THE SYNTHESIS AND CHARACTERIZATION OF SOME N-SUBSTITUTED CYCLOSILOXAZANES AND CYCLODISILAZANES

> Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY TERENCE J. SWIHART 1969







ABSTRACT

THE SYNTHESIS AND CHARACTERIZATION OF SOME N-SUBSTITUTED CYCLOSILOXAZANES AND CYCLODISILAZANES

By

Terence J. Swihart

In recent years reports concerning attempts to prepare N-alkali cyclosiloxanes and their silyl derivatives have appeared. These reports list attempted reactions of sodium amide or phenyllithium with cyclosiloxazanes. This approach was unsuccessful and resulted in the indiscriminate cleavage of siloxane bonds.

This work describes the preparation of some N-lithium salts of polydimethylcyclosiloxazanes and their rearrangement in tetrahydrofuran to form cyclodisilazanes. Also described is the preparation of some silyl derivatives of cyclosiloxazanes and cyclodisilazanes.

It has been found that stoichiometric conversion of polydimethylcyclosiloxazanes to the N-substituted lithium salt proceeds at 25° with <u>n</u>-butyllithium in <u>n</u>-hexane. Further, the lithium salt, 2,2,4,4,6,6-hexamethyl-5-lithio-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane, has been shown to react with triorganohalosilanes in a mixture of tetrahydrofuran (THF) and <u>n</u>-hexane at 25° to yield the N-substituted triorganosilyl derivative, reaction (i).

$$Me_{2}Si(OSiMe_{2})_{2}NH + \underline{n}-BuLi \xrightarrow{THF} Me_{2}Si(OSiMe_{2})_{2}N-Li + Butane$$

$$LiCl + Me_{2}Si(OSiMe_{2})_{2}N-SiMe_{2}Vi \xrightarrow{THF, \underline{n}-hexane} (i)$$

While the reaction of triorganohalosilanes with 2,2,4,4,6,6,-8,8-octamethyl-3,7-dilithio-1,5-dioxa-3,7-diaza-2,4,6,8tetrasilacycloöctane, or with 2,2,4,4,6,6,8,8-octamethyl-7lithio-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacycloöctane results in a ring contraction according to the reactions (ii) and (iii) below.



It has further been shown that the reaction of 2,2,4,4,6,6,8,8octamethyl-3,7-dilithio-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacycloöctane with dimethyldichlorosilane yields a crystalline polymer of low molecular weight containing cyclodisilazane units along the backbone of the polymer. The reaction and proposed structure is presented below.



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AND CYCLODISILAZANES

Ву

Terence \mathbf{J} . Swihart

A THESIS

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Dedication

To My Grandparents, John and Angeline Kowalczyk

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NOMENCLATURE

The organosilicone compounds reported herein are named according to the ACS draft No. 10, of July 5, 1968, which is based on IUPAC Comptes undus de la Quinzieme Conference, Amsterdam (1949), pages 127-132. Rule D-421 was followed which describes the use of replacement nomenclature in subsection C-0.6 (cf. rule B-4).

Examples:

Linear chains

7 6 5 4 3 2 1 H₃Si-NH-NH-CH₂-SiH₂-S-SiH₃

2-Thia-5,6-diaza-1,3,7-trisilaheptane

<u>Rings</u>



2,2-Dimethyl-1-oxa-4-thia-2-silacyclohexane-6-one



2,2,4,4,6,6-Hexamethyl-5-trimethylsilyl-1,3-dioxa-5-aza-

2,4,6-trisilacyclohexane.

I. INTRODUCTION

As it would be impractical to survey the entire field of silicon-nitrogen chemistry, reference is given to R. Fessenden and J. S. Fessenden who present an excellent review article in the area of silicon-nitrogen chemistry through December of 1959 (1). The silicon-nitrogen chemistry which does, however, relate to this thesis is outlined in the following paragraphs.

Silicon-nitrogen chemistry had been, until the late 1950's, an area of neglect. This is surprising when one considers the abundant possibilities inherent in siliconnitrogen chemistry. The recent upsurge of research in this area is due in large part to the advent of commercially available siloxane materials, which require as starting materials large quantities of various chlorosilanes. Chlorosilanes are also the chief starting materials used in the preparation of silicon-nitrogen compounds.

Silicon-nitrogen compounds are most generally prepared by the reaction of an \equiv SiCl group with an H-N= group.

 $R_3SiCl + 2 R'NH_2 R_3SiNHR' + R'NH_3Cl.$

This reaction is reversible, the halosilane being obtainable from the silylamine and the amine salt (2,3). It has been

shown that the bromo- and iodo-silanes are more reactive towards a given amine than the corresponding chlorosilane (4).

It is interesting to note that the silicon-nitrogen bond is unique in the sense that a mesomeric equilibrium involving the $d\pi$ -p π orbitals of silicon and nitrogen, respectively, is established (5).

This interaction of $d\pi$ -p π orbitals imparts a type of double bond character to the silicon-nitrogen bond (6).

$$-\sin N$$
 \rightarrow $-\sin \theta = N$

The extent of this $d\pi$ -p π interaction is in large measure dependent upon the nature of the substituents on silicon (7,8,9,10).

The type and degree of organic or halide substitution on silicon also affects the chemical reactivity of chlorine on silicon (11). Normally halosilanes react rapidly with secondary and primary amines, with the exception of fluorosilanes which have been found to react only with metallated amines (12,13).

Tertiary amines do not react with halosilanes but do, however, interact with the tri- and tetra-halogenated silanes to form various complexes (14,15,16,17).

Ammonia reacts with most halosilanes to form silylamines.

 $R_3SiX + 2 NH_3 \longrightarrow R_3SiNH_2 + NH_4X$

The stability of silylamines towards silazane formation

appears to be very dependent upon steric factors. For example,

 $H_3SiCl + 2 NH_3 \longrightarrow 1/3(H_3Si)_3N + 2/3NH_3 + NH_4Cl (22).$

Silazane formation is generally thought to occur by way of condensation of the silylamines (6).

 $2R_3SiNH_2 \longrightarrow (R_3Si)_2NH + NH_3$

Krüger and Rochow capitalized on the condensation behavior of silylamines to prepared cyclopolydimethylsiloxazanes from α, ω -dichloropolydimethylsiloxanes (23).



A more recent paper by J. G. Murray and R. K. Griffith describes the preparation of dimethyl and phenylmethyl homopolymer and diphenyldimethyl copolymer cyclic siloxazanes (24).

Of the many reactions which silazanes and siloxazanes undergo, that of metallation of the nitrogen linked to silicon is especially interesting. These materials, silyl substituted alkali metal amides, are easily prepared by the metallation of bis(silyl)amines with organic alkali metal compounds, alkali amides and alkali hydrides (25-29).

 $(R_3Si)_2NH + NaNH_2 \longrightarrow (R_3Si)_2NNa + NH_3$ $(R_3Si)_2NH + NaH \longrightarrow (R_3Si(_2NNa + H_2)$ $(R_3Si)_2NH + R'Li \longrightarrow (R_3Si)_2NLi + R'H$ (where R' = propyl, butyl or phenyl)

The alkali metals themselves will also function as metallating agents for bis(silyl)amines in special cases (12,30). This approach requires a suspension of the alkali metal in styrene or in a naphthalene-tetrahydrofuran mixture.

These metallated silyl-substituted alkali metal amides are unique intermediates which are used primarily for the synthesis of materials otherwise made with great difficulty (31-35).

W. Fink of Monsanto extended the techniques developed for the preparation of linear silyl-substituted alkali metal amides to the preparation of mono-, di-, tri-, or tetra-N-lithio cyclosilazanes (36). The addition of the appropriate amount of chlorotrimethylsilane to these materials yielded N-silyl-substituted cyclosilazanes (36,37).



cyclosilazane.

Breed and Elliot, and at a later date W. Fink, used this approach to prepare some N-chlorodimethylsilyl derivatives of cyclosilazanes (37,38). Upon further exploration of this chemistry, W. Fink found the reaction of dichlorodimethylsilane with the dilithiated cyclotrisilazane to yield 1,3bis(chlorodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane rather than the expected silylated cyclotrisilazane.



+ $[Cl-Me_2Si]_2NH$ + 2 LiCl

It is interesting to note that 1,3-bis(chlorodimethylsilyl)-2,2,4,4,-tetramethylcyclodisilazane can be prepared directly from the reaction of hexamethylcyclotrisilazane with



Related to the work of Breed, Elliot, and Fink, is the attempt by Rochow and Krüger to metallate cyclosiloxazanes. Rochow and Krüger report that attempted metallation of cyclosiloxazanes with phenyllithium and sodium amide in refluxing n-hexane results in the cleavage of the silozane bond (22). In support of these findings Wannagat reports the cleavage of the Si-O bond in attempts to metallate bis(alkoxysilyl) amines with organolithium compounds (40). J. F. Hyde has also reported the cleavage of siloxane bonds with sodium amide under rather drastic conditions (41). Until very recently there was no literature information which outlined the metallation of a linear or cyclic siloxazane. The first report of the successful metallation and silylation of cyclosiloxazanes was made at the 1968 Spring American Chemical Society Meeting in San Francisco. The reported work was drawn from a portion of this thesis and was reported by this author.

dichlorodimethylsilane (39).

Shortly thereafter a brief communication was published by R. P. Buch, N. C. Lloyd and C. A. Pearce which indicates the reaction of butyllithium with some cyclosiloxazanes, as did we, and also indicates the disproportionation and subsequent ring contraction of some of these salts during their reaction with monochlorosilanes to yield cyclodisilazane structures (42). No characterization data is presented. Also no mention is made of the preparation of polymeric materials from the lithiated cyclosiloxazanes, which is outlined in this thesis.

II. RESEARCH OBJECTIVES

The primary purpose of this research was to describe a technique which would facilitate the metallation of siloxazanes. These metallated siloxazanes could serve as reactive intermediates from which new compounds could be synthesized.

The possible reaction of metallated siloxazanes with various chlorosilanes would be of particular interest.



If it could be demonstrated that this reaction occurs with a high degree of specificity, new areas of research would be opened.

Should the following two factors established;

- that the metal salts of the siloxazanes can be prepared,
- (2) that the metal salts of the siloxazanes react specifically in the manner,

 $(\equiv si)_2 NLi + Clsi \equiv \longrightarrow (\equiv si)_3 N + LiCl,$

then a reaction of the following type, to demonstrate the

possibility of preparing block copolymers would be attempted.



The possibility of being able to exercise very exact structural control in the preparation of new polymers and true block copolymer systems via the above reaction is immediately apparent. The preparation of such materials is the suggested third phase of this research.

