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REACTIONS OF SILIRANES WITH ELEMENTAL SULFUR AND WITH t-BUTYL MERCAPTAN. PREPARATION OF THE 2,3-DITHIA-1-SILACYCLOPENTANE RING SYSTEM

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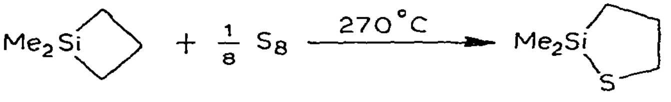
Summary

The reaction of 1,1-dimethyl-*trans*-2,3-bis(2′,2′-dimethylcyclopropylidene)-1-silirane with S_8 gives a mixture of four isomeric products derived from incorporation of one sulfur atom and a cyclopropylcarbinyl-to-butenyl type rearrangement. This silirane reacts with t-butyl mercaptan to give a product of mercaptan addition in which a cyclopropylcarbinyl-to-butenyl rearrangement also has occurred. Hexamethylsilirane reacts with S_8 to give 1,1,4,4,5,5-hexamethyl-2,3-dithia-1-silacyclopentane in high yield. These reactions are discussed in terms of free radical mechanisms.

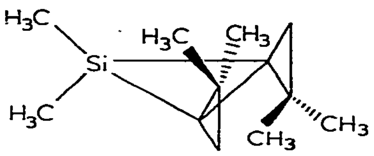
Introduction

Siliranes (silacyclopropanes) are extremely reactive compounds, much more so than the members of the next larger SiC_n ring system, the silacyclobutanes [1]. Among the rare insertion reactions which have been reported for the silacyclobutane system is the ring expansion which occurs when 1,1-dimethyl-1-silacyclobutane and elemental sulfur are heated at 270° C in a sealed tube (eq. 1) [2]. In view of the higher reactivity of the siliranes, it was of interest to see if such insertion also would occur on reaction of sulfur with siliranes, and, if so, under what conditions.

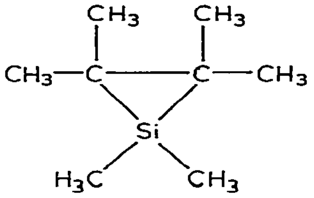


(1)

We have examined the reaction of elemental sulfur with siliranes I [3] and II [4]. Of these, II is considerably more reactive. Of special interest are the

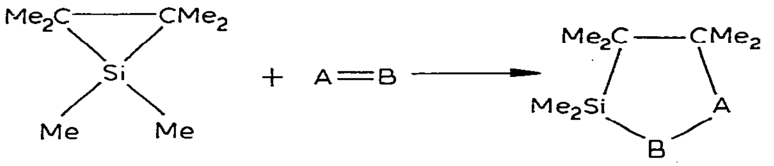


(I)



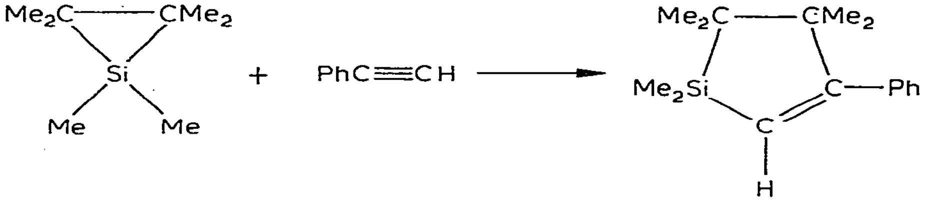
(II)

facile two-atom insertions (eq. 2 and 3) which II was found to undergo [5,6]. Available evidence suggests that these are radical processes [6].



(2)

$(A{=}B \;=\; R_2C{=}O,\ ArCH{=}NR,\ ArC(R){=}CH_2,\ CH_2{=}CR{-}CR'{=}CH_2)$



(3)

Results and discussion

When 1,1-dimethyl-*trans*-2,3-(2′,2′-dimethylcyclopropylidene)-1-silirane, I, was added to an excess of sulfur in tetrahydrofuran (THF) at room temperature under nitrogen, a slightly exothermic reaction ensued. Upon completion of the reaction (3 h at room temperature), the excess sulfur was filtered and the filtrate was distilled. A liquid product was obtained in 70% yield. Its analysis by gas chromatography (GLC) showed the presence of two major components which could be separated from one another. The combustion analysis and mass spectrum of each corresponded to $C_{12}H_{22}SSi$, i.e., to the product of insertion of one sulfur atom into I, and our initial hypothesis was that we were dealing with two isomeric products, III and IV *.

