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Silylethylenediamine Compounds

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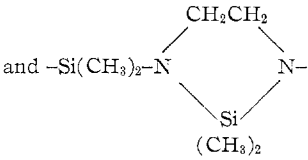
The products of reaction of ethylenediamine with dimethyldichlorosilane consist of a mixture of linear and cyclic units of the type $-Si(CH_3)_2NHCH_2CH_2NH-$ and , in a ratio of about 1:2. By heating the products to 300°, or by treating them with $(CH_3)_3SiCl$, polymers of the pure cyclic species are obtained. Similar reaction with ethylenediamine forms products with a higher ratio of the linear component.

Introduction

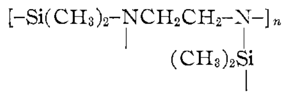
The subject of silicon–nitrogen compounds has received considerable attention during the past few years.[1] Renewed interest in this long-neglected area was in part initiated by the search for polymers whose properties might supplement those of the silicones, and in part by the peculiar features of the Si–N bond. In our laboratory a detailed study of these aspects of silicon–nitrogen compounds was started with the investigation of products from the condensation reaction of dihalosilanes and organic diamines.[2]

The reaction of ethylenediamine with dimethyldichlorosilane in a 2:1 molar ratio produced a polymeric substance with a molecular weight of 2000. Based on chemical analysis and on the quantities of starting materials and reaction products, its structure was assumed to be

$$[-Si(CH_3)_2NHCH_2CH_2NH-]_n$$

A

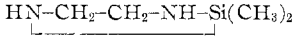
Catalytic amounts of complexing metal salts caused cleavage of ethylenediamine out of this primary material, leading to a product for which the preliminary cross-linked structure had been postulated by the chemical analysis to be



$$[-Si(CH_3)_2-\underset{|}{N}CH_2CH_2-\underset{\substack{|\\(CH_3)_2Si\\|}}{N}-]_n$$

B

Both products suffer changes in elemental composition when stored for long periods at room temperature. The chemical analyses reflect the altered nature of the products, but do not allow any conclusions about their molecular structure. Obviously there are several possibilities for the structural arrangement of the building unit of product B, leading either to linear coupling of ten-membered rings or five-membered rings, or to extensive random cross linking. Furthermore, the preliminary structure of A appears rather problematic in retrospect if one considers the well known tendency of Si–N compounds to form small-membered ring compounds.[3] One might expect the monomeric ring



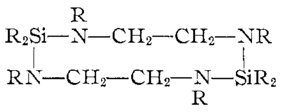
$$HN-CH_2-CH_2-NH-Si(CH_3)_2$$

A′

(which has never been reported[4]), rather than polymer A. The reaction between ethylenediamine and $(CH_3)_2SiCl_2$ became even less lucid when Henglein and Lienhard[5] reported the results of their independent investigation of the reaction. Applying only slightly different conditions, they obtained a material of the elemental composition corresponding to structure B.

It appeared necessary to us to attack this problem with improved analytical methods. In particular, an unambiguous method for the exact determination of the structure of the products without chemical degradation had to be found.

In the previous papers of this series[4,6] it has been shown that structural questions like this can be solved by n.m.r. investigations. Chemical and spectroscopic studies on the well-defined monomeric products of the reaction of $(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3$ and different chlorosilanes had shown that only two basic structural types of silylethylenediamine compounds can be obtained, *i.e.*, a linear unit or a cyclic species incorporating the 1,3-diaza-2-silacyclopentane ring system. In no case was a compound with a ten-membered ring system (C)



$$\begin{array}{c} R_2Si-\overset{R}{N}-CH_2-CH_2-NR \\ |\qquad\qquad\qquad\qquad| \\ RN-CH_2-CH_2-\underset{R}{N}-SiR_2 \end{array}$$

C

obtained. Apparently the five-membered species is the least reactive and most stable arrangement.

Linear and cyclic structures may easily be differentiated by their n.m.r. spectra because the CH_2

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[1] U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964); R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961).

[2] R. Minné and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 5625, 5628 (1960).

[3] C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960, p. 343.

[4] D. Kummer and E. G. Rochow, *Z. anorg. allgem. Chem.*, **321**, 21 (1963).

