

THE FORMATION AND PROPERTIES OF SOME CYCLIC

COMPOUNDS OF SILICON AND TIN

by

JENNIFER MARY DOBSON

*Thesis*

54 7.25 DOB

190560

5 MAR 1976

A Thesis presented for the Degree of Master of Philosophy  
in the University of Aston in Birmingham.

September 1975.

## SUMMARY

Six and seven membered cyclic compounds of silicon and tin were prepared and investigated at low temperatures, using nuclear magnetic resonance spectroscopy. An attempt was made to prepare a suitable cyclic compound of tin, which would be capable of existing in geometrically isomeric forms. It was hoped that, having prepared such a compound, it would be of great value in studying the reaction mechanisms of tin. However, the compound was not successfully prepared and it was therefore decided to investigate further cyclic compounds of silicon, such as the siloxanes.

Siloxanes are obtained principally from the hydrolysis of diorganohalosilanes. The hydrolysis of certain diorganohalosilanes, such as dimethyldichlorosilane and methylphenyldichlorosilane has been extensively investigated but little work has been reported on the hydrolysis of ethylmethyldichlorosilane. In this work, the hydrolysis of ethylmethyldichlorosilane has been investigated and the results obtained were found to be in agreement with those obtained for other diorganohalosilanes. The interest in the hydrolysis of this halosilane, was due to the possibility of the products existing in stereoisomeric forms, but although a considerable amount of time was spent in finding suitable instrumental conditions, no separation of the isomers was achieved.

The addition of glycerol to the hydrolysis of diorganohalosilanes was investigated. A study was made, of both the hydrolysis of ethylmethyldichlorosilane and dimethyldichlorosilane with added glycerol and the results obtained were compared with previous experiments.

Siloxanes were also obtained from both the hydrolysis and hydrogenolysis of bis(benzyloxy)ethylmethylsilane. The proportions of siloxanes obtained, from both reactions, were compared with those

obtained from the hydrolysis of the diorganohalosilane.

A further investigation was carried out into the hydrogenolysis of bis(benzyloxy)methylphenylsilane.

This work was carried out between 1970 and 1975 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

*J. M. Dobson*

J.M.Dobson.

### ACKNOWLEDGEMENTS

I would like to express my sincere thanks to Dr.A.Holt for his supervision and encouragement, over a fairly extended period, of this mainly part-time work. My thanks also to Mrs.R.Clenton, Mr.E.Hartland and Mr.P.Turner for the various spectra they prepared.

I would also like to thank the Staffordshire County Council and the Governors of the Stafford College of Further Education, for granting secondment to enable me to complete this work.

C O N T E N T S

		Page
CHAPTER ONE.	Six and seven membered cyclic compounds of silicon and tin	1
I.1.	Introduction	1
I.2.	Stereochemical aspects	2
I.3.	Cyclic organosilicon compounds	6
I.4.	Nuclear magnetic resonance spectroscopy studies of cyclic organosilicon compounds	9
	Results	10
	Discussion	10
I.5.	Cyclic organotin compounds	11
I.6.	Nuclear magnetic resonance spectroscopy studies of cyclic organotin compounds	13
CHAPTER TWO	The formation of cyclic organosiloxanes by the hydrolysis of diorganohalosilanes	15
II.1.	Introduction	15
II.2.	The hydrolysis of diorganodichlorosilanes	16
II.3.	The hydrolysis of ethylmethyldichlorosilane	17
	Results	18
	Discussion	
II.4.	The addition of glycerol to the hydrolysis of ethylmethyldichlorosilane	28
II.5.	The addition of glycerol to the hydrolysis of dimethyldichlorosilane	31
	Results	31
	Discussion	31

	Page
CHAPTER THREE. The formation of cyclic organosiloxanes by the hydrolysis and hydrogenolysis of diorganodialkoxysilanes	32
III.1. Introduction	32
III.2. The preparation and stability of organoalkoxysilanes	32
III.3. The hydrolysis of organoalkoxysilanes	33
III.4. The hydrolysis of bis(benzyloxy)ethylmethylsilane	33
Results	33
Discussion	35
III.5. The hydrogenolysis of organoalkoxysilanes	36
III.6. The hydrogenolysis of bis(benzyloxy)ethylmethylsilane	37
Results	38
III.7. The hydrogenolysis of bis(benzyloxy)methylphenylsilane	39
Results	40
III.8. Discussion of the hydrogenolysis results	41
EXPERIMENTAL	42
The preparation of tetraphenyltin	44
The preparation of triphenyltin chloride	44
The preparation of methyltriphenyltin	44
The preparation of methylphenyltin dibromide	45
The preparation of 3-methyl adipic acid	46
The preparation of 3-methyldiethyl adipate	46
The preparation of 3-methylhexan 1,6-diol	47
The preparation of 3-methyl 1,6-dibromohexane	47

	Page
The preparation of 1-methyl-1-phenylsilacycloheptane	48
The preparation of 1-methyl-1-phenylsilacyclohexane	48
The preparation of 1,4-dimethyl-1-phenylsilacycloheptane	49
The preparation of 1-methyl-1-phenylstannacyclohexane	49
The preparation of ethylmethyldichlorosilane	50
The hydrolysis of ethylmethyldichlorosilane	50
The hydrolysis of ethylmethyldichlorosilane and dimethyldichlorosilane with added glycerol	53
The preparation of bis(benzyloxy)ethylmethylsilane	55
The hydrolysis of bis(benzyloxy)ethylmethylsilane	56
The preparation of bis(benzyloxy)methylphenylsilane	57
The hydrogenolysis of bis(benzyloxy)ethylmethylsilane	57
The hydrogenolysis of bis(benzyloxy)methylphenylsilane	58
REFERENCES	60



TABLES AND FIGURES

Page

FIGURES

1.	Reaction scheme for the preparation of 3-methyl 1,6-dibromohexane	8
2.	Chromatogram obtained for the hydrolysis product of ethylmethyldichlorosilane	18a
3.	Mass Spectra obtained for peaks 1, 2 and 3	20
4.	Structures of the three major components obtained from the hydrolysis of ethylmethyldichlorosilane	23
5.	Chromatogram obtained for the hydrolysis product of bis(benzyloxy)ethylmethyilsilane	34
6.	Chromatogram obtained for the hydrogenolysis product of bis(benzyloxy)ethylmethyilsilane	38
7.	Chromatogram obtained for the hydrogenolysis product of bis(benzyloxy)methylphenyilsilane	40

TABLES

I.	Nuclear magnetic resonance spectroscopy results for six and seven membered cyclic organosilicon compounds	10a.
II.	The hydrolysis of ethylmethyldichlorosilane with an excess of water - variation of concentration and temperature	23a
III.	The addition of glycerol to the hydrolysis of ethylmethyldichlorosilane	28a
IV.	The addition of glycerol to the hydrolysis of dimethyldichlorosilane	31a

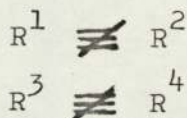
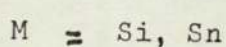
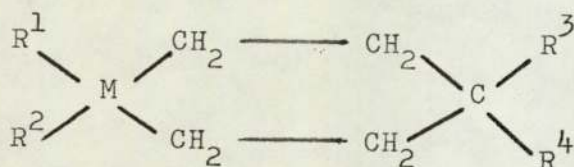
## CHAPTER ONE

### Six and seven membered cyclic compounds of silicon and tin

#### I. 1. Introduction

The ring compounds investigated were the six and seven membered ring compounds of silicon and tin. In these compounds, the silicon and tin atoms are linked to two carbon atoms of a cyclic system. In comparison to the corresponding carbon compounds, which have been extensively investigated, comparatively little is known about the silicon compounds and even less about those of tin. The information which is available seems to deal mainly with the preparation of these compounds. The reactivity of cyclic organosilicon compounds has been investigated<sup>1</sup>, and it appears that the order of reactivity is 5 > 7 > straight chain > 6. This is the same as that found for the corresponding carbon compounds.

The ring compounds initially prepared and investigated contained substituents attached to the silicon and tin atoms. An attempt was then made to prepare suitable cyclic compounds which could exist in geometrically isomeric forms, for example a compound of the type : -



A compound of this type would be of particular importance in the case of tin, since it would be invaluable in studying the reaction mechanisms of organo tin compounds.

Organotin compounds have become of increasing practical importance, due mainly, to the discovery of industrial applications for these compounds. They are very versatile compounds and are used as P.V.C. stabilisers, fungicides, for wood preservation, in food packaging and in marine anti-fouling paint. This range of applications should increase in the future, because it has been found that environmentally, organotin compounds are less damaging than other organometallics, since they degrade to give non-toxic residues.

It was thought that information about the reaction mechanisms of organotin compounds could be obtained by studying the reactions of optically active organotin compounds. This has proved successful in the case of silicon<sup>2</sup> and it was thought that a similar study could be applied to tin. However difficulties have been encountered in the preparation of optically active organotin compounds.

Pope and Peachey<sup>3</sup> reported the preparation of ethylmethylpropyltin-iodide but this work has never been repeated. Peddle and Redl<sup>4</sup> investigated compounds of the type  $R' R'' R''' Sn X$  where X is a halogen, and found that there is rapid equilibration of configuration of the tin atom, which would preclude resolution. They attributed this to the presence of the labile tin-halogen bond, and found<sup>5</sup> that in compounds with four carbon-tin bonds, this equilibration of configuration is much slower than with the halides and may be slow enough to permit resolution of these compounds. Recently, an optically active tetraorganotin compound has been obtained through asymmetric synthesis<sup>6</sup>.

Owing to the practical difficulties encountered earlier in resolving organotin compounds, it was thought that geometrical isomers of suitable cyclic organotin compounds might be easier to separate.

## I. 2. Stereochemical aspects

There are various factors which affect the stability of a particular conformation. These factors include angle strain, torsional strain and

various types of non-bonded interactions, such as Van der Waal's strain (steric strain) and dipole-dipole interactions. All of these factors, working together or opposing each other, determine the net stability of a conformation.

The stereochemistry of six membered carbon rings has been extensively pursued. It has been well established by thermochemical measurements that the cyclohexane ring is free of angle strain. Two puckered, i.e. non planar, models of cyclohexane can be constructed, in which the valence bonds of all the carbon atoms are at the tetrahedral angle ( $109^{\circ}28'$ ) and which are therefore free of angle strain. These are the rigid or chair form (a) and a mobile form (b) which can be readily distorted into a variety of shapes some of which resemble a boat.



(a)



(b)



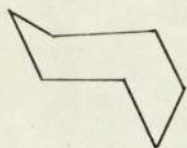
(c)

In the chair form (a) not only is there no angle strain but there is no torsional strain either. The chair form can be converted to that of the boat, by the flipping up of one carbon atom or vice versa. During the transformation, some angular distortion is required because several bonds have to be rotated at the same time. In the boat form (b), there is no angle strain but there is considerable torsional strain, together with Van der Waal's strain due to crowding between the hydrogens. As a result of these unfavourable interactions the boat is considerably less stable than the chair. Considering the model of the boat form, it becomes clear that the boat form represents only one of the flexible conformations. Besides this form, other flexible forms, termed twist forms (c) are possible, in which both torsional strain and Van der Waal's strain are reduced.

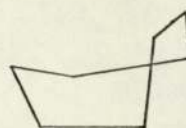
In the chair shaped cyclohexane ring there are two possible kinds of bonds, namely six axial bonds which lie parallel to the trigonal axis and six equatorial bonds which form an angle of  $109^{\circ}28'$  with the trigonal axis. Cyclohexane itself, in which only hydrogens are attached to the carbon atoms is not only free of angle strain and torsional strain but free of Van der Waal's strain as well. However when a hydrogen is replaced by a larger atom or group, crowding occurs and it is found that a given atom or group has more room in an equatorial position than in an axial position. Therefore the most stable chair conformations are those in which the largest groups are in equatorial positions. The situation becomes a little more complicated, with the introduction of two substituents into the cyclohexane ring. The introduction of a second substituent makes possible two diastereoisomeric forms, a cis and a trans compound. The second substituent can be introduced into the 2,3 or 4 position in relation to the first substituent.

Seven membered rings are subject to torsional strain and are therefore less stable than the six membered rings. Less information has appeared concerning the conformations of cycloheptane in comparison to the detailed studies of cyclohexane. Chair and boat forms of cycloheptane can be constructed and like the chair and boat forms of cyclohexane, they can be transformed into each other by conversion. The problem of the conformations of the cycloheptane ring has been investigated by several workers<sup>7</sup>. Hendrickson<sup>8</sup> has calculated with the aid of a computer, the energies of the possible conformations of cycloheptane depending on the various geometric parameters. This has presented a detailed representation of the conformations of cycloheptane.

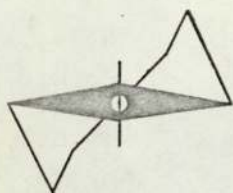
The two types of conformations are termed the chair (d) and boat form (e) as with cyclohexane. In contrast to cyclohexane, both forms of cycloheptane are flexible and capable of pseudorotation.



(d)



(e)



(f)

However in the chair (d) as well as in the boat (e) conformation, an interaction which cannot be neglected appears between the hydrogens on carbon atoms three and six. To avoid this the chair and boat forms go into the conformation where the interaction energy is at a minimum, thus assuming the twist-chair conformation (f) and a corresponding twist-boat conformation. In this way the 3,6-H-H interactions are not entirely avoided but are reduced, so that an additional valence angle distortion appears.

In comparison to the information available about six and seven membered carbon rings, few stereochemical studies have been carried out on the ring compounds of silicon and tin. The introduction of a silicon atom into a six membered ring does not appear to alter the conformation. Since the covalent radius of silicon is more than 50% larger than that of carbon (C 7.7nm, Si 11.7 nm), it is not immediately apparent that the six membered silicon ring will be able to assume a strainless staggered conformation like that of cyclohexane. However, it has been shown<sup>1</sup> by geometrical calculations that it is in fact correct. The structure and steric energies of silacyclohexane and the various methylsilacyclohexanes have been calculated by force field methods<sup>9</sup>. Silacyclohexane

is predicted to exist in a modified chain conformation in which the ring is more flattened than cyclohexane in the region of silicon and is more puckered in the region of C<sub>4</sub>. The seven membered silicon ring, like cycloheptane, is strained. Since the tetrahedral bond angles at silicon should be more deformable than those at carbon, some relief of internal strain may take place, when the carbon atom is replaced by silicon in the seven membered ring.

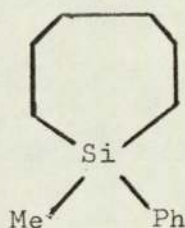
One of the few studies<sup>10</sup>, concerned with the stereochemistry of cyclic organotin compounds indicates that the six membered ring shows considerable strain. This is in contrast to the six membered rings of carbon and silicon and is due to the large covalent radius of the tin atom (Sn 14.0 nm), which is practically almost double that of carbon. The seven membered ring by comparison shows no strain:

### I. 3. Cyclic organosilicon compounds

The first cyclic organosilicon compounds to be prepared were cyclopentamethylchlorosilane and its dimethyl and diethyl derivatives which were prepared by Bygden<sup>11,12</sup> in 1915. The method employed for introducing silicon into the six membered ring, was by treating silicon tetrachloride with the Grignard reagent prepared from 1,5-dibromopentane. An improved modification of Bygden's work has been used by latter workers<sup>13</sup>, who successfully prepared five, six and seven membered rings containing silicon. It was found that the yield was highest for the six membered ring, somewhat lower for the five membered and very much lower for the seven membered ring. This result is in agreement with many other well known reactions involving ring closure.

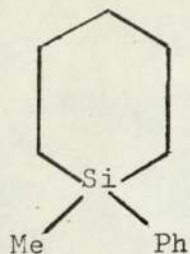
The following three cyclic organosilicon compounds were prepared :-

1.



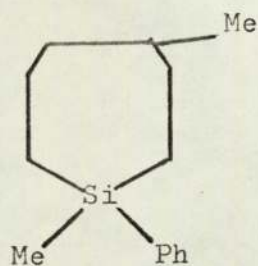
1-methyl-1-phenylsilacycloheptane

2.



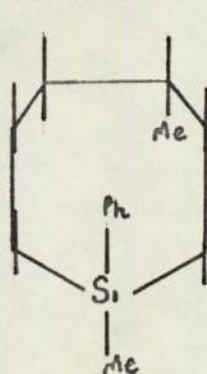
1-methyl-1-phenylsilacyclohexane

3.

