

SYNTHESIS AND TRANSFORMATIONS OF 2,4,4,7-TETRAMETHYL-4-SILA- NAPHTHO[3,2-*b*]THIOPHEN-9-ONE

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*The catalytic dehydrocyclization of dimethyl(5-methyl-2-thienyl)(2,4-dimethylphenyl)silane accompanied by a skeletal rearrangement gives 2,4,4,7-tetramethyl-4,9-dihydro-4-silanaphtho[3,2-*b*]thiophene, which was oxidized to 2,4,4,7-tetramethyl-4-silanaphtho[3,2-*b*]thiophen-9-one, whose structure was solved by X-ray diffraction structural analysis. Various chemical transformations of the ketone synthesized were performed including radical bromination by bromosuccinimide, condensation with furfural in the presence of KOH, reduction by LiAlH₄, and nitration by acetyl nitrate.*

Keywords: aluminum–chromium catalyst, 2,4,4,7-tetramethyl-4-silanaphtho[3,2-*b*]thiophen-9-one, bromination, reduction, dehydrocyclization, condensation, nitration.

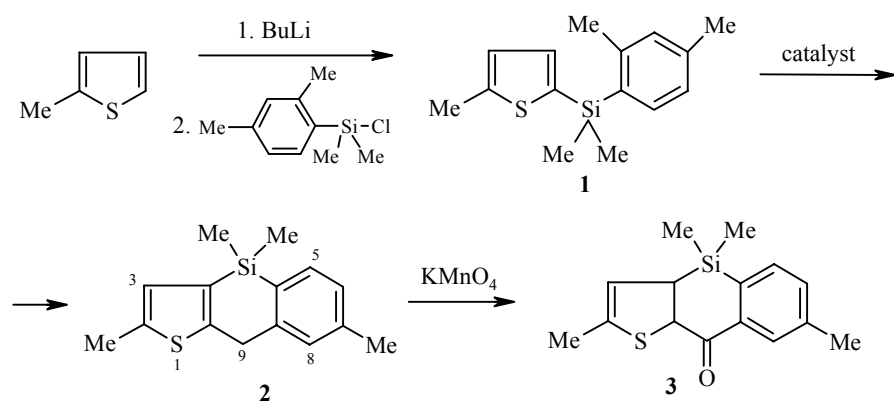
In a previous study [1], we demonstrated the feasibility of using an aluminum–chromium catalyst for the high-temperature transformations of silicon derivatives of thiophene. A study of these transformations permitted us to synthesize new condensed organosilicon heterocycles with various functional groups [2, 3].

In the present work, the dehydrocyclization of dimethyl(5-methyl-2-thienyl)(2,4-dimethylphenyl)silane (**1**) obtained upon the consecutive treatment of 2-methylthiophene by butyllithium and dimethyl(2,4-dimethylphenyl)chlorosilane, accompanied by a skeletal rearrangement, was carried out on an industrial aluminum–chromium catalyst (IM-2204) at 560–570°C. The yield of the liquid catalyzate was 85–90%. The product of the dehydrocycloisomerization of starting silane **1** was 2,4,4,7-tetramethyl-4,9-dihydro-4-silanaphtho[3,2-*b*]thiophene (**2**). The composition and structure of **2** as well as of the products of its subsequent transformations described below are in good accord with the elemental analysis and spectral data (see Experimental). The oxidation of **2** by KMnO₄ in acetone gave ketone **3** ($\nu_{C=O}$ at 1630 cm⁻¹ in the IR spectrum). An X-ray diffraction study of **3** unequivocally confirmed the structure of the dehydrocyclization product.* The molecule occupies a special position in the "m" crystallographic plane. The atomic coordinates and isotropic temperature parameters, valence angles, and bond lengths are given in Tables 1–3. The data in Tables 2 and 3 indicate that the bond lengths and angles in ketone **3** have ordinary values [4].

The tricyclic condensed system of ketone **3**, containing a thiophene ring and silanaphthalene fragment with a carbonyl group, has several potential active sites and thus holds interest as a starting reagent for the construction of various new compounds.

* This investigation was carried out by V. A. Tafeenko, to whom the authors express their deep gratitude.

