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Abstract

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A NEW METHOD FOR OBTAINING ALKYLDICHLOROGERMANES AND ALKYLTRICHLOROGERMANES

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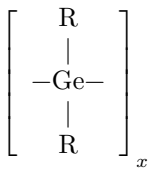
Whereas alkyldichlorosilanes (RCl_2SiH) can readily be obtained and, on their basis, diverse methods for the synthesis of various organosilicon compounds are being widely developed, alkyldichlorogermanes (RCl_2GeH) still remain an unstudied and practically inaccessible class of compounds. The only known route to the preparation of these compounds consists in replacing the hydrogen atoms in $RGeH_3$ by one reagent or another [1–3]. This method requires the availability of scarcely accessible $RGeH_3$ and complicated apparatus for the gaseous lower members of the homologous series.

An attempt to alkylate $HGeCl_3$ with Grignard or organolithium reagents, both according to the literature and according to our data, does not lead to success [4–7]. In these cases exclusively polymeric products of the composition



are formed. Therefore it was decided to use other organometallic compounds for this purpose.

We found [8] that, when trichlorogermane containing $\sim 30\%$ $GeCl_4$ is mixed with tetramethyltin, an exothermic reaction occurs, leading to a rather complex mixture of substances, from which the following compounds were isolated:

$$(CH_3)_4Sn \xrightarrow{HGeCl_3+GeCl_4} CH_4\ (\sim 30\%) + CH_3GeCl_2H\ (\sim 43\%)^* + \\ + CH_3GeCl_3\ (\sim 25\%); + (CH_3)_2SnCl_2\ (26\%); \\ (CH_3)_3SnCl\ (\sim 57\%). \qquad (1)$$

However, if this reaction is carried out with etherate of $HGeCl_3$ [9], only two compounds are formed:

$$(CH_3)_4Sn + HGeCl_3 \xrightarrow{\text{ether}} HGeCl_2CH_2CH_3\ (80\%) + (CH_3)_3SnCl\ (70\%).$$

Other alkyldichlorogermanes can be obtained in an analogous way. However, in these cases, along with RCl_2GeH, appreciable amounts of $RGeCl_3$ are formed and, in addition, hydrogen and the corresponding hydrocarbon are evolved:

$$(C_2H_5)_4Sn + HGeCl_3 \xrightarrow{\text{ether}} HGeCl_2C_2H_5\ (45\%) + C_2H_5GeCl_3\ (31\%)+$$
$$+ (C_2H_5)_3SnCl + H_2 + C_2H_6.$$

$$(C_6H_5)_4Sn + HGeCl_3 \xrightarrow{\text{ether}} HGeCl_2C_6H_5\ (\sim 5\%) + C_6H_5GeCl_3\ (45\%).$$

Replacement of tetraethyltin by tetraethyllead also leads to the formation of these same compounds, in somewhat different ratios:

$$(C_2H_5)_4Pb + HGeCl_3 \rightarrow HCl_2GeC_2H_5\ (60\%) + C_2H_5GeCl_3\ (\sim 20\%).$$

The structure of the obtained CH_3HGeCl_2, in addition to elemental analysis and spectra, is proved by its ability to add to ethylene and by further

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* Here and below, yields for germanium and tin compounds are given, respectively, calculated on the germanium- or tin-containing starting component of the reaction.

into the known ethyltrimethylgermane:

$$CH_3GeCl_2H \xrightarrow{CH_2=CH_2} C_2H_5GeCH_3Cl_2 \xrightarrow{CH_3MgX} C_2H_5Ge(CH_3)_3.$$

It is also curious to note that, although $HGeCl_3$ cannot be alkylated with a Grignard reagent, under these conditions $RGeHCl_2$ are converted in good yields into the corresponding trialkylgermanes:

$$C_2H_5HGeCl_2 \xrightarrow{CH_3MgBr} (C_2H_5)GeH(CH_3)_2 \quad (74\%).$$

It could have been assumed that part of the substances formed in reaction (I) (for example, CH_3GeCl_3) owed their origin to $GeCl_4$, always present in $HGeCl_3$

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

in an amount of about 30%. But it turned out that tetrachlorogermane does not react with tetramethyltin even on boiling*. At the same time tetraethyllead reacts with $GeCl_4$ with formation of ethyltrichlorogermane:

Fig. 1

Fig. 2

$$(C_2H_5)_4Pb + GeCl_4 \rightarrow (C_2H_5)_3PbCl + C_2H_5GeCl_3 \quad (90\%).$$

Taking into account the availability of $(C_2H_5)_4Pb$, this method of preparing ethyltrichlorogermane may prove to be one of the best.