Contraction (Second

III. PART I. THE PREPARATION OF α,ω-DICHLOROPOLY-DIMETHYLSILOXANES AND THE CONVERSION OF THESE MATERIALS TO POLYDIMETHYLCYCLOSILOXAZANES

A. Experimental

1. Preparation of α, ω -Dichloropolydimethylsiloxanes

a. <u>Materials</u>

Polydimethylcyclosiloxanes obtained from the Dow Corning Corporation were used without further treatment. The hydrogen chloride was a product of the Mathieson Company and was of 99% minimum purity.

b. Synthesis and Characterization

The α, ω -dichloropolydimethylsiloxanes were prepared according to the method of J. F. Hyde and P. L. Brown (43). This is a high pressure equilibration technique. Eight liters of a mixture of polydimethylcyclosiloxanes was added to two liters of distilled water and allowed to react under 250 p.s.i. of HCl for seven hours at 25[°] in a sixteen liter glass-lined pressure kettle. The pressure kettle was equipped with a pressure and temperature gauge. The pressure and temperature were recorded automatically as a function of time. The pressure kettle was stirred continuously during the seven hour reaction time. The stirrer was sealed with a mechanical rotating seal produced by the Durasal Company.

After the materials had been equilibrated for seven hours stirring was discontinued. The aqueous phase was then separated from the siloxane phase, under pressure, through a drain attached to the bottom of the kettle. The pressure on the kettle was relieved through a vent valve and the chlorosiloxane phase was drained into two four liter glass containers. A partial vacuum was applied to each container to remove any dissolved HCl. A five liter ground glass onenecked flask, equipped with a thermometer well, was charged with 3430 grams of the prepared α,ω -dichloropolydimethylsiloxanes. This charged flask was attached to a five-foot distillation column, 7.5 cm inner diameter; packed with porcelein saddles. The distillation column was equipped with a distillation head, an automatic take off device, and a fraction cutter.

The boiling point, per cent Cl as an indication of stoichiometry, and the calculated and found molecular weight based on the end group analysis, was compiled in Table I. Figures 1-4 represent the vapor phase chromatographs of the distilled fractions which were used as intermediates. The per cent hydrolyzable chlorine was determined by titration to the phenolphthalein end point with 0.1 N alcoholic KOH in a 50/50 ethanol-water hydrolysis medium.

The vapor phase chromatograph used in this work and in the identification of all of the volatile compounds was an F and M 500, equipped with a 2' x 1/4" column packed with

TABLE I

	Boiling	Per ce	nt Cl	Molecular	Weight
ClMe ₂ Si(OSiMe ₂) _x Cl	Point	Calc'd	Found	Calc'd	Found*
X = 1	42.5 ⁰ at 21 mm	34.97	34.92	203	203
X = 2	75.5 ⁰ at 16 mm	25.63	25.53	277	278
X = 3	101 ⁰ at 13 mm	20.22	20.20	351	351
X = 4	116.5 ⁰ at 7.5 mm	16.70	16.68	425	425

* Molecular weight found is based on end group analysis for per cent hydrolyzable chlorine.



Figure 1. Vapor phase chromatograph of 1,3-dichloro-1,1,3,3tetramethyl-2-oxa-1,3-disilapropane.



Figure 2. Vapor phase chromatograph of 1,5-dichloro-1,1,3,3,5,5-hexamethyl-2,4-dioxa-1,3,5trisilapentane.



Figure 3. Vapor phase chromatograph of 1,7-dichloro-1,1,3,3,4,4,7,7-octamethyl-2,4,6-trioxa-1,3,5,7tetrasilaheptane.



Figure 4. Vapor phase chromatograph of 1,9-dichloro-1,1,3,3,5,5,7,7,9,9-decamethyl-2,4,6,8-tetraoxa-1,3,5,7,9-pentasilanonane.

chromosorp W. The conditions were kept constant throughout the research reported herein. Sample size = $1 - 10 \ \mu$ l. heating rate = $21^{\circ}/\text{min.}$, flow rate = $60 \ \text{ml. of } N_2/\text{min}$, 100 milliamps, temperature range $75-300+^{\circ}$.

2. The Preparation of Some Polydimethylcyclosiloxazanes

a. <u>Materials</u>

The preparation, identification and purification of the starting materials, the α, ω -dichloropolydimethylsiloxanes, is outlined in Part I experimental section A. <u>n</u>-Hexane, dried over sodium metal, was used as a solvent without any further treatment. Ammonia gas obtained from the Mathieson Company was dried over alkaline earth hydroxides prior to being used.

b. Synthesis and Characterization

The general procedure used for the preparation of the polydimethylcyclosiloxazanes is outlined below. The apparatus used was a three liter, three necked flask equipped with a reflux condenser, stirrer, sparger and addition funnel. The α, ω -dichloropolydimethylsiloxanes in <u>n</u>-hexane were converted to polydimethylcyclosiloxazanes by treatment with ammonia gas at atmospheric pressure. The <u>n</u>-hexane solution containing the starting material was slowly added to a large volume of <u>n</u>-hexane which was constantly swept with ammonia gas. After the addition of the starting material was discontinued and the reaction mixture was filtered to remove the ammonium chloride.

The ammonium chloride and the product, is formed according to the following reaction:

The reaction temperature during the ammination process was maintained below 30° C by controlling the rate of addition of the α, ω -dichloropolydimethylsiloxane. After the product was filtered, the filtrate was vacuum distilled at less than 25° to remove the volatile ammonia gas and n-hexane. The materials were then purified by vacuum distillation. Table II lists the compounds which were isolated. Table III lists the calculated and found per cent C, H, N and Si. Some of the physical properties of the pure materials are listed in Table IV. The distilled yield of the prepared materials is also listed in Table IV and is based on the amount of starting α, ω -dichloropolydimethylsiloxane. Infrared spectra were obtained on each pure material and is presented in Figures 5-10. The infrared and H^1 nuclear magnetic resonance (H^1 nmr) data obtained on these materials is discussed in the following sections.



STRUCTURE REPRESENTATION OF THE POLYDIMETHYLCYCLO-SILOXAZANES PREPARED AND ISOLATED

TABLE II



- (I) 2,2,4,4,6,6-Hexamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane.
- (II) 2,2,4,4,6,6,8,8-Octamethyl-1,3,5-trioxa-7-aza-2,4,6,8tetrasilacycloöctane.
- (III) 2,2,4,4,6,6,8,8,10,10-Decamethyl-1,3,5,7-tetraoxa-9aza-2,4,6,8,10-pentasilacyclodecane.
 - (IV) 2,2,4,4,6,6,8,8-Octamethyl-1,5-dioxa-3,7-diaza-2,4,6,8tetrasilacycloöctane.

continued

- (V) 2,2,4,4,6,6,8,8,10,10,12,12-Dodecamethyl-1,3,7,9tetraoxa-5,11-diaza-2,4,6,8,10,12-hexasilacyclododecane.
- (VI) 2,2,4,4,6,6,8,8,10,10,12,12-Dodecamethyl-1,5,9-trioxa-3,7,11-triaza-2,4,6,8,10,12-hexasilacyclododecane.
TABLE III

CHARACTERIZATION DATA OF THE POLYDIMETHYLCYCLOSILOXAZANES PREPARED

				lemental Analy	sis			
	•	Calculat	:ed			Found		
Compound	υ	Н	N	Si	с С	Н	N	Si
		- P ercenta	ıge			Percent	age	8
(<u>I</u>)	32.58	8.60	6.33		37.6 37.8	8.35 8.40	5.84 5.90	
(11)	32.54	8.47	4.74	1	32.9 32.7	8.73 8.64	4.45 4.46	; ;
$(\overline{111})$	32.52	8.40	3.79	1	32.8 32.8	8.40 8.32	3.67 3.69	ł
(<u>11</u>)	32.65	8.84	9.52		32.8 32.8	9.30 9.27	9.26 9.19	
(<u>۸</u>	32.57	8.59	6.33	38.1	32.3 32.4	8.83 8.78	6.42 6.47	37.8
$(\overline{I\Lambda})$	32.65	8.84	9.52	38.0	32.7 32.3	9.16 9.21	9.36 9.32	39.0

Per cent Yiel 40.4 72.4 29.0 52.0 10.2	Refractive Index at 25 ⁰ 1.4065 1.4117-8 1.4145 1.4292-3* 1.4220-1	Boiling Point 36 ⁰ at 5.3 mm 40 ⁰ at 0.7 mm 58 ⁰ at 0.3 mm 51 ⁰ at 0.65 mm 73-75 ⁰ at 0.15 mm
10.2 5.2	1.4220-1 1.4355-6	73-75 ⁰ at 0.15 mm 92 ⁰ at 0.45 mm
C 02	* 1 0007 7	51 ⁰ at 0 65 mm
29.0	1.4145	58 ⁰ at 0.3 mm
72.4	1.4117-8	40 ⁰ at 0.7 mm
40.4	1.4065	36 ⁰ at 5.3 mm
Per cent Yiel	Refractive Index at 25 ⁰	Boiling Point

TABLE IV

SOME PHYSICAL PROPERTIES OF THE POLYDIMETHYLCYCLOSILOXAZANES PREPARED

Compound IV is solid at room temperature, * Refractive index run on super-cooled liquid. melting point of (IV) is 37⁰

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B. General Discussion

The class of compounds known as cyclosiloxazanes have steadily attracted the attention of an increasing number of scientists since the first cyclosiloxazane was prepared in 1959 by Sokolov' (44).

An extension of this interest in the use of polydimethylcyclosiloxazanes as intermediates for the preparation of N-substituted organosilylcyclosiloxazanes, prompted the synthesis of a series of known and new polydimethylcyclosiloxazanes for use as reactive intermediates.

These materials were prepared according to Rochow (23) wherein the α, ω -dichloropolydimethylsiloxanes were amminated in an organic solvent. The desired cyclosiloxazanes were produced in fair yields.

$$Me$$
x ClSi(OSiMe₂)_zCl + 3x NH₃
Me
25^o
n-hexane
H Me
(OSiMe₂)_z
+ 2x NH₄Cl
y

The cyclosiloxazanes which were prepared from the appropriate α, ω -dichloropolydimethylsiloxane are shown in Table II.

It is interesting to note that, although ammination of 1,5-dichloro-1,1,3,3,5,5-hexamethyl-2,4-dioxa-1,3,5-tri-silapentane produced compound (<u>I</u>) in a distilled yield of 40%,

the next highest homolog (\underline{V}) could not, at first, be isolated from the same reaction mixture. As can be seen in Figure 11 the presence of this compound or of compound (\underline{VII}) shown below was indicated by the vapor phase chromatograph of the reaction mixture.

 $\begin{array}{ccc} Me_{2} & H\\ I & I\\ H_{2}NSi(OSiMe_{2})_{2}N(OSiMe_{2})_{3}NH_{2} \end{array}$

(VII)

It is felt that the increased temperature required to effect distillation, did in fact effect the polymerization of compound (\underline{V}) due to the presence of NH₄Cl as a trace contaminant.

Rochow and Kruger have reported that NH_4Cl is a catalyst for the polymerization of cyclosiloxazanes to polysiloxazanes (23).



Thus, in the second attempt to prepare compound (\underline{V}) extreme care was taken, by more thorough filtration, to eliminate trace amounts ammonium chloride. This resulted in the successful isolation of compound (\underline{V}), and later compound (\underline{VI}) by distillation.