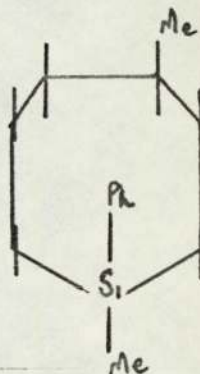


1,4-dimethyl-1-phenylsilacycloheptane

The interest in the third compound was due to the possibility that it could exist in geometrically isomeric forms.



cis



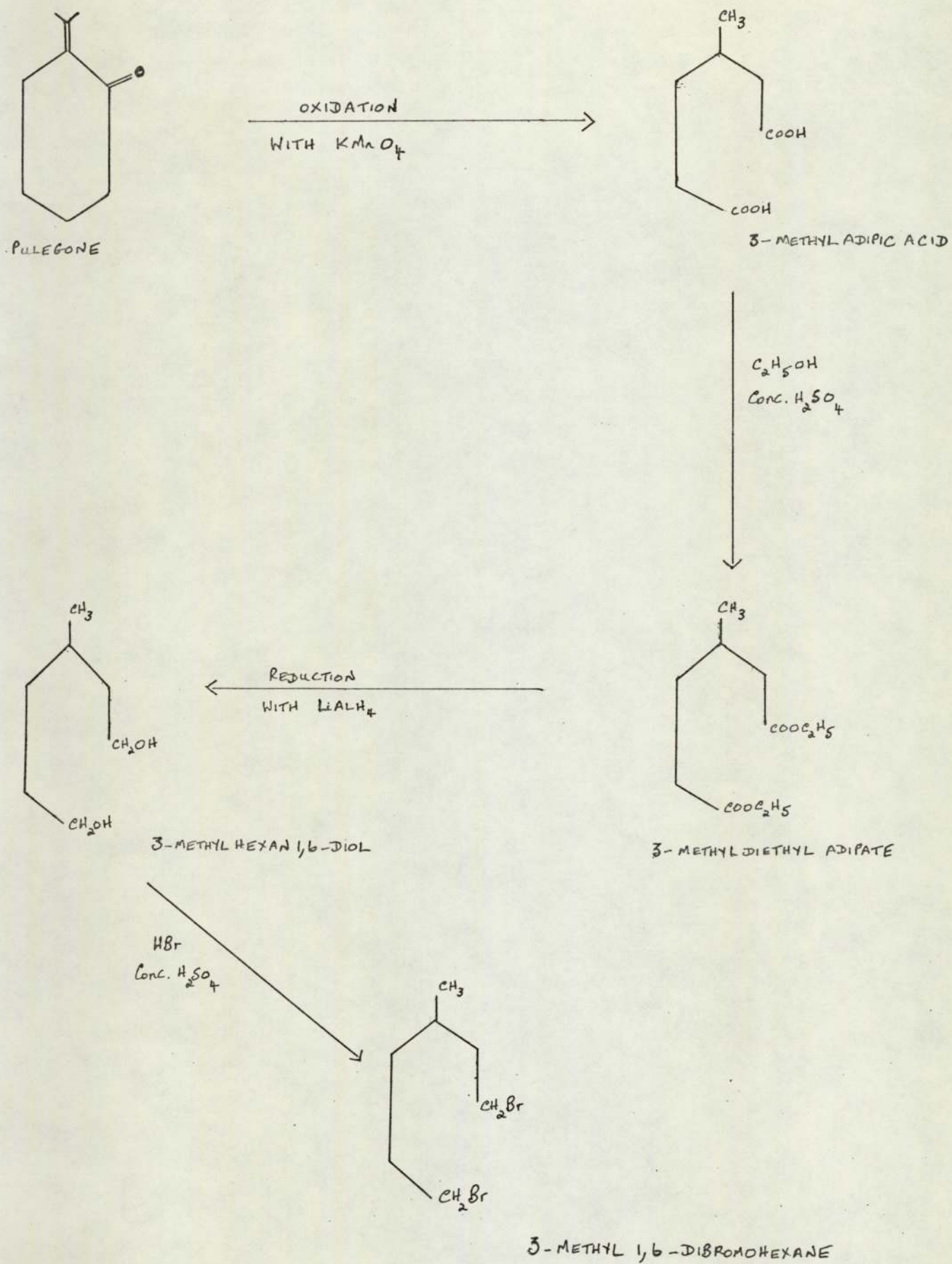
trans

The three compounds were all analysed by nuclear magnetic resonance spectroscopy at progressively lower temperatures.

All three compounds were prepared by the reaction between methylphenyldichlorosilane and the Grignard reagent prepared from the appropriate dihalide. For 1,4-dimethyl-1-phenylsilacycloheptane, the dihalide used was 3-methyl 1,6-dibromohexane which was obtained from a series of reactions, shown in Fig.1, with the terpene pulegone as the starting material. Oxidation of pulegone gave 3-methyladipic acid, which on esterification followed by reduction, gave the required dibromide



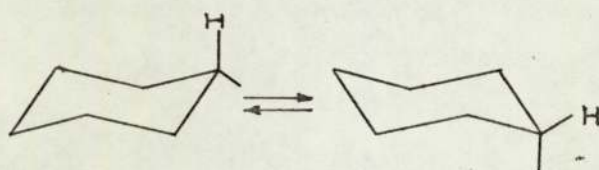
Fig.1. Reaction scheme for the preparation of 3-methyl 1,6-dibromohexane



#### I.4. Nuclear magnetic resonance spectroscopy studies of cyclic organo-silicon compounds

Rotation about single bonds can change the environment of a given proton and hence can affect both its chemical shift and its coupling with other protons.

The transformation of one chair form of cyclohexane into another involves rotation about single bonds.



Although there are two kinds of protons, six equatorial protons and six axial protons, there is a single nuclear magnetic resonance signal for all twelve since their average environments are identical. The speed of rotation about the single bonds is so fast that the nuclear magnetic resonance spectrometer only sees protons in their average environment. However if the temperature is lowered, resulting in a slowing down of the rotations about the single bonds, then a nuclear magnetic resonance spectrum would be obtained that reflects the 'instantaneous environments' of protons in each conformation. This is found to be the case for cyclohexane for as it is cooled down the sharp peak observed at room temperature is seen to broaden and then to split into two peaks at about  $-70^{\circ}\text{C}$ .

Variable temperature proton magnetic resonance spectroscopy and total proton magnetic resonance line shape analysis have been used to determine the activation parameters for chair-chair interconversion in cyclopentamethylenedimethylsilane<sup>14</sup>.

A low temperature study was carried out with the six and seven membered cyclic organosilicon compounds. The positions of the methyl

and phenyl groups were examined to see if there was any change in their position in the spectrum, indicating a change in their environment.

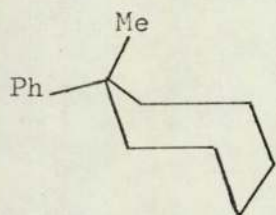
## Results

### Table 1.

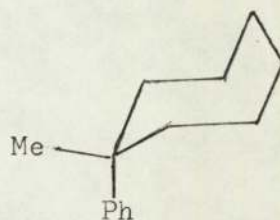
The table shows the results obtained for 1-methyl-1-phenylsilacycloheptane and 1-methyl-1-phenylsilacyclohexane. The results obtained on analysing 1,4-dimethyl-1-phenylsilacycloheptane showed that the compound had not been successfully prepared

## Discussion

The results show that there is some variation at  $-70^{\circ}\text{C}$  in the position of the phenyl group of the seven membered ring but not with the six membered. This would be expected, considering that the six membered ring, being free of strain is more stable than that of the seven. It is assumed that the variation in the position of the phenyl group is due to the fact that it has changed from an equatorial position (1) to that of an axial position (2)



(1)

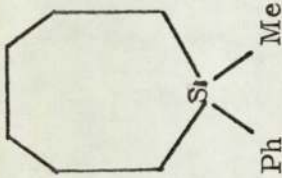
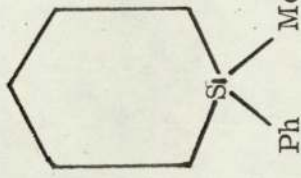


(2)

At  $-90^{\circ}\text{C}$  the situation appears to be similar to the earlier temperatures, indicating that the conformation formed at  $-70^{\circ}\text{C}$  is unstable, and quickly reverts back to the earlier conformation (1), with the phenyl group in the equatorial position.

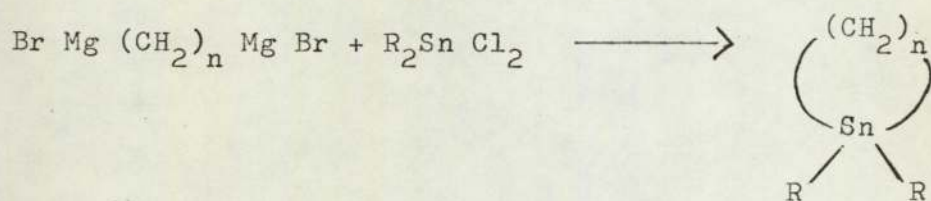
Table I

Nuclear magnetic resonance spectroscopy results for six and seven membered cyclic organosilicon Compounds.

Compound	Temp. °C.	Reference	Methyl group $\tau$	Phenyl group $\tau$
	33.4	Tetramethylsilane	9.80	2.40 - 3.00
	-30	"	9.80	2.45 - 3.00
	-50	"	9.79	2.40 - 2.95
	-70	"	9.81	2.60 - 3.15
	-90	"	9.79	2.45 - 3.00
1 - methyl - 1 - phenyl silacycloheptane	33.4	"	9.80	2.40 - 2.90
	-70	"	9.80	2.40 - 2.95
	-90	"	9.80	2.45 - 2.95
				
1 - methyl - 1 - phenyl silacyclohexane				

## I. 5. Cyclic organotin compounds

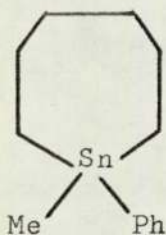
In 1917 the first ring compounds containing tin were reported by Gruttner and Krause<sup>15</sup>, but the field lay largely neglected until recent years. The ring compounds initially synthesised were the 1,1-diethyl and 1,1-dimethyl derivatives of stannacyclohexane, which were obtained in the same way as the cyclic organosilicon compounds, by the reaction between a Grignard reagent and a suitable tin dihalide. The synthesis employing Grignard reagents has been found to be suitable for the preparation of other ring compounds of tin, namely the stannacyclopentanes and stannacycloheptanes<sup>10</sup>.



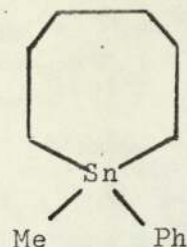
$$n = 4, 5, 6$$

$$\text{R} = \text{Me, Et, Bu, neoC}_5\text{H}_{11}, \text{Ph}$$

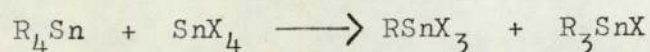
In this work the first ring compound to be investigated was that of a seven membered ring with a methyl and a phenyl group attached to tin: -



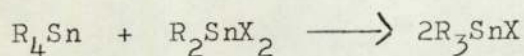
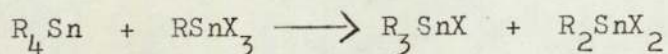
The preparation like that used for the silicon compounds involved the reaction between 1,6-dibromohexane and a suitable tin dihalide. The tin dihalide was methylphenyltin dibromide, which was obtained in a series of reactions from tetraphenyltin.



The tetraphenyltin, having been prepared from phenyl magnesium bromide and tin tetrachloride, was reacted with further tin tetrachloride to give triphenyltin chloride. Redistributions reactions of tin have been reviewed<sup>16</sup>. At temperatures 0 - 50°C there is one dominant spontaneous reaction



This reaction is complete over a wide range of concentrations and molar ratios before other reactions are observed. Subsequent reactions occur at high temperatures and depend upon the initial molar ratio of the reactants. When  $\text{R}_4\text{Sn} : \text{SnX}_4 \gg 1$  the subsequent reactions are



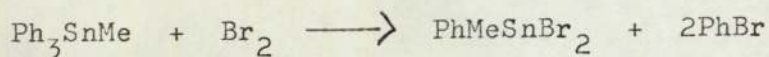
The overall reaction is  $3\text{R}_4\text{Sn} + \text{SnX}_4 \longrightarrow 4\text{R}_3\text{SnX}$

The triphenyltin chloride prepared was then reacted with methylmagnesium iodide to give methyltriphenyltin. The next stage involved the cleavage of tin-carbon bonds by halogen. The halogen used was bromine, which was dissolved in carbon tetrachloride and added dropwise at 0°C to avoid uncontrolled cleavage reactions. When unsymmetrical organotin compounds are treated with one molecular proportion of halogen it is necessary to be able to predict which group will be preferentially removed. From a number of studies of the cleavage reactions of unsymmetrical compounds such as  $\text{R}_3\text{SnR}'$  sequences have been obtained, showing the relative ease with which groups are cleaved from tin, for example<sup>17</sup>:

o-tolyl > p-tolyl > phenyl > benzyl > vinyl > methyl > ethyl >  
propyl > isobutyl > butyl > isoamyl > amyl > hexyl > heptyl > octyl

However these sequences have been compiled from reactions using differing cleavage reagents, under a variety of conditions, and careful examination of the literature reveals a number of contradictions<sup>18</sup>. This situation has been clarified in a series of papers by Gielen and Nasielski<sup>19,20</sup>, who have studied the kinetics of bromo- and iodo-demetalation of a number of tetraalkyltin compounds in a range of solvents. They found that in polar solvents, e.g. methanol, acetic acid, there is a high degree of selectivity in halodemetalation whereas in solvents such as chlorobenzene, which are of low polarity, the degree of selectivity is low. A claim<sup>21</sup>, that bromine in carbon tetrachloride reacts selectively with either tributylethyltin or tributylpropyltin to produce the alkyl bromide with the lowest molecular weight, was not confirmed by other workers<sup>22</sup>.

In this work cleavage of the tin-phenyl bond in methyltriphenyltin was found to take place fairly rapidly on addition of bromine in carbon tetrachloride at 0°C. The reaction was followed, by monitoring the amount of bromobenzene produced using gas-liquid chromatography and it was found to be complete after thirty minutes.



#### I. 6. Nuclear magnetic resonance spectroscopy studies of cyclic organotin compounds

The seven membered cyclic organotin compound was analysed in a similar way to that of the corresponding silicon compound. However, the nuclear magnetic resonance spectroscopy results showed that the compound had not been successfully prepared.

Due to the disappointing results obtained with the seven membered cyclic organotin compound no further ring compounds of tin were attempted. Having obtained some successful results with the silicon compounds, it was decided to look at further cyclic organosilicon compounds, such as the siloxanes, in which the silicon is directly attached to another heteroatom.



## CHAPTER TWO

The formation of cyclic organosiloxanes by the hydrolysis of diorganohalosilanes.

### II.1. Introduction

Simple cyclic organosiloxanes owe their commercial importance to the fact that they form an intermediate stage in the production of silicones. Silicones which are linear or cross-linked polyorganosiloxanes possess many specific properties, which have guaranteed them a great variety of applications. In the electrical industry, silicones are used as insulators, this use being based on their good dielectric properties and heat and cold resistance. This good heat resistance, together with a resistance to weathering recommends their use in the paint industry and their hydrophobic nature is utilised by manufacturers of car and furniture polishes. Silicone oils are used as hydraulic fluids, owing to their excellent viscosity-temperature relationship, stability to oxidation, non-corrosive properties and low volatility. The low physiological harmlessness of silicones has led to their extensive application in pharmacy, medicine and cosmetics.

