INVESTIGATIONS INTO THE FORMATION AND CLEAVAGE OF SILOXANES

BY

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SUMMARY

The hydrolysis of dimethyldichlorosilane and methylphenyldichlorosilane, with an excess of water, was carried out under various conditions. The initial product, a silane diol, usually undergoes condensation very readily to give mixtures of open chain α,ω-siloxane diols and cyclic siloxanes. These mixtures were quantitatively analysed by column and gas chromatography, the proportions of cyclic to linear siloxanes and the proportions of cyclic trimer, tetramer and pentamer being obtained. With the methyl phenyl cyclosiloxanes, which exist in stereoisomeric forms, product isomer ratios were also determined. The effects of varying the solvent, temperature, concentration, time for reaction, etc., on the product ratios are discussed from the point of view of competing reactions during the condensation of the initial hydrolysis products, relative stability of possible products, further reaction of products with the hydrochloric acid present, etc.

On treatment with acid or base, oligomeric cyclic siloxanes can be polymerised to high molecular weight materials. In this work the initial stage of the reaction of some cyclic siloxanes with acid and base was investigated. The acid reaction was pursued mainly with regard to the effect of acid on the initially formed cyclic products in the hydrolysis of diorganodichlorosilanes. Analytical results obtained by thin layer, column and gas chromatography and proton resonance spectroscopy are mentioned. It was found that, in general, the initial effect of acid or base on a cyclic trimer was to convert it to the corresponding cyclic tetramer.

Many low molecular weight open chain stannosiloxanes have been reported but little mention has been made of cyclic types. A brief examination of some potential methods for the preparation of cyclic polyphenylstannosiloxanes is described.

This work was carried out between 1967 and 1970 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

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CONTENTS

CHAPTER 3 An examination of some possible methods for preparing cyclic polyphenylstannosiloxanes

TABLES

INTRODUCTION

Silicones, linear or crosslinked polyorganosiloxanes, are the only semi inorganic polymers in widespread use. Since their commercial introduction in the early 1940's enormous increases in their production and range of uses have occurred. This unique and versatile group of materials, consisting of oils, elastomers and resins, have found such diverse applications as lubricants, water repellents, hydraulic fluids, heat transfer media, electrical insulators, mold release agents, and as constituents of paints, polishes, pharmaceuticals and cosmetics. The technological importance of these materials arises from a remarkable combination of properties. A high thermal and chemical, particularly oxidative, stability is combined with water repellency, electrical insulating properties, and in the case of the methyl silicones, the lowest known coefficient of viscosity change with temperature.

The technological production of silicones consists, in general, of three processes:

1. The production of monomeric silicon functional organosilanes.
2. The hydrolysis of mainly diorganodichlorosilanes

to produce a mixture (usually) of cyclic and linear oligomeric siloxanes.

3. The formation of high polymers from the species obtained in 2. by equilibration-polymerisation processes and then, for some applications, cross linking.

Of the three processes the first is the most difficult technologically. The development of silicone production closely followed the development of methods for the large scale production of monomeric silanes. One important process is a direct synthesis from alkyl halide and silicon in the presence of a catalyst such as copper. The reaction produces a range of silanes but the type mainly required for silicone production is R_2SiX_2. Only by very careful optimisation of the conditions can the reaction be made to proceed satisfactorily and to give products in the desired proportion. The resulting silanes sometimes have close boiling points and difficulties arise in their separation by fractional distillation.

Although the technical execution of the other two main processes in silicone production is considerably easier than the first, these processes have elicited much interest and have been extensively investigated, particularly with regard to polydimethyl compounds.

Some aspects of the two latter processes are investigated in this work. In general the hydrolysis of diorganodichlorosilanes gives a mixture of cyclic siloxanes and linear siloxanediols. The proportions of cyclic and linear products and the distribution of cyclic species can be made to vary widely according to the conditions of hydrolysis. Silicones are based mainly on polydimethylsiloxanes and the hydrolysis of dimethyldichlorosilane has received much attention. The evaluation of the products of hydrolysis was formerly a tedious process involving fractional distillation. More recently the much more convenient technique of gas chromatography has been employed and this is used extensively in this work. Although some work is reported on the hydrolysis of dimethyldichlorosilane, the main emphasis here is on the hydrolysis of methylphenyldichlorosilane. This has been much less investigated than the former reaction but is of interest particularly because of the possibilities for stereoisomerism in the products. A feature of the work is the inclusion of some low temperature (-75°C.) hydrolysis experiments.

In the third stage of the technical production of silicones, an oligomeric siloxane such as the cyclic tetramer, is polymerised by the action of acid or base. The average chain length of the product can be controlled by the admixture of a disiloxane to provide monofunctional silicon units. The greater the proportion of this "chain stopper", the lower the average chain length. The reaction is an equilibration and a mixture of oligomers and polymers is obtained. After removal of the catalyst the former can be removed by vacuum distillation. In this work the initial stage of the reaction of some cyclic siloxanes with acid and base was investigated. The acid reaction was pursued mainly from the point of view of the effect of acid on the initially formed cyclic products in the hydrolysis of diorganodichlorosilanes. In general the initial effect of acid or base on a cyclic trimer is to convert it to the corresponding cyclic tetramer. In the case of the methyl phenyl cyclic siloxanes, product isomer ratios were examined.

The great success of silicones in a variety of technological applications has prompted a search, during the last two decades, for inorganic polymers with even more desirable combinations of properties. Amongst materials that have been investigated are heterosiloxanes, i.e. siloxanes in which some of the silicon atoms have been replaced by heteroatoms giving the grouping Si-O-M, where M is at least divalent. Little progress seems to have been made towards the production of improved polymers but many low molecular weight model compound heterosiloxanes, particularly with boron, aluminium, titanium and tin as heteroatoms, have been prepared and investigated. Of particular interest is the possibility of the existence of interconvertible oligomeric rings and polymeric chains, as with the siloxanes and several other heteroatom systems. In one of the most numerous groups of heterosiloxanes, the stannosiloxanes, examples of cyclic types seem to be almost completely absent from the literature. The possibility of the abovementioned ring-chain relationship applying to the stannosiloxanes suggested an investigation into possible methods for preparing cyclic stannosiloxanes. A brief examination of some of these methods for cyclic polyphenylstannosiloxanes is described.

CHAPTER 1

The formation of cyclic organosiloxanes by the hydrolysis of chlorosilanes.

1.1 Introduction.

i. The hydrolysis of chlorosilanes.[1,2]

The hydrolysis of organochlorosilanes is one of the central processes in the production of high molecular weight siloxanes or silicones. The initial reaction in the hydrolysis is the formation of a silanol and hydrochloric acid;

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{Cl} + \mathrm{H_2O} \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HCl}.$$

The ease of this hydrolysis depends on the functionality of the silane. For a given organic group the order of reactivity is;

$$\left(\mathrm{SiCl_4} > \right] \mathrm{RSiCl_3} > \mathrm{R_2SiCl_2} > \mathrm{R_3SiCl}.$$

Silanols show a marked tendency to undergo spontaneous condensation to form siloxanes;

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} \; + \; \mathrm{HO}-\overset{|}{\underset{|}{\mathrm{Si}}}- \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- \; + \; \mathrm{H_2O}.$$

This tendency for spontaneous condensation increases with the number of -OH groups bound to the silicon atom and also depends on the nature of the organic group. As condensation usually accompanies the hydrolysis reaction, it also depends on the conditions under which the hydrolysis is carried out. Of particular importance here is the hydrochloric acid formed during the hydrolysis, the silanol condensation being promoted by acid.

The three different groups of organochlorosilanes give markedly different types of product in simple hydrolysis reactions.

A triorganochlorosilane gives the triorganosilanol as the initial product. If this condenses then the hexaorganodisiloxane will be the final product. e.g. Trimethylchlorosilane with excess water gives hexamethyldisiloxane:

$$2(\mathrm{CH_3})_3\mathrm{SiCl} \; + \; \mathrm{H_2O} \longrightarrow (\mathrm{CH_3})_3\mathrm{SiOSi}(\mathrm{CH_3})_3 \; + \; 2\mathrm{HCl}$$

With diorganodichlorosilanes the diorganosilanediol initially formed can undergo condensation more readily than in the above case to give a variety of cyclic siloxanes and open chain siloxanediols. The nature of the organic groups and the conditions of the hydrolysis have a profound effect on the course of the reaction and hence the nature of the products. The effect of varying some of these factors, particularly with regard to the nature of the cyclic products, is described subsequently.

The organosilanetriols that may be formed initially during the hydrolysis of organotrichlorosilanes are extremely unstable and usually condense to give highly cross linked polymeric materials which are often brittle solids. Only a very few silanetriols have been isolated, e.g. phenylsilanetriol, $PhSi(OH)_3$, has been obtained by careful hydrolysis of phenyltrichlorosilane using the theoretical amounts of water and aniline, the latter as a hydrogen chloride acceptor.[3] Under certain conditions, instead of condensing to polymeric materials, the silanetriols may condense to low molecular weight "spherocyclic" polysiloxanes, $(RSiO_{3/2})_n$. These consist of three dimensional structures of fused siloxane rings.

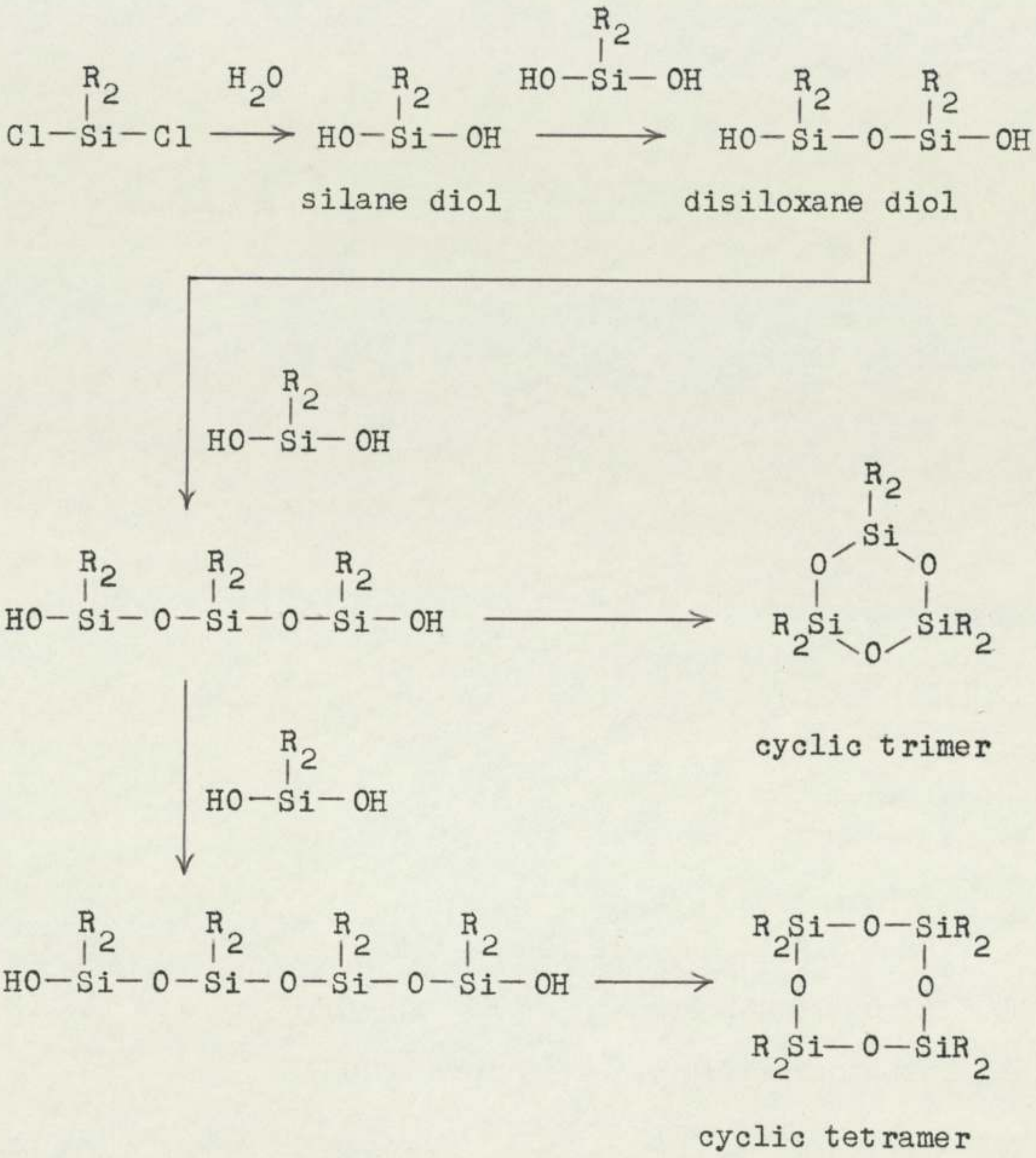
The cohydrolysis of mixtures of chlorosilanes of different functionality is used to produce materials with controlled molecular weight and structure.

e.g. R_3SiCl, mixed with R_2SiCl_2, acts as a chain stopper.

$RSiCl_3$ or $SiCl_4$, mixed with R_2SiCl_2, brings about cross linking, etc. In this way, with further processing in some cases, a large number of low molecular weight and polymeric siloxanes exhibiting a variety of structural features can be obtained.

ii. The hydrolysis of diorganodichlorosilanes.

A general scheme for the hydrolysis of diorganodichlorosilanes with excess water is:



Cyclic dimers, $(R_2SiO)_2$, have not been isolated, presumably because of the strain that would be present in the ring. Monomers, $R_2Si{=}O$, are also unknown, because of the inability of silicon to form double bonds.

The silane diol is only a significant final product of hydrolysis if the organic groups present can stabilise the molecule sufficiently to prevent condensation under the prevailing conditions, e.g. diphenylsilanediol has been obtained from diphenyldichlorosilane in 93% yield by hydrolysis in the presence of toluene and t-amyl alcohol.[4] Otherwise a mixture of cyclic and linear species is usually produced. For a given diorganodichlorosilane the relative proportions of cyclic and linear products and also the proportions of individual cyclic products can vary very widely according to the conditions of hydrolysis.

Some factors that can affect the hydrolysis:

1. Temperature. The dependence of product proportions on temperature is reported later in this work for the dimethyl and methyl phenyl systems. The reaction is exothermic so temperature control must be exercised during the course of the reaction.
2. pH of the aqueous medium. During addition of the chlorosilane to a fixed amount of water, the aqueous layer becomes progressively more acid due to the formation of hydrogen chloride. This progressive change in one of the major factors affecting the reaction during the course of the reaction can be avoided in continuous flow reactors or by the continuous addition of alkali so as to keep the pH constant. This method is particularly applicable where a diol is the desired product,[5] the condensation of diols being promoted by acid and also by alkali. For some applications an acid or alkaline solution can be used for the hydrolysis. With diphenyldichlorosilane, acid favours the formation of the cyclic trimer, $(Ph_2SiO)_3$, and alkali the tetramer, $(Ph_2SiO)_4$.[4]

3. The solvent system. Single or mixed solvents, miscible or immiscible with water can be employed. A high dilution of intermediate diols in an immiscible solvent can promote intramolecular condensation at the expense of intermolecular. An immiscible solvent also protects the diols from the catalytic effect of the aqueous medium. It is also possible for the solvent to participate in the reaction. Alcohols used either alone or mixed with water, reduce the tendency for silanols to condense and even out the hydrolysis rates of different chlorosilanes in cohydrolysis reactions.

4. Time for reaction. The initial reaction of the chlorosilane with water is usually more rapid than the subsequent condensation of the diols.[6] Hence the overall time for the reaction can affect the degree of condensation that occurs. The cyclic products can also react with the aqueous medium and be interconverted or equilibrated, as will be shown subsequently.

5. Alternative sources of water.
e.g. Salt hydrates such as $FeSO_4.7H_2O$, $CuSO_4.5H_2O$, etc.
Compounds such as $NaHCO_3$ and $NaHSO_3$.

With dimethyldichlorosilane the use of such compounds has given hydrolysates poor in low molecular weight siloxanes.

6. Hydrolysis with a deficiency of water. If the reaction is carried out using less water than is required for complete hydrolysis, the chlorosilanol and chlorosiloxanes may be formed. This partial hydrolysis of dichlorosilanes affords a convenient route to individual siloxane diols.[4,7]

The appropriate dichlorosiloxane may be separated from the partial hydrolysis reaction mixture by fractional distillation and then hydrolysed to give the corresponding diol. The formation of these chloro compounds as intermediates during the complete hydrolysis has been demonstrated by following the reaction conductimetrically.[6]

iii. Some theoretical aspects of cyclosiloxane formation during hydrolysis reactions.

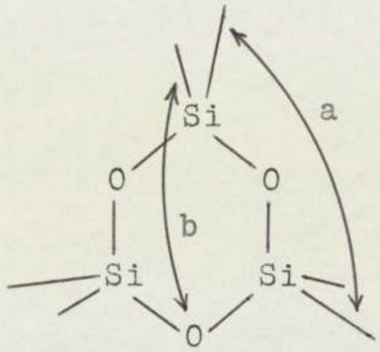
The general scheme given at the beginning of section ii. shows that two types of competitive reaction occur. These are cyclisation and addition of another monomer unit to increase the chain length. Cyclisation will take place readily if the skeletal bond angles are suitable for ring closure and if bond rotation can occur so that end groups can come together and combine. Mathematical analyses on the basis of these considerations have been carried out for the equilibration of cyclic and linear polydimethylsiloxanes. Some measure of agreement with experimental results has been obtained.[8]

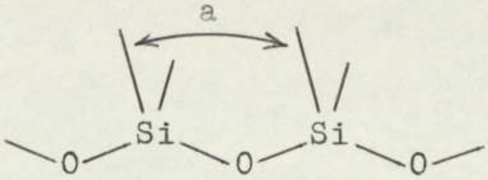
The Pauling electronegativity values for silicon and oxygen are 1.8 and 3.5 respectively. This comparatively large difference indicates that the Si-O bond has considerable ionic character. Bonds of this type have more angular flexibility than the purely covalent type and can exhibit considerable variation without much increase in internal energy or strain. This factor contributes to the formation of a range of low molecular weight cyclic species in hydrolytic and equilibration processes rather than the formation of one particular stable compound. This is a characteristic feature of siloxane chemistry. There are, however, some variations in the ease of formation and stability of the lower cyclic oligomers.

