THE REACTION OF TRICHLOROGERMANE WITH CONJUGATED DIENES

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Fig. 1

Figure 1: Fig. 1

Abstract

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THE REACTION OF TRICHLOROGERMANE WITH CONJUGATED DIENES

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Trichlorogermane ($HGeCl_3$) adds exothermically to the multiple bonds of practically any unsaturated compounds without any catalysts or activators ([1]).

At the same time, the addition of trichlorosilane ($HSiCl_3$) to these same compounds proceeds exclusively in the presence either of catalysts (Pt, H_2PtCl_6, etc.) or of radical activators. Nevertheless, the structures of the compounds obtained in these two cases do not differ in principle.

The addition of trichlorosilane to butadiene and other conjugated dienes proceeds exclusively in the 1,4-position ([2,3])

$$CH_2{=}CH{-}CH{=}CH_2 + HSiCl_3 \xrightarrow{Pt/C} CH_3CH{=}CHCH_2SiCl_3$$

Fig. 1

Therefore, the reaction of butadiene with trichlorogermane proved unexpected: it led to a narrow fraction which, on the basis of elemental and spectral analyses, consisted of a mixture of two compounds, one of which contained two chlorine atoms*. After methylation of this mixture, gas-liquid chromatography showed the presence likewise of two compounds. These compounds (III) and (IV) were successfully separated on a rectification column, with mutual admixture not exceeding 1% (chromatogram)

$$CH_2{=}CHCH{=}CH_2 \xrightarrow{HGeCl_3} Cl_3GeCH_2CH{=}CHCH_3 + Cl_2Ge\begin{matrix}CH_2{-}CH\\ \|\\ CH_2{-}CH\end{matrix} \xrightarrow{CH_3MgCl} \longrightarrow$$

$$\longrightarrow (CH_3)_3GeCH_2CH{=}CHCH_3 + (CH_3)_2Ge\begin{matrix}CH_2{-}CH\\ \|\\ CH_2{-}CH\end{matrix}$$

(I) (II)

(III) (IV)

The ratio between compounds I and II varies from experiment to experiment within the range from 1 : 3 to 1 : 9. In addition to elemental analysis, the structures of compounds I, II, III, and IV are firmly established by comparison of their Raman and IR spectra with the spectra of known silicon compounds analogous in structure ([7,8]). (The spectral analysis was carried out by L. A. Leites, the UV spectrum was taken by V. A. Petukhov (Fig. 1), and the NMR spectrum by M. L. Khidekel.)

The nuclear magnetic resonance spectra of compounds II and IV (see Fig. 2) reveal only two kinds of protons for compound II and three kinds for IV, which also confirms the structures of these compounds.

Isoprene also reacts with trichlorogermane with formation of hetero-

* For a preliminary communication, see ([4]).

cyclic compound V:

$$CH_2=C(CH_3)-CH=CH_2 \xrightarrow{HGeCl_3} \begin{array}{c} CH=C-CH_3 \\ \quad | \quad | \\ CH_2 \quad CH_2 \\ \quad \backslash \quad / \\ \quad\quad Ge \\ \quad / \quad \backslash \\ Cl \quad Cl \end{array} \text{(V)} + Cl_3GeCH_2C(CH_3)=CHCH_3 \text{ (VI)} \xrightarrow{CH_3MgCl}$$

$$\longrightarrow \begin{array}{c} CH=C-CH_3 \\ \quad | \quad | \\ CH_2 \quad CH_2 \\ \quad \backslash \quad / \\ \quad\quad Ge \\ \quad / \quad \backslash \\ CH_3 \quad CH_3 \end{array} \text{(VII)} + (CH_3)_3GeCH_2C(CH_3)=CHCH_3 \text{ (VIII)}$$

The ratio between compounds V and VI is approximately 1 : 3. However, piperylene under these same conditions forms exclusively linear addition products:

$$CH_3CH=CHCH=CH_2 \xrightarrow{HGeCl_3} CH_3CH_2CH=CHCH_2GeCl_3 + CH_3CH=CHCH(CH_3)GeCl_3 \longrightarrow$$

$\xrightarrow{CH_3MgCl}$ $CH_3CH_2CH = CHCH_2Ge(CH_3)_3$ (IX)+$CH_3CH = CHCH(CH_3)Ge(CH_3)_3$. (X)

The structure of compounds V–X was determined on the basis of spectral analysis. The formation of heterocyclic compounds II and V can be explained as 1,4-addition to butadiene and isoprene of dichlorogermanium ($GeCl_2$), formed according to the scheme:

$$HGeCl_3 \rightleftarrows H^+[GeCl_3]^- \rightleftarrows HCl + GeCl_2$$

This assumption is supported by the fact that the spectrum of $HGeCl_3$, similar to the spectrum of $HSiCl_3$, changes sharply in hydrochloric acid solution and becomes identical to the spectrum of a solution of $GeCl_2$ in hydrochloric acid and similar to the spectrum of $H^+[SnCl_3]^-$ (5).

