

THE PREPARATION OF ACYLOXYSILANES,
THEIR REACTION WITH GRIGNARD REAGENTS,
AND THE PREPARATION OF SOME Si-N BONDED COMPOUNDS

by

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INTRODUCTION AND REVIEW OF LITERATURE

The organic compounds of silicon which have been the subject of much scholarly research during the past 90 years, are a promising field, emerging from the laboratory and finding a place in industry. The silicon esters and the Si-N bonded compounds are not new in silicon chemistry, but they have not been studied extensively. Looking at the history of silicon esters, they were first prepared by Fiedel and Ladenberg (3) in 1867. They prepared silicon tetraacetate from silicon tetrachloride and acetic anhydride. Silicon tetraacetate was prepared by Volnov (19) in 1939 in a different way. He used silicon tetrachloride and organic acetates. Silicon tetraacetate was again prepared in 1947 by Schuyten et al. (16) from silicon tetrachloride and sodium acetate using anhydrous benzene as a diluent. Petrov and Itkina (12) prepared silicon tetrabutyrate from silicon tetrachloride and butyric acid in the same year. Lanning (9, 10) prepared silicon tetrapropionate and silicon tetrabenzoate in 1953 and 1954 respectively, from the sodium salts of the organic acids and silicon tetrachloride. Lanning and Moore (11) prepared a series of silicon esters such as silicon tetratrichloroacetate and silicon tetracrotonate, etc. Anderson and Hager (1) in 1959 prepared a series of organosiliconfluoro esters and studied their properties.

Lanning (10) and Lanning and Moore (11) prepared several silicon esters and treated those esters with ethylmagnesium bromide, which gave as products alcohols, ketones, and silicones.

The present investigation was initiated to prepare some biologically active compounds by first preparing the silicon esters and then reacting with Grignard reagents to get a ketone or alcohol which could be biologically active. α -Naphthaleneacetic acid, which is a root growth hormone, and 2,4-dichlorophenoxyacetic acid, which is a weed killer, were used to prepare the silicon esters. These two compounds gave the respective silicon esters which were then treated with ethylmagnesium bromide. The silicon esters were prepared at very low temperature.

The next immediate investigation was to prepare some Si-N bonded compounds. This phase of study had more or less been neglected since the time the first bonds of this type were established around 1873 (18). Perhaps this may be due to the fact such compounds have had no industrial application. This feeling was manifested in 1936 during The Bakerian Lecture by Kipping (8). He stated, in part:

Very few substances containing silicon and nitrogen atoms directly united have been prepared since it was shown by J. E. Reynolds that silicon tetraphenylamide, $\text{Si}(\text{NHPh})_4$, is completely decomposed not only by water but also by alcohol. Even when a molecule contains only one silicon-nitrogen link, it is still very unstable towards water, and although certain compounds of this type have been prepared from the chlorides, SiR_2Cl , they are of little interest.

The evidence of J. E. Reynolds to which Kipping referred was published in 1889 (13). J. E. Reynolds reported the formation of tetraanilino silane by the reaction of aniline in benzene with silicon tetrachloride. This same reaction had been investigated by Harden (6) in 1887. He reported the production of one equivalent of dianilindichlorosilane and two of aniline

hydrochloride. In 1950, J. C. Winters (24) prepared successfully tetraanilino silane. In 1959, Ulrich Wannagat and Walter Liehr (20, 21) prepared a series of Si-N bonded compounds with hydrazine. They prepared mono(triethylsilyl) and bis(triethylsilyl)hydrazines from triethylchlorosilane and hydrazine. They also prepared mixed alkyl or aryl substituted hydrazine silicon compounds. Ulrich Wannagat and H. Niederprum (22) prepared the compound, $\text{Ph}_2\text{Si}(\text{NHNMe}_2)_2$ by the reaction of dichlorodiphenylsilane and dimethyl hydrazine. In the same year, Sergeeva et al. (17), prepared more alkyl substituted hydrazine silicon compounds. Later, Sarju Prasad and K. N. Chatterjee (15) prepared a series of silicon-nitrogen bonded compounds by the reaction of silicon tetrachloride with amines and heterocyclic bases.

This investigation was initiated to prepare more silicon-nitrogen bonded compounds by using other nitrogen containing organic compounds. During the preliminary search of compounds suitable for the preparation of Si-N bonded compounds, several amines and azo compounds were tried. Of these, p-aminoazobenzene and N,N-dimethylaminoazobenzene were selected, as these compounds react with silicon tetrachloride very readily. It was found that these reactions go to completion at low temperatures.

EXPERIMENTAL

Preparation of Silicon Esters

The method and apparatus used in preparing the silicon esters from silicon tetrachloride and sodium salts of organic

acids were similar to that of Schuyten et al. (16) and to Lanning (9, 10). The silicon tetrachloride was purified by distillation. The sodium salts of organic acids were prepared by the reaction of the calculated amount of sodium bicarbonate with the pure acid and then dried by heating them to their melting points. Anhydrous benzene and anhydrous diethyl ether were used as solvents. It was found that the reactions in anhydrous diethyl ether were better than in anhydrous benzene, as the removal of the products was more satisfactory with the diethyl ether.

