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Phenyltrichlorogermane Synthesis by the Reaction of Chlorobenzene and the Dichlorogermylene Intermediate Formed from Elemental Germanium and Tetrachlorogermane

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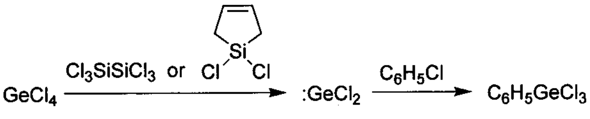
Phenyltrichlorogermane was synthesized with high selectivity, 96%, from elemental germanium, tetrachlorogermane, and chlorobenzene using no catalyst, almost all germanium and tetrachlorogermane being converted. Dichlorogermylene was formed as a reaction intermediate by the reaction of germanium with tetrachlorogermane and inserted into the C−Cl bond of chlorobenzene to yield phenyltrichlorogermane.

Introduction

In 1947, Rochow reported the direct synthesis of dimethyldichlorogermane by the reaction of elemental germanim with gaseous methyl chloride at 320−360 °C.[1] Since that time, various organic halides,[1−5] such as ethyl chloride,[1,3] propyl chloride,[4,5] and chlorobenzene,[1,5] also have been reported to react with elemental germanium in the presence of a copper or silver catalyst to afford organohalogermanes. Furthermore, we have recently found a new reaction for synthesizing alkyltrichlorogermanes directly from elemental germanium, hydrogen chloride, and an alkene using a copper catalyst.[6] The direct synthesis is a very simple method to synthesize organogermanes, and elemental germanium as a germanium source is readily available.

Organogermanes can be synthesized using a germylene intermediate.[7−9] Chernyshev et al. have reported the gas-phase synthesis of various organochlorogermanes using dichlorogermylene formed in the gas-phase reaction of tetrachlorogermane with dichlorosilylene, which was obtained by the pyrolysis of hexachlorodisilane or 1,1-dichlorosilacyclopent-3-ene.[8,9] For example, phenyltrichlorogermane was obtained by the dichlorogermylene insertion into the carbon−chlorine bond in chlorobenzene (eq 1).[9] The drawbacks of this reaction are that the disilane and the silacyclopentene are not easily obtainable and that stoichiometric amounts of silicon-containing byproducts are formed.



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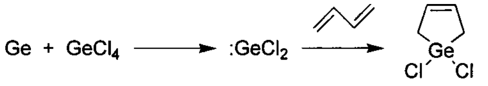
Berliner et al. have reported that elemental germanium reacts with tetrachlorogermane to afford dichlorogermylene in the absence of a catalyst.[10,11] The dichlorogermylene thus formed reacted with butadiene under the vapor-phase flow conditions to form 1,1-dichlorogermacyclopent-3-ene (eq 2), whose yield was, however, only 15%.[10] This reaction has the advantages that elemental germanium and tetrachlorogermane as sources of dichlorogermylene are more readily available than hexachlorodisilane or the silacyclopent-3-ene and



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that no byproducts are produced in the formation of the germylene.

Here, we show that batch reaction of elemental germanium, tetrachlorogermane, and chlorobenzene, in which dichlorogermylene is an intermediate, gives phenyltrichlorogermane as sole product in high conversions.

Experimental Section

Germanium grains (purity: 99.99%, size: <45 μm) were washed with stirring in a 46% HF aqueous solution for 1 h at room temperature, rinsed with deionized water, and dried using a rotary evaporator. The germanium grains (6.9 mmol), tetrachlorogermane (0.87–4.4 mmol), and chlorobenzene (200 mmol) were charged into a 120 mL stainless steel (SUS 316) autoclave, and then nitrogen, 30 atm pressure, was added. The autoclave was heated at 300 and 350 °C while stirring the reaction mixture. The pressure finally reached 67 and 75 atm, respectively. The reaction was stopped at 4, 8, 15, or 40 h, and the reaction mixture was cooled and filtered. Toluene (1 mL) was added to the reaction liquid as an internal standard. The products were analyzed quantitatively by gas chromatography and identified by GC–MS. Tetrachlorogermane and germanium conversions are defined by the following equations.

$$\text{tetrachlorogermane conversion (\%)} = 100 - \frac{\begin{array}{c}\text{amount of tetrachlorogermane}\\ \text{remaining after the reaction (mmol)}\end{array}}{\begin{array}{c}\text{amount of tetrachlorogermane}\\ \text{charged (mmol)}\end{array}} \times 100$$

$$\text{germanium conversion (\%)} = \frac{\begin{array}{c}[\text{sum of amounts of germanes (mmol)}] - \\ [\text{amount of tetrachlorogermane charged (mmol)}]\end{array}}{\text{amount of germanium charged (mmol)}} \times 100$$

