Heteroatom Chemistry
Volume 7, Number 1, 1996

Studies on Organosilicon Reactive Intermediates VIII Synthesis and Photochemistry of Di(α-thienyl)hexamethyltrisilane

Shihui Wu,* Yumei Luo, and Fei Liu

Department of Chemistry, Fudan University, Shanghai 200433, China

Shiming Chen

Center of Analytical and Measurement, Fudan University, Shanghai 200433, China

Received 17 May 1995; revised 12 July 1995

ABSTRACT

*The synthesis of di(α-thienyl)hexamethyltrisilane (*1*) is described. In the photolysis of* 1 *with cyclohexene and methanol, an apparent radical reaction occurred. We suspect that the sulfur atom of the thienyl group strongly stabilizes an initially formed silyl radical. This idea was supported both by identifying typical radical reaction products and examining the ESR spectrum of an adduct obtained by use of a radical trap.*

INTRODUCTION

Considerable attention has been focused on the electronic state of photolytically generated silylenes in recent years, and many studies that deal with the insertion of these intermediates into single bonds and with their addition to multiple bonds have been reported [1,2,3,4]. In search of triplet silylenes, Boudjouk et al. [5] and Pae et al. [6] have generated di-*tert*-butylsilylene and diadamantylsilylene, respectively, hoping that the bulky substituent groups on the silylene would stabilize the triplet silylene. They found that both silylenes have a high degree of stereoselectivity in olefin addition reactions and concluded that the bulky substituted silylenes still have singlet reacting states. Much less interest has been shown in the reaction of the silylene containing two heterocycles with olefins. Recently, we have found that the reaction of photochemically generated di(α-furyl)silylene with cyclohexene and methanol results in formation of products arising from the formal addition of the silylene to the multiple bond [7]. In this article we report the results for the photolysis of di(α-thienyl)hexamethyltrisilane in the presence of cyclohexene, methanol, or both.

RESULTS AND DISCUSSION

Synthesis of 2,2-Di-(α-thienyl)hexamethyltrisilane

Linear trisilanes can often be made by coupling dichlorosilanes RR'$SiCl_2$ with trimethylchlorosilane in THF and HMPA as shown in Scheme 1. However, attempts to prepare 2,2-di(α-thienyl)hexamethyltrisilane are more difficult by this approach. Dich-

$$RR'SiCl_2 \quad + \; 2\,Me_3\,SiCl \xrightarrow[THF]{Mg\text{ - }HMPA} \quad (Me_3Si)_2SiR\,R'$$

SCHEME 1

---

*To whom correspondence should be addressed.

1042-7163/96/010045-07

lorodi(α-thienyl)silane cannot be obtained easily, because the mixture formed in the coupling reaction between dichlorodi(α-thienyl)silane and trimethylchlorosilane is too complex for us to be able to separate the product efficiently. Therefore, synthesis of 1 was achieved by starting from 2,2-dichlorohexamethyltrisilane. For 2,2-di(α-thienyl)hexamethyltrisilane, the best yield was 79.7%, obtained by reacting the α-thienyllithium with 2,2-dichlorohexamethyltrisilane in ethyl ether as shown in Scheme 2.

Photolysis of 2,2-Di(α-thienyl) hexamethyltrisilane

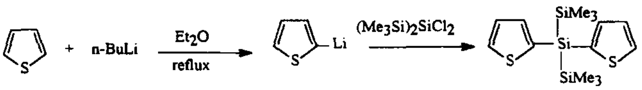
Irradiation of 1 in the presence of cyclohexene and methanol was carried out with a medium-pressure 450 W mercury lamp. Unusual results were obtained (Scheme 3).

We immediately surmised that either dithienylsilylene could be a triplet silylene or that the reaction products were formed from reactions of radicals. A good yield of trimethylsilyldi(α-thienyl)silane (5), which was obtained from the photolysis of 1 in the cyclohexene-methanol 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 a large excess of carbon tetrachloride in pentane solution (Scheme 4).

