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The preparation, properties and reactions of B-diethylaminoethoxy-methylsilanes

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The Preparation, Properties and Reactions of
 β -diethylaminoethoxy - methylsilanes

This paper is offered in partial fulfillment of
the requirements for the degree of Master of Science
in Union College.

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Approved:

Howard E. Sheffer

May, 1952

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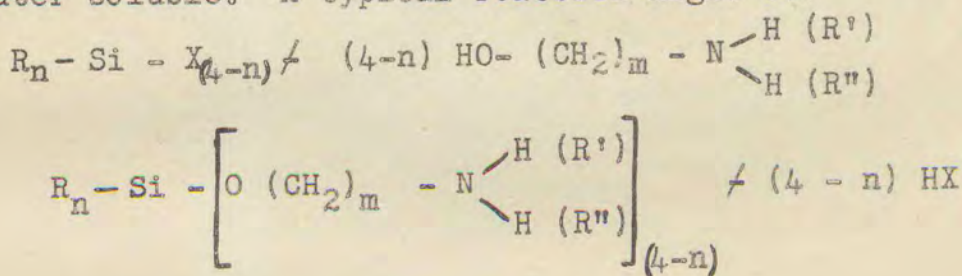
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The Preparation, Properties and Reactions of β -diethylaminoethoxy - methylsilanes

INTRODUCTION

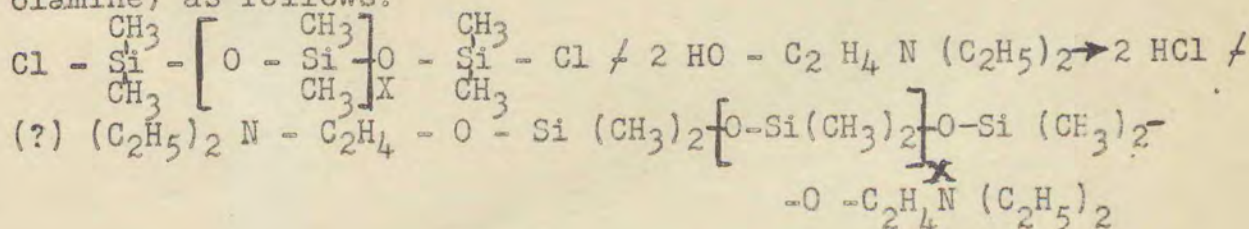
In the course of work on the application of silicones to textiles and paper, chiefly to impart water repellency thereby, it has been found that the most desirable method for industrial operations is from water solution. Methods for preparing emulsions of silicones have been developed and such materials are available commercially. However, it would still be of interest to obtain a material which is directly water soluble and which is either a silicone itself, or can be simply and easily converted to a silicone in situ.

These facts were brought out by Dr. D. P. Spalding (1) in a discussion of his work on attempting to prepare quaternary amine compounds involving methyl chlorosilanes. It occurred to the author that another approach might be through the reaction of organo-halogenosilanes with the class of compounds known as alkanolamines. The Si-X groups might react preferentially with the carbinol groups and leave the amine end free to undergo salt formation reactions and thus be made water soluble. A typical reaction might be:



Subsequent hydrolysis of the $-Si-O-CH_2-$ linkage would regenerate the alkanolamine (or its salt) and also would produce a silicone compound.

To test the idea, Dr. Spalding and the author decided to try the reaction of mixed methylchlorosiloxanes with (impure) β -diethylaminoethanol (also known as diethylethanolamine) as follows:



The reaction was run in toluene and with about 100% excess of the ethanolamine to act as an acceptor for HCl. Upon distillation of the solvent, a brownish pasty mass was obtained which was insoluble in water. When methyl iodide was added to a toluene solution of this material, a precipitate was obtained which was soluble in water. On standing a few hours, the aqueous solution separated an oily phase, indicating hydrolysis had taken place.

With this experience as a background, it was deemed advisable to investigate preparations from simple chlorosilanes in order to establish the course of the reaction and to learn more of the subsequent reactions of the products.

A search was made of the literature to see if similar work had been reported previously. None was found, but material on related compounds was found in Rochow (2), on methyl "Cellosolve" derivatives of methylchlorosilanes by Burkhard (3, 4), on 2-chloroethoxy silanes by Sauer (5), on silazane compounds by Sauer and Hasek (6), and on quaternary ammonium compounds containing silicon by Lewis (7).

EXPERIMENTAL

I. Preparations and Properties of Products

It was decided to work with β -diethylaminoethanol for two principal reasons: a) it is monofunctional in carbinol, thus producing simple derivatives; and b) it is a tertiary amine, thus lending itself to quaternization with alkyl halides.

Physical properties of β -diethylaminoethanol as given in the 1952 edition of "Physical Properties of Synthetic Organic Chemicals", Carbide and Carbon Chemicals Company are as follows:

Structural formula: $(C_2H_5)_2 NC_2H_4OH$

Molecular weight: 117.19

Specific gravity: 0.8851, 20/20°C

Vapor pressure: 760 MM at 162.1°C (B.P.)
1.4 MM at 20°C

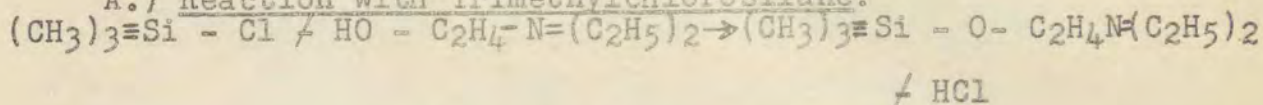
Miscibility with water: Complete.

Figure II contains a plot of the vapor pressure - 1/T relationship.

Some of the material available in this laboratory was old stock from Sharples Chemicals Co. and Carbide and Carbon Chemicals Co. and was badly discolored. This was purified by distillation at atmospheric pressure, retaining fractions boiling from 160° - 166°C overhead from a Vigreux column fitted with fractionating head. The product was almost colorless and with a somewhat ammoniacal, but pleasant odor. Later, a quan-

tity of $\text{Et}_2\text{NC}_2\text{H}_4\text{OH}$ was obtained from Eastman Kodak and was used with no further purification.

A.) Reaction with Trimethylchlorosilane:



In order to take up the HCl formed by reaction, 100% excess over theory of the ethanolamine was used.

