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Abstract

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SYNTHESIS AND TRANSFORMATIONS OF TRIALKYLSILYLETHYNYLVINYL ALKYL ETHERS

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Synthesis based on diacetylene has opened up a broad possibility for obtaining a whole series of ethynylvinyl alkyl ethers possessing high reactivity. Various reactions with ethynylvinyl alkyl ethers have been widely studied in the works of Herberts (^{1}), Frank (^{2}), and other investigators ($^{3-7}$), in which the synthesis and their interaction with alcohols, ketones, and mercaptans are described. Diacetylene and its monosubstituted derivatives form the corresponding magnesium bromide derivatives ($^{8-10}$), the interaction of which with various carbonyl compounds and carbon dioxide is described in the literature (^{11}). Earlier (^{12}) we studied the interaction of diacetylene with trialkylsilane chlorides according to the scheme:

$$\mathrm{HC \equiv C - C \equiv CH \xrightarrow{C_2H_5MgBr} BrMgC \equiv C - C \equiv C - MgBr \xrightarrow{R_3SiCl}}$$

$$\mathrm{\rightarrow R_3SiC \equiv C - C \equiv C - SiR_3.} \qquad (1)$$

Dornow and Ische (^{13,14}) obtained the magnesium bromide derivative of ethynylvinyl methyl and ethynylvinyl ethyl ethers and condensed them with diethyl carbonate and with ethyl orthocarbonate.

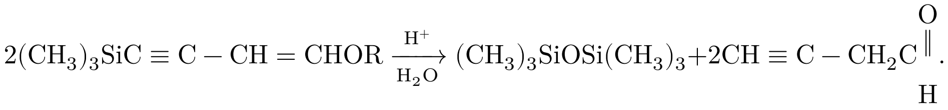
The purpose of the present investigation is to study the interaction of ethynylvinyl alkyl ethers with trialkylsilane chlorides. The synthesis of trialkylsilylethynylvinyl alkyl ethers was carried out via the Mg-organic derivative, obtained not in tetrahydrofuran solution, as in Dornow and Ische, but in ether:

$$\mathrm{C_2H_5MgBr + HC \equiv C - CH = CHOR \rightarrow BrMgC \equiv C - CH = CHOR;} \qquad (2)$$

$$\mathrm{BrMgC \equiv C - CH = CHOR + R_3SiCl \rightarrow R_3SiC \equiv C - CH = CHOR + MgClBr.} \qquad (3)$$

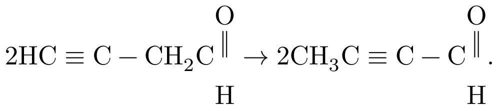
Reactions (2) and (3) proceed under very mild conditions.

The trialkylsilylethynylvinyl butyl ethers obtained resemble, in their chemical properties, ethynylvinyl alkyl ethers that do not contain silicon (they are also readily hydrolyzed by 2% H_2SO_4), but they also have their own distinctive features. Hydrolysis carried out in order to prove the structure of the trialkylsilylethynylvinyl alkyl ethers showed that, in this case, cleavage at the Si—C bond occurs:



$$2(CH_3)_3SiC \equiv C-CH=CHOR \xrightarrow[H_2O]{H^+} (CH_3)_3SiOSi(CH_3)_3 + 2CH \equiv C-CH_2C\overset{O}{\underset{H}{\|}}.$$

The butyn-1-al-4 formed as a result of the reaction isomerizes into tetrolic aldehyde:

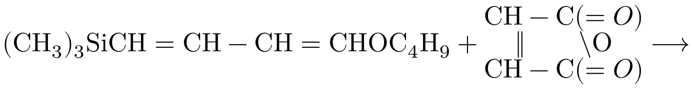


$$2HC \equiv C-CH_2C\overset{O}{\underset{H}{\|}} \rightarrow 2CH_3C \equiv C-C\overset{O}{\underset{H}{\|}}.$$