The preparations of tetra(2,4-dichlorophenoxyacetoxy)silane and tetranaphthaleneacetoxy silane were carried out by adding 3 ml. (5.19 g.) of silicon tetrachloride dissolved in 50 ml. of ether dropwise into a slurry of 1.5 times the calculated amount of anhydrous sodium salts dispersed in 150 ml. of ether. A salt-ice bath was used, thereby lowering the temperature to -12° C. The silicon tetrachloride was added in small amounts every one-half hour for one and one-half hours. The mixture was stirred mechanically during the addition of silicon tetrachloride and for about two and one-half hours afterwards. The stirring was stopped when the ether solution gave no chlorine test with silver nitrate. The sodium chloride and excess sodium salt were removed by filtration using suction. The residue was washed with 50-100 ml. of anhydrous ether. Immediately after filtering, the filtrate was stored in a cold room at 4° C.

The filtrate was concentrated under reduced pressure and when all the ether was removed, a white crystalline material was

obtained. This material was dried at 80° C. in an oven.

Reaction of Silicon Esters With Grignard Reagents

The reaction of silicon esters with Grignard reagents was carried out with tetra(2,4-dichlorophenoxyacetoxy)silane and tetra(α -naphthaleneacetoxy)silane. These reactions of silicon esters with the Grignard reagents gave ketones and silicones.

The first set of reactions was carried out by adding dropwise a dilute diethyl ether solution of the silicon ester through a dropping funnel into the stoichiometric amount of Grignard reagents prepared from ethyl bromide in the usual manner. After the addition was completed, the mixture was stirred mechanically and maintained at the boiling point for one hour. The Grignard complex was hydrolyzed in an ammonium chloride solution containing some ice. Some dilute sulfuric acid was added afterwards to dissolve the magnesium precipitate. The ether layer was separated and dried with calcium sulfate. After the evaporation of ether, an oily liquid and some white crystals were obtained.

Reaction of Tetra(2,4-dichlorophenoxyacetoxy)silane With Ethylmagnesium Bromide

The apparatus and the method for the preparation of 2,4-dichlorophenoxyethyl ethyl ketone were very similar to those used by Lanning (9, 10) to prepare 3-ethyl-3-pentanol and triphenyl carbinol. A dilute ether solution containing 4 g. of tetra(2,4-dichlorophenoxyacetoxy)silane was added through a

dropping funnel, drop by drop into the stoichiometric amount of Grignard reagent prepared from ethyl bromide in the usual manner. The mixture was stirred mechanically. When all the silane was added, the mixture was boiled gently for one hour. The Grignard complex was hydrolyzed in ammonium chloride solution containing some ice. Some dilute sulfuric acid was added afterwards to react with the magnesium hydroxide precipitate.

The ether layer was separated, washed with water, and dried with calcium sulfate. This anhydrous ether solution was concentrated under reduced pressure. When all the ether had evaporated, white crystals along with a light yellow oily liquid was left at the bottom of the flask. By various methods, it was found that the products obtained were:

1. 2,4-dichlorophenoxyacetic acid
2. A ketone
3. Light yellow oil

In order to remove the acid, the ether layer was extracted with five per cent sodium hydroxide which removed all the acid completely. Then it was extracted with water and then dried over calcium sulfate. After the removal of acid and the drying, the ether was evaporated completely under reduced pressure, when white crystalline material along with light yellow oil was obtained. This product was washed with Skelly-F which removed the oil.

The purified white crystalline material had a melting point of 66.5° C. and gave a positive ketone test with 2,4-dinitrophenylhydrazine. This white crystalline material was the 2,4-

dichlorophenoxyethyl ethyl ketone. The molecular weight was determined by Beckmann method (2). It gave a value of 234.4, while the calculated value was 233.

Since it was suspected that there might be some alcohol also present, adsorption chromatography was tried to separate the mixture. It was found that only ketone and the oil were present.

Reaction of Tetra(*o*-naphthaleneacetoxy)silane With Ethylmagnesium Bromide

The preparation and the method used here were the same as those used for the reaction of tetra(2,4-dichlorophenoxyacetoxy)silane with ethylmagnesium bromide. The ether layer was separated and dried over calcium sulfate. The anhydrous ether solution was shaken with five per cent sodium hydroxide to remove any naphthalene acetic acid formed by hydrolysis. Then the ether solution was dried again over calcium sulfate.

When the ether was evaporated completely, an oily layer mixed with some crystals was obtained. It was difficult to remove the crystals from the oil. On testing the mixture for carbonyl groups, it gave a positive test with 2,4-dinitrophenylhydrazine. The product therefore could contain a ketone. Chemical analysis showed that the oil contained a silicon compound and the infrared spectrum indicated that a silicone was present.

Preparation of Dichlorodi(*p*-aminoazobenzene)silane

The method and apparatus used in preparing these Si-N

bonded compounds were similar to those used in the preparation of silicon esters. The silicon tetrachloride was purified by distillation. The p-aminoazobenzene was dried at 100° C. Anhydrous benzene was used as solvent.

