METAL ALKOXIDE-INDUCED CLEAVAGE OF SILICON-NITROGEN BONDS IN UNSYMMETRICALLY ALKOXYLATED DISILAZANES

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ABSTRACT

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The purpose of this study was to synthesize unsymmetrically alkoxylated disilazanes and to investigate the ease with which sodium methoxide and aluminum isopropoxide cleaved silicon-nitrogen bonds as a function of the number of alkoxy groups bonded to silicon. Also, investigated was the possibility of obtaining linear silicon-nitrogen polymers from the cleavage of the silicon-nitrogen bond by the metal alkoxides.

Two disilazanes, 1,2-dimethoxy-1,1,2,2-tetramethyldisilazane (I) and 1-methoxy-1,1-dimethyl-2,2,2-triethoxydisilazane (II) were prepared according to the following generalized equation, where $R = CH_3$ or C_2H_5:

$$(RO)_3SiCl + (CH_3O)(CH_3)_2SiCl + 3NH_3 \longrightarrow 2NH_4Cl + (CH_3O)(CH_3)_2SiNHSi(OR)_3.$$

Small amounts of the corresponding symmetrical compounds are also formed.

Metal alkoxides were found to cleave the silicon-nitrogen bond in Compounds (I) and (II) to give alkoxysilanes and compounds containing extended silicon-nitrogen frameworks. The latter compounds range from linear oligomeric oils to highly crosslinked solids. Vapor phase chromatographic studies of the products of the various reactions indicated that the cleavage of the silicon-nitrogen

bond in the presence of metal alkoxides was a complex process. Sodium methoxide cleaved the silicon-nitrogen bond to the more alkoxylated silicon in compound (I), but cleaved the silicon-nitrogen bond with the less completely alkoxylated silicon in compound (II). Aluminum isopropoxide did not appear to distinguish between the two silicon-nitrogen bonds in compound (I). However, for compound (II) the silicon-nitrogen bond involving the silicon with three ethoxy groups bonded to it was cleaved more readily by aluminum isopropoxide than was the corresponding bond to the singly methoxylated silicon.

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By

Ronald Eugene Goldsberry

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To My Mother, Mrs. Constance Goldsberry

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I. INTRODUCTION

NOMENCLATURE

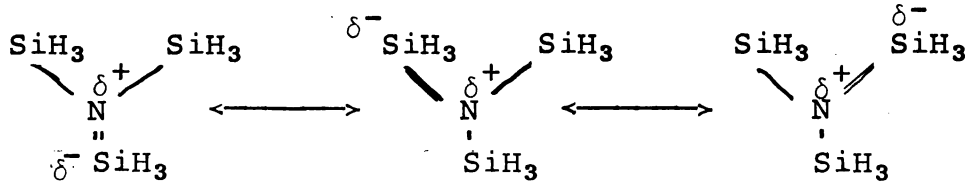
The Committee on Nomenclature of the American Chemical Society and the Commission on the Nomenclature of Organic Chemistry of the International Union of Pure and Applied Chemistry have adopted a system for naming organosilicon compounds. Compounds derived from the structure H_3SiNH_2 are called silylamines, with the use of appropriate prefixes to designate substitution. The system of prefix designation for nitrogen substitution becomes quite cumbersome when more than one nitrogen is attached to silicon. In these cases the amine grouping is designated as a substitutent of the silane.

The generic name silazane is given to the series $H_3Si(NHSiH_2)_nNHSiH_3$. Compounds of this series are called disilazanes, trisilazanes, etc. depending upon the number of silicon atoms in the molecule. Two spellings of this generic name are found in the literature, silazane and silazine, with the former being preferred. Compounds of the type $(H_2SiNH)_n$ are given the generic name cyclosilazanes, the prefix depending upon the number of silicon atoms in the ring.

HISTORICAL

The study of silicon-nitrogen compounds embraces both inorganic and organic chemistry. Although silicon-nitrogen compounds, such as silylamines, differ markedly from their carbon analogs with respect to chemical behavior, the organic nature of this class of compounds should not be underemphasized. An excellent review article[1] exists, which bridges both fields of chemistry and reviews publications through December, 1959, with a few important references from papers published in 1960.

Trisilylamine and tri(methylsilyl)amine have been shown by infrared and Raman spectra[2,3,4] and electron-diffraction[5] data to be co-planar molecules.[6] Also, the silicon-nitrogen bond in trisilylamine is shorter than the calculated silicon-nitrogen single bond distance but longer than the calculated double bond distance. These factors have been interpreted in terms of the ability of the "lone pair" of electrons of nitrogen to be donated to the empty d orbital of the silicon ($d\pi$ - $p\pi$ overlap).



The polarity of the Si-N bond in substituted trisilylamines is decreased and the basicity is lowered as compared with their methyl substituted isostructural counterparts.[7] This may be observed for example in the formation of complexes of silylmethylamines with trimethylboron;[8] neither trisilyamine nor methyldisilylamine form a complex, dimethylsilyamine forms a weak complex and trimethylamine a more stable one. The compounds $(CH_3SiH_2)_3$ and $(CH_3SiH_2)_2NCH_3$ do not form complexes with trimethylboron, but $(CH_3SiH_2)N(CH_3)_2$ does.[9]

The considerable difference between the electronegativities of silicon and nitrogen contributes to a high thermal stability of the Si-N bond but, at the same time, is responsible for its susceptibility to solvolysis[10] by polar solvents. In the infrared spectra of trialkylsilylamines, nitrogen-hydrogen bond stretching and deformation frequencies are similar to those found for normal amines.[11] The silicon-nitrogen asymmetric stretching frequency in the simple amines has been observed in the 900-1000 cm^{-1} region.[12,3,4] Other tabulations and published spectra are available.[13,14,15,16,17] The mass-spectral analysis of hexamethyldisilazane has been reported,[18] as have the nuclear magnetic resonance spectra of hexamethyldisilazane,[19] hexamethyl-cyclotrisilazane,[18] and other silylamines.[7]

Synthesis of Silicon-Nitrogen Compounds

The action of ammonia, primary and secondary amines on a halosilane results in the formation of a silicon-nitrogen bond. Comparative yield data as a function of the nature of the halogen are not available in a sufficiently sterically hindered system for the differences in reactivity to be detected. From the data available, the bromo- and iodosilanes appear more reactive toward a given amine than do the chlorosilanes.[20] Owing to their availability, however, the chlorosilanes are most frequently employed. The halide released during the course of the reaction is precipitated as the amine hydrohalide. The reaction is reversible, with the halosilane being obtained from the silylamine and the amine salt.[21]

$$R_3SiCl \ + \ 2R'NH_2 \rightleftharpoons R_3SiNHR' \ + \ R'NH_3Cl$$

By analogy with the chemistry of the corresponding carbon compounds, the reaction of a monohalosilane with ammonia should yield a variety of silicon-nitrogen products. However, owing to the electronic and steric natures of the compounds involved, only one or, in a few cases, two reaction products are formed. When the non-halogen substituents attached to silicon are hydrogen, there is a definite tendency for complete silylation of the amine.[22,23,24] When silyl chloride is treated with ammonia, trisilyamine can be obtained in 80 per cent yield.[22]

$$H_3SiCl + NH_3 \longrightarrow (H_3Si)_3N + 3HCl$$

The product of the reaction is dependent on the size of the alkyl substituent on silicon. The tendency for complete silylation of the amine is decreased as the size of the groups attached to silicon is increased. With trimethylchlorosilane, only hexamethyldisilazane can be isolated.[25,26,27,28,29] An attempt to obtain trimethylsilylamine by the use of excess liquid ammonia failed. This failure was probably caused by rapid condensation of the silylamine to the disilazane during attempted isolation.

$$(CH_3)_3SiCl + NH_3 \longrightarrow (CH_3)_3Si\overset{H}{N}-Si(CH_3)_3$$

Tris(trimethylsilyl)amine can, however, be formed by the use of the lithium[30] or sodium[6] salt of hexamethyldisilazane.

$$[(CH_3)_3Si]_2NLi + (CH_3)_3SiCl \longrightarrow [(CH_3)_3Si]_3N$$

The preference for formation of silyamine, is again observed in the reaction of triethylchlorosilane with ammonia. In this reaction, triethylsilylamine is the major product, the disilazane being the minor product.[31,32]

$$(C_2H_4)_3SiCl + NH_3 \longrightarrow (C_2H_5)_3SiNH_2$$

The disilazane may be obtained by treating the silylamine with triethylchlorosilane at a higher temperature.[33] With higher trialkylchlorosilanes, only silylamines have been reported as products.[34,35]

Trialkoxychlorosilanes react with ammonia and amines in the same general fashion as do trialkyl and triarylhalosilanes. Both trimethoxy and triethoxychlorosilanes yield the corresponding disilazanes when treated with ammonia,[36] while triisopropoxy[37] and tributoxychlorosilanes[38,39] yield only the silylamines. A further increase in the size of the alkoxy group has no effect upon the products obtained.

$$(CH_3O)_3SiCl + NH_3 \longrightarrow [(CH_3O)_3Si]_2NH$$

$$(C_4H_9O)_3SiCl + NH_3 \longrightarrow (C_4H_9O)_3SiNH_2.$$

In recent years a considerable amount of research has been devoted to the synthesis of inorganic polymers with properties which would enable them to function as elastomers, resins, and lubricants at extreme tempertures. Such a polymer, methyl silicone, a polyorganosiloxane usually represented as $[(CH_3)_2SiO]_n$, is a straight-chain polymer containing alternating silicon and oxygen atoms. Since the N-H group is isoelectronic with oxygen, one might expect to be able to obtain substances analogous to the silicones in which the N-H groups replace oxygen atoms. A possible route to substances of this kind is illustrated by the reaction of dimethyldichlorosilane with ammonia according to the equation:

$$n(CH_3)_2SiCl_2 + 3nNH_3 \longrightarrow [(CH_3)_2SiNH]_n + 2nNH_4Cl$$

Thus the synthesis of polymers, based on a silicon-nitrogen framework, that have optimum stability toward hydrolysis and high temperature and have a highly linear structure has been an active research area.

One should note, however, that the hydrogen atom attached to nitrogen in these polyorganosilazanes should be capable of further substitution by other dimethyldichlorosilane molecules to give a crosslinked polymeric material. This is one feature which has stimulated the recent interest in silicon-nitrogen polymers. Also, due to the considerable $d\pi$ - $p\pi$ interaction between the silicon and nitrogen atoms, arising from contributions of the "lone pair" of electrons on nitrogen to the empty d orbitals of silicon, the silicon framework is bonded together more rigidly than the flexible silicon-oxygen framework of the siloxanes.

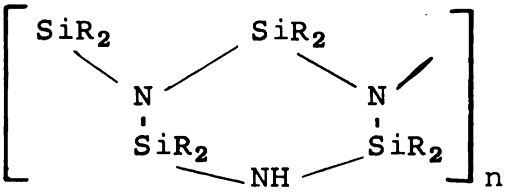
It is also well known that silicon-nitrogen compounds as a rule tend to split off ammonia in the presence of water and alcohols and give the analogous siloxanes. This tendency to hydrolyze is related directly to the number of silicon atoms bonded to the nitrogen atom and hence to the degree of $d\pi$-$p\pi$ bonding in the molecule. For example, as one proceeds from a primary to a tertiary silylamine, the tendency towards hydrolysis becomes progressively smaller. This indicates that delocalization of the electron pair into <u>d</u> orbitals of the silicon atom minimizes the attack on the nitrogen atom and leads to a more stable compound. Therefore, if one wants to obtain a hydrolytically stable silicon-nitrogen polymer, one must "tie up" the electron pair on the nitrogen atom either by complexation with a metal ion or by tri-substituting the nitrogen atoms with silicon atoms. Steric factors are also important.

The factors mentioned above are not the main difficulties encountered in the preparation of silicon-nitrogen analogs to the silicones. When one, in fact, carries out the reaction between dimethyldichlorosilane and ammonia under the normal conditions for obtaining polysiloxanes, one does not obtain a high polymer at all, but instead obtains cyclic compounds. Hexamethylcyclotrisilazane, $[(CH_3)_2SiNH]_3$, and octamethylcyclotetrasilazane $[(CH_3)_2SiNH]_4$, can be prepared in approximately 80 per cent yield by this method.[40] This strong tendency to form rings precludes the use of simple methods for obtaining organosilazane polymers. This ring-formation tendency is also found in siloxanes, but to a much smaller extent;[41] the ring-chain equilibrium is understood and can be manipulated. Recently, however, by using special methods, several types of linear silicon-nitrogen polymers have been prepared. The polymers range from oils and greases to waxes and rubbers; some are extremely stable while others decompose in moist air to liberate ammonia and form the corresponding siloxanes.

Since dimethyldichlorosilane reacts with ammonia to form mixtures of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane, plus a small amount of polymer, the silizane rings must be either opened and the fragments joined to form a linear polymer or the rings themselves must be connected in some manner. Andrianov attempted to prepare polysilazanes by treatment of hexamethylcyclotrisilazane with potassium hydroxide.[42] At 165°C, some cleavage of the silicon-carbon bonds occurred with the formation of methane. Only highly crosslinked polysilazanes could be isolated from the reaction mixture. A basic catalysis involving a base in the ammonia system, i.e., sodium amide, is also unsatisfactory. It has been shown that this reagent metalates the NH groups in the cyclic starting material rather than splitting the silicon-nitrogen bonds.[43]

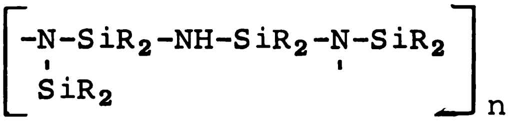
Krüger studied the use of ammonium halides, which are acids in the ammonia system, as possible polymerization catalysts.[44] It had previously been noted by Anderson that silicon-nitrogen bonds could be broken in the presence of inorganic halides.[45] Polymers were obtained which ranged from waxes to very tough elastomers which showed remarkable thermal stability and considerable hydrolytic stability. The silazane polymers were found to have approximately 2/3 of their nitrogen atoms completely substituted. This would indicate either of two structures:

I



or

II



where R = CH_3. Structure I is the more probable structure, for it is well known that silazanes tend to form small rings.[46,47] However, there is no need to assume perfect ordering of the ring structures; and, therefore, the polymers are probably a mixture of structure I and structure II.

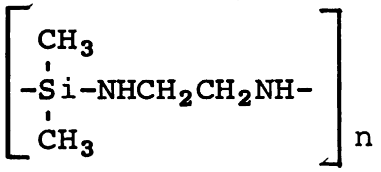
Krüger also isolated two highly cross-linked polymers by heating freshly-distilled hexamethylcyclotrisilazane with 1% of ammonium bromide to 280°C, for several hours. A dark brown material resulted having properties between those of a rubber and those of a wax. The other polymer was prepared by carrying out the reaction of dimethyldichlorosilane with ammonia to obtain a mixture of cyclic trimer and tetramer, and then heating this crude reaction mixture at 280°C for several hours in the presence of 5% ammonium bromide as a catalyst. A white, waxy material resulted which looked very much like polyethylene; both compounds were flexible, but not elastic.[44]

By mixing 55 grams of cyclotrisilazane and 3 grams of methyltrichlorosilane with 5% of ammonium bromide and heating the mixture while bubbling ammonia through it, Krüger obtained an elastic, waxy polymer which melted at 178-190°C. This polymer was crosslinked through silicon and tertiary nitrogen.

A polymer cross-linked through vinyl groups and tertiary nitrogen was prepared by Krüger by heating a mixture of 40 grams of cyclotrisilazane, 10 grams of trimethyl-trivinylcyclotrisilazane and 5% of ammonium bromide. A rubber which swelled in carbon tetrachloride was obtained.

