REACTIVE INTERMEDIATES IN CARBON-FUNCTIONAL ORGANOSILICON REACTIONS.

By

SILVANA MARIA MIFSUD.

A Thesis presented for the
degree of Doctor of Philosophy
in the University of Aston in
Birmingham.

January, 1978.

SUMMARY

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Addition, substitution and reduction were observed to occur as competing processes in the reaction between vinyltrichlorosilane and isopropylmagnesium bromide, whereas only addition and reduction were observed in the reaction between vinyltrichlorosilane and tert-butylmagnesium chloride.

Unsuccessful attempts were made to prepare compounds containing silacyclopropane rings via Grignard cyclisation reactions of sterically hindered (2-bromoethyl)dialkylchlorosilanes.

Sterically hindered (2-bromoethyl)trialkylsilanes were prepared and some reactions investigated. To account for the substitution product as well as the cleavage product from the solvolysis of (2-bromoethyl)tri-n-butylsilane, a mechanism involving attack of the carbonium ion intermediate as the rate-determining step is proposed. Rearrangement of (2-hydroxyethyl-2,2-d_2)tri-n-butylsilane with phosphorus tribromide and thionyl chloride was observed. The carbonium ion $Bu_3SiCH_2CH_2^+$ proposed as an intermediate in the rearrangement reaction was trapped using the silane transfer reaction. Observations indicate that if nucleophilic attack takes place at silicon, formation of the Grignard reagent from (2-halogenoalkyl)trialkylsilane is unlikely to occur; whereas if nucleophilic attack does not take place at silicon then Grignard formation is possible.

No rearrangement was observed between chloromethyltri-n-butylsilane and a nucleophilic reagent such as sodium ethoxide or an electrophilic reagent such as aluminium chloride.

An exploratory study of the pyrolysis of silacyclobutanes was undertaken with a view to the detection of silicon-carbon π-bonded intermediates.

Synthesis reactions
organosilicon compounds.

This work was carried out between 1973 and 1976 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

Silvana M. Mifsud

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ACKNOWLEDGEMENTS

I would like to express my thanks to Dr. A. W. P. Jarvie for her supervision and encouragement of this work: to Dr. S. J. Moss for his help and advice with the work on silacyclobutanes; to Miss S. Simpson for typing this thesis and to Mrs. V. Clenton, Mr. E. Hartland, Mr. M. Houghton and Mr. M. Perry for the various spectra they prepared.

I am also indebted to the Science Research Council for the provision of a grant.

S. M. M.

ERRATA

Page 17, line 16 - for '1-naphthyllithiumsilane' read '1-naphthyltriethoxysilane.'

Page 97, line 17 - for 'tetrahydrofuran (60 ml.) magensium' read 'tetrahydrofuran (60 ml.) was added dropwise to a slurry of magnesium.'

Page 104, line 22 - for '(intensity 2) singlet' read '(intensity 2) multiplet τ 8·7 (intensity 2) singlet.'

Whenever the word 'ether' occurs unqualified in this text reference to diethyl ether is implied.

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CHAPTER ONE

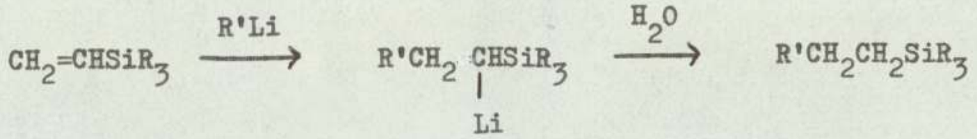
INTRODUCTION

The size of substituents on silicon profoundly affects the reactions and reactivity of silicon containing species. For example, the hydrolysis of certain organohalogenosilanes produces silanols, siloxanes or both. However, it has been observed that the presence of large groups on silicon hinders the condensation of silanols to siloxanes.[1] The same is true for silyl nitrogen compounds.[2] The work reported herein is concerned with the preparation and study of reactions of sterically hindered carbon-functional silicon derivatives. Alpha and beta-halogenoalkyl derivatives, as well as silacyclobutyl derivatives with large substituents on silicon were prepared. Chapter one is concerned with some of the problems encountered in the preparation of some of these sterically hindered compounds. Chapter two is devoted to the reactions of the sterically hindered beta-halogenoalkyl derivatives. We investigated this group of compounds in the greatest detail. Chapter three is concerned with some exploratory studies of alpha-halogenoalkylsilanes and silacyclobutyl compounds.

I. Reaction of vinyltrichlorosilane with sterically hindered Grignard reagents.

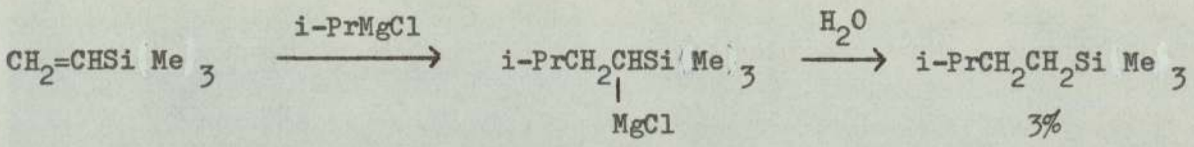
The addition of Grignard reagents to vinyl groups usually occurs in conjugated systems. Condensation is more likely to occur with the more reactive Grignard reagents such as tert-butylmagnesium chloride, benzylmagnesium chloride and p-chlorobenzylmagnesium chloride, [3a]

The addition of organolithium compounds to vinylsilanes is well documented.[4]

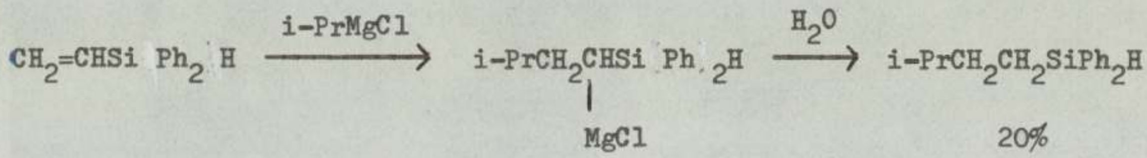


$$CH_2{=}CHSiR_3 \xrightarrow{R'Li} R'CH_2\underset{|\atop Li}{CH}SiR_3 \xrightarrow{H_2O} R'CH_2CH_2SiR_3$$

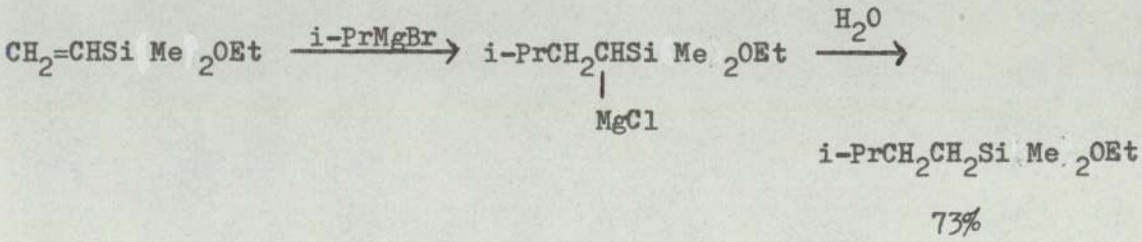
On the other hand, only a couple of reports can be found in the literature concerning the addition of Grignard reagents to vinylsilanes. Seyferth[4d] reported an addition between phenylmagnesium bromide and triethylperfluorovinylsilane. Spialter and co-workers[5] have shown that some Grignard reagents add to the vinyl group of vinylsilanes and that the extent of the reaction is sensitive to the substituents attached to the silicon atom.



$$CH_2{=}CHSiMe_3 \xrightarrow{i\text{-}PrMgCl} i\text{-}PrCH_2\underset{|\atop MgCl}{CH}SiMe_3 \xrightarrow{H_2O} \underset{3\%}{i\text{-}PrCH_2CH_2SiMe_3}$$



$$CH_2{=}CHSiPh_2H \xrightarrow{i\text{-}PrMgCl} i\text{-}PrCH_2\underset{|\atop MgCl}{CH}SiPh_2H \xrightarrow{H_2O} \underset{20\%}{i\text{-}PrCH_2CH_2SiPh_2H}$$

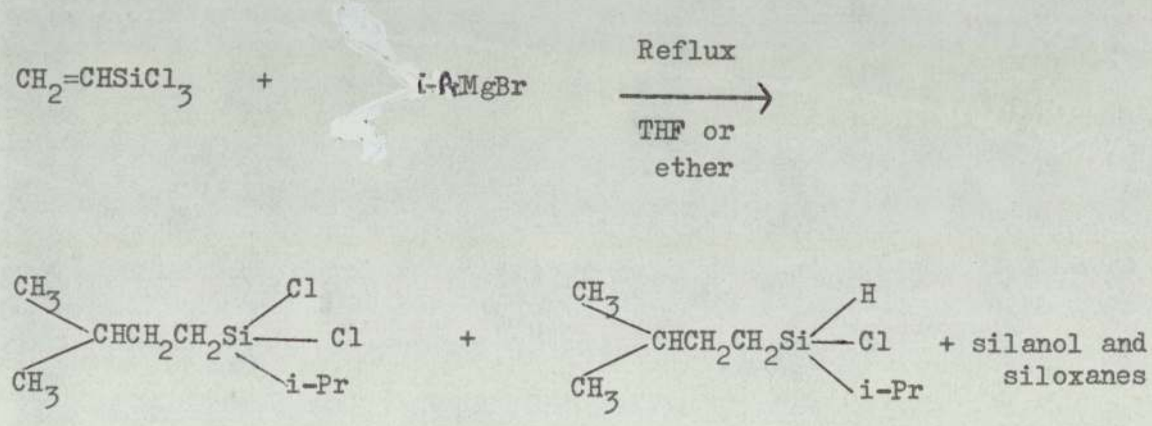


$$CH_2{=}CHSiMe_2OEt \xrightarrow{i\text{-}PrMgBr} i\text{-}PrCH_2\underset{|\atop MgCl}{CH}SiMe_2OEt \xrightarrow{H_2O} \underset{73\%}{i\text{-}PrCH_2CH_2SiMe_2OEt}$$

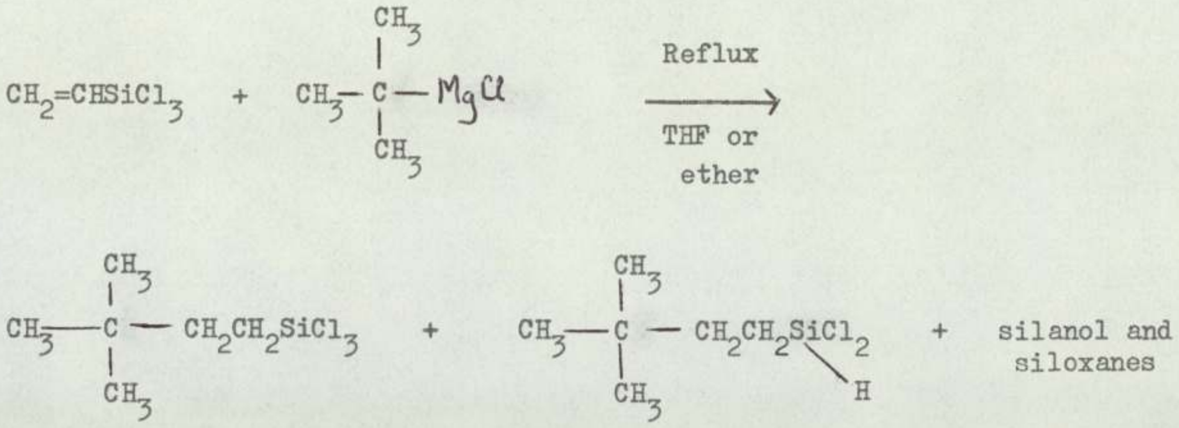
Alkoxysilanes and chlorosilanes generally undergo displacement reactions with organomagnesium compounds. However, these investigators obtained only addition products when mono and dialkoxyvinylsilanes were treated with secondary and tertiary Grignard reagents but obtained a mixture of addition and substitution products when trialkoxyvinylsilanes were treated in a similar manner. They observed that with the monochlorovinylcompounds the addition/substitution processes depended on the Grignard reagent used.

Although we were aware of the work of Spialter on the addition of Grignard reagents to vinylsilanes, we investigated initially the reaction of vinyltrichlorosilane with tert-butylmagnesium chloride and isopropylmagnesium bromide as a possible route to sterically hindered vinylsilanes. It seemed possible that with vinyltrichlorosilane itself we might be able to introduce one or even two tert-butyl or isopropyl groups, since two bulky cyclohexyl groups can be introduced into a molecule such as phenyltrichlorosilane by use of excess cyclohexylmagnesium chloride.[6] Steric hindrance only arises with the third cyclohexyl group.

When vinyltrichlorosilane was treated with excess isopropylmagnesium bromide, the major products of the reaction were identified as a mixture of 2-methylbutylisopropyldichlorosilane and 2-methylbutylisopropylchlorosilane together with some silanol and siloxanes.



Again, when vinyltrichlorosilane was treated with excess tert-butylmagnesium chloride, the major products of the reaction were identified as 2, 2-dimethylbutyltrichlorosilane and 2, 2-dimethylbutyldichlorosilane together with some silanol and siloxanes.



$$CH_2{=}CHSiCl_3 + CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}MgCl \xrightarrow[\text{THF or ether}]{\text{Reflux}} CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2CH_2SiCl_3 + CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2CH_2SiCl_2H + \text{silanol and siloxanes}$$

No starting material was recovered from either of these reactions. Clearly what we observed is addition, substitution and reduction occurring as competing processes. Spialter and co-workers only observed addition/substitution or additionalthough they were dealing with disubstituted alkoxy or chlorovinylsilanes.

In the reaction of vinyltrichlorosilane with isopropylmagnesium bromide the addition/substitution processes appear to occur to the same extent, with reduction occurring to less than 15%. On the other hand, in the reaction of vinyltrichlorosilane with tert-butylmagnesium chloride no substitution was observed but rather addition of the tert-butyl group to the vinyl group. Again reduction occurred to less than 15%. These observations would suggest that the addition process predominates in the above reactions and if this is the case, then the resistance to substitution can be explained.

When trichlorosilane is treated with isopropylmagnesium bromide in ether only two isopropyl groups are introduced even when the Grignard reagent is in excess.[7] Thus, if addition of the isopropyl group to the vinyl group occurs as a first step in the reaction,

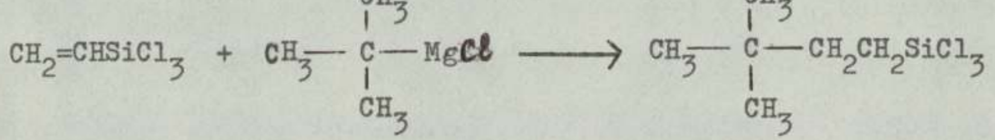
$$CH_2{=}CH_2SiCl_3 \quad + \quad i\text{-}PrMgBr \longrightarrow Me_2CHCH_2CH_2SiCl_3$$

it would seem unlikely that more than one isopropyl group could now be introduced into the molecule already carrying one sterically hindered group.

The lack of substitution in the reaction of tert-butylmagnesium chloride with vinyltrichlorosilane can be similarly explained. There is even greater hindrance to the introduction of the tert-butyl group than to the isopropyl group; tert-butyl-lithium at 70° is necessary for the introduction of two such groups.[8]

$$\text{t-BuSiCl}_3 \quad + \quad \text{t-BuLi} \quad \longrightarrow \quad \text{t-Bu}_2\text{SiCl}_2$$

Thus with addition of the tert-butyl group to the vinyl group,



$$CH_2{=}CHSiCl_3 \; + \; CH_3\!-\!\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\!-\!MgCl \;\longrightarrow\; CH_3\!-\!\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\!-\!CH_2CH_2SiCl_3$$

no substitution is possible in this molecule now carrying such a large group.

The ease with which these sterically hindered Grignard reagents add to vinylsilanes is rather surprising. These additions could be explained by the activating effect of the chloro group since its large -I effect would reduce the electron density at silicon, thereby increasing the atom's tendency to accept electron density from the vinyl group via backbonding. If a methylene group is attached between the olefinic function and silicon no addition occurs. In this case no $d\pi - p\pi$ backbonding is possible. Backbonding is quite an important factor in the chemistry of silicon[9,10] and there is spectral support for $d\pi - p\pi$ interaction between the olefinic function and silicon of vinylsilanes.[11-12]

The reaction of a Grignard reagent with a chlorosilane is thought to proceed by nucleophilic attack at silicon via a trigonal bipyramidal pentacoordinate intermediate. This intermediate is depicted as having the chlorine and the entering groups occupying the axial positions. The R group of the Grignard reagent would then be in close proximity to a silicon bonded vinyl group, allowing either vinyl addition or displacement to occur from a common mechanistic pathway. Most displacement reactions involving chlorosilanes proceed with inversion of configuration.[13a]

These additions seem to depend on the following factors:

a) The nature of the Grignard reagent.

b) The olefinic function must be attached directly to the silicon atom.

c) Activating groups should also be attached to the silicon atom.

The reduction of the chloro group on vinylchlorosilanes by sterically hindered Grignard reagents has not been previously observed. However, reduction of the last chloro group of chlorosilanes by sterically hindered Grignard reagents has been observed in the past.

In 1933 Cusa and Kipping[14] were the first to report that on treating phenyltrichlorosilane with cyclohexylmagnesium bromide, phenyldicyclohexylsilane was obtained. These investigators suggested that dicyclohexylphenylsiliconmagnesium bromide was formed as an intermediate which upon hydrolysis gave dicyclohexylphenylsilane.

$$C_6H_5SiCl_3 + 2C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2C_6H_5SiCl + 2MgBrCl$$

$$(C_6H_{11})_2C_6H_5SiCl + C_6H_{11}MgBr \longrightarrow C_6H_{11}Cl + (C_6H_{11})_2C_6H_5SiMgBr$$

$$(C_6H_{11})_2C_6H_5SiMgBr + H_2O \longrightarrow (C_6H_{11})_2C_6H_5SiH + MgOHBr$$

This seems an unlikely explanation as several workers[15] have failed to prepare stable Grignard type silicon-magnesium compounds.

More recently Brook and Wolfe[16] treated triphenylchlorosilane with cyclohexylmagnesium bromide at 100° for 24 hours and obtained 44% triphenylsilane and 22% cyclohexene.

At about the same time Harvey, Nebergall and Peak[17] repeated the work of Cusa and Kipping on the reaction of phenyltrichlorosilane with cyclohexylmagnesium bromide. These workers found that dicyclohexylphenylsilane is formed prior to hydrolysis which shows that Cusa and Kipping's mechanism is not correct. They found that cyclohexene is a reaction product, a fact overlooked by the previous workers. They also found that Grignard reagents containing the cyclopentyl, isopropyl and tert-butyl groups react with phenyltrichlorosilane to form dicyclopentyl, diisopropyl and ditert-butylphenylsilane. This suggests the following scheme:

$$C_6H_5SiCl_3 + 2C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2C_6H_5SiCl + 2MgBrCl$$

$$(C_6H_{11})_2C_6H_5SiCl + C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2C_6H_5SiH + C_6H_{10} + MgBrCl$$

They suggest that a beta hydrogen is involved in the reduction. Additional evidence is provided by the reaction of o-tolylmagnesium bromide and phenyltrichlorosilane where the silicon-chlorine bond is not reduced.

Valade and co-workers[18] studied the reduction of compounds of the type $R_nSi\xi_{4-n}$ ($\xi = Cl, OCH_3$) by organomagnesium compounds at high temperature ($\geqslant 80$). These workers observed that when tetrasubstitution was impossible then reduction occurred to approximately 70%. However, when tetrasubstitution was possible reduction fell to approximately 50%. They also observed that when steric hindrance becomes very pronounced, not only is tetrasubstitution hindered but to some extent so is trisubstitution. Thus with sterically hindered Grignard reagents reduction of the third as well as the fourth labile group can occur.

As a continuation of this work, Valade[19] investigated the reaction of triorganosilanes of the type $R_3Si\xi$ (ξ = Cl or OCH_3) with sterically hindered Grignard reagents at temperatures greater than 100°. They found that the reduction of triorganosilanes $R_3Si\xi$ to silanes R_3SiH by tert-butylmagnesium chloride proceeds by two simultaneous processes: the direct reduction by the organomagnesium and the indirect reduction by magnesium hydride arising from the thermal decomposition of the Grignard reagent.

$$t\text{-}C_4H_9MgCl \longrightarrow \tfrac{1}{2}MgH_2 + \tfrac{1}{2}MgCl_2 + t\text{-}C_4H_{9(-H)}$$

They concluded that in the reduction of a silicon-chlorine bond reduction by magnesium hydride rather than by transfer of a beta hydrogen predominates. These reductions by magnesium hydride are stereospecific and comparable to reductions by lithium aluminium hydride. However, this mechanism applies to reactions carried out at temperatures greater than 100°.

All the reductions discussed so far deal with reductions of the fourth silicon-chlorine bond or possibly with the third as well as the fourth silicon-chlorine bond. What we in fact observed was reduction of the third chloro group in the case of the reaction of vinyltrichlorosilane with isopropylmagnesium bromide and of the second chloro group in the case of the reaction with tert-butylmagnesium chloride. It, therefore, seems that in the reaction of chlorosilanes with sterically hindered Grignard reagents reduction of the fourth chloro group does not necessarily occur.

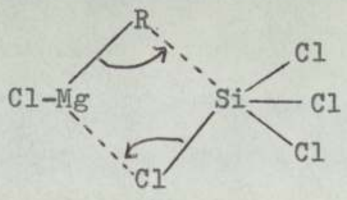
The above observation is supported by the work of Valade et al[20] who studied the reaction of silicon tetrachloride with sterically hindered Grignard reagents. They suggest that these reactions proceed as follows:

$$SiCl_4 \xrightarrow{RMgCl} HSiCl_3 + R_{(-H)} \xrightarrow{RMgCl} RSiHCl_2$$

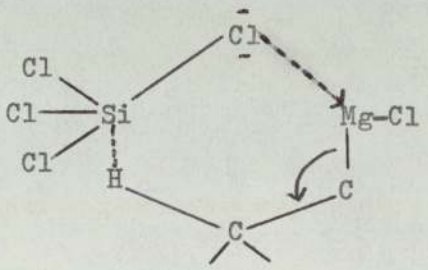
$$\xrightarrow{RMgCl} R_2SiHCl$$

The silicon tetrachloride is first reduced to trichlorosilane and substitution then occurs. They observed that reduction still occurred even if an excess of silicon tetrachloride was employed with the Grignard reagent. They obtained the same product R_2SiHCl on treatment of trichlorosilane with the Grignard reagent RMgCl as on treatment of silicon tetrachloride with the Grignard reagent. This observation suggests that trichlorosilane is indeed formed in the first step. This is an example of reduction occurring at the first silicon-chlorine bond.

These workers conclude that the silicon-hydrogen bond results from competition between the classical substitution reaction (a) and the hydrogen transfer (b).



(a)



(b)

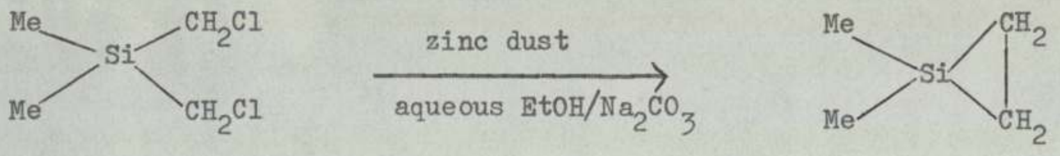
The more unfavourable (a) becomes the more likely that reduction (b) will occur. When R is small the carbon-magnesium bond is not efficiently protected and results only in substitution taking place. However, when R becomes too cumbersome mechanism (a) is inhibited and only mechanism (b) is observed.

Similar reductions with sterically hindered organolithium compounds have also been observed. These reductions will be discussed later.

Thus the reaction of vinyltrichlorosilane with sterically hindered Grignard reagents has been observed to proceed with substitution, addition and reduction occurring as competing processes. The reduction of the silicon-chlorine bond takes place at the second or third silicon-chlorine bond contrary to previous observations where reduction took place at the fourth silicon-chlorine bond.

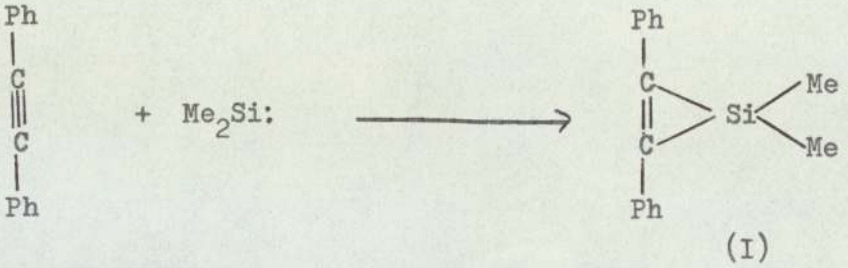
II. Attempted preparation of Silacyclopropanes

Many reports of unsuccessful attempts to prepare compounds containing a silacyclopropane or propene ring may be found in the literature. Roberts[21] attempted to synthesize 1,1-dimethylsilacyclopropane by treating bis(chloromethyl)dimethylsilane with zinc dust.



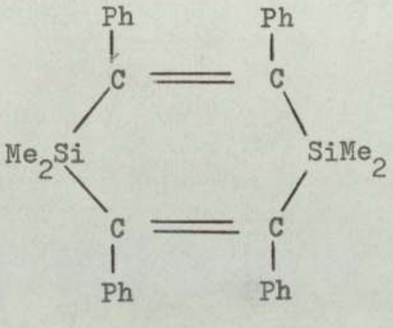
Cyclopropanes are normally generated under the above conditions. However, Roberts obtained chloromethyltrimethylsilane and a small amount of tetramethylsilane.

Some years ago, Vol'pin et al[22] predicted that silacyclopropenes should be a stable class of organosilicon compounds on the basis of anologies to the cyclopropenium cation. However, the initial claim by these workers that they had prepared 1,1-dimethyl-2,3-diphenyl-1-silirene (I) by addition of dimethylsilylene to diphenylacetylene was later disproved.



(I)

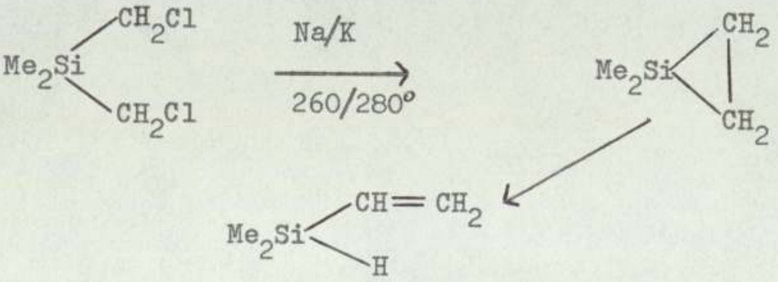
The highly stable product of their reaction was shown to be the dimer (II).[23]



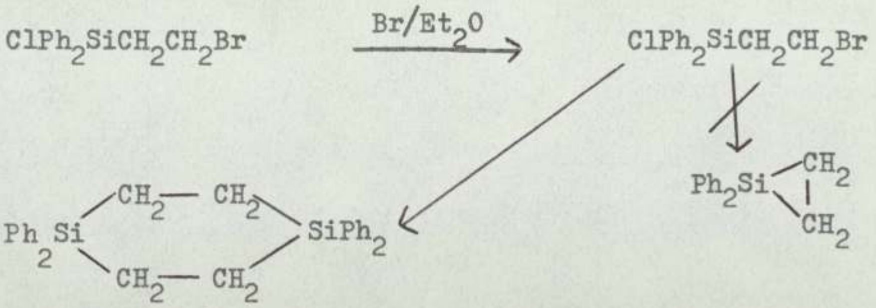
(II)

Conolly and Urry[24] studied the Wurtz reaction of chloromethyltrimethylsilane in a variety of solvents. To account for some of their products, they suggested that 1,1-dimethylsilacyclopropane was formed as an intermediate although the compound was not isolated.

Skell and Golstein[25] studied the vapour phase reaction of bis(chloromethyl)dimethylsilane with sodium/potassium. To account for the presence of vinyldimethylsilane in the products, 1,1-dimethylsilacyclopropane was suggested as an intermediate.