Electron diffraction studies have been carried out on some of the polydimethylcyclosiloxanes and bond angles, bond distances, and ring conformations have been determined.[9,10] The O-Si-O angle shows little variation from the tetrahedral value (109° 28'). Various values in the region 120°-145° have been quoted for the Si-O-Si angle. It seems agreed, however, that this angle in the cyclic tetramer is larger than in the trimer. The Si-O-Si angle in gaseous hexamethyldisiloxane, which is presumably unstrained, is similar to that in the eight membered and larger rings. It therefore appears that the eight membered and larger rings are unstrained whereas the six membered trimer ring is slightly strained. This seems to be confirmed by thermochemical measurements which indicate that hexamethylcyclotrisiloxane has a strain energy of up to 9Kcal./mole.[11] It has been well established that the six membered siloxane ring is planar, or nearly so, and the eight membered and larger rings puckered. The origin of the planarity of the six membered ring could be polar repulsion between the skeletal atoms.

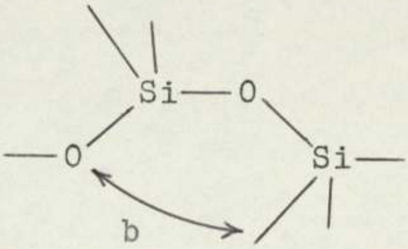
The yields of individual polydimethylcyclosiloxanes in hydrolytic and equilibration processes are consistent with the above physical considerations. The amount of trimer obtained is almost invariably very much less than the amount of tetramer. In the hydrolysis of dimethyldichlorosilane according to the scheme, at the trisiloxanediol stage chain lengthening, rather than cyclisation, will be the preferred process. At the tetrasiloxanediol stage, however, cyclisation to the unstrained octamethylcyclotetrasiloxane will take place readily. The cyclic pentamer and higher cyclics are usually formed in smaller amounts. The cyclic trimer is very much more reactive chemically than the tetramer (Chap. 2) and further reduction in the amount of trimer occurs because it reacts with the hydrochloric acid present to form other products. The condensation reactions of the siloxanediols leading to chain lengthening and cyclisation and also the cleavage of cyclosiloxanes are catalysed both by acids and bases.

The acid hydrolysis of diphenyldichlorosilane yields hexaphenylcyclotrisiloxane.[4] Presumably at the trisiloxane stage, cyclisation must be favoured rather than chain lengthening. It has been suggested that the phenyl groups, which must be responsible for this effect, can be involved in several types of steric interaction.[12] I and II (P.14) represent two extreme types of open chain conformation. It is evident that a and b types of repulsion would be more significant in the open chain conformations I and II respectively than in the cyclic siloxane. A more general and quantitative examination of the effect of substituents on the position of equilibrium in ring closure reactions has been made in terms of the enthalpy and entropy of cyclisation.[13]



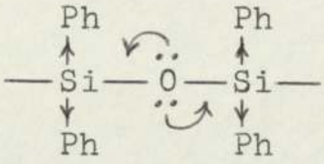


I



II

Hexaphenylcyclotrisiloxane is also very much more resistant to cleavage by acids than the corresponding methyl compound, hence once formed it does not tend to react further. The initial step in the acid cleavage of siloxanes is presumably protonation of an oxygen atom. This will happen very much less readily when electron withdrawing phenyl groups, rather than methyl groups, are present. This effect also doubtless contributes to



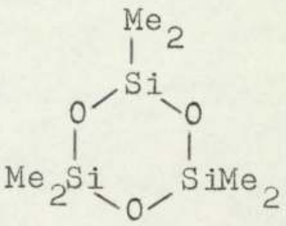
$$-\underset{\underset{\text{Ph}}{\downarrow}}{\overset{\overset{\text{Ph}}{\uparrow}}{\text{Si}}}-\ddot{\underset{..}{\text{O}}}-\underset{\underset{\text{Ph}}{\downarrow}}{\overset{\overset{\text{Ph}}{\uparrow}}{\text{Si}}}-$$

the comparative reluctance with which diphenylsilanediol undergoes condensation.

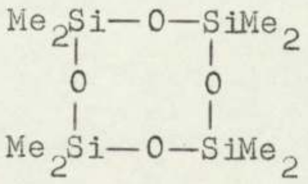
It is interesting to note that on contact with strong bases the phenyl trimer is converted to tetramer (Chap. 2). Hence hydrolysis or condensation reactions under alkaline conditions give tetramer and not trimer.

1.2 The hydrolysis of dimethyldichlorosilane.

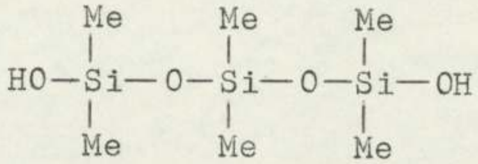
The hydrolysis of dimethyldichlorosilane with excess water yields a mixture containing substantial amounts of polydimethylcyclosiloxanes together with linear polydimethylsiloxane-α,ω-diols. The composition has been stated to vary between 20 and 50% cyclosiloxanes.[14] Some typical products are:



Hexamethylcyclotrisiloxane



Octamethylcyclotetrasiloxane



$$\mathrm{HO-\underset{Me}{\overset{Me}{\underset{|}{\overset{|}{Si}}}}-O-\underset{Me}{\overset{Me}{\underset{|}{\overset{|}{Si}}}}-O-\underset{Me}{\overset{Me}{\underset{|}{\overset{|}{Si}}}}-OH}$$

Hexamethyltrisiloxane-1,5-diol

The lower molecular weight diols are only observed in any quantity if special precautions are taken during the hydrolysis because of the ease with which they condense. The simultaneous addition of dimethyldichlorosilane and ammonia to water, so as to keep the solution neutral, yields tetramethyl-1,3-disiloxanediol in good yield.[5]

Dimethylsilanediol is much more difficult to obtain, because of the extreme ease with which it undergoes condensation. It has been obtained, by hydrolysis of the chlorosilane, using a procedure similar to the one mentioned earlier for the preparation of phenylsilanetriol.[3] Another method, in which strictly neutral conditions can be more easily maintained, is by the hydrolysis of dimethyldimethoxysilane with boiling water.[15] The use of an excess of alkali during the hydrolysis of dimethyldichlorosilane promotes condensation but leads to the formation of high molecular weight linear polymers, rather than cyclic oligomers.[14]

In the present work the effect of varying three factors in the hydrolysis of dimethyldichlorosilane with an excess of water has been investigated and the results are summarised in Table I (P.17). Gas chromatography, rather than the fractional distillation that has been used formerly,[14] affords a quick and convenient method of analysing the hydrolysis products for cyclic siloxanes. Where only the three lower cyclosiloxanes are being determined, as in this work, the gas chromatography may be carried out isothermally at about 100°C. When a larger range of cyclics are determined, it is desirable to use a temperature program.[16] The cyclic siloxanes are progressively eluted in order of increasing molecular weight and the peak areas are compared. Linear siloxane diols are not eluted. Cyclic siloxanes higher than the pentamer, which are present in quite small amounts, were not determined. The figures for "% of cyclic siloxanes

Table I

The hydrolysis of dimethyldichlorosilane with an excess of water under various conditions.

Time for addition of water: About 1¼ hours.

Chlorosilane/solvent: 1/5 by volume at 0°C. and 1/15 at -75°C.

Solvent	Temperature, °C.	Trimer/Tetramer	Tetramer/Pentamer	% of cyclic siloxanes in product
1. Addition of water to chlorosilane:				
Ether	0	Trace/100	66/34	42
Ether	-75	35/65	90/10	24
Acetone	0	0/100	56/44	34
Acetone	-75	9/91	68/32	13
2. Addition of chlorosilane to water:				
Ether	0	15/85	91/9	23
Ether	-75	58/42	93/7	6
Acetone	0	0/100	82/18	27
Acetone	-75	Trace/100	0/0	Trace

in product" are the percentages of trimer + tetramer + pentamer compared to the maximum possible yield of cyclic material.

Discussion of results.

1. Order of addition of reactants.

During the initial stages of the addition of water to the chlorosilane, the water will react completely and a mixture of α,ω-dichlorosiloxanes will be formed. These will be progressively hydrolysed during further addition of water to siloxanediols which then may undergo condensation. After an excess of water has been added, the siloxanes are exposed to hydrochloric acid and may undergo further modification.

When the chlorosilane is added to water, complete hydrolysis will occur rapidly and the products will be exposed to a progressively increasing concentration of hydrochloric acid.

2. Solvent.

One effect that can be ascribed to the miscibility of the solvent with water is the degree of exposure of the products of the reaction to hydrochloric acid. Overall the yields of cyclic siloxanes using acetone as solvent are somewhat less than with ether. There is a marked effect on the yield of trimer, however. This is doubtless due to the ease with which the trimer reacts with hydrochloric acid.

3. Temperature.

Little work seems to have been done on the low temperature hydrolysis of chlorosilanes. A dry ice-acetone bath is an obvious cooling medium to use, giving a temperature (-75°C.) well below that commonly used for hydrolysis.

In each pair of experiments the rise in temperature from -75 to 0°C. causes a substantial increase in the yield of cyclic products. At the same time the cyclic siloxane profile changes in favour of pentamer at the expense of trimer. At the higher temperature the siloxane chains are growing larger and cyclising more rapidly. The cyclic trimer, once formed, probably reacts more rapidly with the hydrochloric acid at the higher temperature.

It is probable that thermodynamic, as well as kinetic effects, operate in controlling product proportions. This is particularly likely in the case of the trimer, which is formed in relatively greater proportion at the lower temperature. The entropy decrease for cyclisation should be relatively greater for the formation of the slightly strained trimer than for the formation of the strain free puckered tetramer, i.e. for cyclisation $\Delta S_{trimer} > \Delta S_{tetramer}$. If, in the equation for the free energy of cyclisation, $\Delta G = \Delta H - T\Delta S$, the enthalpy term is largely independent of temperature, then the temperature dependent $T\Delta S$ term would thermodynamically favour the formation of trimer at the lower temperature.

It has been observed elsewhere that hydrolysis in a strongly acid medium favours the formation of oligomeric cyclosiloxanes.[14] A further series of hydrolyses were done with a view to maximising the yield of cyclic trimer. This was attempted by rapidly running a dilute solution of dimethyldichlorosilane in diethyl ether into ether plus a large volume of hydrochloric acid. In this way the reaction products, in dilute solution in ether, will only be in contact with the aqueous acid for a short time. This should favour the acid sensitive trimer. In the previous series of hydrolyses the long reaction times resulted from a desire to keep the temperature of the mixture constant. In these experiments the temperature rose 6 or 7°C. during the 4 minutes of addition of the chlorosilane. The mixture was then stirred for a further 2 minutes. The hydrolysis products were again analysed by gas chromatography using a standard injection of pure tetramer in order to establish the yields of cyclic products. The results are summarised in Table II (P.21).

The first of these experiments, where plain water is used for the hydrolysis and where only a trace of trimer is produced, indicates that cyclisation is a comparatively slow process. After each experiment there was a delay of at least a day before the gas chromatographic analysis was carried out. Thus the first result indicates that the acid free mixture of siloxanediols shows little tendency to undergo cyclisation at room temperature. The other results show that cyclisation and chain lengthening is strongly catalysed by acid. With increasing concentration of acid, the yield of trimer increases sharply and reaches a maximum at about 6 M acid. Competing with trimer producing cyclisation will be

Table II

The hydrolysis of dimethyldichlorosilane with hydrochloric acid of various concentrations.

Time for reaction: 4 + 2 minutes.
Average temperature: 0°C.
Chlorosilane /solvent (total): 1 /20.

Molarity of hydrochloric acid	Trimer/ Tetramer	Tetramer/ Pentamer	% of cyclic siloxanes in product
0	-	-	Trace (mainly trimer)
4	46 /54	95 /5	15
6	26 /74	84 /16	46
8	6 /94	84 /16	66
10.5	5 /95	79 /21	32

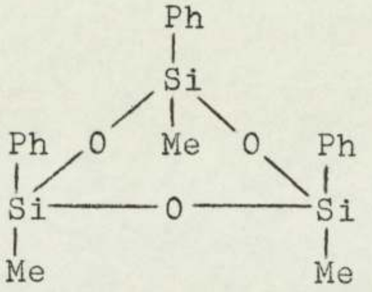
chain lengthening. This process predominates over trimer formation above an acid concentration of about 6 M. The increasing formation of pentamer supports this. Above an acid concentration of about 8 M the overall yield of the three lower cyclic siloxanes drops sharply. This is presumably due to further chain lengthening, possibly accompanied by cyclisation to higher cyclic oligomers. It was shown (Chap. 2) that, in dilute solution in ether exposed to 7.5 M hydrochloric acid at 20°C., the trimer has a half life of about 20 minutes. It would appear, therefore, that reaction of the trimer with acid would play comparatively little part in these experiments, at least up to 7.5 M acid.

1.3 The hydrolysis of methylphenyldichlorosilane.

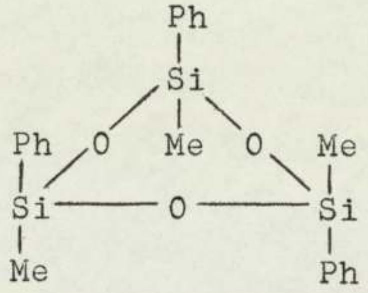
The hydrolysis of methylphenyldichlorosilane has not been as extensively investigated as that of dimethyldichlorosilane. The former reaction is, however, of particular interest because the products can exist in stereoisomeric forms due to the presence of two different groups on each silicon atom. The hydrolysis, like that of dimethyldichlorosilane, gives a mixture, depending on the conditions, of cyclic and linear species.[17] The two isomeric cyclic trimers are readily separated.[18,19] The four tetramers are more difficult to deal with, but with the aid of crystallisation procedures, gas and column chromatography and nuclear magnetic resonance spectroscopy, they have been separated and configurations assigned.[18,20,21] These configurations, together with those of the trimers, are set out on P. 23. For convenience, in subsequent discussion, the trimers will be referred to as cis or trans and the tetramers will be denoted by the letters A,B,C and D.

In the series of experiments reported here, an excess of water was added to a stirred mixture of the chlorosilane in solvent. The effect of varying the following factors was investigated:

The 2,4,6-trimethyl-2,4,6-triphenylcyclotrisiloxanes:

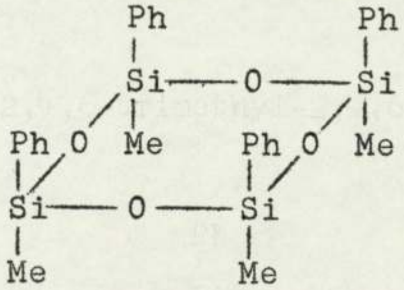


cis

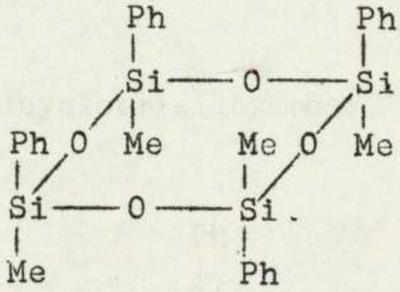


trans

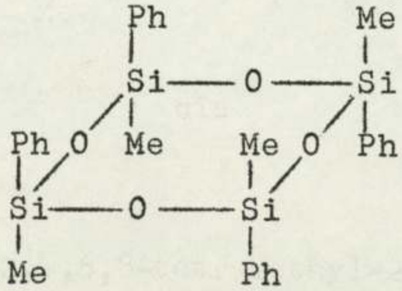
The 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxanes:



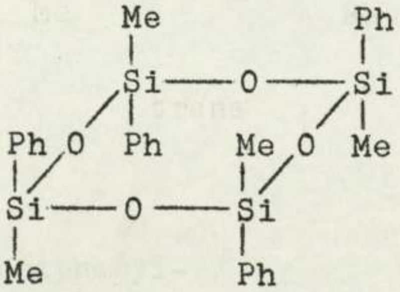
A



B



C



D

1. Temperature.
2. Nature of solvent.
3. Quantity of solvent.
4. Time for addition of water.

The percentages of cyclic siloxanes in the hydrolysis products were estimated by column chromatography. Cyclic siloxanes were eluted while linear siloxane diols were retained on the column. The separated cyclic siloxanes were then analysed by gas chromatography.[20,21] It was again assumed that peak areas are proportional to the masses of components present and analyses were made on this basis by comparison of peak areas.

Each experiment, both the hydrolysis and the analysis of the hydrolysis products, was carried out in duplicate. In general the variation in numerical results from duplicate experiments was no more than the variation in the results from different analytical determinations on the same hydrolysis product. The results presented in the following tables are averages not only of duplicate experiments but also of different analyses of the same product.

Results and discussion.

1. Variation of time for addition of water.

Table III (P. 25).

In each of the hydrolyses, the chlorosilane in the reaction flask will have been completely hydrolysed after the addition of only a small proportion of the water. As was mentioned earlier, during the early stages of the

Table III

The hydrolysis of methylphenyldichlorosilane. i. Variation of time for addition of water.

Solvent: Ether. Chlorosilane/Ether: 1/5 by volume.

Temperature: 30^{o}C. Mole ratio of chlorosilane/water: 1/20.

Time for addition of water, minutes	% of cyclic siloxanes in product	Trimer/ Tetramer	Trimer: cis/trans	Tetramer: A/(B+C+D)	Tetramer/ Pentamer
10	41	74/26	20/80	12/88	100/0
20	54	59/41	17/83	16/84	96/4
60	60	47/53	16/84	15/85	87/13
120	67	33/67	19/81	19/81	73/27

hydrolysis a homogeneous solution of unreacted chlorosilane, α,ω-chlorosiloxanes and hydrogen chloride in the solvent is obtained. At a certain, usually clearly defined, point the solution becomes cloudy and heterogeneous. For most of the time the initially formed hydrolysis products are simply being stirred with hydrochloric acid. During this time methylphenylsiloxanediols undergo condensation to give cyclic or longer chain linear products. The progressively increasing proportion of cyclic siloxanes in the hydrolysis product suggests that the siloxane diols condense comparatively slowly. The increasing proportion of pentamer supports this. Work reported in Chap. 2 suggests that with an immiscible solvent, such as ether, cyclic siloxanes already formed will undergo little further modification. However an overall decrease in the yield of cyclic trimer is observed. It seems likely that trimer initially formed reacts with hydrogen chloride during the final part of the homogeneous stage giving other products.

