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Chemistry of Germanium Atoms. II. Reactions of Thermally Evaporated Germanium Vapor with Organic Halides[1,2]

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Thermally generated germanium atoms were found to react with organic halides by insertion into carbon-halogen bonds. The resulting germylenes abstracted halogens from organic halides to form trihalogermyl derivatives. Tetrahalogermanes were also formed by the abstraction of halogens with germanium atoms.

The study of a group 4B element-vapor reaction has been of considerable interest in organometallic chemistry and organic synthesis during the last few decades.[3] With this method, it is proving feasible to synthesize organometallic compounds containing group 4B elements which would be difficult, if not impossible, to prepare by other methods and to study their reactive intermediates. The study of carbon and silicon atoms as homologue of the germanium atom has been fairly well investigated, while the chemical properties of germanium atoms have been little studied.[4–8] In this paper, we report on the reactions of thermally evaporated germanium vapor (atoms) with organic halides.

The reactions of carbon atoms and silicon atoms with compounds containing carbon-halogen bonds for good trapping agents have been reported.[9,10] Under these circumstances, we have undertaken a co-condensation of germanium atoms with organic halides. The present finding is valuable for understanding not only the chemical properties of germanium atoms but also organogermanium intermediates in solutions.

Results and Discussion

The apparatus described in the Experimental section was used. Germanium metal was evaporated at a temperature of ca. 1200—1300 °C using a filament of tungsten in vacuo (ca. 5×10^{-3} Torr, 1 Torr=133.322 Pa) at a rate of ca. 10 mg min^{-1}.[11] During the vaporization of germanium metal, an excess of organic halide was introduced, as vapor, into a reaction flask. Germanium atoms and organic halide vapor was co-condensed on the walls of the reaction vessel which was cooled at 77 K. The color of co-condensation product, thus prepared, was muddy brown. After the germanium evaporation and introduction of the organic halide were completed, the reaction flask was warmed to room temperature. The co-condensation product of germanium atoms and organic halide vapor turned black. The products were identified by comparing their GC-MS and retention times on GLC with those of authentic samples. The yields of products were calculated by GLC with an internal standard.

The reactions of thermally vaporized germanium atoms with organic halides were examined. The products containing germanium are summarized in Table 1.

The reaction of germanium atoms with CCl_4 produced $GeCl_4$ (<10%), CCl_3GeCl_3 (7.0%), CCl_3CCl_3 (6.5%), and several high-boiling-point products (No. 1). The high-boiling-point products obtained did not contain germanium atoms. McGlinchey and Tan reported on a similar co-condensation of germanium atoms with CCl_4, but did not observe the formation of $GeCl_4$.[7] The yields of products were increased when a mixture of germanium atoms/copper atoms and germanium atoms/chromium atoms was used (Nos. 2 and 3, respectively). The formation of CCl_3GeCl_3 shown in Table 1 is explained by the insertion of germanium atoms into C-Cl bonds of CCl_4 to form $ClGeCCl_3$. The resulting germylene is known to abstract chlorines.[12] The compound $GeCl_4$ presumably arises as a result of abstraction of four chlorine atoms from CCl_4 by germanium atoms in a stepwise manner. The reason for increased yields of products for germanium atoms/copper atoms and germanium atoms/chromium atoms is not clear.

Other tetrahalomethanes showed a similar behavior; the reactions of germanium atoms with $CFCl_3$ and $BrCCl_3$ gave mainly $CFCl_2GeCl_3$ (1.6%) and CCl_3GeBr_3 (7.8%), respectively (Nos. 4 and 5).

The reaction of germanium atoms with $CHCl_3$ gave $CHCl_2GeCl_3$ (8.0%) as trihalogermyl compounds (No. 6). When CH_2Cl_2 and CH_2Br_2 were used as substrate, the trihalogermyl compounds formed were $CH_2ClGeCl_3$ (0.3%) and $CH_2BrGeBr_3$ (0.7%), respectively (Nos. 7 and 8).

Taking the results (Nos. 1—8) shown in Table 1 into consideration, the order of decreasing reactivity towards carbon-halogen insertion by germanium atoms is CeBr>C-Cl≫C-F. This may be a reflection of the carbon-halogen bond strengths.

The reaction of germanium atoms with MeI produced GeI_4 (14.0%), $MeGeI_3$ (11.0%), and Me_2GeI_2 (0.5%) (No. 9). Other alkyl iodides showed a similar behavior; the reactions of germanium atoms with EtI, *n*-PrI, *i*-PrI, and *n*-BuI gave $EtGeI_3$ (2.8%) (No. 10), *n*-$PrGeI_3$ (2.7%) (No. 11), *i*-$PrGeI_3$ (5.3%) (No. 12), and *n*-$BuGeI_3$ (1.0%) (No. 13), respectively. Compound GeI_4 was also produced in all reactions of germanium atoms with alkyl iodides. No reactions occurred with alkyl monobromides and alkyl monochlorides.

