SYNTHESIS OF N-METHYL-N-PHENYLAMINOMETHYLTRIMETHYLSILANE AND N,N-DIMETHYLANILINOMETHYLTRIMETHYLSILYL IODIDE

by

Mark S. Lichtenstein III UC 1970

Submitted in partial fulfillment
of the requirements for
Honors in the Department of Chemistry

UNION COLLEGE
May, 1970

ABSTRACT

LICHTENSTEIN, MARK S. Synthesis of N-Methyl-N-Phenylaminomethyltrimethylsilane and N,N-Dimethylanilinomethyltrimethylsilyl-Iodide. Department of Chemistry, May 1970

N-Methyl-N-Phenylaminomethyltrimethylsilane (I) has been prepared by heating an ethereal solution of lithium N-Methylanilide and chloromethyltrimethylsilane in a sealed flask for two days at 110°.

The peak ratios in the NMR spectrum of the product did not correspond to those expected for I but suggested a different product, N-Methyl-N-Trimethylsilylaniline (II). Elemental analysis favored II although it could also be interpreted to support I. The spectra of derivatives, and the substance's stability to hydrochloric acid were characteristic of I. Tentative identification of ethylene as a by-product, and a small degree of reaction with hydrochloric acid support the presence of II, but only as an impurity. This hypothesis has been verified by gas chromatography, which showed the major product to be 94% pure and only one significant impurity present. The mass spectrum, however, showed no major peak at m/e 179, the molecular weight of II. The parent peak at m/e 193, and a molecular weight of 197 ± 2% determined by vapor phase osmometry provide convincing evidence in support of I.

The methyl iodide and HCl salts of N-Methyl-N-Phenylaminomethyltrimethylsilane have been prepared and their identity confirmed by their NMR spectra.

This Thesis

Submitted by

Mark S. Lichtenstein

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

John T. Sowa

TABLE OF CONTENTS

LIST OF FIGURES

INTRODUCTION

In recent years considerable effort has been spent in synthesizing compounds to be used in studies to determine the extent of $d\pi$-$p\pi$ bonding in certain organosilicon compounds. Messe (1) has summarized the recent, and often questioned evidence on $d\pi$-$p\pi$ bonding and has placed the objectives of these studies in perspective.

For our study it was necessary to synthesize the following sets of related compounds.

A	B
1. $Ph\text{-}O\text{-}CH_2\text{-}SiMe_3$	1. $CH_3\text{-}O\text{-}CH_2\text{-}SiMe_3$
2. $Ph\text{-}S\text{-}CH_2\text{-}SiMe_3$	2. $CH_3\text{-}S\text{-}CH_2\text{-}SiMe_3$
3. $Ph\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}}\text{-}CH_2\text{-}SiMe_3$	3. $Et_2N\text{-}CH_2\text{-}SiMe_3$

Compounds A-1, A-2, B-1, and B-3 have been prepared with little difficulty. However, synthesis of A-3 by methods analogous to those used in preparing the other compounds proved to be unsuccessful. This project has therefore been devoted to synthesizing A-3 and some of its derivatives.

DISCUSSION

The first method, which was successful in preparing $Et_2N-CH_2-SiMe_3$ (1) and $Ph-NHCH_2-SiMe_3$ employed the direct S_N2 of chloride by the amine (Reaction 1)

1. $2\ Ph-\underset{CH_3}{N}-H + Cl-CH_2-SiMe_3 \longrightarrow Ph-\underset{CH_3}{N}-CH_2SiMe_3 + Ph-\underset{CH_3}{N}-H \cdot HCl$

Refluxing the reaction mixture resulted in the formation of methylaniline hydrochloride and other products which could not be separated. The NMR and infrared spectra of the liquid phase, after filtration of the precipitated amine hydrochloride, were uninterpretable.

Strong bases, such as sodium metal and sodium hydride, were then incorporated in the reaction mixture to form the anion of the amine, a stronger nucleophile than the free amine. Again, the products resisted separation and the spectra provided little help in their identification.

Since the two bases used above were insoluble in the reaction medium, and the sodium salt of N-methylaniline perhaps too insoluble to affect the reaction, it seemed desirable to make the lithium salt. Lithium compounds are generally more soluble in organic reagents than their sodium counterparts. The following reactions were therefore proposed.

$$Ph-Li + Ph-\underset{CH_3}{N}-H \longrightarrow Ph-\underset{CH_3}{N}-Li + PhH$$

2. $Ph-\underset{CH_3}{N}-Li + Cl-CH_2-SiMe_3 \longrightarrow Ph-\underset{CH_3}{N}-CH_2-SiMe_3 + LiCl\ (solid)$ (I)

The NMR spectrum of I should show an aromatic absorption and singlets due to N-methyl, methylene, and silylmethyl protons in a 5:3:2:9 ratio. The actual spectrum of the product showed only three sets of peaks: an aromatic absorption at 7.3 - 6.3 ppm, a singlet at 2.7 ppm, and a silylmethyl singlet arbitrarily

positioned at 0.0 ppm in a 4.8:3.5:6.0 ratio. Even if the N-methyl and methylene protons of I had the same chemical shift, the ratio predicted would be 5:5:9.

The low value of the peak at 2.7 ppm could be explained on the basis of a second possible product (II) formed by the S_N2 displacement of the chloromethyl group in chloromethyltrimethylsilane by the base (Reaction 3).

3. $Ph\text{-}\underset{\underset{CH_3}{|}}{N}\text{-}Li + Cl\text{-}CH_2\text{-}SiMe_3 \longrightarrow Ph\text{-}\underset{\underset{CH_3}{|}}{N}\text{-}SiMe_3 + Li\text{-}CH_2Cl$ (II)

The NMR spectrum of II would exhibit three sets of peaks in the ratio of 5 (aromatic) : 3 (N-methyl) : 9 (silylmethyl). The displacement of electronegatively substituted carbon atoms bound to silicon by strong bases has been well documented by Eaborn (2). Considering the relatively drastic conditions employed in Experiment III such a displacement might have been expected.

The elemental analysis performed by Micro-Analylis, Inc. favored product II, although it could also be interpreted to support structure I.

The molecular weight determination by vapor phase osmometry indicated a molecular weight of 197 $\pm$ 2%, supporting structure I.

Experiment IV was performed to detect gaseous products whose presence might confirm the occurrence of Reaction 3. One of the products, $Li\text{-}CH_2Cl$, is highly reactive and would be expected to either abstract a proton from the reaction medium, forming methyl chloride (bp -24°, mp -97°) or form carbene and lithium chloride. The carbene could then undergo an insertion reaction or dimerize, forming ethylene (bp -104°, mp -181°). No NMR absorption was observed for methyl chloride but a peak at 5.3 ppm relative to TMS suggested the presence of ethylene or dichloromethane (bp 41° , mp -97°). Decolorization of bromine provided additional evidence for the presence of ethylene. An infrared spectrum of the gas would further aid in its identification, and such an experiment is currently in progress. The amount of gas produced was quite small, indicating

that Reaction 3, if it occurs at all, is only a minor side reaction.

Salts of the product from Experiment III appear to support compound I. The methyl iodide salt would be expected to show four peaks in a ratio of 5 (aromatic) : 2 (methylene) : 6 (N-methyl) : 9 (silylmethyl). The actual spectrum showed the predicted four peaks in a 5:2:6:9 ratio. The spectrum of the HCl salt was somewhat less informative but nevertheless supported structure I. No N-H peak was observed due to exchange with acetone but the three sets of peaks in a ratio of 5 (aromatic) : 5 (methylene and N- methyl combined) : 7.6 (silylmethyl) was closer to the 5:5:9 ratio expected for I than the 5:3:9 ratio expected for II.

Since II could not be prepared by direct combination of chloromethyltrimethylsilane and N-methylaniline, it was of interest to compare the methyl iodide salt of N-trimethylsilylaniline with the HCl salt of the product isolated in Experiment III. If the product of Experiment III were compound II, the spectra of both salts would be identical. The infrared spectra proved that the salts were different but furnished little additional information. The NMR spectrum of the hydro iodide salt of II, prepared by the addition of methyl iodide to N-trimethylsilylaniline, showed no silylmethyl absorption, indicating cleavage of the Si-N bond. Cleavage of Si-N bonds by acids have been well substantiated (2,3). A reaction of this sort is illustrated by Equation 4.

4. $Ph\text{-}\underset{\underset{H}{|}}{N}\text{-}SiMe_3 + HX \longrightarrow Me_3SiX + PhNH_2$

Si-N bonds are also cleaved by amine hydrochlorides when the silicon halide is volatile and can distill from the system (3). Reaction 5 is a typical example.

5. $Ph\text{-}\underset{\underset{H}{|}}{N}\text{-}SiMe_3 + PhNH_3X \longrightarrow Me_3SiX + 2\ PhNH_2$

The HI salt of II prepared by the addition of methyl iodide to N-trimethylsilylaniline should cleave according to analogous reactions.

If the product from Experiment III were a mixture of compounds I and II, acid cleavage of II (Reaction 6) would give an indication of its composition. Experiment VI-B has shown this hypothesis to be true. Upon reaction with conc. hydrochloric acid an immiscible layer separated which exhibited a single silylmethyl NMR absorption.

6. $Ph\text{-}\underset{CH_3}{N}\text{-}SiMe_3 + 2HCl \longrightarrow Me_3SiCl + Ph\text{-}\underset{CH_3}{NH_2}Cl$

Making the HCl layer alkaline liberated a base whose NMR spectrum corresponded to that expected for I. Comparison of the gas chromatographs of the starting material and the acid treated product revealed that an impurity (presumably II) initially present, had been quantitatively converted to N-methylaniline. The mass spectrum, however, showed no major peak at 179, the molecular weight of II.

Preparation of I <u>via</u> Reactions 7 and 8 yielded a product identical to that isolated in Experiment III.

7. $Ph\text{-}Li + Ph\text{-}\underset{H}{N}\text{-}CH_2\text{-}SiMe_3 \longrightarrow Ph\text{-}\underset{Li}{N}\text{-}CH_2\text{-}SiMe_3 + PhH$

8. $Ph\text{-}\underset{Li}{N}\text{-}CH_2\text{-}SiMe_3 + CH_3I \longrightarrow Ph\text{-}\underset{CH_3}{N}\text{-}CH_2\text{-}SiMe_3 + LiI$

A mass spectrum of the product from Experiment III gave a parent peak of 193, strongly supporting compound I.