Results and Discussion

The reaction of germanium, tetrachlorogermane, and chlorobenzene at 300 °C gave phenytrichlorogermane selectively. Figure 1a shows the changes of germane product amounts as a function of reaction time. All data were obtained from individual runs. The amount of tetrachlorogermane decreased with reaction time, and almost all tetrachlorogermane was consumed after 8 h. The phenyltrichlorogermane amount increased at twice the rate of tetrachlorogermane consumption. At 8 h, 98% of the total amount of all organogermanes was phenyltrichlorogermane. In the direct synthesis from elemental germanium and chlorobenzene using a copper catalyst, diphenyldichlorogermane and phenyltrichlorogermane were formed both with ca. 50% selectivity.[12] This product distribution is quite different from that obtained in the present study. Additionally, a catalyst such as copper is not prerequisite for our phenyltrichlorogermane synthesis. This suggests that a direct synthesis was not involved. Actually, when the reaction of elemental germanium with chlorobenzene was carried out in the absence of copper, the germanium was hardly converted (0.7% conversion) and no diphenyldichlorogermane, which is one of the main products of the direct synthesis, was formed.[12] According to eq 3, the reaction of germanium and tetrachlorogermane leads to the formation of 2 equiv of dichlorogermylene.[6,10,11] Dichlorogermylene can easily react with chlorobenzene to give phenyltrichlorogermane[9] as shown in eq 4. Thus, the conversion of 1 mol of tetrachlorogermane should result in the formation of 2 mol of phenyltrichlorogermane (eq 5). As shown in Figure 1a, at the initial stages of the reaction, the rate of phenyltrichlorogermane formation was almost twice as great as that of tetrachlorogermane consumption. This result is consistent with eq 5, indicating the intermediacy of dichlorogermylene. At 15 and 40 h, the formation of a very small amount of diphenyldichlorogermane was observed. This probably is caused by the disproportionation of phenyltrichlorogermane (eq

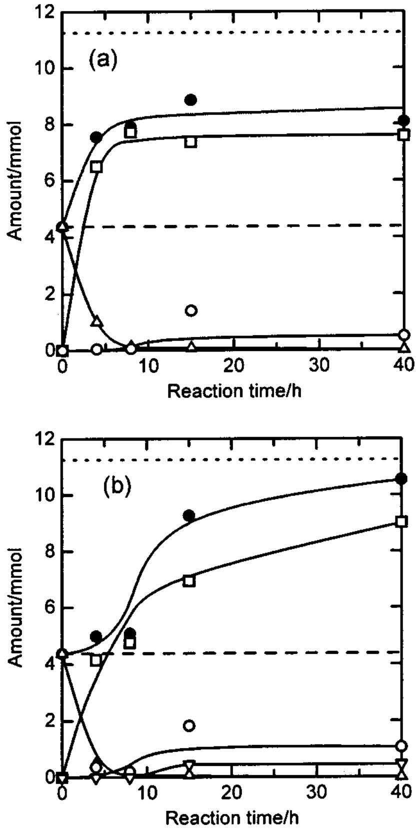

Figure 1. Time courses of the amounts of germanes in the reaction at 300 °C (a) and 350 °C (b): Phenyltrichlorogermane (□), diphenyldichlorogermane (○), triphenylchlorogermane (▽), tetrachlorogermane (△), and the sum of germanes (●). The amounts of elemental germanium, tetrachlorogermane, and chlorobenzene charged in the autoclave were 6.9, 4.4, and 200 mmol, respectively. Dashed and dotted lines represent the amount of tetrachlorogermane charged and the sum of amounts of elemental germanium and tetrachlorogermane charged, respectively.

$$\text{Ge} + \text{GeCl}_4 \longrightarrow 2\ \text{:GeCl}_2 \tag{3}$$

$$\text{:GeCl}_2 + \text{C}_6\text{H}_5\text{Cl} \longrightarrow \text{C}_6\text{H}_5\text{GeCl}_3 \tag{4}$$

$$\text{Ge} + \text{GeCl}_4 + 2\ \text{C}_6\text{H}_5\text{Cl} \longrightarrow 2\ \text{C}_6\text{H}_5\text{GeCl}_3 \tag{5}$$

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[12] The reaction of elemental germanium (6.88 mmol) and chlorobenzene (200 mmol) with copper(I) chloride catalyst (2.27 mmol) was carried out in a 120 mL autoclave at 350 °C for 60 h. The germanium conversion was 76%, and the selectivities for phenyltrichlorogermane, diphenyldichlorogermane, and triphenylchlorogermane were 53%, 45%, and 2%, respectively.

Table 1. Effect of the Amount of Tetrachlorogermane Charged on the Total Amount of All Germanes and the Conversion of Elemental Germanium in the 15 h Reaction[a]

reaction temp (°C)	amount of $GeCl_4$ charged/mmol	total amount of all germanes/mmol	elemental germanium conversion (%)
300	0.88	1.7	12
	2.2	4.5	48
	4.4	8.8	64
	8.8*	17*	100*
350	1.8	4.1	33
	0.88	3.5	38
	4.4	9.3	71

[a] The amounts of elemental germanium and chlorobenzene charged in the autoclave were 6.9 (* 8.8) and 200 mmol, respectively.