On the other hand, the reaction of germanium atoms with PhBr produced Ph_2GeBr_2 (0.05%) and Ph_3GeBr (0.01%) (No. 16). With PhCl, germanium atoms reacted to give only PhH and Ph-Ph. The reactivity observed for polyhalomethanes and alkyl iodides is not consistent with those for aryl halides used in this study. The reactions of germanium atoms with aryl halides may involve a radical-initiated process.[13]

Blank experiments were carried out under identical conditions. As a result, the products shown in Table 1 were attributable to the interaction of germanium atoms with the starting organic halides.

A probable pathway for the products shown in Table 1 is outlined in Scheme 1. Thermally evaporated germanium atoms possess a ^3P ground state. ^3P germanium atoms inserted into a carbon-halogen bond of organic halides to form triplet divalent species (germylenes) (Eq. 1). The intially formed triplet germylenes rapidly relax to the singlet state (Eq. 2). The ground state of R_2Ge (R=H, Me) and GeI_2 has been shown to be a singlet by quantum chemical calculations and chemical reactions.[14–16] The singlet germylenes abstract halogens from organic halides in a stepwise manner characteristic of germyl radicals (Eq. 3). Halogen abstraction has also been reported for singlet germylenes.[12]

Table 1. The Reaction of Germanium Atoms with Organic Halides[a]

No.	Substrate	Products (Yield/%[b])
1	CCl_4	$GeCl_4$ (<10[c]), CCl_3GeCl_3 (7.0)
2[d]	CCl_4	$GeCl_4$ (<10[c]), CCl_3GeCl_3 (12.0)
3[e]	CCl_4	$GeCl_4$ (<10[c]), CCl_3GeCl_3 (10.4)
4	$CFCl_3$	$GeCl_4$ (0.6), $CFCl_2GeCl_3$ (1.6)
5	$BrCCl_3$	$GeCl_4$ (5.8), $GeBrCl_3$ (0.6), $GeBrCl_3$ (0.6), $GeBr_4$ (0.7), $CCl_3GeBrCl_2$ (0.6), CCl_3GeBr_3 (7.8)
6	$CHCl_3$	$GeCl_4$ (15.0), $CHCl_2GeCl_3$ (8.0)
7	CH_2Cl_2	$GeCl_4$ (1.6), $CH_2ClGeCl_3$ (0.3)
8	CH_2Br_2	$GeBr_4$ (2.0), $CH_2BrGeClBr_3$ (0.7)
9	MeI	GeI_4 (14.0), $MeGeI_3$ (11.0), Me_2GeI_2 (0.5)
10	EtI	GeI_4 (17.0), $EtGeI_3$ (2.8)
11	*n*-PrI	GeI_4 (3.0), *n*-$PrGeI_3$ (2.7)
12	*i*-PrI	GeI_4 (5.1), *i*-$PrGeI_3$ (5.3)
13	*n*-BuI	GeI_4 (1.0), *n*-$BuGeI_3$ (1.0)
14	*n*-BuBr	No product
15	*n*-BuCl	No product
16	PhBr	Ph_2GeBr_2 (0.05), Ph_3GeBr (0.01)
17	PhCl	No product

a) Reactions were performed at room temperature for 1.5 h. b) Yields of products were determined on the basis of the amount of the germanium metal consumed on the assumption that all of the vaporized germanium metal completely reacted with organic halides. c) The retention time of $GeCl_4$ on GLC was overlapped with that of CCl_4. The yields of $GeCl_4$ could not be accurately determined by GLC. d) A mixture of germanium atoms and copper atoms. e) A mixture of germanium atoms and chromium atoms.

$$\dot{\mathrm{G}}\mathrm{e}\colon (^3\mathrm{P}) + \mathrm{R{-}X} \longrightarrow {}^3[\mathrm{R{-}}\overset{\cdot}{\underset{\cdot}{\mathrm{G}}}\mathrm{e{-}X}] \qquad (1)$$

$${}^3[\mathrm{R{-}}\overset{\cdot}{\underset{\cdot}{\mathrm{G}}}\mathrm{e{-}X}] \longrightarrow {}^1[\mathrm{R{-}}\overset{\cdot\cdot}{\mathrm{Ge}}\mathrm{{-}X}] \qquad (2)$$

$$\begin{tikzcd} {}^1[\mathrm{R{-}}\overset{\cdot\cdot}{\mathrm{Ge}}\mathrm{{-}X}] \arrow[r, "\mathrm{R{-}X}"] \arrow[dr, "\mathrm{R{-}X}"'] & \mathrm{R\dot{G}eX_2} \arrow[r, "\mathrm{R{-}X}"] & \mathrm{RGeX_3} \quad (3) \\ & \mathrm{R_2GeX_2} \quad (4) & \end{tikzcd}$$

Scheme 1. The mechanism for germylene intermediates.

