Direct Synthesis of Organotrichlorogermanes by the Reaction of Elemental Germanium, Hydrogen Chloride, and Alkene

Masaki Okamoto*

Department of Applied Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

Takehiko Chikamori, Takuya Asano, and Eiichi Suzuki*

Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8550, Japan

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The reaction of elemental germanium, hydrogen chloride, and ethylene with copper(I) chloride catalyst gave ethyltrichlorogermane with a 66% selectivity, tetrachlorogermane also being formed. The addition of tetrachlorogermane to the reaction system increased the formation rate of ethyltrichlorogermane. The reaction of germanium, tetrachlorogermane, and butadiene resulted in the formation of 1,1-dichlorogermacyclopent-3-ene. These results indicate the intermediacy of dichlorogermylene, which is formed by the reaction of elemental germanium with tetrachlorogermane. In place of ethylene, allyl chloride was fed with hydrogen chloride. Allyltrichlorogermane was obtained with a 92% selectivity together with a small amount of tetrachlorogermane. It is highly plausible that the formation of allyltrichlorogermane is caused by the insertion of dichlorogermylene intermediate to the carbon−chlorine bond of allyl chloride.

Introduction

Elemental germanium reacts with methyl chloride with use of a copper catalyst to form methylchlorogermanes.[1,2] This is called “direct synthesis” since organogermanes are synthesized directly from elemental germanium. The reactions of germanium with various alkyl and aryl halides have also been reported for the direct synthesis of alkylhalogermanes and arylhalogermanes, respectively.[2−5] Only organic halides are reactive to directly synthesize organogermanes. In refs 2−5 copper and silver have been used as the catalysts, and these metals have formed the germanium−metal intermetallic compounds, in which germanium atom reacts with organic halides.

Hydrogen chloride also reacts with elemental germanium to form trichlorogermane and tetrachlorogermane with a copper catalyst,[4,6] even with no catalyst.[7]

In this work, a new method of direct synthesis of organogermane was developed and the reaction mechanism was examined. Here, we have found that alkyltrichlorogermane was synthesized by the reaction of elemental germanium and hydrogen chloride in the presence of alkene.

Results and Discussion

Reaction of Elemental Germanium, Hydrogen Chloride, and Ethylene. When the mixture of germanium and 20 wt % of copper(I) chloride was pretreated at 450 °C for 1 h in a helium stream, 4% of germanium charged reacted with copper(I) chloride to form tetrachlorogermane. After the pretreatment, the reaction of elemental germanium, hydrogen chloride, and ethylene was carried out at 450 °C. Ethyltrichlorogermane was formed together with tetrachlorogermane. The changes of formation rates of ethyltrichlorogermane and tetrachlorogermane with time are shown in Figure 1. Both the rates increased with reaction time to the maxima around 1 h, and then gradually decreased. The overall selectivity and yield of ethyltrichlorogermane for 7 h were 61% and 15%, respectively, the germanium

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* Address correspondence to these authors. M.O.: phone +81-3-5734-2625, fax +81-3-5734-2878, e-mail mokamoto@apc.titech.ac.jp. E.S.: phone +81-3-5734-2118, fax +81-3-5734-2878, e-mail esuzuki@o.cc.titech.ac.jp.

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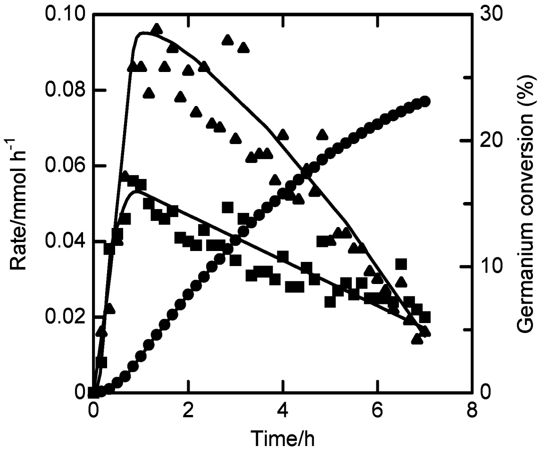


Figure 1. Time courses of the germanium conversion (circle) and the formation rates of ethyltrichlorogermane (triangle) and tetrachlorogermane (square) in the reaction of germanium, hydrogen chloride, and ethylene. The pretreatment was carried out at 450 °C for 1 h. The reaction temperature was 450 °C. The amount of germanium charged in the reactor was 2.76 mmol. The catalyst amount was 20 wt %. The flow rates of hydrogen chloride and ethylene were 5 and 10 mmol h^{-1}, respectively.

