CHEMISTRY

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1961

SovietRxiv

Abstract

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CHEMISTRY

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THE ACTION OF TRIETHYLSILANE ON ACETYLENIC γ-GLYCOLS IN THE PRESENCE OF Pt/C AND H_2PtCl_6

In previous communications we ([1,2]) investigated the interaction of triethylsilane with secondary and tertiary vinylethynylcarbinols in the presence of Pt/C and $0.1\,M$ $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. It was found that, in the presence of Pt/C, both secondary and tertiary vinylethynylcarbinols give products of addition at the triple bond according to the scheme:

$$\begin{array}{c} R \quad OH \\ C{-}C{\equiv}C{-}CH{=}CH_2 \\ \quad R \end{array} + (C_2H_5)_3SiH \longrightarrow \begin{array}{c} R \quad OH \\ C{-}C{=}CH{-}CH{=}CH_2 \\ R \quad Si(C_2H_5)_3 \end{array} \qquad \text{(I)}$$

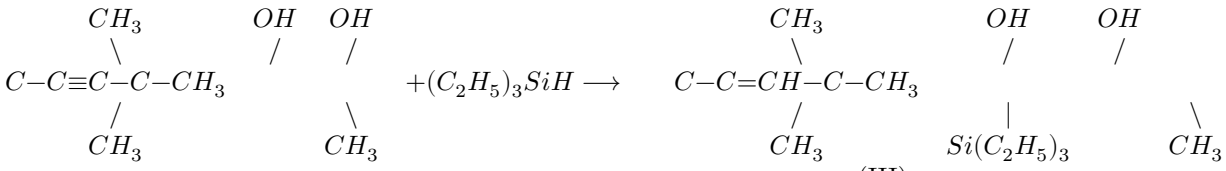
Very interesting results were obtained in the presence of $0.1\,M$ $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol ([2]). It turned out that, in the case of this catalyst, tertiary vinylethynylcarbinols add triethylsilane according to scheme (I), whereas secondary vinylethynylcarbinols add according to scheme (II), i.e., the products obtained are not products of addition at the triple bond, but organosilicon ethers:

$$RCHOH{-}C{\equiv}C{-}CH{=}CH_2 + (C_2H_5)_3SiH \longrightarrow \begin{array}{c} OSi(C_2H_5)_3 \\ RCH{-}C{\equiv}C{-}CH{=}CH_2 \end{array} \qquad \text{(II)}$$

However, besides the nature of the alcohol, the amount of catalyst is also important; in the case of *n*-propylvinylethynylcarbinol, with 2 ml of catalyst the reaction proceeds according to scheme (II), whereas with 1 ml it proceeds both according to scheme (I) and according to scheme (II) simultaneously.

Continuing the work, we decided to study the interaction of triethylsilane with acetylenic γ-glycols in the presence of Pt/C and H_2PtCl_6. We used primary (butynediol), secondary (dimethylbutynediol), and tertiary (tetramethylbutynediol and symmetrical dimethyldiethylbutynediol) glycols.

In the case of Pt/C, tetramethylbutynediol added triethylsilane with formation of an ethylenic glycol according to the scheme:



(III)

Under these conditions, symmetrical dimethyldiethylbutynediol did not react with triethylsilane. Among the products of the reaction of butynediol with triethylsilane, one fraction, according to analytical data, corresponds to the vinyl ether of triethylsilanol, $(C_2H_5)_3SiOCH{=}CH_2$.

The reactions studied were repeated using $0.1\,M$ $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. It turned out that, in the case of tetramethylbutynediol, the reaction proceeds more readily and with higher yields than with Pt/C, according to the same scheme. If symmetrical dimethyldiethylbutynediol did not react with

with triethylsilane with Pt/C, then with H_2PtCl_6 the reaction proceeds according to scheme (III) with a yield of 36% of theory. The primary glycol-butynediol reacts according to scheme (III), whereas the secondary glycol forms a product of simultaneous addition at the triple bond and at the hydroxyl:

$$CH_3CHOH{-}C{\equiv}C{-}CHOH{-}CH_3 + 2(C_2H_5)_3SiH \rightarrow$$

$$\rightarrow CH_3CHOH{-}C{=}CH{-}CH{-}CH_3$$

$$\begin{matrix} OSi(C_2H_5)_3 \\ / \end{matrix} \qquad \begin{matrix} Si(C_2H_5)_3 \\ | \end{matrix}$$

