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REACTIONS OF 4,4,9-TRIMETHYL-4,9-DIHYDRO-4-SILA-NAPHTHO[3,2-*b*]THIOPHEN-9-ONE WITH NUCLEOPHILIC AND ELECTROPHILIC REAGENTS

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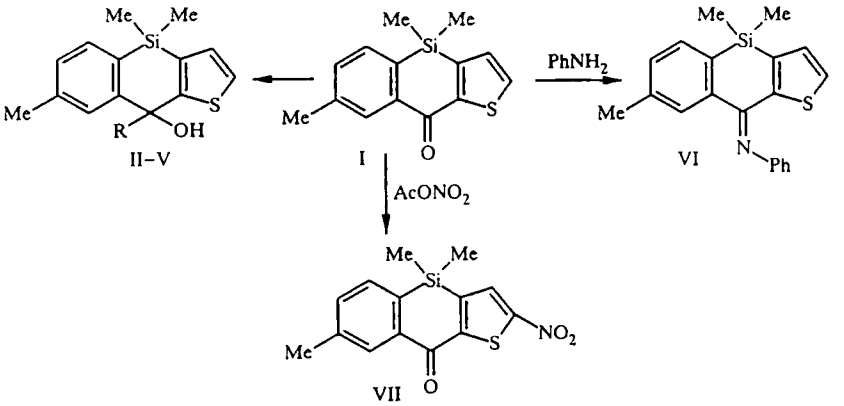
We have studied the reaction of 4,4,9-trimethyl-4,9-dihydro-4-silanaphtho[3,2-b]-thiophen-9-one with organometallic compounds, lithium aluminum hydride, sodium borohydride, aniline, and acetyl nitrate. We have obtained secondary and tertiary dihydrosilanaphtho[3,2-b]thiophen-9-ols and 9-phenyliminodihydro-silanaphtho[3,2-b]thiophene. We have established that nitration of dihydrosilanaphthothiophen-9-one occurs at the α position of the thiophene moiety.

Of the tricyclic condensed heterocycles containing silicon in a central partially hydrogenated six-membered ring, dihydrosilanaphthothiophenes have remained practically unstudied. This heterocyclic system was synthesized for the first time in 1989 [1]. The functional derivatives of tricyclic silicon-containing heterocycles, due to their characteristic stereochemistry, have attracted attention as synthons for obtaining analogs of known psychotropic compounds [2], and also their hydroxy derivatives as diuretics, antiarrhythmics [3], and inhibitors of the sodium–calcium exchange pump [4]. In this connection, we have studied reduction of 4,4,9-trimethyl-1,9-dihydro-4-silanaphtho[3,2-*b*]thiophen-9-one (I) and its reaction of organo-magnesium compounds, aniline, and acetyl nitrate.

Dihydrosilanaphthothiophenone I is easily reduced at 20°C to the corresponding dihydrosilanaphthothiophen-9-ol II by sodium borohydride in methanol or lithium aluminum hydride in ether.



II R = H, III R = Et, IV R = $CH_2C{\equiv}CH$, V R = Ph

Treatment of ketone I with ethylmagnesium iodide, propargylmagnesium bromide, and phenyllithium results in tertiary alcohols III-V in high yields. In the IR spectra of alcohols II-V, we observe a narrow absorption band from the OH group at

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TABLE 1. PMR Spectral Parameters for Dihydrosilanaphtho[3,2-*b*]thiophenes I-VII

