REACTIONS OF CHLOROSILANES WITH AMINES

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by

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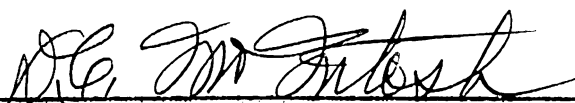
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INTRODUCTION

It has been shown that the alkylchlorosilanes can condense with cellulose by splitting out hydrogen chloride (10). It is also known that primary and secondary amines can react with chlorosilanes by splitting out hydrogen chloride forming compounds having nitrogen-silicon bonds (9).

On this basis, the present investigation was intended to cause reaction of a dichlorosilane with a dye and then with a hydroxyl group in cellulose or with an amino group in protein fibers to obtain a fast-dyed material.

Although diphenyldichlorosilane reacts with rosaniline, the reaction is complex and no way was found to make use of the products. It was, therefore, decided to study the reactions of simpler amines with chlorosilanes.

HISTORICAL

The study of organosilicon compounds started about the end of the nineteenth century. The earlier work along this line was carried out by Friedel, Crafts, and Ladenburg. From the beginning of the twentieth century until about 15 years ago, the investigations were largely carried out by Kipping in England. During the past 15 years, scientists and industrialists in this country have made great strides in the investigation of the properties and uses of these compounds.

The position of silicon with respect to carbon in the periodic table has led to an analogy between compounds of silicon and carbon. Although much has been learned about organosilicon compounds, there remains a vast amount of unexplored possibilities.

The reaction of trimethylchlorosilane with ammonia is known (8,9). Trimethyl-N-methylaminosilane (N-trimethylsilylmethylamine), N-methyl-hexamethyldisilazane (N,N-bis[trimethylsilyl]methylamine), trimethyl-N-ethylaminosilane (N-trimethylsilylethylamine), and trimethyl-N,N-diethyl-aminosilane (N-trimethylsilyldiethylamine) have been prepared by reacting trimethylchlorosilane with the respective amines (9). Either triethyl-silane or triethylbromosilane with ethylamine in the presence of lithium produced triethyl-N-ethylaminosilane (N-triethylsilylethylamine) (7), and in a search for a compound containing an asymmetric silicon atom, Kipping (6) prepared ethylphenyl-n-propyl-N-p-tolylaminosilane (N-ethylphenyl-n-propylsilyl-p-toluidine) from ethylphenyl-n-propylchlorosilane and p-toluidine. No other aminosilanes having an alkyl or aryl radical on the nitrogen atom are mentioned by Burkhard, Rochow, Booth, and Hartt (4) or have been found in the literature.

The history of triphenylmethane dyestuffs dates back to about the middle of the nineteenth century with the discovery of a red dye first named fuchsine. This dye was produced and used before its constitution or chemical mechanism of formation was investigated. A few years after its discovery, Hoffman showed the dye to be the salt of a base which he called rosaniline. Otto and Emil Fischer then demonstrated that rosaniline upon reduction followed by diazotization and boiling with alcohol produced triphenylmethane. This proved that the reduced rosaniline was a primary amine.

The mechanism of color formation of the triphenylmethane dyes is in most cases no longer in doubt. It is believed that the color is due to both the quinoid structure and the groups present.

From the colorless leuco base of rosaniline, there can be obtained, on mild oxidation, the colorless carbinol base. The base loses water to form the red imine base that will react with hydrochloric acid to give the red salt, rosaniline hydrochloride.

leuco base   carbinol base   imine base   rosaniline hydrochloride
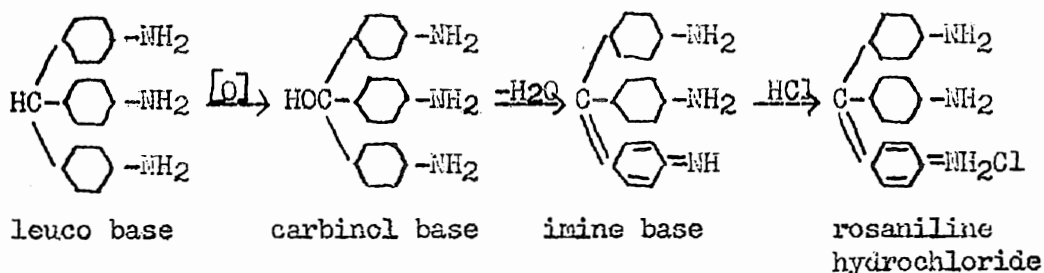
The leuco base of malachite green shows the same type of reactions.