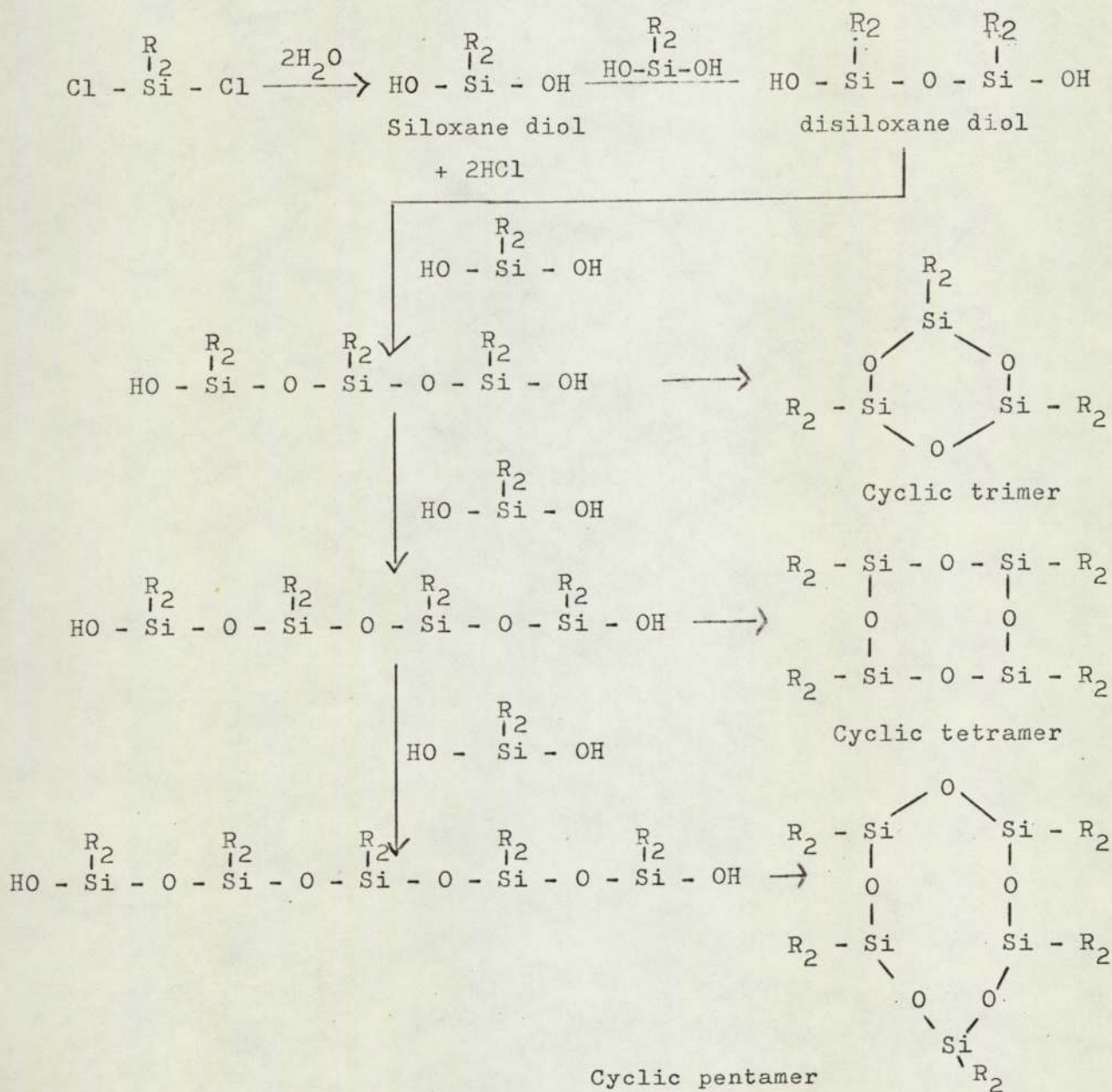
The preparation of organosiloxanes involves the hydrolysis of organohalosilanes, usually the diorganodichlorosilane being used. The products of hydrolysis are usually a mixture of linear and cyclic oligomeric organosiloxanes. The final stage of silicone production involves the formation of high polymers from the hydrolysis products, by equilibration-polymerisation processes followed in certain cases by cross-linking.

The hydrolysis of diorganodichlorosilanes has elicited much interest and has been extensively investigated. Silicones are based mainly on polydimethylsiloxanes and therefore the hydrolysis of dimethyl-

dichlorosilane has received much attention. Some work is reported on the addition of glycerol to the hydrolysis of dimethyldichlorosilane. The hydrolysis of methylphenyldichlorosilane has also been fully investigated, the hydrolysis being of particular interest because of the possibilities of stereoisomerism in the products. Relatively little has been reported on the hydrolysis of ethylmethyldichlorosilane<sup>23,24</sup> and the main emphasis of this work is on the hydrolysis of this compound.

## II.2. The hydrolysis of diorganodichlorosilanes

The hydrolysis of diorganodichlorosilanes gives a mixture of cyclic and linear siloxanes. The hydrolysis follows the general scheme shown below : -



The mechanism of siloxane formation during the hydrolysis of the dichlorosilane can be considered as two steps : -

(a) formation of the silanediol

(b) condensation of this to the siloxane.

It appears that the condensation of the silanediol rather than hydrolysis of the halide is the rate determining step<sup>25,26</sup>.

Although both cyclic and linear species are usually formed in the same reaction, the proportion of each may depend on the reaction conditions employed. Certain factors which can affect the hydrolysis are : - temperature, time for reaction, solvent system, pH of the aqueous medium, using a deficiency of water and the use of alternative sources of water, such as salt hydrates.

The hydrolysis of dimethyldichlorosilane with excess water gives a mixture of polydimethylcyclosiloxanes and linear polydimethylsiloxane- $\alpha,\omega$  - diols. Depending on the method of working the proportion of polydimethylcyclosiloxanes is between 20% and 50%<sup>27</sup>. Methylphenyldichlorosilane has also be found to give a mixture of cyclic and linear species depending on the conditions employed<sup>28</sup>. This hydrolysis is of particular interest, because the products can exist in stereoisomeric forms. The two isomeric cyclic trimers have found to be readily separated<sup>29,30</sup>. The four tetramers have also been separated, and configurations assigned<sup>29,30,31</sup>.

### II.3. The hydrolysis of ethylmethyldichlorosilane

By comparison with the dimethyl and methylphenyl systems, the hydrolysis of ethylmethyldichlorosilane has not been fully investigated. Like the methylphenyl system, this is of particular interest since the products can exist in stereoisomeric forms, due to the presence of two different groups on each silicon atom.

Experimentally an excess of water was added to a stirred mixture of the chlorosilane in solvent. The effect of varying the following factors was investigated (i) temperature (ii) quantity of solvent (iii) order of addition of reactants.

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-liquid chromatography. It was assumed that peak areas are proportional to the masses of components present and analyses were made on this basis by comparison of peak areas.

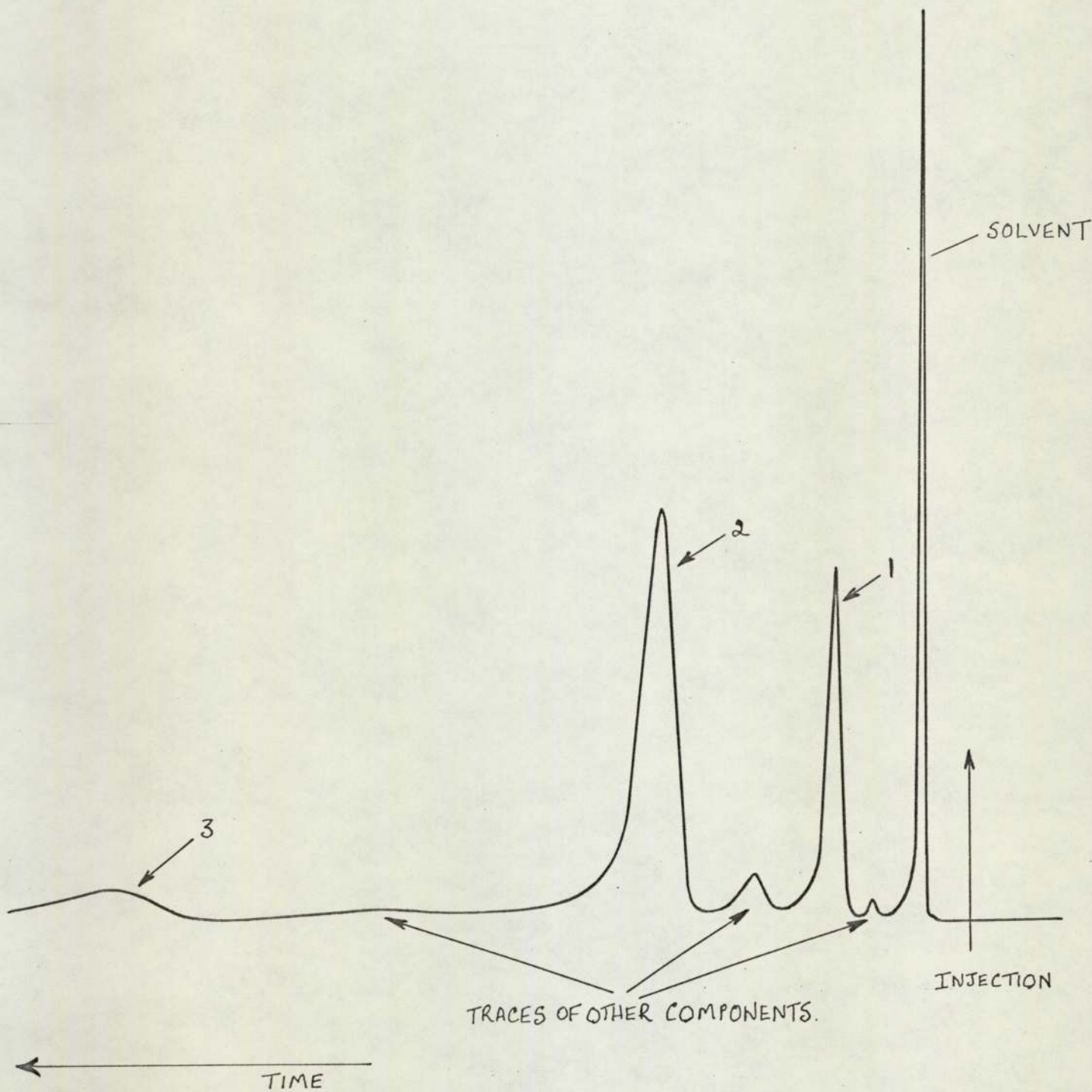
## Results

### (a) Gas-Liquid chromatography results.

A typical gas chromatogram for the cyclic siloxanes is shown in Fig.2. The chromatogram shows the presence of three major components denoted by peaks 1, 2 and 3. There are also traces of three other components. The three major components were suspected as being the cyclic trimer, tetramer and pentamer. Evidence as to the exact identity of the three main components was obtained by molecular weight determinations.

Initially a partial separation of the components was obtained using column chromatography. An attempt was then made to separate the components using a preparative gas-liquid chromatograph. Various fractions were collected and the molecular weight of each of these was determined using mass spectrometry. However from the results obtained, no positive identification could be obtained for the three major components. A second attempt using a combined gas-liquid chromatograph and mass spectrometer proved more successful.

Fig.2. Chromatogram obtained for the hydrolysis product of ethylmethyldichlorosilane.



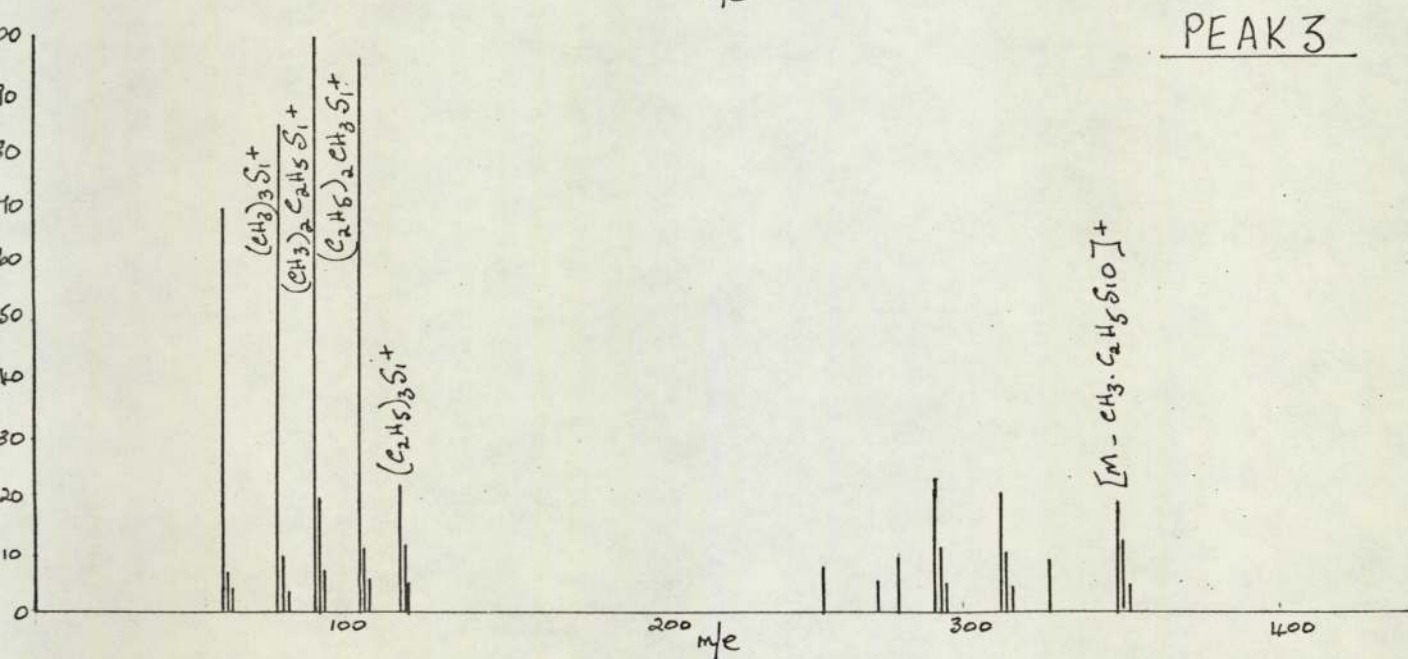
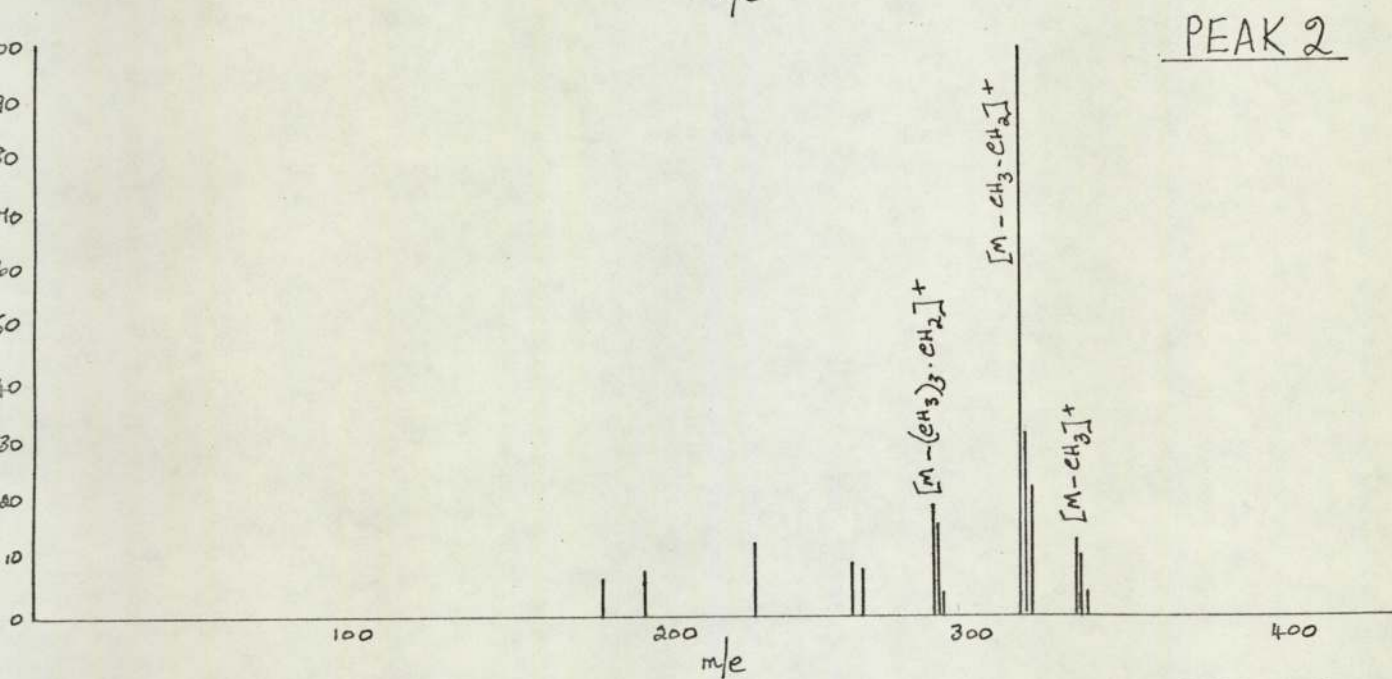
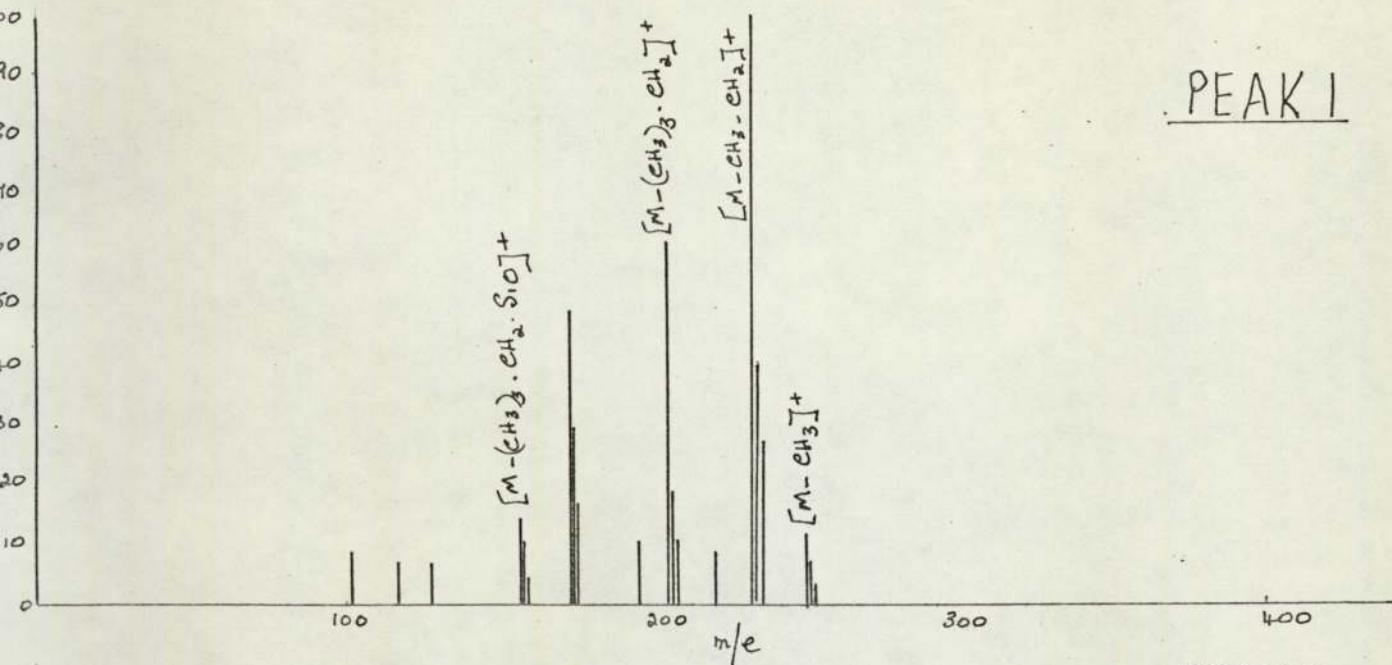
(b) Mass Spectrometry results.

