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Abstract

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ADDITION OF $HGeCl_3$ TO HALOGEN-SUBSTITUTED ETHYLENES

DEHYDROCHLORINATION OF α,β-DICHLOROETHYLTRICHLOROGERMA

In a previous work (1) we established that trichlorogermane ($HGeCl_3$), unlike trichlorosilane ($HSiCl_3$), adds vigorously at room temperature to a variety of olefins and their derivatives without catalysts.

In the present investigation we studied the addition of $HGeCl_3$ to various chlorinated ethylenes (from $ClCH = CH_2$ to $Cl_2C = CCl_2$), to which the addition of $HSiCl_3$ is practically almost impossible. For example, the addition of methyldichlorosilane to vinyl chloride can be effected only in an autoclave at 160° and in the presence of a catalyst—platinum on carbon (2). However, even under these conditions the yield of α-chloroethylmethyldichlorosilane does not exceed 7% of theory

$$ClCH{=}CH_2 + HSiCH_3Cl_2 \xrightarrow{Pt/C} CH_3ClCHSiCl_2CH_3.$$

With still lower yields, despite the use of initiators and severe experimental conditions, addition of $HSiCl_3$ and CH_3Cl_2SiH to dichloroethylene, trichloroethylene, and tetrachloroethylene occurs (3,4). Meanwhile, trichlorogermane, as we have established in the present investigation, adds readily to the abovementioned chloroethylenes without any catalysts.

For example, when vinyl chloride is bubbled through trichlorogermane, the addition proceeds with self-heating, which is also observed when trichlorogermane is mixed with dichloroethylene, trichloroethylene, and tetrachloroethylene. In the last case, however, the self-heating is barely noticeable.

The most unexpected result, however, is that in the interaction of vinyl chloride and trichlorogermane, not α-, but β-chloroethyltrichlorogermane was formed:

$$ClCH{=}CH_2 + HGeCl_3 \to ClCH_2CH_2GeCl_3 \ (33\%).$$

In connection with this circumstance, we investigated the order of addition of $HSiCl_3$ to vinyl chloride. It turned out that $HSiCl_3$, despite the use of such a vigorous catalyst as chloroplatinic acid, just like CH_3Cl_2SiH, adds to vinyl chloride only in an autoclave, forming α-chloroethyltrichlorosilane in only 6% yield

$$ClCH{=}CH_2 + HSiCl_3 \rightarrow Cl_3SiCHClCH_3.$$

Thus it was established that trichlorogermane adds to vinyl chloride in a different order than trichlorosilane, which is probably connected with a different mechanism of the addition reaction of the two reagents. Cleavage of HCl from α,β-dichloroethyltrichlorogermane was carried out by us both with quinoline and with aluminum chloride.

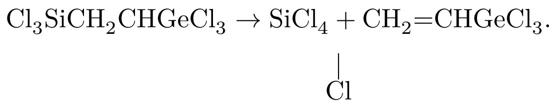
Previously (^{5,6}), a similar elimination by both reagents was studied using the example of an analogous organosilicon compound ($Cl_3SiCHClCH_2Cl$). It proved that in the present case as well the regularities noted earlier are preserved, i.e., quinoline eliminates the β-chlorine atom, whereas aluminum chloride eliminates the α-chlorine atom.

$$Cl_3GeCHClCH_2Cl \begin{array}{l} \xrightarrow{AlCl_3} Cl_3GeCH{=}CHCl\ (80\%) \\ \xrightarrow[\text{Quinoline}]{} Cl_3GeCCl{=}CH_2\ (42\%). \end{array}$$

The mechanism of dehydrochlorination by aluminum chloride was at one time explained (^{7,8}) for α,β-dichloroalkyltrichlorosilanes by rearrangement of the β-carbonium ion formed, with migration of the trichlorosilyl group from the α-carbon atom to the β-carbon atom. It is probable that in the present case the same rearrangement mechanism occurs:

$$Cl_3GeCHClCH_2Cl \xrightarrow{AlCl_3} [Cl_3GeCHClCH_2^{\oplus} \rightarrow Cl^{\oplus}CH{-}CH_2GeCl_3] \rightarrow Cl_3GeCH{=}CHCl.$$

An attempt to eliminate HCl with quinoline from $Cl_3SiCH_2CHClGeCl_3$ led only to β-cleavage:



$$\underset{\displaystyle Cl}{Cl_3SiCH_2CHGeCl_3} \rightarrow SiCl_4 + CH_2{=}CHGeCl_3.$$

The α- and β-chlorovinyltrichlorogermanes possess curious properties. α-Chlorovinyltrichlorogermane, after several hours, spontaneously polymerized into an opaque, solid substance of milky color. As is known, α-chloro(or bromo)vinyltrichlorosilanes behave analogously (^{6,9}).

β-Chlorovinyltrichlorogermane, like its silicon analogue ([5,9,10]), on titration with a 0.1 *N* alkali solution saponifies all three chlorine atoms.