It was found by R. N. Minné[48] and independently by K. Lienhard[49] that a polymeric material could be obtained from the reaction of ethylenediammine with dimethyldichlorosilane. The two polymers obtained were reported as having the following structures:

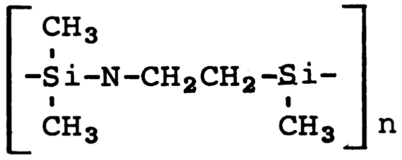
A



$$\left[\begin{array}{l} CH_3 \\ -\overset{|}{\underset{|}{Si}}-NHCH_2CH_2NH- \\ CH_3 \end{array}\right]_n$$

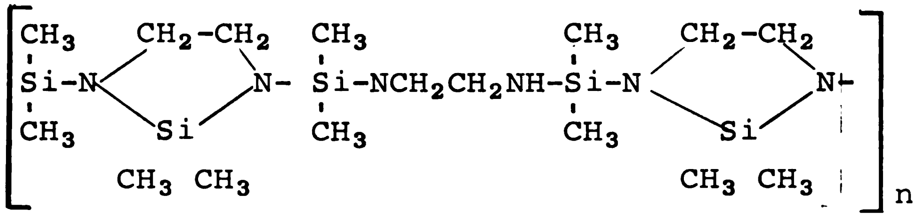
and

B



$$\left[\begin{array}{llll} CH_3 & & & \\ -\overset{|}{\underset{|}{Si}}-N-CH_2CH_2-\underset{|}{Si}- & & & \\ CH_3 & & CH_3 & \end{array}\right]_n$$

Subsequent research in this area by D. Kummer[50,47] let to two more polymers: polymer I in xylene and polymer II in benzene. From analytical data on polymer I and polymer II it was found that neither of the two pure compositions, A or B, had been obtained. Instead, a mixture of both structures is present in both polymer I and polymer II, and the proposed average structure is given by Kummer[50] as:



The presence of the five-membered rings in the polymer is supported by IR[51] measurements and by double-resonance high resolution NMR.[52] In no case could the pure linear compound of Minné be obtained, even with an excess of ethylenediamine.

Attempts have been made to polymerize N,N',N"-nonamethylcyclotrisilazane.[53] So far little success has been achieved, for it seems that the cyclic compounds are much too stable. The advantage of obtaining an N-methylsilazane is that cross-linking through the nitrogen atoms would be prohibited, and a linear polymer should, therefore, result.

Finally, low-molecular-weight linear silicon-nitrogen polymers, were prepared by Weibrecht.[54] In this method, sym-dimethoxy-tetramethyldisilazane and the corresponding tri and tetrasilazanes were prepared by the treatment with anhydrous ammonia. Prolonged heating of the disilazane in the presence of sodium methoxide, aluminum methoxide and isopropoxide, and potassium tertiarybutoxide led to liquid polysilazanes containing 5 to 6 silicon atoms, as well as to some other, high molecular weight silicon-nitrogen substances of a more complicated nature.

Synthesis of Alkoxy Silanes

The most important method of obtaining organosilicon alkoxides and phenoxides involves treatment of an organosilicon chloride with an alcohol or a phenol:

$$\equiv Si{-}Cl + ROH \longrightarrow \equiv SiOR + HCl.$$

Partial replacement of halogen is clearly possible in a polyhalogen compound:

$$Et_2SiCl_2 + EtOH \longrightarrow Et_2SiCl(OEt) + HCl.$$

The alcoholysis reaction is reversible although the equilibrium normally lies well in favor of the products in the presence of an excess of the alcohol; therefore, it is desirable to remove the hydrogen chloride either by boiling it out of the reaction mixture or by reaction with a base. More serious than the reversibility is the fact that if the hydrogen chloride is not removed, it can react with the alcohol to give the alkyl chloride and water. The latter can then hydrolyze the organosilicon alkoxide or chloride.

Sodium alkoxides or phenoxides may be used in place of alcohols. They are not only the effective reagents but can serve as acceptors as well. A solution of sodium alkoxide in alcohol is a much more active reagent than the alcohol alone, and is particularly useful in introducing alkoxy groups in highly hindered systems.

II. EXPERIMENTAL

REAGENTS

Silicon tetrachloride and dimethyldichlorosilane were supplied by Dow Corning and used without further purification. Methanol was refluxed over magnesium and absolute ethanol was used without further purification. All solvents were dried over sodium wire.

PREPARATION OF HEXAMETHOXYDISILAZANE

1. Preparation and Purification

Hexamethoxydisilazane was prepared according to the method of Weibrecht and Rochow.[54] In this procedure, silicon tetrachloride and a stoichiometric amount of methanol in solution were reacted to give trimethoxychlorosilane. Ammonia gas was added to this solution to give the desired product.

In a typical experiment five-tenths of a mole of silicon tetrachloride was added to one liter of dry carbon tetrachloride in a 3-liter, 3-necked, round-bottom flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel. One and five-tenths moles of methanol was added dropwise and HCl evolution began immediately. After all of the methanol had been added, the reaction mixture was refluxed for 1.5 hours and the apparatus flushed with dry nitrogen to remove traces of hydrogen chloride. The trimethoxychlorosilane, which was presumably the product of this reaction, was not isolated. Rather, ammonia gas was added directly to the hexane solution described above and ammonium chloride precipitation was observed immediately. Concurrently, there was a rapid rise in temperature which caused the hexane to reflux without external heating. Ammonia addition was continued for five hours until the reaction mixture began to cool.

The hexane solution was separated from the very large amount of NH_4Cl by suction filtration. The ammonium chloride was then washed with 2 liters of hexane, and the two hexane fractions were combined. Undoubtedly, this washing of the ammonium chloride was one of the most crucial steps in maximixing the yield. Much of the desired product would otherwise almost certainly have been left clinging to the NH_4Cl. The hexane was distilled out of the mixture, and when the temperature had risen to 95°C, it appeared as though all of the hexane had been removed. The remaining liquid was fractionally distilled at atmospheric pressure using a 15 inch column packed with glass helices. The normal boiling point of hexamethoxydisilazane is 220°C. Forty and three tenths grams of material boiling between 220°-223°C were collected, which corresponded to a 63% yield of hexamethoxydisilazane.

2. Nuclear Magnetic Resonance Spectrum of Hexamethoxydisilazane

The proton nuclear magnetic resonance spectrum of the hexamethoxydisilazane was obtained in 50% carbon tetrachloride solution as solvent with tetramethylsilane as the reference, using a Varian A-60 Spectrometer. The spectrum showed one peak which was assigned to the methoxy protons at $\delta = 3.60$ downfield from TMS.

This indicates that all of the methoxy groups in the molecule are in the same chemical environment. This is entirely consistent with what would be expected for $(CH_3O)_3\text{-Si-NH-Si-}(OCH_3)_3$.

PREPARATION OF 1-METHOXY-1,1-DIMETHYL-2,2,2-TRIMETHOXYDISILAZANE

1. Preparation and Purification

The 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane was prepared in a manner similar to that described for the preparation of hexamethoxydisilazane in the preceding section. A typical run is described below:

Two moles of dimethyldichlorosilane was added to one liter of dry *n*-hexane in a 3-liter, 3-necked, round-bottom flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. Similarly, two moles of silicon tetrachloride was added to one liter of dry *n*-hexane. Two moles of methanol was added dropwise to the flask containing the dimethyldichlorosilane, and six moles of methanol was added to the flask containing the silicon tetrachloride. Hydrogen chloride evolution began immediately. After all of the methanol had been added, the reaction mixtures were refluxed for 1.5 hours and in each case the reaction vessels were flushed with dry nitrogen to remove traces of hydrogen chloride. The methoxydimethylchlorosilane and trimethoxychlorosilane which were presumably the products of these reactions were not isolated. Rather, ammonia gas was added directly to the combined hexane solutions described above, and ammonium chloride precipitation was observed immediately. Concurrently, there was a rapid rise in temperature which caused the hexane to reflux without external heating. The hexane solution was separated from the very large amount of NH_4Cl by suction filtration. Ammonia gas was again added to the hexane solution described above and the resulting mixture filtered by suction to remove the NH_4Cl. This process was repeated until an excess of ammonia was present indicating the reaction was complete. In each case, the ammonium chloride was washed with hexane, and the hexane fractions were combined. The hexane was distilled out of the mixture, and when the temperature had risen to 95°C, it appeared as though all of the hexane had been removed. The liquid boiling above 95°C at atmospheric pressure corresponded to a 73% yield of crude disilazanes. This liquid was fractionally distilled at 10 mm. pressure, using a 15 inch, insulated column packed with glass helices and yielded the fractions shown in Table I.

Table I. Distillation of 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane.

Fraction	BP°C (10 mm)	BP°C (760 mm)
I	47-49	163-165
II	53-55	170-175
III	65-71	185-190
IV	75-78	197-200
V	82-84	205
VI	86-90	210
VII	92-95	220
VIII	higher boiling oily material	

2. Discussion of Analytical Data

Analytical data obtained for Fraction V were compared with the values calculated for 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane. These data are shown in Table II.

Table II. Elemental analysis of 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane

	Calculated %	Found %
Carbon	32.10	32.23
Hydrogen	8.49	8.54
Silicon	25.	25.10
Nitrogen	6.24	6.31
Molecular Weight	225.40	230.

The agreement between the calculated and found percentages of the various elements leaves little doubt that this substance is indeed the desired 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane.

3. Infrared Spectra

The infrared spectra of Fractions I through VIII were obtained on pure liquid films between NaCl discs and Nujol mulls using a Unicam SP-200 Spectrophotomer. (See Figure 1, Appendix I.) All of the spectra were essentially identical and most of the peaks in the spectra could be assigned by comparison to values reported by Smith[55] for some alkoxysilicon compounds and also the infrared absorption frequencies of hexamethylcyclotrisilane discussed by Kriegsmann.[17]

The infrared absorption frequencies, their relative intensities and tentative assignments are given in Table III.

This infrared spectrum is entirely consistent with what might be expected for a molecule such as 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane. All of the important frequencies have been observed.

4. Nuclear Magnetic Resonance Studies of Fractions I Through VIII

The proton nuclear magnetic resonance spectra of all fractions were obtained as described in the preceding section. The spectrum of Fraction I shows only 2 peaks, one of which is assigned to methyl protons at $\delta = 0.09$ downfield from TMS

Table III. Infrared absorption frequencies of 1,1-dimethyl-2,2,2-trimethoxydisilazane

Frequency cm^{-1}	Intensity*	Assignment
3278	m	symmetric N-H stretch
2900	s	symmetric C-H stretch, methyl
2800	m	symmetric C-H stretch, methoxy
1460	w	
1405	w	antisymmetric C-H deformation
1250	vs	symmetric C-H deformation characteristic of $Si-CH_3$
1190	s	$SiOCH_3$ rock
1100	vs	C-O stretch
960	vs	Si-N-Si stretch
850	vs	Si-O stretch
810	vs	
725	w	

*m = medium, s = strong, vs = very strong, and w = weak.

and the other due to methoxy protons at $\delta = 3.50$. Integration gave a ratio of methyl protons to methoxy protons of 2:1. Since there was only one methyl and one methoxy peak, all of the methoxy groups must find themselves in the same environment. The NMR spectrum and boiling point of Fraction I agree with those reported for 1,2-dimethoxy-1,1,2,2-tetramethyldisilazane.

The spectra of Fractions II, III, IV, V, and VI all contain three peaks, one of which was assigned to methyl protons at $\delta = 0.09$ downfield from TMS and the other two, due to methoxy protons, one at $\delta = 3.50$ and the second at $\delta = 3.60$ both downfield. (See Figure 1, Appendix II.)

The ratio of total methoxy to methyl protons and methoxy protons at $\delta = 3.60$ to those at $\delta = 3.50$ of Factions II through VI are given in Table IV.

Table IV. Comparison of NMR peaks from the distillation of 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane

Fraction	$\frac{\text{MeO}}{\text{Me}}$	$\frac{\text{MeO at } \delta = 3.60}{\text{MeO at } \delta = 3.50}$
II	1.3	1.4
III	1.5	1.8
IV	1.7	2.9
V	1.99	2.96
VI	2.1	3.8

The methoxy peak found at $\delta = 3.60$ and total methoxy becomes progressively larger in going from Fraction II to VI.

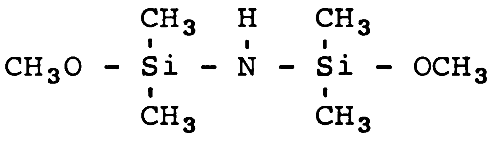
This illustrates that while there is only one type of methyl group present, structurally, there are two distinct types of methoxy groups.

The spectrum of Fraction VII showed one peak which was assigned to the methoxy protons at $\delta = 3.60$ downfield from TMS. This indicates that all of the methoxy groups are in the same chemical environment.

The spectrum of Fraction VIII showed eight peaks. The methyl peak at $\delta = 0.09$ downfield from TMS is split into four peaks, while the methoxy peak at $\delta = 3.50$ is split into two peaks and the methoxy peak at $\delta = 3.60$ is split into two peaks. This indicates that the methyl and methoxy groups both find themselves in four different chemical environments.

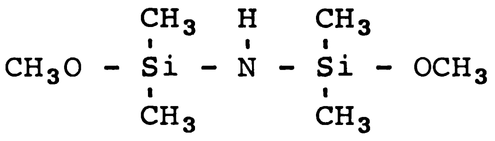
From the NMR data as well as the results of the elemental analysis and the infrared spectra, the following structures can be written for Fractions I through VIII:

I



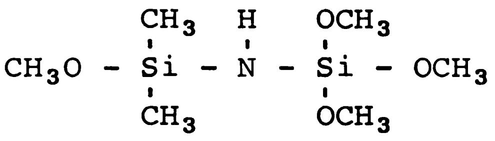
$$CH_3O - \overset{CH_3}{\underset{CH_3}{Si}} - \overset{H}{N} - \overset{CH_3}{\underset{CH_3}{Si}} - OCH_3$$

II, III, and IV azeotropic mixtures of



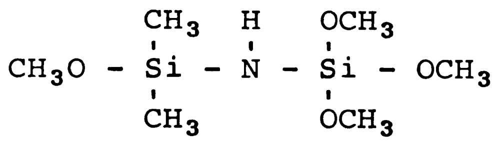
$$CH_3O - \overset{CH_3}{\underset{CH_3}{Si}} - \overset{H}{N} - \overset{CH_3}{\underset{CH_3}{Si}} - OCH_3$$

and



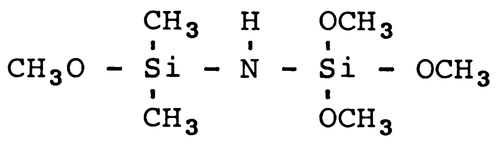
$$CH_3O - \overset{CH_3}{\underset{CH_3}{Si}} - \overset{H}{N} - \overset{OCH_3}{\underset{OCH_3}{Si}} - OCH_3$$

V



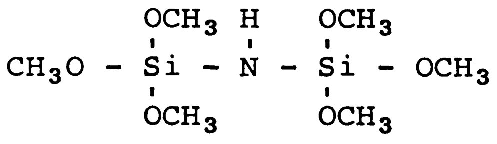
$$\mathrm{CH_3O-\overset{CH_3}{\underset{CH_3}{Si}}-\overset{H}{N}-\overset{OCH_3}{\underset{OCH_3}{Si}}-OCH_3}$$

VI Azeotropic mixture



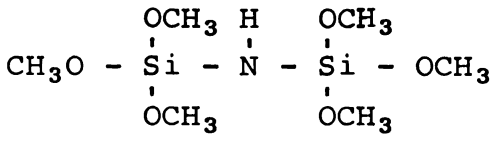
$$\mathrm{CH_3O-\overset{CH_3}{\underset{CH_3}{Si}}-\overset{H}{N}-\overset{OCH_3}{\underset{OCH_3}{Si}}-OCH_3}$$

and



$$\mathrm{CH_3O-\overset{OCH_3}{\underset{OCH_3}{Si}}-\overset{H}{N}-\overset{OCH_3}{\underset{OCH_3}{Si}}-OCH_3}$$

VII



$$\mathrm{CH_3O-\overset{OCH_3}{\underset{OCH_3}{Si}}-\overset{H}{N}-\overset{OCH_3}{\underset{OCH_3}{Si}}-OCH_3}$$

VIII Low molecular weight mixed silazane polymers.

5. Summary

A small amount of a substance collected at 47°C was shown by NMR to be the symmetrical compound, 1,2-dimethoxy-1,1,2,2-tetramethyldisilazane. A small amount of another substance, boiling at 92-95°C, was identified as hexamethoxydisilazane. Although azeotropic mixtures of the various disilazanes were obtained, it was possible to isolate a fraction which boiled at 82-84°C (b.p. = 205°C at 740 mm) in 35-40% yield. This compound will henceforth be designated as compound (I).