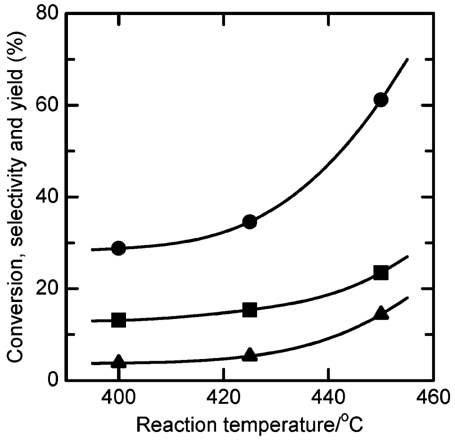


Figure 2. Effect of reaction temperature on the germanium conversion (square), the selectivity (circle), and the yield (triangle) of ethyltrichlorogermane. The pretreatment was carried out at 450 °C for 1 h. The amount of germanium charged in the reactor was 2.76 mmol. The catalyst amount was 20 wt %. The flow rates of hydrogen chloride and ethylene were 5 and 10 mmol h^{-1}, respectively.

conversion for 7 h being 24%. No formation of ethyl chloride was observed, indicating that this reaction is not a general direct synthesis from germanium and ethyl chloride. The reaction shown in this work is a new method of direct synthesis of organogermanes.

On the other hand, in the absence of ethylene only tetrachlorogermane was formed, the germanium conversion for 7 h being 23%. No formation of trichlorogermane was observed. In some reports,[4,6,7] trichlorogermane, not tetrachlorogermane, has been reported as a main product for the reaction of germanium and hydrogen chloride. Thus, under our reaction conditions, the germanium−hydrogen bond in trichlorogermane was completely converted to the germanium−chlorine bond by an attack of hydrogen chloride.

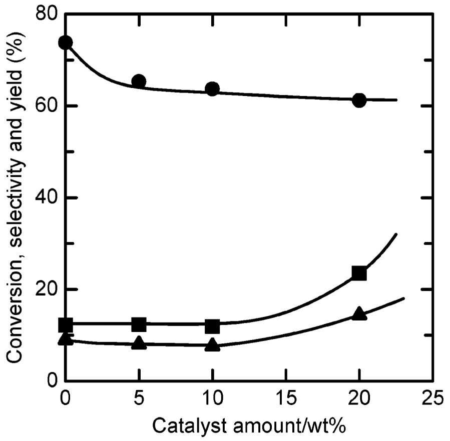


Figure 3. Effect of the catalyst amount on the germanium conversion (square), the selectivity (circle), and the yield (triangle) of ethyltrichlorogermane. The pretreatment was carried out at 450 °C for 1 h. The amount of germanium charged in the reactor was 2.76 mmol. The reaction temperature was 450 °C. The flow rates of hydrogen chloride and ethylene were 5 and 10 mmol h^{-1}, respectively.