Table 1

Compound	B.p., °C/mm	Yield, %	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.
$ClCH_2CH_2GeCl_3$ *	75/15	32.5	1.5092	1.7637	41.06	40.35
$ClCH_2{-}ClCHGeCl_3$	88/12	62	1.5240	1.8390	46.07	45.20
$Cl_3C_2H_2GeCl_3$	92/9	55.3	1.5341	1.9000	50.95	50.028
$CHCl_2{-}CCl_2GeCl_3$	123/25	48	1.5378	1.9243	56.11	54.862
$CH_2{=}CClGeCl_3$	151	41.6	1.5002	–	–	–
$CHCl{=}CHGeCl_3$	164–165	80	1.5139	1.7690	40.92	40.88

* Literature data ([12,13]): b.p. 188° (756), n_D^{20} 1.5094; d_4^{20} 1.7587.

of chlorine. Thus, here the cleavage with liberation of acetylene, which we expected and which is characteristic of quasi-complex compounds ([11]) (for example: $Cl_3PbCH{=}CHCl$ and $Cl_3SnCH{=}CHCl$), did not take place. The properties of the 5 germanium compounds synthesized for the first time are presented in Table 1.

Experimental Part

β-Chloroethyltrichlorogermane $ClCH_2CH_2GeCl_3$. A stream of vinyl chloride was passed for one hour through 15 g of trichlorogermane ([1]). At first, strong heating was observed. After cooling, the contents of the flask were heated on a hot plate at 80° for another hour. Vacuum ⋯

By distillation, 6.5 g of β-chloroethyltrichlorogermane was isolated. B.p. 75° (15 mm). Yield 32.5%. The Raman spectra and the infrared spectrum completely coincide with those for β-chloroethyltrichlorogermane obtained earlier by another route [12,13]. Titration with 0.1 *N* NaOH, using phenolphthalein, of a sample of β-chloroethyltrichlorogermane in ~70% ethanol leads exactly to saponification of four chlorine atoms, but only over the course of a day.

α,β-Dichloroethyltrichlorogermane $ClCH_2CHClGeCl_3$. To 30 g of trans-dichloroethylene, with stirring, 54 g of trichlorogermane was added at such a rate that the temperature of the liquid did not rise above ~80°. The contents of the flask were then heated for half an hour at 80° and distilled under vacuum. 51 g of α,β-dichloroethyltrichlorogermane was obtained, b.p. 88° (12 mm). Yield 62%. With 0.1 *N* alkali, exactly four chlorine atoms were titrated.

Trichloroethyltrichlorogermane $Cl_3GeC_2H_2Cl_3$. Under the conditions of the preceding experiment, from 20 g of trichloroethylene and 27 g of trichlorogermane, 26 g of trichloroethyltrichlorogermane was obtained, b.p. 92° (9 mm).

Yield 55.3%. Titration with 0.1 *N* alkali leads to saponification of 4 chlorine atoms.

Tetrachloroethyltrichlorogermane $Cl_2CHCl_2CGeCl_3$. After mixing 20 g of tetrachloroethylene and 18 g of trichlorogermane, heating of the contents of the flask at 80-90° was continued for 2 h. 16.5 g of tetrachloroethyltrichlorogermane was obtained, b.p. 123° (25 mm). Yield 48%. With 0.1 *N* alkali, four chlorine atoms were titrated.

α-Chlorovinyltrichlorogermane $CH_2 = CClGeCl_3$. A mixture consisting of 27.7 g of α,β-dichloroethyltrichlorogermane and 13 g of quinoline was slowly distilled from a Favorskii flask up to ~200°. By redistillation of the condensate, 10 g of α-chlorovinyltrichlorogermane was isolated, b.p. 151° (753 mm). Yield 41.5%. Only three chlorine atoms were titrated.

β-Chlorovinyltrichlorogermane $ClCH = CHGeCl_3$. 20 g of α,β-dichloroethyltrichlorogermane with 0.2 g of aluminum chloride was slowly distilled from a Favorskii flask. By redistillation, 16 g of β-chlorovinyltrichlorogermane was isolated, b.p. 164–165°. Yield 80%. With 0.1 *N* alkali, exactly three chlorine atoms were titrated.

α-Chloroethyltrichlorosilane $CH_3ClCHSiCl_3$. In a 250-ml autoclave in a glass vessel were placed 68 g of $HSiCl_3$, 32 g of vinyl chloride, and 0.5 ml of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol (0.1 *N* solution). Heating of the autoclave at 120° was continued for 4 h. On distillation, 19 g of ethyltrichlorosilane was isolated (b.p. 98-103°), whose Raman spectrum completely coincided with that reported in the literature. Yield 20% of theory. From the fraction with b.p. 136–139°, 6 g was obtained. Yield 6%. The Raman spectrum of this fraction corresponded to α-chloroethyltrichlorosilane; with 0.1 *N* alkali, three chlorine atoms were titrated. Ethyltrichlorosilane was apparently formed as a result of the following reactions:
$Cl_3SiH + ClCH = CH_2 \rightarrow Cl_4Si + CH_2 = CH_2$;
$CH_2 = CH_2 + HSiCl_3 \rightarrow C_2H_5SiCl_3$. The spectra were recorded by L. A. Leites.

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