2. Variation of solvent and temperature.

Table IV (P. 27).

The general effect of increasing the temperature is similar to that for increasing the time of reaction. The proportion of cyclic siloxanes in the product increases, the trimer /tetramer ratio decreases and the yield of pentamer increases. It is apparent that the rate of siloxanediol condensation and cyclisation increases with increasing temperature. In acetone solution, at the two higher temperatures, the trimer /tetramer ratio

Table IV

The hydrolysis of methylphenyldichlorosilane. ii. Variation of solvent and temperature.

Time for addition of water: 2 hours. Chlorosilane/solvent: 1/5 by volume.

Mole ratio of chlorosilane/water: 1/20.

Solvent	Temperature °C.	% of cyclic siloxanes in product	Trimer/ Tetramer	Trimer: cis/trans	Tetramer: A/(B+C+D)	Tetramer/ Pentamer
Ether	-75	8	54/46	22/78	7/93	100/0
Ether	0	61	52/48	19/81	17/83	83/17
Ether	30	67	33/67	19/81	19/81	73/27
Acetone	-75	8	38/62	19/81	7/93	100/0
Acetone	0	58	3/97	-	7/93	70/30
Acetone	30	75	1/99	-	7/93	70/30

is much lower than with ether as solvent. This is undoubtedly due to the reaction of initially formed trimer with hydrochloric acid to give other products (Chap. 2). This occurs because the reaction mixture remains homogeneous for a longer period with acetone as the solvent than with ether.

3. Variation of concentration of the chlorosilane solution and temperature. Table V (P. 29).

Varying the concentration of chlorosilane in the solvent apparently has no effect on the yield of cyclic siloxanes. The yield of trimer, as would be expected from previous discussion, is reduced as the concentration increases. An increased yield of pentamer, in the two more concentrated solutions, can be ascribed to the increased concentration of siloxanediols favouring condensation to longer chains and then cyclisation rather than earlier cyclisation to smaller rings.

The additional reaction that was done, using tetrahydrofuran as solvent, gives a much reduced yield of trimer, as would be expected, but not at the expense of the overall yield of cyclics.

Stereochemical aspects of methylphenylsiloxane formation.

The first stage in the hydrolysis of methylphenyldichlorosilane in the presence of an excess of water results in the formation of methylphenylsilanediol. This can condense to give meso and racemic 1,3-dimethyl-1,3-diphenyldisiloxanediols.[7] On further condensation with another molecule of methylphenylsilanediol, three isomeric

Table V

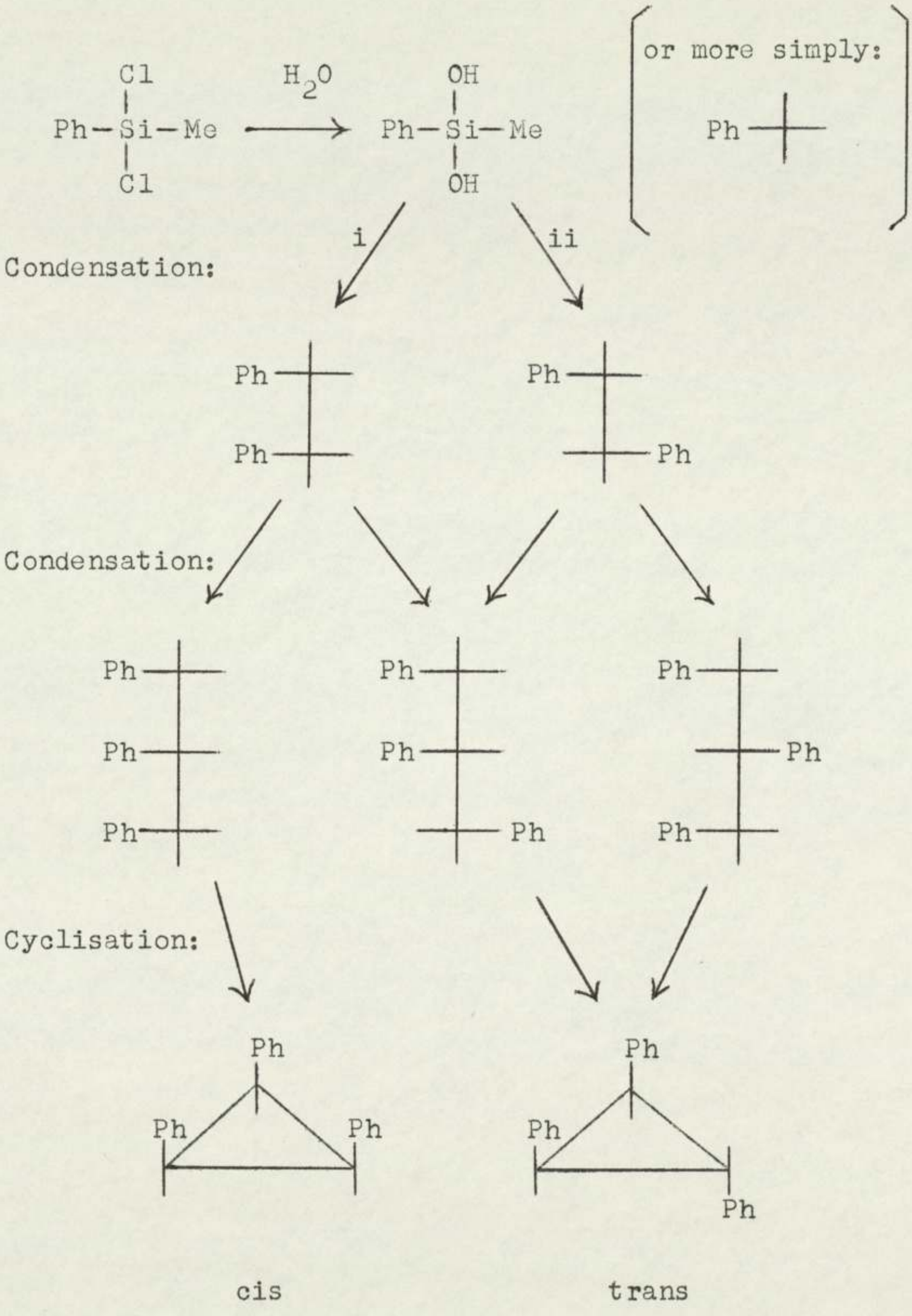
The hydrolysis of methylphenyldichlorosilane. iii. Variation of concentration of the chlorosilane solution and temperature.

Time for addition of water: 1 hour. Solvent: Ether.

Mole ratio of chlorosilane/water: 1/20.

Chlorosilane/ solvent (by volume)	Temperature, °C.	% of cyclic siloxanes in product	Trimer/ Tetramer	Trimer: cis/trans	Tetramer: A/(B+C+D)	Tetramer/ Pentamer
1/1	0	59	21/79	13/87	10/90	70/30
1/1	30	59	16/84	16/84	10/90	72/28
1/2	0	57	38/62	16/84	13/87	82/18
1/2	30	60	16/84	16/84	11/89	68/32
1/5	30	60	47/53	16/84	15/85	87/13
An additional reaction, using tetrahydrofuran as solvent:						
1/5	30	59	6/94	-	11/89	82/18

1,3,5-trimethyl-1,3,5-triphenyltrisiloxanediols will be formed. On cyclisation these will give the two isomeric trimethyltriphenylcyclotrisiloxanes:



According to the scheme shown on P. 30 , if all possible reactions take place with equal ease, the cis and trans trimers will be formed in the ratio 1 : 3. If the initial stages of the reaction take place in the presence of an excess of chlorosilane, α,ω-dichlorosiloxanes will be formed instead of siloxanediols. The ratio of cyclic products eventually formed will, of course, be the same.

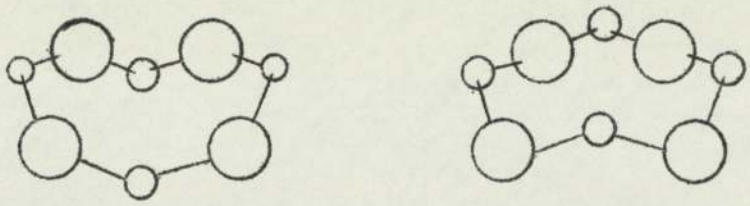
In all the hydrolysis reactions carried out the yield of cis trimer is less than the theoretical 25%. This can be due either to the cis trimer being less favoured in the reaction scheme or to it being attacked by hydrochloric acid more rapidly than the trans trimer. Steric factors are certainly significant in siloxane formation when phenyl groups are present (P. 13), hence reaction i in the scheme could well be less favoured than ii. Similarly with the next stage of condensation. It has been shown (Chap. 2) that there are distinct differences in the reaction of the cis and trans trimers with hydrochloric acid. There is probably a difference in the rate of reaction, but this was not definitely established. In the case of the reaction of the trimers with potassium hydroxide, however, it was definitely shown that the cis trimer is more reactive than the trans (Chap. 2). It is probably significant that the highest cis /trans trimer ratio was obtained with ether as solvent at -75°C. These are the conditions where it would be most expected.

As mentioned previously, it has been shown, by electron diffraction,[10] that hexamethylcyclotrisiloxane has a planar ring. If the methyl phenyl trimers also have planar rings, then the cis trimer will carry the three bulky phenyl groups on one side of the siloxane ring. Steric repulsion between the phenyl groups will raise the internal energy of the cis trimer compared to that of the trans. It would therefore be expected that the cis trimer would form less readily than the trans and be more reactive.

During the hydrolysis, further condensation of the trisiloxanediols with methylphenylsilanediol followed by cyclisation will give the four tetramers. An extension of the reaction scheme given previously indicates a theoretical ratio for tetramers A,B,C and D of 1 : 4 : 2 : 1. A similar scheme, involving condensation between two molecules of disiloxanediol followed by cyclisation, gives the same ratio.

The analytical results for the percentages of tetramer A in the mixtures of tetramer show a spread on either side of the theoretical value of 12.5%. This is in contrast to the trimer case. In general the use of ether as a solvent with a long reaction time, a dilute solution of chlorosilane and ordinary temperatures seem to favour the formation of tetramer A in yields greater than the theoretical.

Unlike hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane has a puckered ring.[9] A number of different conformations are possible for an eight membered puckered ring. The "crown" arrangement in the sulphur molecule, S_8, is one well known example. Electron diffraction studies[9] have shown that octamethylcyclotetrasiloxane probably has the "cradle" conformation. This gives the most symmetrical arrangement for an eight membered puckered ring with eight identical substituents on the four silicon atoms.



"Cradle" "Crown"

Two conformations of an eight membered ring.

With the methyl phenyl tetramers, greater separation of the bulky phenyl groups might be possible with the assumption of other conformations by the siloxane ring, particularly in the case of tetramer A where the phenyl groups are all on one side of the ring. Models show that a large number of possibilities exist. Some work on thermal stabilities showed that although the cis trimer is significantly less thermally stable than the trans, no difference was found between the four tetramer isomers.[22] It thus appears that conformational flexibility of the siloxane ring is able to even out any differences in internal energy due to steric repulsion. The fairly wide deviations in the percentage of tetramer A on either side of the theoretical amount cannot therefore be ascribed to possible differences in the stabilities of the tetramer isomers.

CHAPTER 2

The acid and base catalysed cleavage of cyclic organosiloxanes.

2.1 Introduction.[1,2]

The term "cleavage of siloxanes" usually refers to the breaking of siloxane bonds, Si-O, rather than the breaking of silicon-carbon bonds. The cleavage reactions are usually reversible and are often accompanied by a redistribution of siloxane bonds. The term cleavage has been associated with the depolymerisation or degradation of high molecular weight polyorganosiloxanes. Here the products might be low molecular weight siloxanes, siloxanols, alkoxysiloxanes, chlorosilanes, etc., depending on the reagents, whether in stoichiometric or catalytic amounts, and conditions used. The reaction is commonly brought about by heat with basic catalysts and here, particularly at high temperatures, the products are usually low molecular weight cyclic siloxanes, the reaction involving both the breaking and reforming of siloxanes bonds.[23] The reverse process, the polymerisation of low molecular weight oligomeric siloxanes, also involves the breaking and reforming of siloxanes bonds. In each case the reaction is one that leads to products of greater thermodynamic stability under the prevailing conditions, i.e. an equilibration. The "cleavage of siloxanes" described in this work involves low molecular weight cyclic organosiloxanes and the initial stages only of their equilibration with acidic and basic catalysts. The products of the reactions most accessible for investigation are not cleavage products as such but new siloxanes formed by a redistribution of siloxane bonds.

The technical production of silicones or high molecular weight polyorganosiloxanes usually involves the "polymerisation" of a low molecular weight oligomer such as a cyclic tetramer. The reaction, an equilibration in which a redistribution of siloxane bonds occurs, can be brought about by heat alone, or more commonly, with acidic or basic catalysts as well. A fully equilibrated siloxane mixture consists mainly of high molecular weight polymer with a much smaller amount of low molecular weight cyclic oligomers. The average molecular weight can be controlled by the addition of a "chain stopper" such as hexamethyldisiloxane:

$$\text{e.g.}\quad n(Me_2SiO)_4 + Me_3SiOSiMe_3 \rightarrow Me_3SiO(Me_2SiO)_{4n}SiMe_3.$$

Although the mechanisms of this reaction are different with acid and base catalysts, the same mixture of siloxane homologues is formed in each case.[24] As would be expected from the nature of the catalysts, the reactions proceed by ionic mechanisms involving heterolytic cleavage of the siloxane bond. This is usually the case in heteroatom systems.

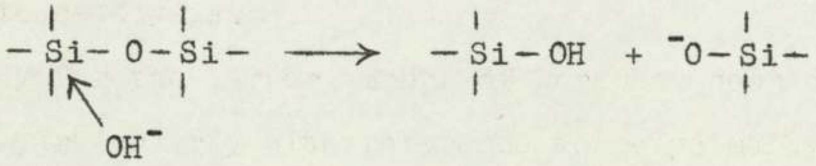
Anionic catalysis.

By far the larger amount of work has been done on this, particularly with reference to polydimethylsiloxanes. Potassium hydroxide is a commonly used base catalyst but the other alkali metal hydroxides have been used, their order of activity being:[25]

$$\text{CsOH} > \text{RbOH} > \text{KOH} > \text{NaOH} > \text{LiOH}.$$

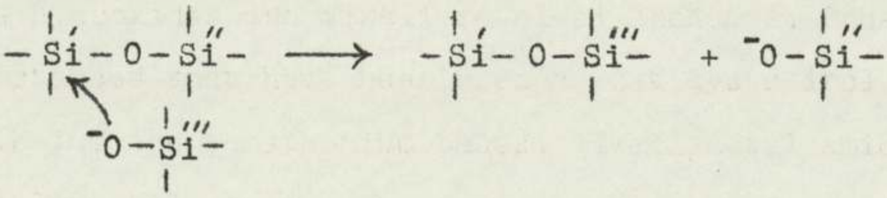
This is presumably due to decreasing ionisation of both the hydroxides and alkali metal silanolates. Other substances that have been used as catalysts include ammonium and phosphonium bases, alkali metal amides, alkali metals, etc.

The first part of the reaction is a nucleophilic attack on silicon followed by cleavage:



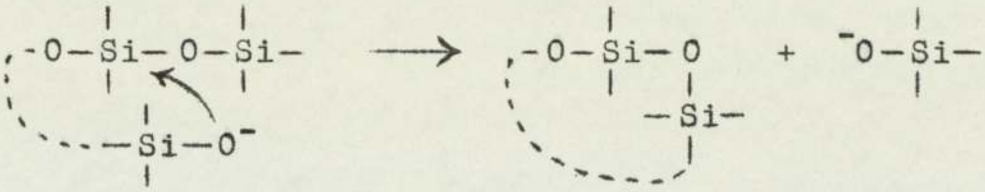
$$-\overset{|}{\underset{|\nwarrow}{\text{Si}}}-\text{O}-\overset{|}{\underset{|}{\text{Si}}}- \longrightarrow -\overset{|}{\underset{|}{\text{Si}}}-\text{OH} + {}^-\text{O}-\overset{|}{\underset{|}{\text{Si}}}-$$
$$\text{OH}^-$$

It has been found that potassium silanolates have comparable activities to potassium hydroxide[26] hence the silanolate ion produced above can propagate the reaction; either attacking a siloxane bond in another molecule:



$$-\overset{|}{\underset{|\nwarrow}{\text{Si}'}}-\text{O}-\overset{|}{\underset{|}{\text{Si}''}}- \longrightarrow -\overset{|}{\underset{|}{\text{Si}'}}-\text{O}-\overset{|}{\underset{|}{\text{Si}'''}}- + {}^-\text{O}-\overset{|}{\underset{|}{\text{Si}''}}-$$
$${}^-\text{O}-\overset{|}{\underset{|}{\text{Si}'''}}-$$

or in the same molecule:



The latter reaction, a cyclisation, leads to the formation of the low molecular weight cyclic oligomers produced in equilibration reactions.

As mentioned above, the acid or base catalysed equilibration of methyl siloxanes in the presence of chain stopper gives the same mixture in each case. With an acid catalyst the average molecular weight (measured by viscosity) increases to a steady maximum value as equilibrium is attained. With a base catalyst the molecular weight rapidly rises to a maximum and then decreases to the same steady value as that obtained with the acid catalyst.[24] This indicates that, with a base catalyst, chain growth involving faster reacting difunctional siloxane units predominates initially. The more slowly reacting monofunctional chain stopping units then break down the long chains initially formed and the molecular weight decreases. This is confirmed by the reactivity of some low molecular weight siloxanes with base.[24] It is :

$$(Me_2SiO)_4 > Me_3SiOSiMe_2OSiMe_3 > Me_3SiOSiMe_3.$$

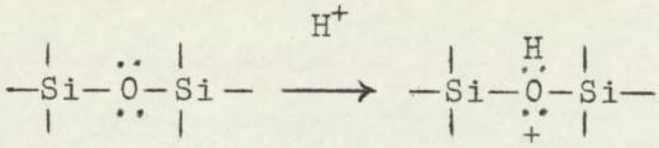
These results are obtained because silicon is more electropositive in the difunctional groups than in the monofunctional.