Figure 11. Vapor phase chromatograph of the ammination products of 1,5-dichloro-1,1,3,3,5,5-hexamethyl-2,4-dioxa-1,3,5-trisilapentane.

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1. H<sup>1</sup> Nuclear Magnetic Resonance Characterization Data
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The prepared cyclosiloxazanes listed in Table II were characterized by H^1 nuclear magnetic resonance (H^1 nmr) and by infrared. The spectroscopic data was found to be in complete agreement with the proposed structures for compounds (<u>I-VI</u>).

The H¹nmr data is presented in Table V, and are without any peculiarity.

The accumulated H^1 nmr data on the cyclosiloxazanes allows some assignment of τ values. The absorption in the range from 9.08 to 9.11 τ in compounds (<u>II</u>), (<u>III</u>), and (<u>V</u>) is attributed to the methyl groups near adjacent siloxane and silazane groups. This premise is based primarily on the H^1 nmr analyses of compounds (<u>III</u>) and (<u>V</u>). As can be seen from the structure of compound (<u>III</u>), a 2 to 3 proton mole



ratio of Me¹ to Me², respectively, is expected. The experimentally measured proton ratio is 12.2 to 17.8 as expected, at τ values of 9.910 and 9.943, respectively. This yields a 2 to 3 molar ratio of Me¹ to Me² as predicted by theory.

TABLE V

Compound	<u>Hydrogen</u> Prot Theory	<u>ton Ratios</u> Found	τ
$(\underline{I}) \overset{**}{Me_2} \overset{Me_2}{\underset{N}{SiMe_2}} $	$\frac{Me^{*}}{Me^{**}} = \frac{6}{12}$	1 peak	9.900
** Me ₂ Si-O-SiMe ₂ (<u>II</u>) H-N O ** * Me ₂ Si-O-SiMe ₂	$\frac{Me^*}{Me^{**}} = \frac{12}{12}$	<u>12.2</u> 11.8	9.947* 9.911**
$(\underline{III}) \qquad Me_{2}^{*}Si - O - SiMe_{2}^{*}$ $(\underline{III}) \qquad 0 \qquad 0$ $Me_{2}^{*}Si \qquad SiMe_{2}^{*}$ $N - H$ Si Me_{2}^{*}	$\frac{\text{Me*}}{\text{Me**}} = \frac{18}{12}$	<u>17.8</u> 12.2	9.943* 9.910**
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1 peak	1 peak	9.930
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\frac{Me^*}{Me^{**}} = \frac{12}{24}$	$\frac{11.7}{24.3}$	9.953 9. 9 08

H¹ NUCLEAR MAGNETIC RESONANCE DATA OF SOME PREPARED POLYDIMETHYLCYCLOSILOXAZANES

continued

Compound	<u>Hydrogen Proton</u> Theory	<u>Ratios</u> Found	τ
$(\underline{VI}) H-N$ $Me_2 Me_2 H Me_2$ $Si-O-Si-N-Si$ $Me_2 Me_2 H Me_2$	0 1 peak	1 peak	9.924

The assignment of the τ values in the range of 9.908-9.911 to the methyl protons adjacent to a silazane and siloxane group is in direct contradiction to a similar assignment made by Rochow and Krüger (45). Based on the available data at that time, Rochow and Krüger quite appropriately assigned the higher frequency absorption, at 9.950 τ , to the methyl protons adjacent to the silazane functions, and the lower frequency absorption at 9.915 τ to the methyl protons in a pure siloxane environment. These assignments were made based on the H¹nmr spectrum of the following compounds.

TABLE VI

H¹ NUCLEAR MAGNETIC RESONANCE DATA OF SOME KNOWN CYCLOSILOXÁZANES AND SILOXANES

		and the second secon
 Compounds	τ	
(Me ₂ SiO) ₃	9.883	
(Me ₂ SiNH) ₃	9.947	
(Me ₂ SiNH) ₄	9.953	
H Me ₂ Si-N-SiMe ₂ I O O	9.915,	9.950 (equal inten- sities, Rochow)
Me ₂ Si-O-SiMe ₂	9.911,	9.947 (equal inten- sities this th e sis)

Compounds (<u>IV</u>) and (<u>VI</u>) which contain only methyl groups adjacent to siloxane and silazane groups exhibit a H^1 nmr

absorption value which is intermediate (9.924-30) to compounds containing methyl silicon groups bordered by silazane or siloxane groups on both sides.

TABLE VII

THE ASSIGNMENT OF CHEMICAL SHIFTS TO SPECIFIC METHYL PROTONS FOR POLYDIMETHYLCYCLOSILOXAZANES

Compound Class	Grouping	τ value of H on C
$I \xrightarrow{H} Me_2 Me_2$ I $\xrightarrow{N-Si-O-Si}_{x=2,3}$	H Me Me N-Si-O-	9.924-9.930
$II - \begin{bmatrix} H & Me_2 \\ I & I \\ N-Si(OSiMe_2) \\ Y \\ Y \\ X \end{bmatrix} x$	H Me Me N-Si-O-	9.908-9.911
for; $y = 3$, $x = 1$	Me Me -0-Si-0-	9.943-9.953
y = 4, x = 1 y = 2, x = 2		

An exception to the above assignments is observed in the H^1 nmr spectrum of compound (I).



Based on the assignments in Table VII, a two to one proton ratio would be predicted at τ values of ~9.908 and ~9.948, respectively. Instead, this compound exhibits no splitting of its signal at 9.900 τ , which is near the expected absorp-H Me Me tion frequency for a N-Si-O grouping from compound class II. Compound (I) would be the first in the homologous series of compound class II where x = 1.

2. Infrared Characterization Data

The infrared data is consistent with the proposed structures (45). However, some peculiarities exist which heretofore have never been recognized in silicon chemistry, but are, however, quite common to carbon chemistry. This is discussed below.

Compounds (V) and (VI) exhibit an unusual double N-H stretching vibration at 3378 and 3347 cm⁻¹. Whereas compounds (I-IV) exhibit but one absorption, at 3410-3380 cm⁻¹, as expected. A splitting of the N-H stretching frequencies would normally be interpreted as an indication of the presence of \equiv Si-NH₂, which exhibits two hydrogen stretching frequencies between 3570 and 3380 cm⁻¹.

However the $-NH_2$ deformation at 1540 cm⁻¹, which is normally quite strong, is absent or at the best is very weak in compounds (<u>V</u>) and (<u>VI</u>). These results, in conjunction with the excellent structure confirmation of compounds (<u>V</u>) and (<u>VI</u>) by H¹nmr and by elemental analysis, would indicate the total absence of \equiv SiNH₂.

The splitting of the N-H vibrational frequency must then be interpreted as an indication of some form of hydrogen bonding of the hydrogen on nitrogen.

Either inter- or intra-molecular hydrogen bonding could be responsible for the splitting of the N-H vibrational frequency. This type of phenomenon is observed in many organic secondary amines, wherein splitting of the N-H vibration occurs because of hydrogen bonding.

Since this phenomenon seems to be unique to silicone chemistry, it was felt that it would be worthwhile to establish the form of the hydrogen bonding involved in compounds (\underline{V}) and (\underline{VI}) . Compound (\underline{V}) was therefore run by infrared at 0.1, 1.0 and 10.0 weight per cent concentrations in CCl₄.

The absorption ratio of the free to the hydrogen bonded N-H stretching vibrations at 3380 cm⁻¹ and 3340 cm⁻¹ respectively, were found to remain relatively constant (~1.38) over the entire concentration range. This ratio was found to decrease to 1.1 for compound (<u>VI</u>) at a ten weight per cent concentration in CCl_4 .



This implies an increase in the amount of hydrogen bonding relative to compound (\underline{V}). No attempt was made to determine the form or forms of hydrogen bonding existent in compound (\underline{VI}).

These data indicate some form of intramolecular hydrogen bonding as being largely responsible for the splitting of the N-H vibrational frequency in compound (\underline{V}). The construction of a molecular model from, Prentice-Hall, <u>Molecular</u> <u>Framework Models</u>, also indicates a favorable grometry for intramolecular hydrogen bonding in compounds (V) and (VI).



The geometry of compound (<u>IV</u>) as indicated by the <u>Molecular Framework Models</u> is unfavorable for the type of interaction displayed by compound (<u>V</u>). Compound (<u>IV</u>) as a result exhibits only the unassociated N-H vibrational frequency at 3400 cm⁻¹, as a ten weight per cent solution in CCl₄.

Based on these analysis it is concluded that the splitting of the N-H vibrational frequency of compound (\underline{V}) at 3380 cm⁻¹ and 3340 cm⁻¹ is in fact largely due to intramolecular hydrogen bonding of the hydrogen on nitrogen to

to the π electrons of another nitrogen atom in the ring.

The dodecamethylcyclohexasiloxazanes, exhibit but one very strong siloxane alborbance at 1062-1066 cm⁻¹. This is in contrast to dodecamethylcyclohexasiloxane (Me₂SiO)₆, which is the first member in the series of permethylcyclosiloxanes to exhibit splitting of the siloxane absorbance at 1097 cm⁻¹ (weak) and 1068 cm⁻¹ (strong). Splitting of the siloxane vibration is, however, exhibited by compounds (<u>II</u>) and (<u>III</u>), respectively.

Rochow and Krüger also reported a splitting of the SiOSi vibration for compound (<u>II</u>) (44). This phenomenon was explained as due to two different SiOSi angles in the same compound. The calculated values for some silazane and siloxane angles as reported by Rochow are presented in Table VIII along with other literature values. Compound (<u>II</u>) is included for comparison. Based on the shift to higher frequencies for compound (<u>III</u>) relative to compound (<u>II</u>) it is apparent that the two different siloxane bonds in compound (<u>III</u>) are much less strained than in compound (II).

This is to be expected since any ring strain in compound (<u>II</u>) would be relieved by a ring expansion via the insertion of a $-Me_2SiO-$ group into compound (<u>II</u>) to yield compound (III).

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	(Me ₂ SiNH) 4	(Me₂SiO)₄	(<u>I</u>) ×=2, y=0	<u>fме₂Si(OSiMe₂ (II) x=3,y=0</u>) x^{NH] y} . (<u>III</u>) x=4 , <u>y</u> =0	$\frac{(\underline{IV})}{x=1, y=0}$
vas, Si−OSi cm ⁻¹	ł	1078	1022	1065 1025	1088 1037	1050
Calcd bond angle	1	141.5	124 ⁰	137 ⁰ 125 ⁰	; ;	132 ⁰
Found bond angle		142.5 ± 50	ļ	!	}	1
Vas, SiNSi cm ⁻¹	928	ł	978	928	942	938
Calcd bond angle	118.5	}	133 ⁰	118.8 ⁰	ł	121.3 ⁰
Found bond angle	117 <u>+</u> 4 ⁰	1	1	ł	ł	1

A COMPARISON OF THE INFRARED SILOXANE ABSORPTION FREQUENCIES FOR SOME POLYDIMETHYLCYCLOSILOXAZANES

TABLE VIII

H MezSi-N-SiMez O MezSi _{Mez} inez 0-Si-O	т-	3390 3390 3390 11259 10081 10081 10081 10081 10081 10081 10081 10000 1000000
H MezSi-N-SiMez O MezSi-O-SiMez	bsorption Frequencies, cm	3390 23960 14412 12559 1028 934 8837 8837 862 694
MezSi-N-SiMez 0 0 0 SiMez	A	3410 2960 14209 14258 1403 990 808 803 803 803 803 803
		v N-H va C-H vs C-H čas CH3 čas CH3 čas CH3 čas StA3 vas SiOSi vas SiOSi vas SiOSi vas Si-C vas Si-C(?)