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We studied radical bromination, condensation with furfural, reduction of the carbonyl group, and nitration of ketone **3**.

Bromination of **3** with two molar equivalents of N-bromosuccinimide in CCl_4 in the presence of a catalytic amount of benzoyl peroxide gave dibromide **4** in 26% yield.

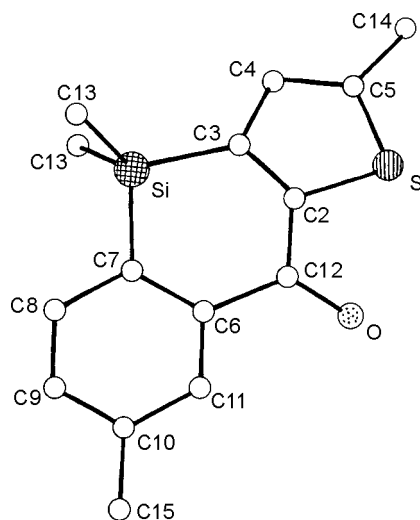
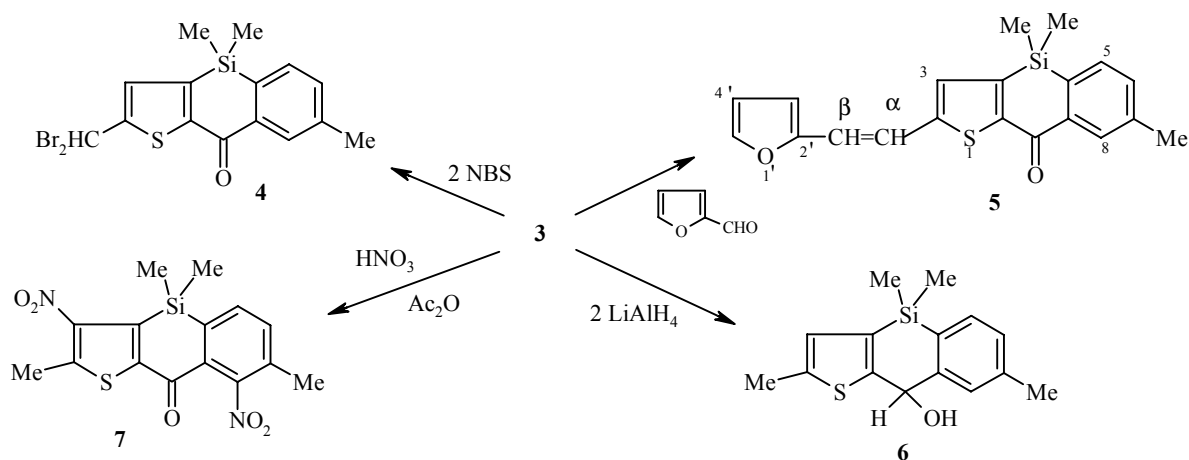


Fig. 1. Molecular structure of compound **3**.

The mass spectrum showed a molecular ion peak with m/z 430 corresponding to the chemical formula. Two decomposition pathways were found. Pathway I features elimination of a bromine atom and formation of an ion with m/z 351 (28%), while Pathway II involves loss of a methyl radical to give an $[M - CH_3]^+$ ion with m/z 415 (8%). The IR spectrum of **4** has a strong carbonyl band at 1625 cm^{-1} and strong bands at $530\text{-}510\text{ cm}^{-1}$, which should be assigned to C–Br stretching vibrations. The ^1H NMR spectrum shows a one-proton singlet for the 2-CHBr₂ group at 4.76 ppm instead of the three-proton singlet of the 2-CH₃ group at 2.54 ppm.

The reaction of ketone **3** with furfural in ethanol in the presence of KOH proceeded through an aldol condensation [5]. Furfurylidene derivative **5** was obtained in 36% yield. The mass spectrum of this compound shows a molecular ion peak with m/z 350 (*I* 40%). The IR spectrum of **5** has $\nu_{\text{C=O}}$ at 1630 cm^{-1} and stretching bands for the –CH=CH– group are observed at 3045 cm^{-1} . The ^1H NMR spectrum shows that **5** has *trans* configuration of the substituents at the double bond ($J_{\alpha\beta} = 16.0\text{ Hz}$) [6].