Although several mass spectroscopic studies on the organic derivatives of silicon have been carried out<sup>32</sup>, these have included very little about siloxanes. The only siloxanes which have been previously investigated are the methylsiloxanes<sup>33,34,35</sup>. In these investigations both linear and cyclic siloxanes were studied and were found to show the following characteristic features on dissociation in the mass spectrometer :-

1. The dissociation of siloxanes like that of other organosilicon compounds goes extremely selectively, the dissociation being even more selective for cyclic siloxanes than for linear.
2. The intensities of the peaks of the molecular ions are extremely small.
3. The (Parent - CH<sub>3</sub>)<sup>+</sup> peak is among the most intense and for cyclic siloxanes this ion is more stable to breakdown than in the case of linear siloxanes.
4. Although a certain part of the fragment ions is formed by removal of hydrocarbon groups from the periphery of the molecule, most of the disintegrations are associated with the breaking of Si - O bonds.
5. There are numerous and often extremely intense metastable ions,
6. Multicharged ions are found to be present.
7. In common with the mass spectra of other organosilicon compounds, hydrogen rearrangements are found to take place.

The mass spectra obtained for peaks 1, 2 and 3 (Fig.2) were examined and found to contain some of the characteristic features mentioned. Diagrams of the mass spectra obtained for peaks 1, 2 and 3 are shown in Fig.3.

Fig.3. Mass spectra obtained for peaks 1,2 and 3.



Peak 1. Intense peaks occur at m/e values of 249, 235 and 205. The peak at m/e 249 is probably due to the loss of a methyl group from the parent ion, this being a common feature in the breakdown of siloxanes. The parent ion therefore has an m/e value of 264 which corresponds to that of the cyclotrisiloxane  $(\text{CH}_3\text{C}_2\text{H}_5)_3\text{Si}_3\text{O}_3$ . Subsequent loss of a  $\text{CH}_2$  group will give the peak at m/e 235, followed by the loss of two methyl groups presumably as an ethane molecule, to give the peak at m/e 205. The next stage would involve the loss of the SiO group and there is a peak at m/e 161 which is probably due to this.

Peak 2. Intense peaks occur at m/e values of 337, 323 and 293. The peak at m/e 337 would be the parent ion, minus a methyl group, thus giving the m/e value of the parent at 352 which is the weight of the cyclotetrasiloxane  $(\text{CH}_3\text{C}_2\text{H}_5)_4\text{Si}_4\text{O}_4$ . Presuming a similar breakdown pattern to that suggested for peak 1, the m/e value at 323 would be loss of a  $\text{CH}_2$  followed by loss of an ethane molecule to give the peak at m/e 293.

Peak 3. Intense peaks occur at m/e values of 352, 308, 294 and then at the lower values of 115, 101, 87 and 73. Unlike the previous two peaks the parent minus a methyl group ion does/<sup>not</sup> seem to be present, as the first most intense peak is at m/e 352. Assuming that the parent ion is that of the cyclopentasiloxane m/e 440, the observed peak at m/e 352 would correspond to the loss of a  $\text{CH}_3\text{C}_2\text{H}_5\text{SiO}$  group from the parent. Subsequent loss of a  $\text{C}_3\text{H}_8$  group, which in line with the two previous spectra would be a  $\text{CH}_2$  group followed by loss of two methyls, would account for the peak at m/e 308. The next peak at m/e 294 would then be due to the loss of a further  $\text{CH}_2$  group. At the lower end of the spectrum the peaks are very intense due to the following



fragment ions formed by hydrogen rearrangements :-



In all of the spectra no peaks were observed corresponding to the presence of multicharged ions. Having assigned plausible structures to the peaks, it was concluded that enough evidence had been obtained for the identification of the three components obtained in the chromatogram (Fig.2). The structures of the three components are shown in Fig.4.

(c) Experimental results.

Variation of concentration and Temperature - Table II

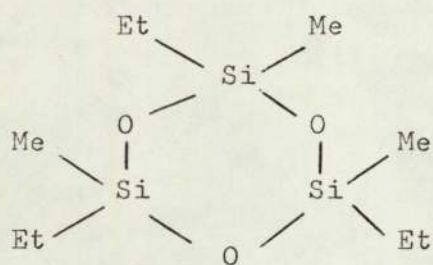
The hydrolysis and the analysis of the hydrolysis product was carried out in duplicate and therefore the results presented in the table are averages of these duplicate experiments.

(1) Addition of water to the chlorosilane - Varying the concentration of the chlorosilane has little effect on the yield of cyclic siloxanes. There is a slight decrease only on reduction of the temperature. The proportion of trimer (cyclotrisiloxane) relative to tetramer (cyclotetrasiloxane) is reduced as the concentration increases. As the temperature and concentration are raised the proportion of pentamer (cyclopentasiloxane) relative to tetramer increases.

(2) Addition of chlorosilane to water - The yield of cyclic siloxanes, although slightly lower, is unaffected by varying the concentration. The proportion of trimer relative to tetramer is greatly increased although reduction of temperature brings about a slight decrease. By comparison the proportion of pentamer relative to tetramer is greatly increased.

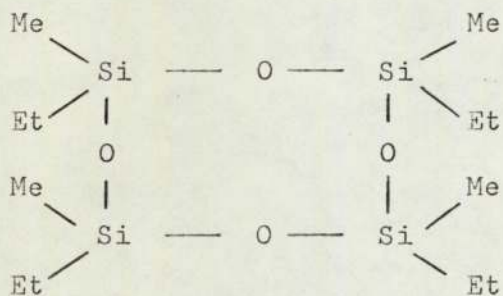
Fig.4. Structures of the three major components obtained from the hydrolysis of ethylmethyldichlorosilane

Peak 1.



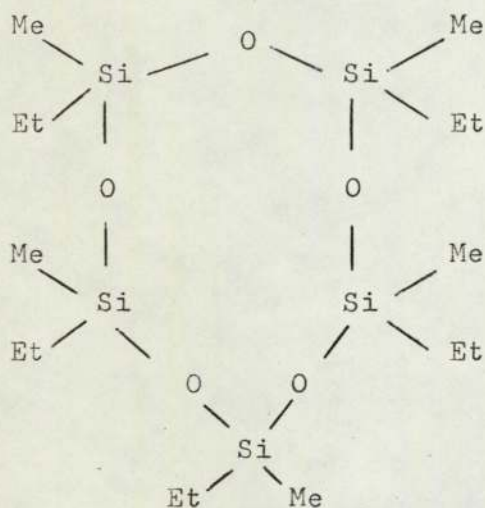
2,4,6-triethyl-2,4,6-trimethylcyclotrisiloxane

Peak 2.



2,4,6,8-tetraethyl-2,4,6,8-tetramethylcyclotetrasiloxane.

Peak 3.



2,4,6,8,10-pentaethyl-2,4,6,8,10-pentamethylcyclopentasiloxane

Table II

The hydrolysis of ethylmethyldichlorosilane with an excess of water - variation of concentration and temperature

Time for addition of water :  $1\frac{1}{4}$  hours  
Solvent : diethyl ether.

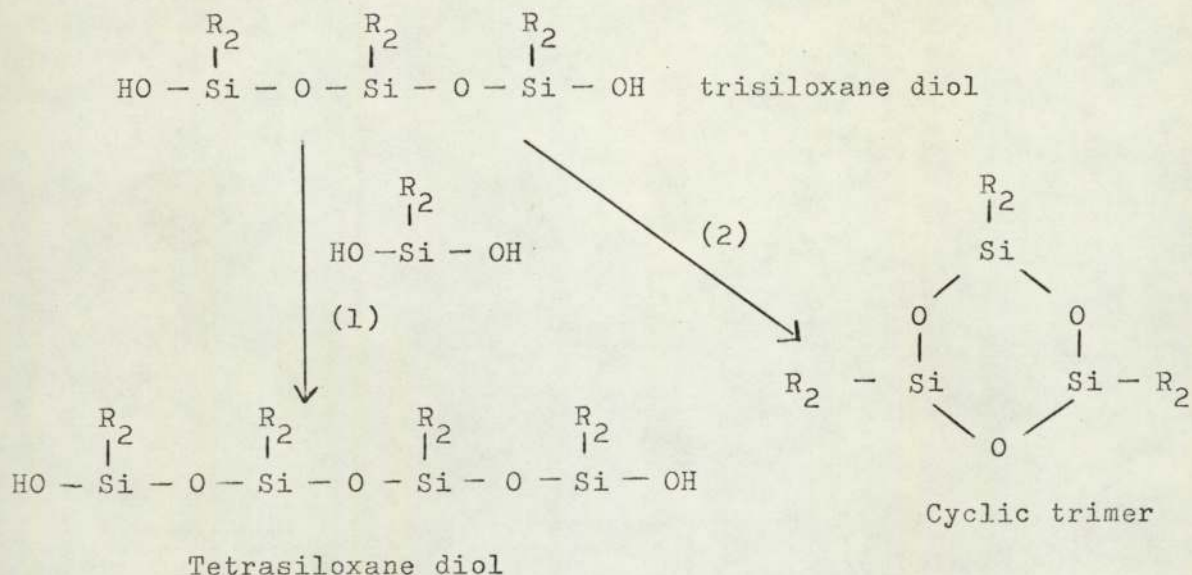
Mole ratio of chlorosilane/water : 1/16

Chlorosilane/Solvent (by volume)	Temperature °C	% of cyclic Siloxanes in product	% Trimer	% Tetramer	% Pentamer
(1) Addition of water to chlorosilane					
1/5	22	71	32	51	17
1/5	0	69	60	38	2
1/1	22	70	27	55	18
1/1	0	67	31	53	16
(2) Addition of chlorosilane to water					
1/5	22	65	56	38	6
1/5	0	65	67	31	2
1/1	22	67	52	42	6
1/1	0	65	58	39	3

Note : The three minor components shown in Fig. 2 total 2% of the hydrolysis product.

## Discussion

During the hydrolysis of organohalosilanes the growing chain can undergo two competitive reactions as shown below:-



Reaction (1) addition of another unit to yield a chain of increased length

(2) cyclisation

There will be a much greater probability of cyclisation taking place if the skeletal bond angles are suitable for ring closure and if the bonds are free to rotate so that the end groups can combine. Several mathematical studies regarding the polydimethylsiloxanes have been carried out regarding the probability of the end groups combining and some measure of agreement with experimental results has been obtained<sup>36</sup>. Concentration is an important factor in deciding whether reaction (1) or (2) will take place. Dilution of the siloxane results in a tendency for intramolecular condensation to predominate over intermolecular condensation, thus yielding cyclic compounds preferentially.

The bond angles, bond distances and ring conformations of the polydimethylsiloxanes have been investigated<sup>37,38</sup>. The O - Si - O angle shows little variation from the tetrahedral value of  $109^{\circ}28'$  and various values in the region  $120^{\circ} - 145^{\circ}$  have been quoted for the

Si - O - Si. The six membered trimer ring is slightly strained and this is confirmed by thermochemical measurements which show that hexamethylcyclotrisiloxane has a strain energy of up to 9 kcal/mole<sup>39</sup>. By comparison, eight membered tetramer and ten membered pentamer rings are unstrained. The structure of the six membered trimer ring has been established as being planar, whereas those of the eight, ten and larger membered rings are puckered.

The presence of ring strain in the trimer is probably one of the factors accounting for its low proportion in the hydrolysis product of organohalosilanes. For dimethyldichlorosilane, the proportion of trimer in the hydrolysis product is found to be about 0.5% compared with around 40% for the tetramer<sup>27</sup>. Therefore according to the reaction scheme (p.16) at the trisiloxanediol stage, chain lengthening rather than cyclisation will be the preferred process. However at the tetrasiloxanediol stage, cyclisation to the unstrained cyclotetrasiloxane will take place readily. The cyclic pentamer and higher cyclics are usually formed in smaller amounts. The proportion of cyclic trimer obtained is further reduced by the fact that it reacts with the hydrochloric acid present to give cyclic tetramer.

The hydrolysis of methylphenyldichlorosilane also gives a higher proportion of tetramer than trimer but in this case the amount of trimer is greater than in the case of dimethyldichlorosilane. The methylphenyl trimer is therefore more resistant to attack by the hydrochloric acid than that of the dimethyl. This is probably due to the presence of electron withdrawing phenyl groups, which will hinder the protonation of the oxygen atom in the initial stage of the acid cleavage of siloxanes.

By contrast the proportion of trimer is greater than that of the tetramer in the hydrolysis product of diethyldichlorosilane as it is

reported<sup>40</sup> that hydrolysis in ether produces 41% of the trimer and 31% of the tetramer.