For comparison of the products of the reactions of primary and secondary glycols with triethylsilane, we decided to obtain the mono- and diesters of these glycols from triethylchlorosilane according to the schemes:

$$RCHOH{-}C{\equiv}C{-}CHOH{-}R + (C_2H_5)_3SiCl \xrightarrow{C_5H_5N} RCHOH{-}C{\equiv}C{-}CHR$$

$$\begin{matrix} OSi(C_2H_5)_3 \\ / \end{matrix} \qquad \text{(IV)}$$

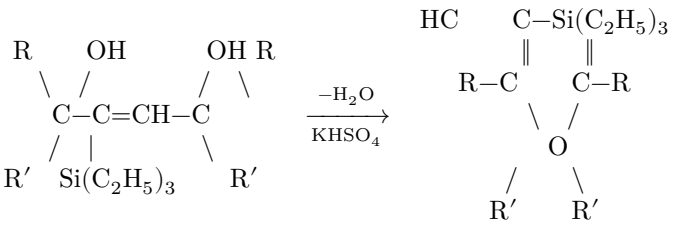
$$\mathrm{RCHOH{-}C{\equiv}C{-}CHOHR} + 2(\mathrm{C_2H_5})_3\mathrm{SiCl} \xrightarrow{2\mathrm{C_5H_5N}} \mathrm{RCH{-}C{\equiv}C{-}CH{-}R}$$

$$\begin{matrix} \mathrm{OSi(C_2H_5)_3}, & \mathrm{OSi(C_2H_5)_3} \\ / & / \end{matrix} \qquad \text{(V)}$$

$$\mathrm{R = H \text{ and } CH_3}.$$

Both reactions were carried out under identical conditions; only the ratios of the reacting components were varied, but it turned out that in both cases only the diester according to scheme (V) was obtained. The esters obtained did not coincide with any of the products of the reactions of the corresponding glycols with triethylsilane.

Organosilicon ethylenic glycols were dehydrated with $KHSO_4$ analogously to ethylenic glycols, with formation of furan compounds according to the scheme:



$$\mathrm{R = H \text{ and } CH_3}; \quad \mathrm{R' = H,\ CH_3 \text{ and } C_2H_5}.$$

Experimental Part

Action of triethylsilane on tetramethylbutynediol in the presence of H_2PtCl_6. Into a three-necked flask equipped with a mechanical stirrer and a reflux condenser were placed 18 g of tetramethylbutynediol, 17 g of triethylsilane, and 1.2 ml of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. The reaction mixture was heated on a boiling water bath. On cooling, the reaction mass crystallized; recrystallization was carried out from benzene; white, shiny needle-shaped crystals were obtained, mp 84.5-86.5°, 26.5 g (after recrystallization), yield 75.5% of theory.

Found, %: OH 12.88; 13.41; C 64.82; H 12.00; Si 10.77
$C_{14}H_{30}SiO_2$. Calculated, %: OH 13.26; C 64.72; H 11.62; Si 10.84

Action of triethylsilane on tetramethylbutynediol in the presence of Pt/C. Into a three-necked flask equipped with a mechanical stirrer and a reflux condenser were placed 18 g of glycol, 17 g of triethylsilane, and 0.15 g of Pt/C.

The reaction mixture was heated on a boiling water bath at 97–98° for 20 h; after cooling to room temperature the mass crystallized; recrystallization from benzene gave white, shiny crystals, mp 84.5–85.5°, 18.5 g, yield 52.89% of theory.

Dehydration of 1,1,4,4-tetramethyl-2-triethylsilylbuten-2-ol-1,4. 7 g of glycol, 1 g of $KHSO_4$, and 0.1 g of dithizone

placed in an apparatus for vacuum distillation. The mixture was heated in vacuo under nitrogen for 30 min at no higher than 100°, after which it was distilled. A fraction with b.p. 74–77° at 2 mm was obtained, 5 g; found n_D^{20} 1.4590; d_4^{20} 0.8666; MR_D 75.71; calculated 75.75; yield 76.9% of theory; no hydroxyl was detected.

