

THE SYNTHESIS AND CHARACTERIZATION
OF SILYLIMIDES

by

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ABSTRACT

The preparation of a series of silylsuccinimides and silylphthalimides is described.

The silylsuccinimides and phthalimides were prepared by the reaction of the potassium imide salt with chlorosilanes. The prepared compounds were characterized by elemental analysis, infrared spectra, proton n.m.r. spectra and mass spectra.

On the basis of infrared and proton n.m.r. spectra, the electronic nature of the Si-N bond of these compounds is discussed.

ACKNOWLEDGEMENTS

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GENERAL INTRODUCTION

HISTORY

Silicon-nitrogen compounds are now very common. A few had been made previous to 1940¹⁻⁴, but it was not until the chlorosilanes became widely available during the 1940's that silicon-nitrogen compounds began to appear with any frequency.

By use of triorganochlorosilanes in reaction with ammonia, primary and secondary amines, a large number of the known silicon-nitrogen compounds were prepared⁴⁻¹⁵. The use of triorganosilanes in preparing silicon-nitrogen compounds is the most versatile of the methods possible. Silylhydrazines¹⁶ (fig 1(a)), silyl-hydroxylamines¹⁷ (fig 1(b)), silylazides¹⁸ (fig 1(c)), disilylamines¹⁹ (fig 1(d)), silylamines²⁰ (fig 1(e)), silazanes²¹ (fig 1(f)), N- and O-silyl derivatives of amino acids²², silylamides^{23,24} (fig 1(g)), silylimides²⁵⁻²⁷ (fig 1(h)) and a large number of compounds formed by the reaction between triorganochlorosilanes and nitrogen containing heterocyclic ring compounds²⁸ (fig 1(i)) are made by using triorganochlorosilane as a starting material.

The dichloro, trichloro and tetrachloro derivatives of organosilyl compounds lead to a smaller group of compounds. Dihalodiorganosilanes can be used to prepare silyldimides^{25,27} (fig 1(j)), cyclotrisilazanes²⁹ (fig 1(k)) and cyclotetrasilazanes³⁰ (fig 1(l)). Triorganosilanes can be used to prepare polysilazanes³¹ (fig 1(m)) and silyltriamines³² (fig 1(n)). Tetrahalosilanes can be used to prepare heterogeneous polymers³³, variously substituted silylamines³⁴ and a number of adducts^{35,36} (fig 1(o)).

All the above compounds prepared by the use of the halosilanes have at least one characteristic in common. The outcome of the reaction will be sterically sensitive. For example, the amine-silylhalogen reactions will show a decreasing tendency to go to completion as the alkyl substituents on silicon increase in size or as the alkyl substituents on the amine increase in size ³¹.

Many methods can be used to prepare a silicon-nitrogen bond. A detailed list of some of these methods can be found in Pierce's book ²⁸ and in other reviews and books ^{31,36-45}.

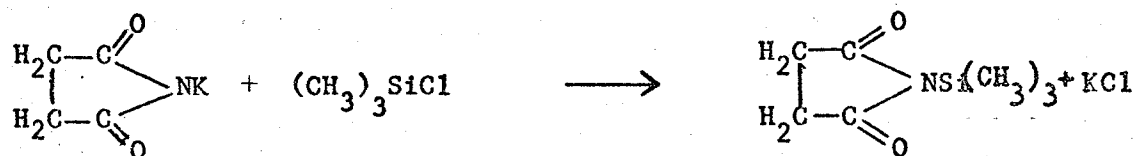
SILYLATION OF HETEROCYCLIC COMPOUNDS

A number of methods can be used in order to silylate heterocyclic rings. Pierce ²⁸ lists the most useful methods. Another review ⁴⁶ covers some other methods. Following Pierce ²⁸, the methods used can be broken down into five essentially different groups. Accordingly, they are (1) the trimethylchlorosilane - based methods, (2) the hexamethyldisilazane - based methods, (3) the silylamine - based methods, (4) the silylamide - based methods and (5) a few miscellaneous methods.

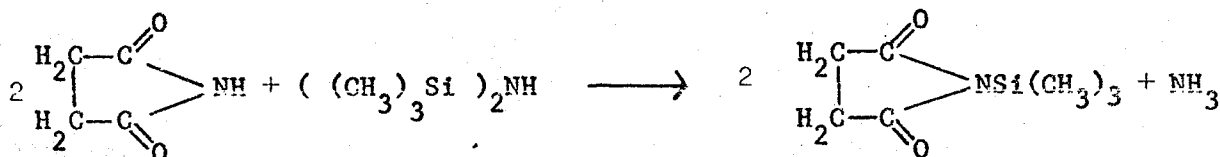
The trimethylchlorosilane-based methods are normally used to silylate alcohols, phenols and a few acids. This work mainly made use of the trimethylchlorosilane - based method which involves the reaction of a triorganochlorosilane with an alkali metal salt of an imide. In this work the cyclic imides used were succinimide and phthalimide. The alkali metal used was potassium. In general a number of the first four above methods have been used to silylate cyclic amides and a few cyclic imides ²⁸.

N-(trimethylsilyl)succinimide has been made by at least six different

methods. The first two methods of preparation have been done by Frainnet et al ⁴⁷. One of the methods he used involves beginning with the sodium or potassium salt of succinimide which can be prepared by a number of different ways ^{25,48} and reacting either of them with trimethylchlorosilane.

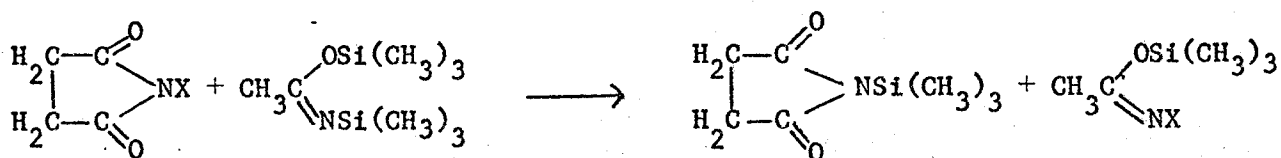


The second method he used is the reaction of hexamethyldisilazane with succinimide which yields N-(trimethylsilyl)succinimide and ammonia.



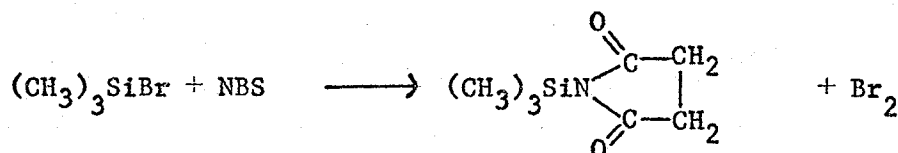
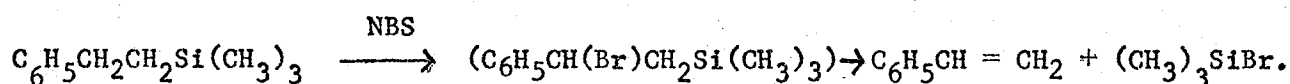
This method was also used by Wannagat ⁴⁹. This method normally yields a clean product with no side reactions. The reaction usually requires refluxing for a number of hours. Frainnet also has prepared N-(triethylsilyl)- and N-(triphenylsilyl)succinimide using both of the above methods.

Further, there are two methods used by Birkofer ^{50,51}. The first of these two methods involves the reaction of N-chloro or N-bromosuccinimide with N-(trimethylsilyl)acetamide to yield N-(trimethylsilyl)succinimide and the N-halomidessilylester.

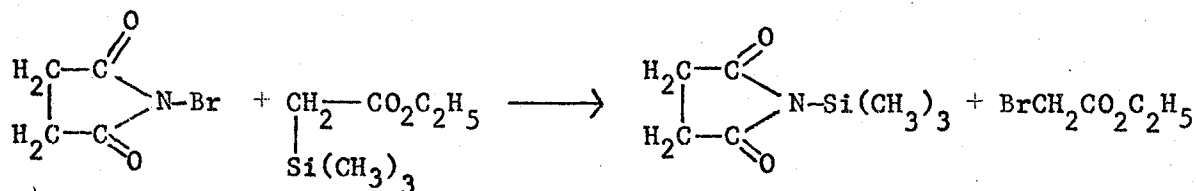


(X = Br, Cl)

The second method found by Birkofer is rather novel. If two moles of N-bromosuccinimide are reacted with 1- phenyl - 2 - trimethylsilylethane, the expected product 1 - phenyl - 1 - bromo - 2 - trimethylsilylethane is not formed or if it is formed, it immediately decomposes into phenylethylene and trimethylsilylbromide. The trimethylsilylbromide then reacts with N-bromosuccinimide to yield N-(trimethylsilyl)succinimide and free bromine. The free bromine then reacts with the phenylethylene.



The fifth method was found by Vernaleken ⁵², wherein, he reacted N-bromosuccinimide with ethyltrimethylsilylacetate to give ethylbromoacetate and N-(trimethylsilyl)succinimide



The last method found was that used by Dickopp ⁵³. His method sees a very large range of application in the silylation of compounds with active hydrogens in general. He reacted trimethylsilylchloride with succinimide in the presence of triethylamine. The triethylamine complexes the free acid.

There is less variety of methods for the preparation of N-(trimethylsilyl)-

phthalimide. N-(trimethylsilyl)phthalimide was prepared by Frainnet ⁴⁷ using the potassium salt of phthalimide and trimethylchlorosilane. He prepared N-(triethylsilyl)- and N-(triphenylsilyl)phthalimide using this method. Recently, this method has been used by Sheckeev et al., ²⁷ to prepare N-(methylethylsilyl)- and N-(methylisopropylsilyl)phthalimide. Similarly, he prepared N-(N'-phthalimidomethylsilyl)- and N-(N'-phthalimidodiethylsilyl)-phthalimide. He used N, N-dimethylformamide as a solvent for these reactions.

Frainnet ⁴⁷ was also able to prepare N-(trimethylsilyl)phthalimide by the reaction of hexamethyldisilazane with phthalimide.

Dickopp ⁵³ used the same method he employed for the preparation of N-(trimethylsilyl)succinimide to prepare N-(trimethylsilyl)phthalimide.

Klebe ²⁴ prepared N-(trimethylsilyl)phthalimide by reacting N,O-bis(trimethylsilyl)acetamide with phthalimide. The B.S.A. acts as a silyl-donor in this exchange reaction with the equilibrium lying far over to the products' side. He carried out this reaction by refluxing in acetonitrile.

Sheckeev et al., ²⁷ prepared N-(methylethylsilyl)phthalimide by refluxing phthalimide with methylethylchlorosilane in pyridine. The pyridine complexes the free acid.

Some other phthalimide compounds have been prepared using silicon containing functional groups, but in these the silicon atom is not directly bonded to the nitrogen atom of the phthalimide. Sommer ⁵⁴ prepared trimethylsilylmethylphthalimide by reacting phthalimide with trimethylsilylmethylchloride in the presence of potassium carbonate and N,N-dimethylformamide. Goubeau ⁵⁵ prepared bis(methylphthalimido)dimethylsilane by reacting potassium phthalimide with bis(chloromethyl)dimethylsilane in N,N-dimethylformamide.

In this work N-(trimethylsilyl)succinimide and N-(trimethylsilyl)-

phthalimide. were prepared using both the potassium salt/chlorosilane method and the imide/hexamethyldisilazane method. Comparison of their infrared spectra and proton n.m.r. spectra indicated that the compounds obtained by both of these methods were identical. By use of the potassium salt/chlorosilane method seven new silylsuccinimides were prepared and five new silylphthalimide compounds were prepared. Two of the new silylsuccinimides were dialkylsilyldisuccinimides.

MECHANISMS OF THE SILYLATION REACTIONS

The reaction methods mainly used in this work are essentially similar to the first step of the Gabriel synthesis used to prepare primary amines and amino compounds ⁵⁶. Also similar to the Gabriel synthesis are the preparations of silylmethylphthalimides and silyldimethylphthalimides from the corresponding silylchlorides and potassium phthalimide ^{54,55}.

When the method is used to synthesize N-alkylphthalimides, the reaction mechanism is thought to be S_N2 , wherein the phthalimide ion reacts at the nitrogen ⁵⁷.

Dimethylformamide is normally used as a solvent for Gabriel reactions because of its ability to dissolve the potassium salt to a small degree and therefore increase the reaction rate. In this work tetrahydrofuran was used as a solvent for all of the reactions because it dissolves many organometallic reagents, ⁵⁸ and is very stable to most organometallic compounds.

A number of detailed studies have been made on the stereochemistry of displacement of Cl^- leaving groups from asymmetric silicon in optically active compounds.

From Sommer's work⁵⁹ there appear four generalizations concerning the reaction behaviour of silylchlorides where the Cl^- ion is considered to be a good leaving group. He finds that predominant inversion of configuration occurs for replacement of Cl^- in R_3SiCl with:

- " a) groups of widely varying basicity
 $\text{H} > \text{OH}, \text{OR}, \text{OSiR} > \text{F}, \text{OCOR}.$
- b) groups of widely varying steric requirements
ie.; $\text{O-t} - \text{C}_4\text{H}_9$ and $\text{H}.$
- c) groups which form bonds to silicon in which $d_{\pi} - p_{\pi}$ bonding is not possible.
eg.; H
- d) groups which form bonds to silicon in which $d_{\pi} - p_{\pi}$ dative bonding is probably significant.
eg., $\text{Si} = \text{OR}, \text{Si} = \text{F}, \text{etc.}$ "

He carried out a wide variety of reactions in various solvents and found that again the predominant stereochemical path of reaction was via inversion of configuration.

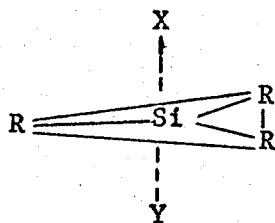
As a result Sommer⁵⁹ formulated the rule that "good leaving groups 'X' whose conjugate acids have a pK_a less than ≈ 6 undergo nucleophilic displacement from R_3SiX with inversion of configuration irregardless of the nature of the solvent and providing only that the attacking reagent furnishes an entering group 'Y' that is more basic than 'X' ". It is important to note that this rule emphasizes basicity rather than electronegativity.

By means of a large review of these stereospecific reactions Sommer further concludes that the reaction rates as well as the reaction mechanisms agree with the use of the concept of basicity of 'X', however the increased ability of 'X' to stabilize negative charge will increase the rate of R_3SiX reaction with nucleophiles.

In accordance with the inversion mechanism for $\text{S}_{\text{N}}2 - \text{Si}$ reactions Sommer

postulates a transition state (I) having the following two requirements:

- (a) a trigonal bipyramid geometry with 'X' and 'Y' occupying apical positions and (b) the bonds of 'X' and 'Y' are longer and weaker than between silicon and the non-reacting organic groups.

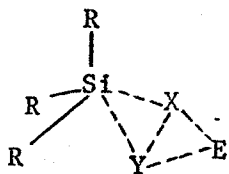


(I)

A fully fledged pentacoordinate Si-structure is not used because of the difficulty of explaining certain other results ⁶⁰.

Sommer ^{7,60} has found for the F⁻ and Cl⁻ leaving groups, when displaced by some organometallic reagents that retention of configuration occurs. Such results are explained on the basis of a S_N1 - Si mechanism where the transition state could be considered to take on one of two equivalent geometries.

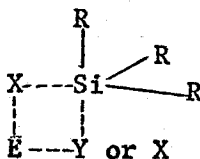
They are either tetragonal pyramid (II) wherein 'X' and 'Y' are both in basal positions or trigonal bipyramid (III), wherein, one is apical and one is equatorial. The electrophile of the organometallic reagent is assumed to be bonded to both 'X' and 'Y' to form quasi-cyclic four member transition states.



(II)

OR

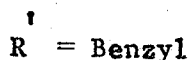
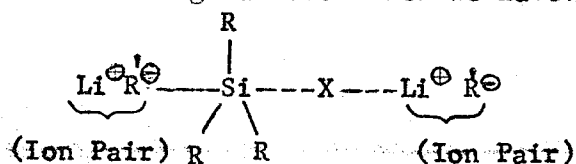
Y or



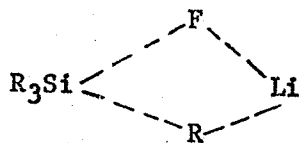
(III)

In either of these mechanisms the rate controlling step will be the breaking of the Si-Cl bond which will have a higher energy (91 kcal/mole) than the energy of the Si-N bond which is being formed (77 kcal/mole) ⁶¹. Thus, the replacing of the Si-Cl bond will be endothermic. Therefore, accompanying the replacement of Si-Cl bond there must be considerable weakening of the Si-Cl bond by the electrophilic attack of the metal ion accompanied by considerable release of energy by formation of a metal chloride salt. These will be the rate controlling consideration. Thus, Sommer proposes the following simple models to explain the above considerations.

For attack of lithium benzyl on a triorganosilylchloride inversion of configuration occurs, especially if the reaction is carried out in a polar solvent. Thus, Sommer invoked the S_N2-Si mechanism involving solvent stabilized ion pairs for the attacking organometallic reagent placed at the two apical positions of configuration. Then we have:



When a non polar solvent is used and where 'X' is a poor leaving group the S_Ni-Si mechanism is invoked to explain the retention of configuration. Where 'X' is a poor leaving group it is also considered by Sommers to be incapable of stabilizing -ve charge which is necessary for the charge separation that occurs in the S_N2-Si mechanism. Then we have the quasi cyclic four membered transition state (IV).

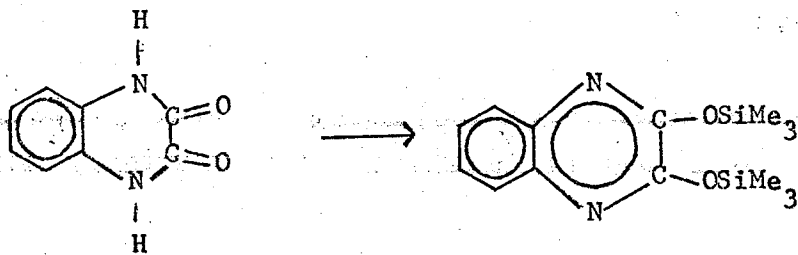


(IV)

This cyclic state is usually used to explain the results when F^- is the leaving group. One further consideration should be noted. All things being equal, of the three transition states mentioned, transition state I, will be the most stable according to valence - shell, electron - pair repulsion theory (V.S.E.P.R.) developed by Gillespie ⁶².

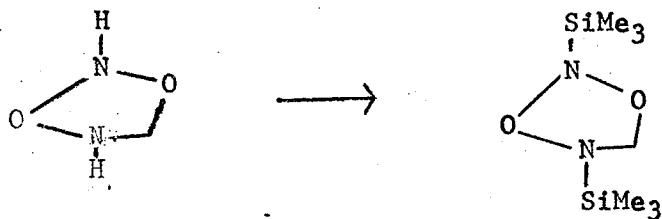
On the basis of these considerations then it seems reasonable to expect that the imide salt/silylchloride reactions would occur by an S_N2 -Si mechanism.

In respect to the silylation of imides and cyclic nitrogen and oxygen containing heterocycles two aspects can confuse the mechanistic picture. There is a tendency during silylation of heterocyclic compounds for the silylating group to favour N-silylation, O-silylation or both depending on the compound. The general rule that has evolved out of the work by Giessler ⁹ is that cyclic imides (and amides) O-silylate if there is significant resonance stabilization of the ring eg:



Otherwise, N-silylation will predominate.

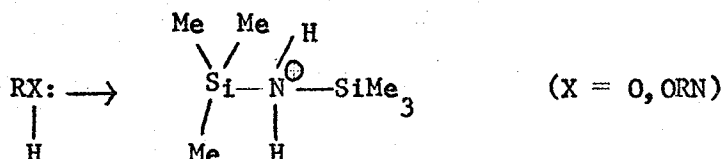
eg.



This rule neglects the possibility of tautomerization having an effect upon the outcome of the reaction. However, in the case of succinimide and phthalimide there is no conclusive evidence for tautomerism, ⁶³. Therefore, since no

resonance stabilization can occur if they are O-silylated, it is concluded that only N-silylation will take place and most likely by the S_N2 -Si mechanism described by Sommer.

In general an S_N2 -Si type of attack is thought to prevail in the reactions of hexamethyldisilazane with the imides. These are reversible reactions which have characteristic equilibriums depending on the conditions of the reaction. Langer⁶⁴ proposes a S_N2 -Si like attack which would give inversion of configuration.



Pump and Wannagat⁶⁵ proposed three mechanisms similar to those already discussed from Sommer's work for the reaction of amides with hexamethyldisilazane, all of which involved nucleophilic attack on the silicon by nitrogen.

REACTIONS OF SILICON NITROGEN COMPOUNDS

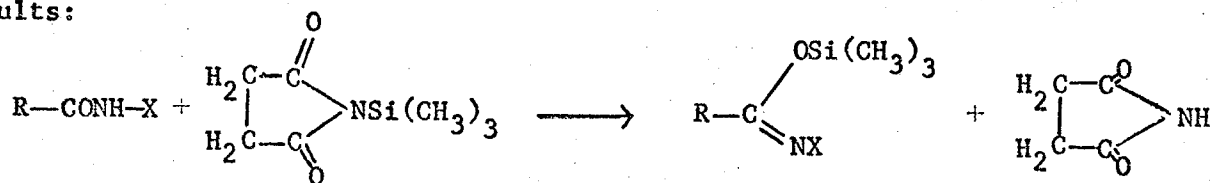
In general, most silicon-nitrogen compounds are very sensitive to water and protic agents. The heterocyclic compounds show a wide range of reactivities but in general they are among the most powerful silyl donating groups.^{28,24} N-(trimethylsilyl)imidazole is a strong enough silyl donor that it will react with α -halogeno-carboxylic esters⁶⁵ which are inert towards free imidazole, and forms N-(trimethylsilyl)imidazoleacetate. In general, they will react with acid chlorides with the elimination of trimethylsilylchloride. Most of the N-trimethylsilyl - heterocyclic nitrogen compounds are thermally stable⁴⁶ if heating is carried out in vacuo. A notable exception to this trend is that of silylated tetrazoles which decompose at temperatures above 100°C. An

excellent review covering some of the behaviour of some of these compounds has been written by Birkofer ⁴⁶.

N-(trimethylsilyl)succinimide has been found by Wannagat ²⁶ to be capable of donation of the trimethylsilyl group to N-methyl-N-hydroxymethyl-formamide, α -phenyl β - (methylamino)ethanol, and N-halomides. Similarly, Wannagat showed that N-(trimethylsilyl)phthalimide could donate to N-halomides.