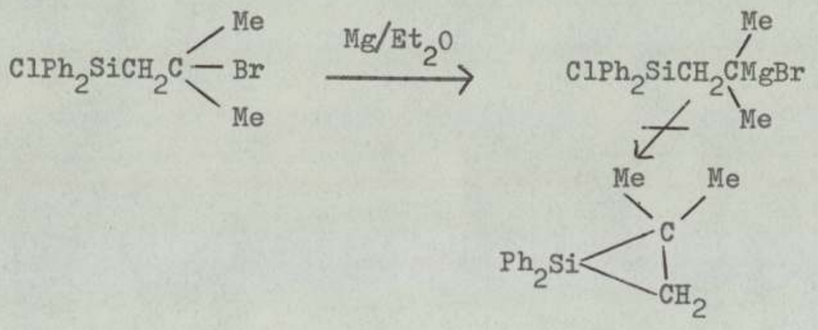
Subsequently, Rowley[26] attempted to prepare silacyclopropanes by the cyclisation of a Grignard reagent. He reacted (2-bromoethyl)diphenylchlorosilane with magnesium in ether.



(I)

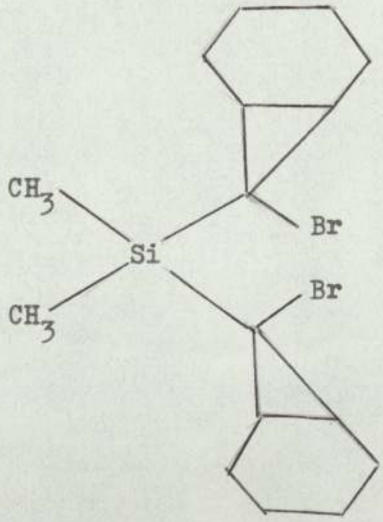
He did not obtain 1,1-diphenylsilacyclopropane but obtained the cyclic dimer (I).

He also attempted the cyclisation of (2-bromo-2-methylpropyl)-diphenylchlorosilane with magnesium in ether.



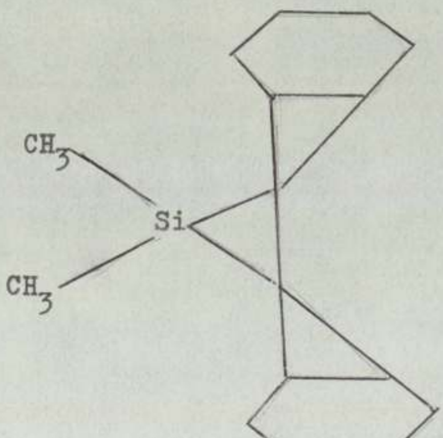
He did not obtain 1,1-diphenyl3,3-dimethylsilacyclopropane but obtained instead a mixture of products.

In 1972 Seyferth[27] prepared the first silacyclopropanes i.e. the substituted 7-siladispiro[2.0.2.1] heptanes. He achieved the synthesis of dispirobicyclo[4.1.0]heptane-7-2'-silacyclopropane-3'-7''-bicyclo[4.1.0]heptane by treating dimethyldichlorosilane with the lithium compound from 7,7-dibromobicyclo[4.1.0.] heptane. He obtained the following silane (I) from the reaction.



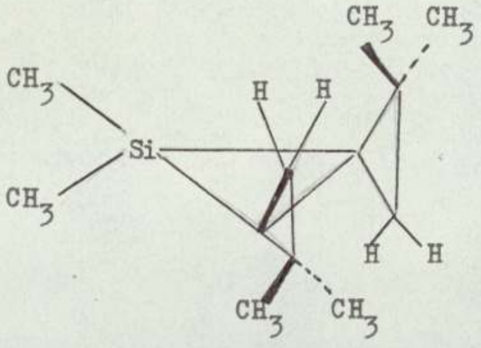
(I)

Treatment of silane (I) in T.H.F. with an excess of magnesium afforded the highly strained silacyclopropane (II).

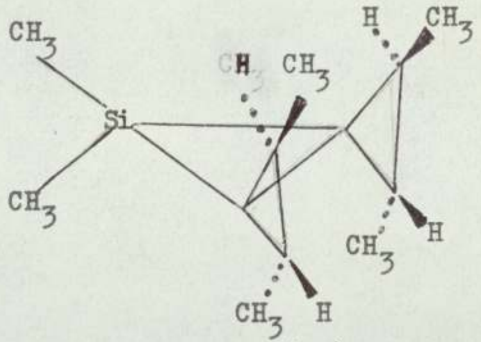


(II)

He was also able to synthesise two other silacyclopropanes in the series. The reaction of the lithium reagents from 1,1-dibromo-trans-2,2-dimethylcyclopropane and 1,1-dibromo-trans-2,3-dimethylcyclopropane with dimethyldichlorosilane afforded the silacyclopropanes (III) and (IV).



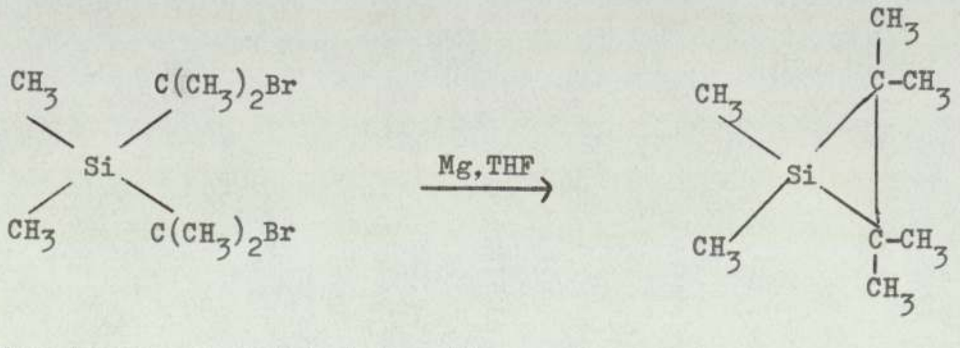
(III)



(IV)

Subsequent investigations indicated that these compounds were quite stable thermally but were exceptionally reactive. Thus compound III, whose chemistry was studied in some detail, was shown to react exothermally at room temperature with reagents which do not normally attack the silicon-carbon bonds of larger silacycloalkanes, such as atmospheric oxygen, water, alcohols, ammonia, hydrogen sulphide and carbon tetrachloride.[27,28] The high reactivity of the silicon-carbon bonds of silacyclopropane is most probably due to the angle strain in the $Si-C_2$ ring.

Seyferth[29] also prepared hexamethylsilirane, a simple isolable silacyclopropane. This synthesis was achieved by treating dimethylbis(α-bromoisopropyl)silane with magnesium in T.H.F.



Thus having established that the synthesis of silacyclopropanes is possible and that it produces a stable class of compound, substituted silacyclopropenes[30] were also synthesised. The syntheses of silacyclopropenes was based on the original reaction of Vol'pin.[22] Seyferth has recently reviewed the preparation and properties of silacyclopropanes.[31]

In the light of these results, it was decided that cyclisation of a Grignard reagent might still be a possible synthetic route to silacyclopropanes provided that the silicon atom carried sterically hindered groups. To this end, beta-halogeno compounds were prepared with two large substituents on silicon as well as a functional group.

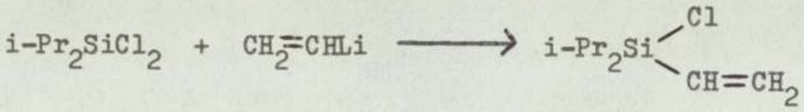
Difficulties were encountered in the syntheses of these compounds, not only because of the competing addition/substitution reaction between vinyltrichlorosilane and sterically hindered Grignard reagents but also because of problems of identification of the isopropyl group in the N.M.R. Thus the desired starting materials were prepared as follows, starting from silicon tetrachloride.

(2-bromoethyl)diisopropylchlorosilane.

Silicon tetrachloride was treated with isopropyllithium in petroleum ether.

$$SiCl_4 + i\text{-}PrLi \longrightarrow i\text{-}Pr_2SiCl_2$$

The diisopropyldichlorosilane produced was then treated with vinyllithium in ether.



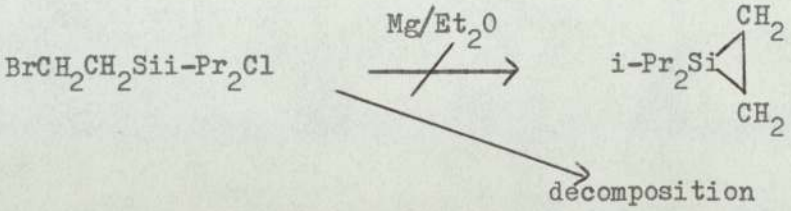
$$i\text{-}Pr_2SiCl_2 + CH_2{=}CHLi \longrightarrow i\text{-}Pr_2Si\begin{matrix}Cl\\ CH{=}CH_2\end{matrix}$$

and finally, hydrogen bromide was bubbled into a solution of diisopropylvinylchlorosilane in carbon tetrachloride.

$$CH_2{=}CHSii\text{-}Pr_2Cl \xrightarrow{HBr} BrCH_2CH_2Sii\text{-}Pr_2Cl$$

The problems of identification of the isopropyl group in the N.M.R.

will be discussed later. Cyclisation of (2-bromoethyl)diisopropylchlorosilane was attempted but there was, however, no indication that the Grignard had been formed. In fact, on treatment of the silane with magnesium in ether, the compound decomposed.



Identification of the decomposition products was not attempted.

(2-bromoethyl)ditert-butylchlorosilane.

This compound was similarly prepared. Ditert-butyldichlorosilane was prepared by the method of Tyler, Sommer and Whitmore.[32] Commercial tert-butyllithium in pentane was used as attempts to prepare tert-butyllithium using lithium wire or a lithium dispersion were unsuccessful.

$$\text{SiCl}_4 + \text{t-BuLi} \longrightarrow \text{t-BuSiCl}_3 + \text{LiCl}$$

$$\text{t-BuSiCl}_3 + \text{t-BuLi} \longrightarrow \text{t-Bu}_2\text{SiCl}_2 + \text{t-BuSiCl}_3 + \text{t-Bu}_2\text{SiClH}$$

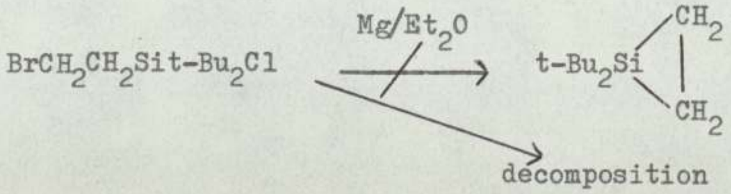
However, the fact that reduction as well as substitution occurred on treatment of tert-butyltrichlorosilane with excess tert-butyllithium is a fact overlooked by Whitmore and co-workers. The ditert-butyldichlorosilane was subsequently treated with vinyllithium in ether.

$$\text{t-Bu}_2\text{SiCl}_2 + \text{CH}_2{=}\text{CHLi} \longrightarrow \text{t-Bu}_2\text{SiCH}{=}\text{CH}_2\text{Cl}$$

Finally hydrogen bromide was bubbled into a solution of ditert-butylvinylchlorosilane in carbon tetrachloride.

$$\text{t-Bu}_2\text{SiCH}{=}\text{CH}_2\text{Cl} \xrightarrow{\text{HBr}} \text{BrCH}_2\text{CH}_2\text{Sit-Bu}_2\text{Cl}$$

Cyclisation of (2-bromoethyl)ditert-butylvinylsilane was attempted. There was no indication that the Grignard reagent had been formed. Once again decomposition occurred on treatment of the silane with magnesium.



No attempt was made to identify the decomposition products. However, what is evident is that sterically hindered (2-halogenoethyl)dialkylchlorosilanes are not suitable materials for the synthesis of silacyclopropanes.

Although the attempts to prepare silacyclopropanes were unsuccessful, the reaction between t-butyltrichlorosilane and tert-butyllithium is both interesting and unexpected. There are several reports in the literature of the reducing action of sterically hindered Grignard reagents on chlorosilanes. However, at the time this investigation was undertaken, the only report of the reducing action of a sterically hindered organolithium compound is in the reaction between 1-naphthyllithiumsilane with excess 1-naphthyllithium.[33]

$$1\text{-}C_{10}H_7Si(OEt)_3 \;+\; 1\text{-}C_{10}H_7Li \;\xrightarrow[170\ -\ 180°]{\text{Kerosene}}\; (1\text{-}C_{10}H_7)_3SiH$$

In the above example the reduction taking place is of a silicon-ethoxy bond with the reduction taking place at the fourth bond. What we observed was reduction of a third silicon-chlorine bond as in the case of the sterically hindered Grignard reagent.

Subsequent to our observations, two reports appeared in the literature concerning the reducing action of tert-butyllithium.[34,35] These two reports are somewhat conflicting. Spialter and Dexheimer[34] conclude that the ditert-butylchlorosilane arises from the reaction of tert-butyltrichlorosilane with excess tert-butyllithium.

$$\text{t-BuLi} + \text{t-BuSiCl}_3 \longrightarrow \text{t-Bu}_2\text{SiCl}_2 + \text{t-BuSiCl}_3 + \text{t-Bu}_2\text{SiClH}$$

On the other hand Doyle and West[35] suggest that it is the ditert-butyldichlorosilane itself that is reduced by the excess tert-butyllithium. The ditert-butylchlorosilane was obtained in approximately 30% yield by these workers and is consistent with our observations. We feel that it is the dichlorosilane that is reduced rather than the trichlorosilane by the excess tert-butyllithium, since we found that the reaction of ditert-butyldichlorosilane with excess tert-butyllithium produces ditert-butylchlorosilane.

However, some of our observations concerning this preparation are not in agreement with those of Doyle and West. These workers prepared tert-butyllithium by the method of Tyler, Sommer and Whitmore. All our attempts to prepare this compound by the method of Whitmore were unsuccessful even though all precautions were observed. Tert-butyllithium was eventually prepared by using a lithium dispersion containing 2% sodium. It is possible that Doyle and West unknowingly used lithium with a high sodium content. Secondly, they claim that ditert-butyldichlorosilane is inert to substitution as it does not react with methyllithium. We found that ditert-butyldichlorosilane reacts slowly with vinyllithium to yield approximately 15% ditert-butylvinylchlorosilane. Lastly, they found that ditert-butyldichlorosilane is not reduced by lithium aluminium hydride although it is reduced by tert-butyllithium. Lithium aluminium hydride reductions of chlorosilanes are less affected than most reactions of sterically hindered organosilanes[9] so it is surprising that no reduction took place. From our experience of syntheses of asymmetric organosilanes, we have found that different batches of lithium aluminium hydride vary considerably in reducing ability and with some batches we found it difficult even to carry out a simple reduction. Although we have no evidence that this is the case in this reaction, we suggest that the lithium aluminium hydride may be at fault.

Weidenbruch and co-workers[36] have also reported similar reductions with isopropyllithium. On treatment of silicon tetrachloride with excess isopropyllithium, they obtained triisopropylchlorosilane and triisopropylsilane in 24% and 42% yields respectively. They also observed the following:

$$\mathrm{MeSiCl_3 + 3i\text{-}PrLi \longrightarrow Me(i\text{-}Pr)_2SiH\ (79\%)}$$

$$\mathrm{MeSiCl_3 + 2i\text{-}PrLi \longrightarrow Me(i\text{-}Pr)_2SiCl\ \ (74\%)}$$

$$\mathrm{Me(i\text{-}Pr)_2SiCl + i\text{-}PrLi \longrightarrow Me(i\text{-}Pr)_3Si\ (3\%) + Me(i\text{-}Pr_2)SiH\ (68\%)}$$

We observed no reduction on treatment of silicon tetrachloride with isopropyllithium since the lithium compound was not used in excess.

These reductions by sterically hindered Grignard reagents (discussed previously) and organolithium compounds only occur if the compounds possess a beta hydrogen. These reductions can be compared with the reduction of carbonyl compounds by Grignard reagents and the subject has been reviewed by Kharasch and Reinmuth.[3]

III. Preparation of sterically hindered (2-bromoethyl)trialkylsilanes.

Although the solvolysis and reactions of (2-bromoethyl)trialkylsilanes have been the subject of many investigations, the solvolysis and reactions of sterically hindered (2-bromoethyl)trialkylsilanes have not been investigated. To this end, a series of sterically hindered (2-bromoethyl)trialkylsilanes were prepared.

The following compounds were synthesised:

(2-bromoethyl)diisopropylmethylsilane
(2-bromoethyl)triisopropylsilane
(2-bromoethyl)tri-n-propylsilane
(2-bromoethyl)tri-n-butylsilane

The synthesis of (2-bromoethyl)tri-n-butylsilane and (2-bromoethyl)tri-n-propylsilane was straight forward. This was carried out by reacting vinyltrichlorosilane with excess of the appropriate Grignard reagent.

$$CH_2{=}CHSiCl_3 + 3RMgX \longrightarrow CH_2{=}CHSiR_3 + MgClX$$

Hydrogen bromide was then bubbled into a solution of the vinyltrialkylsilane in carbon tetrachloride. (2-bromoethyl)tri-n-butylsilane and (2-bromoethyl)tri-n-propylsilane were found to be very stable. These compounds were in fact kept in a refrigerator for over a year. Analysis indicated that no decomposition had occurred during this time.

Difficulties were encountered, however, with the synthesis of (2-bromoethyl)diisopropylmethylsilane and (2-bromoethyl)triisopylsilane. It will be recalled that when vinyltrichlorosilane was treated with isopropylmagnesium bromide, addition, substitution and reduction occurred as competing processes. The expected products, vinyldiisopropylchlorosilane or vinyltriisopropylsilane, were not isolated. Similar products were also obtained from the reaction of methylvinyldichlorosilane with isopropylmagnesium bromide. Therefore vinyltrichlorosilane is not a suitable starting material for the synthesis of sterically hindered (2-bromoethyl)trialkylsilanes.

The problem with these isopropylsilicon compounds was one of identification of the group by means of N.M.R. The signal for an isopropyl group normally appears in the N.M.R. as a doublet and a septet, however, we observed that this is not the case when isopropyl is attached to silicon. Therefore, some of the intermediate compounds were prepared by more than one route to help with the problem of identification.

(2-Bromoethyl)diisopropylmethylsilane

This compound was prepared by treating methyltrichlorosilane with excess isopropylmagnesium bromide in ether. A mixture of diisopropylmethylchlorosilane and diisopropylmethylsilane was obtained. The preparation was repeated, this time treating methyltrichlorosilane with isopropyllithium. The isopropyllithium was not used in excess and thus only diisopropylmethylchlorosilane was isolated. The two chlorosilanes thus produced had the same boiling points and identical N.M.R. spectra were obtained for these compounds.

$$\text{MeSiCl}_3 + \text{excess i-PrMgBr} \longrightarrow \text{Mei-Pr}_2\text{SiCl} + \text{Mei-Pr}_2\text{SiH}$$

$$\text{MeSiCl}_3 + \text{i-PrLi} \longrightarrow \text{Mei-Pr}_2\text{SiCl}$$

Subsequently diisopropylmethylchlorosilane was treated with vinyllithium in ether and diisopropylmethylvinylsilane isolated.

$$\text{Mei-Pr}_2\text{SiCl} + \text{CH}_2{=}\text{CHLi} \longrightarrow \text{Mei-Pr}_2\text{SiCH}{=}\text{CH}_2$$

The synthesis was completed by bubbling hydrogen bromide into a solution of the pure diisopropylmethylvinylsilane in carbon tetrachloride. The usual distorted triplet arising from $-CH_2Br$ for this class of compounds was observed in the N.M.R. Figure 1 illustrates the N.M.R.

spectra obtained for the synthesis of (2-bromoethyl)diisopropylmethylsilane.

(2-Bromoethyl)triisopropylsilane

The reaction between silicon tetrachloride and isopropyllithium in petroleum ether was found to be a rather messy reaction accompanied by a poor yield. Trichlorosilane was found to be an excellent starting material for the introduction of several bulky groups. Thus the above was prepared by treating trichlorosilane with excess isopropylmagnesium bromide in T.H.F. Triisopropylsilane was isolated in good yield.

$$\mathrm{HSiCl_3} \;+\; \text{(excess) i-PrMgBr} \;\longrightarrow\; \text{i-}\mathrm{Pr_3SiH}$$

A spectrum of triisopropylsilane in carbon tetrachloride with added benzene was also recorded. Aromatic solvents can be used in N.M.R. as shift reagents and this spectrum was recorded in order to obtain a better resolution of the Si-H. However, a spectrum identical to (I) figure 2 was obtained.

Triisopropylchlorosilane was prepared by the addition of chlorine gas into an ice-cold solution of triisopropylsilane in carbon tetrachloride. The addition was followed by G.L.C. and afforded an almost quantitative yield of triisopropylchlorosilane. Subsequently triisopropylchlorosilane was treated with vinyllithium and triisopropylvinylsilane isolated.

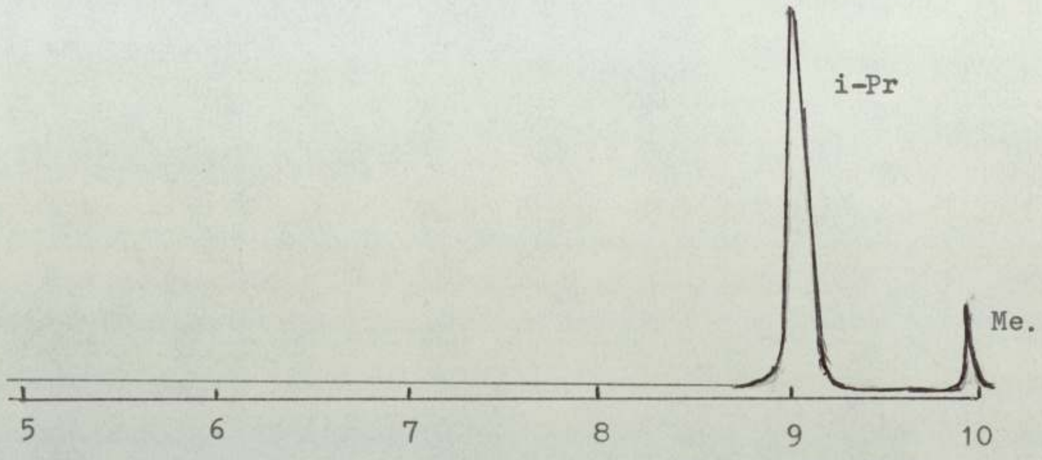
$$\mathrm{iPr_3SiCl} \;+\; \mathrm{CH_2{=}CHLi} \;\longrightarrow\; \mathrm{iPr_3SiCH{=}CH_2}$$

The synthesis was completed by bubbling hydrogen bromide into a solution of the pure triisopropylvinylsilane in carbon tetrachloride. The usual distorted triplet arising from $-\mathrm{CH_2Br}$ for this class of

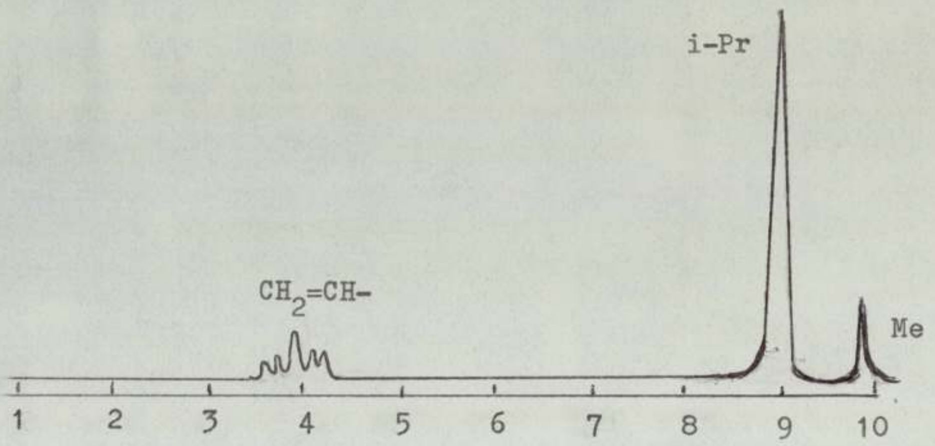
FIG.1.

N.M.R. spectra of isopropylsilanes.

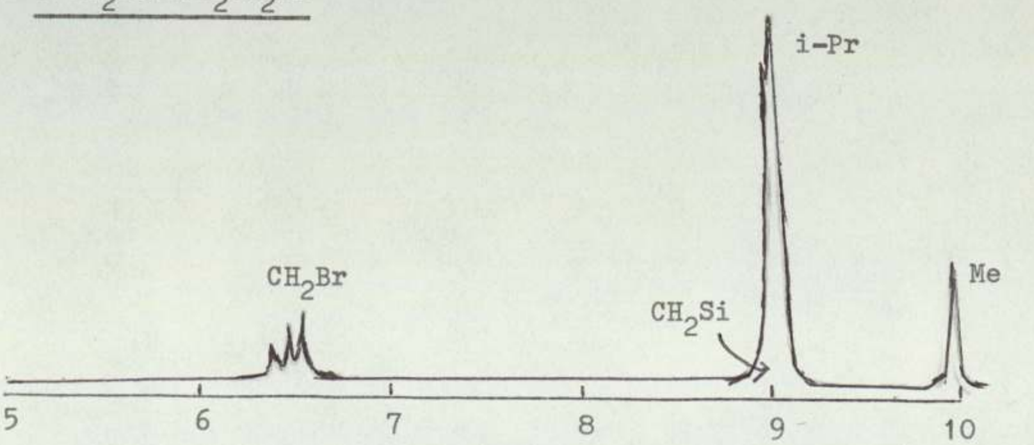
(I) i-$Pr_2MeSiCl$.



(II) i-$Pr_2MeSiCH=CH_2$



(III) i-$Pr_2MeSiCH_2CH_2Br$



compounds was observed in the N.M.R. Figure 2 illustrates the N.M.R. spectra obtained for the synthesis of (2-bromoethyl)triisopropylsilane.

It will be observed from the diagrams in figures 1 and 2 that the signal for the isopropyl group on silicon appears as a singlet at approximately τ 9 in the N.M.R. Only one one occasion during our investigations the isopropyl group had any resemblance to a doublet. The ethyl group on silicon often appears as a singlet in the N.M.R. although this depends on its environment and thus the isopropyl group on silicon appears to behave analogously.

(2-bromoethyl)diisopropylmethylsilane and (2-bromoethyl)-triisopropylsilane appeared to be thermally unstable and decomposed before they were fully investigated. Unfortunately we were unsuccessful with the preparation of the highly hindered betahalogenosilanes. However, from our experience with the isopropylsilanes it is likely that the highly hindered betahalogenosilanes would also be thermally unstable.

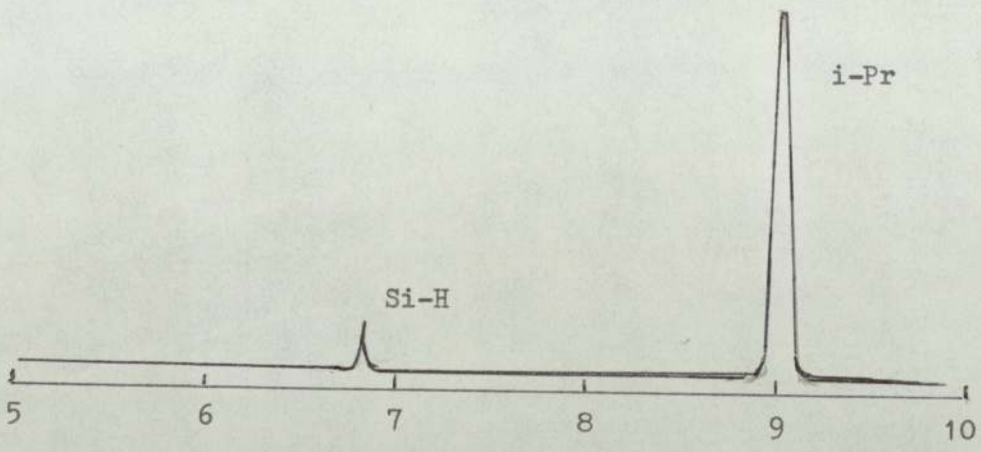
Finally we attempted to synthesise (2-bromoethyl)di-n-butylchlorosilane since we believed that this compound on cyclisation might yield a silacyclopropane. However, we were not able to obtain complete addition of hydrogen bromide to di-n-butylvinylchlorosilane. It seems that in this particular case an equilibrium of addition/elimination was set up. When the original material, di-n-butylvinylchlorosilane, was treated with n-butylmagnesium bromide then tri-n-butylvinylsilane was obtained. This demonstrates that the di-n-butylvinylchlorosilane was not at fault and that some sort of equilibrium set up is responsible for the incomplete addition observed.

