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CYCLOSILTHIANES

II*. STEREOISOMERS OF METHYLETHYL- AND METHYLVINYLCYCLOSILTHIANES

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SUMMARY

1,3,5-Trimethyl-1,3,5-triethylcyclotrisilthiane (I) was prepared by treating methylethyldichlorosilane with hydrogen sulfide in the presence of pyridine. 1,3,5-Trimethyl-1,3,5-trivinylcyclotrisilthiane (II) was prepared in a similar manner from methylethyldichlorosilane.

The PMR spectrum of these cyclosilthianes is interpreted in terms of a mixture of conformational isomers. The PMR spectrum of these substances in solution did not allow a distinction among the chair and boat forms possible for the cyclosilthiane ring.

Continued refluxing of (I) or (II) resulted in the isolation of a 50/50 mixture of *cis* and *trans*-1,3-dimethyl-1,3-diethylcyclodisilthiane (III), (IV) and 1,3-dimethyl-1,3-divinylcyclodisilthiane (V), (VI) respectively.

When (II) was heated or prepared at higher temperature, the PMR spectrum of the product contained resonances in the methyl region indicating the presence of additional methylvinylcyclosilthianes. Polymeric methylvinylsilthiane was isolated as one of the products formed when (II) is heated.

INTRODUCTION

Part I of this series[1] reported the synthesis of *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane and *cis*- and *trans*-1,3-dimethyl-1,3-diphenylcyclodisilthiane. *trans*-1,3,5-Trimethyl-1,3,5-triphenylcyclotrisilthiane exists in the boat form in the crystalline state[2] and NMR studies in solution indicate the presence of boat and possibly chair conformations. In this paper, we report the synthesis and properties of some of the possible stereoisomers of methylethyl and methylvinyl substituted cyclosilthianes.

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[*] For Part I, see ref. 1.
[**] Abstracted in part from the Ph.D. thesis of L. J. Pazdernik, University of Iowa, 1970. Present address: Chemistry University of Montreal, Quebec, Canada.

RESULTS AND DISCUSSION

Synthesis of compounds

Treatment of methylethyl- or methylvinyldichlorosilane with hydrogen sulfide in the presence of base yielded the corresponding cyclotrisilthiane smoothly at room temperature according to eqn. 1.

$$3\,R_1R_2SiCl_2+6\,C_5H_5N+3\,H_2S \rightleftarrows (R_1R_2SiS)_3+6\,C_5H_5N\cdot HCl \qquad (1)$$

$$\begin{aligned}&(I),\ R_1=CH_3,\ R_2=C_2H_5\\&(II),\ R_1=CH_3,\ R_2=C_2H_3\end{aligned}$$

Both cyclotrisilthianes (I) and (II) were characterized by their elemental analysis and molecular weight in solution.

Upon refluxing (I) and (II) at reduced pressure and distilling the lowest boiling fraction, both (I) and (II) were converted to a mixture of *cis*- and *trans*-cyclodisilthianes according to eqn. 2.

$$2(R_1R_2SiS)_3 \rightleftarrows 3(R_1R_2SiS)_2 \qquad (2)$$

$$\begin{aligned}&(III)\ R_1=CH_3, && R_2=C_2H_5, && \textit{cis}\\&(IV)\ R_1=CH_3, && R_2=C_2H_5, && \textit{trans}\\&(V)\ R_1=CH_3, && R_2=C_2H_3, && \textit{cis}\\&(VI)\ R_1=CH_3, && R_2=C_2H_3, && \textit{trans}\end{aligned}$$

These compounds were characterized as cyclodisilthianes by their mass spectra. The PMR spectrum of each product in the methyl region consisted of two closely spaced resonances of approximately equal intensity.

