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Abstract

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PROPERTIES OF 1,1-DICHLORO- AND 1,1-DIMETHYLGERMANACYCLOPENTENES-3

Recently Mironov and Gar (^1) found that the reaction of trichlorogermane with divinyl in the absence of solvents leads to $CH_3CH{=}CHCH_2GeCl_3$ (I) and to the unsaturated germanium heterocycle—1,1-dichloro-1-germanacyclopentene-3 (II). The authors explained the formation of II by 1,4-addition to divinyl of $GeCl_2$, formed according to the scheme:

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

In connection with our work in the field of the chemistry of silicon and germanium analogs of carbenes (^2, ^3), we continued the study of this reaction. In particular, we investigated in greater detail the physical and chemical properties of the now accessible 1,1-dichloro- and 1,1-dimethylgermanacyclopentenes-3.

It turned out that, upon interaction of an excess of divinyl with $HGeCl_3$ in the temperature range from −80 to −50°, along with compounds I and II (overall yield, in agreement with (^1), 60–80% of theory, content of II 80–95%), higher-molecular organogermanium compounds are also formed. Thus we isolated a dimeric oligomer (yield 5%), most closely corresponding to the structure $H(-CH_2CH{=}CHCH_2GeCl_2-)_2Cl$ (III), as well as liquid and solid polymers (weight ratio 10:1), consisting predominantly of the same elementary units $-CH_2CH{=}CHCH_2GeCl_2-$(overall yield 15–30%, molecular weight >1500).

The obtained monomeric, dimeric, and polymeric organogermanium chlorides are readily alkylated (arylated) under the action of an excess of RMgX, forming the corresponding germanium-hydrocarbon compounds. In particular, methylation of II leads to 1,1-dimethyl-1-germanacyclopentene-3 (IV) in 80–90% yield. The identical heterocycle IV was also obtained by us, although in yields of only 2–5%, by two organometallic routes: 1) from divinyl, $(CH_3)_2GeCl_2$, and lithium under the conditions of our previous work (^2, ^3); 2) from 1,4-dibromobutene-2, $(CH_3)_2GeCl_2$, and lithium in diethyl ether at 10°.

In accordance with the structure assigned to II, its NMR spectrum contains only two singlet signals (τ 7.93 and 3.87 ppm), which correspond to two types of protons present in a ratio of 2:1. The spectrum of the methylated ring IV is

Fig. 1. NMR spectra of the methylated dimer III and of the liquid polymer obtained from $HGeCl_3$ and divinyl

Figure 1: Fig. 1. NMR spectra of the methylated dimer III and of the liquid polymer obtained from $HGeCl_3$ and divinyl

identical to the NMR spectrum of this compound reported by the authors (^1) (τ 9.69, 8.57, and 4.11 ppm) and indicates the presence in this compound of three types of protons in an approximate ratio of 3:2:1. It should also be noted that the spectrum of IV is highly similar to the spectrum of its silicon analog—1,1-dimethylsilacyclopentene-3 (τ 9.82, 8.69, and 4.12 ppm).

Under conditions of quantitative hydrogenation in a "duck"apparatus over Raney Ni in ethanol at 20°, IV adds exactly an equimolar amount of hydrogen, being converted in 100% yield into 1,1-dimethyl-1-germanacyclopentane. Like acyclic allylsilanes (^4), IV very readily, at 0-5°, adds electrophilic dichlorocarbene, formed from $HCCl_3$ and tert-C_4H_9OK in *n*-hexane (adduct yield 60-70%).

II, analogously to $(CH_3)_2GeCl_2$ (^3), readily reacts with metallic lithium in tetrahydrofuran (THF) at 0-20°, forming mainly a polymer, insoluble in water and organic solvents, with mp 440° (decomp.). The formation of an organogermanium polymer, outwardly very similar to polydimethylgermylene $[(CH_3)_2Ge<]_n$ (^3), probably also proceeds with the intermediate participation of the corresponding germanium carbene. However, this polymer, unlike polydimethylgermylene (^3), contains, according to elemental analysis and IR spectra, considerably-

amounts of oxygen (1.5-2 atoms per Ge atom) in the form of Ge—O and, possibly, carbonyl groups. Oxidation of this polymer apparently occurs when it is washed free of lithium and LiCl with a mixture of CH_3OH and CH_3COOH and water in air.

We next investigated the catalytic dehydrogenation of IV. As was to be expected, this unsaturated heterocycle is dehydrogenated considerably more readily and more completely than substituted sila- and germacyclopentanes ([5], [6]). Thus, at 450° over $Al_2O_3 \cdot Cr_2O_3 \cdot K_2O$ (84 : 14 : 2) or at 350-400° over 10% Pt/C, the conversion of IV is ~60%, with an H_2 content in the gaseous dehydrogenation products of 96-98%, whereas 1,1-dimethylgermacyclopentane is not changed at all under these conditions. However, we were unable to isolate 1,1-dimethylgermacyclopentadiene-2,4 in pure form from the dehydrogenation product because of its extremely great tendency to undergo condensation, probably mainly of the diene-condensation type. In the NMR spectra of the liquid products of dehydrogenation of IV (fraction with b.p. 26-37° at 0.6 mm, n_D^{20} 1.4991), intense signals were found at 9.86 and 9.68 ppm (CH_3 groups at Ge atoms situated in different environments) and considerably weaker signals at 8.36 and 7.66 (respectively CH_2 and CH groups at Ge), as well as 4.12 and 2.91 ppm.