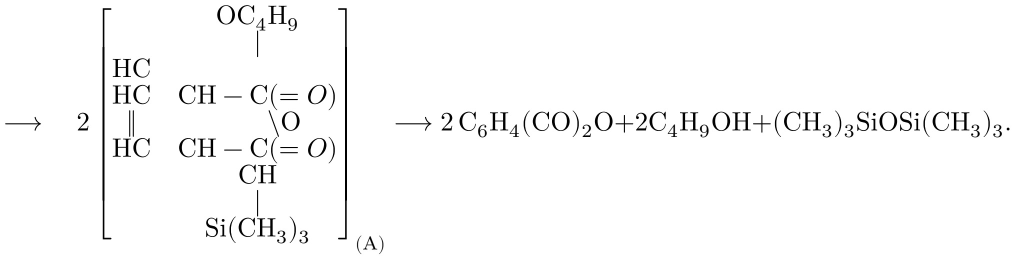
Unlike ethynylvinyl alkyl ethers that do not contain silicon, trialkylsilylethynylvinyl alkyl ethers are not hydrogenated over $PtO_2 \cdot H_2O$ or over Pd deposited on calcium sulfate (15), but are hydrogenated only over a mixture of 2% $Pd/CaCO_3$ and 5% Pt/C. Stepwise hydrogenation gave trimethylsilylbutoxy-1,3-butadiene

$$(CH_3)_3SiC \equiv C-CH=CHOR \xrightarrow{H_2} (CH_3)_3SiCH=CH-CH=CHOR.$$

On condensation of the latter with maleic anhydride an adduct (A) is formed, with subsequent elimination (16) of butyl alcohol and trimethylsilanol, which under the reaction conditions gives hexamethyldisiloxane. It was established that the adduct is phthalic anhydride.



$$(CH_3)_3SiCH=CH-CH=CHOC_4H_9 + \begin{array}{l} CH-C(=O) \\ \| \qquad \backslash O \\ CH-C(=O) \end{array} \longrightarrow$$



$$\longrightarrow 2\,[\text{A}] \longrightarrow 2\,C_6H_4(CO)_2O + 2C_4H_9OH + (CH_3)_3SiOSi(CH_3)_3.$$

The silicon-containing ethynylvinyl butyl ether, on heating with butanol without a catalyst, and also in the presence of 1-2% alkaline or acidic catalyst, does not give the acetal of trimethylsilylbutyn-1-al-4.

Experimental Part

Synthesis of ethynylvinyl butyl ether

A 2% alcoholic solution of KOH was placed in a round-bottom flask equipped with a stirrer and a reflux condenser. The system was purged with dry nitrogen, after which diacetylene was passed, with a stream of nitrogen, into the reaction mixture heated to 70–75°. After completion of the reaction the mixture was washed 3–4 times with water, dried over ignited potash, and distilled in vacuo. The characteristics of the ethynylvinyl and trialkylsilylethynylvinyl butyl ethers obtained are given in Table 1.

Table 1

Name of ether	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Found, % C	Found, % H	Found, % Si	Calculated, % C	Calculated, % H	Calculated, % Si
Ethynylvinyl butyl ether*	61.5°/12	1.4712	0.8664	40.04	38.16	77.1	9.70	–	77.36	9.85	–
Trimethylsilylethynylvinyl butyl ether	110–112°/15	1.4695	0.8589	63.73	63.68	67.05	10.23	14.12	67.28	10.27	14.30
Triethylsilylethynylvinyl butyl ether	105–106°/7	1.4895	0.8886	77.10	77.57	70.40	10.90	11.82	70.52	11.01	11.78

* In addition to the ether, acetal was isolated.

Synthesis of trimethylsilylethynylvinyl butyl ether

$(CH_3)_3SiC \equiv C - CH = CHOC_4H_9$. In a three-necked flask ⋯

with a stirrer, equipped with a condenser, dropping funnel, and thermometer, ethylmagnesium bromide was prepared from 2.9 g of magnesium and 13.1 g of C_2H_5Br. To the ethylmagnesium bromide cooled to −10°, 14.5 g of ethynylvinyl butyl ether was added dropwise at room temperature with stirring. The mixture was stirred at 20° for 4-5 h, and then 13 g of trimethylsilyl chloride was added dropwise. After an hour the reaction mixture was left overnight, and the next day the reaction mixture was stirred for another 3 h; then the precipitate was filtered off and the filtrate was distilled in a stream of nitrogen. On distillation the following fractions were isolated: I) 24–38°/14 mm; II) 110–112°/15 mm.

Fraction I is unreacted trimethylsilyl chloride, slightly contaminated with the trimethylsilylethynylvinyl butyl ether obtained.