Thus, sterically hindered (2-bromoethyl) trialkylsilanes can be

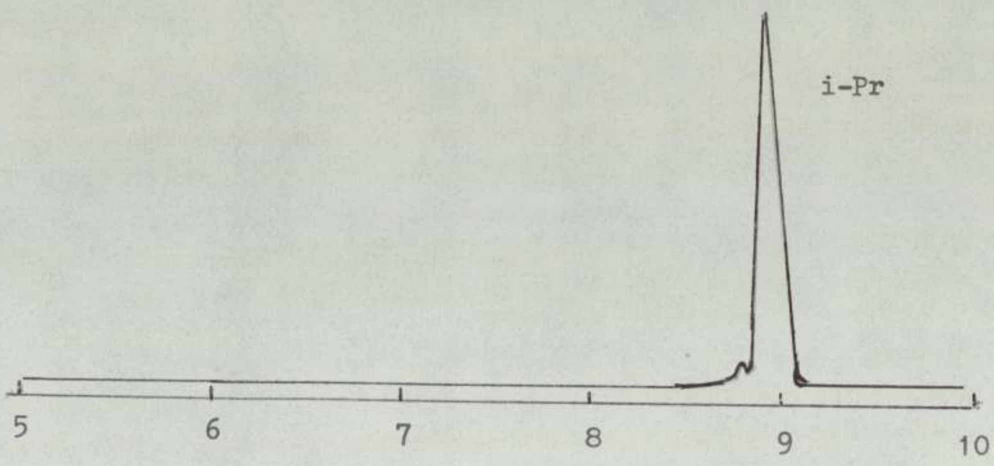
FIG. 2.

N.M.R. spectra of isopropylsilanes

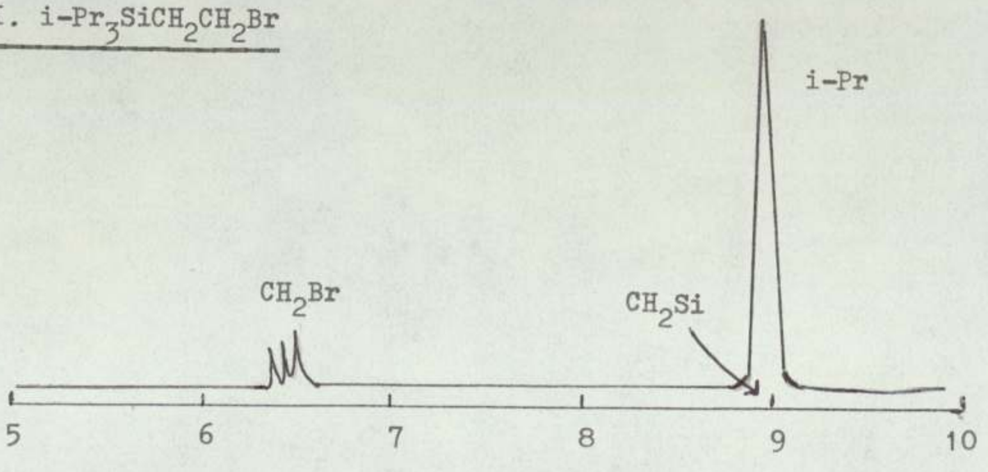
I. i-Pr$_3$SiH



II. i-Pr$_3$Cl



III. i-Pr$_3$SiCH$_2$CH$_2$Br



prepared successfully although they appear to be thermally unstable. On the other hand, (2-bromoethyl)trialkylsilanes carrying "bulky" groups such as butyl can be synthesised very easily. This "bulk" appears to confer on them added stability since these compounds showed no signs of decomposition even after one year.

CHAPTER TWO

REACTIONS OF STERICALLY HINDERED (2-BROMOETHYL)TRIALKYLSILANES

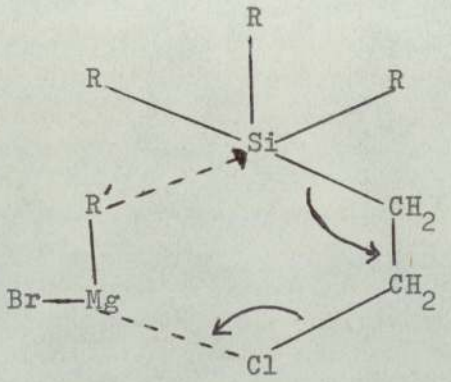
1. Introduction

Interest in the chemistry of beta-halogenoalkylsilanes arose because of their unusual physical and chemical properties in comparison with other halogenoalkysilanes. Many investigators have studied the reactions of beta-halogenoalkylsilanes with various reagents and by way of illustrating the properties of this type of compound some examples will be cited. Ushakov and Itenberg[37] were the first to note the exceptional reactivity of beta-halogenoalkylsilanes $R_3SiCH_2CH_2X$ as compared with the alpha R_3SiCH_2X and gamma-halogenoalkylsilanes $R_3Si(CH_2)_3X$. Later, Sommer and Whitmore[38] carried out a detailed investigation on the reactivity of alpha and beta-halogenoalkylsilanes and found a striking difference in the reactivity of the latter.

Subsequently, Sommer and co-workers[39] found that the reactivity towards basic reagents of chlorine atoms in the beta position differed from those in the alpha position. Thus they observed that the titration of alpha-chloropropyltrichlorosilane and gamma-chloropropyltrichlorosilane with dilute alkali gave titres corresponding to chlorine attached to silicon only, whereas the titration of beta-chloropropyltrichlorosilane gave a titre value corresponding to chlorine attached to silicon and carbon.

As a continuation of this work, Sommer and co-workers[40] studied the reaction of beta-chloroethyltrichlosilane with Grignard reagents.

They found that the stepwise addition of methylmagnesium bromide proceeded smoothly to replace three chlorine atoms. On addition of the fourth equivalent of methylmagnesium bromide, ethylene and tetramethylsilane were formed, instead of the expected n-propyltrimethylsilane. The following cyclic intermediate was proposed to account for the elimination of ethylene.



$$Cl_3SiCH_2CH_2Cl + 4MeMgBr \longrightarrow Me_4Si + CH_2{=}CH_2 + 4MeBrCl$$

Sommer and co-workers[41] also studied the reaction of beta-halogenoalkylsilanes with electrophilic reagents such as aluminium chloride. They showed that these reagents also brought about desilicohalogenation.

$$Et_2ClSiCH_2CH_2Cl \xrightarrow{AlCl_3} Et_2SiCl_2 + CH_2{=}CH_2$$

They also observed the case of thermal elimination of beta-chloroethyltriethylsilane compared with the alpha-chlorinated compound. They suggested that in thermal beta-eliminations "ionic" bond cleavage was involved, but free radical cleavage could not be ruled out. Thus from pyrolysis at 80°, the following were obtained:

$$Et_3SiCH_2CH_2Cl \xrightarrow{80^\circ} Et_3SiCl_3 + CH_2{=}CH_2$$

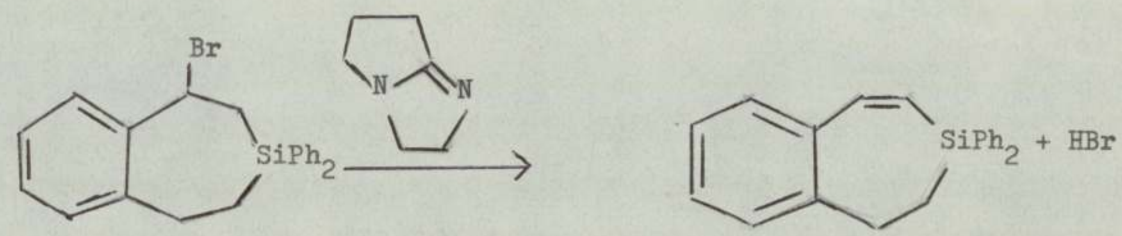
On the other hand, dehydrohalogenation was observed when chloroethyltrichlorosilane was treated with aluminium chloride.

$$Cl_3SiCH_2CH_2Cl \xrightarrow{AlCl_3} Cl_3SiCH{=}CH_2 \qquad (42)$$

similarly

$$Cl_3SiCH_2CHClCH_2Cl \xrightarrow{AlCl_3} Cl_3SiCH_2CH{=}CHCl \qquad (43)$$

It seems that phenyl groups are capable of stabilizing the silicon-carbon bond in the same way as chlorine and preventing desilicohalogenation. This is illustrated by the following reaction:

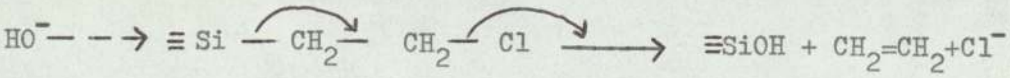


However, in the corresponding compound with methyl groups on silicon, complete desilicohalogenation was observed.[44] The amount of desilicohalogenation thus increases when the electronegative halogen atoms on silicon are replaced by electron donating alkyl substituents.

The beta-halogenoalkylsilanes are so susceptible to nucleophilic attack that they undergo fragmentation in protic solvents.[45]

$$Me_3SiCH_2CH_2Cl \xrightarrow{ROH} Me_3SiOR + CH_2{=}CH_2 + HCl$$

A mechanism for the solvolysis of beta compounds was first proposed by Sommer and co-workers.[40]



$$HO^- \dashrightarrow \equiv Si - CH_2 - CH_2 - Cl \longrightarrow \equiv SiOH + CH_2{=}CH_2 + Cl^-$$

They suggested that the reaction of beta-halogenoalkylsilanes with alkali is analogous to the E2 mechanism for beta-eliminations from alkyl halides. Many mechanisms have been put forward by various workers since Sommer first attempted to formulate a mechanism for the solvolysis of these compounds. The solvolytic reaction is the most thoroughly studied beta-elimination involving organosilicon compounds and will be discussed at length in the next section.

It can be seen from the preceeding examples that the majority of reactions of beta-halogenoalkylsilanes involve cleavage of the silicon-carbon bond and the formation of olefin.

Likewise, the beta-hydroxytrialkylsilanes readily decompose when treated with dilute acid.[45]

$$Me_3SiCH_2CHOHCH_3 \xrightarrow{H^+/H_2O} (Me_3Si)_2O + CH_3CH = CH_2$$

Many compounds such as ketosilanes[46] of the type R_3SiCH_2COR, the corresponding esters,[47] acids[46] and cyanides[48] are readily cleaved by a variety of reagents.

$$Me_3SiCH_2COCH_3 + EtOH \longrightarrow Me_3SiOEt + CH_3COCH_3$$

$$Me_3SiCH_2CN + H_2O \longrightarrow Me_3SiOH + CH_3N$$

In the above examples, the compounds have a double or triple bond in a beta position to the silicon atom. The allylsilanes $R_3SiCH_2CH = CH_2$ and the benzylsilanes $R_3SiCH_2C_6H_5$ have also been observed to show unusual spectral properties and high reactivity towards electrophilic reagents.[49] Reactions involving silicon-carbon bond cleavage have been summarised by Eaborn and Bott[50] and the subject has been reviewed by Jarvie.[51]

It was subsequently observed that the (2-bromoethyl)triphenylsilanes did not behave in a similar manner to the beta-halogenoalkylsilanes. Jarvie and her colleagues[52] from the reaction between (2-bromoethyl)triphenylsilane and magnesium, obtained a stable Grignard reagent $Ph_3SiCH_2CH_2X$. They did not obtain any of the cleavage products normally associated with the reactions of beta-halogenoalkylsilanes.

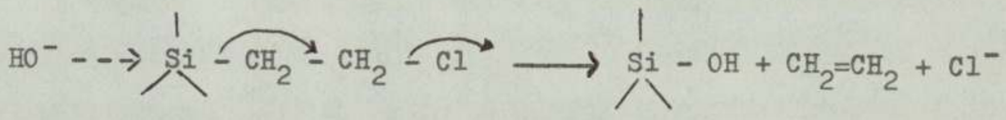
As a continuation of this work, Bourne[53] studied the solvolysis of (2-bromoethyl)triphenylsilane and (2-bromopropyl)triphenylsilane in T.H.F./water. He found that (2-bromoethyl)triphenylsilane was resistant to solvolysis and that (2-bromopropyl)triphenylsilane afforded an almost quantitative yield of the substitution product $Ph_3SiCH_2CHOHCH_3$.

These workers[52,53] attributed the stability of the triphenylsilyl systems mainly to electronic factors although they also considered steric factors. Therefore in order to resolve this problem, a series of sterically hindered (2-bromoethyl)trialkylsilanes was prepared and some reactions were investigated.

Sommer[13] studied the steric effects of substituents on the rates of solvolysis of $R_3SiCH_2CH_2Cl$ compounds. He found that the rates of solvolysis proceed in the order $Me_3Si > Et_2MeSi > PhMe_2Si > (m\text{-}CF_3C_6H_4)Me_2Si$. It is evident that the rate of reaction is slowed down as the size of the substituent on silicon is increased. These solvolytic processes are postulated to occur via a carbonium ion mechanism. If the rate-determining step is the formation of the carbonium ion, Sommer's observation is not in agreement with the carbonium ion theory. However, if formation of the carbonium ion is not the rate-determining step but instead slow attack of the so-formed carbonium ion is rate-determining, then we might expect reaction at carbon to to compete with reaction at silicon. Therefore to determine the validity of the carbonium ion mechanism, the solvolysis of sterically hindered (2-bromoethyl)trialkylsilanes was investigated.

2. The solvolysis of sterically hindered (2-bromoethyl)trialkylsilanes.

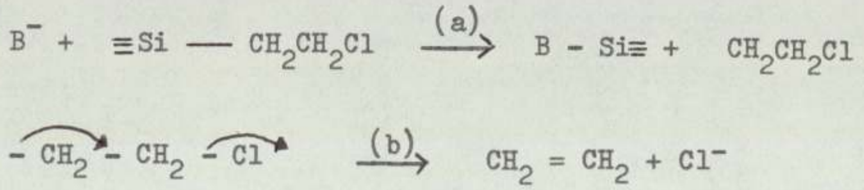
The solvolytic reaction is one of the most thoroughly investigated beta-elimination involving organosilicon compounds. Many mechanisms have been formulated for the solvolysis of beta-halogenoalkylsilanes and these will be presently discussed. Sommer and co-workers[40] were the first to propose a mechanism for the solvolysis of beta-halogenoalkylsilanes.



$$HO^- \dashrightarrow \mathrm{Si} - CH_2 - CH_2 - Cl \longrightarrow \mathrm{Si} - OH + CH_2{=}CH_2 + Cl^-$$

They suggested that the reaction of beta carbon-chlorine bonds with alkali is analogous to the E2 mechanism proposed for beta-eliminations from alkyl halides. The only difference between the two reactions is that the base attacks tetracovalent silicon instead of a combined hydrogen atom.

In a subsequent study of beta-eliminations, Sommer[41] elaborated on his original mechanism.



$$B^- + \equiv\mathrm{Si} - CH_2CH_2Cl \xrightarrow{(a)} B - \mathrm{Si}\equiv + \quad CH_2CH_2Cl$$

$$-CH_2 - CH_2 - Cl \xrightarrow{(b)} CH_2 = CH_2 + Cl^-$$

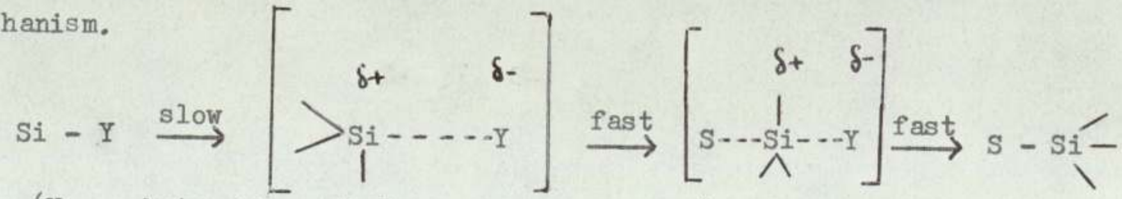
Step (a) which is rate-controlling is aided by an increased concentration of nucleophilic anions (B^-). Thus (a) and (b) were assumed to be effectively simultaneous. This mechanism is also similar to that established for E2 eliminations of ordinary alkyl halides.

Sommer and Baughman[54] whilst trying to establish the existence of siliconium ions carried out quantitative studies of the kinetics of beta-eliminations at silicon. They used compounds of type $(CH_3)_3SiCH_2CH_2Cl(I)$, in which the leaving group is beta-chloroethyl and the silicon carries three organic groups. Solvolysis of compount I in aqueous ethanol at 30° followed a first-order rate law with excellent precision, gave good correlation of variation in rate constant with variation in solvent composition over the range 50% - 80% aqueous ethanol by volume according to the Winstein-Grunwald equation, $\log (k/k_o) = mY$[55] and yielded a value of m, 1·02, which indicated that compound I and tert-butyl chloride are about equally susceptible to the ionizing power of the solvolysis medium. They also concluded from their observations that solvolysis rates of compound I are not sensitive to the nucleophilic character of the solvent, but are strongly dependent on its ionizing power. The approximately equal rate constants in corresponding media of compound I and tert-butyl chloride implied that there is strong participation of electron-release from silicon in the rate-controlling transition state, without simultaneous nucleophilic attack by solvent at the silicon atom. On these grounds and since the Hammett rho factor = -2·15, the following reaction,

$$(CH_3)_3\ SiCH_2CH_2Cl + EtOH + H_2O \longrightarrow (CH_3)_3SiOR + CH_2{=}CH_2 + HCl$$

Where R = H or OEt.

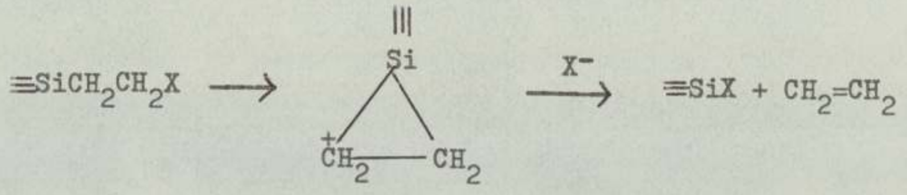
may be described as proceeding by a limiting siliconium ion mechanism.



(Y = beta-chloroethyl, S = Solvent.)

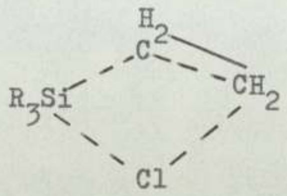
Essentially, cleavage of the carbon-silicon bond is proposed as the rate-determining step with the formation of a carbanion together with a carbonium ion.

Subsequently, Baughman[56] suggested that the initial step in the reaction was the rate-determining cleavage of the carbon-halogen bond. The entropies of activation and Hammett rho factor indicated that in the transition state there was considerable positive change accumulation, relative to the starting state. He essentially proposed a silacyclopropenium type intermediate with cleavage of the silicon-carbon bond occurring in a fast step.



The Hammett rho factor for this reaction was shown to be -2·15, which suggests that electron release enhances the rate of reaction.[13] This evidence supports both mechanisms but does not distinguish between the "limiting siliconium ion mechanism" and the "cyclic mechanism." Baughman also studied the effect of changing the halogen from chlorine to bromine on the base catalysed rate. He observed a seventeen-fold increase of the base-catalyzed rate and suggested that the "limiting siliconium ion mechanism" may not be correct.

Eaborn et al[57] later criticised the results of Sommer and Baughman as inconclusive and capable of many interpretations. They point out that formation of the carbanion $ClCH_2CH_2^-$ is unlikely as solvolytic cleavages of carbon-silicon bonds involving formation of carbanions which are more stable e.g. $Me_3SiC\equiv CPh$ take place more slowly than the decomposition of beta-chloroethyltrimethylsilane and are also strongly base catalysed. They suggested that the ready unimolecular solvolysis of the compound $Me_3SiCH_2CH_2Cl$ is related to the ease of thermal decomposition of beta-chloroalkylsilicon compounds and to the tendency for intramolecular transfer of halogen from carbon to silicon. The gas-phase decomposition of these compounds apparently involves a four-centre unimolecular process, with the following intermediate:



They proposed that the operation of such a process in solution, provided there was change separation in the transition state, would be consistent with Sommer and Baughman's results.

Sommer[13] studied the polar and steric effects of substituents on the rates of some beta-halogenoalkylsilanes.

$$R_3SiCH_2CH_2Cl + R'OH \longrightarrow R_3SiOR' + CH_2{=}CH_2 + HCl$$

These reactions follow a first-order rate law.

$$\frac{-d\left[R_3SiCH_2CH_2Cl\right]}{dt} = k_1\left[R_3SiCH_2CH_2Cl\right]$$

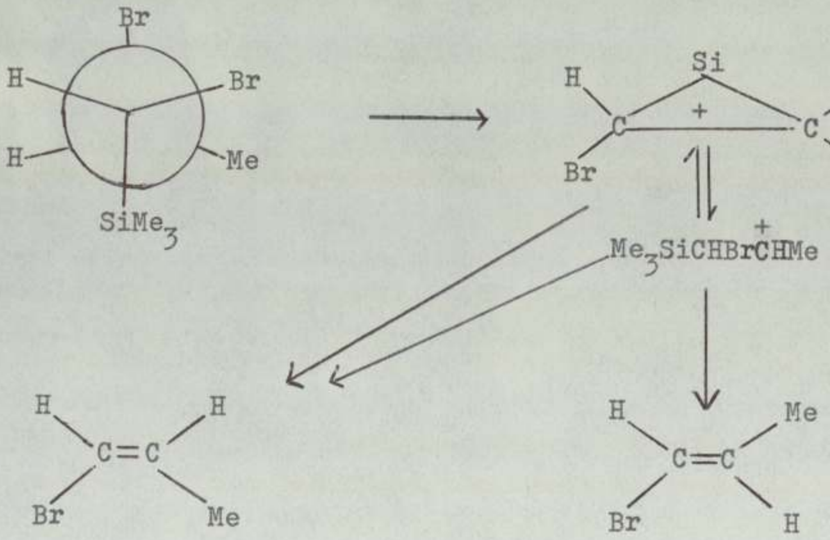
The following was observed.

Structural effects on initially neutral solvolysis rates of $R_3SiCH_2CH_2Cl$ in 70% ethanol at 70 C

R_3Si	Me_3Si	Et_2MeSi	$iPrMe_2Si$	$PhMe_2Si$	$(m\text{-}CF_3C_6H_4)Me_2Si$
k/k_o	1·000	0·955	0·652	0·0955	0·0123

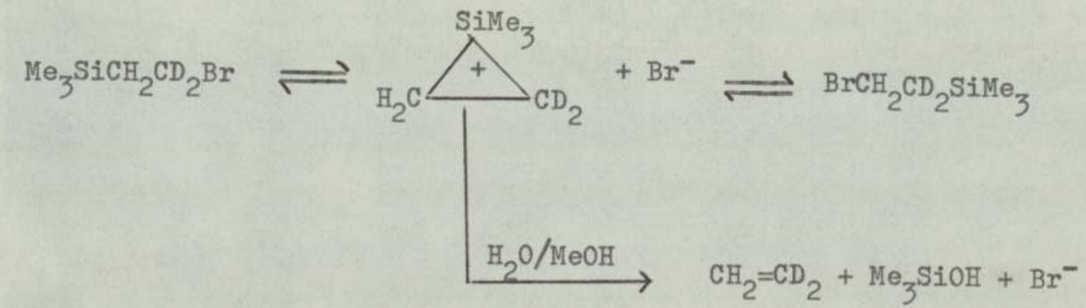
A rho factor of -2·15 was obtained showing that electron-donating groups enhance the rate of reaction. Sommer concluded that steric factors for the reaction series he investigated probably resulted from "steric hindrance to solvation of a developing cationic charge at the silicon atom."

It has been shown by Jarvie and her colleagues[58] that the solvolysis of erythro 1,2-dibromosilane in aqueous ethanol results in highly stereospecific trans-elimination of trimethylbromosilane. The stereospecificity of the reaction decreases with increasing ionic strength of the medium. The predominantly trans elimination observed suggests an E2 mechanism, however, previous kinetic results would suggest an E1 mechanism. To explain the trans stereospecificity, they proposed a mechanism similar to the ones originally postulated by Cram.[59]



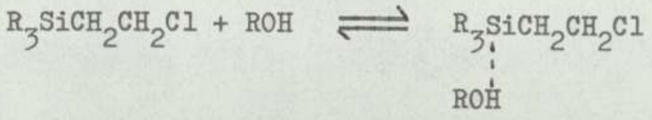
The reaction follows two paths, one involving silicon participation with the developing positive change and trans-elimination, the other involving a classical carbonium ion and non-stereospecific elimination. In the more highly ionic solvents the classical carbonium ion is more stable and a greater proportion of the non-stereospecific products is produced. This mechanism proposed by Jarvie is similar to the cyclic mechanism postulated by Baughman. Jarvie and co-workers obtained further support for the proposal that the rate-determining step involved carbon-halogen cleavage was obtained from a study of secondary deuterium isotope effects.

Further support for the silacyclopropenium ion mechanism is also provided by the work of Eaborn et al.[60] They found that when the solvolysis of the compound $Me_3SiCH_2CD_2Br$ by aqueous methanol is allowed to proceed to about 50% completion, the recovered bromide contains $Me_3SiCD_2CH_2Br$ and $Me_3SiCH_2CD_2Br$ in 1:2 ratio. They conclude that the migration of the Me_3Si group is consistent with a mechanism involving anchimerically assisted ionization of the carbon-bromine bond to give a silacyclopropenium ion.



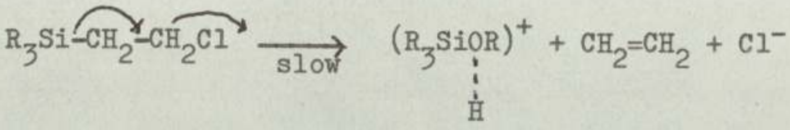
Thus from the preceeding solvolytic reactions discussed, a mechanism has emerged applicable to the simple alkyl substituted beta-halogenosilanes. These processes occur by way of an E1 type mechanism via a carbonium ion intermediate. Studies involving deuterated molecules suggest that a non-classical carbonium ion is formed as a reaction intermediate.

However, Corriu et al[61] studied some eliminations of beta-functional compounds in order to establish the existence of siliconium ions as intermediates in these reactions. They found that the compound $ClCH_2CH_2SiPh_3$ is more resistant to solvolysis and is also thermally stable in comparison with the corresponding trimethyl derivatives. They suggest that if the limiting siliconium ion mechanism were possible, it should be enhanced by the presence of phenyl groups on silicon whereas they observed the opposite. They conclude that the nucleophilicity of the solvent and steric effects are main factors controlling these reactions. They propose the following mechanism, with the silicon atom co-ordinated with the solvent in a pre-equilibrium state:



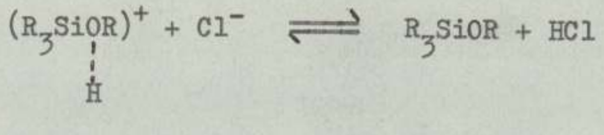
$$R_3SiCH_2CH_2Cl + ROH \rightleftharpoons \underset{\overset{\vdots}{ROH}}{R_3SiCH_2CH_2Cl}$$

(1)



$$R_3Si\text{-}CH_2\text{-}CH_2Cl \xrightarrow[\text{slow}]{} \underset{\overset{\vdots}{H}}{(R_3SiOR)^+} + CH_2{=}CH_2 + Cl^-$$

(2)



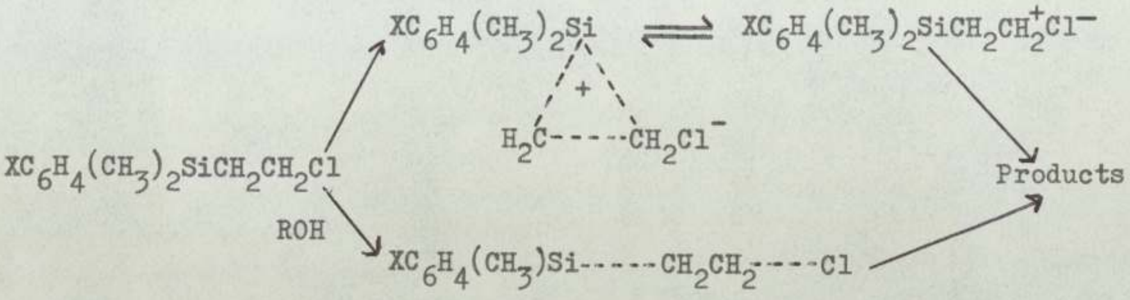
$$\underset{\overset{\vdots}{H}}{(R_3SiOR)^+} + Cl^- \rightleftharpoons R_3SiOR + HCl$$

(3)

According to Corriu and co-workers, the above mechanism takes into account all the previous established observations made for beta-halogenosilanes.

