Chemistry

I. M. Gverdtsiteli, T. P. Guntsadze,

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Abstract

Full Text

Chemistry

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

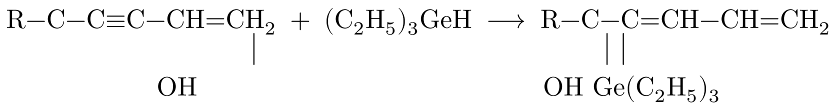
Synthesis and Dehydration of Some Diene Germanium-Containing Carbinols

In previous works ([1], [2]) we studied the action of $(C_2H_5)_3SiH$ on vinylacetylenic carbinols in the presence of Pt/C catalysts and a 0.1 *M* solution of H_2PtCl_6 in isopropyl alcohol. It was found that with Speier's catalyst the reaction proceeded under milder conditions than with the Pt/C catalyst: at room temperature, with better yields, and faster. It was of interest to study the behavior of $(C_2H_5)_3GeH$ ([3]) in reaction with vinyl ethynyl carbinols under the same conditions (Speier' s catalyst).

For this purpose we carried out the synthesis of several tertiary carbinols, namely dimethyl-, methylethyl-, tetramethylene-, and pentamethylene-divinylgermanium carbinols (in the presence of Speier' s catalyst), and their dehydration.

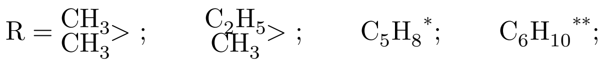
As a result of the investigations it was found that the reaction between $(C_2H_5)_3GeH$ and the above-mentioned carbinols proceeds more smoothly than in the case of $(C_2H_5)_3SiH$: in each synthesis two fractions were isolated (whereas in the case of $(C_2H_5)_3SiH$ several fractions were obtained), less catalyst was required (1 ml instead of 2 ml), and the yields increased to 70-80% (instead of 55-60%).

The reaction proceeded according to the scheme:



$$\underset{\text{OH}}{\text{R}-\text{C}}-\text{C}\equiv\text{C}-\text{CH}=\underset{|}{\text{CH}_2} + (C_2H_5)_3GeH \longrightarrow \underset{\text{OH}}{\text{R}-\text{C}}-\underset{\text{Ge}(C_2H_5)_3}{\text{C}}=\text{CH}-\text{CH}=\text{CH}_2$$

where



$$R = \genfrac{}{}{0pt}{}{CH_3}{CH_3}> ; \quad \genfrac{}{}{0pt}{}{C_2H_5}{CH_3}> ; \quad C_5H_8{}^{*}; \quad C_6H_{10}{}^{**};$$

Dehydration of the diene compounds in the presence of $KHSO_4$ proceeded with good yields (74-82%); however, in the case of cyclopentyl and cyclohexyl radicals, partial decomposition was observed during distillation and, accordingly, the yield of the dehydrated product decreased (33-50%).

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

Experimental Part

Action of $(C_2H_5)_3GeH$ **on dimethylvinylethynylcarbinol.**
15 g of dimethylvinylethynylcarbinol, 1 ml of a 0.1 *M* solution of H_2PtCl_6 in isopropyl alcohol, and 23 g of $(C_2H_5)_3GeH$ were placed in a three-necked flask with a stir—

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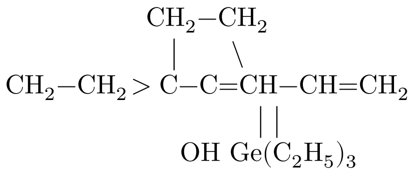

$CH_2{-}CH_2{>}C(OH){-}C(CH_2{-}CH_2){=}CH{-}CH{=}CH_2$, $Ge(C_2H_5)_3$

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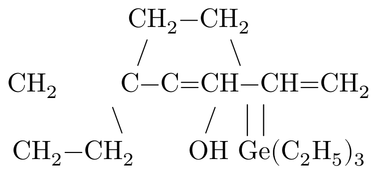