PREPARATION OF
1-METHOXY-1,1-DIMETHYL-2,2,2-TRIETHOXYDISILAZANE

1. Preparation and Purification

The method of preparation of the 1-methoxy-1,1-dimethyl-2,2,2-triethoxydisilazane was analagous to that used in the preparation of 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane.

Two moles of dimethyldichlorosilane was added to one liter of dry n-hexane in a 3-liter, 3-necked, round-bottom flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. Similarly, two moles of silicon tetrachloride was added to one liter of dry n-hexane. Two moles of methanol was added dropwise to the flask containing the dimethyldichlorosilane and six moles of absolute ethanol was added to the flask containing the silicon tetrachloride. Hydrogen chloride evolution began immediately. After all of the methanol and ethanol had been added, the reaction mixtures were refluxed for 1.5 hours and in each case the reaction vessels were flushed with dry nitrogen to remove traces of hydrogen chloride. The methoxydimethylchlorosilane and triethoxychlorosilane which were presumably the products of the reactions were not isolated. Rather, ammonia gas was added directly to the combined hexane solutions described above and ammonium chloride precipitation was observed immediately. This reaction, like the others, was also found to be exothermic. The hexane solution was separated from the NH_4Cl by suction filtration. Ammonia gas was again added to the hexane solution described above and the resulting mixture filtered by suction to remove the NH_4Cl. This process was repeated until an excess of ammonia was present indicating that reaction was complete. In each case the ammonium chloride was washed with hexane, and the hexane fractions were combined. The hexane was distilled out of the mixture, and when the temperature had risen to 95°C it appeared as though all of the hexane had been removed. The liquid boiling above 95°C at atmospheric pressure corresponded to a 75% yield of the crude mixed disilazanes. This liquid was fractionally distilled at 10 mm pressure, using a 15 inch, insulated column packed with glass helices and yielded the fractions shown in Table V.

Table V. Distillation of 1-methoxy-1,1-dimethyl-2,2,2-triethoxydisilazane

Fraction	BP°C (10 mm)	BP°C(760 mm)
I	47-49	163-165
II	67-71	190
III	73-75	195-197
IV	80-86	205-210
V	90-92	215
VI	107-110	245-250
VII	112-150	255-290

2. Infrared Spectra

The infrared spectra of Fractions I through VI were obtained on pure liquid films between NaCl discs and Nujol mulls using a Unicam SP-200 Spectrophotometer. All of the spectra were identical to the spectra of the 1,1-dimethyl-2,2,2-trimethoxydisilazane discussed in the previous section. This is consistent since the 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane and 1-methoxy-1,1-dimethyl-2,2,2-triethoxydisilazane molecules are so similar.

3. Nuclear Magnetic Resonance Studies of Fractions I, V, and VI

The proton nuclear magnetic resonance spectra were obtained as described in the previous section.

The spectrum of Fraction I was identical to the spectrum of Fraction I from the preparation of 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane. There were two peaks present, one of which is assigned to methyl protons at $\delta = 0.09$ downfield from TMS and the other due to methoxy protons at $\delta = 3.50$. Integration gave a ratio of methyl protons to methoxy protons of 2:1.

The spectra of Fractions V and VI showed nine peaks. (See Figure 2, Appendix II.) There was a singlet at $\delta = 0.9$ downfield from TMS, assigned to methyl on silicon; a triplet at $\delta = 1.24$ downfield, assigned to methyl protons in the ethoxy groups; a singlet at $\delta = 3.50$ downfield, due to methoxy on silicon; and a quartet at $\delta = 3.90$ downfield, attributed to methylene protons in the ethoxy groups. The ratios of methyl to ethoxy to methoxy protons in Fractions V and VI were 2:5:1 and 10:42:1, respectively. For Fraction V, this corresponds to a ratio of methyl to ethoxy to methoxy groups in the molecules of 2:3:1 and for Fraction VI a ratio of 10:25:1. The spectra further indicated that that both of the methyl groups as well as all three of the ethoxy groups were in the same chemical environment.

4. Vapor Phase Chromatography

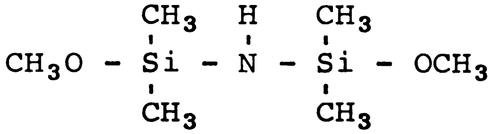
The gas chromatographic analysis was done using an Aerograph A-90-P chromatograph equipped with a 20% SE 30, 60/80 chromosorb wax column.

Fractions I and V showed one major peak. This indicates that these fractions were pure compounds. The retention times of these fractions were identical to the retention times of sym-dimethoxytetramethyldisilazane and 1-methoxy-1,1-dimethyl-2,2,2-triethoxydisilazane, respectively.

Fractions II, III, IV and VI showed two major peaks. The retention time of the first major peak for Fractions II, III, and IV was the same as the retention time of Fraction I. The retention time of the second major peak for Fractions II, III, and IV, and the first major peak for Fraction VI was identical to the retention time of Fraction V. The retention time of the second major peak for Fraction VI was the same as the retention time of hexaethoxydisilazane.

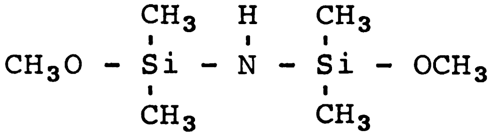
From the gas chromatographic analysis as well as the results from the NMR data, the nitrogen analysis and the infrared spectra, the following structures can be written for Fractions I through VI:

I

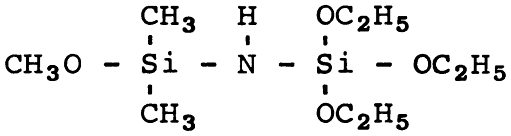


$$CH_3O-\underset{CH_3}{\overset{CH_3}{Si}}-\overset{H}{N}-\underset{CH_3}{\overset{CH_3}{Si}}-OCH_3$$

II, III, and IV azeotropic mixtures of

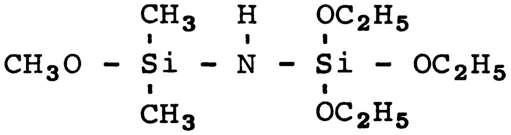


$$CH_3O-\underset{CH_3}{\overset{CH_3}{Si}}-\overset{H}{N}-\underset{CH_3}{\overset{CH_3}{Si}}-OCH_3$$



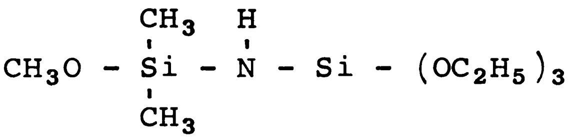
$$CH_3O-\underset{CH_3}{\overset{CH_3}{Si}}-\overset{H}{N}-\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}-OC_2H_5$$

V

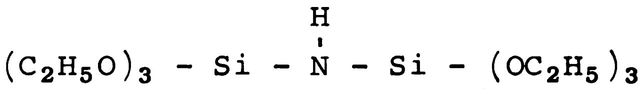


$$CH_3O-\underset{CH_3}{\overset{CH_3}{Si}}-\overset{H}{N}-\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}-OC_2H_5$$

VI Azeotropic mixture of



$$CH_3O-\underset{CH_3}{\overset{CH_3}{Si}}-\overset{H}{N}-Si-(OC_2H_5)_3$$



$$(C_2H_5O)_3-Si-\overset{H}{N}-Si-(OC_2H_5)_3$$

5. Summary

Fractional distillation of a mixture of crude disilazanes from the preparation of 1-methoxy-1,1-dimethyl-2,2,2-triethoxydisilazane yielded a small amount of 1,2-dimethoxy-1,1,2,2-tetramethyldisilazane. A fraction was isolated which boiled at 90-92°C (b.p. 215 at 760 mm) in

42% yield, compound V, 1-methoxy-1,1-dimethyl-2,2,2-triethoxydisilazane. This compound will be referred to as Compound (II). Azeotropic mixtures of the various disilazanes were also obtained, including a mixture which contained hexaethoxydisilazane.

SILICON ANALYSIS

Porcelain crucibles were fired in a muffle furnace at 700°C to constant weight and stored in a desiccator over $Mg(ClO_4)_2$. Weighed samples (0.2 - 0.3 g) of the disilazane were added to the crucibles which were cooled in dry ice. Concentrated sulfuric acid (3-5 cc) was then slowly added to the samples. The crucibles were removed and allowed to warm to room temperature. They were placed in a muffle furnace and the temperature slowly raised to 900°C over a period of 12-16 hours. The crucibles and contents were removed from the furnace and stored over $Mg(ClO_4)_2$ until cool and reweighed to obtain the weight of SiO_2 formed. The per cent silicon was calculated using the expression

$$\%Si = \frac{0.467 \times \text{wt } SiO_2}{\text{sample weight}} \times 100 .$$

NITROGEN ANALYSIS

A weighed sample of disilazane (0.2-0.3g) was dissolved in aqueous ethanol and several drops of bromocresol purple added. Excess standard hydrochloric acid was added and back titrated with standard sodium hydroxide to the indicator color of a blank that was run previously. The per cent nitrogen was calculated using the expression

$$\%N = \frac{\text{Volume of standard acid x N of acid x 14}}{\text{Sample weight}} \text{ x } 100.$$

PREPARATION OF ALKOXY SILANES

The alkoxy silanes were prepared according to the method of Peppard, Brown, and Johnson.[56] To avoid repetition of experimental details, the data pertaining to the alkoxy silanes are presented in tabular form and, except as otherwise noted, the preparation of dimethoxydiethoxysilane described below may be considered as typical.

The reaction was carried out in a 500-ml, three-necked flask fitted with a mechanical stirrer, dropping funnel, and gas exit tube, all openings being protected by calcium chloride tubes. To 0.5 mole of silicon tetrachloride contained in the flask was added, with cooling and over a period of two and one-half hours, one mole of ethanol and one mole of methanol.

The mixture was then transferred to the boiling flask of an all-glass fractionating column and heated rapidly to free it of dissolved hydrogen chloride. Fractional distillation of the remaining liquid yielded the following:

$Si(OMe)_4$	121^0
$EtOSi(OMe)_3$	$133-135^0$
$(EtO)_2Si(OMe)_2$	$143-146^0$
$(EtO)_3SiOMe$	$155-157^0$
$Si(OEt)_4$	166.1^0 .

Physical constants of alkoxy silanes in order of increasing molecular weight are presented in the following table:

Table VI. Physical constants of some alkoxy silanes

Formula	Name	B.P.(lit)	Ref.
$(CH_3)_2Si(OCH_3)_2$	dimethyldimethoxysilane	82.2°	- 57
$(CH_3)_2SiOCH_3(OC_2H_5)$	dimethylmethoxyethoxysilane	----	
$(CH_3)_2Si(OC_2H_5)_2$	dimethyldiethoxysilane	113.8°	- 57
$Si(OCH_3)_4$	tetramethoxysilane	121°	- 58
$(CH_3)_2OCH_3Si(O\text{-}\underline{i}\text{-}C_3H_7)$	dimethylmethoxyisopropoxysilane	----	
$(CH_3O)_3Si(OC_2H_5)$	trimethoxyethoxysilane	$133\text{-}135^\circ$	- 59
$(CH_3O)_2Si(OC_2H_5)_2$	dimethoxydiethoxysilane	$143\text{-}146^\circ$	- 59
$(CH_3O)_3Si(O\text{-}\underline{i}\text{-}C_3H_7)$	trimethoxyisopropoxysilane	----	
$(CH_3O)Si(OC_2H_5)_3$	methoxytriethoxysilane	$155\text{-}157^\circ$	- 60
$Si(C_2H_5O)_4$	tetraethoxysilane	----	
$(C_2H_5O)_3Si(O\text{-}\underline{i}\text{-}C_3H_7)$	triethoxyisopropoxysilane	----	
$(CH_3O)(C_2H_5O)Si(O\text{-}\underline{i}\text{-}C_3H_7)_2$	methoxyethoxydiisopropoxysilane	----	

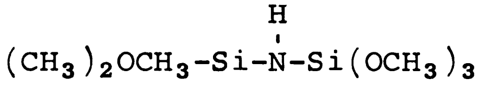
PYROLYSIS OF
1-METHOXY-1,1-DIMETHYL-2,2,2-TRIMETHOXYDISILAZANE

In an investigation of the properties of some alkoxysilazanes, Buerger and Wannagat[60] found that pyrolysis of hexamethoxydisilazane at 200°C in a sealed tube led to the formation of cross-linked polymers, accompanied by the evolution of tetramethoxysilane.

1. Pyrolysis of the Disilazane in a Sealed Tube

In order to study the pyrolysis of 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane, 20 ml of the disilazane was heated at 200-225°C for 24 hours in a sealed Pyrex tube. The tube was opened after it was cooled in a dry ice bath. No attempt was made to isolate all of the pure components of the pyrolysis mixture. Rather, the retention times on a vapor phase chromatographic column were found for previously prepared pure samples of all of the possible alkoxysilanes and known mixtures of them. (See Figure 1, Appendix III.) The constituents of the pyrolysis mixtures were then identified by comparison of their retention times with the retention times of the pure compounds. From the areas under the peaks of the vapor phase chromatograms of the mixtures (See Figure 2, Appendix II.), the approximate mole ratios of the constituents were estimated. All of the peaks could be assigned without question. In Table VII the alkoxysilanes found, are listed in order of increasing retention times on the column. The major portion of the mixture was unchanged starting material. From Table VII, it is seen that a small amount of the sample decomposed with the formation of dimethyldimethoxysilane and tetramethoxysilane.

Table VII. Pyrolysis of compound (I) at 200°C.

Volatile Products	Approx. Mole Ratios
$(CH_3)_2Si(OCH_3)_2$	1
$(CH_3O)_4Si$	3
 $(CH_3)_2OCH_3\text{-}Si\text{-}\overset{H}{N}\text{-}Si(OCH_3)_3$	$\frac{-Si(CH_3)_2OCH_3\cdot}{-Si(OCH_3)_3} = \frac{1}{3}$

2. Pyrolysis of the Disilazane at Atmospheric Pressure

A sample of 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane was refluxed under nitrogen for 24 hours in a 100 ml. round-bottom flask equipped with a water-cooled reflux condenser and a calcium chloride drying tube. The mixture was cooled to room temperature and then analyzed by VPC as described in the previous section. A small amount of dimethyldimethoxysilane and tetramethoxysilane formed; however, the major portion of the starting material was recovered unchanged. Again, the ratio of dimethyldimethoxysilane to tetramethoxysilane was 1:3.

3. Pyrolysis of the Disilazane in the Presence of Sodium Methoxide

The following series of experiments were performed to test the catalytic effect of various nonaqueous bases on the polymerization of 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane. These experiments were all carried out in the absence of a solvent. The disilazane and the catalyst, under examination, were mixed and the system heated to the reflux temperature of the disilazane.

a. Experimental Procedure: In a typical experiment 0.110 mole of the disilazane was mixed with 1.85×10^{-2} mole of sodium methoxide in the absence of a solvent and refluxed for 24 hours in a 100 ml., round-bottom flask equipped with a water-cooled reflux condenser. The condenser was connected through two Leiden gas washing bottles to a reservoir of 50 ml. of 0.1160 N hydrochloric acid which took up any ammonia generated during the pyrolysis. Ammonia was given off during the heating process, and after 24 hours, the reaction mixture consisted of a clear, slightly yellow liquid. Upon cooling and standing for several hours, a crystalline solid separated from the liquid. The liquid fraction was decanted from these crystals and the two unknowns were studied separately. Back titration of the hydrochloric acid with 0.201 N sodium hydroxide was used to determine the amount of ammonia produced. Table VIII shows the results obtained in two typical experiments. Ammonia in a 1:1 mole ratio to the quantity of sodium methoxide was formed regardless of the amount of disilazane.

The NMR spectrum of the solid was identical to that of the disilazane except that the methyl protons were shifted 0.24 ppm up field. The solid was known to be the sodium compound of 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane from the results of a similar experiment by

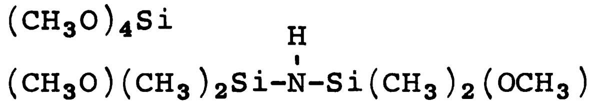
Weibrecht and Rochow.[54] Therefore, the solid was not further analyzed.