If the carbinol base of rosaniline is alkylated or arylated the dye-character is not lost but is altered. As methyl or ethyl groups are added the color changes progressively from red to violet. Addition of a molecule of acid to rosaniline hydrochloride changes the color to violet. Upon further addition of acid, the color becomes blue.

Aqueous solutions of malachite green are blue. Acids change the color through green to orange-red.

As the absorption band of a substance is shifted toward the visible, it approaches the violet end of the spectrum (2). In successive stages, the absorption can be pushed across the spectrum and ultimately reaches the red end, or even beyond with a second band appearing from the violet side. The colors visible to the eye as this happens are: greenish-yellow, yellow, orange, red, purple, blue, green. These are not true spectral colors but a combination of all the colors not absorbed but transmitted to the eye.

EXPERIMENTAL

Materials used.

Diphenyldichlorosilane.

One hundred seventy grams (1 mole) of silicon tetrachloride was cooled to 0° in a flask provided with a stirrer, reflux condenser, and dropping funnel. A carefully prepared ethereal solution of phenylmagnesium bromide (2.5 moles) in 1300 ml. of dry ether was added over a period of one and one-half hours.

The contents of the flask were then left at room temperature for 12 hours. During this time, vigorous stirring was necessary to prevent the precipitated magnesium salt from forming a solid cake.

The mixture was then refluxed three hours to complete interaction. The ethereal solution was filtered as rapidly as possible. In order to prevent hydrolysis of the chlorosilanes by moisture in the air, the magnesium salt was not allowed to dry. The salt was twice washed with ether.

The filtrate and washings were then evaporated on a hot-water bath. Toward the end of this operation, a large quantity of crystals was precipitated. As the crystals were formed, they adhered to the walls of the flask. The remaining liquid was decanted into a smaller flask and evaporation continued.

When the removal of the ether was complete, more crystals had been formed. The brownish-yellow oil was poured into a Claisen flask and distilled at 42 mm. pressure.

After traces of ether and bromobenzene were removed, the temperature rose to 120° and remained constant while a pink liquid was distilled.

A light pink oil was distilled from 170-180°. This fraction consisted principally of diphenyldichlorosilane.

A third fraction was collected from 180-190°. Crystals, probably triphenylchlorosilane, were deposited in the condenser and receiving receptacle.

The distillation was stopped and the crystals were washed down with carbon tetrachloride.

The fraction consisting principally of diphenyldichlorosilane was redistilled at 44 mm. pressure. At 160-180°, 5 ml. of liquid was collected. About 90 ml. of rose-yellow oil was collected from 180-200°. Above 200°, about 15 ml. was collected. The 180-200° fraction was the diphenyldichlorosilane used.

Diphenyldichlorosilane was also purchased from Anderson Laboratories, Adrian, Michigan.

Trimethylchlorosilane.

One hundred seventy grams (1 mole) of silicon tetrachloride in 800 ml. of dry ether was cooled to 0° in a three-liter flask provided with a stirrer, reflux condenser, and dropping funnel. Three moles of methylmagnesium bromide in 1500 ml. of dry ether was added over a period of two and one-half hours. Vigorous stirring was necessary to prevent caking of the magnesium salt.

The mixture was stirred for 12 hours at room temperature. Stirring was stopped, the crystals allowed to cake, and the ethereal solution was siphoned from the solid. The cake was then broken up and washed with two 500-ml. portions of dry ether and separated by filtration.