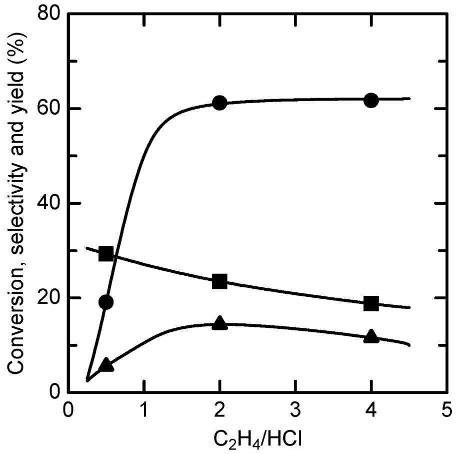


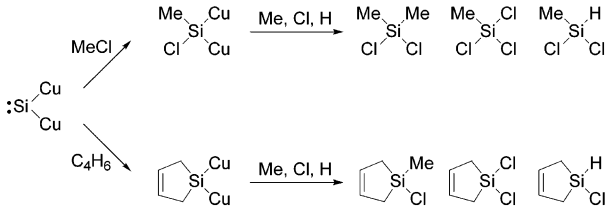
Figure 4. Effect of the ratio of ethylene to hydrogen chloride on the germanium conversion (square), the selectivity (circle), and the yield (triangle) of ethyltrichlorogermane. The pretreatment was carried out at 450 °C for 1 h. The amount of germanium charged in the reactor was 2.76 mmol. The catalyst amount was 20 wt %. The reaction temperature was 450 °C. The total flow rate of hydrogen chloride and ethylene was kept at 15 mmol h^{-1}.

The effect of reaction temperature on the product distribution was examined. Figure 2 shows the germanium conversion, the selectivity, and the yield of ethyltrichlorogermane for the 7-h reaction. Both the selectivity and the conversion increased with reaction temperature.

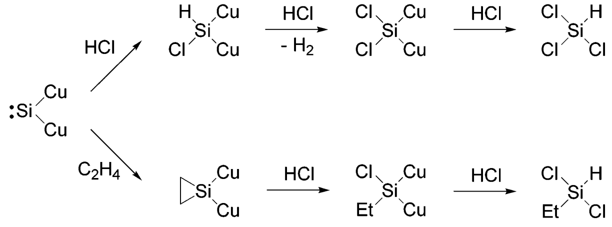
The amount of copper(I) chloride catalyst was varied. As shown in Figure 3, even without the catalyst, the reaction proceeded and ethyltrichlorogermane was formed with a 74% selectivity. With use of 5 wt % of copper(I) chloride, the selectivity for ethyltrichlorogermane decreased, while the germanium conversion did not change. When the catalyst amount was further increased, the selectivity slightly decreased and the conversion increased.

The ratio of ethylene to hydrogen chloride greatly affected the reaction results as shown in Figure 4. At a ratio of 0.5, the selectivity for ethyltrichlorogermane was very low, 19%, while above 2, it was constant at 61%. The germanium conversion slightly declined at a higher ratio.

It is well-known[8] that silicon, a congener of germanium, also reacts with methyl chloride to afford dimethyldichlorosilane, which is a raw material of silicones. We have elucidated the reaction mechanism involving a surface silylene intermediate (:$SiCu_2$) on the silicon surface as shown in eq 1.[9] When the reaction of elemental silicon with methyl chloride was carried out in the presence of butadiene as a silylene-trapping reagent, silacyclopent-3-enes were formed as the products trapped by butadiene, together with methylchlorosilanes.



Furthermore, the intermediacy of surface silylene in the reaction of silicon with hydrogen chloride has also been revealed.[10] The reaction of silicon with hydrogen chloride gave di-, tri-, and tetrachlorosilanes,[11] while the reaction in the presence of alkene resulted in the formation of alkyldichlorosilane together with chlorosilanes.[10] The alkyldichlorosilane formation also indicates that surface silylene is the reaction intermediate. The key step of the organosilane formation is the reaction of alkene with the silylene as shown in eq 2.



Trapping an intermediate of the methylchlorogermane synthesis from elemental germanium was attempted with butadiene. The mixture of methyl chloride and 1,3-butadiene (CH_3Cl/C_4H_6 was changed between 2 and 20) was fed at 400−500 °C to the reactor, in which the mixture of germanium (2.76 mmol) and copper(I) chloride (10 wt %) was charged. The reaction products were methylchlorogermanes and dimers of butadiene. The selectivities for dimethyldichlorogermane, methyltrichlorogermane, and trimethylchlorogermane were 91%, 6%, and 3%, respectively. No detection of germacyclopent-3-enes was observed, indicating that the intermediate in the direct synthesis of methylchlorogermanes is not surface germylene (:$GeCu_2$). This strongly suggests that surface germylene is not the intermediate of the ethyltrichlorogermane formation in the reaction of germanium, hydrogen chloride, and ethylene either.