The reactions described in this work were all carried out at 20 or 50°C. Increasing the temperature increases the rate of polymerisation, of course, but seems to have little effect on the composition of the equilibrium mixture produced. However at high temperatures, i.e. 350-400°C., the equilibrium concentration of lower polydimethylcyclosiloxanes does increase slightly. If these are distilled off, complete degradation can be brought about.[23] Other factors that can influence polymerisation include the nature of the substituent groups on silicon, the ring size, and solvents. These effects are referred to in later discussion.

Acidic catalysis.

Unlike anionic catalysis, where the base acts as an electron donor and adds to the silicon atom, acidic catalysis involves initially the siloxane oxygen atom which acts as an electron donor to a proton or some other electron accepting species of the Lewis acid type.

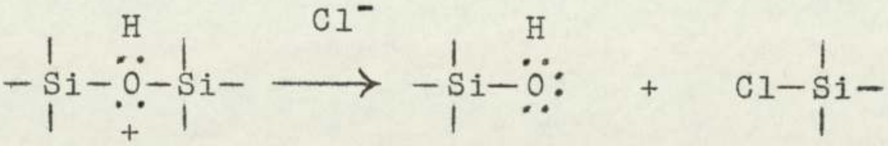
e.g.



$$\mathrm{-\overset{|}{\underset{|}{Si}}-\underset{..}{\ddot{O}}-\overset{|}{\underset{|}{Si}}-} \xrightarrow{H^{+}} \mathrm{-\overset{|}{\underset{|}{Si}}-\underset{+}{\overset{H}{O}}-\overset{|}{\underset{|}{Si}}-}$$

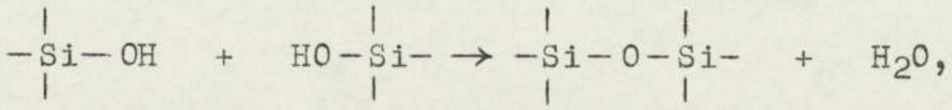
Cleavage could then occur through nucleophilic attack on an adjacent silicon atom.

e.g.



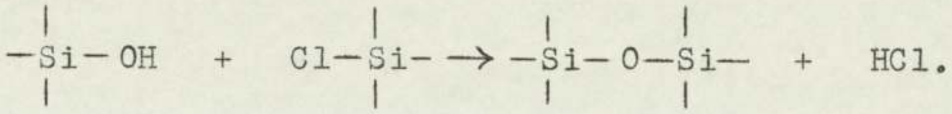
$$\mathrm{-\overset{|}{\underset{|}{Si}}-\underset{+}{\overset{H}{O}}-\overset{|}{\underset{|}{Si}}-} \xrightarrow{Cl^{-}} \mathrm{-\overset{|}{\underset{|}{Si}}-\overset{H}{\ddot{O}}\!:} \quad + \quad \mathrm{Cl-\overset{|}{\underset{|}{Si}}-}$$

Redistribution of siloxane bonds could then follow from reactions of the type:



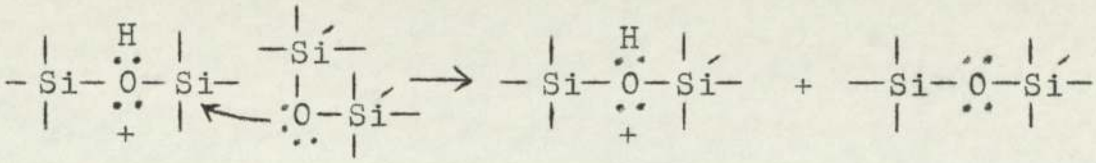
$$-\mathrm{Si}-\mathrm{OH} + \mathrm{HO}-\mathrm{Si}- \rightarrow -\mathrm{Si}-\mathrm{O}-\mathrm{Si}- + \mathrm{H_2O},$$

and

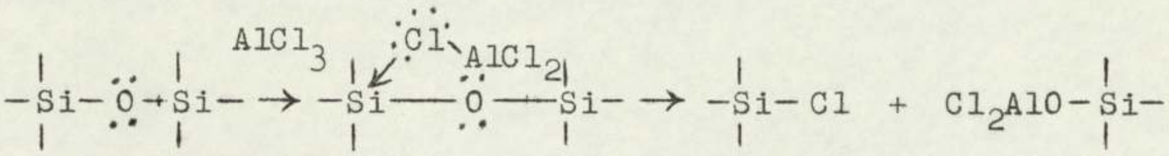


$$-\mathrm{Si}-\mathrm{OH} + \mathrm{Cl}-\mathrm{Si}- \rightarrow -\mathrm{Si}-\mathrm{O}-\mathrm{Si}- + \mathrm{HCl}.$$

Another possibility involves a nonprotonated oxygen atom on another or the same molecule:



Typical Lewis acid catalysts are iron III chloride-hydrogen chloride complex, aluminium chloride, tin IV chloride, etc. A typical mode of reaction could be:



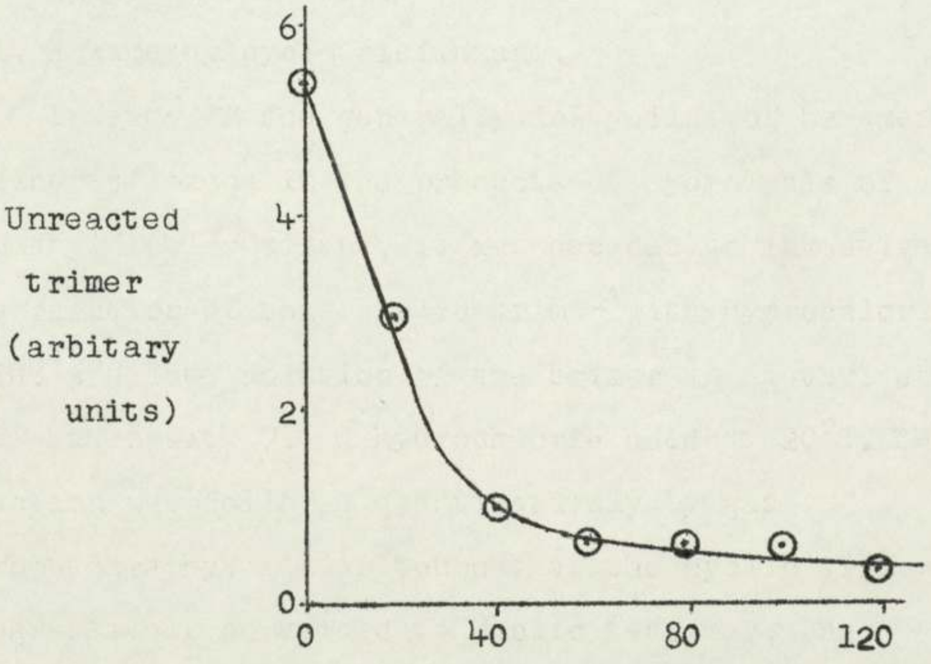
During the hydrolysis of chlorosilanes, initially formed siloxanes are usually exposed to the hydrochloric acid also formed in the reaction. In this work the catalytic effect of hydrochloric acid on cyclic siloxanes was investigated mainly from this point of view.

The initial stage of the reaction of some cyclotrisiloxanes with potassium hydroxide was also investigated. In each case the initial product, formed in varying yields, was the cyclotetrasiloxane. With the methyl phenyl siloxanes particular attention was paid to the stereochemical aspects of the reaction.

2.2 The reaction of cyclic organosiloxanes with hydrochloric acid.

i. Hexamethylcyclotrisiloxane.

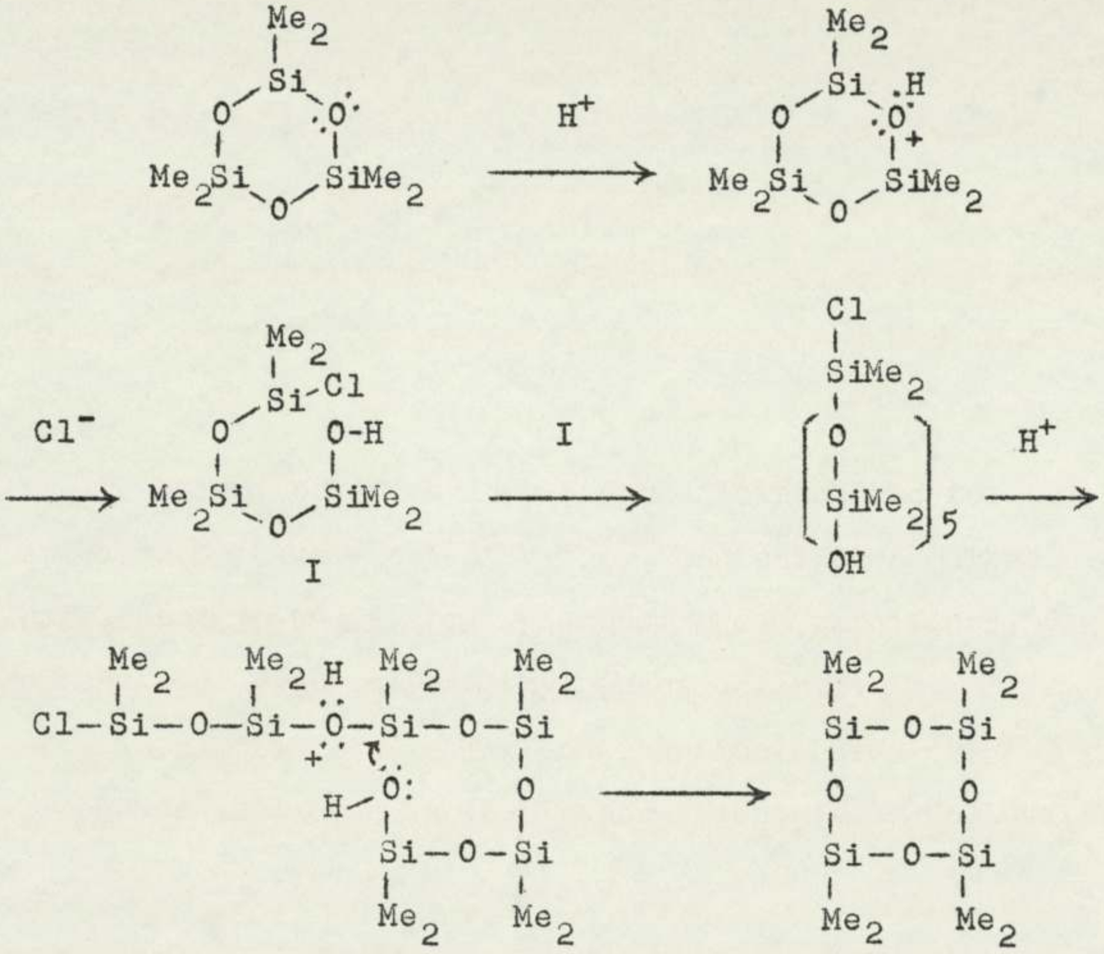
In view of the generally low yeilds of hexamethylcyclotrisiloxane in the products of hydrolysis of dimethyldichlorosilane, it was decided to investigate the reaction of this cyclic trimer with hydrochloric acid. A dilute solution of the trimer in diethyl ether was shaken with 7.5 M hydrochloric acid at 20°C. The reaction was followed quantitatively by gas chromatography. It was found that the cyclic trimer is progressively converted to cyclic tetramer. The consumption of the trimer is shown by the graph. This indicates a half life for the trimer of about 20 minutes under the conditions used. After 24 hours the product of



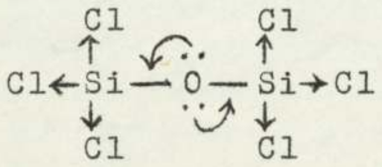
<u>The reaction of hexamethylcyclotrisiloxane with hydrochloric acid</u>.

the reaction, octamethylcyclotetrasiloxane, had not appeared to have reacted further, indicating a marked difference in the stability, under these conditions, of the two lower polydimethylcyclosiloxanes.

A possible scheme for the reaction, based on processes mentioned in the Introduction, is as follows:



As mentioned earlier, the siloxane bond shows considerable ionic character due to the electronegativity difference of silicon and oxygen. The nature of the bond can be further modified by the substituents on the silicon atom, particularly the tendency for oxygen lone pair electrons to partially enter the unfilled 3d orbitals of the silicon atom giving a dπ-pπ component to the bond. Pure silicon-oxygen double bonds are unknown but partial double bond formation may be invoked to explain various chemical effects. The variations in Si-O-Si bond angle that are found in simple disiloxanes can be explained on this basis. For pure single bonds at the oxygen an angle of 90° might be expected and for pure double bonds an angle of 180°. The intermediate values that are found in practice might be due to, or might cause, partial double bond character. The oxygen bond angle in hexamethyldisiloxane has been quoted as $130^\circ \pm 10^\circ$ and that in hexachlorodisiloxane as $175^\circ \pm 5^\circ$.[2] The electronegative chlorine atoms would be expected to increase the dπ-pπ contribution and hence widen the bond angle. Associated with this effect is a



$$\mathrm{Cl}\leftarrow\underset{\underset{\mathrm{Cl}}{\downarrow}}{\overset{\overset{\mathrm{Cl}}{\uparrow}}{\mathrm{Si}}}\!-\!\mathrm{O}\!-\!\underset{\underset{\mathrm{Cl}}{\downarrow}}{\overset{\overset{\mathrm{Cl}}{\uparrow}}{\mathrm{Si}}}\rightarrow\mathrm{Cl}$$

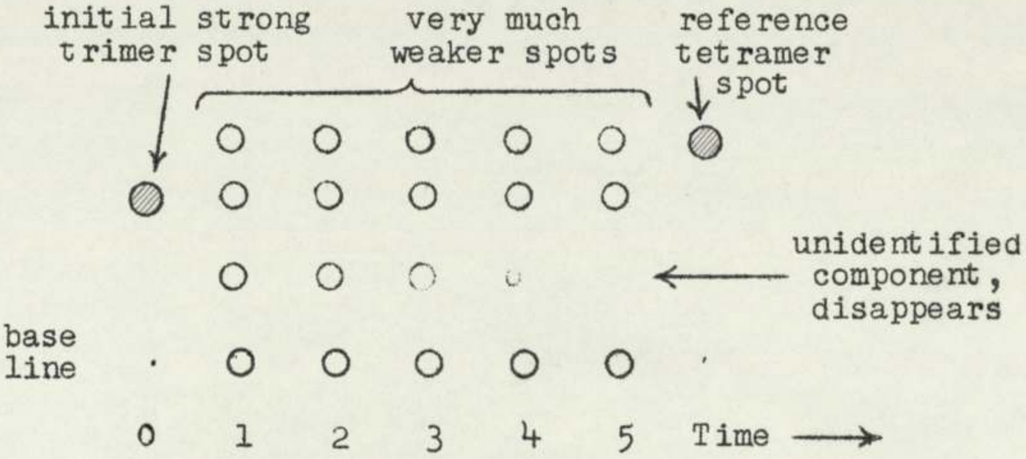
<u>Hexachloro-disiloxane</u>.

strengthening of the Si-O bond and a decrease in its ionic character. The ease with which electrophilic attack on the oxygen lone pairs occurs will obviously depend on the nature of the groups present on the silicon atoms. It has been found that the sensitivity of simple disiloxanes to protonation and cleavage decreases with increasing electron attraction of the groups on the silicon atoms.[27]

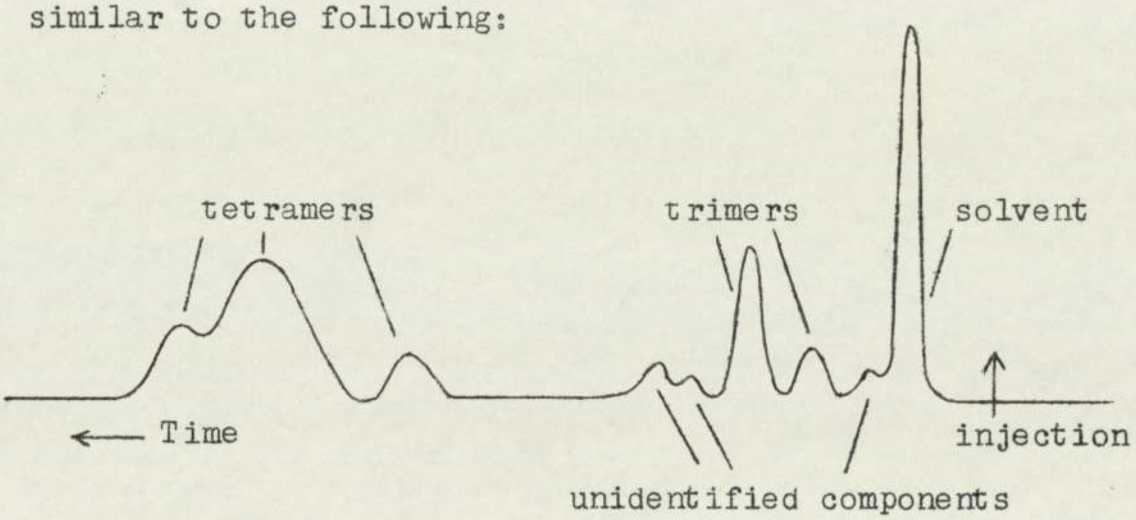
In the case of the lower cyclic methyl siloxanes, the distinctly smaller Si-O-Si bond angle in the trimer as compared with the tetramer might be associated with decreased double bond character and hence greater availability of the oxygen electron pairs for donation to protons. Associated with this would be a greater polarity of the bond and therefore enhancement of possibilities for the subsequent nucleophilic attack on the silicon atom and ring opening. It would be expected that the marked difference in stability of the methyl trimer and tetramer to attack by aqueous acid would be associated with a kinetic effect resulting from one of the above mentioned factors rather than with their comparatively slight intrinsic difference in stability.

ii. The trimethyltriphenylcyclotrisiloxanes.