More recently Chvalovsky et al[62] carried out a kinetic study of the solvolysis of (2-chloroethyl)aryldimethylsilanes of the type $XC_6H_4(CH_3)_2SiCH_2CH_2Cl$ (where X = p-CH_3,H,p-F,p-Cl,m-Cl,m-CF_3) in aqueous ethanolic (95-50%) and methanolic (96·8-60%) media at 50°. They found that all members of the series are solvolysed by the same mechanism, except when the solvolytic media used is 96·8% methanol and 95% ethanol, although they observed no change in the kinetics of the reaction.

These investigators suggest that two mechanisms are possible for the solvolysis of these compounds. Both mechanisms proceed via a rate-determining cleavage of the carbon-chlorine bond, but in one case with participation of the solvent and in the other without. The proportion of the solvent-assisted process increases with increasing nucleophilicity of the solvent and with increasing electronegativity of the substituents attached to the aromatic ring. The solvent-assisted process becomes important only in media of low ionizing power especially in the solvolysis of compounds substituted by electronegative groups.



R = H, alkyl.

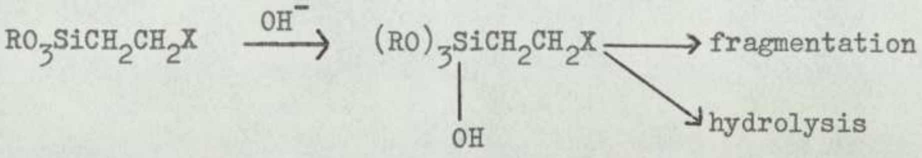
Gregory[63] studied the base and acid catalysed solvolytic fragmentation of (2-halogenoethyl)trialkoxysilanes. He found that the fragmentation of (2-halogenoethyl)trialkoxysilanes involved a two-stage process in which either hydrolysis of the trialkoxysilane or fragmentation of a hydrolysis product is rate limiting, depending on the pH.

At pH > 7, he found that (2-chloroethyl)triethoxysilane reacted 3·8 times slower than (2-chloroethyl)trimethoxysilane, whereas (2-bromoethyl)trimethoxysilane reacted only marginally faster than the corresponding chloro compound. He suggests that at pH > 7, the rate-limiting step does not involve carbon-halide bond cleavage and proposes two mechanisms for the reaction.

(a) The first step in the reaction may be the hydrolysis of the trialkoxysilane, followed by rapid fragmentation of the product.

$$\begin{tikzcd} (RO)_3SiCH_2CH_2X \arrow[r, "kOH'\,\left[OH^-\right]", "slow"'] & (HO)_n(RO)_{n-3}SiCH_2CH_2X \arrow[d, "fast"] \\ & \text{products.} \end{tikzcd}$$

(b) Alternatively, addition of the hydroxide ion to silicon giving a pentacovalent adduct, could be rate limiting. This adduct can undergo either fragmentation or loss of alkoxide, the latter leading to hydrolysis



$$RO_3SiCH_2CH_2X \xrightarrow{OH^-} (RO)_3\underset{\displaystyle OH}{\underset{|}{Si}}CH_2CH_2X \longrightarrow \text{fragmentation},\ \text{hydrolysis}$$

At pH3, he found that the rates of solvolysis of (2-chloroethyl)-trimethoxy and triethoxysilane were the same, whereas (2-bromoethyl)-trimethoxysilane reacted some 13 times faster than the corresponding chloro compound. He suggests that the reaction followed in acid solution is not the solvolysis of the alkoxysilanes but of a common derivative.

$$RO_3SiCH_2CH_2X \xrightarrow{\text{fast}} (HO)_3SiCH_2CH_2X \xrightarrow{\text{slow}} \text{products}$$

These bimolecular fragmentation reactions are similar to the one originally postulated by Sommer for the solvolysis of beta-halogenoalkylsilanes. It is obvious from these results that beta-eliminations involving silicon proceed by more than one pathway, depending on the nature of the silicon substituents and the leaving group on carbon.

However, the effects of phenyl groups on silicon had not been examined until Bourne[53] investigated the reactions of (2-bromoethyl)triphenylsilane and (2-bromopropyl)triphenylsilane in protic solvents. (2-bromoethyl)triphenylsilane was recovered unchanged from a variety of solvolytic media and (2-bromopropyl)-triphenylsilane did not eliminate propylene in tetrahydrofuran/water but instead afforded (2-hydroxypropyl)triphenylsilane in almost quantitative yield.

$$Ph_3SiCH_2CHMeBr \xrightarrow{THF/Water} Ph_3SiCH_2CHMeOH$$

He attributed the stability and the decrease in carbon-silicon bond cleavage to electronic effects. It has already been mentioned that the phenyl group like the trichloro group exerts a stabilizing effect on the carbon-silicon bond. The Cl_3SiCH_2 group is believed to be electron-withdrawing, thus he proposes that likewise the group Ph_3SiCH_2 might also be expected to display electron-withdrawal and lead to a more stable system. The Taft σ^{*}[64] value for the Ph_3SiCH_2 group (+ 0·09) indicates that the group is indeed electron-withdrawing.

It has already been mentioned that the aim of preparing a series of sterically hindered (2-bromoethyl)trialkylsilanes was two-fold.
(a) To determine whether steric or electronic effects are responsible for the stability of the (2-bromoalkyl)triphenylsilanes.
(b) To determine the validity of the carbonium ion theory as applied to the solvolysis of sterically hindered (2-bromoethyl)trialkylsilanes.
To this end, the solvolysis of (2-bromoethyl)methyldiisopropylsilane, (2-bromoethyl)triisopropylsilane , (2-bromoethyl)tri-n-butylsilane and (2-bromoethyl)tri-n-propylsilane was investigated.

(2-bromoethyl)methyldiisopropylsilane and (2-bromoethyl)-triisopropylsilane were treated with methanol/ether and T.H.F./water and the resulting mixtures stirred at room temperature for five hours. Examination of the products indicated that in all cases the compounds were recovered unchanged. Unfortunately we were not able to repeat the experiments in order to determine whether these compounds are resistant to solvolysis, or whether the rate of the reaction was slowed down due to steric hindrance, since these compounds were found to be thermally unstable. Bott and co-workers[57] have suggested that the ready unimolecular solvolysis of beta-halogenoalkylsilanes was related to the ease of thermal decomposition. However, this statement does not support our observations concerning the isopropylsilanes where thermal decomposition is accompanied by a resistance to solvolysis. In this case, steric hindrance by the isopropyl groups is more likely to account for the behaviour of these compounds.

(2-bromoethyl)tri-n-propylsilane was similarly treated with methanol/ether and T.H.F./water mixtures and the expected products obtained.

$$Pr_3SiCH_2CH_2Br \xrightarrow{MeOH/ether} Pr_3SiOMe + CH_2=CH_2 + Br^-$$

$$Pr_3SiCH_2CH_2Br \xrightarrow{THF/Water} Pr_3SiOH + CH_2=CH_2 + Br^-$$

However, it was observed that (2-bromoethyl)tri-n-propylsilane showed a marked resistance to solvolysis since the reaction mixtures had to be refluxed for 24 hours for the reaction to occur.

(2-bromoethyl)tri-n-butylsilane was also similarly treated with methanol/ether and T.H.F./water but in this case the reaction mixture was refluxed for five days for the reaction to proceed to completion. Examination of the resulting mixtures revealed that the expected product had been obtained from the methanol/ether solvolysis.

$$Bu_3SiCH_2CH_2Br \xrightarrow{MeOH/ether} Bu_3SiOMe$$

However, examination of the products obtained from the T.H.F./water solvolysis indicated that this reaction was more complex than expected since the cleavage product hydroxytri-n-butylsilane was obtained together with another compound. G.L.C. analysis indicated the presence of two compounds in the reaction mixture in a ratio of approximately 1:10. The reaction mixture was separated on a silica gel column and the unknown (amounting to approximately 10% of total) established to be another hydroxy compound and probably was

(2-hydroxyethyl)tri-n-butylsilane. Thus with this knowledge we set out to establish the presence of (2-hydroxyethyl)tri-n-butylsilane in the solvolysis product.

(2-hydroxyethyl)tri-n-butylsilane was synthesised and this compound was shown to have the same G.L.C. retention time as the unidentified hydroxy solvolysis product. The unknown was established to be (2-hydroxyethyl)tributylsilane since its I.R. and N.M.R. spectra were identical to those of the known compound.

Thus solvolysis of (2-bromoethyl)tri-n-butylsilane in T.H.F./water affords the substitution product (2-hydroxyethyl)tri-n-butylsilane as well as the cleavage product hydroxytri-n-butylsilane.

$$Bu_3SiCH_2CH_2Br \longrightarrow Bu_3SiOH + Bu_3SiCH_2CH_2OH$$

Clearly this reaction does not follow any of the mechanistic pathways proposed so far.

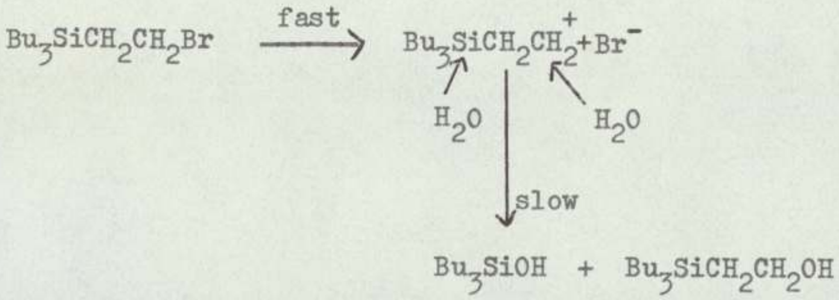
The mechanism proposed by Jarvie and supported by Eaborn suggests that the solvolysis of beta-halogenoalkylsilanes occurs as a two stage process with formation of a silacyclopropenium ion as the rate-determining step followed by rapid attack of this intermediate by the solvent. Clearly this mechanism would not explain the formation of (2-hydroxyethyl)tri-n-butylsilane in the reaction.

On the other hand, the mechanism proposed by Corriu and co-workers should be applicable to the tri-n-butyl system since it is supposed to take into account steric factors. However, simultaneous silicon-carbon and carbon-halide bond cleavage excludes the possibility of obtaining the substitution product from the reaction. Thus this mechanism is not applicable to the solvolysis of sterically hindered beta-halogenoalkylsilanes.

The solvolysis may be solvent assisted as suggested by Chvalovsky and co-workers. However, these workers observed that the solvent-assisted process predominates when beta-halogenosilanes are substituted with electron-withdrawing groups whereas we are dealing with electron-donating groups. This mechanism is also unlikely to provide an explanation for our observations.

Eaborn and co-workers[65] have shown from ab-initio calculations on silyl-substituted alkanes, alkyl-radicals and carbonium ions that the carbonium ion is destabilized by an alpha-silyl group but stabilized by a beta-silyl group in comparison with the carbon analogues. On the other hand, they found that replacement of alpha or beta-methyl by silyl has little effect on the stability of the radicals or alkanes. These workers conclude that the results of these calculations suggest that the relative rates of SN1 solvolysis are largely determined by the relative stabilities of the carbonium ions formed in these reactions.

The products from the solvolysis of (2-hydroxyethyl)tri-n-butylsilane arise from competing reaction at both silicon and carbon. Thus, if the reaction occurs by an initial fast step involving ionization of the carbon-bromine bond and formation of a carbonium ion followed by a slow rate-determining step involving solvent attack of the intermediate, then attack at both carbon and silicon is possible. The carbonium ion formed may or may not be bridged although Eaborn[65] has shown by calculation that a non-classical bridged structure for the $SiH_3CH_2CH_2^+$ cation is more stable than a classical open structure.



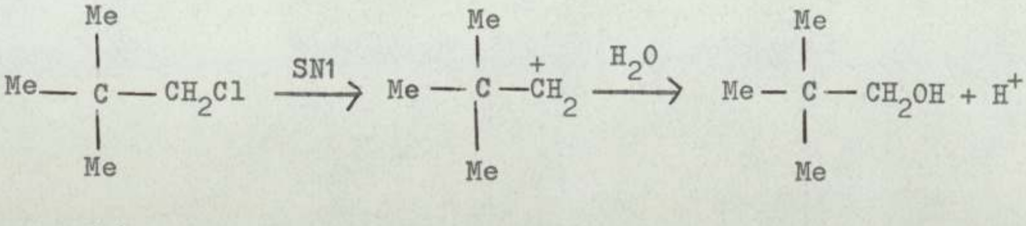
This mechanism allows for the formation of the substitution product as well as the cleavage product.

Kinetic measurements were carried out on (2-bromoethyl)-trimethylsilane, (2-bromoethyl)tri-n-propylsilane and (2-bromoethyl)tri-n-butylsilane. The rates of solvolysis were found to proceed in the order $Me_3SiCH_2CH_2Br$ > $Pr_3SiCH_2CH_2Br$ > $Bu_3SiCH_2CH_2Br$ with (2-bromoethyl)tri-n-butylsilane showing a 200-fold decrease and (2-bromoethyl)tri-n-propylsilane showing a 105-fold decrease in the rate of solvolysis relative to (2-bromoethyl)trimethylsilane.

This investigation of sterically hindered (2-bromoethyl)-trialkylsilanes suggests that beta-halogenoalkylsilanes can follow more than one solvolytic pathway depending on the substituents present on silicon. The carbonium ion mechanism is in agreement with our observations provided that, at least for the sterically hindered compounds, the solvolysis is envisaged as proceeding by a two step mechanism where slow attack of the carbonium ion by the solvent is the rate-determining step. This mechanism would then allow the formation of the cleavage product as well as the substitution product. Our observations also suggest that steric factors rather than electronic factors are responsible for the increased resistance to solvolysis as the size of the substituents on silicon increases although electronic factors should not be overlooked.

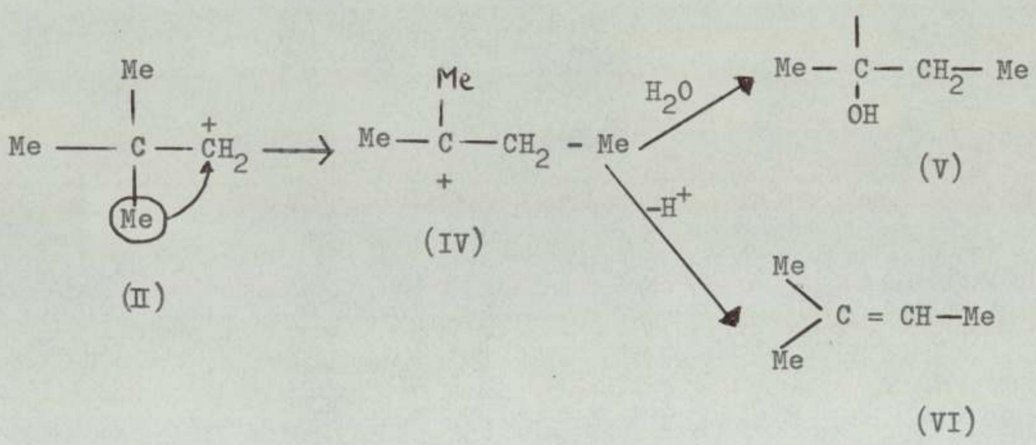
3. Rearrangement of (2-hydroxyethyl -2,2-d_2)tri-n-butylsilane with phosphorus tribromide and thionyl chloride

Rearrangement of carbonium ions are encountered in reactions proceeding with the formation of these ions. For example[66] the hydrolysis of neopentyl chloride (I) under conditions favouring the SN1 mechanism might be expected to yield neopentyl alcohol (III)



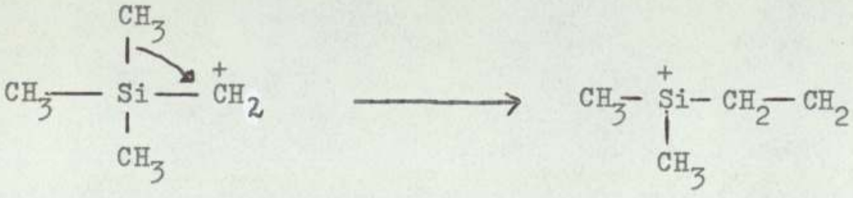
(I) (II) (III)

However, no neopentyl alcohol is obtained, the only alcoholic product is found to be t-amyl alcohol (V); this is due to carbonium ion II rearranging to yield the ion (IV).



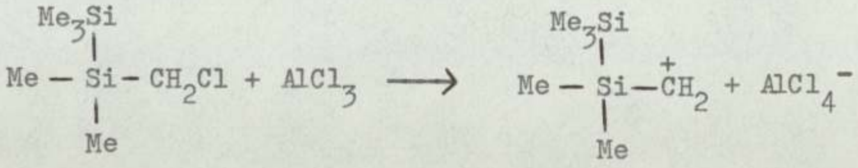
Some of the elimination product (VI) is also obtained. This is an example of the Wagner-Meerwein rearrangement.

Rearrangements involving migration of alkyl,[67,68] aryl[57] and trialkyl[69] groups from silicon to carbon are known. They are analogous to Wagner-Meerwein rearrangements of organic chemistry.

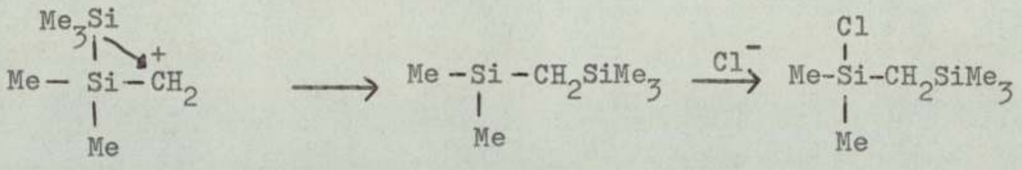


Processes which would be expected to form carbonium-ions with the charge adjacent to silicon lead to rearrangement. Kumada and co-workers[70] observed that the migration of a trimethylsilyl group from silicon to carbon, took place in the presence of aluminium chloride.

$$\mathrm{Me_3SiSiMe_2CH_2Cl \xrightarrow{AlCl_3} Me_2ClSiCH_2SiMe_3}$$

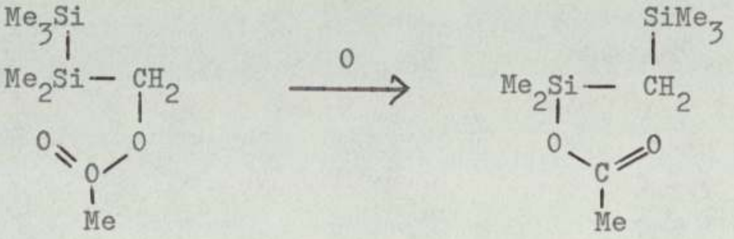


$$\mathrm{Me{-}\underset{Me}{\overset{Me_3Si}{Si}}{-}CH_2Cl + AlCl_3 \longrightarrow Me{-}\underset{Me}{\overset{Me_3Si}{Si}}{-}\overset{+}{C}H_2 + AlCl_4^-}$$



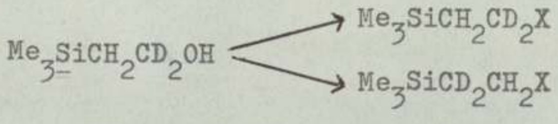
$$\mathrm{Me{-}\underset{Me}{\overset{Me_3Si}{Si}}{-}\overset{+}{C}H_2 \longrightarrow Me{-}\underset{Me}{Si}{-}CH_2SiMe_3 \xrightarrow{Cl^-} Me{-}\underset{Me}{\overset{Cl}{Si}}{-}CH_2SiMe_3}$$

Examples of reactions where migration of the trimethylsilyl group to a beta-carbon takes place are also known, such a process has been observed by Kumada et al.[71] They postulate a cyclic transition state in the 1, 2 migration of the trimethylsilyl group from silicon to carbon.



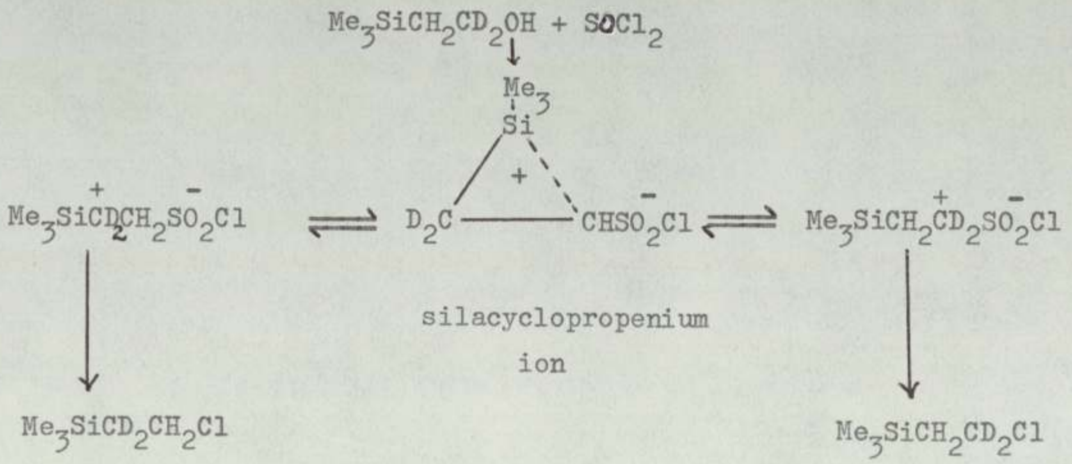
Reactions between alcohols and thionyl chloride or phosphorus bromide are considered to proceed via ion-pair intermediates. These reactions generally proceed without rearrangement, however, in some cases rearrangements have been observed to occur. Roberts and Mazur[72] found that cyclobutanol and cyclopropylcarbinol reacted with thionyl chloride to give mixtures of chlorides, and similar mixtures were obtained from each alcohol. Comparable results were obtained on treatment of the alcohols with phosphorus tribromide. Similar rearrangements were noted by Whitmore and Johnston[73] on treatment of isopropylmethylcarbinol with thionyl chloride to give tert-amyl chloride and by Wallis and Bowman[74] on treatment of 2-methyl-2-phenylbutan-1-ol obtained 1-phenyl-2-chloro-2-methylbutane.

It has been shown by Jarvie and her co-workers[58] that on treatment of (2-hydroxyethyl-2,2-d_2)trimethylsilane with thionyl chloride or phosphorus tribromide, rearrangement occurs and a mixture of isomeric halides is obtained.



X = Cl or Br

The following scheme was suggested to account for the migration observed.



A similar scheme is proposed for the reaction of phosphorus tribromide, in which the ratio of alpha to beta deuterated compounds is identical with that of the reaction with thionylchloride.

In the following discussion, the alpha-deuterated compound refers to the compound which has the deuterium atoms linked to the carbon atom beta to the silicon; whilst the beta-deuterated compound refers to the compound which has the deuterium atoms attached to the carbon atom in the alpha position.

These workers[58] observed that the quantity of alpha-deuterated compound produced (55%) is greater than the quantity of beta-deuterated compound produced. (45%). Roberts and Mazur suggest that the product obtained from a given carbonium ion reaction depends to a large extent on the relative carbonium ion stabilities. Thus it would seem that this reaction does proceed via a carbonium ion and that the product ratio is a reflection of the relative stabilities of the carbonium ions. The higher stability of the alpha-deuterated carbonium ion is not surprising when one considers the greater inductive effect of deuterium and the fact that more effective hyperconjugation is possible with a beta-hydrogen atom than with a beta-deuterium atom.[75]

As a continuation of this work Jarvie and Bourne[76] investigated the reaction of phosphorus tribromide and thionyl chloride with compounds of the type $R_3SiCH_2CD_2OH$ (where R = Me_3, $PhMe_2$, Ph_2Me or Ph_3) and in all these cases they obtained the same proportion of the alpha-deuterated product $R_3SiCH_2CD_2X$ and the beta-deuterated product $R_3SiCD_2CH_2X$.

A similar rearrangement was observed by Eaborn and co-workers[60] when the solvolysis of the bromide $Me_3SiCH_2CD_2Br$ by aqueous methanol was allowed to proceed to 50% completion. They conclude that the migration of the tri-methylsilyl-group is consistent with a mechanism involving anchimerically assisted ionization of the carbon-bromine bond to give a silacyclopropenium ion.

This rearrangement reaction, irrespective of the nature of the carbonium ion intermediate, has been suggested to involve the interaction of silicon with the developing positive charge at the beta-carbon atom. The reaction outlined by Jarvie was repeated with (2-hydroxyethyl-2,2-d_2)tri-n-butylsilane to determine whether butyl substituents on silicon would alter the ratio of the products observed and to establish that the solvolysis of (2-bromoethyl)tri-n-butylsilane proceeds with the formation of a carbonium ion intermediate.

(2-Hydroxyethyl-2,2-d_2)tri-n-butylsilane was synthesised and analysed by N.M.R. The spectrum consisted of a singlet at τ 6.1 of intensity one (due to the proton of the hydroxyl group) and multiplets at τ 8.6, τ 9.0 and τ 9.4 of intensity twelve, eleven and six (due to the tri-n-butylsilyl group and methylene attached to silicon, with absorption of the latter at τ9.0). (2-hydroxyethyl-2,2-d_2)tri-n-butylsilane was treated with thionyl chloride and phosphorus tribromide. Examination of the reaction products by N.M.R. revealed that migration of the tri-n-butylsilyl group had occurred in both cases and thus established that a rearrangement was taking place.

Thus, on reaction of this alcohol with phosphorus tribromide, as well as the expected multiplet between τ 8·6 and τ 9·4 due to n-butyl and methylene on silicon, a singlet at τ 6·4 attributable to ($-CH_2Br$) was observed. Similarly in the reaction with thionyl chloride a singlet at τ6·3 attributable to ($-CH_2Cl$) was also observed. The ratio of the intensity of the singlet to the multiplet was approximately 1:36. The peaks were broadened as is typical of deuterated melecules but no proton spin coupling was observed. The relative intensity of the singlet to multiplet also made it possible to calculate the percentage of each isomer formed. In each case the quantity of alpha-deuterated compound produced (60%) was greater than the quantity of beta-deuterated compound produced (40%). A scheme similar to that proposed by Jarvie may be drawn up except that in this case a bridged ion may or may not be formed.

Thus butyl substitution instead of methyl substitution on silicon has little effect on the quantity of rearranged product observed since approximately the same quantity of alpha and beta compounds were obtained from the reactions. It does, however, provide further evidence that silicon interacts with the developing charge on the beta-carbon atom and suggests that the solvolysis of (2-bromoethyl)tri-n-butylsilane proceeds via a carbonium ion intermediate.

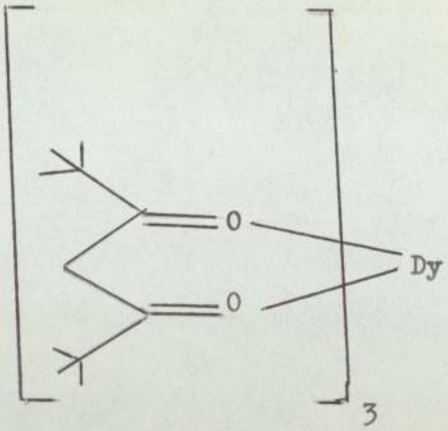
4. The effect of Lanthanide shift reagents on the N.M.R. spectra of (2-hydroxyethyl)tri-n-butylsilane and (2-hydroxyethyl-2,2-d_2)tri-n-butylsilane.

Shift reagents[77] are used in N.M.R. spectroscopy to reduce the equivalence of the nuclei by altering their magnetic environment. There are two types of shift reagents a) aromatic solvents. b) paramagnetic complexes. These complexes function by co-ordinating to suitable donor atoms in the compound under investigation thus expanding their co-ordination shell and forming a new complex in solution.