[5] F. A. Henglein and K. Lienhard, *Makromol. Chem.*, **32**, 218 (1959); K. Lienhard, Dissertation, TH Karlsruhe, 1959.

[6] D. Kummer and J. D. Baldeschwieler, *J. Phys. Chem.*, **67**, 98 (1963).

resonances of the ring characteristically are about 0.30 p.p.m. downfield from the CH_2 signals of the linear compounds. Furthermore the infrared spectra of the five-membered rings display a characteristic sharp absorption at 1340 cm.$^{-1}$ which does not appear in the infrared spectra of the linear compounds.[4,5] Armed with these facts from study of the model compounds, a study of the reaction products from ethylenediamine and dimethyldichlorosilane was begun.

Experimental

All experiments were carried out in an atmosphere of dry nitrogen.

Product I (1:2 Molar Ratio).—Over a 30-min. period, 17.4 g. (0.15 mole) of dimethyldichlorosilane was added with stirring to 18 g. (0.3 mole) of anhydrous ethylenediamine diluted with 80 ml. of xylene. The temperature of the reaction mixture was kept below 30° by means of an ice bath. After all the chlorosilane had been added, stirring was continued for 10 min. at room temperature and then the reaction flask was warmed gradually to the reflux temperature of xylene. At about 80° the fine white suspension of amine hydrochloride congealed to a yellowish mass, leaving a pale yellow supernatant liquid. After 50 min. of reflux the mixture was allowed to cool. The solid material was separated by suction filtration through a medium glass frit, washed three times with petroleum ether, and then dried. It weighed 23 g. (calculated for ethylenediamine dihydrochloride 20 g.). *Anal.* Calcd. for $C_2H_6N_2Cl_2$: N, 21.0; Cl, 53.4. Found: N, 20.73; Cl, 51.74.

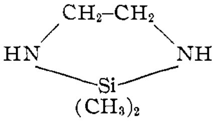
The solution was freed from xylene at reduced pressure (1 mm.) at room temperature. To remove the last traces of xylene the residue was then heated to 70–100° for 2 hr. at 1 mm. The xylene which was distilled from the residue during this time contained no ethylenediamine; yield, 12 g. of a very viscous oil.

Products III and IV were prepared in the same way as I, with one exception: the dimethyldichlorosilane was diluted in both cases with an equal volume of xylene. The products were very viscous oils.

Product II was prepared in the same way as I, except that the ethylenediamine was diluted with 30 ml. of benzene. Slightly impure ethylenediamine dihydrochloride (22 g.) was obtained (calcd. 20 g.). *Anal.* Calcd. for $C_2H_6N_2Cl_2$: N, 21.0; Cl, 53.4. Found: N, 20.68; Cl, 51.63. The bulk of the benzene was distilled from the colorless solution at normal pressure and the rest by heating the residue at 1 mm. to 180° for 4 hr. No ethylenediamine was found in the volatile substance (benzene). A very viscous oil (11 g.) was obtained.

Product V (Molar Ratio 1:1).—Anhydrous ethylenediamine (6 g., 0.1 mole), $(CH_3)_2Si[N(C_2H_5)_2]_2$ (19.4 g., 0.1 mole), and 60 ml. of mesitylene were refluxed for 2 hr. The mixture was distilled to remove the lower-boiling reaction products (diethylamine and unreacted ethylenediamine) and the solvent. The soft waxy residue (10 g.) was freed from mesitylene by heating for 2 hr. to 100° *in vacuo*.

This preparation differs from that of Henglein and Lienhard[5] in that a solvent was used in this case. The higher reaction temperature which is finally reached without solvent favors the formation of a ring compound, as is shown by our experiments (see product VI). The solvent had been added in this experiment to see whether the monomeric compound



could be obtained by the dilution principle. However, not a trace of the ring could be detected in the distillate (as indicated by the n.m.r. spectrum).

Product VI.—III (14 g.) was heated to 370° for 5 hr. at 1 mm. pressure. Ethylenediamine (0.6 g., identified by its n.m.r. spectrum) was isolated in a trap cooled with liquid nitrogen. Two grams of oligomers was distilled over at 300–320° (1 mm.). The residue (10.4 g.) was a brown viscous resin (VI), insoluble in cold benzene but soluble when melted and mixed with hot benzene.

