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Photolysis of 1,1,2,2-tetramethyl-1,2-bis-(2′-thienyl)disilane

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Abstract

Photolysis of 1,1,2,2-tetramethyl-1,2-bis-(2′-thienyl)disilane (I) in methanol/benzene leads to dimethyl-bis-(2′-thienyl)silane (III), 2-methoxydimethylsilylthiophene (IV) and 2-dimethylsilylthiophene (V) as a major products. The mechanism of this reaction, has been explored by use of methanol-d_4. The predominant pathway leading to IV and V appears to involve direct reaction of methanol with the photoexcited state of I.

While the photolysis of aryl substituted disilanes has been extensively studied, the photolysis of heteroaryl substituted disilanes has not. Most of the products formed by photolysis of aryl substituted disilanes in the presence of methanol have been accounted for by three major pathways. These involve silylene and silene reactive intermediates. It has been proposed that these intermediates are formed by recombination [1] and disproportionation [1,2] of an initial pair of silyl radicals formed by homolytic scission of the Si–Si bond of the photoexcited aryl substituted disilane. The initial silyl radical pair has been successfully trapped with 1,1-di-t-butylethylene to give relatively long lived adduct radicals which can be detected by EPR spectroscopy [3]. The secondary silylene and silene intermediates have been trapped by reaction with various agents such as methanol as outlined in Scheme 1 [1].

We should like to report that the photolysis of 1,1,2,2-tetramethyl-1,2-bis-(2′-thienyl)disilane (I) in benzene/methanol yields methoxydimethylsilane (II), dimethyl-bis-(2′-thienyl)silane (III), 2-methoxydimethylsilylthiophene (IV) and 2-dimethylsilylthiophene (V) as major products. Control experiments have shown that III, IV, and V are stable under these reaction conditions. In the absence of light, I is stable in benzene/methanol. We believe that II and III are probably formed by a pathway analogous to eq. 1 of Scheme 1. Thus recombination of the initial 2′-thienyldimethylsilyl radical (VI) pair yields III and dimethylsilylene which reacts with methanol to give II. Products IV and V can be formed by disproportionation of

