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CYCLOSILTHIANES

I. STEREOISOMERS OF PHENYLMETHYLCYCLOSILTHIANES*

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SUMMARY

trans-1,3,5-Trimethyl-1,3,5-triphenylcyclotrisilthiane (I) was prepared by treating methylphenyldichlorosilane with hydrogen sulfide in the presence of pyridine. Compound (I) exists in the boat form in the solid state. Rapidly interconverting twist boat or boat forms and possibly chair forms of (I) are believed to be present in solution on the basis of PMR data. Upon distillation at reduced pressure, (I) is converted into an equimolar mixture of *cis* and *trans* isomers of 1,3-dimethyl-1,3-diphenylcyclodisilthiane (II), and (III). One of these isomers was isolated by recrystallization from solution. The interconversion of the *cis,trans*-isomers (II) and (III) was found to be complete in 30 min at 179° in 1,2,4-trichlorobenzene. The interconversion of cyclosilthianes (I), (II), and (III) in solution was studied by NMR.

INTRODUCTION

Organo cyclosilthianes, sulfur analogs of organo siloxanes; were prepared by Étienne and co-workers[1] in 1952. The method of preparation consisted of treating diorganosilicon halides with hydrogen sulfide in the presence of an organic base such as pyridine. Both cyclodisilthianes containing a four member ring and cyclotrisilthianes containing a six member ring were isolated depending on the procedure used for isolation and purification of the products. These compounds differ from organo siloxanes considerably in their chemical reactivity and structure[2]. The six member ring appears to be most stable at ambient temperatures although the six member ring converts to the four member ring upon heating. The equilibrium constant for this interconversion reaction seems to vary with the substituents on the ring. Structural studies on the conformation of the six member ring are inclusive, but rule out a planar ring form. We have initiated a study of the stereoisomers of the organo cyclosilthianes that result when the silicon atom in the ring has unlike substituents.

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cis- And *trans*-isomers can result for the six membered ring as well as the four membered ring depending on the number of similar substituents on one side of the ring. Analogous *cis,trans*-isomers have been reported for siloxanes[3]. However, in the silthiane system four member rings are also stable.

The existence of these stereoisomers allows a study of the interconversion of these interesting ring systems as well as the possibility of a dependence of the chemical reactivity of substituents on silicon on the conformation of the ring. The conformation of the cyclotrisilthiane ring in solution is unknown and the existence of stereoisomers of this ring provides interesting compounds for conformational studies in solution. This paper presents the details of the synthesis of methylphenylcyclosilthianes and the isolation and characterization of some of the stereoisomers possible for this system. Early results of this work were reported briefly in a preliminary communication[4].

RESULTS AND DISCUSSION

Synthesis

When phenylmethyldichlorosilane is treated with hydrogen sulfide in the presence of pyridine at ambient temperature, 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I) can be isolated as a white crystalline substance in yields up to 99%. This reaction is summarized by eqn. 1.

$$3\ CH_3C_6H_5SiCl_2 + 6\ H_2S + 6\ C_5H_5N \xrightarrow{\text{hexane}} (CH_3C_6H_5SiS)_3 + 6\ C_5H_5NHCl \quad (1)$$

This compound melts between 112.5–114° and was characterized as 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane by its molecular weight in solution and its elemental analysis. The compound is moisture sensitive.

Geometrical isomers and ring conformation

The formulation of a reasonable structure for this substance requires some discussion. Three forms are possible for the silicon–sulfur six membered ring. These are a planar ring, a chair, and the boat or twist boat. Some structural information is available for hexamethylcyclotrisilthiane.

By comparing the dipole moment observed for hexamethylcyclotrisilthiane with that calculated for model structures, Kurita and Konda[5] suggest that the molecule is predominantly in the chair form with the possibility of a small amount of boat form present. Data obtained from an electron diffraction study of hexamethylcyclotrisilthiane could be interpreted using a chair or boat model but not a planar model[6]. The Raman and infrared spectra of $[(CH_3)_2SiS]_3$ have been reported by Kriegsmann and Clauss[7]. Within the limitation of their frequency assignment, the data was best interpreted in terms of a boat conformation.