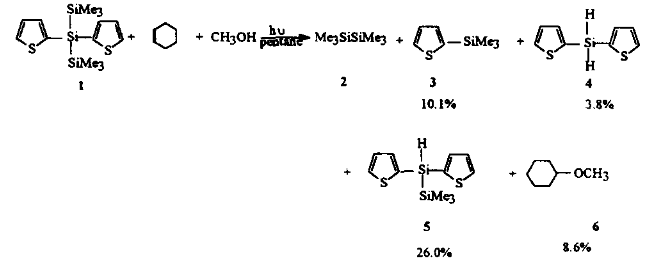
The main products were as follows: (α-thienyl)trimethylsilane, trimethylsilyldi(α-thienyl)chlorosilane, hexachloroethane, and bis(trimethylsilyl)(α-thienyl)chlorosilane, which were formed through homolytic scission. The isolation of these products showed that the Si–Si bond of radicals 10 and 11 did not undergo further homolytic cleavage (Scheme 5). There are several reports of analogous reactions, in which silyl radicals abstract a chlorine atom [8,9,10].

We then tried to gain further understanding of a possible radical mechanism of the reaction by use of the following experiment. The photolysis of 1 was carried out in either cyclohexene or methanol (Scheme 6).

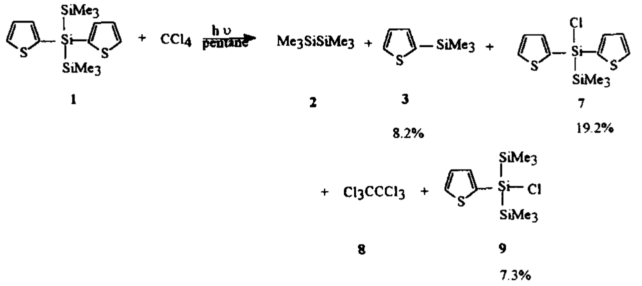
These results suggest that an initially formed trimethylsilyldi(α-thienyl)silyl radical could abstract hydrogen from either methanol or cyclohexene to



