SYNTHESIS AND DISPROPORTIONATION OF METHYLCHLOROGERMANIUM HYDRIDES

G. Ya. Zueva, N. V. Serezhkina,

T. I. Khaustova, and V. A. Ponomarenko

Direct synthesis is extensively used to obtain various alkylhalosilanes, including the hydrogen-containing types RSiHCl₂ and R₂SiHCl [1], and a number of lower alkylhalogermanes [2, p. 212]. However, at tempts to synthesize hydrogen-containing organogermanium compounds by this method have been unsuccessful. All known methods for the synthesis of organohalogermanium hydrides have started from organogermanium compounds which already possess the Ge-H bond [2, p. 147]. Stagewise hydrogenation of the more readily available alkylhalogermanes has not met with success.

For the first time we have partly replaced chlorine in alkylchlorogermanes by hydrogen by means of organosilicon hydrides: CH₃SiHCl₂, (CH₃)₂SiHCl₁, (C₂H₅)₃SiH, and C₆H₅SiHCl₂ [3).

The proposed method is simple and is performed by boiling a mixture of the corresponding organohalogermanes with one of these organosilicon hydrides in the presence of 1-2% AlCl₃. Using this procedure, by the reaction

$$RGeCl_3 + RSiHCl_2 \xrightarrow{AlCl_3} RGeHCl_2 + RSiCl_3$$

we obtained methyldichlorogermane with a 70% yield [3]. However, in the preparation of methyldichlorogermane we noted that in addition to the main product CH_3GeHCl_2 , appreciable amounts (10-20%) of (CH₃)₂GeCl₂ are always present in the reaction products. When the reaction mixture is left to stand above AlCl₃ for a considerable period, the $(CH_3)_2$ GeCl₂ content increases to 70-80%, and the CH₃GeHCl₂ content correspondingly decreases to 20-30%. But if AlCl₃ is removed from the reaction mixture as soon as the reaction is completed, its initial composition does not subsequently change. Boiling of CH₃GeHCl₂ above AlCl₃ in absence of CH₃SiHCl₂ leads mainly to formation of CH₃GeCl₃, and although (CH₃)₂GeCl₂ is formed the amounts are much smaller. An investigation of these reactions by physical methods (IR, NMR, and mass spectra) enabled us to postulate two conversion schemes of methyldichlorogermane; scheme A (in the presence of $AlCl_3$)

> $\begin{array}{l} 2\mathrm{CH}_{3}\mathrm{GeHCl}_{2} \xrightarrow{\mathrm{AICl}_{4}} \mathrm{CH}_{3}\mathrm{GeCl}_{2} + \mathrm{CH}_{3}\mathrm{GeH}_{2}\mathrm{Cl} \\ 2\mathrm{CH}_{3}\mathrm{GeH}_{2}\mathrm{Cl} \xrightarrow{\mathrm{AICl}_{3}} \mathrm{(CH}_{3})_{2}\mathrm{GeCl}_{2} + \mathrm{GeH}_{4} \end{array}$ $\underbrace{\text{AlCl}_3}_{4\text{CH}_3\text{GeHCl}_2} \xrightarrow{\text{AlCl}_3} 2\text{CH}_3\text{GeCl}_3 + (\text{CH}_3)_2\text{GeCl}_2 + \text{GeH}_4$

and scheme B (in the presence of AlCl₃ and CH₃SiHCl₂.

 $CH_{3}GeHCl_{2} + CH_{3}SiHCl_{2} \xrightarrow{AlCl_{3}'} CH_{3}GeH_{2}Cl + CH_{3}SiCl_{3}$ $2CH_3GeH_2Cl \xrightarrow{AlCl_3} (CH_3)_2GeCl_2 + GeH_4$ $\frac{\text{AlCl}_{a}}{2\text{CH}_{3}\text{GeHCl}_{2} + 2\text{CH}_{3}\text{SiHCl}_{2} \longrightarrow (\text{CH}_{a})_{2}\text{GeCl}_{2} + \text{GeH}_{4} + 2\text{CH}_{3}\text{SiCl}_{3}}$

P. N. Lebedev Physical Institute, Academy of Sciences of the USSR, Moscow. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 912-915, April, 1976. Original article submitted July 29, 1975.

