SYNTHESIS AND SOME REACTIONS OF α-SILAACETYLENIC KETONES OF THE THIOPHENE SERIES

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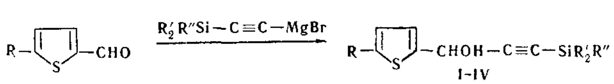
The oxidation of secondary silaacetylenic alcohols of the thiophene series with active manganese dioxide in ethereal solution has given the corresponding ketones.

Silaacetylenic ketones of the thiophene series are of definite interest as the starting materials for the synthesis of various organosilanes containing the thiophene nucleus.

We have previously [1] recorded the synthesis of some silaacetylenic alochols of the thiophene series obtained by the reaction of ethynylsilanes with thiophene-2-carbaldehyde under the conditions of the Iotsich reaction. In the present paper we describe the preparation of some new thienylsilaacetylenic alcohols by the reaction of trialkylsilylethynylmagnesium bromides with thiophene-2-carbaldehyde and 5-bromothiophene-2-carbaldehyde:



I R=H, R'=R''=C_2H_5; II R=Br, R'=CH_3, R''=C_2H_5; III R=H, R'=R''=CH_3;
IV R=H, R'=CH_3, R''=C_2H_5

The alcohols I-IV were oxidized with active manganese dioxide in ethereal solution at room temperature to the corresponding silaacetylenic ketones V-VIII (See Table 1). The reaction took place smoothly and was complete in 5-8 h, being followed by thin-layer chromatography. The silaacetylenic ketones V-VIII have higher boiling points and are less stable on storage than the corresponding thienylacetylenic ketones [2].

In contrast to the thienylacetylenic ketones, the silicon-containing ketones do not form pyrazoles by reaction with hydrazine. The reason is probably a qualitative difference in the electronic structure of the C ≡ C bond as a result of the interaction of the vacant 3d orbitals of the silicon atom and the π electrons of the acetylenic bond.

Using 1-(2-thienyl)-3-triethylsilylprop-2-yn-1-ol (IV) as an example, the selective hydrogenation of the silaacetylenic alcohols in ethereal solution on a Pd/$BaCO_3$ catalyst was studied. Without preparative isolation, the silavinyl alcohol IX obtained was oxidized with active manganese dioxide to the corresponding ketone X. To prove its structure, the latter was also obtained by independent synthesis – by the addition of triethylsilane to the triple bond of 1-(2-thienyl)prop-2-yn-1-one (XI) in the presence of 0.1 N chloroplatinic acid.

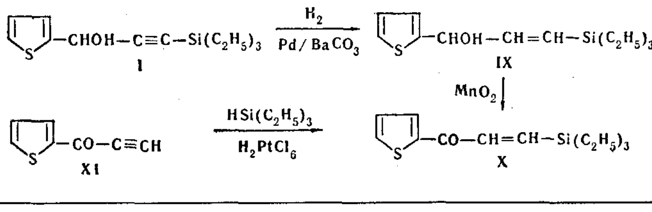


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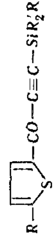
TABLE 1.



R—(thienyl)—CO—C≡C—SiR'₂R''

Compound	R	R'	R''	bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	Found %				Empirical formula	Calculated %				Yield, %	2,4-Dinitrophenylhydrazone		
																	mp, °C (from ethanol)	N, %	
							C	H	S	Si		C	H	S	Si			found	calc.
V	H	C_2H_5	C_2H_5	139—141 (3)	1,5485	1,0621	62,86	7,61	13,02	11,20	$C_{13}H_{18}OSSi$	62,40	7,20	12,80	11,20	55	199—200	13,00	13,01
VI	H	CH_3	CH_3	116—118 (3)	1,5250	1,0544	57,58	5,75	14,96	13,15	$C_{10}H_{12}OSSi$	57,69	5,77	15,38	13,46	62	239—241	14,43	14,20
VII	H	CH_3	C_2H_5	114—115 (2)	1,5475	1,0630	59,43	6,52	14,49	12,43	$C_{11}H_{14}OSSi$	59,45	6,31	14,41	12,61	68	229—231	13,92	13,78
VIII	Br	CH_3	C_2H_5	129—131 (2)	—	—	—	—	10,48	—	$C_{11}H_{13}BrOSSi$*	—	—	10,63	—	41	249—251	12,47	12,36

*Found %: Br 26.53. Calculated %: Br 26.58.