The reaction vessel was a three-necked, round bottom, one-liter flask fitted with agitator, addition funnel, thermometer, and reflux condenser. Figure I illustrates the set-up used. Into the flask were placed 128.9 gm (1.1 mole) $\text{HO}-\text{C}_2\text{H}_4-\text{N}(\text{C}_2\text{H}_5)_2$ and 100 gm of residue-free toluene. Into the addition funnel were placed 54.2 gm (0.5 mole) $\text{Me}_3\text{Si}-\text{Cl}$ and 100 gm of residue-free toluene. The $\text{Me}_3\text{Si}-\text{Cl}$ used was commercial grade G. E. 81008 which usually contains some hexane isomers and a little SiCl_4 as impurities. The quantity of toluene was chosen such that the postulated product would be obtained as approximately 30% solution and the resulting slurry of aminehydrochloride would be readily stirred.

The methylchlorosilane solution was added to the ethanolamine solution in about 1 1/4 hours. The addition rate was controlled so that the reaction temperature remained below the boiling point of $\text{Me}_3\text{Si}-\text{Cl}$ (56.5°C). After the addition was completed, the mixture was stirred for an additional half hour.

The product slurry was filtered with suction and the filter cake was washed with two - 100 ml portions of fresh toluene, which were added to the filtrate. During the filtration, the filtrate which was clear at first, developed a precipitate of fine crystals; the material was re-filtered and the precipitate saved separately.

The clear filtrate was then distilled under reduced pressure to remove the toluene, leaving a yellowish high boiling residue. This amounted to 83. gm, or 87.8% of a theoretical 94.6 gm yield. Upon standing over night, fine white needles precipitated and were filtered from the product.

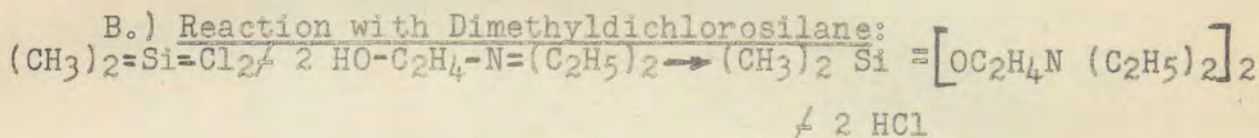
A small portion of the "product" was distilled in a claisen flask to determine boiling range and thermal stability. Unreacted ethanolamine was obtained in greater amount than the original excess and then a "product cut" at $172 - 185^\circ\text{C}$. Still pot material turned very dark brown at $190 - 200^\circ\text{C}$.

A re-distillation was attempted at atmospheric pressure, using a small packed column with fractionating head. A cut boiling at 176°C (760 MM) was collected, but decomposition in the still pot at $180 - 185^\circ$ was taking place so rapidly that atmospheric pressure distillation was abandoned. A Vigreux

column with fractionating head was set up for reduced pressure distillation. The crude product yielded a major fraction boiling at 80 - 82°C at 31 MM. These vapor pressure - temperature data are plotted in Figure II. After all the mishandling and decompositions encountered, yield figures were of no significance.

The product was a mobile, water-white liquid with a definitely ammoniacal, but pleasant odor which was different from that of the ethanolamine. It was insoluble in water, but soluble in toluene, hexane, and ether.

Upon treatment with aqueous alkali, the principal salt-like by-product regenerated $\text{HO-C}_2\text{H}_4\text{N-Et}_2$.

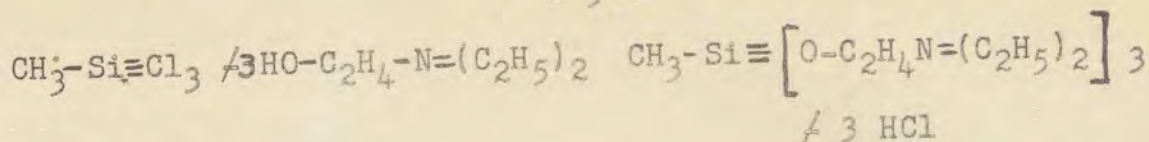


The same apparatus and general technique were used as for preparation (A) above. Charge to the reaction flask was 257.8 gm (2.2 moles) $\text{HO-C}_2\text{H}_4\text{-N-Et}_2$ and 145 gm toluene. Into the addition funnel were placed 64.5 gm (0.5 mole) $\text{Me}_2\text{Si Cl}_2$ and 145 gm toluene. The $\text{Me}_2\text{Si Cl}_2$ was commercial grade G.E. 9999 which contained approximately 0.5 mol % Me Si Cl_3 as impurity. Addition was completed in about 1 1/4 hours, followed by a 20 minute stirring period and three days standing. The product solution was separated from the amine hydrochloride by suction filtration of the slurry and washing with portions of additional toluene. Again, the filtrate was clear at first, but developed a precipitate on standing, which was separated by gravity filtration.

The clear product solution was distilled under reduced pressure to strip out toluene; when this was done, a brownish precipitate was present in the residual liquid. This was removed by filtration and the liquid was fractionated under vacuum with a nitrogen bleed in the Vigreux column. After removing residual toluene and unreacted ethanolamine, a major cut was obtained at 147 - 155° C and 16 - 18 MM, with the flat at 151 - 153° and 17 MM. This fraction was 101. gm or 69.6% of theoretical yield of 145.2 gm. This fraction was redistilled to yield a product boiling at 130 - 131°C at 7MM. These vapor pressure - temperature data are plotted in Figure II.

The product was a mobile, water-white liquid with an odor reminiscent of crushed weeds. Density $22^\circ/40^\circ = 0.8853$ gm/ml; refractive index, $n_{20}^D = 1.4348 \pm .0001$. It was insoluble in water, soluble in ^Dtoluene, hexane, and ether. Combustion showed alkyl silicone type of flame with white smoke and a silica residue.

C.) Reaction with Methyltrichlorosilane:



Again the reaction equipment was as outlined above. Charge to flask was 386.8 gm (3.3 moles) of HO C₂H₄N Et₂ and 196 gm toluene; 196 gm toluene and 74.8 gm (0.5 mole) of Me Si Cl₃ were added from the addition funnel over a two hour period. The ethanolamine was Kodak material, while the Me Si Cl₃ was commercial G.E. 81017 which contained about 5. mol % Me₂Si Cl₂ as impurity. Some difficulty was encountered in efficient stirring because of the large volume of by-product solid and about 200 ml additional toluene were added to get better agitation. The mixture was stirred for 3/4 hour after the Me Si Cl₃ solution was all added. The product solution was separated from the solids by suction filtration and the filter cake was re-slurried in toluene, filtered, and washed on the filter with fresh toluene. These washings were added to the original solution. After standing, this filtrate also developed a crystalline precipitate which was removed prior to distilling away the toluene.

After removal of toluene under reduced pressure, the crude product was hazy and was filtered while it was still warm. Upon cooling, the originally clear filtrate precipitated needle-like crystals.