Compound	2) δ, ppm (*J*, Hz)								
	2-H	3-H	5-H	6-H	8-H	$Si(CH_3)_2$	7-CH_3	9-R	9-OH
I	7,75 d, J_{23} = 4,9	7,31 d, J_{23} = 4,8	7,57 d, J_{56} = 7,5	7,41 d.d, J_{56} = 7,5; J^*_{68} = 1,8	8,27 d, J^*_{68} = 1,8	0,45 s	2,44 s	–	–
II	7,37 d, J_{23} = 4,9	7,16 d, J_{23} = 4,9	7,51 d, J_{56} = 7,3	7,18 br.d. , J_{56} = 7,3	7,51 br.d	0,48 (s), 0,38 (s)	2,39 s	5,89 d, $J_{H,OH}$ = 7,6	2,25 d, $J_{H,OH}$ = 7,6
III	7,34 d, J_{23} = 5,0	7,11 d, J_{23} = 5,0	6,47 d, J_{56} = 7,1	7,16 br.d , J_{56} = 7,1	7,70 br.d	0,44 (s), 0,37 (s)	2,41 s	$CH_3CH_AH_B$; 0,62 (t), 2,06 (m), 1,96 (m), J_{CH_2,CH_3} = 7,4; J_{AB} = 13,3	2,70 s
IV	7,38 d, J_{23} = 4,9	7,14 d, J_{23} = 4,9	7,50 d, J_{56} = 7,3	7,19 d. d, J_{56} = 7,3; J^*_{68} = 1,5	7,77 d, J^*_{68} = 1,5	0,46 (s), 0,40 (s)	2,42 s	$HC{=}CH_AH_B$; 2,0 (t), 2,93 (m), 2,82 (m), J_{CH,CH_2} = 2,6; J_{AB} = 16,4	3,04 s
V	7,34 d, J_{23} = 5,0	7,10 d, J_{23} = 5,0	7,49 d, J_{56} = 7,8	7,14 d.d, J_{56} = 6,8; J^*_{68} = 1,8	7,59 d, J^*_{68} = 1,8	0,48 (s), 0,29 (s)	2,33 s	C_6H_5 m 7,1...7,35	3,03 br. s
VI	7,40 d, J_{23} = 4,9	7,13 d, J_{23} = 4,9	7,56 d, J_{56} = 7,3	7,32 br.d , J_{56} = 7,3	8,38 br.d	0,47 s	2,46 s	C_6H_5N – *o*-H 6,85; *m*-H 7,34; *p*-H 7,14	–
VII	–	8,03 s	7,59 d, J_{56} = 7,5	7,48 d.d , J_{56} = 7,5; J_{68} = 1,5	8,25 br.d	0,51 s	2,57 s	–	–

*Measured from the {7-CH_3} double resonance spectrum.

3530 cm^{-1} (for compounds II) and 3520 cm^{-1} (for compounds III-V); consequently, due to steric hindrances, the hydroxyl group is found in the free state or very weakly associated.

The structure of alcohols II and V has been confirmed by PMR spectroscopy (Table 1) and mass spectrometry. The PMR spectra of compounds II-V are characterized by the presence of doublet signals from 2-H and 3-H protons with spin–spin coupling constants typical of thiophene derivatives, $^3J_{23} \sim 5$ Hz [5]. The signals from the 6-H and 8-H protons are strongly broadened as a result of spin–spin coupling with protons in the 7-CH_3 methyl group, which is confirmed by the {7-CH_3} double resonance spectra. Decoupling the methine protons made it possible to measure J_{68} in the spectra of compounds I, IV, and V. Signals from the proton in the OH group are observed in the 2.25-3.04 ppm region; and in the spectrum of the secondary alcohol II, this signal is a doublet with $^3J_{OH,9H} = 7.6$ Hz. The chemical shifts and spin–spin coupling constants of the protons in the substituents at $C_{(9)}$ in the spectra of compounds II-V correspond to the values observed in the spectra of compounds with similar groups. In the alcohols III and IV having a methylene group bonded with $C_{(9)}$, the protons in this group are not magnetically equivalent and are recorded as complex multiplets with geminal spin–spin coupling constants $^2J_{AB}$, equal to 13.3 and 16.4 Hz respectively.

In the mass spectrum* of the secondary alcohol II, we observe a molecular ion peak with 260(100), corresponding to its empirical formula, which has the maximum intensity. In the mass spectra of the tertiary alcohols III-V, the intensity of the molecular ion peak is no greater than 1.1%. The major direction for decomposition of the M^+ ions in compounds II-V is connected with elimination of a radical from $C_{(9)}$. In the mass spectra of the tertiary alcohols III-V, this ion (259) has the maximum intensity, while in the mass spectrum of the secondary alcohol II it has an intensity of 30%. Then the $[M-R]^+$ ion eliminates a methane molecule, forming the fragmentary ion 243. The other direction for fragmentation of the M^+ ions is connected with cleavage of a methyl group from the silicon atom. In the secondary alcohol II, this fragmentation channel is one of the major ones. The intensity of the $[M-CH_3]^+$ 245 ion peak is 62%.

Condensation of ketone I with aniline was done at 120-140°C in the presence of aluminum chloride [6]. In the mass spectrum of the azomethine VI formed, the 333 molecular ion peak has maximum intensity (100%). The IR spectrum is characterized by the appearance of a vibrational stretching band for the C=N bond at 1590 cm^{-1}.

