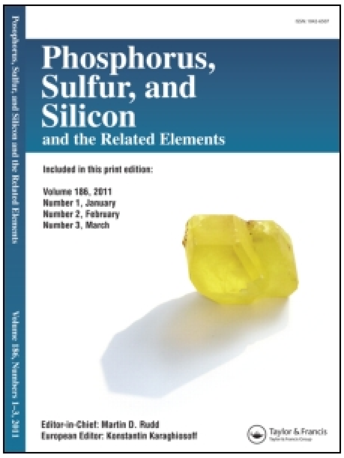

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SYNTHESIS AND PHOTOCHEMISTRY OF 2-(α-FURYL)-2-(α-THIENYL)HEXAMETHYLTRISILANE

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*The synthesis of 2-(α-furyl)-2-(α-thienyl)hexamethyltrisilane is described. Photolysis of **2** in the presence of cyclohexene and methanol led to apparent radical reaction. It is proposed that the sulfur atom of thienyl group strongly stabilized an initially formed silyl radical. This idea was supported by identifying typical radical reaction products.*

Keywords: Photochemistry; synthesis; trisliane

INTRODUCTION

In recent years, considerable attention has been devoted to investigation of silylene intermediates, and many papers that deal with addition of silylenes to carbon-carbon multiple bonds have been reported.[1–4] The reaction of the silylene intermediates generated by photolysis of polysilanes has been found to proceed simultaneously by two different pathways: one involves polymerization of the silylene itself; the other comprises the reaction with a trapping agent that is added to intercept the species. The so-called "Skell-rule" states[5] that singlet carbenes add to olefin stereospecifically, whereas triplet carbenes do not. Unlike carbenes for which both singlet and triplet ground states are known, most known silylenes have singlet ground states. Thus far, only Ando et al. have reported a nonstereospecific addition.[6] They found that bulky dimesityl and bis (2,4,6-triisopropylphenyl) silylene gave nonstereospecific adducts. However, their work has been refuted by Conlin and co-workers.[7] In search of triplet ground state silylenes, Boudjouk et al.[8] and Gaspar et al.[9] have generated di-*t*-butyl silylene and diadmantyl silylene, respectively, hoping that bulky substituent groups on the silylene would stabilize the triplet ground state silylene. They found that both silylenes have a high degree of stereospecificity for the olefin

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addition reactions and concluded that the bulky substituent group silylenes still have the singlet state. Recently, in addition to the silylene extrusion, the 1,3-silyl migration to the corresponding cyclic silaethene product has been reported to be a major photochemical pathway of 2,2-diphenyltrisilanes.[10]

In this article we report the synthesis of a trisilane containing two different heterocyclic substituents hoping that the unshared electrons and richer electron density in the heterocycle might have some effect on the empty orbital of silicon. The results for photolysis of 2-(α-furyl)-2-(α-thienyl) hexamethyltrisilane in the presence of cyclohexene and methanol are also reported.

RESULTS AND DISCUSSION

Synthesis of 2-(α-furyl)-2-(α-thienyl)hexamethyltrisilane

Linear trisilane $RR'Si(SiMe_3)_2$ can often be made of coupling dichlorosilanes $RR'SiCl_2$ with trimethylchlorosilanes in THF as shown in Eq 1. However, attempts to make trisilanes with two different heterocyclic substituent failed (Scheme 1).

$$RR'SiCl_2 + 2Me_3SiCl \xrightarrow[\text{THF}]{\text{Mg-HMPA}} RR'Si(SiMe_3)_2$$

