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Chemistry of Germanium Atoms. III. Reactions of Thermally Evaporated Germanium Vapor with Hydrogermanes1)

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Synopsis. Thermally generated germanium atoms were found to react with hydrogermanes by insertion into germanium–hydrogen bonds. The resulting germylenes were inserted again in a germanium–hydrogen bond to form trigermanes.

We previously reported on the reactions of germanium atoms, thermally generated from a tungsten filament, with organic halides (polyhalomethanes, alkyl halides, and aryl halides), and the characterization of several new organogermanium halides.1) We now describe the reactions of germanium atoms with hydrogermanes (R_3GeH, R=Me; Et).

The fact that compounds containing group-4B element-hydrogen bonds like carbon–halogen bonds are good trapping agents for carbon atoms2) and silicon atoms3) made this class of substrates a logical choice for a germanium atom reaction. The present study is valuable for understanding not only the chemical properties of germanium atoms but also of the reactive intermediates in solutions.

Results and Discussion

Germanium atoms were generated by evaporation from a tungsten filament using essentially the same apparatus as has been described in the literature (ca. 1200—1300 °C and 5×10^{-3} Torr, 1 Torr=133.32 Pa).4) Germanium metal was evaporated at a rate of ca. 10 mg min^{-1} for 50 min, while an excess of hydrogermane was co-condensed on the walls of a quartz reaction flask containing the crucible and a perforated inlet tube through which the hydrogermane was introduced. The reaction flask was immersed in liquid nitrogen during germanium evaporation. After the germanium evaporation and introduction of the hydrogermane was completed, the reaction flask was warmed to room temperature and allowed to stand for 1.5 h. After removing the reaction flask from a vacuum line, the products were identified by comparing their GC-MS and retention times on GLC with those of authentic and similar samples. The yields of products were calculated by GLC with an internal-standard method.

The reaction of germanium atoms with trimethylgermane (Me_3GeH) produced 1,1,3,3-tetramethyltrigermane, $(Me_3Ge)_2GeH_2$, (0.2%) and hexamethyldigermane, $Me_3GeGeMe_3$, (1.0%). With triethylgermane (Et_3GeH) as the substrate, germanium atoms produced 1,1,3,3-tetraethyltrigermane, $(Et_3Ge)_2GeH_2$, (0.2%) and hexaethyldigermane, $Et_3GeGeEt_3$, (0.4%). Very small quantities of several unidentified products were formed in both reactions. This is the first observation of the insertion of germanium atoms into germanium–hydrogen bond of hydrogermanes by thermally vaporized germanium atom, so far as we know.

The condensation of hydrogermanes alone was carried out under identical conditions, except for germanium vaporization. As a result, hexamethyldigermane and hexaethyldigermane were formed in 0.1 and 0.2% yields, respectively. No trigermanes were detected.

The mechanism of double insertion is reasonable for the formation of products (Eqs. 1—3):5)

$$\dot{G}\dot{e}: + H\text{-}GeR_3 \longrightarrow {}^3[H\text{-}\underset{\cdot}{\dot{G}}e\text{-}GeR_3] \qquad (1)$$

$${}^3[H\text{-}\underset{\cdot}{\dot{G}}e\text{-}GeR_3] \longrightarrow {}^1[H\text{-}\dot{G}\dot{e}\text{-}GeR_3] \qquad (2)$$

$${}^1[H\text{-}\dot{G}\dot{e}\text{-}GeR_3] + H\text{-}GeR_3 \longrightarrow H_2Ge(GeR_3)_2 \qquad (3)$$

$$R = Me;\ Et$$

Thus, germanium atoms of the ^3P ground state, thermally evaporated, were inserted into germanium-hydrogen bonds of hydrogermanes (Eq. 1). The initially formed triplet germylenes rapidly relaxed to their singlet states, since the ground states of germylenes have been shown to be singlets by quantum chemical calculations and chemical reactions6—8) (Eq. 2). The singlet germylenes insert again into germanium-hydrogen bonds to form trigermanes (Eq. 3).

The digermanes are considered to be derived from the germyl radicals generated by the hydrogen-abstraction of the hydrogermanes with singlet germylenes ($HGeGeR_3$) or germanium atoms. Therefore, the formation of trihydrogermanes (H_3GeGeR_3) or tetrahydrogermane (GeH_4) may be expected. However, these germanium compounds could not be detected. A similar mechanism has been proposed for the co-condensation of thermally vaporized germanium atoms with organic halides.1)

Experimental

^{1}H NMR spectra were recorded on a Varian FT 80A, with tetramethylsilane as an internal standard. GC-MS spectra were obtained on a JEOL JMS-DX 303 mass spectrometer. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. Gas chromatography was performed on a Shimadzu GC-6A and 8A with lm 20% SE30 and 30% Apiezon L columns.

Materials. Me_3GeH and Et_3GeH were prepared by the reduction of the corresponding chlorides with lithium aluminum hydride in ether.9) $Me_6Ge_2$10) and $Et_6Ge_2$11) were prepared as described in the cited references.

Reactions of Germanium Atoms with Hydrogermanes. As a typical example, the reaction of germanium atoms with trimethylgermane (Me_3GeH) is described. Germanium atoms were produced by using essentially the same apparatus and conditions as described in the literature.[1] Germanium metal (0.5 g, 6.9 mmol) was vaporized at a temperature of 1200—1300 °C by using a resistively heated, alumina-coated tungsten spiral crucible, in vacuo (ca. 5×10^{-3} Torr), at a rate of 10 mg min^{-1}. During vaporization of the germanium metal, Me_3GeH (ca. 10 cm^3) was co-condensed on the walls of a quartz reaction flask. The color of the co-condensation product of germanium vapor and Me_3GeH vapor at 77 K is bluish-black. The crucible was maintained at 1200—1300 °C and reaction flask was immersed in liquid nitrogen during germanium the vaporization and the introduction of Me_3GeH. Then, the reaction flask was warmed to room temperature and allowed to stand for 1.5 h. The co-condensation products were characterized by comparing their GC-MS and retention times on GLC with those of authentic and similar compounds. The amounts of products were determined by GLC with an internal standard method. Me_6Ge_2 and $(Me_3Ge)_2GeH_2$ were formed in 1.0 and 0.2% yields, respectively. Small quantites of several unidentified products were also produced. The yields of products were determined on the basis of the germanium metal consumed by supposing that the germanium metal, except for germanium metal that remained in the crucible, completely reacted with Me_3GeH vapor. Therefore, by taking into consideration that the unreacted germanium metal becomes attached to the walls of a reaction flask, the yields of products may be underestimated.

Identification of Products. The known compounds (Me_6Ge_2 and Et_6Ge_2) were identified by comparing their GC-MS and retention times on GLC with those of authentic samples. The unknown compounds were carefully identified by comparing their GC-MS with those of similar samples and parent peaks and cleavage patterns while considering the natural abundance of germanium (ratio, $^{70}Ge/^{72}Ge/^{73}Ge/^{74}Ge/^{76}Ge=56/75/21/100/21$). $(Me_3{}^{74}Ge)_2{}^{74}GeH_2$ (parent ion at peak $m/z=314$); $m/z=309$ (11), 206 (39), 191 (21), and 119 (100). $(Et_3{}^{74}Ge)_2{}^{74}GeH_2$ (parent ion peak at $m/z=394$); $m/z=394$ (28), 365 (3), 312 (4), 223 (17), 161 (100), 133 (82), and 105 (16).

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