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Abstract

Full Text

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ORGANOLITHIUM SYNTHESIS OF GERMANIUM-HYDROCARBON COMPOUNDS FROM DIMETHYLDICHLOROGERMANE

SOME REACTIONS WITH POSSIBLE INTERMEDIATE FORMATION OF $(CH_3)_2Ge$

Recently we showed (1) that dimethyldichlorosilane reacts readily with lithium in tetrahydrofuran (THF), leading, in the presence of arylethylenes, to the formation of the corresponding aryl-substituted silacyclopentanes and silicon-hydrocarbon polymers, and, in the absence of olefins, to a mixture of polymeric products of the general formula $[(CH_3)_2Si <]_n$. In this connection we suggested the possibility of the intermediate formation in these reactions of dimethylsilylene—the silicon analogue of carbenes:

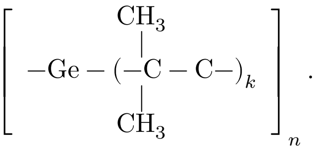
$$(CH_3)_2SiCl_2 \xrightarrow[THF]{Li} (CH_3)_2Si(Li)Cl \xrightarrow{-LiCl} (CH_3)_2Si: \rightarrow \text{ etc.}$$

At the same time, Vol' pin, Koreshkov, and Kursanov (2) showed the formation of this carbenoid also on boiling dimethyldichlorosilane with sodium in xylene and on thermal cleavage of the polymer $[(CH_3)_2Si <]_{55}$.

Taking into account the closeness of many chemical properties of analogous silicon and germanium compounds, analogous behavior in the above-mentioned reactions with alkali metals might have been expected for dimethyldichlorogermane. Indeed, the latter, like $(CH_3)_2SiCl_2$, reacted readily and vigorously with lithium in THF, forming at 20-45° chiefly the cyclic hexamer $[(CH_3)_2Ge <]_6$, m.p. 211-213°, readily soluble in most organic solvents (yields up to 80%). At a lower temperature ($\sim 0°$), along with this cyclohexamer and other THF-soluble products, $\sim 50\%$ of a polymer insoluble in organic solvents was obtained, rather close in composition to polydimethylgermylene $[(CH_3)_2Ge <]_n$. This polymer is a gray amorphous powder with a melting interval of 200-240°, and in its hydrophobicity and other properties it closely resembled polydimethylsilylene $[(CH_3)_2Si <]_n$ (1). The formation of these polymeric germanium-hydrocarbon products is well explained by a carbenoid scheme, including the intermediate formation of dimethylgermylene (dimethylgermanylene)—the germanium analogue of carbenes:

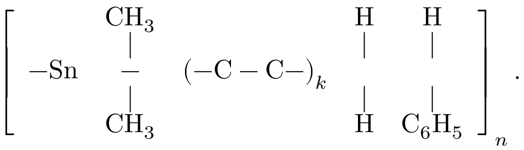
$$n(\mathrm{CH_3})_2\mathrm{GeCl_2} \xrightarrow[-n\mathrm{LiCl}]{2n\mathrm{Li}} n(\mathrm{CH_3})_2\mathrm{Ge(Li)Cl} \xrightarrow{-n\mathrm{LiCl}} n(\mathrm{CH_3})_2\mathrm{Ge}: \rightarrow [(\mathrm{CH_3})_2\mathrm{Ge}<]_n.$$

Like dimethyldichlorosilane, $(CH_3)_2GeCl_2$ reacted with alkali metals also in the presence of arylethylenes. Thus, from $(CH_3)_2GeCl_2$, styrene, and lithium (molar ratio 1 : 2 : 4) in THF at a temperature of ~ 0°, X, X'-diphenyl-1,1-dimethylgermanacyclopentane was obtained (yield ~ 40%) and a germanium-hydrocarbon polymer of the general type



$$\left[-\mathrm{Ge}-\left(-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{C}-\right)_k\right]_n.$$

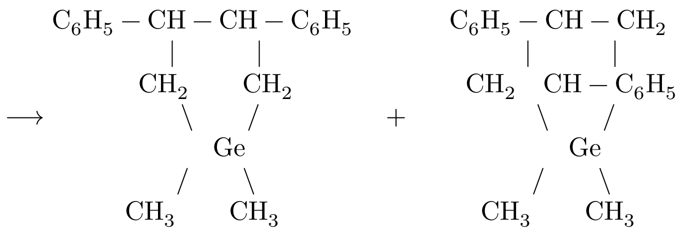
Under the same conditions, vinyltoluene and $(CH_3)_2GeCl_2$ gave, along with polymeric products, ~ 45% of theory of ditolyldimethylgermanacyclopentane. The reaction proceeded analogously with other aryl-substituted ethylenes and conjugated dienes. In contrast to $(CH_3)_2SiCl_2$ and $(CH_3)_2GeCl_2$, dimethyldichlorostannane, on treatment with lithium and styrene in THF at temperatures from 0 to 67°, forms, as we showed jointly with V. I. Shiryaev, exclusively polymeric products of probable structure



$$\left[-\mathrm{Sn}\ \overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{-}}\ (-\mathrm{C}-\mathrm{C}-)_k\ \overset{\mathrm{H}}{\underset{\mathrm{H}}{|}}\ \ \overset{\mathrm{H}}{\underset{\mathrm{C_6H_5}}{|}}\right]_n.$$