EXPERIMENTAL

I. Synthesis of Phenoxymethyltrimethylsilane

A) Preparation of Potassium Phenoxide

38.0g (.404 mole) phenol on 75ml of 95% ethanol and 22.4g (.400mole) potassium hydroxide in 200ml of 95% ethanol were mixed together in a 400ml beaker. After heating 10 min on a smlaa hotplate the solution was concentrated on a rotary evaporator until a sludge remained. The sludge was dissolved in 50ml of acetone and the potassium phenoxide precipitated by the addition of 200ml of ether. The precipitate was filtered by suction, washed several times with small portions of ether and sucked dry. Last traces of ether were removed by storing the product overnight in a vacuum desiccator at water aspirator pressure.

B) Preparation of Phenoxymethyltrimethylsilane

To a 100ml flask fitted with a reflux condenser and a magnetic stir-bar wes added 45ml of methanol, 13.2g (.10 mole) potassium phenoxide and 12.2g (.10 mole) chloromethyltrimethylsilane. The mixture was refluxed and stirred.

Within a few hours, KCl began to precipitate. After three days of refluxing the solid was filtered off and the filtrate distilled through a 5" column packed with glass beads. After most of the solvent and unreacted silane had been distilled, a solid (probably KCl and/or unreacted PhOK) appeared in the distilling flask making further distillation impossible. An NMR spectrum of the liquid remaining in the flask indicated it was the desired product (Figure 1).

Ether was added to the distilling flask and the solid was broken with a glass rod. The suspension was then transferred to a separatory funnel, 50ml water added, and the mixture shaken. The brown aqueous layer was discarded and the ether layer washed twice with 25ml portions of water, dried with anhydrous sodium sulfate, and filtered. The ether was removed on a rotary evaporator, leaving approximately 5ml of phenoxymethyltrimethylsilane.

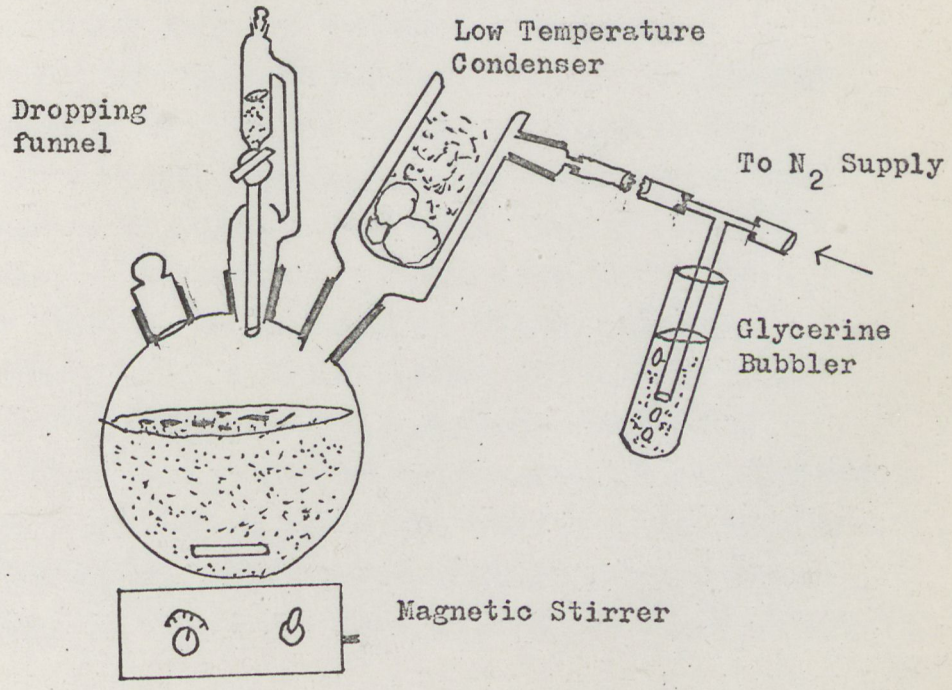
II. Preparation of Phenyllithium (5)

All apparatus was dried in an oven, cooled in a desiccaor, flushed with dry nitrogen prior to use and assembled in a glove-bag under a nitrogen atmosphere. The reaction itself was also run under nitrogen.

Lithium wire (4.0g, .576 mole) was wiped of its protective grease coating and cut into small pieces (ca. 2cm), letting the pieces fall directly into a 500ml three-neck flask containing 150ml of sodium dried ether and a magnetic stir-bar. The flask was fitted with a low temperature condenser and a 50ml pressure equallizing dropping funnel containing 39g (.25 mole) of bromo-benzene, and a glass stopper in the third neck. Provisions were made to run the reaction under a dry nitrogen atmosphere (see accompanying diagram).

After addition of bromobenzene, the mixture was stirred for 10 min, allowed to settle, and filtered through glass wool into a glass stoppered flask.

To determine the concentration of the phenyllithium, aliquots were pipetted into 125ml Erlenmeyer flasks, hydrolyzed with distilled water, and titrated with standard HCl using phenol-phthalein for the indicator.



III. Reaction of Phenyllithium with N-Methylaniline and Chloromethyltrimethylsilane

A 100ml flask containing 10.7g (.10 mole) N-methylaniline, equipped with a magnetic stir-bar and a pressure equalizing dropping funnel containing 57ml of 1.67M phenyllithium (.095 mole) in ether, was attached to a dry nitrogen supply and cooled in an ice bath. The phenyllithium was added slowly with stirring. To this solution was added 12.25g (.10 mole) chloromethyltrimethylsilane. A small portion was placed in an NMR tube which was cooled in dry ice-acetone and sealed under nitrogen. The remainder was transferred to a 100ml round-bottom flask (the neck of which had been previously tapered to a diameter of approximately 6mm) and sealed in a similar fashion.

The flask and NMR tube were immersed in a heating bath thermostatted at 40°. An NMR spectrum of the solution after 20 hrs indicated that no reaction had occurred. The tube and flask were then transferred to a 110° drying oven. Within 30 min a white precipitate had formed. NMR spectra were recorded periodically for several days until no further changes were observed (Figure 2)

The sharp singlet at 7.1 ppm (relative to the silylmethyl absorption in chloromethyltrimethylsilane) and the absence of the broad amino hydrogen absorption of N-methylaniline confirmed conversion to the lithium salt and formation of benzene.

Reaction between chloromethyltrimethylsilane and the lithium salt of N-methylaniline was observed through the decay of the N-methyl singlet at 2.73 ppm, the formation of a new peak at 2.78 ppm, and the formation of a second silylmethyl peak at -.03 ppm.

Upon completion of the reaction the flask was opened, 50ml of water added to dissolve the precipitated lithium chloride, and the mixture shaken in a separatory funnel. The aqueous layer was extracted with 25ml ether and then discarded. The combine ether layers were dried over anhydrous calcium chloride and filtered. Evaporation of the ether left approximately 20ml of a high boiling residue. Thin layer and gas chromatography indicated the presence of two major components, one of which corresponded to N-methylaniline.

Distillation through a 5" X ½" Hempel column packed with glass beads under a nitrogen atmosphere yielded two fractions. The fraction boiling at 39°- 40°/1mm was characterized by NMR and infrared spectra as N-methylaniline. The second fraction (ca. 10ml) boiled at 70°- 71°/1mm. The small amount of tarry residue remaining in the distilling flask was discarded.

The infrared spectrum of a thin film of the second fraction (Figure 3) showed no N-H stretching frequencies in the 3400 cm^{-1} region. Other than this feature, the infrared spectrum of the product closely resembled the spectrum of N-methylaniline.

The NMR spectrum (Figure 4) showed three areas of interest: an aromatic absorption at 7.3 - 6.3 ppm, a singlet at 2.7 ppm, and a singlet in the silylmethyl region arbitrarily positioned at 0.0 ppm. The ratios were 4.8:3.5:6.0, respectively. The ratios expected for the desired product, N-methyl-N-phenylaminomethyl-trimethylsilane, are 5:3:2:9 or 5:5:9 if the N-methyl and methylene protons have the same chemical shift.

IV. Detection of Gaseous By-products Generated in Experiment III

The reagents were prepared according to the procedure outlined in Experiment III, but this time sealed under vacuum as follows. A reaction vessel (Figure 5) was constructed from 35mm Pyrex tubing, provided with a 3mm o.d. stem to serve as a break seal and a 10mm o.d. side arm with a seal-off constriction for addition of reagents and attachment to the vacuum system. The reagents (already mixed) were added through the side arm, washed down with dry ether and frozen in liquid nitrogen. The 3mm stem was then sealed. The side arm was connected to the vacuum system at F (Figure 5), which was repeatedly evacuated and filled with nitrogen through stopcock H several times. The system was evacuated a final time and the side arm sealed off at the thickened constriction.

The sealed reaction vessel was immersed in a heating bath thermostatted at 95°. Sometime during the night, after at least 5 hrs heating at 95°, the thermometer broke and the temperature rose to 184°. An aliquot heated in a sealed NMR tube revealed a complete reaction after overnight heating at the elevated temperature.

The reaction vessel was placed in the break seal apparatus, I, and connected to the vacuum system via a ball-and-socket joint at F. Stopcocks C, E, and G were opened and the fore pump turned on. When the pressure on the McCleod gauge was .2mm, trap B was immersed in liquid nitrogen, and the oil diffusion pump, A, containing 50ml of dioctyl phthalate, set into operation. Vessel I was immersed in liquid nitrogen but the contents of the reaction flask never froze completely. When the McCleod gauge registered less than .001mm, stopcock C was closed, the 3mm stem broken by turning fork J, and the Dewar of liquid nitrogen removed from I. A small Dewar of liquid nitrogen was then placed around one of the NMR tubes located at K. No condensation was observed in the NMR tube until I was warmed with an infrared heat lamp sufficiently to melt the frost which had accumulated on its outside surface.

When the tube had been filled to a depth of approximately 2" with condensate, it was sealed off. Two similar tubes were prepared. The NMR spectrum (Figure 6) showed, in addition to ether, a peak at 7.2 ppm (benzene) and at 5.3 ppm. Two sources of this second peak are dichloromethane and ethylene.

One of the tubes was frozen in liquid nitroged, opened, and placed upside down in a 10 X 75mm test tube containing 10% alcoholic silver nitrate. Upon warming to room temperature, the contents mixed with the silvef nitrate solution but no precipitate was formed. The other tube was frozen, opened, and placed upside down in a 10 X 75mm test tube containing dilute (light yellow) bromine in carbon tetrachloride. Within 5 min the solution was decolorized. A blank was run on sodium dried ether, but the solution remained yellow.

In a similar experiment bromine was bled into the vacuum system through stopcock H and collected in an NMR tube along with the ether solution. Within 5 min after the tube was sealed off and warmed to room temperature, the solution lost its color.

V. Derivatives of Product from Experiment III

A) Methyl Iodide Salt

To a 10ml Erlenmeyer flask was added 5ml of methyl iodide and .5ml of the product from Experiment III. The solution was heated a few minutes to initiate the reaction and allowed to cool. The white crystals were filtered through a coarse sintered glass filter and washed with acetone. The crystals were dissolved in a small amount of methanol and reprecipitated with benzene. After filtering and washing with ligroine (bp 30°- 60°) the product was stored overnight in a vacuum desiccator at 2mm. The crystals melted at 197°- 199°.