Table VIII. Stoichiometry of the pyrolysis of Compound (I) with sodium methoxide

	I	II
Moles of disilazane	1.11×10^{-1}	1.16×10^{-1}
Moles of sodium methoxide	8.43×10^{-3}	5.08×10^{-3}
$\frac{\text{Moles of soidum methoxide}}{\text{Mole of disilazane}}$	7.59×10^{-2}	4.379×10^{-2}
Moles of NH_3 liberated during pyrolysis	8.02×10^{-3}	4.97×10^{-3}
$\frac{\text{Moles of ammonia}}{\text{Moles of sodium methoxide}}$	9.55×10^{-1}	9.78×10^{-1}

The liquid fraction was analyzed by VPC. The volatile constituents of the liquid fraction were identified by comparison of their retention times on a vapor phase chromatographic column with retention times of the pure compounds. (Figure 3, Appendix III.) Table IX lists the alkoxysilanes found in order of increasing retention times on the column.

Table IX. Alkoxy silanes produced from the pyrolysis of Compound (I) with sodium methoxide

Metal Alkoxide	Volatile Products	Approximate Mole Ratios
$NaOCH_3$	$(CH_3)_2Si(OCH_3)_2$	1
	$(CH_3O)_4Si$	3
	 $(CH_3O)(CH_3)_2Si\text{-}\overset{H}{N}\text{-}Si(CH_3)_2(OCH_3)$	2
	$\frac{-Si(CH_3)_2(OCH_3)}{-Si(OCH_3)_3}$	1/3

The liquid fraction was finally distilled at 10 mm pressure until all of the volatile material had been removed and a polymeric material was left behind as a residue. This solid was found to be insoluble in water, dilute hydrochloric acid, dilute sodium hydroxide, methanol, benzene, hexane and carbon tetrachloride. It was decomposed slowly by hot, concentrated sulfuric acid. Nitrogen and silicon analyses have been obtained. However, the apparent formation of silicon carbide under the conditions usually used to determine per cent carbon and hydrogen led to non-reproducible carbon and hydrogen analyses. The presence of an infrared band corresponding to N-H stretching is taken as evidence that the silicon-nitrogen chains are not completely cross-linked through tertiary nitrogen. The analytical data are given in Table X.

Table X. Elemental analysis of the polymer from the pyrolysis of compound (I) with sodium methoxide

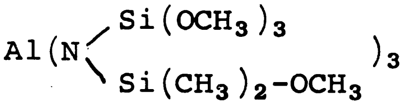
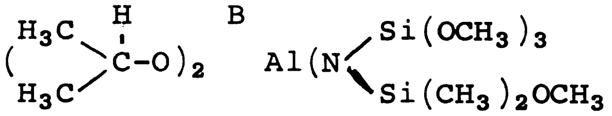
% Nitrogen Calculated	100% linear	100% crosslinked
	17.75	12.76
Found Percentages		
% Carbon	16.60, 16.42	
% Hydrogen	4.66, 4.74	
% Nitrogen	13.93, 13.98	
% Silicon	36.48	

These data show that the polymer is quite highly crosslinked.

b. Nitrogen Analysis: A weighed sample was decomposed under concentrated sulfuric acid in a Kjeldahl flask and gently heated for 2 hours. The polymer decomposed with SiO_2 as one of the products. An excess of concentrated sodium hydroxide was then added to the Kjeldahl flask and the distillate was collected in 50 ml. of standard hydrochloric acid to which several drops of methyl red had been added. A blank was run and the sample was then titrated with standard sodium hydroxide to the indicator color of the blank.

4. Pyrolysis of the Disilazane in the Presence of Aluminum Isopropoxide

a. Experimental Procedure: 0.114 mole of the disilazane and 3.9×10^{-3} moles of aluminum isopropoxide were mixed in the absence of a solvent and refluxed for 24 hours in exactly the same manner employed in the previous polymerization studies. The reaction mixture was a rosy orange color and a solid remained on the side of the flask. After cooling, the liquid fraction was decanted from the solid and the two studied separately. Back titration of the standard hydrochloric acid with standard sodium hydroxide showed 2.97×10^{-3} moles of ammonia were liberated. This is approximately a 1:1 mole ratio of the ammonia liberated to the quantity of aluminum isopropoxide.

The solid was washed with hexane to remove impurities. It was soluble in hydrochloric acid but insoluble in hexane, carbon tetrachloride, benzene and tetrahydrofuran. A qualitative test with the aluminon reagent indicated the presence of aluminum. The NMR of the solid was not taken since the solid was insoluble in all organic solvents attempted. However, the infrared spectrum of the solid was identical to the starting material including a peak corresponding to the N-H stretching frequency. The amount of aluminum was determined by the 8-hydroxyquinoline precipitation method. The per cent aluminum found was 3.09. If the aluminum salt has the formula A  $\mathrm{Al}\left(\mathrm{N}\begin{array}{l}\diagup \mathrm{Si(OCH_3)_3}\\ \diagdown \mathrm{Si(CH_3)_2{-}OCH_3}\end{array}\right)_3$, the calculated per cent aluminum would be 3.682. If the aluminum salt has the formula B  $\left(\begin{array}{l}\mathrm{H_3C}\\ \mathrm{H_3C}\end{array}\!>\!\overset{\mathrm{H}}{\mathrm{C}}\mathrm{{-}O}\right)_2\ \mathrm{Al}\left(\mathrm{N}\begin{array}{l}\diagup \mathrm{Si(OCH_3)_3}\\ \diagdown \mathrm{Si(CH_3)_2OCH_3}\end{array}\right)$, the per cent aluminum would be 7.32. The per cent aluminum found is low when compared with the calculated per cent aluminum for both possible structures. The found percentage is closer to the first proposed structure, but this possibility may be ruled out on steric factors alone. The agreement between the found and calculated percentage for the second structure is clearer when it is observed that the calculated percentage is approximately twice as great as the found per cent aluminum and the infrared spectrum shows a band corresponding to N-H stretching. Thus, a mixture of polysilazanes similar to structure two with only one-half of the hydrogens on nitrogen replaced by aluminum may be proposed.

The liquid fraction was analyzed by VPC (See Figure 4, Appendix III) in order to identify the volatile constituents. Table XI lists the alkoxysilanes found in order of increasing retention time on the column.

Table XI. Alkoxy silanes produced from the pyrolysis of Compound (I) with aluminum isopropoxide

Volatile Products	Approx. Mole Ratios
$(CH_3)_2Si(OCH_3)_2$	10
$(CH_3O)_4Si$	10
$(CH_3)(CH_3O)\text{-}Si\text{-}(O\text{-}\underline{i}\text{-}C_3H_7)$	2
$(CH_3O)_3\text{-}Si\text{-}(O\text{-}\underline{i}\text{-}C_3H_7)$	1

$$\frac{-Si(CH_3)_2(OCH_3)}{-Si(OCH_3)_3} = \frac{1}{1}$$

Finally, in an attempt to isolate a polymeric material, the liquid fraction was distilled at 10 mm pressure until all of the volatile material was removed. If the temperature is not controlled, a polymeric solid similar in properties to the one from the reaction of sodium methoxide and Compound (I) is obtained. Also it appeared as though silicon carbide was formed when this polymer was analyzed for carbon and hydrogen. However, if the liquid is carefully distilled at a low temperature and at 10 mm pressure, a mixture of oligomeric oils is obtained. The oligomeric oils were soluble in a variety of common organic solvents. The NMR spectrum (See Figure 3, Appendix II) of the oils, taken in carbon tetrachloride as solvent, showed a methyl to methoxy ratio of 1 to 1.9, essentially the same as that for the starting material. However, three structurally different kinds of methyl (predominately one) and five structurally different methoxy groups (predominately two) were identified by the spectrum. The methyl to methoxy ratio in the oligomeric oils is consistent with the ratio of methoxydimethylsilyl to trimethoxysilyl groups shown to have been cleaved by the composition of the mixture of volatile pyrolysis products. The analytical data for the two different polymers are given in Table XII.

Table XII. Elemental analysis of the polymers from the pyrolysis of Compound (I) with aluminum isopropoxide

% Nitrogen Calculated	100% linear	100% crosslinked
	10.52	11.63
	Found Percentages	
	Solid Polymer	Oligomeric Oils
% Carbon	12.4, 12.21	27.06, 26.96
% Hydrogen	4.11, 3.84	6.98, 7.19
% Nitrogen	11.48	9.15, 9.09
% Silicon	35.29	28.8 , 28.72

The infrared spectrum of the oligomeric oil indicated that essentially most of the N-H bond remained intact during the pyrolysis. Therefore, it appears on this evidence as though this oil is a linear organopolysilazane. The solid polymer is highly crosslinked.

b. <u>8-Hydroxyquinoline Method for the Determination of Aluminum</u>: Weighed samples (0.2-0.32 g.) of the sample

were added to 100 ml of distilled water. This solution was made acidic with concentrated hydrochloric acid and warmed to 60-70^{o}C. The insoluble material was separated from the supernatant liquid by suction filtration. A slight excess of a 5 per cent 8-hydroxyquinoline solution in 2M acetic acid was added to the liquid allowing 1 ml of reagent for each 3 mg. of aluminum present. Slowly, 2M ammonium acetate solution was added until a precipitate formed and then an additional 25 ml was added to increase the buffering action. The supernatant liquid was yellow from the excess reagent. The solution was cooled for 30 minutes and then the precipitate was collected in a sintered glass crucible, previously dried to constant weight in the oven. The precipitate was washed with cold water until the washings were colorless. The crucible and precipitate were dried for an hour at 120-140^{o}C, cooled in a desiccator and weighed. The dried precipitate has the formula $Al(C_9H_6ON)_3$. The per cent aluminum was calculated using the expression

$$\%Al = \frac{27 \text{ x wt } Al(C_9H_6ON)_3}{459 \text{ x sample weight}} \text{ x } 100$$

PYROLYSIS OF
1-METHOXY-1,1-DIMETHYL-2,2,2-TRIETHOXYDISILAZANE

The polymerization studies of this disilazane were run parallel to the studies on 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane; therefore, experimental details will be eliminated.

1. Pyrolysis of the Disilazane in a Sealed Tube

A sealed tube containing 20 ml of the disilazane was heated in an oven at 200-225°C for 24 hours. A clear yellow liquid remained in the tube. The liquid was shown by VPC (Figure 5, Appendix III) to contain the following constituents.

Table XIII. Alkoxy silanes produced from the pyrolysis of Compound (II) at 200°C

Volatile Products	Approx. Mole Ratio
$(CH_3)_2Si(OCH_3)_2$	10
$(CH_3)_2Si(OCH_3)(OC_2H_5)$	40
$(CH_3)_2Si(OC_2H_5)_2$	30
$Si(OCH_3)_2(OC_2H_5)_2$	5
$Si(OCH_3)(OC_2H_5)_3$	48
$Si(OC_2H_5)_4$	98

$$\frac{Si(OEt)_3}{Si(CH_3)_2OCH_3} = \frac{1.9}{1}$$

From Table XIII, it is seen that the sample decomposed with the formation of alkoxysilanes. However, the major portion of the starting material was recovered unchanged. Distillation of the pyrolysis mixture to dryness without the formation of nonvolatile materials indicated that a solid polymer was not formed.

2. Pyrolysis of the Disilazane in the Presence of Sodium Methoxide

Eleven one-hundredths of a mole of disilazane and

1.85×10^{-2} mole of sodium methoxide were refluxed for 24 hours in the absence of a solvent. The ammonia liberated during the reaction was trapped in a reservoir of standard hydrochloric acid. After 24 hours, the pyrolysis mixture consisted of a brownish-yellow liquid with a crystalline solid in the bottom of the flask. After cooling, the liquid and solid were separated. Back titration of the hydrochloric acid with standard sodium hydroxide indicated 1.91×10^{-2} mole of ammonia was liberated. This is a 1:1 mole ratio of ammonia to the quantity of sodium methoxide. The solid was washed with hexane and identified on the basis of its sensitivity to moisture, proton NMR spectrum, which was identical to that of the pure starting material except for an up-field shift of the methyl proton resonances, and its IR spectrum. This solid is the sodium salt of 1-methoxy-1,1-dimethyl-2,2,2-triethoxydisilazane.

The volatile constituents of the liquid fraction were characterized by VPC (Figure 6, Appendix III). Table XIV lists the alkoxysilanes found in order of increasing retention times on the column.

A polymeric solid was also isolated from this mixture which had all the properties of the polymer from the reaction of sodium methoxide with Compound I. The analytical data are given in Table XV.

These data and the fact that the infrared spectrum of this polymer showed a band corresponding to N-H stretching indicate that while the polymer is crosslinked, it is not completely crosslinked through tertiary nitrogen.

Table XIV. Alkoxy silanes produced from the pyrolysis of Compound (II) with sodium methoxide

Volatile Products	Approx. Mole Ratios
$(CH_3)_2Si(OCH_3)_2$	6
$(CH_3)_2(CH_3O)Si(OC_2H_5)$	18
$(CH_3)_2Si(OC_2H_5)_2$	24
$(CH_3O)_4Si$	6
$(CH_3O)_3Si(OC_2H_5)$	1
$(CH_3O)_2Si(OC_2H_5)_2$	5
$(CH_3O)Si(OC_2H_5)_3$	12
$(C_2H_5O)_4Si$	10

$$\frac{-Si(CH_3)_2(OCH_3)}{-Si(OC_2H_5)_3} = \frac{3}{2}$$

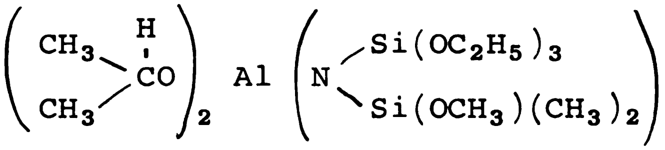
Table XV. Elemental analysis of the polymer from the pyrolysis of Compound (II) with sodium methoxide

%Nitrogen Calculated	100% linear	100% crosslinked
	14.8	10.6
	Found Percentages*	
% Carbon	14.74, 14.40	
% Hydrogen	4.14, 3.93	
% Nitrogen	14.42, 13.9	
% Silicon	35.85	

*Carbon and hydrogen results nonreproducible due to the possible formation of SiC.

3. Pyrolysis of the Disilazane in the Presence of Aluminum Isopropoxide

A mixture of 0.092 mole of the disilazane and 1.651 x 10^{-3} mole of aluminum isopropoxide was refluxed for 24 hours. The ammonia liberated, 1.49 x 10^{-3} moles, was in a 1:1 mole ratio to the quantity of aluminum isopropoxide. The pyrolysis mixture consisted of a solid and a liquid. The solid was similar in all respects to the solid obtained from the reaction of aluminum isopropoxide with 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane. The solid was insoluble in all attempted solvents and the aluminon test was positive. The infrared spectrum showed a band corresponding to the N-H stretching frequency and the per cent aluminum found was 3.27. The calculated percentage for the following structure is 6.569:



$$\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!\overset{H}{C}O\right)_2 Al \left(N\!<\!\begin{matrix}Si(OC_2H_5)_3\\Si(OCH_3)(CH_3)_2\end{matrix}\right)$$

The calculated percentage is approximately twice as great as the found percentage. Since the infrared spectrum contains a band corresponding to N-H stretching, it is proposed that the solid is composed of a mixture of polysilazanes similar to structure B with one-half of the hydrogens on nitrogen replaced by aluminum. The volatile constituents of the liquid fraction were analyzed by VPC (See Figure 7, Appendix III) and in Table XVI the alkoxysilanes, found, are listed in order of increasing retention times on the column.

Table XVI. Alkoxy silanes produced from the pyrolysis of Compound (II) with aluminum isopropoxide

Volatile Products	Approx. Mole Ratios
$(CH_3)_2Si(OCH_3)_2$	4
$(CH_3)_2(OCH_3)Si(OC_2H_5)$	20
$(CH_3)_2Si(OC_2H_5)_2$	20
$(CH_3O)_4Si$	4
$(CH_3O)_2Si(OC_2H_5)_2$	1
$(CH_3O)Si(OC_2H_5)_3$	8
$(C_2H_5O)_4Si$	12
$(C_2H_5O)_3Si(O\text{-}\underline{i}\text{-}C_3H_7)$	12
$(CH_3O)(C_2H_5O)Si(O\text{-}\underline{i}\text{-}C_3H_7)_2$	20
Starting material	40
$(CH_3O)Si(CH_3)_2\text{-}[NHSi(CH_3)_2]_2NHSi(OCH_3)(CH_3)_2$	40

$$\frac{-Si(CH_3)_2(OCH_3)}{-Si(OC_2H_5)_3} = \frac{3}{4}$$

In addition to the volatile pyrolysis products from the liquid fraction, high molecular weight silicon-nitrogen compounds were formed. When the liquid was distilled at 10 mm pressure and at a high temperature, an unreactive solid was formed which was insoluble in acid, base, and organic solvents.

