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PYROLYSIS OF 1,1,2,2-TETRAMETHYL-1,2-DISILA-3,6-DITHIACYCLOHEXANE; EVIDENCE FOR DIMETHYLSILATHIONE [$(CH_3)_2Si{=}S$] INTERMEDIATES

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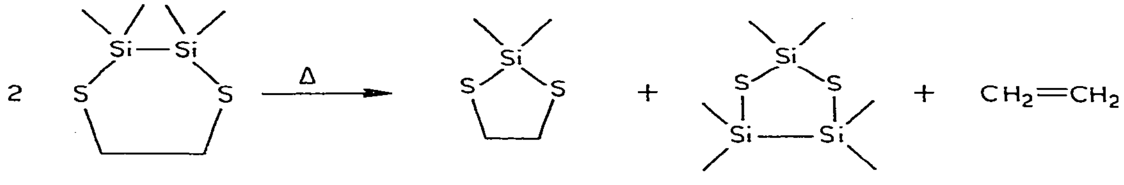
Summary

The pyrolysis of 1,1,2,2-tetramethyl-1,2-disila-3,6-dithiacyclohexane (I) yields 1,1-dimethyl-1-sila-2,5-dithiacyclopentane (II), 1,1,2,2,4,4-hexamethyl-1,2,4-trisila-3,5-dithiacyclopentane (III) and ethylene in equal amounts. While pyrolysis of a mixture of I and tetramethylcyclodisilthiane yields equal amounts of II, III, and no ethylene. Finally, pyrolysis of a mixture of I and hexamethylcyclotrisiloxane yields 1,1,3,3,5,5,7,7-octamethyl-2,4,6-trioxo-1,3,5,7-tetrasila-8-thiacyclooctane. Possible mechanisms to explain these results are presented. In addition, the first example of insertion of dimethylsilylene into a silicon—sulfur single bond is reported.

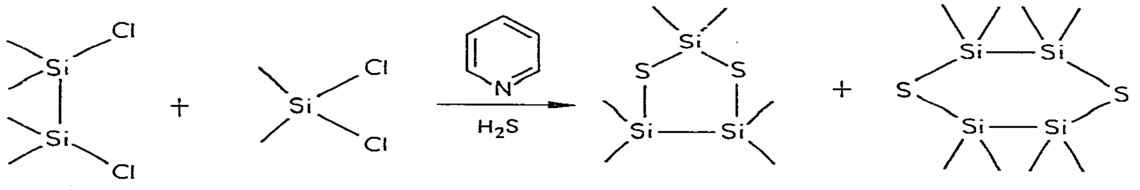
There has been considerable interest in the last ten years in reactions which involve intermediates which possess silicon—carbon [1—7], silicon—oxygen [1, 8—10], silicon—nitrogen [11,12], silicon—silicon [13—16] and silicon—sulfur [17,18] double bonds. Of these intermediates, those which possess silicon—sulfur double bonds have been the least studied. We should like to report our results on the pyrolysis of 1,1,2,2-tetramethyl-1,2-disila-3,6-dithiacyclohexane (I) which may be explained by reaction pathways which involve dimethylsilathione [$(CH_3)_2Si{=}S$] as a reactive intermediate.

The synthesis of I was achieved by reaction of 1,2-dichlorotetramethyldisilane with ethanedithiol in the presence of pyridine. Although I is a six-membered heterocycle, slow addition of both difunctional reagents to a vigorously stirred solution of pyridine was required to minimize polymer formation. Even so, the yield of I was low (35%). Heating a solution of I in t-butylbenzene at 215°C for several days ($t_{1/2} \simeq 1$ d) gave 1,1-dimethyl-1-sila-2,5-dithiacyclopentane (II) [19] (78%), 1,1,2,2,4,4-hexamethyl-1,2,4-trisila-3,5-dithiacyclopentane (III) (72%), and ethylene (88%). Yields are based on the stoichiometry of the reaction as written.