Product VII.—III (39 g.) was dissolved in 300 ml. of diethyl ether and 50 g. of $(CH_3)_3SiCl$ was added. At the reflux temperature of ether a fine white suspension appeared. After 12 hr. the reaction mixture was cooled and the white precipitate (*ca.* 3 g.) was removed by suction filtration. The yellow solution was freed of ether and excess $(CH_3)_3SiCl$ at reduced pressure at 30° and was distilled. Four grams of a liquid [b.p. 146–148° (65 mm.)] was isolated, consisting mainly of 1,3-bis(trimethylsilyl)-2.2′-dimethyl-1,3-diaza-2-silacyclopentane [b.p. 47° (1 mm.)][4] (identified by its n.m.r. spectrum). The residue was then heated *in vacuo* (1 mm.) to *ca.* 320° for 6 hr. During this period 2 g. of methylchlorosilanes (isolated in a trap cooled with liquid nitrogen) and 2 g. of a soft waxy material, which condensed on the cooler parts of the reaction flask, were removed from the residue. The formation of the methylchlorosilanes is explained by the presence of terminal $\equiv$SiCl groups in the original reaction product. The groups are formed by an exchange reaction of $(CH_3)_3SiCl$

$$=N-Si(CH_3)_2-N= \; + \; (CH_3)_3SiCl \longrightarrow =N-Si(CH_3)_2Cl \; + \; (CH_3)_3SiN=$$

At higher temperatures this reaction is reversed and chlorosilanes are evolved

$$=N-Si(CH_3)_2Cl \; + \; Cl(CH_3)_2Si-N \longrightarrow =N-Si(CH_3)_2-N= \; + \; (CH_3)_2SiCl_2{}^{5}$$

The residue (28 g.) was a brown fusible resin soluble in hot benzene.

Reaction of III and Ethylenediamine.—Product III has a ring/chain unit ratio of *ca.* 3:1 (Table III). A molecular unit of three rings and one linear ethylenediamine group has a molecular weight of 632. To convert this unit into a pure linear configuration, three ethylenediamine units are needed for each such polymeric unit. According to this calculation, 14.5 g. of III was allowed to react with 4 g. of ethylenediamine under reflux for 2 hr. An n.m.r. spectrum showed unreacted ethylenediamine. The mixture was refluxed for another period of 4 hr. There was still free ethylenediamine present, which was removed by heating to 70° for 4 hr. The chain/ring ratio of the product changed from 1.00:0.70 to 1.00:1.32 during this process (checked by n.m.r. spectra before and after the heating).

The reaction of III with ethylenediamine was repeated with the following variations: (a) use of a great excess of the diamine, (b) different reaction times, ranging from 2 to 24 hr., (c) use of xylene as a solvent, and (d) reflux of the reaction mixture in the presence of ethylenediamine dihydrochloride. Analytical data for all products are given in Table I.

Results

The products obtained by the methods of Minné[2] and Henglein and Lienhard[5] (products I and II) differed surprisingly little in their analytical composition (Table I). In no case did the composition correspond to that of either the pure linear silylamine (A) or the silazane (B) (Table I). It is obvious from Table I that a mixture of the linear and the silazane building units must be present. Further and more detailed information on the structure of the products was derived from spectroscopic investigations.

The n.m.r. spectra of the products are qualitatively very similar, in accordance with the microanalytical results. They include three strong sharp peaks at

TABLE I

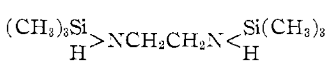
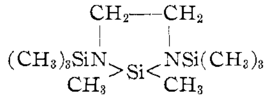
ANALYTICAL DATA

	C, %		H, %		N, %		
Linear str. unit	Calcd.	Found	Calcd.	Found	Calcd.	Found	Mol. wt.
$[-Si(CH_3)_2NHCH_2CH_2NH-]$	41.33		10.41		24.10		
Cross-linked str. unit							
$[-Si(CH_3)_2NCH_2CH_2NSi(CH_3)_2-]$	41.80		9.36		16.25		
Product I	41.70[a]	41.54	9.71[a]	9.63	18.88[a]	19.03	*Ca.* 1500
Product II	41.65[a]	41.51	9.69[a]	9.76	18.77[a]	18.66	*Ca.* 2400
Product VI	41.80	41.22	9.36	9.23	16.25	16.03	Unknown
Product VII	41.80	41.19	9.36	9.31	16.25	15.68	Unknown

[a] These values are calculated on the basis of the integration ratios of the ring and chain units in the respective structures (as given by the relative intensities of the CH_2 proton signals in their n.m.r. spectra (Table III) for mixtures of the pure silylamine and silazane compounds).