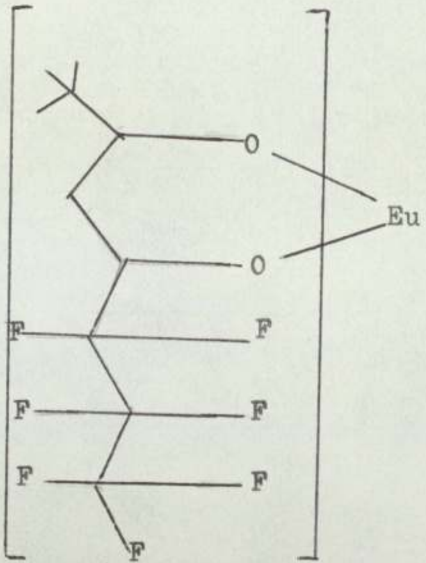
First row transition metal complexes can be used as shift reagents although they exhibit adverse effect on the resolution of N.M.R. spectra by causing severe line broadening. Lanthanide-complexes are used in preference as these produce far less linewidth broadening.

The lanthanide shift reagent basically consists of a six co-ordinate metal complex which readily expands its co-ordination in solution to accept further ligands. The substrate co-ordinates to the lanthanide shift reagent [LSR] because it contains heteroatoms which exhibit some degree of Lewis basicity. A 1:1 complex is thought to be formed between the LSR and the substrate in a normal N.M.R. solvent. The N.M.R. positions of the associated nuclei in the substrate differ from those in the uncomplexed state owing to the magnetic interactions with the metal ion in the complexed substrate. The equilibrium in solution between these species is rapid, so that only a single average signal is recorded for each nucleus in the different environments. The whole spectrum is not just displaced but a differential expansion of the spectrum will be observed due to such factors as the distances of the nuclei from the metal ion. Therefore the main use of [LSR] is in effectively increasing the resolution and in many cases producing first-order spectra.

The N.M.R. spectra of the tri-n-butylsilyl compounds under investigation are rather complex in the region τ 8·0 ——— 10·0. Thus in order to try to obtain a better resolution of this highly complex region, lanthanide shift reagents were initially added to a carbon tetrachloride solution of the undeuterated and deuterated (2-hydroxyethyl)tri-n-butylsilane and the N.M.R. spectra recorded. The reaction between (2-hydroxyethyl-2,2-d_2)tri-n-butylsilane and phosphorus tribromide was repeated, lanthanide shift reagent was added to the reaction mixture in carbon tetrachloride and the N.M.R. spectra recorded. The spectra recorded are shown in figure 3. The two lanthanide shift reagents used were $Dy(dpm)_3$ and $Eu(fod)_3$.



Tris(dipivaloymethanolo-
dysprosium III $Dy(dpm)_3$



Tris(1,1,1,2,2,3,3,-
heptafluoro-7,7-
dimethyl octane-4,6 dionato)
Europium (III) $Eu(fod)_3$

It can be seen from the recorded N.M.R. spectra shown in figure 3 that the use of lanthanide shift reagents with the hydroxy compounds did not produce the expected resolution of their N.M.R. spectra. The spectra obtained in fact were confusing and could not be interpreted. The use of lanthanide shift reagents was therefore discontinued in this investigation.

5. Trapping of the 2-(tri-n-butylsilyl)ethyl cation using the silane hydride transfer reaction.

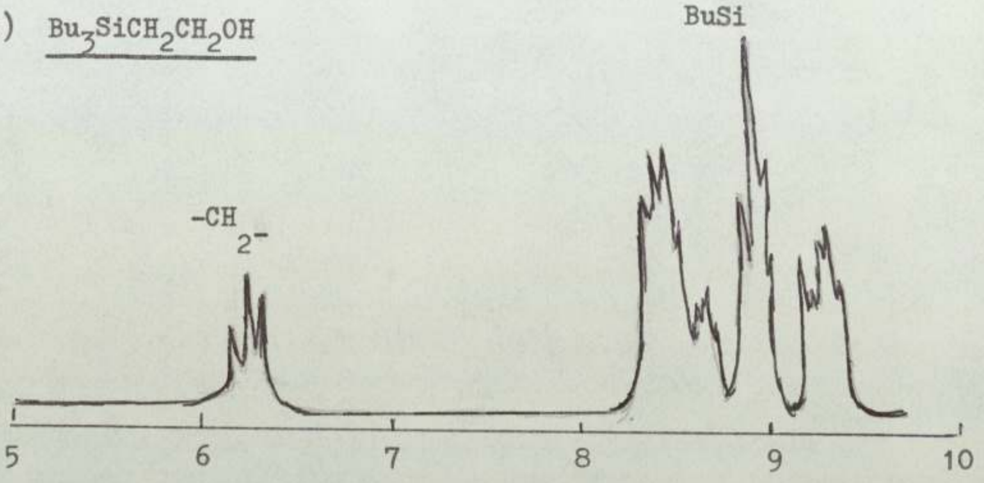
Some carbonium ions containing the triarylmethyl and related cations have been identified by isolation of their crystalline salts (chiefly perchlorates and complex halides). The most widely used technique has been their detection in highly acid media by spectroscopic means. N.M.R., I.R. and U.V. provide evidence for the existence of such species in these solutions. Primary and secondary carbonium ions formed in these media tend to rearrange to the more stable tertiary ions. Therefore most of the recorded carbonium ion spectra are of the tertiary ions.

Since silicon is more electropositive than carbon, silanes are

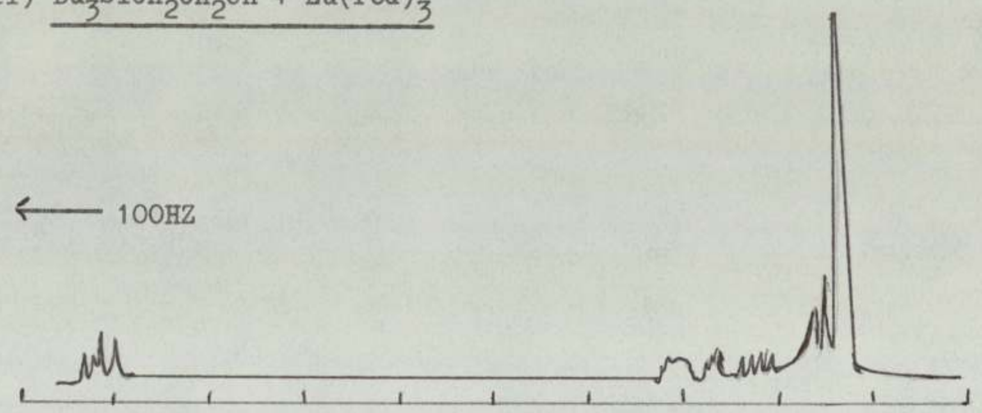
FIG. 3

N.M.R. spectra of (2-hydroxyethyl)tri-n-butylsilane and (2-hydroxyethyl-2,2-d_2)tri-n-butylsilane with lanthanide shift reagents

(I) $Bu_3SiCH_2CH_2OH$



(II) $Bu_3SiCH_2CH_2OH + Eu(fod)_3$



(III) $Bu_3SiCH_2CD_2OH$

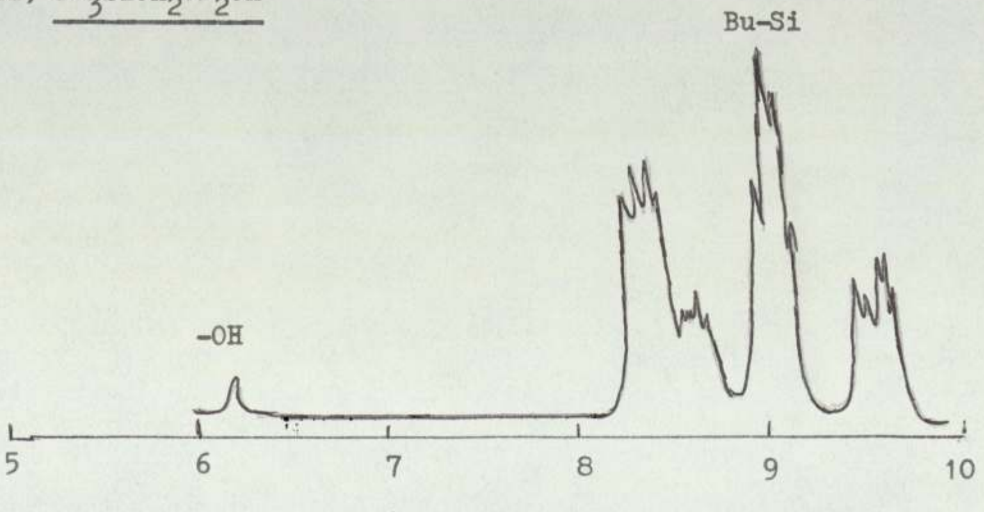
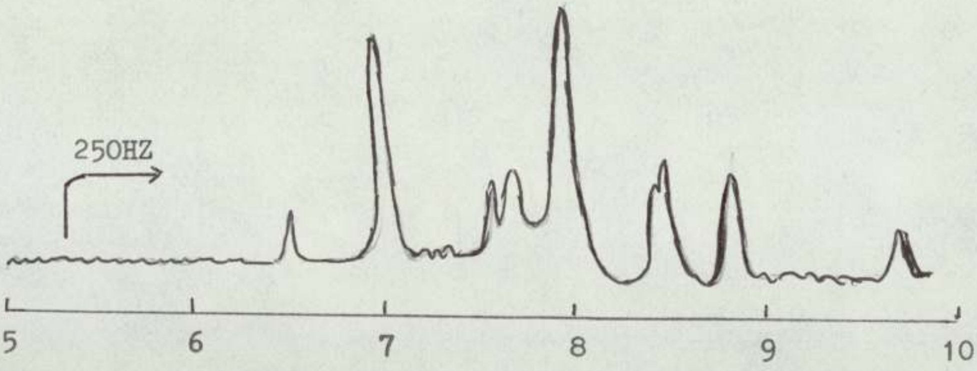
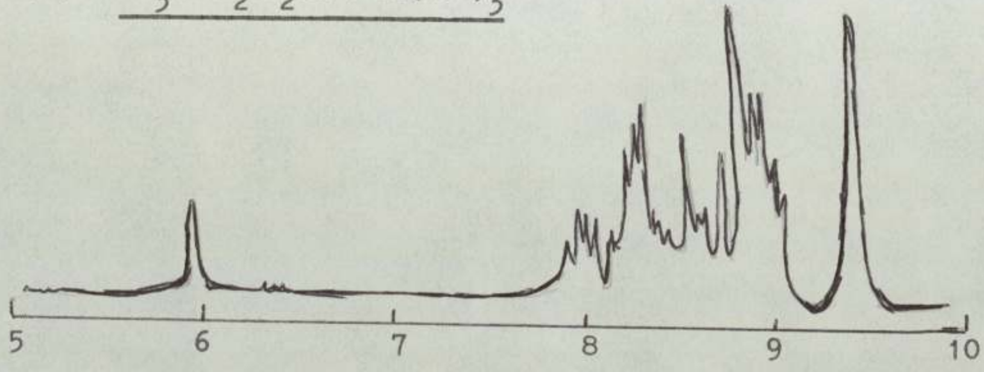


FIG. 3.

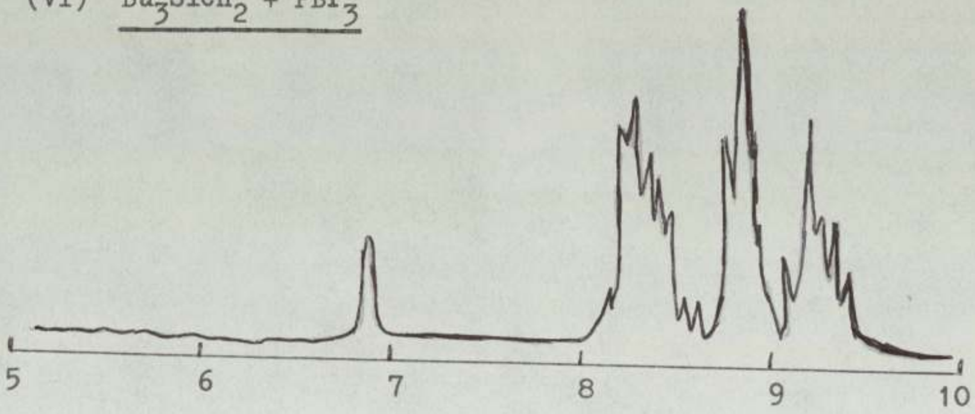
(IV) $Bu_2SiCH_2CD_2OH + Dy(dpm)_3$



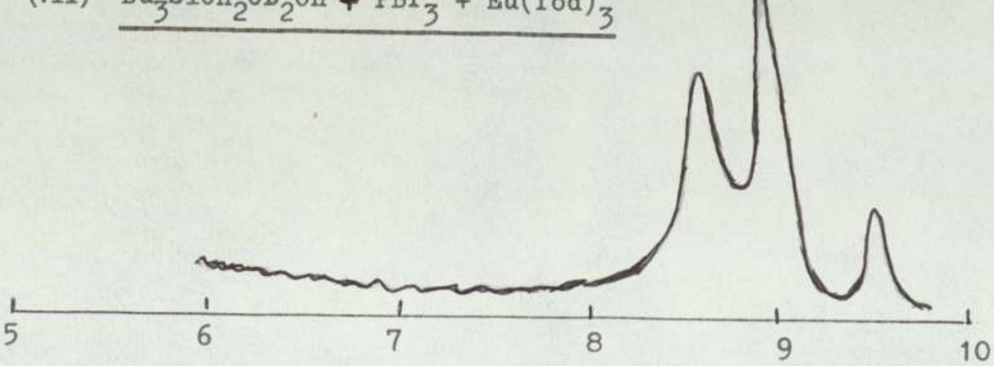
(V) $Bu_3SiCH_2CD_2OH + Eu(fod)_3$



(VI) $Bu_3SiCH_2 + PBr_3$



(VII) $Bu_3SiCH_2CD_2OH + PBr_3 + Eu(fod)_3$



good hydride donors to carbonium ions.

$$(CH_3)_3SiH + (CH_3)_3C^+ \longrightarrow (CH_3)_3Si^+ + (CH_3)_3CH$$

Thus Whitmore et al[78] using silanes as hydride donors obtained n-hexane fron n-hexyl chloride and isopentane from neopentyl chloride. It was observed that in these reactions rearrangement to the more stable carbonium ion had taken place.

More recently, Carey and Tremper,[79,80] using this technique with the appropriate alcohol and trifluoroacetic acid in methylene chloride or chloroform, have generated carbonium ions of the arylmethyl type, some tertiary alkyl and some cyclopropylmethyl cations. They found that under mild conditions only those alcohols which form relatively stable carbonium ions are reduced to the corresponding alkanes. They conclude that this indicates that abstraction from silicon requires a true carbonium ion intermediate. Protonated alcohols or encumbered carbonium ions do not appear capable of abstracting hydrides from silanes.

Bourne[53] used this technique in an attempt to trap the 2-(trimethylsilyl)ethyl cation. He carried out the reaction in methylene chloride and chloroform using (2-hydroxyethyl)trimethylsilane, trifluoroacetic acid and triethyl or triphenylsilane under a variety of conditions. He found that no reaction occurred at -15°C. At higher temperatures, the only products detected were hexamethyldisiloxane and 2-(trimethylsilyl)ethyltrifluoroacetate. He also carried out the reaction using the dideuterated alcohol $Me_3SiCH_2CD_2OH$ and failed to detect structures of the type $Me_3SiCD_2CH_2X(X=OH,OCOCF_3)$, thus providing further evidence that the carbonium ion $Me_3SiCH_2CD_2^+$ had not been formed.

In view of the apparent stabilization of the carbonium ion $Bu_3SiCH_2CH_2^+$, it seemed possible that this ion might be detectable under suitable experimental conditions. Trapping the carbonium ion using the silane transfer reaction still seemed a possible route.

The reaction was carried out using (2-hydroxyethyl)tri-n-butylsilane. Analysis of the products of the reaction carried out at -15° using the alcohol, triisopropylsilane and methylene chloride indicated that no reaction had occurred. Triisopropylsilane was used rather than triphenylsilane or triethylsilane because it was readily available. The reaction was repeated at room temperature and analysis indicated that the reaction mixture consisted of ethyltri-n-butylsilane formed by hydride transfer to the carbonium ion $Bu_3SiCH_2CH_2^+$, the trifluoroacetate ester together with unreacted alcohol.

$$Bu_3SiCH_2CH_2OH \xrightarrow[CH_2Cl_2]{i\text{-}Pr_3SiH/CF_3CO_2H} Bu_3SiCH_2CH_3 + Bu_3SiCH_2CH_2OCOCF_3$$
$$+ Bu_3SiCH_2CH_2OH$$

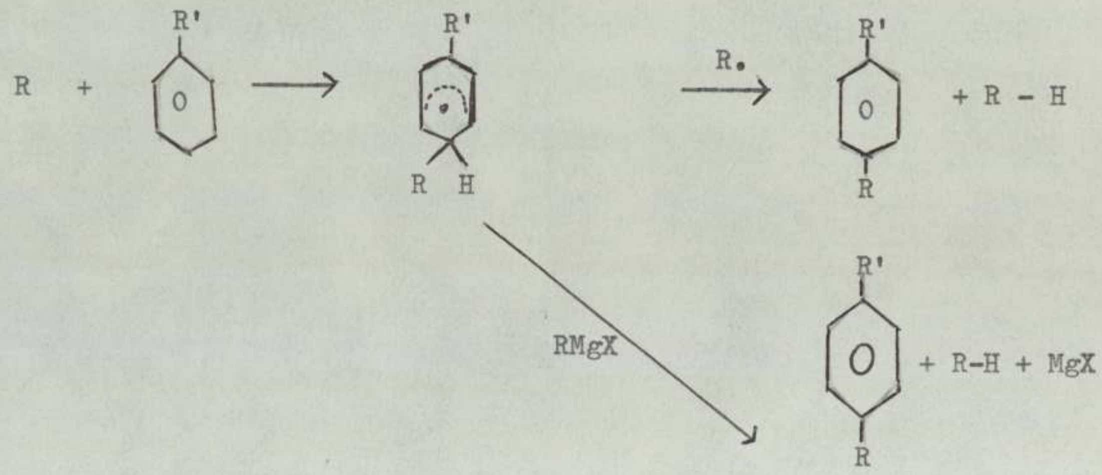
Thus it seems that the 2-(tri-n-butylsilyl)ethyl cation is stable under these reaction conditions and can be trapped. This reaction further establishes that reactions of (2-bromoethyl)tri-n-butylsilane can take place with the formation of a carbonium ion.

6. Reaction of sterically hindered (2-bromoethyl)trialkylsilanes with magnesium.

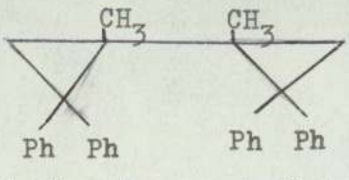
The radical nature of Grignard formation was first suggested by Kharasch and Reinmuth.[3] More recently Walborsky and Aronoff[81] carried out a study of the mechanism of Grignard formation. These workers investigated the interaction of organic halides with magnesium in ether solvents by means of the optically active 1-methyl-2,2-diphenylcyclopropyl halide system, which provides a stereochemical tool for the purpose.

Their results indicate that the reaction proceeds with overall retention of configuration and that the optical purity and yield of the Grignard reagent increases in the order $I < Br < Cl$. They also found that reactions carried out in perdeuterated ethers show that of the processes involved in the generation of the Grignard reagent, solvent cleavage is only of minor importance.

Previous studies on the formation of Grignard reagents in aromatic solvents suggest that the following processes could be occurring on the magnesium surface.[82]

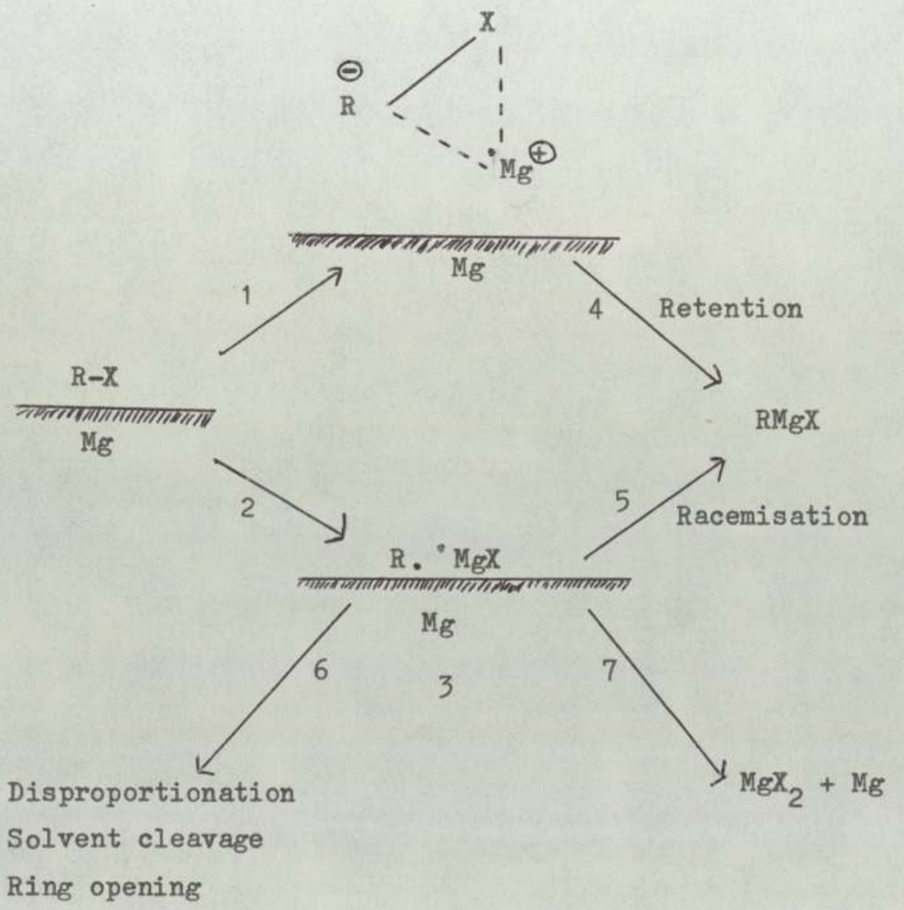


It has been suggested that the isolation of dimeric products from Grignard reaction is a strong indication that radicals are involved in this reaction.[3] Walborsky and Aronoff obtained the closed dimer



as a reaction product and suggest that this not only points to involvement of radical intermediates but taken with the lack of solvent cleavage is a strong indication of the surface bound nature of these intermediates.

These workers propose the following mechanism for Grignard formation.



These processes are assumed to take place on the surface of the magnesium. Interaction of the cyclopropyl halide and magnesium by pathway (1) gives a radical anion in close association with a univalent magnesium cation. In their case the tight anion radical cation radical pair collapses by pathway (4) to the Grignard reagent with complete retention of configuration. Collapse may also proceed by pathway (3) to a loose radical pair which may also be formed directly from magnesium by pathway (2). In the loose radical pair racemization takes place. Combination of the cyclopropyl radical with magnesium halide radical produces racemic Grignard reagent. The organic radical may escape capture by magnesious halide and undergo disproportionation, ring opening and dimerization. It may also attack the benzene rings of adsorbed species and to a small extent the solvent.

However, as the halogen is changed from iodide to bromide to chloride, the bond strength increases and more energy is required to add an additional electron to the carbon halogen bond. Consequently the lifetime of the intermediate radical ion decreases in this order and the reaction becomes more concerted resulting in less loose radical pair formation and thus less racemization and loss of material to side processes is observed.

They obtained a drastically reduced yield of the bromo Grignard in ether compared with T.H.F. while the yield of the side products increased. They observed no difference in the stereochemistry of the reaction. This is probably due to the different abilities of the two solvents to stabilize the intermediates involved. Stabilization of the radical anion is not so great in ether, therefore more loose radical pair is formed in this solvent. Magnesium (I) halide is also less stabilized, therefore more of it is destroyed by pathway (7). Thus much of the radical instead of forming racemic Grignard reagent is diverted to side product in ether. There need not be any change in the stereochemistry of the reaction even though the yield of Grignard is reduced since the relative amounts of material which result in Grignard reagent from pathway (4) and (5) can remain constant.

Finally, they found that in spite of the surface nature of the reaction neither the physical state of the magnesium nor its state of purity has any effect on the stereochemistry of the reaction.

Grignard reagents of the alpha, gamma and omega-halogenoalkylsilanes (n = 1,3,4) may be obtained in high yields (e.g. Me_3SiCH_2MgCl-[83] 95%) although their formation is sometimes accompanied by significant quantities of the dimer[84]:-

$$Ph_3Si(CH_2)_4Br + Mg + CO_2 \longrightarrow \begin{array}{c} Ph_3Si(CH_2)_4CO_2H \\ + \quad (60\%) \\ \left[Ph_3Si(CH_2)_4\right]_2 \quad (20\%) \end{array}$$

However, some unusual reactions of triphenylsilyl-substituted compounds have been reported. Brook et al[85] observed the following:-

$$Ph_3SiCH_2Br + Mg \xrightarrow[\text{ether}]{CO_2} Ph_3SiMe \ (89\%)$$

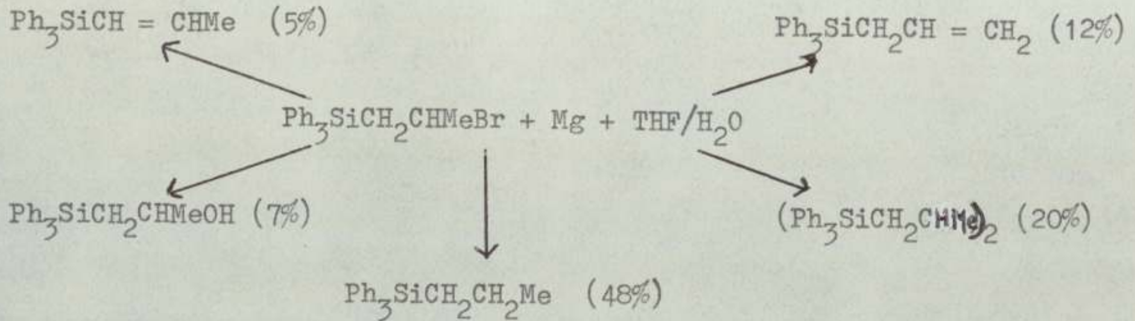
and in a similar reaction, Gilman et al[86] obtained the acid $Ph_3Si(CH_2)_3CO_2H$ in only 8% yield from the gamma-substituted compound $Ph_3Si(CH_2)_3Br$. Our attempt to prepare the Grignard from chloromethyl-tri-n-butylsilane was unsuccessful.

Beta-halogenoalkylsilanes do not normally react with magnesium to produce the organometallic reagent. However, Jarvie and her colleagues[52] have reported some unusual reactions of the triphenylsilyl substituted compounds with magnesium. They found that (2-bromoethyl)triphenylsilane reacted with excess magnesium to produce ethyltriphenylsilane and 1,4-bis(triphenylsilyl)butane in 64% and 24% yields respectively.

$$Ph_3SiCH_2CH_2Br + Mg \xrightarrow{H^+/H_2O} Ph_3SiCH_2CH_3 + (Ph_3SiCH_2CH_2)_2$$

They did not obtain any of the cleavage products such as hexaphenyldisiloxane or hydroxytriphenylsilane normally observed in the reactions of beta-halogenoalkylsilanes. When the reaction was quenched with deuterium oxide, the ethyltriphenylsilane isolated contained 100% of the deuterium atom.

They also investigated the reaction between (2-bromopropyl)-triphenylsilane and magnesium and found it to proceed according to the following scheme:-



Again they did not observe carbon-silicon bond cleavage. In contrast to the primary compound, they found that attempted deuterolysis gave n-propyltriphenylsilane which did not contain deuterium.

It has already been mentioned that beta-halogenosilanes do not normally react with magnesium to produce Grignard reagents. In view of the increasing resistance to solvolysis of sterically hindered (2-bromoethyl)trialkylsilanes it seemed probable that these compounds might produce Grignard reagents on treatment with magnesium.

The products obtained from attempts to prepare the Grignard reagents are summarized in Table I. Reactions were attempted in both diethyl ether and tetrahydrofuran.