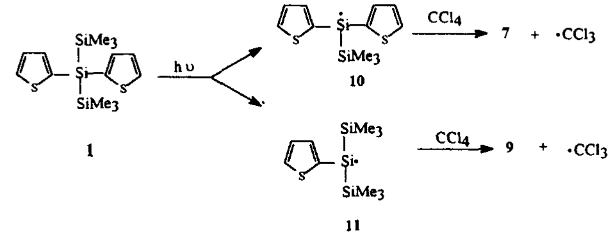
SCHEME 2



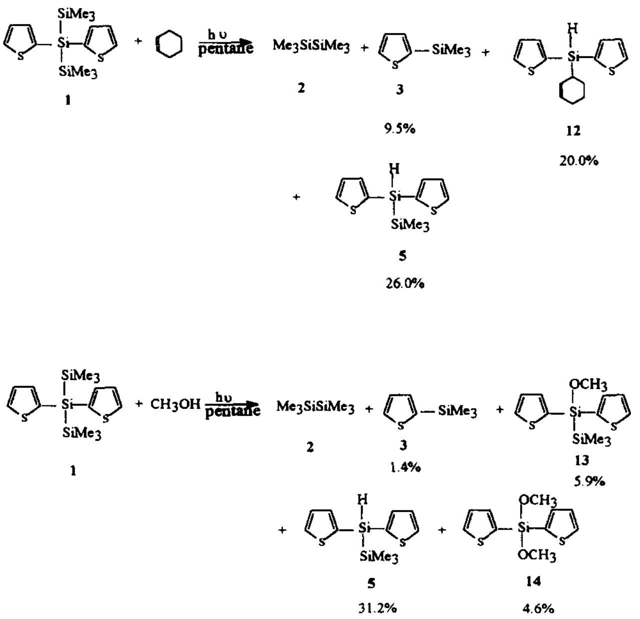
SCHEME 3



SCHEME 4



SCHEME 5



SCHEME 6

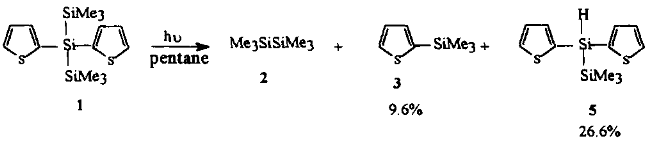
give 5. Compound 13 could arise from reaction of the trimethylsilyldi(α-thienyl)silyl radical with methanol and compound 14 from reaction of the methoxydi(α-thienyl)silyl radical with methanol. In these reactions, nucleophilic assistance of a methoxy group onto the silicon atom of radicals to form complex would be important [11]. An analogous result was obtained when the photolysis of 1 was carried out in pentane solution without the presence of a trapping agent. After the solvent was removed, most of the residue was the starting trisilane. In addition to much unchanged 1, compounds 3 and 5 were also obtained (Scheme 7).

We believe that trimethylsilyldi(α-thienyl)silane (5) was generated from the reaction of the trimethylsilyldi(α-thienyl) radical with methanol or cyclohexene. Further cleavage of the Si–Si bond of compound 5 and subsequent abstraction of hydrogen by the di(α-thienyl)silyl radical would give di(α-thienyl)silane (4).

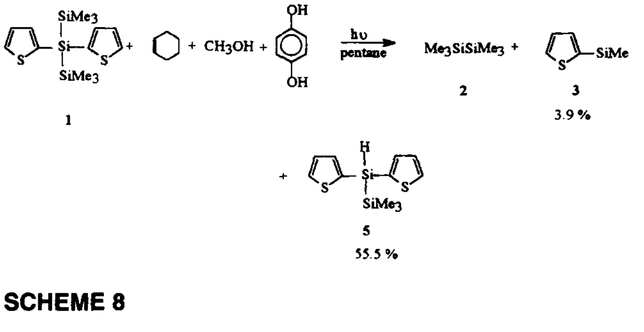
Furthermore, when hydroquinone as a radical trap was present in the reaction mixture, the radical reaction is stopped at the primary stage, and only compound 5 was obtained as a major product.

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 [7], and di(α-thienyl)hexamethyltrisilane? The only difference in these substrates is the replacement of the oxygen atom in the furan ring by a sulfur atom. A possible explanation is the large $\sigma_{j\cdot j}$ value of sulfur, which shows that sulfur has a great stabilizing effect on a free radical [12].

In order to confirm the initial formation of a silyl radical, we used ESR spectroscopy to detect the presence of trapped products in the photolysis of the trisilane 1. After irradiation of a mixture of trisilane 1 and 2,4,6-tri-*tert*-butylnitrosobenzene (BNB) for 1 hour, the ESR spectra of the trapped radicals shown in Figure 1 were obtained. The ESR spectra seem to show that the hyperfine multiplets match the number of γ-hydrogen in the radicals. In fact, two species of radical had been converted into "stable" spin adducts, one being the silyl radical converted into a spin adduct with BNB, another being formed by the former adduct and BNB again. The photolysis of a solution of BNB alone produced no spectrum in a short time [13]. The peak heights and widths of the signals were recorded, along with their decay characteristics. We found that the decay of one group of peaks was faster than that of the other group of peaks. Our data show that two species of adduct are present at the same time (Scheme 8). There is little difference between the two species of radical when the spin trapping agent converts them to "stable" spin adducts. The hyperfine splitting value *a* and the value of *g* are comparable with those of a typical nitroxide in an organic solution.



SCHEME 7



SCHEME 8

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 and Shimadzu IR 408 spectrophotometers. Nuclear magnetic resonance spectra were recorded on a JNM-PMX 60 SI (60 MHZ, JEOL) spectrometer and a 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 0.25 mm diameter and 30 m length SE-30 capillary columns, equipped with 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 made on a 6.3 mm × 3 m 20% SE-30 aluminum column. Electron spin resonance spectra were taken on a Bruker ER-200D-SRC spectrometer.