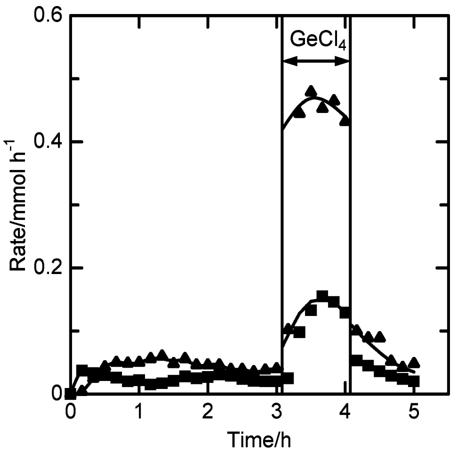
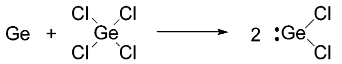
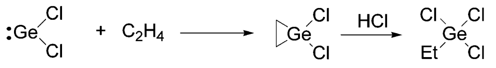


Figure 5. Effect of the tetrachlorogermane addition to the noncatalyzed Ge−HCl−C_2H_4 reaction system on the effluent rates of ethyltrichlorogermane (triangle) and tetrachlorogermane (square). The pretreatment was carried out at 450 °C for 1 h. The reaction temperature was 450 °C. The amount of germanium charged in the reactor was 2.76 mmol. No catalyst was used. The flow rates of hydrogen chloride and ethylene were 5 and 10 mmol h^{-1}, respectively. The flow rate of tetrachlorogermane added was 0.32 mmol h^{-1}.

It has been reported that tetrachlorogermane reacts with elemental germanium without a catalyst to form dichlorogermylene, which is easily trapped by butadiene[12] and chlorobenzene[13] to give 1,1-dichlorogermacyclopent-3-ene and phenyltrichlorogermane, respectively. It is highly plausible that dichlorogermylene is produced by the reaction of elemental germanium and tetrachlorogermane thus formed by the Ge−HCl reaction (eq 3) and that the dichlorogermylene formed is the intermediate in the ethyltrichlorogermane formation (eq 4). It has been reported that the 1,1-dichlorogermacyclopropane intermediate is formed by the reaction of dichlorogermylene with ethylene.[14]


(3)

$$\mathrm{Ge} + \mathrm{GeCl_4} \longrightarrow 2\ {:}\mathrm{GeCl_2}$$



(4)

To examine the intermediacy of dichlorogermylene, tetrachlorogermane was added to the feed during the reaction of germanium, hydrogen chloride, and ethylene. The result with no catalyst is shown in Figure 5. The reaction started with flowing the mixture of hydrogen

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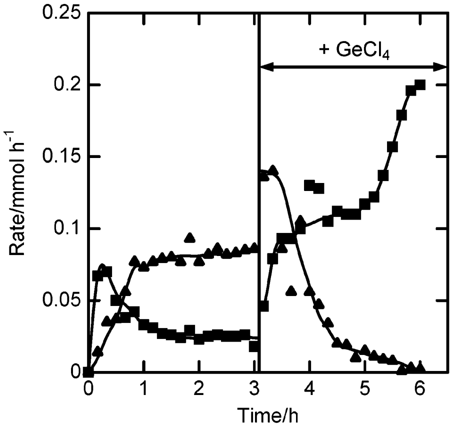


Figure 6. Effect of the tetrachlorogermane addition to the catalyzed Ge$-$HCl$-$C$_2$H$_4$ reaction system on the effluent rates of ethyltrichlorogermane (triangle) and tetrachlorogermane (square). The pretreatment was carried out at 450 °C for 1 h. The reaction temperature was 450 °C. The amount of germanium charged in the reactor was 2.76 mmol. The catalyst amount was 20 wt %. The flow rates of hydrogen chloride and ethylene were 5 and 10 mmol h^{-1}, respectively. The flow rate of tetrachlorogermane added was 0.32 mmol h^{-1}.