Table I

Compound	Product
$BrCH_2CH_2SiMei\text{-}Pr_2$	No reaction. Silane recovered unchanged.
$BrCH_2CH_2Sii\text{-}Pr_3$	No reaction. Silane recovered unchanged.
$BrCH_2CH_2SiPr_3$	Pr_3SiOH(72%) hexaphenyldisiloxane (16%)
$BrCH_2CH_2SiBu_3$	$EtSiBu_3$(60%), BuSiOH (21%)

The reaction between (2-bromoethyl)diisopropylmethylsilane or (2-bromoethyl)triisopropylsilane and magnesium did not produce the Grignard reagent. However, examination of the reaction products revealed that in both cases the starting material had been recovered unchanged. Since no fragmentation was observed for these compounds it is possible that an impurity, a trace of moisture, or incorrect experimental conditions hindered the formation of the Grignard reagents.

The reaction between (2-bromoethyl)tri-n-propylsilane and magnesium did not produce the Grignard reagent. Examination of the reaction products revealed that in this case hydroxytri-n-propylsilane and hexaphenyldisiloxane had been formed in 72% and 16% yields respectively. No ethyltri-n-propylsilane was detected in the reaction mixture. Thus this compound is not suitable for Grignard formation since the reaction only leads to the fragmentation products.

The reaction between (2-bromoethyl)tri-n-butylsilane and magnesium afforded ethyltri-n-butylsilane and hydroxytri-n-butylsilane in 60% and 21% yields respectively. The reaction was repeated and subsequently quenched with deuterium oxide. Examination of the ethyltri-n-butylsilane formed indicated that less than 10% deuterium incorporation had taken place. The fact that such a small percentage of deuterium was incorporated in the hydrolysis product of the Grignard $Bu_3SiCH_2CH_2MgBr$ suggests that the media may not be suitable, the compound may be unstable under the experimental conditions employed, or that abstraction from the solvent had taken place by the radical.

These observations suggest that with beta-halogenoalkylsilanes, if nucleophilic substitution takes place at silicon, the compound is unlikely to form the Grignard reagent. However, as the size of the substituents on silicon increases, there is a marked increase in the resistance to solvolysis and a decrease in carbon-silicon bond cleavage. Therefore, for beta-halogenoalkylsilanes which display a decrease in carbon-silicon bond cleavage, formation of the Grignard reagent is possible.

7. Reaction of (2-bromoethyl)tri-n-propylsilane and (2-bromoethyl)tri-n-butylsilane with aluminium chloride.

Sommer and co-workers[41] originally investigated the reaction of beta-halogenoalkylsilanes with aluminium chloride. These investigators found that electrophilic reagents such as aluminium chloride brought about desilicohalogenation provided that the substituents on silicon are sufficiently electropositive. They observed that $Et_3SiCH_2CH_2Cl$, $Et_2ClSiCH_2CH_2Cl$ and $Et_2FSiCH_2CH_2Cl$ eliminated ethylene when treated with small amounts of aluminium chloride. The following E1 type mechanism was proposed for the elimination:

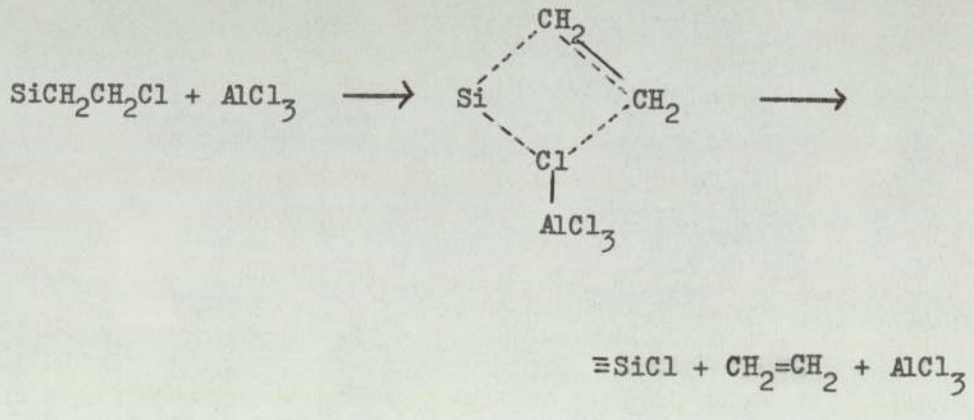
$$\equiv SiCH_2CH_2Cl \;+\; AlCl_3 \xrightarrow{(a)} \equiv SiCH_2CH_2^{+} \;+\; AlCl_4^{-}$$

$$\equiv Si - CH_2CH_2^{+} \xrightarrow{(b)} CH_2 = CH_2 \;+\; \equiv Si^{+}$$

$$\equiv Si^{+} \;+\; AlCl_4^{-} \xrightarrow{(c)} \equiv Si - Cl \;+\; AlCl_3$$

Aluminium chloride is known to aid ionization of the carbon-chlorine bond. Thus, step (a) gives a beta carbonium ion. Step (b) involves electron release from electropositive silicon to electron deficient carbon. Step (c) which may be simultaneous with or subsequent to (b), gives a chlorosilane by combination of chloride ion with "siliconium ion," thus regenerating the catalyst.

However, these reactions are no longer thought to occur via an E1 type mechanism and are now believed to occur via a four-centre process.[57]



On the other hand, dehydrohalogenation is observed if the substituents on silicon are electronegative.[42]

$$Cl_3SiCH_2CH_2Cl \xrightarrow{AlCl_3} Cl_3SiCH = CH_2$$

(2-bromoethyl)tri-n-propylsilane and (2-bromoethyl)tri-n-butylsilane were treated with aluminium chloride. A mixture of tri-n-propylbromosilane and tri-n-propylchlorosilane and a mixture of tri-n-butylbromosilane and tri-n-butylchlorosilane were obtained. Both reactions were accompanied by the evolution of ethylene. The products obtained indicate that desilicohalogenation has taken place.

$$Pr_3SiCH_2CH_2Br \xrightarrow{AlCl_3} Pr_3SiCl + Pr_3SiBr + CH_2 = CH_2$$

$$Bu_3SiCH_2CH_2Br \xrightarrow{AlCl_3} Bu_3SiCl + Bu_3SiBr + CH_2 = CH_2$$

No report can be found in the literature of a reaction between (2-bromoethyl)triphenylsilane and aluminium chloride. However, if the anomalous behaviour of the (2-bromoalkyl)triphenylsilanes is due to the triphenylsilyl group behaving as an electron-withdrawing group then dehydrohalogenation should be observed on treatment of the above with aluminium chloride. Since desilicohalogenation is observed when (2-bromoethyl)tri-n-propylsilane and (2-bromoethyl)tri-n-butylsilane are treated with aluminium chloride this would suggest that the fragmentation observed in this case is probably due to the positive character of the carbonium ion formed in the course of this reaction.

Conclusion

This investigation demonstrates that sterically hindered (2-bromoethyl)trialkylsilanes show a resistance to solvolysis. The carbonium ion theory is in agreement with our observations provided that a slow rate-determining step involving attack of the carbonium ion by the solvent is envisaged.

The rearrangement of (2-hydroxyethyl-2,2-d_2)tri-n-butylsilane establishes that the solvolysis takes place with formation of a carbonium ion and that butyl substitution on silicon instead of methyl has little effect on the ratio of the rearranged products obtained. Trapping the 2-(tri-n-butylsilyl)ethyl cation by the silane transfer reaction further establishes that reactions of (2-bromoethyl)tri-n-butylsilane can take place with the formation of a carbonium ion.

The increased stability of these compounds with increasing size of substituents on silicon is demonstrated by the reaction of (2-bromoethyl)tri-n-butylsilane with magnesium to form the organometallic compound rather than the cleavage product.

These observations therefore suggest that the increased stability of (2-bromoethyl)triphenylsilanes is not due to electronic factors as it has been suggested but is due to steric factors although electronic factors should not be overlooked.

CHAPTER THREE

REACTIONS OF CHLOROMETHYLTRI-n-BUTYLSILANE AND THE PYROLYSIS OF SILACYCLOBUTANES

I. REACTIONS OF CHLOROMETHYLTRI-n-BUTYLSILANE

Our interest in the alpha-halogenoalkylsilane $ClCH_2SiBu_3$ arose because of the rearrangement of aryldimethylsilylchlorides induced by nucleophilic reagents observed by Eaborn.[87] Chloromethyltri-n-butylsilane was prepared in order to establish if a compound carrying three large alkyl groups would undergo a similar rearrangement and thus give some indication if steric factors are involved.

1. Preparation of Chloromethyltri-n-butylsilane

This compound was prepared by treating chloromethyltrichlorosilane with excess n-butylmagnesium bromide. However, as well as the expected product chloromethyltri-n-butylsilane, methyltri-n-butylsilane was also obtained. These two compounds were isolated in a 3:1 ratio.

However, Mironov and Pagonkina[88] have shown that cleavage of silicon-carbon bond does not occur in reactions of the compounds $Cl_3Si(CH_2)_nCl$ with Grignard reagents, when n = 1, 3 or 4, and the carbon-halogen bond is also unreactive in such experiments.

$$Cl_3Si(CH_2)_nCl \xrightarrow{\text{Xs RMgX}} R_3Si(CH_2)_nCl$$

$$n = 1, 3 \text{ or } 4$$

Grignard reagents from the halogenoalkylsilanes $R_3Si(CH_2)_nCl$ (n = 1, 3 or 4) may be obtained in high yields (e.g. Me_3SiCH_2MgCl - 95%).[83]

although we were unable to obtain an organometallic compound on treatment of chloromethyltri-n-butylsilane with lithium or magnesium in tetrahydrofuran or ether. However, some unusual reactions of the triphenylsilyl-substituted compounds have been reported. Brook et al[85] observed the following reaction:-

$$Ph_3SiCH_2Br + Mg \xrightarrow[ether]{CO_2} Ph_3SiMe \quad (89\%)$$

Brook[85] also found that the alpha compound underwent halogen-metal exchange with n-butyllithium. In this case carbonation of the intermediate organolithium compound gave the acid in high yield.

$$Ph_3SiCH_2Br + n\text{-}BuLi \longrightarrow Ph_3SiCH_2Li \xrightarrow{CO_2} Ph_3SiCH_2CO_2H \quad (78\%)$$

Halogen-metal exchange reactions are commonly encountered in organolithium chemistry.[89]

$$R'X + RLi \rightleftharpoons R'Li + RX$$

The reactions have generally been interpreted as heterolytic processes and it appears that at equilibrium lithium becomes attached to the most electronegative organic group. A few such exchanges have been established using organomagnesium compounds[90] but all these involve strongly electronegative substituents which can stabilize a carbanionic state. Attempts to observe exchange involving simple alkyl or aryl groups were apparently unsuccessful and Kharasch and Reinmuth[3] have suggested that "functional exchange between an organic halide and an organomagnesium compound is a relatively rare reaction."

Jarvie[91] investigated the reaction of bromomethyltriphenylsilane with n-butylmagnesium bromide in ether, tetrahydrofuran and benzene and obtained methyltriphenylsilane and n-amyltriphenylsilane as the major products. Deuteration studies showed that about 40% of the Grignard reagent Ph_3SiCH_2MgBr was produced in benzene but in ethereal solvents the methyltriphenylsilane was formed entirely by hydrogen abstraction from the solvent. Metal transfer took place only in benzene.

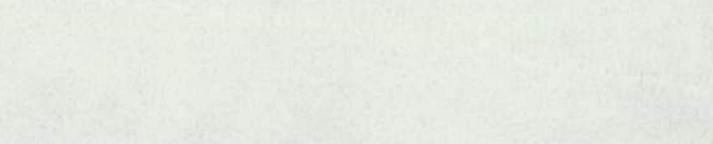
Thus, in the reaction between chloromethyltributylsilane $ClCH_2SiBu_3$ and excess n-butylmagnesium bromide, halogen-metal exchange is unlikely to have occurred to produce methyltri-n-butylsilane. However, the observation by Mironov and Pagonkina[88] that the carbon-halogen bond is unreactive in such experiments clearly does not apply to the reaction we investigated. The methyltri-n-butylsilane was probably produced as follows:

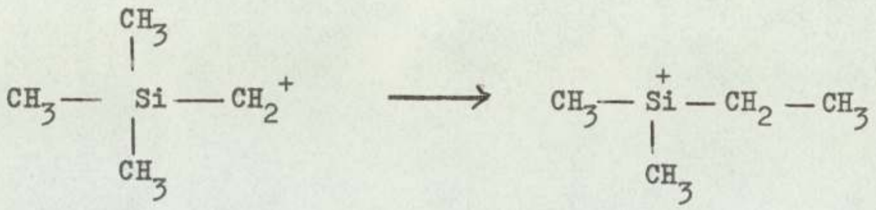
1) chloromethyltrichlorosilane reacted with excess n-butylmagnesium bromide to produce chloromethyltri-n-butylsilane.
2) chloromethyltri-n-butylsilane subsequently reacted with n-butylmagnesium bromide to produce methyltri-n-butylsilane either by metal transfer or by hydrogen abstration from the solvent.

2. Reaction of Chloromethyltri-n-butylsilane with Sodium in Ethanol and Sodium Ethoxide.

Several examples may be found in the literature of intramolecular migrations of alkyl groups from a silicon atom to an adjacent electron-deficient carbon atom.[68,69,92] These rearrangements being of the Wagner-Meerwein type.

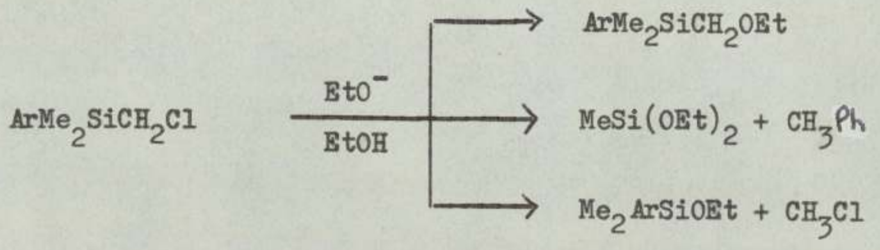
e.g.





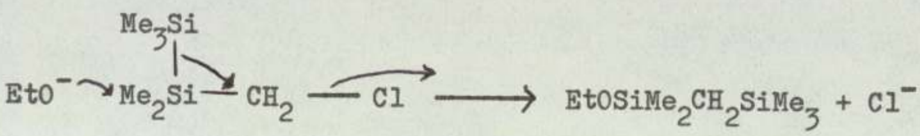
$$(CH_3)_3Si-CH_2^+ \longrightarrow CH_3-\overset{+}{Si}(CH_3)-CH_2-CH_3$$

Eaborn and Jeffrey[87] were the first to report examples of organosilicon rearrangements induced by nucleophilic reagents. When aryldimethylsilylchlorides are treated with sodium ethoxide in ethanol, toluene derivatives, Aryl-CH_3, are formed together with products of substitution at the carbon atom and of cleavage of Si-CH_2Cl bonds.



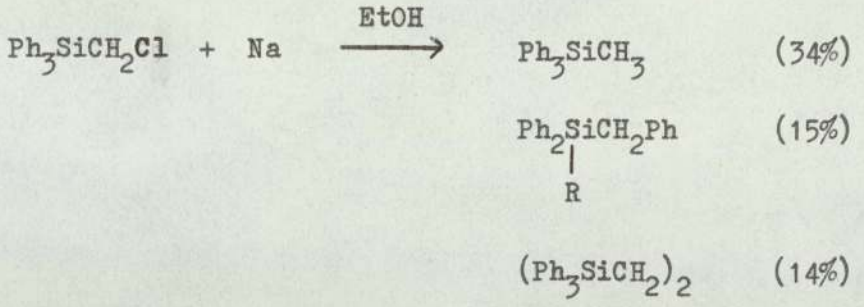
It was suggested that the toluene derivatives arose from the cleavage of silicon-benzyl bonds formed by intramolecular migration of the aryl group from silicon to a neighbouring carbon atom under the influence of nucleophilic attack of ethoxide ion at silicon.

Kumada and co-workers[93] have shown that trimethylsilyl groups also migrate under similar conditions:



and that this kind of rearrangement occurs generally with alkoxides NaOR in the corresponding alcohol ROH, where R = Me, Et and i-Pr.

Subsequently Siriveschaphan[94] observed that an anologous rearrangement occurred on treatment of chloromethyltriphenylsilane with sodium in ethanol.



$$\mathrm{Ph_3SiCH_2Cl} + \mathrm{Na} \xrightarrow{\mathrm{EtOH}} \mathrm{Ph_3SiCH_3} \quad (34\%)$$

$$\mathrm{Ph_2}\underset{\mathrm{R}}{\underset{|}{\mathrm{Si}}}\mathrm{CH_2Ph} \quad (15\%)$$

$$(\mathrm{Ph_3SiCH_2})_2 \quad (14\%)$$

She observed that this migration only occurred during the period that the sodium was dissolving in ethanol. When the same reaction was carried out using preformed sodium ethoxide, instead of sodium in ethanol, no rearrangement was observed.

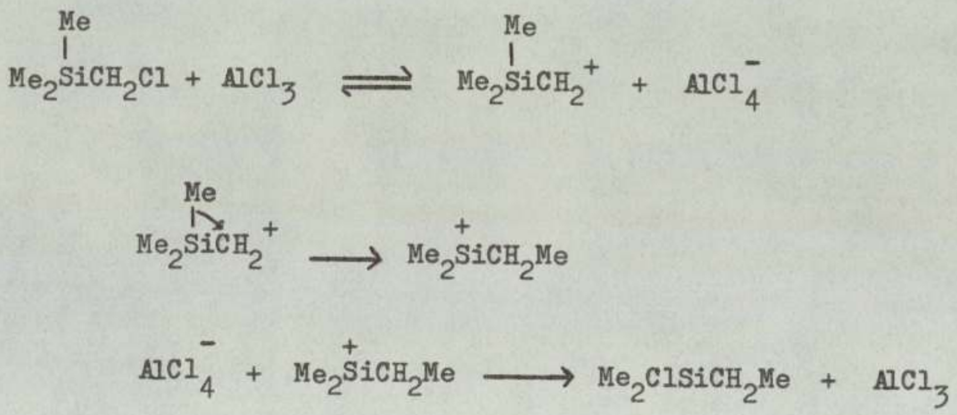
In the light of these observations, it was thought of interest to substitute the phenyl groups for bulky groups such as n-butyl and determine whether such a rearrangement would still take place.

Chloromethyltri-n-butylsilane was treated with sodium in ethanol at reflux temperature. Examination of the reaction products after one hour revealed the presence of methyltri-n-butylsilane together with a small amount of starting material. No rearrangement was observed. These observations suggest that the bulky butyl group hinders the reaction and that the presence of a phenyl group induces the migration. Although metal/alcohol solutions have been used extensively for reductions, very little can be found in the literature concerning the mechanism of the reaction of alkyl halides in such media.[95] The reduction of chloromethyltri-n-butylsilane and chloromethyltriphenylsilane with sodium in alcohol suggests that it is a general reaction for alpha-halogenoalkylsilanes.

Chloromethyltri-n-butylsilane was subsequently treated with sodium ethoxide in ethanol. After three days, examination of the reaction mixture revealed that it consisted mainly of starting material together with 20% of the substitution product $Bu_3SiCH_2OCH_2CH_3$. Normally both substitution and cleavage are observed in the reaction of alpha-halogenoalkylsilanes with sodium ethoxide.[96] It would appear that bulky groups stabilize the molecule preventing carbon-silicon bond cleavage and permitting nucleophilic substitution at carbon.

3. Reaction of Chloromethyltri-n-butylsilane with Aluminium Chloride

When chloromethyltrimethylsilane is treated with aluminium chloride, the following rearrangement is observed.[92]

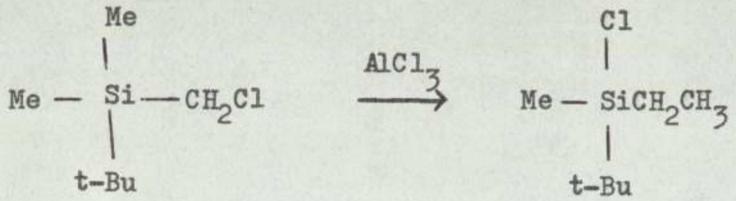


$$Me_2\overset{Me}{Si}CH_2Cl + AlCl_3 \rightleftharpoons Me_2\overset{Me}{Si}CH_2^+ + AlCl_4^-$$

$$Me_2\overset{Me}{Si}CH_2^+ \longrightarrow Me_2\overset{+}{Si}CH_2Me$$

$$AlCl_4^- + Me_2\overset{+}{Si}CH_2Me \longrightarrow Me_2ClSiCH_2Me + AlCl_3$$

It has been observed that the tert-butyl group migrates less readily than the methyl group, as indicated by the following example:[97]



$$Me-\underset{t\text{-}Bu}{\overset{Me}{Si}}-CH_2Cl \xrightarrow{AlCl_3} Me-\underset{t\text{-}Bu}{\overset{Cl}{Si}}CH_2CH_3$$

We observed no rearrangement on treatment of chloromethyltri-n-butylsilane with aluminium chloride. In fact the material was recovered unchanged. Thus it seems that steric effects of bulky groups such as butyl prevent the rearrangement.

Our observations suggest that chloromethyltri-n-butylsilane reacts with n-butylmagnesium bromide to yield methyltri-n-butylsilane by metal transfer or by hydrogen abstraction from the solvent. Chloromethyltri-n-butylsilane reacts with sodium in ethanol to yield methyltri-n-butylsilane, and with sodium ethoxide 20% of the substitution product is obtained. Thus, in the case of sodium in ethanol electronic effects hinder the rearrangement observed for the analogous triphenylsilyl system, whereas with sodium ethoxide steric effects afford added stability to the molecule and only nucleophilic substitution at carbon is observed. Finally it seems that steric effects are responsible for the fact that chloromethyltri-n-butylsilane does not rearrange on treatment with aluminium chloride.

II. THE PYROLYSIS OF SILACYCLOBUTANES

1. Introduction

Several workers have used the 1,1-disubstituted silacyclobutanes to generate $\left[R_2Si = CH_2\right]$ intermediates by photochemical and pyrolytic means. The most common cited evidence for the transient existence of silaalkenes is the formation of the head-to-tail dimers 1,3-disilacyclobutanes from the pyrolysis of 1,1-disubstituted silacyclobutanes, although the transient existence of these species has also been established by trapping with suitable reagents. Most of the evidence to date has been based on product analysis and the intermediacy of these species has not been confirmed by other techniques. Furthermore only the products which have been isolated and discussed are those derived from $\left[>Si = C<\right]$ intermediates; usually these have only accounted for a fairly small percentage of the products.

Our interest in these compounds i.e. silacyclobutanes was twofold (1) to discover what the other products were and how they were formed and (2) to investigate systems other than the methyl substituted system in order to determine how substituents affected the pattern under more controlled conditions. With this purpose in mind, a series of silacyclobutanes was synthesised.

2) Carbon-silicon ($p\pi - p\pi$) bonds

Contrary to earlier beliefs that second row elements do not participate in $p\pi - p\pi$ bonding, there is some evidence now for the existence or otherwise of compounds in which silicon is involved in olefin type linkage. The subject has been reviewed by Attridge[98] and by Jutzi.[99] Carbon is atypical of the Group IVB elements in being the only one able to form stable, multiply-bonded molecules. The other group IVB elements despite having equivalent valence shell configuration to carbon seem reluctant to adopt trigonal or digonal co-ordination in their compounds. The two most quoted reasons for the lack of multiple bonding in these compounds are a lack of good $p\pi - p\pi$ overlap and "inner shell" repulsions.

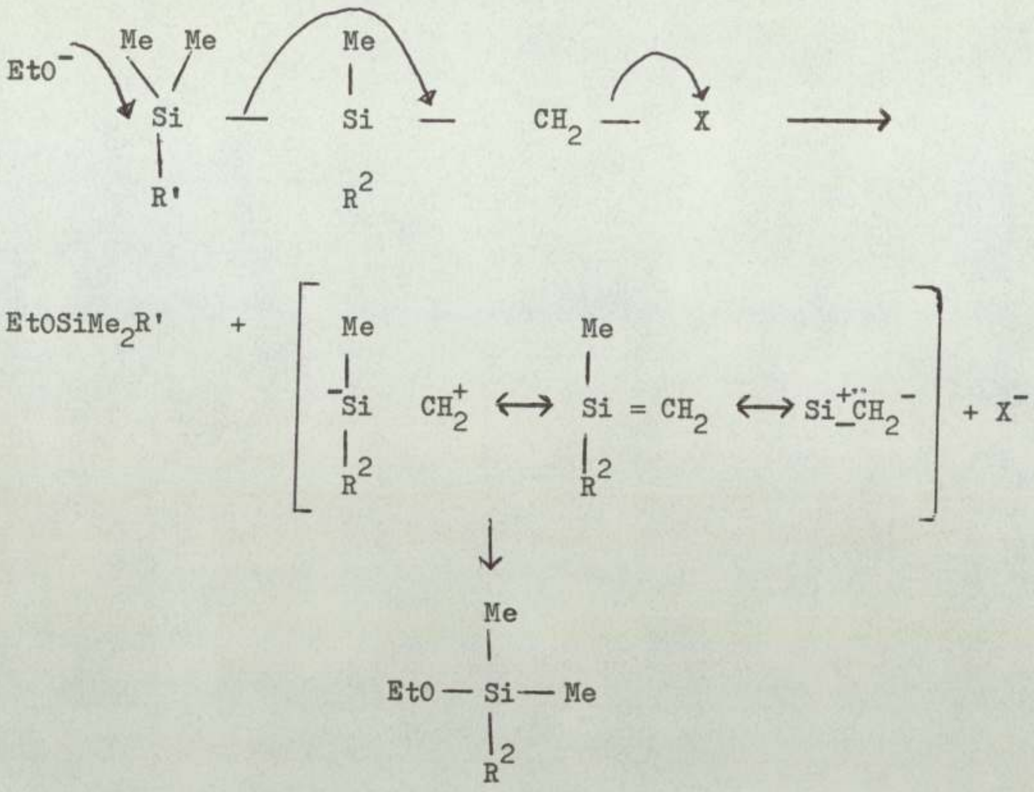
Recently several reports dealing with theoretical aspects of multiple bonding in silicon have appeared in the literature. Walsh[100] analysed the kinetic data obtained from the pyrolitic studies by Gusel'nikov and Flowers[101] and Davidson and Lambert[102] where $[(CH_3)_2Si = CH_2]$ and $[CH_3SiH = CH_2]$ are proposed as reaction intermediates. Walsh calculated that the π-bond between silicon and carbon is about half as strong as that in olefins.

Subsequently, Curtis[103] carried out extended Huckel (EHMO) calculations on silaethylene $H_2C{=}SiH_2$ and disilaethylene $H_2Si{=}SiH_2$. These calculations indicate that the carbon-silicon double bond is exceedingly polar and expected to be very reactive, behaving like a carbanion-siliconium ion combination. In this bond system the interaction between 2pπ(C) and 3pπ(Si) electrons is not particularly effective. This is not due so much to inadequate orbital overlap but to energy mismatching of carbon 2p and silicon 3p orbitals. This is in large part responsible for the weakness of the π-bond. However, in contrast to this last statement Dewar et al[104] predict the carbon-silicon π-bond to be quite strong.

Damrauer and Williams[105] carried out CNDO/2 (complete neglect of differential overlap) calculations on silaethylene and fluorine substituted silaethylenes. Their calculations suggest that the carbon-silicon double bond is stable owing to substantial π-bond order and short silicon-carbon bond length and that it is extremely reactive as a result of the highly polar silicon-carbon bond.

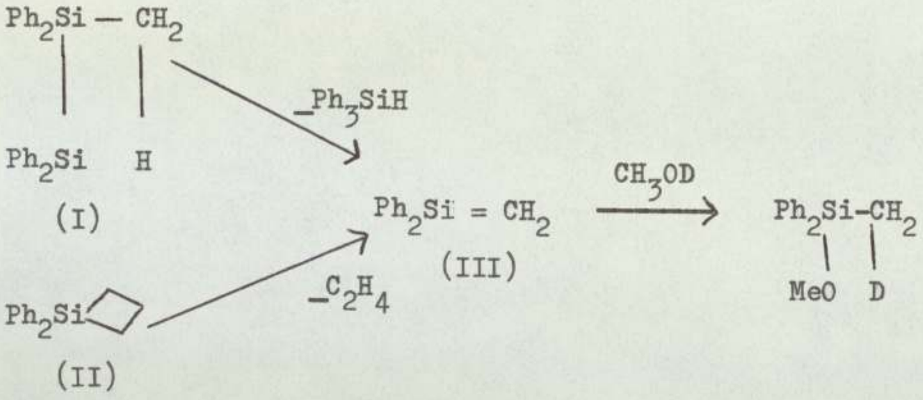
More recently Blustin[106] investigated the bond in carbon and silicon by the Floating Spherical Gaussian Orbital (FSGO) calculations. These calculations suggest that the carbon-silicon bond becomes more polar with increasing bond order. He concludes from orbital density comparisons that although silicon has equivalent valence shell to carbon, it might be too electropositive to form multiple bonds with a high enough π-bond energy.