ACCUMULATED INFRARED SPECTRA OF SOME CYCLOSILOXAZANES

TABLE IX

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continued

Mez-Si-N-Si-Mez MezSi Mez-Si-O-Si-Mez Mez-Si-O-Si-Mez	es, cm ⁻¹	3380 3340 2964 1409 11257 11257 11257 11257 11252 873 873 873 700
$Me_{2}-Si-N-Si-Me_{2}$ $Me_{2}Si$ $Me_{2}Si$ $Me_{2}-Si-N-Si-Me_{2}$	Absorption Frequencie	3380 3340 2962 2966 1409 1257 1409 877 877 877 807
$Me_{z} - Si - N - Si - Me_{z}$ $Me_{z} - Si - N - Si - Me_{z}$ $Me_{z} - Si - N - Si - Me_{z}$		3380 2964 1409 1261 1261 1066 899 867 899 867 899 867 899 867 899
		v N-H v N-H va C-H vs C-H vs C-H čas CH3 čs CH3 čs CH3 vas SiNSi p CH3 p CH3 p CH3 p CH3 vas Si-C() vas Si-C()

TABLE IX--continued

IV. PART II. THE PREPARATION OF SOME N-SUBSTITUTED LITHIUM SALTS OF POLYDIMETHYLCYCLOSILOXAZANES

A. Experimental

1. Materials

The preparation and purification of the polydimethylcyclosiloxazane starting materials is described in Part I. Reagent grade <u>n</u>-hexane obtained from the Fisher Scientific Company was used as a solvent without further treatment. Butyllithium was obtained from the Foote Chemical Company and was used without any further treatment. It is sold as 15.18% butyllithium in <u>n</u>-hexane, the specific gravity being approximately 0.68 g./ml. at 25° .

2. Synthesis and Characterization

The general technique used for the preparation of lithium salts of the polydimethylcyclosiloxazanes is outlined below. A sample of distilled cyclosiloxazane was weighed in a 60 ml. flask. A rubber stopper, containing a piece of glass tubing and equipped with a septum, was inserted into the neck opening of the flask. The system was then purged with dry nitrogen gas, with the septum removed, through a vent leading from the side of the neck of the flask. Upon completion of the nitrogen gas purge, the system was vented

to the atmosphere by connecting some tubing to the side arm on the flask. A tube filled with Drierite was attached to the tubing.

The appropriate number of moles of butyllithium was introduced through the septum with a calibrated syringe. The following reaction took place.

Reaction I

$$\xrightarrow{H}_{i}$$

$$\xrightarrow{-Si-N-Si-} + CH_3(CH_2)_3Li \xrightarrow{\underline{n}-hexane} CH_3(CH_2)_2CH_3 + \xrightarrow{}_{i}$$

$$\xrightarrow{-Si-N-Si-}_{Li}$$

The reaction is quite exothermic. However, it was possible to maintain the temperature below 30° by controlling the rate of addition of butyllithium, the lithium salt of the cyclic siloxazane precipitated from solution as a finely divided white solid. After the addition of butyllithium was completed, the reaction mixture was cooled to -60° C by using dry ice. The sample was then vacuum filtered at that temperature under a nitrogen atmosphere. The solid product was washed twice with small portions of <u>n</u>-hexane, cooled to -60° C, and once with <u>n</u>-hexane at 25° . The precipitate was then transferred to a glass container, sealed and weighed immediately to determine the amount of product obtained. The product was stored over CaSO₄ in a vacuum desiccator. A vacuum of 1 mm. was applied to the desiccator for two hours to remove trace amounts of <u>n</u>-hexane. The products were then removed for analysis. The lithium salts of the cyclosiloxazanes were characterized by their infrared and H¹nmr spectra and by per cent lithium. A list of the materials prepared is presented in Table X. The per cent yield based on the starting amount of the cyclosiloxazane, the ratio of the moles of butane found to moles of butane calculated according to Reaction I, and the per cent lithium as an indication of stoichiometry are listed in Table XI. The infrared spectra of compounds <u>VIII-XII</u> are presented in Figures 12-16. The H¹nmr spectra (and infrared data) are accumulated in Tables XIV and XII.

B. General Discussion

A variety of reactions describing the preparation of metallated disilazanes have been reported within recent years (25-29). These metallated disilazanes have been used primarily as reactive intermediates for the formation of tris(sily1)amines (31-35).

$[R_3Si]_2NNa + R_3SiCl \longrightarrow [R_3Si]_3N + NaCl$

Rochow (44), attempted to extend this work to the preparation of N-substituted sodium cyclosiloxazanes through the reaction of sodium amide or phenyllithium with the respective cyclosiloxazane in toluene or ether. These early attempts



STRUCTURE REPRESENTATION OF THE N-LITHIUM POLYDIMETHYLCYCLOSILOXAZANES PREPARED



- (<u>VIII</u>) 2,2,4,4,6,6-Hexamethyl-5-lithio-1,3-dioxa-5-aza-2,4,6trisilacyclohexane.
 - (<u>IX</u>) 2,2,4,4,6,6,8,8-Octamethyl-7-lithio-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacycloöctane.
 - (<u>x</u>) 2,2,4,4,6,6,8,8,10,10-Decamethyl-9-lithio-1,3,5,7tetraoxa-9-aza-2,4,6,8,10-pentasilacyclodecane.

continued



- (XI) 2,2,4,4,6,6,8,8-Octamethyl-3,7-dilithio-1,5-dioxa-3,7diaz-2,4,6,8-tetrasilacycloöctane.
- (XII) 2,2,4,4,6,6,8,8,10,10,12,12-Dodecamethyl-3,7,11trilithio-1,5,9-trioxa-3,7,11-triaza-2,4,6,8,10,12hexasilacyclododecane.

XI	
TABLE	

CHARACTERIZATION DATA OF THE N-LITHIUM POLYDIMETHYLCYCLOSILOXAZANES PREPARED

	Percei	nt Li	Moles of Butane Evolved According	Per cent
Compound	Calcd.	Found	to Reaction I, Ratio of Found/Calcd.	YleId
(IIIA)	3.08	3.05	1.18	94
	2.32	2.38	1.04	58
(X)	1.87	1.86	1.09	82
(<u>IX</u>)	4.54	4.79	1.08	93
(<u>IIX</u>)	4.54	4.18		94



Figure 12. Infrared spectrum of 2,2,4,4,6,6-hexamethyl-5-lithio-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane.



Figure 13. Infrared spectrum of 2,2,4,4,6,6,8,8-octamethyl-7-lithio-1,3,5-trioxa-7-aza-tetrasilacycloöctane.


Figure 14. Infrared spectrum of 2,2,4,4,6,6,8,8,10,10decamethyl-9-lithio-1,3,5,7-tetraoxa-9-aza-2,4,6,8,10-pentasilacyclodecane.



Figure 15. Infrared spectrum of 2,2,4,4,6,6,8,8-octamethyl-3,7-dilithio-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacycloöctane.



Figure 16. Infrared spectrum of 2,2,4,4,6,6,8,8,10,10,12,12dodecamethyl-3,7,11-trilithio-1,5,9-trioxa-3,7,11triaza-2,4,6,8,10,12-hexasilacyclododecane.

by Rochow were reported to result in cleavage of the siloxane bond and the subsequent formation of polymeric material, presumably a polysiloxazane.

Rochow and Krüger (44), further reported that there was no evidence for metallation of the disilazane linkage. However, these experimenters employed only non-polar solvents as the reaction media in their attempts to metallate the silazane linkage.

Since most of the available metallating agents are salts, it was felt that their reaction with the disilazane linkage could be enhanced by increasing the ionizing or polar character of the reaction medium.

Attempts to metallate compound (\underline{I}) with sodium amide, calcium hydride, sodium hydride and metallic sodium were therefore carried out in dry acetonitrile at 50°. Under these conditions there was no evidence for metallation of H the -N- group, nor was there any evidence for cleavage of the siloxane bond. The dimethylcyclosiloxazanes did not react in any manner under these conditions with any of the aforementioned metallating reagents. Each reaction was followed by vapor phase chromatography on a modified 710 F and M dual column chromatograph.

The work of W. Fink (36,37), wherein N-substituted lithiocyclosiloxazanes were prepared by treating hexamethylcyclotrisilazane with butyllithium, suggested a possible reaction between butyllithium and cyclosiloxazanes. It was felt that the reaction should be carried out at low temperature to minimize the possibility of siloxane cleavage, which was reported by Rochow in the reaction of phenyllithium with cyclosiloxazanes.

The following reaction was attempted and was found to proceed quantitatively in <u>n</u>-hexane at room temperature with the evolution of butane gas:

 $Me_{2}Si(OSiMe_{2}) + BuLi \xrightarrow{n-hexane}_{room temp} Me_{2}Si(OSi + N-Li) + Butane$

This reaction is general for a large number of cyclosiloxazanes. The compounds listed in Table X were prepared in high yields.

The metallation of the cyclosiloxazanes with butyllithium does not appear to lead to the formation of any species other than the products listed in Table X. This is evidenced by infrared, H^1 nmr per cent lithium, and the high yields of the desired species. A discussion of the characterization data is offered in the following sections.

C. Infrared Spectroscopic Analysis of the N-Substituted Lithium Salts of Polydimethylcyclosiloxazanes

The Si-C asymmetric vibration at 800-810 cm⁻¹ in the N-lithic cyclosiloxazanes corresponds to the previously reported values for related compounds such as the cyclo-siloxazanes and cyclosiloxazes (45). The Si-CH₃ symmetric

deformation, which commonly occurs from 1250-80 cm⁻¹, falls to frequencies of 1245-1253 cm⁻¹ for compounds (<u>VIII-XII</u>); this is unusually low for the Si-CH₃ deformation absorption frequency.

There is no indication of Si-Bu in the infrared spectra of compounds (<u>VIII-XII</u>). This is indicated largely by the absence of a strong absorption between 870-890 cm⁻¹ which is indicative of Si-Bu. Also the absorptions normally associated with Si-Bu at 1470 and 1390 cm⁻¹, which are largely in the same range as the Nujol absorptions, are not detectable as absorption shoulders on the Nujol peak.

This analysis is in agreement with the contention that no siloxane cleavage is observed in the reaction of butyllithium with the cyclosiloxazanes in <u>n</u>-hexane at 25° .