Further studies showed that actually four products are formed in the reaction of I with elemental sulfur. In addition to the two GLC peaks corresponding to the major products, which were isolated as pure compounds, there was another smaller peak in the gas chromatogram. Originally thought to be due to

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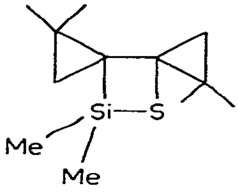
* The products of the I/S_8 reaction were reported as III and IV in our 1975 review of the silirane chemistry developed at M.I.T. [7]. In view of the subsequent studies described in this paper, this claim was premature and must be withdrawn as erroneous. Also incorrect was the structure assigned to the product of the reaction of I with t-butyl mercaptan which is discussed below.

an impurity, it was collected and its NMR spectrum indicated that it consisted



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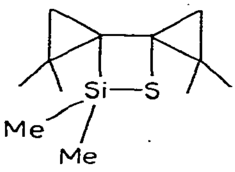
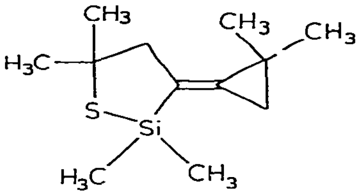


(IV)

of two components. Infrared and ^{1}H and ^{13}C NMR studies showed the four products to be V, VI, VII and VIII in 18/9/3/1 ratio.



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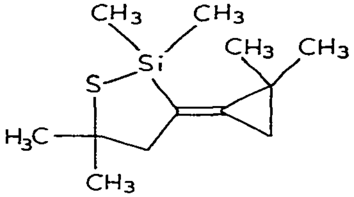

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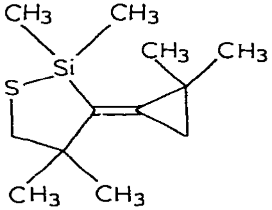

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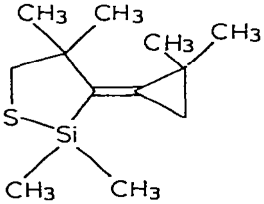
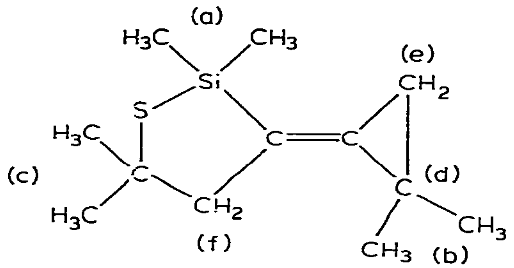


(VIII)

The spectra of all four compounds were almost identical. The methylenecyclopropane C=C IR stretch [8] at 1740 cm^{-1} was observed in the IR spectrum of each of the separately collected GLC peaks. With the ^{1}H NMR information that four products were present and that all were structurally similar, and, knowing that the methylenecyclopropane unit was present in each, the structural assignments were made in the following manner. The most abundant product, V, was collected (GLC) and examined by ^{13}C NMR spectroscopy. The decoupled spectrum showed three methyl singlets (quartets in the off-resonance proton-decoupled spectrum), two methylene singlets (triplets in the off-resonance proton-decoupled spectrum) and two singlets which did not change in the off-resonance, proton-decoupled spectrum. The olefinic region of the spectrum was not scanned. The $\text{Si—}\underline{\text{C}}\text{H}_3$ resonance (a; δ_C 2.53) and the $\text{C—}\underline{\text{C}}\text{H}_3$ resonances (b, c; δ_C 24.86 and 33.39) were easily assigned. The closely spaced peaks at δ_C 17.87 and 18.07 (singlet and triplet, respectively, in the off-resonance proton-decoupled spectrum) were assigned to the cyclopropane carbon