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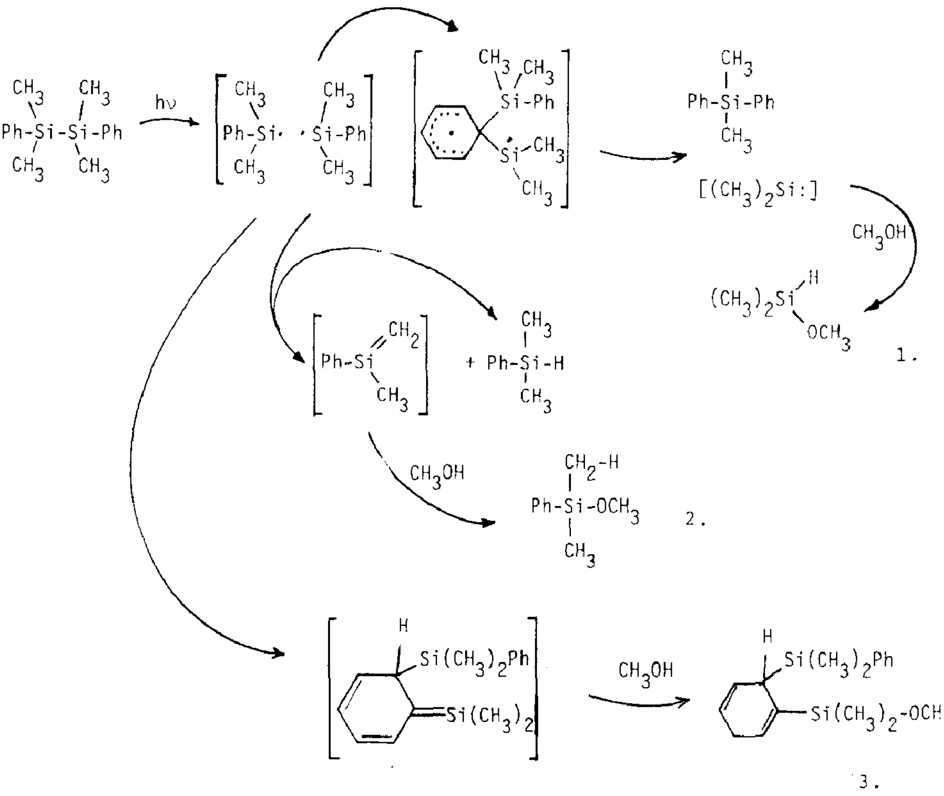
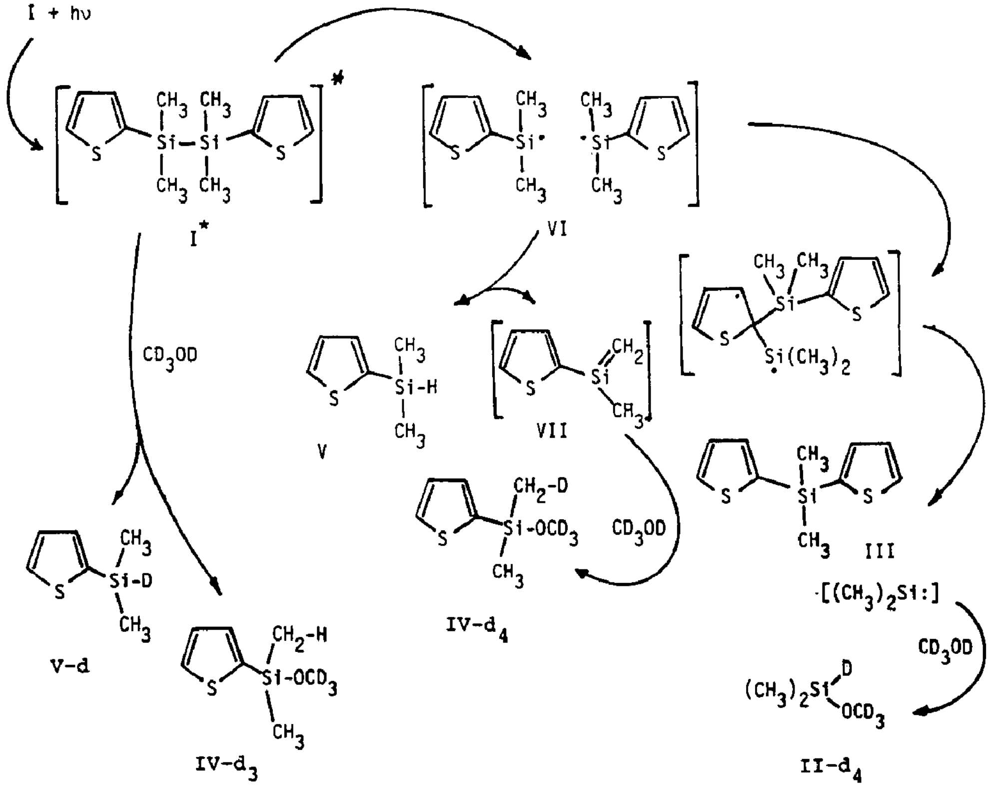


Scheme 1. Photochemical pathways of aryl substituted disilanes.

VI to yield V and methyl-2-thienylsilene (VII). Addition of methanol across the polar Si–C double bond of VII will yield IV. This reaction sequence is analogous to that outlined in eq. 2 of Scheme 1. If the photolysis of I is carried out in the presence of methanol-d_4, this pathway should yield IV-d_4 and V-d_0. IV-d_4 results from the addition of methanol-d_4 across the polar Si–C double bond of VII. However, analysis of the products formed in the photolysis of I in methanol-d_4 indicates that in addition to 23 to 37% of IV-d_4 and V-d_0, IV-d_3 and V-d_1 are formed as major products (65–77%). These are most reasonably accounted for by a direct reaction of the solvent methanol-d_4 with the photoexcited Si–Si bond of I. This type of process has never been observed as a major pathway in the photolysis of aryl-substituted disilanes previously [4]. These processes are outlined in Scheme 2. Photolysis of I in benzene in the absence of methanol yields V (15%) and III (58%). No products which might arise from dimerization of VII such as 1,3-dimethyl-1,3-bis-(2′-thienyl)-1,3-disilacyclobutane were detected. Finally, no products analogous to those formed via eq. 3 of Scheme 1 were found.