Compounds containing silicon-carbon double bonds have frequently been postulated to explain reaction products. For example in the cleavage of 1-halogenomethyl-1-phenyldisilanes by sodium ethoxide, Kumada et al[107] propose $[\gt Si = CH_2]$ as unstable reaction intermediates.



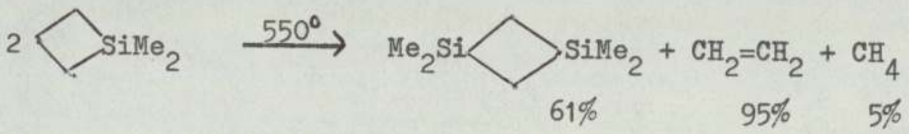
Many other examples may be found in the literature of silicon-carbon double bond species being postulated as reaction intermediates. However, it is only recently that more definite proof of these short-lived species has been obtained from photochemical experiments and pyrolysis reactions.

Reactive carbon-silicon double-bond intermediates have been generated by photochemically induced homolysis as mentioned above. For example from the photolysis of both pentaphenylmethyldisilane[108] and 1,1-diphenyl-1-silacyclobutane[109] in cyclohexane at 2537A Sommer obtained 1,1-diphenyl-1-silaethylene which can be trapped as $Ph_2SiOMeCH_2D$ with methanol-d_1.

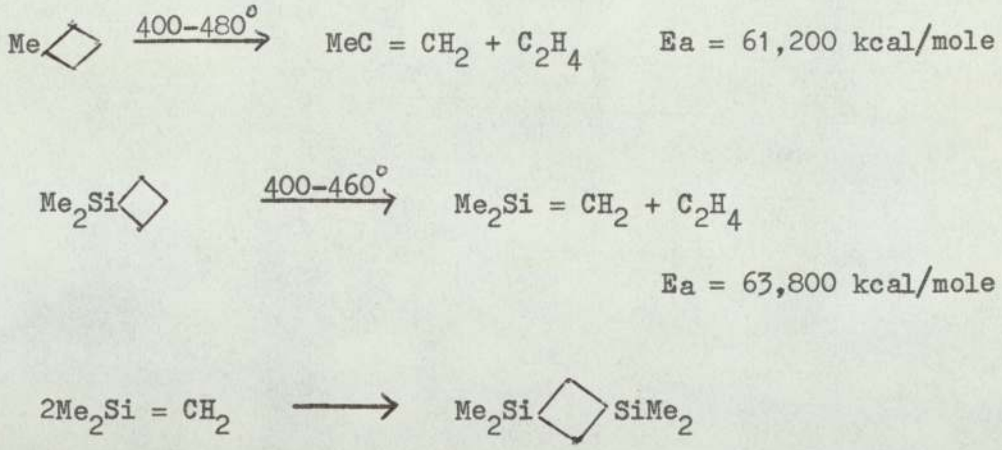


Numerous other examples of carbon-silicon double bond intermediates generated in this manner may be found in the literature.

Reactive carbon-silicon double-bond intermediates may also be generated from pyrolysis reactions. Evidence is now accumulating for the existence of these species in pyrolysis reactions especially those involving silacyclobutanes. Thermal decomposition of monosilacyclobutanes was first reported in 1966. It was shown that these compounds behaved differently during gas-phase pyrolysis from liquid phase reaction in which polymerisation occurs. Nametkin and co-workers[110] reported that vapour phase pyrolysis of silacyclobutanes between 550-750° led to 1,3-disilacyclobutanes.



Gusel'nikov and Flowers[101] carried out a kinetic study of the gas-phase thermal decomposition of 1,1-dimethylsilacyclobutane in order to establish a mechanism for the reaction. They found that the Arrhenius parameters of this decomposition are similar to those found for the decomposition of alkylcyclobutanes.



Ea = 61,200 kcal/mole

Ea = 63,800 kcal/mole

Gusel'nikov and Flowers suggest that $Me_2Si = CH_2$ is formed as an intermediate and that it is because of the low stability of the silicon-carbon double bond that rapid dimerisation occurs to give the disilacyclobutane. They also found that the reaction is inhibited by ethylene and that this is probably due to the reversibility of the initial step of the decomposition. To support this statement, prop-1-ene was used as an inhibitor in some experiments and they obtained a compound tentatively identified as 1,1,3(or 2)-trimethylsilacyclobutane.

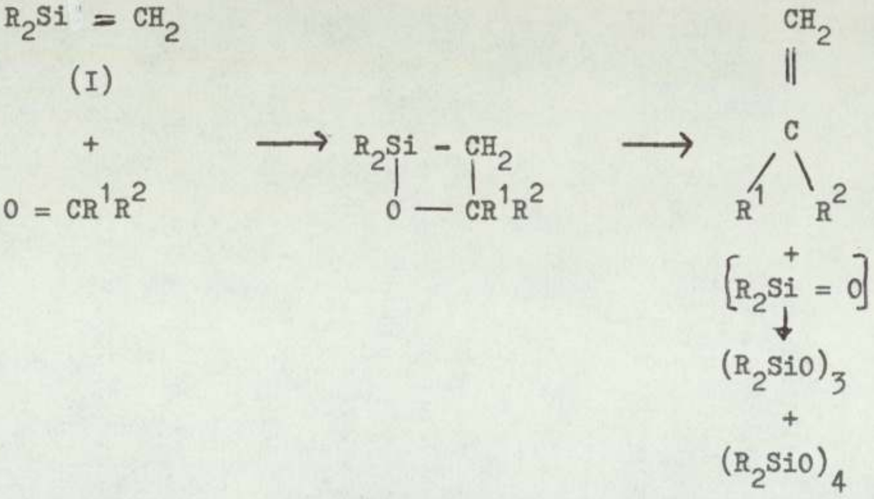
Subsequently Barton and McIntosh[111] pyrolysed 1,1-dimethylsilacyclobutane at 650° and the pyrolysate was allowed to deposit on a sodium chloride plate at -196°. Barton and McIntosh were thus able to observe the I.R. of an unstable species which they suggest is $[Me_2Si = CH_2]$. At -196° the spectrum of the pyrolysis product was essentially that of 1,1-dimethylsilacyclobutane except for a new sharp band at 1407 cm^{-1}. As the cell was warmed slowly, the band at 1407 cm^{-1} disappeared at -120°. Finally, they observed that conditions for the detection of the intermediate are crucial as for example at 800°, the pure dimer 1,1,3,3_tetramethyldisilacyclobutane was obtained. However, recently three groups of workers[112] have independently studied the I.R. spectra of silaalkenes isolated in Ar matrices. These workers place no emphasis on bands near 1410 cm^{-1}, the apparent region of the Si = C stretching mode according to Barton and McIntosh.

Thus it seems that their initial assignment is incorrect.

It seems that carbon-silicon double bonds are not exclusively generated from silacyclobutane. For example, Clifford and co-workers[113] obtained carbon-silicon double bond intermediates from the pyrolysis of tetramethylsilane. Barton and Kline[114] found that the compound 2,3-Bis(trifluoromethyl)-3,7,dimethyl-7-silabicyclo [2.2.2.] octa-2,5-diene is a good source of silaalkene. More recently Ando and co-workers[115] have reported that the gas-phase decomposition of silylphenylketones is also a possible route for the formation of carbon-silicon double bond intermediates.

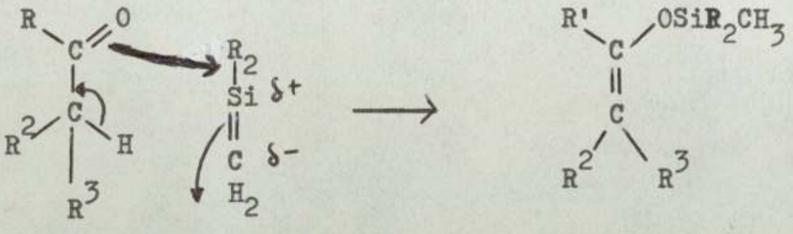
Sommer and co-workers have reported, as mentioned previously, the generation of carbon-silicon double bond intermediates from the photochemically induced reactions of methylpentaphenyldisilane[108] and 1,1-diphenylsilacyclobutane.[109] As a continuation of this work, Sommer carried out a detailed study of the reactivity of carbon-silicon double bond intermediates generated from the pyrolysis of silacyclobutanes with such compounds as aldehydes, ketones and nitriles.

These workers[116] observed that pyrolysis of 1,1 dimethylsilacyclobutane and subsequent trapping with a non-enolizable ketone such as benzophenone was found to give high yields of 1,1 diphenylethylene together with cyclic siloxanes. They proposed the following pseudo-Wittig mechanism for the reaction:



$$\underset{(I)}{R_2Si=CH_2} + O=CR^1R^2 \longrightarrow \begin{array}{cc} R_2Si\ - & CH_2 \\ | & | \\ O\ - & CR^1R^2 \end{array} \longrightarrow CH_2=CR^1R^2 + [R_2Si=O] \rightarrow (R_2SiO)_3 + (R_2SiO)_4$$

They also observed that when the reaction was carried out with potentially enolizable ketones as trapping agents, the reaction followed a different pathway. The intermediate (I) is suggested to react with enolizable ketones and aldehydes by a mechanism involving proton abstraction. These investigators suggested the following mechanism for the formation of the silyl enol ethers.



(I)

Sommer[117] obtained further support for this mechanism from the co-pyrolysis of acetonitrile-d_3 with 1,1-dimethylsilacyclobutane at 610° obtaining deuteriotrimethylsilyldeuterioacetonitrile $N \equiv C-CD_2-Si(CH_2D)Me_2$.

In subsequent studies Sommer and co-workers[118-121] observed the following order of reactivity of substrates towards $[Me_2Si = CH_2]$: $Ph_2C = O > ROH, ArOH \gg m\text{-}ClC_6H_4NH_2 > CH_3CN$. They also observed that within a given class of substrates, polar effects were generally unimportant although steric effects caused a decrease in rate. They established the dipolar nature of the carbon-silicon double bonds from reactions of 1,1-dimethylsilaethene with silicon halides. They also established that the initial step in the thermal decomposition of silacyclobutane takes place via C_2-C_3 bond scission and not $Si-C_4$ bond scission. Finally they obtained a pattern for general chemical behaviour of these carbon-silicon double bond intermediates.

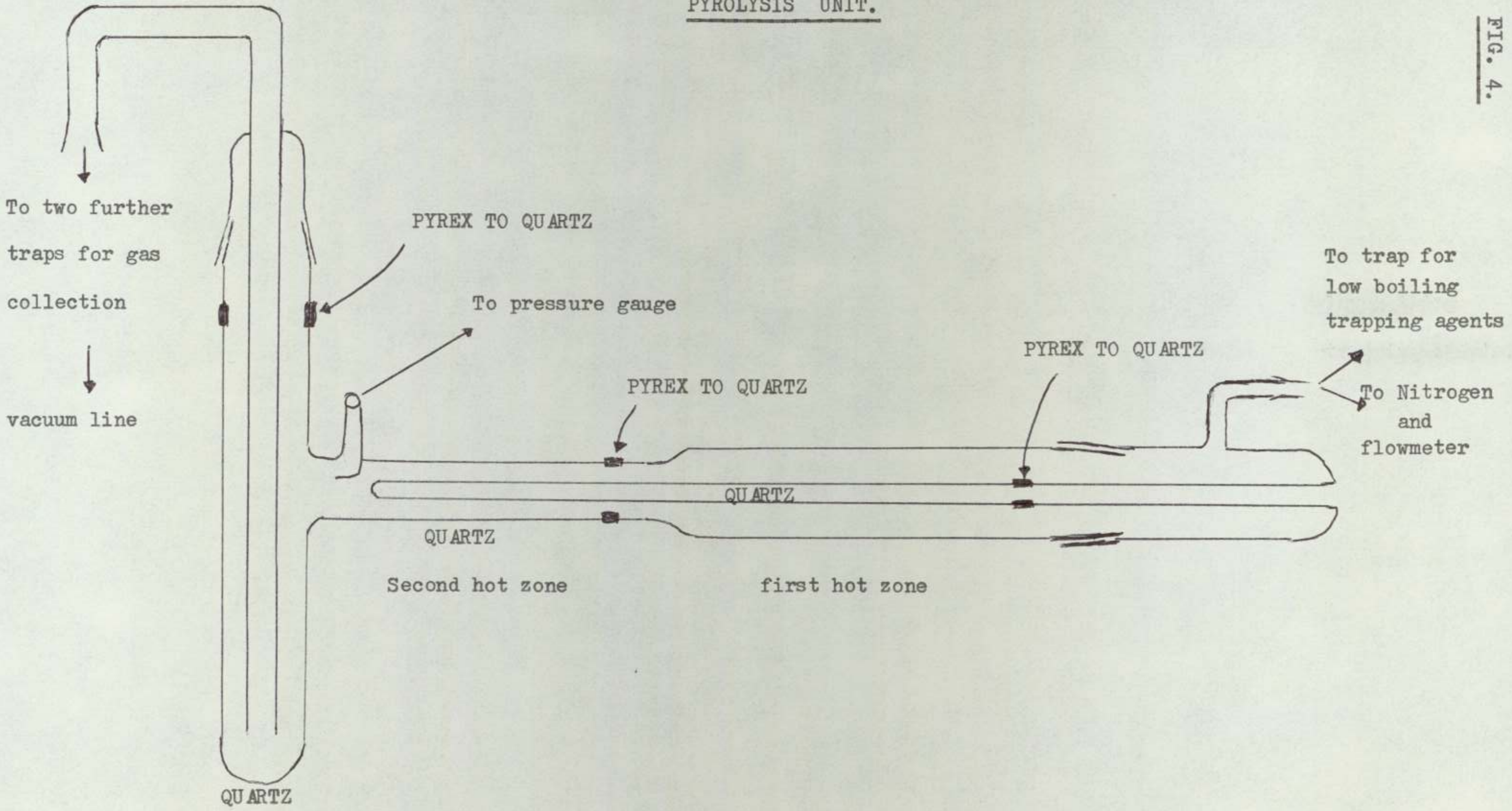
3. The Pyrolysis of Silacyclobutanes.

It has already been mentioned in the introduction that the purpose of preparing and subsequently pyrolysing the silacyclobutanes was to determine what other products are formed since there is a large discrepancy between the quantity of starting materials and products. Thus the work of Sommer and co-workers[116] involving the pyrolysis of silacyclobutanes with aldehydes and ketones was repeated. The pyrolysis unit used was essentially similar to the one used by Sommer but with a certain number of modifications. The pyrolysis unit is shown diagramatically on the next page. We felt that the system needed to be modified in order to minimise some of the problems involving this type of work.

The main differences between the system used by Sommer and the one used for this investigation involve the manner of injecting and hence pyrolysing the compound and the manner of heating the pyrolysis unit. Sommer injected a mixture of the silacyclobutane and the trapping agent straight onto the hot zone and the length of the pyrolysis tube was heated to 610°. On the other hand, we placed the silacyclobutane under investigation in a boat inside the pyrolysis unit. The length of the pyrolysis tube heated was split into a first hot zone and a second hot zone. The boat was placed initially into the first hot zone and when the system had attained the correct pressure and temperature, the sample in the boat (by means of its magnetic handle) was moved into the second hot zone. The temperature of the first hot zone was found to be very critical as this temperature determined the amount of polymer formed from the silacyclobutane. The ideal temperature for the first hot zone was found to be approximately 100° and for the second hot zone approximately 600°. However, when a very volatile silacyclobutane such as silacyclobutane or 1,1-dimethylsilacyclobutane was pyrolysed, the first hot zone was

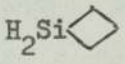
FIG. 4.

PYROLYSIS UNIT.

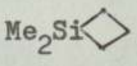


not heated. The trapping agent, if volatile, was placed in a separate trap and carried over as the sample under investigation was pyrolysed. The majority of trapping agents were not particularly volatile and in these cases a mixture of silacyclobutane and trapping agent was placed directly in the boat. The temperature of the pyrolysis tube was measured by an iron-constantant thermocouple placed against the outside of the tube at the centre of the oven. Nitrogen was used as the carrier gas in all the experiments.

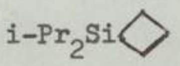
The following silacyclobutanes were synthesised and investigated.



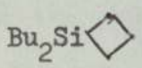
- silacyclobutane



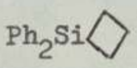
- 1,1-dimethylsilacyclobutane



- 1,1-diisopropylsilacyclobutane

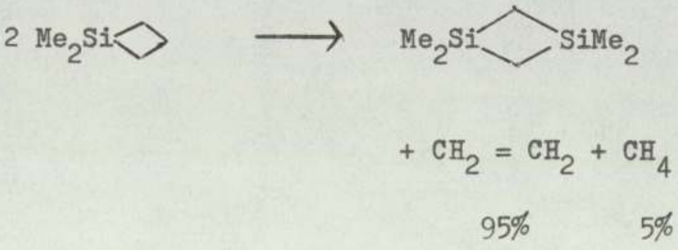


- 1,1-di-n-butylsilacyclobutane



- 1,1-diphenylsilacyclobutane

Pyrolyses of silacyclobutanes are more complex than they may appear at first sight. The only report in the literature dealing with the pyrolysis of a silacyclobutane and the analysis of the gaseous products is by Nametkin and co-workers.[110] The workers pyrolysed 1,1-dimethylsilacyclobutane and obtained the following products.

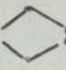


Thus the silacylcobutanes synthesised were pyrolysed without trapping agents and the pyrolysates(including the gaseous products) were analysed in order to determine all the products formed.

a) Silacyclobutane

This compound was pyrolysed at 560° with the first hot zone of the pyrolysis unit not heated. The gaseous mixture was analysed by G.L.C., I.R. and mass spectrometry. These indicate that the gaseous mixture was essentially ethylene together with a trace of starting material. The amount of ethylene liberated suggests that 48% of the compound was pyrolysed however only a trace of the starting material was recovered. The disilacyclobutane was not formed in this case but instead a yellowish green polymeric substance was deposited on the sides of the pyrolysis unit. Analysis of this substance proved rather difficult as the compound was not soluble in any of the solvents available.

b) 1,1-dimethylsilacyclobutane

This compound was pyrolysed at 611° with the first hot zone of the pyrolysis unit not heated. Estimation from the quantity of ethylene evolved suggests some 65% yield of the disilacyclobutane Me_2Si$SiMe_2$. The ethylene was not subjected to full analysis as in other experiments as it is rather difficult to establish the presence of methane in a sample of ethylene.

c) 1,1-diisopropylsilacyclobutane

This compound was pyrolysed at 611° and the first hot zone of the pyrolysis unit was heated to 100°. Estimation from the quantity of ethylene evolved suggests some 83% dimerisation to the silacyclobutane. However, I.R., G.L.C. and the mass spectrum indicate that the compound is not pure ethylene but that it consists of 57% ethylene and 43% prop-1-ene. Therefore, only 47% of the dimer is obtained in this case.

d) 1,1-di-n-butylsilacyclobutane

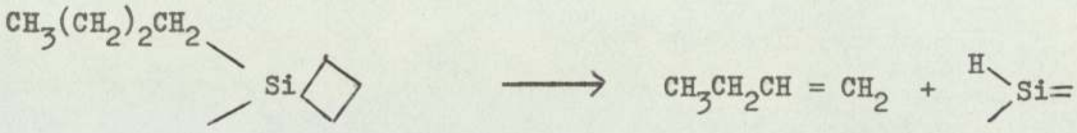
This compound was pyrolysed at 611° and the first hot zone of the pyrolysis unit heated to 100°. The gaseous mixture was subjected to analysis as in the previous case. Estimation from the volume of ethylene evolved suggests some 82·9% dimerisation. However, analysis indicates the gaseous mixture to be composed of 16% but-1-ene and 84% ethylene. Therefore, 69% of the dimer is obtained in this case.

e) 1,1-diphenylsilacyclobutane

This compound was initially pyrolysed at 611° with the first hot zone heated to 200°. Under these conditions it was found that about 50% of the sample polymerised in the boat. The experiment was repeated heating the first hot zone to 100°. Under these conditions very little polymerisation was obtained. Estimation from the amount if ethylene evolved suggests 70·9% dimerization. The sample was subjected to analysis as in previous cases and this indicates the gaseous mixture to be composed of 20% benzene and 80% ethylene. Therefore this reaction leads to 57% dimerisation. The pyrolysate consisted of a solid layer and a liquid layer. The liquid was identified as the dimer and the solid tentatively identified as 1,3-dimethyl-1,1,3,3-tetraphenyldisiloxane.

Examination of the I.R. spectra of the pyrolysate of 1,1-diisopropylsilacyclobutane, 1,1-di-n-butylsilacyclobutane, and 1,1-diphenylsilacyclobutane reveal a band at 2115 cm^{-1} of weak intensity. These bands indicate the presence of a silicon-hydrogen bond in the pyrolysates but as these absorptions, i.e. Si-H, are usually of strong intensity, the weak bands obtained suggest that only small amounts of the Si-H compounds are present.

The presence of prop-1-ene and but-1-ene in the gaseous mixtures, as well as in the silicon-hydrogen compounds, arises from the cleavage of the $>\mathrm{Si}<^{R}$ bond. For example,



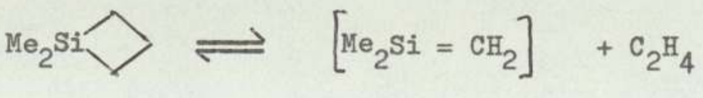
Thermal decomposition[50] of some tetraorganosilanes has been shown to proceed as suggested above:

$$R_3SiCH_2CH_2R^1 \longrightarrow R_3SiH + CH_2 = CHR^1$$

It should be emphasized at this stage that our work was complicated due to the breakdown of the mass spectrometer and for this reason we were not able to fully identify some of our products from these reactions. The investigation of 1,1-diisopropylsilacyclobutane was discontinued, since it was felt that with such a high proportion of isopropyl-silicon bond cleavage the pyrolysis of this silacyclobutane with trapping agents would be too complex. We had intended to prepare other sterically hindered 1,1-disubstituted silacyclobutanes at the onset of this investigation. However, since isopropyl-silicon bond cleavage occurred to such a large extent in the case of the diisopropyl compound, this possibility was not pursued. It can be seen from this initial investigation that the pyrolysis of silacyclobutane is more complex than Sommer and other workers have suggested.

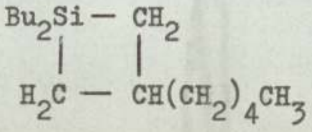
e) Pyrolysis of 1,1-di-n-butylsilacyclobutane and 1,1-diphenylsilacyclobutane with oct-1-ene as a trapping agent.

Gusel'nikov and Flowers[101] suggested that olefins hinder the pyrolysis of silacyclobutanes and that this inhibition is due to the reversible nature of the primary reaction.

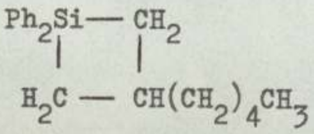


They obtained a compound tentatively identified as 1,1,3 (or 2) - trimethylsilacyclobutane from the pyrolysis of the 1,1 dimethylsilacyclobutane with prop-1-ene.

1,1-Di-n-butylsilacyclobutane and 1,1-diphenylsilacyclobutane were pyrolysed at 611° with oct-1-ene as the trapping agent. Examination of the resulting pyrolysates indicated that the expected compounds



and



had not been formed and that the dimerisation has been hindered to some extent. In both cases the starting compounds were the main products of the reaction together with about 10% of the disilacyclobutanes. Clearly these observations are not in agreement with those of Gusel'nikov and Flowers although these workers were investigating the 1,1-dimethyl system. Thus it seems that no reaction occurs between oct-1-ene and the 1,1 disubstituted silacyclobutanes with large substituents such as butyl or phenyl.

f) Pyrolysis of silacyclobutanes with aldehydes and ketones.

It has already been mentioned that complications arose in these reactions due to alkyl or aryl-silicon bond cleavage and the breakdown of the mass spectrometer. Thus we were not able to identify all the siloxanes formed from the reaction of silacyclobutanes with aldehydes and ketones. All trapping agents were pyrolysed on their own and analysis indicates that these did not suffer any decomposition during pyrolysis.

Pyrolysis of 1,1-di-n-butylsilacyclobutane with benzaldehyde.

1,1-Di-n-butylsilacyclobutane was pyrolysed at 611° with benzaldehyde. In a similar experiment with the dimethyl system, Sommer obtained benzene (35%), styrene (40·3%) hexamethylcyclotrisiloxane (4·4%) and octamethylcyclotrisiloxane (32%). G.L.C. of the pyrolysate indicates the presence of benzene (10%) and styrene (50%) together with a small amount of starting material and disilacyclobutane. It is difficult to establish if hexa-n-butylcyclotrisiloxane or octa-n-butylcyclotetrasiloxane were formed as a mass determination of the siloxane was not available.

Pyrolysis of 1,1-di-n-butylsilacyclobutane with pentan-2-one.

Sommer obtained a 2-(trimethylsiloxy)pent-1-ene and 2-(trimethylsiloxy)pent-2-ene as the major products from the pyrolysis of 1,1-dimethylsilacyclobutane with pentan-2-one. We did not obtain analogous products from the pyrolysis of 1,1-di-n-butylsilacyclobutane with pentan-2-one but obtained 1,3-dimethyl-1,1,3,3-tetra-n-butyldisiloxane $(Bu_2SiCH_3)_2O$ as the major product together with a small quantity of starting material and disilacyclobutane.

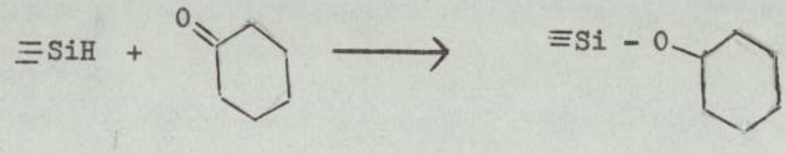
Pyrolysis of 1,1-di-n-butylsilacyclobutane and 1,1-diphenylsilacyclobutane with heptanal.

Sommer obtained oct-1-ene (19·2%), hexamethylcyclotrisiloxane (10·8%), octamethylcyclotetrasiloxane (2·3%), and 1-(trimethylsiloxy)-1-heptene (5·5%) from the pyrolysis of 1,1-dimethylsilacyclobutane and heptanal and oct-1-ene (33%) and hexaphenylcyclotrisiloxane (0·1%) from the pyrolysis of 1,1 diphenylsilacyclobutane and heptanal. We obtained oct-1-ene (4%) and 1,3-dimethyl 1,1,3,3-tetra-n-butyldisiloxane from the pyrolysis of 1,1-di-n-butylsilacyclobutane and heptanal together with starting material and disilacyclobutane. Similarly we obtained oct-1-ene (< 1·0%) and 1,3-dimethyl-1,1,3,3-tetraphenyldisiloxane from 1,1-diphenylsilacyclobutane together with starting material and disilacyclobutane.

Pyrolysis of 1,1-di-n-butylsilacyclobutane and 1,1-diphenylsilacyclobutane with cyclohexanone.

Sommer obtained 1-(trimethylsiloxy)cyclohexene (33·7%), methylenecyclohexane (6%) and hexamethylcyclotrisiloxane (5%) from the pyrolysis of 1,1-dimethylsilacyclobutane with cyclohexanone. Pyrolysis of 1,1-di-n-butylsilacyclobutane with cyclohexanone afforded methylenecyclohexane (6%) and another product identified as cyclohexene (4%) from its G.L.C. retention time. Similarly pyrolysis of 1,1-diphenylsilacyclobutane afforded methylene cyclohexane (5%) and cyclohexene (4%). No mass determinations were available for these experiments.

Sommer did not obtain cyclohexene as a reaction product and the presence of this compound in these reactions is rather difficult to explain. However, pyrolysis of silacyclobutanes has been shown to produce silicon-hydrogen bonds. If these compounds react with the ketone or more precisely if the ketone adds to these compounds, then:



The cyclohexene may then be formed from cleavage of the oxygen-carbon bond.

