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Abstract

Full Text

Chemistry

I. M. Gverdtsiteli, T. P. Guntsadze, Corresponding Member of the USSR Academy of Sciences A. D. Petrov

The Action of $HGe(C_2H_5)_3$ on Primary and Secondary Vinylacetylene Carbinols

In a previous paper ([1]) we described the synthesis and dehydration of certain tertiary germanium-containing diene carbinols. It was established that, in the reaction of $HGe(C_2H_5)_3$ with tertiary carbinols (Speier catalyst), the reaction proceeded in only one direction—the diene germanium-containing carbinols were obtained. In the present communication we give the results of the interaction of primary and certain secondary vinylacetylene carbinols with $HGe(C_2H_5)_3$ in the presence of Speier catalyst under the same conditions.

It turned out that, in the case of primary and secondary carbinols, the reaction proceeds in two directions: in addition to the diene germanium-containing carbinol I, a digermanium carbinol II is obtained

$$\mathrm{R{-}\underset{\mathrm{OH}}{CH}{-}C{\equiv}C{-}CH{=}CH_2 + HGe(C_2H_5)_3 \rightarrow R{-}\underset{\mathrm{OH}}{CH}{-}C(Ge(C_2H_5)_3){=}CH{-}CH{=}CH_2} \qquad \text{(I)}$$

$$\mathrm{R{-}\underset{\mathrm{OH}}{CH}{-}CH{-}CH{=}CH{-}CH_2{-}Ge(C_2H_5)_3} \quad \overset{\mathrm{Ge(C_2H_5)_3}}{\downarrow} \qquad \text{(II)}$$

where

$$\mathrm{R = CH_3{-},\ C_3H_7{-},\ C_6H_5{-}.}$$

In the case of the phenyl radical the reaction proceeded under different conditions: whereas the other syntheses took place at room temperature, here, despite the increased amount of catalyst (2 ml), the reaction did not begin until the contents of the flask were heated on a boiling water bath. The maximum temperature of the reaction mixture reached 145° (in the other cases it did not exceed 120°). As a result of the reaction, from the first fraction a product was isolated which could be distilled at atmospheric pressure (719 mm) at 220–221°.

Having determined the constants and carried out elemental analysis, we established that the substance obtained is a product of β-cleavage

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(I) $R-CH-\underset{\underset{Ge(C_2H_5)_3}{|}}{C}(OH)=CH-CH=CH_2 \rightarrow (C_2H_5)_3GeOH \rightarrow (C_2H_5)_3Ge-O-Ge(C_2H_5)_3$.

As is known, organogermanium compounds with the germanium atom in the β-position relative to the functional group undergo β-cleavage under the action of various reagents, and this property is more strongly expressed in organogermanium compounds than in organosilicon compounds of the same type ([2]).

In paper ([3]), the β-cleavage of silicon-containing compounds synthesized by the authors is explained by the action of the catalyst H_2PtCl_6 or of the products of its partial reduction ($PtCl_4$, $PtCl_2$). In our case, in view of the sufficient stability of the compounds we obtained, we explain the process of β-cleavage by the same factor, i.e., by an excess of the rather acidic Speier catalyst and by the high temperature.

Table 1

No.	Compound obtained	Yield, % of theory	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D found, %	MR_D calc., %
1	$CH_2OH-CH_2-C(Ge(C_2H_5)_3)=CH-CH=CH_2$	40	129–131/4	1.5030	1.0471	72.43	70.03
2	$CH_2OH-CH_2-CH(Ge(C_2H_5)_3)-CH=CH-CH_2-Ge(C_2H_5)_3$	7	153–154/1	1.5160	1.1423	110.15	109.064
3	$CH_3-CH(OH)-C(Ge(C_2H_5)_3)=CH-CH=CH_2$	54	99/2	1.5012	1.0215	70.54	70.01
4	$CH_3-CH(OH)-CH(Ge(C_2H_5)_3)-CH=CH-CH_2-Ge(C_2H_5)_3$	5	147–150/2	1.4980	1.1269	107.74	107.86
5	$C_3H_7-CH(OH)-C(Ge(C_2H_5)_3)=CH-CH=CH_2$	56	123–124/4	1.4970	1.0457	79.63	79.32
6	$C_3H_7-CH(OH)-CH(Ge(C_2H_5)_3)-CH=CH-CH_2-Ge(C_2H_5)_3$	11	188–189/4	1.4990	1.1034	119.61	119.36
7	$C_6H_5-CH(OH)-C(Ge(C_2H_5)_3)=CH-CH=CH_2$	41	163–164/3	1.5482	1.0775	90.67	89.51
8	$C_6H_5-CH(OH)-CH(Ge(C_2H_5)_3)-CH=CH-CH_2-Ge(C_2H_5)_3$	9	196–200/2	1.5320	1.1329	131.07	129.59