Structure of cyclotrisilthianes

Limited information is available concerning the structure of the cyclotrisilthiane ring. Hexamethylcyclotrisilthiane has been shown to be non-coplanar in the vapor phase by electron diffraction studies[3]. By comparison of the measured dipole moment of hexamethylcyclotrisilthiane with that calculated for a chair and boat model, Kurita and Kondo[4] suggested that the compound was predominantly in the chair form with possibly some of the boat form present. On the basis of infrared and Raman data, Kriegsman and Clauss[5] concluded that hexamethylcyclotrisilthiane exists in the boat conformation in the liquid state. The preliminary results of an X-ray diffraction study of *trans*-1,3,5-trimethyl-1,3,5-triphenylcyclotrisilthiane indicate that the compound is in the boat conformation in the crystalline state[2]. The PMR spectrum of this compound in solution has been interpreted in terms of rapidly interconverting boat forms although the chair form could not be ruled out[1]. Thus, the conformation of the cyclosilthiane ring in solution is far from established.

Assuming that the cyclotrisilthiane ring is non-coplanar, chair and boat or twist boat conformations are possible for the ring.

In the chair conformation, *cis* and *trans* isomers are possible (see Fig. 1). In the *cis* isomer, all substituents on the silicon of one kind are either axial or equatorial (a, b, Fig. 1). In the *trans* isomer, two substituents of one kind are either axial or equatorial (c, d, Fig. 1).

In the boat conformation, eight isomers are possible and these are shown in Fig. 1, structures e–j.

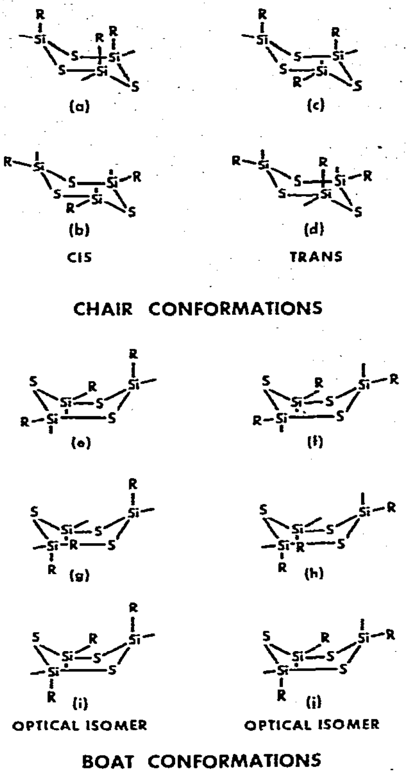

Fig. 1. Conformations and stereoisomers possible for unsymmetrically substituted cyclotrisilthianes.

PMR results; cyclotrisilthianes

The PMR spectra of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilthiane (II) contains resonances in the vinyl proton region centered at 3.92 τ and three resonances in the methyl region at 9.25, 9.28 and 9.32 τ (see Fig. 2 and Table 1). The integration ratio of the protons in the vinyl and methyl region is one within experimental error. The patterns of resonances in the vinyl region is complex and is less useful than the resonances in the methyl region for structural interpretation.

The integration ratio of the resonances in the methyl region at 9.25, 9.28 and 9.32 τ is 1/2/1 respectively. The position of these resonances is solvent dependent but the pattern and relative positions remain the same. Low temperature NMR studies were hampered due to the lack of solubility of methylvinylcyclotrisilthiane.

A variable temperature PMR study was completed on a neat sample of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilthiane (II). As the temperature increased from 35 to 180°, the three methyl resonances of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilthiane (II) moved toward each other by 1.50 Hz. There was no apparent change in the vinyl resonances and the integrated areas of the methyl resonances.

Consideration of the PMR spectra in the methyl region expected from the chair and boat or twist boat isomers reveals that no single isomer can account for this spectrum. Methyl–vinyl proton coupling is ruled out by the fact the chemical shifts are unchanged in the 60 or 100 MHz spectrum.