The ether was distilled through an eight-ball snyder-type column. Crystals formed in the boiling flask during this distillation. When the either was removed, the liquid was transferred to another flask; and the same column was used to distill the methylchlorosilanes. A liquid distilled over at 38° that contained some ether but fumed in moist air. The temperature rose rapidly to $63-64^{o}$, and a few milliliters of liquid came over. The temperature rose slowly to 75° and a rose-colored liquid distilled. The fraction distilled at $63-64^{o}$ was trimethylchlorosilane.

Trimethylchlorosilane was also purchased from Anderson Laboratories.

Preparation of Solutions.

A saturated aqueous solution of rosaniline hydrochloride was prepared.

An ether solution of the color base of rosaniline was prepared by adding alkali to an aqueous solution of rosaniline hydrochloride, filtering and dissolving the precipitated base in ether. The solution was dried over anhydrous potassium carbonate after it was found that calcium sulfate (drierite) and calcium chloride adsorbed the color base.

A saturated solution of rosaniline hydrochloride in anhydrous acetone was prepared.

A carbon tetrachloride solution of the color base of malachite green was prepared by adding alkali to an aqueous solution of the dye. The precipitate was isolated by filtration and dissolved in anhydrous carbon tetrachloride.

A 7% solution by volume of diphenyldichlorosilane in anhydrous ether was prepared.

A 7% solution by volume of diphenyldichlorosilane in anhydrous acetone was prepared.

Reactions of Dyes.

Diphenyldichlorosilane with rosaniline base.

Excess diphenyldichlorosilane in ether was added to an ether solution of rosaniline base. A dark purple precipitate was formed. The precipitate and mother liquor were poured onto a watch glass and the ether was evaporated. After evaporation, a yellow residue remained which was partially soluble in water to give a red solution. The water-insoluble part of the residue was a tar, assumed to be polymerized diphenylsilanediol.

Diphenyldichlorosilane in ether was added, drop by drop, to the ether solution of rosaniline base. A color change from red through purple to blue was noticed.

Diphenyldichlorosilane in ether was added, drop by drop, to an ether solution of rosaniline base containing a few drops of pyridine. The color change was from red to purple to blue.
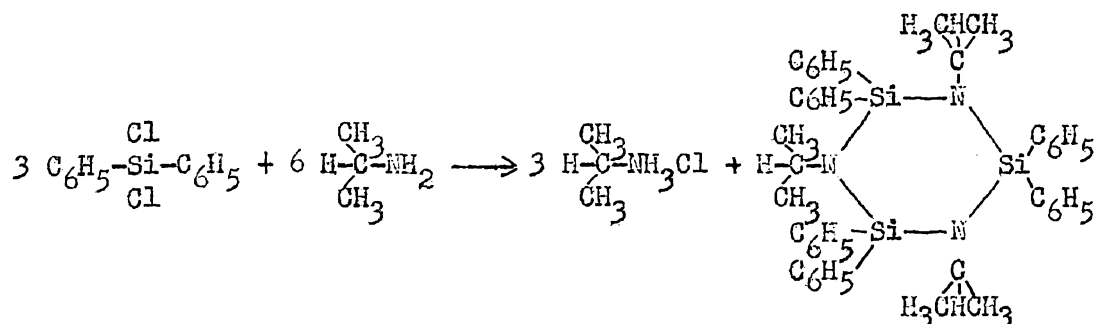
Diphenyldichlorosilane in acetone was added, drop by drop, to an acetone solution of rosaniline hydrochloride that contained enough benzylamine to decolorize it. The original red color of the dye was produced and a white precipitate was formed. Upon further addition of diphenyldichlorosilane the color of the solution was changed to blue. The ethereal solution was decanted, and the precipitate washed with acetone. When dried, this solid had a melting point of 249°. The melting point of benzylamine hydrochloride is 248°. The crystals were then dissolved in water and silver nitrate solution was added. A white precipitate of silver chloride was formed.

Diphenyldichlorosilane with malachite green base.

Diphenyldichlorosilane solution in ether was added to malachite green base in carbon tetrachloride. The color of the mixture changed from green through yellow to orange-red.