In work involving reaction of cyclic siloxanes other than polymethyl, it was found convenient to follow the course of the reactions by thin layer chromatography. This is not possible with the lower polydimethylcyclosiloxanes because they are too volatile. In each experiment, an individual methyl phenyl trimer isomer, dissolved in solvent, was shaken with 6 M hydrochloric acid at $20^{o}C.$, the course of the reaction being followed by thin layer chromatography. With diethyl ether as solvent there was no sign of reaction after 24 hours. Thus the methyl phenyl trimers are very much less reactive than hexamethylcyclotrisiloxane. This is doubtless due to the electron withdrawing phenyl groups strengthening the siloxane bond and reducing the availability of the oxygen lone pairs. The methyl phenyl trimer can be made to react, however, in homogeneous solution. With sufficient acetone or tetrahydrofuran to give a largely homogeneous solution, the following type of thin layer chromatogram was obtained in each case:



It appears that the trimer rapidly reacts to give mainly non eluted material, i.e. open chain siloxane diols. The three very faint eluted components consist of an unidentified material that gradually disappears together with methyl phenyl trimer and tetramer. The two latter remain approximately constant in intensity with possibly the trimer becoming slightly weaker and the tetramer slightly stronger. With each solvent there was no significant difference between the cis and trans isomers. After 1 hours exposure to hydrochloric acid the reaction products were worked up and analysed by gas chromatography using standard injections. The two isomers with acetone as solvent each gave chromatograms similar to the following:



With tetrahydrofuran as solvent the traces were similar but all peaks were considerably smaller and the "unidentified components" were almost absent. In both pairs of experiments the peaks from the trans trimer were about twice the size of those from the cis one. The relative proportions of each component were about the same in each case. All the chromatograms were obtained at the high sensitivity setting on the instrument. At "normal" sensitivity, where a solution of pure trimer of the same strength gave a large peak, the reaction product solutions gave no peaks. By visual inspection, the isomer ratios in the chromatograms appeared to approximate to the theoretical ratios mentioned in Chap. I.

Gas chromatography confirms the thin layer results and in addition indicates that "equilibration" of the cyclic siloxanes has occurred. It is evident that in homogeneous solution, acid catalysed cleavage of the six membered ring takes place readily, with equilibration of configuration at the silicon atoms, to give mainly open chain products.

In the hydrolysis experiments reported in Chap. I, the final concentration of hydrochloric acid formed was approximately 6 M, the same as that used in these experiments. With acetone as solvent, yields of cyclic siloxanes up to 75% were obtained. The amount of acetone used, however, was not sufficient to give homogeneous solutions.

iii. The tetramethyltetraphenylcyclotetrasiloxanes.

The individual methyl phenyl tetramer isomers, in dilute solution in acetone or tetrahydrofuran, were shaken with 6 M hydrochloric acid at 20°C. for 1 hour. After working up, the reaction products were analysed by gas chromatography. Each reaction product gave a large peak corresponding to unreacted tetramer together with one or more smaller peaks corresponding to the other tetramer isomers. Trimer peaks were not observed. With acetone as solvent between about 10 and 35% of the original tetramer had reacted to give other isomers. Inspection of the peaks indicated that the extent of reaction was in the order:

$$A \simeq D > B > C.$$

With tetrahydrofuran as solvent up to about 12% of the original tetramer reacted and the order was:

$$B > A \simeq D > C.$$

Estimates of the proportions of isomers A,B,C and D were made from the peak areas. In some cases peaks B and C are quoted together, due to poor resolution.

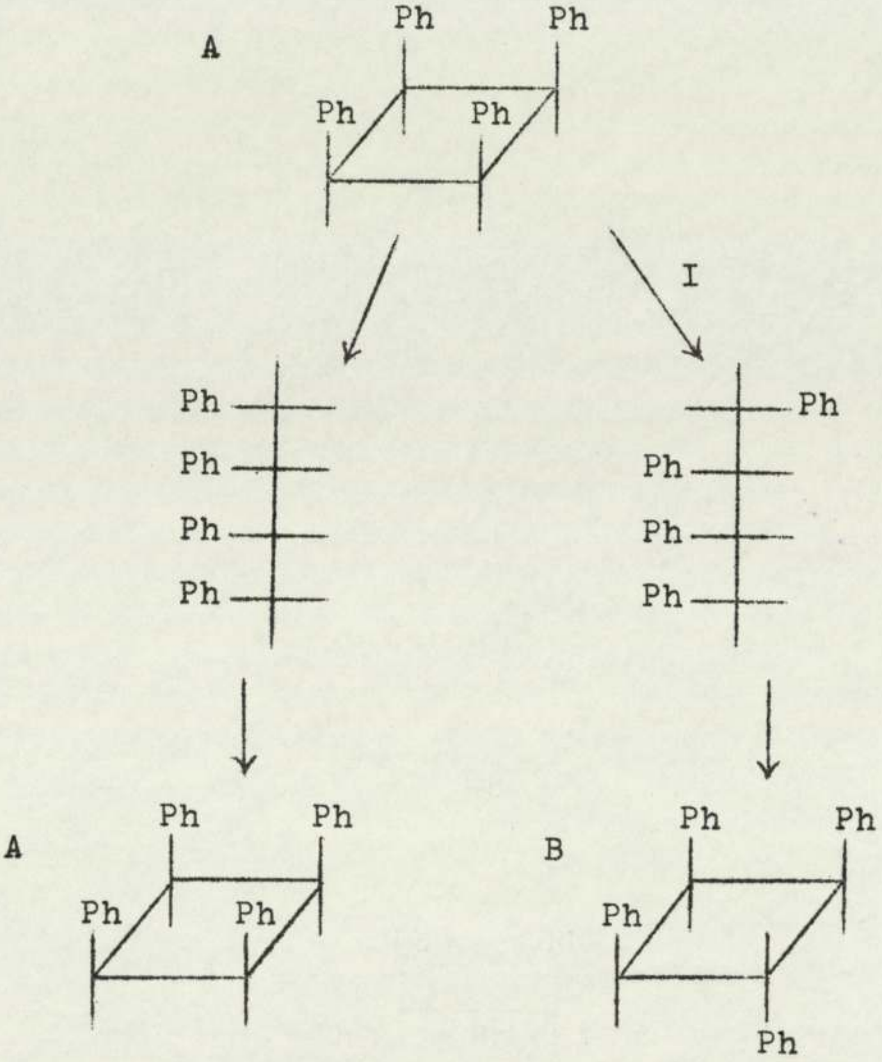
Acetone as solvent:

<table>
<tr><th rowspan="2">Tetramer isomer used:</th><th colspan="4">% of tetramer isomers in product:</th></tr>
<tr><th>A</th><th>B</th><th>C</th><th>D</th></tr>
<tr><td>A</td><td>64</td><td>21</td><td>9</td><td>6</td></tr>
<tr><td>B</td><td>17</td><td colspan="2">83</td><td>0</td></tr>
<tr><td>C</td><td>0</td><td>8</td><td>90</td><td>2</td></tr>
<tr><td>D</td><td>10</td><td>16</td><td>6</td><td>68</td></tr>
</table>

Tetrahydrofuran as solvent:

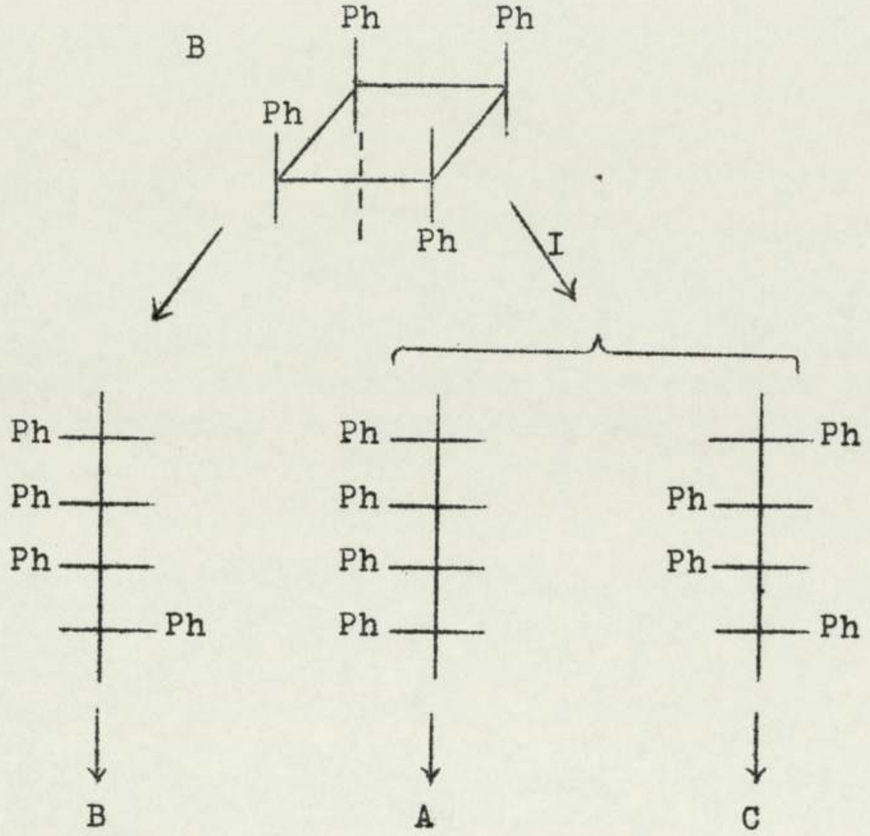
<table>
<tr><th></th><th>A</th><th>B</th><th>C</th><th>D</th></tr>
<tr><td>A</td><td>92</td><td>8</td><td>0</td><td>0</td></tr>
<tr><td>B</td><td>7</td><td colspan="2">88</td><td>5</td></tr>
<tr><td>C</td><td>0</td><td>trace</td><td>100</td><td>0</td></tr>
<tr><td>D</td><td>0</td><td>8</td><td>0</td><td>92</td></tr>
</table>

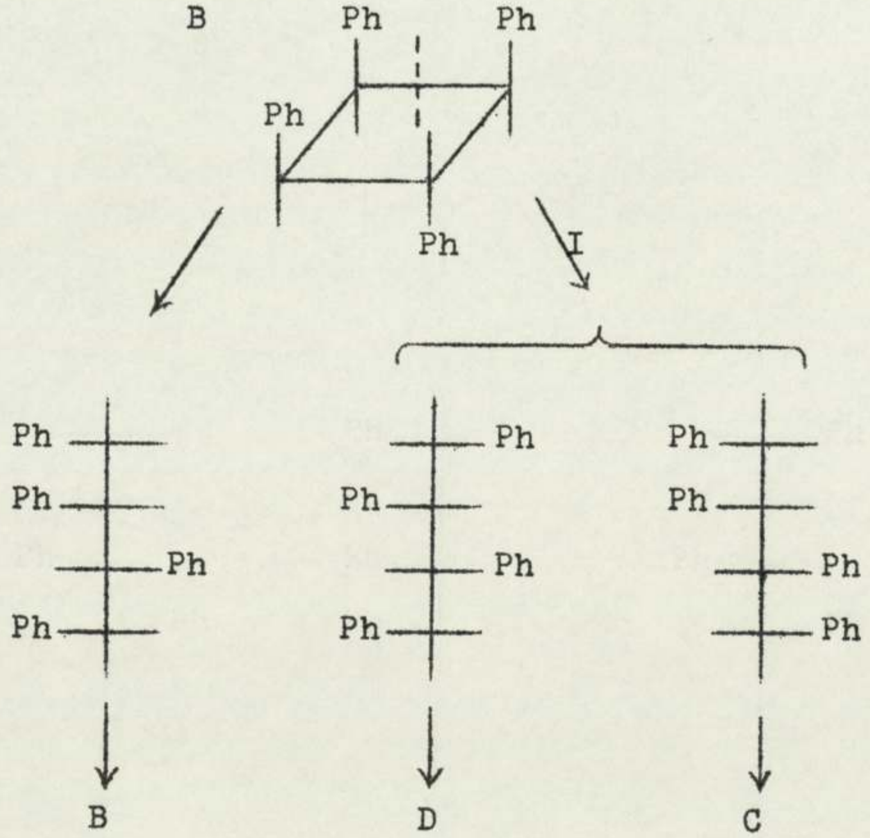
The reaction probably consists of cleavage of the ring followed by rapid recyclisation. The formation of other tetramer isomers in the products indicates that the reaction is not stereospecific, the silicon atom at which cleavage occurs undergoing equilibration of configuration on ring opening. For example tetramer A could give two linear siloxanes on ring opening, which would then recyclise to give tetramers A and B:



I = inversion of configuration at a terminal silicon atom.

In a similar way tetramer C would give C and B and tetramer D would give D and B. The scheme for tetramer B is more complex. There are two modes of cleavage, each accompanied by two inversion products:


B
Ph
Ph
Ph
Ph
I
Ph
Ph
Ph
Ph
B
A
C


B
Ph
Ph
Ph
Ph
I
Ph
Ph
Ph
Ph
B
D
C

On recyclisation, isomers A, B, C and D will be formed in the ratio 1 : 4 : 2 : 1. With tetrahydrofuran as solvent the products of the reaction conform to this scheme. With acetone as solvent it is evident that a second stage of reaction has taken place, particularly with tetramers A and D as initial reactants. With tetramer A, for example, tetramers C and D appear in the products. According to the above scheme, these could only be formed as a result of further reaction of the initial product, B. If two stages of reaction occur, i.e. if each molecule of tetramer undergoes cleavage and recyclisation twice, then the expected ratios of products would be as follows:

Original tetramer:	Ratios of tetramers expected after two stages of reaction:			
	A	B	C	D
A	5	8	2	1
B	2	8	4	2
C	1	8	6	1
D	1	8	2	5

There will now, of course, be very much less agreement with experiment because the different isomers react at different rates. In particular with tetramers B and D as initial reactant, tetramer A seems to be favoured in the products. This could be the result of a greater stability of A compared to B and D. A similar effect was noticed in some of the products of hydrolysis of methylphenyldichlorosilane, as described in Chap. I.

The effect, however, was only noticed with ether as solvent, not acetone.

It is clear from this work that tetramer C is the most resistant to aqueous acid. As a result of the flexibility of the eight membered puckered ring, this isomer might assume a conformation allowing maximum separation of the phenyl groups and hence maximum stability. Alternatively, or in addition, the conformation may hinder one of the cleavage processes such as protonation of oxygen or nucleophilic attack on silicon. The ease of protonation might be affected by a slight widening of the Si-O-Si angle reducing the availability of the lone pairs on the oxygen.

2.3 The reaction of cyclic organosiloxanes with potassium hydroxide.

i. Hexamethylcyclotrisiloxane.

The equilibration of polydimethylcyclosiloxanes, particularly the tetramer, has been extensively investigated.[1,2] In this work the initial stages of the reaction of hexamethylcyclotrisiloxane with potassium hydroxide was briefly investigated. Solutions of the trimer in benzene and diethyl ether were shaken with powdered potassium hydroxide at 20°C. Portions of the solution were withdrawn at intervals and analysed by gas chromatography. With benzene as solvent the trimer reacted slowly, about 25% being consumed after 4 hours and 95% after 24 hours. At the same time slight formation of tetramer was observed. With ether the reaction was rather more rapid and only a slight trace of trimer was left after 24 hours. Slightly more tetramer was formed in this case. These reactions are discussed later.

ii. Hexaphenylcyclotrisiloxane.

The reaction was carried out as above, i.e. a solution of hexaphenylcyclotrisiloxane in solvent was shaken with powdered potassium hydroxide. The course of the reaction, however, is more conveniently followed by thin layer chromatography. During development the cyclic siloxanes are differentially eluted but open chain siloxanes remain on the base line. With p-xylene as solvent at a temperature of 20°C., no reaction was observed after 40 minutes but after 24 hours the trimer had almost completely reacted and a component with the same R_f value as octaphenylcyclotetrasiloxane was formed. $R_{f(\text{trimer})} - R_{f(\text{tetramer})} \simeq 0.1$. The reaction was repeated at 50°C. and a progressive conversion of the trimer into the other component was observed, the conversion being complete after about 2 hours. The reaction was repeated on a larger scale at 50°C. for 2 hours, followed by column chromatography on the product. Open chain siloxanes and potassium silanolates were retained on the column but cyclic siloxanes were washed through. A 49% recovery of cyclic material was obtained. From this a material with a melting point (196°C.) and infra red spectrum identical to those of octaphenylcyclotetrasiloxane was isolated.

iii. The trimethyltriphenylcyclotrisiloxanes.

The individual isomers were reacted with powdered potassium hydroxide in various solvents as above. Again the course of the reaction was followed by thin layer chromatography and again a progressive conversion of the trimer into tetramer could be readily observed. The stereoisomeric methyl phenyl trimers and tetramers are not resolved by thin layer chromatography. i.e. the trimers have one R_f value and the tetramers another. These R_f values varied somewhat from one plate to another but in general: $R_{f(\text{tetramer})} - R_{f(\text{trimer})} \simeq 0.1$. Note that the order of the R_f values is the reverse of that found for the polyphenyl trimer and tetramer.

On continuing the reaction, the tetramer was then gradually consumed, but at a much slower rate than the trimer was initially. In some thin layer chromatograms, faint spots corresponding to the formation and then disappearance of up to six other components were also observed. These effects were not investigated further.

The reactions were repeated on a larger scale using the times necessary for the trimer to be just consumed. The products were subjected to column chromatography in order to obtain yields of cyclic siloxanes. The results, so far, from the two sets of experiments are summarised in Table VI (P. 54).

It was confirmed by gas chromatography and nuclear magnetic resonance that the products obtained above were mixtures of the stereoisomeric tetramers and the mixtures were analysed quantitatively by these techniques. The gas

Table VI

The reaction of the trimethyltriphenylcyclotrisiloxanes with potassium hydroxide.