Anhydrous ether was heated with sodium and distilled under a nitrogen atmosphere before use. Pentane and methanol were distilled and then dried over molecular sieves. Cyclohexene was distilled before use, and 2,2-dichlorohexamethyltrisilane [6,15] and 2,2-diphenylhexamethyltrisilane [14,15] were prepared by literature procedures.

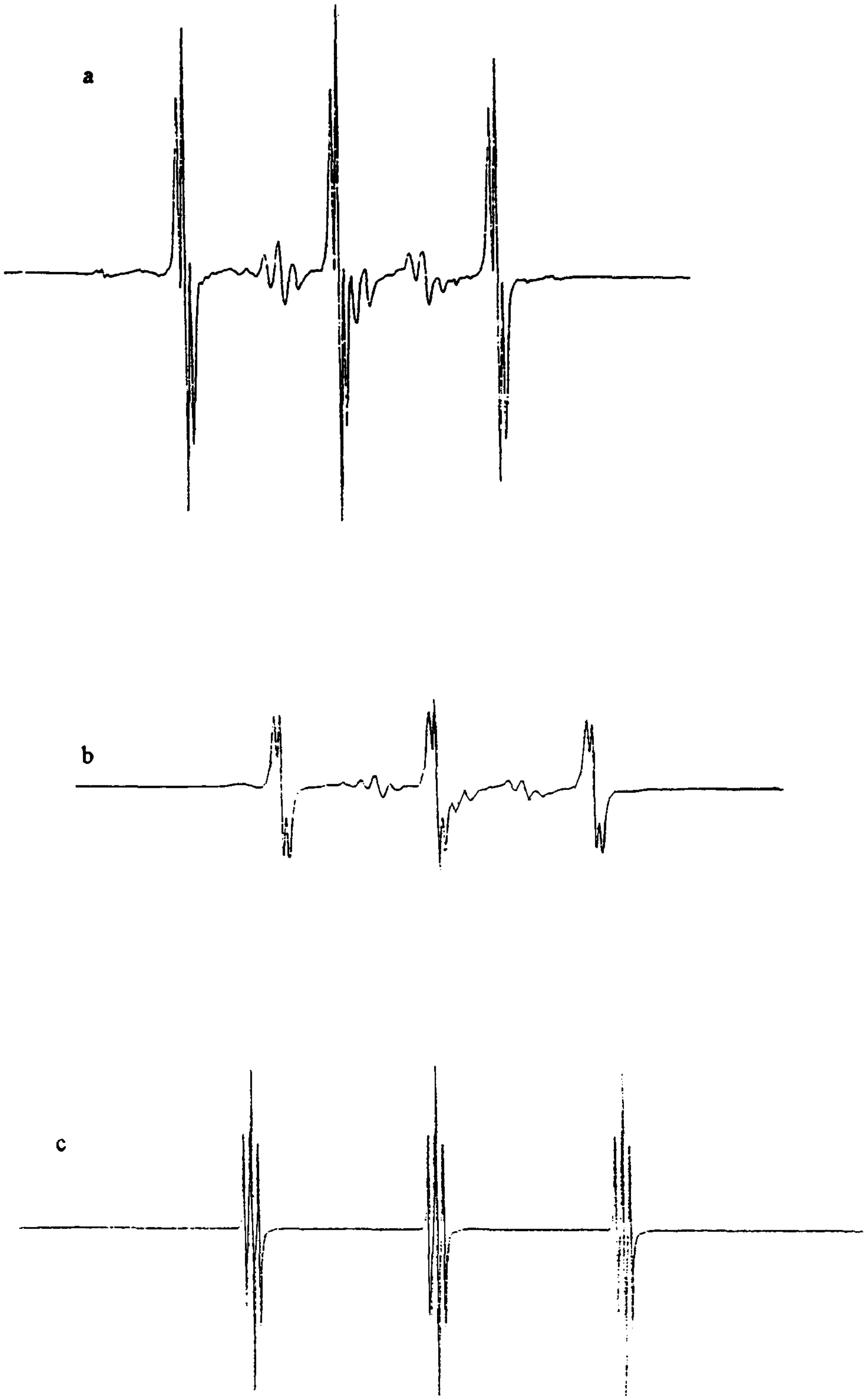
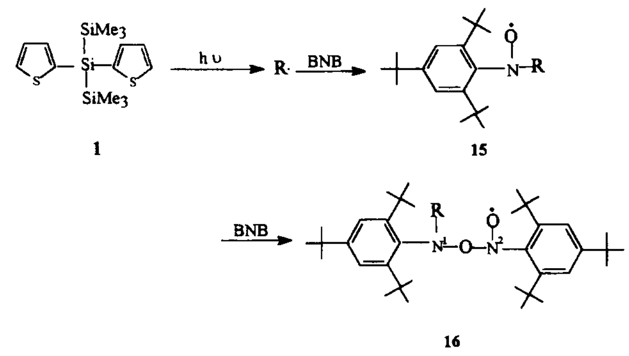