In addition to these products, several minor products were detected: 1,1,2,2-tetramethyldisiloxane (VIII), 1,1,3,3-tetramethyl-1,3-bis-(2′-thienyl)disiloxane (IX) and 1,1,3,3-tetramethyl-1-(2′-thienyl)disiloxane (X) were found. VIII probably results from insertion of dimethylsilylene into the O–H single bonds of trace amounts of water [5,6]. Reaction of water with the photoexcited state of I is expected to yield 2-thienyldimethylsilanol (XI) and V. Condensation of XI will yield IX, while insertion of dimethylsilylene into the O–H single bond of XI will give X. Finally



Scheme 2. Photochemical pathways of 1,1,2,2-tetramethyl-1,2-bis-(2′-thienyl)tetramethyldisilane.

phenyl-2′-thienyldimethylsilane (XII) is found (1%). This product probably results from reaction of 2′-thienyldimethylsilyl radicals with the benzene solvent. Radical aromatic silylation reactions have been previously observed [7–9].

Experimental

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on an IBM Bruker WP-270-SY spectrometer operating in the Fourier transform mode. ^{13}C NMR spectra were run with broad band proton decoupling. Five to ten percent solutions in chloroform-*d* were used to obtain these spectra. Chloroform was used as an internal standard for ^{1}H and ^{13}C NMR. All chemical shifts reported were externally referenced to TMS. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have at least two methyl groups bonded to them [10]. IR spectra were recorded on a Perkin–Elmer PE-281 spectrometer. Spectra were taken on neat films on NaCl plates. UV spectra were recorded on a Shimadzu UV-260 spectrometer. Spectral quality hexane was used to prepare solutions for UV spectra. Low resolution mass spectra were recorded on a Finnigan MAT Incos 50 GCMS instrument, equipped with a Varian 3400 gas liquid phase chromatograph with a 30 m × 0.25 mm DB-5 capillary column as the inlet, at an ionizing voltage of 70 eV. Photolysis reactions were analyzed on a Hewlett Packard (HP) 5710A gas liquid phase chromatograph equipped with an HP 3380A integrator and a 10′ × 1/8″ stainless steel column packed with 10% SE-30 on Chromosorb W. Naphthalene was added to reaction mixtures after photolysis to serve as an internal standard. Product yields reported are corrected for recovered starting material I and for GC sensitivities of major photo-products. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

THF was distilled from a deep blue solution of sodium benzophenone ketyl immediately prior to use.

All reactions were carried out under an atmosphere of purified nitrogen in a flame dried glassware.

Photolysis reactions were analyzed by GC as well as GC/MS. Authentic samples of reaction products (II, III, IV, V, IX and XII) were prepared. They were fully characterized. 1,1,2,2-Tetramethyldisiloxane (VIII) was purchased from Petrarch. GC retention times and GC/MS of authentic samples were identical with those of photo-products. X, a minor product, was only identified by GC/MS.

Methoxydimethylsilane (II) was prepared by reaction of dimethylchlorosilane with trimethylorthoformate. It had properties in complete agreement with literature values [11].

1,2-Dichloro-1,1,2,2-tetramethyldisilane was prepared from hexamethyldisilane (Petrarch) by reaction with trimethylchlorosilane and anhydrous aluminum chloride in 88% yield. It had properties in complete agreement with literature values [12].

1,1,2,2-Tetramethyl-1,2-bis(2′-thienyl)disilane (I)