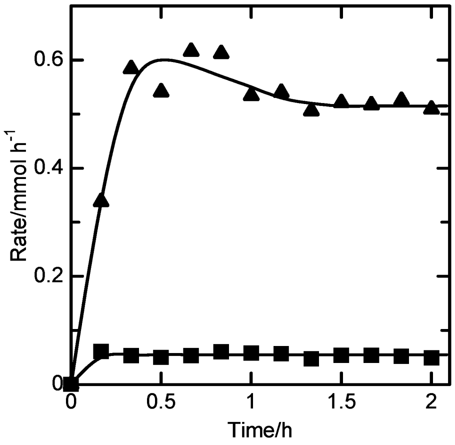


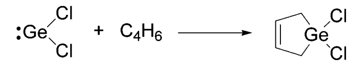
Figure 7. Changes in the formation rates of 1,1-dichlorogermacyclopent-3-ene (triangle) and tetrachlorogermane (square) with time in the noncatalyzed Ge$-$GeCl$_4-$C$_4$H$_6$ reaction. The pretreatment was carried out at 450 °C for 1 h. The reaction temperature was 450 °C. The amount of germanium charged in the reactor was 2.76 mmol. No catalyst was used. The flow rates of tetrachlorogermane, butadiene, and helium were 0.32, 5, and 10 mmol h^{-1}, respectively.

chloride and ethylene, and at 3.1 h, 0.32 mmol h^{-1} of tetrachlorogermane was added to the flow. Just after adding tetrachlorogermane, the effluent rate of ethyltrichlorogermane rapidly increased. When the tetrachlorogermane flow was stopped at 4.1 h, the amount of ethyltrichlorogermane formed decreased. The change of the ethyltrichlorogermane rates before and after the addition of tetrachlorogermane was twice as much as the conversion rate of tetrachlorogermane. This strongly indicates that the reaction shown in eq 5 occurs.

$$\mathrm{Ge} + \mathrm{GeCl_4} + 2\,\mathrm{C_2H_4} + 2\,\mathrm{HCl} \longrightarrow 2\,\mathrm{EtGeCl_3} \qquad (5)$$

Figure 6 shows the effect of the tetrachlorogermane addition in the reaction with the catalyst. At 3.1 h, tetrachlorogermane was fed to the reactor together with hydrogen chloride and ethylene. The rate of ethyltrichlorogermane increased just after the addition; however, the difference between the rates before and after the addition was smaller than the 2-fold rate of consuming tetrachlorogermane. Perhaps a part of tetrachlorogermane converted reacts with metallic copper to form an intermetallic compound of germanium and copper together with chlorine. Actually, chlorine was formed, and a decrease of the volume of the germanium$-$catalyst mixture due to the consumption of elemental germanium was not observed. The increase of the ethyltrichlorogermane rate just after the addition of tetrachlorogermane was smaller than that with no catalyst. This suggests that copper inhibits the formation of dichlorogermylene from germanium and tetrachlorogermane. Thus, tetrachlorogermane reacts with germanium on the surface of elemental germanium, not on the surface of the copper$-$germanium intermetallic compound where chlorogermanes are formed rapidly by the reaction of germanium with hydrogen chloride.

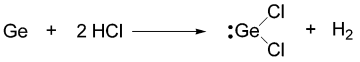
Further to prove the intermediacy of dichlorogermylene, the reaction of germanium and tetrachlorogermane was carried out in the presence of 1,3-butadiene as a germylene-trapping reagent. 1,1-Dichlorogeramcyclopent-3-ene was formed as the butadiene-trapped product (eq 6). This result is in agreement with the report of



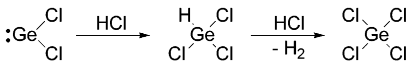
(6)

the synthesis of 1,1-dimethylgermacyclopent-3-ene by methylation of 1,1-dichlorogermacyclopent-3-ene produced from dichlorogermylene and butadiene.[12] Figure 7 shows the time courses of effluent rates of tetrachlorogermane and 1,1-dichlorogermacyclopent-3-ene. The formation rate of the trapped product was equal to the 2-fold conversion rate of tetrachlorogermane, also indicating the intermediacy of dichlorogermylene.