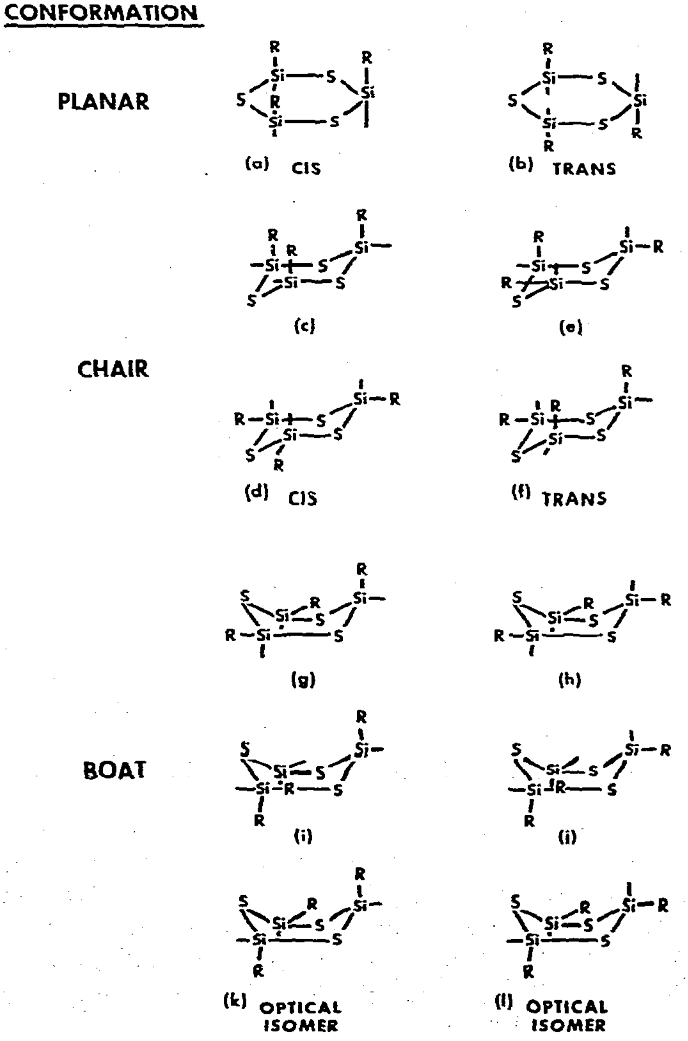
These results as well as the results of a variable temperature PMR study of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane discussed later rule out the planar ring.

When the silicon atom in the cyclosilthiane ring contains unlike groups, geometrical isomers are possible for the six membered and four membered rings. In the case of the six membered ring, three similar substituents or two similar substituents can be on one side of the ring. These are designated *cis* and *trans* isomers respectively. The four membered ring can have one or two similar substituents on one side of the ring and these are designated *trans* or *cis* respectively. The six membered cyclotrisilthiane ring can exist in a planar, chair, or boat or twist boat conformation. The isomers possible for each conformation are shown in Table 1.

The results[8] of a preliminary structure determination by X-ray crystallography indicate that the silicon–sulfur ring of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane is in the boat conformation with the methyl and phenyl groups orientated as shown in structure 1 in Table 1.

TABLE 1

CONFORMATIONS AND STEREOISOMERS POSSIBLE FOR 1,3,5-TRIMETHYL-1,3,5-TRIPHENYLCYCLOTRISILTHIANE



(a) CIS (b) TRANS

(c) (e)

(d) CIS (f) TRANS

(g) (h)

(i) (j)