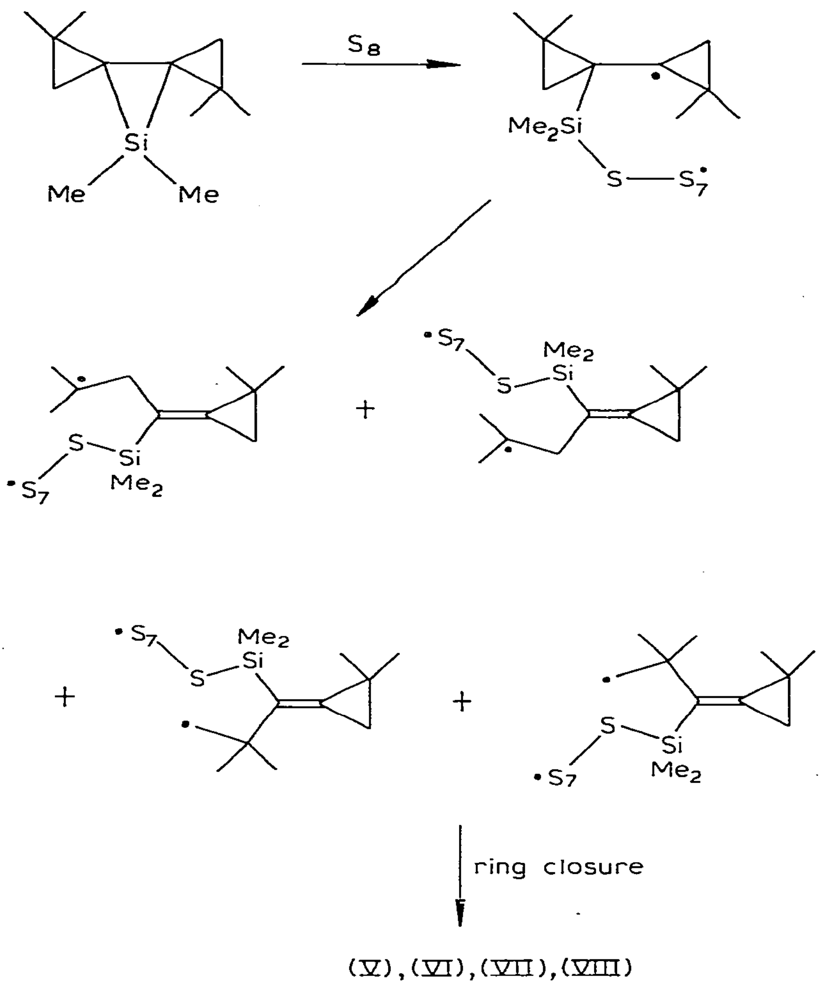
atoms d and e. The low field triplet (f; δ_C 53.56) was assigned to the allylic methylene carbon atom. The low field singlet (g; δ_C 54.05) was assigned to the quaternary carbon atom bonded to the sulfur atom. The presence of the allylic methylene group and the low field quaternary carbon atom rules out structures III and IV. Structure V rather than VI was assigned to the major product on the grounds that the less hindered isomer, V, should be the more abundant one. Compound VI was assigned the structure shown because it and V showed singlets in the ^{1}H NMR spectrum at δ 2.67 ppm attributable to the allylic methylene group. Compounds VII and VIII could not be separated by GLC, but a ^{1}H NMR spectrum of a mixture of these compounds showed two resonances at δ 2.80 and 2.82 ppm attributable to methylene groups bonded to sulfur. Integration of these resonances established that the two components of this GLC peak were present in 3/1 ratio. The assignment of these as VII and VIII, respectively, rather than VIII and VII, is less certain.

The formation of products V—VIII can be explained if a radical mechanism is invoked for the I/S_8 reaction, for compounds V—VIII are products of a cyclopropylcarbinyl rearrangement. This process, in which a cyclopropylcarbinyl radical rearranges to the more stable butenyl radical, is well known in free radical chemistry [9]. Scheme 1 shows the formation of these products. The stabilities of the rearranged radicals are presumed to decrease from the least hindered tertiary radical to the most hindered primary radical. This is also the order of the product distribution.

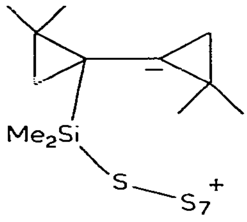
Such a radical mechanism seems appealing in view of the known two-atom insertions into hexamethylsilirane, which seem to be radical processes [6]. As a recent review [10] states, reactions of elemental sulfur can involve a variety of as yet poorly defined neutral or charged sulfur species which formally can react as diradicals, radical cations or ionic dipoles, so a radical process of the type suggested certainly is possible. The formally related reactions of silacyclobutanes [11] with S_8, which take place at 250—270°C and give monosulfur insertion products, 1-sila-2-thiacyclopentanes and 1-germa-2-thiacyclopentanes, respectively, have been discussed [2,11,12] in terms of a "nucleophilic degradation mechanism". In this proposed process an incipient carbanion derived from the sila- or gemacyclobutane is the nucleophile which attacks a ring-opened, bipolar sulfur molecule. However, these reactions, which require rather drastic conditions, are not necessarily mechanistically related to the I/S_8 reaction.