Laukmanis and Feltyn have studied the kinetics using dichlorogermylene as an intermediate in the reaction of germanium and hydrogen chloride with no catalyst (eq 7).[15] It is plausible that dichlorogermylene also originates from germanium and hydrogen chloride without use of copper(I) chloride as well as from germanium and tetrachlorogermane and that the reactions of hydrogen chloride and ethylene with the formed dichlorogermylene lead to the tetrachlorogermane (eq 8) and ethyltrichlorogermane (eq 4), respectively.



$$\mathrm{Ge} + 2\,\mathrm{HCl} \longrightarrow :\mathrm{GeCl_2} + \mathrm{H_2} \qquad (7)$$



$$:\mathrm{GeCl_2} \xrightarrow{\mathrm{HCl}} \mathrm{HGeCl_3} \xrightarrow[-\,\mathrm{H_2}]{\mathrm{HCl}} \mathrm{GeCl_4} \qquad (8)$$

Reaction of Elemental Germanium, Hydrogen Chloride, and Allyl Chloride. The direct synthesis of allylchlorogermanes by the reaction of elemental germanium and allyl chloride has been reported.[4,5] The products were allyltrichlorogermane and diallyldichlorogermane, whose selectivities were 60% and 40%, respectively.[5] Allyl chloride can easily react with dichlorogermylene to afford allyltrichlorogermane.[16] It was expected that allyltrichlorogermane could be selectively

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[15] Laukmanis, L. A.; Feltyn, I. A. *Inorg. Mater.* **1968**, *4*, 1275.

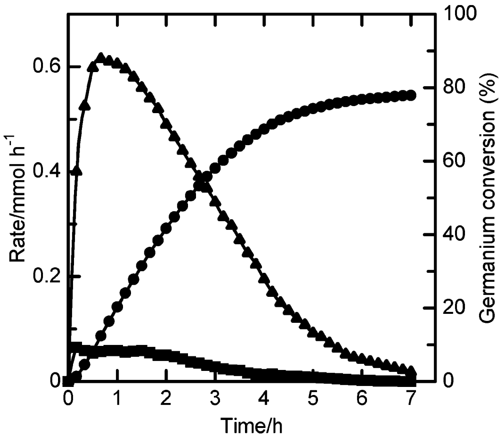
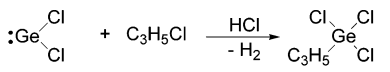


Figure 8. Time courses of the germanium conversion (circle) and the formation rates of allyltrichlorogermane (triangle) and tetrachlorogermane (square) in the reaction of germanium, hydrogen chloride, and allyl chloride. The pretreatment was carried out at 450 °C for 1 h. The reaction temperature was 260 °C. The amount of germanium charged in the reactor was 2.76 mmol. The catalyst amount was 10 wt %. The flow rates of hydrogen chloride and allyl chloride were 10 and 5 mmol h^{-1}, respectively.

obtained by the reaction of germanium, hydrogen chloride, and allyl chloride.

When 10 mmol h^{-1} of hydrogen chloride and 5 mmol h^{-1} of allyl chloride were fed to the reactor at 260 °C, allyltrichlorogermane was formed with a high selectivity. Figure 8 shows the time course of the reaction. The formation rate of allyltrichlorogermane was almost 10 times larger than that of tetrachlorogermane at 1 h, and the germanium conversion reached 78% at 7 h. The overall selectivity for allyltrichlorogermane for 7 h was 92%, its yield being 72%. In the absence of hydrogen chloride, diallyldichlorogermane and allyltrichlorogermane were formed with 70% and 30% selectivities, respectively, the germanium conversion being 83%. Adding hydrogen chloride to the reaction of germanium and allyl chloride enhanced the selectivity for allyltrichlorogermane.

Diallyldichlorogermane was mainly formed in the absence of hydrogen chloride. The fact that the diorganodichlorogermane was a main product is the same as that in the direct synthesis of methylchlorogermanes. This indicates that copper catalyzes the reaction of germanium and allyl chloride to form diallyldichlorogermane mainly. On the other hand, no formation of diallyldichlorogermane was observed in the presence of hydrogen chloride. This strongly suggests that allyltrichlorogermane is not formed by the catalysis of copper. Therefore, it is concluded that allyltrichlorogermane is formed by the insertion of dichlorogermylene to the carbon−chlorine bond in allyl chloride (eq 9).



$$:\mathrm{GeCl_2} + \mathrm{C_3H_5Cl} \xrightarrow[-\mathrm{H_2}]{\mathrm{HCl}} \mathrm{C_3H_5GeCl_3} \qquad (9)$$