Usually, azomethines of asymmetric tricyclic compounds are formed as mixtures of *Z* and *E* isomers, which has been confirmed by double sets of a number of signals in their PMR spectra [7]. However, in the PMR spectrum of azomethine VI (Table 1), we observe only one singlet from each group of equivalent protons, and all the signals from aromatic protons (except for the 5-H doublet) are strongly broadened; the signal from the 8-H proton is more broadened; at 20°C, the width of this signal at half-height $\Delta\nu$ is 6 Hz. Raising the temperature of the solution up to 30°C leads to even more broadening of this signal: $\Delta\nu$ is 15 Hz. In this case, the signals from the rest of the aromatic protons are only slightly broadened. The observed broadening of the indicated signals and the anomalous broadening of the 8-H signal when the temperature is raised can be explained by dynamic effects, probably connected with inversion of the nitrogen atom.

Nitration of ketone I with acetylnitrate at −5°C [8] occurred at the α position of the thiophene moiety. In the IR spectrum of the 2-nitro-substituted dihydrosilanaphthothiophene VII, we observe bands for the stretching vibrations of the nitro group at 1356 and 1536 cm^{-1}. The C=O stretching vibrations appear at 1646 cm^{-1}. In the mass spectrum, there is a 303 (28%) molecular ion peak corresponding to its empirical formula. The major directions for its decomposition are due to elimination of OH and CH_3 from the silicon with formation of the fragmentary ions 286 (100%) and 288 (10%).

A singlet signal is located downfield in the PMR spectrum of compound VII at 8.03 ppm. The increment due to the effect of the nitro group on the chemical shifts of the 3-H protons, $\Delta\nu$ 0.7-0.9 ppm, calculated from the chemical shifts of the corresponding protons in the spectra of thiophene and a number of its 2-nitro derivatives [5], made it possible to estimate the value of the chemical shift for the 3-H proton in compound VII (δ(3-H) = 7.31 + $\Delta\delta$ = 8.01-8.21 ppm) starting from the shift for 3-H in the spectrum of the original compound I (Table 1). Based on this estimate, the singlet with chemical shift 8.03 ppm was assigned to the 3-H proton. If the nitro group were located on the $C_{(3)}$ carbon, the singlet for the 2-H proton would be registered downfield (δ(2-H) = 7.75 + $\Delta\delta$), in the 8.45-8.65 ppm region.

In the spectra of compounds I, VI, and VII, the chemical shifts of the protons in the methyl groups bonded to the silicon atom coincide, which suggests a planar conformation of the tricyclic moieties of these molecules in solution.

*Here and in the following, we give the *m/z* (I_{rel}, %) values for the ion peaks.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in KBr pellets. The mass spectra were obtained on an MKh-1303 with a system for direct injection of the sample into the ion source, with ionizing voltage 70 eV. The PMR spectra of the solutions of the compounds in $CDCl_3$ were recorded on a Bruker WP-200 spectrometer at 20°C, internal standard TMS. Column chromatography was done on L 100/160 μm silica gel. For TLC, we used Silufol UV-154 plates with an adherent layer of silica gel.

4,9-Dihydro-4,4,7-trimethyl-4-silanaphtho[3,2-*b*]thiophen-9-ol (II). Sodium borohydride (0.1 g, 2.6 mmoles) was introduced in portions into a solution of 0.4 g (1.6 mmoles) ketone I in 60 ml methanol at 20°C. After 2 h (TLC monitoring), the reaction mixture was poured onto ice and then extracted with ether. The extract was dried with magnesium sulfate. The residue after driving off the ether was crystallized from hexane. Obtained: 0.3 g (71%) alcohol II, colorless crystals, mp 120-122°C, R_f 0.56 (hexane–ethyl acetate, 6:1). Mass spectrum, *m/z* (I_{rel}, %): 260 (M^+, 100); 259(50); 245 (62); 243(13); 230(25); 227(19); 195(25); 194(19); 115(25); 91(38). Found, %: C 64.66; H 6.20. $C_{14}H_{16}OSSi$. Calculated, %: C 64.61; H 6.15.