A calculated amount of silicon tetrachloride, about 6.7 ml. (10 g.), dissolved in 50 ml. of anhydrous benzene was added dropwise into a slurry of 47 g. of p-aminoazobenzene dispersed in 200 ml. of benzene. The reaction vessel was kept in an ice bath and the silicon tetrachloride was added in small amounts every one-half hour for one and one-half hours. The mixture was stirred mechanically during the addition of silicon tetrachloride and for about two and one-half hours afterwards. A red violet substance separated out which is the hydrochloride of p-aminoazobenzene.

The solid, p-aminoazobenzene hydrochloride, was removed by filtering the mixture through a Selas crucible. The filtrate was stored in a bottle and kept in the cold room at 4° C.

The following methods were employed to obtain crystalline products from the filtrate:

1. The filtrate was subjected to reduced pressure and when all the benzene was removed, a red powder was obtained. This powder was treated with carbon disulfide. It was found that only a portion of the powder dissolved in carbon disulfide. The insoluble portion was removed by filtration. The filtrate was subjected to reduced pressure and when all the carbon disulfide was removed, fine needle shaped crystals were obtained. By infrared spectrum, it was found that the needle shaped crystals

were p-aminoazobenzene itself. From this, it was concluded that the red powder was a mixture containing p-aminoazobenzene, its hydrochloride and the product.

2. The filtrate was subjected to reduced pressure, thereby concentrating the solution. When Skelly F solvent was added to this concentrated solution, a colored substance precipitated. This substance was removed by filtration and found to contain some silicon.

The remaining filtrate was subjected to reduced pressure and when all the solvent was removed, red crystals were obtained. By infrared spectrum, it was found that the red crystals were p-aminoazobenzene. This test also indicated that the filtrate obtained from the original reaction was a mixture.

A different method had to be adopted to separate various constituents from the mixture. So, adsorption chromatography was used for the separation of this mixture.

Separation Using Adsorption Chromatography

Adsorbents selected for the study were: tricalcium phosphate, supercel, one to one by weight; magnesia (Westvaco 2641), supercel, one to one by weight; alumina, supercel, one to one by weight; and silicic acid (Mallinckrodt AR, 100 mesh), supercel, one to one by weight. It was found that the silicic acid-supercel mixture was a good adsorbent. A 1 x 18 inch adsorption tube was attached to a suction flask. The adsorbent was added, under vacuum, to the tube in small portions and was tamped firmly with a cork mounted on a glass rod. The final length of the adsorbent

column was 15 inches. About two to three ml. of the benzene solution of the filtrate was poured into the column. When all the solution had been drawn into the adsorbent, additional benzene was added just to moisten the entire column of adsorbent. When benzene as the eluting agent was added, different bands were obtained. By using benzene, carbon disulfide, and acetone, it was possible to remove all the bands. The results obtained are given as follows:

Eluting agent	Fraction	Nature of the substance	Presence of silicon	Infrared analysis
Benzene	A	Sticky substance	No	----
	B	Red crystals	No	P-aminoazobenzene
Carbon disulfide		Red crystals	No	P-aminoazobenzene
Acetone	A	Red powder	Yes	Silica
	B	Sticky substance	Yes	Product
	C	Red powder	Yes	Silica

Benzene A, B, and carbon disulfide did not contain silicon. Acetones A and C had silicon in them but it was found to be due to some silicic acid dissolving in acetone. Acetone B gave a good infrared spectrum having most of the peaks of p-aminoazobenzene. A qualitative test for silicon and chlorine was positive. So this fraction should be the product.

From the chromatographic separation, it was found that most of the p-aminoazobenzene present in the filtrate could be removed

by washing with CS_2 and a little benzene. So the filtrate obtained from the original reaction was subject to reduced pressure and when all the benzene was removed, a red powder was obtained. This powder was washed first with carbon disulfide and then with benzene, thereby removing all the unreacted *p*-aminoazobenzene. The remaining solid left behind was the product.

Preparation of Tetra(*N,N*-dimethylaminoazobenzene)-silane Tetrachloride

The method and apparatus used in the preparation of tetra(*N,N*-dimethylaminoazobenzene)silane tetrachloride was same as that used in the preparation of tetra(*p*-aminoazobenzene)silane. Anhydrous benzene was used as solvent. A salt-ice bath was used in this case, thereby lowering the temperature to -12°C . The reaction mixture was stirred mechanically for four hours. The addition of silicon tetrachloride to the benzene solution of *N,N*-dimethylaminoazobenzene resulted in the separation of a red colored precipitate. This precipitate was separated by filtration and the filtrate was stored in the cold room at 4°C .

Using chromatography technique as before, two fractions were obtained with benzene as solvent. These fractions were found to be *N,N'*-dimethylaminoazobenzene. A third fraction obtained with acetone gave a different spectrum in infrared. This was found to be the same as the precipitate, separated out by the addition of silicon tetrachloride to benzene solution of *N,N'*-dimethylaminoazobenzene. The precipitate was dried at 90°C . and analyses were carried out on this material.