The rather unusual reactivity of the methyl group in the α -position to the thiophene fragment in ketone **3** in the above transformations may be explained by the *-I* effect of the sulfur atom and effect of the close-lying carbonyl group, which facilitates delocalization of the unpaired electron arising in the bromination of the α -thienyl radical and stabilization of the carbanion formed under base catalysis conditions in the reaction with furfural.

The reduction of ketone **3** by LiAlH₄ in absolute ether at 20°C leads to 2,4,4,7-tetramethyl-4,9-dihydro-4-silanaphtho[3,2-*b*]thiophen-9-ol (**6**) in 75% yield. The mass spectrum of **6** shows a molecular ion peak with m/z 274 corresponding to the chemical formula. The strongest peak is found for the ion with m/z 259, corresponding to the elimination of a CH₃ group. The IR spectrum of alcohol **6** shows a peak for the OH group at 3500 cm^{-1} .

The nitration of arylsilanes is a difficult problem in light of the instability of the Si–C_{aryl} bond toward the action of acids. The yield of the nitration product depends on the reaction conditions and selection of the nitrating agent [7-9]. Ketone **3** was treated with fuming nitric acid in acetic anhydride at -20°C. Dinitro derivative **7** was isolated as the major product in 32% yield. The IR spectrum of **7** has bands for the nitro group at 1350 and 1540 cm^{-1} and carbonyl group absorption at 1640 cm^{-1} .

TABLE 1. Coordinates of the Non-hydrogen Atoms ($\times 10^4$) and Temperature Parameters in the Structure of **3**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
S	4277.7(8)	2500	189(2)	4.44(3)
Si	5893.8(9)	2500	-2597(2)	3.87(3)
O	5258(2)	2500	2394(5)	5.4(1)
C(2)	5023(3)	2500	-259(7)	3.6(1)
C(3)	5127(3)	2500	-1844(7)	3.7(1)
C(4)	4578(3)	2500	-2663(8)	4.7(1)
C(5)	4093(3)	2500	-1745(8)	4.3(1)
C(6)	6101(3)	2500	750(7)	3.4(1)
C(7)	6350(3)	2500	-771(7)	3.6(1)
C(8)	6964(3)	2500	-849(8)	5.1(2)
C(9)	7314(3)	2500	438(9)	5.2(2)
C(10)	7078(3)	2500	1920(8)	4.3(1)
C(11)	6468(3)	2500	2061(7)	3.8(1)
C(12)	5444(3)	2500	1055(7)	3.7(1)
C(13)	6036(3)	446(7)	-3806(5)	5.6(1)
C(14)	3444(3)	2500	-2210(1)	6.4(2)
C(15)	7500	2500	3353(9)	6.2(2)

TABLE 2. Bond Lengths (*l*) in **3**

Bond	<i>l</i> , Å	Bond	<i>l</i> , Å
S–C(2)	1.726(6)	C(5)–C(14)	1.517(10)
S–C(5)	1.705(7)	C(6)–C(7)	1.417(8)
Si–C(3)	1.846(6)	C(6)–C(11)	1.395(8)
Si–C(7)	1.871(6)	C(6)–C(12)	1.506(8)
Si–C(13)	1.859(5)	C(7)–C(8)	1.388(9)
O–C(12)	1.219(7)	C(8)–C(9)	1.354(10)
C(2)–C(3)	1.376(8)	C(9)–C(10)	1.374(10)
C(2)–C(12)	1.470(9)	C(10)–C(11)	1.382(9)
C(3)–C(4)	1.425(9)	C(10)–C(15)	1.552(9)
C(4)–C(5)	1.347(10)		