The NMR spectrum (Figure 7) in DMSO-d6 showed a low field aromatic absorption at 8.3 - 7.6 ppm, and singlets at 4.05, 3.82, and (arbitrarily) at 0.0 ppm in a 5:2:6:9 ratio.

B) HCl Salt

25ml of concentrated hydrochloric acid and 40ml of ether were shaken in a separatory funnel. Upon separation, the aqueous layer was discarded and the ether phase dried over anhydrous sodium sulfate. 0.5ml of the product from Experiment III was added to 25ml of the HCl solution. The solution immediately became cloudy and within a few minutes white crystals formed. The salt was filteted through a coarse sintered glass filter, washed with carbon tetrachloride, and sucked dry. The product was recrystallized from acetone and dried 15 min at 110°. A wide melting range (132°- 140°) indicated the product was impure.

The NMR spectrum in acetone-d6 (Figure 8) showed a low field aromatic absorption 8.2 - 7.3 ppm, two peaks at 3.28 and 2.24 ppm which merged together, and a silylmethyl peak arbitrarily set at 0.0 ppm. The ratios were 5:5:7.6, respectively. Assuming that the proton exchanged rapidly with the acetone solvent, and that the peaks at 3.28 and 3.24 ppm represent the methylene and N-methyl absorption of the desired product, the ratios would be expected to be 5:5:9.

VI. Stability of the Product from Experiment III

A) Reaction with Alcohol

To a 50ml flask was added 20ml of methanol and 1ml of the product from Experiment III. The solution was refluxed 3 hrs and and the alcohol removed with a rotary evaporator. An NMR spectrum of the residue indicated no reaction had taken place.

B) Reaction with Concentrated Hydrochloric Acid

To a 25ml flask was added 10ml of concentrated hydrochloric acid and 1ml of the product from Experiment III. White crystals immediately formed but upon warming an immiscible layer separated. The mixture was refluxed 15 min to complete any reaction which had occurred.

The upper layer was extracted with 10ml of ether, dried over anhydrous calcium chloride, and concentrated to approximately 2ml. The NMR spectrum showed, in addition to ether, only one peak in the silylmethyl region at .06 ppm relative to TMS.

The aqueous layer was boiled to remove any volatile products which may have escaped ether extraction, cooled, and made alkaline with sodium hydroxide. The immiscible layer which separated was extracted with ether. The ether layer was dried over anhydrous calcium chloride and the ether removed by a rotary evaporator. The NMR spectrum (Figure 9) was identical in appearance to that of the starting material, except the ratios were 5:5:8.2 rather than 5:3.5:6. This corresponded closely to the 5:5:9 ratio expected for N-methyl-N-phenylaminomethyltrimethylsilane.

The acid treated product and the starting material were compared by gas chromatography (six feet DC-710 Silicon Oil Column, 20 psi He, 190°) and the peak areas approximated by triangulation. The starting material showed two peaks: R.T. 1.55 min (N-methylaniline,.95%),4.05 min (93.7%), and 5.30 min (5.35%). The acid treated product showed only two peaks: R.T. 1.55 min (N-methylaniline, 6.2%) and 4.05 min (93.8%). Apparently the impurity at R.T. 5.30 min had been converted to N-methylaniline upon acid treatment.

VII. Preparation of N-Methyl-N-Trimethylsilylaniline

To a 100ml flask equipped with a reflux condenser and a drying tube was added 23.4g (.22 mole) N-methylaniline and 10.8g (.10 mole) trimethylchlorosilane. The solution was refluxed overnight. No change in the NMR spectrum was observed. After refluxing 5 days, only an insignificant amount of product formed, and upon distillation only N-methylaniline, bp 35°/1mm was recovered. A tarry residue in the distilling flask proved to be mainly impure N-methylaniline.

VIII. Preparation of N-Trimethylsilylaniline (3)

To a 50ml Erlenmeyer flask containing 25g (.27 mole) aniline and cooled in an ice bath, was added 10.0g (.093 mole) trimethylchlorosilane. A precipitate formed immediately. The mixture was removed from the ice bath, allowed to stand 30 min, filtered, and washed with ligroine (bp 100°- 115°). The ligroine was removed on a rotary evaporator and the residual liquid distilled under reduced pressure. After distillation of aniline at 34°/1mm, the fraction boiling at 48°/1mm was collected (bp (lit) = 206°/760mm, 98°-99°/19mm). The NMR spectrum (Figure 10) of this fraction showed an aromatic absorption at 7.25 - 6.40 ppm, a broad singlet (N-H) at 3.05 ppm, and a silylmethyl singlet arbitrarily positioned at 0.0 ppm in the expected 5:1:9 ratio.

IX. Methyl Iodide Salt of N-Trimethylsilylaniline

To a 25ml flask equipped with a reflux condenser was added 1ml N-trimethylsilylaniline and 10ml methyl iodide. Crystals formed after several hours of refluxing and the mixture refluxed overnight. The crystals were filtered, washed with ether, and stored overnight in a vacuum desiccator at 3mm. The NMR spectrum showed no silylmethyl absorption, indicating cleavage of the Si-N bond.

X. Preparation of N-Phenylaminomethyltrimethylsilane (5)

A) To a 250ml flask fitted with a reflux condenser and a drying tube was added 37g (.4 mole) aniline (distilled over zinc), 12.25g (.10 mole) chloromethyltrimethylsilane, and 80ml ligroine (bp 100°-115°). The mixture was refluxed for a week. During this period solid accumulated in the condenser sealing it. The resulting

increase in pressure loosened the condenser and most of the solvent evaporated. The remaining liquid was distilled at reduced pressure yielding about 5ml of product, bp 72°/1mm.

The NMR spectrum (Figure 11) showed an aromatic absorption at 8.0 - 6.8 ppm, and singlets at 3.50 (N-H), 2.55 (methylene), and, arbitrarily, 0.0 ppm (silylmethyl). The ratios of 5.1:1.0:1.9:8.4 correspond closely to the expected 5:1:2:9 ratio.

B) A 100ml flask containing 22.5g (.24 mole) aniline and 12.25g (.10 mole) chloromethyltrimethylsilane was refluxed overnight. The aniline hydrochloride precipitate was filtered and washed with ether. The ether was removed from the filtrate on a rotary evaporator and the residual liquid distilled under reduced pressure. The fraction (approximately 5ml) boiling at 72° was collected. This method of preparation is to be preferred over method A.

XI. Methyl Iodide Salt of N-Phenylaminomethyltrimethylsilane

A solution of 10ml methyl iodide and 1ml N-phenylaminomethyltrimethylsilane was refluxed overnight. No reaction had occurred. 10ml methanol was added to increase the polarity and the solution refluxed overnight. Upon evaporation of the methanol and methyl iodide only a gummy residue of impure starting material remained.

XII. Preparation of N-Methyl-N-Phenylaminomethyltrimethylsilane

A 25ml flask containing 2.15g (.012 mole) N-phenylaminomethyltrimethylsilane, fit with a pressure equalizing dropping funnel containing .0123 mole phenyllithium in ether, was attached to a dry nitrogen supply and cooled in a dry ice - acetone bath. The phenyllithium was added slowly with magnetic stirring. When addition was complete, 1ml (016 mole) methyl iodide was added and the solution was warmed to room temperature. A precipitate formed within a few minutes. After 40 hrs of stirring water was added and the organic layer separated. The aqueous layer was extracted once with 5ml of ether and discarded. The combined ether phases were dried over anhydrous calcium chloride, filtered, and the ether evaporated. The NMR spectrum was identical to the spectrum of the product from Experiment III.

XIII. Analyses

A) Elemental Analysis (Micro-Analysis, Inc., Wilmington, Del.)
Sample ML-3 (Experiment III)

	% Found	Molar Ratio		
		A	B	Average of A and B
C	69.83	12.63	10.48	11.56
H	9.57	20.70	17.20	18.95
N	7.73	1.20	1.00	1.10
Si*	12.87	1.00	.83	.90

* By difference

B) Molecular Weight by Vapor Phase Osmometry
(Schenectady Chemicals, Inc.)

M.W. = 197 ± 2%

C) Mass Spectrum (Rennselaer Polytechnic Institute)
m/e of Parent Peak = 193
There was no major peak at m/e 179, the molecular weight of N-Methyl-N-Trimethylsilylaniline.