The filtered crude product was distilled in the Vigreux column at reduced pressure with nitrogen bleed to remove unreacted ethanolamine and residual toluene. The major fraction was collected at 182 - 183°C at 6 MM. This fraction was re-distilled for further purification and yielded a heart cut boiling at 169 - 170° at 4 MM. These data are plotted in Figure II. The final yield of heart cut was low, only 26. gm; this was 13.3%, based on a theoretical yield of 195.8 gm.

The product was a mobile liquid with a faint yellowish cast and with practically no odor. Density 22°/4° = 0.9148 gm/ml; refractive index, $n_D^{20} = 1.4427 \pm 0.0001$. It was insoluble in water, but soluble in toluene, hexane, and ether. Combustion showed the bright flame associated with alkyl silicone, with white fumes and a silica residue.

D.) Reaction with Trimethylchlorosilane in the Presence of Pyridine:

This was the same reaction as (A), above except that the stoichiometric amount of pyridine was used to act as an acceptor for HCl. The same apparatus was used; into the reaction flask were charged 128.9 gm (1.1 mole) of HO C₂H₄N Et₂, 79.1 gm (1.0 mole) pyridine, and 189 gm toluene. The mixture in the addition funnel was 108.5 gm (1.0 mole) Me₃Si Cl and 189 gm toluene. The reaction produced a thick slurry that needed to be diluted with an additional 250 ml toluene in order to obtain sufficient agitation. The addition was completed in about one hour and the mixture allowed to stir for an additional half hour.

The slurry was filtered and the filter cake was re-slurried, filtered again and then washed twice with toluene. The filtrate, which smelled strongly of pyridine, developed a crystalline precipitate on standing. After filtration, the solution was distilled under reduced pressure; toluene and pyridine were removed, leaving a mass of brown crystals in the still pot. These crystals were water soluble, but insoluble in ether, thus effecting a separation from the residual pyridine. The extracted crystals showed no silica residue on combustion. The residual liquid associated with these crystals contained, in addition to the pyridine, a silicon bearing compound; combustion test showed a silica residue. The original precipitate from the reaction was water soluble and left a silica residue on combustion. It was undoubtedly the hydrochloride of the aminoethanol derivative that was formed because the basicity of the latter was greater than that of the pyridine. This approach was not pursued further because nothing was known about the hydrolytic stabilities of the desired products, and these would be factors in any process to obtain the free amino compounds.

E.) Reaction with Trimethylchlorosilane - Repeat.

This was a repetition of process (A), except that quantities of reagents were doubled in order to obtain more material to work with. The final heart cut re-fractionation yielded 142 gm of material boiling at 60 - 61°C at 10 MM. These data were added to the plot for the product of (A), above. Density $20^{\circ}/4^{\circ} = 0.8289$ gm/ml; refractive index, $n_D^{20} = 1.4199 \pm 0.0001$. Combustion showed alkyl silicone type of flame, white smoke, and white silica residue. The yield was about 75% of theory.

II. Analytical and Identification Work

It was expected that the reaction of $\text{HO-C}_2\text{H}_4\text{N-Et}_2$ with methylchlorosilanes would follow the course already well-known for alcohols (8) and form the corresponding substituted ethoxy compounds. This was already corroborated in the preliminary experiments by the presence in the product of an amine group that could be quaternized. Also, the tertiary amine group would not be expected to form silazane compounds as do primary and secondary amines (9). Accordingly, it was deemed sufficient to demonstrate the presence of silicon in the finished products, to establish the amount of nitrogen in the compounds, to establish structure by comparison of infra-red spectrograms with known standards, and to compare experimental specific refractions with the summed bond refractions.

A.) The presence of silicon was demonstrated, as pointed out above, by combustion of the materials on a stainless steel spatula and comparing with the known behavior of methyl silicones. The aminoethoxy derivatives ignited rapidly and burned with a bright flame, giving off white smoke and leaving a silica residue, as do methyl silicones.

B.) Nitrogen was determined by using a semi-micro Kjeldahl technique as described in a pamphlet published by the

Hengar Company of Philadelphia, Pa. As a standardization procedure, analyses were first run on β -diethylaminoethanol itself. For this, some previously redistilled material was fractionated to a heart cut boiling at 159 - 160°. Compounds, B, C, and E were then run in turn. Results are given in Table I:

TABLE I
% N, Determined by Semi-micro Kjeldahl Method

Compound	% N, Found	% N, Theory
$\text{HO}-\text{C}_2\text{H}_4-\text{N}=(\text{C}_2\text{H}_5)_2$	11.36	11.95
$(\text{CH}_3)_3\text{Si}-\text{O}-\text{C}_2\text{H}_4-\text{N}=(\text{C}_2\text{H}_5)_2$ "E"	7.32	7.40
$(\text{CH}_3)_2\text{Si}=[\text{OC}_2\text{H}_4-\text{N}=(\text{C}_2\text{H}_5)_2]_2$ "B"	9.09	9.64
$\text{CH}_3-\text{Si}=[\text{OC}_2\text{H}_4-\text{N}=(\text{C}_2\text{H}_5)_2]_3$ "C"	10.53	10.73

These results indicate that the postulated compounds were very probably obtained.

C.) Infra-red spectra for compounds "B", "C", and "E" were run by Mr. D. L. Harms of the General Electric Schenectady Works Laboratory on their Baird Associates I. R. Spectrophotometer with NaCl prism. Interpretation of these spectra by Mr. Harms and Dr. J. G. Morse of G. E. Silicone Products Engineering, Waterford, N. Y. aided materially in applying these data towards establishing the identity of these compounds. Figures III, IV, V, VI and VII reproduce the spectrograms that were obtained.