The mechanism of formation of germanacyclopentanes and organogermanium polymers is probably analogous to the mechanism we proposed (1) for the case of dichlorosilanes, and includes both the interaction of products of lithium addition to styrenes with $(CH_3)_2GeCl_2$, and, apparently, direct addition of the intermediately formed $(CH_3)_2Ge:$ to these olefins, for example:

$$\mathrm{C_6H_5CH(Li)CH_2Li} + (\mathrm{CH_3})_2\mathrm{GeCl_2} \xrightarrow{-2\mathrm{LiCl}} \mathrm{C_6H_5\dot{C}HCH_2} \longrightarrow$$
$$(\mathrm{CH_3})_2\mathrm{Ge}: + \mathrm{C_6H_5CH} = \mathrm{CH_2} \longrightarrow$$



$$\xrightarrow{C_6H_5CH{=}CH_2} \left[-Ge\,(CH_3)_2-(-CH_2-CH(C_6H_5)-)_k\right]_n \qquad (k \geqslant 1).$$

In particular, the possibility of a carbenoid scheme for the course of this reaction is supported by the fact that even GeJ_2, stable under ordinary conditions, exhibits the properties of carbenes and adds to tolane (2,3).

The structure of the cyclic and linear organogermanium hydrocarbon compounds obtained by us was confirmed by data from elemental analysis and determination of molecular weights, as well as by IR spectra (Fig. 1). The latter were taken by E. D. Lubuzh on a UR-10 spectrometer in a thin layer of substance for liquid compounds (layer thickness 0.02 mm) or in dry KBr for solid products (pressed disks of $\sim$ 2 mg of substance and 200 mg KBr). In this connection, as was to be expected, the IR spectra of the cyclohexamer and polymer of dimethylgermylene (Fig. 1, ,) are very similar both to one another and to the spectrum of the cyclotetramer of dimethylsilylene (Fig. 1,), isolated by us from the products of interaction of $(CH_3)_2SiCl_2$ with lithium in THF (m.p. 194-197°). An analogous similarity is also observed in the spectra of diphenyl-substituted germana- and silacyclopentanes (Fig. 1, ,). In addition, the structure of dodecamethylcyclohexagermane $[(CH_3)_2Ge]_6$ is confirmed by NMR spectral data,* which show the presence in this compound of only one type of protons (chemical shift relative to the signal of C_6H_6, 5.9 m.u.).

Experimental Part**

Dimethyldichlorogermane was obtained, according to (4), from metallic germanium (with the addition of 20 wt.% copper) and methyl chloride at a temperature of $360 \pm 20°$, and purified by distillation on a column: b.p. 118-119° (750 mm), n_D^{20} 1.4612. Found, %: Cl 41.1, 41.2. $C_2H_6GeCl_2$. Calculated, %: Cl 40.9.

According to (4): b.p. 119° (735 mm); n_D^{29} 1.4555.

All experiments with lithium were carried out in an atmosphere of dry purified nitrogen.

Dimethylgermylene polymers $[(CH_3)_2Ge]_n$. **Experiment No. 1.** 26 g (0.15 mole) of dimethyldichlorogermane was added over 1 h to a mixture, stirred

Fig. 1. IR spectra of organogermanium hydrocarbon compounds and their silicon analogs

Figure 1: Fig. 1. IR spectra of organogermanium hydrocarbon compounds and their silicon analogs

with a glass stirrer, of 3.5 g (0.5 g-atom) of lithium powder and 60 ml of absolute THF at 40-46°. The contents of the flask were then stirred until the hydrolyzable chlorine disappeared (∼ 1.5 h), diluted with ether, and filtered from the excess Li and LiCl (precipitate on the filter completely dissolved in water). After evaporation of the ether and THF, ~12 g of a white crystalline mass was obtained, which consisted mainly of dodecamethylcyclohexagermane, fine white needles with m.p. 211-213° (after 4-5 recrystallizations from aqueous ethanol).

Found, %:	C 23.93, 23.64;	H 6.35, 6.14;	Ge 69.80, 69.52
$C_{12}H_{36}Ge_6$. Calculated, %:	C 23.39;	H 5.90;	Ge 70.71

Mol. wt.: found (cryoscopically in C_6H_6) 613, 633; calculated 615.6.