The cyclopropylcarbinyl-to-3-butenyl rearrangement is also observed in the organolithium and organomagnesium series [13,14]. The occurrence of such a carbanion mechanism in our reaction would require nucleophilic attack by the S_8 species at silicon with resulting Si—C bond heterolysis to generate a cyclo-

SCHEME 1

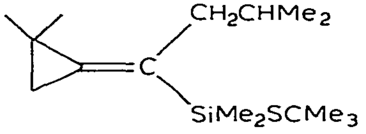


propylcarbinyl carbanion, IX. Rearrangement of the latter then could give the observed products. Such a reaction course seems less likely but cannot be dismissed out of hand.

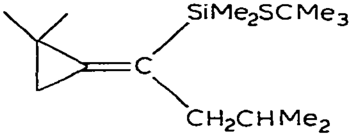


(IX)

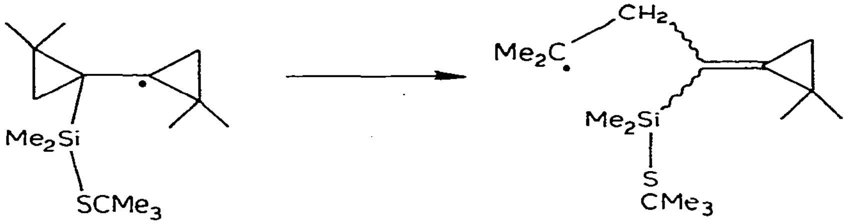
Indirect support to the suggested radical mechanism for the I/S_8 reaction is given by the finding that t-butyl mercaptan, a member of a class of compounds which are prone to free radical processes [15], also reacts with the dispiro-silirane I to give products in which one of the cyclopropane rings has been opened. When these reactants were heated in tetrahydrofuran solution at reflux for 4.5 h, two products were formed in 4/1 ratio. These were collected and identified by means of their IR and ^{1}H NMR spectra as X and XI. Both showed ν(C=C) at 1720 cm^{-1}. In the reaction between I and t-butyl mercaptan the radical XII very likely is the initially formed intermediate. This species, a cyclopropylcarbinyl radical, then rearranges to the more stable *cis/trans* butenyl radical pair, XIII. Hydrogen atom abstraction from Me_3CSH then gives X and XI. The free radical addition of mercaptans to olefins requires an initiator such as a peroxide [15]. In the present reaction, the facility with which silirane I undergoes autoxidation to give peroxidic products [1] should guarantee that trace amounts of such peroxides will be present to initiate a free radical chain process.



(X)

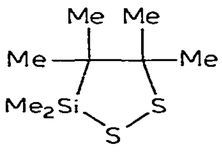


(XI)



(XII) (XIII)

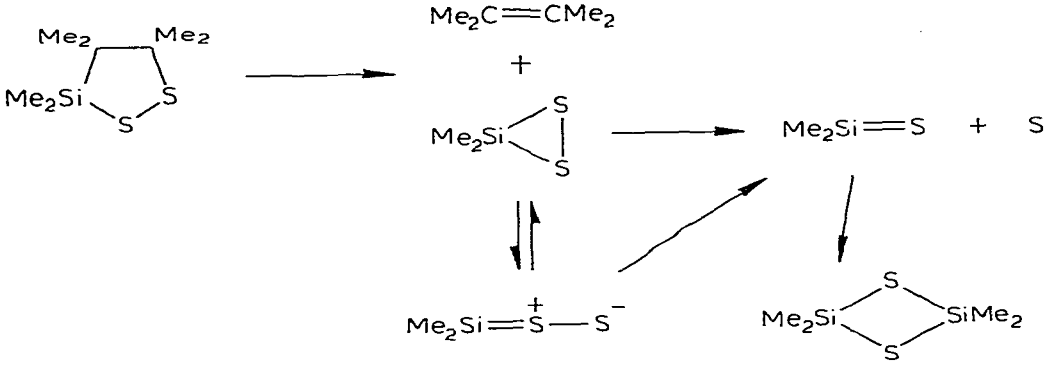
The reaction of hexamethylsilirane with S_8 in tetrahydrofuran proceeded at room temperature and was mildly exothermic. A single product was formed which could be isolated by GLC as a volatile yellow solid, m.p. 90—91°C. It was identified as 1,1,4,4,5,5-hexamethyl-2,3-dithia-1-silacyclopentane, XIV, on the basis of its analysis, mass spectrum and proton NMR spectrum. The mass spectrum of XIV showed a large fragment ion at *m/e* 122 which was attributable to $[Me_2SiS_2]^+$ and the molecular ion at *m/e* 206. This product is very readily decomposed on attempted analysis or isolation by gas chromatography. If great care is not taken, then tetramethylene is the only volatile product observed. However, when the GLC column has been conditioned by repeated