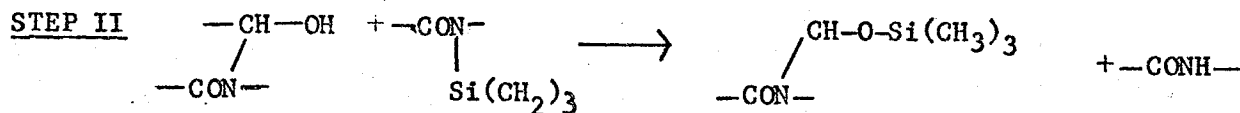
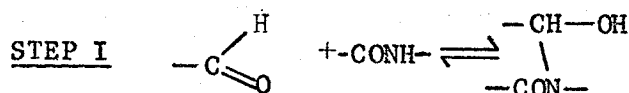
Birkofer ⁵⁷ has done a number of reactions between N-halomides and N-(trimethylsilyl)succinimide. The following equation expresses his

results:

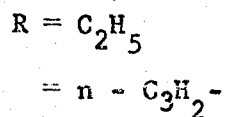
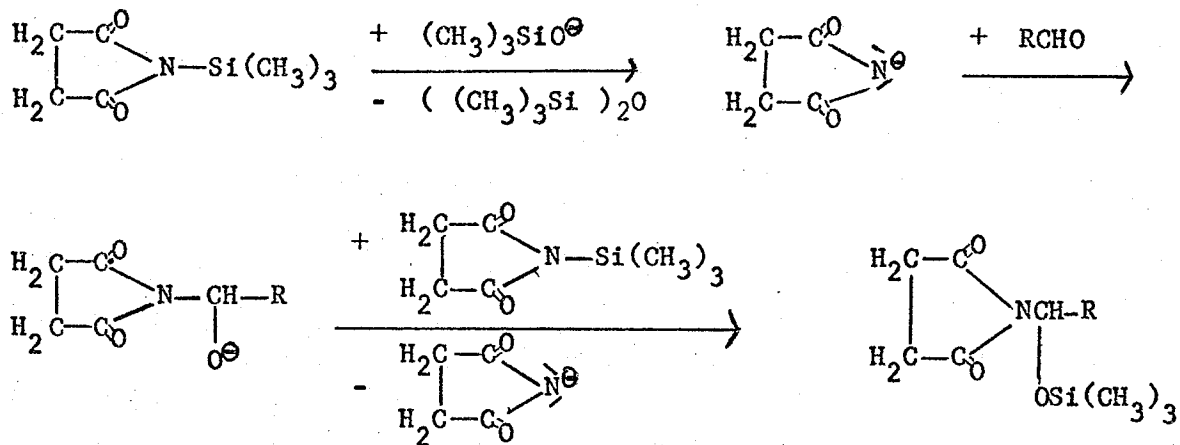


<u>R</u>	<u>X</u>	<u>R</u>	<u>X</u>
CH ₃ -	Cl	CH ₃ -	Cl
C ₆ H ₅ -	Cl	C ₆ H ₅ -	Cl
(CH ₃) ₂ CH-	Br	(CH ₃) ₃ CH-	Br

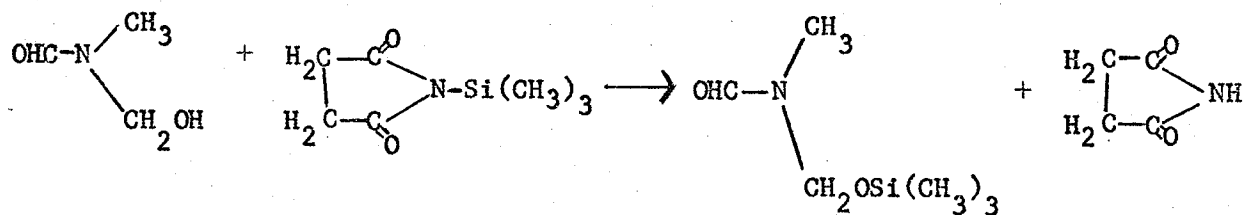
Birkofer has also found that reactions between N-(trimethylsilyl)-amides and various aldehydes occur, wherein, there is an attack of the silyl group on the oxygen of the aldehyde followed by coupling of the α -carbon of the aldehyde to the nitrogen of the amide. According to Birkofer this is a two step mechanism, which he writes as follows:



With N-(trimethylsilyl)succinimide the reaction between it and aldehydes apparently occurs very slowly. However, in the presence of a catalyst like $\text{NaOSi}(\text{CH}_3)_3$ the reaction occurs very quickly, according to following scheme;



The reaction between N-(trimethylsilyl)succinimide and an N-(methylhydroxy)amide was done by Böhm⁶⁸. However, here the silyl group attacks the methyl oxygen of the hydroxyl group and reacts as follows:



MASS SPECTRA OF Si - N BOND CONTAINING COMPOUNDS

Very little mass spectra data is available on Si-N bond containing compounds. A larger amount of effort, however, has been expended on silyl

ethers because of their extensive use for purification and identification purposes.

The mass spectra of α -functional organosilicon compounds and their organic analogues differ. This difference has been attributed to the extended delocalization found frequently in silicon compounds . This is illustrated by a comparison between the fragmentation pattern of tetraphenylmethane and tetraphenylsilane, wherein, important fragments of the tetraphenylsilane are due to unsaturated silicon moieties.⁶⁹

Some general trends in fragmentation patterns appear for the trimethylsilylethers and these can in some cases be generalized to the silicon-nitrogen bond containing compounds. Diekman⁷⁰ found that of the two possible fragmentations open to trimethylsilylethers the more favourable is the loss of a methyl from the molecule (M-15) giving in most cases the base peak. This base peak is regarded as the progenitor of most other fragments. Hydrogen transfer with elimination of an olefin is also a predominant fragment after the (M-15) ion has been formed in silylethers.

Diekman, from the mass spectra of benzyltrimethylsilylethers and para-substituted benzyltrimethylsilylethers found that the trimethylsilyl group was not a particularly good fragment director, M-CH₃ is a predominant fragment, the trimethylsilyl cation is present and the molecular ion is normally a very small amount of the total ion current.

The mass spectrum of N-(trimethylsilyl)benzylamine has the same major fragmentation pattern as that of the benzyltrimethylsilylethers. The M-CH₃ ion peak is almost as large as the base ion peak. The trimethylsilyl cation is found in greater abundance. Unlike the ethers a major source of fragmentation occurs via the loss of -CH = NH to produce $C_6H_5^{\dagger}Si(CH_3)_2$ and $(CH_3)_3Si^{\dagger}$.

Both ways of α -fragmentation are represented. Other benzyltrimethylsilylamines exhibit the same general behaviour. N-methyl - N-(trimethylsilyl)benzylamine shows a much different behaviour in terms of rearrangement, but the (M-15) peak still is the base peak ⁷⁰.

From Aylet's work ^{71,72}, N-phenylsilylamine gave a molecular ion peak, a M-2 ion supposed to be $\text{SiH}_2 = \text{NPh}^+$ (illustrating again the unsaturated nature of some silicon containing fragments) and the rest of the ions are due to the organic moiety; dimethylaminosilane gives the molecular ion, M-1, M-2, M-3, corresponding each to successive loss of hydrogen from silicon, after which the Si-N bond breaks.

The mass spectra of a number of silazanes have been done by Silbiger et al. ⁷³ For hexamethylcyclotrisilazane and octamethylcyclotetrasilazane the intensity of the molecular ion peak was small and the base peak was due to (M-15) ion in both. They both exhibit the ability to lose ammonia and methane from the M-15 ion and both exhibit the presence of doubly charged ions found for most of the above compounds. The other silazanes exhibit similar behaviour.

No mass spectra of silylimides or similar compounds were found. However, by considering the analogous organic compounds one would expect some similarities. For N-n-butylsuccinimide ⁷⁴ it is found that there is a relatively abundant molecular ion, there are less intense peaks due to α -, β - and γ -cleavage, there are peaks due to hydrogen transfer from the β - and γ -carbons and there is loss of CO from the ring. Also the ring tends to cleave into two fragments, $\cdot\text{CH}_2\text{CH}_2\text{C} \equiv \text{O}^+$ and/or $\text{RNC} \equiv \text{O}^+$. The spectra of aromatic phthalimides have been run and the loss of CO_2 from the imide is a major path to fragmentation for these compounds ⁷⁵.

N.M.R. SPECTRA OF SI-N BOND CONTAINING COMPOUNDS

Most of the proton n.m.r. studies of the Si-N bond containing compounds have been attempts to clarify the electronic nature of the Si-N bond, since there is some uncertainty as to the exact nature of this bond. The reason for this uncertainty is that many silicon containing compounds exhibit a behavior which can not be attributed to simple inductive effects. An example of this is the n.m.r. studies of silyl-substituted butadienes done by Bock ⁷⁶. For these experiments he finds that the silyl group on the butadiene behaves as an acceptor of electron density with respect to the carbon analogues. This he suggested was due to the participation of empty silicon 3d orbitals in the pi-system of butadiene because it would rationalize the fact that the -I effect was greater than +I effect of the silicon. However, there exists no documented example of multiple bonding between silicon and any other element. Therefore, these pi-interactions (referred to as $d_{\pi}-p_{\pi}$ interaction) are difficult to prove or disprove in any final way.

Since the Si-N bond is very likely to approach the multiple bonding extreme because of the availability of the nitrogen lone pair, proton n.m.r. studies of the compounds in this work could be a good source of evidence concerning $d_{\pi}-p_{\pi}$ interactions in the ground state. This is true because the nuclear magnetic resonance of a particular nucleus is sensitive to the electron density at that particular nuclei in the molecule.

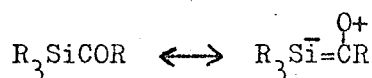
For N-trimethylsilyl-substituted heterocyclic compounds that contain a Si-N bond, "the chemical shifts of the methyl protons may be regarded as a measure of the extent to which the silicon atom shares the lone pair of electrons on the nitrogen atom of the Si-N bond, increasing δ -

values corresponding to reduced shielding." ⁴⁶ This statement is made by Birkofer on the basis of a comparison between N-trimethylsilyl-substituted compounds and the analogous N-t-butyl compounds, wherein, he finds that the chemical shifts of the methyl protons on the trimethylsilyl moiety are reduced by back donation of the nitrogen to the silicon.

INFRARED SPECTRA OF Si-N BOND CONTAINING COMPOUNDS

It has been found by Brook that organosilicon compounds having a carbonyl adjacent to silicon exhibits infrared properties considerably different in behavior from those of its carbon analogues ⁷⁷. The carbonyl absorption appears at remarkably low frequencies; 1645 cm⁻¹ for acetyl or propionyl silanes.

It has been suggested that these anomolous effects might be due to interaction of the unshared pair electrons of the oxygen atom of the carbonyl with the unoccupied but accessible d-orbitals of the silicon ⁷⁸. It seems reasonable that if such d_π-p_π interactions were associated with the anomolous spectral properties of α-silylketones that little effect would be observed for β-ketosilanes because of the poor overlap of the carbonyl oxygen with the silicon atom. Brook found that the carbonyl absorption frequency for the β-ketosilanes were the same as the carbon analogues. Thus, only when the silicon atom is directly attached to the carbonyl group are these anomolous effects observed and these are attributed to d_π-p_π interactions which can be represented by the following resonance structures.



However, an alternate explanation has been proposed. The SiR_3 groups are electron releasing with respect to their carbon analogues. As a result of electron release into the carbonyl adjacent to the silicon atom the carbonyl bond polarity would increase and therefore the carbonyl absorption frequency would decrease. This is opposite to the effect of placing an electron withdrawing group adjacent to the carbonyl which tends to decrease the bond polarity, thereby increasing the double bond character of the carbonyl and thus, raise the absorption frequency of the carbonyl 79.

Therefore, as can be seen the effect of the SiR_3 group adjacent to the carbonyl could be due to either the $+I_{\text{SiR}_3}$ effect, the $d_{\pi}-p_{\pi}$ effect, or to a combination of both.

For the imides prepared resonance structures can be written. The resonance interactions of the imide moiety will lower the carbonyl absorption frequency because the bond polarization of the carbonyl will be increased.



However, resonance interaction between the Si-N bond will tend to shift the electron density away from the the carbonyl reducing the bond polarity of the carbonyl bond. Therefore, if $d_{\pi}-p_{\pi}$ bonding occurs between the Si-N bond of these molecules to a large extent it will have the same effect as an electron withdrawing group and the carbonyl absorption frequency will increase. Thus, if $d_{\pi}-p_{\pi}$ bonding is a large effect, the carbonyl absorption frequency will be greater in the silyl-substituted imides than in the unsubstituted imides.

The $+I_{\text{SiR}_3}$ effect will increase the bond polarization of the carbonyl and therefore the carbonyl absorption frequency will decrease. Thus, if the $+I_{\text{SiR}_3}$ effect is large the carbonyl frequency will be lower in the silyl-substituted imides than in the unsubstituted imides.

Thus, the infrared spectra of these compounds should indicate which effect is the larger.

CONCLUSION

The compounds prepared in this work are useful in two ways. They supply more data concerning the electronic nature of a Si-N bond. They are useful precursors in silyl donor reactions where the final products desired have various R groups on the silicon. They are particularly good because of their powerful silyl donor properties and because the imide produced in such exchange reactions can be easily separated from the desired product since they are insoluble in most organic reagents.

GENERAL PROCEDURE, APPARATUS AND REAGENT

GENERAL

Due to the air and moisture sensitivity of most of the compounds, either used as starting materials or prepared, the handling of these compounds was carried out as much as possible either in a conventional vacuum gas rack or under a dry nitrogen atmosphere. When it was necessary to expose air sensitive compounds to the atmosphere, such exposure was kept at a minimum. All apparatus used to manipulate these compounds were dried at 120°C for three hours and flushed with dry nitrogen. A syringe was used to handle the chlorosilanes and hexamethyldisilazane. Microanalysis and molecular weight determinations (Rast method) was performed by Dr. Alfred Bernhardt at the Mikroanalytisches Laboratorium im Max - Planck - Institute, Mulheim, Germany.

INSTRUMENTAL

Infrared spectra were recorded by a Perkin-Elmer, Model 337, grating spectrophotometer, linear in wave number and covering the range of 4000-400 wave numbers. Liquid compounds were run as films between KBr discs. Solid compounds prepared were run as nujol mulls between KBr discs. The spectrum of the carbonyl stretching region and the silicon-hydrogen stretching region were run as 10^{-2} M and 10^{-1} M solutions respectively in dry chloroform using a KBr liquid cell of thickness 0.1 mm. All peak positions were determined to $\pm 1.0 \text{ cm}^{-1}$ using polystyrene for calibration.

All nuclear resonance spectra were recorded on a Varian A56/60 Analytical N.M.R. Spectrophotometer. Proton n.m.r. spectra were run as 10 mole percent solutions in deuterated chloroform. The protonated chloroform present as an

impurity in the deuterated chloroform was used as the internal reference standard where possible. Where this peak was masked by other peaks, the spectrum was run in deuterated chloroform, and then a drop of chloroform was added to give a reference peak. All samples were run in the same thin walled quartz n.m.r. sample tube at 40°C. The sample tube was pressure capped during spectra runs.

All mass spectra were run on a Hitachi, Perkin-Elmer, R.M.U. -6D mass spectrometer. The chamber temperature was 230±5°C. The ion source was run at 50 e.v. Solid samples were introduced directly to the ion source. Liquid samples were vapourized into the gas inlet system.

A Rinco variable temperature oven was used to fractionally distill liquid samples.

CHEMICALS

All the chlorosilanes used except trimethylchlorosilane (Matheson Coleman and Bell) were obtained from Penninsular Chemresearch Incorporated, and used without further purification.

Succinimide (Aldrich Chemical Company) was purified by two recrystallizations from water and dried in vacuo.

Phthalimide (Aldrich Chemical Company) was purified by two recrystallizations from water and dried in vacuo.

Potassium metal (Fischer Scientific Company) was used without further purification.

Hexamethyldisilazane (Pierce Chemical Company) was used without further purification.

Potassium phthalimide (Matheson, Coleman and Bell) was not suitable for

these reactions. It contained some impurity which led to unwanted products.

Tetrahydrofuran (T.H.F.) was refluxed vigorously for one hour over lithium aluminum hydride under dry nitrogen and then was distilled into the reaction flasks directly for use.

The chloroform was dried and purified according to Vogel⁸⁰.

Benzene was dried over sodium wire for three days and then distilled.

Anhydrous ethylether (Fisher Scientific Company) was used directly.

Pentan-1-ol (Fisher Scientific Company) was distilled with benzene to remove water; the fraction that was used boiled at 129-131°C.

EXPERIMENTAL

PART 1

CHLOROSILANES AND POTASSIUM SUCCINIMIDE

REACTION OF POTASSIUM METAL WITH SUCCINIMIDE

Potassium metal (1.17 g, 29.9 mmole) was cut into small pieces under dry cyclohexane. These pieces were added to succinimide (3.00 g, 30.3 mmole) in 35 ml of dry T.H.F. under dry nitrogen in a 250 ml two-necked round-bottom flask fitted with a reflux condenser. The mixture was refluxed at a moderate rate with stirring for two hours. A thick white precipitate was formed, identified as potassium succinimide. A small but undetermined amount of potassium metal did not react. The reaction mixture was cooled to 0°C in an ice bath prior to the addition of the chlorosilanes. This reaction was repeated for each reaction of potassium succinimide with a chlorosilane.

REACTION OF POTASSIUM SUCCINIMIDE WITH TRIMETHYLCHLOROSILANE

Trimethylchlorosilane (3.17 g, 29.0 mmole) was added slowly to a stirred mixture of potassium succinimide (4.10 g, 29.9 mmole) at 0°C, under dry nitrogen. A fine white precipitate was formed, identified by the silver nitrate test as a water soluble chloride salt presumed to be potassium chloride. Suction filtering through a sintered glass (M porosity) filter gave a pale yellow liquid filtrate. After pumping off the T.H.F. and unreacted trimethylchlorosilane, vacuum distillation gave a clear, colourless liquid identified as N-(trimethylsilyl)succinimide (1.51 g, 8.81 mmole, 30%, b.p. 120°C at 10⁻²mm).

Anal. calcd. for C₇H₁₃NO₂Si: C, 49.09; H, 7.65. Found: C, 49.25; H, 8.03.

The infrared spectrum (liquid phase, neat) is shown in figure 2(a). The infrared spectrum ($10^{-2}M$ solution) gave the value for the most intense carbonyl absorptionband as 1689 cm^{-1} .

Two singlets, one at 2.64 p.p.m. and one at 0.42 p.p.m. were found for the proton n.m.r. spectrum. The relative areas of the two peaks were found to be 4.1:9.2 and they were assigned to the $\text{SiNCO}(\text{CH}_2)_2\text{CO}$ and $-\text{Si}(\text{CH}_3)_3$ groups respectively.

The mass spectrum (Table 1(a)) was obtained by vapourizing the liquid sample into the gas inlet system at $100\pm 5^\circ\text{C}$.

TABLE 1(a) The ten most abundant peaks for the mass spectrum of N-(trimethylsilyl) succinimide.

<u>m/e</u>	<u>% Relative Abundance</u>
156	43.4
149	15.7
148	31.4
147	100.0
131	9.6
93	28.9
75	22.9
73	28.9
66	15.7
55	16.9

The molecular ion ($m/e = 171$) has an abundance equal to $<1\%$. Four peaks ($m/e = 217, 189, 184, 175$) appear above the parent ion. No metastable peaks were found.

REACTION OF POTASSIUM SUCCINIMIDE WITH TRIETHYLCHLOROSILANE

Using the above procedure, triethylchlorosilane (4.50 g, 29.9 mmole) was reacted with potassium succinimide (4.10 g, 29.9 mmoles), was filtered, and the T.H.F. and unreacted triethylchlorosilane were pumped off to yield a pale yellow liquid - solid mixture. Vacuum distillation of this mixture yielded a

clear colourless liquid identified as N-(triethylsilyl)succinimide. (2.05 g, 9.61 mmole, 32%, b.p. 150°C at 10⁻² mm).

Anal. calcd. for C₁₀H₁₉NO₂Si : C, 56.29; H, 8.98. Found: C, 55.92; H, 9.08.

The infrared spectrum (liquid phase, neat) is shown in figure 2(b). The infrared spectrum (10⁻²M solution) gave the value for the most intense carbonyl absorption peak as 1685 cm⁻¹.

Two singlets, one at 2.68 p.p.m. and one at 0.99 p.p.m., were found for the proton n.m.r. spectrum. The relative areas of the two peaks were 4.0:16.2 and these were assigned to the $\text{SiNCO}(\text{CH}_2)_2\text{CO}$ and the $(\text{CH}_3\text{CH}_2)_3\text{Si}$ groups respectively (fig 4(a)). The proton n.m.r. spectrum (neat, liquid phase) of the $(\text{CH}_3\text{CH}_2)_3\text{Si}$ - group on a 50 cycle sweep width showed that this singlet was unsymmetrical (fig 4(b)). The proton n.m.r. spectrum (10 mole percent solution in benzene) of the $(\text{CH}_3\text{CH}_2)_3\text{Si}$ group on a 50 cycle sweep width gave a multiplet (fig 4(c)). The proton n.m.r. spectrum (10 mole percent in chloroform) on a 500 cycle sweep width, when varied in temperature from -80°C to +40°C in 20°C steps showed no change in the peaks except for natural line width broadening at low temperatures.

The mass spectrum (table 1(b)) was obtained by vapourizing a liquid sample into the gas inlet system at 100 ± 5°C.

TABLE 1(b) The ten most abundant peaks for the mass spectrum of N-(triethylsilyl)succinimide.

<u>m/e</u>	<u>% Relative Abundance</u>
218	43.5
187	67.1
186	100 *
185	100 *
157	76.5
104	100.0
101	29.4
76	100.0
73	42.4
56	74.1

* Off scale

The molecular ion ($m/e = 213$) has an abundance of less than 1%. Five measurable metastable peaks are found at $m/e = 55.8$, 58.8 , 133.1 , 166.0 and 138.1 .

This mass spectrum was repeated two times and the ion at $m/e = 218$ remained in both at approximately the same abundance.

REACTION OF DIMETHYLCHLOROSILANE WITH POTASSIUM SUCCINIMIDE

Using the above procedure, dimethylchlorosilane (4.75 g, 29.5 mmole) was reacted with potassium succinimide (4.10 g, 29.9 mmole), was filtered, and the T.H.F. and unreacted dimethylchlorosilane were pumped off to yield a pale yellow liquid - solid mixture. Vacuum distillation yielded a clear colourless liquid identified as N-(dimethylsilyl)succinimide. (2.09 g, 12.3 mmole, 28%, b.p. 120°C at 10^{-2}mm).

Anal. calcd. for $\text{C}_6\text{H}_{11}\text{NO}_2\text{Si}$: C, 45.84; H, 7.05, Found: C, 45.93; H, 7.35.

The infrared spectrum (liquid phase, neat) is shown in figure 2(c). The infrared spectrum (10^{-2}M solution) gave the value for the most intense carbonyl absorption peak as 1717 cm^{-1} . The infrared spectrum (10^{-1}M solution) gave the value for the most intense carbonyl absorption peak as 1698 cm^{-1} and gave the value for the Si-H absorption peak as 2192 cm^{-1} .

A septet, a singlet and a doublet, at 4.68 p.p.m. ($J = 3.6 \pm 0.1$ cps), 2.66 p.p.m., and at 0.42 p.p.m. ($J = 3.7 \pm 0.1$ cps) respectively were found for the proton n.m.r. spectrum. The relative areas of the three sets of peaks were found to be 0.8:4.0:6.4 and they were assigned to the SiH , $\text{SiNCO}(\text{CH}_2)_2\text{CO}$ and $(\text{CH}_3)_2\text{Si} =$ groups respectively.

This compound was found to be particularly air sensitive.

REACTION OF ALLYLDIMETHYLCHLOROSILANE WITH POTASSIUM SUCCINIMIDE

Using the above procedure, allyldimethylchlorosilane (4.03 g, 29.9 mmoles) was reacted with potassium succinimide (4.10 g, 29.9 mmole) was filtered, and the T.H.F. and unreacted allyldimethylchlorosilane were pumped off to yield a pale yellow liquid - solid mixture. Vacuum distillation yielded a clear colourless liquid identified as N-(allyldimethylsilyl)succinimide (2.07 g, 10.5 mmole, 35%, b.p. 170°C at 10⁻²mm).