Figure 1

Ø-O-CH_2-$SiMe_3$

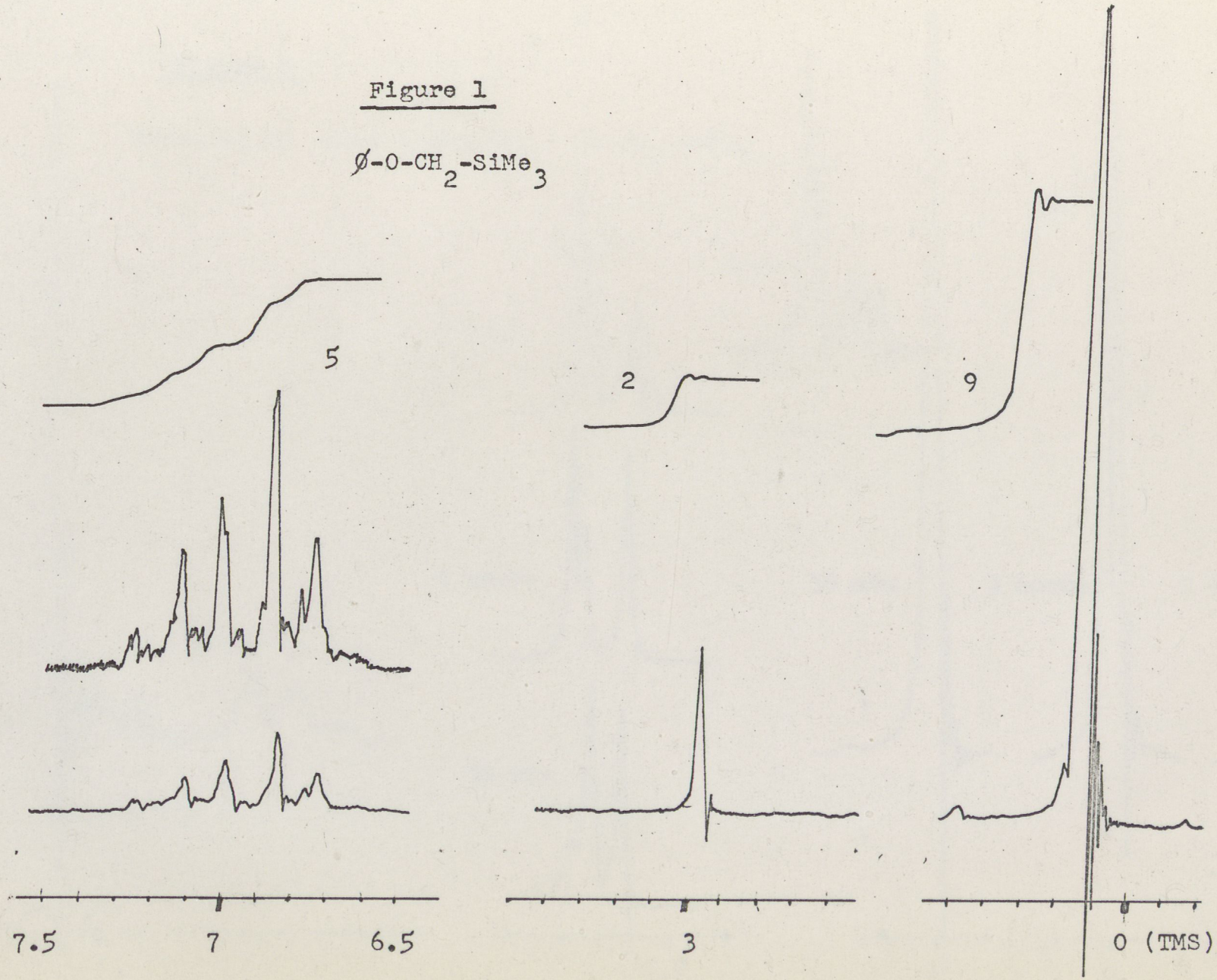
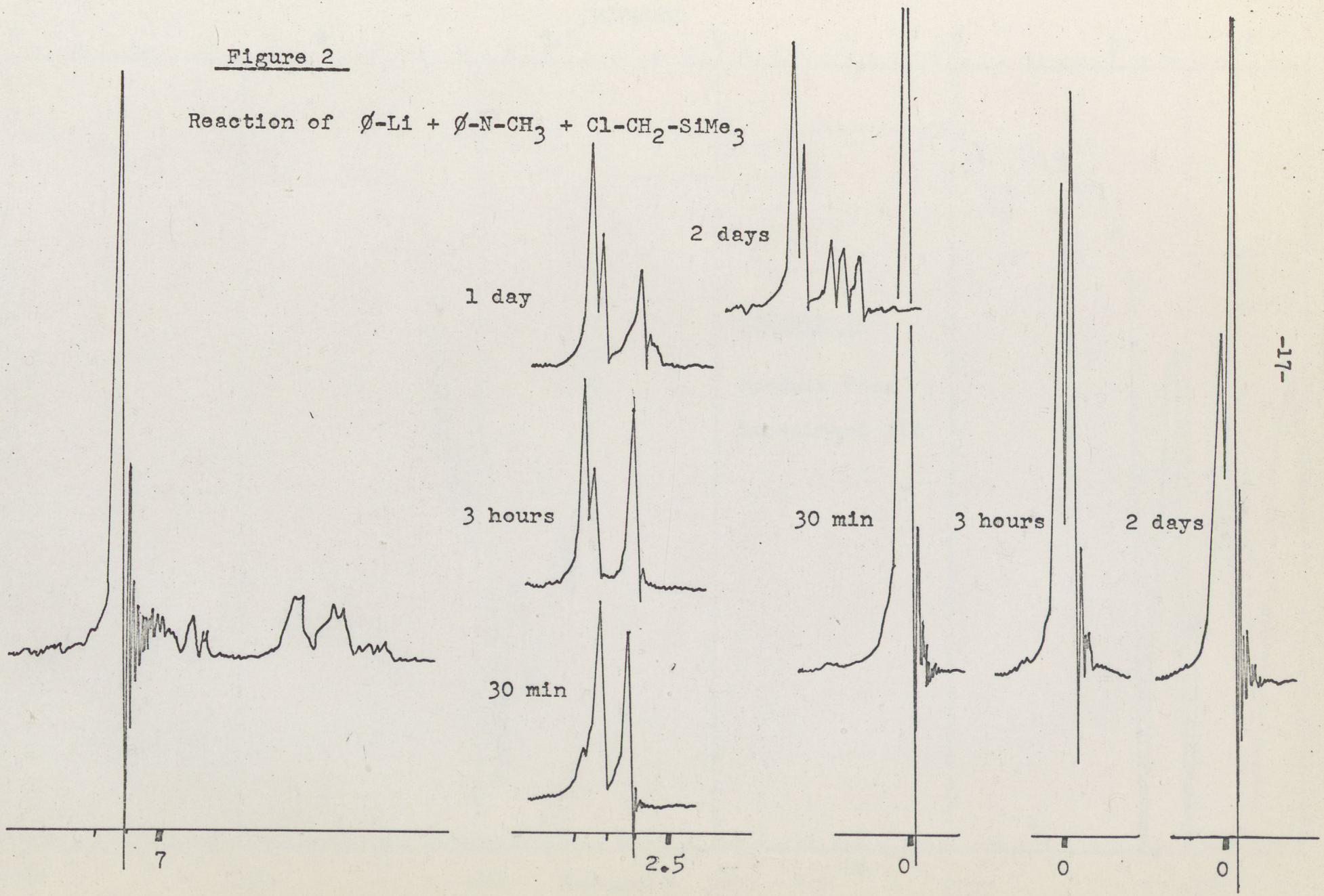