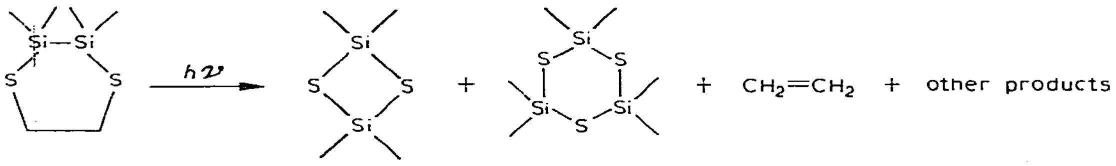


(I) (II) (III)

While II is a known compound, III is not. Its structure was determined by the usual spectral methods, elemental analysis, and by synthesis of an authentic sample by reaction of dimethyldichlorosilane, 1,2-dichlorotetramethyldisilane, and hydrogen sulfide in the presence of pyridine. In addition to III, 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrasila-3,6-dithiacyclohexane was formed in this reaction [20].

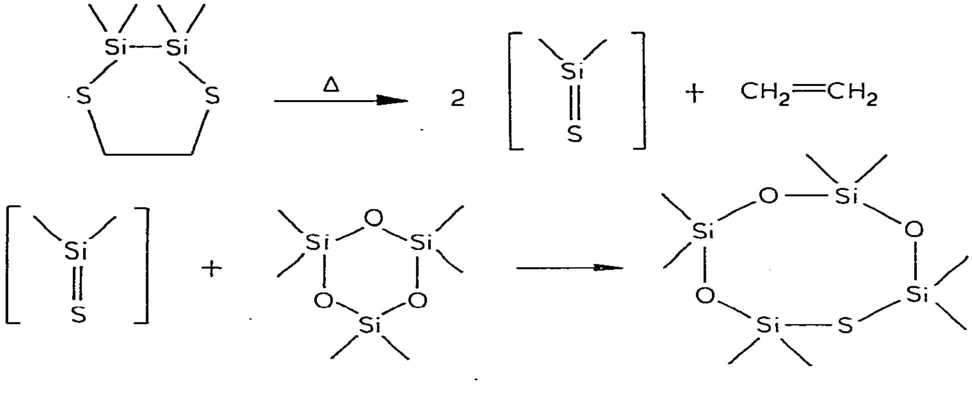


While our understanding of the photolysis of I is fragmentary at this time, our preliminary results nevertheless provided us with a clue as to the mechanism of the pyrolysis reaction. Thus photolysis (2537 Å) of a degassed solution of I in cyclohexane yields tetramethylcyclodisilthiane (IV) [21,22] (26%), hexamethylcyclotrisilthiane (V) [22] (13%), ethylene (40%), and a number of other products. We were intrigued with the possibility that IV, V, and ethylene might result from an initial $[\pi 2s, \pi 2s, \pi 2s]$ cyclo-reversion [23,24] reaction of I to yield ethylene and two dimethylsilathione intermediates which dimerize in a head to tail manner to yield IV or trimerize to yield V.



(IV) (V)