6). In fact, when 3.1 mmol of phenyltrichlorogermane in 20 mL of *n*-decane solvent was heated at 300 °C for 15 h, 0.24 mmol of diphenyldichlorogermane was formed together with tetrachlorogermane.

$$2\ C_6H_5GeCl_3 \longrightarrow (C_6H_5)_2GeCl_2 + GeCl_4 \qquad (6)$$

The effect of the amount of tetrachlorogermane charged was examined. Table 1 includes the results at 300 °C for 15 h. The sum of tetrachlorogermane, phenyltrichlorogermane, and diphenyldichlorogermane amounts was twice as great as that of tetrachlorogermane charged, and phenyltrichlorogermane was almost the sole germanium compound formed. This strongly supports the intermediacy of dichlorogermylene, formed by the reaction of germanium with tetrachlorogermane. On increasing the tetrachlorogermane amount to 4.4 mmol, the conversion of elemental germanium increased to 64%. When equal molar amounts of elemental germanium (8.8 mmol) and tetrachlorogermane (8.8 mmol) were used, the conversions of germanium and tetrachlorogermane were 100% and 97%, respectively, and the selectivity for phenyltrichlorogermane among organochlorogermanes was 96%.

On raising the reaction temperature to 350 °C, the time course of the reaction changed greatly. The result is shown in Figure 1b. At the beginning of the reaction, the amount of phenyltrichlorogermane formed was almost the same as that of tetrachlorogermane consumed; that is, elemental germanium hardly reacted. This strongly suggests that the substitution of chlorine in tetrachlorogermane for a phenyl group (eq 7) is the dominant process occurring. The reaction of tetrachlorogermane (4.4 mmol) and chlorobenzene (200 mmol) in the absence of elemental germanium at 350 °C for 8 h in the autoclave was carried out as a control. The conversion of tetrachlorogermane was 55%, and phenyltrichlorogermane and diphenyldichlorogermane were obtained in 52% and 3% yields, respectively. This indicates that the phenylation occurred at the beginning of the reaction of elemental germanium, tetrachlorogermane, and chlorobenzene. At 4 h in Figure 1b, 5.8 mmol of dichlorobenzene was also formed, and chlorine was not detected. Apparently, the chlorine formed as a byproduct of the substitution is completely consumed in forming dichlorobenzenes and hydrogen chloride (eq 8). Actually, hydrogen chloride was detected by GC–MS.[13] After 4 h, diphenyldichlorogermane and triphenylchlorogermane were formed together with phenyltrichlorogermane. The total amount of all germanes was larger than double the amount of tetrachlorogermane charged, indicating that elemental germanium was still consumed even after the consumption of all tetrachlorogermane. This suggests that tetrachlorogermane is formed by the disproportionation of phenyltrichlorogermane (eq 6) and/or that phenylchlorogermylene, which reacts with chlorobenzene to give diphenyldichlorogermane, is formed as an intermediate in the reaction of elemental germanium with phenyltrichlorogermane (eq 9). Triphenylchlorogermane most likely was formed by the disproportionation of diphenyldichlorogermane (eq 10).

$$GeCl_4 + C_6H_5Cl \longrightarrow C_6H_5GeCl_3 + Cl_2 \qquad (7)$$

$$C_6H_5Cl + Cl_2 \longrightarrow C_6H_4Cl_2 + HCl \qquad (8)$$

$$Ge + C_6H_5GeCl_3 \longrightarrow :Ge(C_6H_5)Cl + :GeCl_2 \qquad (9)$$

$$2\ (C_6H_5)_2GeCl_2 \longrightarrow (C_6H_5)_3GeCl + C_6H_5GeCl_3 \qquad (10)$$

Table 1 includes the effect of the amount of tetrachlorogermane charged in the autoclave. Under all conditions, the total amount of all germanium compounds was larger than twice the amount of tetrachlorogermane, also suggesting that the reactions shown by eqs 6 and 9 are operative.

Conclusions

Phenyltrichlorogermane was synthesized selectively from elemental germanium, tetrachlorogermane, and chlorobenzene without using a catalyst. The reaction intermediate is dichlorogermylene, which is formed by the reaction of germanium with tetrachlorogermane. The reaction and the procedure used in this work are very simple, and the starting materials are readily obtainable.

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[13] Probably the hydrogen chloride reacted partly with elemental germanium to give tetrachlorogermane ($Ge + 4\ HCl \rightarrow GeCl_4 + 2\ H_2$), whose reaction with chlorobenzene afforded dichlorobenzenes and chlorine again (eq 8). The effect of the chain of these reactions on the germanium conversion is small because the reaction of 4 mol of hydrogen chloride gives 1 mol of germanium consumed and a part of hydrogen chloride remained in the reaction mixture.