Figure 2

Reaction of Ø-Li + Ø-N-CH_3 + Cl-CH_2-$SiMe_3$



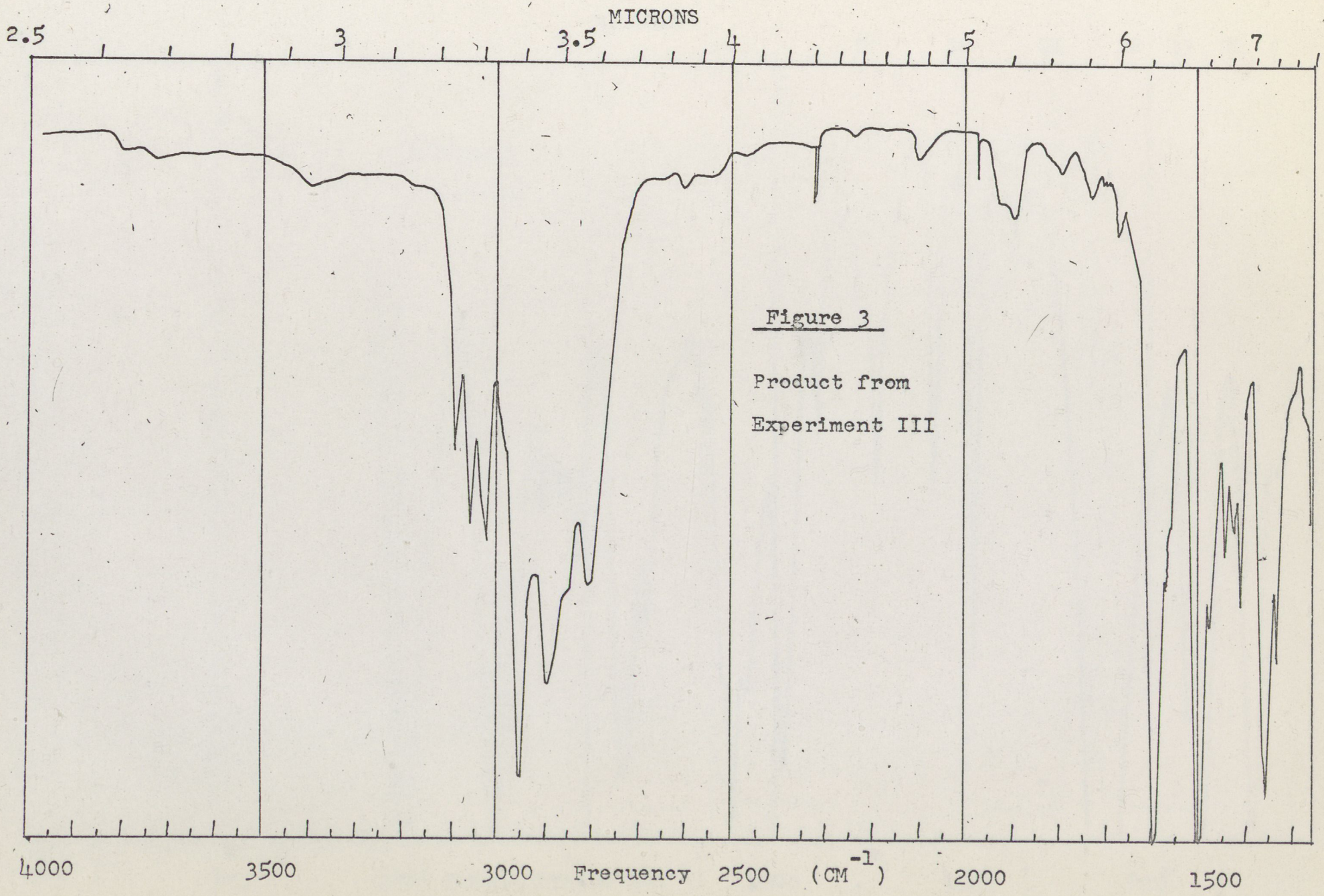


Figure 3

Product from

Experiment III

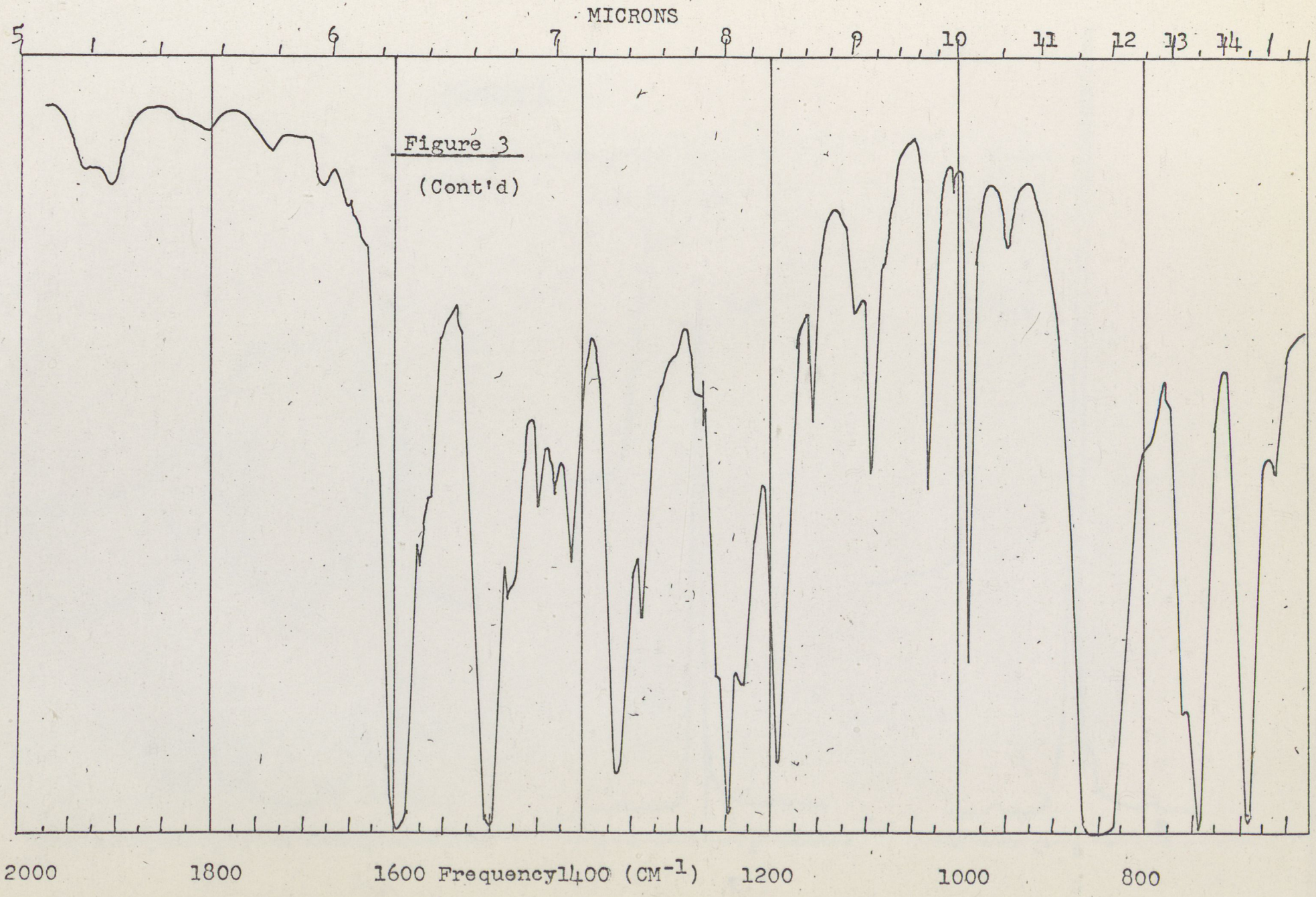


Figure 3

(Cont'd)