The IR spectra of the ketones V-VIII have the characteristic frequencies of the thiophene ring – 756, 1024, 1440, 1539, and 3115 cm^{-1}. The absorption band of the C ≡ C bond appears clearly in the 2160-2180 cm^{-1} region. Absorption bands at 850 and 1245 cm^{-1} relate to the $Si(C_2H_5)_3$ group. The stretching vibrations of the carbonyl are represented by an absorption band between 1640 and 1663 cm^{-1}. The lowering of the frequency of the vibrations of the C = O group is due to the conjugation effect.

EXPERIMENTAL

1-(2'-Thienyl)-3-triethylsilylprop-2-yn-1-ol (I). With stirring and cooling (0°C), 11.2 g (0.1 mole) of thiophene-2-carbaldehyde was added to the Iotsich reagent prepared from 2.4 g (0.1 g-atom) of magnesium, 10.9 g (0.1 mole) of ethyl bromide, and 14 g (0.1 mole) of triethylethynylsilane in ether. The mixture was stirred at room temperature for 3 h and was left overnight. Then it was decomposed with water and NH_4Cl solution. The aqueous layer was separated off and extracted with ether. The organic layer and the ethereal extracts were washed with water and 5% hydrochloric acid and were dried with potassium carbonate. The ether was evaporated off and the residue was distilled in vacuum. The yield of I was 10.6 g (42%). Bp 138-140°C (2 mm); n_D^{20} 1.5330; d_4^{20} 1.025. Found %: C 61.98; H 7.66; S 13.35; Si 10.64. MR$_D$ 76.50. $C_{13}H_{20}SSi$. Calculated %: C 61.90; H 7.94; S 12.70; Si 11.11; MR$_D$ 76.67.

1-(5'-Bromo-2'-thienyl)-3-(ethyldimethylsilyl)prop-2-yn-1-ol (II). This was obtained in a similar manner to I from 9.6 g (0.05 mole) of 5-bromothiophene-2-carbaldehyde, 5.6 g (0.05 mole) of ethylethynyldimethylsilane, 1.2 g (0.05 g-atom) of magnesium, and 5.45 g (0.05 mole) of ethyl bromide. Yield of II, 5.1 g (34%). Viscous oil. Bp 160-163°C (5 mm). Found %: Br 26.00; S 10.82; Si 9.18. $C_{11}H_{15}BrOSSi$. Calculated %: Br 26.40; S 10.56; Si 9.24.

1-(2'-Thienyl)-3-(trimethylsilyl)prop-2-yn-1-ol (III) and 3-(ethyldimethylsilyl)-1-(2'-thienyl)prop-2-yn-1-ol (IV) were obtained as described previously [1].

1-(2'-Thienyl)-3-(triethylsilyl)prop-2-yn-1-ol (V). In portions, 5.2 g (0.06 mole) of active manganese dioxide was added to a solution of 4 g (0.015 mole) of I in dry ether and the mixture was stirred at room temperature for 6 h. Then the precipitate was filtered off and repeatedly washed with ether. The ethereal solution was dried with magnesium sulfate and evaporated, and the residue was distilled in vacuum. The yield of V was 2.2 g (55%). 1-(2'-Thienyl)-3-(trimethylsilylprop-2-yn-1-one) (VI), 3-(ethyldimethylsilyl)-1-(2'-thienyl)prop-2-yn-1-one (VII), and 1-(5'-bromo-2'-thienyl)-3-(ethyldimethylsilyl)prop-2-yn-1-one (VIII) were obtained similarly (see Table 1).

1-(2'-Thienyl)-3-(triethylsilyl)prop-2-en-1-one (X). a. A hydrogenation vessel was charged with 4.2 g (0.016 mole) of I, 50 ml of ethanol, and 2 g of $Pd/BaCO_3$ catalyst (5% of Pd), and hydrogen was passed in while the vessel was shaken on a mechanical device. An amount of hydrogen close to the calculated amount (248 ml) was absorbed in 12 h. The catalyst was filtered off and the solvent was evaporated. Without preparative isolation, the alcohol IX was oxidized with manganese dioxide (in a similar manner to V) to form the ketone X. Bp 148-150°C (3 mm), n_D^{20} 1.5380, d_4^{20} 1.0310. Found %: C 62.16; H 7.85; S 13.18; Si 10.81; MR_D 76.50. $C_{13}H_{20}OSSi$. Calculated %: C 61.90; H 7.94; S 12.70; Si 11.11; MR_D 76.26.

b. To 5 g (0.04 mole) of the ethynyl thienyl ketone XI were added 4.6 g (0.04 mole) of triethylsilane and two drops of a 0.1 N solution of chloroplatinic acid. The mixture was heated at 60-70°C for 1 h, cooled, and distilled in vacuum. The yield of X was 4.5 g (47%); bp 132-134°C (1 mm); n_D^{20} 1.5378; d_4^{20} 1.0314.

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