The Action of Triethylsilane on Diacetylenic Glycols in the Presence of $\mathrm{H_2PtCl_6}$

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Abstract

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The Action of Triethylsilane on Diacetylenic Glycols in the Presence of H_2PtCl_6

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Many works have been devoted to the preparation of unsaturated oxygen-containing organosilicon compounds. In 1956, A. D. Petrov and L. L. Shchukovskaya ([1]) first synthesized β-containing alcohols by addition of triethylsilane to ethynylcarbinols in the presence of Pt/C. Subsequently, A. D. Petrov, I. M. Tverdtsiteli, and K. I. Cherkezishvili ([2,3]) studied the reaction of triethylsilane with vinylethynylcarbinols and acetylenic γ-glycols in the presence of Pt/C catalysts and a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. They established that, in the case of a glycol in the presence of Speier' s catalyst, the primary glycol reacts with addition at the triple bond, whereas the secondary one forms a product of simultaneous addition at the triple bond and at the hydroxyl group.

It was of interest to study the behavior, in analogous reactions, of glycols of the diacetylenic series that are more complex in structure. In this case, owing to the presence in the molecule of two hydroxyl and two acetylenic groups, it seemed possible for the reactions to proceed in different directions. Study of the reaction products indicates that the reaction proceeds only in one direction, in particular with addition of $HSi(C_2H_5)_3$ to one triple bond of the glycol; the resulting product I then decomposes with formation of product II (β-cleavage), which subsequently is converted into siloxane (III). In addition, the product I obtained undergoes dehydration with formation of product IV.

[structural scheme]

$$R(OH)C{-}C{\equiv}C{-}C{\equiv}C{-}C(OH)(R)(R') \xrightarrow[H_2PtCl_6\cdot 6H_2O]{+HSi(C_2H_5)_3} R(OH)C{-}C{=}CH{-}C{\equiv}C{-}C(OH)(R)(R') \quad (I)$$

$$\longrightarrow (C_2H_5)_3SiOH \quad (II)$$

$$(C_2H_5)_3SiOH \longrightarrow (C_2H_5)_3SiOSi(C_2H_5)_3 \quad (III)$$

$$R_2C{=}C(Si(C_2H_5)_3){-}CH{-}C{\equiv}C{-}C(OH)(R)(R') \quad (IV)$$

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

At first we regarded the product of partial dehydration (IV) as a monoether formed by addition of $HSi(C_2H_5)_3$ to one hydroxyl group.

To verify this, we decided to synthesize monoethers of these glycols by the action of triethylchlorosilane in pyridine:

$$R(OH)C{-}C{\equiv}C{-}C{\equiv}C{-}C(OH)(R)(R') \xrightarrow[C_5H_5N]{+ClSi(C_2H_5)_3} R(OSi(C_2H_5)_3)C{-}C{\equiv}C{-}C{\equiv}C{-}C(OH)(R)(R') + R(OSi(C_2H_5)_3)C{-}C{\equiv}C{-}C{\equiv}C{-}C(OSi(C_2H_5)_3)(R)(R') ;$$

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

The constants of the monoethers obtained did not coincide with the constants of the substance under investigation. This led us to the conclusion that, in the course of the reaction, triethylsilane does not react with the hydroxyl groups of the glycol.

The formation of a partial dehydration product was established both by study of the substance itself (IV) and by study of the oxidation products. The simultaneous formation of dehydration products of alcohols and products of β-cleavage in the synthesis of β-alcohols from $(CH_3)_3SiCH_2MgCl$ and a series of carbinol compounds was noted by A. D. Petrov et al. ([4]), which introduced a substantial addition to Whitmore' s cleavage scheme.

Table 1

No.	Compound obtained	Yield of theor., %	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.
1	$(CH_3)_2C(OH)C{\equiv}C{-}C{\equiv}C{-}C(OH)(CH_3)_2$	59	121/2	1.4890	0.9225	88.04	86.86
2	$CH_2{=}C(CH_3)C{\equiv}C{-}C{\equiv}C{-}C(OH)(CH_3)_2$	11	143/3	1.5002	0.9072	84.07	84.84
3	$CH_2{=}C(CH_3)C{\equiv}C{-}C{\equiv}C{-}CH_2OH$	18	96/3	1.4976	0.8799	81.89	82.42
4	$CH_3C(OH)(C_2H_5)C{\equiv}C{-}C{\equiv}C{-}C(OH)(CH_3)_2$	12	127/2	1.4920	0.9251	97.01	96.12
5	$CH_3CH{=}C(CH_3)C{\equiv}C{-}C{\equiv}C{-}C(OH)(CH_3)(C_2H_5)$	22	122/2	1.4920	0.9046	93.67	94.10
6	$CH_3CH{=}C(CH_3)C{\equiv}C{-}C{\equiv}C{-}CH{=}CH_2$	24	113/4	1.5100	0.8822	92.88	90.45
7	$(CH_3)_2C(OSi(C_2H_5)_3)C{\equiv}C{-}C{\equiv}C{-}C(OSi(C_2H_5)_3)(CH_3)_2$	39	176/3	1.4700	0.8938	123.00	121.55
8	$(CH_3)_2C(OSi(C_2H_5)_3)C{\equiv}C{-}C{\equiv}C{-}C(OH)(CH_3)_2$	15	136/3	1.4720	0.9037	85.80	84.9
9	$CH_3C(OSi(C_2H_5)_3)(C_2H_5)C{\equiv}C{-}C{\equiv}C{-}C(OSi(C_2H_5)_3)(CH_3)(C_2H_5)$	55	176/3	1.4739	0.8942	132.63	134.19
10	$CH_3C(OSi(C_2H_5)_3)(C_2H_5)C{\equiv}C{-}C{\equiv}C{-}C(OH)(CH_3)(C_2H_5)$	22	161/3	1.4790	0.9170	95.23	94.19