In a 100 ml three-neck round-bottom flask equipped with a reflux condenser, a rubber septum and a 0.5″ diameter ultrasound horn was placed 2-chlorothiophene (6.6 g, 55 mmol), magnesium turnings (1.45 g, 60 mmol) and 60 ml of THF. The ultrasound horn was connected to a Tekmar 500 W 20 KHz ultrasound generator. The reaction mixture was sonicated at 30% power for 3 h while the flask was cooled to 25 °C in a water bath. At this time almost all of the magnesium had been consumed. 1,2-Dichloro-1,1,2,2-tetramethyldisilane (4.7 g, 25 mmol) was added to the reaction mixture via a syringe through the rubber septum over a 10-min period. The reaction mixture was allowed to stand overnight and was transferred to a 250 ml Erlenmeyer flask. Magnesium salts were precipitated by addition of 100 ml of pentane. These were removed by filtration and the salts were washed with an additional 100 ml of pentane. The combined organic phase was washed twice with 100 ml portions of water. It was then dried over anhydrous magnesium sulfate, filtered and the solvents removed by evaporation under reduced pressure. The residue was distilled through a 10 cm vacuum jacketed Vigreux column. A fraction b.p. 92–94 °C/0.1 mmHg, 6.0 g, 85% yield was obtained. It solidified on standing to a solid m.p. 39–40 °C. I had the following spectral properties. ^{1}H NMR δ: 0.41 (s,12H), 7.176 (d of d,1H $J = 1.7$ and 3.3 Hz), 7.186 (d of d,1H, $J = 3.3$ and 4.8 Hz), 7.60 (d of d,1H, $J = 1.7$ and 4.8 Hz). ^{13}C NMR δ: −2.69, 128.25, 130.69, 134.48, 137.68. ^{29}Si NMR δ: −24.36. IR ν: 3080, 3060, 2935s, 1530, 1400s, 1320, 1242, 1207s, 1074, 978s, 820s, 775s cm^{-1}. UV λ_{max} 244 nm, $\epsilon = 24{,}700$. GCMS m/e (rel. intensity): 284(1.17), 283(1.62), 282(6.58) $M^{+\cdot}$, 269(2.14), 268(2.78), 267(12.04) $M - 15^+$, 209(4.23), 194(3.88), 193(7.30), 192(42.72), 179(1.62), 178(2.66), 177(17.46), 143(11.48), 142(15.84), 141(100.00), 117(1.98), 116(2.15), 115(16.52), 111(12.88), 97(12.59), 83(16.80), 75(20.34), 73(12.20). Elemental Anal. Found: C, 50.87; H, 6.55. $C_{12}H_{18}S_2Si_2$ calcd.: C, 51.00; H, 6.42%.

Dimethyl-bis-(2′-thiophenyl)silane (III)

In a 100 ml three-neck round-bottom flask equipped with a reflux condenser, rubber septum and an ultrasound horn was placed dimethyldichlorosilane (1.29 g, 10 mmol), 2-chlorothiophene (2.95 g, 25 mmol), magnesium turnings (0.6 g, 25 mmol) and 50 ml of THF. The reaction mixture was sonicated for 1 h at a 30% power level while the flask was cooled in a water bath. The reaction mixture was poured into a 250 ml separatory funnel and 50 ml of methylene chloride was added. The organic phase was extracted twice with water, dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The residue was distilled through a 10 cm vacuum jacketed Vigreux column. A central fraction b.p. 73–75 °C/0.1 mmHg, 1.78 g, 80% yield was obtained. If had the following spectral properties. ^{1}H NMR δ: 0.83 (s,6H), 7.38 (d of d,2H, $J = 3.5$ and 4.5 Hz), 7.52 (d of d,2H, $J = 1$ and 3.5 Hz), 7.825 (d of d,2H, $J = 1$ and 4.5 Hz). ^{13}C NMR δ: -0.03, 128.3, 131.3, 135.4, 137.56. ^{29}Si NMR δ: -14.91. UV λ_{max} 236.8 nm, $\epsilon = 29{,}900$. GCMS *m/e* (rel. intensity): 226(4.58), 225(6.02), 224(34.29) $M^{+\cdot}$, 211(13.38), 210(16.83), 209(100.00) $M-15^+$, 185(1.26), 184(1.29), 183(8.94), 166(2.77), 151(2.54), 143(2.09), 142(1.04), 141(7.69), 134(4.27), 125(3.62), 115(3.91), 111(8.29), 101(3.36), 99(1.52), 98(3.62), 97(5.22), 89(2.03), 85(4.55), 75(17.28). ^{1}H NMR [12] and IR [14] are in agreement with literature values. Elemental Anal. Found: C, 53.26; H, 5.25. $C_{10}H_{12}S_2Si$ calc: C, 53.57; H, 5.36%.