All the derivatives of the methylchlorosilanes show the absence of the strong peak corresponding to -OH group at 2.9μ (except compound "E", which apparently contained a little $\text{HOC}_2\text{H}_4\text{N Et}_2$ as impurity). Peaks in the $3.4 - 3.6 \mu$ region indicate -CH (CH_3) and -CH (C_2H_5), with those at 3.4μ , corresponding to CH_3 being well defined in the derivatives. In the $6.8 - 7.8 \mu$ region are absorptions characteristic of the aminoethanol. Compound "E" gives a strong absorption at 8.0μ ; "B" at 7.95μ ; and "C" at 7.90μ . These well-defined peaks correspond to the $(\text{CH}_3)_3\text{Si}-$, $(\text{CH}_3)_2\text{Si} =$, and $\text{CH}_3-\text{Si} \equiv$ configurations, respectively. All the derivatives show the Si - O broad band in the $9 - 9.5 \mu$ region (10) which is absent in the ethanolamine. In addition, compound "E" shows a peak at $11.85 - 11.80 \mu$ corresponding to $(\text{CH}_3)_3\text{Si} - \text{O}$ (11). Compound "B" has the peak at 12.5μ which corresponds to $\text{CH}_3-\text{Si} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \end{smallmatrix}$ (11). Vibrations in com-

pound "C" that should correspond to 11.47μ and 12.62μ absorptions for $\text{CH}_3 - \text{Si} - \text{O}$ (11) are masked. However, pertinent dif-

ferences appear in the spectra for compounds "B" and "C" in the $11 - 13 \mu$ region: "B" has a double vibration in the $11 - 12 \mu$ range, a single vibration in the $12 - 13 \mu$ range; "C" has a single mode in the $11 - 12 \mu$ region, a doublet between 12 and

13 μ . A further characteristic is a peak at 10.5 μ which Mr. Harms (12) ascribes to $\sim \text{O}-\text{C}_2\text{H}_4\text{N}=\text{Et}_2$, which is absent in the ethanolamine spectrum, but which is present in the spectra of the derivatives in increasing intensity as the number of such groups attached to Si increases.

D.) Sauer (13) demonstrated the value of the Lorentz-Lorenz relationship:

$$\text{Molar refraction} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}, \text{ where}$$

n = index of refraction of pure substance at given temperature, (D line of Na used)

d = density at the same temperature

M = molecular weight

for determining structure of organosilicon compounds by means of the additive bond refractions. Using Sauer's values for the molar group refractions associated with Si:

$$\text{CH}_3 - \text{Si} = 7.573 \text{ ml}$$

$$\text{Si} - \text{O} = 1.751 \text{ ml}$$

and molar group refractions for organic compounds as given in Weissberger (14) and Glasstone (15):

$$-\text{O}- (\text{ether}) = 1.643 \text{ ml}$$

$$-\text{CH}_2- = 4.618 \text{ ml}$$

$$\text{N (tertiary amine)} = 2.840 \text{ ml}$$

$$\text{H} = 1.100 \text{ ml}$$

molar refractions were calculated for the assumed structures of compounds "B", "C", and "E". The additive and constitutive properties of groups making up the molecules were made use of, but corrections for deviations from strict additivity (14, 15) were not used. Also, in calculating specific refractions for compounds "B" and "C", an assumption was made that Δd was of the order of $\sim .0001 \text{ gm/ml/deg C}$ in order to compensate for densities taken at $22^\circ/4^\circ$, while N_D values were at 20°C . The calculated molar refractions were divided by the corresponding molecular weights to get specific refractions for comparison with experimentally determined values.

Results are given in Table II:

TABLE II

Specific Refractions, $R_D = \frac{n^2 - 1}{n^2 \cdot d} \cdot \frac{1}{d} \left(\frac{\text{ml}}{\text{gm}} \right)$

Compound	Calculated	Found
"E" $\text{Me}_3\text{Si}-\text{O}-\text{C}_2\text{H}_4-\text{N}=\text{Et}_2$	0.300	0.305
"B" $\text{Me}_2\text{Si} = [\text{O}-\text{C}_2\text{H}_4-\text{N}=\text{Et}_2]_2$	0.300	0.295
"C" $\text{Me}-\text{Si} = [\text{O}-\text{C}_2\text{H}_4-\text{N}=\text{Et}_2]_3$	0.296	0.290

III. Reactions of the Compounds

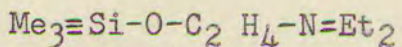
The reactions of these β -diethylaminoethoxy silanes that would be of greatest immediate interest would be those with water and with alkyl halides to form water soluble quaternary compounds. The stability of the quaternaries in water would also be of practical interest. Only limited reactions were tried in order to survey general behavior, with no attempts made to study reaction rates quantitatively.

A.) Hydrolytic Reactions

One-hundredth molar quantities of the three compounds were weighed into test tubes. To these, three times the stoichiometric amount of water for cleavage of the Si - O - C bonds was added as follows:

- distilled water
- 5% HCl (aq.)
- 5% Na OH (aq.)
- distilled water, plus ether in volume equal to the compound.

These were shaken thoroughly and examined over a period of time, with re-shaking as necessary. Results were as follows:

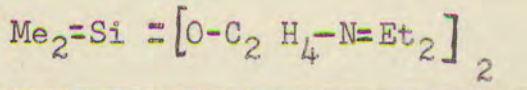


Little or no apparent attack by distilled water over a period of two days.

No attack within two days by 5% HCl.

No attack at first by 5% NaOH, but was being hydrolysed to $\text{Me}_3\text{Si OH}$ at end of three hours, hydrolysis complete within a day.

No attack by ether - water system.

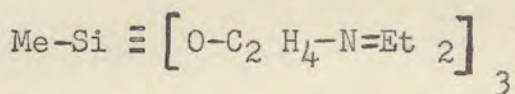


No attack at first, then a slow conversion to a single phase liquid by distilled water; completed at end of two days.

Hydrolysed rather rapidly to an oil by 5% HCl, with a slight heat effect. On standing two days the two phase system converted to a single phase oily liquid.

Rapid hydrolysis with 5% NaOH to a single phase oily liquid, with considerable heat effect. On standing a day, a second phase separated.

Slow hydrolysis by ether - water system; remains two phase at all times.



Distilled water hydrolyses the compound rapidly, with a large heat effect, to a single phase oily liquid. This slowly increases in viscosity to a soft gel in one hour.

With 5% HCl, hydrolysis is as rapid, but gelation of the single phase, viscous liquid was slower; about $3\frac{1}{2}$ hours were needed to set to a soft gel.

When 5% NaOH was shaken with the compound, rapid hydrolysis occurred and the single phase liquid became a brittle gel within a few minutes.

In the water - ether system, hydrolysis was rapid, but the system remained two phase and polymerization was slower; two days were required to get a soft gel throughout.

These results indicate hydrolytic stabilities in pure water of a lower order than Burkhard's methyl "Cellosolve" derivatives (3, 4). Hydrolysis is promoted by alkali and retarded by acid, and hydrolytic stability decreases with increasing functionality of the silicon. Addition of a solvent has a retarding effect on hydrolysis in water and on polymerization. The formation of single phase hydrolysis products is an interesting effect which should be investigated further.