From the hydrolysis results obtained for ethylmethyldichlorosilane it appears that the tetramer is the major product. Like the hydrolysis of both dimethyldichlorosilane and methylphenyldichlorosilane the proportion of pentamer is low. The presence of electron donating ethyl groups would facilitate protonation of the oxygen atom and therefore the trimer would react readily with the hydrochloric acid present. However since a low proportion of trimer is not found to be the case other factors, such as the size of the groups attached to silicon, are important. It is found that the reactivity of the Si - O - Si bond in acid catalysed polymerisation is strongly dependent on the nature of the organic groups attached to silicon. The reactivity decreases rapidly as the size of the aliphatic radical is increased or if aromatic substituents are present. Ethyl groups like phenyl groups are found to be involved in several types of steric interaction<sup>41</sup>. However this type of repulsion suggested would be more significant in the open chain conformation than in the cyclic siloxane.

In the hydrolysis of ethylmethyldichlorosilane, the chlorosilane will have been completely hydrolysed after the addition of only a small proportion of the water. The hydrolysis mixture will consist of a homogeneous solution of unreacted chlorosilane,  $\alpha$ - $\omega$ -chlorosiloxanes and hydrogen chloride in the solvent. At a certain point the solution becomes cloudy and heterogeneous. The initially formed hydrolysis products are being stirred with hydrochloric acid resulting in the diols undergoing condensation to cyclic or longer chain linear compounds. The results (Table II) show that increasing the concentration decreases the proportion of trimer. This is

because the increasing concentration produces a high concentration of hydrochloric acid with which the trimer will react to give the tetramer. In the two more concentrated solutions the yield of pentamer is increased. This is due to the fact that the increasing concentration of siloxanediols favours condensation to longer chains followed by cyclisation, than earlier cyclisation to smaller rings. Decreasing the temperature also has the effect of increasing the proportion of pentamer as the rate of siloxanediol condensation and cyclisation increases with increasing temperature. These results obtained for ethylmethyldichlorosilane are in agreement with those obtained for the hydrolysis of dimethyldichlorosilane and methylphenyldichlorosilane which have been fully investigated.

Varying the order of addition of reagents in the hydrolysis of ethylmethyldichlorosilane, although slightly decreasing the proportion of cyclic siloxanes, is found unexpectedly to increase the proportion of trimer (Table II). It is probable that the concentration of hydrochloric acid resulting during this addition, is lower than in the case where the water is added to the chlorosilane, resulting in the increased proportion of the trimer. The corresponding decrease in the proportion of pentamer supports the view that the siloxanediol formed, favours early cyclisation to the smaller ring products such as the trimer.

As previously mentioned, the hydrolysis of ethylmethyldichlorosilane was chosen for investigation because of the possibility of the products existing in stereoisomeric forms. A considerable amount of time was spent analysing the hydrolysis products, but no separation of the isomers was achieved. There is no chemical reason why these do not exist, so it is concluded that the exact conditions for their separation were not found.

#### II.4. The addition of glycerol to the hydrolysis of ethylmethyl-dichlorosilane

A further series of hydrolysis experiments were carried out, this time adding the trihydric alcohol, glycerol to the reaction mixture. The purpose of this work was to find if this addition altered the amount of cyclic material and if there was any change in the proportions of the individual cyclic siloxanes.

#### Results - Table III.

Increasing the proportion of glycerol appears to result in a gradual decrease in the percentage of the cyclic siloxanes. The proportion of trimer relative to tetramer increases as the amount of glycerol added increases. The increase in the proportion of trimer results in a corresponding decrease in the proportion of pentamer.

#### Discussion

The initial product formed in the hydrolysis of a diorganohalosilane is the silanediol (reaction scheme p. 16) which then rapidly condenses to give the siloxane. The tendency to condensation increases with the number of hydroxyl groups bonded to the silicon atom and decreases with the number, size and bulkiness of the organic groups. Factors which affect the condensation are the concentration, the electronegativity of the substituents and the pH value of the system.

In order to obtain a silanediol which is sensitive to condensation certain modifications have to be implemented in the hydrolysis process. One of these is the use of alcohol alone or in combination with a non-reactive solvent and it has been reported<sup>42</sup> that good yields of silanediols have been obtained using this method.

Having increased the yield of silanediol by preventing its



Table III

The addition of glycerol to the hydrolysis of ethylmethyldichlorosilane

Time for addition of water :  $1\frac{1}{4}$  hours

Solvent : diethyl ether.

Temperature : 22°C.

Mole ratio of chlorosilane/water : 1/16

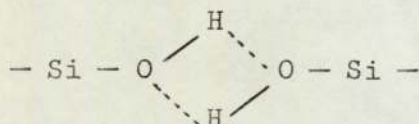
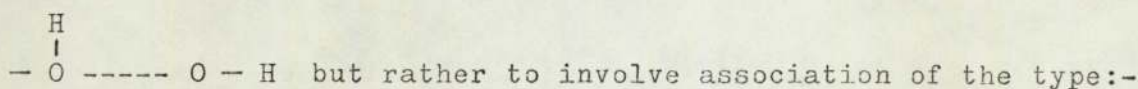
Volume ratio of chlorosilane/ether : 1/5

Moles of glycerol added	% of cyclic Siloxanes in product	% Trimer	% Tetramer	% Pentamer
0	71	32	51	17
0.025	67	50	40	10
0.05	60	65	30	5
0.1	56	77	22	1

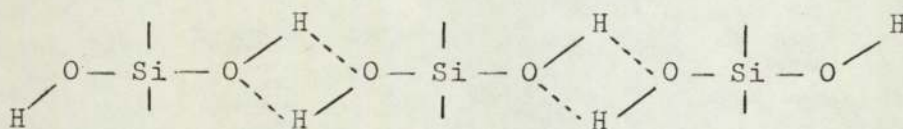
Note : The three minor components shown in Fig. 2 total 2% of the hydrolysis product.

condensation, the proportion of cyclic material will therefore be reduced. This is observed in the hydrolysis of ethylmethyldichlorosilane when glycerol is added to the reaction mixture. Of the cyclic materials obtained, it is the cyclic trimer which increases in concentration at the expense of the cyclic tetramer and pentamer. Therefore the glycerol stabilises the silanediol initially formed thus reducing its tendency to undergo condensation to the siloxane.

Examination of the crystal structures of simple silanediols<sup>43</sup> has shown the presence of strong intermolecular hydrogen bonding. The hydrogen bonding appears not to be of the usual linear type :-

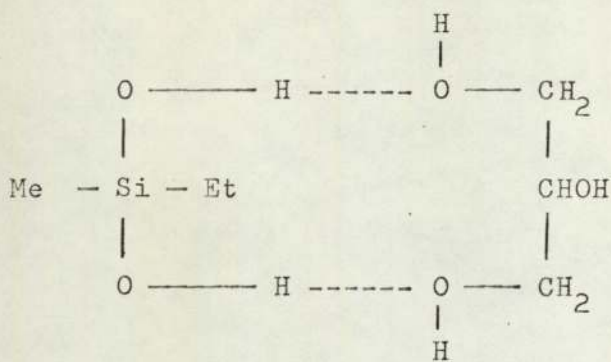


This bonding is found to lead to the formation of molecular chains as shown below :-



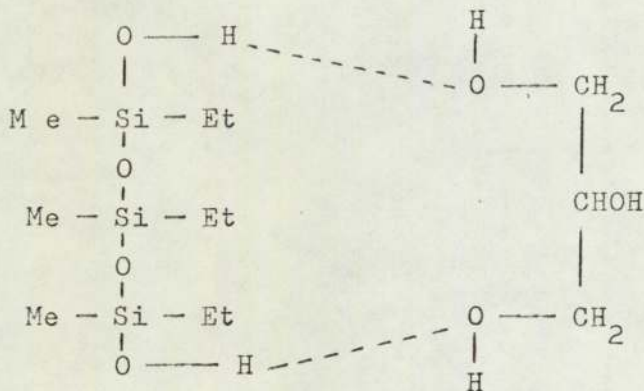
In the diorganosilane-diols there is also interaction between neighbouring chains so that they are arranged parallel to each other in a plane. The sheets thus constructed form a layer structure, with the alkyl groups of neighbouring sheets contacting back to back.

The increased stability of the silanediol can therefore be accounted for in terms of hydrogen bonding which can take place between the silanediol and the glycerol as shown in the following diagram



- - - - - hydrogen bonding

Although condensation to the linear siloxanediols does take place, it appears that the cyclisation of these is affected, resulting in the reduced proportion of cyclic material. The linear siloxanediols formed are also stabilised by hydrogen bonding with glycerol as shown in the diagram below. This stabilisation therefore affects the ability to cyclise and therefore the proportion of cyclic siloxanes is reduced as is found to be the case



- - - - - hydrogen bonding

Of the cyclic siloxanes obtained, it is noticeable that it is the trimer which is the major product, indicating that condensation to longer chains followed by cyclisation becomes increasingly difficult.

## II.5. The addition of glycerol to the hydrolysis of dimethyldichloro- silane

The hydrolysis of dimethyldichlorosilane has been the subject of numerous investigations. The products of hydrolysis are approximately equal amounts of polydimethylcyclsiloxanes and linear polydimethyl- $\alpha$ - $\omega$ -diols. In this work the hydrolysis was carried out in the presence of glycerol with the purpose of observing the effect that this would have on the proportions of the individual cyclic siloxanes.

### Results - Table IV.

Similar to the previous experiments with ethylmethyldichlorosilane, the proportion of trimer rapidly increases as the proportion of glycerol increases. There is also a corresponding decrease in the proportion of pentamer .

### Discussion

The increased proportion of trimer relative to the other cyclic siloxanes indicates that, condensation to the smaller chains followed by cyclisation is favoured. This is presumably due to the presence of hydrogen bonding as explained in the previous section (II.4)

Table IV

The addition of glycerol to the hydrolysis of dimethyldichlorosilane

Time for addition of water: 1 1/4 hours

Solvent: diethyl ether.

Temperature: 22°C.

Mole ratio of chlorosilane/water: 1/13  
 Volume ratio of chlorosilane/ether: 1/5

Moles of glycerol added	% Trimer	% Tetramer	% Pentamer
0	trace	71	29
0.025	2	82	16
0.05	17	70	13
0.1	31	58	11

## CHAPTER THREE

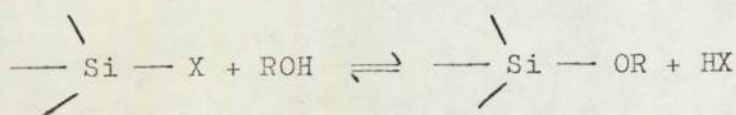
The formation of cyclic organosiloxanes by the hydrolysis and hydrogenolysis of diorganodialkoxysilanes.

### III.1. Introduction

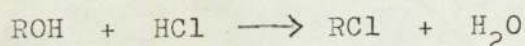
Organosiloxanes can also be obtained from the hydrolysis and hydrogenolysis of organoalkoxysilanes. After the organohalosilanes they are the most interesting silanes in silicone chemistry. Like the corresponding diorganohalosilanes the hydrolysis and hydrogenolysis of diorganodialkoxysilanes leads to a mixture of linear and cyclic oligomeric organosiloxanes.

### III.2. The preparation and stability of organoalkoxysilanes

Organoalkoxysilanes are prepared by the reaction of organohalosilanes with alcohol



The reaction is reversible so it is essential that the hydrogen halide is removed. This is done by adding a base such as pyridine<sup>44</sup> or a tertiary amine<sup>45</sup>. This removal is all the more important, in view of the fact that the hydrogen halide can react with the alcohol.

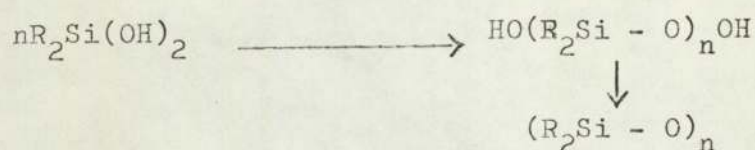
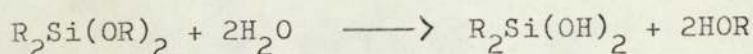


The resulting water would hydrolyse the silicon halide and the silicon alkoxide to give silanols and siloxanes.

Organoalkoxysilanes can be susceptible to attack by atmospheric moisture and oxygen on prolonged standing. It has been reported that both benzyloxytrimethylsilane<sup>46</sup> and benzyloxytriethylsilane<sup>47</sup> decompose on long standing. This work therefore includes investigations into the stability of the organoalkoxysilanes prepared.

### III.3. The hydrolysis of organoalkoxysilanes

The reaction follows the same pattern as for organohalosilanes formation of the diol followed by condensation to linear and cyclic siloxanes.



Unlike the hydrolysis of organohalosilanes, the initial stage leads to the formation of an alcohol and not an acid. Because of this organoalkoxysilanes can be employed to produce silanols sensitive to condensation, e.g. dimethylsilane-diols can be prepared from dimethyldiethoxysilane and dimethyldimethoxysilane<sup>48,49</sup> and the hydrolysis of phenyltrimethoxysilane gives good yields of phenylsilanediol<sup>50</sup>.

The experimental procedure is similar to that for the organohalosilanes. The hydrolysis can be greatly accelerated by the addition of small amounts of acid especially those acids which can be easily removed by washing such as hydrochloric, oxalic and acetic acids.<sup>51.</sup>

### III.4. The hydrolysis of bis(benzyloxy)ethylmethylsilane

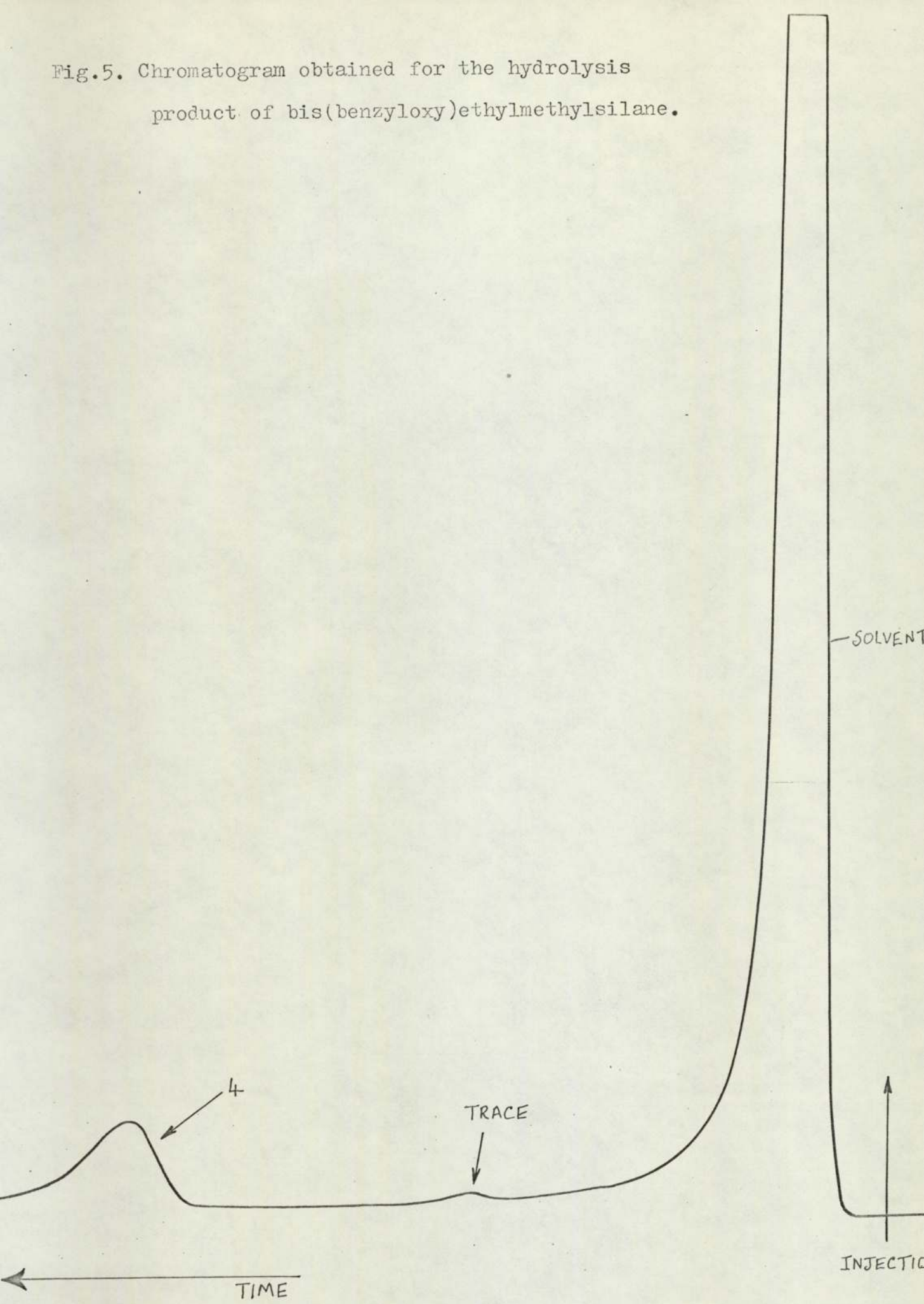
Experimentally the dialkoxysilane in solvent was added to a stirred excess of water containing a small amount of hydrochloric acid. The hydrolysis was carried out for the same length of time as that for the organodichlorosilane. The hydrolysis product was worked up and analysed in a similar manner to that obtained from the organodichlorosilane.