2-Methoxydimethylsilylthiophene (IV)

IV was prepared by reaction of V with methanol catalyzed by tris-(triphenylphosphine) rhodium(I) chloride [15–18]. In a 50 ml two-neck round-bottom flask equipped with a Teflon covered magnetic stirring bar was placed 2-dimethylsilylthiophene (V) (0.68 g, 4.6 mmol), 15 ml of freshly distilled benzene, and 0.2 ml of methanol. Nitrogen was bubbled through the solution for 10 min. Tris-(triphenylphosphine) rhodium(I) chloride (5 mg) was added to the solution. The flask was sealed with two rubber septa. The reaction mixture was stirred at room temperature overnight. The volatile solvents were removed by evaporation under reduced pressure. The residue was distilled through a 5 cm vacuum jacketed Vigreux column. A fraction b.p. 45–46 °C/0.5 mmHg was obtained 0.6 g, 72% yield. It had the following spectral properties. ^{1}H NMR δ: 0.25 (s, 6H), 3.27 (s,3H), 7.045 (d of d,1H, $J = 3.2$ and 4.3 Hz), 7.18 (d of d,1H, $J = 3.2$ and 1 Hz), 7.47 (d of d,1H, $J = 4.3$ and 1 Hz). ^{13}C NMR δ: -1.33, 50.62, 128.14, 131.17, 135.02, 137.26. ^{29}Si NMR δ: -6.18. IR ν: 1400, 1395, 1255, 1080, 1050, 785 cm^{-1}. GCMS *m/e* (rel. intensity) 175(0.28), 174(2.51), 173(3.55), 172(29.33) $M^{+\cdot}$, 160(0.74), 159(8.15), 158(11.70), 157(100.0) $M-15^+$ 130(0.38), 129(4.02), 128(5.54), 127(51.15), 99(1.91), 98(1.52), 97(17.82), 61(2.12), 60(1.99), 59(26.38). Elemental Anal. Found: C, 48.98; H, 6.92. $C_7H_{12}OSSi$ calc: C, 48.94; H, 6.98%.

2-Dimethylsilylthiophene (V)

In a 100 ml three-neck round-bottom flask equipped with an reflux condenser, an ultrasound horn and a rubber septum was placed 60 ml of THF, magnesium turnings (1.46 g, 60 mmol) and 2-chlorothiophene (5.6 ml, 50 mmol). The reaction flask was cooled in a water bath while the reaction mixture was sonicated for 1 h at a 30% power level. At this time, almost all of the magnesium had been consumed.

Dimethylchlorosilane (6.5 ml, 60 mmol) was added dropwise via a syringe into the reaction mixture. After 0.5 h, the reaction mixture was transferred to a 500 ml separatory funnel, 200 ml of pentane and 10 ml of water was added. The organic phase was washed with water, dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The residue was distilled through a 10 cm vacuum jacketed Vigreux column. A fraction b.p. 74–75°C/60 mmHg, 13 g 92% yield was obtained. ^{1}H NMR δ: 0.762 (d,6H, $J = 3.7$ Hz), 5.00 (sept. 1H, $J = 3.7$ Hz), 7.52 (d of d,1H, $J = 3.2$ and 4.1 Hz), 7.66 (d of d,1H, J 2.3 and 3.2 Hz), 7.91 (d of d,1H, $J = 2.3$ and 4.1 Hz). ^{13}C NMR δ: −2.79, 128.19, 130.96, 135.02, 136.00. ^{29}Si NMR δ: −22.97. IR ν: 2960s, 2120s, 1400, 1245, 1210, 990, 870, 830, 695 cm^{-1}. GCMS m/e (rel. intensity) 145(0.25), 144(2.62), 143(5.05), 142(31.02) $M^{+\cdot}$, 141(14.06) $M-1^+$, 129(10.21), 128(13.63), 127(100.00) $M-15^+$, 126(1.97), 115(3.01), 103(1.60), 102(1.80), 101(19.01), 87(1.21), 86(2.02), 85(7.19), 84(3.34), 83(3.71), 82(1.36), 81(1.60), 78(2.60), 77(5.06), 76(1.92), 75(14.41), 73(1.84), 69(4.17), 58(10.03). The ^{1}H NMR [13] and IR [14] were consistent with literature values.