Experimental Part

Methyldichlorogermane CH_3Cl_2GeH **(I).** A. To 60 g of $(CH_3)_4Sn$, with stirring, etherate of $HGeCl_3$, prepared [9] from 70 g of crude $HGeCl_3$, was added dropwise. The mixture boiled during this operation. After standing for an hour, distillation on a column gave 40 g of I, yield 80%, b.p. 101.5° (750 mm); n_D^{20} 1.4701, d_4^{20} 1.6356, MR_D 27.21; MR_D calculated 27.34; IR spectrum, see Fig. 1.

Found, %: C 7.86, 8.15; H 2.68, 2.69; Cl 43.90, 44.30; Ge 45.60, 45.30 CH_4GeCl_2. Calculated, %: C 7.53; H 2.53; Cl 44.44; Ge 45.51

Raman spectrum of I ($\Delta\nu$, cm^{-1}):

150 (3 sh); 179 (3 sh); 191 (1); 396 (10 sh); 430 (0); 571 (1 sh); 625 (5 sh); 670 (2 sh); 707 (2 sh); 1168 (1); 1240 (1); 1261 (1); 1355 (1); 1410 (1 sh); 2132 (6 sh); 2925 (10); 3005 (3 sh).

In addition, 45 g of $(CH_3)_3SnCl$ was isolated, b.p. 152-153° (755 mm); m.p. 34°. Yield 67%. Literature data [10]: b.p. 152-154° (760 mm); m.p. 37°. In the residue, 7 g with m.p. ~ 300°.

* A reaction is observed between $GeBr_4$ and R_4Sn, but it is not possible to isolate individual compounds in this case.

B. To 25 g of $(CH_3)_4Sn$ was added 30 g of $HGeCl_3$. This evolved 1200 ml of gas consisting of 90.5% CH_4 and 9.5% hydrogen. Fractionation on a column gave 16 g of $(CH_3)_3SnCl$, b.p. 150° (760); m.p. 37°, yield 57%; 8 g of $(CH_3)_2SnCl_2$

IR spectrum of $C_2H_5GeHCl_2$, transmission vs. ν

Figure 3: IR spectrum of $C_2H_5GeHCl_2$, transmission vs. ν

IR spectrum of $(CH_3)_2GeC_2H_5H$, transmission vs. ν

Figure 4: IR spectrum of $(CH_3)_2GeC_2H_5H$, transmission vs. ν

with b.p. 190° (760); m.p. 105–107°, yield 21.4%; and 15 g of a mixture (chromatographic and spectral analyses) of $CH_3GeCl_3 + CH_3GeHCl_2$ with b.p. 100–110° (760), yield 55%.

Ethyldichloromethylgermane $C_2H_6Cl_2GeCH_3$ (II). Through 10 g of I, while boiling, ethylene was passed for 6 h. Fractionation on a column gave 10.5 g of II, yield 90%, b.p. 149° (750 mm); n_D^{20} 1.4600; d_4^{20} 1.4381, MR_D 36.13; MR_D calculated 36.00; for the IR spectrum, see Fig. 2.

$C_3H_8GeCl_2$. Found, %: Cl 37.70, 37.65
Calculated, %: Cl 37.80

Raman spectrum of II ($\Delta\nu$, cm^{-1}):

152 (2); 185 (2sh); 306 (1); 351 (0); 384 (10); 400 (3sh); 578 (9sh); 633 (3); 979 (1sh); 1027 (1sh); 1120 (0); 1161 (1sh); 1235 (2sh); 1261 (0); 1306 (0); 1346 (0); 1426 (1); 1461 (1); 2877 (2); 2917 (10); 2929 (1); 2667 (1); 3004 (1sh).