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Fig. 1. Amount of GeH_4 formed during the reaction vs the AlCl₃ content (%): 1) 2; 2) 5; 3) 10.

TABLE 1. Composition of the Products of the Reaction of $(CH_3)_2$ -GeCl₂ with CH_3SiHCl_2 in the Presence of $AlCl_3$

Reac-	(CH ₃) ₂ GeCl ₂ , % AlCl ₃ , %			(CH _a) ₃ GeCl, % AlCl ₃ , %			(CH ₃) ₂ GeHCl, %		
tion									
time, h	2	5	10	2	5	10	2	5	10
$ \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{array} $	79 71 65 58 46	$ \begin{array}{r} 66 \\ 58 \\ 46 \\ 22 \\ 20 \end{array} $	57 48 29 12 10	$ \begin{array}{c c} & 13 \\ & 16 \\ & 22 \\ & 27 \\ & 43 \\ \end{array} $	22 28 36 60 64	32 41 54 78 88	8 13 13 15 11	12 14 18 18	11 11 17 10 2

As we see from scheme A, in absence of methyldichlorosilane, boiling of CH_3 -GeHCl₂ with AlCl₃ leads to its disproportionation with formation of CH_3GeCl_3 and CH_3GeH_2Cl . Methylchlorogermane in turn apparently very rapidly (we failed to detect it) undergoes disproportionation with formation of $(CH_3)_2GeCl_2$ and GeH_4 . The amounts of CH_3GeCl_3 , $(CH_3)_2GeCl_2$, and GeH_4 formed agree with the proposed scheme.

If CH_3SiHCl_2 is present in the reaction (scheme B), which is the case when CH_3GeCl_2 reacts with an excess of CH_3SiHCl_2 and $AlCl_3$, first one chlorine atom and then another one are apparently replaced by hydrogen in the CH_3GeCl_3 , after which the disproportionation of CH_3GeH_2Cl takes place. In fact, in this case CH_3GeCl_3 is not formed and GeH_4 is evolved in a much greater amount than in absence of CH_3SiHCl_2 (see Experimental Method).

Hence it is clear that depending on the conditions (the amount of $AlCl_3$ and CH_3SiHCl_2 , and temperature) the reaction of CH_3GeCl_3 with CH_3SiHCl_2 in the presence of $AlCl_3$ may give either CH_3GeHCl_2 (70%) or $(CH_3)_2GeCl_2$ (80%). No CH_3GeH_2Cl is detected, because under these conditions (in the presence of $AlCl_3$ and CH_3SiHCl_2) it is apparently extremely unstable and undergoes disproportionation.

The compound $(CH_3)_2$ GeHCl is also unstable in the presence of AlCl₃. We failed to direct the reaction toward its preferential formation. However, if CH_3 GeH₂Cl was not detected, the $(CH_3)_2$ GeHCl content of the reaction products reached 10-20%. Instead of the expected $(CH_3)_2$ GeHCl we obtained trimethylchlorogermane with a 70-80% yield. Formation of $(CH_3)_2$ GeCl is accompanied by evolution of GeH₄. The reaction probably takes place by scheme C:

 $\begin{array}{l} (\mathrm{CH}_3)_2\mathrm{GeCl}_2 + \mathrm{CH}_3\mathrm{SiHCl}_2 \xrightarrow{\mathrm{AICl}_3} (\mathrm{CH}_3)_2\mathrm{GeHCl} + \mathrm{CH}_3\mathrm{SiCl}_3 \\ \\ \underline{4(\mathrm{CH}_3)_2\mathrm{GeHCl}} \xrightarrow{\mathrm{AICl}_3} 2(\mathrm{CH}_3)_3\mathrm{GeCl} + \mathrm{i}\mathrm{CH}_3)_2\mathrm{GeCl}_2 + \mathrm{GeH}_4 \\ \\ \hline \\ \underline{4(\mathrm{CH}_3)_2\mathrm{GeCl}_2 + 4\mathrm{CH}_3\mathrm{SiHCl}_2} \xrightarrow{\mathrm{AICl}_3} 2(\mathrm{CH}_3)_3\mathrm{GeCl} + (\mathrm{CH}_3)_2\mathrm{GeCl}_2 + \mathrm{GeH}_4 + 4\mathrm{CH}_3\mathrm{SiCl}_3 \end{array}$