B.) Preparation of Quaternary Amine Salts

Ethyl halides were chosen for this work so as not to complicate matters by effects arising from unsymmetrical substituents. One-hundredth molar amounts of the three compounds were reacted with slightly over stoichiometric quantities of ethyl chloride, - bromide, and - iodide. Results obtained were as might be anticipated; for any one aminoethoxysilane compound, the reactivity order was $\text{EtI} > \text{Et Br} > \text{Et Cl}$. For any one ethyl halide, the reactivity order was trifunctional (Si) > difunctional > monofunctional. Thus, were obtained a number of reactions,

such as EtI with $\text{Me-Si} \equiv [\text{O-C}_2\text{H}_4\text{-N=Et}_2]_3$ which gave a rapid development of a dry, waxy solid salt, to Et Cl with $\text{Me}_3\equiv\text{Si-O-C}_2\text{H}_4\text{-N=Et}_2$ which apparently did not react at all.

The three quaternary iodides were examined for hydrolytic stability. All dissolved readily in distilled water. The mono-functional gave a cloudy solution that cleared on standing. Evaporation of water yielded a salt-like residue which showed trace of silicone on ignition. The difunctional material was a hazy solution that remained so. Evaporation of water gave salt crystals that showed no signs of silica on ignition. The reason for this behavior is puzzling. Combustion tests on all the iodides showed silica residues. The trifunctional material hydrolysed at once to a white gel resembling $(\text{Me Si O } 1.5)_n$. It would appear that hydrolytic stabilities of the water soluble quaternary amine salts are very poor.

SUMMARY

Three new β -diethylaminoethoxy-methyl silanes have been prepared and characterized. By the system of nomenclature proposed by Sauer (16) and substantially approved by the A.C.S. Committee on Nomenclature, Spelling, and Pronunciation (17), these compounds are:

β -diethylaminoethoxy - trimethylsilane
 $(\text{C}_2\text{H}_5)_2\text{N-C}_2\text{H}_4\text{-O-Si} \equiv (\text{CH}_3)_3$;

bis (β -diethylaminoethoxy) - dimethyl silane,

$[(\text{C}_2\text{H}_5)_2\text{N-C}_2\text{H}_4\text{-O}]_2\text{Si} = (\text{CH}_3)_2$; and

tris (β -diethylaminoethoxy) - methyl silane

$[(\text{C}_2\text{H}_5)_2\text{N-C}_2\text{H}_4\text{-O}]_3\text{Si-CH}_3$.

The stability towards hydrolytic cleavage at the $\text{-Si-O-CH}_2\text{-}$ linkage has been studied. Hydrolytic stability decreases with increasing number of the aminoethoxy groups on silicon. Hydrolytic cleavage is most rapid in contact with dilute alkali, followed by distilled water, and least when in contact with dilute acid. Hydrolysis in the presence of a partially miscible solvent (ether) and distilled water is of the same order or slightly less than water alone, and polymerization of the resulting silicone is retarded due to solvent dilution effect.

The preparation of quaternary amine salts was attempted with ethyl halides. The rates of formation of the salts increased with increasing numbers of the aminoethoxy groups on silicon, and with increasing atomic number of the halogen. A brief study of the water soluble quaternary salts showed poor hydrolytic stability

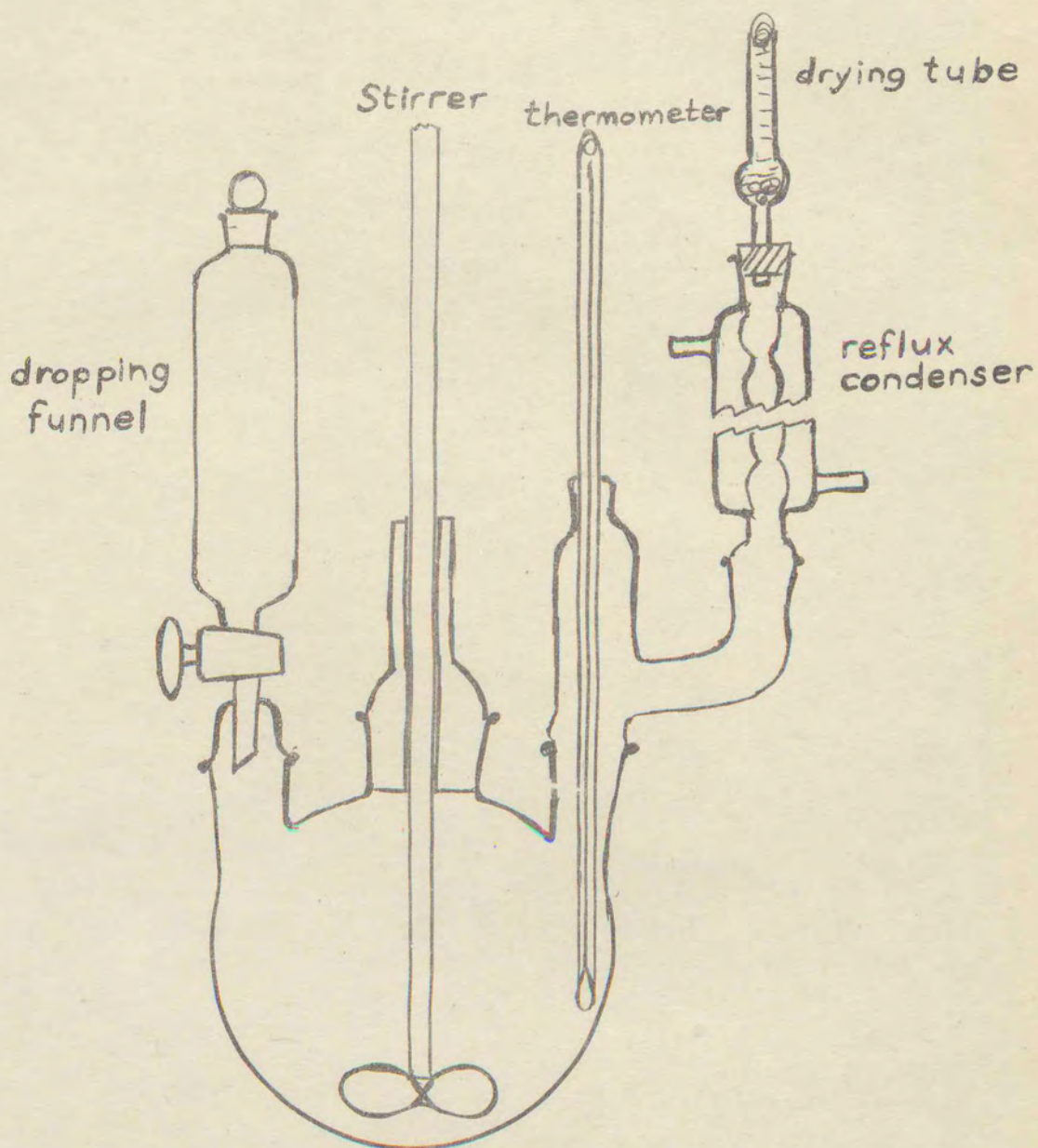
at the Si - O - CH₂ - bond. Because of this poor stability, the quaternary amine salts would not be suitable for the application originally envisioned. However, the hydrolytic behavior of the aminoethoxy - methyl silanes themselves may lead to a suitable material or process.