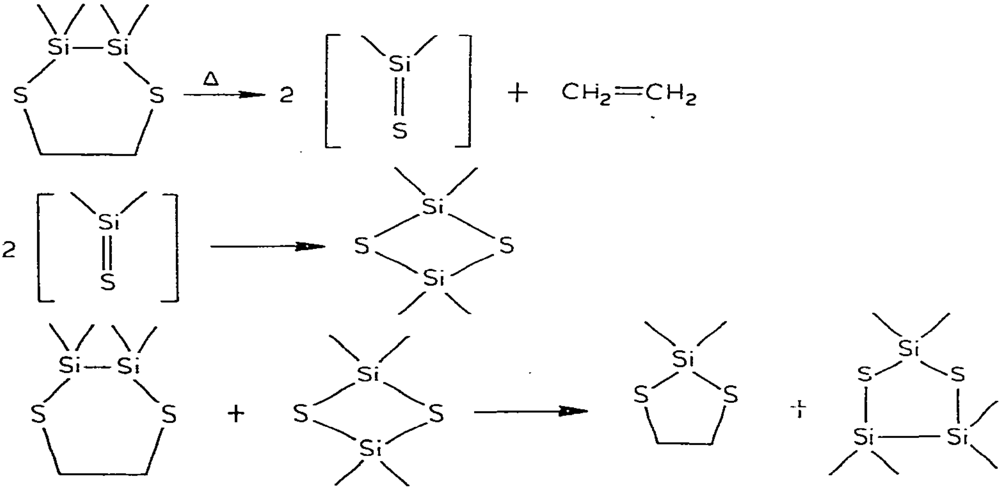
If the mechanism of the pyrolysis reaction of I is related to the photochemical reaction of I, then the first step might yield ethylene and two dimethylsilathione intermediates. To test this possibility, a solution of I and hexamethylcyclotrisiloxane (VI) was heated at 215°C for several days. Hexamethylcyclotrisiloxane has been used to trap intermediates possessing silicon—carbon [9, 25], silicon—oxygen [9,26], silicon—nitrogen [11], and even silicon—sulfur double bonds [17,18]. 1,1,3,3,5,5,7,7-Octamethyl-2,4,6-trioxo-1,3,5,7-tetrasila-8-thiacyclooctane (VII) [18] the expected product of insertion of a dimethylsilathione intermediate into a silicon—oxygen single bond of VI, was produced in 24% yield, along with II (32%), III (26%), and ethylene.



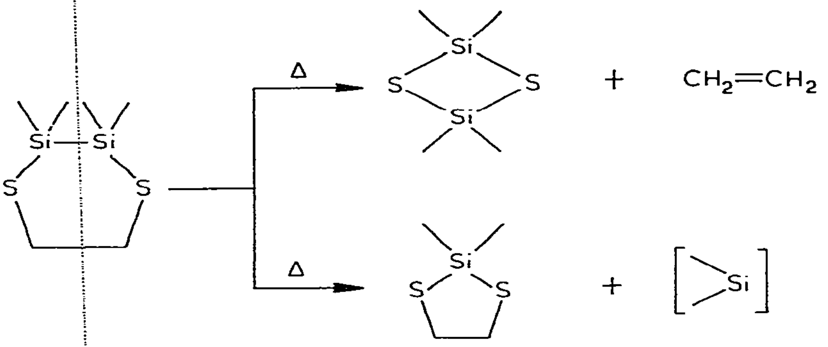
(VI) (VII)

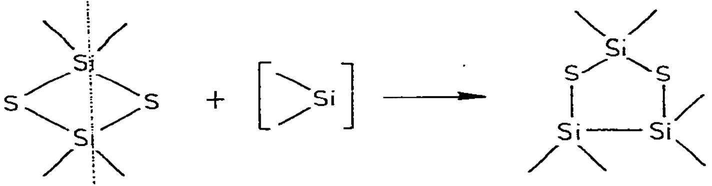
The observation that IV, the expected product of dimerization of two dimethylsilatione intermediates reacts rapidly at 215°C ($t_{1/2} \approx 15$ min) with I to yield almost equal amounts of II, III and a small amount of V provides additional support for this proposal. The formation of a small amount of V in this reaction is expected since IV and V are known to be in rapid thermal equilibrium [27,28].

Thus we believe that the pyrolysis of I to yield II, III, and ethylene in approximately equal amounts occurs by a three step mechanism. The first step involves a $[\pi 2s, \pi 2s, \pi 2s]$ cyclo-reversion reaction of I to yield ethylene and two dimethylsilathione intermediates. This step is apparently slow. In the presence of VI these dimethylsilathione intermediates can partially be trapped to yield VII. In the absence of VI, the second step is head to tail dimerization of the dimethylsilathione intermediates to yield IV. The third step involves a rapid redistribution between I and IV to yield II and III. Control experiments have demonstrated the stability of both II and III to the long and strenuous thermal reaction conditions.