Table XVII gives the analytical data found for this polymer.

The presence of an infrared band corresponding to N-H stretching is taken as evidence that the silicon nitrogen chains are not completely crosslinked through tertiary nitrogen. When the liquid was distilled at 10 mm pressure

Table XVII. Elemental analysis of the crosslinked polymer from the pyrolysis of Compound (II) with aluminum isopropoxide

	Found Percentages*
% Carbon	15.85
% Hydrogen	4.85
% Silicon	38.15

*Carbon and hydrogen analyses are not fully reliable.

Table XVIII. Elemental analysis of the oligomeric oil from the pyrolysis of Compound (II) with aluminum isopropoxide

	Found Percentages
% Carbon	29.41, 29.28
% Hydrogen	7.21, 7.26
% Nitrogen	10.77, 10.69
% Silicon	29.20, 29.34

and with a small amount of heat a mixture of oligomeric oils was obtained. The NMR data (See Figure 4, Appendix II) obtained for the oligomeric oils showed there were more than two structurally different methyl groups as indicated by three peaks, two sharp and one broad. The ethoxy and methoxy proton resonances were also broad. A methyl to ethoxy to methoxy ratio of 2:3:1 was found. These ratios are also consistent with the vapor phase chromatographic analysis of the mixture of alkoxysilanes formed during the pyrolysis. The infrared spectra of these oligomeric oils indicate that essentially most of the N-H bonds remained intact during the pyrolysis. The elemental analysis data for this polymer are given in Table XVIII.

It appears on this evidence as though this oil is a linear organopolysilazane.

III. SUMMARY

Prolonged heating of Compounds (I) and (II) at 200°C results in slight decomposition to the corresponding alkoxy silanes with most of the starting material remaining unchanged. Hexamethyldisilazane and 1,2-dimethoxy-1,1,2,2-tetramethyldisilazane have been shown to be thermally stable,[54] while hexamethoxydisilazane when heated to 200°C, decomposes almost completely.[60]

Sodium methoxide and aluminum isopropoxide cleaved the silicon-nitrogen bond in Compound (I) with the formation of predominantly dimethyldimethoxy and tetramethoxy silane, the corresponding sodium or aluminum salt of the disilazane and high molecular weight polymers. For sodium methoxide, the number of trimethoxysilyl groups lost was three times that for methoxydimethylsilyl. For aluminum isopropoxide, there was an equal number of both groups lost. Since the cleavage is thought to involve a nucleophilic attack by the alkoxide ion on the electrophilic silicon atom and also, due to the electron withdrawing power of oxygen atoms bonded to silicon, it is reasonable on electrostatic grounds to expect the trimethoxysilyl group to be the predominant cleavage product. Therefore, one would predict that the susceptibility of a particular silicon atom to nucleophilic attack by alkoxide should increase as the number of alkoxy groups bonded to that silicon increases. However, this reasoning is based on electrostatic reasoning, alone, and does not take into account steric hindrance due to the groups bonded to silicon or the relative nucleophilic strengths of the attacking alkoxide ions. Steric hindrance appears to be least important and electrostatic factors predominate for attack by sodium methoxide on Compound (I), whereas, steric effects to a significant extent determined the site of attack by aluminum isopropoxide. The weaker base, aluminum isopropoxide, in the presence of the disilazane and under mild conditions gave a somewhat linear polymer, but only solid polymers, crosslinked through nitrogen, could be isolated with sodium methoxide.

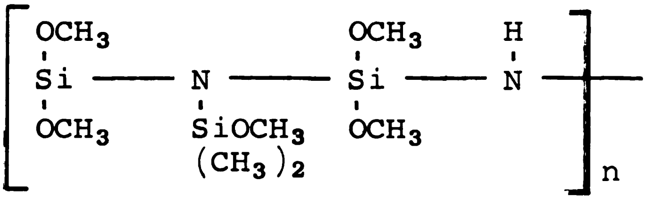
Compound (II) contains the slightly bulkier ethoxy groups bonded to silicon. The polymers and salts formed from the cleavage reaction with sodium methoxide and aluminum isopropoxide were similar to those formed from the cleavage of Compound (I). However, a larger number of alkoxysilanes were produced from the cleavage of Compound (II). This is due to the fact that this disilazane contains two different kinds of alkoxy groups and the unequivocally established fact that alkoxy groups bonded to silicon exchange readily.[61] Therefore, the final product is a complicated mixture of all of the possible rearranged alkoxysilanes. Steric factors seemed to have been important in both cases involving the attack of the alkoxy group on the more hindered silicon atom.

The cleavage of the dimethylmethoxysilicon-nitrogen bond by the more basic methoxide ion was 3/2 as great as the cleavage of the triethoxysilicon-nitrogen bond. The methoxide ion preferred to attack the less hindered silicon atom. The more discriminating aluminum isopropoxide showed a slightly greater preference for attack at the more electrophilic but hindered silicon atom and the ratio of dimethylmethoxysilyl groups cleaved to triethoxysilyl groups is 3:4. The difference in nucleophilicity between sodium methoxide and aluminum isopropoxide probably accounts for the difference in the degree of condensation observed for these two bases.

The solid polymers were insoluble in all attempted solvents and gave unreliable carbon and hydrogen analyses due to the formation of silicon carbide. This evidence indicates that these solids are highly crosslinked polymers of undetermined structure.

Probable structures were determined for the liquid polymers on the basis of their elemental analysis, physical properties, NMR and IR data. Structures involving a linear silicon-nitrogen framework along with the retention of at least a fraction of the N-H bonds contain too high a percentage of nitrogen to be in agreement with analysis. The per cent nitrogen calculated for the completely crosslinked case is also higher than the found value. Similarly, linear polymers with completely silylated nitrogen must also be rejected. These lead to theoretical nitrogen percentages which are too low. Therefore, these extremes must be rejected as probable structures unless the oligomeric oils are considered to be a mixture.

The simplest formula calculated from the elemental analyses for Compound (I) is $(Si_3C_7H_2O_5N_2)$. IR data indicated the presence of a N-H bond and NMR data show that the methyl to methoxy ratio is 1:2. The following structure in which one-half of the total nitrogen is completely substituted is proposed as a probable structure:

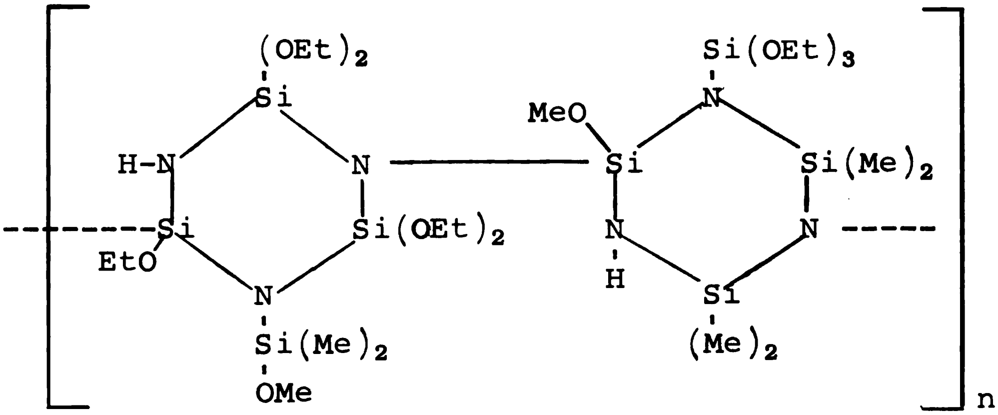


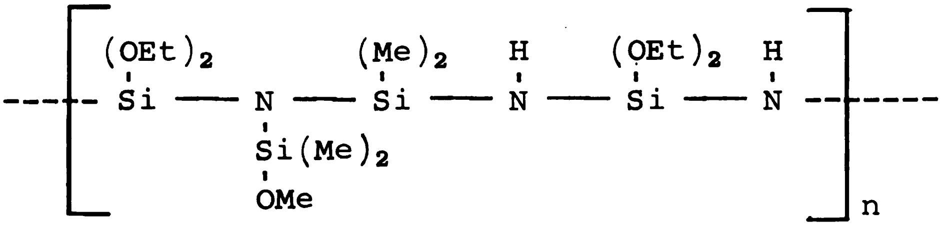
$$\left[\underset{\mathrm{OCH_3}}{\overset{\mathrm{OCH_3}}{\mathrm{Si}}} - \underset{\substack{\mathrm{SiOCH_3}\\ \mathrm{(CH_3)_2}}}{\mathrm{N}} - \underset{\mathrm{OCH_3}}{\overset{\mathrm{OCH_3}}{\mathrm{Si}}} - \overset{\mathrm{H}}{\mathrm{N}} - \right]_n$$

It is assumed that the methyl and methoxy groups can be interchanged along the chain.

The empirical formula for the polymer from Compound (II) is $(Si_4C_{10}H_{27}O_5N_3)$. The IR data show that the nitrogen is not completely substituted and the ethoxy to methyl to methoxy ratio was shown to be 3:2:1 from NMR data. These data and the large body of evidence that silazanes tend to form 6 and 8 membered rings make plausible a mixture of the average structures shown on page 51.

The results obtained in the alkoxide cleavage experiments suggest that the much touted $d\pi$ - $p\pi$ interaction between silicon and nitrogen, while obviously important in some systems, should not be considered as the silicon-nitrogen chemist's panacea. For unsymmetrically alkoxylated





$$-\left[\overset{(OEt)_2}{Si} - \underset{\underset{OMe}{Si(Me)_2}}{N} - \overset{(Me)_2}{Si} - \overset{H}{N} - \overset{(OEt)_2}{Si} - \overset{H}{N} \right]_n-$$

disilazanes a large $d\pi - p\pi$ interaction would have the net effect of weakening the silicon-nitrogen bond to the less (rather than more) highly alkoxylated silicon. The experimental results reported in this thesis are more in agreement with what would be predicted for an, at best minimal $d\pi - p\pi$ contribution to the bonding and can be explained in terms of the largely uncompensated electron withdrawing power of alkoxy groups bonded to silicon.

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APPENDICES

APPENDIX I

INFRARED SPECTRUM OF COMPOUND (I)

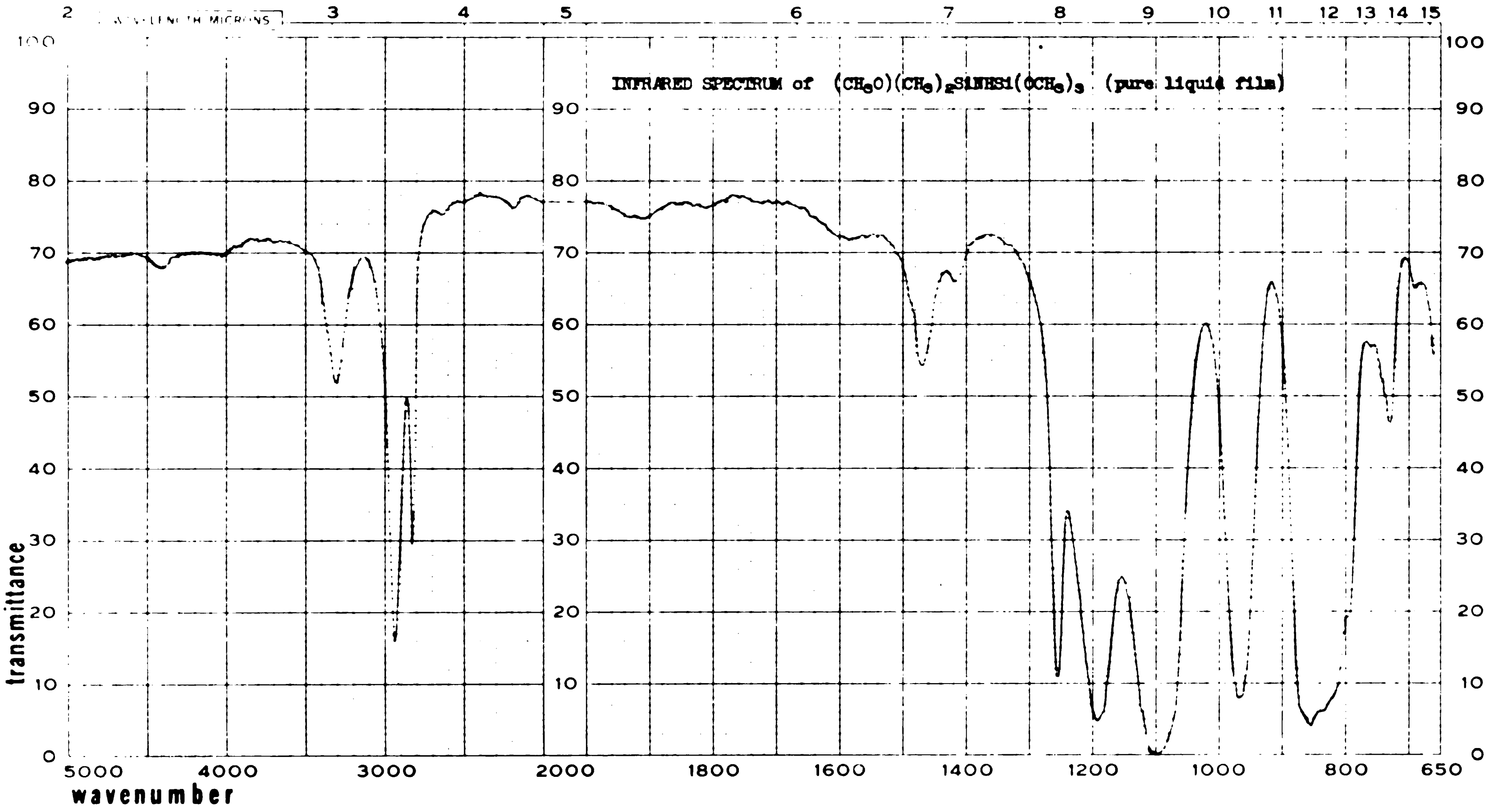


Figure 1. Infrared spectrum of 1-methoxy-1,1-dimethyl-2,2,2-trimethoxydisilazane.

APPENDIX II

PROTON NMR SPECTRA OF DISILAZANES

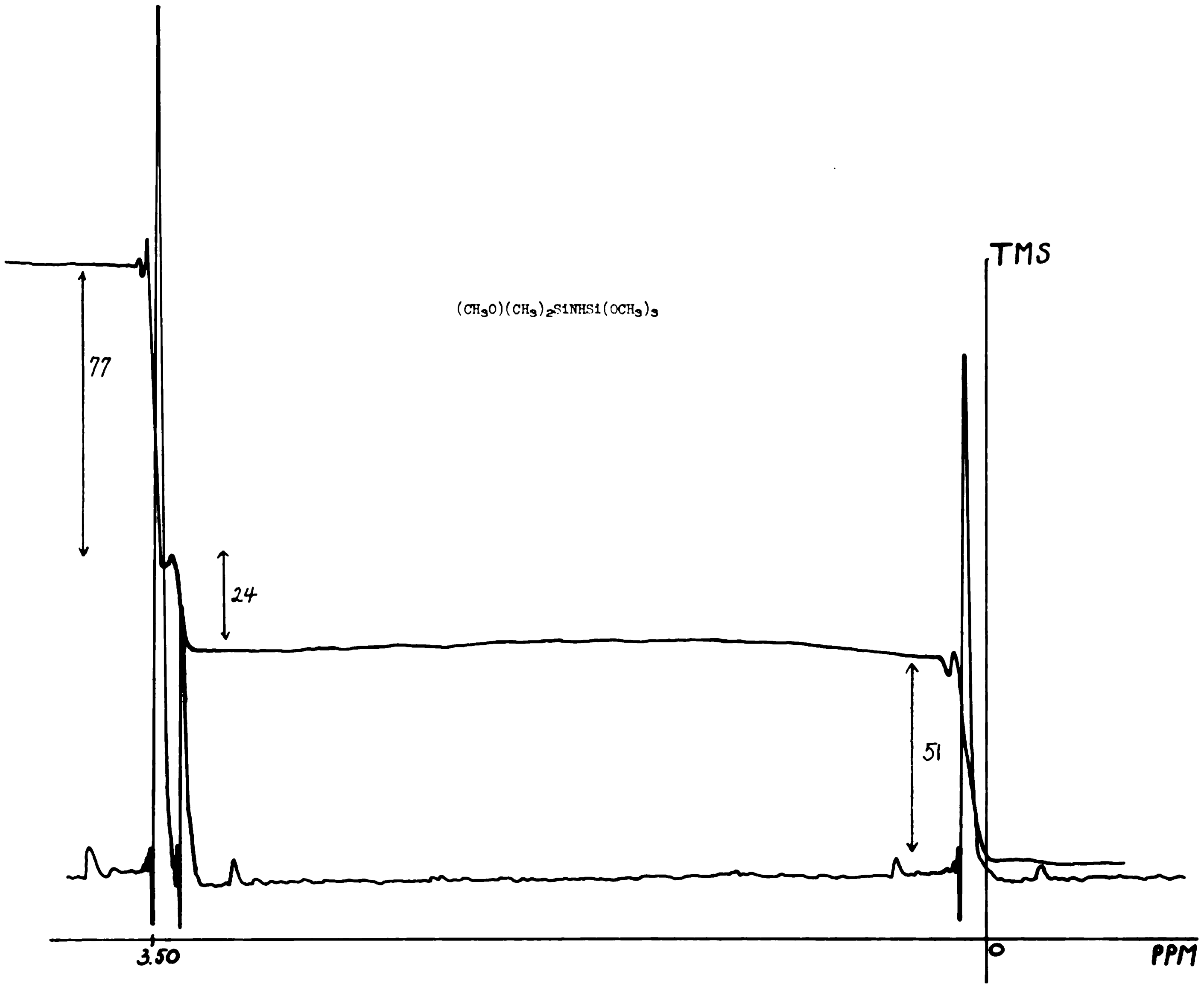


Figure 2. Proton NMR spectrum of Compound (I).