Anal. calcd. for C₉H₁₅NO₂Si : C, 54.28; H, 7.66. Found: C, 55.18; H, 8.04.

The infrared spectrum (liquid phase, neat) is shown in figure 2(d). The infrared spectrum (10⁻²M solution) gave the value for the most intense carbonyl absorption peak as 1696 cm⁻¹.

A singlet at 2.65 p.p.m., a doublet at 1.91 p.p.m., a singlet at 0.43 p.p.m., a multiplet centred at 5.89 p.p.m. and a multiplet centred at 4.82 p.p.m. were found for the proton n.m.r. spectrum. The relative areas of the peaks were 4.5:2.5:6.2:1.4:2.2 and they were assigned to the SiCO(CH₂)₂CO, CH₂ = CH - CH₂ -, = Si(CH₃)₂, CH₂ = CH - CH₂ -, and the CH₂ = CH - CH₂ - groups respectively.

The mass spectrum table 1(c) was obtained by vapourizing a liquid sample into the gas inlet system at 100 ± 5°C.

TABLE 1(c) The ten most abundant peaks for the mass spectrum of N-(allyldimethylsilyl) succinimide.

<u>m/e</u>	<u>% Relative Abundance</u>
217	16.5
190	11.8
185	38.8
184	100 *
156	17.6
103	100.0
75	92.9
72	15.3
55	28.2
45	16.5

* Off Scale

The molecular ion (m/e 197) appears with less than 1.0% abundance.

Two measurable metastable peaks were found at m/e = 54.6 and 57.7 .

REACTION OF PHENYLMETHYLCHLOROSILANE WITH POTASSIUM SUCCINIMIDE

Using the above procedure, phenylmethylchlorosilane (4.68 g, 29.9 mmole) was reacted with potassium succinimide (4.10 g, 29.9 mmole), was filtered, and the T.H.F. and unreacted phenylmethylchlorosilane were pumped off to yield a pale yellow liquid-solid mixture. Vacuum distillation yielded a clear colourless liquid identified as N-(phenylmethylsilyl)succinimide (1.95 g, 8.89 mmole, 19%, b.p. 200°C at 10⁻²mm).

Anal. calcd. for C₁₁H₁₃ NO₂Si : C, 60.25; H, 5.97. Found: C, 60.24; H, 6.49.

The infrared spectrum (liquid phase, neat) is shown in figure 2(e). A small amount of succinimide impurity is evident from this spectrum. The infrared spectrum (10⁻²M solution) gave the value for the most intense carbonyl absorption peak as 1670 cm⁻¹. The infrared spectrum (10⁻¹M solution) gave the value for the most intense carbonyl absorption peak as 1697 cm⁻¹ and gave the value for the Si-H absorption peak as 2200 cm⁻¹ fig 3(b).

A singlet at 2.66 p.p.m., a quartet at 5.22 p.p.m. (J = 3.6 ± 0.1 cps), a doublet at 0.70 p.p.m. (J = 3.6 ± 0.1 cps) and a multiplet centred at 7.49 p.p.m., were found for the proton n.m.r. spectrum. The relative areas of the peaks were 5.0:1.0:3.3:6.6 and they were assigned to the $\text{Si-CH}_2\text{CO}$, Si-H , SiCH_3 and $\text{C}_6\text{H}_5\text{Si}$ groups respectively.

The mass spectrum (table 1(d)) was obtained by vapourizing a liquid sample into the gas inlet system at 130°C ± 5°C.

TABLE 1(d) The ten most abundant peaks for the mass spectrum of N-(phenylmethylsilyl)succinimide.

<u>m/e</u>	<u>% Relative Abundance</u>
217	68.5
189	52.5
175	40.5
161	31.6
147	47.4
105	42.1
99	100.0
77	42.1
56	57.9
28	100.0

The molecular ion ($m/e = 219$) had an abundance of 13.2%. One metastable peak was found at $m/e=165.0$.

REACTION OF DIPHENYLMETHYLCHLOROSILANE WITH POTASSIUM SUCCINIMIDE

Using the above procedure, diphenylmethylchlorosilane (6.94 g, 29.9 mmole) was reacted with potassium succinimide (4.10 g, 29.9 mmole), was filtered, and the T.H.F. and unreacted phenyldimethylchlorosilane were pumped off to yield a pale yellow solid. The solid was dissolved in dry benzene, insoluble succinimide was filtered off and a white crystalline solid was obtained by recrystallization which was identified as N-(diphenylmethylsilyl)succinimide. (2.04 g, 6.94 mmole, 25%, m.p. 88-90°C).

Anal. calcd. for $C_{17}H_{17}NO_2Si$: C, 69.12; H, 5.80. Found C, 68.85; H, 5.83.

The infrared spectrum (nujol mull) is shown in figure 2(f). The infrared spectrum ($10^{-2}M$ solution) gave the value for the most intense carbonyl absorption peak as 1696 cm^{-1} .

A singlet at 2.55 p.p.m., a singlet at 0.98 p.p.m. and a multiplet centred at 7.34 p.p.m. were found for the proton n.m.r.. The relative peak

areas were 4.5:3.0:10.8 and they were assigned to the $\text{SiNCO}(\text{CH}_2)_2\text{CO}$, SiCH_3 and $(\text{C}_6\text{H}_5)_2\text{Si} =$ groups respectively.

Attempts to purify this compound by sublimation led to an increase in the impurity peaks found in the proton n.m.r. spectrum of the sublimate as compared with the spectrum of the recrystallized product. Sublimation was carried out at 70°C at 10^{-4}mm of Hg.

The mass spectrum (table 1(e)) was obtained for a sample temperature of $25 \pm 5^\circ\text{C}$.

TABLE 1(e) The ten most abundant peaks for the mass spectrum of N-(diphenylmethylsilyl)succinimide.

<u>m/e</u>	<u>% Relative Abundance</u>
295	13.8
281	24.1
280	100.0
218	44.9
199	27.6
195	15.5
181	12.1
137	20.7
99	12.1
28	10.3

Two metastable peaks were observed at $m/e=266.1$ and 254.5 .

REACTION OF PHENYLDIMETHYLCHLOROSILANE WITH POTASSIUM SUCCINIMIDE

Using the above procedure phenyldimethylchlorosilane (5.10 g, 29.9 mmole.) was reacted with potassium succinimide (4.10 g, 29.9 mmole) was filtered, and the T.H.F. and unreacted phenyldimethylchlorosilane were pumped off to yield a pale red solid. Recrystallization from dry benzene yielded a white solid identified as N-(phenyldimethylsilyl)succinimide. (1.38 g, 5.95 mmole, 20%, m.p. $47-49^\circ\text{C}$).

Anal. calcd. for $\text{C}_{12}\text{H}_{15}\text{NO}_2\text{Si}$: C, 61.77; H, 6.48, Found: C, 62.33; H, 6.43.

The infrared spectrum (nujol mull) is shown in figure 2(g). The infrared spectrum ($10^{-2}M$ solution) gave the value for the most intense carbonyl absorption peak as 1695 cm^{-1} .

A singlet at 2.58 p.p.m., a multiplet centred at 7.50 p.p.m. and a singlet at 0.72 p.p.m. were found for the proton n.m.r. spectrum. The relative peak areas were 4.0:4.35:5.1 and they were assigned to the $\text{=SiNCO(CH}_2\text{)}_2\text{CO}$, $\text{=SiC}_6\text{H}_5$ and $\text{=Si(CH}_3\text{)}_2$ groups respectively.

REACTION OF DIMETHYLDICHLOROSILANE WITH POTASSIUM SUCCINIMIDE

Using the above procedure, potassium metal (3.96 g, 99.0 mmole) was reacted with succinimide (10.02 g, 101 mmole) in 70 ml dry T.H.F. Dimethyldichlorosilane (6.50 g, 50.4 mmole) was reacted with the potassium succinimide (13.83 g, 101 mmole), was filtered and the T.H.F. and unreacted dimethyldichlorosilane were pumped off yielding a pale yellow liquid-solid mixture. The mixture was dissolved in dry benzene and the insoluble succinimide was filtered off. Vacuum distillation of the filtrate for four days yielded a viscous clear pale yellow liquid identified as N-(N'-succinimidodimethylsilyl)succinimide. (1.29 g, 5.04 mmole, 10%, b.p. 100°C at 10^{-4}mm).

Anal. calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_4\text{Si}$: C, 47.24; H, 5.54. Found: C, 46.73; H, 5.70.

The infrared spectrum (liquid phase, neat) is shown in figure 2(h).

A singlet at 0.77 p.p.m. and a singlet at 2.64 p.p.m. were found for the proton n.m.r. spectrum. The relative peak areas were 6.0:9.6 and they were assigned to the $\text{=Si(CH}_3\text{)}_2$ and two $\text{-NCO(CH}_2\text{)}_2\text{CO}$ groups respectively.

This compound was particularly sensitive to moisture.

REACTION OF METHYL VINYLDICHLOROSILANE WITH POTASSIUM SUCCINIMIDE

Following the above procedure, methylvinylchlorosilane (7.06 g, 50.5 mmole) was reacted with potassium succinimide (5.01 g, 50.5 mmole), was filtered, and the T.H.F. and unreacted methylvinylchlorosilane were pumped off to yield a pale yellow solid-liquid mixture. The mixture was dissolved in dry benzene and the insoluble succinimide was filtered off. Vacuum distillation of the filtrate for four days yielded a pale yellow liquid identified as N-(N'-succinimidomethylvinylsilyl)succinimide. (1.34 g, 5.04 mmole, 10%, b.p. 100°C at 10⁻⁴mm).

No analysis was obtained due to the instability of this compound.

The infrared spectrum (neat, liquid phase) is shown in figure 2(i).

The presence of a small amount of succinimide impurity can be detected from this spectrum.

A singlet at 2.63 p.p.m., a singlet at 0.89 p.p.m. and a multiplet centred at 6.08 p.p.m. were found for the proton n.m.r. spectrum. The relative peak areas were 10.2:3.0:4.6 and they were assigned to the two $\text{-NCO(CH}_2\text{)}_2\text{CO}$, ≡SiCH_3 and $\text{CH}_2 = \text{CH-Si}$ groups respectively.

PART II

POTASSIUM PHTHALIMIDE AND CHLOROSILANES

REACTION OF POTASSIUM PENTOXIDE WITH PHTHALIMIDE

Following the method of Hammick and Lockett⁸¹ phthalimide (5.4 g, 36.8 mmole) was dissolved in 70 ml of pentan-1-ol at 100°C and then added to a solution of potassium pentoxide in 60 mls of pentan-1-ol at 100°C (made by adding potassium metal (2.15 g, 55.0 mmoles) to 60 ml of pentan-1-ol). A white precipitate was formed. The mixture was cooled to 0°C, filtered, washed with three 20 ml portions of anhydrous ethylether and dried to yield a white solid identified as potassium phthalimide (5.1 g, 27.6 mmoles, 75%).

REACTION OF POTASSIUM PHTHALIMIDE WITH TRIMETHYLCHLOROSILANE

Potassium phthalimide (5.11 g, 27.6 mmole) was added to 50 ml dry T.H.F. in a 150 ml, two necked, round-bottomed flask with a reflux condenser. Trimethylchlorosilane (2.99 g, 27.6 mmole) was added slowly with stirring. The reaction was heated to 60°C for 15 minutes, then cooled to 0°C, filtered through a sintered glass filter (M) and the T.H.F. and unreacted trimethylchlorosilane were pumped off to yield a white solid. The solid was dissolved in dry benzene, the insoluble phthalimide was filtered off and a white crystalline solid was recrystallized from the filtrate and identified as N-(trimethylsilyl)phthalimide (2.63 g, 12.0 mmole, 44%, m.p. 65-67°C).

Anal. calcd. for $C_{10}H_{13}NO_2Si$: C, 60.24; H, 5.98. Found: C, 60.41; H, 6.01.

Molecular weight calcd: 219, Found: 209.

The infrared spectrum (nujol mull) is shown in figure 2(j). The infrared

spectrum ($10^{-2}M$ solution) gave the value for the most intense carbonyl absorption peak as 1700 cm^{-1} .

A singlet at 0.80 p.p.m., and a multiplet centred at 7.69 p.p.m. were found for the proton n.m.r. spectrum. The relative peak areas were 9.3:4.0 and they were assigned to the $-\text{Si}(\text{CH}_3)_3$ and $-\text{Si}-\text{NCOC}_6\text{H}_4\text{CO}$ groups respectively.

The mass spectrum (table 1(f)) was obtained at a sample temperature of 33°C .

TABLE 1(f) The ten most abundant peaks of the mass spectrum of N-(trimethylsilyl)phthalimide

<u>m/e</u>	<u>% Relative Abundance</u>
205	42.1
204	100 *
161	23.7
160	100.0
130	92.1
102	85.5
76	18.4
75	17.1
28	21.1
18	23.7

*Off scale

Two metastable peaks were observed at $m/e=80.1$ and 125.5 . The molecular ion at $m/e=219$ had an abundance of 3%.

REACTION OF TRIETHYLCHLOROSILANE WITH POTASSIUM PHTHALIMIDE

Using the above procedure, triethylsilylchlorosilane (8.0 g, 53.4 mmole) was reacted with potassium phthalimide (10.0 g, 54.1 mmole), was filtered, and the T.H.F. and the unreacted triethylchlorosilane were pumped off yielding a liquid-solid mixture. Vacuum distillation of this mixture yielded a clear colourless liquid identified as N-(triethylsilyl)phthalimide (4.3 g, 16.5 mmole, 48 %, b.p. 112°C at 10^{-2}mm).

Anal. calcd. for $C_{14}H_{19}NO_2Si$: C, 64.32; H, 7.34. Found: C, 64.06; H, 7.34.

The infrared spectrum (neat, liquid phase) is shown in figure 2(k). The infrared spectrum ($10^{-2}M$ solution) gave the value for the most intense carbonyl absorption peak as 1701 cm^{-1} .

A singlet at 1.00 p.p.m. and a multiplet centred at 7.73 p.p.m. (relative to internal chloroform) were found for the proton n.m.r. spectrum (10 mole percent solution). (fig 5(a)). The relative peak areas were 15.4:4.0 and they were assigned to the $(CH_2CH_2)_3Si$ - and $\underline{\underline{SiNCOC_6H_4CO}}$ groups respectively. The proton n.m.r. (neat, liquid phase) spectrum for a 50 cycle scan width of the singlet assigned to the $-Si(CH_2CH_2)_3$ group revealed that the singlet was unsymmetrical. (fig 5(b)). The proton n.m.r. spectrum (10 mole percent solution in deuterated benzene) of the $-Si(CH_2CH_2)_3$ group on 50 cycle scan width gave a multiplet. (fig 5(c)). A 50 cycle scan of the phenyl protons gave two sets of peaks that were mirror images and separated by approximately 9.6 c.p.s. (fig 5(d)).

REACTION OF DIMETHYLCHLOROSILANE WITH POTASSIUM PHTHALIMIDE

Using the above procedure, dimethylchlorosilane (3.3 g, 35.1 mmole) was reacted with potassium phthalimide (6.46 g, 34.9 mmole), was filtered, and the T.H.F. and unreacted dimethylchlorosilane were pumped off yielding a white solid. Recrystallization from dry benzene yielded a white crystalline solid identified as N-(dimethylsilyl)phthalimide. (4.6 g, 22.4 mmole, 64%, m.p. 63-65°C).

Anal. calcd. for $C_{10}H_{11}NO_2Si$: C, 58.51; H, 5.40. Found: C, 58.71; H, 5.03.

Molecular weight calcd: 205. Found: 199

The infrared spectrum (nujol mull) is shown in figure 2(1). The infrared spectrum ($10^{-2}M$ solution) gave the value for the most intense carbonyl absorption peak as 1706 cm^{-1} . The infrared spectrum ($10^{-1}M$ solution) gave the value for the most intense carbonyl absorption peak as 1710 cm^{-1} and gave the value for $\nu(\text{Si-H})$ as 2188 cm^{-1} (fig 5(c)).

A doublet centred at 0.50 p.p.m. ($J = 3.4 \pm 0.1 \text{ cps.}$). A septet centred at 6.58 p.p.m. ($J = 3.4 \pm 0.1 \text{ cps.}$), and a multiplet centred at 7.72 p.p.m. were found for the proton n.m.r. spectrum. The relative peak areas were 7.8:1.0:5.4 and they were assigned to the $-\text{Si}(\text{CH}_3)_2$, $-\text{Si-H}$ and $-\text{Si}(\text{COC}_6\text{H}_4\text{CO})$ groups respectively.

REACTION OF ALLYLDIMETHYLCHLOROSILANE WITH POTASSIUM PHTHALIMIDE

Using the above procedure, allyldimethylchlorosilane (4.56 g, 34.2 mmole) was reacted with potassium phthalimide (6.34 g, 34.2 mmole), was filtered, and the T.H.F. and unreacted allyldimethylchlorosilane were pumped off yielding a white solid. Recrystallization from dry benzene yielded a white crystalline solid identified as N-(allyldimethylsilyl)phthalimide. (4.5 g, 18.4 mmole, 55%, m.p. $27-29^\circ\text{C}$).

Anal. calcd. for $\text{C}_{13}\text{H}_{15}\text{NO}_2\text{Si}$: C, 63.65; H, 6.16. Found: C, 63.86; H, 6.20.

The infrared spectrum (nujol mull) is shown in figure 2(m). The infrared spectrum ($10^{-2}M$ solution) gave the value for the most intense carbonyl absorption peak as 1694 cm^{-1} .

A multiplet centred at 1.97 p.p.m., a multiplet centred at 7.86 p.p.m., a multiplet centred at 5.77 p.p.m., a multiplet centred at 4.86 p.p.m. and a singlet at 0.46 p.p.m. were found for the proton n.m.r. spectrum. The

relative peak areas were 2.2:4.6:1.0:2.0:6.4 and they were assigned to the $\text{CH}_2 = \text{CH}-\text{CH}_2-\text{Si}^-$, $\text{Si}^-\text{COC}_6\text{H}_5\text{CO}$, $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{Si}^-$, $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{Si}^-$, and $\text{Si}(\text{CH}_3)_2$ groups respectively.

REACTION OF PHENYLMETHYLCHLOROSILANE WITH POTASSIUM PHTHALIMIDE

Using the above procedure, phenylmethylchlorosilane (5.00 g, 32.0 mmoles) was reacted with potassium phthalimide (6.09 g, 32.8 mmole) was filtered, and the T.H.F. and unreacted phenylmethylchlorosilane were pumped off to yield a white solid. Recrystallization from dry benzene yielded a white crystalline solid identified as N-(phenylmethylsilyl)phthalimide (5.52 g, 19.6 mmole, 64%, m.p. 226-229°C).

Anal. calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_2\text{Si}$: C, 67.39; H, 4.90. Found: C, 67.65; H, 4.67.

The infrared spectrum (nujol mull) is shown in figure 2(n). The infrared spectrum (10^{-2}M solution) gave the value for the most intense carbonyl absorption peak as 1707 cm^{-1} . The infrared spectrum (10^{-1}M solution) gave the value for the most intense carbonyl absorption peak as 1706 cm^{-1} and gave the value for the Si-H stretching band as 2194 cm^{-1} . (fig 3(d)).

A multiplet centred at 7.68 p.p.m., a quartet centred at 5.39 p.p.m. ($J = 3.6 \pm 0.1$ cps.), a multiplet centred at 7.31 p.p.m. and a doublet centred at 9.82 p.p.m. ($J = 3.6 \pm 0.1$ cps) were found for the proton n.m.r. spectrum. The relative peak areas were 1.0:2.9:9.3: and were assigned to the Si^-H , Si^-CH_3 groups and the nine protons of the $\text{Si}^-\text{C}_6\text{H}_5$ and $\text{Si}^-\text{COC}_6\text{H}_4\text{CO}$ groups. The multiplet centred at 7.31 p.p.m. was assigned to the $\text{Si}^-\text{C}_6\text{H}_5$ group and the multiplet at 7.68 p.p.m. was assigned to the $\text{Si}^-\text{COC}_6\text{H}_4\text{CO}$ groups.

REACTION OF PHENYLDIMETHYLCHLOROSILANE WITH POTASSIUM PHTHALIMIDE

Using the above procedure, phenyldimethylchlorosilane (5.72 g, 33.6 mmole) was reacted with potassium phthalimide (5.72 g, 30.9 mmole) was filtered, and the T.H.F. and unreacted phenyldimethylchlorosilane were pumped off to yield a white solid. Recrystallization from dry benzene yielded a white crystalline solid identified as N-(phenyldimethylsilyl)phthalimide. (3.41 g, 12.1 mmole, 40%, m.p. 87-89°C).

Anal. calcd. for $C_{16}H_{15}NO_2Si$: C, 68.30; H, 5.37. Found: C, 68.47; H, 5.59.

The infrared spectrum (nujol mull) is shown in figure 2(o). The infrared spectrum ($10^{-2}M$ solution) gave the value for the most intense carbonyl absorption peak as 1695 cm^{-1} .

A multiplet centred at 7.74 p.p.m., a multiplet centred at 7.37 p.p.m. and a singlet at 0.87 p.p.m. were found for the proton n.m.r. spectrum. The relative peak areas were 8.8:6.0 and they were assigned to all the phenyl protons (9 in all) and the $[-Si(CH_3)_2]$ group respectively. The multiplet centred at 7.37 p.p.m. was assigned to the $[-SiC_6H_5]$ group and the multiplet centred at 7.74 p.p.m. was assigned to the phenyl protons of phthalimide.

The mass spectrum (table 1(g)) was obtained at a sample temperature of $23 \pm 5^\circ C$.

TABLE 1(g). The ten most abundant peaks for the mass spectrum of N-(phenyldimethylsilyl)succinimide.

<u>m/e</u>	<u>% Relative Abundance</u>
268	32.5
267	100.0
266	100 *
222	90.8
204	72.1
203	32.6
195	24.4
130	100.0
102	98.8
76	22.1

*Off scale

The molecular ion ($m/e = 281$) had an abundance of 10%. Three metastable peaks were observed at $m/e=185.7, 251.9$ and 80.1 .

REACTION OF DIPHENYLMETHYLCHLOROSILANE WITH POTASSIUM PHTHALIMIDE

Using the above procedure diphenylmethylchlorosilane (8.1 g, 34.9 mmole) was reacted with potassium phthalimide (6.6 g, 35.6 mmole), was filtered, and the T.H.F. and unreacted diphenylmethylchlorosilane were pumped off to yield a white solid. Recrystallization from dry benzene yielded a white crystalline solid identified as N-(diphenylmethylsilyl)phthalimide. (5.4 g, 15.1 mmole, 46%, m.p. $109-111^{\circ}\text{C}$).

Anal. calcd. for $\text{C}_{21}\text{H}_{17}\text{NO}_2\text{Si}$: C, 72.48; H, 5.17. Found: C, 72.70; H, 4.79.

The infrared spectrum (nujol mull) is shown in figure 2(p). The infrared spectrum (10^{-2}M solution) gave the value for the most intense carbonyl absorption peak as 1713 cm^{-1} .

A singlet at 1.25 p.p.m., a multiplet centred at 7.52 p.p.m. and a multiplet centred at 7.85 p.p.m. were found for the proton n.m.r. spectrum. The relative peak areas were 3.0:13.8 and they were assigned to the SiCH_3 group and the phenyl protons of the molecule (14 in all). The multiplet at 7.85 p.p.m. was assigned to the phenyl protons of phthalimide and the multiplet at 7.52 p.p.m. was assigned to the $\text{Si}(\text{C}_6\text{H}_5)_2$ group.