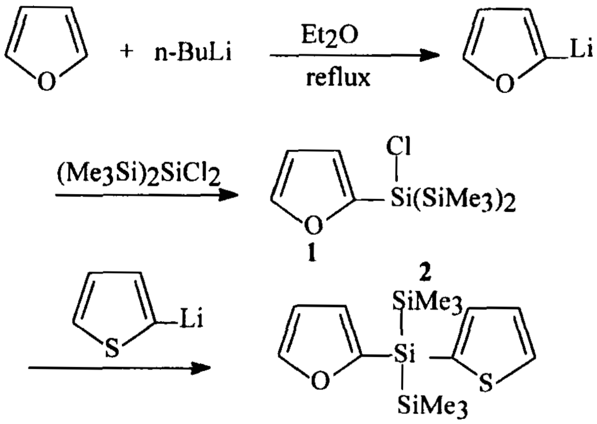
SCHEME 1

Dichloro(α-furyl)(α-thienyl)silane cannot be obtained easily and, moreover, in the next step, the mixture is too complex to separate the expected product easily. Synthesis of the appropriate trisilane was achieved by starting from 2,2-dichlorohexamethyltrisilane. For trisilane, the best results were obtained by reacting the α-thienyl lithium with 2,2-dichlorohexamethyltrisilane in ethyl ether to give 2-chloro-2-(α-thienyl)hexamethyltrisilane (**1**). The intermediate compound was reacted with excess (α-furyl) lithium, a colorless oil separated as shown (Scheme 2).

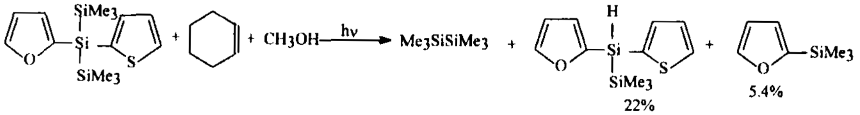
Photolysis of Compound 2

Photolysis of compound **2** in cyclohexene and methanol irradiation of **2** in the presence of cyclohexene, methanol, and pentane with a medium-pressure 450 W mercury pressure lamp is discussed. Unusual results were obtained (Scheme 3).

We immediately surmised that the products were derived from reactions of radicals. A good yield of trimethylsilyl(α-furyl) (α-thienyl)



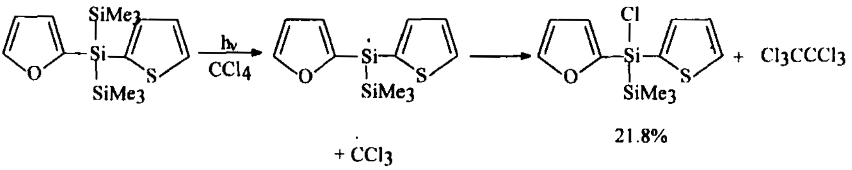
SCHEME 2



SCHEME 3

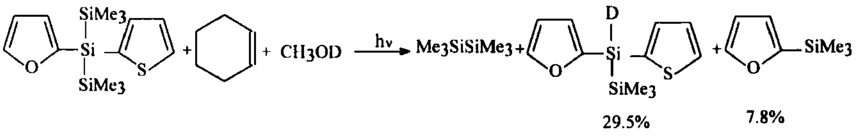
silane, which was obtained from the photolysis of **2** in the methanol-cyclohexene system, makes a triplet silylene seem unlikely. Therefore, we undertook an experiment in which we tried to capture reactive intermediates by carrying out the photolysis in the presence of large excess of carbon tetrachloride in pentane solution.

The main products were trimethylsilyl(α-furyl)(α-thienyl)chlorosilane and hexachloroethane, which were formed through homolytic scission. The isolation of products showed that the Si-Si bond of the radical disilane did not undergo further homolytic cleavage (Scheme 4). There are several reports of analogous reaction, in which silyl radicals abstract a chlorine atom.[11–13]



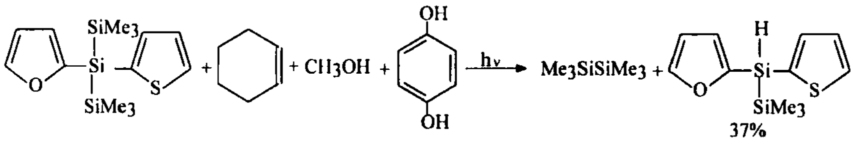
SCHEME 4

Then we invested photolysis of **2** in the presence of cyclohexene and methanol-d_1 respectively (Scheme 5). The results suggest that an initially formed trimethylsilyl(α-furyl)(α-thienyl)silyl radical could abstract hydrogen from methanol illustrated that the radical was not active enough to abstract hydrogen from cyclohexene.