Found %:	C	70.60;	70.47;	H	12.10;	12.20;	Si	11.30;	11.20
$C_{14}H_{28}CSi$. Calculated %:	C	70.00;		H	11.66;		Si	11.66	

According to the analytical data, the substance obtained corresponds to 2,2,5,5-tetramethyl-3-triethylsilyldihydrofuran.

Action of triethylsilane on symmetrical dimethyldiethylbutynediol in the presence of H_2PtCl_6. Under the conditions of the preceding experiment, 10 g of dimethyldiethylbutynediol, 8 g of triethylsilane, and 2 ml of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol were taken. After distillation the following fractions were obtained: I 43° (7 mm), 1.4 g; II 85–92° (2 mm), 2.2 g; III 92–100° (2 mm) (crystallized); IV 145–147° (2 mm), 6.5 g.

For fraction IV found: n_D^{20} 1.4870; d_4^{20} 0.9372; MR_D 87.74; calculated MR_D 88.47; found %: OH 10.11; 11.60; calculated %: OH 11.92; yield 36% of theory.

Found %:	C	67.67;	67.65;	H	12.38;	12.12;	Si	9.26;	9.55
$C_{16}H_{34}O_2Si$. Calculated %:	C	67.13;		H	11.88;		Si	9.75	

The substance obtained is symmetrical 1,1,4,4-dimethyldiethyl-2-triethylsilylbutene-2-ol-1,4, a colorless, very viscous liquid.

Dehydration of 1,1,4,4-dimethyldiethyl-2-triethylsilylbutene-2-ol-1,4. 3.88 g of the substance, 2 g of $KHSO_4$, and 0.1 g of dithizone were taken. After 20 min of boiling, distillation gave a fraction with b.p. 89–90° (2 mm), 2 g; yield 55% of theory; found n_D^{20} 1.4670, d_4^{20} 0.8838; MR_D 84.15; calculated MR_D 85.01; no hydroxyl was detected.

Found %:	C	71.35;	71.68;	H	12.14;	12.22;	Si	9.75;	10.14
$C_{16}H_{32}OSi$. Calculated %:	C	71.64;		H	11.94;		Si	10.44	

The synthesized substance is a mobile colorless liquid, 2,5-dimethyl-2,5-diethyl-3-triethylsilyldihydrofuran.

Action of triethylsilane on butynediol in the presence of Pt/C. 21 g of butynediol, 29 g of triethylsilane, and 0.2 g of Pt/C were taken. After 20 h of heating on a boiling water bath, part of the reaction mass crystallized; the mixture was filtered, and the filtrate (30 g) was distilled; first the unreacted triethylsilane distilled off, 14 g; by distillation of the remaining part the following fractions were obtained: I–96–97° (10 mm), 5.5 g; II–97.5–146° (3 mm), 0.9 g; III–131° (2 mm), 1.3 g; IV–139° (2 mm), 1.5 g.

Fraction I had n_D^{20} 1.4414, d_4^{20} 0.8578; found MR_D^{ex} 48.68; calculated 49.09; yield 16% of theory; no hydroxyl was detected.

	Found %:	C 60.71;	H	11.22;	Si	18.12
$C_8H_{18}OSi$.	Calculated %:	C 60.77;	H	11.39;	Si	17.72

According to the analytical data, the substance corresponds to the vinyl ether of triethylsilanol.

Action of triethylsilane on butynediol in the presence of H_2PtCl_6. Under analogous conditions, 21 g of glycol, 29 g of triethylsilane, and 2 ml of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol were taken. After distillation the following fractions were obtained: I–44° (5 mm), 7.6 g; II–65° (2 mm), 1.8 g; III –104–125° (2.5 mm), 5 g, crystals (butynediol); IV–127–129° (2 mm), 5 g; V–139–146° (3 mm), 11.7 g; VI–150° (2 mm), 7.8 g.