Figure 4

Experiment III Reaction Product

bp 72°/1mm

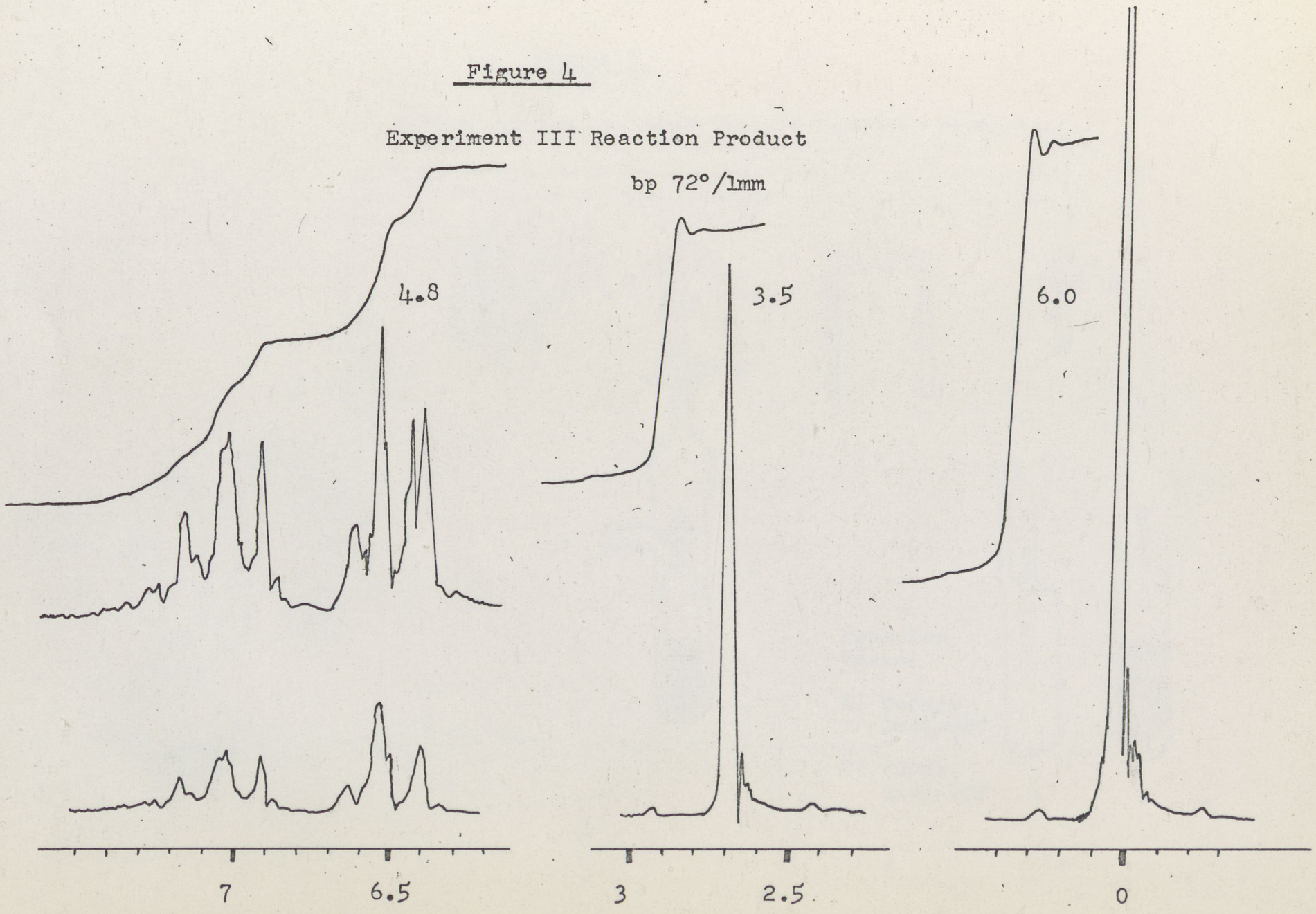


Figure 5

Vacuum System for Detection of Volatile Products

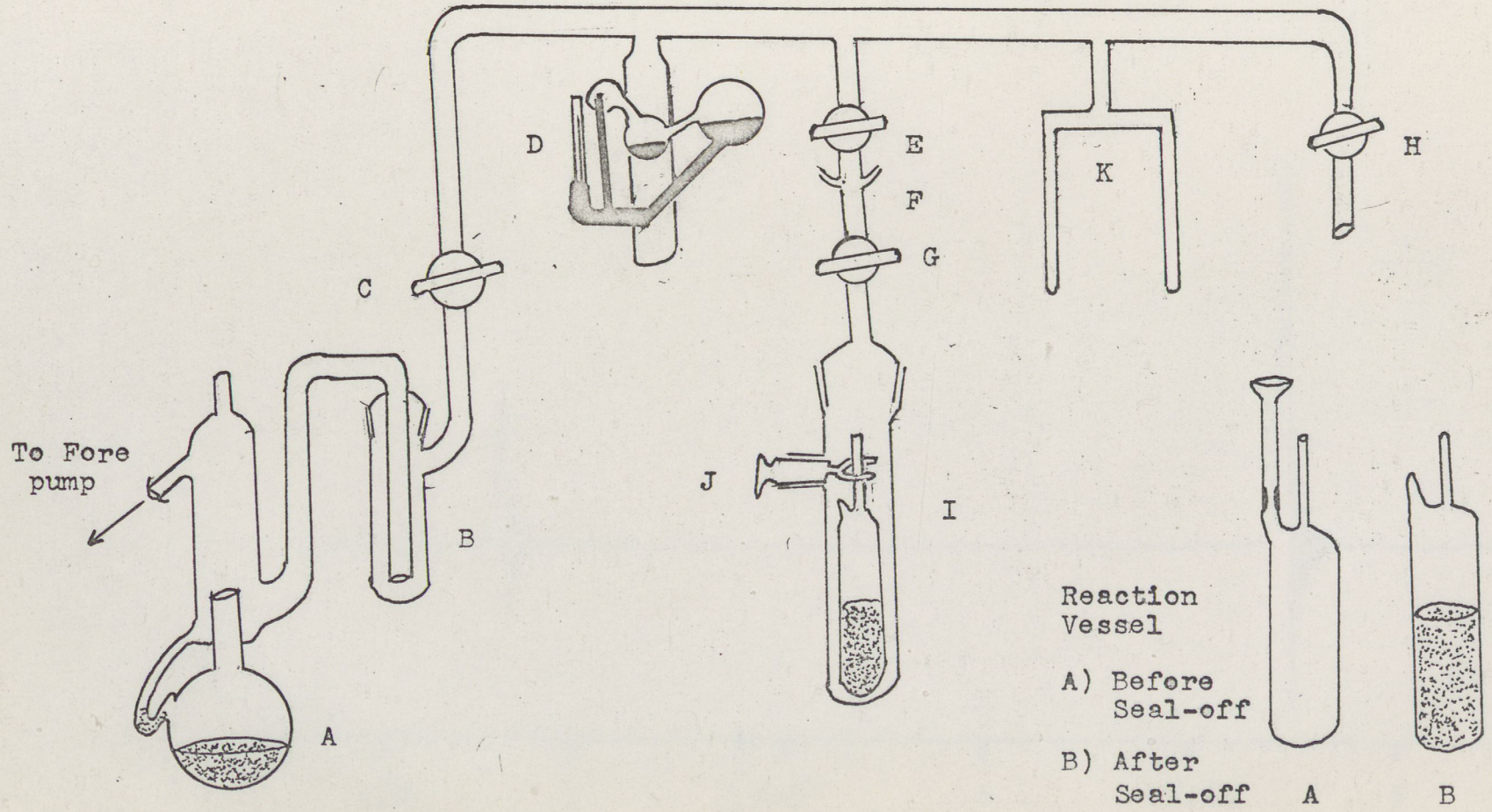


Figure 6

Volatile Products Collected from Vacuum System

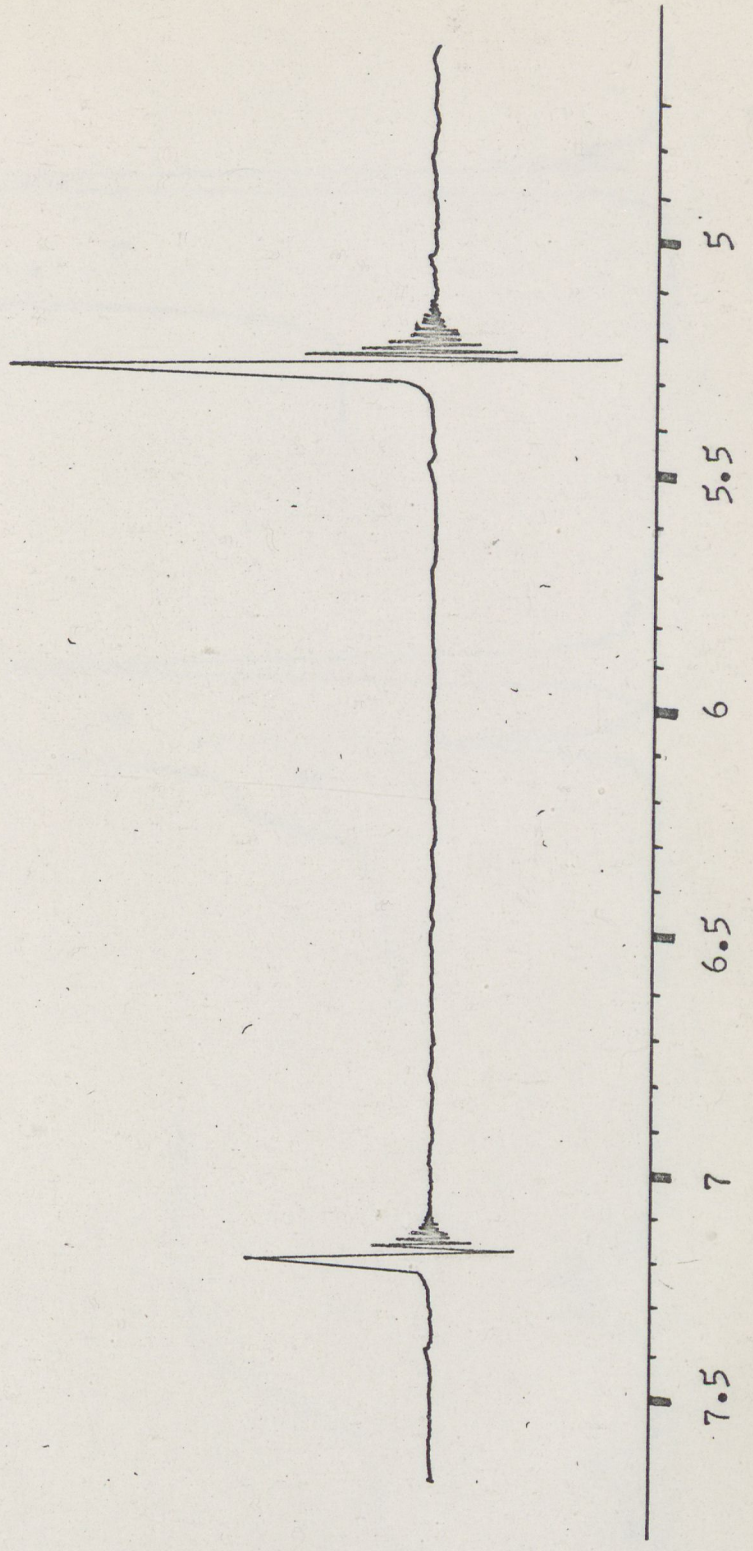


Figure 7

Methyl Iodide Salt of Ø-N-CH_2-$SiMe_3$
CH_3

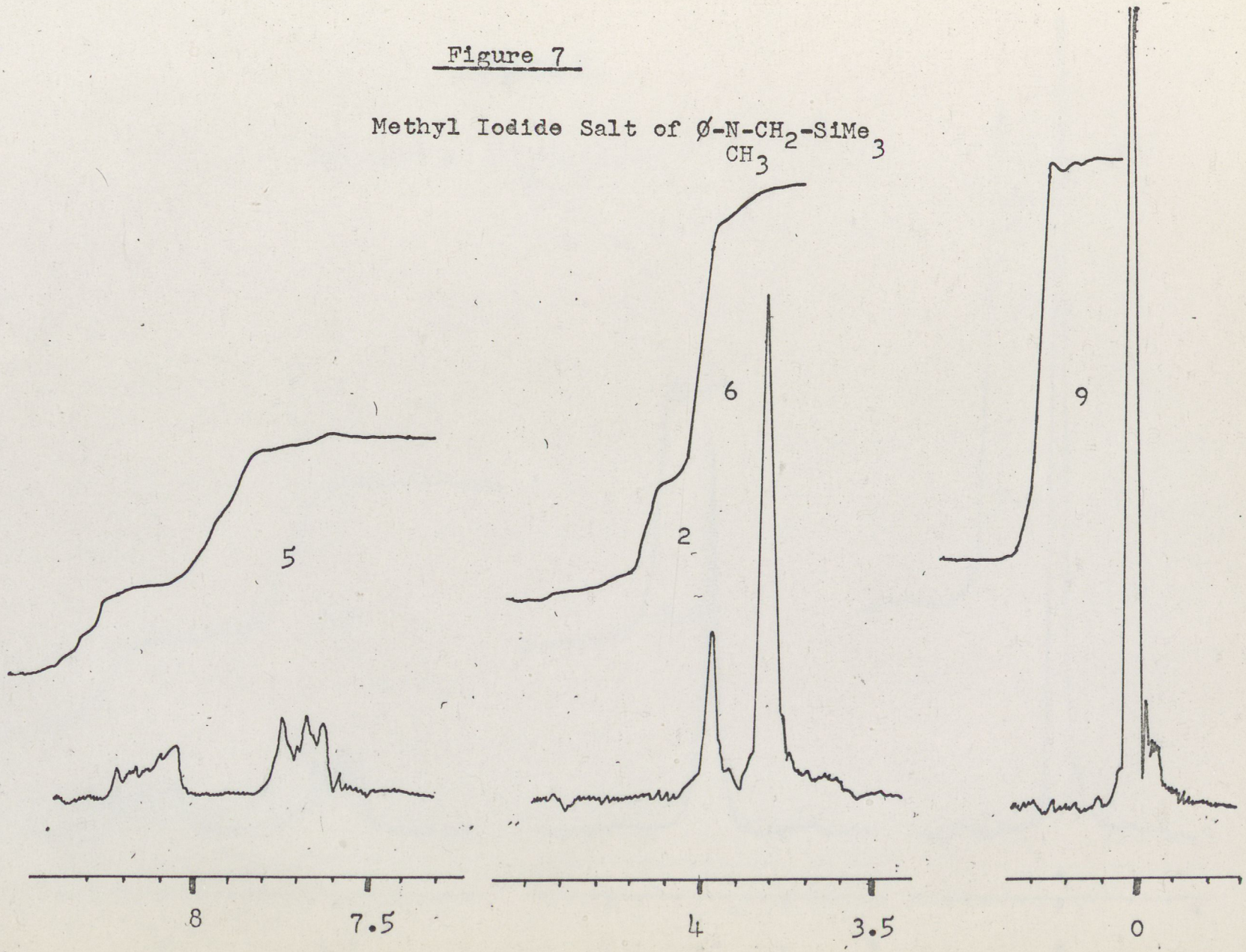