TABLE II

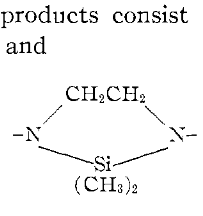
PROTON CHEMICAL SHIFTS OF ORGANOSILYLETHYLENEDIAMINE COMPOUNDS

	Chemical shifts,[a] τ units ± 0.02					
Compound	CH_2 (ring)	CH_2 (chain)	NH	$-Si(CH_3)_2-$		$-Si(CH_3)_3$
 $(CH_3)_3\underset{H}{Si}{>}NCH_2CH_2N{<}\underset{H}{Si(CH_3)_3}$	. . .	7.38	9.42	. . .		9.99
	7.04	. . .	. . .	9.89		9.94
				a[b]	b[b]	c[b]
Products I–IV, VIII	7.03	7.37	9.24	9.87	9.91	9.97
Product V	7.03	7.37	?	9.87	9.91	9.97
Products VI and VII	7.03	. . .	. . .	9.87	9.91	. . .

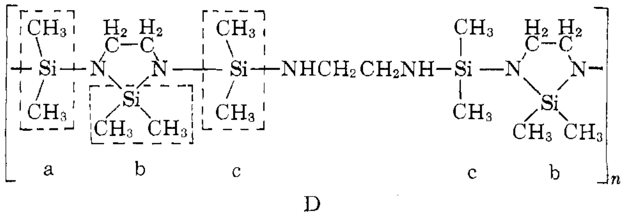
[a] Measured in dilute CCl_4 solution with $Si(CH_3)_4$ as internal standard. [b] For explanation see formula D.

τ 9.97, 9.91, and 9.87, a complex multiplet centered at τ 7.37, a broadened peak at τ 7.03, and a very broad peak centered at τ 9.24 (Table II). By comparison with the monomeric compounds (Table II) these features are easily assigned to $SiCH_3$ groups (signals (τ) at 9.97–9.87), NH protons (9.24), CH_2 protons of the linear $=NCH_2CH_2N=$ group (7.37), and CH_2 protons of the five-membered 1,3-diaza-2-silacyclopentane system (7.03). The presence of the five-membered rings as structural units of the polymers is also supported by chemical evidence from the abovementioned monomeric compounds and by the infrared spectra containing the sharp band at 1340 cm.$^{-1}$ characteristic of the ring and the NH absorption of 3400 cm.$^{-1}$ which is indicative of linear $-NHCH_2CH_2NH-$ units.

Neglecting for the moment the presence of all other types of linear and cross-linked units (which will be shown to be absent or to be present in only small amounts later), the n.m.r. spectra provide the following results: (a) The products consist of a framework of $-NHCH_2CH_2NH-$ and



units which are connected by $-Si(CH_3)_2-$ units. (b) The ratio of these two groups is given by the relative intensities of the linear and cyclic CH_2 proton signals. Three further repetitions of the reactions of Minné[2] and of Henglein and Lienhard[5] under varying conditions produced material with the same structural units, differing only in the ratio of linear to cyclic units (which lies in the range of 1:1.5 to 1:3). The n.m.r. data for these products are given in Tables II and III. In no case could a purely linear structure (A) or a purely cyclic structure (B) be identified. The results indicate that the choice of the solvent and the temperature of the reaction has no specific influence on the structure of the products formed. (c) In general, a product will have more cyclic units the higher and the longer it is heated, especially after the solvent has been removed. This curing effect is responsible for the differences of the reported products. Minné's material, when freshly prepared, has a higher percentage of linear units than the Henglein–Lienhard material, but appears to lose ethylenediamine on standing for long periods of time, leading to a composition of decreased chain-to-ring ratio. Product II had a chain-to-ring ratio of 1:2.26 shortly after its preparation. (d) Taking the above results, the structure of all the first five products (I–V) may be depicted as



