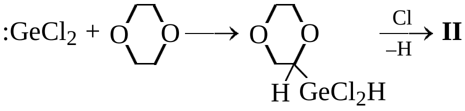
II
(1)

Complex **I** is a molecular *n*,ν complex [4]. The dissociation rate constants k_2 for such complexes and the equilibrium (2) constants are usually quite high and close to the collision factor [5, 6].

$$\mathbf{I} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_4H_8O_2 + :GeCl_2. \tag{2}$$

Complex **I** is a crystalline substance. Therefore, in reaction (1) we used dioxane not only as a reagent but also as a solvent.

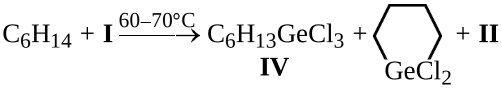
Compound **II** is likely to be formed by :$GeCl_2$ insertion into the C–H bond, leading to an unstable dichlorogermyl dioxane derivative **III**. Further substitution in compound **III** of the hydrogen atom on germanium by chlorine yields compound **II**.



III
(3)

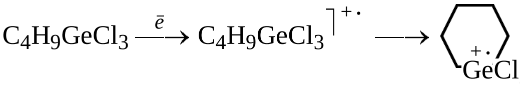
Such transformation of dichlorosilyl derivatives into trichlorosilyl is well-documented. Thus, for instance, the exchange reaction of $ArCH_2SiCl_2H$ (Ar = phenyl, *o*- and *p*-tolyl, etc.) with silicon subchlorides produces $ArCH_2SiCl_3$ [7].

Organogermanium compounds are also formed in the presence as :$GeCl_2$ acceptors of other C–H compounds. Thus, the reaction of hexane with complex **I** resulted in formation of trichlorohexylgermane (**IV**), 1,1-dichloro-1-germacycloheptane (**V**), and compound **II** in yields of 20.5, 7.6, and 6.8%.



V
(4)

Compounds **II** and **IV** are probably formed by reactions like (3), whereas compound **V** may be formed by dehydrochlorination of compound **IV**. Such dehydrochlorination of butyltrichlorogermane to give a heterocycle have been observed under electron impact [8].



(5)

Heating of complex **I** with hexamethyldisilane results in preferential formation of 1,1,1-trichloro-3,3,4,4,4-pentamethyl-1-germa-3,4-disilabutane (**VI**) in an yield of 12.8%. The yield of compound **II** is as low as 2.7%.

$$Me_3Si\text{–}SiMe_3 + \mathbf{I} \xrightarrow{60–70°C} \underset{\mathbf{VI}}{Cl_3Ge\text{–}CH_2\text{–}SiMe_2\text{–}SiMe_3} + \mathbf{II} \tag{6}$$

Thus, we showed for the first time that organogermanium compounds can be prepared by reactions of the dioxanedichlorogermylene complex with compounds containing C–H bonds.

EXPERIMENTAL

Reaction products were analyzed by GC–MS. The mass spectra were obtained on a Hewlett–Packard HP-5971A GC–MS system at an ionizing voltage of 70 V. Separation was performed on an 0.032 × 2500-cm DB-5 capillary column (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 dioxanetrichlorogermylene complex was prepared by the procedure described in [3].

Reaction of complex I with hexane. Compound **I**, 6.7 g, and 5 ml of hexane were placed in a Bunsen flask with a magnetic stirrer and a reflux condenser. The mixture was heated at 60–70°C and stirred for 60 h. When the reaction was complete, the reaction mixture consisted of two phases, liquid (9.1 g) and solid (2.0 g). By GC–MS data, the liquid phase contained 2.55 g of dioxane, 4.0 g of hexane, and 1.57 g of compound **IV** [mass spectrum, *m*/*e* (I_{rel}, %): 229 (2) $(M - Cl)^+$, 179 (11) $(GeCl_3)^+$, 85 (81) $(C_6H_{13})^+$], 0.5 g of compound **V** [mass spectrum, *m*/*e* (I_{rel}, %): 228 (19) ($M^{+\cdot}$), 192 (50) $(M - HCl)^{+\cdot}$, 144 (7) $(GeCl_2)^{+\cdot}$, 84 (53) $(C_6H_{12})^{+\cdot}$], and 0.52 g of compound **II** [mass spectrum, *m*/*e* (I_{rel}, %): 179 (6) $(GeCl_3)^+$, 87 (100) $(C_4H_7O_2)^+$]. The solid phase contained mostly germanium subchlorides of the approximate polymer composition $(GeCl_x)_n$, where x = 1.4–1.5. The yields of compounds **IV**, **V**, and **II** per taken compound **I** were 20.5, 7.6, and 6.8%.

Reaction of complex I with hexamethyldisilane (VII). The same reaction vessel as in the previous experiment was charged with 15.8 g of compound **I**, 10 g of compound **VII**, and 7.2 g of dioxane. The reaction mixture was stirred at 60–70°C for 69 h. When the reaction was complete, the reaction mixture consisted of two phases, liquid (23.5 g) and solid (5.5 g). The liquid phase contained 12.2 g of dioxane, 8.0 g of compound **VII**, 2.81 g of compound **VI** [mass spectrum, *m*/*e* (I_{rel}, %): 324 (2) ($M^{+\cdot}$), 309 (2) $(M - Me)^+$, 251 (58) $(M - Me_3Si)^+$, 201 (47) $(M - Me_3Si - MeCl)^+$, 179 (18) $(GeCl_3)^+$, 73 (100) $(Me_3Si)^+$], and 0.49 g of compound **II**. The solid phase contained mostly germanium subchloride of the approximate polymer composition $(GeCl_x)_n$, where x = 1.3–1.4. The yields of compounds **VII** and **II** per taken compound **I** were 12.8 and 2.7%.

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