Figure 8

HCl Salt of Ø-N-CH_2-$SiMe_3$
CH_3

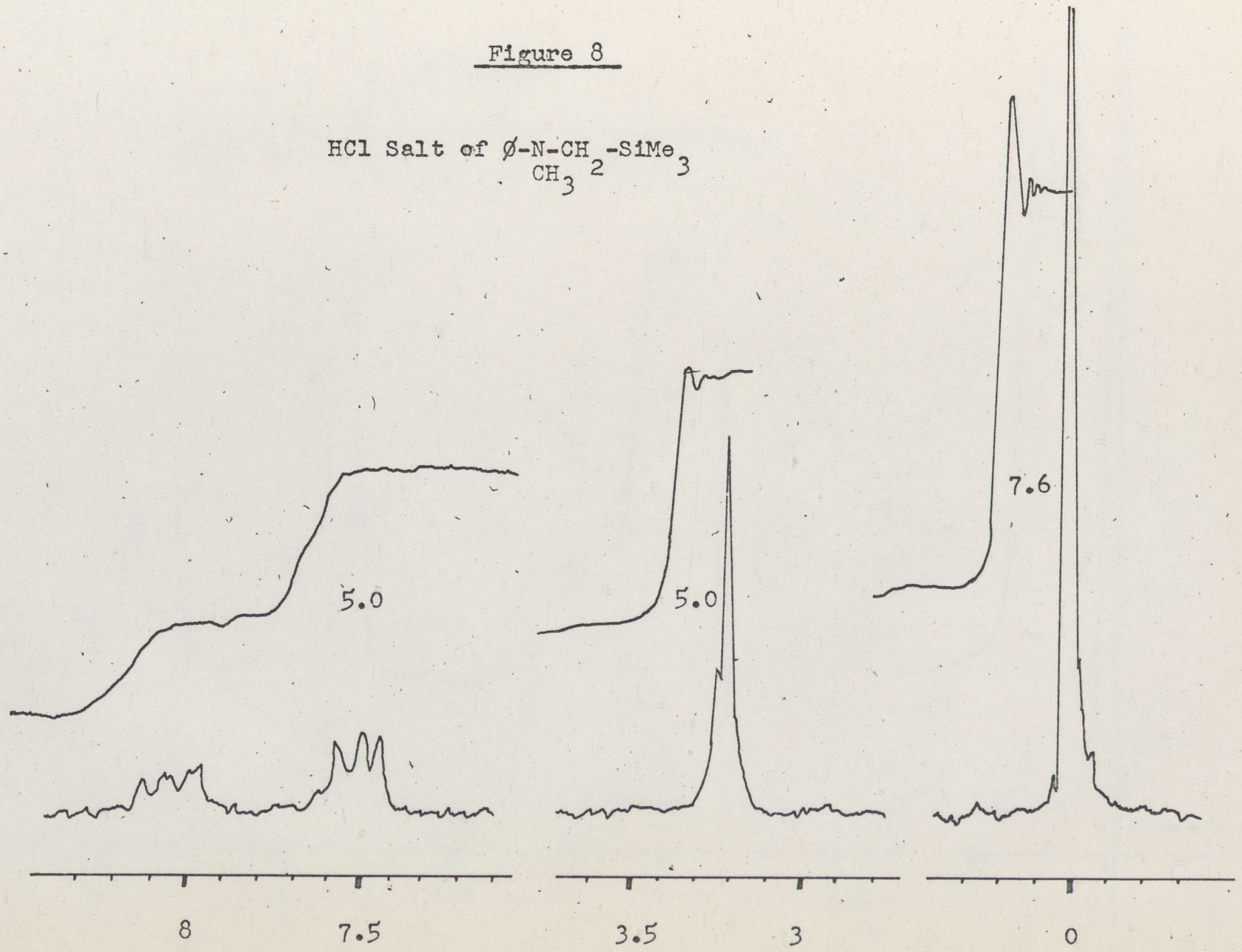


Figure 9

Product from Experiment III (ϕ-N-CH_2-$SiMe_3$)
After Acid Treatment
CH_3

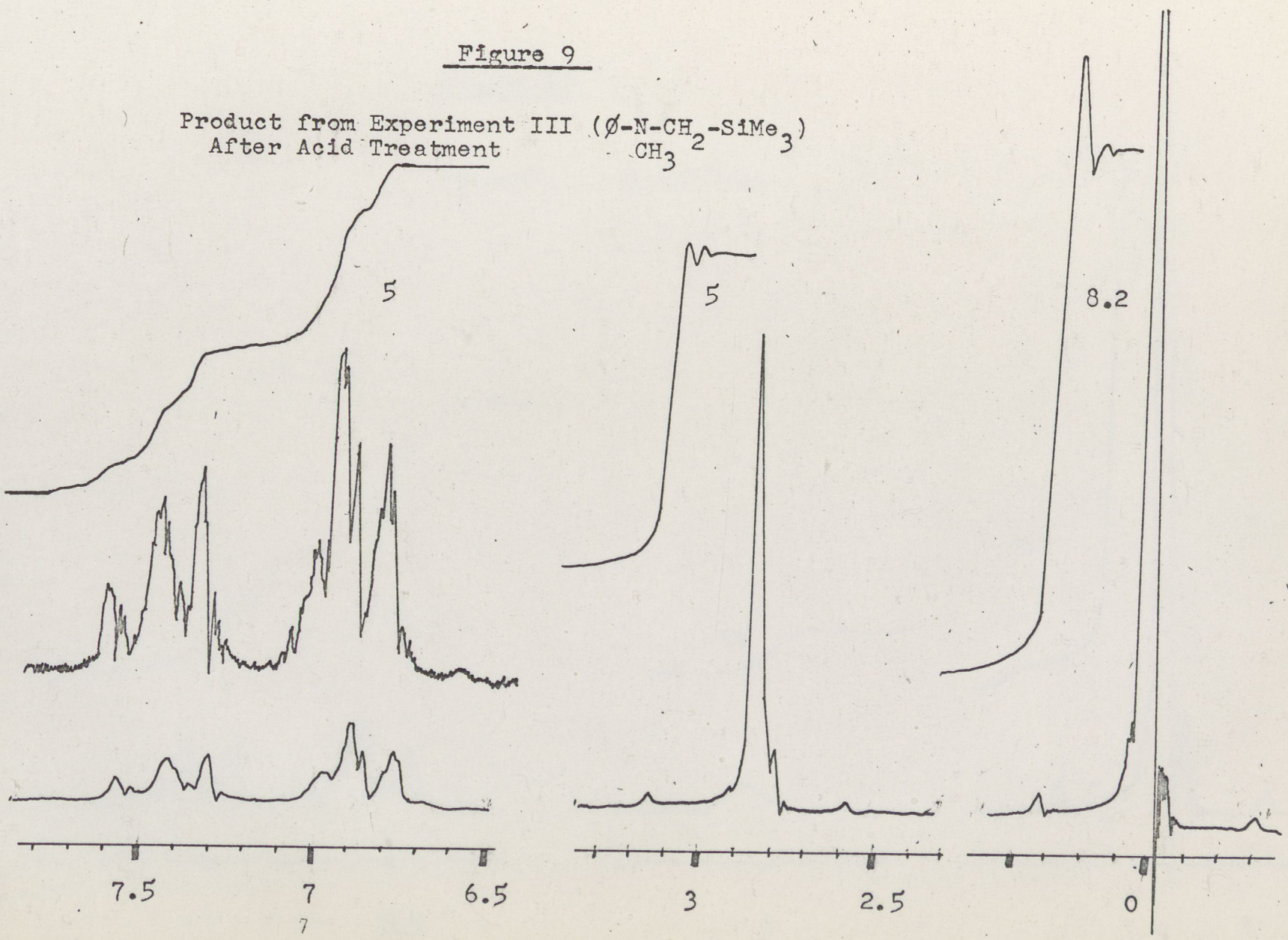


Figure 10

Ø-N-SiMe$_3$ bp 48°/1mm
H

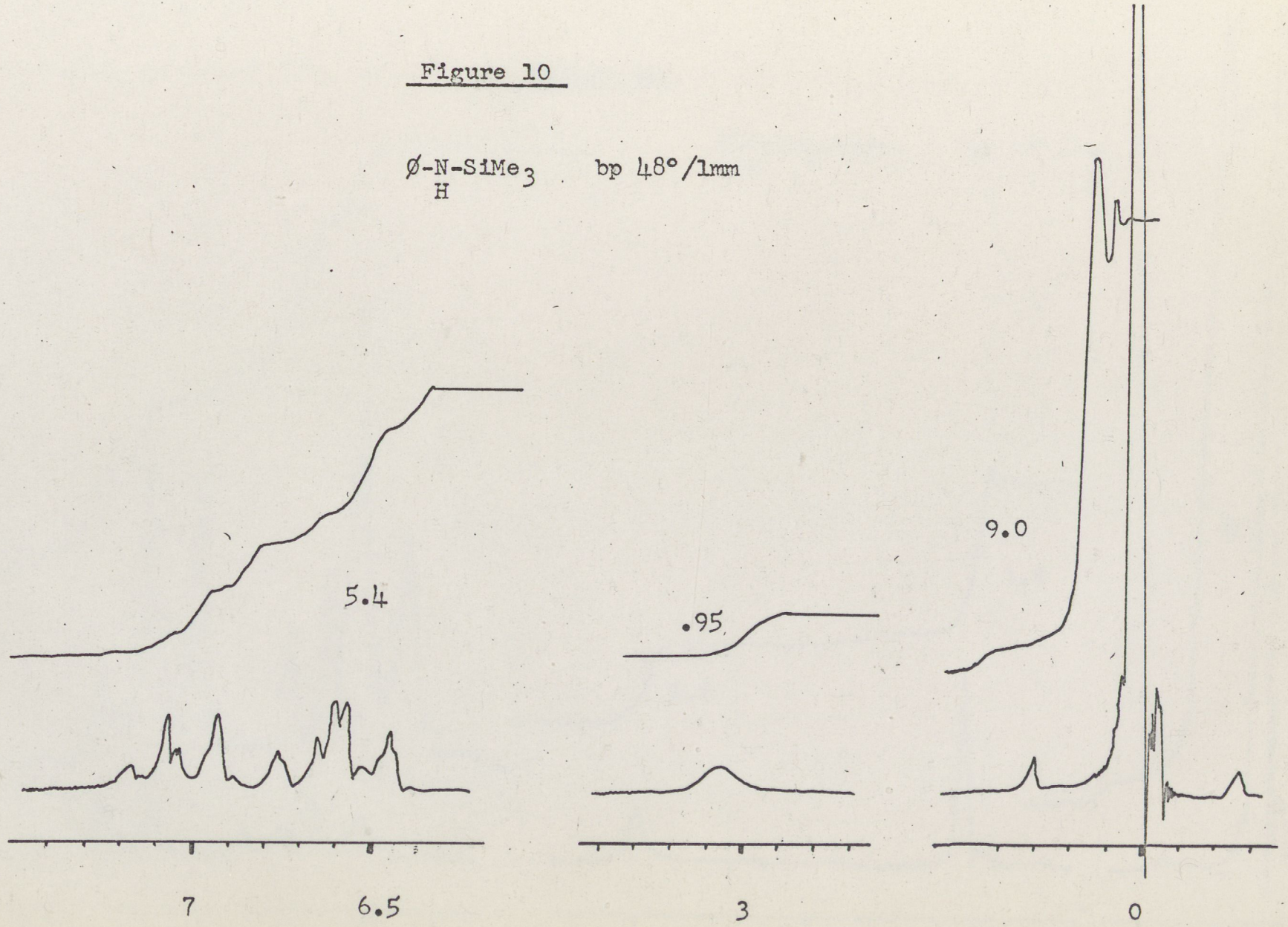
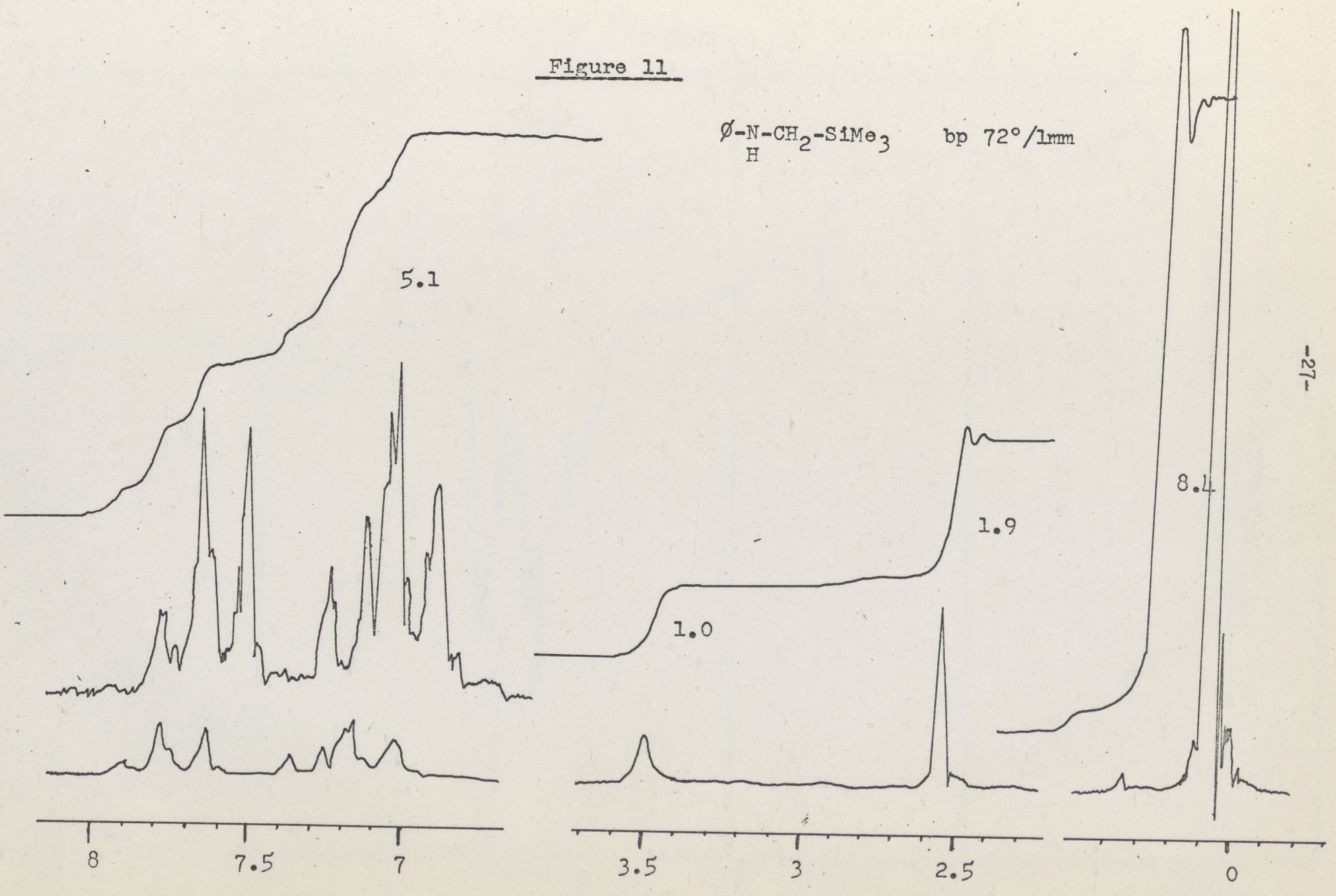
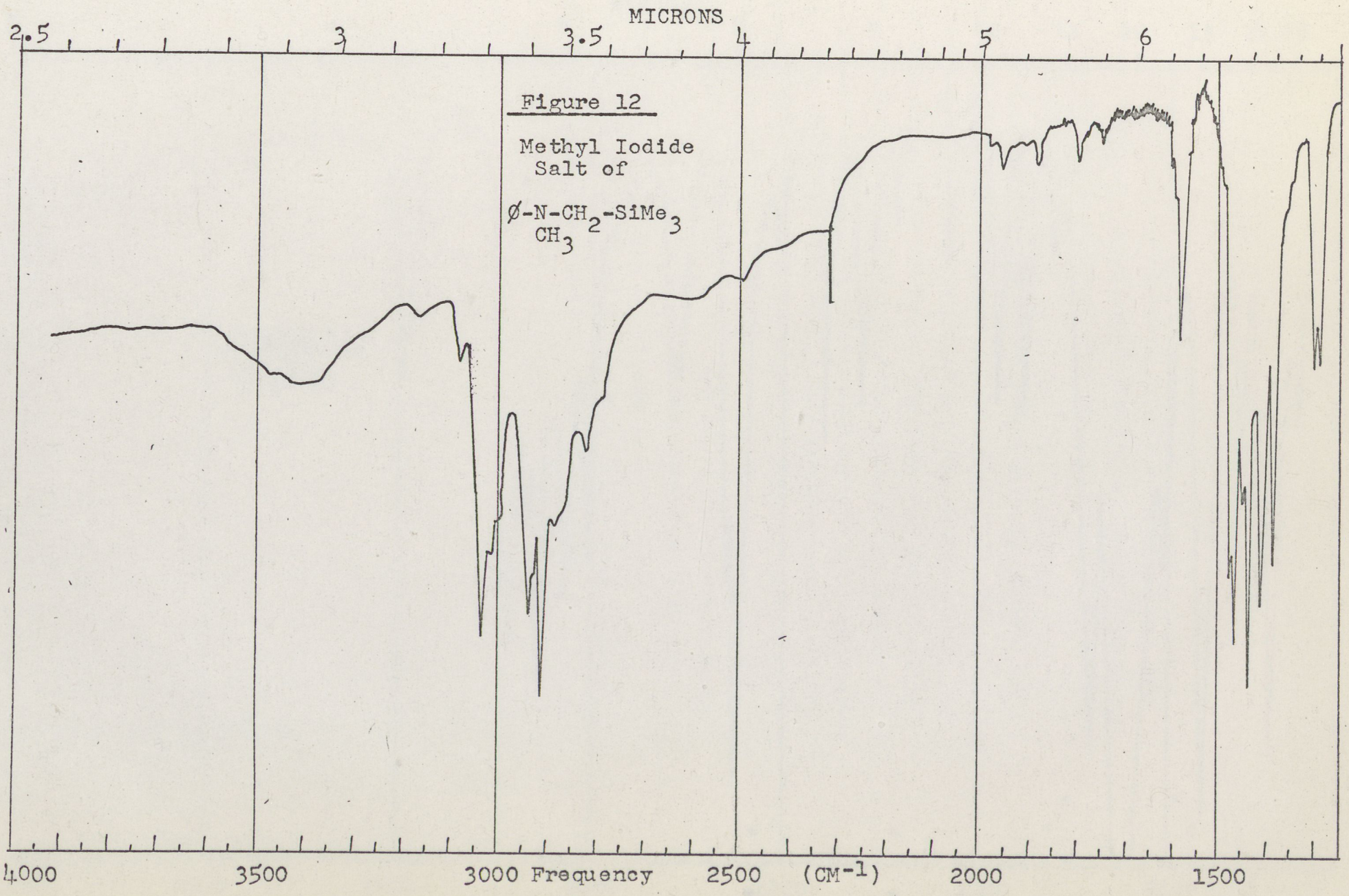