In the remaining syntheses, in our opinion, because of the comparatively small amount of catalyst (0.5–1 ml), β-cleavage evidently occurs to a lesser extent, and it is not possible to isolate $(C_2H_5)_6Ge_2O$ because of its small amount.

The formulas and properties of the compounds synthesized by us are given in Table 1.

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Experimental Part

Action of $HGe(C_2H_5)_3$ **on** β**-vinylethynylethanol.** 14 g of the starting carbinol, 1 ml of 0.1 M H_2PtCl_6 in isopropyl alcohol, and 24 g of $HGe(C_2H_5)_3$ were placed in a three-necked flask with a mechanical stirrer. A vigorous reaction began and was complete after 1 h. By distillation in vacuum under nitrogen, fractions were isolated: I 36–106° (4 mm), 2.2 g; II 129–131° (4 mm), 15.5 g; III 153–154° (1 mm), 5.1 g; the remaining mass polymerized (4.5 g).

For fraction II, n_D^{20} 1.5030; d_4^{20} 1.0471.

Found, %: C 55.42, 56.02; H 9.20, 9.32; Ge 28.39, 28.31;
(OH) 6.50; 7.20

$C_{12}H_{24}GeO$. Calculated, %: C 56.11; H 9.35; Ge 28.28;
(OH) 6.66

MR_D found 72.43, calculated 70.03; yield 40% (of theory). The synthesized substance, 3-triethylgermylhexadienol-3,5,1, is a colorless, mobile liquid.

For fraction III, n_D^{20} 1.5150; d_4^{20} 1.1423.

Found, %: C 51.43, 51.50; H 10.01, 9.93; Ge 34.20, 34.46;
(OH) 4.50, 4.15

$C_{18}H_{40}Ge_2O$. Calculated, %: C 51.77; H 9.58; Ge 34.80;
(OH) 4.08

MR_D found 110.150; calculated 109.064; yield 7%.
The substance obtained–ditriethylgermyl-3,5-hexenol-3,1–is a colorless, viscous liquid.

Action of $HGe(C_2H_5)_3$ **on methylvinylethynylcarbinol.** Under the conditions of the preceding experiment, 20 g of the starting carbinol, 0.5 ml of Speier catalyst, and 34 g of $HGe(C_2H_5)_3$ were taken.

By distillation in vacuum under nitrogen the following were obtained: fraction I up to 99° (2 mm), 2.4 g; II 99° (2 mm), 29 g; III 147—150° (2 mm), 4.5 g; the remaining mass polymerized.

For fraction II, n_D^{20} 1.5012; d_4^{20} 1.0725.

Found, %: C 56.05, 56.14; H 9.65, 9.49; Ge 28.05, 28.13;
(OH) 6.86, 6.30

$C_{12}H_{24}GeO$. Calculated, %: C 56.09; H 9.34; Ge 28.27;
(OH) 6.55

MR_D found 70.54; calculated 70.01; yield 54%.
The synthesized substance–hexadiene-3,5,3-triethylgermyl-2-ol–is a viscous liquid of pale-yellow color.

For fraction III, n_D^{20} 1.4980; d_4^{20} 1.1269.

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Found, %: C 52.14, 52.38; H 9.48, 9.72; Ge 33.21, 33.03;
(OH) 2.89, 3.73

$C_{18}H_{40}Ge_2O$. Calculated, %: C 51.71; H 9.58; Ge 33.63;
(OH) 3.92

MR_D found 107.94; calculated 107.86; yield 5%.
The substance obtained—ditriethylgermyl-3,5-hexanol-3,2—is a viscous liquid of yellow color.