The mass spectrum (table 1(h)) was obtained at a sample temperature of $25 \pm 5^{\circ}\text{C}$.

TABLE 1(h) The ten most abundant peaks of the mass spectrum of N-(diphenylmethylsilyl)phthalimide.

<u>m/e</u>	<u>% Relative Abundance</u>
329	28.6
328	100.0
266	39.3
222	8.9
148	10.7
130	52.6
105	14.3
104	8.9
102	32.2
76	12.5

Three metastable peaks were observed at $m/e=80.1, 245.9$ and 185.1 . The molecular ion at $m/e=343$ had an abundance of 7.1%.

PART III

HEXAMETHYLDISILAZANE AND THE IMIDES

REACTION OF HEXAMETHYLDISILAZANE WITH SUCCINIMIDE

Succinimide (2.54 g, 25.4 mmole) was added to 100 mls of dry T.H.F. in a 150 ml round-bottom, two-necked flask fitted with a reflux condenser. Hexamethyldisilazane (3.84 g, 23.4 mmole) was added. The reaction was refluxed and stirred at moderate rates under dry nitrogen for 6 hours. The T.H.F. and unreacted hexamethyldisilazane were pumped off yielding a solid-liquid mixture. Vacuum distillation yielded a colourless clear liquid identified as N-(trimethylsilyl)succinimide. (1.1 g, 6.4 mmole, 25%, 120°C at 10⁻² mm). The infrared and proton n.m.r. spectra of this compound were identical to those of the N-(trimethylsilyl)succinimide prepared by the reaction of potassium succinimide and trimethylchlorosilane.

REACTION OF HEXAMETHYLDISILAZANE WITH PHTHALIMIDE

Using the above procedure phthalimide (3.68 g, 25.0 mmole) was reacted with hexamethyldisilazane (3.78 g, 23.0 mmole), the solvent and hexamethyldisilazane were pumped off to yield a white solid. Recrystallization from dry benzene yielded a white crystalline solid identified as N-(trimethylsilyl)phthalimide. (2.14 g, 9.7 mmole, 38%, m.p. 65-67°C). The infrared and proton n.m.r. spectra of this compound were identical to those of the N-(trimethylsilyl)phthalimide prepared from the reaction of potassium phthalimide and trimethylchlorosilane.

PART IV

PHYSICAL PROPERTIES OF THE STARTING MATERIALS

SUCCINIMIDE

The infrared spectrum (nujol mull) is shown in figure 5(q). The infrared spectrum ($10^{-2}M$ solution) gave the value for the most intense carbonyl absorption peak as 1717 cm^{-1} .

The mass spectrum (table 1(i)) was run at $25 \pm 5^{\circ}C$.

TABLE 1(i) The ten most abundant peaks for the mass spectrum of succinimide.

<u>m/e</u>	<u>% Relative Abundance</u>
100	5.8
99	100.0
70	5.8
56	61.6
55	8.1
28	74.5
27	10.5
26	8.1
18	30.1
17	5.8

PHTHALIMIDE

The infrared spectrum (nujol mull) is shown in figure 5(r). The infrared spectrum ($10^{-2}M$ solution) gave the value for the most intense carbonyl absorption peak as 1736 cm^{-1} .

The mass spectrum (table 1(j)) was run at $25 \pm 5^{\circ}C$.

CHLOROSILANES

In table 2 are listed δ -values of the chlorosilanes used as starting materials. The δ -values are relative to internal chloroform and obtained for 10 mole percent solutions in deuterated chloroform.

TABLE 1(j) The ten most abundant peaks for the mass spectrum of phthalimide.

<u>m/e</u>	<u>% Relative Abundance</u>
148	5.9
147	49.5
105	94.1
104	100.0
103	51.7
76	64.7
75	12.9
74	11.8
50	58.9
28	4.7

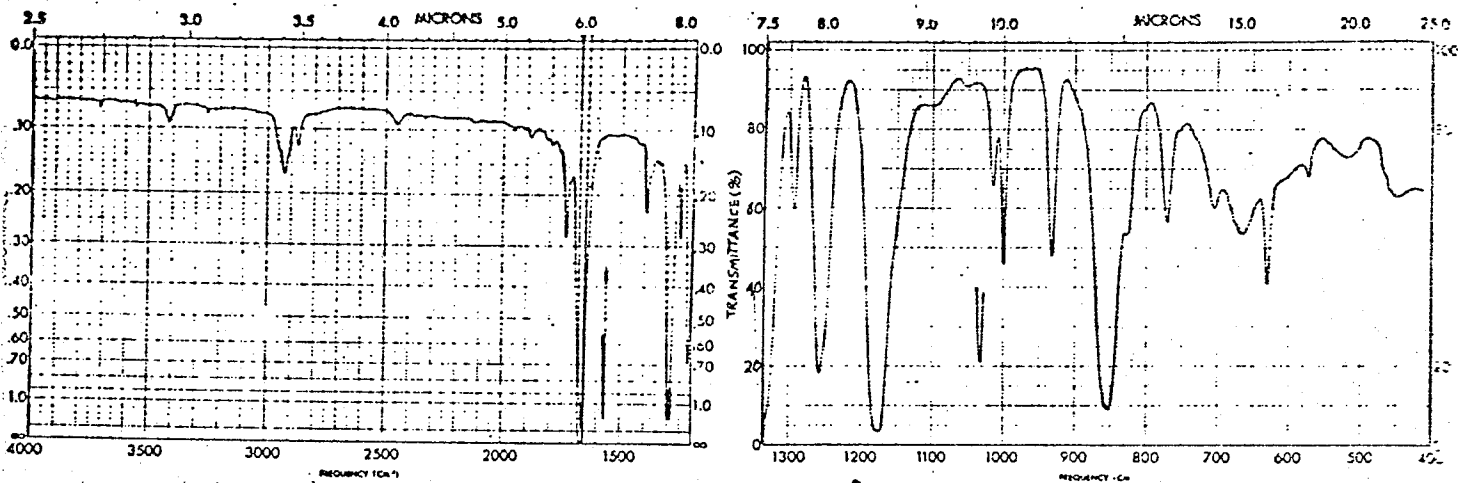
TABLE 2. δ (ppm) values for R groups of chlorosilanes used as starting materials.

COMPOUND	δ (p.p.m.) R					
	CH ₃	CH ₃ CH ₂	C ₆ H ₅	H	CH ₂ = CH CH ₂	CH ₂ = CH - CH ₂ CH CH ₂
(CH ₃) ₃ SiCl	0.53 s					
(CH ₃ CH ₂) ₃ SiCl		0.95m				
(CH ₃) ₂ HSiCl	0.59 d, J=3.1			4.90 sep, J=3.1		
C ₆ H ₅ (CH ₃) ₂ SiCl	0.75 s		7.36m			
(C ₆ H ₅) ₂ CH ₃ SiCl	1.01 s		7.60m			
C ₆ H ₅ CH ₃ HSiCl	0.88 d, J=3.3		7.53m	5.39 q J=3.2		
CH ₂ = CH-CH ₂ (CH ₃) ₂ SiCl	0.51 s					1.87m 5.83m 5.19m
(CH ₃) ₂ SiCl ₂	J.89 s					
CH ₂ = CHCH ₃ SiCl ₂	0.95 s				6.08m 6.18m	

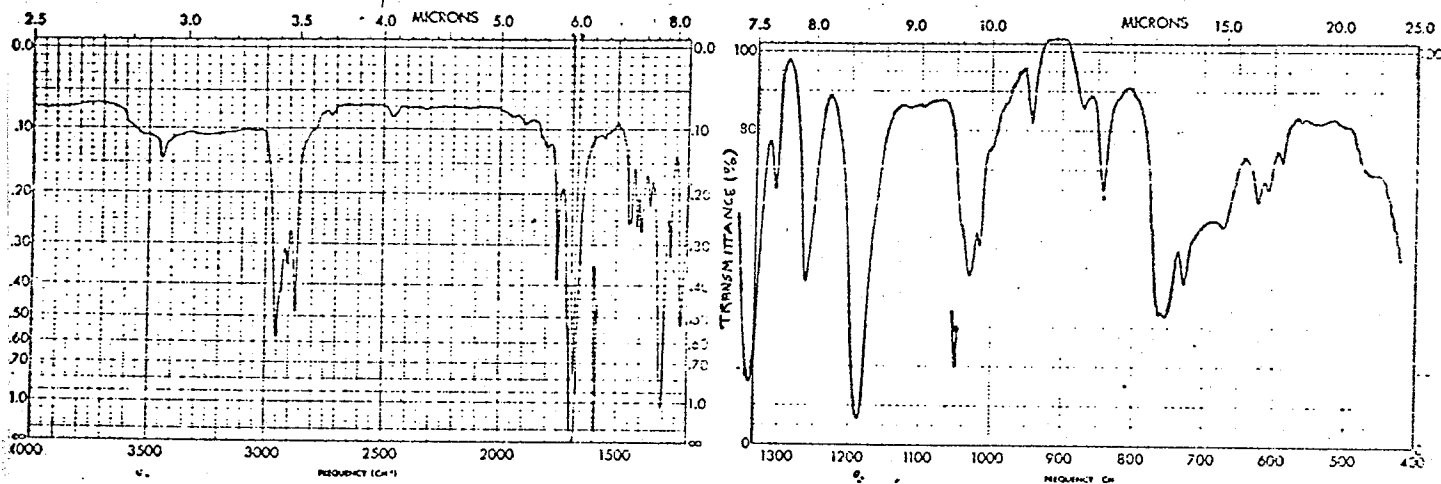
CHCl₃ was used as the internal standard. s=singlet, d=doublet, m=multiplet, q=quartet and sep=septet.

FIGURE 2

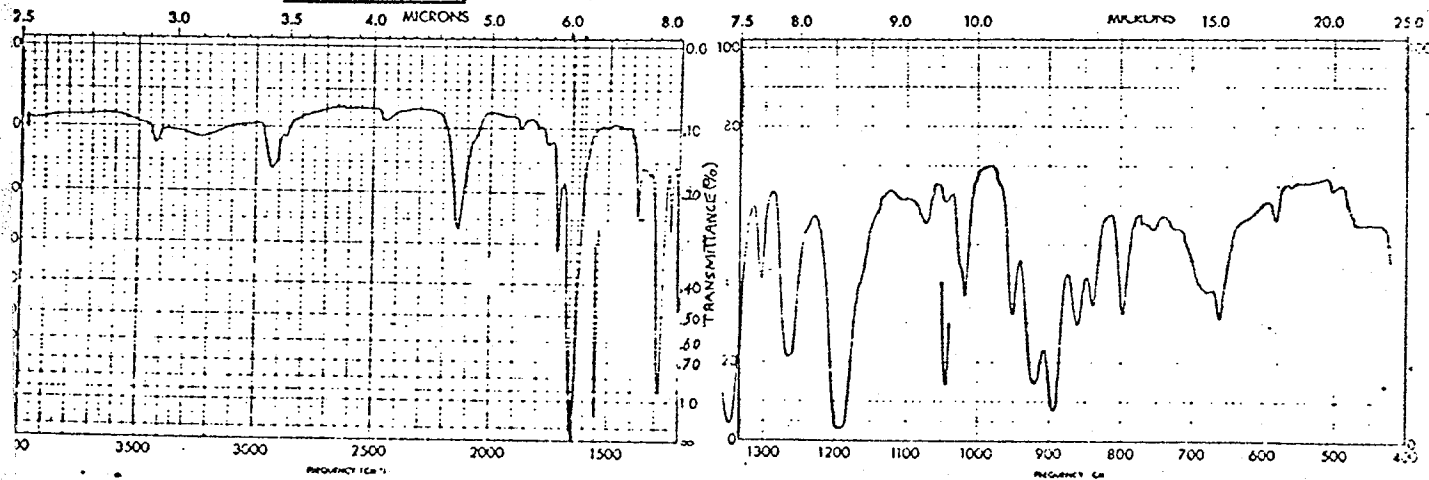
Infrared Spectra of $R_3SiNC(CH_2)_2CO$ and $R_3SiNCOC_6H_4CO$



a) $(CH_3)_3SiNC(CH_2)_2CO$, liquid phase, neat.

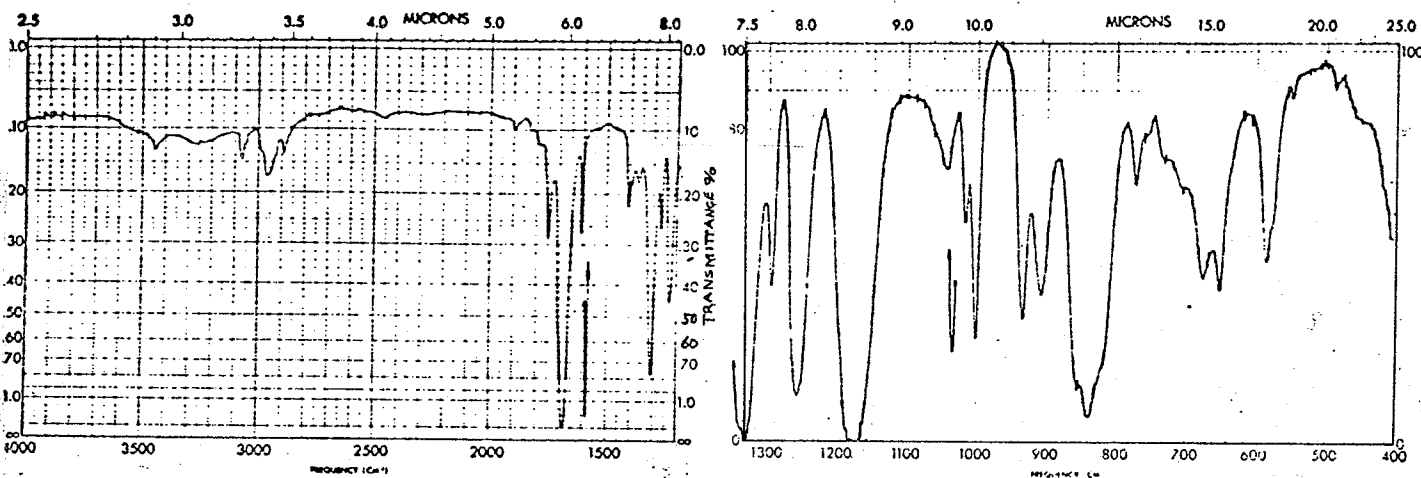


b) $(CH_3CH_2)_3SiNC(CH_2)_2CO$, liquid phase, neat.

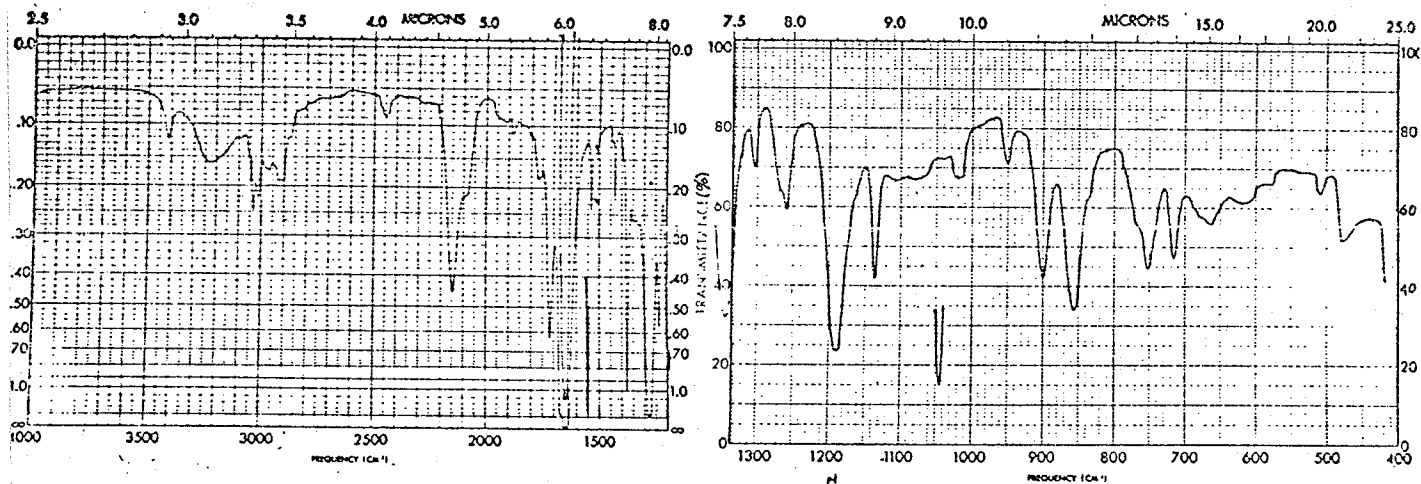


c) $(CH_3)_2HSiNC(CH_2)_2CO$, liquid phase, neat.

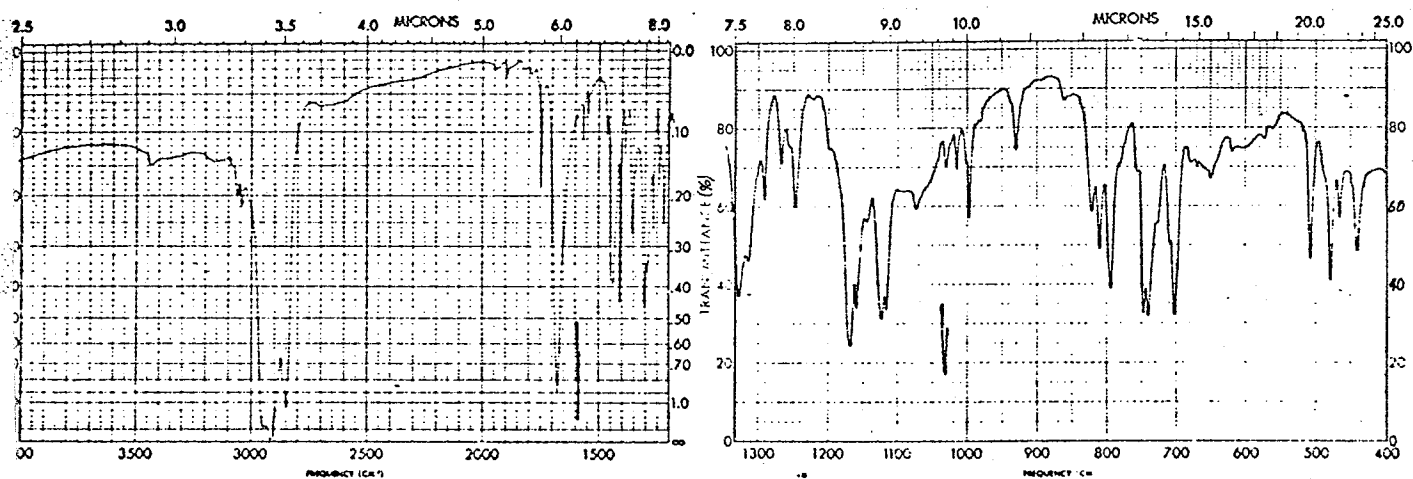
FIGURE 2 (con't)



d) $\text{CH}_2=\text{CHCH}_2(\text{CH}_3)_2\text{SiNCO}(\text{CH}_2)_2\text{CO}$, liquid phase, neat.

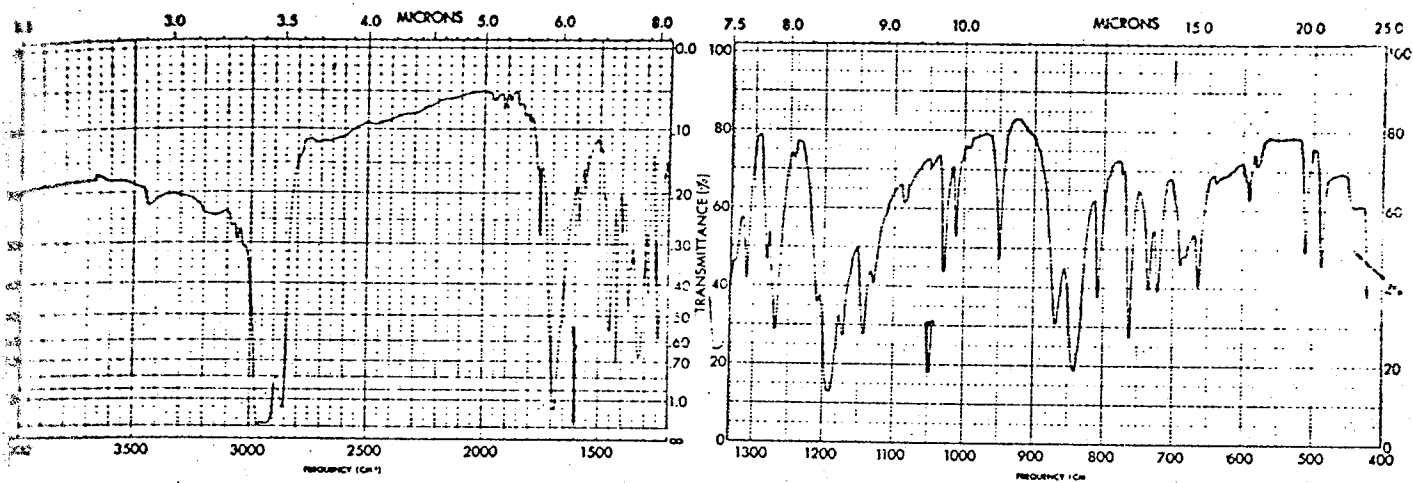


e) $\text{C}_6\text{H}_5\text{CH}_3\text{HSiNCO}(\text{CH}_2)_2\text{CO}$, liquid phase, neat.

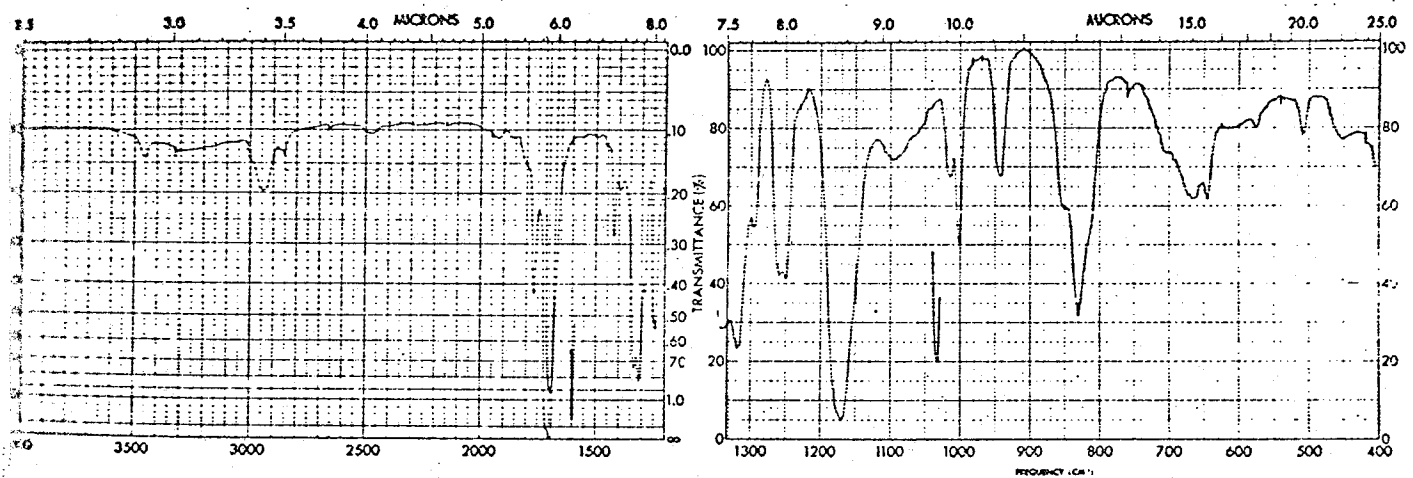


f) $(\text{C}_6\text{H}_5)_2\text{CH}_3\text{SiNCO}(\text{CH}_2)_2\text{CO}$, nujol mull.