(k) OPTICAL ISOMER (l) OPTICAL ISOMER

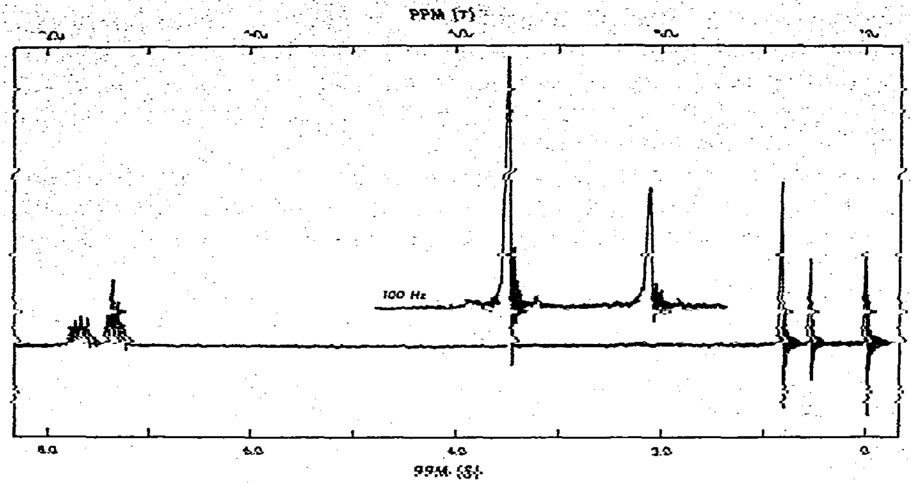


Fig. 1. PMR spectra of compound (I) in CCl_4. Inserted spectrum is 100 Hz scan of the methyl proton region.

The PMR spectra of compound (I) in carbon tetrachloride solution at room temperature consists of complex multiplets centered at 2.30 and 2.67 τ and two singlets in the methyl region at 9.17 and 9.45 τ. This spectrum is shown in Fig. 1. The area under the 9.17 τ resonance was twice that under the 9.45 resonance. The proton resonance in the methyl region is most sensitive to structural changes in the molecule and is most easily interpreted.

The proton resonances in the phenyl region are interpreted in the following way. The multiplet centered at 2.30 τ is assigned to the two protons *ortho* to the silicon atom and the multiplet at 2.67 τ is assigned to the three remaining *meta* and *para* hydrogens. The integration ratio of these multiplets is in the ratio of two to three.

The temperature dependence of the two proton resonances in the methyl region was studied in five solvents ranging in temperature from −65° to 179°. The variable temperature data is presented in Table 2. In this temperature range, the proton resonances were observed to shift their positions with little indication of changes in line shapes or intensity. The resonance at 9.45 τ shifts over a much wider range than does the 9.17 τ resonance.

Thus, the NMR data indicate that the proton resonances are temperature dependent and that the methyl groups are in two environments. Two methyl groups are identical and different from the third. Isomers in the chair and boat or flexible conformation can account for the observed NMR data.

trans Isomers in the chair form are consistent with methyl groups in two environments in the ratio 2/1. The *trans* chair isomer with two methyl groups in the axial position (structure e, Table 1) seems most likely on steric grounds. A Dreiding model of the alternate *cis* chair isomer with two phenyl groups in the axial position (structure f, Table 1) indicates severe steric crowding between the benzene rings.

Boat form conformations g, h, i and j, Table 1, all have two methyl groups in one environment which differs from the third.

TABLE 2

VARIABLE TEMPERATURE PMR STUDY OF $[CH_3(C_6H_5)SiS]_3$

Solvent[a]	Temperature (°C)[b]	9.17τ (Hz)	9.45τ (Hz)	ΔHz	Temperature (K)
C_6H_{12}	73	45.5	31.8	13.7	346
	37	44.6	30.3	14.3	310
$\frac{0.0402\ g}{0.592\ ml}$	29	44.4	30.0	14.4	302
C_5H_{10}	32	44.7	30.5	14.2	305
	+1	44.5	29.1	15.4	274
	−19	43.9	28.3	15.6	254
$\frac{0.0399\ g}{0.756\ ml}$	−37	43.2	27.2	16.0	236
	−56	42.4	25.8	16.6	217
	−65	41.5	25.0	16.5	208
CS_2	32	46.9	29.2	17.7	305
	+1	46.6	27.3	19.3	274
	−19	46.4	26.2	20.2	254
$\frac{0.0598\ g}{0.468\ ml}$	−37	46.4	24.8	21.6	236
	−56	45.8	23.1	22.7	217
	−65	46.2	21.3	24.9	208
CS_2	+20	47.0	29.0	19.0	293
	− 9	48.0	28.0	20.0	264
	−28	48.2	26.5	21.7	245
$\frac{0.0598\ g}{0.786\ ml}$	−46	47.5	25.0	22.5	227
	−65	47.6	23.6	24.0	208
1,2,4-$Cl_3C_6H_3$	167	54.0	40.0	14.0	440
	150	54.0	39.6	14.4	423
	110	54.0	39.0	15.0	380
	74	54.0	38.0	16.0	347
$\frac{0.0999\ g}{0.563\ ml}$	37	54.0	36.5	17.5	310
	32	54.0	36.8	17.2	305
Triglyme	179	50.0	37.0	13.0	452
	143	50.0	36.0	14.0	416
$\frac{0.60\ g}{2.0\ ml}$	115	50.2	35.0	15.2	388
	68	50.0	33.8	16.2	341
	38	50.0	31.0	19.0	311

[a] The solvents used were cyclohexane, cyclopentane, carbon disulfide, 1,2,4-trichlorobenzene and 161 glyme $[CH_3(OCH_2CH_2)_3OCH_3]$. The fraction listed under every solvent is the weight of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane in grams divided by the total volume of the solution in milliliters. [b] Methanol and ethylene glycol PMR standards were used to determine the probe temperature.