As in the case of the cyclosiloxazanes, the N-lithiocyclosiloxazanes also exhibit a splitting of the SiOSi vibration. The position of the dual absorbancies is apparently dependent upon the size of the ring, as well as the position and number of nitrogen atoms having displaced the oxygen atoms in the ring. In general the siloxane and silazane stretching vibrations shift to lower frequencies as the size of the ring is decreased. This is indicative of increasing ring strain as the ring size is reduced.

The observed dual SiOSi absorbances as a function of structure are presented in Table XII. As was previously mentioned in Part I, splitting of the siloxane vibration is also observed in high molecular permethylcyclosiloxanes.

Group			Compound		
Assignments	$(\overline{III}\overline{\Lambda})$	(<u>XI</u>)	(X)	(<u>IX</u>)	(\overline{IIX})
		Absorpt	ion Frequenci	es, cm ⁻¹	
н - и л	3360	3350	3350	3350	3380
စ်s CH ₃	1245	1250	1248	1248	1253
<i>λ</i> N-H) ?	1140	1165	1170	1160	1180
vas SiOSi	1022	1066	1075	1058	1115
vas SiOSi	985	1020	1020	1020	1075
vas SiNSi					066
vas SiNSi	905	928	932	945	950
ρ CH ₃				890	
p CH ₃		858	855	862	848
vas SiC	812	810	805	808	800
vas SiC	802				

TABLE XII

INFRARED SPECTRA OF SOME N-SUBSTITUTED LITHIOCYCLOSILOXAZANES

The absorption at $1140-1180 \text{ cm}^{-1}$ is difficult to explain. This is normally the position assigned to the N-H bending vibration. However, the N-H stretching frequency at 3340-3380 cm⁻¹ is extremely weak, indicating very little -SiNH- was formed as a result of hydrolysis of -SiNLi- while preparing the Nujol mulls. The SiBu group is known to absorb at 1190-1200 cm⁻¹ but the absorption typical of SiBu at 870-890 cm⁻¹ is absent from the infrared spectra.

D. The Determination of the Stoichiometry of the Metallation of Cyclosiloxazanes with Butyllithium

Experimental

A sample of distilled cyclosiloxazane was weighed in a 50 ml flask containing a side arm inlet equipped with a rubber septum. This flask was attached to a 100 ml calibrated gas burette. The system was purged with dry nitrogen after which a known amount of butyllithium was introduced through the septum from a calibrated syringe. Upon complete addition of the butyllithium the flask was shaken and then allowed to stand for one hour at 24.8°. The mercury levels in the gas burette was adjusted with the mercury reservoir during the evolution of the butane gas so as not to pressurize the system during the reaction. The difference between the final and the original mercury reading in ml was taken as the volume of butane evolved at 746 mm at 24.8°. The results for the cyclosiloxazanes run in this system are given in Table XIII. The volume of butane evolved at 746 mm was corrected to 760 mm using the gas law.

This data indicates the metallation of the cyclosiloxazanes is quantitative and proceeds according to reaction I below:



The data also show the following most probable side reactions do not occur to any extent, as might be measurable by the aforementioned technique, based on the moles of butane evolved.

 $\begin{array}{rcl} Me_{2}Si(OSiMe_{2}) & H \\ & H \\ & & \\ &$

That is, the reactions above would not require the evolution of butane--if either of these reactions were to occur in large measure then the established stoichiometry according to reaction I would be invalid.

The premise that the reaction is essentially quantitative is further substantiated by the high yields of compounds $(\underline{I}-\underline{V})$ and by the spectral data which are discussed in the following section.

uH Evolved Found	0.0026	0.00246	0.00193	0.00276
* <u>Moles of B</u> Calcd.	0.00221	0.00244	0.00198	0.00262
Volume (V.) of BuH Evolved, ml.	59.6	56 ° 0	43.8	63.0
(ml.) Final	62.8	58.8	44.0	64.2
<u>Hg level</u> Initial	3.2	2.8	0.2	1.2
Moles of BuLi Added	0.00283	0.00290	0.00210	0.00306
Moles of siloxazane	0.00221	0.00244	0.00198	0.00131
Cyclo- siloxazane	(<u>ī</u>)	$(\overline{11})$	(111)	

MOLES OF BUTANE EVOLVED FOR THE REACTION OF BUTYLLITHIUM WITH VARIOUS POLYDIMETHYLCYCLOSILOXAZANES

TABLE XIII

* Corrected to 760 mm.

E. <u>The Ring Contraction of Some N-Substituted Lithium</u> <u>Salts of Polydimethylcyclosiloxazanes</u>

W. Fink and Breed and Elliot indicate the N-substituted lithium cyclosilazanes, upon reaction with silylating reagents, undergo a disproportionation and subsequent ring contraction to yield the cyclodisilazane structure (46,47).

The recent work of Bush, Floyd and Pearce is related to that of Breed and Elliot, wherein some N-substituted lithium cyclosiloxazanes were reported to have undergone a ring contraction to yield cyclodisilazane structures (42). Compound (<u>XI</u>) was reported to have undergone "ring contraction" in 1,2-dimethoxyethane in six hours at room temperature. The reaction of this material with chlorotrimethylsilane yielded the cyclodisilazane.



These investigators attribute this ring contraction to a transannular nucleophilic rearrangement of the initially formed N-lithium salt as represented below.



Ring contraction of this sort does not occur to any measurable extent in <u>n</u>-hexane. This is evidenced by the absence of the typical (strong infrared) cyclodisilazane absorptions at 875-900 cm⁻¹ and at 1025 cm⁻¹ in the infrared spectra of the N•substituted lithium cyclosiloxazanes isolated from the reaction of butyllithium with the cyclosiloxazanes in <u>n</u>-hexane.

Also, the H¹ nmr data presented in Table III are consistent with the proposed structures for the N-lithium salts. The chemical shifts typical of N,N'-bis(dimethylsilyl)tetramethylcyclodisilazane structures are at approximately 9.75 and 10.00 τ for the ring methyls and the methyl groups on silicon adjacent to the ring, respectively (46).

Compound (<u>XI</u>), which is most likely to undergo ring contraction, shows but one peak at 9.829 τ . If in fact compound (<u>XI</u>) had formed the smaller ring, as in the example below, an integrated area ratio of 12:12 would be expected at τ 9.75 and 9.9-10.0.



Further evidence for the maintenance of the basic cyclosiloxazane structure, after lithiation, is indicated from the reaction of chlorodimethylvinylsilane with the isolated N,N'-dilithium salt, compound (XI), in THF at room temperature. The infrared spectrum (Figure 17) of the undistilled reaction product does not display the typical strong cyclodisilazane absorbtions at 875-900 cm⁻¹. Instead, it indicates that the following material is the primary product:

$$Me_{2}Si-O-SiMe_{2}$$

$$ViMe_{2}Si-N$$

$$Me_{2}Si-O-SiMe_{2}$$

which could only be formed from the corresponding N,N'-dilithium salt.

However, attempts to prepare the N-lithium salts of compounds (<u>II</u>) and (<u>IV</u>) in THF, followed by an <u>in situ</u> silylation of the salts with a monochlorosilane yielded only the siloxysilylated cyclotrisilozane and cyclodisilazane. The reaction scheme leading to these products of smaller ring size is written below.



Only compound (\underline{I}) yielded the expected silyl derivative when the above reaction scheme was followed.

These data indicate that the lithiation reaction can be controlled and directed by the proper choice of solvent for the reaction medium.

BuLi + $[Me_2Si(OSiMe_2)NH]_2 \xrightarrow{\underline{n}-hexane} [Me_2Si(OSiMe_2)NLi]_2$ BuLi + $[Me_2Si(OSiMe_2)NH]_2 \xrightarrow{\underline{n}-hexane} He_2$ BuLi + $[Me_2Si(OSiMe_2)NH]_2 \xrightarrow{\underline{n}-hexane} HF$

The various silulation reactions are discussed in the next section.

LOS I LOXAZANES	t Values	9.851a 9.798b	9.825a 9.849b	9.833 ^a 9.846b 9.857 ^c	9.829	9.801
TED LITHIUM CYC	ht Ratios Found	2.00 ^a 0.98 ^b	1.00 ^a 0.89 ^b	2.00 ^a 1.97 ^b 1.04 ^c	1 1 1	
SOME N-SUBSTITU	Peak Heig Calcd	2:1	с ,	2°2:1	1	
NANCE DATA OF S	of Peaks Found	2	N	м	Ч	τ
NETIC RESO	Number Calcd	2	N	ю	Ч	Ţ
H ¹ NUCLEAR MAG	Compound	(IIIA)	(X T)	(X)	(<u>x</u>)	(<u>TIX</u>)

TABLE XIV



Figure 17. Infrared spectrum of the reaction product of chlorotrimethylsilane and 2,2,4,4,6,6,8,8-octamethyl-3,7-dilithio-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacycloöctane.

V. PART III. THE PREPARATION OF SOME N-SILYL DERIVATIVES OF POLYDIMETHYLCYCLOSILOXAZANES AND OF POLYDIMETHYLCYCLODISILAZANES

A. Experimental--Procedure I

1. Materials

Tetrahydrofuran which was used as a solvent was freshly distilled from CaH_2 . The chlorosilanes used in these reactions were obtained from the Dow Corning Corporation and were distilled prior to being used.

2. Synthesis and Purification

The following technique was used for the preparation of all the distilled silv derivatives of the polydimethylcyclosiloxazanes.

A one liter, three-necked, round-bottom flask, equipped with a reflux condenser, stirrer, and an addition port stoppered with a rubber septum, was charged with a weighed amount of a cyclosiloxazane. To the cyclosiloxazane was added 200 percent by weight of tetrahydrofuran. The system was purged for five minutes with nitrogen gas, dried over CaSO₄. To this solution, with constant stirring, was added the correct number of moles of butyllithium from a glass syringe by slow addition through the addition port containing

the rubber septum. The temperature of the medium was maintained below 30° by controlling the addition rate of butyllithium. The reaction medium remained a homogeneous liquid system during and after the addition of the required amount of butyllithium for all polydimethylcyclosiloxazane systems investigated, with one exception. In the conversion of compound (<u>IV</u>) to its lithium salt, the lithium salt did not remain completely soluble in the THF-<u>n</u>-hexane solvent system. Instead, a portion or all of the lithium salt of compound (<u>IV</u>) precipitated from solution as a white, finely divided, solid.

After the addition of butyllithium was completed, the reaction mixture was stirred for from 0.5 to 2.5 hours at room temperature. A weighed amount of the desired monochlorosilane was then added dropwise from a 125 ml. addition funnel equipped with a drying tube. This reaction displayed an apparent induction period. No exothermic reaction is detected within the first five minutes after the addition of five to ten percent of the chlorosilane, nor is any lithium chloride precipitated from the reaction mixture. However, upon the addition of 20 to 25 per cent of the chlorosilane, a very exothermic reaction occurs with the immediate formation of lithium chloride.