1,1,3,3-Tetramethyl-1-3-bis(2′-thienyl)disiloxane (IX)

IX was prepared by reaction of V (4.00 g, 28.0 mmol) with water (0.25 g, 14 mmol) in benzene (30 mL) catalyzed by tris-(triphenylphosphine) rhodium(I) chloride (10 mg). This reaction was similar to that used to prepare IV, except that the reaction was heated to 60°C for 24 h. IX was purified by fractional distillation through a 10 cm vacuum jacketed Vigreux column. A fraction b.p. 105–107°C/20 mmHg, 2.6 g, 60% yield was collected. It had the following spectral properties. ^{1}H NMR δ: 0.43 (s,12H), 7.20 (d of d,1H, $J = 3.4$ and 4.6 Hz), 7.35 (d of d,1H, $J = 0.8$ and 3.4 Hz), 7.61 (d of d,1H, $J = 0.8$ and 4.6 Hz). ^{13}C NMR δ: 0.89, 128.14, 131.01, 134.64, 138.28. ^{29}Si NMR δ: −5.02. GCMS m/e (rel. intensity): 301(0.97), 300(5.81), 299(6.80), 298(32.26) $M^{+\cdot}$, 286(1.09), 285(6.25), 284(7.57), 283(36.05) $M-15^+$, 203(0.60), 202(1.64), 201(12.18), 200(16.49), 199(100.0), 143(1.12), 142(1.48), 141(12.26), 134(9.73), 92(14.97), 84(13.45).

1,1,3,3-Tetramethyl-1-(2′-thienyl)disiloxane (X)

GC/MS m/e (rel. intensity) 218(4.42), 217(9.03), 216(30.80) $M^{+\cdot}$, 215(5.44) $M-1^+$, 204(2.63), 203(13.57), 202(25.50), 201(100.00) $M-15^+$, 200(3.17), 199(15.67), 187(2.15), 186(3.73), 185(15.90), 151(7.21), 150(8.80), 149(58.42), 143(4.19), 142(2.42), 141(16.50), 135(5.98), 134(4.48), 133(12.71), 132(33.38), 119(7.48), 118(4.71), 117(31.96).

Phenyl-2′-thienyldimethylsilane (XII)

XII was prepared by the reaction of phenyldimethylchlorosilane (Petrarch) with 2′-thienylmagnesium chloride as above. It was purified by fractional distillation b.p. 71–72°C/0.4 mmHg. A 96% yield was obtained. It had the following spectral properties. ^{1}H NMR δ: 0.63 (s,6H), 7.44(d of d,1H, $J = 3.4$ and 4.6 Hz), 7.54 (d of d,1H, $J = 0.6$ and 3.4 Hz), 7.615 (d of d,3H, $J = 2$ and 5 Hz), 7.82 (d of d,2H, $J = 3.8$ and 4.6 Hz). ^{13}C NMR δ: −1.22, 127.88, 128.15, 129.33, 131.07, 134.00, 135.31, 137.89, 138.00. ^{29}Si NMR δ: −11.28. IR ν: 3070, 3020, 2960, 2900, 1430, 1410, 1250, 1220, 1110, 990, 855, 835, 810, 780, 730, 705 cm^{-1}. UV λ_{max} 235.2 nm, $\epsilon = 24{,}140$. GCMS m/e (rel. intensity): 220(2.64), 219(5.17), 218(33.27) $M^{+\cdot}$, 206(1.38), 205(10.15), 204(18.28), 203(100.00) $M-15^+$, 141(10.51) $M-\mathrm{Ph}^+$, 135(7.90) $M-\text{thienyl}^+$, 115(7.69), 105(14.05), 77(10.09), 75(21.10). Elemental Analysis Found: C, 65.97; H, 6.53. $C_{12}H_{14}SSi$ calc: C, 66.06; H, 6.42%.