D

TABLE III

RELATIVE PROTON RESONANCE INTENSITIES[a] OF ORGANOSILYLETHYLENEDIAMINE STRUCTURES

	Relative intensities of signals					
	Cyclic CH_2	Linear CH_2	NH		$SiCH_3$	
	Found	Found	Found	Calcd.[b]	Found	Calcd.[b]
I	1.96	[1.00]	0.54	0.50	7.54	7.39
II	2.13	[1.00]	0.5	0.50	7.79	7.89
III	3.03	[1.00]	0.53	0.50	10.23	10.59
IV	1.79	[1.00]	0.5	0.50	7.00	6.86
V	3.03	[1.00]	?		10.76	10.59
VI	[1.00]	...	...	...	2.94	3.00
VII	[1.00]	...	...	...	3.12	3.00
VIII	1.32	[1.00]	0.52	0.50	5.49	5.46

[a] The term "relative intensities" as used throughout this work, and quite generally elsewhere, actually refers to the relative areas of the different signals as obtained by the integrating circuit of the n.m.r. spectrometer. [b] The calculated values were obtained on the assumption that the numbers of protons in the linear group (formula D), $CH_2:NH:SiCH_3$, stood in the ratio of 2:1:3, and the numbers in the cyclic group stood in the ratio 1:0:3.

This picture is substantiated by the good agreement of the calculated and found relative intensities of the cyclic and linear CH_2, NH–, and $SiCH_3$– proton resonances and by the microanalytical findings and the calculated elementary composition. In both cases the calculated values were based on the chain-to-ring ratio of the particular polymer as obtained from the n.m.r. spectra. The results are summarized in Tables I and III.

Discussion of the N.m.r. Spectra

The strict treatment of all structural possibilities of the silylethylenediamine products must include the following moieties: For the linear ethylenediamine group, structures d, e, f, and g and for the cyclic h and j. The presence of appreciable amounts of the species d, f, g, and j in the polymers can be excluded on grounds of spectroscopic evidence. The absence of the NH_2 infrared bands at 3300–3400 and 1540–1570 cm.$^{-1}$ excludes group d. A decision between the possibilities e, f, and g can be made in favor of e by an analysis of the linear CH_2 group proton resonance at τ 7.37 in the p.m.r. spectra of the polymers. The CH_2 resonance consists of an asymmetrical "triplet structure" (Figure 1) of the type which also was observed for the respective resonances of $(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3$, $RNHCH_2CH_2NHR$, where R is a 1,3-diaza-2-silacyclopentane group,[6] and a number of organic compounds of the type $R_1NHCH_2CH_2NHR_2$ $(R_1 = R_2)$.[7]

$$\equiv Si{-}NH{-}CH_2CH_2{-}NH_2$$

d

$$\equiv Si{-}NH{-}CH_2CH_2{-}NHSi\equiv$$

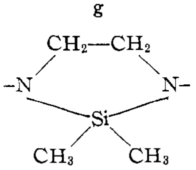
e

$$(\equiv Si)_2NCH_2CH_2NHSi\equiv$$

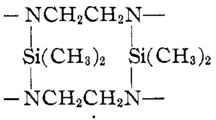
f

$$(\equiv Si)_2NCH_2CH_2N(Si\equiv)_2$$

g



h



$$\begin{array}{c} -NCH_2CH_2N- \\ |\qquad\quad | \\ Si(CH_3)_2\ \ Si(CH_3)_2 \\ |\qquad\quad | \\ -NCH_2CH_2N- \end{array}$$