Methods of Chemical Analysis

The silicon analysis was carried out by the method of Hyde and DeLong (7). In order to get an accurate silicon analysis by this method, it was necessary to use fuming nitric acid.

The nitrogen analysis was carried out by the Kjeldahl (4) method. In the case of the silicon derivative of *N,N*-dimethylaminoazobenzene, a micro Kjeldahl analysis for nitrogen was carried out.

The chloride analysis was carried out by the Carius (5) method. This method was accurate. A method by which the chlorine was converted to sodium chloride, using sodium metal and then determining the chlorine as silver chloride, did not give accurate results.

The infrared spectrum of the silicon esters and Si-N bonded compounds were obtained with a Perkin-Elmer, Model 137, Infrared Spectrometer. The compounds tested were made into pellets with potassium bromide. The pellets were made by grinding one mg. of the compound with 500 mg. of potassium bromide.

RESULTS AND DISCUSSION

Two silicon esters, tetra(2,4-dichlorophenoxyacetoxy)silane and tetra(-naphthaleneacetoxy)silane, were prepared by the Schuyten, Weaver, and Reid method (16). Two Si-N bonded compounds, namely, dichlorodi(*p*-aminoazobenzene)silane and tetra(*N,N*-dimethylaminoazobenzene)silane tetrachloride, were also prepared. The analysis of these compounds are listed in Table 1.

Table 1. The analysis of silicon esters and Si-N bonded compounds.

Compound	Yield %	% of Si		% of N		% of Cl	
		Calcu- lated	Found	Calcu- lated	Found	Calcu- lated	Found
$[\text{C}_6\text{H}_4(\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O}))_4\text{Si}]_4$	63.3	3.097	3.05	---	---	30.96	30.71
$[\text{C}_6\text{H}_4(\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O}))_4\text{Si}]_4$	55.92	3.65	3.649	---	---	---	---
$[\text{C}_6\text{H}_4(\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{N})_2\text{SiCl}_2]$	74.4	5.68	5.56	17.06	17.01	14.62	14.02
$\text{Si}[\text{C}_6\text{H}_4(\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}(\text{CH}_3)_2)_4\text{Cl}_4]$	78.5	2.61	2.56	15.6	15.1	13.3	13.07

In all these preparations, low temperature was necessary. The compounds were quite stable at room temperature. These compounds were quite stable as they neither melted nor decomposed below 120° C. Moisture should be avoided in order to prevent any decomposition. The products obtained in the case of Si-N bonded compounds were dark red solids.

In the case of the reaction of p-aminoazobenzene with silicon tetrachloride, the dichlorodi(p-aminoazobenzene)silane was in the filtrate and the solid that separated out was the hydrochloride of p-aminoazobenzene. This was verified by comparing the spectrum of the solid obtained from the reaction and the hydrochloride prepared in the laboratory.

The reaction of dimethylaminoazobenzene with silicon tetrachloride was quite rapid. As soon as the silicon tetrachloride was added, a red violet colored solid separated out. This solid was found to be the product, and the filtrate had only the unreacted N,N-dimethylaminoazobenzene. The product thus obtained, seemed to be ionic. In the analysis for chlorine, when concentrated nitric acid and silver nitrate were added to the product, silver chloride precipitated immediately.

Anhydrous benzene was found to be the best solvent for the preparation of Si-N bonded compounds and anhydrous ether was best for the silicon esters. The silicon esters reacted very readily with water and alcohols. The Si-O-Si-O bonding being more stable than Si-O-C^O-R bonding, accounts for the esters reactivity.

Both the silicon esters, tetra(2,4-dichlorophenoxyacetoxy)-

silane and tetra(α -naphthaleneacetoxy)silane, were white crystalline solids. The Si-N bonded compounds were both dark red crystalline solids. The ketone obtained from the reaction of tetra(2,4-dichlorophenoxyacetoxy)silane and ethylmagnesium bromide was white crystalline solid and the silicone oil was a light yellow oil.

The infrared spectra of all these compounds were determined between 3 and 15 μ . The spectra of tetra(2,4-dichlorophenoxyacetoxy)silane, tetra(α -naphthaleneacetoxy)silane, dichlorodip-(p-aminoazobenzene)silane and tetra(N,N-dimethylaminoazobenzene)silane tetrachloride are shown in Plates I and II. All of the silicon esters had significant strong absorption bands between 9.2 and 9.4 μ , which correspond to values reported by Richards and Thompson (14) to be characteristic of the Si-O bond. The bands between 5.7 and 5.95 μ are due to C=O bond. These bands occur in organic esters and are found in the spectra of all the acyloxy silanes studied. No anhydride was present as no bands occur between 5.48 and 5.62 μ . In each of the silicon esters, the bands corresponding to the original compound were present along with the characteristic Si-O bond which was a new band in the spectrum. These spectral studies, along with the analysis, indicated that the two silicon esters have been prepared.

