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Abstract

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THE ACTION OF $HGe(C_2H_5)_3$ ON DIACETYLENIC GLYCOLS IN THE PRESENCE OF H_2PtCl_6

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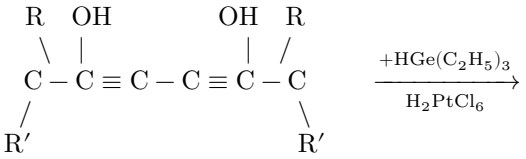
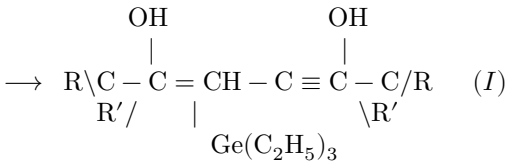
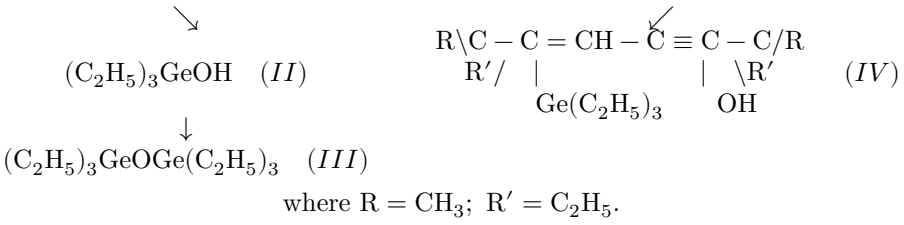
I. M. Gverdtsiteli and T. P. Doksopulo ([1]) studied the reaction of triethylsilane with diacetylenic glycols in the presence of Speier' s catalyst (0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol). They established that the reaction proceeds in one direction, namely with addition of the Si—H bond to one triple bond of the glycol. It was of interest to study the behavior of triethylgermane in analogous reactions. V. F. Mironov and N. G. Dzhurinskaya ([2]) found that the tendency toward β-cleavage in germanium compounds is more pronounced than in silicon compounds.

It turned out that, for the addition reaction to proceed, it is necessary to use half as much catalyst as in the reaction of addition of $HSi(C_2H_5)_3$ to diacetylenic glycols (with the yields increasing to 70–80%); otherwise the reaction proceeds vigorously, and when R and $R' = CH_3$, a series of fractions is obtained whose structure cannot be established; while in the case $R = CH_3$, $R' = C_2H_5$, the products obtained are the β-cleavage product $(C_2H_5)_3GeOGe(C_2H_5)_3$ (III) and a product of partial dehydration (IV). Evidently, β-cleavage and partial dehydration, just as in silicon-containing vinylacetylenic glycols, occur during the reaction and are caused by the presence of the catalyst. The reaction scheme may be expressed as follows:







where $R = CH_3$; $R' = C_2H_5$.

We studied the action of triethylgermane on germanium-containing vinylacetylenic glycols in the presence of H_2PtCl_6. It turned out that $HGe(C_2H_5)_3$ adds to the triple bond of the glycol only when $R, R' = CH_3$, upon heating the reaction mixture at 120° for one hour, with a small yield (13%). As a result, a germanium-containing dienic glycol is obtained.

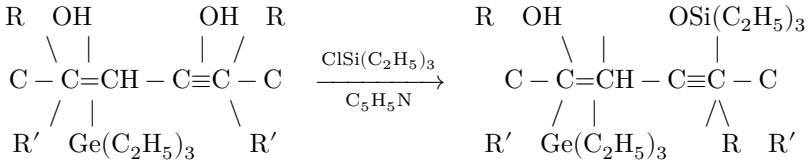
We carried out the dehydration of germanium-containing vinylacetylenic glycols. The dehydration is accompanied by decomposition, and the yields are correspondingly insignificant (7–9%). The interaction of germanium-containing vinylacetylenic glycols with triethylchlorogermane and with