(XIV)

injection of aliquots of the reaction mixture, analysis and collection of XIV is possible. Even then, the GLC yield (38%) is considerably less than the yield of XIV determined in the reaction mixture by NMR spectroscopy using an internal standard (97%). Without doubt, the GLC instability of XIV is based on its reaction with OH functionality on the solid support.

In the absence of hydroxyl functionality, XIV was found to be remarkably stable. An experiment in which a sample of XIV was heated in $CCl_4/CHCl_3$ solution in an evacuated, sealed NMR tube showed its half-life at 130°C to be 11 h. It appeared to be completely stable at 80°C. The products of its decomposition were found to be tetramethylethylene and tetramethylcyclodisilthian, XV. A plausible decomposition mechanism is shown in eq. 4. The stability of XIV is striking when compared to that of its carbon analogs. The unsubstituted 1,2-dithiolane has been found to be a non-isolable, extremely photosensitive oil which polymerized rapidly at room temperature [16]. Increasing methyl substitution (3,3-dimethyl- and 3,3,5,5-tetramethyl-1,2-dithiolane) has been found to stabilize the dithiolane structure, such compounds being isolable as yellow oils which polymerize on standing [16a]. The instability of this ring system was postulated to result from ring strain, which was predicted to be between 16 and 30 kcal/mol [17]. In the 2,3-dithia-1-silacyclopentane (or 3-sila-1,2-dithiolane) system such ring strain would be lessened somewhat as a result of the longer Si—C and Si—S bonds in the ring. Also, a stabilizing donation of some electron density from lone pairs on sulfur to vacant *d* orbitals on silicon may be discussed.



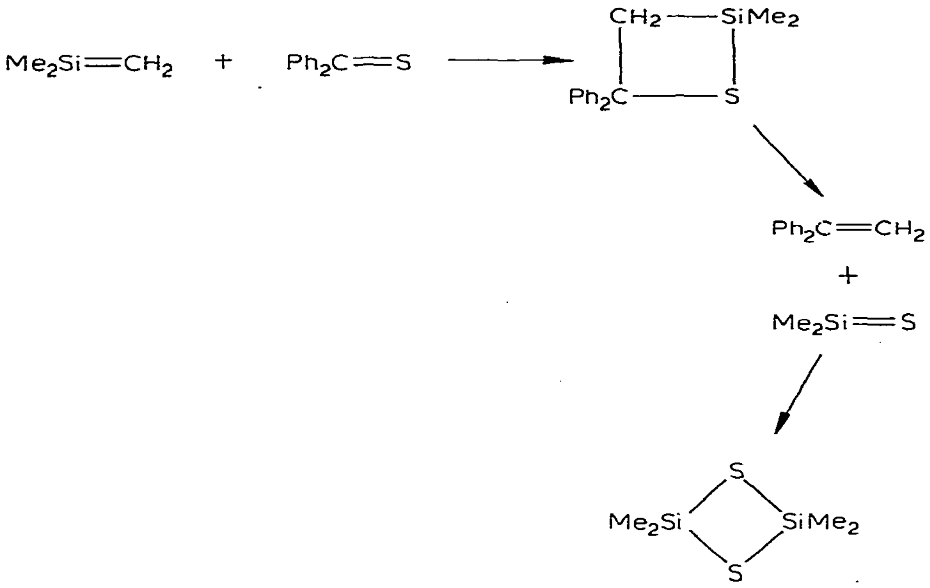
(4)

(XV)

The decomposition process shown in eq. 4 is, of course, only speculation. The SiS_2 ring system is not a known one, but it would be expected to be quite labile. The $Me_2Si{=}S$ intermediate is, as reported by Sommer and McLick [18], a transient species in the reaction of $Me_2Si{=}CH_2$, generated by pyrolysis of 1,1-dimethyl-1-silacyclobutane at 611°C, and thiobenzophenone (eq. 5).

The reaction of hexamethylsilirane with the S_8 molecule may also be discussed in terms of a radical mechanism, but a polar process is by no means excluded.