SCHEME 5

We believe that trimethyl(α-furyl)(α-thienyl)silane was generated from the reaction of the trimethylsilyl(α-furyl)(α-thienyl)silyl radical with methanol. Furthermore, when hydroquinone as a radical trap was present in the reaction mixture, the radical reaction is stopped at the primary stage, and only trimethyl(α-furyl)(α-thienyl)silane was obtained as a major product (Scheme 6).



SCHEME 6

Now, a question emerges: What is the reason for the difference between the photolytic reactions of di(α-furyl)hexamethyltrisilane, in which a silylene is an important intermediate,[14] and (α-furyl)(α-thienyl)hexamethyltrisilane? The only difference in these substrates is the replacement of the oxygen atom in a furan ring by a sulfur atom. A possible explanation is the large $\sigma_{j,j}$ value of sulfur, which shows that sulfur atom has a great stabilizing effect on a free radical.[15]

(α-Furyl)(α-thienyl)hexamethyltrisilane (**2**) can be synthesized easily by α-thienyl lithium and dichlorohexamethyltrisilane, the product (α-thienyl)hexamethyl-chrolotrisilane was reacted with α-furyl lithium producing **2**. Photolyses of **2** in the presence of cyclohexene and methanol led to normal radical reaction.

EXPERIMENTAL

Boiling points were uncorrected. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on Nicolet 5DX FT-IR spectrophotometer and Shimadzu IR 408 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a JNM-PMX 60 SI (60MHZ, JEOL) spectrometer and Bruker MSL-300 spectrometer. Mass spectra were obtained on a Finnigan-MAT 4501 GC/MS spectrometer. Analytical gas chromatography was performed on a Shanghai 103 gas chromatograph (flame ionization detector) with nitrogen as carrier gas, using a 0.25 mm diameter and 30 M length SE-30 capillary column using an internal standard on the basis of the unreacted starting trisilane, and data were calculated on an HP 3390A integrator. Preparative gas chromatography was performed on a Shanghai 102 gas chromatograph with a thermal conductivity detector, hydrogen being used as carrier gas. The collections were conducted on a 6.3 mm × 3 m 20% SE-30 aluminum column.

Anhydrous ether was heated with sodium and distilled under nitrogen atmosphere before use, n-pentane and methanol were distilled and then dried with molecular sieves, cyclohexene was distilled before use, 2,2-dichlorohexamethyltrisilane and 2,2-diphenylhexamethyltrisilane were prepared by literature procedure.[5,16,17]

Synthesis of Compound 1

To a solution of 2.0 g (23.8 mmol) thiophene in dry diethyl ether (20 mL) at ambient temperature was added a 1.24 M solution of n-BuLi (16 mL, 19.8 mmol) in hexane dropwise with stirring. The mixture was refluxed for 7 h, and then permitted to stand overnight at room temperature. The solution of α-thienyl lithium was added to a mixture of 4 g (16.3 mmol) of 2,2-dichlorohexamethyltrisilane and ether 10 mL slowly. After the addition was complete, stirring was continued at room temperature for 1 h, then refluxed for 3.5 h. The salt was filtered under nitrogen atmosphere before the solvent was removed under vacuum on a rotary evaporator. The residue was distilled to give 4.4 g (92%) of colorless oil boiling at 78–80/0.28 mmHg. ^{1}H NMR (δ in $CDCl_3$, ppm), 0.20 (s, 18H), 7.10–7.33 (m, 2H), 7.55 (d, 1H).