FIGURE 1 The field sweep of the spectrometer was calibrated with DPPH (g = 2.0057). (a) ESR spectrum of radical after trapping by 2,4,6-tri-*tert*-butylnitrosobenzene. (b) This spectrum was recorded for the same sample after 20 min. (c) a simulation of spectrum (a), is composed of two spectra that are simulations of two groups of parameters for two species of radical, respectively.



R= silyl radical

Parameters for two species are given below:

19: g =2.0053, ΔH=0.054 mT, a= 2.19 mT

20: g =2.0053, ΔH=0.054 mT, $a_{N'}$=2.19 mT, $a_{N'}$=0.088 mT

SCHEME 9

Synthesis of 2,2-Di(a-thienyl) hexamethyltrisilane

To a solution of thiophene (11.7 g, 0.139 mol) in dry ether, an *n*-hexane solution of *n*-butyllithium (0.12 mol, 136 mL) was added dropwise under stirring. The mixture was refluxed for 4 hours and then permitted to stand overnight at room temperature. 2,2-Dichlorohexamethyltrisilane 11.0 g (0.045 mol) 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 × 30 mL). The combined extracts were then dried over anhydrous $MgSO_4$. Solvents were removed under vacuum with the use of a rotary evaporator. The residue was distilled, 12.2 g (79.7%) of a colorless oil being collected, b.p. 100–102°C/0.2 mm Hg. A pure sample was collected from a 3 m 20% SE-30 chromatography column. UV (in cyclohexane) λ_{max} = 238 nm. IR (cm^{-1}): 3104, 3074, 2950, 2896, 1398, 1321, 1243, 1213, 1082, 1052, 980. ^1H NMR (δ in $CDCl_3$, ppm) 0.24 (s, 18H), 7.27 (m, 2H), 7.34 (m, 2H), 7.80 (m, 2H). MS *m*/*z* (%): 340 (M^+, 28.84), 325 (M^+ − 15, 100), 257 (M^+ − 83, 93.26), 73 (Me_3Si, 33.99). Anal. calcd. for $C_{14}H_{24}S_2Si_3$: C, 49.35; H, 7.10. Found: C, 48.86; H, 6.77.

Photolysis of 2,2-Di(a-thienyl)hexamethyltrisilane in Cyclohexene and Methanol

A mixture of compound 1 (164 mg, 0.48 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 12 hours in a water-cooled bath using a medium-pressure 450 W mercury lamp (Shanghai Yaming). After irradiation, the tube was placed in a liquid nitrogen bath and opened, and the solvent was removed under ordinary pressure. The residue was analyzed by VPC, and the pure products were collected by preparative gas chromatography.

Hexamethyldisilane $Me_3SiSiMe_3$ (2). *m*/*z*(%): 146 (M^+, 10.72), 131 (M^+ − 15, 23.62), 73 (Me_3Si, 100).

(a-Thienyl)trimethylsilane [16] $(C_4H_3S)SiMe_3$ (3). *m*/*z*(%): 156 (M^+, 26.03), 141 (M^+ − 15, 100), 83 (C_4H_3S, 12.93), 73 (Me_3Si, 45.58). IR (cm^{-1}): 3060 (w, =CH), 2985 (s, CH_3), 2920 (m, CH_3), 1492, and 1400 (C_4H_3S), 1210. ^1H NMR (CCl_4, CH_2Cl_2 as inner standard, ppm) 0.30 (s, 9H, $SiMe_3$), 7.00–7.80 (m, 3H, C_4H_3S).