Once the reaction has started, the addition of more chlorosilane results in the immediate formation of more lithium chloride and an increase in the temperature of the

reaction mixture. The temperature of the reaction mixture was maintained below 35[°] by regulating the addition rate of the chlorosilane. The chlorosilane was always added in a slight excess to insure the complete reaction of all lithium on nitrogen. After the addition of the chlorosilane was completed, the reaction mixture was stirred for one to two hours at room temperature. Ammonia gas dried over sodium hydroxide was passed into the reaction mixture to convert any unreacted chlorosilane to the disilazane according to the equation below.

 $2 R_3 SiCl + excess NH_3 (g) - NH_4 Cl + (R_3 Si)_2 NH$

This step was necessary because hydrogen chloride which could form from the hydrolysis of unreacted chlorosilane, would react with \equiv Si-N \equiv bonds. After the reaction mixture had been amminated, it was vacuum filtered to remove the lithium chloride and ammonium chloride. The calculated lithium chloride and ammonium chloride from the total reaction always correlated well with the observed values. The filtrate was strip distilled to remove the low boiling volatile solvents. Distillation over a spinning band column was used to purify the remaining high boiling product.

The silyl derivatives of the lithiated cyclosiloxazanes, which were isolated according to procedure A, are presented in Table XV. Table XVI lists the starting materials, procedure used, the product formed and the percent yields.

Other physical properties and the elemental analysis are presented (Table XVII). The spectral data is accumulated in Tables XVIII and XIX, Figures 18-21.

B. <u>Preparation--Procedure II</u>

A weighed amount of compound (XI) was placed in a large amount of THF. To this solution was immediately added the required amount of chlorodimethylvinylsilane to yield the N,N'-disilyl derivative of compound (XI). The reaction was exothermic. The reaction was allowed to proceed for one hour at room temperature after which the THF and unreacted chlorotrimethylsilane was removed under reduced pressure. The product was then filtered and analyzed by infrared. The infrared spectrum indicated the formation of the following material.

The analysis of the infrared spectrum is discussed in the following sections.

C. <u>General Discussion</u>

As was reported in Part II, the N-lithio derivatives of cyclosiloxazanes can be readily prepared and isolated from

TABLE XV

STRUCTURE REPRESENTATION OF SOME N-SILYL DERIVATIVES OF CYCLOSILOXAZANES AND CYCLODISILAZANES



Distilled	yield, per cent	67.0	74.5	81.6	75.0	
Droduct	Formed	$(\overline{\mathbf{XIII}})$	$(\overline{\Lambda IX})$	(<u>XX</u>)	(<u>I/X</u>)	$(\frac{1}{x^{\text{IINX}}})$
Drocedure	Used	A	A	A	A	а
Chlorosilane	Used	ViMe ₂ SiCl	ViMe ₂ SiCl	ViMe ₂ SiCl	Me ₃ SiCl	ViMe ₂ SiCl
Starting	Material	(<u>T</u>)	(11)	$(\overline{\Lambda I})$	$(\overline{\Lambda I})$	

TABLE XVI

CORRELATION CHART OF STARTING MATERIALS AND PRODUCTS FORMED FROM THE ATTEMPTED SILVLATIONS OF VARIOUS CYCLOSILOXAZANES

* See page 71.

	-	Refractive		Eler	nental A	Analysis -	7	
Compound	Boint	Index at 250	<u>%</u>	AH MH	NN	¥ 22	MH MH	NR N
(<u>IIIX</u>)	96 ⁰ at 11mm	1.4416	39.35	8.85	4.59	39.4 39.4	9.02 8.99	
$(\overline{\Lambda I X})$	107 ⁰ at 5mm	1.4328	37.99	8.70	3.69	37.4 37.6	8.69 8.50	3.53 3.60
(<u>x</u> x)	121.5 ⁰ at 3mm	1.4337	41.55	60.6	6.06	41.6 41.6	9.15 9.38	6.12 6.06
$(\overline{\mathbf{X}\mathbf{N}\mathbf{I}})$	115 ⁰ at 3mm	1.4205	38.35	9.58	6.49	38.1 38.5	9.75 9.66	6.31 6.28

TABLE XVII

CHARACTERIZATION DATA FOR THE N-SILYL DERIVATIVES OF CYCLOSILOXAZANES AND CYCLODISILAZANES

	(IIVX)	3370(v.w.)			1408(s) 1250(s)	1160(w) 1035(s)	 	955(s) 025/2)		 880(w)	840(w) 800(s)
	(<u>T/X</u>)	1	2960(s) 2902(w)	1 4 2 9 (tim)	1408(s) 1255(s)	1070(s)	1018(vs) 		890(s)	13)000	 802(s)
Compound	(<u>xv</u>)	8	3 058(w) 2960(s) 2900(w)	1590(w)	1408(s) 1252(s)	1068(s)	1015(vs) 950(w)		883 (s)	(m)040 	802
	$(\overline{\Lambda I X})$	1 1	3050(w) 2962(s) 2904(w)	1592(w)	1408(s) 1255(s)	 1025(s) *	 990(s)	945(s) 015(c)		870(w)	850(w) 804(s)
	(<u>IIIX)</u>	1	3050(w) 2962(s) 2904(w)	1590 (w)	1404(s) 1255(s)	 1029(s)	 990(s) 950(w)	932 (s) 94 2 (s)	12/370	870(w)	850(w) 804(s)
		н-и л	∨ С − Н	ט ק ט ט	óas CH ₃ ós CH ₃	γ N-H vas SiOSi	Vas Si ₂ N Vas SiOSi C-H	Vas Si ₂ N	V SizN	p CH ₃	p CH3 vas Si-C

CHARACTERISTIC INFRARED GROUP ABSORPTIONS FOR COMPOUNDS XIII-XVII

TABLE XVIII

^{*} Shoulder at ~1060 cm⁻¹.

SIV Me2

TABLE XIX

H¹ NUCLEAR MAGNETIC RESONANCE CHARACTERIZATION DATA





<u>n</u>-hexane. However, attempts to prepare the N-lithio derivative of compounds (<u>II</u>) and (<u>IV</u>) in THF followed by an <u>in situ</u> silylation with a monochlorosilane resulted in the rearrangement of the N-lithio derivative and subsequent ring contraction according to the reactions written below.

Of the cyclosiloxazanes treated according to procedure I, only the N-lithio derivative of compound (\underline{I}) yielded the expected product from THF according to the reaction below.

$$\begin{array}{c|c} Me_{2}Si(OSiMe_{2})_{2}NH & \xrightarrow{THF} & Me_{2}Si(OSiMe_{2})_{2}NSiR_{3} \\ \hline \\ 2) R_{3}SiCl & & & & & \\ \hline \\ (\underline{I}) & & & + LiCl \end{array}$$

Ring contraction of the N-lithio-derivative of compound (\underline{I}) very probably did not occur in procedure I since this would have necessitated the formation of a cyclodisiloxazane of the sort:

The formation of this compound would be energetically unfavored and in addition would be extremely reactive towards Li^+O^-Si , which would also be formed in tetrahydrofuran as a result of a ring contraction according to the reaction below.

Although the formation of compound (<u>XVIII</u>)^a is unlikely, the rearrangement of the N-lithio salts of cyclosiloxazanes affords an approach that could, under the correct reaction conditions, possibly yield a cyclodisiloxazane.

With relation to procedure II, it is important to note that the formation of the triorganosilyl derivative of compound (<u>IV</u>) without ring contraction was indicated by infrared. Procedure II was carried out by placing the N,N'-dilithio derivative of compound (<u>IV</u>), isolated from <u>n</u>-hexane, in THF and immediately treating the salt with an excess of chlorodimethylvinylsilane.

The reaction product, freed of volatiles, showed the typical absorption for the SiOSi assymetric vibration at 1035 cm⁻¹ and two strong absorptions at 935 cm⁻¹ and 955 cm⁻¹ for the two forms of Si₂N present in compound (<u>XVII</u>). The absorptions typical of the silyl-substituted cyclodisilazane at 880-900 cm⁻¹ and at 1015-1040 cm⁻¹ were not observed (Table XVIII).

These data indicate a critical rate dependence of the rearrangement of the lithiated cyclosiloxazanes to smaller rings upon the polarity or ionizing ability of the solvent reaction media. This explains why compound (<u>XVII</u>) was indicated by infrared when procedure II was employed. Other investigators have indicated that the ring contraction of the N,N'-dilithio salt of compound (<u>IV</u>) to the cyclodisilazane requires six hours in 1,2-dimethoxyethane. The ring contraction of that same salt in tetrahydrofuran is obviously much faster (Procedure I, page 68).

D. <u>A Discussion of the Spectral Data of 2,2,4,4,6,6</u>-<u>Hexamethyl-5-dimethylvinylsilyl-1,3-dioxa</u>-<u>5-aza-2,4,6-trisilacyclohexane</u> (XIII)

Compound (<u>XIII</u>) prepared according to Procedure I, was distilled in a yield of 67 per cent and was characterized by elemental analysis and by infrared and H^1 nmr. The infrared spectrum of compound (<u>XIII</u>) shows two types of siloxane vibrations at absorptions of 1028 cm⁻¹ and 990 cm⁻¹. The N-hydrogen and lithium analogs of compound (XIII) also

exhibit two siloxane vibrational absorbances at approximately 1020 cm⁻¹ and 985 cm⁻¹. There also appears to be present two Si₂N vibrational absorbances at 930 cm⁻¹ and 911 cm⁻¹ which are probably due to the two forms of Si₂N stretching vibrations one would expect for the more strained Si₂N ring stretching vibration and for the pendant silicon-nitrogen-silicon ring stretching vibration.

It is important to note the invariance of the double siloxane absorptions at 1028 and 990 cm⁻¹ throughout the following series: $Me_2Si(OSiMe_2)_2N-X$ (X = H-, Li-, ViMe_2Si-). This is a critical observation since it indicates that the unit -N Si has not contracted during the silylation of the lithium salt of (<u>I</u>). If ring contraction would have occurred, subsequent silylation with a monochlorosilane would have yielded the following compound:

This compound should yield two siloxane vibrational absorbances at approximately 1060 cm⁻¹ and at a frequency much less than 990 cm⁻¹ for the pendant siloxane and ring siloxane vibration, respectively. As was stated earlier, this behavior is in fact not evidenced in the infrared spectrum of compound (XIII). Also the Si₂N vibrational frequency for the cyclodisilazane unit is normally between 880-900 cm⁻¹. The Si₂N linkage in compound $(\underline{XVIII})^{b}$ should also be strained. However, no shift to a lower Si₂N vibrational frequency is noted.

Further structure confirmation indicating the proposed structure is found in the H¹ nmr data. Compound XIII yields a methyl proton ratio of 6:12:6 at τ values of 9.772, 9.807, and 9.905, respectively (Table XIX). This is in agreement with the structure assignment of compound (XIII).

E. Infrared and H¹ Nuclear Magnetic Resonance Structure <u>Confirmation of 2,2,4,4,6,6-Hexamethyl-5-[(dimethyl-vinylsiloxy)dimethylsilyl]-1,3-dioxa-5-aza-</u> <u>2,4,6-trisilacyclohexane</u> (XIV)

The infrared spectrum of compound (<u>XIV</u>) indicates two forms of siloxane vibration which show absorbances at 1025 cm^{-1} and 990 cm^{-1} . This appears to be typical of the cyclotrisiloxazane unit shown below.