#### Results

##### (a) Gas-Liquid chromatography results

A chromatogram of the hydrolysis product is shown in Fig.5.

Fig.5. Chromatogram obtained for the hydrolysis product of bis(benzyloxy)ethylmethyilsilane.





One major component (peak 4) is indicated together with a slight trace of another component. Evidence as to the exact identity of the major component was obtained in a similar manner to that used in the hydrolysis of the dichlorosilane, by the use of a gas-liquid chromatograph combined with a mass spectrometer.

(b) Mass Spectra results

Peak 4 - intense peaks at m/e values of 249, 235 and 205. Less intense peak at m/e 161. The mass spectrum of the component was found to be identical with that obtained for peak 1 (Fig.3) in the hydrolysis product of ethylmethyldichlorosilane. The compound was therefore presumed to be the cyclic trimer  $(\text{CH}_3\text{C}_2\text{H}_5)_3\text{Si}_3\text{O}_3$ . The minor component was assumed to be a siloxanediol.

(c) Stability

After keeping for six months in a stoppered flask the bis(benzyloxy) ethylmethyldichlorosilane showed no signs of decomposition.

Discussion

Compared with the Si-hal bond, the Si-OR bond found in the alkoxy-silane has a more pronounced covalent character and therefore its sensitivity to hydrolysis is considerably lower. In addition the hydrolysis is also affected by the nature of the radical R in the organic group. The sensitivity of alkoxy groups to hydrolysis decreases with an increasing number of carbon atoms in the group, aryloxy groups being less easily split off by hydrolysis than lower alkoxy groups. The silanes with the most reactive alkoxy groups are the organomethoxy and organoethoxysilanes which have gained interest as intermediates for the production of silicones. The reactivity of alkoxy groups is also affected by the nature and extent of the organic

substitution of the silicon atoms. If several relatively large organic groups are bound to the silicon, the reaction of an Si - OR bond can be considerably reduced by steric hindrance.

By comparison with ethylmethyldichlorosilane, bis(benzyloxy)-ethylmethyldichlorosilane appears to be less sensitive to hydrolysis, for after an equivalent length of time only a small proportion of cyclic trimer is obtained. This is presumably due to the fact that the benzyloxy groups present are only slowly cleaved by hydrolysis.

### III.5. The hydrogenolysis of organoalkoxysilanes

Organoalkoxysilanes have been found to be cleaved by hydrogen at atmospheric pressure and room temperature to give a hydrocarbon plus siloxane. It has been reported<sup>46</sup> that bis(benzyloxy)dimethylsilane reacted to give cyclic trimer as the major component together with smaller amounts of the cyclic tetramer and linear siloxanediol. Bis(benzyloxy)diphenylsilane was also found to give 40% of the cyclic trimer although in this case the major product was diphenylsilanediol.

However other workers<sup>52</sup> have reported that alcohols are the main products formed when trimethyl and triphenylsilyl ethers are hydrogenolised.

Experimentally the reactions were carried out in a glass hydrogenation apparatus at room temperature and pressure, the reaction being followed by measuring the decrease in volume of the hydrogen. The reaction mixture was examined for volatile products by gas-liquid chromatography using standard reference solutions. Solid products were isolated by removal of solvent followed by characterisation by infra-red spectroscopy.

### III.6. The hydrogenolysis of bis(benzyloxy)ethylmethyilsilane

#### Results

##### (a) Gas-Liquid chromatography and Infra-red spectroscopy results

Examination of the reaction mixture by gas-liquid chromatography failed to indicate the presence of the expected toluene. A further examination for the presence of benzyl alcohol also proved unsuccessful. The sample was then examined by nuclear magnetic resonance spectroscopy and this indicated the presence of toluene in the reaction mixture.

After removal of the majority of the solvent, examination using infra-red spectroscopy showed the presence of siloxane in the product. The presence of a hydroxy group was also indicated this being due to the presence of siloxanediol in the reaction mixture.

Fig.6 shows the chromatogram obtained for the residue. Two major components, peaks 5 and 6, are indicated together with a trace of another component. The identification of peaks 5 and 6 was carried out using a combined gas-liquid chromatograph and mass spectrometer as used for the hydrolysis products.

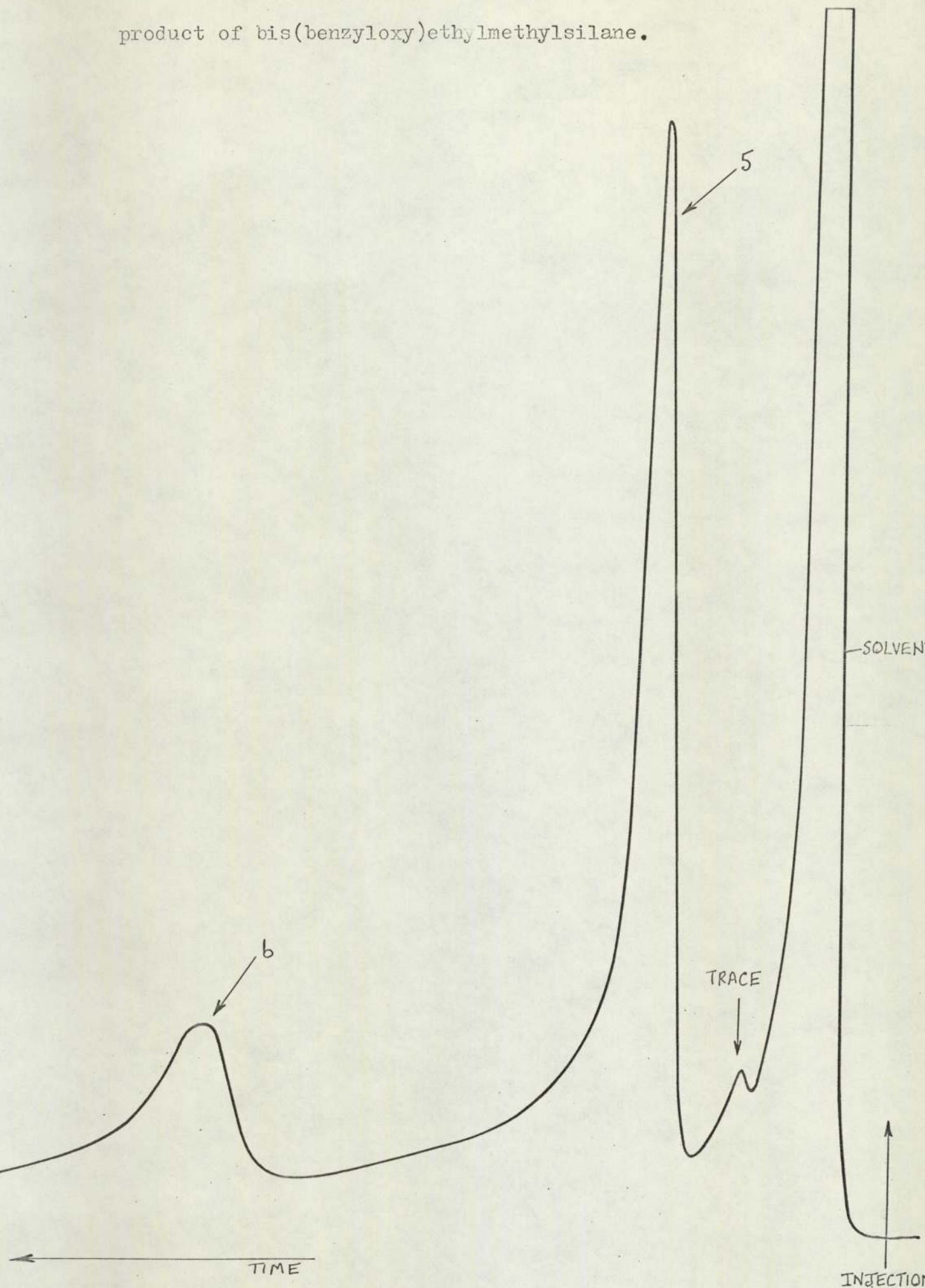
##### (b) Mass Spectrometry results

Generally the two components showed fewer intense peaks than those obtained from the hydrolysis products. This could be due to a change in instrumental conditions as they were analysed at a different time to those obtained from the hydrolysis experiments.

Peak 5 - Intense peaks were obtained at m/e values of 249 and 235. Other peaks at m/e 205 and 161.

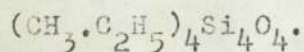
This spectrum was identical with that obtained for peak 1 (Fig.3) in the hydrolysis product. It was therefore assumed that the component was the trimer  $(\text{CH}_3 \cdot \text{C}_2\text{H}_5)_3\text{Si}_3\text{O}_3$ .

Fig.6. Chromatogram obtained for the hydrogenolysis product of bis(benzyloxy)ethylmethylsilane.



Peak 6 - Intense peaks were observed at  $m/e$  values of 337 and 323.

Although fewer intense peaks were observed the pattern of fragmentation was similar to that obtained for peak 2 (Fig.3) and it was therefore assumed that the component was the tetramer



### III.7. The Hydrogenolysis of bis(benzyloxy)methylphenylsilane

In addition to the hydrogenolysis of bis(benzyloxy)ethylmethylsilane the hydrogenolysis of bis(benzyloxy)methylphenylsilane was also investigated. This alkoxysilane was prepared by the reaction between methylphenyldichlorosilane, and benzyl alcohol in the presence of pyridine in a similar manner to that used for the bis(benzyloxy)-ethylmethylsilane.

#### Results

This work was in fact done prior to that for the bis(benzyloxy)-ethylmethylsilane and no analysis using mass spectrometry was carried out on the products of the hydrogenolysis.

#### (a) Gas-liquid chromatography and Infra-red spectroscopy results

Examination by gas-liquid chromatography using standard reference solutions confirmed the presence of toluene in the product. The majority of the solvent was then removed and the residue examined using gas-liquid chromatography and infra-red spectroscopy. Examination by infra-red spectroscopy showed the presence of siloxane together with siloxanediol.

A chromatogram of the residue is shown in Fig.7.

As no further investigations were made, it is difficult to exactly identify the peaks in the above chromatogram. However it can be suggested that peaks 'a' and 'b' are the isomeric methylphenyl trimers and 'c' and 'd' the partially separated tetramers.

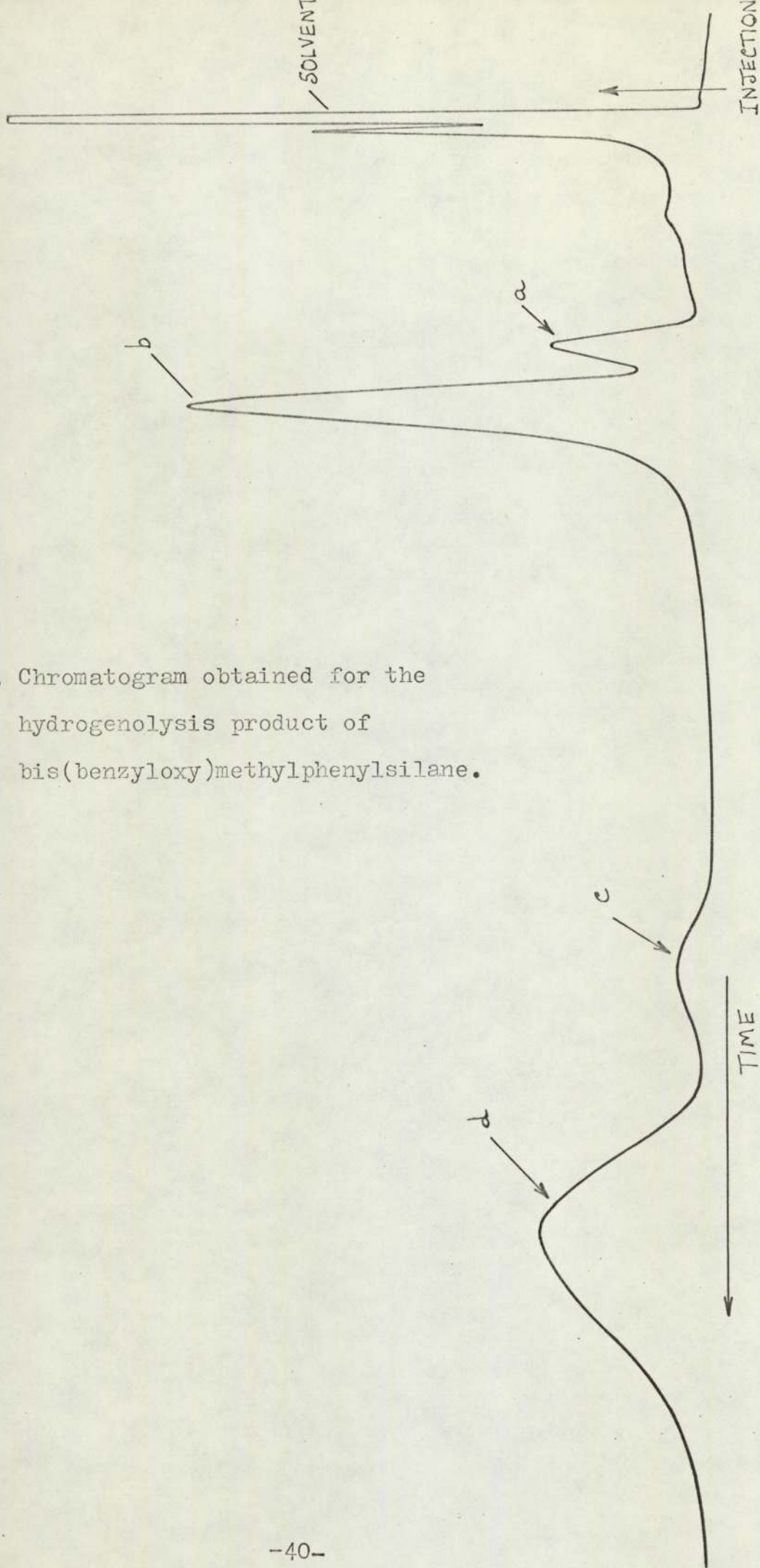


Fig.7. Chromatogram obtained for the hydrogenolysis product of bis(benzyloxy)methylphenylsilane.

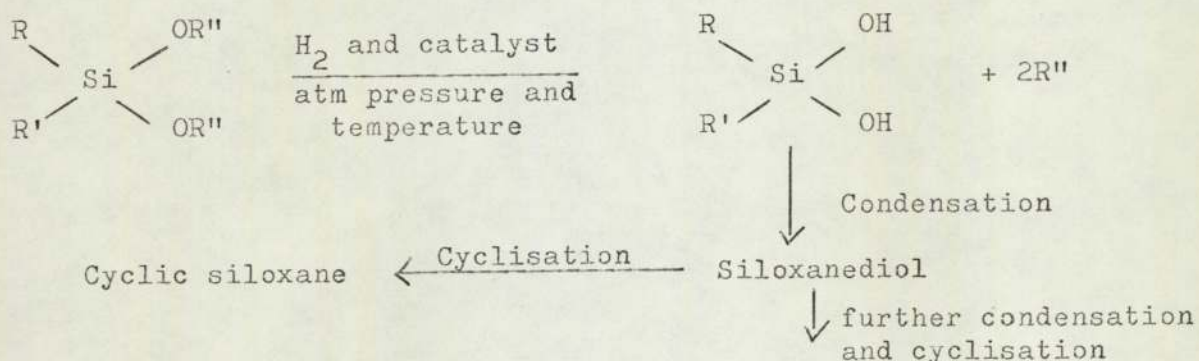
### III.8. Discussion of the hydrogenolysis results

The hydrogenolysis results were found to be in agreement with the previous results<sup>46</sup>, yielding a hydrocarbon plus siloxane.