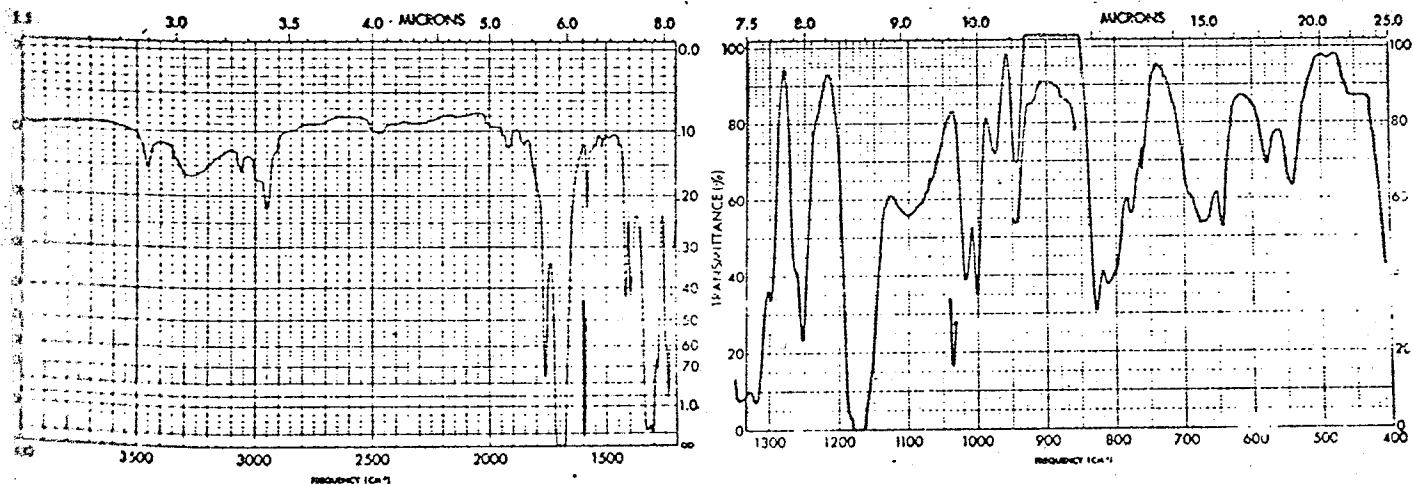
FIGURE 2 (con't)



1) $C_6H_5(CH_3)_2Si(NCO(CH_2)_2CO)_2$, nujol mull.

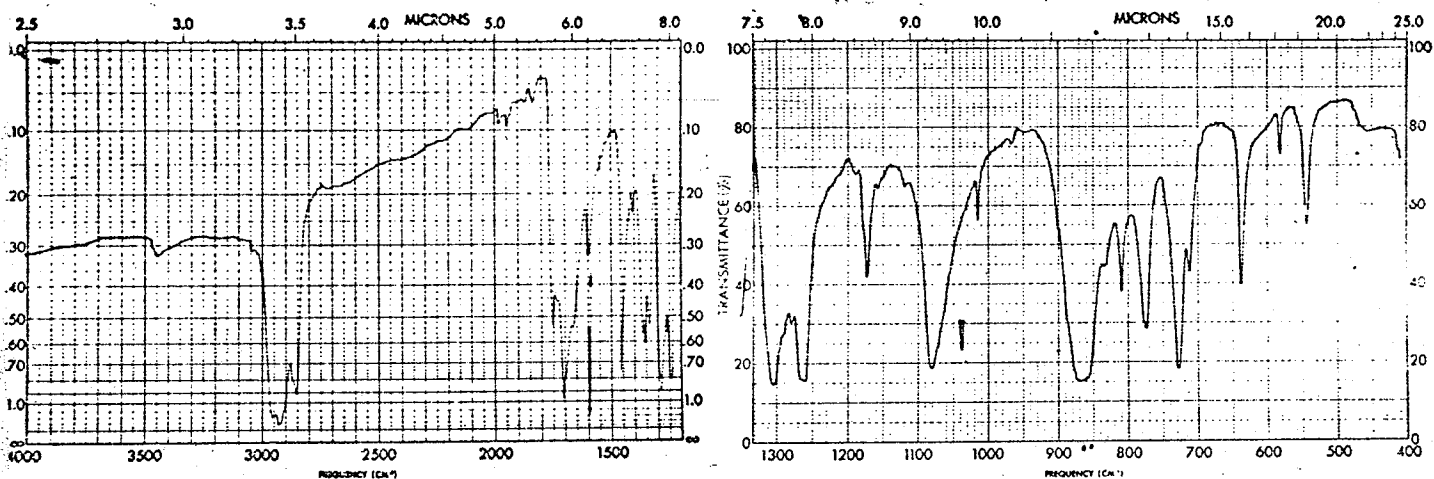


2) $(CH_3)_2Si(NCO(CH_2)_2CO)_2$, liquid phase, neat.

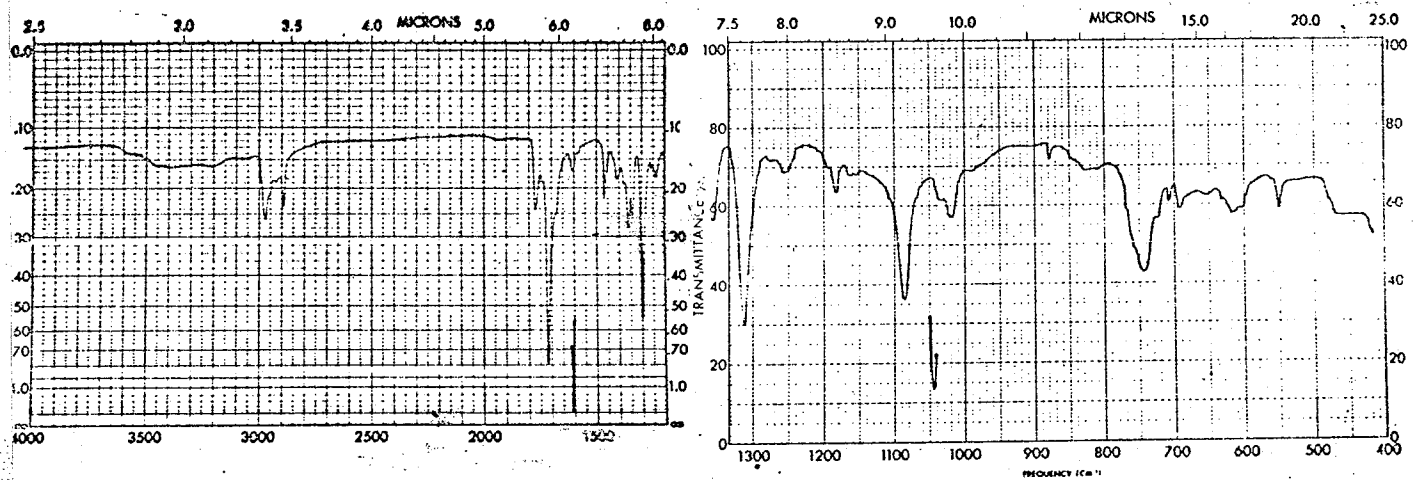


3) $CH_3CH_2=CHSi(NCO(CH_2)_2CO)_2$, liquid phase, neat.

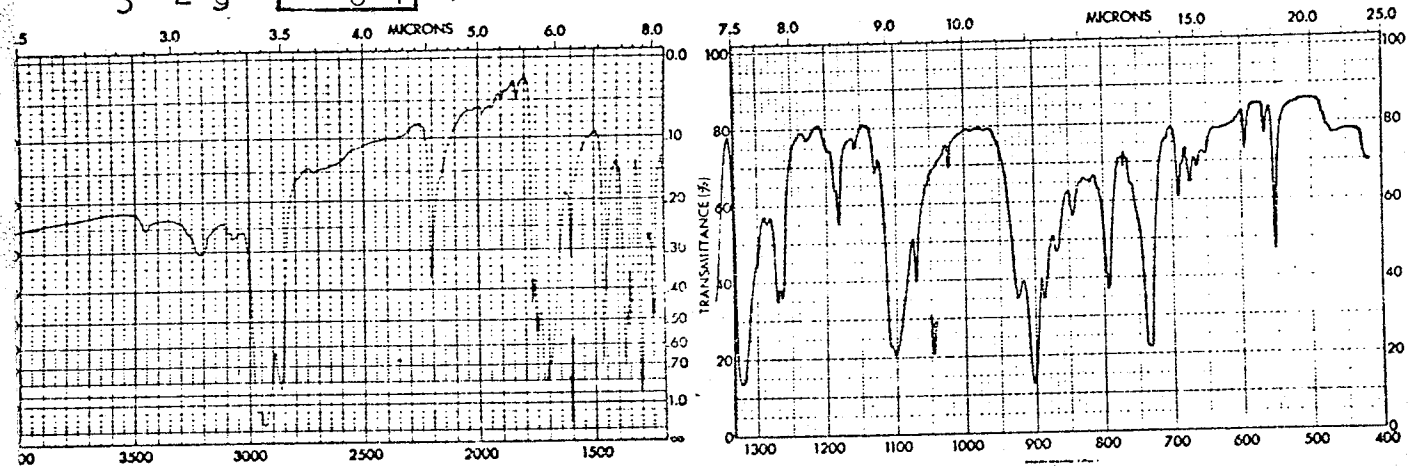
FIGURE 2 (con't)



j) $(\text{CH}_3)_3\text{SiNCOC}_6\text{H}_4\text{CO}$, nujol mull.

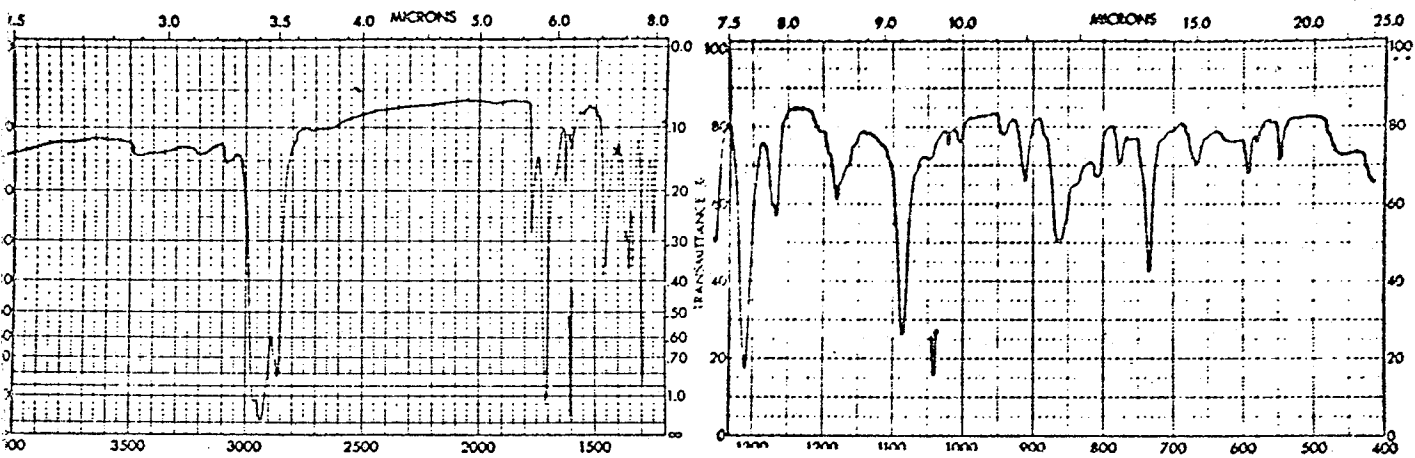


k) $(\text{CH}_3\text{CH}_2)_3\text{SiNCOC}_6\text{H}_4\text{CO}$, liquid phase neat.

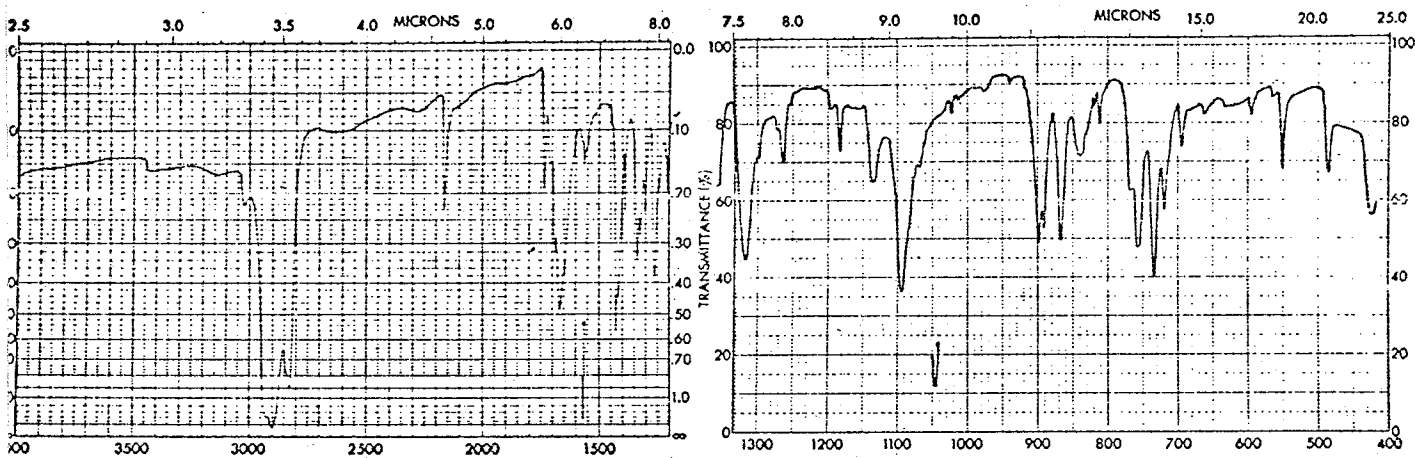


l) $(\text{CH}_3)_2\text{HSiNCOC}_6\text{H}_4\text{CO}$, nujol mull.

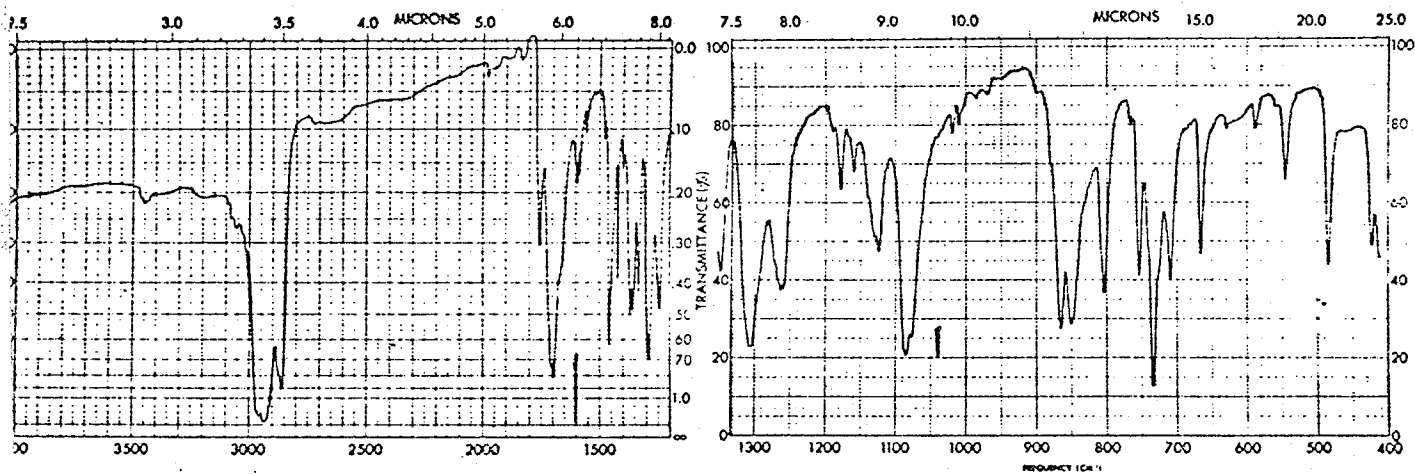
FIGURE 2 (con't)



m) $(\text{CH}_3)_2\text{CH}_2=\text{CHCH}_2\text{S-NCOC}_6\text{H}_4\text{CO}$, nujol mull.

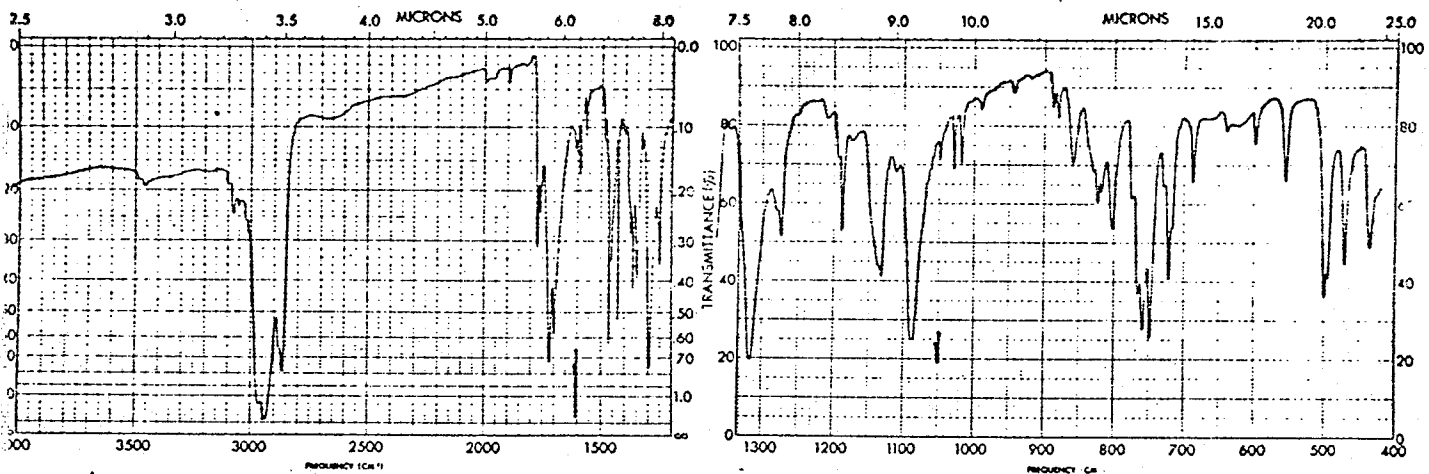


n) $\text{C}_6\text{H}_5\text{CH}_3\text{HS-NCOC}_6\text{H}_4\text{CO}$, nujol mull.

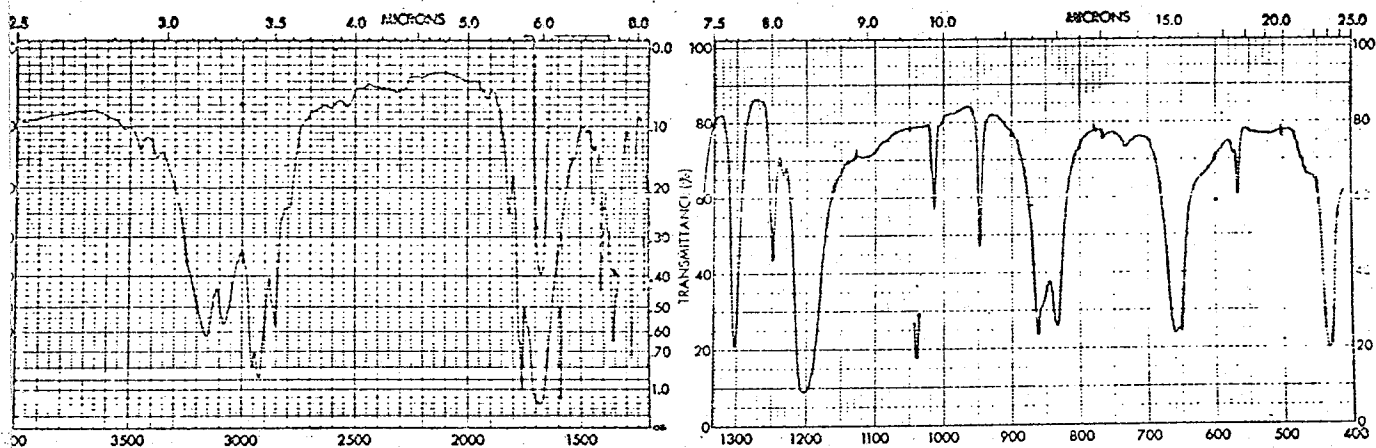


o) $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{S-NCOC}_6\text{H}_4\text{CO}$, nujol mull.

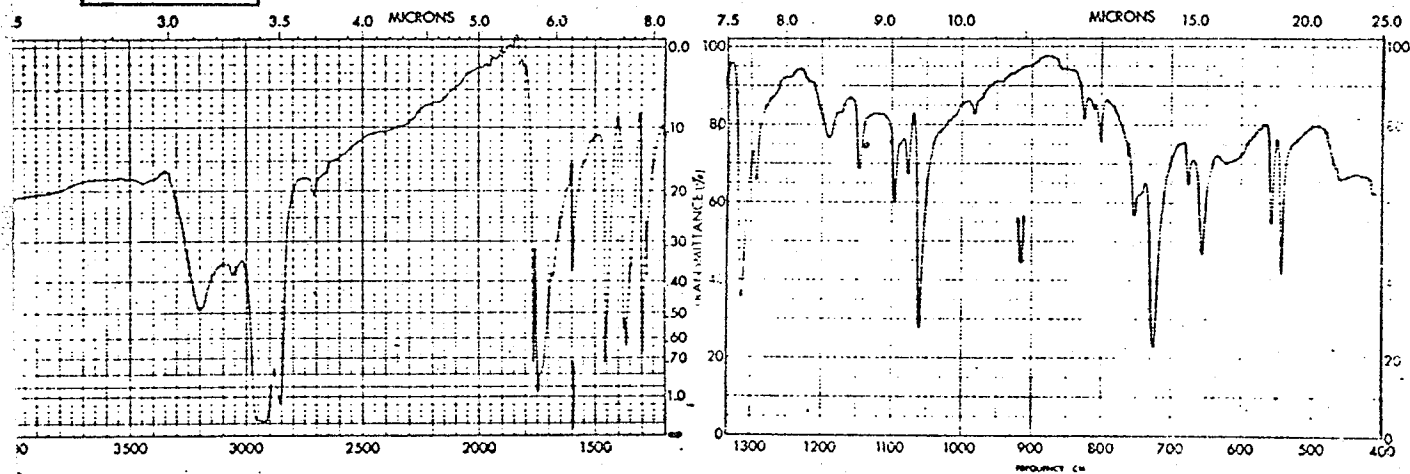
FIGURE 2 (cont'd)



o) $(C_6H_5)_2CH_3SiCOC_6H_4CO$, nujol mull.



) $HNC(CH_2)_2CO$, nujol mull.



) $HNCOC_6H_4CO$, nujol mull.

FIGURE 3(a,b,c,d.)