Figure 11




MICRONS
2.5
3
3.5
4
5
6
Figure 12
Methyl Iodide
Salt of
Ø-N-CH2-SiMe3
CH3
4000
3500
3000 Frequency
2500
(CM-1)
2000
1500

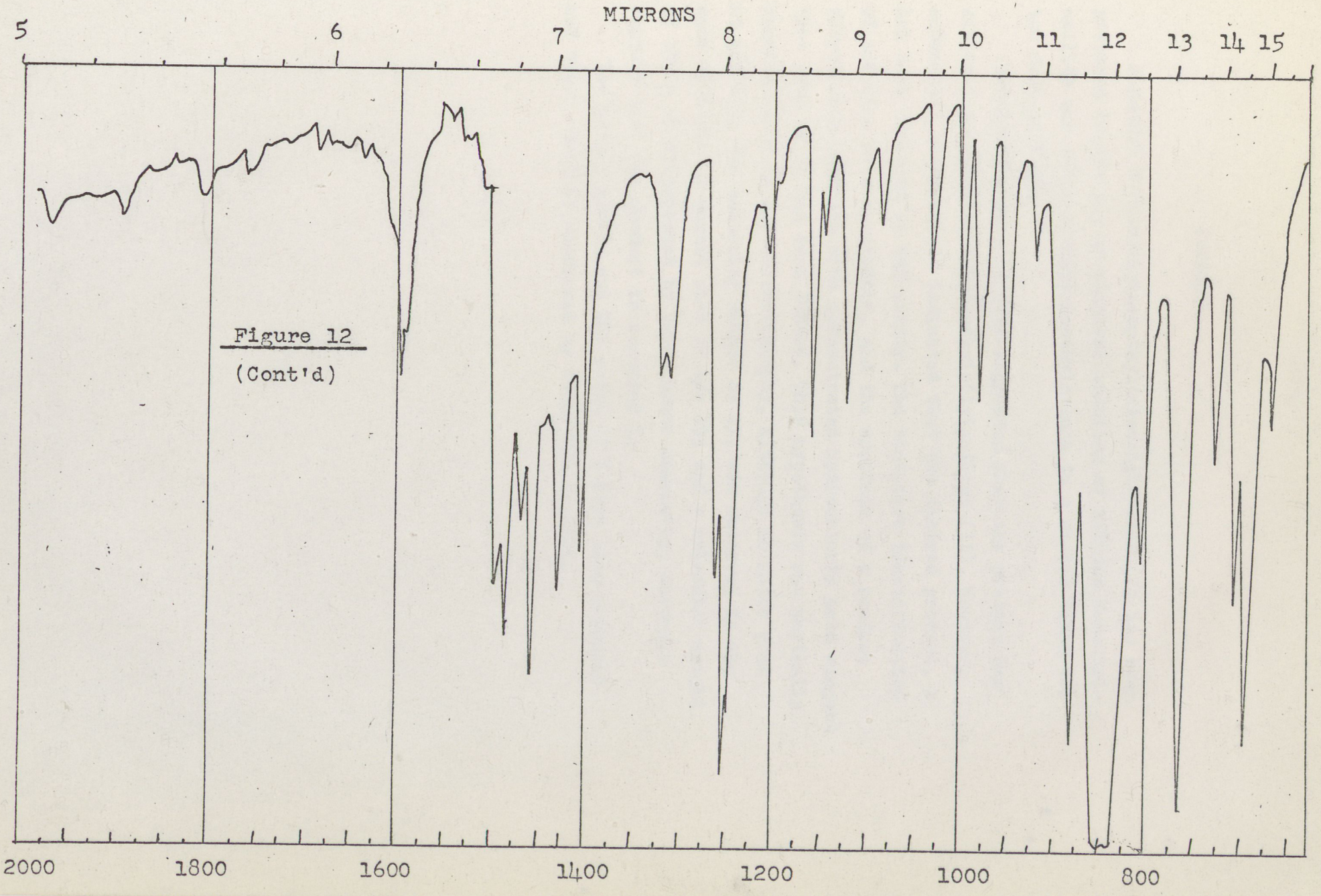


Figure 12
(Cont'd)

SUMMARY

N-Methyl-N-Phenylaminomethyltrimethylsilane (I) has been prepared by heating an ethereal solution of lithium N-methylanilide and chloromethyltrimethylsilane in a sealed flask for two days at 110°.

Conflicting sets of data suggested that the product was either I or N-Methyl-N-Trimethylsilylaniline (II). However, subsequent measurements indicated that the desired product, I, had been isolated in 94% purity. The tentative identification of ethylene as a by-product, and the spectrum of a product formed upon reaction with concentrated hydrochloric acid suggest that some of II had been formed. This hypothesis was partially substantiated by gas chromatography, although no major peak at m/e 179, the molecular weight of II, was observed in the mass spectrum. A parent peak at m/e 193 and a molecular weight of 197 ± 2% established by vapor phase osmometry, strongly suggest that the product is compound I.

The methyl iodide and HCl salts of I have been prepared and their identity confirmed by their NMR spectra.

BIBLIOGRAPHY

1. Messe, Mark; Union College (May 1970)
2. Eaborn, C.; Organosilicon Compounds, (Butterworths Scientific Publications, 1960)
3. Anderson, H.H.; J. Am. Chem. Soc. 73,5802 (1951)
4. Jones, R,G. and Gilman, H.; Organic Reactions 6 353 (1951)
5. George, P.D. and Elliott, J.R.; J. Am. Chem. Soc. 77,3495 (1955)