The reaction of hexamethylsilirane with t-butyl mercaptan in THF solution at room temperature gave $Me_2(Me_2CHCMe_2)SiSCMe_3$ in 72% yield [19]. This product gives no indication of the mechanism of the reaction since it is the one



(5)

(isolated in 15% yield)

which would be expected in either a polar or a radical chain process. The fact that hexamethylsilirane is unreactive toward t-butanol but reacts readily with t-butyl mercaptan suggests that the latter has access to a different mechanism, i.e., that in contrast to the polar mechanism by which alcohols must react, the mercaptan can react by a free radical mechanism.

Experimental

General comments

The siliranes were prepared as described previously [3,4]. All reactions and manipulations involving these siliranes were carried out under argon in glassware which had been flame-dried and allowed to cool in an atmosphere of dry argon. Silirane transfers were made by syringe or cannula. Hexamethylsilirane was stored, transferred, and in some cases, brought into reaction as an approximately 0.35 *M* solution in THF. For those reactions which employed a different solvent, the THF was removed by trap-to-trap distillation (65—70 mm, 25° C, into a receiver which was cooled with liquid nitrogen).

Infrared spectra were measured using a Perkin—Elmer 456A grating infrared spectrophotometer, proton NMR spectra using Varian T-60 or Perkin—Elmer R-20 or R-22 spectrometers. Chemical shifts are reported in ppm downfield from internal tetramethylsilane. ^{13}C NMR spectra were obtained using a Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 computer or a Jeol FNM HFX-60Q spectrometer. Mass spectra were obtained using a Hitachi—Perkin—Elmer RMU-6 mass spectrometer or a Varian MAT-44, both operating at 70 eV.

Reaction of silirane I with elemental sulfur

A mixture of 1.67 g (8.5 mmol) of the silirane and 1.0 g (31 mmol) of elemental sulfur in 15 ml of dry THF was prepared in a 50 ml three-necked, round-bottomed flask, which was equipped with a reflux condenser, a thermometer extending in the reaction mixture, a rubber septum and an argon inlet tube. A small initial exotherm was noted. The mixture was stirred for 3 h at room temperature, then was filtered and concentrated at reduced pressure. The residue was distilled at 48°C(0.01 mmHg) to give 1.31 g (70%) of liquid product. Examination by GLC (20% UC-W98 silicone on Chromosorb W at 160°C) showed the presence of two major components in 1/2 ratio, as well as of some minor products. Component 1 showed the molecular ion, $M^+ = 226$, in its mass spectrum. (Found: C, 64.03; H, 10.27; S, 13.70. $C_{12}H_{22}SSi$ calcd.: C, 63.63; H, 9.79; S, 14.16%.) Component 2 also showed $M^+ = 226$ in its mass spectrum. (Found: C, 63.84; H, 10.00; S, 13.93%.)

This reaction was reperated on the same scale using the same procedure except for a 15 h reaction time. After filtration of unconverted sulfur, trap-to-trap distillation of the filtrate gave 1.463 g of a yellow solution. GLC analysis (20% General Electric Co. SE-30 silicone rubber gum on Chromosorb W, at 154°C) showed three product peaks in 18/9/4 ratio. Structural assignments were made on the basis of the following information.

Compound V. n_D^{25} 1.4986. IR (cm^{-1}, thin film): 3030w, 2960vs, 2920s, 2880(sh), 2870s, 2820m, 2710w, 1740m, 1457m, 1445(sh), 1400m, 1380m, 1368(sh), 1365s, 1295m, 1275w, 1247vs, 1235(sh), 1200m, 1150m, 1120m, 1090m, 1027m, 970m, 935m, 920m, 855vs, 838vs, 825vs, 795vs, 780vs, 690s. ^1H NMR (C_6D_6, C_6D_5H): δ 0.52 (s, 6H, Si—CH_3), 0.82 (s, 2H, cyclopropyl H), 1.15 (s, 6H, cyclopropyl CH_3), 1.55 (s, 6H, S—C—CH_3) and 2.67 ppm (s, 6H, S—C—CH_2). ^{13}C (proton-decoupled; C_6D_6/C_6D_5H): δ_C 2.53 (s, Si—CH_3), 17.87 (s, cyclopropyl $\underline{C}$—CH_3), 18.07 (s, cyclopropyl CH_2), 24.86 (s, cyclopropyl C—$\underline{C}H_3$), 33.39 (s, S—C—$\underline{C}H_3$), 53.56 (s, S—C—$\underline{C}H_2$) and 54.05 ppm (s, S—C). In the off-resonance proton-decoupled spectrum, the resonances at 18.07 and 53.56 ppm became triplets, those at 2.53, 24.86 and 33.39 ppm became quartets and those at 17.87 and 54.05 ppm remained singlets. GLC yield: 45%.