Fig. 1. IR spectra of organogermanium hydrocarbon compounds and their silicon analogs

Experiment No. 2. To 3.2 g of small pieces of lithium in 70 ml of THF, with stirring by a steel mechanical stirrer of the turbine type, 17.2 g (0.1 mole) of dimethyldichlorogermane in 20 ml of THF was added (~0°, 1¼ hours), after which the mixture was stirred for a further 1½ hours at 5-10° (hydrolyzable chlorine is absent from the mixture). The precipitate that separated, partly soluble in water and containing $[(CH_3)_2Ge<]_n$, LiCl, and Li, was filtered off, thoroughly washed with ether, freed from pieces of lithium, and treated successively with methanol and cold distilled water (until a negative test for chloride ion). The precipitate was then dried in a vacuum desiccator. Yield of dry polymer ~5 g (49%), a gray amorphous powder, m.p. 200-240°.

Found, %:	C 22.64, 22.60;	H 5.49, 5.41;	Ge 68.74, 68.93
$[C_2H_6Ge]_n$. Calculated, %:	C 23.39;	H 5.90;	Ge 70.71

This polymer is insoluble in ordinary organic solvents and is characterized by high hydrophobicity.

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* Taken by A. S. Khachaturov on a JNM-317 spectrometer in CCl_4 solution (concentration ∼ 40%) using toluene as the external standard.
** Performed with the participation of V. N. Medvedev.

The tetrahydrofuran solution (filtrate) remaining after separation of the precipitate was evaporated in vacuo; ∼ 4 g of soluble low-molecular-weight products were obtained, containing a cyclohexamer of dimethylgermanium and other compounds. In a similar experiment, also carried out with a steel mechanical stirrer but at 10—20°, the yield of the organogermanium polymer insoluble in THF and water was considerably lower.

X, X'-Diphenyl-1,1-dimethylgermanacyclopentane. A mixture of 17.2 g (0.1 mole) of dimethyldichlorogermane and 21 g (0.2 mole) of styrene was added over 25 min, with vigorous stirring by a steel stirrer, to 3 g of lithium in 100 ml of THF (temperature from 0 to +5°). After 20 min of subsequent stirring, a sample of the hydrolyzate of the mixture was alkaline to phenolphthalein. The reaction products were worked up as in the experiments with $(CH_3)_2SiCl_2$ [1]. The yield of diphenyldimethylgermanacyclopentane was 12.5 g (40.5% of theory), b.p. 140—141° (0.2 mm), n_D^{20} 1.5920, d_4^{20} 1.1688.

$C_{18}H_{22}Ge$. Found, %: C 69.57, 69.60; H 7.18, 7.26; Ge 23.18, 23.32
Calculated, %: C 69.52; H 7.14; Ge 23.34

Mol. wt.: found 313; calculated 311.0.

The yield of the germanium-hydrocarbon polymer was 21.5 g; a light-yellow resin, readily soluble in ether, THF, and benzene. After two reprecipitations from ethereal solution with methanol and drying in vacuo, it was a white powder with a melting interval of 74—89°; mol. wt. 2790, 2960 (cryoscopically in C_6H_6).

In another analogous experiment carried out at a temperature from −5 to +5°, 15 g (40%) of the corresponding germanacyclopentane and 21.5 g of polymer were obtained (from 0.12 mole of $(CH_3)_2GeCl_2$ and 0.22 mole of styrene).

X, X'-Ditolyl-1,1-dimethylgermanacyclopentane. Obtained analogously to diphenyldimethylgermanacyclopentane from 17.2 g (0.1 mole) of dimethyldichlorogermane, 24 g (0.2 mole) of freshly distilled vinyltoluene (n_D^{20} 1.5424), and 3 g (0.43 g-atom) of lithium in 65 ml of THF at 0° (35 min). Yield 14.5 g (43%), b.p. 150—151° (0.18 mm), n_D^{20} 1.5825, d_4^{20} 1.1346.

$C_{20}H_{26}Ge$. Found, %: C 71.36, 71.07; H 7.69, 7.68; Ge 20.85, 20.93
Calculated, %: C 70.89; H 7.69; Ge 21.42

Mol. wt.: found 322, 312; calculated 338.8.

The non-distilling residue (a yellow glassy mass, yield 18.5 g) was reprecipitated twice from ethereal solution with methanol, after which it was a white powder melting at 58—70°; mol. wt. 1280, 1220 (cryoscopically in C_6H_6). The IR spectrum of this polymer, recorded in a "solid solution" of KBr, showed the presence of benzene rings (intense bands at 1599, 1523, and 1456 cm^{-1}), CH_2

groups (2920 cm^{-1}), and also CH_3 groups attached to germanium (1236, 790, and 705 cm^{-1}) and to carbon (2967 cm^{-1}).

When the above-described experiment was carried out at 28—37°, the yield of ditolyldimethylgermanacyclopentane (b.p. 145—147° at 0.15 mm, n_D^{20} 1.5798, d_4^{20} 1.1337) was 11 g (33%), and that of polymer 20.2 g.

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