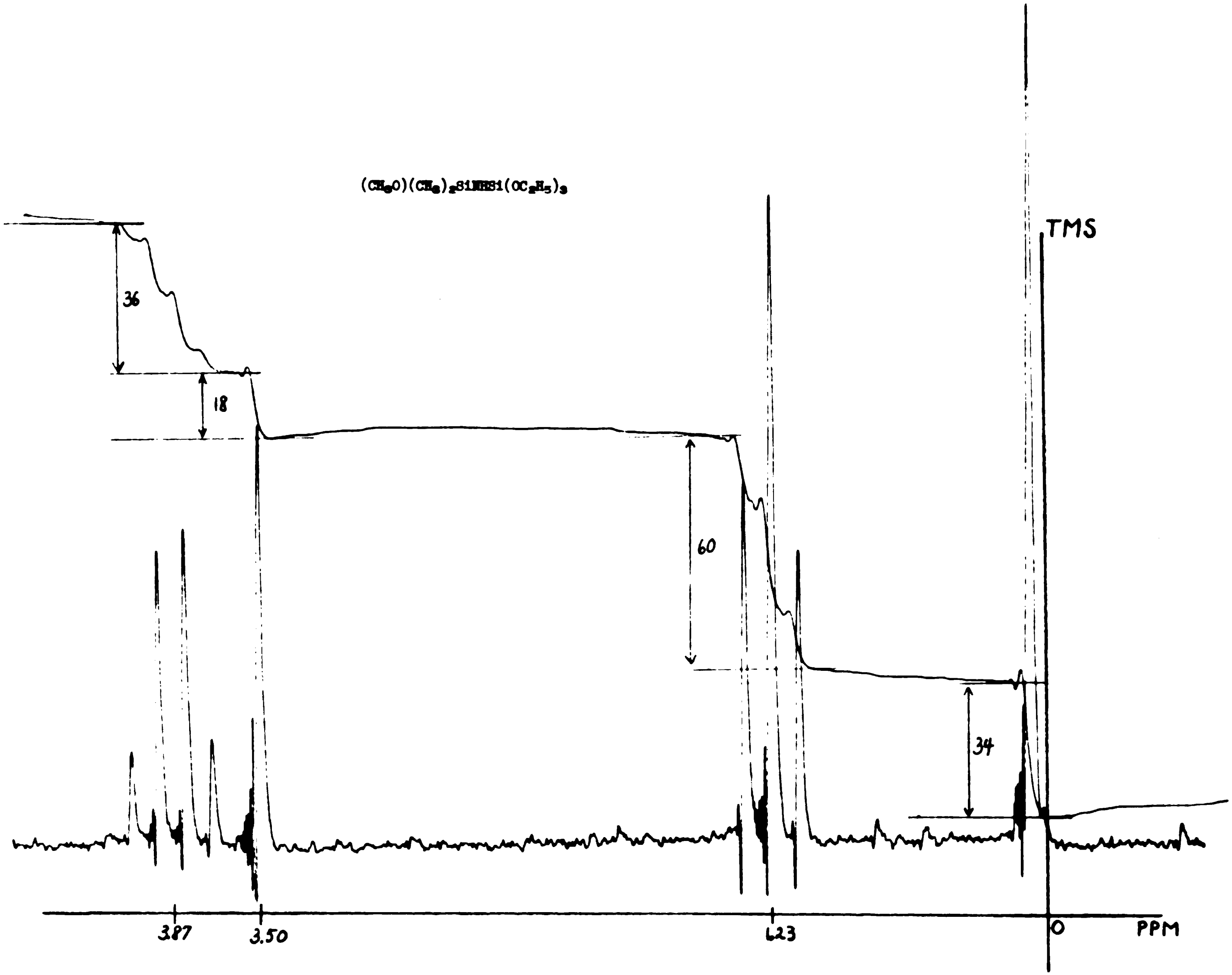


Figure 3. Proton NMR spectrum of Compound (II).

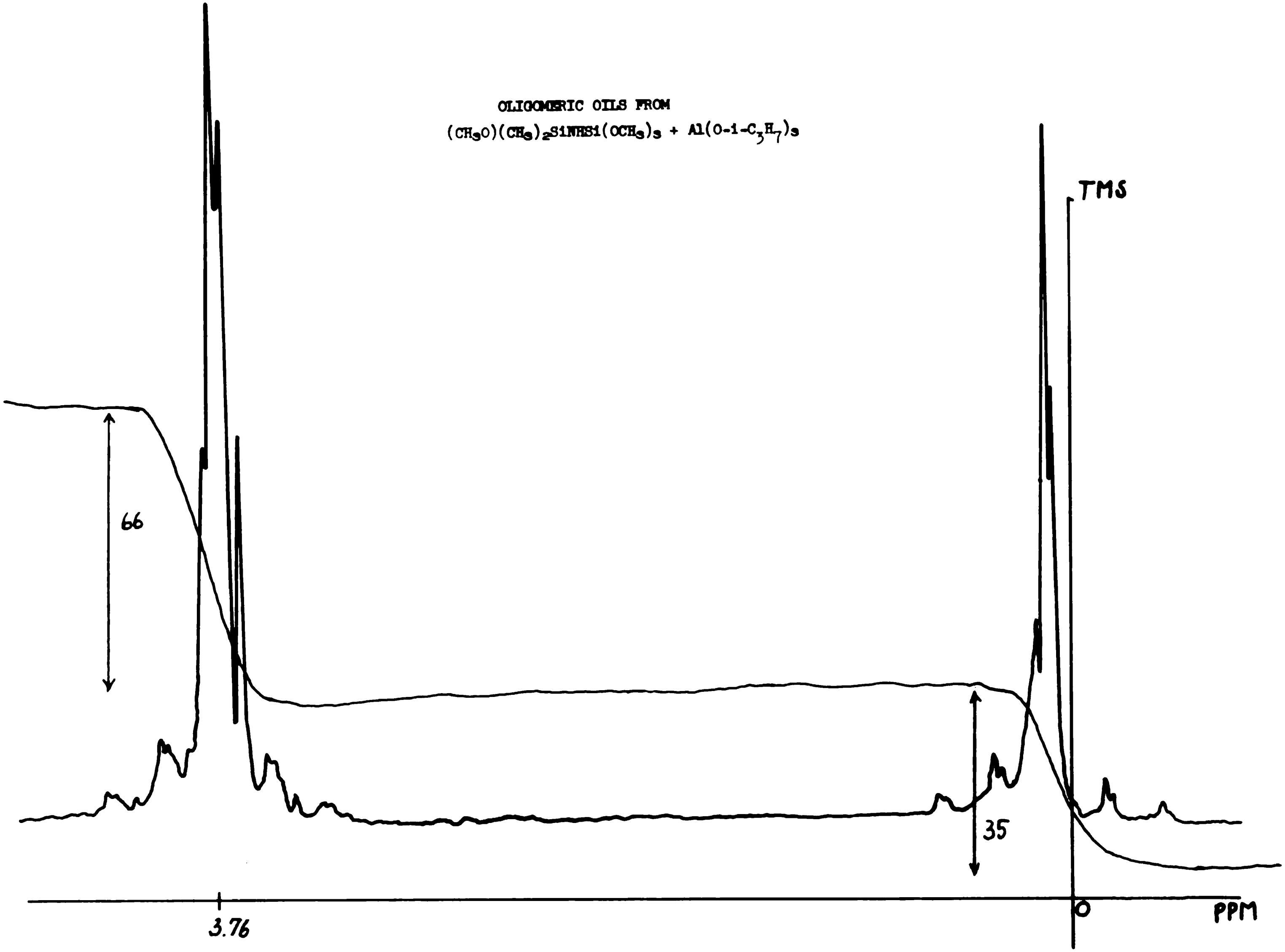


Figure 4. Proton NMR spectrum of the oligomeric oil from the pyrolysis of Compound (I).

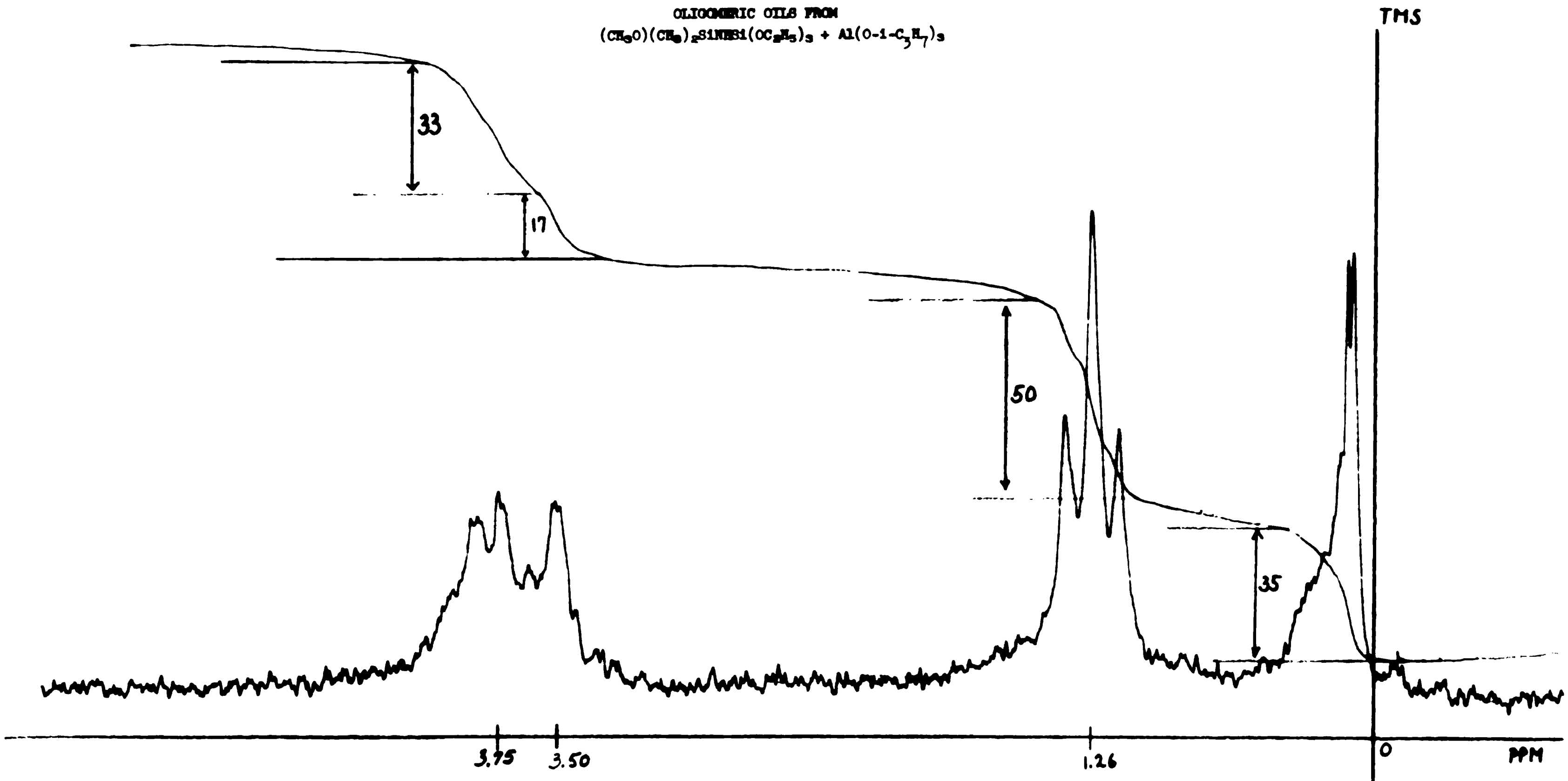


Figure 5. Proton NMR spectrum of the oligomeric oil from the pyrolysis of Compound (II).