In the case of Si-N bonded compounds, there were several new bands obtained. J. C. Winters (24) prepared tetraanilinosilane and tetra(N-methylanilino)silane. He did chemical and infrared studies on the structure of these compounds containing

Si-N bonds. Winter assigned the bands that appeared at 7.18-7.24, 9.2-9.3, 10.77-10.86, 11.07-11.09, and 12.41-12.72 μ to Si-N bonding. Waterman-Delft (23) also prepared a series of silicon nitrogen compounds, namely, trichloroethylaminosilane, dichlorodiethylaminosilane, chlorotriethylaminosilane, and tetraethylaminosilane, and obtained infrared spectra of all these compounds. A comparison of all these spectra with the spectra of diethylamine was made. It was found that the bands that occur between 7.45 and 7.48, 9.38 and 9.41, 9.69 and 9.78, 10.66 and 10.8, and 12.6 and 12.68 μ are new bands and may be due to Si-N bonding. In this work, strong new bands were obtained at 7.18, 9.2, 9.7, and 12.4 μ for the product dichlorodi-(p-aminoazobenzene)silane and new bands at 7.18 and 9.35 μ for the product tetra(N,N-dimethylaminoazobenzene)silane tetrachloride may be due to Si-N bonds. Weak peaks occurred in the spectrum of (N,N-dimethylaminoazobenzene)silane tetrachloride at 9.7 and 12.4 μ . Comparing the work of Winter, Waterman-Delft, and this work, the bands that occur between 7.1 and 7.3, 9.1 and 9.4, 9.69 and 9.71, and at 12.4 μ may be due to Si-N bonding. Dichlorodi(p-aminoazobenzene)silane gave bands at 9.8 and 14.3 μ which were due to the Si-Cl bond. Tetra(N,N-dimethylaminoazobenzene)silane tetrachloride gave a band at 6.42 μ which may be due to ionic chloride.

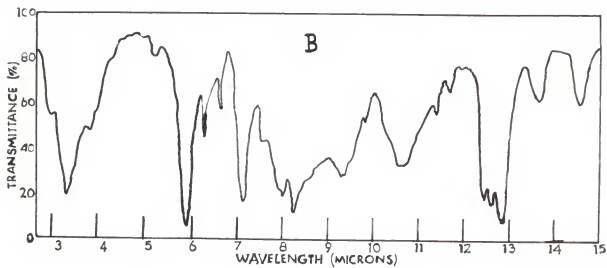
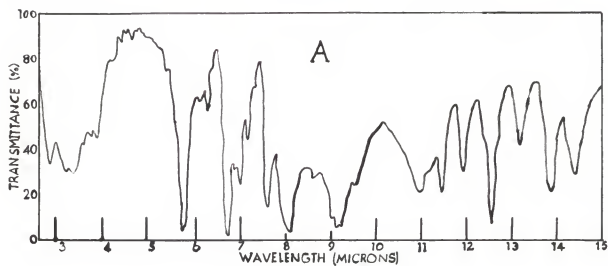
In order to determine where the silicon attaches in the structure of aminoazobenzene, several compounds were tried. It was found that the silicon tetrachloride did not react with

EXPLANATION OF PLATE I

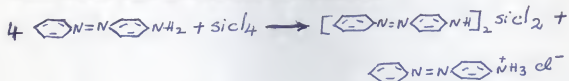
The Infrared Spectra of Silicon Esters

- A. Tetra(2,4-dichlorophenoxyacetoxy)silane.
- B. Tetra(α -naphthaleneacetoxy)silane.

PLATE I



azobenzene and thus indicated that there was no breakage of N=N bond. When p-aminoazobenzene was treated with silicon tetrachloride, the product dichlorodi(p-aminoazobenzene)silane was obtained. This reaction indicated that the hydrogen in the amino group can be replaced as follows:



The hydrogen chloride was removed as p-aminoazobenzene hydrochloride. This reaction was carried out for four hours with continuous stirring.

When N,N-dimethylaminoazobenzene was treated with silicon tetrachloride, the product separated immediately upon the addition of silicon tetrachloride, indicating that it was an addition reaction. The preparation of tetra(N,N-dimethylanilino)silane was attempted. When silicon tetrachloride was added to N,N-dimethylaniline, the product obtained was very unstable towards atmospheric moisture and decomposed very readily.

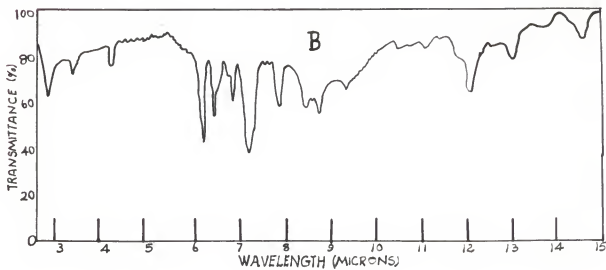
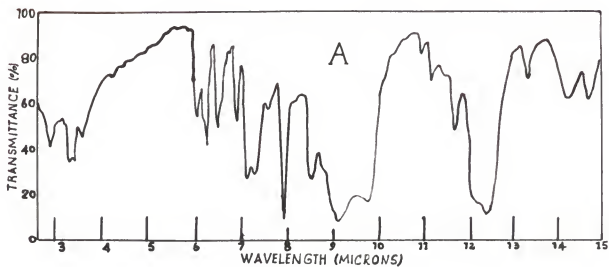
In order to study the reactions of the silicon esters, the esters were treated with ethylmagnesium bromide. Tetra(2,4-dichlorophenoxyacetoxy)silane treated with ethylmagnesium bromide and subsequent hydrolysis gave a ketone and a silicone oil. The ketone was a white crystalline material, melting at 66.5° C. In reviewing the literature, no information was available on this ketone. Therefore, it is probably a new compound. The reaction mechanism of tetra(2,4-dichlorophenoxyacetoxy)silane is given in Plate III. The infrared spectrum of the ketone is given in