Conformations g and j seem unlikely since they are obtained by flipping the *cis* chair forms c, d Table 1. Isomers c, d, g, j form a set and any member of this set can be obtained from another member by ring inversion or rotations about bonds.

It is not possible to obtain structures e, f, h, i, k, l from structures c, d, g, j without breaking bonds. Since the NMR evidence rules out the *cis* chair isomers c and d, it is unlikely that any of the members of the set c, d, g, j, exist in significant concentration in solution. In summary, the *trans* chair isomer e, (Table 1) and the boat isomers h, i (Table 1) all having methyl groups in two environments in the ratio of two to one are consistent with the observed PMR spectra. It is also possible that the observed PMR spectrum is the time-averaged result of contributions from several rapidly interconverting structures. Rapidly interconverting boat or twist boat isomers h, i, k, l, (Table 1) as well as the *trans* chair isomer e (Table 1) could be present in equilibrium leading to the observed time averaged spectrum. The presence of rapidly interconverting isomers in solution is consistent with the observed solvent and temperature dependence of the PMR spectrum.

The barrier to interconversion among conformations of silicon–carbon ring compounds has recently been investigated by two groups of workers. Using low temperature PMR data from the ring protons in cyclopentamethylenedimethylsilane, Jensen and Bushweller[9] estimated a value of $\Delta F^{\neq}$ 5.5 ± 0.25 kcal/mole at −157° for the barrier for the chair to twist boat interconversion in this compound. Murray and Kaplan[10] estimated an upper limit for the free energy of the chair boat interconversion of 1,1,4,4-tetramethyl-1,4-disilacyclohexane to be less than 6 kcal/mole at −160°. This is a low value for the potential barrier to ring conformer interconversion and is suggestive that rings containing silicon may have a low barrier to conformer interconversion.

The potential energy difference between the flexible forms of *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane is unknown and attempts to measure this barrier by NMR were unsuccessful.

Conversion to the four membered ring

Cyclotrisilthianes are known to convert to cyclodisilthianes upon heating[2,12,13,16]. With unlike groups on the silicon atom, *cis* and *trans* isomers are possible for the four membered ring compound. This ring interconversion is given in eqn. 2.

$$2\,(CH_3C_6H_5SiS)_3 \rightarrow \underset{(II),\ (III)}{3\,(CH_3C_6H_5SiS)_2} \qquad (2)$$

When (I) was distilled at reduced pressure, a solid distillate was obtained. The PMR spectrum of this solid dissolved in carbon tetrachloride contained two resonances in the methyl region of equal intensity at 8.92 (II) and 8.95 τ (III) (see Fig. 2). Two multiplets were also present in the phenyl region centered at 2.30 and 2.67 τ. The ratio of the integrated areas of these two resonances was 2/3.

Isolation of the substance with a methyl proton resonance at 8.95 τ proved to be relatively easy. Recrystallization of the solid obtained as the distillate from boiling n-hexane yielded a white crystalline solid melting in the range of 137–139°. The PMR spectrum of this solid dissolved in carbon tetrachloride contained a single resonance in the methyl region at 8.95 τ in addition to phenyl resonances centered around 2.30 and 2.67 τ. This substance was characterized as 1,3-dimethyl-1,3-diphenylcyclodisilthiane by its molecular weight in solution and its elemental analysis. Concentration of solution remaining after crystallization of the cyclodisilthiane with the methyl proton resonance at 8.95 τ yielded more of this isomer and *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I).