Reaction number	Cyclo-trisiloxane used	Solvent	Volume of solvent to 1 mMole of siloxane, cu. cm	Temperature, °C.	Approximate time T for trimer to react, minutes	% yield of cyclic siloxanes after time T
1	cis	p-xylene	10	50	8	77
2	trans	p-xylene	10	50	20	78
3	cis	p-xylene	10	20	90	46
4	trans	p-xylene	10	20	180	88
5	cis	ether	10	20	20	91
6	trans	ether	10	20	40	99
7	cis	ether	2	20	3	20
8	trans	ether	2	20	6	57
9	cis	THF	10	20	0.75	40
10	trans	THF	10	20	1.5	50

chromatograms obtained were sufficiently good for reasonable estimates of the proportions of all four isomers to be made from peak areas. Nuclear magnetic resonance provided an independent method of tetramer isomer analysis. Methyl proton shifts for the four isomers occur in the region τ 9.5 - 9.9.[21] In three of the isomers, A, C and D, the four methyl groups are similarly situated enviromentally and a single methyl proton resonance is obtained for each isomer. In the fourth, B, three methyl resonances are obtained. Isomer composition can be readily obtained by measurement of peak areas for the resonances on an expanded methyl-silicon spectrum. In general the figures obtained by the two methods were in good agreement. They are quoted separately in Table VII (P. 56).

In most of the gas chromatograms a small single peak corresponding to a small amount of unreacted trimer was observed. In the two reactions with tetrahydrofuran as solvent, however, two peaks in each case were observed. These peaks corresponded with the two trimer isomers and were in approximately the theoretical 1 : 3 ratio.

Discussion of results.

Although the reactions were not carried out under identical conditions, it is evident that hexamethyl- and hexaphenylcyclotrisiloxanes have comparable reactivities in these experiments and that the trimethyltriphenylcyclotrisiloxanes are very much more reactive. The order of reactivities of hexamethyl- and trimethyltriphenyl-

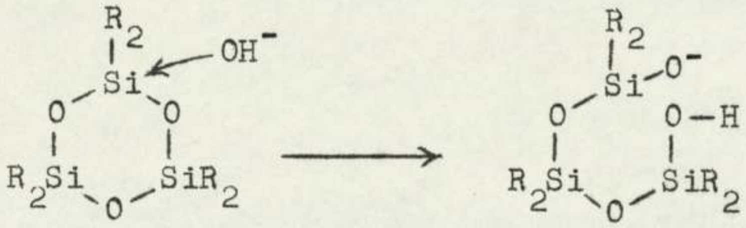
Table VII

The reaction of the trimethyltriphenylcyclotrisiloxanes with potassium hydroxide.

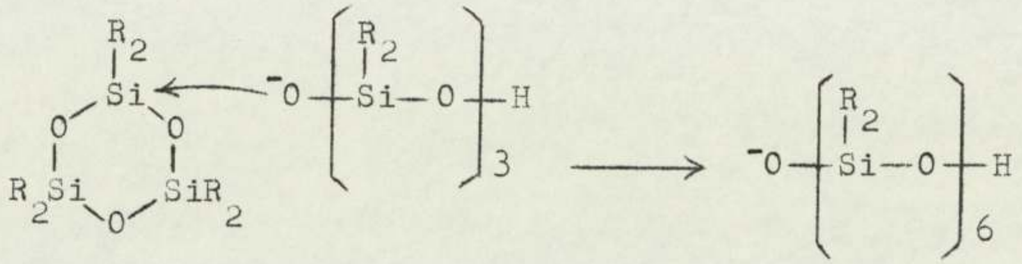
Reaction number	Proportions of tetramer isomers in the reaction products.							
Tetramer:	A		B		C		D	
Analysis by:	GLC	NMR	GLC	NMR	GLC	NMR	GLC	NMR
1	30	32	58	52	9	13	3	3
2	8	6	66	55	18	33	8	6
3	-	30	-	59	-	8	-	3
4	-	3	-	58	-	28	-	11
5	28	29	56	56	10	12	6	3
6	9	10	70	60	14	20	7	10
7	39	42	55	51	6	6	0	1
8	1	1	55	54	34	33	10	12
9	13	15	52	54	26	22	9	9
10	9	7	54	56	22	25	15	12

cyclotrisiloxanes with base are the reverse of what they are with acid. This is to be expected from the probable reaction mechanisms in each case. In the acid cleavage, the protonation of oxygen will be inhibited by electron withdrawing groups, such as phenyl, on the silicon. The base reaction presumably proceeds by way of nucleophilic attack on silicon. This will be promoted by electronegative groups on the silicon. On this basis the hexaphenyl trimer would be expected to be much more reactive than the methyl phenyl trimer. As this is not so, a steric factor involving the two bulky phenyl groups probably predominates in this case.

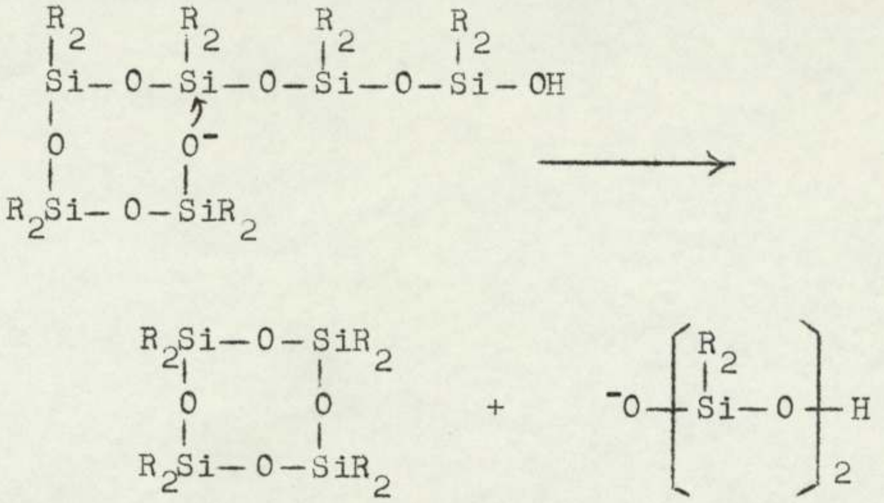
The initial stage of the base catalysed polymerisation of cyclotrisiloxanes will be a nucleophilic attack by hydroxide ion on silicon followed by a cleavage of the ring:



It has been found that potassium polydimethylsilanolates have an approximately equal catalytic activity to potassium hydroxide.[26] Hence it may be assumed that the reaction is propagated by nucleophilic attack of silanolate ion on silicon:



The hexasilanolate ion may then undergo cyclisation, again by nucleophilic attack, to give the cyclic tetramer and a disilanolate ion:



The disilanolate ion then attacks the trimer to give a pentasilanolate ion. This can then cyclise to give tetramer and a monosilanolate ion, etc.

Studies on the statistics of ring closure, based on bond angles and chain conformations for polydimethylsiloxanes, indicate that the cyclic tetramer is the predominant cyclic product.[8] It has been shown that polydimethylsiloxanes, other than the tetramer, undergo anionic polymerisation more rapidly than the tetramer.[28] This is, of course, to be expected in the case of the trimer, with its ring strain energy, and the reactions described in this work are a consequence of it. It also applies, however, to the higher rings even though, like the tetramer, they are unstrained. The activation energies for the reaction of the methyl tetramer and the higher rings have been found to be the same. As a result of this the differing reactivities have been ascribed to the effect of entropy changes on the formation of the pentacovalent transition state.[28] If similar considerations apply to the methyl-phenyl and phenyl cyclics then it is evident that the cyclic tetramer will be the only significant initial product of the reaction.

The times required for the methyl phenyl trimer to be consumed varied considerably with solvent and temperature but under the same conditions the trans trimer took, in general, about twice as long to react as the cis isomer. This is probably a reflection of the differing stabilities of the isomers resulting from steric interaction between the bulky phenyl groups. The polarity of the solvent appears to have a marked effect on the rate of the reaction, the order of decreasing polarity and decreasing rate of reaction being:

tetrahydrofuran $>$ diethyl ether $>$ p-xylene.

This effect is to be expected from the ionic nature of the reaction. The greater ionisation and hence availability of the silanolate ions in the more polar solvents should increase the rate of reaction.

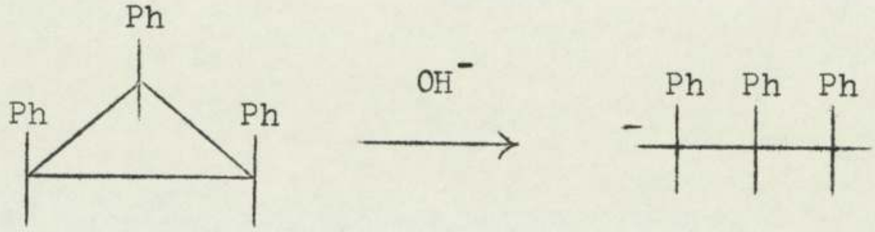
Between 20 and 99% of the original weight of methyl phenyl trimer was recovered as tetramer. The rest of the material was converted into open chain potassium silanolates. In each pair of experiments the trans trimer gave the highest yield of cyclic products, the greatest difference being with concentrated solutions in ether (reactions 7 and 8). With the more dilute solutions in ether (reactions 5 and 6), much higher yields of cyclic products were obtained, an almost quantitative yield of cyclic tetramers being obtained from the trans trimer (reaction 6).

In the times taken for all the original trimer to react, the more concentrated solutions, which give a reduced yield of tetramers, give more stereospecific products, i.e. the differences in product proportions (particularly of isomers A and D) are greatest (reactions 7 and 8). In the more dilute solutions in ether (reactions 5 and 6) more equilibration of the tetramer mixture occurred. Yields of isomers A, C and D from the cis and trans trimers are closer together than in the concentrated solutions. In experiments with the very much less polar p-xylene as solvent at 50°C. (reactions 1 and 2) the stereoselectivity of the product is about the same as with ether at 20°C. (reactions 5 and 6).

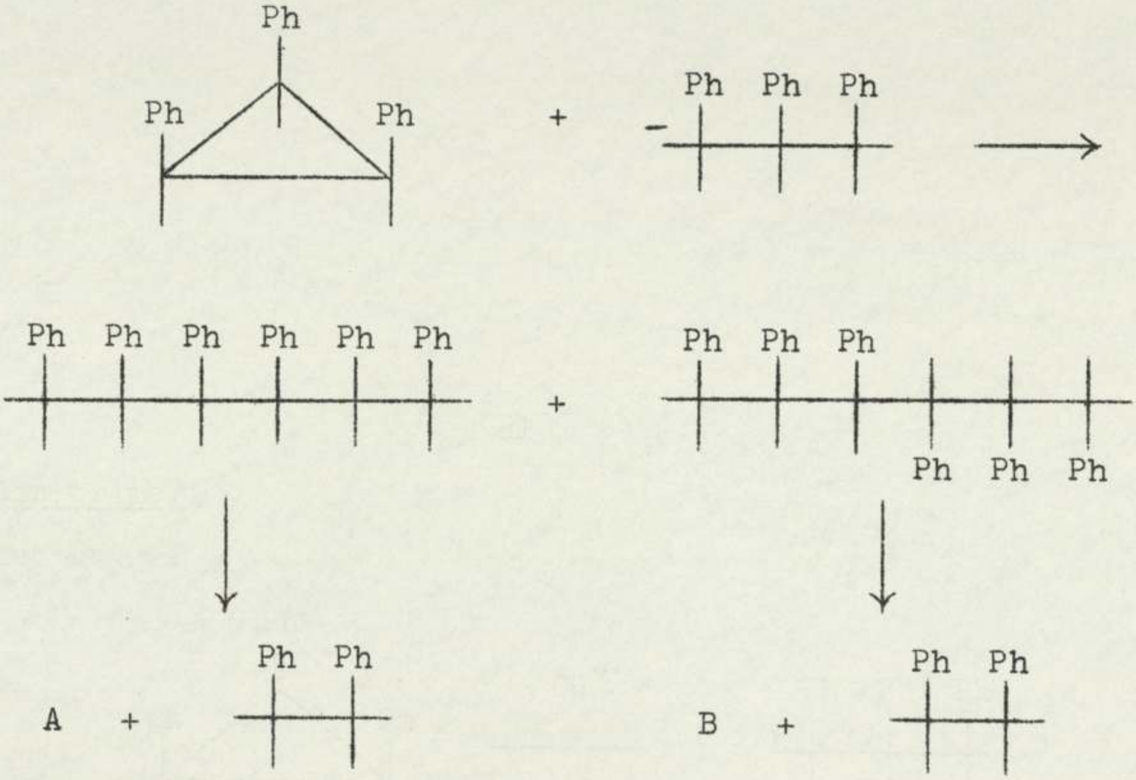
The cis and trans methyl phenyl trimer reaction products in the most stereoselective reactions (7 and 8) can be accounted for by the following scheme, based on steps described previously. Simplified formulae, indicating the stereochemistry, are used for the methyl phenyl siloxanes. One end of each open chain species is anionic.

Cis trimer

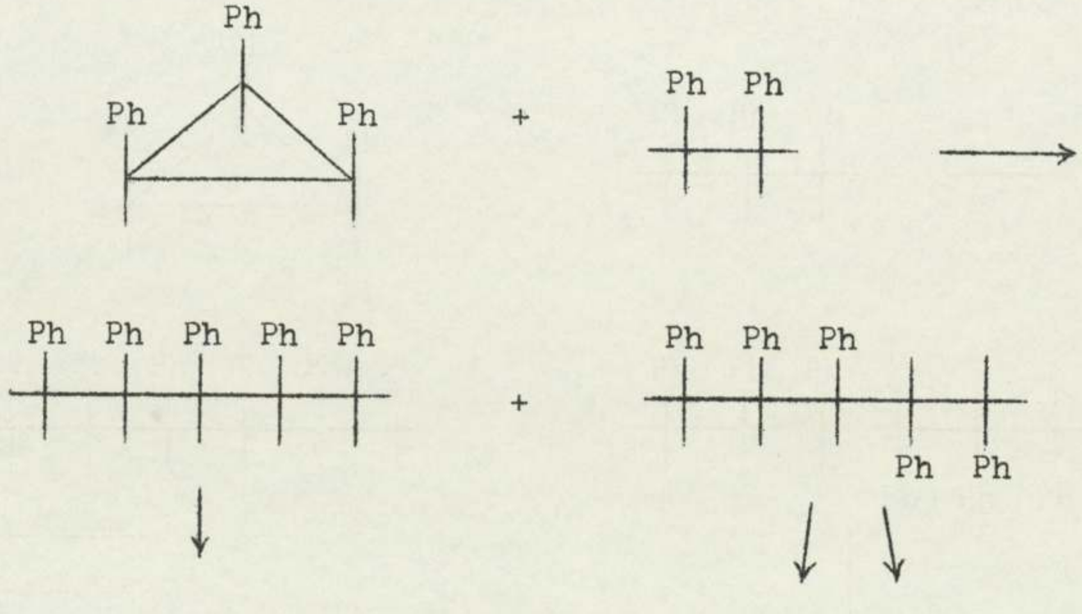
1st stage:

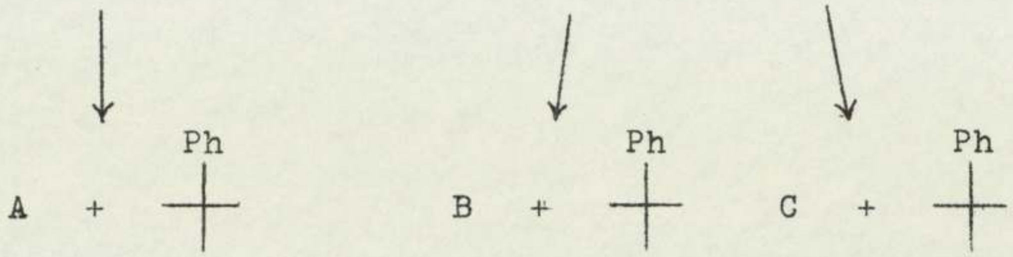


2nd stage:

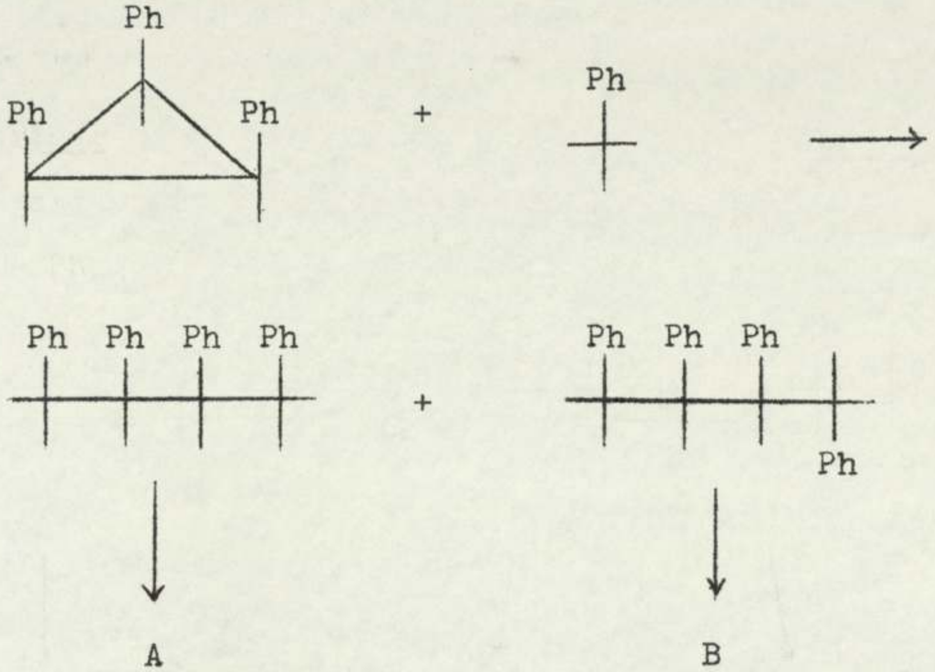


3rd stage:





4th stage:

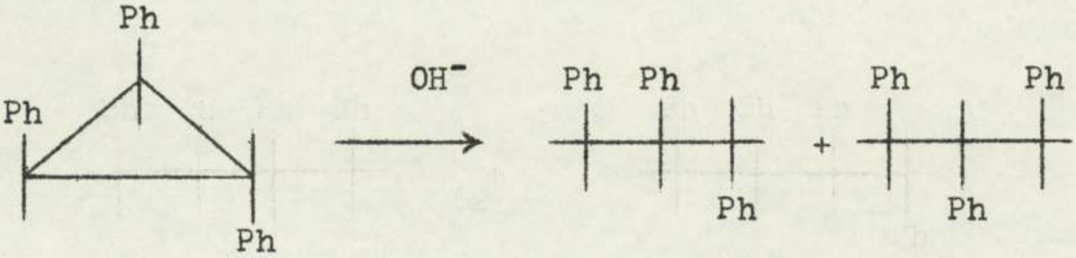


This scheme indicates, after four stages of reaction, the following isomer proportions:

$$A > B \gg C, \text{ no } D.$$

Trans trimer

1st stage:



The two different silanolate ions can react with the trimer to give a number of different hexasilanolate ions which on cyclisation would give three tetramers (B, C and D). Although a large number of further reactions are then possible, it is evident that the isomer proportions would be: B $>$ C $>$ D $\gg$ A.