EXPLANATION OF PLATE II

The Infrared Spectra of Si-N Bonded Compounds

- A. Dichlorodi(p-aminoazobenzene)silane.
- B. Tetra(N,N-dimethylaminoazobenzene)silane tetrachloride.

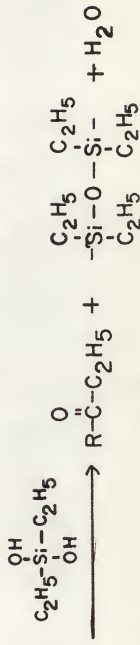
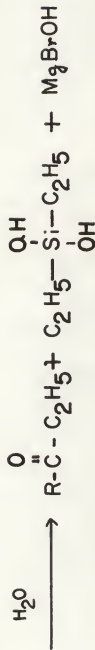
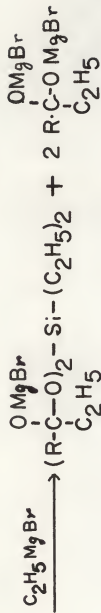
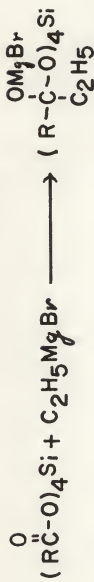
PLATE II



EXPLANATION OF PLATE III

Reaction of tetra(2,4-dichlorophenoxyacetoxy)silane with the stoichiometric amount of Grignard reagents.

PLATE III



EXPLANATION OF PLATE IV

The infrared spectra of 2,4-dichlorophenoxyethyl ethyl ketone.

PLATE IV

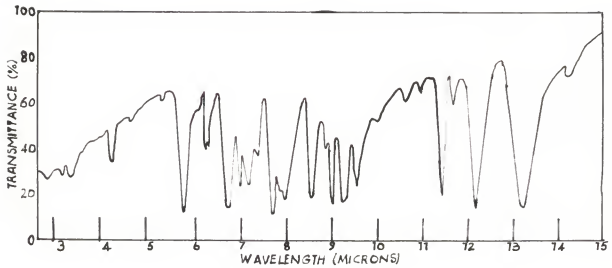


Plate IV. The 2,4-dinitrophenylhydrozone derivative of this ketone had a melting point of 133° C. The percentage of the silicone oil obtained was 2.1 per cent. The ethyl silicone was a light yellow oil. Since it was difficult to get the pure silicone oil, as some ketone was also mixed along with it, the infrared spectrum showed both silicone and ketone peaks. This reaction was an additional proof for the formation of tetra(2,4--dichlorophenoxyacetoxy)silane.

The reaction of tetra(α -naphthaleneacetoxy)silane with ethylmagnesium bromide gave a ketone mixed with silicone oil. The percentage of silicone oil obtained was found to be 35 per cent. The mixture of silicone oil and the ketone gave a positive test for ketone with 2,4-dinitrophenylhydrazine. The adsorption chromatography technique was tried to separate this mixture, but it was not very successful. The infrared spectrum taken on this material had all the characteristic bands of a silicone and a ketone.

The molecular weights of most of the compounds could not be determined in benzene because of the high molecular weight. The molecular weight of the 2,4-dichlorophenoxyethyl ethyl ketone determined by Beckmann method (2) gave a value of 234.4. The calculated value for the ketone was 233. This is additional data in confirming the presence of the ketone.

SUMMARY

New compounds, tetra(2,4-dichlorophenoxyacetoxy)silane and tetra(α -naphthaleneacetoxy)silane have been prepared by the

method of Schuyten et al. (16) and Lanning (9, 10). The reactions were carried out at -12°C . Anhydrous diethyl ether was a good reaction medium for preparing these silicon esters, as it was easy to remove the products from the solvent. Tetra(2,4-dichlorophenoxyacetoxy)silane and tetra(α -naphthaleneacetoxy)silane were both white crystalline compounds. They do not melt but decompose above 130°C .

Both the silicon esters, tetra(2,4-dichlorophenoxyacetoxy)silane and tetra(α -naphthaleneacetoxy)silane were treated with ethylmagnesium bromide. Alcohols, ketones, and silicones are the products to be expected when ethylmagnesium bromide reacts with an ester. An alcohol was not obtained from either of the silicon esters under the conditions in which these experiments were conducted. Ketones were obtained from both the silicon esters. The ketone, 2,4-dichlorophenoxyethyl ethyl ketone, which was obtained by the reaction of tetra(2,4-dichlorophenoxyacetoxy)silane and ethylmagnesium bromide, had a melting point of 66.5 and a molecular weight of 234.4 . It gave a phenylhydrazone derivative with 2,4-dinitrophenylhydrazine which had a melting point of 133°C . The product obtained by the reaction of tetra(α -naphthaleneacetoxy)silane with ethylmagnesium bromide, gave a positive ketone test with 2,4-dinitrophenylhydrazine. But, the ketone could not be separated from the silicone oil. The silicone oils obtained were both ethyl silicones. The ketone, 2,4-dichloromethyl ethyl ketone, probably is a new compound.