j

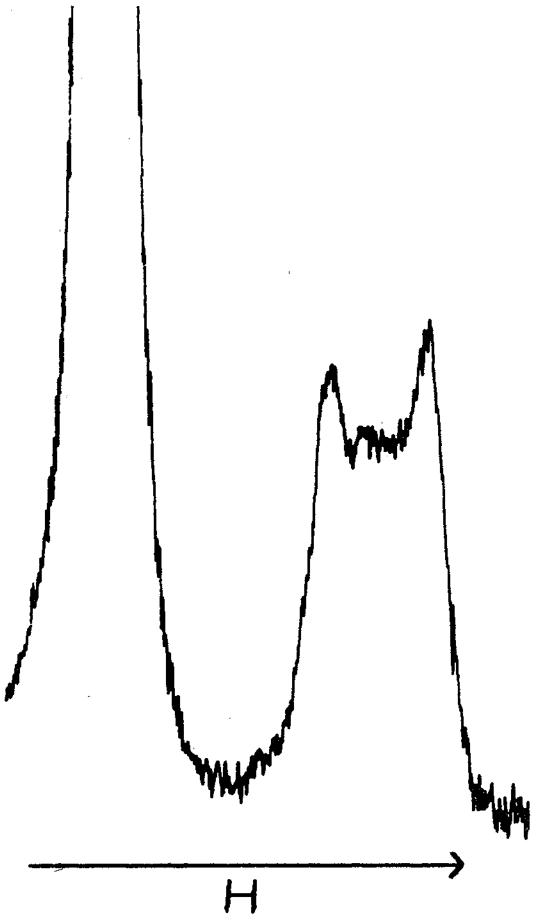


Figure 1.—CH_2 proton resonance of product I at 60 Mc. in dilute CCl_4 solution. The sharp resonance signal of the ring CH_2 protons is incompletely shown because the instrument was adjusted for maximum clarity of the chain CH_2 proton response.

The presence of f and g groups cannot be excluded completely by this argument in view of the broad and not very well-resolved spectrum, but since the CH_2 signals of f and g are very different from that of e,[6] the observation of a pure $RNHCH_2CH_2NHR$ signal indicates that only small amounts (if any) of f and g could be present. The best argument in favor of e and against appreciable amounts of f and g and the cross-linked type (j) is provided by the relative intensities of the proton signals.

When e, f, and g are units of a structure they have relative $CH_2:NH:SiCH_3$ proton ratios of 4:2:6 (e), 4:1:9 (f), and 4:0:12 (g). The presence of f and g would be reflected both in decreased NH and increased $SiCH_3$ intensities relative to the CH_2 intensity when compared with the pure unit e. It will be seen from Table III that this is not the case. All values

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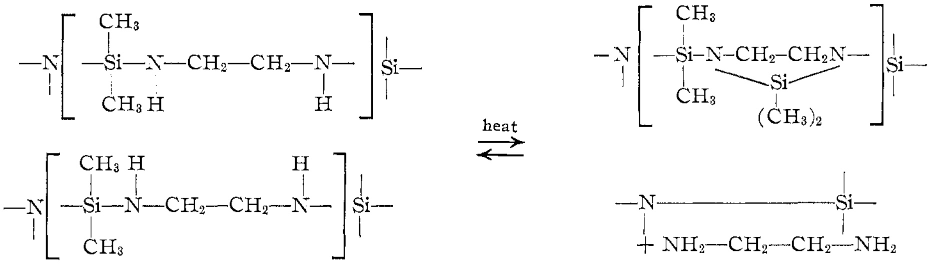
(7) G. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1961); G. Dudek, R. H. Holm, and J. D. Baldeschwieler, unpublished results.

SCHEME I

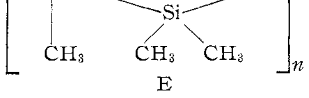


support the presence of unit e. In the case of the cross-linked type (j), the above reasoning would only be true if the chemical shift of the CH_2 proton resonance of this ten-membered ring system would coincide with that of the linear groups. For the purpose of the calculation this can be assumed, however, since the presence of CH_2 proton signals of j in a region other than the linear CH_2 resonance region was definitely excluded.

The limit for such considerations is set by the accuracy of the determination of the relative intensities. The presence of smaller amounts of the different groups in the polymers therefore cannot be excluded. In the light of the above interpretation the assignment of the $SiCH_3$ proton resonances of the polymers renders no difficulties and adds further proof to the proposed structures.