ACKNOWLEDGMENTS

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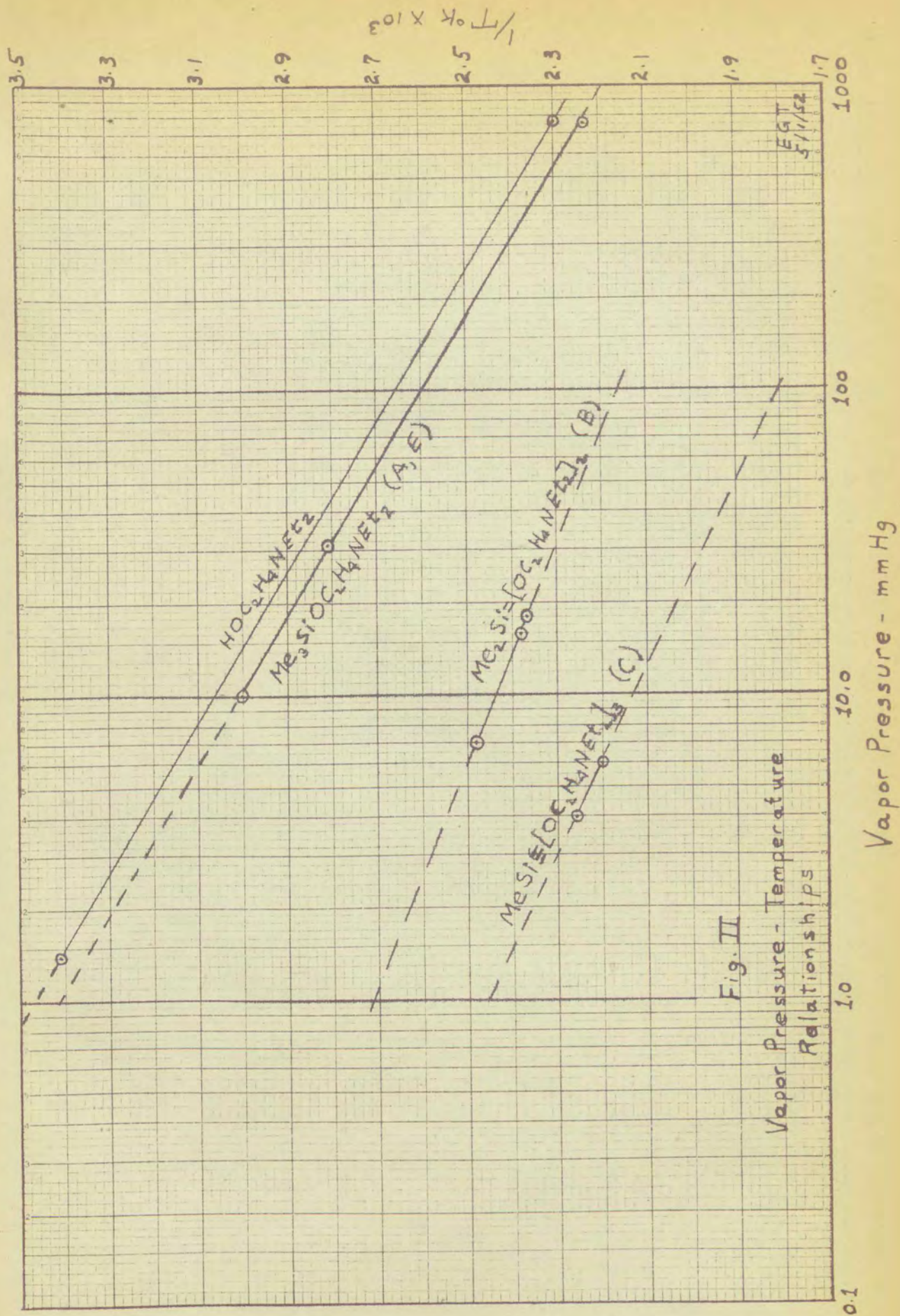
BIBLIOGRAPHY

- (1) Dr. D. P. Spalding - Silicone Dept., General Electric Co.,
Private Communication.
- (2) E. G. Rochow - Chemistry of the Silicones - 2nd Edition,
John Wiley & Sons, New York (1951)
- (3) C. A. Burkhard - J. Org. Chem 13, 879 (1948)
- (4) C. A. Burkhard - ibid 15, 106 (1949)
- (5) R. O. Sauer - J.A.C.S 67, 1548 (1945)
- (6) R. O. Sauer and R. H. Hasek - ibid 68, 241 (1946)
- (7) R. N. Lewis - General Electric Co. Research Laboratory
Private Report (1948)
- (8) Rochow - loc cit pp. 56-58
- (9) Rochow - loc cit pp. 58-59
- (10) Richards and Thompson - J. Chem. Soc. Part I, 124 (1949)
- (11) R. W. Schaefer - Private G. E. Co. report, reviewing
infra-red data on silicones.
- (12) D. L. Harms - Private Communication.
- (13) R. O. Sauer - J.A.C.S. 68, 954 (1946)
- (14) Weissberger (ed.) - Physical Methods of Organic Chemistry
Interscience Publishers, New York, (1949), Chap. XX.
- (15) Glasstone - Textbook of Physical Chemistry, 2nd edition,
D. Van Nostrand Co., New York, (1946), Chap. VIII.
- (16) R. O. Sauer - J. Chem. Education 21, 303 (1944)
- (17) Report of Committee on Nomenclature, Spelling, and
Pronunciation - Chem. Eng. News 24, 1233 (1946)



1000 ml., 3-neck flask
§ joints

Apparatus used for syntheses



I. R. SPECTROPHOTOMETER
NaCl PRISM

NO. 2662				
DATE		INDEX		
4/29/52				
SAMPLE				
DIETHYLAMINOETHANOL				
$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \begin{matrix} \diagup \\ \diagdown \end{matrix} NC_2H_4OH$				
reference compound				
FROM TANKOWSKI				
SAMP. CELL=,031 MM		CMS.		
REF. CELL R.S. MM		CMS.		
CHEM.	MG.	MG.		
SOLV.				
VOL.	C.C.	%	C.C.	%
F.S.	SOLID	C.	GAS	MM