Di(a-thienyl)silane $(C_4H_3S)_2SiH_2$ (4). *m*/*z*(%): 196 (M^+, 73.32), 45 (HCS, 100).

Di(a-thienyl)-trimethylsilylsilane $(C_4H_3S)_2(SiMe_3)SiH$ (5). *m*/*z*(%): 268 (M^+, 29.77), 253 (M^+ − 15, 65.40), 73 (Me_3Si, 100), 45 (HC S, 90.60). IR (cm^{-1}): 3100, 2950, 2875, 2125, 1500, 1375, 1250, 1225, 1100, 1000, 800, 775. ^1H NMR (CCl_4, CH_2Cl_2 as inner standard, ppm): 0.30 (s, 9H, $SiMe_3$), 5.07 (s, 1H, SiH), 7.00–7.67 (m, 6H).

Methoxycyclohexane $C_6H_{11}OCH_3$ (6). *m*/*z*(%): 114 (M^+, 8.65), 99 (M^+ − 15, 6.73), 41 ($-CH_2CH=CH_2$, 100).

Photolysis of Compound 1 *in Carbon Tetrachloride*

A mixture of compound 1 (178 mg 0.52 mmol), 3 mL of carbon tetrachloride, and 10 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 12 hours in a water-cooled bath using a medium-pressure 450 W mercury lamp. 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 $Me_3SiSiMe_3$ (2). *m/z*(%): 146 (M$^+$, 44.28), 131 (M$^+$ − 15, 86.25), 73 (Me_3Si, 100).

(α-Thienyl)trimethylsilane $(C_4H_3S)SiMe_3$ (3). *m/z*(%): 156 (M$^+$, 30.06), 141 (M$^+$ − 15, 100), 83 (C_4H_3S, 13.84), 73 (Me_3Si, 18.30). ^{1}H NMR (CCl_4, CH_2Cl_2 as inner standard, ppm): 0.30 (s, 9H), 7.13–7.70 (m, 3H).

Chloro-di(α-thienyl)silane $(C_4H_3S)_2(SiMe_3)SiCl$ (7). *m/z*(%): 304 (M$^+$ + 2, 12.23), 303 (M$^+$ + 1, 7.18), 302 (M$^+$, 37.23), 267 (M$^+$ − 35, 31.91), 194 (M$^+$ − 35–73, 25.80), 73 ($SiMe_3$, 100).

Hexachloroethane Cl_3CCCl_3 (8). *m/z*(%): 205 (12.91), 203 (35.59), 201 (49.85), 199 (34.98), 119 (57.21), 117 (53.60), 82 (45.95), 94 (ClCCCl, 100), 47 (77.18). IR (cm^{-1}): 830 (w), 770, 670 (m). mp: 235–236°C (sealed tube).

Chlorobis(trimethylsilyl)(α-thienyl)silane $(C_4H_3S)(SiMe_3)_2SiCl$ (9). *m/z*(%): 292 (M$^+$, 2.10), 277 (M$^+$ − 15, 31.90), 257 (M$^+$ − 35, 100), 169 (M$^+$ − 73–35, 20.65), 73 ($SiMe_3$, 63.55). Starting material.

Photolysis of Compound 1 *in Cyclohexene*

A mixture of compound 1 (165 mg, 0.49 mmol), 3 mL of cyclohexene, and 15 mL of pentane was placed in a 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 VPC, and the pure products were collected by preparative gas chromatography.

Hexamethyldisilane $Me_3SiSiMe_3$ (2). *m/z*(%): 146 (M$^+$, 17.61), 131 (M$^+$ − 15, 100), 73 (Me_3Si, 100).