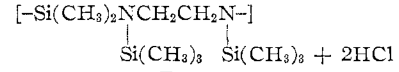
Three different types of $Si(CH_3)_2$ groups (in dashed lines a, b, c with a proton ratio of 1:2:2) can be recognized in D. This corresponds to the observation of the three distinct $SiCH_3$ proton signals, which are listed in Table II. By comparison with the $SiCH_3$ chemical shifts of the two monomeric compounds of Table II, the signal at τ 9.97 was assigned to group c, the signal at τ 9.91 to group a, and the signal at τ 9.87 to group b. The calculated and observed relative intensities are in substantial agreement with this assignment. The assignment of the signal at 9.97 to group c was verified by chemical reactions (see next paragraph).

Rearrangement Reactions.—All the products, when heated for several hours to 300–350° *in vacuo*, suffer changes which are also observed in aging. Ethylenediamine is evolved and can be isolated in a cooled trap. Further condensation of the products occurs, and tacky gums are produced. The internal changes are revealed by the n.m.r. spectra. The chain CH_2 proton signal of the original material gradually disappears, as well as the $SiCH_3$ proton signal at τ 9.97, leaving the ring CH_2 signal at τ 7.03, which is slightly broadened, and the two $SiCH_3$ signals at τ 9.87 and 9.91, which are of equal intensity. No new signals appear. The relative intensities of the CH_2 signal and the combined $SiCH_3$ signals are about 1:3, which is the ratio calculated for the pure ring E (Tables II and III). The microanalytical data for VI (Table I) and the infrared spectrum (characteristic ring peak at 1340 cm.$^{-1}$, no NH peak at 3400 cm.$^{-1}$) are in full agreement with this formula and correspond to the product obtained by Henglein and Lienhard by a similar procedure.[5]


E

The disappearance of the $SiCH_3$ signal of the starting material at τ 9.97 is a direct proof that the signal is due to a $Si(CH_3)_2$ group connecting a chain and ring unit. If the polymers are heated to still higher temperatures (>400°), decomposition occurs with formation of lower boiling liquids and a dark porous residue. The cleavage of ethylenediamine, as in Scheme I, is reversible to a certain degree. When III was heated in the presence of ethylenediamine, the reaction proceeded in the direction of the lower arrow. When the excess of ethylenediamine was removed at 30–40° *in vacuo*, products with a maximal ratio of one chain to 0.6 ring unit were obtained (identified by their n.m.r. spectra). These materials are extremely unstable at higher temperatures. Although they contain free ethylenediamine only in small amounts (~5%) at 30–40° (which can easily be identified in the n.m.r. spectrum), they cleave off ethylenediamine in considerable quantities when one tries to remove the residual free ethylenediamine at temperatures above 40°. A product completely free of ethylenediamine was obtained by heating it for 4 hr. to 70° *in vacuo*, and it had a chain/ring ratio of 1:1.32 (VIII, Tables II and III). It was impossible even with a great excess of ethylenediamine to obtain or even identify in the ethylenediamine solution a substance with a pure chain structure. Such a configuration apparently is very unstable and rearranges partially to the cyclic structure, until finally a sufficient number of the latter species stabilizes the residual linear groups. This evidently is the case when a ratio of about 1:1 is reached and every linear unit is separated from the next linear group by a ring unit. Solvents or ethylenediamine dihydrochloride have no discernible effect upon the reaction.

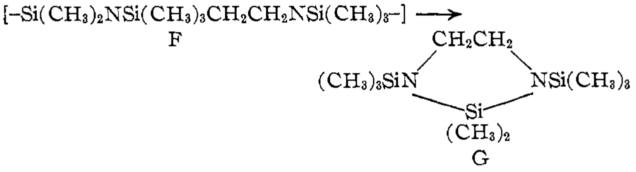
The same tendency for the transformation of chain units into ring units is observed when products with chain units were allowed to react with $(CH_3)_3SiCl$ in an attempt to improve their hydrolytic stability by replacing the NH by the $NSi(CH_3)_3$ group



$$[\text{-Si(CH}_3)_2\text{NHCH}_2\text{CH}_2\text{NH-}] + 2(\text{CH}_3)_3\text{SiCl} \longrightarrow [\text{-Si(CH}_3)_2\underset{\text{Si(CH}_3)_3}{\text{N}}\text{CH}_2\text{CH}_2\underset{\text{Si(CH}_3)_3}{\text{N}}\text{-}] + 2\text{HCl}$$