A shoulder on the strong absorption peak at 1025 cm⁻¹ occurs at approximately 1000 cm⁻¹. This absorbance is felt to be a disiloxane absorbance due to the N-siloxysilyl pendant group, ViMe₂SiOSiMe₂—N < . As in compound (<u>XIII</u>), this material also exhibits two absorption bands at 945 and 915 cm⁻¹ which indicates the two forms of Si₂N vibrations in compound (XIV). The absorption band at 915 cm^{-1} is very probably due to the strained Si₂N vibration in the ring.

The H¹ nmr data lends further credance to structure (\underline{XIV}) . Chemical shifts were observed at 9.807, 9.819, 9.826, and 9.909 τ with a methyl proton ratio of 12:6:6:6 which is identical to the required proton ratio (Table XIX). If silylation of the N-lithium salt of compound (<u>II</u>) had proceeded without ring contraction, the required methyl proton ratio of the resulting product below would be 6:12:12.

F. Infrared and H¹ Nuclear Magnetic Resonance Structure Confirmation of 2,2,4,4-Tetramethyl-1,3-bis[(dimethylvinylsiloxy)dimethylsilyl]-1,3-diaza-2,4-disilacyclobutane and of 2,2,4,4-tetramethyl-1,3bis[(trimethylsiloxy)dimethylsilyl]-1,3diaza-2,4-disilacyclobutane (XV), (XVI)

Compounds (<u>XV</u>) and (<u>XVI</u>) both show very strong absorptions at 880-900 cm⁻¹ and at 1015-1020 cm⁻¹. These absorption bands are indicative of a silylated cyclodisilazane structure (47):

The Si₂N absorption bands between 900-950 cm⁻¹ commonly associated with silazanes and tris-silylamines are not

present in the infrared spectra of compounds (<u>XV</u>) and (<u>XVI</u>). The one disiloxane vibration is observed at 1068 and 1070 cm^{-1} for compounds (<u>XV</u>) and (<u>XVI</u>), respectively.

The H¹ nmr spectra of compound (<u>XV</u>) revealed chemical shifts at 9.748, 9.875, and 10.000 τ with a methyl proton ratio of 12:12:12, which is in agreement with the proposed structure (46). Neither of the other two possible isomeric structures shown below would yield the correct methyl proton ratios.

$$viMe_2Si-N \xrightarrow{Si-O-Si}_{N-SiMe_2Vi} (\underline{XIX})$$

$$Me_{2}$$

$$Me_{2}$$

$$Ne_{2}$$

$$Si-0$$

$$SiMe_{2}$$

$$SiMe_{2}$$

$$Me_{2}$$

$$SiMe_{2}$$

$$SiMe_{2}$$

$$SiMe_{2}$$

$$Me_{2}$$

$$SiMe_{2}$$

Compound (\underline{XIX}) should yield a 12:24 methyl proton ratio while compound (\underline{XX}) should yield a ratio of 6:6:6:6:12.

Further evidence for the proposed structure is offered from the work of Breed and Elliot (47) wherein they have assigned a chemical shift of 9.76-9.79 τ for silylmethyl protons attached to a cyclodisilazane ring. Also the pendant, N-silylmethyl protons exhibit a chemical shift of 10.000 τ . The H¹ nmr spectrum of compounds (<u>XV</u>) and (<u>XVI</u>) are in full agreement with these assignments.
In conclusion the methyl proton ratio of compound (\underline{XVI}) is 3:2:2 which is what is predicted by theory (Table XIX).

VI. PART IV. THE PREPARATION OF SOME LINEAR POLYMERIC MATERIALS CONTAINING ALTERNATING SILOXANE AND CYCLODISILAZANE UNITS AS THE BACKBONE OF THE POLYMER

A. Experimental

1. Materials

The dichlorodimethylsilane was obtained from the Dow Corning Corporation. It was distilled before being used. The preparation and purification of bis(chlorodimethyl)disiloxane is described in Part I.

2. Preparation

A general procedure used to prepare these polymeric materials is outlined as follows.

A weighed amount of the cyclosiloxazane was placed in a 300 milliliter, three-necked flask equipped with a stirrer, addition funnel and rubber septum. To this reaction flask was added enough THF to yield a 40 weight per cent solution of compound (\underline{IV}). The system was then purged with dry nitrogen gas. After the nitrogen gas purge was discontinued, butyllithium in slight excess was added through the rubber septum from a calibrated syringe to form the lithium salt.

Stirring of the reaction mixture was continued for thirty minutes after the addition of butyllithium was completed. The chlorosilane or chlorosiloxane was then added from the

separatory funnel. Upon the addition of the chlorosilane or chlorosiloxane the reaction medium became hazy, after which lithium chloride began to form.

The reaction mixture did not warm until the precipitate began to form. Only lithium chloride precipitates from solution, as the polymer remains in solution.

The reaction mixture was stirred at 25° for two hours, after which ten weight per cent of chlorodimethylvinylsilane was added based on the starting amount of compound (<u>IV</u>). Upon the addition of the monochlorosilane, the reaction mixture was stirred for an additional thirty minutes. The system was then purged with dry ammonia gas to convert any unreacted monochlorosilane to the disilazane according to the reaction below.

 $ViMe_2SiCl \xrightarrow{excess NH_3(q)} [ViMe_2Si]_2NH + NH_4Cl$

Following this step, the reaction mixture was vacuum filtered to remove the lithium chloride and any ammonium chloride that was formed. The filtrate was devolatilized by vacuum distillation. The product residue was, at this point, slightly cloudy. It was therefore dissolved in <u>n</u>-hexane, pressure filtered and strip distilled to remove the volatiles to leave a clear product. Table XX lists the mole ratios of reactants used to prepare the polymers. Tables XXI and XXII and Figures 22-23 list the infrared and nuclear magnetic resonance data, while Table XXIII, represents the thermal gravimetric analysis data of the prepared polymers.

LVINYLSILYL- ,2,4,4- B;		[ClMe ₂ Si] ₂ 0		0.0358
α, ω -DIMETHY SNTANE-1, 3-(2 ID OF POLYMER OCTAMETHYL- 5-(2,2,- SUTANE)]	s Used	Me ₂ SiCl ₂	0.0459	
DF POLYMER A; 5,5-TRISILAPE DBUTANE)], AN DBUTANE)], AN 5,5,5,7,7-C 5,3,5,5,7,7-C AHEPTANE-1,3 DISILACYCLOF	s of Reactant	BuLi	0.0920	0.0722
JSED IN THE PREPARATION (-HEXAMETHYL-2,4-DIOXA-1,3 L,3-DIAZA-2,4-DISILACYCL(CHYLVINYLSILYL-POLY[1,1,3 CHYLVINYLSILYL-POLY[1,1,3 S-TRIOXA-1,3,5,7-TETRASII STRAMETHYL-1,3-DIAZA-2,4-	Moles	-fwe ₂ Si(OSiMe ₂)NH] 2	0.0459	0.0352
MOLES OF REACTANTS U POLY [1,1,3,5,5,5,5,5,5,5,5,5,5,5,5,5,5,5,5,5,		Preparation of	Polymer A	Polymer B

TABLE XX

TABLE XXI

INFRARED SPECTRA OF POLYMER A AND POLYMER B

••••••••••••••••••••••••••••••••••••••	Polymer A	Polymer B	
ν С-Н	2960(s) 2902(w)	2962(s) 2902(w)	
ν C=C	1590(v.w.)	1590(v.w.)	
δ_{as} CH ₃	1408(m)	1408(m)	
်း CH 3	1255(s)	1257(s)	
va s Si OSi	1075(s)	1080(s)	
ν SinSi	1000(v.s.)	1005(v.s.)	
v SiNSi	945(w.m.)	940(w)	
v SiNSi	885(s)	887(s)	
v Si- C	850(m)	850(m)	
vas Si-C	802(s)	802(s)	









TABLE XXII

H¹ NUCLEAR MAGNETIC RESONANCE SPECTRA OF POLYMER A AND POLYMER B

τ Values	9.738ª 9.973b 9.984c 9.81 8 d	9.746a 9.959b 9.982c 9.818d
<mark>n Ratios</mark> Found	2ª;3 ^{b+c}	2ª.4b+c
<u>Methyl Proto</u> Calcd	2ª:2b:1 ^c	2ª:2b:2 ^c
e Peaks Found	3(strong) 1(weak)d	3(strong) 1(weak)d
<u>Number of M</u> Calcd	3(strong) 1(weak)d	3(strong) 1(weak)
20lymer	А.	ů

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B. General Discussion

The following reaction sequence is proposed based on the polymeric materials, isolated and characterized by infrared and H^1 nmr data. The structure verification of the polymers and their physical and thermal properties are discussed in the following sections.

Reaction Sequence



The reaction intermediate indicated in square brackets is conjectured.

Step 5, which follows, involves the conversion of the unreacted chlorodimethylvinylsilane to the disilazane via ammination with ammonia gas. The step is included to eliminate the possible formation of hydrogen chloride from the hydrolysis of any unreacted chlorosilane. Hydrogen chloride, if formed, would react with the cyclodisilazane unit in the polymer. This is undesirable.

Compound (<u>XI</u>) is listed in the reaction sequence for the sake of convenience. The true intermediate or intermediates formed which result in the formation of the cyclodisilazane unit have not been identified. For the sake of simplicity in the following sections, let Polymer A and Polymer B to be representative of the polymer structure written above where x = 1 and x = 2, respectively.

C. <u>Spectroscopic Confirmation of α, ω-Dimethylvinylsilyl-poly[1,1,3,3,5,5-hexamethyl-2,4-dioxa-1,3,5-trisila-pentane-1,3-(2,2,4,4-tetramethyl-1,3-diaza-2,4-disilacyclobutane)]</u>, Polymer A; and of α, ω-<u>Dimethylvinylsilyl-poly[1,1,3,3,5,5,7,7-cotamethyl-2,4,6-trioxa-1,3,5,7-tetra-silaheptane-1,3-(2,2,4,4-tetra-methyl-1,3-diaza-2,4-disila-cyclobutane)]</u>, Polymer B

Polymers A and B both show very strong absorptions at 880-890 cm⁻¹ and at 1000-1005 cm⁻¹. These absorption bands are indicative of a silylated cyclodisilazane structure. This assignment was recently indicated by Breed and Elliot (47).

The Si₂N absorption band, between 900 and 950 cm⁻¹, common to both disilazane and tris-silylamine structures, was also evident in the infrared spectra of Polymers A and B as a weak band at 940-945 cm⁻¹ (Figures 22 and 23). However, no NH absorption was observed at 1140-1180 cm⁻¹. This would indicate that the infrared absorption at 940-945 cm⁻¹ is due to some form of tris-silylamine structure other than that exhibited by the N,N'-silylated cyclodisilazane.