Compound VI. n_D^{25} 1.4998. IR (cm^{-1}, neat film): 3030w, 2960vs, 2930s, 2870(sh), 2820w, 2720w, 1740w, 1455(sh), 1450m, 1420(sh), 1400m, 1380m, 1370(sh), 1365m, 1290m, 1245s, 1235(sh), 1200m, 1150m, 1120m, 1085m, 1045m, 1010m, 970m, 940m, 900m, 850vs, 835s, 820vs, 780vs, 720m and 690s. ^1H NMR (C_6D_6/C_6D_5H): δ 0.51 (s, 6H, Si—CH_3), 0.97 (s, 2H, cyclopropyl H), 1.17 (s, 6H, cyclopropyl CH_3), 1.56 (s, 6H, S—C—CH_3) and 2.66 ppm (s, 2H, S—C—CH_2). GLC yield: 22%.

The third peak was found upon examination by proton NMR spectroscopy to consist of two components, VII and VIII. The following information was obtained *on the mixture*: n_D^{25} 1.4995. IR (cm^{-1}, thin film): 3020w, 2980vs, 2920s, 2890(sh), 2870m, 2720vw, 1725w, 1460m, 1450m, 1415m, 1400m, 1375m, 1370m, 1358m, 1280m, 1247vs, 1200m, 1168m, 1120m, 1095m, 1045m, 1025m, 995m, 955m, 920m, 890m, 855s, 830vs, 808s, 780vs, 730m, 700(sh) and 680s. ^1H NMR (C_6D_6/C_6D_5H): δ 0.50 (s, 6H, Si—CH_3, both isomers), 0.76 (s, cyclopropyl H, VII) and 0.94 (s, cyclopropyl H, VIII), total integration, 2H, 1.07 (s, cyclopropyl CH_3, VIII) and 1.13 (s, cyclopropyl CH_3, VII), total integration, 6H, 1.23 (s, S—C—C—CH_3, VII) and 1.26 (s, S—C—C—CH_3, VIII), total integration, 6H, 2.80 (s, S—CH_2, VII) and 2.82 (s, S—CH_2, VIII), total integration, 2H. The mass spectrum of the mixture showed the molecular ion at *m/e* 226. GLC yield, VII + VIII: 8%; VII/VIII ratio, by NMR: 3/1.

Reaction of silirane/I with t-butyl mercaptan

A solution of 1.53 g (22 mmol) of t-butyl mercaptan (Eastman) and 0.466 g (2.4 mmol) of silirane I in 5 ml of THF was heated at reflux under argon with stirring for 4.5 h. Subsequent GLC analysis (10% Apiezon L on Chromosorb W, 170°C) showed the presence of two products in 4/1 ratio. These were collected and identified as X and XI, respectively. In another reaction carried out using 3.92 mmol of silirane I, the reaction mixture was distilled to give 0.69 g (64%) of the isomer mixture, b.p. 75°C at 0.03 mmHg. (Found, X,XI mixture: C, 67.46; H, 11.48. $C_{16}H_{32}SSi$ calcd.: C, 67.53; H, 11.34%.) The molecular ion, M^+, *m/e* 284, was observed in the mass spectra of X and XI.

^1H NMR (CS_2/dioxane): Compound X: δ 0.43 (s, 6H, $Si-CH_3$), 0.78—0.93 (m, 8H, $CH-C\underline{H}_3$ and cyclopropyl H), 1.24 (s, 6H, cyclopropyl CH_3), 1.41 (s, 9H, $S-C-CH_3$), 1.60—2.03 (m, 1H, $C\underline{H}-CH_3$) and 2.18 ppm (d, *J* 6.5 Hz, 2H, $CH-C\underline{H}_2$). Compound XI: δ 0.43 (s, 6H, $Si-CH_3$), 0.81—0.97 (m, 8H, $CH-C\underline{H}_3$ and cyclopropyl H), 1.21 (s, 6H, cyclopropyl CH_3), 1.40 (s, 9H, $S-C-C\underline{H}_3$), 1.60—2.05 (m, 1H, $C\underline{H}-CH_3$), and 2.18 ppm (d, *J* 6.5 Hz, $CH-C\underline{H}_2$).