TABLE 3. Bond Angles (ω) in **3**

Angle	ω , deg.	Angle	ω , deg.
C(2)–S–C(5)	91.3(3)	C(7)–C(6)–C(12)	123.4(5)
C(3)–Si–C(7)	103.0(3)	C(11)–C(6)–C(12)	116.5(5)
C(3)–Si–C(13)	110.9(2)	C(6)–C(7)–C(8)	116.2(6)
C(7)–Si–C(13)	111.6(2)	C(7)–C(8)–C(9)	122.9(6)
C(3)–C(2)–C(12)	130.0(6)	C(8)–C(9)–C(10)	121.6(6)
C(2)–C(3)–C(4)	109.6(6)	C(9)–C(10)–C(11)	117.8(6)
C(3)–C(4)–C(5)	114.9(6)	C(9)–C(10)–C(15)	119.4(6)
C(4)–C(5)–C(14)	129.2(7)	C(11)–C(10)–C(15)	122.8(6)
C(7)–C(6)–C(11)	120.0(5)	C(6)–C(11)–C(10)	121.5(6)
O–C(12)–C(2)	119.7(6)	O–C(12)–C(6)	120.1(5)
C(2)–C(12)–C(6)	120.2(5)		

The direction of the replacement of the hydrogen atoms at positions 3 and 8 is attributed to the electron-donor effect of the two methyl groups and electron-withdrawing effect of the carbonyl group. The lack of signals for protons at C₍₃₎ and C₍₈₎ in the ¹H NMR spectrum supports the positions proposed for the nitro groups.

EXPERIMENTAL

The mass spectra were taken on an MS-25 RFA mass spectrometer. The IR spectra were taken on UR-20 and IR-435 spectrometers for KBr pellets and neat samples. The ¹H NMR spectra were obtained on WP-80 and WM-400 (400 MHz) spectrometers in CDCl₃ with TMS as the internal standard. Thin-layer chromatography was carried out on Silufol UV-254 plates with an attached layer.

X-ray Diffraction Study of 3. Monocrystals of **3** were studied on an Enraf Nonius CAD-4 four-circle automatic diffractometer with λ MoK α radiation, graphite monochromator, and ω - θ /2 θ scanning. The major crystallographic data are as follows: $a = 22.573(8)$, $b = 7.355(3)$, $c = 8.551(3)$ Å; $V = 1419.6$ Å³, space group $Pnma$; $Z = 4$. A total of 1517 nonzero reflections were observed in the range $\theta \leq 28^\circ$, of which 1266 with $I > 3\sigma(I)$ were used for refinement of the positional and temperature parameters. The pattern was found using the MULTAN program and SDP program package. Refinement of the positional and temperature parameters of the non-hydrogen atoms was carried out anisotropically using the full-matrix approximation. The hydrogen atoms were localized from the Fourier map and refined isotropically. The final $R = 5.4\%$.

Dimethyl(5-methyl-2-thienyl)(2,4-dimethylphenyl)silane (1). A sample of butyllithium (12.9 g, 0.2 mol) in hexane (120 ml) was added in a nitrogen stream to a solution of 2-methylthiophene (20 g, 0.2 mol) in absolute ether (150 ml) at from -5 to 0°C. The mixture obtained was stirred at this temperature for 30 min and then cooled to -20°C. A solution of dimethyl(2,4-dimethylphenyl)chlorosilane (40 g, 0.2 mol) in ether (50 ml) was added. The reaction mixture was stirred for 5 h at the same temperature, maintained for 12 h at room temperature, and then decomposed by adding aqueous ammonium chloride (100 ml). The organic layer was separated and dried over MgSO₄. The residue after distilling off the solvent was fractionated to give 31.5 g (60%) of compound **1**; bp 153-156°C (6 mm Hg), n_D^{20} 1.5630, R_f 0.73 (5:1 hexane–ethyl acetate on Silufol UV-254). IR spectrum, ν , cm⁻¹: 820, 1250 (Si(CH₃)₂). Mass spectrum, m/z (I_{rel} , %): [M]⁺ 260 (100), [M-15]⁺ 245 (65). Found, %: C 69.31; H 7.52; S 12.15. C₁₅H₂₀SSi. Calculated, %: C 69.23; H 7.69; S 12.30.