Photochemical reactions

All photochemical reactions were conducted in flame dried quartz tubes. In each case 0.1 mmol of I was photolyzed. Solutions of I in benzene/methanol were prepared and placed in the photolysis tubes. Argon gas was then bubbled through the solutions for 10 min. The tubes were then sealed with a rubber septum. They were placed next to a quartz photolysis well containing a 500 W Hanovia medium pressure mercury lamp which was immersed in a water bath maintained at 20 °C. It has been difficult to accurately determine the amount of II formed due to its volatility. The deuterium content of IV and V was determined by analysis of GCMS data. The deuterium content of IV was carried out by comparison of the ratios of the intensities of the $M^{+\cdot}$, $M+1^{+\cdot}$ and $M+2^{+\cdot}$ peaks observed to calculated values. Analysis of the deuterium content of V and X is complicated due to a significant $M-1^+$ peak found in the spectra of unlabeled V and X. For this reason, the analyses were done using the $M-15^+$ peak. This ion is formed by cleavage of a methyl group from silicon. There is only a small complicating $M-15-1^+$ ion associated with it [19].

Control photolysis experiments

Solutions were prepared, composed of 0.1 mol of III, IV, or V in benzene (3 ml)/methanol (0.8 mmol) as above. After photolysis for 10 h, these were analyzed by GC/MS. All of the starting materials III, IV, or V were recovered unreacted.

Photolysis experiment no. 1. I was dissolved in benzene (3 ml) and methanol (0.8 mmol) and was photolyzed for 2 h. Thirty percent of I was recovered. The following photoproducts were detected: II, III (11%), IV (47.7%) and V (44.2%).

Photolysis experiment no. 2. I was dissolved in benzene (3 ml) and methanol-d_3 (2 mmol) and was photolyzed for 3 h. Two percent of I was recovered. II-d_3, III (15%), IV-d_3 (36.9%), V (36.4%) and IX (9%) were detected.

Photolysis experiment no. 3. I was dissolved in benzene (3 ml) and methanol-d_4 (1 ml). The solution was photolyzed for 5 h. Nine percent of I was recovered.The following photoproducts were detected: II-d_4, III (20%), IV-d_3 (32.7%) and IV-d_4 (2.7%), V (7.7%) and V-d (21.7%), X (0.5%) and X-d (5.3%), and XII (1%).

Photolysis experiment no. 4. I was dissolved in benzene-d (1 ml) and methanol-d_4 (2 mmol). This solution was photolyzed for 5 h. No I was recovered. II-d_4, III (20%), IV-d_3 (20.8%) and IV-d_4 (1.2%), V (6.8%) and V-d (19.2%), VIII (8%), X (0.5%), X-d (7.5%).

Photolysis experiment no. 5. I was dissolved in benzene (3 ml). The solution was photolyzed for 2 h. Forty-four percent of I was recovered.The following photo-products were detected: III (58%), V (15.6%), VIII (1%), IX (4%), X (7%) and XII (5.5%).

Control experiment. I (0.1 mmol) was dissolved in benzene (3 ml) and methanol-d_3 (1 ml). This solution was kept in the dark for 14 h. Analysis of the solution demonstrated the complete recovery of I.

GCMS data for the parent ion cluster of 2-methoxydimethylsilylthiophene (IV)

Experiment	no. 1	no. 2	no. 3	no. 4
m/e	Rel. intensity			
178		0.25	0.69	0.50
177		2.26	4.22	3.26
176		3.77	9.60	6.88
175	0.28	27.27	44.07	35.87
174	2.51			
173	3.5			
172	29.33			

GCMS data for parent, $M-1^+$ and $M-15^+$ ion clusters for 2-dimethylsilylthiophene (V)

Experiment	no. 1	no. 2	no. 3	no. 4
m/e	Rel. intensity			
146			0.27	0.24
145	0.25	0.20	2.57	2.52
144	2.62	2.20	4.28	4.14
143	5.05	4.83	30.88	31.53
142	31.02	25.98	8.63	10.09
141	14.06	10.85	11.08	13.16
131			0.92	0.95
130	0.86	1.05	10.68	10.63
129	10.21	8.57	17.00	17.03
128	13.63	15.29	100.00	100.00
127	100.00	100.00	29.43	34.22
126	1.97	1.43	1.70	

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