We also investigated the variation of the composition of the reaction products with the amount of $AlCl_3$ added. The results of the investigation are listed in Table 1, from which it will be seen that the $(CH_3)_2GeCl$ content of the reaction products increases with the $AlCl_3$ content. Figure 1 is a plot of the amount of GeH_4 formed during the reaction vs the amount of $AlCl_3$ added.

Using this method we replaced chlorine by hydrogen in trimethylchlorogermane:

$$(CH_3)_3GeCl + CH_3SiHCl_2 \xrightarrow{AlCl_3} (CH_3)_3GeH + CH_3SiCl_3$$

As would be expected, in this case replacement is far more difficult. Thus by boiling $(CH_3)_3$ GeCl with CH_3 SiHCl₂ in the presence of 2% of AlCl₃ for 30 h we obtained $(CH_3)_3$ GeH only with a 30% yield. However, an increase in the AlCl₃ content to 10% enables one to obtain $(CH_3)_3$ GeH with a 44% yield after only 5 h. The authors of [2, p. 149] described the disproportionation of certain ethyl- and phenylhalogermanium hydrides in the presence of AlCl₃ and drew the conclusion that the stability of organohalogermanium hydrides decreases with an increase in the number of halogen atoms in the molecule:

$$R_2(X)GeH \rightarrow R(X)GeH_2 \rightarrow R(X_2)GeH$$

Our data show that in the presence of $AlCl_3$ the stability of methylchlorogermanium hydrides decreases in the series: $CH_3GeHCl_2 > (CH_3)_2GeHCl > CH_3GeH_2Cl$.

EXPERIMENTAL METHOD

Gas-liquid chromatographic analyses were performed by the method in [4] on an LKhM-8D chromatograph. The IR spectra were registered by a UR-20 spectrometer in a thin layer in a cell 0.02 mm thick. The PMR spectra was registered by an RYa-2308 spectrometer (60 MHz) in a CCl_4 solution, the internal standard was benzene. The mass spectra were registed on an MI-1305 device.

<u>Methyldichlorogermane</u>. A mixture consisting of 93 g (0.6 moles) of CH_3GeCl_3 , 110 g (0.95 moles) of CH_3SiHCl_2 , and 4 g (2%) of AlCl₃, was boiled for 7 h at 55-59°C until evolution of gas began. Heating was then immediately stopped and AlCl₃ was separated from the liquid products, the mixture being twice subjected to vacuum distillation. The composition of the organogermanium compounds was as follows: CH_3GeHCl_2 78%, CH_3GeCl_3 15%, and $(CH_3)_2GeCl_2$ 7%. After distillation in a rectifying column with 20 theoretical plates we obtained 48 g (63%) of CH_3GeHCl_2 , bp 101-102°C (750 mm), n_D^{-20} 1.4689, d_4^{20} 1.6432 (see [5], p. 164) Found; MR 27.15. Calculated: MR 27.32. Infrared spectrum 2115 cm⁻¹ (Ge-H); PMR spectrum (δ , ppm): 0.56 sec (Ge-H).

Dimethylchlorogermane. A mixture of 10.2 g (0.05 moles) CH_3GeCl_3 , 15 g (0.13 moles) CH_3SiHCl_2 , and 2.5 g (10%) AlCl₃ was boiled for 3 h. The composition of the organogermanium compounds was as follows: $(CH_3)_2GeCl_2 \ 80\%$, $CH_3GeHCl_2 \ 20\%$.