2,4,4,7-Tetramethyl-4,9-dihydro-4-silanaphtho[3,2-*b*]thiophene (2). A solution of **1** (5 g, 20 mmol) in benzene (10 ml) was passed through a quartz reactor containing catalyst (10 g) at a rate of 0.5-0.7 h⁻¹ at 560-570°C and then benzene (10 ml) was passed. The residue (4.1 g) after distilling off benzene from the catalyzate was crystallized from ethanol to give 1.1 g (22%) of compound **2** as colorless crystals; mp 106-107°C, R_f 0.72 (5:1 hexane–ethyl acetate). IR spectrum, ν , cm⁻¹: 800, 1260 (Si(CH₃)₂). Mass spectrum, m/z (I_{rel} , %): [M]⁺ 258 (100), [M-15]⁺ 243 (30). ¹H NMR spectrum, δ , ppm (J , Hz): 0.35 (6H, s, (Si(CH₃)₂); 2.35 (3H, s, 7-CH₃); 2.47 (3H, s, 2-CH₃); 4.26 (2H, s, 9,9-H₂); 6.74 (1H, s, 3-H); 7.50 (1H, d, J = 7.5, 5-H); 7.12 (1H, m, 6-H). Found, %: C 69.71; H 6.90; S 12.55. C₁₅H₁₈SSi. Calculated, %: C 69.76; H 6.97; S 12.40.

2,4,4,7-Tetramethyl-4-silanaphtho[3,2-*b*]thiophen-9-one (3). Potassium permanganate was added in small portions to a solution of **2** (0.4 g, 1.7 mmol) in acetone (50 ml) until a stable pink color appeared. The MnO₂ precipitate was filtered off and acetone was evaporated. The residue was crystallized from hexane to give 0.32 g (90%) of compound **3** as yellow crystals; mp 129-130°C, R_f 0.5 (4:1 hexane–ethyl acetate). IR spectrum, ν , cm⁻¹: 1630 (C=O). Mass spectrum, m/z (I_{rel} , %): [M]⁺ 272 (42), [M-15]⁺ 257 (100). ¹H NMR spectrum, δ , ppm (J , Hz): 0.42 (6H, s, Si(CH₃)₂); 2.40 (3H, s, 7-CH₃); 2.54 (3H, s, 2-CH₃); 6.98 (1H, s, 3-H); 7.56 (1H, d, J = 7.5, 5-H); 7.39 (1H, d, J = 7.5, 6-H); 8.27 (1H, s, 8-H). Found, %: C 66.21; H 5.81. C₁₅H₁₆OSSi. Calculated, %: C 66.17; H 5.88.

2-Dibromomethyl-4,4,7-trimethyl-4-silanaphtho[3,2-*b*]thiophen-9-one (4). A sample of bromosuccinimide (0.5 g, 3 mmol) and a catalytic amount of benzoyl peroxide were added to a solution of **3** (0.4 g, 1.47 mmol) in CCl₄ (50 ml). The mixture was irradiated with a 500 W incandescent lamp and heated at reflux for 15 min and then stirred for 20 min at 20°C. The succinimide precipitate was filtered off and the solvent was distilled off the filtrate. The precipitate was separated on a silica gel column with 7:1 hexane–ethyl acetate as the eluent to give 0.16 g (26%) of compound **4** as colorless crystals; mp 166-168°C (hexane), R_f 0.68 (3:1 hexane–ethyl acetate). IR spectrum, ν , cm⁻¹: 510, 530 (C–Br), 1625 (C=O). Mass spectrum, m/z (I_{rel} , %): [M]⁺ 430 (30), [M-15]⁺ 415 (8), [M-Br]⁺ 351 (28). ¹H NMR spectrum, δ , ppm (J , Hz): 0.47 (6H, s, Si(CH₃)₂); 2.42 (3H, s, 7-CH₃); 4.76 (1H, s, 2-CHBr₂); 6.94 (1H, s, 3-H); 7.42 (1H, d, J = 7.0, 6-H); 7.59 (1H, d, J = 7.0, 5-H). Found, %: C 41.81; H 3.31; Br 37.09; S 7.52. C₁₅H₁₄Br₂OSSi. Calculated, %: C 41.88; H 3.28; Br 37.15; S 7.45.