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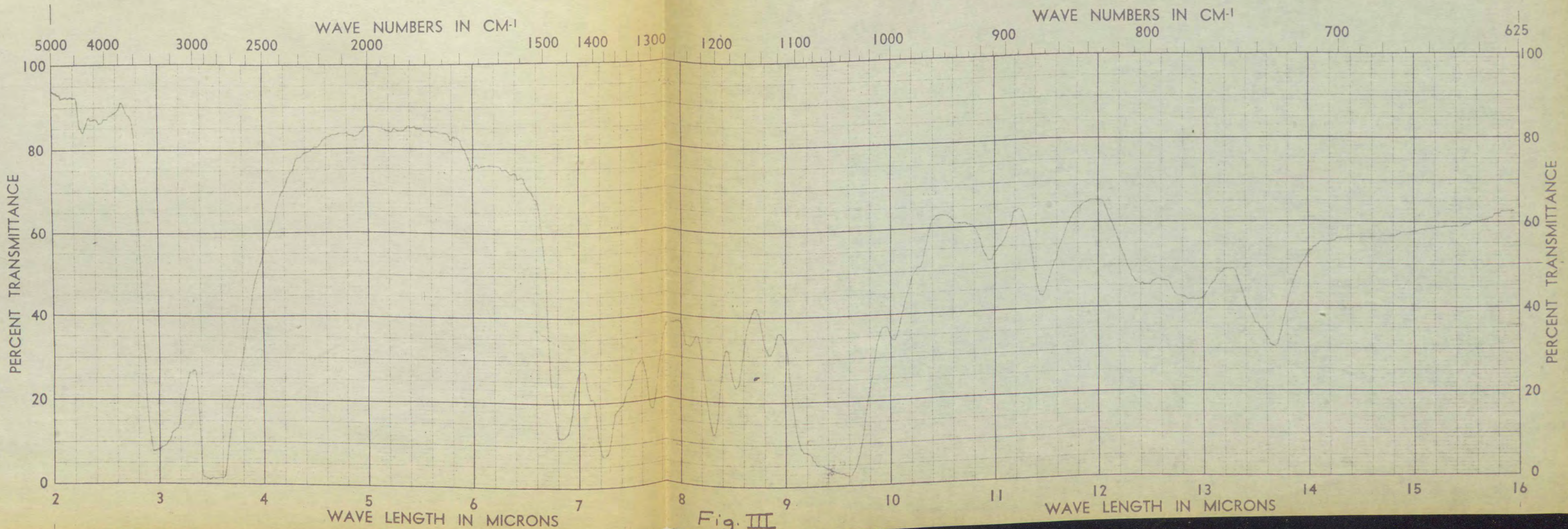


Fig. III

I. R. SPECTROPHOTOMETER
NaCl PRISM

NO. 2665				
DATE 4/29/52		INDEX		
SAMPLE #5 $ME_3SiOC_2H_4NET_2$ "E"				
-17-				
FROM TAJKOWSKI				
SAMP. CELL= .031 MM		CMS.		
REF. CELL R.S. MM		CMS.		
CHEM.	MG.	MG.		
SOLV.				
VOL.	C.C.	%	C.C.	%
F.S. SOLID	C.	GAS	MM	

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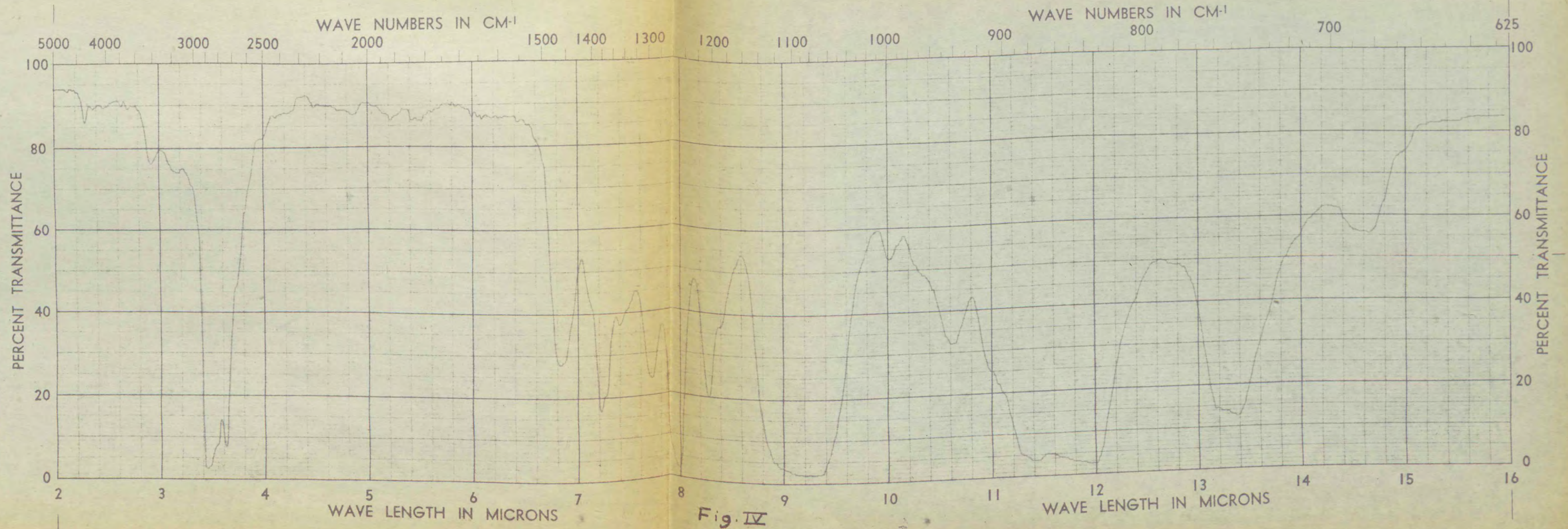


Fig. IV

I. R. SPECTROPHOTOMETER
NaCl PRISM

NO. 2683				
DATE		INDEX		
4/30/52				
SAMPLE				
#5				
$\text{Me}_3\text{SiOC}_2\text{H}_4\text{NEt}_2$				
"E"				
-01- increased resolution				
FROM TANKOWSKI				
SAMP. CELL		CMS.		
SAND CELL		APPROX. MM		
REF. CELL		R.S. MM		
CHEM.	MG.	MG.	MG.	MG.
SOLV.				
VOL.	C.C.	%	C.C.	%
F.S. SOLID	C.	GAS	MM	