It was concluded that salt formation was taking place in the foregoing experiments, and that the color of this salt prevented any visual observation of condensation products. This conclusion was substantiated by the fact that some of the diphenyldichlorosilane had been hydrolyzed to diphenylsilanediol, the presence of which was proved by its polymerization to crystalline hexaphenylcyclotrisiloxane. This material was separated, washed, dried, and the melting point determined. The melting point was $187-189^{\circ}$. A mixture of these crystals with crystals of hexaphenylcyclotrisiloxane made by the method of Burkhard (3) had a melting point of $187-188^{\circ}$.

From a new bottle of diphenyldichlorosilane, purchased from Anderson Laboratories, new solutions were prepared, and the same tests performed. The results were the same.
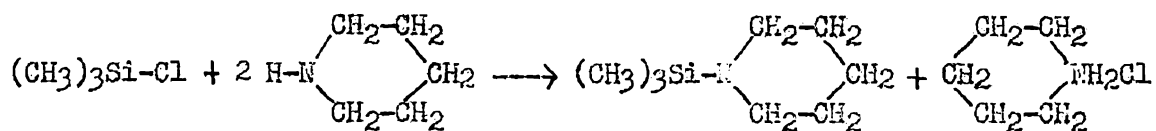
Reaction of trimethylchlorosilane with piperidine.

$$(CH_3)_3Si-Cl + 2\ H-N\overset{CH_2-CH_2}{\underset{CH_2-CH_2}{\diagdown}}CH_2 \longrightarrow (CH_3)_3Si-N\overset{CH_2-CH_2}{\underset{CH_2-CH_2}{\diagdown}}CH_2 + CH_2\overset{CH_2-CH_2}{\underset{CH_2-CH_2}{\diagdown}}NH_2Cl$$

The first two attempts to prepare N-trimethylsilylpiperidine failed owing to moisture in the piperidine. It was found best to dry the piperidine over sodium hydroxide, reflux with sodium metal until all reaction ceased, and distill. The piperidine was then stored over sodium until used.

Ten and eighty-five hundredths grams (0.1 mole) of trimethylchlorosilane in 50 ml. of dry ether was added over a period of thirty minutes to an ice-cold solution of 17.85 g. (0.21 mole) of piperidine in 100 ml. of dry ether. A water bath was used to reflux the mixture for 30 minutes. The white solid was washed with 150 ml. of dry ether and separated by filtration. The cake was then washed with 50 ml. of dry ether.

The ether was removed from the ethereal solution under reduced pressure using an aspirator. The remaining liquid was distilled at atmospheric pressure in a Vigreux flask. After traces of ether, hexamethyldisiloxane, and piperidine were removed, a fraction was taken from 110-150°. There was no leveling off of the temperature in this range. The melting point of this fraction was determined with an alcohol thermometer in a bath of dry ice and methyl alcohol. The melting point was -41 to -44°.

On sodium fusion of a portion of this fraction, a test was obtained for cyanide ion but not for chlorine. On ignition of a portion of this fraction, a white solid remained which was insoluble in dilute hydrochloric acid, indicating the presence of silicon.

After standing for 24 hours, this fraction was redistilled. Most of the material distilled at 106° (boiling point of piperidine) and only about 0.5 ml. distilled slowly at $139-140^\circ$. The supply of piperidine was exhausted before other properties could be determined.

Reaction of trimethylchlorosilane with morpholine.

$$(CH_3)_3Si-Cl + 2 HN\begin{smallmatrix}CH_2-CH_2\\ \\CH_2-CH_2\end{smallmatrix}O \longrightarrow (CH_3)_3Si-N\begin{smallmatrix}CH_2-CH_2\\ \\CH_2-CH_2\end{smallmatrix}O + O\begin{smallmatrix}CH_2-CH_2\\ \\CH_2-CH_2\end{smallmatrix}NH_2Cl$$
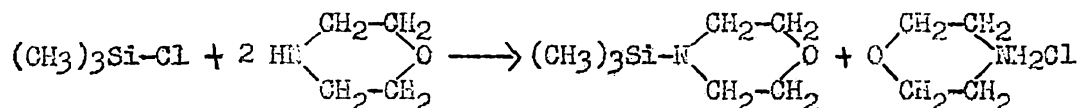
To 36.54 g. (0.42 mole) of ice-cold morpholine (dried by the same method used to dry piperidine) in 200 ml. of dry ether was added 21.7 g. (0.2 mole) of trimethylchlorosilane in 100 ml. of dry ether. The trimethyl-chlorosilane solution was added over a period of one hour. The mixture was shaken intermittently during this time. The mixture was allowed to come to room temperature and stand for 24 hours. The white solid was leached with 100 ml. of dry ether, separated by filtration, and washed with two 50-ml. portions of dry ether.

