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Abstract

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Some Reactions of Transformation of Silicon-Containing Vinylacetylene Glycols

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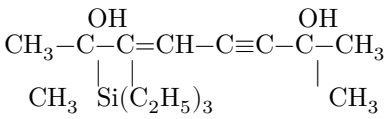
In a previous communication we considered the synthesis of silicon-containing vinylacetylene glycols[1] by the action of triethylsilane on diacetylene glycols in the presence of Speier' s catalyst—H_2PtCl_6—in isopropyl alcohol. Along with this, it seemed of interest to us to study their reactivity: to determine the influence of the triethylsilyl group on the behavior of the molecule of a silicon-containing vinylacetylene glycol in certain chemical reactions, in particular in hydrogenation reactions and in reactions involving the action of triethylsilane and triethylchlorosilane.

As we established earlier[1], when $HSi(C_2H_5)_3$ acts on diacetylene glycols in the presence of H_2PtCl_6, the reaction proceeds with addition of $HSi(C_2H_5)_3$ to only one triple bond, while the other triple bond remains intact. It was of interest to determine whether the other triple bond of the silicon-containing vinylacetylene glycol would enter into the addition reaction with $HSi(C_2H_5)_3$.

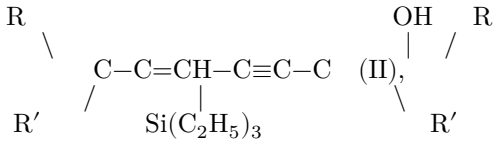
Various authors[2–4] have studied the addition of trichlorosilane to various diallyl derivatives of silicon in the presence of H_2PtCl_6, and it was found that addition of $HSiCl_3$ occurs both at one double bond and at two double bonds.

Our investigations showed that triethylsilane does not add to the triple bond of the silicon-containing vinylacetylene glycol in the presence of Speier' s catalyst even when the reaction mixture is heated to 120°. On distillation of the reaction mixture, the unreacted starting products were isolated—$HSi(C_2H_5)_3$ and the silicon-containing glycol



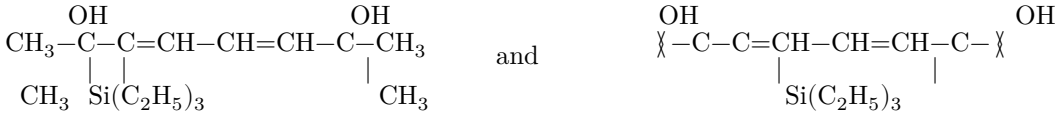
as well as products of β-cleavage I and partial dehydration II,

$$(C_2H_5)_3SiOSi(C_2H_5)_3 \text{ (I)},$$



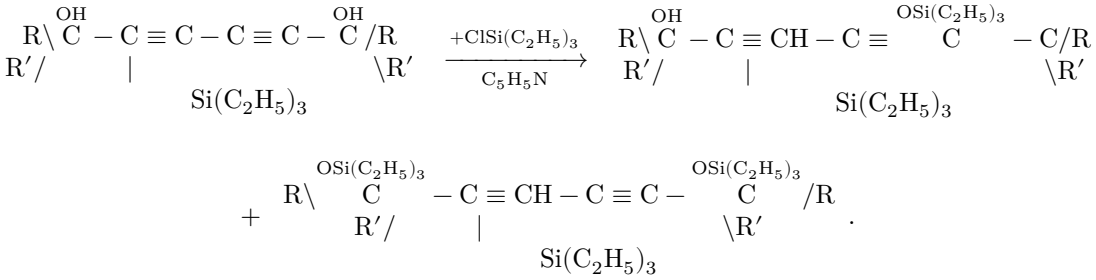
whose formation is caused by heating of the glycol with the β-position of OH to Si in the presence of H_2PtCl_6[1].