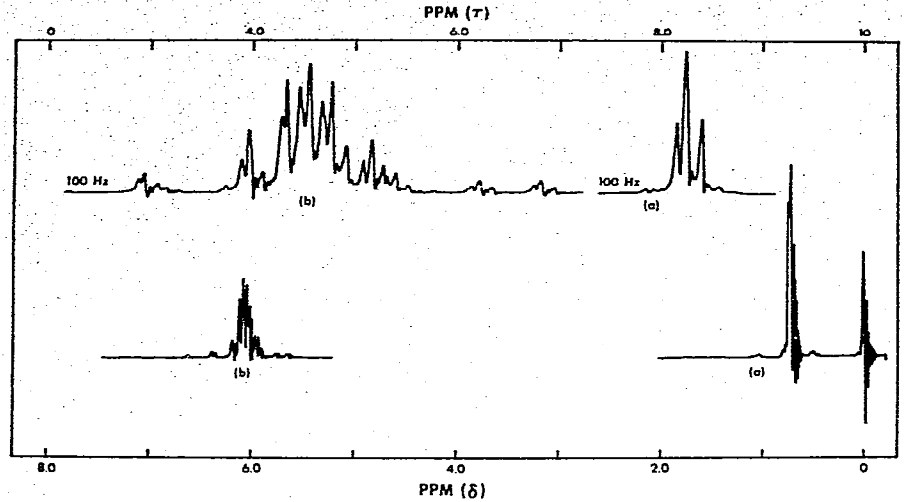

Fig. 2. PMR spectra of 1,3,5-trimethyl-1,3,5,-trivinylcyclotrisilthiane (II).

TABLE 1

PROTON MAGNETIC RESONANCE SPECTRA[a] OF CYCLOSILTHIANES

	R_1	$R_2\ (CH_3)$
$CH_3C_2H_5SiCl_2$	8.91 (5)	9.28 (3)
$(C_2H_5SiS)_3$	8.91	
$(CH_3C_2H_5SiS)_3$[b] (I)	8.99 (5)	9.39 (3)
$(CH_3C_2H_5SiS)_3$[c,e] (I)	8.97, 8.99	0.675, 0.66, 0.62
$(CH_3C_2H_5SiS)_3$[d,e] (I)	8.99	0.629, 0.619, 0.6036
$(CH_3C_2H_5SiS)_2$[c,e] (III), (IV)	8.96	0.664, 0.672
$(CH_3C_2H_3SiS)_2$[c] (V), (VI)	3.94	9.20, 9.23
$(CH_3C_2H_3SiS)_3$[c] (II)	3.92	9.25, 9.28, 9.32

[a] Relative integrated intensities in parentheses after τ values. [b] In carbon tetrachloride. [c] In carbon disulfide. [d] In benzene. [e] Obtained on HA100. [f] Center of multiplet.

The PMR spectrum of (II) in the methyl region can be accounted for by assuming the presence of two or more isomers or conformations in solution. On the basis of the PMR solution data, it is not possible to differentiate between the boat or chair conformations. Various combinations of chair, boat, or boat and chair conformations could be present.

For example, a 1/3 molar mixture of *cis* and *trans* chair isomers could yield the observed methyl PMR spectra. The two equivalent methyl groups in the *trans* chair form could be assigned to the 9.27 τ resonance and the remaining methyl group assigned to the 9.30 τ resonance. The equivalent methyl groups in the *cis* form could account for the 9.25 τ resonance.

Boat conformations e, f, g, h (Fig. 1) contain methyl groups in two environments in a 2/1 ratio and the PMR spectra of these forms would be similar to that expected for the *trans* chair isomers.

It is possible that the conformers are rapidly interconverting and that the observed PMR spectrum is time averaged. On the basis of the NMR data alone it is not possible to distinguish between the various possible ring forms and stereoisomers that could be present in solution. A similar situation exists in the case of the interpretation of the solution PMR spectra of methylphenylcyclotrisilithiane[1].

The PMR spectrum of 1,3,5-trimethyl-1,3,5-triethylcyclotrisilthiane (I) is somewhat anomalous and quite subject to solvent shifts. The PMR spectrum obtained at 60 MHz or 100 MHz employing routine scan conditions in carbon tetrachloride or carbon disulfide consists of single resonances at 8.99 and 9.39 τ. The integration ratio of these resonances is in the ratio of 5/3 respectively. To further investigate the degeneracy of the ethyl protons, the PMR spectra of some other compounds containing an ethyl group on silicon was investigated. The NMR spectrum of methylethyldichlorosilane consisted of single resonances at 8.91 and 9.28 τ in carbon tetrachloride solution with the integration ratio of 5/3. Hexaethylcyclotrisilthiane dissolved in carbon tetrachloride exhibited a single resonance at 8.91 τ.