On the other hand, singlet germylenes also undergo double insertions (Eq. 4).

C-X bonds of organic halides may also be activated by clusters rather than germanium atoms.

Experimental

^1H 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 1 m 5% and 20% SE30 columns.

Materials. Organic halides are commercially available and purified prior to use. Copper metal, chromium metal, $GeCl_4$, and GeI_4 are commercially available. CCl_3GeCl_3,[17] $MeGeI_3$,[18] Me_2GeI_2,[18] $EtGeI_3$,[19] *n*-$PrGeI_3$,[19] *n*-$BuGeI_3$,[19] Ph_2GeBr_2,[20] Ph_3GeBr,[21] were prepared as described in the cited references.

Reactions of Germanium Atoms with Organic Halides. As a typical example, the reaction of germanium atoms with chloroform ($CHCl_3$) is described. Germanium atoms were produced by using essentially the same apparatus 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 at 6.0—7.0 V, 15A, which was connected to copper electrodes, in vacuo (ca. 5×10^{-3} Torr) at a rate of 10 mg min^{-1}. During vaporization of the germanium metal, $CHCl_3$ (ca. 15 cm^3) was co-condensed on the walls of a quartz reaction flask containing crucible and a perforated inlet tube through which $CHCl_3$ was introduced as vapor. The crucible was maintained at 1200—1300 °C and the reaction flask immersed in liquid nitrogen during germanium vaporization and the introduction of $CHCl_3$. After germanium vaporization and the introduction of $CHCl_3$ were completed, the reaction flask was warmed to room temperature and allowed to stand for 1.5 h. Products were identified by comparing their GC-MS and retention times on GLC with those of authentic samples. The amounts of products were calculated by GLC with an internal-standard method. $GeCl_4$ (15.0%), $CHCl_2GeCl_3$ (8.0%), and several high boiling products were produced. The high boiling products were confirmed to exclude germanium atoms by GC-MS. 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 $CHCl_3$ vapor. Therefore, by taking into consideration that the unreacted germanium metal attaches on the walls of a reaction flask, the yields of products may be underestimated.

Identification of Products. The known compounds 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 by parent peaks and cleavage patterns considering the natural abundance of germanium (ratio, $^{70}Ge/^{72}Ge/^{73}Ge/^{74}Ge/^{76}Ge=56/75/21/100/21$). $^{74}Ge,^{79}Br^{35}Cl_3$ (parent ion peak at $m/z=258$), $m/z=222$ (22), 179 (22), 153 (15), and 74 (17). $^{74}Ge^{79}Br_3{}^{35}Cl$ (parent ion peak at $m/z=346$), $m/z=347$ (10), 268 (60), 153 (54), 109 (80), and 74 (7). $CF^{35}Cl_2{}^{74}Ge^{35}Cl_3$ (parent ion peak at $m/z=280$), $m/z=$ 245 (18), 179 (26), 101 (100), 82 (36), and 66 (6). $C^{35}Cl_3{}^{74}Ge^{79}Br_3$ (parent ion peak at $m/z=428$), $m/z=428$ (1), 395 (12), 350 (4), 312 (100), 231 (8), 153 (53), 119 (50), 82 (30), and 74 (10). $C^{79}Br^{35}Cl_2{}^{74}Ge^{79}Br_3$ (parent ion peak at $m/z=$ 474), $m/z=475$ (0.4), 440 (1), 394 (11), 350 (3.5), 312 (22), 231 (3), 163 (100), 153 (27), and 74 (6). $CH^{35}Cl_2{}^{74}Ge^{35}Cl_3$ (parent ion peak at $m/z=262$), $m/z=227$ (2), 179 (18), 144 (2), 109 (18), and 83 (100). $CH_2{}^{35}Cl^{74}Ge^{35}Cl_3$ (parent ion peak at $m/z=228$), $m/z=194$ (17), 179 (65), 159 (100), 144 (12), 109 (65), and 74 (20). $CH_2{}^{79}Br^{74}Ge^{79}Br_3$ (parent ion peak at $m/z=404$), $m/z=405$ (24), 327 (77), 313 (100), 232 (26), 153 (44), and 74 (6).

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