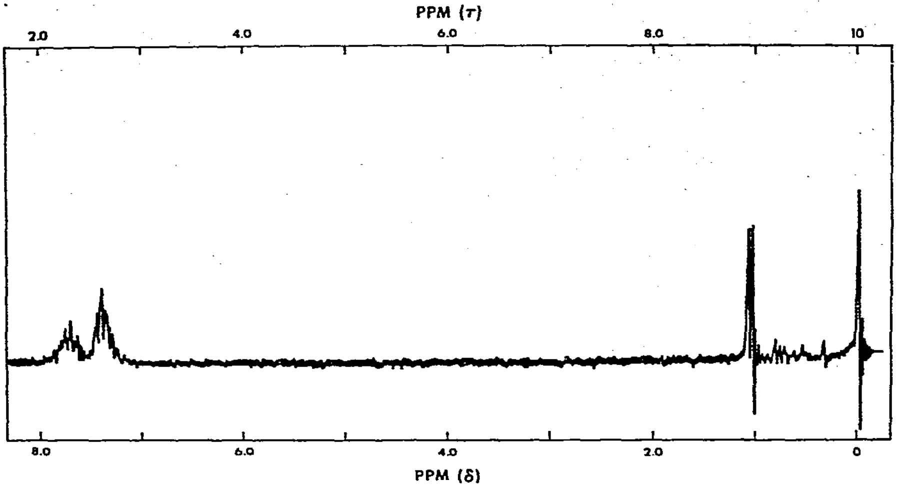


Fig. 2. PMR spectra of a mixture of 1,3-dimethyl-1,3-diphenylcyclodisilthiane in carbon tetrachloride.

Isolation of the isomer with the methyl proton resonance at 8.92 τ proved to be difficult. This isomer is relatively unstable in solution and rapidly converts to the cyclodisilthiane isomer with the methyl proton resonance at 8.95 τ and *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I). The molecular weight of this isomer in solution was estimated by determining the molecular weight of a solution consisting of this isomer and smaller concentrations of other isomers.

The PMR spectrum in the methyl region was used to estimate the concentrations of the various species present. The calculated and observed molecular weight was in good agreement. Although both isomers possible for the four member ring were observed no data was obtained to allow the assignment of the *cis* or *trans* structure to these two compounds.

Effect of temperature on the product distribution of cyclosilthianes

When the preparation of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I) was carried out at 160° in xylene with cyclohexylamine as the base, analysis of the product by PMR spectroscopy indicated the presence of a mixture of some complexity. The PMR spectrum in carbon tetrachloride contained resonances in the methyl region at 8.92, 8.95, 9.07, 9.10, 9.17, 9.23, 9.27, 9.38, 9.45 and 9.48 τ. Cyclosilthianes exhibiting PMR at 8.92, 8.95, 9.17 and 9.45 have been characterized. The species corresponding to the resonance at 9.07 τ always appears when either *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I) or 1,3-dimethyl-1,3-diphenylcyclodisilthiane (II), (III) is heated in various solvents. On this basis, we have tentatively assigned this resonance to *cis*-1,3,5-triphenylcyclotrisilthiane (IV) structure (d) Table 1. This compound is very unstable and readily interconverts to more stable isomers, as we were unable to isolate it from solution. This compound may be in the *cis* chair conformation structure d, (Table 1) with three methyl groups axial or some combination of interconverting twist boat conformation in solution with a single methyl proton resonance due to averaging processes.

Any meaningful structure assignment of the remaining resonances will require molecular weight data. These species may be cyclotetrasilthianes or other conformations of the six and eight member rings or even larger ring cyclosilthianes.

Thermal interconversion of stereoisomers

When *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I) was maintained at 200° for several weeks, analysis of a sample of the resulting mixture dissolved in carbon tetrachloride by NMR revealed resonances at 8.92, 8.95, 9.07, 9.17, and 9.45 τ. Only *trans*-cyclotrisilthiane (I) and cyclodisilthiane (III) could be isolated from this mixture.

The rates of interconversion of the various stereoisomers of cyclosilthianes were qualitatively estimated by NMR experiments.

Attempts were made to obtain equilibrium constants for the following equilibria:

$$\underset{\text{(I)}}{2(CH_3C_6H_5SiS)_3} \rightleftharpoons \underset{\text{(II, III)}}{3(CH_3C_6H_5SiS)_2}$$

and:

$$\underset{\text{(III)}}{(CH_3C_6H_5SiS)_2} \rightleftharpoons \underset{\text{(II)}}{(CH_3C_6H_5SiS)_2}$$

Difficulty was obtained achieving equilibrium due to thermal instability of the compounds which seemed to be quite sensitive to traces of impurities. 1,3,5-Trimethyl-1,3,5-triphenylcyclotrisilthiane (I) converted to 1,3-dimethyl-1,3-diphenylcyclodisilthiane (II), (III) on distillation at 200° under reduced pressure. The disilthiane did not convert to the trisilthiane at room temperature nor did the isomer conversion possible for the disilthiane occur in the solid state. In solution the dimer interconversion occurs slowly at room temperature and reaches equilibrium at 180° in 85 min.