The ether was removed under reduced pressure with an aspirator and the residual liquid was distilled in a Vigreux flask at atmospheric pressure. After traces of ether, hexamethyldisiloxane, and morpholine were removed, N-trimethylsilylmorpholine distilled at 164.5° (736 mm.). d_{20}^{20} 0.9064, n_D^{20} 1.4327. Molar refraction: Calcd. (11) for N-trimethylsilylmor-pholine, 46.83. Found: 45.57. Neutral equivalent: Calcd., 159. Found: 152.6, 153.9.
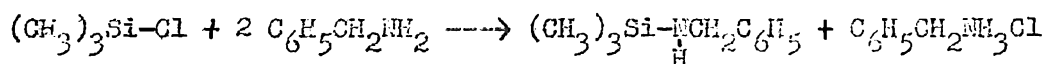
Reaction of trimethylchlorosilane with di-n-butylamine.

$$(CH_3)_3Si-Cl + HN(C_4H_9)_2 \longrightarrow (CH_3)_3Si-N(C_4H_9)_2 + (C_4H_9)_2NH_2Cl$$
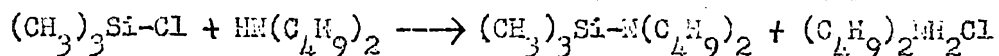
To 27.09 g. (0.21 mole) of dry ice-cold di-n-butylamine in 100 ml. of dry ether was added 10.85 g. (0.1 mole) of trimethylchlorosilane in 50 ml. of dry ether. The trimethylchlorosilane was added over a period of one hour. The mixture was allowed to come to room temperature and was refluxed for 14 hours. The mixture was filtered, and the white solid washed with two 50-ml. portions of dry ether.

The ether was removed under reduced pressure, and the remaining liquid distilled from a Vigreux flask at atmospheric pressure. After traces of ether, hexamethyldisiloxane, and di-n-butylamine were removed, N-trimethyl-silyl-di-n-butylamine was distilled at 200-201°. d_{20}^{20} 0.7964. n_D^{20} 1.4277. Neutral equivalent: Calcd. for $C_{11}H_{27}NSi$, 191. Found: 190.9, 188.5.

Reaction of trimethylchlorosilane with benzylamine.

$$(CH_3)_3Si-Cl + 2 C_6H_5CH_2NH_2 \longrightarrow (CH_3)_3Si-\underset{H}{N}CH_2C_6H_5 + C_6H_5CH_2NH_3Cl$$

To an ice-cold solution of 22.5 g. (0.21 mole) of benzylamine in 100 ml. of dry ether was added 10.8 g. (0.1 mole) of trimethylchlorosilane in 50 ml. of dry ether. The addition was made during one hour. The mixture was then refluxed for 12 hours. The white precipitate was filtered from the ethereal solution, and the precipitate washed with two 50-ml. portions of dry ether. The ether was then evaporated under reduced pressure, and the remaining liquid distilled from a Vigreux flask.

After traces of ether and hexamethyldisiloxane were removed and the temperature had been raised to about 180°, violent foaming occurred. The foam seemed to condense at the top of the column, leaving a column of liquid which was thrown over into the distillate receiver. Reduced pressures did not cause the foaming to subside. When the temperature was raised above the boiling point of benzylamine (184°), foaming ceased, and distillation proceeded normally at atmospheric pressure.

N-trimethylsilylbenzylamine distilled at 211.5°. d_{20}^{20} 0.9055. n_D^{20} 1.4830.