Synthesis of Compound 2

To a solution of 2.4 g (35 mmol) of furan in dry diethyl ether (20 mL) at ambient temperature was added a 1.24 M solution of n-BuLi 25 mL (31 mmol) in hexane dropwise with stirring. The mixture was stirred at room temperature for 2 h, and then refluxed for 8 h. 2-Chloro-2-(α-thienyl)hexamethyltrisilane (4.4 g, 15 mmol) in 10 mL of ether was added dropwise. The solution was refluxed overnight. After having been treated with 20 mL of water, the reaction mixture was transferred to a separatory funnel and diluted with 20 mL of ether. The layers were separated and the aqueous layer was extracted with additional ether (3 × 20 mL). The combined extracts were then dried over anhydrous $MgSO_4$, Solvents were removed under vacuum with use of a rotary evaporator. The residue was distilled, 4.1 g (84%) of a colorless oil being collected, b.p. 106–110/0.1 mmHg. A pure sample was collected from a 3 m, 20% SE-30 chromatography column. UV (in cyclohexane) λ_{max} = 240 nm. ^1H NMR (δ in $CDCl_3$, ppm), 0.20 (s, 18H), 6.35 (m, 1H), 6.69 (m, 1H), 7.14 (m, 1H), 7.29 (m 1H), 7.58 (m, 1H), 7.67 (m, 1H), MS *m/z* (%): 324 (M^+, 1.25), 251 (M^+ - 73, 11.26), 73 (Me_3Si, 100). Anal. calcd. for $C_{14}H_{24}OSSi_3$: C, 51.79, H, 7.45. Found: C, 51.65, H, 7.69.

Photolysis of Compound 2-(α-thienyl)-2-(α-thienyl)hexamethyltrisilane in Cyclohexene and Methanol

A mixture of compound **2** (377 mg, 1.16 mmol), 2 mL of cyclohexene, 2 mL of methanol, and 15 mL of pentane was placed in a quartz tube equipped with a greaseless gas-tight Teflon vacuum stopcock. This solution was repeatedly degassed by the freeze-thaw method. The tube was closed and the reaction mixture was irradiated for 10 h in a water-cooled bath using a medium-pressure 500 W mercury lamp (Shanghai Yaming). After irradiation, the tube was placed in a liquid nitrogen bath and opened, the solvent was removed under ordinary pressure. The residue was analyzed by VPC and the pure products were collected by preparative gas chromatography.

Hexamethyldisilane $Me_3SiSiMe_3$ *m/z* (%): 146 (M^+, 44.28), 131 (M^+, 86.25), 73 (Me_3Si, 100) α-Trimethylfuran[18] $C_4H_3OSiMe_3$ *m/z* (%): 140 (M^+, 5.12), 125 ($M^=$-15, 100), 73 (Me_3Si, 15.12) (α-furyl)(α-thienyl) trimethylsilylsilane $(C_4H_3O)(C_4H_3S)(Me_3Si)SiH$ *m/z* (%) 252 (M^+, 1.92), 185 (M^+-67, 12.20), 169 (M^+-83, 5.90), 73 (Me_3Si, 100). ^1H NMR (δ in $CDCl_3$) 0.10 (s, 9H), 5.33 (s, 1H, Si-H), 6.35 (m, 1H), 6.69 (m, 1H), 7.14 (m, 1H), 7.29 (m 1H), 7.58 (m, 1H), 7.67(m, 1H).

Photolysis of Compound 2 in Carbon Tetrachloride

A mixture of compound **2** (377 mg, 1.16 mmol), 2 mL of cyclohexene, 2 mL of methanol, and 15 mL of pentane was placed in quartz tube equipped with a greaseless gas-tight Teflon vacuum stopcock. This solution was repeatedly degassed by the freeze-thaw method. The tube was closed, and the reaction mixture was irradiated for 10 h in a water-cooled bath using a medium-pressure 500 W mercury lamp (Shanghai

Yaming). After irradiation, the tube was placed in a liquid nitrogen bath and opened, the solvent was removed under ordinary pressure. The residue was analyzed by VPC and the pure products were collected by preparative gas chromatography.