(α-Thienyl)trimethylsilylsilane $(C_4H_3S)SiMe_3$ (3). *m/z*(%): 156 (M$^+$, 9.03), 141 (M$^+$ − 15, 30.11), 73 ($SiMe_3$, 100).

Trimethylsilyldi(α-thienyl)silane $(C_4H_3S)_2(Me_3Si)$-SiH (5). *m/z*(%): 268 (M$^+$, 31.06), 267 (M$^+$ − 1, 7.64), 195 (M$^+$ − 73, 15.37), 73 (Me_3Si, 100). ^{1}H NMR (CCl_4, CH_2Cl_2 as inner standard, ppm): 0.30 (s, 9H, $SiMe_3$), 5.07 (s, 1H, SiH), 7.00–7.67 (m, 6H).

3-Cyclohexenyl-di(α-thienyl)silane $(C_4H_3S)_2(C_6H_9)SiH$ (12). *m/z*(%): 276 (M$^+$, 26.20), 275 (M$^+$ − 1, 67.46), 195 (M$^+$ − 81, 100).

Photolysis of Compound 1 *in Methanol*

A mixture of compound 1 (185 mg, 0.54 mmol), 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 treated in the same manner as described previously. The solvent was removed under ordinary pressure. The residue was analyzed by VPC, and the pure products were collected by preparative gas chromatography.

Hexamethyldisilane $Me_3SiSiMe_3$ (2). *m/z*(%): 146 (M$^+$, 24.90), 131 (M$^+$ − 15, 100), 73 (Me_3Si, 91.90).

(α-Thienyl)trimethylsilane $(C_4H_3S)SiMe_3$ (3). *m/z*(%): 156 (M$^+$, 27.30), 141 (M$^+$ − 15, 100), 73 (Me_3Si, 21.36).

Di(α-thienyl)trimethylsilylsilane $(C_4H_3S)_2(SiMe_3)$-SiH (5). *m/z*(%): 268 (M$^+$, 56.42), 253 (M$^+$ − 15, 65.52), 73 ($SiMe_3$, 100). ^{1}H NMR (CCl_4, CH_2Cl_2 as inner standard, ppm): 0.30 (s, 9H, $SiMe_3$), 5.07 (s, 1H, SiH), 7.00–7.67 (m, 6H).

Methoxydi(α-thienyl)trimethylsilylsilane $(C_4H_3S)_2(SiMe_3)\,SiOCH_3$ (13). *m/z*(%): 298 (M$^+$, 7.87), 283 (M$^+$ − 15, 100), 267 (M$^+$ − 31, 28.54), 215 (M$^+$ − 83, 50.72), 73 (Me_3Si, 71.68). ^{1}H NMR (CCl_4, CH_2Cl_2 as inner standard, ppm): 0.30 (s, 9H), 3.90 (s, 3H), 7.10–7.70 (m, 6H).

Dimethoxydi(α-thienyl)silane $(C_4H_3S)_2Si(OCH_3)_2$ (14). *m/z*(%): 256 (M$^+$, 100), 225 (M$^+$ − 31, 4.75), 173 (M$^+$ − 83, 14.85), 59 ($SiOCH_3$, 50.18).

Photolysis of Compound 1 *in Pentane*

A mixture of compound 1 (180 mg, 0.53 mmol) and 12 mL of pentane was placed in a 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 VPC, and the pure products were collected by preparative gas chromatography.

Hexamethyldisilane $Me_3SiSiMe_3$ (2). *m/z*(%): 146 (M$^+$, 38.21), 131 (M$^+$ − 15, 100), 73 (Me_3Si, 77.34).

(α-Thienyl)trimethylsilane $(C_4H_3S)SiMe_3$ (3). *m/z*(%): 156 (M$^+$, 19.50), 141 (M$^+$ − 15, 100), 73 (Me_3Si, 2.84).

Di(α-thienyl)trimethylsilylsilane $(C_4H_3S)_2(SiMe_3)$-

SiH (5). *m/z(%)*: 268 (M^+, 39.58), 253 ($M^+ - 15$, 20.05), 195 ($M^+ - 73$, 14.01), 185 ($M^+ - 83$, 12.95), 73 (Me_3Si, 100).