When the PMR spectrum of 1,3,5-triethyl-1,3,5-trimethylcyclotrisilthiane (I) dissolved in carbon disulfide was obtained under conditions of better resolution the ethyl resonance at 8.99 τ broadened considerably and sometimes a second resonance was observed slightly downfield whose intensity was about one third that of the upfield resonance. To check the reasonableness of the degeneracy on the ethyl group, the calculated spectrum of the ethyl region by LAOCOONIII (input parameters: 5 protons, chemical shift 150 Hz, $J_{vic}=12$ Hz, $J_{gem}=-10$ Hz) shows 32 resonances of varying intensities which have the same chemical shift, thus it is possible to account for this result.

The PMR spectrum of 1,3,5-trimethyl-1,3,5-triethylcyclotrisilthiane (I) in the methyl region consisted of a single resonance in carbon tetrachloride and carbon disulfide under routine scan conditions. When dissolved in acetone-d_6 or benzene-d_6, three resonances appeared in the methyl region. The pattern was very similar to that exhibited by 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilthiane (II). The PMR spectrum of 1,3,5-trimethyl-1,3,5-triethylcyclotrisilthiane (I) in benzene obtained under conditions of slow scan and high resolution at 100 MHz is shown in Fig. 3. The integration ratio of these three resonances is approximately 1/2/1. The PMR spectrum in acetone-d_6 is

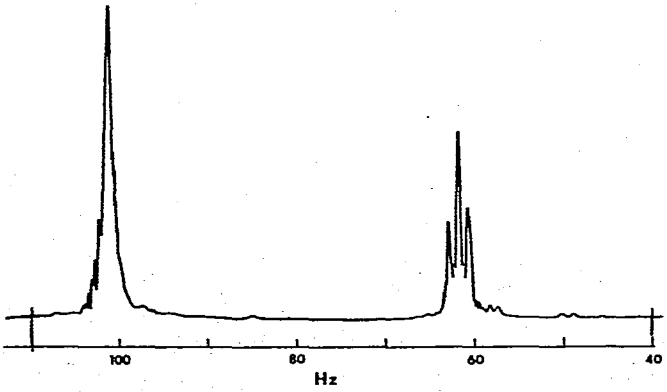

Fig. 3. 100 MHz PMR spectrum of 1,3,5-trimethyl-1,3,5-triethylcyclotrisilthiane (I) in benzene.

similar although the three resonances are farther apart and the upfield resonance is shifted by a larger amount.

The situation concerning structural interpretation of this spectrum is the same as that for 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilthiane (II). The spectrum cannot be accounted for in terms of a single conformation and various proportions of chair and boat isomers can account for the observed spectra. No variable temperature PMR data were obtained for this compound.

Cyclodisilthianes

Organocyclotrisilthianes are known to convert to cyclodisilthianes on heating and this equilibrium in the case of hexamethylcyclotrisilthiane has been studied by NMR[6].

When the silicon atom contains unlike organic groups, *cis, trans* isomers are possible for the four membered ring. *cis*- and *trans*-Methylphenylcyclodisilthianes have been reported in the first paper in this series[1].

Continued refluxing of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilthiane (II) at reduced pressure and subsequent distillation and collection of the low boiling fraction yields a mixture of the *cis*- and *trans*-cyclodisilthianes in equal amounts. The PMR spectrum in the methyl region of the distillation product from 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilthiane (II) dissolved in carbon disulfide consists of two resonances at 9.20 and 9.23 τ of equal intensity (see Table 1 and Fig. 4).

The stability of these cyclodisilthianes seems to be dependent on the presence of trace concentrations of materials capable of catalyzing their conversion to methylvinylcyclotrisilthianes since the half-life of these substances at room temperature varied from preparation to preparation. The sensitivity of the equilibria involving the conversion of methylcyclosilthianes to traces of catalysts has also been reported[6]. When isolated free from cyclotrisilthianes, they were stable for weeks at room temperature neat or in solution. When present as a component in a mixture of cyclosilthianes they converted to cyclotrisilthianes in a few days.