Since the silicon-containing vinylethynyl glycols obtained by us are comparatively stable—on storage (6–8 months) they do not undergo significant transformations and distill without separation of β-cleavage products—we assume that both partial dehydration and β-cleavage occur during the reaction

in the presence of the catalyst H_2PtCl_6, or of the products of its partial reduction ($PtCl_4, PtCl_2$). We carried out dehydration of the silicon-containing vinylethynyl glycols with $KHSO_4$; the yields of the dehydrated products were small (19–24%); dehydration is accompanied by β-cleavage.

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

Experimental Part

Action of triethylsilane on 2,7-dimethyl-3,5-octadiynediol-2,7 in the presence of H_2PtCl_6. A three-necked flask with a mechanical stirrer and a reflux condenser was charged with 16.6 g of the glycol; after melting by heating, 24 g of $HSi(C_2H_5)_3$ and 2 ml of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol were added. The reaction proceeded vigorously, with evolution of heat, and was completed in 1–2 hours. The reaction mixture was distilled in vacuo under nitrogen. The following fractions were obtained: fraction I: 34–35°/3 mm, 4.5 g; fraction II: 90–113°/3 mm, 0.9 g; fraction III: 114°/3 mm, 3 g; fraction IV: 121°/2 mm, 16.8 g. Fraction I: (b.p. 34–35°/3 mm, n_D^{20} 1.4350, d_4^{20} 0.8632) —triethylsilanol, which on standing is converted into hexaethyldisiloxane (n_D^{20} 1.4330, d_4^{20} 0.8460). For fraction III: n_D^{20} 1.5002, d_4^{20} 0.9072,

$C_{16}H_{28}OSi$. Found, %: OH 7.2; 7.5; C 72.81; 72.62; H 10.28; 10.44; Si 10.70; 10.96
Calculated, %: OH 6.32; C 72.72; H 10.66; Si 10.66

MR_D found 84.07, calculated 84.84.
The substance obtained, 2,7-dimethyl-3-triethylsilyloctadien-1,3-yn-5-ol-7, is a mobile liquid of pale yellowish color.

For fraction IV: n_D^{20} 1.4890, d_4^{20} 0.9225.

$C_{16}H_{30}O_2Si$. Found, %: OH 11.82; 12.34; C 68.15; 67.87; H 10.73; 10.54; Si 10.04; 10.32
Calculated, %: OH 12.13; C 68.11; H 10.64; Si 9.93

MR_D found 88.04, calculated 86.86.
The synthesized substance, 2,7-dimethyl-3-triethylsilylocten-3,5-diol-3,8, is a thick liquid of pale yellowish color.

Dehydration of 2,7-dimethyl-3-triethylsilylocten-3,5-diol-2,7. Seven grams of the substance, 7 g of fused $KHSO_4$, and 0.2 g of dithizone were placed in an apparatus for vacuum distillation, heated under nitrogen at not above 100° for 40 min, after which distillation was carried out. The following fractions were obtained: fraction I: b.p. 34–35°/3 mm, $(C_2H_5)_3SiOH$, 1.5 g; fraction II: 96°/3 mm, 1.1 g; the remaining mass polymerized. For fraction II: n_D^{20} 1.4976, d_4^{20} 0.8799.

$C_{16}H_{26}Si$. Found, %: C 78.47; 78.69; H 10.79; 11.01; Si 11.81; 11.94
Calculated, %: C 78.04; H 10.62; Si 11.34

MR_D found 81.89, calculated 82.42. The dehydrated substance, 2,7-dimethyl-3-triethylsilyloctatrien-1,3,7-yn-5, is a readily mobile, colorless liquid.

Action of triethylsilane on 3,8-dimethyl-4,6-decadiynediol-3,8. Under analogous conditions, 19.6 g of the glycol, 24 g of $HSi(C_2H_5)_3$, and 2 ml of 0.1 M H_2PtCl_6 in isopropyl alcohol were taken. After distillation the following fractions were obtained: fraction I: b.p. 34–35°/3 mm (silanol), 3 g; fraction II: 100–121°/3 mm, 1.5 g; fraction III: 122°/2 mm, 5.2 g, and fraction IV: 129°/2 mm, 16.5 g. For fraction III: n_D^{20} 1.4920, d_4^{20} 0.9043.