Two Si-N bonded compounds, dichlorodi(p-aminoazobenzene)silane and tetra(N,N-dimethylaminoazobenzene)silane tetrachloride,

were prepared by a similar method to that used for the preparation of silicon esters. Instead of sodium salts, the pure azo compounds were used. These reactions were also carried out at -12°C . Anhydrous benzene was a good reaction medium. The difficulty in removing the precipitates was rectified by using a Selas crucible. Both dichlorodi(p-aminoazobenzene)silane and tetra(N,N-dimethylaminoazobenzene)silane tetrachloride were dark red crystalline materials.

The infrared spectra of silicon esters and the Si-N bonded compounds were determined between 3 and 15μ . All of the silicon esters had significant absorption bands between 9.2 and 9.4μ which are characteristic Si-O bond. The bands between 5.7 and 5.95μ are due to -C=O bond. These peaks occur in organic esters and are found in the spectra of all the acyloxy silanes studied. No anhydride was present as no bands occur between 5.48 and 5.62μ . In each of the silicon esters, the bands corresponding to the original compound were present along with the characteristic Si-O bond which was a new band in the spectrum. These spectral studies, along with the analysis, indicated that the two silicon esters have been prepared.

In the case of Si-N bonded compounds, new bands were obtained. Dichlorodi(p-aminoazobenzene)silane gave new bands at 7.28 , 9.2 , and 12.4μ , which were due to Si-N bond. Bands at 9.8 and 14.3μ were due to Si-Cl bond. Tetra(N,N-dimethylaminoazobenzene)silane tetrachloride gave new bands at 7.19 and 9.35μ . This was due to Si-N bond. The band at 6.42μ was

probably due to ionic chloride. These spectral studies, along with the analysis, indicated that these Si-N bonded compounds were prepared.

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BIBLIOGRAPHY

- (1) Anderson, H. H., and T. C. Hager.
Organosilicon fluoroesters. *Journal of the American Chemical Society*, 81:1584-6, 1959.
- (2) Beckmann, L.
Molecular weight determination. *Physical Chemistry*, 2:683, 1888.
- (3) Friedel, C., and A. Ladenberg.
Uberdas Intermediar Anhydrid Von Kieselsaure Und Essigsaeure, *Annalen Der Chemie*, 145:174, 1888.
- (4) Furman, N. H.
Scott's standard methods of chemical analysis. Vol. I, Ed. II:632 and 2492, New York: D. Van Nostrand Co., Inc.
- (5) Furman, N. H.
Scott's standard methods of chemical analysis. Vol. I, Ed. II:265, New York: D. Van Nostrand Co., Inc.
- (6) Harden, Arthur.
On the action of silicon tetrachloride on the aromatic amide compounds. *Journal of Chemical Society*, 51:40-47, 1887.
- (7) Hyde, J. F., and R. C. DeLong.
Condensation product of the organo-silane diols. *Journal of the American Chemical Society*, 63:1194, 1941.
- (8) Kipping, Fredrick S.
Organic derivatives of silicon. *Proc. Royal Soc.*, A159:139-148, 1937.
- (9) Lanning, F. C.
Preparation and properties of silicon tetrapropionate. *Journal of the American Chemical Society*, 75:1194, 1953.
- (10) Lanning, F. C.
Silicon tetrabenzoate. *The Journal of Organic Chemistry*, 23:288, 1958.
- (11) Lanning, F. C., and M. Moore.
The preparation of acyloxysilanes and their reaction with Grignard reagents. *The Journal of Organic Chemistry*, 23:288, 1958.