Table 1

No.	Compound obtained	Yield, % of theory	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated
I	$(CH_3)_2C(OH)C(C_2H_5)_3$	80	152/2	1.4990	1.0630	80.61	88.89
II	$(CH_3)_2C(OH)C(Ge(C_2H_5)_3)=CH-C(Ge(C_2H_5)_3)=CC(OH)(CH_3)_2$	13	165/2	1.4803	1.0921	120.78	120.73
III	$CH_2=C(CH_3)C(C_2H_5)_3$	7	124/2	1.4400	0.8560	52.31	52.84.99
IV	$(CH_3)_2C(OH)C(Ge(C_2H_5)_3)=CH-C(OH)C(Ge(C_2H_5)_3)=CC(OH)(CH_3)_2$	27	172/3	1.4940	1.0027	127.91	125.62
V	$(CH_3)(C_2H_5)C(OH)C(Ge(C_2H_5)_3)=CH-C\equiv CC(OH)(CH_3)(C_2H_5)$	70	164/2	1.4964	1.0534	98.40	96.10

No.	Compound obtained	Yield, % of theory	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated
VI	$CH_3CH=C(CH_3)-C\equiv C-C(CH_3)(CH_3)-O-Ge(C_2H_5)_3$	56	146–148/2	1.4500	1.0428	98.12	96.19
VII	$CH_3CH=C(CH_3)-C\equiv C-C(CH_3)(CH_3)-O-Ge(C_2H_5)_3$	25	125/2	1.4560	1.0309	94.27	94.19
VIII	$(CH_3)(C_2H_5)C(OH)-C\equiv C-C(OH)(CH_3)(C_2H_5)$	40	167/1	1.4700	1.0306	136.00	134.92

with triethylchlorosilane in a pyridine medium. As was found, triethylchlorogermane does not react at all with the indicated glycols even when the reaction mixture is heated to 105–110° for 10 h, evidently because of its slight hydrolyzability; triethylchlorosilane with the same glycols forms only monosilyl ethers (heating of the reaction mixture to 120° for 3 h), whereas with silicon-containing glycols triethylchlorosilane gives both mono- and disilyl ethers ([3]), and under milder conditions (heating on a water bath for 1.5 h). As can be seen, the triethylgermyl radical lowers the reactivity of the hydroxyl groups



where $R = CH_3$; $R' = CH_3,\ C_2H_5$.

The formulas and properties of the substances obtained by us are given in Table 1.

Experimental part

Action of triethylgermane on 2,7-dimethyl-3,5-octadiynediol-2,7. In a three-necked flask with a mechanical stirrer, reflux condenser, and thermometer were placed 16.6 g (0.1 mole) of the glycol; after melting, 20 g of triethylgermane and 1 ml of Speier' s catalyst were added. The reaction proceeded vigorously at a temperature of 118° and was completed—

lasted 30 min. By vacuum distillation under nitrogen the following fractions were obtained: I 90–150° (3 mm), 0.9 g; II 152° (2 mm), 26 g. For fraction II: n_D^{20} 1.4990, d_4^{20} 1.0630; MR_D found 89.61, calculated 88.89; yield 80% (of theory).

Found, %: C 58.97, 58.58; H 9.79, 9.80; Ge 22.69, 22.81; (OH) 11.24, 10.90 $C_{16}H_{30}O_2Ge$. Calculated, %: C 58.78; H 9.18; Ge 22.22; (OH) 10.46

The substance obtained, 2,7-dimethyl-3-triethylgermyl-octyn-3,5-diol-2,7, is a mobile yellowish liquid.

Action of triethylgermane on 2,7-dimethyl-octyn-3,5-diol-2,7. A mixture of 7 g of the substance, 3.5 g of $HGe(C_2H_5)_3$, and 0.5 ml of H_2PtCl_6 was heated for 1 h at 120°. Vacuum distillation gave the fractions: I up to 150° (2 mm), 1 g; II 150–152° (2 mm), 3.9 g (unreacted glycol); III 163–165° (2 mm), 1.4 g. For fraction III: n_D^{20} 1.4893, d_4^{20} 1.0921; MR_D found 128.81, calculated 129.73; yield 13%.