Fig. 2. IR spectra of methylated dimer III (a) and of a liquid polymer obtained from IV and AlBr3 (b)

Figure 2: Fig. 2. IR spectra of methylated dimer III (a) and of a liquid polymer obtained from IV and AlBr3 (b)

Fig. 1. NMR spectra of the methylated dimer III and of the liquid polymer obtained from $HGeCl_3$ and divinyl.

II and IV very readily polymerize with ring opening, thereby forming polymers which, in appearance and in molecular and proton spectra, are similar to those obtained directly from divinyl and $HGeCl_3$. Thus, II polymerizes on boiling under atmospheric pressure, and IV when heated with 2-3 mol.% $AlBr_3$ under the conditions ([7]); in the latter case at 100-120° polymerization occurs almost instantaneously:

$$\text{II} \xrightarrow{t} [-CH_2CH{=}CHCH_2GeCl_2-]_n \rightarrow$$

$$CH_3MgBr \longrightarrow [-CH_2CH{=}CHCH_2Ge(CH_3)_2-]_n \xleftarrow[AlBr_3]{t} \text{IV}$$

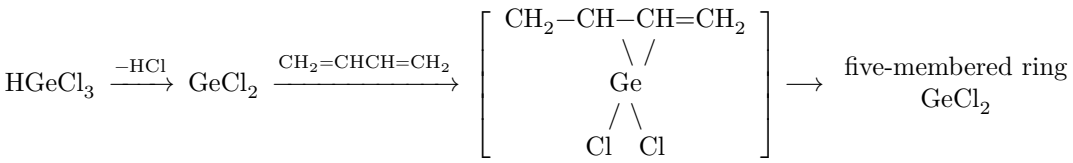
The structure of the dimeric and polymeric oligomers formed from II and IV or directly from divinyl and $HGeCl_3$, as compounds of the general type $X[-CH_2CH{=}CHCH_2GeR_2-]Y$ (R = Cl or CH_3, X and Y = H and Cl or CH_3), is proved by the considerable similarity of their proton spectra to the spectra of the corresponding monomeric heterocycles II and IV. In particular, the NMR spectra of the methylated dimer III and of the polymers (Fig. 1), being very similar to one another, indicate the presence in these compounds, as in ring IV, of three principal types of protons corresponding to the unit $CH_2CH{=}CHCH_2Ge(CH_3)_2$ (τ 9.83-9.9; doublet 8.47-8.49 and 8.30-8.36; 4.72-4.75 ppm). At the same time, the proton signals of the product

methylation of dimer III are shifted, it is true, only very slightly, toward the weaker field, i.e., somewhat closer to the signals of IV. Similarly, the IR spectrum of the methylated dimer III (Fig. 2a) essentially coincides completely with the IR spectra of the methylated polymers formed directly from $HGeCl_3$ and divinyl or upon boiling II. The IR spectra of the polymers obtained by the action of $AlBr_3$ on IV (Fig. 2b) or from divinyl, $(CH_3)_2GeCl_2$, and Li in THF also contain all the lines of the spectra of the above-mentioned dimers and polymers, along with several additional weak lines (in particular, 3070 and 1640 cm^{-1}, characteristic of a terminal methylene group).

Fig. 2. IR spectra of methylated dimer III (a) and of the liquid polymer obtained from IV and $AlBr_3$ (b)

The mechanism of formation of the above-mentioned organogermanium compounds from $HGeCl_3$ and divinyl, apparently, may indeed be connected with

the intermediate participation in this reaction of $GeCl_2$, the germanium analogue of dichlorocarbene. In this case the first step is probably the 1,2-addition of $GeCl_2$ to divinyl with formation of the unstable polarized three-membered heterocycle V, which then undergoes an intramolecular ionic rearrangement into the stable five-membered ring II:



(V) (II)

However, a purely ionic mechanism for the formation of II is also not excluded. The formation of dimeric and polymeric products corresponding to 1,4-addition of $GeCl_2$ to divinyl is apparently also connected with the intermediate participation of V or of the corresponding biion, since the heterocycle II itself does not polymerize under these conditions either with hydrogen chloride or with trichlorogermane. Along with this, as noted above, so-called normal (probably electrophilic) addition of $HGeCl_3$ to divinyl also takes place here, with formation of butenyltrichlorogermane, which according to (1) has structure I. In this connection, in accordance with the proposed mechanism, the use of polar solvents, for example simple ethers, should facilitate both the generation of $GeCl_2$ from $HGeCl_3$ (8) and the conversion of V into II (or polymer). Indeed, when divinyl was passed through an ethereal solution of trichlorogermane (8) at $\sim 20^\circ$, II proved to be, essentially, the only monomeric reaction product (yield $\sim 65\%$ with a yield of I $\sim 1\%$). Under the same conditions, but in an *n*-hexane medium, 21% of I is formed (with a yield of II 41%).