Conclusion

Ethyltrichlorogermane was directly obtained with a 66% selectivity by the reaction of elemental germanium, hydrogen chloride, and ethylene. This reaction is a new method of direct synthesis of organogermane. The reaction intermediate is dichlorogermylene, which reacts with ethylene to form the germanium−carbon bond. The intermediate is formed by the reaction of elemental germanium and tetrachlorogermane and by the reaction of germanium with hydrogen chloride in the absence of the catalyst. The copper catalyst enhances only the formation of tetrachlorogermane from germanium and hydrogen chloride and inhibits the formation of dichlorogermylene by the reaction of germanium and tetrachlorogermane.

When the reaction of germanium with allyl chloride in the presence of hydrogen chloride was carried out, allyltrichlorogermane was obtained with a 92% selectivity and a 72% yield. The dichlorogermylene intermediate inserts to the carbon−chlorine bond of allyl chloride to form allyltrichlorogermane.

Experimental Section

Reaction Procedure. Elemental germanium grains (purity 99.99%, impurity: Ca 0.001, Fe 0.001, Mg 0.001 wt %) were sieved between 45 and 63 μm and washed by 46% hydrofluoric acid for 2 h with stirring to remove oxide overlayers. Copper(I) chloride was used as a catalyst because it can readily react with elemental germanium to form germanium−copper alloys which are reactive sites for the direct synthesis. The germanium grains (2.76 mmol, 200 mg) and copper(I) chloride grains (45−63 μm, Cu/(Ge + CuCl) = 0−20 wt %) were mixed vigorously and charged in a fixed-bed flow reactor (quartz, i.d. 10 mm). The mixture was pretreated at 450 °C for 1 h in a 20 mL $\min^{-1}$ stream of helium, before the mixture of hydrogen chloride (5 mmol h^{-1}) and ethylene (10 mmol h^{-1}) was fed to the reactor at 450 °C. The reaction products were identified by GC-MS, and the formation rates of the products were analyzed by gas chromatography. The selectivity, the yield, and the germanium conversion are defined by the following equations.

$$\text{selectivity (\%)} = \frac{\text{amount of the product (mmol)}}{\text{sum of amounts of Ge-containing products (mmol)}} \times 100$$

$$\text{yield (\%)} = \frac{\text{amount of the product (mmol)}}{\text{amount of the Ge charged in the reactor (2.76 mmol)}} \times 100$$

$$\text{Ge conversion (\%)} = \frac{\text{sum of amounts of Ge-containing products (mmol)}}{\text{amount of the Ge charged in the reactor (2.76 mmol)}} \times 100$$

Products. (a) Ethyltrichlorogermane: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (3H, t, J = 7.8 Hz, CH_2CH_3), 2.06 (2H, q, J = 7.8 Hz, CH_2CH_3); ^{13}C NMR (300 MHz, $CDCl_3$) δ 7.26, 26.05; GC-MS *m*/*e* (rel intensity) $[M - C_2H_5]^+$ and/or $[M - Cl]^+$ 167(4), 168(8), 169(11), 170(18), 171(20), 172(25), 173(17), 174(16), 175(9), 176(7), 177(6), 178(6), 179(8), 180(5), 181(6), 182(2), 183(2), $[C_2H_5]^+$ 29(100). (b) 1,1-Dichlorogermacyclopent-3-ene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.16 (4H, broad s, $CHCH_2$), 6.17 (2H, br s, $CHCH_2$); ^{13}C NMR (300 MHz, $CDCl_3$) δ 25.00, 128.77; GC-MS *m*/*e* (rel intensity) M^+ 194(0.6), 195(0.7), 196(1.2), 197(1.1), 198(1.7), 199(0.8), 200(0.9), $[C_4H_6]^+$ 54(100). (c) Allyltrichlorogermane: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.88 (2H, d), 5.35 (1H, m), 5.36 (1H, m), 5.85 (1H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ 37.26, 121.79, 126.04; GC-MS *m*/*e* (rel intensity) M^+ 216(2), 217(1), 218(4), 219(3), 220(6), 221(2), 222(4), 224(2), $[C_3H_5]^+$ 41(100).

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