Fraction II—13.6 g (yield 50.7%) of trimethylsilylethynylvinyl butyl ether, b.p. 110–112°/15 mm, n_D^{20} 1.4695; d_4^{20} 0.8589. MR_D found 63.73; calculated* 63.68.

Found, %:	C 67.05; H 10.23; Si 14.12
$C_{11}H_{20}OSi$. Calculated, %:	C 67.28; H 10.27; Si 14.30

Under analogous conditions, triethylsilylethynylvinyl butyl ether was synthesized in 52.3% yield, b.p. 105–106°/7 mm, n_D^{20} 1.4895; d_4^{20} 0.8886, MR_D found 77.16, calculated 77.57.

Found, %:	C 70.40; H 10.90; Si 11.82
$C_{14}H_{26}OSi$. Calculated, %:	C 70.52; H 11.01; Si 11.78

Hydrolysis of trimethylsilylethynylvinyl butyl ether. a) Into a 200-ml flask, with 25 ml of 2% H_2SO_4 and 15 ml of $NaHSO_3$, a thin-walled ampoule containing a 0.1-0.2 g sample of the ether was placed. In the closed flask the ampoule containing the ether was broken by vigorous shaking, and the reaction mixture was left for 30 min. The aldehyde that had not reacted with $NaHSO_3$ was titrated with 0.1 *N* iodine solution. Hydrolysis proceeded to 74%. Triethylsilylethynylvinyl butyl ether is hydrolyzed under the above conditions to 79.5%.

b) 3 g of trimethylsilylethynylvinyl butyl ether and 10 ml of 2% H_2SO_4 were stirred with heating to 50° for 1 h in a flask equipped with a reflux condenser, stirrer, and thermometer. To the reaction mixture in ethanol solution there was added a freshly prepared solution of 2,4-dinitrophenylhydrazine. The mixture was left overnight. The resulting 2,4-dinitrophenylhydrazone was then filtered off and recrystallized from ethyl alcohol. 2,4-Dinitrophenylhydrazone of tetrolaldehyde was

> obtained, m.p. 135°. Literature data (^{17}): m.p. 136° for the 2,4-dinitrophenylhydrazone of tetrolaldehyde. A mixed melting-point test showed no depression.

Analytical data for the hydrazone:

Found, %:	C 48.25; 48.17; H 3.32; 3.25; N 22.36; 22.62
$C_{10}H_8N_4O_4$. Calculated, %:	C 48.39; H 3.24; N 22.57

Stepwise hydrogenation of trimethylsilylethynylvinyl butyl ether. Into a "duck" hydrogenation vessel were placed 4 g of the ether in methanol and a mixture of catalysts, 2% Pd/$CaCO_3$ and 5% Pt/C. The air was displaced with hydrogen, and hydrogenation began. After absorption of 540 ml of hydrogen (22°, 743 mm), hydrogenation was stopped. Theoretically, under these conditions 510 ml of hydrogen should be absorbed. The catalyst was filtered off, the methanol was distilled off, and the product obtained was subjected to distillation in a stream of nitrogen. A product was isolated, b.p. 88–89°/7 mm, n_D^{20} 1.4580; d_4^{20} 0.8532. MR_D found 63.45, calculated 63.52. Yield 57% (2.28 g).

* Molecular refraction was calculated taking into account the group refraction of $-C \equiv C - C{=}C$, equal to 3.8.

Condensation of $(CH_3)_3SiCH = CH - CH = CHOC_4H_9$ with maleic anhydride. 1.5 g of trimethylsilyl-1-butoxy-4-butadiene-1,3 (b.p. 88-89°/7 mm, n_D^{20} 1.4580) was placed in a flask equipped with a reflux condenser and a thermometer, and a solution of 2 g of maleic anhydride in 50 ml of benzene was added. No heating was observed. The mixture was heated on a water bath for 1 hour, then the benzene was distilled off and the residue was distilled. Fractions were obtained: I) 96-99°/25 mm, II) 156-162°/25 mm.

Fraction I was maleic anhydride that had not entered into the reaction. After recrystallization of fraction II from petroleum ether, 0.27 g of the adduct was obtained (yield 25.7%), m.p. 130°. A mixed-melting-point test of the adduct obtained with phthalic anhydride showed no depression of the melting point.

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