The cis trimer scheme indicates a 50% yield of tetramer A, the maximum attained (in reaction 7) is about 40%. The results do indicate, however, a considerable degree of stereospecificity in some of the reactions. The tendency towards equilibration of the products is greatest with the most polar solvent, tetrahydrofuran (reactions 9 and 10). Here, although there are still slight differences between the cis and trans trimer products, the proportions of tetramer A, B, C and D in the products approach the theoretical 1 : 4 : 2 : 1 mentioned in Chap. I.

CHAPTER 3

An examination of some possible methods for preparing cyclic polyphenylstannosiloxanes.

3.1 Introduction.

The possibilities for alternant heteroatom systems, particularly from the first two rows of Groups III to VI, are numerous. Many of these systems, where both cyclic oligomers and linear polymers may be formed, have been extensively investigated.[12] By far the most useful group of such compounds are the linear and crosslinked polyorganosiloxanes. The normal way of modifying the properties of these materials is to vary the degrees of polymerisation and crosslinkage and to alter the organic substituent groups on the silicon atoms. An alternative approach is replacement of some or all, of one or other, of the heteroatoms by other atoms. If the oxygen atoms are replaced by carbon, nitrogen or sulphur, materials that are stable mainly in the cyclic oligomeric form, rather than as polymers, are obtained. Replacement of some of the silicon atoms by other atoms, particularly those of Group IV elements, might be more promising. So far, however, little progress seems to have been made in the production of technologically useful polymers by this method.

A considerable number of low molecular weight heterosiloxanes, i.e. siloxanes where some of the silicon atoms have been replaced by atoms with a valency of 2 to 5, have been obtained.[29] The principal replacement elements are boron, aluminium, titanium, tin and phosphorus. A variety of borosiloxanes have been obtained. These include low molecular weight linear and cyclic, and polymeric linear and crosslinked types.[2] With the possible exception of tin, Group IV elements do not seem to have produced such a wide range of heterosiloxanes as boron. With carbon, both cyclic and polymeric methyleneoxysiloxanes have been obtained. These compounds are less stable than those with a multi-carbon atom group, instead of a single carbon atom, or those with carbon directly linked to silicon.[2] Comparatively few germanosiloxanes have been reported, probably due to the expense of organogermanium compounds. Most attention, amongst Group IV heterosiloxanes, has been devoted to the stannosiloxanes.

Although many open chain low molecular weight stannosiloxanes have been reported, there seems to be an almost complete absence of mention of cyclic types. In a recent review,[30] amongst about 50 open chain stannosiloxanes, only two cyclic types were listed. This contrasts with the borosiloxanes where a number of cyclic types have been obtained.[31] In view of the extreme ease with which cyclic siloxanes are formed, the ready formation of the stannosiloxane linkage, Si-O-Sn, and the 20 years or so during which stannosiloxanes have been reported, it might seem surprising that there has not been more mention of cyclic stannosiloxanes in the literature.

3.2 The stannosiloxane linkage.

The replacement of a silicon atom in the siloxane linkage, Si-O-Si, by a heteroatom such as tin has a considerable effect on the nature of the bond and the character of the compound. These effects will depend on the electronegativity, atomic radius, and the availability of energetically and sterically favoured d-orbitals in the heteroatom. The less electronegative tin atom results in a more polar bond than with silicon. This increases the tendency to ionic reactions, such as hydrolytic attack, resulting in the stannosiloxane bond being generally weaker than the siloxane. Contributing to the weakening of the bond is a reduced $p\pi \rightarrow d\pi$ component. This also allows the d-orbitals of the tin atom to be more available for accepting pairs of electrons from other atoms. This leads to a marked tendency for the tin atoms in stannoxanes to increase their co-ordination number above 4.

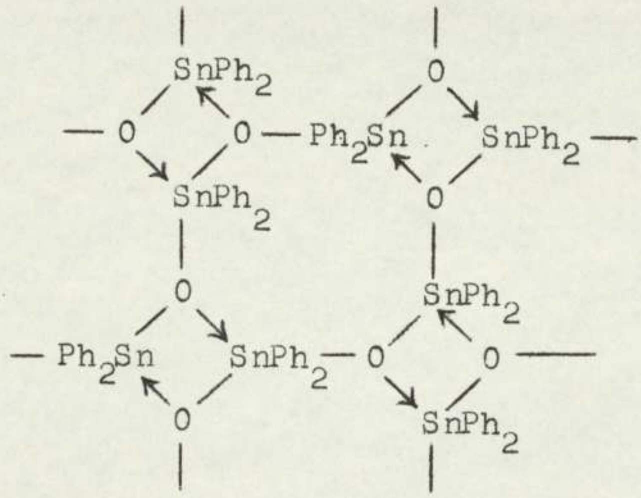
A comparison of high molecular weight siloxanes of the type $(R_2SiO)_n$ with the corresponding tin compounds, $(R_2SnO)_n$, clearly displays the effect of co-ordination with the tin atoms. The silicon compounds are liquids, the well known silicone oils, but the tin compounds are infusible, insoluble solids. A typical example is diphenyltin oxide, $(Ph_2SnO)_n$. This has a highly crosslinked three dimensional structure in which the tin atoms have a co-ordination number of 5, resulting from lone pairs of electrons on oxygen atoms being donated to nearby tin atoms.[33] Replacement of some of the silicon atoms in a siloxane chain by tin can increase the viscosity of the oil or produce properties of the "bouncing putty" variety. This latter material is normally a borosiloxane polymer in which the boron atoms act as electron acceptors.

3.3 Some methods of forming the stannosiloxane linkage and attempts to apply these methods to the formation of cyclic polyphenylstannosiloxanes.

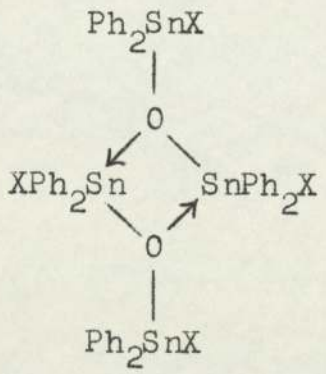
i. Cohydrolysis.

The cohydrolysis of mixtures of silicon and tin organohalides has been successfully applied to the preparation of a few simple open chain stannosiloxanes.[32] The method is only likely to be successful if the rates of hydrolysis of the silicon and tin compounds are comparable and if the inevitable side reactions can be reduced to an acceptable level. Yields of desired product should be highest if at least one of the reacting partners is a monofunctional silicon or tin compound. If both reactants are difunctional, as would be required for the formation of cyclic stannosiloxanes, then the product possibilities multiply. In the case of phenyl compounds, however, encouragement is given by the fact that good yields of single products can be obtained by the hydrolysis of diphenyldichlorosilane under suitable conditions.[4]

The complete hydrolysis of diphenyltin dichloride, which requires alkaline conditions, gives a quantitative yield of diphenyltin oxide. This is an infusible, insoluble polymeric material thought to be based on cyclic stannoxane units:[33]



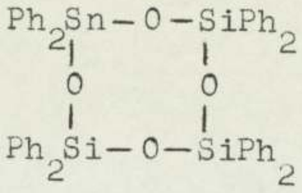
From the partial hydrolysis, intermediate products of the following type have been isolated:



X = Cl or OH

Since the hydrolysis of diphenyltin dichloride requires alkaline conditions and under these conditions diphenyldichlorosilane gives the cyclic tetramer, an attempt was made to obtain I by hydrolysing a 3 : 1

I



mixture of diphenyldichlorosilane and diphenyltin dichloride. An excess of ammonia with diethyl ether as solvent was used. Only a very small amount of insoluble material, presumably diphenyltin oxide, remained at the end of the reaction. The ether solution yielded a white solid whose infra red spectrum indicated the presence of OH groups and the possible presence of the stannosiloxane linkage, Sn-O-Si. This group gives an intense and characteristic absorption in the region 980-940 cm^{-1} [32,34,35] Most of the other compounds involved in this work are free of absorptions in this region. Neighbouring absorptions occur at 1100-1000 cm^{-1} (Si-O) and 750-650 cm^{-1} (phenyl).

Thin layer chromatography indicated the presence of at least four substances in the hydrolysis product, of which two were probably siloxane diols. Cyclic siloxanes seemed to be absent. Column chromatography permitted the separation and identification (by infra red comparison) of tetraphenyl-1,3-disiloxanediol and hexaphenyl-1,5-trisiloxanediol. A smaller amount of an unresolved mixture containing the disiloxanediol and two other substances was also obtained. If any of the desired product was formed in the reaction, it was only produced in very small yield. Partial hydrolysis products of diphenyltin dichloride were probably formed as well.

This experiment was not pursued further. Obvious further lines of investigation include the use of different solvent systems, different temperatures, and the replacement of ammonia by strong alkali.

ii. The reaction of diphenyltin dichloride with organosilicon diols.

a) Using alkali metal derivatives of diols.

The reaction between alkali metal silanolates and organotin halides appears to be one of the principal processes for the preparation of stannosiloxanes.[34,35]

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}^-\mathrm{M}^+ \quad + \quad \mathrm{X}-\overset{|}{\underset{|}{\mathrm{Sn}}}- \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Sn}}}- \quad + \quad \mathrm{MX}$$

Where at least one of the reactants is monofunctional, excellent yields of the appropriate product are readily obtained. In one isolated mention of a reaction where both reactants were difunctional, a "waxy polymeric" product was obtained.[36]

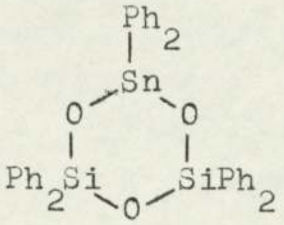
Reactions involving the lithium derivative of diphenylsilanediol and the sodium derivative of tetraphenyl-1,3-disiloxanediol, each with diphenyltin dichloride, were attempted. In each case products (m.p. 180-190°C.) with similar infra red spectra were obtained. These spectra, which were characteristic of

Sn-Ph compounds, such as diphenyltin dichloride (m.p. 42°C), showed no indication of the presence of Si-O-Sn and little sign of Si-Ph.

b) Reaction in the presence of a base.

The condensation of disiloxanediols with dichlorosilanes or dichlorodisiloxanes in the presence of triethylamine has been used as a method for preparing individual methyl phenyl cyclic trimer and tetramer isomers.[21] Apart from a patent,[36] reference to the condensation of a Si-OH compound with an organotin halide in the presence of a base was not found in the literature examined.

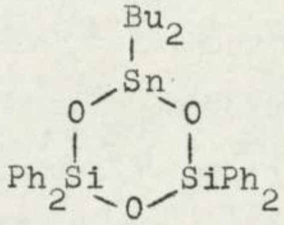
The method was tried with tetraphenyl-1,3-disiloxanediol and diphenyltin dichloride in an attempt to obtain the corresponding cyclic stannosiloxane:



Experiments were carried out using diethyl ether and tetrahydrofuran as solvents with triethylamine as the base. A small amount of a pure substance, apparently containing the Si-O-Sn linkage (intense absorption at about 945cm^{-1}), was isolated. Corresponding cyclotri- and tetrasiloxanes are readily distinguished by infra red spectroscopy. The Si-O-Si absorption for a cyclic trimer occurs at 1020-1010cm^{-1} and at 1090-1080cm^{-1} for a cyclic tetramer.[38] In this case the Si-O-Si absorption was at 1020cm^{-1} and the whole 1200-975cm^{-1} region was very similar to that for hexaphenylcyclotrisiloxane. The substance, which was not obtained in sufficient quantity for a full analysis, could be the required product. An apparently identical substance was obtained by the following method.

iii. The reaction of diphenyltin oxide with organosilicon diols.

It has recently been found that organoheterometalloxanes could be prepared by azeotropic dehydration between a hydroxy compound and an organometallic oxide in benzene, toluene, etc.[37] Among a number of open chain stannosiloxanes, one cyclic type is mentioned:



An attempt was made to prepare the corresponding polyphenyl compound by reacting diphenyltin oxide with diphenylsilanediol or tetraphenyl-1,3-disiloxanediol. In each case the oxide and diol were refluxed in benzene. Water was produced during the first 10-15 minutes and was collected in a Dean and Stark trap. The product from the disiloxanediol experiment yielded a material apparently identical to that obtained in ii,b) above. Again, unfortunately, only a very small quantity was obtained.

It would appear probable, from the method of synthesis and the infra red spectrum, that the small amount of pure substance obtained is one of the desired products, hexaphenylcyclostannoxydisiloxane. Further work would need to be done on the optimisation of conditions for these reactions if useful yields of product were to be obtained. The difficulty lies mainly in the fact that these reactions, involving two difunctional materials, can readily lead to a multiplicity of products.

One or two other possible reactions were not investigated, e.g. transesterification between a tin acetate and an alkoxysilane has been used successfully for stannosiloxane formation.[34]

EXPERIMENTAL

Gas-liquid chromatographic analyses were carried out on a Pye series 104 chromatograph using a katharometer detector. A $9' \times \frac{1}{4}$ inch column of 20% MS 2430 silicone gum on fire brick with hydrogen as carrier gas (flow rate: 50 ml/minute) was used. The column temperatures are mentioned in the appropriate sections. 2-10 microlitre injections of either a neat liquid or a solution in benzene were used. Standard injections were used when a quantitative comparison between different samples was required. The areas under the peaks were determined by tracing the peaks onto uniform paper, cutting out and weighing. The ratio of the components was taken as the ratio of their peak areas. During the course of a substantial amount of quantitative gas chromatography it became evident, from successive analyses of the same sample, the use of standards, etc., that results were usually reliable to within about 1 part in 10. Reasonable consistency was also obtained with the results from proton resonance spectra.

Column chromatography was carried out using Hopkins and Williams' Silica Gel M.F.C. or Whatman's

Silica Gel S.G. 32 as column materials. Elution was by a 20 : 80 mixture of benzene and light petroleum (b.p. 60-80°C.).

Thin layer chromatography was carried out on 6 x 6 inch glass plates spread with a 0.25mm thick layer of Silica Gel G supplied by E. Merck Ltd. After development with a 17 : 83 mixture of benzene and light petroleum (b.p. 60-80°C.) or other solvent where stated, and drying, components were located by spraying the plate with a 2% solution of potassium permanganate in 20% sulphuric acid.

For the last two techniques, A.R. solvents supplied by Fisons Ltd. were used. Chlorosilanes, supplied by Midland Silicones Ltd., were redistilled before use. Cyclic siloxanes were prepared at the University of Aston in Birmingham mainly by H. J. Hickton and J. Thompson. Other chemicals were mainly reagent grade and were supplied by Messrs. Hopkins and Williams.

Proton resonance spectra were obtained using a Perkin-Elmer R10 spectrometer operating at 60 MHz and 35°C. Tetramethylsilane was used as an internal reference. This technique was mainly used as a method of quantitative analysis of mixtures of methyl phenyl cyclotetrasiloxanes by comparison of the peak areas of the methyl proton resonances. The machine integrals were unsatisfactory due to varying base lines resulting from impurities. More reliable results were obtained by a comparison of peak areas on the basis of peak height multiplied by half height width.

Infra red spectra were recorded on a Perkin-Elmer Infracord 237.

Physical constants are taken mainly from Bazant, et al.[39]

Chapter 1

The hydrolysis of dimethyldichlorosilane.

a) With water.

1. Addition of water to chlorosilane.

Dimethyldichlorosilane (5ml) and diethyl ether (25ml) was placed in a 50ml 3-necked flask fitted with a tap funnel, stirrer and thermometer. The flask was placed in an ice-salt bath at -1°C. Water (10ml) was added to the rapidly stirred mixture during $1\frac{1}{4}$ hours, the temperature being kept at 0 ± 0.5°C. The ether layer was then transferred to a separating funnel and washed with water until free of acid. After drying over calcium chloride the ether solution was evaporated on a rotary evaporator.

The experiment was repeated using acetone as solvent but after the hydrolysis the reaction mixture was made just alkaline with ammonia solution, using pH indicator paper, then the solvent was evaporated off. The resulting aqueous mixture was extracted with ether. After washing with water the ether extract was dried and evaporated.

These experiments were repeated but at a temperature of -75 ± 2°C., obtained by placing the flask in a dry ice-acetone bath. The water was introduced into the flask in a very fine stream from a fine pipette.

2. Addition of chlorosilane to water.

Water (10 ml) was placed in a 50 ml 3-necked flask fitted as in 1. and cooled in an ice-salt bath at -1°C. Dimethyldichlorosilane was added during 1 hour, the temperature being kept at 0 ± 0.5°C. The mixture was then stirred for a further $\frac{1}{4}$ hour. The ether layer was worked up as in 1.

The experiment was repeated with acetone as solvent, the working up being as in 1. with acetone as solvent.

These experiments were repeated at -75°C. but using a mixture of water (10 ml) and solvent (50 ml) in a 250 ml flask. This mixture was cooled to -75°C. with vigorous stirring before the reaction. With diethyl ether as solvent a fine suspension of ice crystals was formed but a largely homogeneous mixture was obtained with acetone.

The products, light colourless oils, were analysed by gas chromatography (column temperature: 100°C.) using standard injections of the neat liquid in conjunction with pure octamethylcyclotetrasiloxane as a standard.

b) With hydrochloric acid of various concentrations.

Experiments were carried out using hydrochloric acid of molarities: 0, 4, 6, 8, 10.5.

Diethyl ether (50 ml) and hydrochloric acid (100 ml) was placed in a 250 ml 3-necked flask fitted as in a) 1.

and cooled to -3°C. in an ice-salt bath. Dimethyldichlorosilane (5 ml) dissolved in diethyl ether (50 ml) was run into the vigorously stirred mixture during 4 minutes. This was accompanied by a temperature rise of about 6°C. After a further 2 minutes stirring the ether layer was rapidly transferred to a separating funnel and worked up as in a) 1.