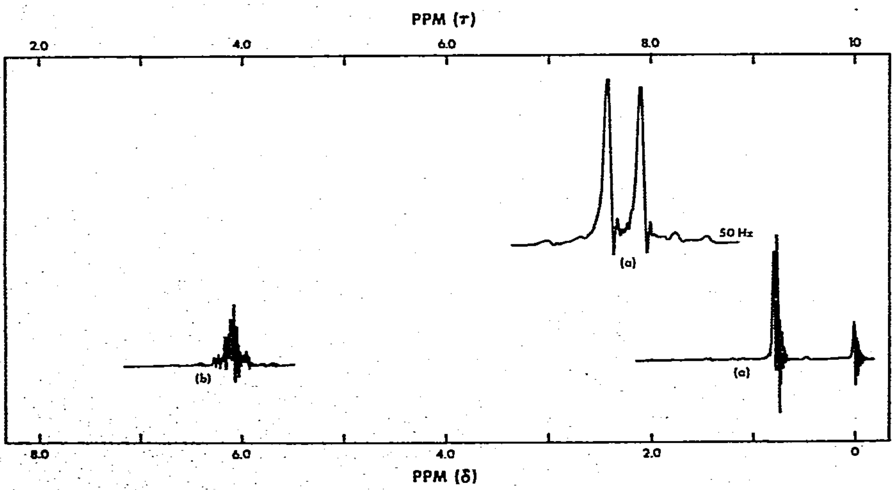

Fig. 4. The PMR spectrum of a mixture of *cis*- and *trans*-1,3-dimethyl-1,3-divinylcyclodisilthiane (V, VI).

Continued refluxing of 1,3,5-trimethyl-1,3,5-triethylcyclotrisilthiane (I) and subsequent distillation of the low boiling fraction at reduced pressure yielded a liquid that was shown to consist of *cis-* and *trans*-cyclodisilthianes in equal amounts by its PMR spectra. The 100 MHz spectrum in the methyl region of this liquid dissolved in carbon disulfide (shown in Fig. 5) consisted of two closely spaced resonances at 0.664 and 0.672 τ. The stability of these isomers was dependent on the presence of other cyclosilthianes and varied with the purity of the sample.

No attempt was made to separate these stereoisomers or to determine their relative configuration.

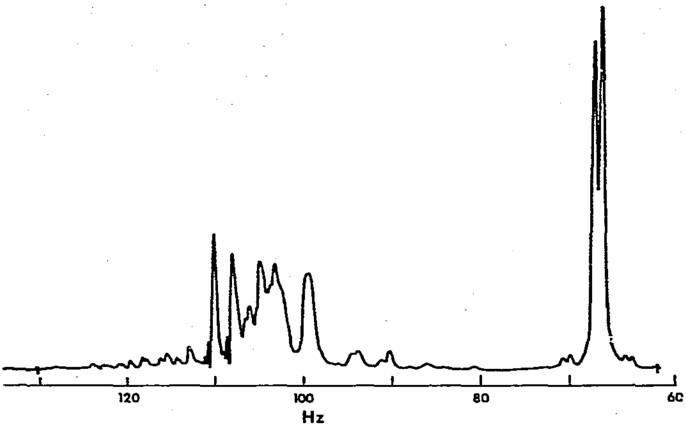

Fig. 5. 100 MHz PMR spectrum of *cis-* and *trans*-1,3-dimethyl-1,3-diethylcyclodisilthiane (III), (IV) in carbon disulfide.

Evidence for other stereoisomers

When the synthesis of methylvinylcyclotrisilthiane was conducted at higher temperatures, the product contained proton resonances in the methyl region at 9.21, 9.24 τ and multiplets consisting of three resonances each centered at 9.27, 9.34, and 9.50 τ. These multiplets also appeared in varying amounts in the fractions obtained when 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilthiane (II) (multiplet at 9.27 τ) was distilled at reduced pressure. These resonances are probably due to other cyclotrisilthianes, or possibly higher ring cyclosilthianes.