Neutral equivalent: Calcd. for $C_{10}H_{17}NSi$, 179. Found: 176.4, 177.1

Reaction of trimethylchlorosilane with benzylaniline.

$$(CH_3)_3Si-Cl + 2\ HN\begin{smallmatrix}C_6H_5\\CH_2C_6H_5\end{smallmatrix} \longrightarrow (CH_3)_3Si-N\begin{smallmatrix}C_6H_5\\CH_2C_6H_5\end{smallmatrix} + ClH_2N\begin{smallmatrix}C_6H_5\\CH_2C_6H_5\end{smallmatrix}$$
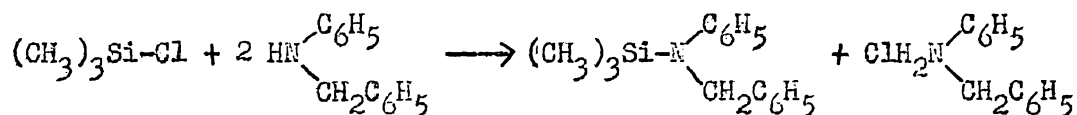
Forty-four grams (0.21 mole) of benzylaniline dissolved in 50 ml. of dry ether was cooled to 0°. Ten and eighty-five hundredths grams (0.1 mole) of trimethylchlorosilane dissolved in 50 ml. of dry ether was added over a period of thirty minutes. The mixture was refluxed in a water bath for thirty minutes. Violent bumping occurred, so almost constant shaking was necessary.

The white crystals were removed by filtration, but after filtration more crystals appeared in the filtrate. This process was repeated three times, and crystals still were present in the filtrate. The filtrate was stoppered and set aside for two weeks. At the end of this time, the ethereal solution had become red in color. The solution was filtered and the filtrate was put under reduced pressure, to evaporate the remaining ether. After the removal of the ether, a red viscous oil was left. This oil was soluble in all organic solvents but could not be crystallized.

A small portion of this oil was cooled in a dry ice-methanol bath, no crystals separated; the oil became a glass. On warming to room temperature, crystals were formed. These crystals were used to seed the remaining oil. Upon standing, large needle like crystals formed, and the mass completely solidified.

Attempts to recrystallize the solid failed. No sharp melting point could be obtained on these red crystals. The melting point was 35-39°. The melting point of benzylaniline is 37°.

Reaction of trimethylchlorosilane with potassium phthalimide.
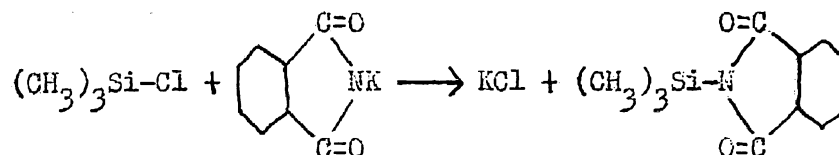
To 13.8 g. (0.075 mole) of potassium phthalimide in a flask with 100 ml. of dry ether, 8.2 g. (0.075 mole) of trimethylchlorosilane was added. Bubbles could be seen rising from the solid. The mixture was refluxed 12 hours; then the ether was distilled.

The solid was then washed with water and separated by filtration. Droplets of oil could be seen in the filtrate. It was found that the cold-water-insoluble portion of this solid was soluble in hot water. This solid was recrystallized from hot water and the melting point determined. The melting point was 234-235°. A mixture of these crystals with phthalimide melted at 234-235°, proving the crystals to be phthalimide.

Neutral Equivalents.

To obtain neutral equivalents, the weighed samples of the dialkylamine were poured into excess 0.1 N sulfuric acid. The excess acid was then back-titrated with 0.1 sodium hydroxide to the methyl orange end point.

DISCUSSION OF RESULTS

In the preparation of diphenyldichlorosilane, it must be stressed that the magnesium salt that precipitates will form a hard, solid cake that cannot be easily broken up. This magnesium salt also forms on evaporation of the ether and causes severe bumping.

In the preparation of trimethylchlorosilane, the same points should be stressed. The magnesium salt will from a cake on precipitation and will crystallize on the walls of the flask when the ether is evaporated.