- (12) Petrov, K. D., and U. I. Itkina.
Preparation of silicon tetrabutryrate and its properties. *Chemical Abstracts*, 42:316, 1948.
- (13) Reynolds, J. Emmerson.
XLVI. Researches on silicon compounds and their derivatives. Part V. On silicotetraphenylamide, para- and ortho silicotetratolylamides, - and - silicote-tranaphtylamide. *Journal of Chemical Society of London*, 55:474-482, 1889.
- (14) Richards, R. K., and H. N. Thompson.
Infrared spectra of compounds of higher molecular weight. Part IV. Silicones and related compounds. *Journal of Chemical Society of London*, 124, 1949.
- (15) Sarju Prasad, and K. N. Chatterjee.
Compounds of silicon tetrachloride with amines and heterocyclic bases. *The Journal of Indian Chemical Society*, 35:901-903, 1958.
- (16) Schuyten, H. A., J. N. Weaver, and J. D. Reid.
Preparation of substituted acetoxysilanes. *Journal of the American Chemical Society*, 69:2110, 1947.
- (17) Sergeeva, Z. I., B. N. Dolgov, and D. D. Tactovich.
Chemical Abstracts, 53:11199, 1959.
- (18) Troost, L., and P. Hautefeuille.
Recherches sur les silicum. *Bull. Soc. Chem.* (2), 19:255-256, 1873.
- (19) Volnov, J. N.
Reactions of silicon tetrachloride with esters. *Journal of General Chemistry (U.S.S.R.)*, 9:2269, 1939.
- (20) Wannagat, U., and Walter Leibr.
Hydrazine silicon compounds. I. Mono and bis(triorganosilyl)hydrazines. *Z Anorg. U. Allgem. Chem.*, 297:129-136, 1958.
- (21) Wannagat, U., and Walter Leibr.
Hydrazine silicon compounds. II. Mixed alkyl- or aryl-substituted hydrazines. *Z Anorg. U. Allgem. Chem.*, 299:341-348, 1959.
- (22) Wannagat, U., and H. Niederprium.
Reactions of diphenyldichlorosilanes with hydrazines. *Angew. Chem.*, 70:745, 1958.

(23) Waterman-Delft.

The saddler standard spectra. Saddler Research Laboratories, 1517 Vine St., Philadelphia 2, Pa., Spectrum Nos. 4464, 4465, 4466, 4467, and 3194.

(24) Winters, J. C.

Chemical and infrared studies on the structure of certain compounds containing silicon-nitrogen bonds. M. S. Thesis submitted at Kansas State University, 1950.

THE PREPARATION OF ACYLOXYSILANES,
THEIR REACTION WITH GRIGNARD REAGENTS,
AND THE PREPARATION OF SOME Si-N BONDED COMPOUNDS

by

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A survey of the available literature in organosilicon compounds disclosed that a great amount of work has been done in the past century. Silicon esters and silicon-nitrogen bonded compounds are not new in this field, but they have not been studied as extensively as other organosilicon compounds.

This investigation was initiated to prepare some biologically active compounds by first preparing the silicon esters and then reacting with Grignard reagents to get a ketone or alcohol which could be biologically active. α -Naphthaleneacetic acid, which is a root growth hormone, and 2,4-dichlorophenoxyacetic acid, which is a weed killer, were used to prepare the silicon esters.

The silicon esters, tetra(α -naphthaleneacetoxy)silane and tetra(2,4-dichlorophenoxyacetoxy)silane, were both prepared by the action of sodium salts on silicon tetrachloride (method of Schuyten, Weaver, and Reid). Both are new compounds. Anhydrous diethyl ether was a good reaction medium for preparing these silicon esters as it was easy to remove the products from the solvent. It was also found that a low temperature of about -12° C. is necessary for the completion of the reaction. They were both white crystalline solids, quite stable at room temperature and react readily with water and alcohol.

The infrared spectra of these silicon esters were determined between 3 and 15μ . Both the silicon esters had significant bands between 9.2 and 9.4μ which were due to Si-O bond. No anhydride was present as there was no band between 5.48 and 5.62μ . These spectral studies, along with the

analysis, indicated these two silicon esters have been prepared.

Both the silicon esters were treated with ethylmagnesium bromide. Alcohols, ketones, and silicones were the products to be expected when Grignard reagents react with an ester. Alcohols were not obtained from either of the silicon esters, but ketones were obtained. The ketone, 2,4-dichlorophenoxyethyl ethyl ketone, which was obtained by the reaction of tetra(2,4-dichlorophenoxyacetoxy)silane and ethylmagnesium bromide, had a melting point of 66.5° C. and a molecular weight of 234.4. It gave a phenylhydrazone derivative with 2,4-dinitrophenylhydrazine which had a melting point of 133° C. The product obtained by the reaction of tetra(α -naphthaleneacetoxy)silane with ethylmagnesium bromide, gave a positive test for ketone with 2,4-dinitrophenylhydrazine. But the ketone could not be separated from the silicone oil. The silicone oils were both ethyl silicones. The ketone, 2,4-dichlorophenoxyethyl ethyl ketone, probably is a new compound.

The second part of the investigation was to prepare some Si-N bonded compounds. These compounds were prepared by direct action of azo compounds with silicon tetrachloride in benzene. The Si-N bonded compounds, dichlorodi(p-aminoazobenzene)silane and tetra(N,N-dimethylaminoazobenzene)silane tetrachloride, were both red crystalline material. They were both stable at room temperature. These compounds were prepared at low temperature, about -12° C. Anhydrous benzene was a good reaction medium.

The infrared spectra of these Si-N bonded compounds were determined between 3 and 15μ . New bands that occurred between

7.18 and 7.28 μ , 9.1 and 9.35 μ , and 12.3 and 12.5 μ were due to Si-N bonds. In the case of dichlorodi(p-aminoazobenzene)silane, bands at 9.8 and 14.3 μ were due to Si-Cl bond. Tetra(N,N-dimethylaminoazobenzene)silane tetrachloride gave a new band at 6.42 μ , which may be due to ionic chloride. These spectral studies, along with the analysis, indicated that these compounds were prepared.