Photolysis of 2,2-Di-(α-thienyl)hexamethyltrisilane in Cyclohexene, Methanol, and Hydroquinone

A mixture of compound 1 (213 mg, 0.63 mmol), 2 mL of cyclohexene, 2 mL of methanol, 106 mg of hydroquinone and 12 mL of pentane was placed in a 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 VPC, and the pure products were collected by preparative gas chromatography.

$Me_3SiSiMe_3$ (2). *m/z(%)*: 146 (M^+, 24.90), 131 ($M^+ - 15$, 100), 73 (Me_3Si, 91.90).

$(C_4H_3S)SiMe_3$ (3). *m/z(%)*: 156 (M^+, 27.30), 141 ($M^+ - 15$, 100), 73 (Me_3Si, 21.36).

$(C_4H_3S)_2(SiMe_3)SiH$ (5). *m/z(%)*: 268 (M^+, 56.42), 253 ($M^+ - 15$, 65.52), 73 ($SiMe_3$, 100). ^1H NMR (CCl_4, CH_2Cl_2 as inner standard, ppm): 0.30 (9H, s, $SiMe_3$), 5.07 (1H, s, SiH), 7.00–7.67 (6H, m). Starting material.

Photolysis of 1 *and Trapping of the Silyl Radical*

A mixture of 20 mg (0.06 mmol) of 1, 0.5 mL (0.25 M) of BNB, and 1 mL of pentane was placed in a quartz tube. This solution was repeatedly degassed by the freeze-thaw method. The tube was closed, and the reaction mixture was irradiated for 1 hour in a water-cooled bath using a medium-pressure 450 W mercury lamp. After irradiation, the ESR spectrum was recorded as soon as possible.

ACKNOWLEDGMENTS

This work was supported by the National Natural Sciences Foundation of China. We also thank Prof. Maitland Jones, Jr. (Princeton University) for his helpful advice and discussions.

REFERENCES

[1] M. Ishikawa, K. Nakagawa, M. Kumada, *J. Organomet. Chem., 152,* 1978, 155.

[2] M. Ishikawa, K. Nakagawa, M. Kumada, *J. Organomet. Chem., 190,* 1980, 117.

[3] P. P. Gaspar, D. Holten, S. Konieczny, *Acc. Chem. Res., 20,* 1987, 329.

[4] D. B. Jacobson, R. Bakhtiar, *J. Am. Chem. Soc., 115,* 1993, 10830.

[5] P. Boudjouk, U. Samaraweera, R. Sooriyakumaran, J. Chrusciel, K. R. Anderson, *Angew. Chem. Int. Ed. Engl., 27,* 1988, 1355.

[6] D. H. Pae, M. Xiao, M. Y. Chiang, P. P. Gaspar, *J. Am. Chem. Soc., 113,* 1991, 1281.

[7] S.-H. Wu, Y.-M. Luo, F. Liu, *Acta Chim Sinca,* in press.

[8] K. Oka, R. Nakao, *Chem. Express, 4,* 1989, 789.

[9] K. Oka, R. Nakao, *Chem. Express, 4,* 1989, 713.

[10] K. Oka, R. Nakao, *Chem. Express, 7,* 1990, 390.

[11] M. Ishikawa, H. Sakamoto, *J. Organomet. Chem., 414,* 1991, 1.

[12] X.-K. Jiang, G.-Z. Ji, *J. Org. Chem., 57,* 1992, 6051.

[13] B. Mile, C. C. Rowlands, P. D. Sillman, M. Filde, *J. Chem. Soc. Perkin Trans., 2,* 1992, 1431.

[14] V. J. Tortorelli, M. Jones, Jr., S.-H. Wu, Z.-H. Li, *Organometallics, 2,* 1983, 759.

[15] R. A. Jackson, C. J. Rhodes, *J. Organoment. Chem., 336,* 1987, 45.

[16] R. A. Benkeser, R. B. Currie, *J. Am. Chem. Soc., 70,* 1948, 1780.