Considering the hydrogenolysis of bis(benzyloxy)ethylmethylsilane both cyclic trimer and tetramer were obtained together with a small amount of another component, probably the siloxanediol whose presence had been indicated by infra-red spectroscopy. By comparison of peak areas it was estimated that the proportions of the components are trimer 63% and tetramer 27%.

The hydrogenolysis of bis(benzyloxy)methylphenylsilane also gives what are assumed to be the cyclic trimer and cyclic tetramer. By comparison of peak areas the proportion of the trimer was estimated to be 48% and that of the tetramer 51%.

The presence of a hydroxy group in the reaction mixture indicates the presence of linear siloxanediols which are formed initially from the silanediol. As in the hydrolysis reactions, the silanediol formed from the cleavage of the alkoxy silane by hydrogen, condenses under the reaction conditions to give the siloxane.



## EXPERIMENTAL

Gas-liquid chromatographic analyses were carried out on a Pye series 104 chromatograph using a katharometer detector. A 5' x ¼ inch column of methylsilicone gum SE30 on firebrick, with helium as the carrier gas (flow rate 60 mls/min) was used. For the analysis of the siloxanes, other instruments were used details of which are mentioned in the relevant sections. 2-10 microlitre injections of either neat liquid or a solution of benzene were used. The areas under the peaks were determined by tracing the peaks on to uniform paper, cutting out and weighing.

Molecular weights were determined using a Pye series 104 chromatograph with a 5' x ¼ inch column of OV-17 silicone gum on chromasorb GAW DMCS (proportions 2½ : 97½) combined with a Micromass 12B mass spectrometer.

60 MHz proton resonance spectra were obtained on a Perkin-Elmer R.10 Spectrometer operating at 35°C. 100 MHz spectra were obtained on a Varian Associates HA 100D instrument. The low temperature study of the cyclic silicon and tin compounds was carried out with the Perkin-Elmer R.10 Spectrometer fitted with a variable temperature accessory. Tetramethylsilane was used as an internal reference throughout.

Infra-red spectra were recorded on either a Perkin-Elmer Infracord 237 or 157G.

Column chromatography was carried out using Fisons Silica Gel (100-200 mesh). Eluents are mentioned in the appropriate sections. For this technique A.R. solvents supplied by Fisons were used.

Chlorosilanes, supplied by Midland Silicones Ltd., were redistilled before use. Other chemicals were supplied by Koch-Light



Ltd. and Messrs. Hopkins and Williams.

For the silicon compounds physical constants were taken mainly from Bazant et al<sup>53</sup>. Infra-red values were taken from Silverstein et al<sup>54</sup>.

Preparation of tetraphenyltin

Phenylmagnesium bromide was prepared according to the method of Voguel<sup>56</sup>, 2.75 mole of each. This was converted to tetraphenyltin using the method of Luijten and Van der Kerk<sup>56</sup>. Redistilled stannic chloride (56 cm<sup>3</sup>, 0.48 mole, 70% of theoretical amount) was added to the cooled phenylmagnesium bromide. After refluxing for two hours followed by cooling, the mixture was decomposed by the addition of ice water (112 cm<sup>3</sup>), followed by cold 10% hydrochloric acid (550 cm<sup>3</sup>). The crude product was filtered off, washed and dried in vacuo at 140°C. The material was recrystallised by means of a continuous extraction with hot benzene. Finally the crystals were washed with benzene and dried in vacuo at 100°C.

Yield 184g (44.9% of theoretical). M.pt. 224°C (Lit<sup>56</sup> 224°C)

Preparation of triphenyltin chloride

This was based on the method of Kocheshkov, Nad and Alexandrov<sup>57</sup>. A mixture of 80g (0.223 mole) of tetraphenyltin and 19.3g (8.7 cm<sup>3</sup>; 0.074 mole) of stannic chloride was heated at 205-215°C for three hours and subsequently at 180-190°C for another three hours. The reaction product on recrystallisation from diethyl ether yielded the following fractions :-

- |     |   |                            |
|-----|---|----------------------------|
| (1) | M.pt 106° - 107°C<br>(Lit <sup>57</sup> 105° - 106°C) | 65.3g (57% of theoretical) |
| (2) | M.pt 100° - 103°C                                     | 17g (15% of theoretical)   |

Preparation of methyltriphenyltin

Methyltriphenyltin was obtained by reacting 23.2g (0.06 mole) of triphenyltin chloride with 0.13 mole of methylmagnesium iodide, prepared from 5.6g of magnesium and 17.8g (7.8cm<sup>3</sup>) of iodomethane in

50cm<sup>3</sup> of anhydrous diethyl ether. The solution of methylmagnesium iodide was cooled and the triphenyltin chloride, partially dissolved in 100cm<sup>3</sup> of diethyl ether, was added with stirring. The mixture was refluxed for one hour. The solution was then decomposed with 20% ammonium chloride. After drying over anhydrous magnesium sulphate the ethereal layer was evaporated leaving an oil which solidified on cooling. The solid was purified by recrystallisation from petroleum ether (b.pt 40-60°C).

Yield 15.2g (67% of theoretical). M.pt 61°C (Lit<sup>58</sup> 60°C)

N.M.R.  $\tau$  (60MHz; CCl<sub>4</sub>) 9.35 (3H, s), 2.1-2.7 (15H, m)

#### Preparation of methylphenyltin dibromide

To a cooled solution (-2°C) of methyltriphenyltin (4.8g 0.017 mole) in carbon tetrachloride (48cm<sup>3</sup>) was added with stirring a solution of bromine (4.2g, 1.31cm<sup>3</sup>) in carbon tetrachloride. After the addition the mixture was refluxed. Samples were withdrawn before and after the addition and compared using gas-liquid chromatography with the theoretical amount of bromobenzene expected from the reaction.

The solution was then evaporated to remove the carbon tetrachloride and excess bromine, leaving a solution containing a small amount of a white solid. Ice cold petroleum ether (b.pt 60-80°C) was then added, dissolving the majority of the solid. The solution was then centrifuged and the supernatant liquid distilled

Yield 3.5cm<sup>3</sup>

N.M.R.  $\tau$  (60MHz; CCl<sub>4</sub>) 9.20 (3H, s), 2.6 - 3.1 (5H, m).

The presence of a multiplet 8.3 - 9.4 indicated that the compound was impure.

### Preparation of 3-methyl adipic acid

This was prepared using the method of Semmler<sup>59</sup>, 25g of pulegone (0.1 mole) were stirred with 50g (0.32 mole) of potassium permanganate in 2000cm<sup>3</sup> of distilled water for four hours, by which time the permanganate had been completely decolourised. The precipitate of manganese dioxide was then removed by filtration. The filtrate was made slightly alkaline by the addition of sodium hydroxide and evaporated to half its volume on a rotary evaporator. The remaining solution was then acidified with concentrated sulphuric acid and the 3-methyl adipic acid extracted with diethyl ether. The ethereal layer, after drying over anhydrous magnesium sulphate was evaporated leaving an oil which solidified on cooling. An unsuccessful attempt was made to recrystallise a portion of the acid by dissolving it in chloroform and then cautiously adding benzene.

Yield 24.6g

M.Pt 81°C (crude product)

(Lit<sup>59</sup> 84.5°C)

### Preparation of 3-methyldiethyl adipate

10g (0.06 mole) of 3-methyl adipic acid were refluxed with 7.7cm<sup>3</sup> of ethanol, 12cm<sup>3</sup> of sodium dried benzene and 0.1cm<sup>3</sup> of concentrated sulphuric acid in a flask fitted with a Dean and Stark trap. The reaction mixture was then poured into an excess volume of water and the benzene layer separated. One extraction of the aqueous layer with diethyl ether was carried out. The combined benzene and ether extracts were then washed with saturated sodium bicarbonate until effervescence ceased, then with water and finally dried over anhydrous magnesium sulphate. The solvents were removed by distillation. A final distillation was carried out to give the ester

Yield  $3.5\text{cm}^3$  (3.64g)

B.pt.  $138^\circ - 139^\circ\text{C}/19\text{mm}$

(Lit<sup>59</sup>,  $126.5^\circ\text{C}/10\text{mm}$ )

N.M.R.  $\tau$  (60MHz;  $\text{CCl}_4$ ) 9.05 (3H, d), 7.6 - 8.8 (13H, m), 5.9 (4H, q).

#### Preparation of 3-methylhexan 1,6-diol

To 1.50g (0.04 mole) of lithium aluminium hydride in  $100\text{cm}^3$  of anhydrous diethyl ether were added with stirring 17g (0.08 mole) of the diethyl ester in  $50\text{cm}^3$  of anhydrous diethyl ether. The ester was added at such a rate to keep the ether steadily refluxing. After the addition the mixture was refluxed for  $1\frac{1}{2}$  hours. Excess lithium aluminium hydride was then decomposed by the addition of ethyl acetate ( $10\text{cm}^3$ ). After separation of the ethereal layer followed by drying over anhydrous magnesium sulphate, the ether was removed by distillation. A final distillation under reduced pressure was carried out to give the product.

Yield  $5\text{cm}^3$  (5.1g)

B.pt.  $160^\circ - 161^\circ\text{C}/15\text{mm}$ .

(Lit<sup>50</sup>,  $155^\circ\text{C}/12\text{mm}$ ).

#### Preparation of 3-methyl 1,6-dibromohexane

To a cooled solution of  $18.9\text{cm}^3$  of hydrogen bromide were added with stirring,  $12.5\text{cm}^3$  of concentrated sulphuric acid. After a short interval 5g of the diol were added dropwise. The mixture was then left in an ice bath for twenty four hours. This was followed by heating on a steam bath for twenty four hours. The mixture was then added to water and the product extracted with diethyl ether. The ethereal layer was then washed successively with saturated sodium bicarbonate and water. After drying over anhydrous magnesium sulphate, the ether was removed by distillation.

Yield 8.4g (84% of theoretical yield)

N.M.R.  $\tau$  (60MHz;  $\text{CCl}_4$ ) 9.05 (3H,d), 7.95 - 8.90 (7H,m) 6.60 (4H,q).

#### Preparation of 1-methyl-1-phenylsilacycloheptane

The Grignard reagent was prepared using the method of Kreuchunas<sup>61</sup>. To 3.04g (0.013 mole) of magnesium in 20cm<sup>3</sup> of anhydrous diethyl ether were added dropwise with stirring 15.3g (0.06 mole) of 1,6-dibromohexane. The reaction was completed by refluxing the solution for thirty minutes. To the resulting Grignard solution was added with stirring 11.49g (9.5cm<sup>3</sup>, 0.06 mole) of freshly distilled methylphenyldichlorosilane in anhydrous diethyl ether (50cm<sup>3</sup>). No immediate reaction was observed during the addition but after refluxing for two hours a white precipitate had been formed. The mixture was then left refluxing for a further five hours to complete the reaction. After this time the solution was decomposed by the addition of 20% ammonium chloride. The ethereal layer was separated, dried and then the ether removed by distillation leaving a white oil.

Yield 12.8g.

N.M.R.  $\tau$  (60MHz,  $\text{CCl}_4$ ) 9.8 (3H, s) 8.2 - 9.3 (12H, m) 2.4 - 3.0 (5H,m).

#### Preparation of 1-methyl-1-phenylsilacyclohexane

The Grignard reagent was first prepared from 3.04g of magnesium and 14.4g of 1,5-dibromopentane in 150cm<sup>3</sup> of anhydrous diethyl ether. To this solution was then added 11.5g (9.5cm<sup>3</sup>, 0.06 mole) of freshly distilled methylphenyldichlorosilane in diethyl ether. The solution was then refluxed and after thirty minutes a white precipitate was observed. Refluxing was continued for a further five hours to complete the reaction. Then the mixture was decomposed and worked up as in the previous preparation. The product was a pale yellow oil.

Yield 12.2g

N.M.R.  $\tau$  (60MHz;  $\text{CCl}_4$ ) 9.8 (3H,s), 8.0 - 9.4 (10H,m) 2.4 - 2.9 (5H,m)

Preparation of 1,4-dimethyl-1-phenylsilacycloheptane

The Grignard solution was first obtained from the previously prepared 3-methyl 1,6-dibromohexane. 0.62g (0.026 mole) of magnesium was reacted with 3.37g (0.013 mole) of the dibromide in anhydrous diethyl ether. To the resulting Grignard solution was added with stirring 2.50g (2.1cm<sup>3</sup> 0.012 mole) of freshly distilled methylphenyl-dichlorosilane in anhydrous diethyl ether. The mixture was then refluxed for a total of twenty two hours. Then it was decomposed and worked up as before, the final product being a dark brown oil.

Yield 2.94g.

N.M.R.  $\tau$  (60MHz;  $\text{CCl}_4$ ) 8.15 - 9.35 (14H,m) 2.2 - 3.0 (5H,m).

Preparation of 1-methyl-1-phenylstannacycloheptane

As previously the Grignard solution was prepared by the reaction of 0.62g (0.026 mole) of magnesium with 3.2g (0.013 mole) of 1,6-dibromohexane in anhydrous diethyl ether. To the solution was then added dropwise with stirring 4.9g (0.013 mole) of the previously prepared methylphenyltin dibromide in anhydrous diethyl ether. After refluxing the mixture for two hours, a white precipitate was observed. Refluxing was then continued for a further five hours and the reaction mixture worked up as before.

Yield 13.19g

N.M.R.  $\tau$  (60MHz;  $\text{CCl}_4$ ) 8.2 - 9.4 (10H,m) 2.5 - 3.1 (5H,m).





an ice-salt bath at  $-2^{\circ}\text{C}$  was used.

Addition of water. This was added dropwise from a tap funnel.

Treatment of reaction products. The ether layer was transferred to a separating funnel and washed well with water until free of acid.

After drying over anhydrous magnesium sulphate, the ether solution was evaporated on a rotary evaporator.

(b) Addition of chlorosilane to water

To  $7\text{cm}^3$  of water in a  $50\text{cm}^3$  three necked flask, fitted with a tap funnel and thermometer, were added dropwise  $3.4\text{cm}^3$  of ethylmethyl-dichlorosilane in  $17.5\text{cm}^3$  of diethyl ether.

Hydrolysis temperature  $22 \pm 0.5$ ,  $0 \pm 0.5^{\circ}\text{C}$ .

Treatment of reaction products. The reaction products were worked up in a similar manner to (a).

The products from both (a) and (b) were colourless viscous oils.

Analysis of the hydrolysis products

Column Chromatography

A weighed amount of each product (about 0.5g) was dissolved in a 20 : 80 mixture of benzene and light petroleum (b.pt.  $60 - 80^{\circ}\text{C}$ ) and placed on a column of silica gel (9" x  $\frac{3}{4}$ ") and eluted with the same solvent ( $300\text{cm}^3$ ). 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.

## Gas-liquid Chromatography

A temperature of 175°C was found to give the best separation of the peaks.

An attempt was made to separate the isomeric siloxanes using the following instruments and conditions : -

(a) Pye 104 Chromatograph - using a 9' x ¼" column of 20% MS 2430 silicone gum on fire brick, with helium as the carrier gas., (flow rate 40 mls/min). Column temperature 197°C.

(b) Philips PV4000 series chromatograph using a flame ionisation detector. A 6' column (diameter 3/16") containing 25% silicone grease on phaseprep A was used. The carrier gas was nitrogen (flow rate 100 mls/min).

## Separation of the components in the hydrolysis product

### (a) Column Chromatography.

1.5g of the hydrolysis product was dissolved in a little petroleum ether (b.pt 60 - 80°C) and placed on a column of silica gel (27" x 2") and eluted with the same solvent (500 cm<sup>3</sup>). The solvent was then changed to a 20 : 80 mixture of benzene and petroleum ether (b.pt. 60 - 80°C) and the process of elution continued. 800 cm<sup>3</sup> of the 20 : 80 mixture were used. The eluate was evaporated on a rotary evaporator and the residues dissolved in a little (1.5cm<sup>3</sup>) petroleum ether (b.pt 60 - 80°C). The residues were analysed using gas-liquid chromatography (column temperature 175°C).

### (b) Preparative gas-liquid chromatography

An attempt was made to separate the components of the hydrolysis/ product using a Pye series 105 Automatic Preparative chromatograph, with a flame ionisation detector. A 20' x ¼" column of 25% silicone gum SE30 on chromasorb W-AW (60 - 80 mesh) was used with nitrogen as the

carrier gas (flow rate 85 mls/min).