IR (cm^{-1}, neat film): Compound X: 3050w, 2955s, 2920(sh), 2895(sh), 2962s, 1718w, 1453m, 1404w, 1370w, 1362s, 1245s, 1210w, 1168w, 1153w, 1120w, 1087w, 1030w, 1010w, 970w, 922w, 831(sh), 820(sh), 810s, 772m and 670m. Compound XI: 3050w, 2957s, 2920s, 2865(sh), 1720w, 1453m, 1405w, 1362m, 1249m, 1212w, 1165w, 1153w, 1121w, 1087w, 1030w, 953w, 921w, 865(sh), 838m, 820(sh), 807m, 772m and 670w.

Reaction of hexamethylsilirane with elemental sulfur

To 0.5 g (1.95 mmol) of S_8 in 5 ml of THF (a saturated solution over undissolved sulfur) in a 25 ml one-necked, argon-purged flask, which was equipped with a magnetic stir-bar and a rubber septum, was added dropwise 0.827 g (2.08 mmol) of concentrated hexamethylsilirane. A slight exotherm was observed. The reaction mixture was stirred for 1 h at room temperature. Subsequent GLC analysis showed the presence of one major product. A 4 ft. × 0.25 in. 10% SE-30 on Chromosorb W column was used, with a column temperature of 130°C. The column must be conditioned by repeated injection of the reaction mixture before each use. This product was collected as a yellow, moisture-sensitive solid, m.p. 90—91°C, by GLC. (Found: C, 46.18; H, 8.64; S, 30.15. $C_8H_{18}S_2Si$ calcd.: C, 46.54; H, 8.79; S, 31.06%.) Mass spectrum, *m/e* (relative intensity): 207 (M^+ + 1, 3), 206 (M^+, 5), 149(14), 148(13), 133(22), 124(13), 123(11), 122(100) ($[Me_2SiS_2]^+$), 107(7), 85(8), 84(17), 83(10), 75(20), 74(8), 73(51), 69(34), 59(25), 58(9), 55(16), 49(10), 47(10), 45(22), 43(32), 41(58), 39(22). IR (cm^{-1}, CCl_4): 2970vs, 2960(sh), 2940(sh), 2900s, 2870s, 1460s, 1440s, 1400m, 1387m, 1375s, 1363s, 1249s, 1195m, 1155m, 1128m, 1115s, 1060m(bd), 1000(sh), 935m, 918m, 890s, 685s and 645m. ^1H NMR (CCl_4/$CHCl_3$): δ 0.37 (s, 6H, CH_3-Si), 1.01 (s, 6H, CH_3-C) and 1.32 ppm (s, 6H, CH_3-C). The yield determined by GLC using dodecane as internal standard, was 38%.

TABLE 1

THERMOLYSIS OF 1,1,4,4,5,5-HEXAMETHYL-1-SILA-2,3-DITHIACYCLOPENTANE IN $CCl_4/CHCl_3$ AT 130°C

Time (h)	Molar quantity of XIV, normalized to 100
0	100
5.5	72
11.0	49
13.25	44
16.75	28
19.75	20

In a separate experiment the yield of the product, XIV, was determined by NMR integration using toluene as internal standard to be 97%.

Thermolysis of 1,1,4,4,5,5-hexamethyl-2,3-dithia-1-silacyclopentane

The thermolysis of a GLC-collected sample of XIV, the title compound, was attempted by heating it in $CCl_4/CHCl_3$ solution in an evacuated, sealed NMR tube. After it had been heated at 140°C for 24 h, it was completely destroyed and new resonances due to tetramethylethylene and tetramethylcyclodisilthian, XV, were observed. (An authentic sample of XV, m.p. 107—108°C; lit. [20] m.p. 108—111°C, was available.)

Repetition of the experiment at 70°C or 95°C gave little evidence for decomposition of XIV. Heating an NMR tube containing a solution of XIV at 130°C in a tube furnace caused the decomposition to proceed at a rate which could be monitored conveniently by NMR analysis. During the decomposition a steady growth of two signals at 1.62 (tetramethylethylene) and 0.79 ppm (XV) was noted, along with a steady decrease of the resonance due to XIV. The decrease of the concentration of XIV was followed by determining the ratio of the 6H methyl resonances of XIV to chloroform, the initial ratio being converted to 100 and subsequent values being reported as % of the initial value. The data obtained are given in Table 1. A first order rate law ($k = 0.07$ h^{-1}) was observed; the half-life of XIV at 130°C is 11 h.

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