The products were analysed as in a).

The hydrolysis of methylphenyldichlorosilane.

These experiments were carried out in duplicate.

Methylphenyldichlorosilane (10 ml) and solvent (50 ml) was placed in a 250 ml 3-necked flask fitted with a tap funnel and thermometer of suitable range. Water (22 ml) was added gradually to the vigorously stirred mixture.

Solvents used: Diethyl ether, acetone, tetrahydrofuran.

Hydrolysis temperatures: 30 ± 0.5, 0 ± 0.5, -75 ± 2 °C.

Temperature control: For experiments at 30°C. the reaction flask was placed in a large volume of water maintained at 28-29°C. by the occasional addition of small amounts of hot water. For short hydrolysis times, lower temperatures were used. For 0°C., an ice-salt bath at -2°C. was used. For -75°C., a dry ice-acetone bath was used.

Times for hydrolysis: These varied from 10 to 120 minutes.

Addition of water: This was dropwise from a tap funnel for the 30 and 0° reactions and in a very fine stream from a fine pipette for the -75° reactions. At -75°

with acetone as solvent the mixture remained clear and homogeneous during the early stages of reaction, becoming white and pasty later. With ether at -75° considerable coagulation occurred at first with a coarse white paste forming later.

Treatment of reaction products.

Ether as solvent: Same procedure as under a) 1. with ether as solvent.

Acetone or tetrahydrofuran as solvent: Same procedure as under a) 1. with acetone as solvent.

The products were colourless viscous oils, some of which partially solidified on standing.

Analysis of hydrolysis products.

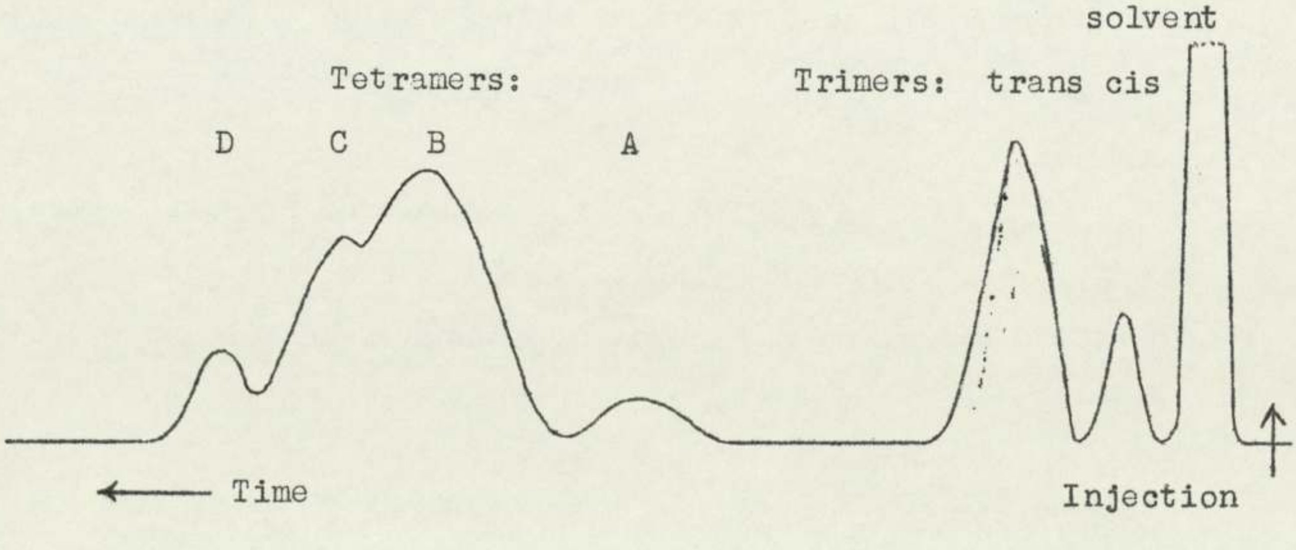
i. Column chromatography.

A weighed amount of each product (about 0.5 g) was dissolved in a 20 : 80 mixture of benzene and light petroleum (b.p 60-80°C.) and placed on a column of Silica Gel S.G. 32 (9 x $\frac{3}{4}$ inch) and eluted with the same solvent (500 ml). Open chain siloxanes were retained on the column while cyclic siloxanes were eluted. The percentage of the latter was obtained by evaporation of the eluate on a rotary evaporator followed by weighing of the residue of cyclic siloxanes. The residues were dissolved in benzene (1.5 ml).

An attempt was made to examine the linear siloxane diols retained on the column. These were eluted with tetrahydrofuran (300 ml) and the resulting solution evaporated. The molecular weights of some residues were determined by a lowering of vapour pressure method. The values obtained (in the region 200-330) suggested the possible presence of 1,3-dimethyl-1,3-diphenyldisiloxanediol (M.W. 290). Difficulties resulting from the use of tetrahydrofuran, such as the extraction of impurities from the column and formation of a considerable residue on evaporation, discouraged further work in this direction.

ii. Gas chromatography.

This was carried out under the conditions mentioned previously, using non standard injections of the solutions obtained in i. A column temperature of 265°C. was found to give base line separation of the isomeric methyl phenyl trimers and optimum separation of the tetramers. Base line separation of tetramer A, partial separation of tetramers B and C, and almost complete separation of tetramer D can be obtained. A Typical gas chromatogram for the mixture of trimers and tetramers is shown below:



Although separation of the tetramers B, C and D is not complete, reasonably reliable estimates of their proportions can be made from their overlapping peak areas (as in Chap. II). In this work, however, due to comparatively small variations in the relative amounts of tetramers B, C and D, only the ratios of A to (B + C + D) were determined.

The pentamers are not eluted at 265°C. Additional runs at 300-310°C. were done in order to get the tetramer/pentamer ratios. The four pentamers, whose stereochemistry does not seem to have been established, are less well resolved than the four tetramers.

Chapter 2

The reaction of cyclic organosiloxanes with hydrochloric acid.

i. Hexamethylcyclotrisiloxane.

Hexamethylcyclotrisiloxane (1.00 g) dissolved in diethyl ether (60 ml) was stirred with 7.5 M hydrochloric acid (25 ml) at 20°C. Portions (5 ml) of the ether layer were withdrawn at 20 minute intervals during 2 hours and also after 24 hours. These were washed with water until free of acid, dried over calcium chloride and evaporated. The residues were dissolved in benzene (0.50 ml) and analysed by gas chromatography (column temperature 100°C.) using standard injections.

ii. The trimethyltriphenylcyclotrisiloxanes.

The trans trimer, m.p. 45°C., (0.1 g) dissolved in diethyl ether (6 ml) was shaken with 6 M hydrochloric acid (2 ml) at 20°C. Portions of the ether layer were withdrawn at intervals during the first 4 hours and then after 24 hours and spotted onto a thin layer plate which was developed as described previously. This procedure was repeated using the trans and cis (m.p. 99.5°C.) trimers with acetone and tetrahydrofuran as solvents but after 1 hour the mixtures were neutralised with ammonia solution and the solvent evaporated off. The residues were extracted with diethyl ether and the extracts washed, dried and evaporated. The residues were dissolved in benzene (0.5 ml) and, together with standard solutions of the two trimers, analysed by gas chromatography (column temperature: 265°C.). The reaction product solutions required a high sensitivity setting on the instrument.

iii. The tetramethyltetraphenylcyclotetrasiloxanes.

Each tetramer isomer (0.1 g), dissolved in acetone (6 ml), was shaken with 6 M hydrochloric acid (2 ml) for 1 hour at 20°C. After working up the mixtures as in ii. above, the residues were dissolved in benzene (0.5 ml) and analysed by gas chromatography (column temperature: 265°C.). The four experiments were repeated with tetrahydrofuran as solvent.

The reaction of cyclic organosiloxanes with potassium hydroxide.

i. Hexamethylcyclotrisiloxane.

Half a pellet of potassium hydroxide (approximately 0.001 mole) was weighed in a closed container and then powdered under benzene using a small pestle and mortar. The resulting suspension was transferred, using a pipette, to a 10 ml flask containing an equimolecular amount of hexamethylcyclotrisiloxane (M.W. 222.5). Benzene was then added to give a total of 5 ml per 0.001 mole of siloxane and the mixture was shaken at 20°C. Portions (0.4 ml) were withdrawn at intervals during 4 hours and then after 24 hours. These were filtered through a small plug of cotton wool, to remove any solid potassium hydroxide, and then sealed into small tubes to prevent loss of solvent. Gas chromatography (column temperature: 100°C.), using standard injections, was carried out on the samples and also on standard solutions of methyl trimer and tetramer.

The experiment was repeated using diethyl ether as solvent.

ii. Hexaphenylcyclotrisiloxane.

The reaction was carried out as in i. except that p-xylene was used as solvent, the mole ratio of potassium hydroxide to siloxane was 1.5 : 1 and the mixture was spotted at intervals during 2 hours and then after 24 hours onto a thin layer plate which was developed in the usual way. The experiment was repeated at a temperature of 50°C. The experiment was further repeated at 50°C. (without the thin layer chromatography) but on a larger scale (0.813 g of siloxane) with a reaction time of 2 hours. The solution was then placed on a column (5 x $\frac{3}{4}$ inch) of Silica Gel M.F.C. and eluted with 20 : 80 benzene-light petroleum (200 ml). The eluate was evaporated to give a solid residue (0.400 g) that was crystallised from glacial acetic acid to give a product with m.p. 196°C. This had an infra red spectrum identical to that of octaphenylcyclotetrasiloxane (m.p. 200°C.[39]).

iii. The trimethyltriphenylcyclotrisiloxanes.

The procedure was again similar to that used in i. Individual trimer isomers (about 0.2 g, 0.0005 mole), an equimolecular amount of powdered potassium hydroxide and solvent (5 ml) was shaken at 20°C. With diethyl ether as solvent, experiments with 1 ml of solvent were also done and with p-xylene a temperature of 50°C. was also used. The reactions were followed by thin layer chromatography and the times taken for the trimer to react were determined. The experiments were repeated on a larger scale (about 1 g of trimer) using these reaction times. The reaction mixtures were worked up as in ii. above and the weights of the residues determined. The residues were colourless viscous oils, some of which partially crystallised on standing. In one case (trans trimer, p-xylene, 50°C.) the crystals were separated, pressed between filter paper and recrystallised from methanol to give a product (m.p. 99°C.) with a proton resonance spectrum identical to that of tetramer isomer C (m.p. 99°C.[21]). In each case portions of the oils (before any crystallisation occurred) were dissolved in benzene and analysed by gas chromatography (column temperature: 265°C.) and dissolved in tetrachloromethane for proton resonance spectrum determination.

The experiments carried out under this section are summarised in Table VI, P. 54.

Chapter 3

Preparation of tetraphenyl tin.

Phenyl magnesium bromide was prepared according to the method of Vogel[40] using magnesium and bromobenzene (2.75 mole of each). This was converted to tetraphenyl tin using the method of Luijten and Van der Kerk.[41] Redistilled stannic chloride (56 ml, 0.48 mole, 70% of theoretical amount) was added to the cooled phenyl magnesium bromide. After refluxing for 2 hours followed by cooling, the mixture was decomposed by addition of ice water (112 ml) followed by cold 10% hydrochloric acid (550 ml). The crude product was filtered off, washed, and dried in vacuo at 140°C. The material was dissolved in hot benzene using a continuous extraction apparatus and the solution allowed to crystallise. Crystals washed with benzene and dried in vacuo at 100°C.

Yield: 75%, m.p. 224°C.(Lit.[41] 224°C.)

Preparation of diphenyltin dichloride.

This was based on the method of Gilman and Gist.[42]

A 250 ml flask fitted with an air condenser was charged with tetraphenyl tin (42.1 g, 0.1 mole) and redistilled stannic chloride (11.5 ml, 0.1 mole). The flask was gradually heated to 180°C. over a period of 1 hour and held at this temperature for a further 2 hours. The resulting oil crystallised after several days at 3°C. The crystals were removed and recrystallised from a little benzene.

Yield: 65%, m.p. 40°C. (Lit.[42] 42-44°C.)

Preparation of diphenyltin oxide.

Diphenyltin dichloride (14.5 g, 0.042 mole) dissolved in ethanol (80 ml) was run, with stirring, into ice cold potassium hydroxide solution (35 ml, containing 0.084 mole KOH) during ½ hour. After stirring for further ¼ hour, the product was filtered off, washed with water and ethanol and dried in vacuo.

Yield: quantitative.

Preparation of tetraphenyl-1,3-disiloxanediol.

This was based on the method of Burkhard.[4] Diphenyldichlorosilane (104 ml, 0.5 mole) dissolved in diethyl ether (125 ml) was placed in a 500 ml 3-necked flask. Water (4.5 g, 0.25 mole) dissolved in dioxan (50 ml) was added dropwise with stirring during 1 hour. Dry nitrogen was blown through the mixture to remove hydrogen chloride. The solvent was distilled off and the residue was distilled under vacuum using a nitrogen bleed. Crude tetraphenyl-1,3-dichlorodisiloxane, b.p. 200-270°C./1mm, was collected. This was redistilled and a fraction b.p. 210-220°C./0.1mm collected. This was dissolved in hexane and left to crystallise at 0°C. Hard white crystals were separated, washed with hexane and dried to give tetraphenyl-1,3-dichlorodisiloxane, m.p. 36°C. (Lit.[4] 38°C.). This material (12.6 g), dissolved in toluene (10 ml), was added during ½ hour to a vigorously stirred mixture of toluene (7.7 ml), tert.-amyl alcohol (16.1 ml) and water (66.6 ml) at 25°C. After further periods of stirring with portions of fresh water, the now neutral organic layer was dried and evaporated to dryness. The residue was crystallised from benzene and n heptane to give tetraphenyl-1,3-disiloxanediol (10 g), m.p. 111°C. (Lit.[4] 113-114°C.)

The cohydrolysis of diphenyldichlorosilane and diphenyltin dichloride.

Diphenyldichlorosilane (5.3 ml, 0.025 mole) and diphenyltin dichloride (2.85 g, 0.0083 mole) dissolved in diethyl ether (35 ml) was added during 45 minutes to a stirred mixture of diethyl ether (70 ml) and aqueous ammonia (35 ml of 4.5 M, a 2 fold excess). After a further 45 minutes stirring the ether layer was washed with water, dried over calcium chloride, and evaporated to give a white solid.

Infra red, KBr disc, included maxima at 3100 cm^{-1} (OH) and 925 cm^{-1} (possibly Si-O-Sn).
Thin layer chromatography was carried out on the products of this and subsequent experiments when the infra red spectrum indicated the possible presence of the stannosiloxane linkage. Much more strongly eluting solvents than are required for cyclic siloxanes were used, e.g. dioxan, chloroform and 5% diethyl ether in chloroform. The acid permanganate spray method of location was much less successful than in the previous work. This was due to difficulty in completely evaporating solvent from the plates. In this case TLC indicated the presence of at least 4 substances of which 2 could be siloxane diols.

The reaction product (0.5 g) dissolved in chloroform was placed on a column of Silica Gel M.F.C. (15 x $\frac{3}{4}$ inch) and eluted with 5% diethyl ether in chloroform. 20 ml fractions were collected, evaporated and weighed. Tetraphenyl-1,3-disiloxanediol (0.2 g approximately) and hexaphenyl-1,5-trisiloxanediol (0.1 g approximately), identified by infra red spectra, were obtained. A much smaller quantity of an unresolved mixture was also obtained.

The reaction of diphenyltin dichloride with organosilicon diols.

a) Using alkali metal derivatives of the diols.

Excess lithium wire was added to a solution of diphenylsilanediol (0.66 g, 0.0305 mole) in sodium

dried diethyl ether (20 ml). After the gentle effervescence had ceased the solution was filtered into a 3-necked flask. Diphenyltin dichloride (1.012 g, 0.0299 mole) in diethyl ether (15 ml) was added with stirring during 20 minutes. After evaporation of the ether the solid residue was warmed with benzene and the mixture filtered. The filtrate deposited a white solid, m.p. 185-190°C.
Infra red, KBr disc: spectrum very similar to that of diphenyltin dichloride.

The above experiment was repeated but using equimolecular amounts of tetraphenyl-1,3-disiloxanediol and diphenyltin dichloride and with sodium instead of lithium. Product, m.p. 185°C.
Infra red, KBr disc: spectrum very similar to that obtained above.

b) Reaction in the presence of a base.

A solution of tetraphenyl-1,3-disiloxanediol (1.2 g, 0.029 mole) and triethylamine (2 ml) in diethyl ether (20 ml) was placed in a 3-necked flask and cooled in ice. A solution of diphenyltin dichloride (1 g, 0.029 mole) in diethyl ether (15 ml) was run in, with stirring, during ½ hour. After stirring for a further 2 hours the white solid was filtered off, and the filtrate evaporated. The experiment was repeated with tetrahydrofuran as solvent.
Thin layer chromatography: each product a mixture of at least 4 substances.

Infra red, KBr disc: virtually identical spectra for each product. Strong absorptions at 945 cm^{-1} (Si-O-Sn).

The tetrahydrofuran reaction product, on slow crystallisation from dioxan, gave a small amount of a single substance (indicated by thin layer chromatography). The Si-O-Sn absorption of this material was less intense than in the crude product and another, weaker, peak was present at 875 cm^{-1}.

The reaction of diphenyltin oxide with organosilicon diols.

Diphenyltin oxide (0.723 g, 0.0025 mole) and diphenylsilanediol (1.175 g, 0.005 mole) in benzene (50 ml) was refluxed for 1 hour in a flask fitted with a condenser and a Dean and Stark trap. Water collected in the trap during the first 15 minutes. A small solid residue was filtered off and the solution evaporated. The experiment was repeated but using diphenyltin oxide (0.0025 mole) and tetraphenyl-1,3-disiloxanediol (1.038 g, 0.0025 mole).

Infra red spectroscopy and thin layer chromatography indicated that the crude products from these experiments were very similar and were also like those from the experiments of b) above. The product from the disiloxane diol experiment, after crystallisation from dioxan, gave a material that appeared to be identical with the purified material obtained in b).

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