Found, %: (OH) 6.84, 6.60; C 53.98, 53.06; H 9.83, 9.67; Ge 29.54, 29.14
$C_{22}H_{46}O_2Ge_2$. Calculated, %: (OH) 7.01; C 54.19; H 9.44; Ge 29.80

2,7-Dimethyl-3,6-di(triethylgermyl)-octadiene-3,5-diol-2,7 is a thick yellow liquid.

Dehydration of 2,7-dimethyl-3-triethylgermyl-octyn-3,5-diol-2,7. A mixture of 3 g of the substance, 1 g of $KHSO_4$ (fused), and 0.1 g of dithizone (antioxidant) was placed in a vacuum-distillation apparatus and distilled under nitrogen. Fractions obtained: I up to 120° (2 mm), 0.3 g; II 121° (2 mm), 0.2 g; the remaining mass polymerized. For fraction II: n_D^{20} 1.5100; d_4^{20} 1.0560. MR_D found 82.31; calculated 84.89; yield 7%.

Found, %: C 65.96, 66.06; H 9.10, 9.08; Ge 24.65, 25.10
$C_{16}H_{26}Ge$. Calculated, %: C 66.07; H 8.94; Ge 24.98

The dehydrated substance, 2,7-dimethyl-3-triethylgermyl-octatrien-1,3,7-yn-5, is a readily mobile pale-yellow liquid.

Action of triethylchlorosilane on 2,7-dimethyl-3-triethylgermyl-octyn-3,5-diol-2,7. Into the reaction flask were introduced 3 g of glycol and 1.5 g of pyridine, and, with constant stirring, 3 g of triethylchlorosilane was added dropwise. A precipitate formed. After all the triethylchlorosilane had been added, the flask was heated at 110–115° for 3 h. The reaction mixture was treated with water, extracted with ether, and dried over calcined Na_2SO_4. After the ether had been distilled off, the residue was vacuum-distilled; fractions obtained: I 83–85° (1 mm), 1.2 g; II 89–171° (3 mm), 0.8 g; III 179° (3 mm), 1.1 g. Fraction I (n_D^{20} 1.4335, d_4^{20} 0.8463) is hexaethyldisiloxane. For fraction III: n_D^{20} 1.4940, d_4^{20} 1.0027; MR_D: found 127.91, calculated 125.62; yield 27%.

Found, %: (OH) 4.03, 3.69; C 59.73, 59.84; H 9.57, 9.60; (Ge+Si) 23.30, 23.15
$C_{22}H_{44}O_2GeSi$. Calculated, %: (OH) 3.88; C 59.92; H 9.98; (Ge+Si) 22.83

The substance obtained, 2,7-dimethyl-3-triethylgermyl-7-triethylsiloxy-octyn-3,5-ol-3, is a dark-yellow mobile liquid.

Action of triethylgermane on 3,8-dimethyl-4,6-decadiyne-diol-3,8. Experiment No. 1. A mixture of 19.4 g (0.1 mole) of glycol, 17 g of $HGe(C_2H_5)_3$, and 2 ml of Speier catalyst was taken. The reaction proceeded instantaneously (with evolution of heat) and ended after an hour. Vacuum distillation gave the fractions: I 90–96° (3 mm), 4 g (distilled together with water); II 146–148° (2 mm), 18.9 g. Fraction I was separated from the water, dried over calcined Na_2SO_4, and redistilled; 3 g of $(C_2H_5)_6Ge_2O$ was obtained, for which

b.p. 95–96° (3 mm), n_D^{20} 1.4615, d_4^{20} 1.1402, MR_D found 80.73, calculated 81.29.

Found, %:	C 42.71, 42.65; H 9.22, 9.30; Ge 43.07, 43.18
$C_{12}H_{30}Ge_2O$. Calculated, %:	C 42.96; H 8.95; Ge 43.31

For fraction II n_D^{20} 1.5200; d_4^{20} 1.0428. MR_D found 98.12, calculated 96.19; yield 56%.