Fraction V was redistilled. Va–60–70° (2 mm) and Vb–127–129° (2 mm), 4 g, were obtained; the remaining part did not distil. Fractions IV and Vb had the same n_D^{20} 1.4880; d_4^{20} 0.9656; found MR_D 60.27; calculated

60.69; found, %: OH 13.26; 15.55; calculated, %: OH 16.92; yield 18% of theory.

$C_{10}H_{22}O_2Si$.	Found, %:	C 60.20;	60.01;	H 11.30;	11.11;	Si 13.35;	13.65	
	Calculated, %:	C 59.40;		H 10.88;		Si 13.86		

The substance obtained by us is 2-triethylsilylbutenediol, a colorless, slightly viscous liquid.

Dehydration of 2-triethylsilylbutenediol. 2 g of the substance, 2 g of $KHSO_4$, and 0.1 g of dithizone were taken; after boiling for 20 min, distillation was carried out, and a fraction with b.p. 70–71° (4 mm), 1.2 g, was obtained; yield 66% of theory. Found n_D^{20} 1.4652; d_4^{20} 0.9031; MR_D 56.34; calculated MR_D 57.23; hydroxyl was not detected.

$C_{10}H_{20}SiO$.	Found, %:	C 65.40;	64.32;	64.75;	H 11.59;	11.47;	11.36;	Si 14.94;	15.21;	14.95	
	Calculated, %:	C 65.22;			H 10.87;			Si 15.22			

According to the analytical data, the substance corresponds to 3-triethylsilyldihydrofuran.

Preparation of $(C_2H_5)_3SiOCH_2—C \equiv C—CH_2OSi(C_2H_5)_3$ **from triethylchlorosilane.** In a three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel were placed 5 g of butynediol and 4.4 g of pyridine, and 8 g of triethylchlorosilane was added dropwise; the mixture warmed strongly and a white precipitate formed. After all of the triethylchlorosilane had been added, the mixture was heated on a boiling water bath for 1.5 h, the precipitate was filtered off, and the product was distilled in vacuo under nitrogen. Fractions I–III were obtained. Fraction III had n_D^{20} 1.4558; d_4^{20} 0.9049; found MR_D 94.25; calculated 95.38; yield 46% of theory. Hydroxyl was not detected.

$C_{16}H_{34}O_2Si_2$.	Found, %:	C 60.86; 60.69;	H 11.60; 11.39;	Si 18.01; 17.20
	Calculated, %:	C 61.14;	H 10.83;	Si 17.84

The synthesized substance is 1,4-diethylsiloxybut-2-yne, a colorless mobile liquid.

Action of triethylsilane on dimethylbutynediol in the presence of H_2PtCl_6**.** Under analogous conditions, 17.6 g of dimethylbutynediol, 18 g of triethylsilane, and 2 ml of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol were taken. After distillation, fractions I–VIII were obtained.

For fraction VII, n_D^{20} 1.4740; d_4^{20} 0.9160; MR_D 105.50; calculated MR_D 106.57; found, %: OH 5.76; calculated, %: OH 5.05; yield 10% of theory.

$C_{18}H_{40}O_2Si_2$.	Found, %:	C 62.31; 62.78;	H 11.99; 11.94;	Si 15.81; 16.02
	Calculated, %:	C 62.79;	H 11.63;	Si 16.32

The substance synthesized by us is 3-triethylsilyl-5-triethylsiloxyhex-3-en-2-ol, a colorless mobile liquid.

Preparation of

$$(C_2H_5)_3SiOCH(CH_3)—C \equiv C—CH(CH_3)OSi(C_2H_5)_3$$

from triethylchlorosilane. 8 g of dimethylbutynediol, 5.4 g of pyridine, and 10 g of triethylchlorosilane were taken. After distillation, fractions I–III were obtained. For fraction III, n_D^{20} 1.4497; d_4^{20} 0.8865; MR_D 103.63; calculated 104.64; yield 16.8% of theory. Hydroxyl was not detected.

$C_{18}H_{38}O_2Si_2$.	Found, %:	C 63.18;	63.15;	H 11.42;	11.84;	Si 16.09;	16.15
	Calculated, %:	C 63.16;		H 11.11;		Si 16.37	

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Received
2 IX 1960

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