The color changes observed in the reactions of the dyes with diphenyldichlorosilane indicated salt formation. Addition of acid to rosaniline base colors the solution red; more acid causes the solution to be violet, and finally blue. The violet color observed is probably not a true spectral color but a combination of the red and blue.

The desired reaction of condensing the amino group of the dye with the diphenyldichlorosilane, by splitting out hydrogen chloride, may have been taking place. It is true that when diphenyldichlorosilane was added to a malachite green solution, the same color changes were observed as when hydrogen chloride was added, and in this case no hydrogen chloride could be produced in the reaction. However, hydrogen chloride could be formed in the diphenyldichlorosilane by hydrolysis from moisture of the air, or it could be formed in the rosaniline reaction mixture by condensation of the amine group with the diphenyldichlorosilane. Another evidence of hydrolysis of the diphenyldichlorosilane was found when crystals of hexaphenylcyclotrisiloxane were identified in the anhydrous acetone solution of diphenyldichlorosilane. This cyclic polymer is a condensation product of diphenylsilanediol which in turn is the hydrolysis product of diphenyldichlorosilane.

The interpretations of the results of these reactions were difficult so it was decided to study the reactions of simpler amines with the chlorosilanes.

The reaction of diphenyldichlorosilane with isopropylamine was attempted to make the nitrogen analog of hexaphenylcyclotrisiloxane. No identifiable products were isolated from this reaction.

When a primary amine is caused to react with trimethylchlorosilane two silylamines may be formed. When a secondary amine is used only one silylamine is possible; therefore, little difficulty should be met in the separation of this compound.

The first simple amine worked with was piperidine. It was found that a very small amount of moisture in the amine or the solvent would cause undesirable reactions with the chlorosilane. The amine must be inert toward sodium metal before it is used, and the solvent dried over calcium chloride or drierite.

Partial success was indicated in the above reaction, since the product boiling at 139-140° contained nitrogen and silicon. There was not enough of this compound to determine the neutral equivalent, and no more piperidine was available.

Dry morpholine reacted as expected, yielding N-trimethylsilylmorpholine, which was characterized. Dry di-n-butylamine reacted to form N-trimethylsilyl-di-n-butylamine, which was characterized. Other secondary alkylamines would be expected to react in the same manner.

Benzylamine, the only primary amine used, gave N-trimethylsilylbenzylamine; however, the yield of the silylamine was smaller than that produced by the secondary amines.

Benzylaniline was the only aromatic amine used. No N-trimethylsilyl-benzylaniline was obtained. Crystals recovered from this reaction could not be recrystallized. They melted at 35-40°.

It was found that the N-trimethylsilyl alkyl secondary amines had a boiling point of approximately 35 to 40° higher than the respective amines. In the case of the primary amine, the boiling-point rise due to the tri-methylsilyl group is about 27°.

The reaction of trimethylchlorosilane with potassium phthalimide was tried once, with the isolation of only phthalimide. The failure to obtain N-trimethylsilylphthalimide may have been due either to the rapid hydroly-sis of N-trimethylsilylphthalimide to phthalimide and trimethylsilanol or to hydrogen chloride impurity in the trimethylchlorosilane.

Further investigations should include: Reaction of trimethylchloro-silane with lower N-alkylanilines; reaction of trimethylchlorosilane with the metallic salts of aromatic secondary amines; reaction of trimethyl-chlorosilane with other primary amines, both alkyl and aryl.

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BIOGRAPHY

Benjamin F. Davis, Jr. was born in Elkhart, Kansas, October 23, 1921. He received his grade school training in Guymon, Oklahoma and in June 1940, he was graduated from Guymon High School. In September of the same year, he enrolled at the Panhandle A. & M. College at Goodwell, Oklahoma. In September of 1942, he registered at Oklahoma A. & M. College where he received the Bacherlor of Science degree in June of 1944.

In August 1944, he entered the U. S. Navy and in June 1946 was discharged as an electronics technician, second class.

In September of 1946, he entered Oklahoma A. & M., where he has been employed as a graduate fellow in the Chemistry Department until the present time.

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