The mechanism of the rapid thermal redistribution reaction between I and IV is not known at present. One possibility involves an α elimination of dimethylsilylene from I to yield II. Rapid insertion of dimethylsilylene into a strained silicon—sulfur single bond of IV would yield III. This seems improbable since the pyrolysis of I would have to occur by two different pathways at approximately equal rates since the yield of II and III are equal.





Further, pyrolysis of I in the presence of *p*-tolyldimethylsilane (VIII) [29], in place of t-butylbenzene as solvent, yields no 1,1,2,2-tetramethyl-*p*-tolyldisilane [30,31], the expected product of insertion of dimethylsilylene into the silicon—hydrogen bond of VIII. These two pieces of evidence cast serious doubt on the intermediacy of a free dimethylsilylene in the thermal redistribution reaction.

However, this possiblity can not be excluded for when dimethylsilylene was generated by photolysis (2537 Å) of a solution of dodecamethylcyclohexasilane [32,33] in the presence of IV, a 26% yield of III was obtained. This is the first example of insertion of a silylene into a silicon—sulfur single bond.

The mechanism of this redistribution reaction as well as the scope of silylene insertion into sulfur—silicon single bonds are under active study.

Experimental

IR spectra were determined as neat liquids on a Perkin—Elmer 281. They were calibrated against known peaks in a polystyrene film. UV spectra were determined in cyclohexane solution on a Beckman Acta M spectrometer. NMR spectra were recorded on a Varian T-60 or XL-100 spectrometer. Spectra were taken using 10% solutions in $CDCl_3$. Samples of all compounds for spectral and elemental analysis were purified by preparative vapor phase chromatography on a Hewlett—Packard F&M 700. Yields of various products were determined by

GLPC. Mass spectra were determined on a DuPont 21-492 at 70 eV. Microanalysis was performed by the California Institute of Technology Microanalytical Laboratory, Pasadena, California, or by Elek Microanalytical Laboratories, Torrance, California.

Preparation of 1,1,2,2,-tetramethyl-1,2-disila-3,6-dithiacyclohexane (I). Into a dry, 500 ml three-necked flask fitted with two pressure equalizing addition funnels and a mechanical stirrer were placed 40 ml of pyridine (freshly distilled from KOH) and either 200 ml of benzene (freshly distilled from sodium) or 200 ml of dichloromethane. 1,2-Dichlorotetramethyldisilane [34] (18.6 g, 0.1 mol) in CH_2Cl_2 was placed in one addition funnel and ethanedithiol (10.3 g, 0.11 mol) in CH_2Cl_2 was placed in the other addition funnel. These solutions were added dropwise at equal rates over 1 h to the vigorously stirred mixture. After addition was complete, the reaction was stirred for 5 h.

Pyridinium hydrochloride was removed by filtration under nitrogen. The solvent and excess pyridine was removed by distillation through a 25 cm Vigreux column at atmospheric pressure. Fractional distillation using the same column gave a fraction (b.p. 68°C/0.1 mmHg, m.p. 23—24°C) found to be I (7.3 g, 35 mmol, 35%). A polymeric residue of 10 g did not distill.

Properties of I: NMR: δ(ppm) 0.43 (s, 12 H), 2.92 (s, 4 H). IR: ν(Si—Me) 1250 cm^{-1}. UV: λ_{max} 2527, ϵ 1370. Mass spectrum: parent *m/e* 208 (8%), (*P* — 15) *m/e* 193 (4%), *m/e* 90 (66%), *m/e* 73 (100%). An analytical sample was purified by preparative GLPC on a 18" × 1/4" 20% SE-30 on Chromosorb P column at 80°C. Anal. Found: C, 34.46; H, 7.74. $C_6H_{16}Si_2S_2$ calcd.: C, 34.56; H, 7.74%.