Reaction of $HGeCl_3$ with divinyl. Experiment No. 1.

117 g of a mixture of $HGeCl_3$ and $GeCl_4$ (~2 : 1) was added over 1 h to 193 g of divinyl (−70°, stirring). Distillation gave 48 g of a fraction with b.p. 51-53° (10 mm), n_D^{20} 1.5180, containing, according to titration data, 88.5% II and 11.5% I, and 9 g of dimer III. The residue (16 g) was a liquid viscous polymer (Cl 33.8%; mol. wt. ~1300), readily methylated with an excess of CH_3MgBr in ether to give a liquid germanium-hydrocarbon polymer with a sharp odor, yield 94%, mol. wt. ~1000 (cryoscopically in C_6H_6).

Found, %: C 44.87, 44.81; H 7.95, 8.02; Ge 46.88, 47.10
$(C_6H_{12}Ge)_n$. Calculated, %: C 45.97; H 7.72; Ge 46.30

Experiment No. 2. To a solution of 100 g of divinyl in 50 ml of *n*-hexane, cooled to −60°, 87 g of an azeotropic mixture of $HGeCl_3$ and $GeCl_4$ (~2 : 1) was added with stirring over 70 min. The temperature was then raised to

~20° and stirring was continued for another 1.5 h. This gave 2.2 g of a solid polymer insoluble in hexane and ether (content of hydrolyzable chlorine 32.6%); methylation of it with CH_3MgBr in a C_6H_6-ether mixture led to a very viscous transparent polymer with a sharp odor, mol. wt. ~1500.

From the soluble products, along with 3 g of dimer III and 16 g of liquid polymer, 37 g of a fraction was isolated with b.p. 55–57° (11 mm), n_D^{20} 1.5188, which, according to titration data and also subsequent methylation and chromatography, contained ~90% II. The isolated dimer III, after twofold distillation in vacuo, had b.p. 138–140° (0.4 mm), n_D^{20} 1.5488.

Found, %: Cl 39.5, 40.2
$C_8H_{13}Ge_2Cl_5$. Calculated, %: Cl 41.1

Methylation of the latter gave the corresponding germanium hydrocarbon, b.p. 65–67° (0.2 mm), n_D^{20} 1.4875, d_4^{20} 1.1212.

Found, %: C 47.37, 47.19; H 8.50, 8.59; Ge 43.61, 43.69
$C_{13}H_{28}Ge_2$. Calculated, %: C 47.37; H 8.55; Ge 44.65

Raman spectrum ($\Delta\nu$, cm^{-1}): 149(1), 166(0), 194(1sh), 414(0), 466(1sh), 569(8sh), 601(6), 638(0sh), 703(0), 783(0), 831(0), 1148(8sh), 1184(2), 1212(0), 1238(1sh), 1304(2), 1406(1sh), 1445(0), 1648(10), 1666(1), 2909(3sh), 2931(1), 2975(2sh).

Experiment No. 3. Gaseous divinyl was passed into a mixture of 52 g of $HGeCl_3$ + $GeCl_4$ (~2 : 1) and 60 ml of absolute ether at ~20° until the two layers disappeared (~5 h). This gave ~2 g of dimer, 7 g of liquid polymer, and 24.5 g of a fraction with b.p. 62–64° (15 mm), n_D^{20} 1.5217, containing 98.5% II. Repeated vacuum distillation of the latter on a column gave pure II, b.p. 52° (10 mm), n_D^{20} 1.5223, d_4^{20} 1.5762.

Raman spectrum ($\Delta\nu$, cm^{-1}): 150(4sh), 168(2), 194(0), 296(0sh), 328(10sh), 383(1), 402(2), 422(3sh), 557(3), 665(3sh), 763(0), 788(1), 903(3), 954(0), 1105(2sh), 1157(1), 1170(1), 1211(3), 1273(0), 1393(4), 1605(3), 1666(1sh), 2920(7sh), 2959(2), 3029(1).

Methylation of II gave IV, yield 80–90%, b.p. 119° (743 mm), n_D^{20} 1.4712, d_4^{20} 1.1273. According to ([1]), b.p. 121° (760 mm), n_D^{20} 1.4723, d_4^{20} 1.1328.

The IR and Raman spectra were recorded by L. A. Leites on UR-10 and ISP-51 spectrometers, respectively. The NMR spectra were recorded on a high-resolution (10^{-8}) JNM-3 radio spectrometer at a frequency of 40 MHz at 20°.

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