CH_2, $C{-}C{=}CH{-}CH{=}CH_2$, $CH_2{-}CH_2$, OH, $Ge(C_2H_5)_3$

Table 1

No.	Compound obtained	B.p., °C (mm Hg)	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Yield, %	Found, % C	Found, % H	Found, % Ge	Calculated, % C	Calculated, % H	Calculated, % Ge	OH, % found	OH, % calculated
1	CH_3 CH_3 [illegible]	112 (6)	1,4954	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	49,59	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7,32
2	$CH_2{=}C{-}$[illegible]	71 (2)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	28,74	—	—
3	C_2H_5 CH_3 [illegible]	98–100 (3)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	CH_3CH CH_3 [illegible]	107–108 (3)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—

No.	Compound obtained	B.p., °C (mm Hg)	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Yield, %	Found, % C	Found, % H	Found, % Ge	Calculated, % C	Calculated, % H	Calculated, % Ge	OH, % found	OH, % calculated
5	[illegible]	116–118 (1)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	24,47	6,30	5,75
6	[illegible]	120–122 (3)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	9,66	[illegible]	[illegible]	9,33	26,06		
7	[illegible]	114–116 (1)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	23,73	6,21	[illegible]
8	[illegible]	139–140 (4)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	9,57	24,81	—	—

mechanical stirrer. After 5 min a vigorous reaction began (the contents of the flask boiled). After approximately an hour the reaction was complete.

By vacuum distillation under nitrogen the following fractions were isolated: I, 93–110° (6 mm), 2.5 g; II, 112° (6 mm), in an amount of 30 g (yield 70%). For fraction II, n_D^{20}1.4954, d_4^{20}1.0390 were found. The substance obtained—2-methyl-3-triethylgermylhexadien-3,5-ol-2—is a yellowish viscous liquid, for which MR_D was calculated as 74.64, found 76.02.

Found, %:	C 57.54; H 9.59; Ge 26.58; (OH) 7.39, 7.50
$C_{13}H_{26}GeO$. Calculated, %:	C 57.64; H 9.60; Ge 26.82; (OH) 7.32

Dehydration of 2-methyl-3-triethylgermylhexadien-3,5-ol-2. 5 g of the substance to be dehydrated, 2.5 g of $KHSO_4$, and 0.1 g of dithizone (antioxidant) were heated in vacuum under nitrogen for 20 min (90–100°), after which distillation was carried out; 3.7 g of 2-methyl-3-triethylgermylhexatriene-1,3,5 was obtained, b.p. 71° (2 mm), n_D^{20}1.5016, d_4^{20}1.0216, a mobile yellow liquid, yield 82%. MR_D calculated 72.62, found 72.92.

Found, %:	C 61.20, 61.10; H 9.57, 9.56; Ge 28.26, 28.32
$C_{13}H_{24}Ge$. Calculated, %:	C 61.90; H 9.50; Ge 28.74

Hydroxyl was not detected.

Action of $(C_2H_5)_3GeH$ **on methylethylvinylethynylcarbinol.** 18.8 g (0.15 mole) of the starting carbinol, 1 ml of Speier' s catalyst, and 24 g (0.15 mole) of $(C_2H_5)_3GeH$ were taken. The reaction proceeded analogously to that described previously.

By vacuum distillation under nitrogen the following fractions were isolated: I, 46-98° (3 mm), 4.5 g; II, 98-100° (3 mm), 33.1 g, yield 79%; for fraction II, n_D^{20}1.4972, d_4^{20}1.0430.

The substance obtained, 3-methyl-4-triethylgermylheptadien-4,6-ol-3, is a yellowish liquid, for which MR_D was calculated as 78.27, found 79.61.

Found, %:	C 52.64, 52.09; H 10.04, 10.01; Ge 25.69, 25.40; (OH) 7.47, 7.31
$C_{14}H_{28}GeO$. Calculated, %:	C 51.98; H 9.83; Ge 25.50; (OH) 6.40

Dehydration of 3-methyl-4-triethylgermylheptadien-4,6-ol-3. 4.26 g (0.015 mole) of the substance, 2.5 g of calcined $KHSO_4$, and 0.1 g of dithizone were taken. The reaction was carried out analogously to that described previously.

The substance obtained, 3-methyl-4-triethylgermylheptatriene-1,3,5, b.p. 107-108° (3 mm), is a yellow mobile liquid, n_D^{20}1.4965, d_4^{20}1.0367. Yield 74% (2.9 g). MR_D calculated 77.35, found 75.52.