4,9-Dihydro-4,4,7-trimethyl-9-ethyl-4-silanaphtho[3,2-*b*]thiophen-9-ol (III). Under a stream of nitrogen at 0°C, a solution of 1.3 g (5 mmoles) ketone I in 60 ml ether was added over the course of 20 min to ethylmagnesium iodide obtained from 0.6 g (26 mmoles) magnesium and 3.9 g (26 mmoles) ethyl iodide in 50 ml absolute ether. This was boiled for 2 h, cooled, and decomposed by a saturated ammonium chloride solution. The ether layer was separated and dried with magnesium sulfate. The residue after driving off the ether was crystallized from heptane. Obtained: 1.1 g (70%) alcohol III, colorless crystals, mp 84-85°C, R_f 0.50 (hexane–ethyl acetate, 5:1). Mass spectrum, *m/z* (I_{rel}, %): 288 (M^+, 0.1); 273(0.2); 259(100); 250(0.2); 243(0.1); 230(1); 160(2); 123(1); 116(2.5); 106(1.1); 92(1.7). Found, %: C 66.70; H 6.91. $C_{16}H_{20}OSSi$. Calculated, %: C 66.66; H 6.94.

4,9-Dihydro-4,4,7-trimethyl-9-propargyl-4-silanaphtho[3,2-*b*]thiophen-9-ol (IV). Using a similar procedure, from 0.89 g (3.4 mmoles) ketone I and propargylmagnesium bromide (from 1 g (43 mmoles) magnesium and 4.76 g (43 mmoles) propargyl bromide in 60 ml ether in the presence of $HgCl_2$), we obtained 0.8 g (77%) alcohol IV, colorless crystals, mp 106-108°C (from hexane), R_f 0.52 (hexane–ethyl acetate, 3:1). Mass spectrum, *m/z* (I_{rel}, %): 298 (M^+, 0.5); 283(0.3); 259(100); 245(3); 244(4.5); 243(5); 216(0.5); 149(5); 135(3). Found, %: C 68.50; H 6.60. $C_{17}H_{18}OSSi$. Calculated, %: C 68.45; H 6.04.

4,9-Dihydro-4,4,7-trimethyl-9-phenyl-4-silanaphtho[3,2-*b*]-thiophen-9-ol (V). Similarly, from phenyllithium obtained from 0.16 g (22 mmoles) lithium and 1.61 g (10 mmoles) bromobenzene in 50 ml absolute ether, and 0.5 g (2 mmoles) ketone I, we synthesized 0.45 g (69%) alcohol V, colorless crystals, mp 150-152°C (from heptane), R_f 0.50 (hexane–ethyl acetate, 3:1). Mass spectrum, *m/z* (I_{rel}, %): 336 (M^+, 1.1); 321(0.5); 259(100); 243(0.5). Found, %: C 71.41; H 6.01. $C_{20}H_{20}OSSi$. Calculated, %: C 71.42; H 5.95.

4,9-Dihydro-4,4,7-trimethyl-9-phenylimino-4-silanaphtho[3,2-*b*]thiophene (VI). A mixture of 0.5 g (1.9 mmoles) ketone I, 2 ml aniline (22 mmoles), and 0.2 g (1.5 mmoles) aluminum chloride was heated for 3 h at 120-130°C. This was cooled and extracted with chloroform. The residue after driving off the chloroform was chromatographed on a column with silica gel, with petroleum ether as the eluent. 0.23 g (36%) azomethine VI were isolated: yellow crystals, mp 84-86°C (from alcohol), R_f 0.60 (petroleum ether–ethyl acetate, 3:1). M^+ 383. Found, %: C 72.00; H 5.80; N 4.09. $C_{20}H_{19}NSSi$. Calculated, %: C 72.07; H 5.70; N 4.20.

4,9-Dihydro-4,4,7-trimethyl-2-nitro-4-silanaphtho[3,2-*b*]thiophen-9-one (VII). A solution of 0.4 g (1.5 mmoles) ketone I in 7 ml acetic anhydride was added to acetyl nitrate obtained from 1 ml fuming (1.45 g/cm^3) nitric acid and 10 ml acetic anhydride at −5°C over the course of 20 min. After 1 h, the reaction mass was poured onto ice and neutralized with soda. The residue was filtered off. After recrystallization from a mixture of heptane and ethyl acetate, we obtained 0.22 g (47%) of the nitro derivative VII, light yellow crystals, mp 216-218°C, R_f 0.7 (hexane–ethyl acetate, 3:1). Mass spectrum, *m/z* (I_{rel}, %): 303 (M^+, 7); 288(4); 286(100). Found, %: C 55.81; H 4.30; N 4.63. $C_{14}H_{13}NO_3SSi$. Calculated, %: C 55.44; H 4.29; N 4.62.

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