Preparation of 1,1,2,2,4,4-hexamethyl-1,2,4-trisila-3,5-dithiacyclopentane (III). A 200 ml two-necked flask was fitted with a gas inlet and a reflux condenser on top of which was a N_2 inlet. 1,2-Dichlorotetramethyldisilane (6.6 g, 35 mmol), dimethyldichlorosilane (5.0 g, 38 mmol), pyridine (10.9 g, 0.14 mol), and benzene (100 ml) were placed in this flask. Hydrogen sulfide was passed into the magnetically stirred solution for 2 h. The solution was stirred overnight, filtered, and the solvent removed by distillation at atmospheric pressure. The residue was fractionally distilled under reduced pressure to give III (2.5 g, 11 mmol, 30%), b.p. 117°C/19 mmHg, and a solid residue which was sublimed under reduced pressure (70°C/0.1 mmHg). It was found to be identical with an authentic sample of 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrasila-3,6-dithiacyclohexane (2.7 g, 9 mmol, 52%) [20].

Properties of III: b.p. 117°C/19 mmHg. NMR δ (ppm) 0.46 (s, 12 H), 0.61 (s, 6 H). IR: ν(Si—Me) 1245 and 1255 cm^{-1}. UV: λ 2273 (sh), ϵ 2175. Mass spectrum: parent *m/e* 238 (8%), Found: 238.015 $C_6H_{18}Si_3S_2$ calcd.: 238.016. (*P* — 15) *m/e* 223 (10%), *m/e* 90 (60%), *m/e* 73 (100%). An analytical sample was purified by preparative GLPC using a 54" × 1/4" 20% SE-30 on Chromosorb P column at 200°C. Anal. Found: C, 29.88; H, 7.23. $C_6H_{18}Si_3S_2$ calcd.: C, 30.20; H, 7.60%.

Solution pyrolysis of I. t-Butylbenzene (freshly distilled from sodium, 236 mg) and I (69 mg, 0.33 mmol) were placed in a NMR tube. The solution was degassed by several freeze-thaw cycles at the vacuum pump. The tube was sealed and heated at 215°C. The reaction was followed periodically by NMR. The methylene protons of I absorbed at δ 2.92 ppm while those in II absorbed at δ 3.08 ppm. Another peak, a singlet at δ 5.5 ppm also increased as the reaction progressed. A solution of ethylene in t-butylbenzene was found to have an identical chemical shift. After 5 d, the reaction was found to be about 70% complete (by NMR). The tube was connected to a flask containing a solution of bromine in CCl_4. The tube was opened and warmed to expel the ethylene into the bromine/CCl_4 solution. The excess bromine was destroyed with a $Na_2S_2O_7$ solution. The organic layer was separated and dried. The presence of 1,2-dibromoethane was confirmed by GLPC (15' × 0.25" 10% DCQF-1 on Chromosorb P column at 130°C) and NMR (by comparison with an authentic sample).

The remaining solution in the pyrolysis tube was analysed by GLPC on a 6' × 0.25" 10% DCQF-1 on Chromosorb W column at 115°C to give II (13 mg, 0.086 mmol, 72%) and III (21 mg, 0.088 mmol, 78%) whose properties were identical to those of authentic samples. The amount of ethylene (NMR) was calculated to be 2.8 mg, 0.10 mmol, 88%. All yields are corrected for recovered I (21 mg, 0.099 mmol, 30%).

Copyrolysis of I and IV. t-Butylbenzene (384 mg), I (53 mg, 0.256 mmol), and IV [21] (51 mg, 0.283 mmol) were placed in a NMR tube which was sealed and heated at 215°C as before. In 15 min, about 46% of I had disappeared and an equivalent amount of II had been formed; this was determined by NMR as above. Heating was continued for 6 h. The tube was connected to a bromine in CCl_4 trap and opened. The reaction mixture was analyzed as before to give III (34 mg, 0.145 mmol, 72%) and II (26 mg, 0.176 mmol, 87%) corrected for recovered I (11 mg, 0.054 mmol, 21%). In addition, hexamethylcyclotrisilthiane (14 mg, 0.051 mmol, 27% based on the amount of IV used) was also found. This yield is calculated based on the following equilibrium: $3[(CH_3)_2SiS]_2 \rightleftharpoons 2[(CH_3)_2SiS]_3$. The NMR of the mixture showed no significant formation of ethylene. Analysis of the bromine trap by GLPC and NMR confirmed that less than 2% 1,2-dibromoethane had been formed.

