SYNTHESIS OF SECONDARY SILICON-CONTAINING ACETYLENIC ALCOHOLS OF THE THIOPHENE SERIES

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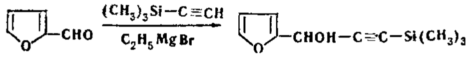
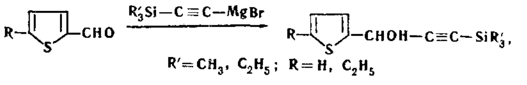
New silicon-containing acetylenic alcohols of the thiophene series have been obtained by the reaction of trialkylsilylacetylenylmagnesium bromides with 2-thiophenealdehydes. Their addition to butyl vinyl ether has given the corresponding acetals.

We have previously [1,2] found new methods for obtaining ethynylsilanes and have pointed out some difference between these compounds and their organic analogs. Among the reactions of the ethynylsilanes, those in which they participate in the form of Iotsich reagents open up great synthetic possibilities. The reaction of trialkylsilylacetylenylmagnesium bromides with carbonyl compounds has led to silicon-containing acetylenic alcohols [3, 4] including 1-(2'-furyl)-3-trimethylsilylprop-2-yn-1-ol, synthesized by the following method [4, 5]:

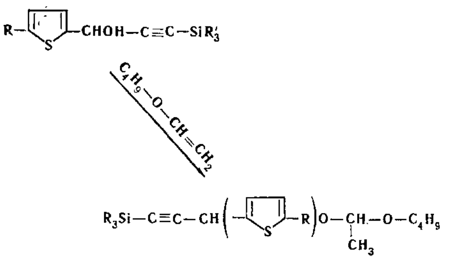


It appeared of interest to study the reaction of trialkylsilylacetylenylmagnesium bromides with 2-thiophenealdehydes and to compare the compounds obtained with their furan analogs. In the present work we have synthesized a number of silicon-containing acetylenic thienyl alcohols in the following way:



The reaction takes place smoothly in ether or tetrahydrofuran. The secondary silicon-containing acetylenic thienyl alcohols, unlike their organic analogs not containing a silicon atom, are stable on storage under ordinary conditions.

The presence of a hydroxy group is shown by the additional of the compounds to butyl vinyl ether:



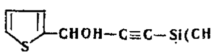
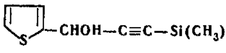
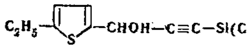
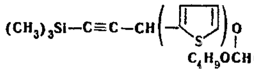
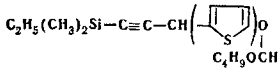
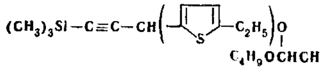
Thus, we have shown a number of methods for the synthesis of silicon-containing acetylenic compounds including a thiophene nucleus.

EXPERIMENTAL

1-(2'-Thienyl)-3-trimethylsilylprop-2-yn-1-ol (I). With stirring and cooling (0° C), 7.2 g (0.064 mole) of 2-thiophenealdehyde was added dropwise to the Iotsich reagent prepared from 1.54 g (0.064 g-atom) of magnesium, 7.0 g (0.064 mole) of ethyl bromide, and 6.3 g (0.064 mole) of ethynyltrimethylsilane in ether. The mixture was stirred for another 1 hr and was decomposed with water and then with 5% hydrochloric acid. The aqueous layer was separated off and extracted with ether. The ethereal solution and the extracts were dried over calcined potassium carbonate. The ether was evaporated off and the residue was distilled in vacuum. The yield of **I** was 7.4 g (see table). IR spectrum (taken on a UR-10 instrument without a solvent in a microlayer): ν(C≡C—Si) 2180 cm^{-1}, ν (OH) 3430 cm^{-1}; ν ($Si(CH_3)_3$) 760, 845, 1253 cm^{-1}; vibrations of the thiophene ring 700, 1034, 3010, 3118 cm^{-1}.