At 200° approximately $\frac{2}{3}$ of cyclotrisilthiane (I) dissolved in 1,2,4-trichlorobenzene was converted into cyclodisilthianes (II), (III) 50% and 11% (IV) after 80 h.

EXPERIMENTAL

General

All syntheses and manipulations of compounds were carried out under nitrogen using standard bench top apparatus or in an inert atmosphere box with constant nitrogen circulation[14]. Some manipulations were carried out in a standard high vacuum apparatus. Hydrocarbon solvents were purified by standard procedures and dried by distillation from a solution containing the blue ketyl radical generated by the addition of benzophenone and sodium to the solvent prior to distillation. Organic bases were dried over potassium hydroxide and distilled prior to use. Methylphenyldichlorosilane was obtained from Dow Corning Corp., Midland, Michigan, and purified by distillation at reduced pressure.

Carbon and hydrogen analyses were obtained by standard micro-analytical combustion techniques. Silicon analysis was done gravimetrically by sulfuric acid digestion in platinum ware[15]. Sulfur analysis was obtained by hydrolyzing samples in a vacuum system and measuring the hydrogen sulfide evolved by the sample.

Molecular weights were determined cryoscopically in benzene under dry nitrogen. All single molecular weight values are reported as the mean of several determinations with the average deviation from the mean.

Proton magnetic resonance spectra were measured with a Varian A-60 or HA 100 nuclear magnetic resonance spectrometer. Tetramethylsilane was used as an internal standard.

Preparation of trans-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I)

A typical preparation consisted of adding methylphenyldichlorosilane (82 ml, 0.5 mol) and pyridine (90 ml, 1.12 mol) to 600 ml of hexane in a one liter flask which had been previously flushed with dry nitrogen. Hydrogen sulfide was passed through the solution for 2.5 h at ambient temperatures. The pyridinium chloride which formed was filtered and extracted in a Soxhlet apparatus using the filtrate as the extracting liquid. 37 g of colorless crystals formed when the solvent cooled to room temperature and another 38 g of crystals was isolated by evaporation of the hexane for a total yield of 75 g (99%). After recrystallization from n-hexane, this substance, m.p. 112.5–114°, was characterized as *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane by its molecular weight, elemental analyses, and PMR spectra. (Found: C, 55.3; H, 5.3; Si, 18.5; S, 21.0. Mol.wt., 457 ± 5. $[CH_3(C_6H_5)SiS]_3$ calcd.: C, 55.2; H, 5.3; Si, 18.4; S, 21.1%. Mol.wt., 457.)

The PMR spectrum in carbon tetrachloride illustrated in Fig. 1 consists of the following resonances with relative integrated intensity after each resonance, 2.30 multiplet (2), 2.67 multiplet (3), 9.17 (2), 9.45 (1) τ.

1,3-*Dimethyl*-1,3-*diphenylcyclodisilthiane* (*III*)

A 200 g sample of crude *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I) was placed in a 500 ml one neck flask connected to a heated 4 ft. zig-zag column that was fitted with a simple distilling head. The distilling head was heated by a soft flame from a Bunsen burner in order to eliminate flooding during the reduced pressure distillation. After some yellow liquid had distilled, a colorless liquid, which solidified upon cooling, distilled at 205–213°/0.5 mmHg with a pot temperature of 287°. The PMR spectrum of this colorless solid contained two methyl resonances at 8.92 and 8.95 τ of equal intensity and phenyl resonances at 2.3 and 2.67 τ (see Fig. 2). Recrystallization, in a drybox, of this solid from boiling n-hexane yielded a white crystalline solid melting at 137–139° which exhibited only one methyl resonance at 8.95 τ and phenyl resonances centered around 2.67 and 2.30 τ. This solid was characterized as 1,3-dimethyl-1,3-diphenylcyclodisilthiane (III) by its molecular weight, elemental analyses and PMR spectra. (Found: C, 55.4; H, 5.3; Si, 18.9; S, 20.9. Mol.wt., 304 ±6. $[CH_3(C_6H_5)SiS]_2$ calcd.: C, 55.2; H, 5.3; Si, 18.4; S, 21.1%. Mol.wt. 305.)