Reaction of CH_3GeHCl_2 with AlCl₃. A mixture of 5.14 g (0.03 moles) CH_3GeHCl_2 and 0.1 g (2%) AlCl₃ was boiled in a flask with a reflux condenser for 5 h until all evolution of gas ceased. A total of 33 ml of GeH_4 was collected. The composition of the liquid organogermanium compounds was as follows: CH_3GeHCl_2 53%, CH_3GeCl_3 29%, $(CH_3)_2GeCl_2$ 18%. The IR spectrum of GeH_4 (ν , cm⁻¹) was as follows: 850, 2115.

<u>Reaction of CH₃GeHCl₂ with CH₃SiHCl₂ and AlCl₃.</u> A mixture of 5.2 g (0.03 moles) CH₃GeHCl₂, 6.6 g (0.06 moles) CH₃SiHCl₂ and 0.25 g (2%) AlCl₃ was boiled for 11 h until evolution of gas ceased. Gas was not evolved during the first 5 h at 53-56°C. In the next 4 h at 70°C we collected 195 ml, and in the following 2 h 55 ml of gas. A total of 250 ml of GeH₄ was obtained. The composition of the liquid organogermanium compounds was as follows: CH₃GeHCl₂ 24%, (CH₃)₂GeCl₂ 76%.

Reaction of $(CH_3)_2GeCl_2$, CH_3SiHCl_2 , and $AlCl_3$. A mixture of 5.4 g (~ 0.03 moles) $(CH_3)_2GeCl_2$, 4.2 g (~ 0.03 moles) CH_3SiHCl_2 , and 0.5 g (5%) $AlCl_3$ was boiled for 5 h at 62-73°C until evolution of gas ceased. A total of 325 ml of GeH₄ was collected. The composition of the organogermanium compounds was as follows: $(CH_3)_2GeCl_2$ 20%, $(CH_3)_3GeCl$ 62%, and $(CH_3)_2GeHCl$ 18%. The presence of $(CH_3)_2GeHCl$ in this mixture is also indicated by the IR and PMR spectra. Infrared spectrum 2085 cm⁻¹ (Ge-H); PMR spectrum (δ , ppm): 1.67 sec (Ge-H).

<u>Trimethylchlorogermane</u>. A mixture of 90 g (~ 0.5 moles) $(CH_3)_2GeCl_2$, 123 g (~ 1 mole) CH_3SiHCl_2 , and 4.5 g (2%) AlCl₃ was boiled for 21 h at 62-73°C until evolution of gas ceased. The composition of the organogermanium compounds was $(CH_3)_3GeCl \ 82\%$ and $(CH_3)_2GeCl_2 \ 18\%$. The mixture obtained was twice subjected to vacuum distillation to remove AlCl₃. As a result of distillation in a rectifying column we obtained 29 g of $(CH_3)_3GeCl \ and \ 17 g \ of \ (CH_3)_2GeCl_2$. The physical constants of $(CH_3)_3GeCl$ were exactly the same as the values given by Mironov and Gar [5, p. 170].

Trimethylgermane. A mixture of 10 g (0.06 moles) (CH₃)₃GeCl, 12.6 g (0.11 moles) CH₃SiHCl₂, and 2.3 g $\overline{(10\%)}$ AlCl₃ was boiled for 5 h in a flask with a rectifying column. The (CH₃)₃GeH formed was periodically removed. We obtained 3.4 g (44%) of (CH₃)₃GeH with a bp of 26°C.

CONCLUSIONS

1. Disproportionation of methylchlorogermanium hydrides in the presence of aluminum chloride has been investigated. The stability of methylchlorogermanium hydrides is governed by the ratio of all the groups entering the molecule and by their nature.

2. The authors have determined the conditions for obtaining CH_3GeHCl_2 and $(CH_3)_3GeH$ by the replacement of chlorine in alkylchlorogermanes by hydrogen by means of organosilicon hydrides.

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