A column temperature of  $205^{\circ}\text{C}$  was used.

(c) Combined gas-liquid chromatography and mass spectrometry

A column temperature of  $120^{\circ}\text{C}$  was used and 0.5 microlitres was injected.

Hydrolysis of ethylmethyldichlorosilane with added glycerol

These experiments were carried out in duplicate.

$6.8\text{cm}^3$  (0.05 mole) of ethylmethyldichlorosilane and  $1.85\text{cm}^3$  (0.025 mole) of glycerol in  $35.0\text{cm}^3$  of diethyl ether were placed in a  $50\text{cm}^3$  three necked flask fitted with a tap funnel and thermometer of suitable range. Water  $14\text{cm}^3$  was added gradually to the vigorously stirred mixture as in the previous hydrolysis experiments.

Hydrolysis temperature  $22 \pm 0.5^{\circ}\text{C}$

Temperature control. The reaction flask was placed in a volume of water maintained at  $21 - 22^{\circ}\text{C}$ .

Treatment of reaction products. These were worked up in a similar manner to those in the previous hydrolysis experiments.

Analysis of reaction products. Similar procedure as for the previous hydrolysis experiments.

Hydrolysis of dimethyldichlorosilane with added glycerol

These experiments were carried out in duplicate.

$6.0\text{cm}^3$  (0.05 mole) of freshly distilled dimethyldichlorosilane together with  $1.85\text{cm}^3$  (0.025 mole) of glycerol in  $30\text{cm}^3$  of diethyl ether were placed in a  $50\text{cm}^3$  three necked flask fitted with a tap funnel and thermometer. Water  $12\text{cm}^3$  was added gradually from the tap funnel to the vigorously stirred mixture.

Hydrolysis temperature       $22 \pm 0.5^{\circ}\text{C}$ .

Temperature control.    The reaction flask was placed in a volume of water maintained at  $21 - 22^{\circ}\text{C}$ .

Treatment of reaction products.    These were analysed using gas-liquid chromatography (column temperature  $100^{\circ}\text{C}$ ).

A control hydrolysis experiment was also carried out involving the hydrolysis of the chlorosilane without the addition of glycerol. The hydrolysis was carried out in a similar manner to the other experiments and the same procedure was used for the analysis of the product.

1. Preparation of bis(benzyloxy)ethylmethyilsilane

In a two necked 500cm<sup>3</sup> flask were placed 20.5cm<sup>3</sup> (0.2 mole) of benzyl alcohol, 16.3cm<sup>3</sup> (0.2 mole) of pyridine and 150cm<sup>3</sup> of diethyl ether. All the reagents had been thoroughly dried. The flask was placed in an ice salt bath maintained at 0°C. The mixture was vigorously stirred while 13.6 cm<sup>3</sup> (0.1 mole) of ethylmethyldichlorosilane in 50cm<sup>3</sup> of diethyl ether was added dropwise from a tap funnel. After the addition the mixture was refluxed for two hours and then was left standing in order to precipitate the pyridine hydrochloride which had been formed during the reaction. The mixture was then filtered and the filtrate washed well with water to remove any last traces of the base. After drying over anhydrous magnesium sulphate the ether was removed by distillation. The impure residue (30.5g) was then purified by column chromatography.

A portion of the residue (5.0g) was dissolved in benzene and placed on a column of silica gel (39" x 1") and eluted with the same solvent (1200cm<sup>3</sup>). After evaporation of the eluate, on a rotary evaporator, 2.9g of product were obtained.

The product was stored in a refrigerator to prevent possible decomposition. In order to study any decomposition which might occur, a portion of the product was kept in a stoppered flask at room temperature. Samples were removed periodically and examined by infrared spectroscopy for any signs of decomposition.

N.M.R.  $\tau$  (60MHz; CCl<sub>4</sub>) 9.90(3H,s), 9.15 (5H,m) 5.35 (4H,s), 2.75 (10H,s)

I.R. (thin film 1060 - 1090cm<sup>-1</sup> (Si - O - C stretching), 1260 cm<sup>-1</sup> (methyl on silicon).

No new bands were observed after the sample had been kept for six months in a stoppered flask.

## 2. Hydrolysis of bis(benzyloxy)ethylmethyilsilane

In a three necked flask fitted with a tap funnel and thermometer were placed  $1.5\text{cm}^3$  of concentrated hydrochloric acid and  $4.5\text{cm}^3$  of water. To the vigorously stirred solution in the flask was added dropwise  $3\text{cm}^3$  (0.01 mole) of bis(benzyloxy)ethylmethyilsilane in  $15\text{cm}^3$  of diethyl ether. The alkoxysilane was added over a period of  $1\frac{1}{4}$  hours.

Hydrolysis temperature  $22 \pm 0.5^\circ\text{C}$ .

Temperature control. The reaction flask was placed in a volume of water maintained at  $21 - 22^\circ\text{C}$ .

Treatment of reaction products. The ether layer was transferred to a separating funnel and washed well with water to remove not only the acid but the benzyl alcohol formed during the reaction. After drying over anhydrous magnesium sulphate the ether layer was evaporated on a rotary evaporator.

Analysis of reaction products. They were analysed in a similar way to the products obtained from the hydrolysis of ethylmethyldichlorosilane.

Gas-Liquid Chromatography. A column temperature of  $107^\circ\text{C}$  was used for the separation.

Combined gas-liquid chromatography and mass spectrometry.

A column temperature of  $110^\circ\text{C}$  was used and 0.5 microlitres injected.

### Mass Spectra

Peak 4 - ions at the following m/e values were shown in the spectrum:-  
249, 250, 251, 235, 236, 237, 220, 205, 206, 207, 193, 179, 180, 181,  
161, 162, 163, 133, 119, 104.

### 3. Preparation of bis(benzyloxy)methylphenylsilane

To a mixture of 27.3cm<sup>3</sup> (0.25 mole) of dried benzyl alcohol and 19cm<sup>3</sup> (0.025 mole) of dried pyridine in 150cm<sup>3</sup> of anhydrous diethyl ether at 0°C, were added with stirring, 20cm<sup>3</sup> (0.013 mole) of freshly distilled methylphenyldichlorosilane in 50cm<sup>3</sup> of diethyl ether. After the addition the mixture was refluxed for two hours and then worked up in a similar manner to the preparation of bis(benzyloxy)ethylmethylsilane. The impure product (32g) was purified in a similar manner using column chromatography.

A portion of the residue (0.9g) was dissolved in benzene and placed on a column of silica gel (20" x 1") and eluted with the same solvent (1200cm<sup>3</sup>). After evaporation of the eluate 0.38g of product were obtained.

N.M.R.  $\tau$  (60MHz; CCl<sub>4</sub>) 9.70 (3H, s), 5.30 (4H, s) 2.3 - 3.0 (15H, m)

I.R. (thin film) 730 cm<sup>-1</sup> (phenyl on silicon)

1000- 1090cm<sup>-1</sup> (Si - O - Si stretching) 1260cm<sup>-1</sup> (methyl on silicon)

#### Hydrogenolysis reactions

The reactions were carried out in a glass hydrogenation apparatus at room temperature and atmospheric pressure.

##### (1) Hydrogenolysis of bis(benzyloxy)ethylmethylsilane

2.86g (0.01 mole) of the dialkoxysilane in 20cm<sup>3</sup> of cyclohexane were stirred with 1g of 10% palladium on charcoal catalyst. The catalyst was filtered off and the filtrate analysed. The solvent was then evaporated and an analysis of the residue carried out.

Time for completing of reaction, 85 minutes.

#### Gas-Liquid chromatography

Filtrate - column temperature of 50°C was used

Residue - column temperature of 150°C was used.

Combined gas-liquid chromatography and mass spectrometry

Residue - column temperature of 150°C was used and 1 microlitre was injected.

Mass Spectra:-

Peak 5 - ions at the following m/e values were shown: -  
249, 250, 251, 235, 236, 237, 205, 206, 207, 161, 133.

Peak 6 - ions at the following m/e values : -  
337, 323, 324, 325.

N.M.R.

Filtrate  $\tau$  (100MHz; CCl<sub>4</sub>) 8.55 (12H,s), 7.7 (3H,s) 5.3 (s),  
2.7 - 2.9 (m).

The multiplet at 2.7 - 2.9 and the singlet at 5.3 indicated that in addition to toluene and cyclohexane there was another compound present which could possibly be benzyl alcohol but there was insufficient evidence to confirm this.

I.R.

Residue (thin film) 1010 - 1110cm<sup>-1</sup> (Si - O - Si stretching)  
1260cm<sup>-1</sup> (methyl on silicon), 3200 - 3400cm<sup>-1</sup> (Si - OH)

(2) Hydrogenolysis of bis(benzyloxy)methylphenylsilane

3.34g (0.1 mole) of the dialkoxysilane in 20cm<sup>3</sup> of cyclohexane were stirred with 1g of 10% palladium on charcoal catalyst. The reaction mixture was treated in a similar way to that in (1).

Time for completion of reaction, 50 minutes.

Gas-liquid chromatography

Filtrate - column temperature of 50°C was used

Residue - column temperature of 272°C was used.



I.R.

Residue (thin film)  $730\text{cm}^{-1}$  (phenyl on silicon)

$1020 - 1100\text{cm}^{-1}$  (Si - O - Si stretching),  $1260\text{cm}^{-1}$  (methyl on silicon)

$3160 - 3480\text{cm}^{-1}$  (Si - OH)

## REFERENCES

1. R. West, *J. Amer. Chem. Soc.*, 76, 6015, (1954).
2. L. H. Sommer, "Stereochemistry, Mechanism and Silicon", McGraw Hill, New York, 1965.
3. W. J. Pope and S. J. Peachey, *Proc. Chem. Soc.*, 16, 42, 116, (1960)
4. G. J. D. Peddle and G. Redl, *Chem. Comm.* 626, (1968).
5. G. J. D. Peddle and G. Redl, Fourth International Conference on Organometallic Chemistry, Bristol, 1969.
6. U. Folli, D. Iarossi and F. Taddei, *J. Chem. Soc., Perkin Transactions II*, 638, (1973).
7. N. L. Allinger, *J. Amer. Chem. Soc.*, 81, 5727, (1959).
8. J. B. Hendrickson, *J. Amer. Chem. Soc.*, 83, 4537, (1961).
9. R. J. Ouellette, *J. Amer. Chem. Soc.*, 96, 2421, (1974).
10. H. Zimmer, C. W. Blewett and A. Brakas, *Tetrahedron Letters*, 13, 1615, (1968).
11. A. Bygden, *Ber.* 48, 1236, (1915).
12. G. Gruttner and M. Wiernik, *Ber.*, 48, 6012, (1954).
13. R. West, *J. Amer. Chem. Soc.* 76, 6012, (1954).
14. C. H. Bushweller, J. W. O'Neil and H. S. Bilofsky, *Tetrahedron*, 27, 3065, (1971).
15. G. Gruttner, E. Krause and M. Wiernik, *Ber.*, 50, 1549, (1917).
16. K. Moedritzer, *Organometal. Chem. Rev.*, 1, 179, (1966).
17. R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, 60, 479, (1960).
18. M. Gielen and J. Nasielski, *J. Organometal. Chem.*, 1, 173, (1963).
19. S. Boué, M. Gielen and J. Nasielski, *J. Organometal. Chem.*, 9, 443, (1967).
20. M. Gielen and J. Nasielski, *J. Organometal. Chem.*, 7, 273, (1967).
21. S. Faleschini and G. Tagliavini, *Gazz. Chim. Ital.*, 97, 1401, (1967).

22. S.Boué, M.Gielen, J.Nasielski, J.Austin and M.Limbourg,  
J.Organometal.Chem., 15, 267, (1968).
23. K.A.Andrianov, M.A.Sipyagina and T.A.Ugarova, J.Gen.Chem., U.S.S.R.  
29, 4019, 1959.
24. A.J.Barry and J.W.Gilkey, U.S.Patent 2,495,363, (1950).
25. L.H.Shaffer and E.M.Flanigen, J.Phys.Chem., 61, 1591, 1595, (1957).
26. W.T.Grubb, J.Amer.Chem.Soc., 76, 3408, (1954).
27. W.Patnode and D.F.Wilcock, J.Amer.Chem.Soc., 68, 358, (1946).
28. J.F.Hyde and R.C.Delong, J.Amer.Chem.Soc., 63, 1194, (1941).
29. C.W.Young, P.C.Servais, C.C.Curie and M.J.Hunter, J.Amer.Chem.Soc.,  
70, 3758, (1948).
30. R.N.Lewis, J.Amer.Chem.Soc., 70, 1115, (1948).
31. H.J.Hickton, A.Holt, J.Homer and A.W.P.Jarvie, J.Chem.Soc., (c),  
149, 1966.
32. D.B.Chambers, F.Glocking and J.R.C.Light, Q.Rev.Chem.Soc., 317,  
(1968).
33. A.G.Sharkey, R.A.Friedel and S.H.Langer, Anal.Chem., 29, 770,  
(1957).
34. V.H.Diebler, F.L.Mohler and R.M.Reese, J.Chem.Phys., 21, 180  
(1953).
35. V.U.Orlov, J.Gen.Chem., U.S.S.R., 37, 2188, (1967);  
Russ, J.Phys.Chem., 43, 13, (1969).
36. J.B.Carmichael and J.B.Kinsinger, Canad. J.Chem., 42, 1996,  
(1964).
37. M.Yokoi, Bull.Chem.Soc., Japan, 30, 100, (1957).
38. E.H.Aggarwal and S.H.Bauer, J.Chem.Phys., 18, 42, (1950).
39. T.Tanaka, Bull. Chem.Soc., Japan, 33, 282; (1960).
40. K.A.Andrianov, I.A.Zubkov, T.A.Krasovskaya and M.A.Kleinovskaya,  
J.Gen.Chem., U.S.S.R., 27, 491, (1957).

41. H.R.Allcock, "Heteroatom Ring Systems and Polymers", Academic Press, New York, 1967, p.89.
42. C.A.Burkhard, J.Amer.Chem.Soc., 67, 2173, (1945).
43. M.Kakudo and T.Watase, J.Chem.Phys., 21, 167, (1953).
44. R.Filler, J.Org.Chem., 19, 544, (1954).
45. W.Simpson, British Patent, 635,726, (1950).
46. A.Holt, A.W.P.Jarvie and J.J.Mallabar, J.Organometal.Chem., 59, 141, (1973).
47. N.E.Glushkova and N.P.Kharitonov, Bull.Acad.Sci., U.S.S.R., Div.Chem.Sci., 81, (1967).
48. J.F.Hyde, J.Amer.Chem.Soc., 75, 2166, (1953).
49. S.W.Kantor, J.Amer.Chem.Soc., 75, 2712, (1953).
50. L.J.Tyler, J.Amer.Chem.Soc., 77, 770, (1955).
51. R.R.McGregor and E.L.Warwick, West German Patent, 881,404, (1942).
52. E.J.Corey and A.W.Venkateswalu, J.Amer.Chem.Soc., 94, 6190, (1972).
53. V.Bazant, V.Chvalovsky and J.Rathousky, "Organosilicon Compounds", Publishing House of the Czechoslovak Academy of Sciences, Prague, 1965,
54. R.M.Silverstein, C.G.Bassler and T.C.Morrill, "Spectrometric Identification of Organic Compounds", Wiley, (3rd Edition), 1974.
55. A.I.Voguel, "Practical Organic Chemistry", 3rd Edition, Longmans, 1962, p.756.
56. J.A.G.Luijten and G.J.M.Van der Kerk, "Investigations into the field of Organotin Chemistry", Tin Research Institute, 1955, p.111.
57. K.A.Kocheshkov, M.M.Nad and A.P.Alexandrov, Ber. 57, 1348, (1934).
58. M.E.Pavlovskaya and K.A.Kocheshkov, Compt.Rend.Acad.Sci., U.S.S.R. 49, 263, (1945).
59. F.W.Semmler, Ber., 25, 3516, (1892).

60. L.Bouveault and G.Blanc, Compt. Rend.Heb.Des.Séances de L'Acad. des Sci., 2, 329, (1903).
61. A.Kreuchunas, J.Amer.Chem.Soc., 75, 4278, (1953).
62. V.F.Mironov and V.V.Nepomnina, Bull.Acad.Sci., U.S.S.R., Div.Chem. Sci., 1188, (1959).