F

Apparently this reaction occurs in the first step (amine hydrochloride is formed), but in a second step cleavage and cyclization of F take place


$[\text{-Si(CH}_3)_2\text{NSi(CH}_3)_3\text{CH}_2\text{CH}_2\text{NSi(CH}_3)_3\text{-}] \longrightarrow$
F
G

When the polymeric reaction product is heated *in vacuo* to remove low-boiling compounds, a liquid is isolated which consists in large part of compound G. The chain units of the original material thus are removed to a high degree, and a ring structure of the approximate composition of E is left (product VII).

The results of this investigation show the strong tendency of silylethylenediamine compounds to form cyclic structures with the 1,3-diaza-2-silacyclopentane basic skeleton, in agreement with earlier results.[4,5] The failure to obtain a purely linear species $[\text{-Si(CH}_3)_2\text{-NHCH}_2\text{CH}_2\text{NH-}]_n$ (A), even in the presence of excess ethylenediamine, underlines the stability of this ring system and the previously discussed ring closure effect.[8]

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[8] In a recent paper Yoder and Zuckerman (*Inorg. Chem.*, **3**, 1329, 1964) erroneously suggest that we indicated that the presence of $\text{NSi(CH}_3)_3$ groups was necessary for the formation of five-membered rings and claim to have found a more general reaction for the formation of cyclic compounds with various alkyl or aryl groups on the nitrogen atoms. We desire to emphasize that the first cyclic silylethylenediamine compounds carrying alkyl as well as silyl substituents on the nitrogen atoms had already been prepared by Lienhard[5] in 1959. Thus it was known quite early that the formation of cyclic silylethylenediamines does not depend upon the presence of the $\text{NSi(CH}_3)_3$ group.

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N-Methylcyclosiloxazanes

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When 1,3-dichlorotetramethyldisiloxane or 1,5-dichlorohexamethyltrisiloxane was treated with methylamine, mixtures of silylamines and cyclosiloxazanes were obtained. The corresponding methylphenylsiloxanes gave only silylamines. All these silylamine derivatives could be converted to cyclosiloxazanes with heat in the presence of ammonium sulfate, and several stereoisomers were separated from the phenyl-substituted cyclosiloxazanes. Like the cyclosilazanes, the cyclosiloxazanes could be polymerized with aromatic diols.

Introduction

Several recent publications have described the synthesis of cyclic siloxazanes derived from ammonia.[1-6] As an extension of the interest of this laboratory in N-substituted cyclosilazanes as intermediates in polymer preparation, the synthesis of N-methylcyclosiloxazanes has been investigated. N-Ethyl-[7,8] and N-butylsiloxazanes[6] have been reported, but it has been observed in the literature that 1,3-bis(methylamino)tetramethyldisiloxane and 1,5-bis(methylamino)hexamethyldisiloxane, which are obtained in good yield from methylamine and the corresponding chlorosilane, resist thermal condensation to ring compounds.[1,2]

Results

The properties and characterization of the siloxazanes and the intermediates in their preparation are reported in Table I. Rather than a single product, methylamine and 1,3-dichlorotetramethyldisiloxane (I) and 1,5-dichlorohexamethyltrisiloxane (II) gave mixtures of cyclic and linear compounds. The reactions were carried out by treating the chlorosilanes in petroleum ether with methylamine at 5–10° and heating the resulting mixtures at reflux for 1 hr.

From the product of treating I with methylamine was isolated 40% of 1,3-bis(methylamino)tetramethyldisiloxane (V), 11% of the linear dimer, methylbis(3-(1-methylamino)tetramethyldisiloxanyl)amine (X), and 31% of the cyclic dimer decamethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (XI). II and methylamine afforded a mixture from which 32% of 1,5-bis(methylamino)hexamethyltrisiloxane (VII) and 45% of the cyclic derivative, octamethyl-1-aza-3,5-dioxa-2,4,6-trisilacyclohexane (XII), were separated. When the phenyl-substituted siloxanes 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane (III) and 1,5-dichloro-

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