In a second experiment, I (24 mg, 0.113 mmol) and IV (39 mg, 0.218 mmol) in t-butylbenzene (292 mg) were heated as above for 180 min. This gave III (18 mg, 0.074 mmol, 80%), II (12 mg, 0.081 mmol, 85%), corrected for recovered I (4 mg, 0.019 mmol, 17%). In addition, hexamethylcyclotrisilthiane (15 mg, 0.055 mmol, 38%) was found.

Solution photolysis of I. A solution of I (52 mg, 0.25 mmol) in spectral grade cyclohexane (390 mg) was placed in a quartz NMR tube. Oxygen was removed by bubbling purified N_2 through this solution for 15 min prior to photolysis. This NMR tube was placed in a quartz water jacket to maintain constant temperature of 25°C. This tube was photolyzed at the center of a circular array of sixteen 12" G.E. germicidal low pressure mercury lamps at 2537 Å for 5 h. The solution was analyzed as before to give IV (9 mg, 0.05 mmol, 26%), V (4 mg, 0.02 mmol, 13%), and ethylene (2 mg, 0.08 mmol, 40%). All yields are corrected for recovered I (10 mg, 0.05 mol, 20%).

Photolysis of dodecamethylcyclohexasilane [32,33] in the presence of IV. A solution of dodecamethylcyclohexasilane (56 mg, 0.16 mmol), IV (65 mg, 0.37 mmol) in spectral grade cyclohexane (555 mg) was degassed, photolyzed for 9 h, and analyzed as before to give III (21 mg, 0.09 mmol, 26%) based on recovered IV (6 mg, 0.03 mmol, 9%).

Solution pyrolysis of II. t-Butylbenzene (335 mg) and II (75 mg, 0.50 mmol) were placed as before in a sealed NMR tube and heated at 215° C for 60 h. NMR indicated no change of starting mixture. This was confirmed by GLPC analysis as before which indicated only recovered II (74 mg, 0.49 mmol, 99%).

Solution pyrolysis of III. t-Butylbenzene (335 mg) and III (119 mg, 0.50 mmol) were placed in a sealed NMR tube and heated at 215° C for 60 h as before. NMR indicated no change of starting mixture. This was confirmed by GLPC analysis as before which gave recovered III (117 mg, 0.49 mmol, 98%).

Copyrolysis of I and VI. I (104 mg, 0.5 mmol) and VI [35] (1.11 g, 5.0 mmol) were heated as before at 215° C for 6 d. The reaction mixture was analyzed by GLPC on a 8' × 0.25" 10% DCQF-1 on Chromosorb W column at 80—130° C to give II (12 mg, 0.08 mmol, 32%), VII (74 mg, 0.24 mmol, 24%) [18], and III (15 mg, 0.065 mmol, 26%). The presence of ethylene was determined by NMR δ 5.5 (s) ppm.

Pyrolysis of I in the presence of VIII [29]. A solution of I (520 mg, 2.5 mmol) in VIII (860 mg) was heated as before in a sealed NMR tube at 215° C for 3 d. The mixure was analyzed by GLPC to give II (127 mg, 0.85 mmol, 72%) and III (168 mg, 0.71 mmol, 60%). Yields are corrected for recovered I (30 mg, 0.14 mmol, 6%) and VIII (830 mg).

No 1,1,2,2-tetramethyl-*p*-tolyldisilane [30,31] was detected.

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