Upon prolonged distillation of 1,3,5-trimethyl-1,3,5-triethylcyclotrisilthiane (I), the pot always contained varying amounts of non-volatile white semi-crystalline material. This material melted over a wide range of temperature and was characterized tentatively as polymeric methylethylsilthiane. The properties of this polymeric mixture were not further studied, although this is the first report of a high molecular weight organosilthiane.

EXPERIMENTAL

General

All syntheses and manipulations were carried out under nitrogen using standard bench top apparatus or in an inert atmosphere box with constant nitrogen circulation[7].

Hydrocarbon solvents were purified by standard procedures[8]. Organic bases were dried over potassium hydroxide and distilled prior to use. Methylvinyldichlorosilane was obtained from Dow Corning Corp., Midland, Michigan, and purified by distillation at reduced pressure.

Methylethyldichlorosilane was prepared by adding a Grignard reagent prepared from ethyl bromide and magnesium to a solution of methyltrichlorosilane in anhydrous ether. The product was purified by distillation, B.p. 100–102°/748 mmHg (Lit.[9] 100°/744 mmHg). The chlorine analysis and PMR spectra of this compound agreed with that expected for methylethyldichlorosilane.

Carbon hydrogen analyses were obtained by standard micro-analytical combustion techniques. 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 on a Varian A60 or HA100 nuclear magnetic resonance spectrometer. Mass spectra were obtained on a CEC model 21-110 instrument.

1,3,5-*Trimethyl*-1,3,5-*triethylcyclotrisilthiane* (*I*)

Methylethyldichlorosilane (87 ml, 0.64 mol) was added to pyridine (115 ml, 1.43 mol) in 500 ml of dry cyclohexane in a three necked flask fitted with a reflux condenser and gas inlet tube. Hydrogen sulfide was passed through the solution for 3 h. The solution warmed as hydrogen sulfide passed into the solution and slowly cooled to room temperature as pyridine hydrochloride precipitated from solution. Pyridine hydrochloride was separated from the solution by filtration and the solvent distilled at 80° leaving a viscous yellow liquid. This liquid was purified by distillation (b.p. 128°/0.5 mmHg) and consisted of only one component by GLC. This colorless oil was characterized as 1,3,5-trimethyl-1,3,5-triethylcyclotrisilthiane (I) by its elemental analysis, molecular weight in solution, mass spectrum, and PMR spectrum. (Found: C, 34.8, H, 7.7. Mol.wt., 312 ± 11. $C_9H_{24}Si_3S_3$ calcd.: C, 34.6; H, 7.7%. Mol.wt., 313.) Mass spectrum: *m/e* 312 (P^+, 1.36%); 297 ($P^+ - 15$, 4.02%); 283 ($P^+ - 29$, 100%). The PMR data are presented in Table 1 and the spectrum is shown in Fig. 3.

1,3-*Dimethyl*-1,3-*diethylcyclodisilthiane* (*III*), (*IV*)

A sample of 1,3,5-trimethyl-1,3,5-triethylcyclotrisilthiane (I) was refluxed at atmospheric pressure for 3 h. The PMR spectrum contained a single methyl proton resonance at 9.38 τ initially and a single ethyl proton resonance. The liquid was refluxed at 0.1 mmHg pressure in a flask filled with a short Vigreux column and a variable reflux ratio fraction cutter head. During 4 h of heating the head temperature rose from 35 to 58°. A fraction boiling at 58°/0.1 mmHg was collected. This fraction was characterized as a mixture of *cis*- and *trans*-1,3-dimethyl-1,3-diethylcyclodisilthiane in approximately equal proportions by its PMR spectrum in solution and its mass spectrum in the vapor phase. The 60 MHz PMR spectrum of this liquid in carbon disulfide contained a single methyl proton resonance at 9.32 τ obtained under routine scan conditions. The spectrum also contained a single resonance at 8.96 τ. The PMR spectrum of this liquid in carbon disulfide obtained at 100 MHz is presented in Fig. 5. This spectrum consisted of two closely spaced resonances at 0.664 and 0.672 τ of approximately equal intensity and a complex multiplet centered at 8.96 τ. Mass spectrum *m/e*: 208 (P^+, 19.8%); 193 (P^+ −15, 8.28%); 179 (P^+ −29, 100%); 151 (P^+ −57, 36.7%).