Action of $HGe(C_2H_5)_3$ **on propylvinylethynylcarbinol.** Under the conditions of the preceding experiment, 13 g of the starting carbinol, 1 ml of Speier catalyst, and 18 g of $HGe(C_2H_5)_3$ were taken.

After fractionation in vacuum under nitrogen, fractions were isolated: I up to 120° (4 mm), 2.3 g; II 123—124° (4 mm), 16.2 g; III 188—189° (4 mm), 5 g; the remaining mass polymerized.

For fraction II, n_D^{20} 1.4970; d_4^{20} 1.0457.

Found, %: C 59.15, 59.12; H 10.01, 9.97; Ge 24.95, 25.11;
(OH) 6.63, 6.40

$C_{14}H_{28}GeO$. Calculated, %: C 59.03; H 9.83; Ge 25.47;
(OH) 6.01

MR_D found 79.63; calculated 79.32; yield 56%.
The synthesized substance—triethylgermyl-5-octadien-5,7-ol-4—is a colorless viscous liquid.

For fraction III, n_D^{20} 1.4990; d_4^{20} 1.0934.

Found, %: C 53.99, 54.07; H 9.55, 9.61; Ge 33.21, 33.09;
(OH) 3.43, 3.06

$C_{20}H_{44}Ge_2O$. Calculated, %: C 54.15; H 9.99; Ge 32.78;
(OH) 3.82

MR_D found 119.61; calculated 119.36; yield 11%.
The substance obtained—ditriethylgermyl-5,8-octenol-6,4—is a viscous liquid of yellow color.

Action of $HGe(C_2H_5)_3$ **on phenylvinylethynylcarbinol.** 18 g of the starting carbinol, 2 ml of Speier catalyst, and 20 g of $HGe(C_2H_5)_3$ were taken. The contents of the flask were stirred for 1-1.5 h. The reaction did not start. As soon as the mixture was heated on a boiling water bath, a very vigorous reaction began (maximum temperature of the reaction mixture 145°).

After distillation in vacuo under nitrogen, the following were obtained: I up to 100° (5 mm), 5 g; II 163-164° (3 mm), 15 g; III 198-200° (2 mm), 5.3 g; the remaining mass polymerized.

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From the first fraction, by distillation at atmospheric pressure (719 mm), a substance was isolated with n_D^{20} 1.4612; d_4^{20} 1.1410.

Found, %:	C 43.20, 43.29;	H 8.71, 8.56;	Ge 43.03;
$C_{12}H_{30}Ge_2O$. Calculated, %:	C 42.96;	H 8.95;	Ge 43.31

Thus, it was established that the substance obtained is the product of β-cleavage, $(C_2H_5)_6Ge_2O$.

For fraction II, n_D^{20} 1.5432; d_4^{20} 1.1075.

Found, %:	C 63.25, 63.76; (OH) 4.40	H 8.19, 8.25;	Ge 22.96, 22.81;
$C_{17}H_{26}GeO$. Calculated, %:	C 63.21; (OH) 5.37	H 8.05;	Ge 22.78;

MR_D found 90.67; calculated 89.51; yield 41%.

The synthesized substance, 1-phenyl-2,4-triethylgermyl-2-penten-1-ol, is a mobile liquid, luminescing in daylight with a yellowish-green color.

For fraction III, n_D^{20} 1.5320; d_4^{20} 1.1329.

Found, %:	C 57.86, 57.70; (OH) 3.13, 3.34	H 8.75, 8.75;	Ge 28.97, 29.15;
$C_{23}H_{42}Ge_2O$. Calculated, %:	C 57.59; (OH) 3.50	H 8.76;	Ge 30.26;

MR_D found 131.078; calculated 129.594; yield 9%.

The substance obtained, 1-phenyl-2,5-ditriethylgermyl-3,1-pentenol, is a viscous liquid, luminescing in daylight with a reddish-green color.

Tbilisi
State University

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CITED LITERATURE

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3. I. M. Gverdtsiteli, T. P. Doksopulo, DAN, 145, No. 4 (1962).

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