Probably, the addition of $GeCl_2$ leads to the formation of a stable compound only in the case of butadiene, since for other unsaturated compounds the unstable three-membered rings that are formed are immediately cleaved by excess HCl, which is always present in the reaction medium:

$$> C = C < \longrightarrow \overset{HGeCl_3 \rightleftarrows HCl + GeCl_2}{\underset{\diagdown\,\diagup}{\overset{C-C}{Ge}}\;\underset{Cl\;Cl}{}} \longrightarrow \overset{HCl}{> CH - C(GeCl_3) <}$$

Only in the case of acetylenic compounds, apparently, can the formation of stable three-membered addition products be expected:

$$-C \equiv C - + HGeCl_3 \rightarrow \overset{C=C}{\underset{Cl\;Cl}{\overset{\diagdown\,\diagup}{Ge}}} + HCl$$

Vol' pin (6) recently suggested that such compounds are stable aromatic systems formed under vigorous conditions in the reaction of acetylene or tolane with GeJ_2.

However, in the reaction of acetylene with trichlorogermane in hexane medium, we were unable to detect the expected three-membered compounds. The reaction proceeded according to the usual scheme:

$$HC \equiv CH + HGeCl_3 \rightarrow CH_2 = CHGeCl_3\ (13\%) + Cl_3GeCH_2CH_2GeCl_3\ (18\%)$$

Carrying out this reaction in ether leads to the formation of a polymer and $Cl_3GeCH = CHGeCl_3$. On the basis of spectral analysis, the structure of this polymer is probably as follows

$$\left[\begin{array}{c} \quad\quad Cl \quad\quad \\ -CH = \overset{|}{C}HGe- \\ \quad\quad Cl \quad\quad \end{array}\right]_n$$

We have so far been unable to add GeJ_2 to butadiene. At -10° no interaction is observed, while at 200° only polymer is formed.

Experimental Part

Interaction of trichlorogermane with butadiene. To 34 g of butadiene, cooled with dry ice to -55 to -60°, 53 g of trichlorogermane was added with stirring. The cooling was then removed, and within an hour the contents of the flask reached room temperature. After heating for one hour at 60°, the contents of the flask were distilled. Obtained were 11 g of $GeCl_4$ and 33 g of a fraction with b.p. 66–67° (17 mm), n_D^{20} 1.5160; d_4^{20} 1.5594.

Fig. 2

Found, %: C 23.76, 23.85; H 3.27, 3.05; Ge 35.09, 34.65
Cl 38.34; 38.17

$C_4H_6GeCl_2$. Calculated, %: C 24.31; H 3.06; Ge 36.74; Cl 35.89
$C_4H_7GeCl_3$. Calculated, %: C 20.52; H 3.01; Ge 31.06; Cl 45.44

Raman spectrum ($\Delta\nu$, cm^{-1}): 155(5), 174(3), 199(1 sh), 303(2 sh), 335(10 sh), 386(3 r), 404(5), 431(4 sh), 506(1), 561(6), 617(0), 634(1 sh), 668(3 sh), 742(0), 766(1), 796(1 sh), 906(6), 959(1), 1074(0), 1107(4 sh), 1160(2 sh), 1173(6 sh), 1212(5), 1269(2 sh), 1315(2), 1401(5), 1456(2), 1609(6), 1662(3), 1669(5), 2926(8 sh), 2968(3 sh), 3036(4).

The lines 1662 and 1669 correspond to compound I, and the frequency 1609 to compound II. In organosilicon compounds of analogous structure, the same frequencies are observed ([7],[8]). On the basis of the relative intensity of these lines, as well as elemental analysis, it may be concluded that the fraction obtained contains $\sim 70\%$ of compound II and $\sim 30\%$ of I.

In other experiments, the amount of compound I in this fraction (n_D^{20} 1.5200) sometimes reaches 90%. On methylation with CH_3MgCl, these fractions give a narrow fraction with b.p. 122–124° (761 mm), n_D^{20} 1.4655–1.4685.