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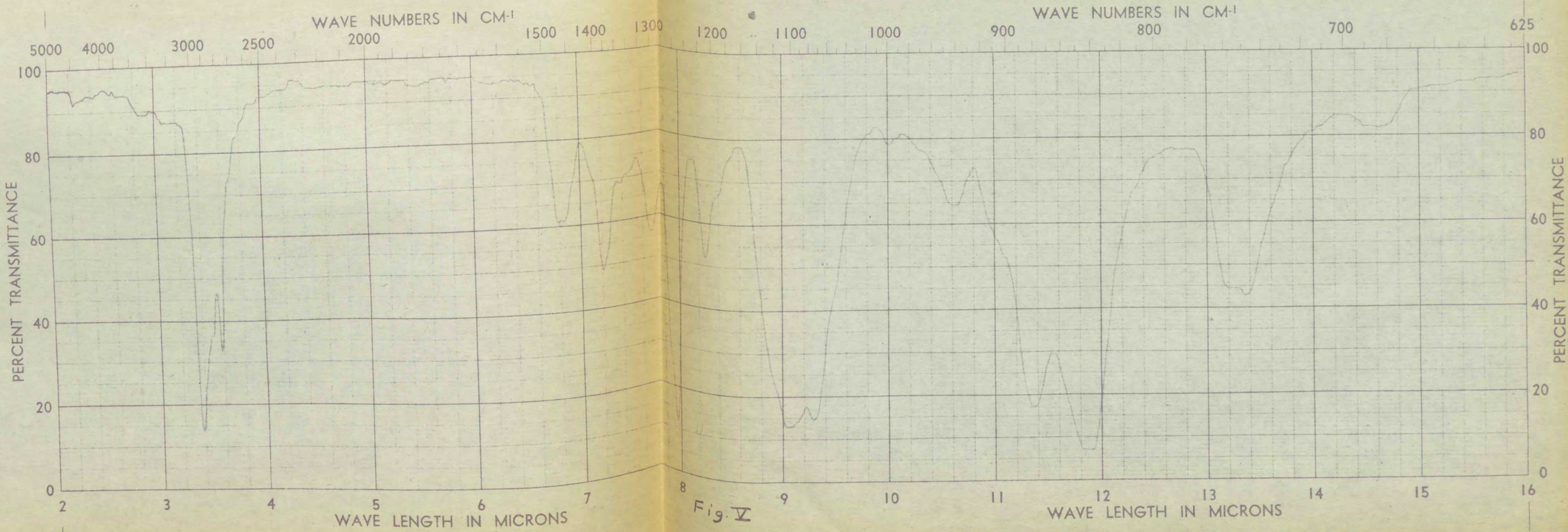


Fig. V

I. R. SPECTROPHOTOMETER
NaCl PRISM

NO. 2663				
DATE 4/29/52		INDEX		
SAMPLE #2 $\text{Me}_2\text{Si}-(\text{O}-\text{C}_2\text{H}_4\text{NET}_2)_2$ "B"				
FROM TAJKOWSKI				
SAMP. CELL= .031 MM		CMS.		
REF. CELL R.S. MM		CMS.		
CHEM.	MG.	MG.		
SOLV.				
VOL.	C.C.	%	C.C.	%
F.S. SOLID	C.	GAS	MM	

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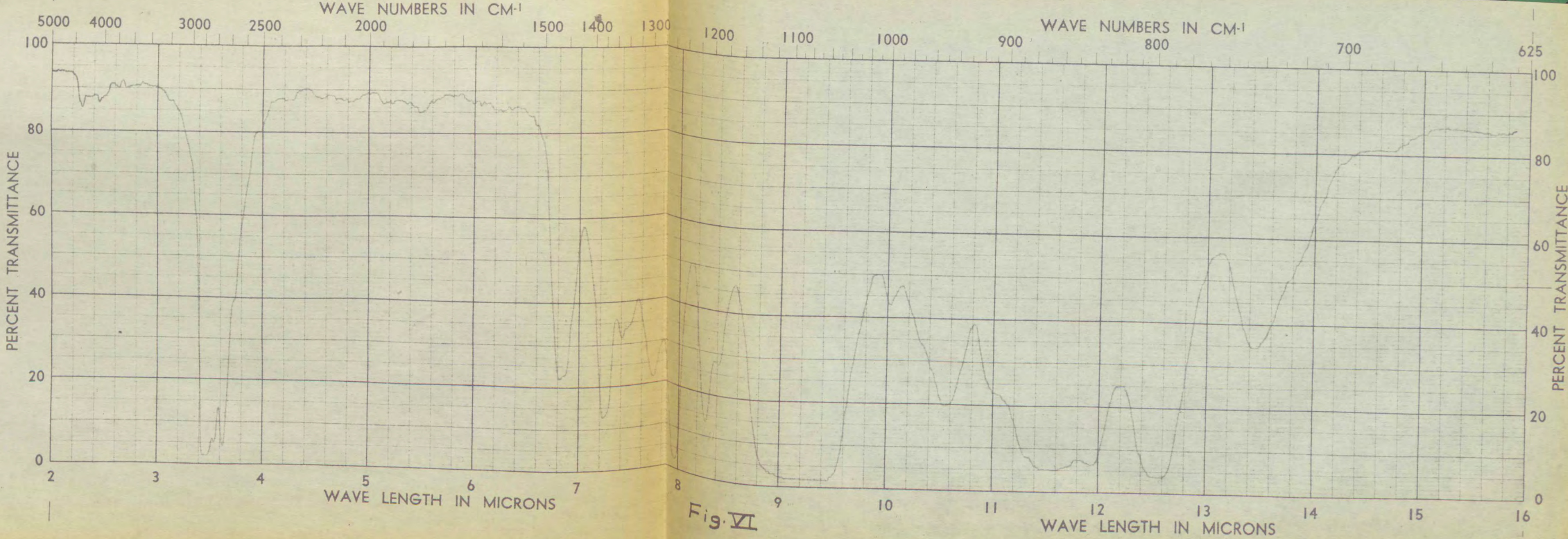


Fig. VI

I. R. SPECTROPHOTOMETER
NaCl PRISM

NO. 2664

DATE	INDEX
4/29/52	

SAMPLE
#3
 $\text{MeSi} \equiv (\text{O}-\text{C}_2\text{H}_4\text{NEt}_2)_3$
"C"

FROM TAJKOWSKI

SAMP. CELL = .031 MM CMS.

REF. CELL R.S. MM CMS.

CHEM.	MG.	MG.

SOLV.

VOL.	C.C.	%	C.C.	%

F.S.	SOLID	C.	GAS	MM

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