Infrared Spectra of 10^{-4} M Solutions of $RR'SiNC(OCH_2)_2CO$ (a,b) and of $RR'SiNCOC_6H_4CO$ (c,d) in chloroform showing $\nu(C=O)$ and $\nu(Si-H)$ in cm^{-1} .

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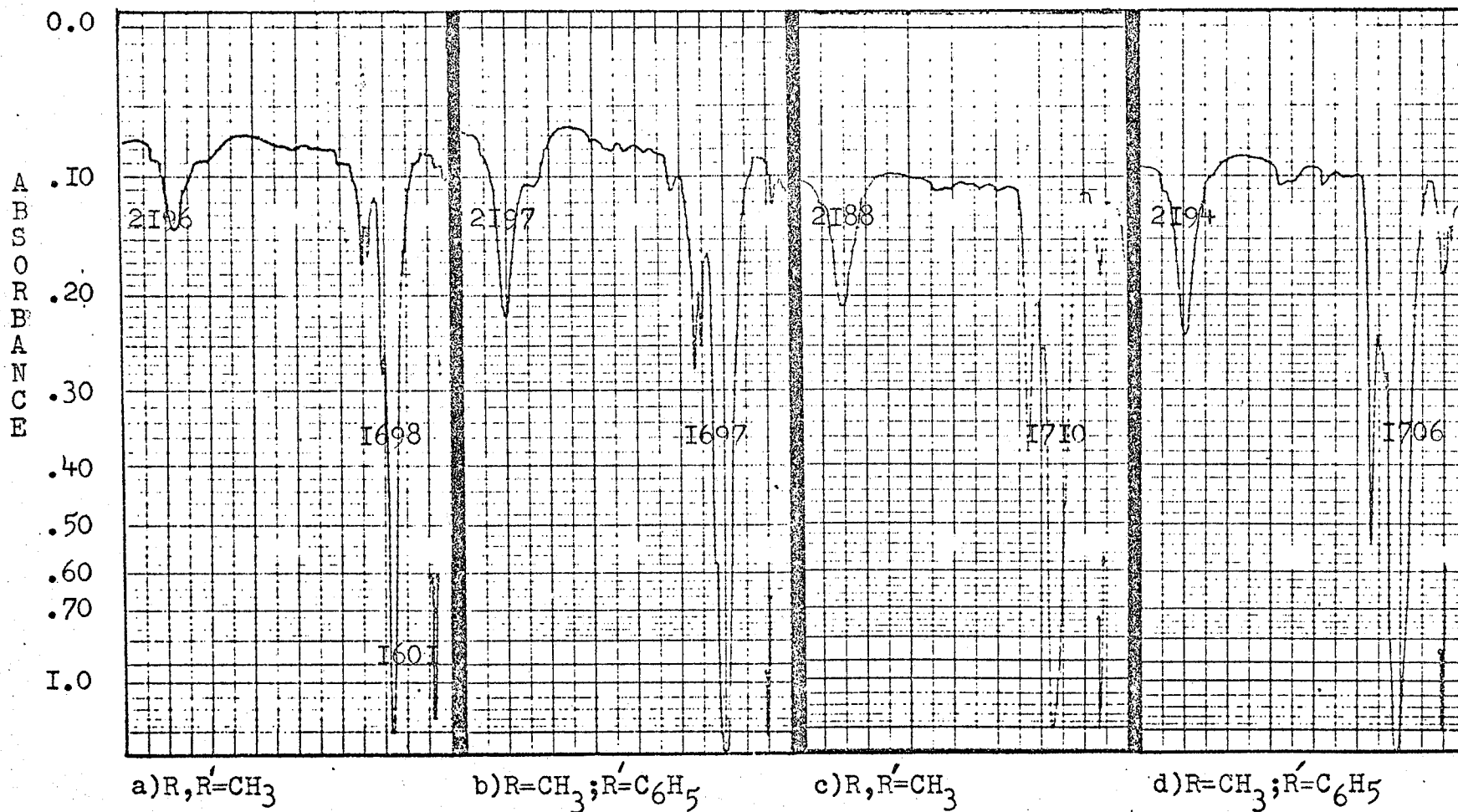
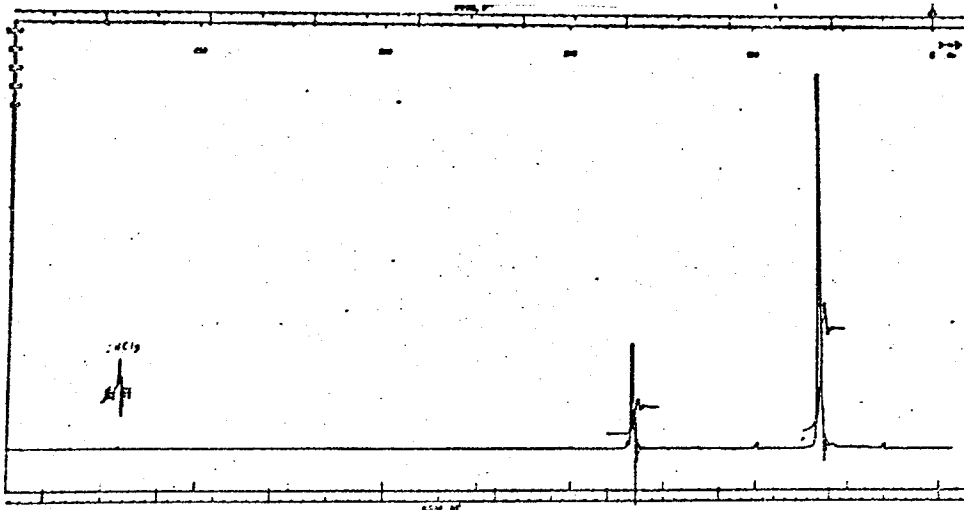
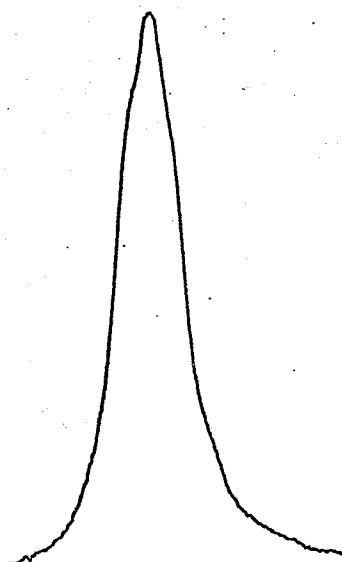


FIGURE 4

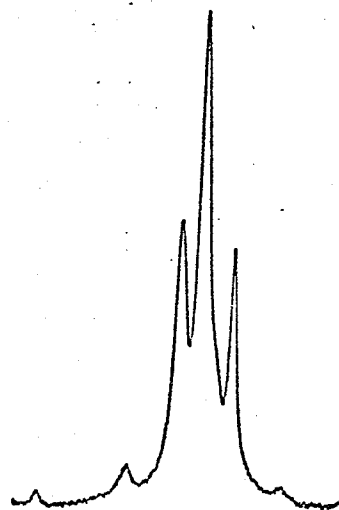
N.M.R. Spectra of N-(triethylsilyl)succinimide



a) N-(triethylsilyl)succinimide, 10 mole percent solution in deuterated chloroform, 500 cycle sweep width.



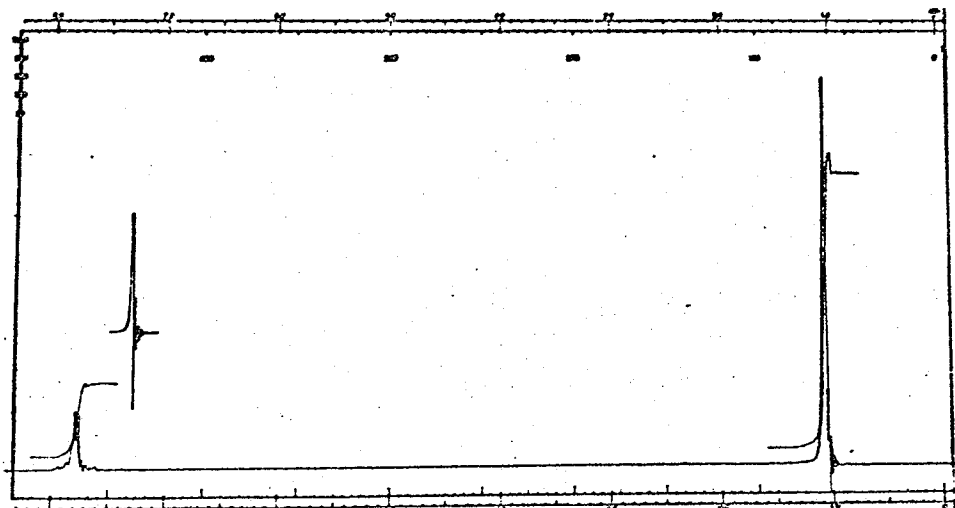
b) 50 cycle scan of $\text{Si}(\text{CH}_2\text{CH}_3)_3$ region, neat liquid sample.



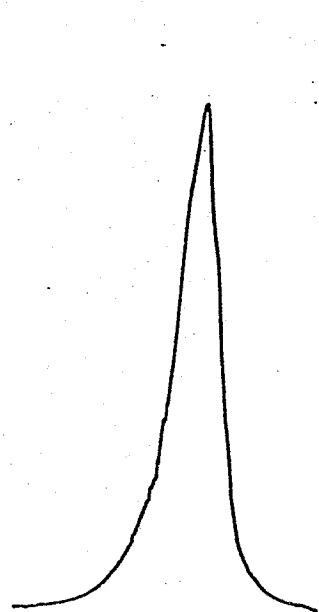
c) 50 cycle scan of $\text{Si}(\text{CH}_2\text{CH}_3)_3$ region, 10 mole percent solution in benzene.

FIGURE 5

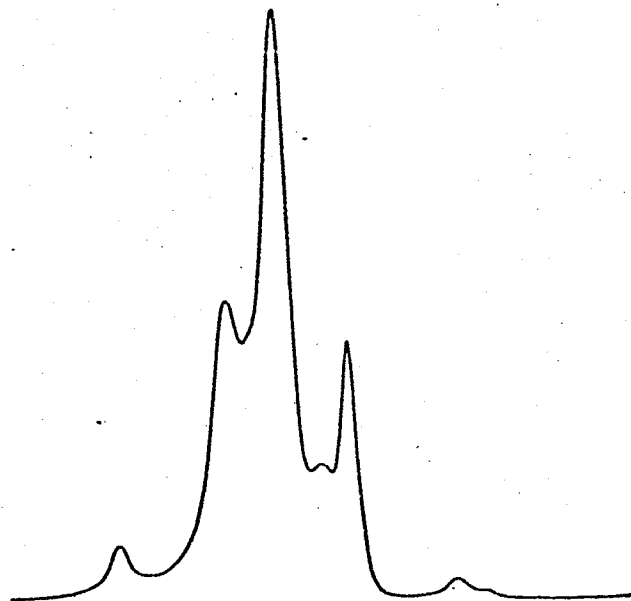
N.M.R. Spectra of N-(triethylsilyl)phthalimide



a) N-(triethylsilyl)phthalimide, 10 mole percent solution in deuterated chloroform, 500 cycle sweep width.



b) 50 cycle scan of $-\text{Si}(\text{CH}_2\text{CH}_2)_3$ region, neat liquid sample.



c) 50 cycle scan width of the $-\text{Si}(\text{CH}_2\text{CH}_2)_3$ region, 10 mole percent solution in deuterated benzene.



d) 50 cycle scan width of $-\text{SiNCOC}_6\text{H}_4\text{CO}$ region, 10 mole percent solution in deuterated benzene.

RESULTS AND DISCUSSIONPART IINFRARED SPECTRASTRUCTURE CONFIRMATION BY INFRARED SPECTRA

Normally, an infrared spectrum can be separated into the fingerprint region and a higher frequency region. For organic compounds only the higher frequency region is particularly useful for structure determination. However, for silicon containing compounds the fingerprint region is also quite useful for this purpose because absorption bands due to bonds between silicon and carbon atoms are about five times more intense than the intensity of the analogous organic bond absorption bands⁸². Therefore, for many Si-R linkages (R = CH₃, C₆H₅, C₂H₅, etc.,) characteristic absorption bands have been identified in the fingerprint region. Moreover, in some cases these bands vary in such a way that Si-R, SiR₂ and SiR₃ (R = CH₃, H, and C₆H₅) groups may be distinguished from one another.

In general the silicon-carbon stretching vibrations occur between 900 and 690 cm⁻¹⁸²⁻⁸⁶. For the -Si(CH₃)₃ group two characteristic absorption bands have been found for the stretching of the Si-C linkage. They occur near 756 cm⁻¹ and near 844 cm⁻¹⁸²⁻⁸⁵. These absorption bands are found to vary little with the fourth substituent on silicon⁸². For N-(trimethylsilyl)phthalimide two bands were found, one at 857 cm⁻¹(s) and one at 756 cm⁻¹(ms). Phthalimide showed no absorption bands for either area. For N-(trimethylsilyl)succinimide two bands were found, one at 850 cm⁻¹(s) and one at 764 cm⁻¹(m). Succinimide, however, shows two absorption bands at 840 and 822 cm⁻¹(ms). Succinimide shows no absorption bands near 760 cm⁻¹.

Therefore, the infrared spectra of these two compounds confirms the presence of the trimethylsilyl group.

For the Si-C stretch in the $\equiv\text{Si}(\text{CH}_3)_2$ group one absorption band is observed near 800 cm^{-1} ^{82-84,86,87} and another is observed near 700 cm^{-1} ⁸⁶. The position of these bands, however, can shift by a large amount depending on the nature of the two other substituents on silicon ⁸⁷. Also the band near 700 cm^{-1} is not particularly useful for structure determination because allyl, phenyl and ethyl substituents absorb in this region ⁸⁴. For N-(dimethylsilyl)succinimide a band at $780\text{ cm}^{-1}(\text{m})$ and a band at $661\text{ cm}^{-1}(\text{mw})$ were found. For N-(N'-succinimidodimethylsilyl)succinimide a band at $810\text{ cm}^{-1}(\text{mw,sh})$ and a band at $700\text{ cm}^{-1}(\text{mw,sh})$ were found. Succinimide shows no absorption bands in the 780 cm^{-1} region and the band that appears at 639 cm^{-1} is accounted for in N-(dimethylsilyl)succinimide by a peak at $643\text{ cm}^{-1}(\text{m})$. For N-(dimethylsilyl)phthalimide a band at $775\text{ cm}^{-1}(\text{m})$ and three bands; $673\text{ cm}^{-1}(\text{mw})$, $660\text{ cm}^{-1}(\text{w})$ and $650\text{ cm}^{-1}(\text{w})$ were found. Phthalimide has only two very weak bands near 800 cm^{-1} but it has two bands at $668\text{ cm}^{-1}(\text{m})$ and $643\text{ cm}^{-1}(\text{m})$.

Because of the complexity of these molecules these assignments may be due to other modes of vibration. However, their presence does not contradict the structures proposed. Other molecules prepared have the $\equiv\text{Si}(\text{CH}_3)_2$ group but due to the presence of other substituents which would interfere no assignments are made to the frequencies that appear in the expected regions.

For the Si-C stretch of the group $\equiv\text{SiCH}_3$ only one absorption band is observed near 800 cm^{-1} ^{83,84,86}. Ebsworth et al., ⁸⁷ found for compounds of the type $(\text{CH}_3 \cdot \text{Si} \cdot \text{H}_2)_n\text{X}$ that this band appeared near 750 cm^{-1} . This absorption band is sensitive to the other substituents on silicon and therefore can be expected to vary alot. Therefore, it is of little use in structure identification unless the compounds are very simple. All the mono methyl

derivatives prepared in this work exhibited a band in the 800 cm^{-1} region.

For all of these various methyl substituted compounds there appear a number of other absorption bands due to the CH_3 group on silicon. In general, they are the Si-CH_3 deformation or rocking vibration near 1260 cm^{-1} , the C-H bending vibrations near 1412 cm^{-1} and the C-H stretching vibrations near 2959 cm^{-1} ^{83,84}. The intensity of the C-H stretching vibration is normally three to four times that found in analogous hydrocarbon compounds ⁸². The deformation or rocking vibrations of the groups $\text{-Si(CH}_3)_2$ and $\text{-Si(CH}_3)$ remain almost constant at 1259 cm^{-1} regardless of the other substituents on silicon ⁸⁷. The Si-C stretching vibration of a Si-phenyl linkage absorbs near 1427 cm^{-1} and therefore confusion can arise in this assignment if the molecule contains both a methyl and a phenyl group linked to the same silicon atom ⁸⁵. The C-H bending vibrations are fairly constant in solution ⁸⁶. The deformation or rocking vibration of the $\text{-Si(CH}_3)_3$ group is somewhat lower being found near 1250 cm^{-1} ⁸⁴.

For the phthalimide derivatives the bands assigned to the C-H bending vibrations all occur in the region $1415\text{-}1399\text{ cm}^{-1}$. None of the C-H stretching bands are noted since all of these compounds except N-(triethylsilyl)phthalimide were run as nujol mulls. The Si-CH_3 rocking or deformation vibrations were found in the region $1247\text{-}1254\text{ cm}^{-1}$. For these compounds the $\text{Si(CH}_3)_2$ and SiCH_3 groups are indistinguishable from the $\text{Si(CH}_3)_3$ group on the basis of this vibration.

For the succinimide derivatives the region near 1412 cm^{-1} has a number of peaks present, however succinimide itself exhibits a number of absorption bands in this region. Therefore, no assignments can be made.

For the C-H stretching vibrations the spectra run as liquid films give two bands, one near 2950 cm^{-1} and one near 2916 cm^{-1} . Succinimide absorbs in the region $2946\text{--}2855\text{ cm}^{-1}$; therefore the higher band is due to the C-H stretch of the methyl groups on silicon only. The disuccinimides show broad absorptions only around 2950 cm^{-1} . The Si-CH₃ rocking or deformation modes of vibration were found in the region $1241\text{--}1266\text{ cm}^{-1}$ with most near 1250 cm^{-1} . Again the Si(CH₃)₃ group cannot be distinguished from the Si(CH₃)₂ or SiCH₃ groups on the basis of this absorption band. The bands of all the dimethyl derivatives except N-(dimethylsilyl)succinimide attributed to this mode of vibration were split into doublets.

In general it can be noted from the above that the most certain indication of a Si(CH₃)_n (n = 1,2,3) group is the presence of an absorption band near 1250 cm^{-1} . Although the Si(CH₃)₃ group can not in the case of these compounds be distinguished from the SiCH₃ or Si(CH₃)₂ groups on the basis of the absorption band near 1250 cm^{-1} , it can be distinguished by the presence of the two strong bands near 850 cm^{-1} and 750 cm^{-1} .

In general the Si-C₂H₅ group exhibits the following characteristic absorption bands, an asymmetric CH₃ bending band at 1462 cm^{-1} , a CH₂ stretching band at 1412 cm^{-1} , a symmetric CH₃ bending band at 1377 cm^{-1} , a Si-CH₂ deformation band at 1238 cm^{-1} and a C - C stretching band at 1012 cm^{-1} . A further band which is not well defined found near 746 cm^{-1} may possibly be assigned to the CH₃ rocking band^{83,85,88,89}. For N-(triethylsilyl)succinimide, the following absorption bands were found, $1457\text{ cm}^{-1}(\text{mw})$, $1404\text{ cm}^{-1}(\text{mw})$, $1380\text{ cm}^{-1}(\text{mw})$, $1241\text{ cm}^{-1}(\text{m})$ and $1002\text{ cm}^{-1}(\text{m})$. Also the C-H stretching bands are very intense (fig 2(b)).

For N-(triethylsilyl)phthalimide, the following bands were found, 1455

$\text{cm}^{-1}(\text{mw})$, $1400 \text{ cm}^{-1}(\text{w})$, $1350 \text{ cm}^{-1}(\text{mw})$, $1239 \text{ cm}^{-1}(\text{w})$ and $1006 \text{ cm}^{-1}(\text{mw})$.

Again, the C-H stretching bands are very intense (fig 2(k)). For these compounds two features appear to be distinctive of the presence of a triethylsilyl group. These are the intensity of the C-H stretching bands and a value for the Si-CH₂ deformation band which is lower than the methyl substituted silyl groups. In studies^{88,89} concerning the usefulness of distinguishing between methyl, ethyl and higher chain aliphatic substituents by use of the Si-CH₂ deformation band, it has been found that care must be used since spectra conditions can shift this value.

In general the most distinctive Si-phenyl absorption bands appear at 1429 cm^{-1} and 1126 cm^{-1} . The 1126 cm^{-1} band is sometimes split into a doublet when two phenyl groups are attached to the same silicon atom^{83,84}. Harvey et al.,⁸⁸ lists the following absorption bands as due to the Si-phenyl group in alkylphenylsilanes; $1595 \text{ cm}^{-1}(\text{w})$, $1486 \text{ cm}^{-1}(\text{m})$, $1431 \text{ cm}^{-1}(\text{s})$, $1186 \text{ cm}^{-1}(\text{m})$, $1116 \text{ cm}^{-1}(\text{vs})$, $1025 \text{ cm}^{-1}(\text{m})$ and $980 \text{ cm}^{-1}(\text{w})$. Two more bands are found by Young et al.,⁸⁵ as also being characteristic. They are a band near 737 cm^{-1} and a band near 699 cm^{-1} . Richards and Thompson⁸⁶ site the region near 750 cm^{-1} as due to the intense bending vibrations of the C-H bonds of the phenyl substituent. The two bands usually found near 1420 cm^{-1} and 1585 cm^{-1} probably correspond to the pair of bands near 1500 and 1600 cm^{-1} which normally occur with aromatic hydrocarbons and simple substituted benzenes⁸⁴.

For all the phenyl substituted compounds except N-(phenylmethylsilyl)phthalimide there appear two bands near 1595 cm^{-1} and 1487 cm^{-1} . The band near 1487 cm^{-1} is not found for N-(phenylmethylsilyl)phthalimide. It is probably masked by the nujol absorption band in this region. All the phenyl substituted compounds exhibit a sharp strong band in the region 1430

cm^{-1} . This band appears to be the most distinctive of the Si-phenyl group for these compounds. The band near 1186 cm^{-1} in these derivatives can be due to the phthalimido and succinimido groups. Only the phenyl derivatives of succinimide show a band near 1126 cm^{-1} . Only the phenyl derivatives of phthalimide show a band near 1116 cm^{-1} . A number of bands appear in the 1025 cm^{-1} and 980 cm^{-1} region for all the derivatives, therefore, no assignments can be made. This region does not appear to be very useful for identifying phenyl derivatives. The situation appears to be the same for the 740 cm^{-1} and 699 cm^{-1} regions.

For the Si-vinyl group the following absorption bands were found by Shull *et al.*,⁸⁷ for vinyltrichlorosilane; a CH_2 asymmetrical stretching band near 3081 cm^{-1} , a C-H stretching band near 3002 cm^{-1} , a symmetrical CH_2 stretching band near 2970 cm^{-1} , a C = C stretching band near 1605 cm^{-1} , a CH_2 deformation band near 1407 cm^{-1} , a CH bending band near 977 cm^{-1} , and a C = CH_2 twisting band near 611 cm^{-1} . The absorption bands for which no other assignments were possible in N-(N'-succinimidovinylmethylsilyl)succinimide were $3066 \text{ cm}^{-1}(\text{w})$, $1585 \text{ cm}^{-1}(\text{w})$ and $993 \text{ cm}^{-1}(\text{m})$.