Found, %:	C 62.65, 62.57; H 9.99, 10.03; Ge 27.21, 27.19
$C_{14}H_{26}Ge$. Calculated, %:	C 62.98; H 9.57; Ge 27.22

Hydroxyl was not detected.

Action of $(C_2H_5)_3GeH$ **on tetramethylenevinylethynylcarbinol.** 20 g of the starting carbinol (0.15 mole), 28 g of $(C_2H_5)_3GeH$, and 1 ml of Speier' s catalyst were taken. The reaction proceeded analogously to the preceding ones. By vacuum distillation under nitrogen the following were obtained: fraction I, 70-116°, 3.3 g; fraction II, 116-118° (1 mm), 32 g of substance. For fraction II, n_D^{20}1.5120, d_4^{20}1.0788, yield 73% of theoretical.

The substance obtained, 1-oxocyclopentyl-1-triethylgermylbutadiene-1,3, is a viscous pale-yellow liquid, for which MR_D was calculated as 81.742, found 82.497.

Found, %:	C 60.32, 60.40; H 10.01, 9.97; Ge 24.99, 24.97; (OH) 6.49, 6.30
$C_{15}H_{28}GeO$. Calculated, %:	C 60.62; H 9.44; Ge 24.47; (OH) 5.75

Dehydration of 1-oxycyclopentyl-1-triethylgermylbutadiene-1,3. 3 g of the substance to be dehydrated, 2 g of $KHSO_4$, and 0.1 g of dithizone were taken. The reaction was carried out analogously to that described earlier.

By distillation in vacuo under nitrogen, a substance was obtained with b.p. 120-122° (3 mm), n_D^{20} 1.5160, d_4^{20} 1.0530. During the distillation, decomposition was observed, as a result of which the yield of the dehydrated product decreased considerably—to 33% (0.9 g).

The substance obtained, 1-cyclopenten-1,1-triethylgermylbutadiene-1,3, is a yellow mobile liquid, for which MR_D was found to be 78.67, calculated 79.806.

Found, %: C 64.42, 64.52; H 9.65, 9.66; Ge 25.42, 25.98

$C_{15}H_{26}Ge$. Calculated, %: C 64.60; H 9.33; Ge 26.06

Hydroxyl was not detected.

Action of $(C_2H_5)_3GeH$ **on pentamethylenevinylethynylcarbinol.** 23 g (0.15 mole) of carbinol, 1 ml of Speier catalyst, and 25 g (0.15 mole) of $(C_2H_5)_3GeH$ were taken. The reaction proceeded analogously to the preceding one.

After distillation in vacuo under nitrogen, the following were obtained: fraction I up to 114° (1 mm), 4 g; fraction II, 144-116° (1 mm), 28 g. For fraction II, n_D^{20} 1.5140, d_4^{20} 1.0777 were found. Yield 69%.

The substance obtained, oxycyclohexyl-1-triethylgermylbutadiene-1,3, is a viscous pale-yellow liquid, for which MR_D was calculated as 86.42, found 86.93.

Found, %: C 60.82, 60.89; H 9.80, 9.75; Ge 23.46, 23.40; (OH) 6.21; 5.97

$C_{16}H_{30}GeO$. Calculated, %: C 61.81; H 9.65; Ge 23.73; (OH) 6.46

Dehydration of 1-oxycyclohexyl-1-triethylgermylbutadiene-1,3. 3.1 g (0.1 mole) of the substance to be dehydrated, 2 g of $KHSO_4$, and 0.1 g of dithizone were taken. The reaction was carried out analogously to the preceding one.

During distillation, as in the case of the cyclopentyl radical, partial decomposition was observed; as a result, 1.5 g of substance was obtained with b.p. 139-140° (4 mm), n_D^{20} 1.5180, d_4^{20} 1.0332. Yield 50%. The substance obtained, 1-cyclohexen-1-1-triethylgermylbutadiene-1,3, is a yellow mobile liquid, for which MR_D was calculated as 84.424, found 85.80.

Found, %: C 65.81, 65.90; H 9.84, 9.80; Ge 24.84, 24.73

$C_{16}H_{28}Ge$. Calculated, %: C 65.62; H 9.57; Ge 24.81

Hydroxyl was not detected.

Tbilisi
State University

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CITED LITERATURE

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3. H. N. Anderson, *J. Am. Chem. Soc.*, **79**, 326 (1957).

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