$C_{18}H_{32}OSi$. Found, %: OH 6.2; 6.4; C 73.61; 73.81; H 11.89; 11.48; Si 9.01; 9.29
Calculated, %: OH 5.68; C 73.97; H 10.96; Si 9.59

MR_D found 93.67, calculated 94.10.
The substance obtained, 3,8-dimethyl-4-triethylsilyldecadien-2,4-yn-6-ol-8, is a mobile liquid of pale greenish-yellow color. For fraction IV: n_D^{20} 1.4920, d_4^{20} 0.9251.

$C_{18}H_{34}O_2Si$. Found, %: OH 10.80; 10.54; C 69.85; 69.64; H 10.51; 10.65; Si 9.45; 9.35
Calculated, %: OH 9.8; C 69.68; H 10.97; Si 9.03

MR_D found 97.21, calculated 96.12.
The synthesized substance is 3,8-dimethyl-4-triethylsilyldecen-4,6-diol-3,7, a thick, low-mobility liquid of pale yellow color.

Dehydration of 3,8-dimethyl-4-triethylsilyldecyne-4,6-diol-3,8. 10 g of the substance, 10 g of $KHSO_4$, and 0.2 g of thiozone were taken. After 40 min of boiling, distillation was carried out; the following fractions were obtained: fraction I: b.p. 34–35°/3 mm (silanol), 3.5 g; fraction II: 113°/3 mm, 2.1 g; the remaining mass polymerized. For fraction II: n_D^{20} 1.51000, d_4^{20} 0.8822.

Found, %: C 79.34; 79.11; H 10.38; 10.51; Si 9.55; 10.01
$C_{18}H_{30}Si$. Calculated, %: C 78.83; H 10.95; Si 10.22

MR_D found 92.88, calculated 91.45.

The dehydrated substance, 3,8-dimethyl-4-triethylsilyldecatriene-2,4,8-yne-6, is a colorless, mobile liquid.

Action of triethylchlorosilane on 2,7-dimethyl-3,5-octadiyne-diol-2,7. Into a three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel were placed 16.6 g of glycol and 15.8 g of pyridine, and 30 g of triethylchlorosilane 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 h. The reaction mixture was then filtered and distilled in vacuo. The following fractions were obtained: fraction I: 50–114°/3 mm, 3 g; fraction II: 115°/3 mm, 4.8 g; fraction III: 115–138°, 2.4 g; fraction IV: 139°, 8.8 g. For fraction II: n_D^{20} 1.4720, d_4^{20} 0.9137.

Found, %: OH 6.32; 6.48; C 68.51; 68.70; H 10.42; 10.30; Si 10.35; 10.68
$C_{16}H_{28}O_2Si$. Calculated, %: OH 5.98; C 68.57; H 10.00; Si 10.00

MR_D found 86.80, calculated 84.93.

The substance obtained, 2,7-dimethyl-2-triethylsiloxyoctadiyne-3,5-ol-7, is a colorless, mobile liquid. For fraction IV: n_D^{20} 1.4700, d_4^{20} 0.8938.

Found, %: C 67.21; 67.35; H 10.50; 10.45; Si 14.15; 13.95
$C_{22}H_{42}O_2Si_2$. Calculated, %: C 67.00; H 10.67; Si 14.21

MR_D found 123.00, calculated 121.55.

The synthesized substance, 2,7-dimethyl-2,7-ditriethylsiloxyoctadiyne-3,5, is a colorless, mobile liquid.

Action of triethylchlorosilane on 3,8-dimethyl-4,6-decadiyne-diol-3,8. Under analogous conditions, 19.6 g of glycol, 15.8 g of pyridine, and 30 g of triethylchlorosilane were taken. After distillation under vacuum, the following fractions were obtained: fraction I: 50–135°/3 mm, 3.4 g; fraction II: 136°, 6.8 g; fraction III: 138–150°, 2.3 g; fraction IV: 153°, 10.8 g. For fraction II: n_D^{20} 1.4790, d_4^{20} 0.9170.

Found, %: OH 6.68; 6.02; C 69.85; 69.64; H 10.51; 10.65; Si 9.45; 9.75
$C_{18}H_{32}O_2Si$. Calculated, %: OH 5.31; C 70.13; H 10.38; Si 9.09

MR_D found 95.23, calculated 94.19.

The synthesized substance, 2,8-dimethyl-3-triethylsiloxydecadiyne-4,6-ol-8, is a colorless, mobile liquid. For fraction IV: n_D^{20} 1.4739, d_4^{20} 0.8942.

Found, %: C 67.89; 67.97; H 10.83; 10.63; Si 13.86; 13.77
$C_{24}H_{46}O_2Si_2$. Calculated, %: C 68.22; H 10.92; Si 13.27

MR_D found 132.63, calculated 134.19.

The synthesized substance, 3,8-dimethyl-3,8-ditriethylsiloxydecadiyne-4,6, is a colorless, mobile liquid.

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