From the spectra of $(\text{CH}_2 = \text{CHCH}_2)_{4-n} \text{SiX}_n$ ($n = 0, 1, 2, 3$) the following bands appear quite clearly associated with the allyl group; they are five bands between 2900 and 3100 cm^{-1} and ten bands near 1645 , 1244 , 1163 , 1042 , 985 , 930 , 890 , 806 , 790 , and 775 cm^{-1} ⁸⁸. For the mono allyl derivative the bands at 1244 and 1163 cm^{-1} become one band near 1220 cm^{-1} , the bands at 930 cm^{-1} shift towards the band at 890 cm^{-1} becoming a shoulder, the band at 806 cm^{-1} becomes very small and the bands near 790 cm^{-1} and 775 cm^{-1} shift to 770 and 757 cm^{-1} respectively. Thompson and Torkington⁸⁹ have assigned various modes of vibration to some of these bands. For N-(allyldimethylsilyl)succinimide

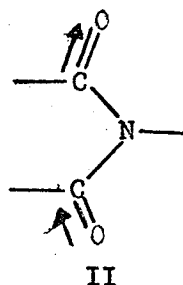
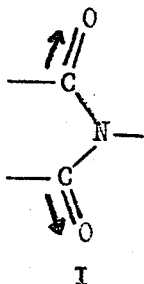
two bands can be found to be specifically associated with the allyl group. They are one band at 3086 cm^{-1} (vw) and one at 1626 cm^{-1} (w). Only one band at 1628 cm^{-1} (mw) can be found for N-(allyldimethylsilyl)phthalimide which is associated with allyl group. Corresponding bands can be found in the rest of spectra but due to the number of absorptions any assignments would be ambiguous.

Silicon hydrogen stretching absorption bands are quite distinctive since they are intense. They appear between 2100 and 2200 cm^{-1} ^{36,90}. N-(phenylmethylsilyl)- and N-(dimethylsilyl)succinimide show Si-H stretching bands at 2203 cm^{-1} (m) and 2190 cm^{-1} (m) respectively. N-(phenylmethylsilyl)- and N-(dimethylsilyl)phthalimide show Si-H stretching bands at 2197 cm^{-1} (m) and 2205 cm^{-1} (m) respectively.

Silicon nitrogen absorption bands vary over a wide range. In general, from the reports surveyed it is concluded that coupling and mixing between various modes of vibration can cause wide variation in the position and the intensity of the Si-N stretching frequency. In compounds where two nitrogen atoms are joined to a single silicon atom in a compound two bands appear near $837-860\text{ cm}^{-1}$ and $786-782\text{ cm}^{-1}$ which are attributed to $\nu_{\text{asym}}(\text{N-Si-N})$ and $\nu_{\text{sym}}(\text{N-Si-N})$ respectively ⁹¹. For compounds of the type R_3SiNH_2 (R = C_2H_5 , n- C_3H_7 , n- C_4H_9 , i- C_3H_7 , C_6H_{11} , H), $\nu(\text{Si-N})$ varied between 824 and 857 cm^{-1} ⁹¹⁻⁹³. For compounds of the type $\text{R}_3\text{SiNR}'\text{R}_2$, $\nu(\text{SiN})$ probably lies around 700 cm^{-1} and is often shifted by mixing ⁹³. The value of $\nu(\text{SiN})$ for the compound $(\text{CH}_3)_3\text{SiNHC}_6\text{H}_5$ was 899 cm^{-1} ⁹³. For the compounds prepared in this work no assignments of bands were made for the Si-N stretching vibration because of the obvious confusion that exists.

All the compounds prepared in this work exhibited two absorption bands

in the carbonyl group frequency region. These two bands are due to the vibrationally coupled symmetric (I) and antisymmetric (II) modes of vibration 94-96 of the two carbonyl groups.



In succinimide they have the values $1773 \text{ cm}^{-1}(\text{s})$ and $1695 \text{ cm}^{-1}(\text{s,br})$ respectively. In phthalimide they have the values $1771 \text{ cm}^{-1}(\text{s})$ and $1750 \text{ cm}^{-1}(\text{s,br})$ respectively. The intensity of these two absorption bands varies depending on the structure of the molecule. If the two carbonyls are in the same plane but have their dipoles aligned opposite to one another there will be no peak due to the symmetric mode of vibration even if there is intense vibrational coupling between the two. Similarly, the vibrational coupling and hence the splitting of these two peaks depends on the structure of the molecule. Of the factors affecting the coupling, the most important is the angle between the carbonyl groups. If the carbonyl groups are coplanar interaction will be at a maximum. If the carbonyl groups are at right angles to one another interaction will be at a minimum. Similar to the anhydrides, the higher less intense band is assigned to the symmetric mode of vibration and the unsymmetric mode of vibration is assigned to the lower frequency more intense absorption band 94.

For the succinimide derivatives prepared the two modes of vibration were split by $66 \pm 6 \text{ cm}^{-1}$. For the phthalimide derivatives prepared the two modes of vibration were split by $50 \pm 7 \text{ cm}^{-1}$. As is shown in figure 2(1,p) two of the phthalimide derivatives show more than two bands in the region $1700\text{-}1770 \text{ cm}^{-1}$.

The clearer example is N-(diphenylmethylsilyl)succinimide, (fig. 2(p)). The multiple absorption bands in this region for these compounds could be due to molecular association in these mulls.

Three conclusions can be drawn from these results: (1) The carbonyls are at a small angle to one another since the splitting is very large. (2) The carbonyl dipoles are not aligned opposite to one another because both bands appear, but the angle can not be large since the intensity of the antisymmetric band is greater than the intensity of the symmetric band. (3) The appearance of the two bands in these spectra is conclusive evidence that O-silylation has not taken place. Absence of the N-H stretching band in these spectra alone is not sufficient proof against O-silylation since N- and O-silylation could have both occurred.

PART IICORRELATIONS OF $\nu(\text{C}=\text{O})$ AND $\nu(\text{Si}-\text{H})$ WITH THE ELECTRONIC NATURE OF THE $\text{Si}-\text{N}$ BOND

From table 3 it can be seen that $\nu_{\text{asym}}(\text{C}=\text{O})$ of the silylsuccinimides and phthalimides are lower than $\nu_{\text{asym}}(\text{C}=\text{O})$ of succinimide and phthalimide.

TABLE 3. $\nu_{\text{asym}}(\text{C}=\text{O})$ of $\text{RNC}(\text{CH}_2)_2\text{CO}$ and $\text{RNCOC}_6\text{H}_4\text{CO}$

<u>R</u>	$\nu_{\text{asym}}(\text{C}=\text{O})\text{RNC}(\text{CH}_2)_2\text{CO}(\text{cm}^{-1})$	$\nu_{\text{asym}}(\text{C}=\text{O})\text{RNCOC}_6\text{H}_4\text{CO}(\text{cm}^{-1})$
H	1717	1736
Me ₃ Si	1689	1700
Et ₃ Si	1685	1707
AlMe ₂ Si	1696	1694
φMeHSi	1670	1700
φ ₂ MeSi	1696	1703
φMe ₂ Si	1695	1695
Me ₂ HSi	1717	1706

Many factors could effect $\nu_{\text{asym}}(\text{C}=\text{O})$ of these molecules ^{83,97}.

They are:

- a). electronegativity of adjacent atoms or groups (inductive effect).
- b). resonance.
- c). fields.
- d). vibrational coupling.
- e). changes in the force constants of adjacent bonds.
- f). phase changes or association.
- g). hydrogen bonding.
- h). solvent effects.
- i). mass and angle effects.

Effects (e), (h), and (i) can be neglected. The solvent and concentration were the same for each compound. A change of mass of an atom adjacent to the carbon of a carbonyl group will affect $\nu(\text{C}=\text{O})$ but even this effect will become negligible when the mass of the atom is greater than 12 ⁹⁸. It is known that as the XCX angle of XCOX changes there will be a corresponding shift in $\nu(\text{C}=\text{O})$ ⁹⁹. However, the ring size of the molecules prepared has not been altered. Therefore, their geometry will remain the same and no change in $\nu(\text{C}=\text{O})$

of this compounds should occur. The change in the force constant of adjacent molecules is connected to the change in the angle $\angle XCX$ and as such will not be expected to affect $\nu(C=O)$ ¹⁰⁰.

As has already been outlined vibrational coupling of the two equivalent carbonyls has led to splitting of the single expected absorption band. Also it has been noted that the position of these two bands will be sensitive to the geometry of the molecule. For the series of compounds prepared no structural changes in the ring containing the carbonyls is expected and therefore no shift in $\nu(C=O)$ will be expected from compound to compound due to this effect. Other vibrational couplings could occur between the carbonyls and adjacent bonds if they have similar vibrational frequencies. However, there are no adjacent bonds which absorb in the same region as the carbonyls.

The effects of association can not be predicted very well, however, they normally do not lead to large shifts except in the case of strong hydrogen bonding¹⁰¹. There is no indication in the case of the succinimide derivatives that association takes place. For the phthalimides, however, association probably occurs for concentrated solutions as in nujol mulls or in the pure phase. Evidence for association in the mulls is exhibited by the infrared spectra of N-(diphenylmethylsilyl)phthalimide which exhibits more than two absorption bands in the carbonyl absorption region. Evidence for association in the pure phase is found in the physical properties of the phthalimide derivatives. N-(trimethylsilyl)phthalimide is a solid with a melting point of 65-67°C whereas N-(triethylsilyl)phthalimide is a liquid. Further, N-(allyl-dimethylsilyl)phthalimide has a melting point of 27-29°C whereas the two phthalimido compounds containing a Si-H group have very much higher melting points when compared with the rest of the compounds. Therefore, it appears that in the pure phase where the SiR_3 groups are very small association occurs

whereas for SiR_3 groups which are large, association takes place to a much smaller extent. However, this association must be very weak because molecular weight determinations of N-(trimethylsilyl)- and N-(dimethylsilyl)-phthalimide (Rast method) showed no indication of association. Therefore, it seems reasonable that for very dilute solutions no association occurs for these derivatives. This conclusion is further supported by the fact that cryoscopic measurements on various diacylamines have showed that when no imide hydrogen is present molecular association is completely suppressed.¹⁰² Finally, Abramovitch¹⁰¹ concludes that for infrared measurements of a number of organic imides the use of chloroform as a solvent rules out the possibility of association and Borisevitch et al.,¹⁰³ finds that for various N-methylated phthalimides no association occurs.

Hydrogen bonding which is a special case of molecular association can also affect $\nu(\text{C}=\text{O})$ ¹⁰⁴. Hydrogen bonding in Si-H bond containing compounds has not been found and if it exists the effects will be small.¹⁰⁹ Hydrogen bonding does exist in the unsubstituted imides.^{95,103} However, when phthalimide is methylated $\nu_{\text{asym}}(\text{C}=\text{O})$ and $\nu_{\text{sym}}(\text{C}=\text{O})$ are found to change so little that Boresivitch et al., concluded that the formation of a hydrogen bond has almost no effect. In a comparison between N-methylsuccinimide and succinimide in a KBr pellet it is found that $\Delta\nu_{\text{asym}}(\text{C}=\text{O})$ is 3 cm^{-1} and $\Delta\nu_{\text{sym}}(\text{C}=\text{O})$ is 5 cm^{-1} ¹⁰⁶. Therefore, it appears that for succinimide and phthalimide the effect of hydrogen bonding is negligible.

It can now be stated that in a comparison of the $\nu(\text{C}=\text{O})$'s of these compounds that the main effects will only be the chemical effects or effects (a), (b) and (c).

The inductive effect is considered to be independent of geometry and to operate along the bonds. The vibrational frequency of a group is altered by

displacements in the electron cloud of that bond. These displacements occur due to changes in the electronegativity of groups adjacent to the vibrating group of interest. In the case of a carbonyl isolated from all effects there is a charge separation with oxygen carrying a partial negative charge. When an electron withdrawing group is placed adjacent to the carbonyl then the negative charge on the oxygen is displaced towards its geometric centre increasing the bond strength and therefore raising $\nu(\text{C}=\text{O})$. When an electron releasing group is adjacent to the carbonyl the bond polarity is increased and $\nu(\text{C}=\text{O})$ decreases ¹⁰⁷.

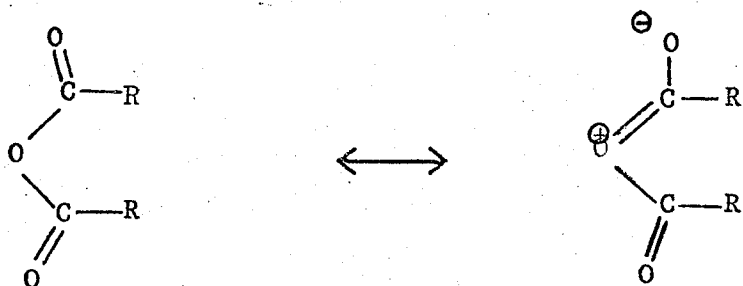
In respect to H a Me_3Si group is electron releasing ^{54,1.08}. On the Gordy scale of electronegativities the Et_3Si and $\phi_3\text{Si}$ groups will only be slightly more electronegative than Me_3Si ^{1.05}. Therefore, it is expected that all the SiR_3 groups encountered in the compounds prepared will be electron releasing with respect to hydrogen. As explained above electron releasing groups adjacent to a carbonyl will cause a decrease in $\nu(\text{C}=\text{O})$. The lowering of $\nu_{\text{asym}}(\text{C}=\text{O})$ for the silyl imides with respect to succinimide and phthalimide correlates well with the expected results of the inductive effect.

Further support for the lowering of $\nu_{\text{asym}}(\text{C}=\text{O})$ when electron releasing groups are attached to the nitrogen of the imides is found for the case of potassium phthalimide. $\nu_{\text{asym}}(\text{C}=\text{O})$ for this salt in a nujol mull is 1685 cm^{-1}
35

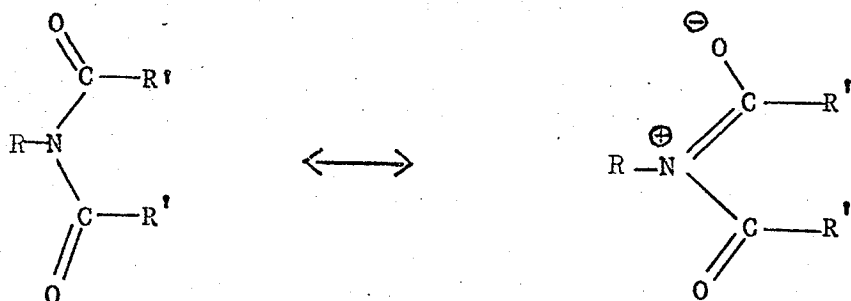
The resonance effect involves the π -electron clouds of multiple bonds. In the general case resonance stabilization with the resultant delocalization of electrons at the expense of the multiple bonds will weaken the multiple bonds and therefore the vibrating frequency of the multiple bond will decrease. The resonance effect is also very sensitive to the structure of the molecule because the atomic orbitals used for the molecular orbital must be orientated

to give maximum overlap. If the structure of the molecule prevents strong overlap of the atomic orbitals then the resonance stabilization will be negligible.

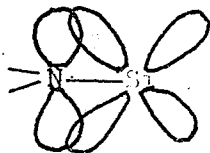
For open chain anhydrides¹⁰⁹ and imides⁹⁵ resonance structures have been proposed to explain the planarity of these molecules eg.,



and



Based on a large amount of work, resonance interaction has been proposed between silicon and nitrogen bonds. These interactions called $d_{\pi} - p_{\pi}$ interactions involve one of the 3d orbitals of silicon and a p orbital of the nitrogen.

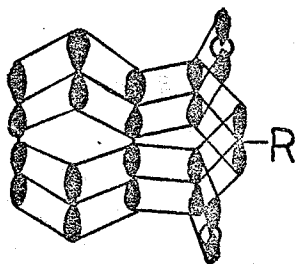


and can be represented simply by⁹¹



Two conclusions can now be drawn concerning the inductive and resonance effects in the succinimides. (1) Either no $d_{\pi} - p_{\pi}$ interaction occurs and $\Delta\nu_{\text{asym}}(\text{C}=\text{O})$ is entirely due to the $+I_{\text{SiR}_3}$ effect or (2) The $+I_{\text{SiR}_3}$ effect is very much larger than the $d_{\pi} - p_{\pi}$ interaction effect.

For the phthalimide derivatives the situation is similar. However, the presence of the phenyl ring allows a delocalized orbital to be constructed over the whole phthalimide molecule.



The consequence of this is that when R is SiR_3 and if it forms a $d_{\pi} - p_{\pi}$ bond it will be in competition with a larger delocalized molecular orbital than in the case of the succinimide derivatives. Secondly, the $+I_{\text{SiR}_3}$ effect of silicon will be displaced over a much larger system of orbitals. As a result both effects will be attenuated.

In figure 6 it can be seen that individual changes in the SiR_3 group on succinimide result in larger changes in $\nu_{\text{asym}}(\text{C}=\text{O})$ than for the same changes in the SiR_3 group on phthalimide. This would be in accordance with the suggestion that the larger delocalized system of the phthalimides would attenuate the $+I_{\text{SiR}_3}$ effect and the $d_{\pi} - p_{\pi}$ interaction effect.

The following conclusions can be drawn concerning the phthalimide derivatives (1) Either no $d_{\pi} - p_{\pi}$ interaction occurs and $\nu_{\text{asym}}(\text{C}=\text{O})$ is entirely due to the $+I_{\text{SiR}_3}$ effect or (2) the $+I_{\text{SiR}_3}$ effect is very much larger than the $d_{\pi} - p_{\pi}$ interactions, and (3) due to the attenuating effect of the delocalized system of phthalimide individual changes in SiR_3 cause small changes

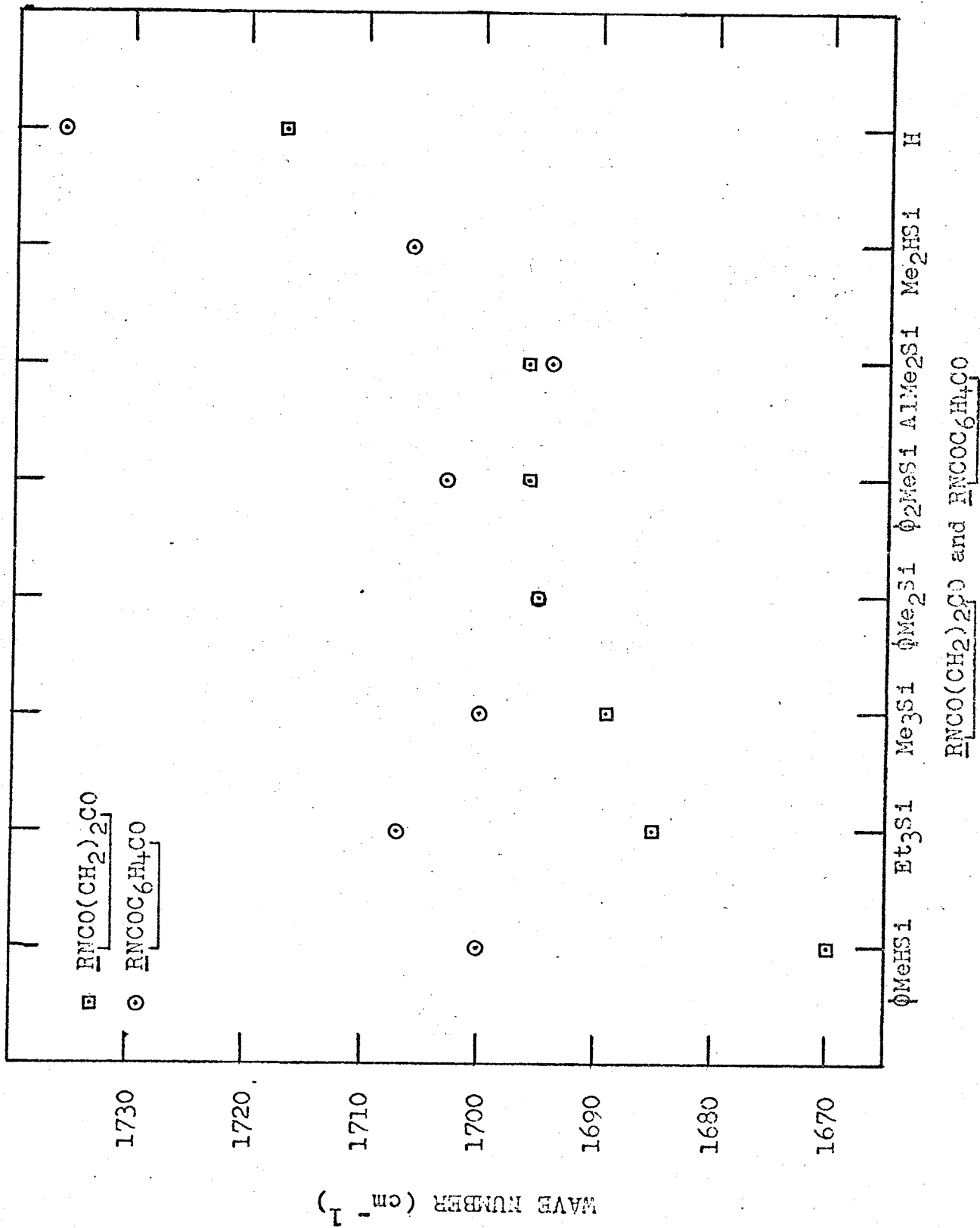
in $\nu_{\text{asym}}(\text{C}=\text{O})$.

For p-substituted benzyltriphenylsilanes good linear plots have been constructed for $\nu(\text{C}=\text{O})$ versus Hammett σ values. However, for these compounds such plots can not be constructed. This could indicate that other effects are causing anomalies. One of these could be field effects or through space effects which would show no ordered effect. More likely, however, the above mentioned effects ruled as negligible can still cause small but incoherent effects.

The values of the $\nu(\text{Si-H})$'s for the Si-H containing derivatives all lie in the region of chlorinated silanes^{102,110}. $\nu(\text{Si-H})$'s can be considered mainly as a measure of the electronegativity of groups attached to silicon^{111,102}. Therefore, the values of the $\nu(\text{Si-H})$'s indicates that the succinimido- and phthalimido groups on silicon are strongly electron withdrawing. This conclusion supports the + I_{SiR_3} effect suggested for those compounds.

FIGURE 6

PLOT of $\nu_{\text{asym}}(\text{C}=\text{O})$ (cm^{-1}) of the $\text{RR}'\text{R}''\text{SiNCO}(\text{CH}_2)_2\text{CO}$ and $\text{RR}'\text{R}''\text{Si-NCOC}_6\text{H}_5\text{CO}$ versus the $\text{RR}'\text{R}''\text{Si}$ groups.



STRUCTURE CHARACTERIZATION BY, PROTON N.M.R.

For all the compounds prepared there were no inconsistencies found between the structure proposed on the basis of the proton n.m.r. spectra and the structure of the compound expected from the reactions. Substituting the succinimido or phthalimido groups for the chlorine atom of the chlorosilanes did not alter the spectra of the unchanged SiR_3 groups except for small chemical shift differences.

The chemical shift of the singlet assigned to the two methylenes of the succinimido group showed almost no variation from compound to compound. Except for two low values (2.55 and 2.58 p.p.m.), the singlet was found to appear in the range 2.62 to 2.68 p.p.m. This is to be expected on the basis of electronic considerations because the hydrogens of the methylenes are four bonds away from the SiR_3 group and therefore should experience little if any of the $+I_{\text{SiR}_3}$ effect. Also, since the methylene groups are not expected to enter into any resonance interactions that may occur in these molecules, they should be relatively unaffected by any resonance interactions in these molecules.