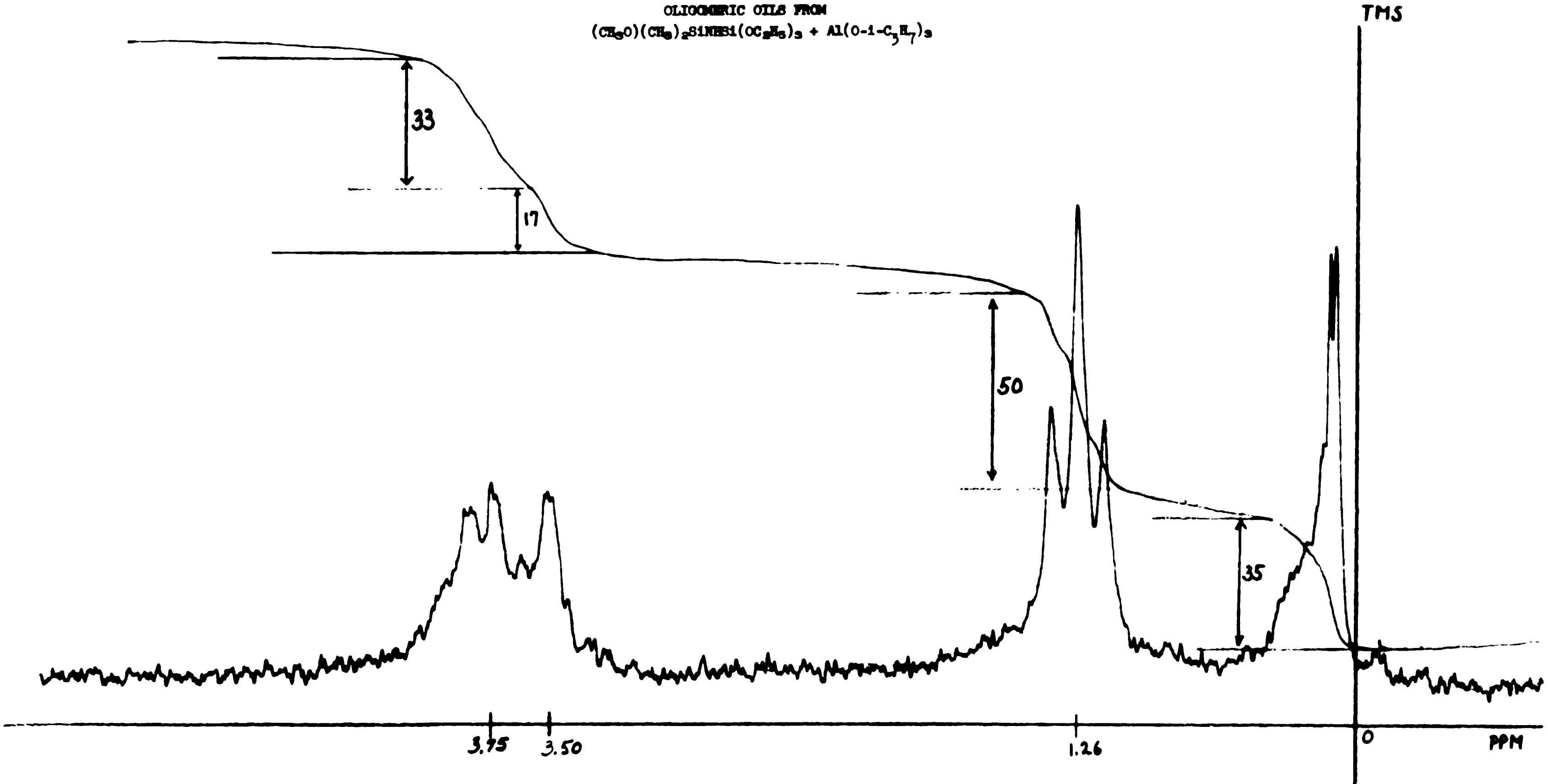
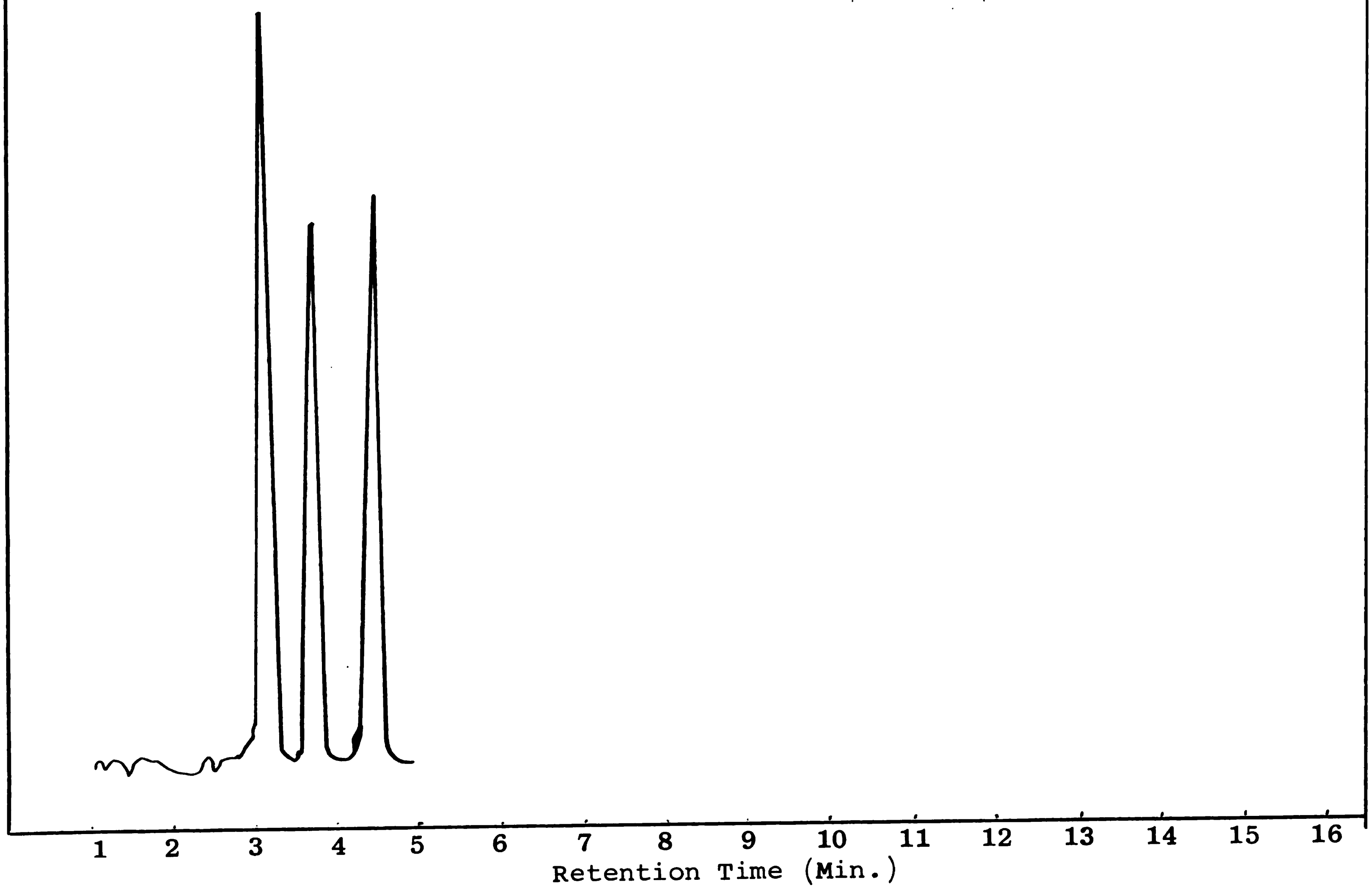


Figure 5. Proton NMR spectrum of the oligomeric oil from the pyrolysis of Compound (II).

APPENDIX III

GAS CHROMATOGRAMS OF ALKOXY SILANES

Figure 6. Gas chromatogram of some known alkoxy silanes. A mixture of
$(MeO)_2Si(Me)_2$
$(EtO)(MeO)Si(Me)_2$
$(EtO)_2Si(Me)_2$



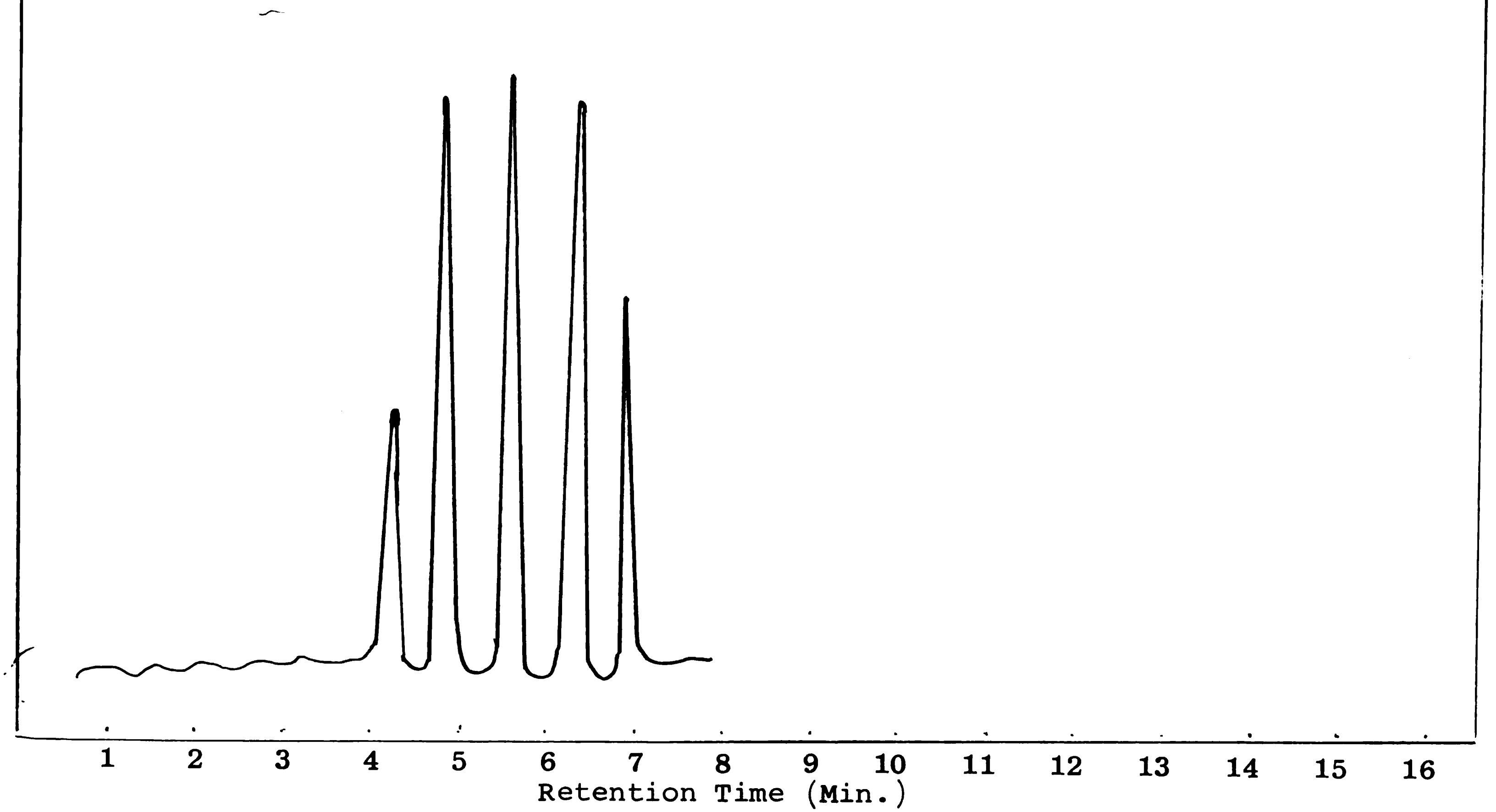


Figure 6. Gas chromatogram of some known alkoxy silanes. A mixture of

$(MeO)_4Si$

$(MeO)_3Si(OEt)$

$(MeO)_2Si(OEt)_2$

$(MeO)Si(OEt)_3$

$(EtO)_2Si(OEt)_2$

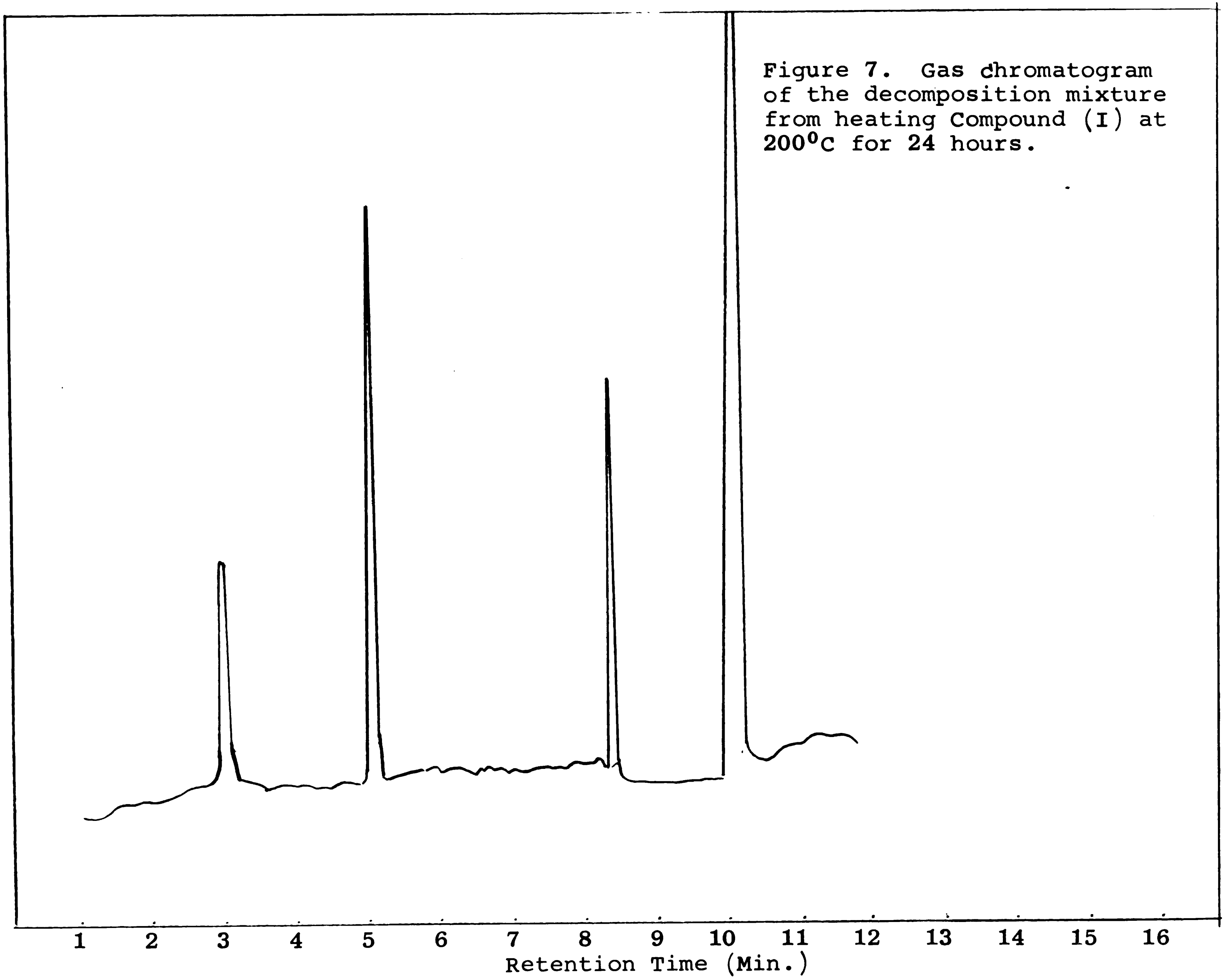


Figure 7. Gas chromatogram of the decomposition mixture from heating Compound (I) at 200^{0}C for 24 hours.