A study of the hydrogenation reaction in the presence of $Pd/CaCO_3$ and Raney nickel catalysts showed that exhaustive hydrogenation of the silicon-containing vinylacetylene glycol does not occur under our conditions; only one triple bond is hydrogenated to a double bond, and a silicon-containing diene glycol is formed. The presence of conjugated diene bonds in the hydrogenated glycols was established by studying the IR spectra of the glycols:



(the frequencies obtained were respectively 1580 and 1576 cm^{-1}).

As regards the action of triethylchlorosilane on silicon-containing vinylacetylene glycols (reaction with hydroxyl groups), here silicon does not exert any noticeable influence on the behavior of the glycol. As in the case of diacetylene glycol.(1), trichlorosilane with a silicon-containing glycol forms both mono- and disilicon ethers:



Experimental part

Action of triethylsilane on 2,7-dimethyl-3-triethylsilyl-octyn-3,5-diol-2,7. Into a three-necked flask with a mechanical stirrer and reflux condenser were placed 10 g of glycol, 7 g of $HSi(C_2H_5)_3$, and 1 ml of a 0.1 M solution of H_2PtCl_6 in isopropyl alcohol. The reaction mixture was heated to 120° for 1-

2 hours, after which it was distilled. The following fractions were obtained: 1. $(C_2H_5)_3SiH$–6.5 g, 2. $(C_2H_5)_3SiOSi(C_2H_5)_3$ 1.4 g (product of β-cleavage), 3.

$$CH_2 = C(CH_3) - C(Si(C_2H_5)_3) = CH - C \equiv C - C(OH)(CH_3) - CH_3$$

(product of partial dehydration) 2.4 g and

$$CH_3 - C(OH)(CH_3) - C(Si(C_2H_5)_3) \equiv CH - C \equiv C - C(OH)(CH_3) - CH_3$$

(unreacted glycol) 3.5 g.

Hydrogenation of 2,7-dimethyl-3-triethylsilyl-octyn-3,5-diol-2,7 with Raney nickel catalyst. 5.64 g (0.02 gram-mole) of glycol, 50 cm^3 of anhydrous ethyl alcohol, and 0.56 g of Raney nickel were placed in a hydrogenation flask. After air had been displaced from the system, absorption of hydrogen began very rapidly and ceased after 10 min. 465 ml of hydrogen was absorbed (instead of the theoretically required 448 ml), sufficient for the hydrogenation of one triple bond. A fresh portion of catalyst, 0.5 g, was added to the flask, but hydrogen absorption did not continue. After separation of the catalyst and distillation of the ethanol, the hydrogenation product was isolated, b.p. 135°/3 mm, 4.85 g.

Found, %: OH 12.82; 11.14; C 68.00; 68.11; H 11.73; 11.70; Si 10.20; 10.16 $C_{16}H_{32}O_2Si$. Calculated, %: OH 12.01; C 67.60; H 11.27; Si 9.85

The substance obtained, 2,7-dimethyl-3-triethylsilyl-octadiene-3,5-diol-2,7, is a mobile, colorless, low-viscosity liquid with a greenish-yellow tint.

Hydrogenation of 2,7-dimethyl-3-triethylsilyl-octyn-3,5-diol-2,7 with $Pd/CaCO_3$ catalyst. 5.64 g of glycol (0.02 gram-mole), 50 cm^3 of anhydrous ethanol, and 0.56 g of $Pd/CaCO_3$ (prepared according to Busch) were placed in a hydrogenation flask. 458 ml of hydrogen was absorbed (instead of the theoretically required 448 ml). The same hydrogenation product was isolated– 2,7-dimethyl-3-triethylsilyl-octadiene-3,5-diol-2,7.

Hydrogenation of 3,8-dimethyl-4-triethylsilyl-decen-4,6-diol-3,8 with $Pd/CaCO_3$ catalyst. Under analogous conditions, 3.1 g of glycol (0.1 gram-mole), 0.3 g of catalyst, and 50 cm^3 of anhydrous ethanol were taken. 232 ml of hydrogen was absorbed (theoretically ···).

required 224 ml). 2.4 g of product was isolated, b.p. 146°/3 mm.