Organic phthalimides like N-2,3-Xylylphthalimide, N-m-tolylphthalimide and bromoethylphthalimide show two multiplets near 7.82 and 8.02 p.p.m. which can be assigned to the two non-equivalent pairs of phenyl hydrogens of the phthalimido group - 112-114. For the phthalimido compounds that contained no Si-phenyl groups the phenyl hydrogens appeared as multiplets centered in the range 7.67 to 7.73 p.p.m. For the phthalimido compounds which contained the Si-phenyl groups, the two multiplets of the Si-phenyl and phthalimido groups could not be assigned on the basis of the integrated peak ratios because of the overlap of the two multiplets. However,

there is no reason to expect a different behavior for the Si-phenyl group containing phthalimides. Therefore, the phthalimido hydrogens were assigned to the lowfield multiplet and the Si-phenyl hydrogens were assigned to the highfield multiplet. On this basis, the multiplets of the phthalimido hydrogens were all centered in the range 7.68 to 7.85 p.p.m. and the multiplets of the Si-phenyl groups were centered in the range 7.31 to 7.55 p.p.m. Including the multiplets of the Si-phenyls for the succinimido and chloro derivatives gave a range of 7.30 to 7.60 p.p.m.

As shown in figures 4(a) and 5(a), the triethylsilyl groups of N-(triethylsilyl)succinimide and N-(triethylsilyl)phthalimide both appear as singlets for the proton n.m.r. of 10 mole percent solutions of these compounds in deuterated chloroform. They appear as singlets because the electron release of silicon into the methylene groups of the ethyl group causes these hydrogens to be as shielded as the methyl hydrogens. Similar effects have been observed in other metal-ethyl compounds ^{115,116}. For the spectra of triethylsilyl region of the neat liquids (fig 4(b), 5(b)), the anisotropic effect of the molecules themselves causes a slight chemical shift difference between the methyl and methylene groups and therefore the singlet appears unsymmetrical. For the proton n.m.r. of the 10 mole percent solutions in benzene (fig 4(c), 5(c)), the chemical shift difference between the methyl and methylene groups is increased enough by non-zero averaging of the anisotropy of the benzene solvent molecules ¹¹⁷ that the spectra of the triethylsilyl groups resembles the spectrum of an A_3B_2 system where $J/v_0\delta$ is near 0.75 ^{118(a)}. This effect is also apparent for the two pairs of non-equivalent phthalimido hydrogens of N-(triethylsilyl)phthalimide, (fig. 5(d)).

There the spectrum resembles the theoretical spectrum of an A_2B_2 system
where J/v_0 is near $0.37^{118(6)}$

ELECTRONIC NATURE OF THE Si-N BOND BY PROTON N.M.R.

As was discussed in the introduction $d_{\pi-p_{\pi}}$ interactions have been used to explain some n.m.r. results. However, it has been found for some Si-N bond containing compounds, that the n.m.r. results could be explained without reference to $d_{\pi-p_{\pi}}$ interactions 119,120,121.

For these compounds comparisons can not be made with the analogous organic compounds as was done by Birkofer because spectra for these compounds have not **been run**.

In Table 4 are found the chemical shift values for the Si-methyl groups of all the chlorosilanes used as starting materials and of the compounds prepared.

Table 4: - values of the Si-methyl groups of compounds $R_{4-x}SiCl_x$,

$R_{4-x}Si[\underline{NCO(CH_2)_2CO}]_x$ and $R_{4-x}Si[\underline{NCOC_6H_4CO}]_x$, (x=1 or 2).

δ (p.p.m.) of the methyl groups of $R_{4-x}Si-$

$R_{4-x}Si-$	$\underline{NCO(CH_2)_2CO}$	-Cl	$\underline{NCOC_6H_4CO}$
Me_3Si-	0.42	0.53	0.80
Me_2HSi-	0.42	0.59	0.50
$AlMe_2Si-$	0.43	0.51	0.51
$\emptyset MeHSi-$	0.70	0.88	0.82
$\emptyset Me_2Si-$	0.72	0.75	0.87
$Me_2Si=$	0.72	0.89	---
$MeViSi=$	0.95	0.95	---
\emptyset_2MeSi-	0.98	1.01	1.25

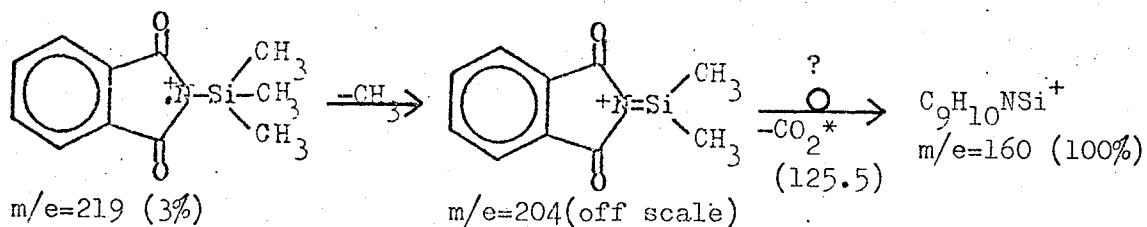
Assuming that molecular association is not a predominant effect and assuming that because an internal standard was used corrections do not have to be made for the bulk diamagnetic shielding one trend can be observed. That is, the methyl groups are deshielded in a regular order as the -I effect of the R groups increases. From the chemical shifts of the methyl protons

it seems apparent that the -I effects of the succinimido, phthalimido and chloro groups are about the same in these compounds. There seems to be no reason on the basis of these data to invoke $d-p$ interactions.

PART V

MASS SPECTRA OF THE SILYLIMIDES

For N-(trimethylsilyl)phthalimide the following scheme can be written which partially explains the mass spectrum obtained.

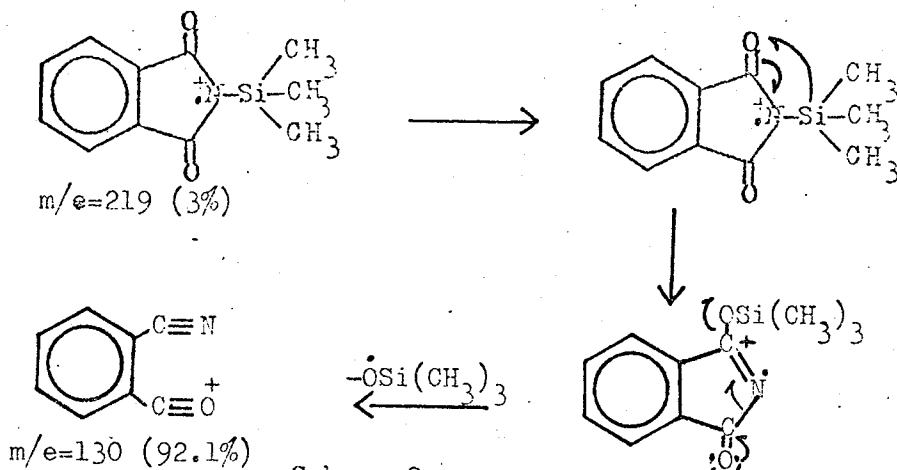


Scheme 1

* An asterisk indicates a transition supported by an appropriate metastable peak.

() After an asterisk surround the measured value of the metastable peak.

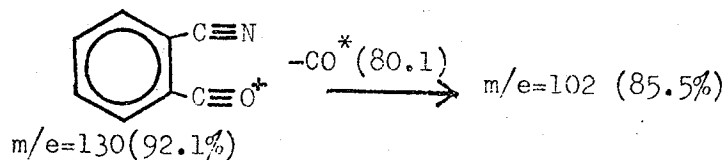
There is a very strong peak at $m/e=130$. This peak is quite prominent in the mass spectra of N-alkylphthalimides and is usually preceded by a peak at $m/e=148$ of similar intensity ¹²². However, in this spectrum the peak at $m/e=148$ was quite small. Therefore, an alternate pathway to the peak at $m/e=130$ is suggested.



Scheme 2

The transition suggested is not supported by a metastable peak but Si-O bonds are very stable and therefore their formation is very favourable.

The peak at $m/e=102$ found in this spectrum can be obtained by the following transition.



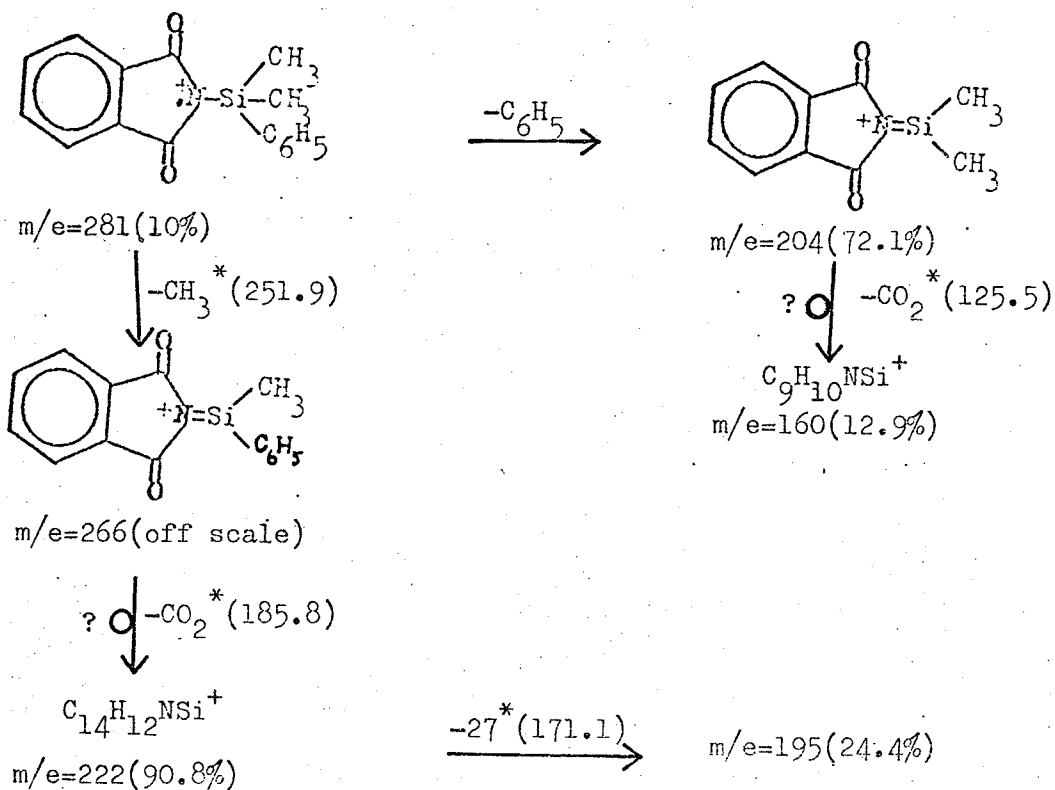
The loss of CO_2 from N-alkylphthalimides has been suggested in two reports 123, 75 to explain prominent M-44 peaks in their mass spectra. In another report the M-44 peaks were said to be due to the loss of CO_2 from thermal isomerization products. For N-(trimethylsilyl)phthalimide the loss of 44 mass units from the peak at $m/e=204$ gives rise to a very intense peak and this transition is supported by the appropriate metastable peak.

The four peaks in table 1(f) lower than $m/e=102$ can be accounted for in a straight forward manner by further fragmentation of the ion at $m/e=102$.

The peaks that appear 1 mass unit above the major fragment peaks can be accounted for by the isotopes C^{13} , Si^{29} , and H^2 naturally present in the molecule.

No significant peak was found to correspond to a trimethylsiliconium ion in this mass spectrum.

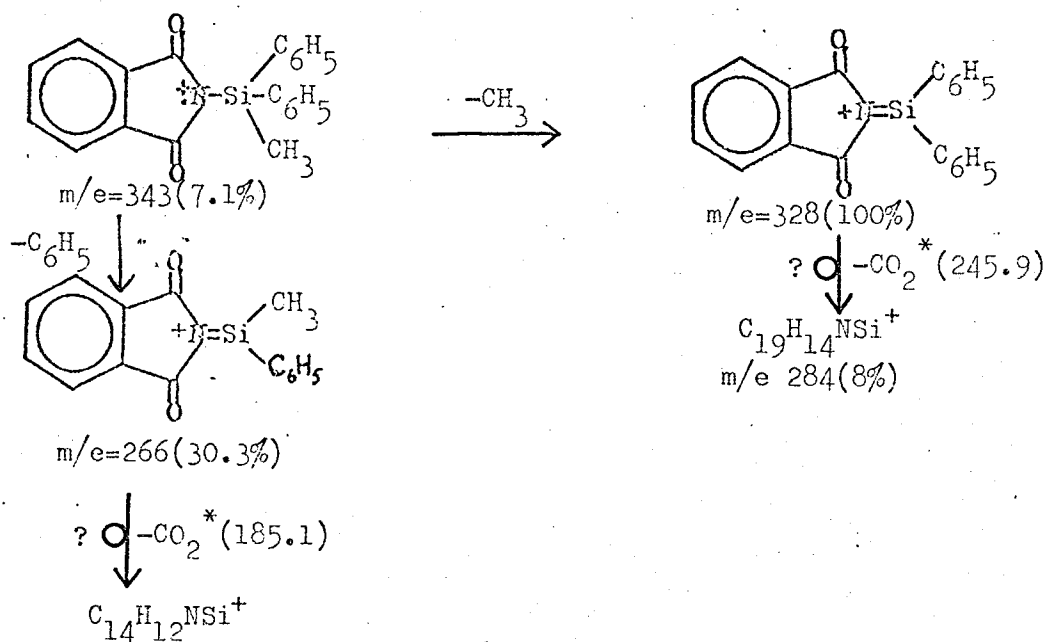
The fragmentation patterns outlined above are further supported by the fact that N-(diphenylmethylsilyl)phthalimide and N-(phenyldimethylsilyl)phthalimide behave in exactly the same way. For N-(phenyldimethylsilyl)phthalimide the following fragmentation pattern is found.



Scheme 3

The peak at $m/e=195$ appears to be a fragment of the peak at $m/e=222$ since there is found in the mass spectrum an appropriate metastable peak.

For *N*-(diphenylmethylsilyl)phthalimide the following fragmentation pattern is found.



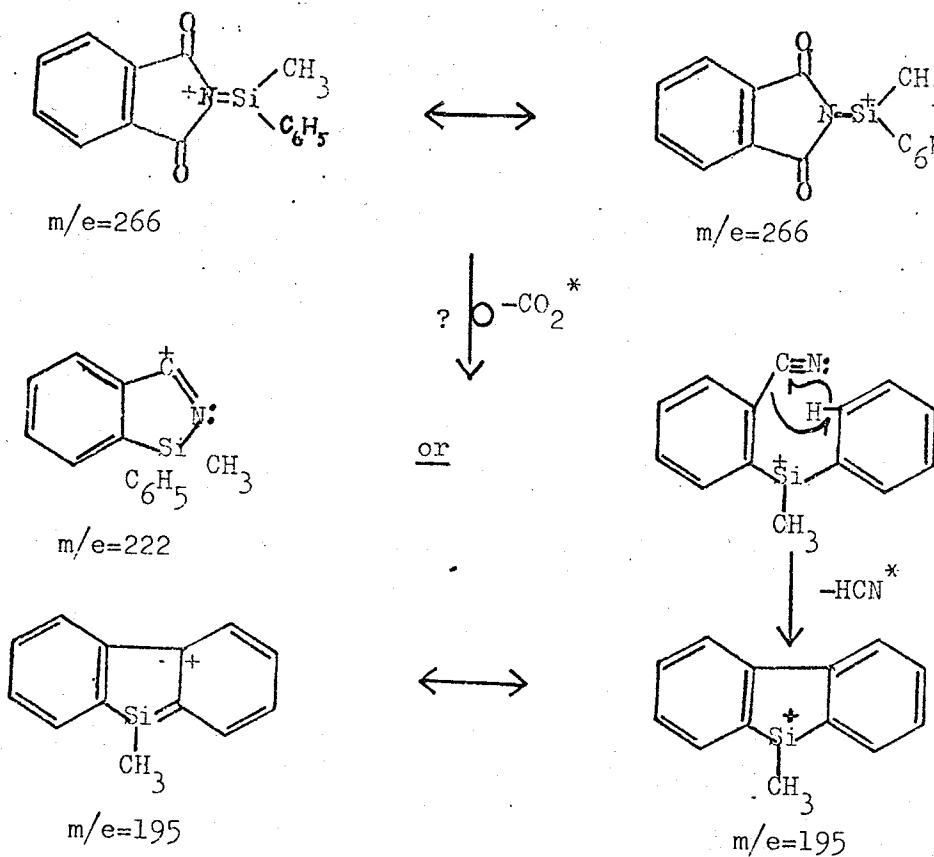
Scheme 4

For both of these compounds the fragment at $m/e=130$ is an intense peak and is followed by the transition to the fragment at $m/e=102$ which is also an intense peak. This transition in each case is supported by the appropriate metastable peak.

The loss of CO_2 appears to occur for all of these compounds. It seems to be a major path of fragmentation of the silylphthalimides. Since the transition involving the loss of CO_2 occurs from fragments of lower mass than the parent ion it seems reasonable to say that this loss does not occur from thermally isomerized products.

Whenever the $\text{M}^+ - \text{CO}_2$ fragment has more than one phenyl ring attached to the silicon a fragment of 27 mass units is lost. The clearest example occurs for the fragment $m/e=222$ of *N*-(phenyldimethylsilyl)phthalimide.

The following scheme can be written to explain this transition.



Scheme 5

For N-(diphenylmethylsilyl)phthalimide two $M^+ - CO_2$ fragments exist which lose a fragment of 27 mass units. However, these transitions are weak and only very weak metastable peaks could be found to support these transitions.

No significant peaks were found in either case that corresponded to either the phenyldimethylsiliconium ion or the diphenylmethylsiliconium ion.

Peaks found below $m/e=102$ can be explained in both cases by the further fragmentation of this ion.

In both cases the ion at $m/e=130$ was found. Its transition to the ion at $m/e=102$ was also found in both cases as well as the appropriate metastable peak to support this transition.

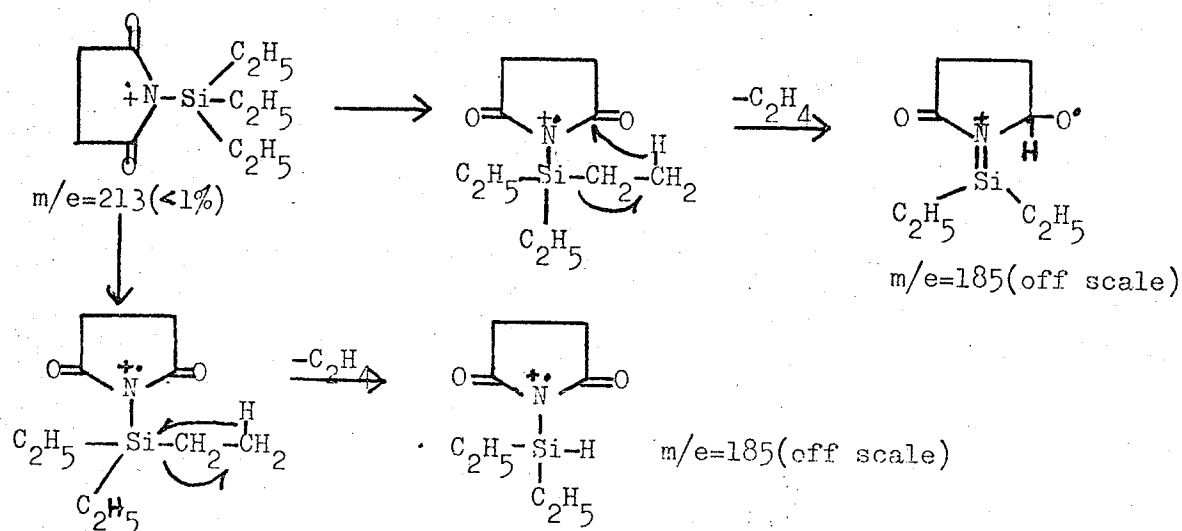
In general the following conclusions can be drawn from these mass spectra. The parent ions appear at very low intensity. Unsaturated silicon containing fragments are consistent with some of the ions formed. The loss of a methyl group from the silicon atom is more favourable than the loss of a phenyl group for these compounds since the $M-15$ ion is the base peak in all of these mass spectra.

The mass spectra of the silylsuccinimides with the exceptions of N-(diphenylmethylsilyl)- and N-(phenylmethylsilyl)succinimide showed peaks above the parent ion. The mass spectra of N-(allyldimethylsilyl)- and N-(phenylmethylsilyl)succinimide could not be solved. Partial fragmentation patterns are presented for the others.

On the basis of the elemental analysis, the proton n.m.r. spectra and the infrared spectra there appears to be no doubt concerning the structure of these compounds. However, these compounds heated to $100^\circ C$ or higher in

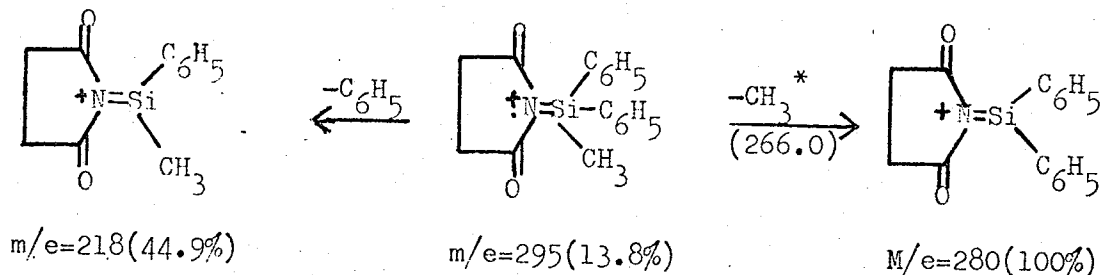
order to obtain a mass spectrum exhibited ions higher than the expected parent ion. Therefore it is suggested that thermal reactions occurred leading to the artifacts found. This effect of heating is supported by the fact Sublimation of N-(diphenylmethylsilyl)succinimide led to an increase in impurities as compared with the unheated recrystallized product.

The following scheme can be written which partially explains the mass spectrum of N-(triethylsilyl)succinimide.

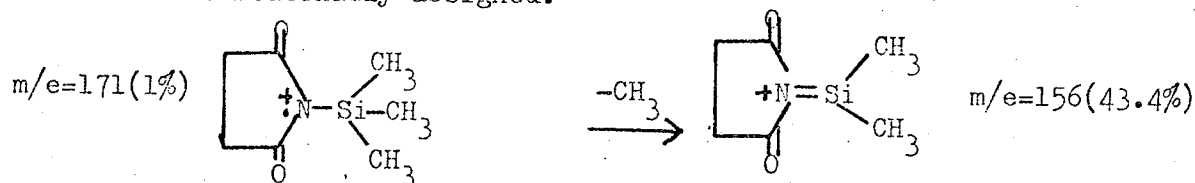


All the rearrangements used in this scheme have been proposed for the fragmentation patterns of the N-alkylsuccinimides ⁷⁴.

For the mass spectrum of N-(diphenylmethylsilyl)succinimide the following scheme can be written.



For N-(trimethylsilyl)succinimide only one transition appeared which could be reasonably assigned.



No peaks appeared in these mass spectra which suggested the presence of siliconium ions.

Based on this very scanty data general conclusions concerning the mass spectra of the silylsuccinimides are not appropriate.

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