Found, %:	(OH) 5.27, 4.99; C 64.34, 64.37; H 10.06, 10.01; Ge 21.50, 21.41
$C_{18}H_{32}OGe$. Calculated, %:	(OH) 5.08; C 64.17; H 9.50; Ge 21.56

The substance obtained, 3,8-dimethyl-4-triethylgermyldecadien-2,4-yn-6-ol-8, is a mobile liquid of pale-yellow color.

Experiment No. 2. Taken were 19.4 g (0.1 mole) of glycol, 17 g of $HGe(C_2H_5)_3$, and 1 ml of Speier' s catalyst. The reaction proceeded more slowly (in comparison with that described above), and after cooling the glycol crystallized out; therefore the contents of the flask were heated to 120° for 1 hour, after which they were distilled. Fractions obtained: I 95–97° (3 mm), 0.8 g $(C_2H_5)_6Ge_2O$; II 98–163° (2 mm), 1.2 g; III fraction 164° (2 mm), 25.1 g. For fraction III n_D^{20} 1.4964, d_4^{20} 1.0534; MR_D found 98.40, calculated 98.19; yield 70%.

Found, %:	(OH) 10.04, 9.27; C 60.53, 60.62; H 9.53, 9.50; Ge 20.83, 20.79
$C_{18}H_{34}O_2Ge$. Calculated, %:	(OH) 9.60; C 60.93; H 9.58; Ge 20.47

The synthesized substance, 3,8-dimethyl-4-triethylgermyldecyn-4,6-diol-3,7, is a slightly mobile yellow liquid.

Dehydration of 3,8-dimethyl-4-triethylgermyldecyn-4,6-diol-3,7. To 3 g of the substance, diluted with 6 ml of dry pyridine, 5 g of $POCl_3$, diluted in dry pyridine (15 ml), was added dropwise. The mixture was heated to 60° for 10 min, after which it was cooled with ice and extracted with hexane. By distillation in vacuum under nitrogen the following fractions were obtained: I 125° (2 mm), 0.25 g; II 125–147° (2 mm), 0.3 g; III 148° (2 mm), 0.5 g. For fraction I n_D^{20} 1.5260; d_4^{20} 1.0309; MR_D found 94.87, calculated 94.19; yield 9%.

Found, %:	C 67.55, 67.60; H 9.12, 9.20; Ge 22.87, 22.52
$C_{18}H_{30}Ge$. Calculated, %:	C 67.79; H 9.41; Ge 22.78

The dehydrated substance, 3,8-dimethyl-4-triethylgermyldecatrien-2,4,8-yn-6, is an easily mobile yellowish liquid. Fraction III (b.p. 125°/2 mm; n_D^{20} 1.5200; d_3^{20} 1.0430) is the product of partial dehydration, 3,8-dimethyl-4-triethylgermyldecadien-2,4-yn-6-ol-8.

Action of triethylchlorosilane on 3,8-dimethyl-4-triethylgermyldecyn-4,6-diol-3,7. Under analogous conditions, 5 g of glycol, 2.3 g of pyridine, and 4.25 g of chlorosilane were taken. After distillation in vacuum, fractions were obtained: I 83° (1 mm), 1.5 g (siloxane); II 135–160° (1 mm), 0.7 g; III 167° (1 mm), 2.6 g. For fraction III n_D^{20} 1.5100, d_4^{20} 1.0305; MR_D 136.009, calculated 134.922; yield 40%.

Found, %:	(OH) 3.76, 3.53; C 61.73, 61.62; H 9.89, 10.03; (Ge + Si) 21.00, 20.86
$C_{24}H_{48}O_2GeSi$. Calculated, %:	(OH) 3.65; C 61.45; H 10.24; (Ge + Si) 21.46

The substance obtained, 3,8-dimethyl-4-triethylgermyl-8-triethylsiloxyldecyn-4,6-ol-3, is a dark-yellow mobile liquid.

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