On rectification on a 30-theoretical-plate column of the final fractions collected from several experiments, compound III was obtained with b.p. 126.8° (760 mm), n_D^{20} 1.4428; d_4^{20} 0.9907: MR_D found 46.22; calculated 45.78.

Fig. 3

Figure 2: Fig. 3

The Raman spectrum of this compound is analogous to the spectrum of $(CH_3)_3SiCH_2CH = CHCH_3$ ([7]) and completely coincides with the spectrum of $-(CH_3)_3GeCH_2CH = CHCH_3$, obtained by another route*. In addition, compound IV was isolated, which after repeated rectifications has the following properties: b.p. 121° (750 mm); n_D^{20} 1.4723; d_4^{20} 1.1328; MR_D found 38.77; calculated 39.07.

Found, %: C 45.87, 45.92; H 7.69, 7.65; Ge 46.16, 46.25

$C_6H_{12}Ge$. Calculated, %: C 45.97; H 7.72; Ge 46.30

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

$$(CH_3)_2Ge\begin{matrix} CH_2-CH \\ \| \\ CH_2-CH \end{matrix}$$

154 (1), 175 (2 sh), 190 (2 sh), 354 (6), 379 (1), 539 (4), 567 (1), 580 (10), 605 (3), 654 (3 sh), 912 (3), 1102 (3), 1146 (1 sh), 1207 (3), 1245 (2 sh), 1402 (3 sh), 1610 (7), 2912 (100 sh), 2980 (3), 3020 (3 sh).

* The communication will be published in *Izv. AN SSSR, Chemical Series*.

IR spectrum, see Fig. 3.

Reaction of trichlorogermane with isoprene. To 50 g of isoprene, cooled to −55°, 39 g of $HGeCl_3$ was added with stirring. After the contents of the flask had reached room temperature, distillation gave 35 g of isoprene, 17 g of $GeCl_4$, and 19 g of a fraction with b.p. 73.5-76.5° (14 mm); n_D^{20} 1.5125; d_4^{20} 1.4678.

Found, %: Ge 32.23, 32.25; Cl 37.87, 38.28
$C_5H_8GeCl_2$. Calculated, %: Ge 34.30; Cl 33.51
$C_5H_9GeCl_3$. Calculated, %: Ge 29.27; Cl 42.87

On the basis of the intensities of the IR-spectrum line at 1635 cm^{-1}, assigned to compound V, and the line at 1668 cm^{-1}, assigned to compound VI, their ratio is approximately equal to 1 : 3.

Fig. 3

After methylation of the fraction obtained, a fraction was isolated with b.p. 78-81° (91 mm), n_D^{20} 1.4643. In the IR spectrum of this fraction, in the frequency region corresponding to vibration of the double bond C=C, two lines are observed –1640 (2), assigned to VII, and 1666 (6), assigned to VIII.

On the basis of analysis of the chromatogram and the IR spectrum, this fraction contains up to 30% of the heterocyclic compound VII.

Reaction of trichlorogermane with piperylene. To 30 g of piperylene, cooled to −60°, 41 g of trichlorogermane was added with stirring. After standing for one hour, the contents of the flask were distilled. This gave 26 g of piperylene, 10 g of $GeCl_4$, and 15 g of a fraction with b.p. 73.5° (13 mm), n_D^{20} 1.5035; d_4^{20} 1.4306; MR_D found 51.31; calculated 50.01.

Found, %: Ge 29.60, 29.50; Cl 42.84, 42.51
$C_5H_9GeCl_3$. Calculated, %: Ge 29.26; Cl 42.89

After methylation of the fraction obtained, a mixture of substances IX–X was isolated in 89% yield, with b.p. 79–79.5° (90 mm); n_D^{20} 1.4500; d_4^{20} 0.9884; MR_D found 50.90; calculated 50.63.

Found, %: C 51.45, 51.59; H 9.72, 9.93; Ge 38.70, 39.00
$C_8H_{18}Ge$. Calculated, %: C 51.43; H 9.71; Ge 38.86

IR spectrum ($\Delta\nu$, cm^{-1}) 148 (1), 194 (2sh), 254 (0), 303 (1sh), 440 (1), 461 (1), 507 (1), 545 (2), 566 (10), 597 (8), 791 (1), 857 (0), 943 (1), 1037 (1sh), 1089 (0sh), 1150 (5sh), 1238 (1sh), 1304 (1), 1373 (1), 1451 (2), 1665 (10), 2869 (2sh), 2914 (5sh), 2976 (2sh).

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