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## LETTERS TO THE EDITOR

# Reaction of Tetrachlorogermane with Vinylmagnesium Chloride

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Glockling *et al.* [1] reported that the reaction of tetrachlorogermane with vinylmagnesium chloride yielded exclusively the complete vinylation products: tetravinylgermane, hexavinyldigermane, and octavinyltrigermane [1]. We showed that the reaction of a freshly prepared solution of vinylmagnesium chloride in THF (without separation of the precipitate) with a solution of $GeCl_4$ in THF yields a mixture of vinylchlorogermanes of various degrees of vinylation, hexavinyldigermane, and octavinyltrigermane:

$$CH_2{=}CHMgCl + GeCl_4 \longrightarrow \underset{8\%}{(CH_2{=}CH)_2GeCl_2}$$
$$+ \underset{24\%}{(CH_2{=}CH)_3GeCl} + \underset{18\%}{(CH_2{=}CH)_4Ge}$$
$$+ \underset{28\%}{(CH_2{=}CH)_3GeGe(CH{=}CH_2)_3}$$
$$+ \underset{16\%}{(CH_2{=}CH)_3GeGe(CH{=}CH_2)_2Ge(CH{=}CH_2)_3}.$$

Treatment of the mixture of vinylgermanes $[(CH_2{=}CH)_2GeCl_2$, $(CH_2{=}CH)_3GeCl$, $(CH_2{=}CH)_4Ge]$ with vinylmagnesium chloride separated from the precipitate of unchanged magneium yielded exclusively tetravinylgermane. Furthermore, the reaction of germanium tetrachloride with vinylmagnesium chloride separated from the precipitate also yielded exclusively tetravinylgermane:

$$CH_2{=}CHMgCl + GeCl_4 \longrightarrow \underset{88\%}{(CH_2{=}CH)_4Ge}.$$

These results allow the following conclusions. First, pervinylated di- and trigermanes are formed by the reaction of trivinylchlorogermane with magnesium metal remaining in the reaction mixture from synthesis of vinylmagnesium chloride. Second, as the number of vinyl groups at the Ge atom increases, the Ge–Cl bond becomes less active in the reaction wity vinylmagnesium chloride and more active in the reaction with magnesium (formation of organogermylmagnesium chlorides); this trend is more pronounced than for the Si–Cl bond in vinylchlorosilanes [2].

$$(CH_2{=}CH)_3GeCl + Mg \xrightarrow{THF} (CH_2{=}CH)_3GeMgCl,$$
$$(CH_2{=}CH)_3GeMgCl + (CH_2{=}CH)_3GeCl$$
$$\longrightarrow (CH_2{=}CH)_3GeGe(CH{=}CH_2)_3 + MgCl_2,$$
$$2(CH_2{=}CH)_3GeMgCl + (CH_2{=}CH)_2GeCl_2$$
$$\rightarrow (CH_2{=}CH)_3GeGe(CH{=}CH_2)_2Ge(CH{=}CH_2)_3 + 2MgCl_2.$$

In the experiments, we used the chemicals meeting the following specifications: tetrahydrofuran, TU (Technical Specifications) 6-02-821–81 (revisions 1, 2); vinyl chloride, OST (Branch Standard) 6-01-23–75; milled magnesium powder (MPF-4), GOST (State Standard) 6001–71 and GOST 804–72; and tetrachlorogermane, TU 6-09-04-257–87.

**Vinylmagnesium chloride.** Vinyl chloride was bubbled through a suspension of 24.3 g of magnesium powder in THF in an inert atmosphere. The reaction was initiated with 1,2-dibromoethane and was performed at 55–60°C. By the end of the reaction, the temperature decreased to 25–30°C.

**Reaction of vinylmagnesium chloride (without separation from the precipitate) with tetrachlorogermane.** A solution of 53.5 g of $GeCl_4$ in 50 ml of THF was added dropwise at a temperature not exceeding 30°C to a solution of vinylmagnesium chloride in THF. The mixture was kept at 20–30°C for 6 h and treated with water. The aqueous layer was separated, and the organic layer was washed with water to remove THF. Fractional distillation of the residue gave broad fractions containing mixtures of vinylchlorogermanes and pervinylpolygermanes. The content of the products in the mixtures was determined by GLC; the products were identified by their retention times.

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The product yields were as follows: divinyldichlorogermane 8%, trivinylchlorogermane 24%, tetravinylgermane 18%, hexavinyldigermane 28%, and octavinyltrigermane 16%.

**Reaction of vinylmagnesium chloride solution, separated from the precipitate, with tetrachlorogermane.** A solution of vinylmagnesium chloride in THF, prepared from 0.5 g-at. of Mg, was allowed to stand for 24 h; the upper layer (transparent brown liquid) was decanted to the reaction flask, and a solution of 21.4 g of $GeCl_4$ in 20 ml of THF was added at a temperature not exceeding 30°C. The mixture was kept at 20–30°C for 6 h, after which it was treated with water. The aqueous layer was separated, and the organic layer was washed with water to remove THF. Fractional distillation of the residue gave 15.8 g (88%) of tetravinylgermane, bp 55–56°C (25 mm Hg), $n_D^{20}$ 1.4688. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 6.247 ($H^1$, $J_{1-2}$ 3.4, $J_{1-3}$ 19.9 Hz), 6.071 ($H^2$, $J_{1-2}$ 13.4, $J_{2-3}$ 3.4 Hz), 5.705 ($H^3$, $J_{1-3}$ 19.9, $J_{2-3}$ 3.4 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 134.6 (CH), 132.8 ($CH_2$)].

The reaction mixtures and products were analyzed by gas–liquid chromatography on an LKhM-80 chromatograph [3000 × 3-mm metallic column; 5% SE-30 on Chromosorb-G-AW-DMCS (0.15–0.18 mm); programmed heating from 50 to 270°C at a rate of 12 deg $min^{-1}$; vaporizer temperature 300°C; thermal conductivity detector, detector temperature 280°C, current 90 mA; carrier gas He, flow rate 30 ml $min^{-1}$].

The $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker AM-360 (360 MHz for $^1H$) and AC-200P (200 MHz for $^1H$) Fourier spectrometers.

## REFERENCES

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