A form of tris-silylamine structure unlike that of the silylated cyclodisilazane could be incorporated into Polymers A or B if the ring contraction of the N,N'-dilithium salt of (IV)was incomplete, according to the partial rearrangement listed below.



Thus, upon subsequent reaction with the dichlorosilane or dichlorosiloxane the unit indicated below would be incorporated into the polymer chain



as an "impurity" and should show a typical Si_2N absorption between 900-950 cm⁻¹. It would appear from infrared that

the amount of the trimer cyclosiloxazane incorporated into the polymer chain relative to the number of cyclodisilazen units is small.

An alternate explanation of the absorption at 940-945 $\rm cm^{-1}$ involves the assignment of this absorption to the out of plane C-H bending vibration due to the vinyl group present as the dimethylvinylsilyl endblocking unit (45). However, the expected accompanying C=C stretching frequency at 1590-1600 cm⁻¹ is of too weak an intensity to compliment the stronger vibration at 940 cm⁻¹.

Based on this analysis, it is felt that the unit



is indeed present in small concentrations as an impurity in Polymers A and B.

The H^1 nmr data would be expected to yield a 2:1:2 methyl proton ratio for Polymer A indicated below



where x = 1. For x = 2 the expected ratio of $Me^{a}/Me^{b}/Me^{c}$ is 2:2:2, where $z = \infty$.

These mole ratios were indeed observed (Table XXII). The chemical shift for the methyl protons in the cyclodisilazane ring and the methyl protons on the adjacent silicon connecting group, $Me^{a}-Me^{C}$, was τ 9.74-9.75 and 9.98, respectively. This is in agreement with the assignment by Breed and Elliot of τ 9.75 and 10.00 for the silylmethyl protons attached to a cyclodisilazane ring (47), and adjacent to the cyclodisilazane rings respectively (Table XXII). Since the polymer was endblocked with the dimethylvinylsilyl group, one would expect to observe a fourth weak band in the H¹ nuclear magnetic resonance spectra for the methyl protons. A peak is evident at τ 9.818. However, since the infrared barely indicates the presence of the vinyl group, it is surprising that H¹ nmr would pick up these methyl protons of the endblocking group.

The correct explanation for the observed weak fourth peak might be to attribute this absorption to the methyl protons (in brackets below) of the cyclotrisiloxazane "impurity".



It is felt that this "impurity" can be eliminated by allowing the N,N'-dilithium salt of compound (<u>IV</u>) more time to ring contract in tetrahydrofuran, prior to reaction with the chlorosilanes.

D. Some Physical Properties of the Prepared Polymers

1. Thermal Stability

The thermal gravimetric analyses of Polymers A and B were gathered so as to indicate qualitatively the thermal stability of these materials under oxidative and nonoxidative conditions. Polymers A and B both exhibited good thermal stability relative to polydimethylsiloxanes as evidenced by a weight loss of only 15 percent at 425° in air (Table XXIII). Polydimethylsiloxane fluids normally undergo extensive siloxane rearrangement at 250° - 350° C (48,49). In air, most polydimethylsiloxanes oxidize appreciably above 250° C (50).

As in the case of polydimethylsiloxanes, polymers A and B exhibit a high weight loss (more than 95 per cent) in helium. This indicates that Polymers A and B, like polydimethylsiloxanes, are subject to thermal rearrangement below $450-500^{\circ}$ C.

The low weight loss of Polymers A and B, 32-36 per cent at $670-710^{\circ}$ C in air, indicates the formation of a crosslinked polymer formed via an oxidative process. The crosslinked material is apparently fairly resistant to thermal rearrangement as is evidenced by the stability of these materials towards the further formation of volatile species between $350-450^{\circ}$ C.

Temperature ^O C	Polvme	<u>er Cent We</u> r A	lght Loss Polymer B	
	Helium	Air	Helium	Air
100	0.3	0.3	0.6	0.4
200	3.7	3.4	5.3	4.1
300	8.0	7.6	11.1	9.9
350	11.6	11.1	15.2	13.2
400	16.9	12.8	20.5	15.1
450	25.3	18.2	27.5	20.0
500	34.0	23.9	41.3	26.3
550	45.4	28.6	59.0	31.5
600	77.2	31.1	88.8	35.8
650	97.5	31.3	99.5	36.0

THERMAL GRAVIMETRIC ANALYSIS OF POLYMER A AND OF POLYMER B'IN HELIUM AND IN AIR

TABLE XXIII

2. <u>Microscopic Identification of the Prepared Polymers</u>

Polymer A was examined in polarized light with crossed nicols and was found to show birefringence, which is an indication of crystallinity. Polymer A is a waxy solid at room temperature but melts at $40-42^{\circ}$. As would be expected, the polymer no longer exhibits birefringence under polarized light at 42° .

Polymer A was allowed to recrystallize from toluene between two glass slides. A photomicrograph was taken of this sample at 100X under polarized light with a 35 mm. camera attached to the microscope. The photomicrograph showed fern-like dendrites and an area of high polymer concentration, containing numerous spherulites growing from nucleation sites.

Polymer B is a liquid at room temperature. It exhibited no birefringence as a solid at -60° under polarized light.

The presence of spherulites in high polymers has been known since Kirchhof took the first picture of this type of crystal formation in 1929 (51). According to Bunn (52) the spherulite structure is the normal manner of crystallization of high polymers.

3. Molecular Weight Determinations

The number average molecular weights of Polymers A and B were determined by vapor phase osmometry. These measurements were performed by the Dow Corning Corporation. Values of 2590<u>+</u>5 per cent and 2,300<u>+</u>5 per cent were found for

Polymers A and B, respectively. This yields the average degree of polymerization as indicated below.



Polymer A; x = 1, z = 6.10Polymer B; x = 2, z = 4.35

4. <u>Hydrolyzability</u>

Polymer A was titrated with 0.1 N aqueous hydrogen chloride in an acetone-toluene-ethanol solution using a back titration technique to yield theory per cent nitrogen based on the proposed structure. The following procedure was employed and is included since it qualitatively indicates the hydrolytic stability of the polymer.

Into a 250 ml iodine flask containing 70 ml of ethanol are placed 0.1327 grams of polymer A. The polymer was not soluble in ethanol. To this mixture was added 13.8 ml of 0.1 N aqueous HCl. After standing for two hours, the polymer appeared to remain intact and apparently did not dissolve. To this mixture was added 20 ml of acetone and 50 ml of toluene which dissolved the polymer. The solution was allowed to stand for one-half hour after which the sample was back titrated with 6.8 ml of 0.1 N alcoholic KOH to neutrality as indicated by brom-cresol purple. This analysis yields 7.38 per cent nitrogen and indicates that the cyclodisilazane structure is subject to hydrolysis in a homogeneous acid solution. The theoretical amount of nitrogen for polymer A based on the molecular weight measurement is 7.68 per cent.

VII. SOME MISCELLANEOUS PHYSICAL PROPERTIES OF THE N-SUBSTITUTED LITHIUM POLYDIMETHYLCYCLOSILOXAZANES

The N-lithium salts are white crystalline solids. Crystallinity was evidenced by birefringence patterns when the salts were exposed to polarized light under crossed nicols. The salts are high melting materials or may decompose at high temperatures prior to reaching their melting point. No obvious change could be detected when compounds (<u>VIII-XII</u>) were heated at 150[°] in sealed vials for one hour. The salts are not pyrophoric, but are, however, quite hygroscopic.

VIII. MISCELLANEOUS

A. Analytical Methods

1. Carbon, Hydrogen, Silicon and Nitrogen Analyses

The carbon, hydrogen, silicon and nitrogen analyses in this investigation were carried out by the Dow Corning Corporation, Midland, Michigan.

2. Chlorine Analysis

The chlorine analysis was carried out by placing a weighed sample of an α, ω -dichlorosiloxane into a 250 ml iodine flask containing about 100 ml of a 50/50 ethanol-water solution.

The solution was then titrated to a phenolphthalein endpoint with 0.1 N alcoholic potassium hydroxide.

3. <u>Hydrolyzable Nitrogen</u>

Hydrolyzable nitrogen was determined by placing a weighed sample of product into a 250 ml iodine flask containing largely ethanol and some distilled water. The solution was then acidified by adding an excess of 0.1 N aqueous hydrochloric acid. The solution was allowed to stand for from one-half to one hour after which the sample was titrated to a brom-cresol purple endpoint with 0.1 N alcoholic potassium hydroxide.

4. Lithium Analysis

The lithium analysis was performed by placing a weighed sample of a N-lithio cyclosiloxazane into a 250 ml iodine flask containing about 100 ml of a 50/50 ethanol-water solution. The solution was then acidified by adding an excess of 0.1 N aqueous hydrochloric acid. The solution was allowed to stand for one hour after which the sample was titrated to a brom-cresol purple endpoint with 0.1 N alcoholic potassium hydroxide. The compound being titrated was assumed to be pure. Thus, the amount of 0.1 N aqueous hydrochloric acid required to titrate the theoretical amount of nitrogen for the specific compound being analyzed was subtracted from the total amount of 0.1 N aqueous hydrogen chloride used. The difference was assumed to be the amount of 0.1 N aqueous hydrogen chloride necessary to neutralize the lithium hydroxide formed as a result of hydrolysis of -\$i-N-Li-.

5. Molecular Weight

The molecular weight of Polymers A and B was determined on a Hewlitt-Packard 302 Vapor Pressure Osmometer which was made available by the Dow Corning Corporation.

6. Spectroscopic Data

The infrared spectra of the polydimethylcyclosiloxazanes were recorded from 400-1300 cm^{-1} as two per cent solutions in carbon disulfide and from 1200 to 4000 cm^{-1}

as ten per cent solutions in carbon tetrachloride on a Perkin Elmer 337 Grating Infrared Spectrophotometer.

The infrared spectra of the N-lithium salts of the cyclosiloxazanes were recorded as Nujol mulls on a Unicam SP-200.

The infrared spectra of the N-silyl derivatives and of Polymers A and B were recorded as ten per cent and as two per cent solutions in carbon tetrachloride and in carbon disulfide respectively. The instrument used was a Perkin Elmer 521 Grating Spectrophotometer.

The H^1 nmr data of the cyclosiloxazanes, the N-silyl derivatives, and of Polymers A and B were recorded as ten per cent solutions in carbon tetrachloride on a Varian A-60 at 50 and 500 cycles per second. The N-lithium salts were recorded as supersaturated solutions in benzene also on a Varian A-60 at 50 and 5000 cycles per second.

7. Photomicrographs

The photomicrograph of Polymer A was taken with a Karl-Zeiss 63040 Ultraphot II.

8. Thermal Gravimetric Analyses

The thermal gravimetric analyses of Polymers A and B were performed by the Dow Corning Corporation. A heating rate of 3° /minute was used for a 60-70 mg sample. The gas flow rate was 50 cc/minute; the air was first dried and then passed through a purifier before being introduced into the sample area. The analysis was carried out at one atmosphere in a 16 mm x 4 mm deep cylindrical platinum cup. BIBLIOGRAPHY

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