Continued removal of n-hexane from the mother liquor in a drybox recrystallization process yielded successively smaller quantities of the 1,3-dimethyl-1,3-diphenylcyclodisilthiane (III). After complete solvent evaporation, the solid remaining was characterized as *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I) by its PMR spectrum.

1,3-*Dimethyl*-1,3-*diphenylcyclodisilthiane* (*II*)

Another workup process conducted in a drybox consisted of grinding the solid which gave rise to equal intensities of methyl resonance at 8.95 and 8.92 τ. This pulverized material was slurried with cold isopentane and filtered. Evacuation of the isopentane from the filtrate caused a solid to crystallize out. The methyl resonance in the PMR spectrum of this solid, m.p. 113–119°, was a singlet at 8.92 τ. This solid was characterized as 1,3-dimethyl-1,3-diphenylcyclodisilthiane by its molecular weight, elemental analyses, and PMR spectra. [Found: C, 55.2; H, 5.3. Mol.wt. 356±5. $[CH_3(C_6H_5)SiS]_2$ calcd.: C, 55.2; H, 5.3; Mol.wt. (based on the molecular formula), 305; mol.wt. (as computed from the PMR methyl integrations) 349.]

The methyl resonances (integrations) of this sample were 8.92 τ (44), 8.95 (10), 9.17–9.45 (9), 9.07 (2) and 9.70 (17). The 9.70 τ resonance is reported to be $(MePhSiO)_4$ and the 9.07 τ is assumed to be the *cis*-trimer.

$$\text{Mol.wt. calcd.} = \frac{\frac{44+10}{2}(304) + \frac{9+2}{3}(456) + \frac{17}{4}(544)}{\frac{54}{2} + \frac{11}{3} + \frac{17}{4}} = 349$$

Removing more of the solvent by evacuation produced a solid which consisted primarily of the cyclodisithiane isomer (III) with its characteristic methyl resonance at 8.95 τ. When the solvent was completely removed, a yellow oil remained. The PMR spectrum of this oil in carbon tetrachloride contained many resonances in the methyl region. These resonances were observed from the product obtained when methyl phenyl dichlorosilane was treated with hydrogen sulfide at higher temperatures. The nature of these resonances will be discussed in the section to follow.

Effect of temperature on cyclosilthiane synthesis

The preparation of *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I) was repeated as described previously while the reaction mixture was maintained at 0°. Less than 10% (7.0 g) of the theoretical yield of *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane identified by its PMR spectrum, was isolated under these conditions.

Methylphenyldichlorosilane (40.3 ml, 0.25 mol) was added to cyclohexylamine (60.5 ml, 0.50 mol) in 500 ml of xylene in a three necked flask filled with a reflux condenser and a gas inlet tube. A fine white precipitate formed when the reagents were mixed. This solution was maintained at 160° while hydrogen sulfide was passed through the reactants for 6 h. Cyclohexylammonium chloride was removed from this solution by filtration and characterized by its melting point m.p. 205–207°. Xylene was removed by vacuum distillation leaving a yellow oil. The PMR of this yellow oil in carbon tetrachloride contained methyl resonances at 8.92, 8.95, 9.07, 9.10, 9.17, 9.23, 9.27, 9.28, 9.38, 9.45, and 9.48 τ in addition to phenyl resonances centered at 2.30 and 2.67 τ. Repeated vacuum distillation yielded an oil with the same methyl resonances. After it had been kept for 4 months, crystals were isolated from the oil and identified as *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I) by their melting point and PMR spectra.