Found, %: OH 11.92; 11.77; C 69.07; 69.35; H 11.72; 11.85; Si 9.09; 8.80 $C_{18}H_{36}O_2Si$ Calculated, %: OH 11.90; C 69.23; H 11.54; Si 8.97

The substance obtained, 3,8-dimethyl-4-triethylsilyldecadien-4,6-diol-3,8, is a colorless, not very viscous liquid with a light yellowish tint.

Hydrogenation of 2,3,8,9-tetramethyl-4-triethylsilyldecadien-4,6-diol-3,8 using $Pd/CaCO_3$ catalyst. 3.38 g of glycol (0.01 g-mol), 0.34 g of $Pd/CaCO_3$ catalyst, and 50 cm^3 of anhydrous ethanol were taken. 232 ml of hydrogen was absorbed (instead of the theoretically required 224 ml). The hydrogenation product was isolated, b.p. 158°/3 mm, 2.75 g; for it:

Found, %: OH 7.63; 8.00; C 70.32; 70.13; H 12.07; 12.35; Si 8.53; 7.93
$C_{20}H_{40}O_2Si$: Calculated, %: OH 7.25; C 70.59; H 11.76; Si 8.24

The substance obtained, 2,3,8,9-tetramethyl-4-triethylsilyldecadien-4,6-diol-3,8, is a thick, mobile, colorless liquid with a slightly greenish tint.

Hydrogenation of 1,4-di(1-oxycyclohexyl)-1-triethylsilylbutyn-1,3 in the presence of $Pd/CaCO_3$. 3.62 g of glycol (0.01 g-mol), 50 cm^3 of ethanol, and 0.36 g of catalyst were taken. 239 ml of hydrogen was absorbed (instead of the theoretically required 224). The hydrogenation product was isolated, b.p. 195°/3 mm, 2.82 g.

Found, %: OH 9.01; 9.54; C 72.76; 72.87; H 11.26; 11.34; Si 7.98; 8.08
$C_{22}H_{40}O_2Si$: Calculated, %: OH 9.29; C 72.53; H 10.99; Si 7.69

The hydrogenated substance, 1,4-di(1-oxycyclohexyl)-1-triethylsilylbutadiene-1,3, is a very thick, somewhat mobile, colorless liquid.

Hydrogenation of 1,4-di(1-oxycyclopentyl)-1-triethylsilylbutyn-1,3 in the presence of $Pd/CaCO_3$. 3.34 g of glycol (0.01 g-mol), 50 cm^3 of anhydrous ethanol, and 0.34 g of catalyst were taken. 231 ml of hydrogen was absorbed (instead of the theoretically required 224 ml). The hydrogenation product was isolated, b.p. 172°/3 mm, 2.63 g.

Found, %: OH 10.36; 10.52; C 71.23; 71.68; H 10.80; 11.00; Si 8.45; 8.60
$C_{20}H_{36}O_2Si$: Calculated, %: OH 10.18; C 71.43; H 10.71; Si 8.33

The hydrogenated substance, 1,4-di(1-oxycyclopentyl)-1-triethylsilylbutadiene-1,3, is a thick, slightly mobile, colorless liquid with a faint greenish tint.

Action of triethylchlorosilane on 2,7-dimethyl-3-triethylsilyloctyn-3,5-diol-2,7. In a three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel were placed 11.5 g of glycol (0.04 g-mol) and 6.5 g of pyridine, and 12 g of $ClSi(C_2H_5)_3$ was added dropwise. A white precipitate formed. After all the triethylchlorosilane had been added, the flask was heated on a boiling water bath for 1.5–2 hours. The reaction mixture was then filtered and distilled in vacuo. Two fractions were obtained: 1) b.p. 149°/3 mm, 5.5 g, and 2) b.p. 162°/3 mm, 4.2 g. For the 1st fraction:

Found, %: OH 4.84; 4.76; C 67.04; 66.69; H 11.70; 11.68; Si 11.62; 11.85
$C_{22}H_{44}O_2Si_2$: Calculated, %: OH 4.42; C 66.66; H 11.11; Si 11.64

The substance obtained, 2,7-dimethyl-3-triethylsilyl-7-triethylsiloxyoctyn-3,5-ol-2, is a mobile yellow liquid. For the 2nd fraction:

Found, %: C 65.41; 66.00; H 11.63; 11.65; Si 16.66; 16.25
Calculated, %: C 65.88; H 11.37; Si 16.47

The substance obtained, 2,7-dimethyl-3-triethylsilyl-2,7-ditriethylsiloxysilyloctyn-3,5, is an easily mobile yellow liquid.