Hexamethyldisilane $Me_3SiSiMe_3$ *m/z*: 146 (M^+, 34.38), 131 (M^+, 56.25), 73 (Me_3Si, 100) Hexachloroethane Cl_3CCCl_3 *m/z* (%): 205 (12.91), 203 (35.59) 201 (49.85), 199 (34.98), 117 (Cl_3C, 100), IR (cm^{-1}): 830 (w), 770, 670 (m). m.p. 235–236 (sealed tube).

Chloro(α-furyl)(α-thienyl)trimethylsilylsilane *m/z*: 271 (M^+-15, 5.34), 251 (25.35), 157 (100). ^1H NMR (δ in $CDCl_3$) 0.10 (s, 9H), 6.37 (m, 1H), 6.71 (m, 1H), 7.14 (m, 1H), 7.29 (m, 1H), 7.58 (m, 1H), 7.67 (m, 1H).

Photolysis of Compound 2 in Cyclohexene and Methanol-*d*

A mixture of compound **2** 370 mg (1.16 mmol), 2 mL of cyclohexene, 2 mL of methanol-d_1, and 15 mL of pentane was placed in quartz tube equipped with a greaseless gas-tight Teflon vacuum stopcock. This solution was treated in the same manner as described previously. The solvent was removed under ordinary pressure. The residue was analyzed by GC-MS and the pure products were collected by preparative gas chromatography.

Hexamethyldisilane $Me_3SiSiMe_3$ *m/z* (%): 146 (M^+, 44.28), 131 (M^+, 86.25), 73 (Me_3Si, 100) α-Trimethylsilylfuran $C_4H_3OSiMe_3$ *m/z* (%): 140 (M^+, 5.12), 125 ($M^=$ -15, 100), 73 (Me_3Si, 15.12).

(α-Furyl)(α-thienyl)trimethylsilylsilane-d_1 (C_4H_3O) (C_4H_3S) (Me_3Si) SiD *m/z* (%) 253 (M^+, 5.02), 238 (M^+ -15, 30.16) 73 (Me_3Si, 100). ^1H NMR (δ in $CDCl_3$) 0.10 (s, 9H), 6.35 (m, 1H), 6.69 (m, 1H), 7.14 (m, 1H), 7.29 (m, 1H), 7.58 (m, 1H), 7.67 (m, 1H).

Photolysis of Compound 2 in Cyclohexene and Methanol, and Hydroquinone

A mixture of compound **2** 370 mg (1.16 mmol), 2 mL of cyclohexene, 2 mL of methanol-d_1, 120 mg of hydroquinone, and 15 mL of pentane was placed in quartz tube equipped with a greaseless gas-tight Teflon vacuum stopcock. This solution was treated in the same manner as described previously. The solvent was removed under ordinary pressure. The residue was analyzed by GC-MS and the pure products were collected by preparative gas chromatography.

Hexamethyldisilane $Me_3SiSiMe_3$ *m/z* (%): 146 (M^+, 11.72), 131 (M^+, 25.72), 73(Me_3Si, 100) (α-Furyl)(α-thienyl)trimethylsilylsilane

(C_4H_3O) (C_4H_3S) $(Me_3Si)SiH$ *m/z*(%) 252 (M^+, 34.52), 237 (M^+ -15, 56.85), 73 (Me_3Si, 100). ^1H NMR (δ in $CDCl_3$) 0.10 (s, 9H), 5.33 (s, 1H, Si-H), 6.35 (m, 1H), 6.69 (m, 1H), 7.14 (m, 1H), 7.29 (m, 1H), 7.58 (m, 1H), 7.67 (m, 1H).

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