Thermolysis of 1,3,5-*trimethyl*-1,3,5-*triphenylcyclotrisilthiane*

A neat sample of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I) was placed in a glass tube fixed with a stopcock and heated at 200° for 3 weeks. The sample was quickly cooled to room temperature whereupon it solidified. A portion was removed

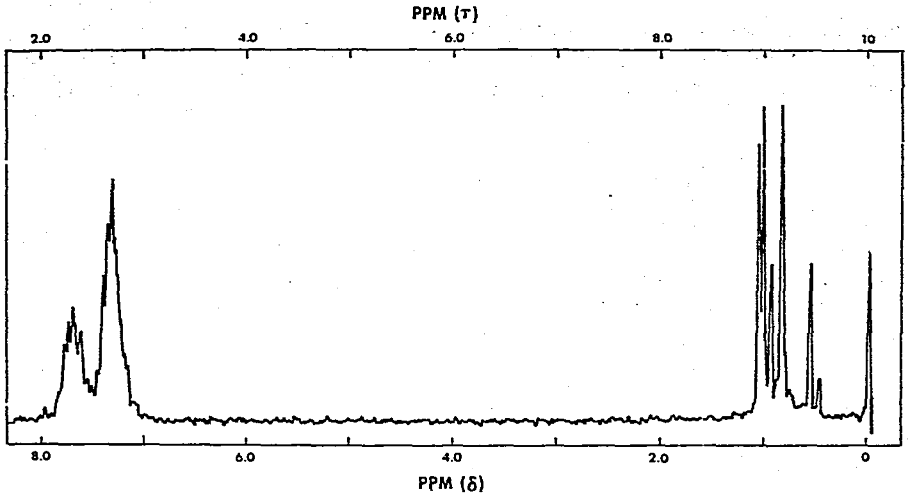


Fig. 3. PMR spectra of the mixture of cyclosilthianes obtained after maintaining compound (I) at 200° for several days.

in the drybox and dissolved in carbon tetrachloride. The PMR spectrum of this equilibrated mixture contained five methyl resonances at 8.92, 8.95, 9.07, 9.17 and 9.45 τ and phenyl resonances at 2.30 and 2.67 τ. See Fig. 3 for a PMR spectrum of this mixture.

The first recrystallization of this solid from n-hexane yielded cyclodisilthiane (III) which had a methyl resonance at 8.95 τ. Further recrystallizations yielded primarily *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I).

Thermolysis of cyclodisilthiane (III)

A 0.82 *M* solution of 1,3-dimethyl-1,3-diphenylcyclodisilthiane (III) in 1,2,4-trichlorobenzene was maintained at 200° in an NMR tube. The sample was cooled to room temperature and a PMR spectrum was obtained at various intervals. Proton resonances characteristic of cyclotrisilthiane (I) at 9.17 and 9.45 τ appeared in the solution together with a resonance at 9.07 τ. After 80 h the composition of the solution consisted of 54% cyclodisilthianes (II), (III) (8.92, 8.95 τ)12% cyclotrisilthiane (IV) (9.07 τ) and 32% cyclotrisilthiane (I) (9.17, 9.45 τ) (see Fig. 3). The proton resonance at 9.07 τ was observed to result when either cyclotrisilthiane (I) or cyclodisilthiane (III) was heated in solution. This resonance was assumed to be due to the *cis* isomer (Table 1) of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane with the three methyl groups in the axial position. This isomer rapidly converted to compound (I) or (III) at room temperature and could not be isolated from solution by distillation or recrystallization.

Thermolysis of cyclotrisilthiane (I)

A 0.186 *M* solution of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane (I) was maintained at 200° in an NMR tube. After 24 h the composition of the solution as estimated by NMR was found to be 32% cyclotrisilthiane (I), 11% cyclotrisilthiane (IV) and 49% cyclodisilthiane (II), (III).

The interconversion of the *cis* and *trans* isomers of 1,3-dimethyl-1,3-diphenylcyclodisilthiane was found to be very rapid at 179° and therefore an equilibrium mixture of these substances is rapidly achieved under the conditions of the above experiments.

Interconversion of cyclodisilthiane isomers (II), (III)

A 0.356 *M* solution of cyclodisilthiane (III) (8.95 τ) in 1,2,4-trichlorobenzene was equilibrated in a NMR tube at 179°. After 14 min the composition of the solution was 57.6% (III) and 42.4% (II). An equilibrium mixture consisting of 51.7% (III) and 48.3% (II) was achieved after 85 min.

To verify that these reactions were quenched at room temperature, the PMR spectrum of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane in 1,2,4-trichlorobenzene showed no change while maintained at ambient temperature for several days. The PMR spectrum of 1,3-dimethyl-1,3-diphenylcyclodisilthiane (III) in 1,2,4-trichlorobenzene did not change upon standing several hours at ambient temperature.

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