Action of triethylchlorosilane on 1,4-(1-oxycyclohexyl)-1-triethylsilylbutyn-1,3. Under the conditions,

Table 1

Substance obtained	Yield, %	b.p., °C	n_D^{20}	d_4^{20}	MR found	MR calc.
$CH_3-C(OH)(CH_3)-C(Si(C_2H_5)_3)=CH-CH=CH-C(OH)(CH_3)-CH_3$	85	135/3 mm	1.4850	0.9238	88.57	88.00
$C_2H_5-C(OH)(CH_3)-C(Si(C_2H_5)_3)=CH-CH=CH-C(OH)(CH_3)-C_2H_5$	76	146/3 mm	1.4855	0.9268	96.09	97.26
$iso-C_3H_7-C(OH)(CH_3)-C(Si(C_2H_5)_3)=CH-CH=CH-C(OH)(CH_3)-C_3H_7-iso$	80	158/3 mm	1.4953	0.9361	105.97	106.56
$C_6H_5-C(OH)-C(Si(C_2H_5)_3)=CH-CH=CH-C(OH)-C_6H_5$	79	195/3 mm	1.5123	0.9905	112.51	111.52
$C_5H_9-C(OH)-C(Si(C_2H_5)_3)=CH-CH=CH-C(OH)-C_5H_9$	79	172/3 mm	1.5114	0.9876	102.57	102.30
$CH_3-C(OH)(CH_3)-C(Si(C_2H_5)_3)=CH-C\equiv C-C(OSi(C_2H_5)_3)(CH_3)-CH_3$	32	149/3 mm	1.4832	0.9068	122.85	123.48
$CH_3-C(OSi(C_2H_5)_3)(CH_3)-C(Si(C_2H_5)_3)=CH-C\equiv C-C(OSi(C_2H_5)_3)(CH_3)-CH_3$	18	162/3 mm	1.4800	0.8947	161.93	160.10
$C_6H_5-C(OH)-C(Si(C_2H_5)_3)=CH-C\equiv C-C(OSi(C_2H_5)_3)-C_6H_5$	24	198/2 mm	1.5080	0.9604	147.73	147.00
$C_6H_5-C(OSi(C_2H_5)_3)-C(Si(C_2H_5)_3)=CH-C\equiv C-C(OSi(C_2H_5)_3)-C_6H_5$	17	223/2 mm	1.5030	0.9536	183.62	183.29

analogous to the preceding ones, 10.86 g of glycol (0.03 g-mole), 5 g of pyridine, and 10 g of triethylchlorosilane were taken. Two fractions were isolated: b.p. 198°/2 mm, 4.2 g, and b.p. 223°/2 mm, 3.5 g (the constants are given in Table 1). For one fraction

Found, %: OH 3.24; 3.07; C 79.85; 70.97; H 11.38; 11.24; Si 11.93; 12.00
$C_{28}H_{52}O_2Si_2$. Calculated, %: OH 3.59; C 70.57; H 10.92; Si 11.76

The substance obtained, 1(1-oxycyclohexyl),4-(1-triethylsiloxycyclohexyl),1-triethylsilylbuten-1,3, is a mobile yellow liquid. For the other fraction

Found, %: C 68.88; 69.25; H 11.35; 11.42; Si 14.04; 14.39;
Calculated, %: C 69.15; H 11.19; Si 14.24

The substance obtained, 1,4-di-di(1-triethylsiloxycyclohexyl),1-triethylsilylbuten-1,3, is a mobile yellow liquid.

The constants of the substances obtained by us are given in Table 1.

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