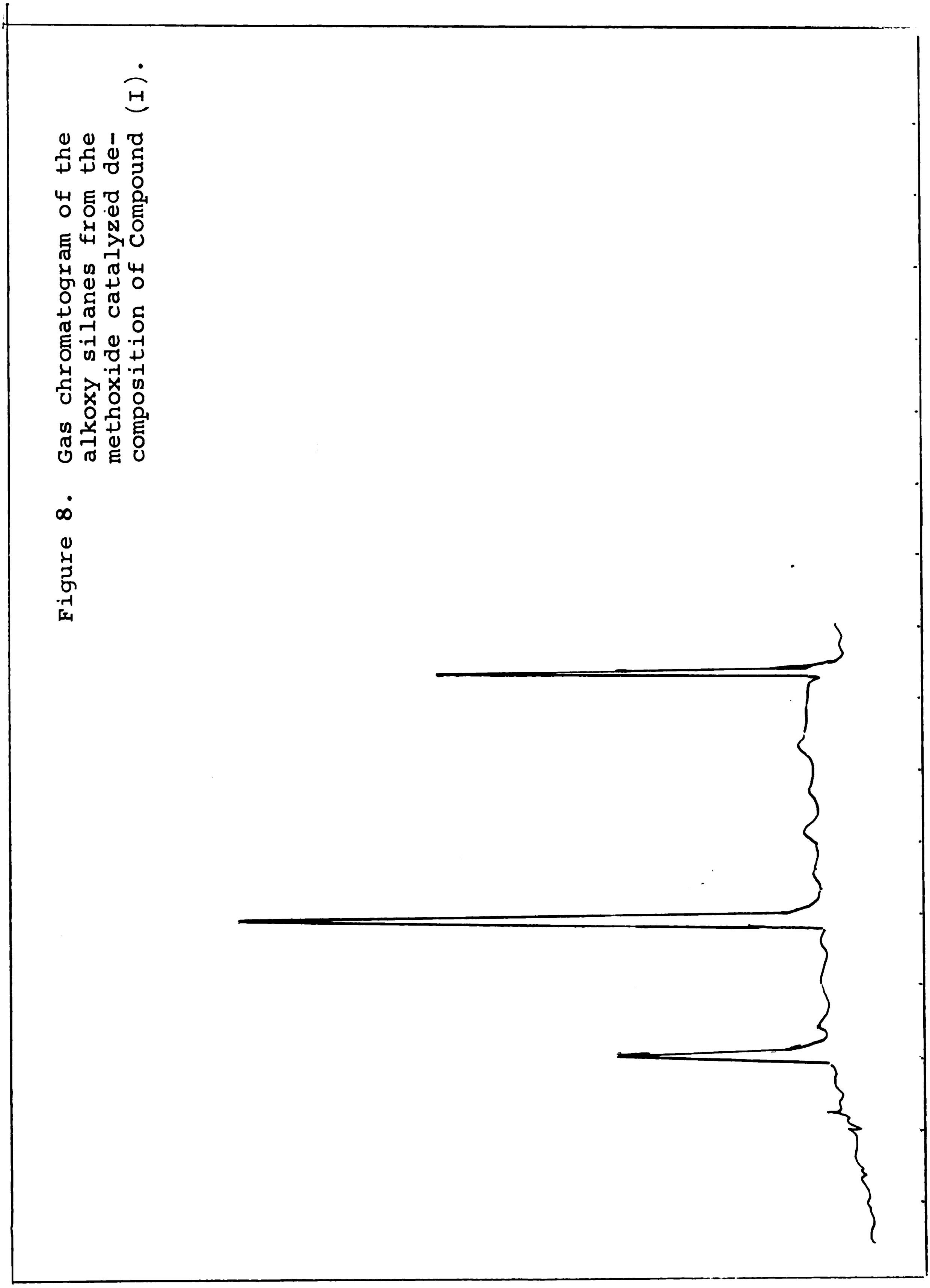
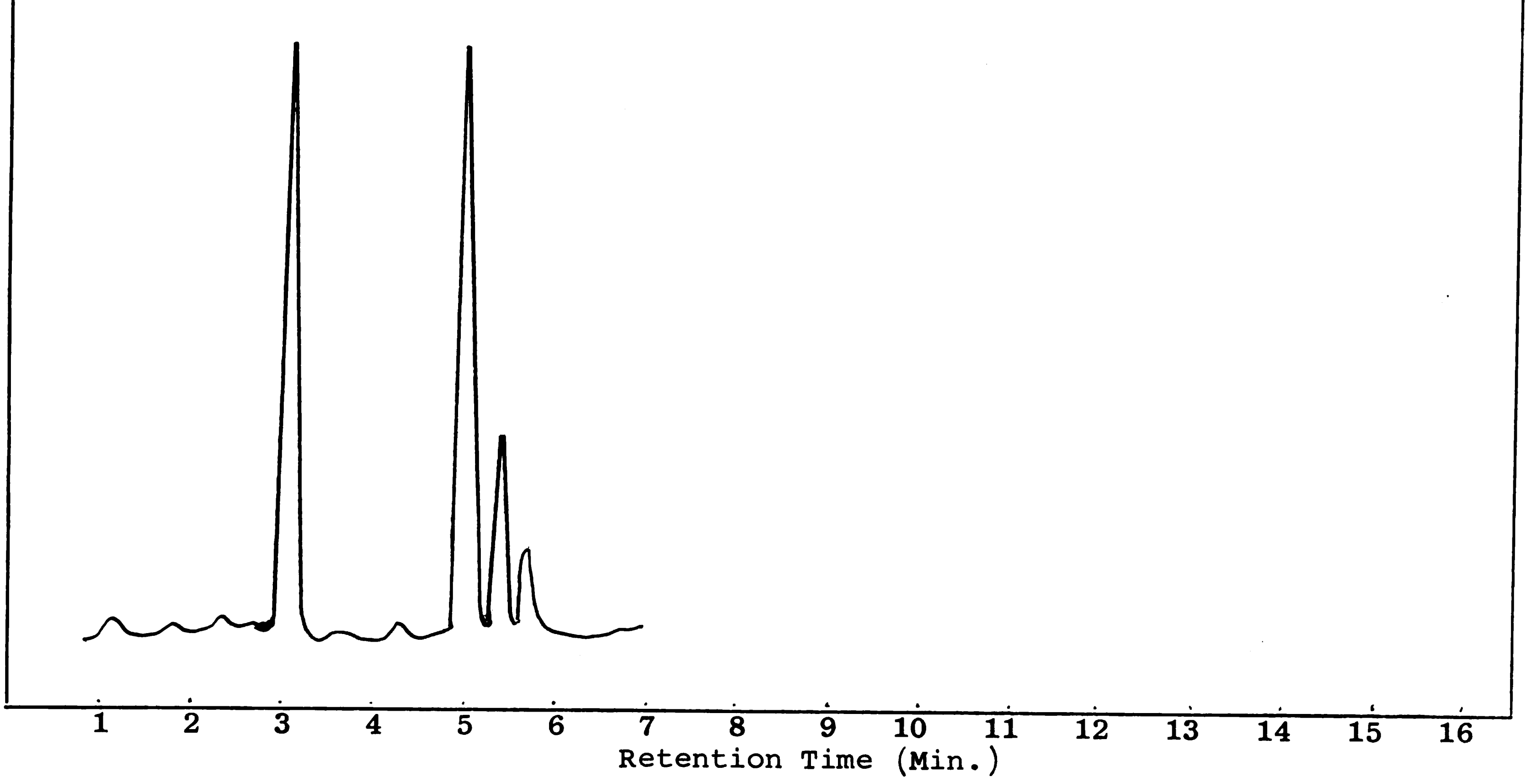


Figure 8. Gas chromatogram of the alkoxy silanes from the methoxide catalyzed decomposition of Compound (I).

Figure 9. Gas chromatogram of the alkoxy silanes from the aluminum isopropoxide catalyzed decomposition of Compound (I).



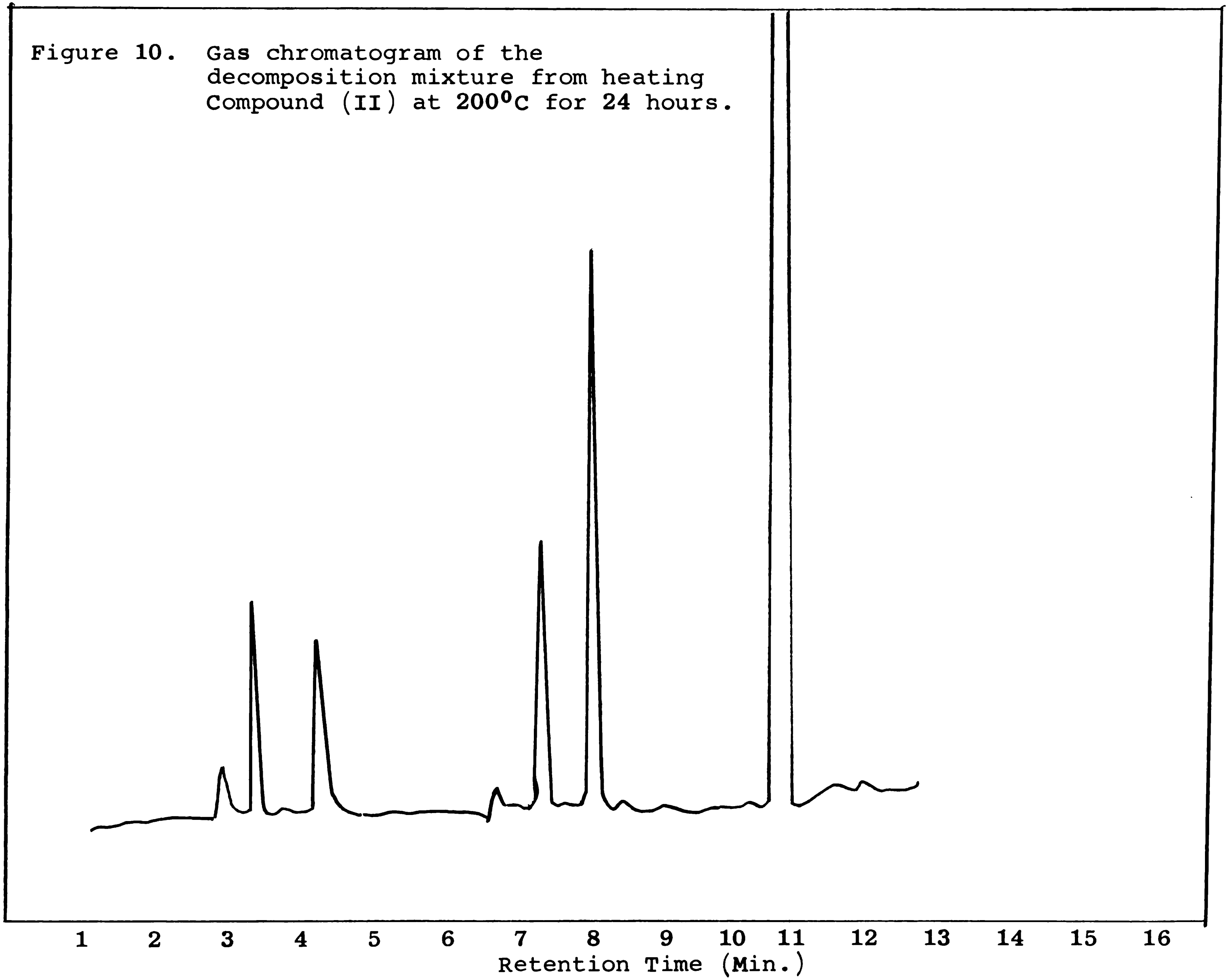


Figure 10. Gas chromatogram of the decomposition mixture from heating Compound (II) at 200^{0}C for 24 hours.

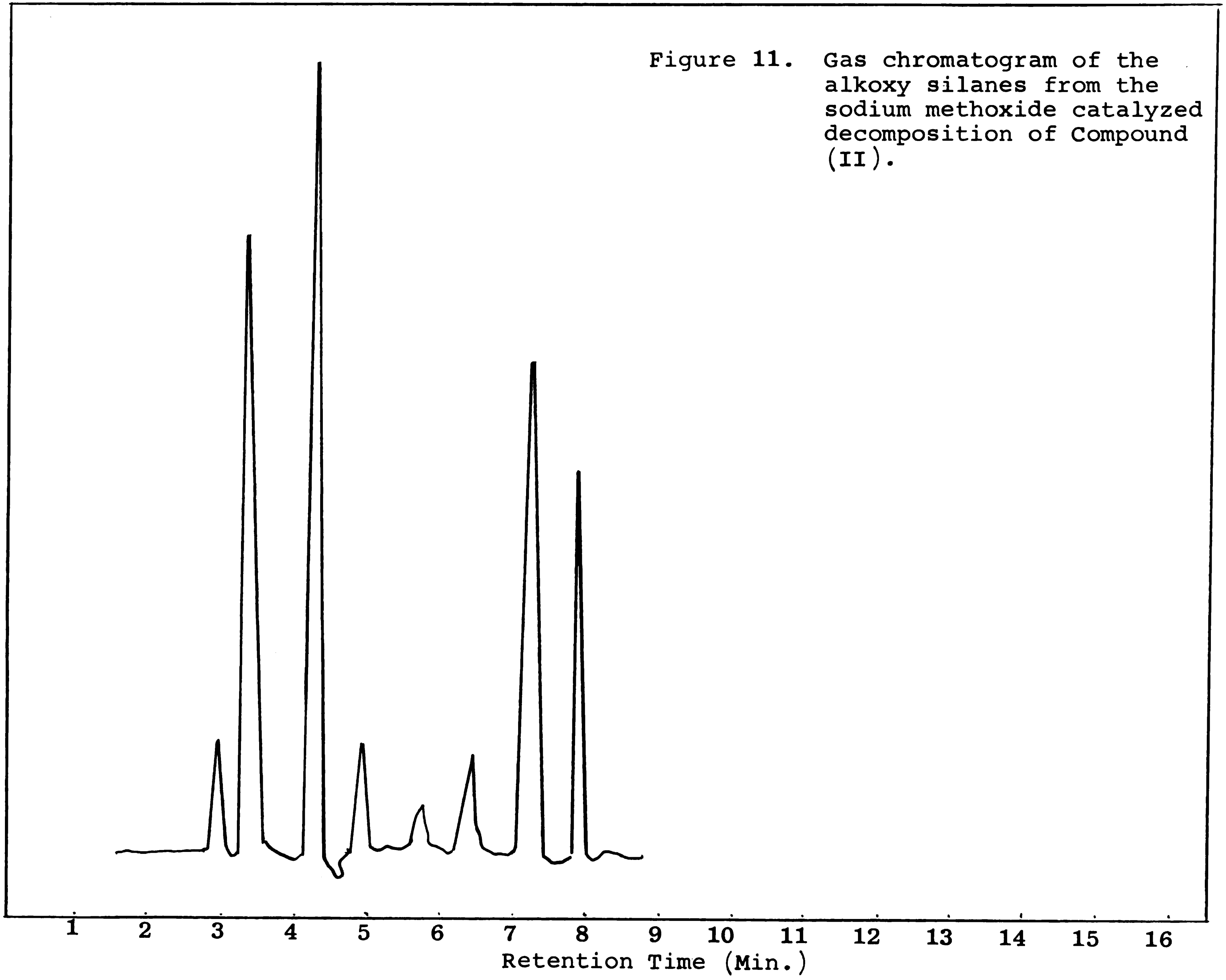


Figure 11. Gas chromatogram of the alkoxy silanes from the sodium methoxide catalyzed decomposition of Compound (II).

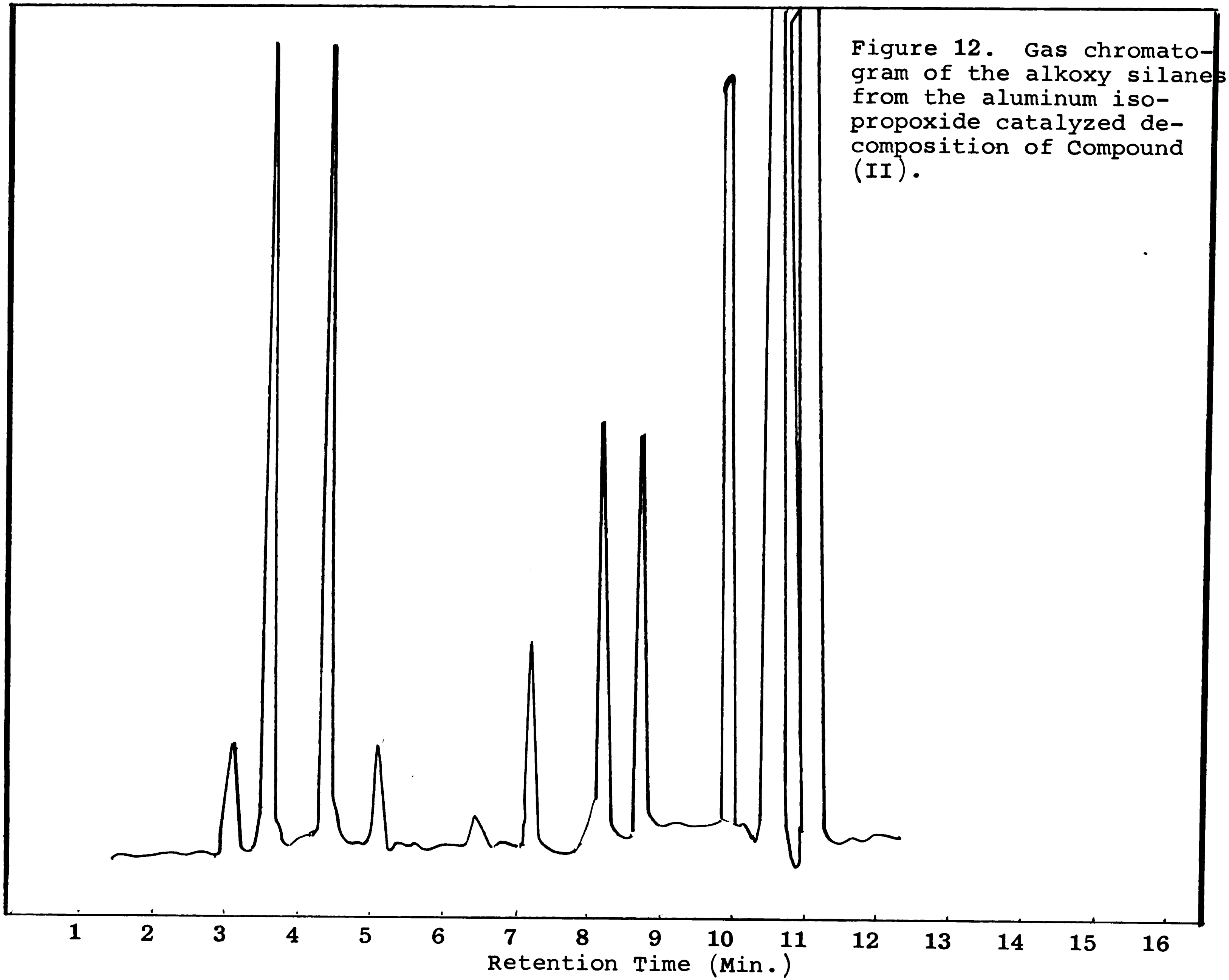


Figure 12. Gas chromatogram of the alkoxy silanes from the aluminum isopropoxide catalyzed decomposition of Compound (II).