1-(2'-Thienyl)-3-dimethylethylsilylprop-2-yn-1-ol (II). This compound was obtained in a similar fashion from 0.86 g (0.036 g-atom) of magnesium, 4.1 g (0.036 mole) of ethyl bromide, 4.14

Physical Constants and Analytical Data of the Compounds Synthesized

Compound	Formula	Bp, °C	n_D^{20}	d_4^{20}	MR_D		Empirical formula	Found, %				Calculated, %				Yield, %
					found	calculated		C	H	S	Si	C	H	S	Si	
I	 CHOH—C≡C—Si(CH₃)₃	116(3)	1.5295	1.0440	62.17	61.66	$C_{10}H_{14}OSSi$	57.15	6.82	15.01	13.20	57.11	6.70	15.24	13.35	54.8
II	 CHOH—C≡C—Si(CH₃)₂C₂H₅	135(5)	1.5286	1.0337	66.91	66.29	$C_{11}H_{16}OSSi$	59.00	6.99	14.04	12.50	58.77	7.18	14.28	12.52	55,1
III	 C₂H₅—CHOH—C≡C—Si(CH₃)₃	132(2)	1.5248	1.0284	71.02	70.92	$C_{12}H_{18}OSSi$	60.66	7.45	13.34	11.54	60.45	7.01	13.44	11.78	48,7
IV	 (CH₃)₃Si—C≡C—CH( )O C₄H₉OCHCH₃	132—133 (3)	1.5012	0.9804	93.35	92.53	$C_{16}H_{26}O_2SSi$	62.23	8.04	11.42	10.15	61.88	8.44	10.32	9.05	82,1
V	 C₂H₅(CH₃)₂Si—C≡C—CH( )O C₄H₉OCHCH₃	126—128 (2)	1.5039	0.9771	98.45	97.16	$C_{17}H_{28}O_2SSi$	62.75	8.18	10.36	8.85	62.91	8.65	9.98	8.64	79,0
VI	 (CH₃)₃Si—C≡C—CH(—C₂H₅)O C₄H₉OCHCH₃	132—133 (1)	1.4928	0.9622	102.23	101.79	$C_{18}H_{30}O_2SSi$	64.15	8.80	9.69	8.03	63.85	8.93	9.46	8.28	85,7

g (0.036 mole) of ethylethynyldimethylsilane and 4.03 g (0.036 mole) of 2-thiophenealdehyde. The yield of II was 4.4. g. IR spectrum ν (C≡C—Si) 2180 cm^{-1}; ν (OH) 3430 cm^{-1}; ν (Si(CH$_3$)$_2$C$_2$H$_5$) 755, 845, 1245 cm^{-1}; vibrations of the thiophene ring 700, 1034, 3020, 3130 cm^{-1}.

1-(2'-Ethyl-5'-thienyl)-3-trimethylsilylprop-2-yn-1-ol (III). This compound was obtained in a similar fashion to I from 0.6 g (0.025 g-atom) of magnesium, 2.7 g (0.025 mole) of ethyl bromide, 2.45 g (0.025 mole) of ethynyltrimethylsilane, and 3.5 g (0.025 mole) of 2-ethyl-5-thiophenealdehyde. The yield of III was 2.9 g. IR spectrum: ν (C≡C—Si) 2180 cm^{-1}; ν (OH) 3435 cm^{-1}; ν (Si)CH$_3$)$_3$) 760, 845, 1251 cm^{-1}; vibrations of the thiophene ring 700, 1056, 3010, 3130 cm^{-1}.

Butyl 1-(2'-thienyl)-3-trimethylsilylprop-2-ynyl acetal (IV). With stirring, a drop of concentrated HCl was added to a mixture of 2.7 g (0.013 mole) of I and 1.3 g (0.013 mole) of butyl vinyl ether. The temperature of the mixture rose to 40°C. To complete the reaction, the mixture was heated at 60°–70°C for another 2 hr and was left overnight. The reaction mixture was neutralized with potassium carbonate and distilled. The yield of IV was 3.2 g (see table).

Butyl 3-dimethylethylsilyl-1-(2'-thienyl)prop-2-ynyl acetal (V). This compound was obtained in a similar fashion to IV from 2.24 g (0.01 mole) of II and 1.0 g (0.01 mole) of butyl vinyl ether. Yield of V 2.6 g.

1-(2'-Ethyl-5'-thienyl)-3-trimethylsilylprop-2-ynyl acetal (VI). This compound was obtained in a similar fashion to IV from 2.4 g (0.01 mole) of III and 1.0 g (0.01 mole) of butyl vinyl ether. The yield of VI was 2.9 g.

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