The temperature at the reflux head increased to 155°/0.1 mmHg and a liquid slightly yellow in color was collected. This liquid was characterized as 1,3,5-trimethyl-1,3,5-triethylcyclotrisilthiane (I) by its PMR spectrum.

1,3,5-*Trimethyl*-1,3,5-*trivinylcyclotrisilthiane* (*II*)

Methylvinyldichlorosilane (81.5 g, 0.598 mol) was added to a solution of pyridine (125 ml, 1.54 mol) in 600 ml of cyclohexane in a three necked flask fitted with a reflux condenser and gas inlet tube. Hydrogen sulfide was passed through this solution for 2 h. During this time the temperature of the reaction mixture rose to 45° and returned to room temperature. Pyridinium hydrochloride that formed during this time was separated from the reaction mixture by filtration and the solvent removed on a rotary evaporator leaving a tan liquid. This liquid was purified by distillation through a 12 cm column filled with glass helices (b.p. 102–105°/0.5 mmHg). This liquid was demonstrated to be free from impurities by GLC. The liquid was characterized as 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilthiane (II) by elemental analysis, solution molecular weight, and spectroscopic properties. (Found: C, 34.6; H, 5.9. Mol.wt., 305±8. $C_9H_{18}Si_3S_3$ calcd.: C, 35.2; H, 5.9%. Mol.wt., 307.) Mass spectrum *m/e*: 306 (P^+, 6.7%); 291 (P^+ −15, 59.6%); 279 (P^+ −27, 41.2%); 252 (P^+ −54, 100%). The PMR spectra are shown in Fig. 2 and tabulated in Table 1.

1,3-*Dimethyl*-1,3-*divinylcyclodisilthiane* (*V*), (*VI*)

A sample of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilthiane (II) was placed in a distillation apparatus consisting of a short Vigreux column fitted with a variable reflux ratio fraction cutter heat. After refluxing for 4 h, a fraction boiling at 71°/0.1 mmHg was collected. This liquid was characterized as a mixture of *cis*- and *trans*-1,3-dimethyl-1,3-divinylcyclodisilthiane (V), (VI) in equal proportions by its PMR spectrum in solution and its mass spectrum in the vapor phase. The PMR spectrum of this liquid consisted of two sharp resonances at 9.21 and 9.24 τ and a complex multiplet centered at 3.92 τ. This spectrum is shown in Fig. 4. The integrated areas under the two methyl proton resonances and the vinyl resonances were equal. Mass spectrum, *m/e*: 204 (P^+, 27.5%): 189 (P^+ −15, 100%); 177 (P^+ −27, 24.5%).

A second fraction boiling over the range 80–105°/0.1 mmHg was collected. The PMR spectrum in the methyl region contained resonances at 9.21 9.24 τ and multiplets consisting of three resonances each with an area ratio of 1/2/1 respectively at 9.27, 9.34 and 9.50 τ. These multiplets were similar to the spectrum shown in Fig. 2. The contents of the distillation pot solidified upon cooling. This solid melted in the range of 95–120° including some material that did not melt at 200°. The material was characterized as polymeric methylvinylsilthiane by its analysis. (Found: C, 34.2; H, 6.0. $[CH_3(C_2H_5)SiS]_n$ calcd.: C, 35.2; H, 5.9%.)

Effect of temperature on product distribution of methylvinylcyclosilthianes

When methylvinyldichlorosilane was treated with hydrogen sulfide in refluxing cyclohexane (80°) in the presence of pyridine, a crude product mixture was obtained whose PMR spectrum in carbon tetrachloride contained resonances at 9.21, 9.24 τ and multiplets of three resonances centered at 9.27, 9.34 and 9.50 τ.

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