Ethyltrimethylgermane $C_2H_5Ge(CH_3)_3$ (III). To CH_3MgCl, prepared from 3 g of magnesium, was added 7 g of II. After the usual treatments, 4 g of III was obtained, b.p. 78° (760 mm); n_D^{20} 1.4080; yield 74%. The Raman spectrum of III completely coincides with the literature spectrum [11].

Fig. 3

Fig. 4

Ethyldichlorogermane $C_2H_5GeHCl_2$ (IV). A. To 80 g of $(C_2H_5)_4Sn$ was added 95 g of $HGeCl_3$ in 150 ml of ether. Heating occurred, and 1700 ml of gas was evolved, consisting of 15% C_2H_6 and 85% H_2. Fractionation on a column gave 30 g of IV with b.p. 129.5° (743); n_D^{20} 1.4750, d_4^{20} 1.5358; MR_D 31.82; MR_D calculated 31.98; yield 45%. For the IR spectrum, see Fig. 3.

Found, %: C 13.55, 13.92; H 3.30, 3.46; Cl 41.20, 41.18; Ge 42.10, 42.00
$C_2H_6GeCl_2$. Calculated, %: C 13.83; H 3.48; Cl 40.85; Ge 41.82

Raman spectrum of IV ($\Delta\nu$, cm^{-1}):

155 (3sh); 174 (1); 279 (1sh); 310 (1); 395 (10b); 409 (1split); 523 (0); 537 (0); 581 (6); 597 (6); 656 (1sh); 681 (0); 709 (1sh); 732 (0); 749 (1); 974 (1sh); 1030 (2); 1118 (0); 1180 (0); 1234 (4); 1290 (0); 1306 (0); 1384 (0); 1421 (0); 1461 (2); 2120 (7b); 2877 (3); 2918 (4sh); 2935 (3); 2968 (2sh).

In addition to IV, 25 g of $C_2H_5GeCl_3$ (V) was isolated with b.p. 141° (743); n_D^{20} 1.4740, d_4^{20} 1.6028; yield 31%, and 80 g of $(C_2H_5)_3SnCl$ with b.p. 210–212°, m.p. 15°. The Raman spectrum of V completely coincides with the literature spectrum [12].

B. To 60 g of $Pb(C_2H_5)_4$, cooled to 0°, 65 g of $HGeCl_3$ etherate was slowly added. Heating occurred and a precipitate of $ClPb(C_2H_5)_3$ separated. The precipitated solid was filtered off, and the filtrate was distilled. This gave 25 g of IV with b.p. 130° (747 mm), n_D^{20} 1.4740, yield 80.5%, and 55 g of Cl—$Pb(C_2H_5)_3$, yield 90%. The IV obtained contains up to 20% V (chromatogram).

Dimethylethylgermane $C_2H_5GeH(CH_3)_2$ (VI). To 8 g of IV, with cooling, was added CH_3MgCl, prepared from 3 g of Mg in ether. After the usual work-up, distillation on a column gave 4.5 g of VI with b.p. 62° (755 mm); n_D^{20} 1.4078; d_4^{20} 1.0077; MR_D 32.48; MR_D, calculated 32.26; yield 74%. For the IR spectrum see Fig. 4.

$C_4H_{12}Ge$.	Found, %: C 35.81, 36.26; H 8.90, 9.08; Ge 54.06
	Calculated, %: C 36.20; H 9.12; Ge 54.69

Ethyltrichlorogermane $C_2H_5GeCl_3$ (V). To 40 g of $(C_2H_5)_4Pb$ was added 26.6 g of $GeCl_4$. The warmed mixture was left overnight, then heated at ~ 100° for one hour, and V was distilled from it under vacuum. Repeated distillation on a column gave 24 g of V, yield 90%; b.p. 140° (750 mm), n_D^{20} 1.4743. The solid residue, 40 g, consists of $(C_2H_5)_3PbCl$, yield 94%.

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Note: Figure translations are in progress. See original paper for figures.