2-(Furfurylidene)methyl-4,4,7-trimethyl-4-silanaphtho[3,2-*b*]thiophen-9-one (5). A mixture of ketone **3** (0.2 g, 0.74 mmol), furfural (0.23 g, 2.39 mmol), and KOH (0.01 g, 0.17 mmol) in ethanol (50 ml) was heated at reflux for 2 h. Ethanol was distilled off and the residue was separated on a silica gel column with 10:1 hexane–ethyl acetate as the eluent to give 0.1 g (39%) of yellow crystalline **5**; mp 162-163°C (heptane), R_f 0.48 (5:1 hexane–ethyl acetate). IR spectrum, ν , cm⁻¹: 1255 (Si(CH₃)₂), 1630 (C=O), 3045 (*trans* –CH=CH–). Mass spectrum, m/z (I_{rel} , %): [M]⁺ 350 (40), [M-15]⁺ 335 (28), [M-93]⁺ 257 (100). ¹H NMR spectrum, δ , ppm (J , Hz): 0.47 (6H, s, Si(CH₃)₂); 2.46 (3H, s, 7-CH₃); 6.45 (2H, d, J = 3.6, 3'-H); 6.94 (1H, d, J = 16, β -H); 7.17 (1H, d, J = 16, α -H); 7.23 (1H, s, 3-H); 7.34 (1H, d, J = 1.8, 5'-H); 7.42 (1H, d, $J_{6,5}$ = 7.5, $J_{6,8}$ = 1.7, 6-H); 7.57 (1H, d, $J_{5,6}$ = 7.5, $J_{5,8}$ = 0.5, 5-H). Found, %: C 68.41; H 5.22; S 9.25. C₂₀H₁₈O₂SSi. Calculated, %: C 68.57; H 5.14; S 9.14.

2,4,4,7-Tetramethyl-4-silanaphtho[3,2-*b*]thiophen-9-ol (6). A sample of LiAlH₄ (0.1 g, 2.6 mmol) was added to a solution of **3** (0.4 g, 1.4 mmol) in absolute ether (10 ml). The reaction mixture was stirred at 20°C until the disappearance of **3** as indicated by thin-layer chromatography. Then, excess LiAlH₄ was decomposed by adding water. The ethereal layer was separated and dried over MgSO₄. Ether was distilled off and the residue was crystallized from hexane to give 0.3 g (75%) of compound **6** as colorless crystals; mp 124-125°C, *R_f* 0.43 (4:1 hexane–ethyl acetate). IR spectrum, ν , cm⁻¹: 3500 (O–H). Mass spectrum, *m/z* (*I_{rel.}*, %): [M]⁺ 274 (70), [M-17]⁺ 257 (55), [M-15]⁺ 259 (100). Found, %: C 65.52; H 6.63; S 11.71. C₁₅H₁₈OSSi. Calculated, %: C 65.69; H 6.57; S 11.68.

2,4,4,7-Tetramethyl-3,6-dinitro-4-silanaphtho[3,2-*b*]thiophen-9-one (7). A solution of **3** (0.5 g, 1.8 mmol) in acetic anhydride (10 ml) was added to a mixture of fuming nitric acid (*d* = 1.51) (2 ml) and acetic anhydride (10 ml) cooled to -20°C. The mixture obtained was maintained at this temperature for 30 min and poured onto ice. The precipitate formed was filtered off, washed with water, and recrystallized from ethyl acetate to give 0.21 g (32%) of compound **7** as light yellow crystals; mp 279-281°C. IR spectrum, ν , cm⁻¹: (C=O), 1540, 1350 (NO₂). Mass spectrum, *m/z* (*I_{rel.}*, %): [M-1]⁺ 363 (30), [M-47]⁺ 315 (100), [M-15]⁺ 347 (15). ¹H NMR spectrum, δ , ppm (*J*, Hz): 0.62 (6H, s, (Si(CH₃)₂)); 2.36 (3H, s, 7-CH₃); 2.93 (3H, s, 2-CH₃); 7.63 (1H, d, *J* = 7.4, 6-H); 7.73 (1H, d, *J* = 7.4, 5-H). Found, %: C 68.70; H 5.34; N 10.68. C₁₅H₁₄N₂O₅SSi. Calculated, %: C 68.72; H 5.36; N 10.71.

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