This investigation reveals that the pyrolysis of silacyclobutanes is far more complex than Sommer and other workers have suggested. Since we observed that alkyl or aryl-silicon bond cleavage as well as the formation of compounds containing silicon-hydrogen bonds accompany the formation of the disilacyclobutanes.

We observed no reaction between oct-1-ene and 1,1-di-n-butylsilacyclobutane and 1,1-diphenylsilacyclobutane. We obtained the starting materials together with some 10% of the disilacyclobutanes in each case from these reactions. It appears that the presence of oct-1-ene hinders the dimerization to a large extent.

We did not obtain the pseudo-wittig products or the silyl enol ethers, the products suggested by Sommer, from the pyrolysis of 1,1-di-n-butylsilacyclobutane and 1,1-diphenylsilacyclobutane with aldehydes and ketones, but obtained siloxanes of the type $(R_2SiMe)_2O$. It seems that if the observations of Sommer for the pyrolysis of 1,1-dimethylsilacyclobutane with aldehydes and ketones are correct, then the pyrolysis of 1,1-disubstituted silacyclobutanes with large substituents with aldehydes and ketones follows a different mechanistic pathway as our products indicate. Although some of these reaction products could arise from $\left[R_2Si = CH_2\right]$ intermediates, the intermediacy of these species needs to be confirmed by other techniques apart from product analysis.

EXPERIMENTAL

All melting points and boiling points are uncorrected, and all experiments involving organometallic compounds were carried out in an atmosphere of purified nitrogen.

N.M.R. Spectra were usually determined at 35° (unless otherwise stated). Routine spectra were recorded at 60 MHz/Sec, using either a Varian Associates A-60A spectrometer or a Perkin-Elmer R-10 model. For the accurate integration of dilute solutions (10% W/V or less), spectra were recorded at 100 MHz/Sec with a Perkin/Elmer R-14 spectrometer. Unless otherwise stated, spectra were recorded from samples of neat liquid or 20% solutions in carbon tetrachloride or deuterochloroform. Absorption positions are quoted relative to tetramethylsilane ($\tau = 10{\cdot}0$) as internal standard. Spectral assignments were based on the data of Mathieson.[122]

I.R. Spectra were obtained using a Perkin-Elmer infracord 237 and the interpretation of absorption bands was based on the texts of Bellamy[123] and Flett.[124] The anticipated silicon-methyl or silicon-phenyl absorptions were observed in all compounds and are not individually recorded.

G.L.C. Analyses were carried out on a Pye-Unicam series 104 instrument using a silicone gum SE30 column (9ft. x $\frac{1}{8}$in. o.d. or 5ft. x $\frac{1}{8}$in. o.d.) with helium as a carrier gas at a flow rate of 50 ml./min. Gas analyses were carried out using a Perkin-Elmer S-11 instrument using a 4m porapak Q column with nitrogen as the carrier gas.

Mass Spectra were determined using an A.E.I. MS9 mass spectrometer. Normal operating conditions consisted of an ionising potential of

70 e.v. and an inlet temperature of 150°C.

Column Chromatographic Separations were performed on a column (approximately $1\frac{1}{2}$ft. x 1 in. diameter) using 'silica gel M.F.C.' Anala R grade solvents were employed in all chromatographic experiments.

Reagents. Organosilanes were kindly donated by Midland Silicones Ltd., and the remaining chemicals were purchased from Messrs. Hopkin and Williams Ltd., or the alternative supplier indicated. The "Anala R" reagents benzene, light petroleum, carbon tetrachloride and diethyl ether were used without further purification. Organometallic reagents were prepared in reagent grade diethyl ether or tetrahydrofuran previously redistilled from lithium aluminium hydride.

A. REACTION OF ISOPROPYLMAGNESIUM BROMIDE AND TERT-BUTYLMAGNESIUM CHLORIDE WITH VINYLTRICHLOROSILANE.

1. Isopropylmagnesium bromide (0·70 mole) in dry diethyl ether (310 ml) was added to vinyltrichlorosilane (32·7g., 0·2 mole) in dry diethyl ether (40 ml) and the resulting mixture heated under reflux for 24 h. The magnesium salts were precipitated by the addition of an excess of light petroleum (b.p. 30-40°) to the cooled mixture and removed by filtration under nitrogen. The solvents were removed by distillation and fractionation afforded (a) 12% of a compound identified as 2-methylbutylisopropylchlorosilane, b.p. 174-178°, N.M.R. (CCl_4 Soln) : multiplet τ 5·4-5·6 (intensity 1), quartet τ 8·6-8·8 (intensity 2), singlet τ 9·0-9·1 (intensity 16); I.R. (neat liquid) : 2140 cm^{-1} (Si-H), 1370 cm^{-1} and 1380 cm^{-1} (gem dimethyl), 1170 cm^{-1} (isopropyl on Si.)
(b) 31% of a compound identified as 2-methylbutylisopropyldichlorosilane, b.p. 210 - 212°, N.M.R. (CCl_4 Soln) : quartet τ 8·6-8·8 (intensity 2), singlet τ 9·0-9·1 (intensity 16); I.R. (neat liquid) : 1370 and 1380 cm^{-1} (gem dimethyl), 1170 cm^{-1} (isopropyl on silicon).

Examination of the residue indicated the presence of siloxanes and silanol. The reaction was repeated in tetrahydrofuran and similar quantities of products were isolated.

Tert-butylmagnesium Chloride (0·5 mole) in dry diethyl ether (220 ml) was added dropwise to vinyltrichlorosilane (32·7 g., 0·2 mole) and the resulting mixture heated under reflux for 3 days. The magnesium salts were precipitated by the addition of an excess of light petroleum (b.p. 30 - 40°) to the cooled mixture and removed by filtration under nitrogen. The solvents were removed by distillation and fractionation afforded (a) 14% of a compound identified as 2,2-dimethylbutyldichlorosilane, b.p. 164 - 168 °, N.M.R. (CCl_4 Soln) : Singlet τ 5·3 (intensity 1)

triplet τ 8·6 - 8·7 (intensity 2) singlet τ 8·95 (intensity 2) singlet τ 9·1 (intensity 9). I.R. (neat liquid) 2135 cm^{-1} Si-H.
(b) 36% of a compound identified as 2,2-dimethylbutyltrichlorosilane, b.p. 182 - 186°, N.M.R. (CCl_4Soln) : triplet τ 8·6 - 8·7 (intensity 2) singlet τ 9·1 (intensity 9) singlet τ 8·95 (intensity 2).

Examination of the residue indicated the presence of siloxanes and silanol. The reaction was repeated in tetrahydrofuran and similar quantities of products were isolated.

B. ATTEMPTED PREPARATION OF SILACYCLOPROPANES.

Diisopropyldichlorosilane was prepared by the addition of isopropyllithium[7] (1 mole) in petroleum ether b.p. 28 - 38° (780 ml) to silicon tetrachloride (84g., 0·5 mole) in petroleum ether (100 ml) and the reaction mixture was refluxed for 6 h. The solvent was removed by distillation and fractionation afforded 65% diisopropyldichlorosilane, b.p. 162°. (lit[36] 56·5°/21mm.). N.M.R. (CCl_4 Soln) : singlet τ9·0.

Diisopropylvinylchlorosilane was prepared by the addition of vinyllithium[125] (0·2 mole) in dry diethyl ether (210 ml) to diisopropyldichlorosilane (36·8g., 0·2 mole) in dry diethyl ether (40 ml). The reaction mixture was heated under reflux for 24 h. The lithium salts were removed by filtration under nitrogen and the solvent removed by distillation. Fractionation afforded 32% diisopropylvinylchlorosilane, b.p. 163 - 164°. N.M.R. (CCl_4 Soln) : multiplet τ 3·8 - 4·2 (intensity 3) singlet τ 9·0 (intensity 14).

(2-bromoethyl)diisopropylchlorosilane diisopropylvinylchlorosilane (8·83g., 0·05 mole) was dissolved in dry carbon tetrachloride (20 ml). Dry hydrogen bromide was bubbled through the solution and when all the vinylic absorption had disappeared (N.M.R. analysis), the products were concentrated firstly by rotary film evaporation and finally under high vacuum. Yield 12·88g. quantitative (clear oil) N.M.R. (CCl_4 Soln) : triplet τ6·2 - 6·4 (intensity 2) singlet τ9·0 (intensity 16).

Di-tertbutyldichlorosilane was prepared according to the method of Whitmore[8] except that commercial t-butyllithium in pentane was employed (ex Ventron - Alfa products) yield 30%, b.p. 194°, (Lit[8] 190°/729mm) N.M.R. (CCl_4 Soln) singlet τ 9·0.

The bi-product - ditert-butylchlorosilane was isolated in approx. 30% yield.

Ditert-butylvinylchlorosilane was prepared by the addition of vinyllithium[125] (0·4 mole) in dry diethyl ether (425 ml) to ditert-butyldichlorosilane (85·2g., 0·4 mole) in dry diethyl ether (80 ml). The reaction mixture was heated under reflux for 24 h and the lithium salts were removed by filtration under nitrogen. The solvent was removed by distillation and subsequent fractionation afforded 15% ditert-butylvinylchlorosilane, b.p. 195°. N.M.R. (CCl_4 Soln) : multiplet τ 3·8 - 4·2 (intensity 3) sharp singlet τ 9·0 (intensity 18).

(2-bromoethyl)ditert-butylchlorosilane ditert-butylvinylchlorosilane (10·22g., 0·05 mole) was dissolved in dry carbon tetrachloride (20 ml). Dry hydrogen bromide was bubbled through the solution and when all the vinylic absorption had disappeared (N.M.R. analysis), the products were concentrated firstly by rotary film evaporation and finally under high vacuum. Yield 14·28g. quantitative (clear oil) N.M.R. (CCl_4 Soln) : Triplet τ 6·2 - 6·4 (intensity 2) sharp singlet τ 9·0 (intensity 20).

(2-bromoethyl)diisopropylchlorosilane (3·08g., 0·012 mole) in dry tetrahydrofuran (60 ml) magnesium (2·0g., 0·082 mole) in dry tetrahydrofuran (10 ml). After the addition reflux was maintained for 24 h. The reaction mixture was then poured into excess light petroleum (b.p. 30 - 40°), filtered and concentrated by rotary film evaporation. The magnesium recovered (1·96g.) suggests that the Grignard reagent had not been formed. Analysis of the viscous brown material recovered suggests that the starting material had decomposed during the reaction.

(2-bromoethyl)ditert-butylchlorosilane (3·46g. 0·012 mole) in dry tetrahydrofuran (60 ml) was added dropwise to a slurry of magnesium (2·0g., 0·082 mole) in dry tetrahydrofuran (10 ml) and the reaction carried out as described in the previous experiment. Examination of the products suggests that Grignard formation had not taken place and that the starting material had decomposed during the reaction.

C. PREPARATION OF STERICALLY HINDERED (2-BROMOETHYL)TRIALKYLSILANES

Tri-n-propylvinylsilane was prepared according to the method of Nagel and Post.[126] Yield 49%, b.p. 75 - 76°/5mm. (Lit[126] 73°/4·5 mm) N.M.R. (CCl_4 Soln) : multiplet τ 3·8 - 4·5 (intensity 3) complex multiplet τ 8·4 - 9·6 (intensity 21) due to propyl on silicon.

Tri-n-butylvinylsilane was prepared as described by Nagel and Post.[126] Yield 60% b.p. 91 - 92°/5mm. (Lit[126] b.p. 99°/6·5mm.). N.M.R. (CCl_4 Soln) : multiplet τ 3·8 - 4·7 (intensity 3) complex multiplet τ 8·5 - 9·7 (intensity 27) due to butyl on silicon.

Diisopropylmethylchlorosilane was prepared by the addition of isopropylmagnesium bromide (0·45 mole) in dry diethyl ether (200 ml) to methyltrichlorosilane (29·9g., 0·2 mole) in dry diethyl ether (40 ml) and the resulting mixture heated under reflux for 24 h. The magnesium salts and solvent were removed in the usual way. Fractionation afforded 55% diisopropylmethylchlorosilane b.pt. 170°. (Lit[36] 62°/37 mm.).

This compound was also prepared by the addition of isopropyllithium (0·4 mole) in petroleum ether (320 ml) to methyltrichlorosilane (29·9g., 0·2 mole) in petroleum ether (40 ml) and the resulting mixture heated under reflux for 6 h. After removal of lithium salts and solvent, fractionation afforded 65% diisopropylmethylchlorosilane b.p. 170° (Lit[36] 62°/37 mm.). N.M.R. (CCl_4 Soln) : Singlet τ 9·1 (intensity 14) singlet τ 9·95 (intensity 3).

Diisopropylmethylvinylsilane was prepared by the addition of vinyllithium[125] (0·2 mole) in diethyl ether (215 ml) to diisopropylmethylchlorosilane (32·9g., 0·2 mole) in diethyl ether (40 ml). The ether was replaced by toluene and the compound heated under reflux for 6 h. The lithium salts and solvent were removed in the usual way and fractionation afforded 35% diisopropylmethylvinylsilane, b.p.

172°C. N.M.R. (CCl_4 Soln) : multiplet τ 3·8 - 4·2 (intensity 3) singlet τ 9·05 (intensity 14) singlet τ 9·95 (intensity 3).

<u>Triisopropylsilane</u> was prepared according to the method of Nametkin et al.[127] Yield 57%, b.p. 60°/10 mm. (Lit[127] 84-86°/35 mm.) N.M.R. (CCl_4 Soln) singlet τ 6·65 (intensity 1) singlet τ 9·0 (intensity 21).

<u>Triisopropylchlorosilane</u> was prepared by passing chlorine gas into a solution of triisopropylsilane in dry carbon tetrachloride (40g./200 ml.) at 0°C. The chlorination was followed by G.L.C. and the chlorine gas stopped when the peak corresponding to triisopropylsilane disappeared. Fractionation afforded a colourless oil. Yield 90%, b.p. 78-80°/1·0 mm. (Lit[36] 47°/4 mm.) N.M.R. (CCl_4 Soln) singlet τ 9·0.

<u>Triisopropylvinylsilane</u> was prepared by the addition of vinyllithium[125] (0·2 mole) in dry diethyl ether (215 ml) to triisopropylchlorosilane (38 5g., 0·2 mole) in dry diethyl ether (40 ml). The ether was removed and the solvent replaced by toluene. The resulting mixture was heated under reflux for 24 h. The lithium salts and solvent were removed in the usual way and fractionation afforded 18% triisopropylvinylsilane, b.p. 172°C. N.M.R. (CCl_4 Soln) multiplet τ 3·8 - 4·2 (intensity 3) singlet τ 8·95 (intensity 21).

In the following preparations, hydrogen bromide was generated by the addition of water to phosphorus tribromide and dried by passing through a trap at - 40°. Carbon tetrachloride was distilled and stored over molecular sieves.

<u>(2-Bromoethyl)diisopropylmethylsilane</u> was obtained by passing hydrogen bromide through a solution of diisopropylmethylvinylsilane (7 8g., 0·05 mole) in carbon tetrachloride (40 ml) until all the

vinylic absorption (N.M.R.) disappeared. This compound was obtained in quantitative yield. Yield 11·4g. N.M.R. (CCl_4 Soln) : triplet τ 6·35 - 6·7 (intensity 2), singlet τ 9·02 (intensity 16) singlet τ 9·95 (intensity 3) (Found : Br 33·8. Calc. for $C_9H_{21}BrSi$: Br, 33·76%).

(2-Bromoethyl)triisopropylsilane was obtained by passing hydrogen bromide through a solution of triisopropylvinylsilane (9·2g., 0·05 mole) in carbon tetrachloride (45 ml.) until all the vinylic absorption (N.M.R.) disappeared. This compound was obtained in quantitative yield. Yield 13·25g. N.M.R. (CCl_4 Soln) : triplet τ 3·9 - 4·2 (intensity 2) singlet τ 9·0 (intensity 23). (Found Br 30·5. Calc. for $C_{11}H_{25}BrSi$: Br 30·3%).

2-Bromoethyltri-n-propylsilane was obtained by passing hydrogen bromide through a solution of tri-n-propylvinylsilane (36·8g. 0·2 mole) in carbon tetrachloride (185 ml) until all the vinylic absorption (N.M.R.) disappeared. This compound was obtained in quantitative yield. Yield 53g. N.M.R. (CCl_4 Soln) : triplet τ 6·3 - 6·6 (intensity 2) complex multiplet τ 8·4 - 9·6 (intensity 23) due to propyl on silicon (Found Br 30·6. Calc. for $C_{11}H_{25}BrSi$: Br 30·3%).

2-Bromoethyltri-n-butylsilane was obtained by passing hydrogen bromide through a solution of tri-n-butylvinylsilane (45g., 0·2 mole) in carbon tetrachloride (225 ml.) until all the vinylic absorption (N.M.R.) disappeared. This compound was obtained in quantitative yield. Yield 57·8g. N.M.R. (CCl_4 Soln) : triplet τ 6·35 - 6·75 (intensity 2) complex multiplet τ 8·4 - 9·6 (intensity 29) due to butyl on silicon. (Found Br 26·4 Calc. for $C_{14}H_{31}BrSi$: Br 26·06%).

Titration of (2-bromoalkyl)silanes

The percentage bromine of (2-bromoalkyl)trialkylsilanes was estimated as follows:

The (2-bromoalkyl)trialkylsilanes (approx. 0·25g.) were carefully weighed into acetone (25 ml.) and standard sodium hydroxide solution (0.IN., 25·0 ml) was added. The solutions were periodically shaken during 4 h. and then back titrated with standard acid using phenolphthalein as indicator. Blank determinations were also carried out in the absence of halide.

Di-n-butylvinylchlorosilane was prepared by the addition of butylmagnesium bromide (0·40 mole) in diethyl ether (180 ml.) to vinyltrichlorosilane (32·7g., 0·20 mole) in diethyl ether (40 ml.). The resulting mixture was heated under reflux for 6 h. The magnesium salts and solvent were removed in the usual way. Fractionation afforded di-n-butylvinylchlorosilane. Yield 67%, b.p. 210-212°. N.M.R. (CCl_4 Soln) : multiplet τ 3·8 - 4·6 (intensity 3) complex multiplet τ 8·4 - 9·6 (intensity 18).

Attempts to add hydrogen bromide to this compound resulted in only 40 - 50% addition even in the presence of benzoyl peroxide. Treatment of di-n-butylvinylsilane with butylmagnesium bromide afforded tri-n-butylvinylsilane.

D. REACTIONS OF STERICALLY HINDERED (2-BROMOETHYL)TRIALKYLSILANES

1. The Solvolysis of sterically hindered (2-bromoethyl)trialkylsilanes.

a) preparation of standards.

Tri-n-butylsilane was prepared according to the method of Gilman et al.[128] Yield 50g., 70%, b.p. 218 - 220° (lit[128] 215 - 220°); N.M.R. (CCl_4 Soln.) : quintet τ 6·25 - 6·45 (intensity 1) complex multiplet τ 8·5 - 9·6 (intensity 27) due to butyl on silicon.

Tri-n-butylchlorosilane chlorine gas was bubbled into a solution of tri-n-butylsilane in dry carbon tetrachloride (50g./200 ml) at 0 C. The chlorination was followed by G.L.C. (temp. 200°) and the chlorination stopped when the peak corresponding to tri-n-butylsilane disappeared. Distillation afforded a colourless oil. Yield 52·9 g., 90%, b.p. 97 - 98°, (1·0 mm), (Lit.,[128] 134 - 139°/16 mm.). N.M.R. (CCl_4 soln.) complex region τ 8·4 - 9·6 due to butyl on silicon.

Ethyl(tri-n-butylsilyl)acetate was prepared by modifying the method of Fessenden and Fessenden.[129] A solution of 46·5g. (0·2 mole) of ethylbromoacetate in 50 ml dry benzene and 50 ml dry diethyl ether was added to 15·8g. zinc wool in 250 ml benzene contained in a flask. The solution was refluxed for two days when most of the zinc was used up. The mixture was acidified, washed and dried. The ester was separated from hydroxytri-n-butylsilane and other by-products by elution with benzene from a silica gel column. Yield 5·8g., 10%, b.p. 115 - 118°/ 0·1 mm.

The physical properties and the I.R. and N.M.R. spectra of this ester were consistent with those reported by Fessenden and Fessenden.[129]

(2-Hydroxyethyl)tri-n-butylsilane was prepared by the slow addition of ethyl(tri-n-butylsilyl)acetate (2·86g., 0·010 mole) in dry diethyl ether (4 ml.) to a stirred suspension of lithium aluminium hydride (0·4g., 0·0096 mole.) in dry diethyl ether (8 ml.). The resulting mixture was stirred for 1 h. after which the excess reducing agent was destroyed by careful hydrolysis with water. The aqueous layer was extracted with ether and the combined extracts dried over magnesium sulphate. Fractionation afforded (2-hydroxyethyl)tri-n-butylsilane. Yield 1·582g., b.p. 123 - 125°/0·2 mm. N.M.R. (CCl_4 Soln.) singlet τ 6·3 (intensity 1) triplet τ 6·1 - 6·3 (intensity 2) complex multiplet τ 8·4 - 9·4 (intensity 29) due to butyl on silicon. (Found : C_2H_4 12·0%. Calc. for $C_{14}H_{32}OSi$ 11·45%).

Hydroxytri-n-butylsilane was prepared as described by Calas et al.[130] Yield 14g., 70%, b.p. 128 - 130°/10 m.m. (Lit. 140 - 141°/26). N.M.R. (CCl_4 Soln.) singlet τ 6·3 (intensity 1) complex multiplet τ 8·5 - 9·6 (intensity 27).

Trimethylvinylsilane was prepared using the method of Nagel and Post;[126] b.p. 54 - 56° (Lit.[123] 54·4 / 745·4 mm.); N.M.R. (neat liquid) : complex multiplet τ 3·7 - 4·6 (intensity 3) singlet τ 9·9 (intensity 9).

(2-Bromoethyl)trimethylsilane was prepared from trimethylvinylsilane and hydrogen bromide using the method of Sommer et al,[131] b.p. 66°/40 mm. (Lit. 64 - 65°/39 mm.); N.M.R. (neat liquid) : multiplet τ 6·5 (intensity 2) singlet τ 10·0 (intensity 9). (Found : titratable Br, 44·7. $C_5H_{13}BrSi$ calcd. titratable Br 44·11%).

b) solvolysis reactions

The attempted solvolysis of (2-bromoethyl)diisopropylmethylsilane.

The halide (0·33g., 0·0014 mole.) was stirred at room temperature with tetrahydrofuran/water (50/50, V/V - total volume 136 ml.) for five hours and the mixture then extracted with ether. After drying over magnesium sulphate, the ethereal layer was evaporated to yield a liquid (0·30g.). Analysis indicated that a quantitative yield of starting halide had been achieved.

In another reaction (2-bromoethyl)diisopropylmethylsilane (0·33g., 0·0018 mole.) in diethyl ether (20 ml.) was stirred at room temperature with methanol (20 ml.) for five hours. Separation and identification of the product obtained indicated that once again a quantitative recovery of the halide had been achieved.

The attempted solvolysis of (2-bromoethyl)triisopropylsilane.

The halide (0·37g., 0·0014 mole.) was stirred at room temperature with tetrahydrofuran/water (50/50, V/V - total volume 136 ml.) for five hours and the mixture then extracted with ether. After drying and evaporating the solvent a liquid was obtained (0·33g.). Analysis indicated that a quantitative yield of the halide had been achieved.

The halide (0·37g., 0·0014 mole.) in diethyl ether (20 ml.) was stirred at room temperature with methanol (20 ml.). Separation and identification of the product obtained indicated that a quantitative yield of the halide had been achieved.

The solvolysis of (2-bromoethyl)tri-n-propylsilane.

The halide (0·37g., 0·0014 mole.) in tetrahydrofuran/water (50/50, V/V - total volume 136 ml.) was heated under reflux for 24 hours. After drying over magnesium sulphate, the ethereal layer was evaporated to yield a liquid (0·21g.). Analysis indicated that this compound was hydroxytri-n-propylsilane. N.M.R. (CCl_4 Soln.) : singlet τ 5·8 (intensity 1) complex multiplet τ 8·4 - 8·9 (intensity 6) triplet τ 8·9 - 9·3 (intensity 6) complex multiplet τ 9·3 - 9·7 (intensity 9).

In another reaction, the halide (0·37g. 0·0014 mole.) in diethyl ether (20 ml.) was heated under reflux with methanol (20 ml.) for 24 hours. Separation and identification of the product obtained (0·25g.) indicated that methoxytri-n-propylsilane had been produced. N.M.R. (CCl_4 Soln.) : Singlet τ 6·8 (intensity 3) multiplet τ 8·4 - 8·8 (intensity 6) triplet τ 8·8 - 9·2 (intensity 6) multiplet τ 9·2 - 9·6 (intensity 9).

The solvolysis of (2-bromoethyl)tri-n-butylsilane.

The halide (0·43g., 0·0014 mole.) in tetrahydrofuran/water (50/50, V/V - total volume 136 ml.) was heated under reflux for five days. After drying over magnesium sulphate, the ethereal layer was evaporated to yield a liquid (0·3g.) G.L.C. (160°) indicated the presence of two compounds in a 1 : 9 ratio and from their retention time were identified as (2-hydroxyethyl)tri-n-butylsilane and hydroxytri-n-butylsilane. The compounds were subsequently separated on a silica gel column. Elution with benzene afforded hydroxytri-n-butylsilane (90%) and with benzene/ether afforded (2-hydroxyethyl)tri-n-butylsilane (10%). The I.R. and N.M.R. spectra of these compounds were identical to those of authentic samples of hydroxytri-n-butylsilane and (2-hydroxyethyl)tri-n-butylsilane.

In another reaction (2-bromoethyl)tri-n-butylsilane (0·43g., 0·0014 mole.) in diethyl ether (20 ml.) was heated under reflux with methanol (20 ml.). Separation and identification of the product (0·29g.) indicated that methoxytri-n-butylsilane had been produced. N.M.R. (CCl_4 Soln.) : singlet τ 6·8 (intensity 3) complex multiplet τ 8·5 - 9·7 (intensity 27).

c) Kinetics

The value of the first order rate constants for $Me_3SiCH_2CH_2Br$, $Pr_3SiCH_2CH_2Br$ and $Bu_3SiCH_2CH_2Br$ were determined by following the rate of ethylene evolution which was observed on a simple apparatus. This consisted of a thermostated reaction vessel, in which a liquid could be shaken, connected to a manometer. The reaction vessel was attached to a shaker and connected to a fixed burette via a flexible coupling. The volume of the burette was kept small in relation to the gas space in the reaction vessel.

The silane was weighed into a small glass-stoppered container, which was introduced into the reaction vessel containing the previously equilibrated solvent. The reaction vessel was reconnected to the manometer and the agitation of the vessel was sufficient to cause the release of the stopper from the container and allow the reaction to proceed. Timing began as soon as the two liquids came into contact.

Kinetic measurements were performed on solutions containing the silane in 80% aqueous ethanol at approximately 25°. The volume of ethylene evolved during the kinetic runs was recorded and was approximately 75 - 90% of the theoretical volume for each of the silanes.

The rate of solvolysis of $Me_3SiCH_2CH_2Br$ was found to be 105 times faster than $Pr_3SiCH_2CH_2Br$ and 200 times faster than $Bu_3SiCH_2CH_2Br$.

2. Rearrangement of (2-hydroxyethyl-2,2-d_2)tri-n-butylsilane with phosphorus tribromide and thionyl chloride.

(2-Hydroxyethyl-2,2-d_2)tri-n-butylsilane was prepared by the slow addition of ethyl(tri-n-butylsilyl)acetate (2·86g. 0·010 mole.) in dry diethyl ether (4 ml.) to a stirred suspension of lithium aluminium deuteride (99% isotopic purity - ex CIBA) (0·4g., 0·0096 mole.) in diethyl ether (8 ml.). The resulting mixture was stirred for one hour after which the excess reducing agent was destroyed by careful hydrolysis with water. The aqueous layer was extracted with ether and the combined extracts dried over magnesium sulphate. Fractionation afforded

(2-hydroxyethyl-2,2-d_2)tri-n-butylsilane, b.p. 125 - 127°/0·2 mm. yield) (1·62g., 67%). N.M.R. (CCl_4 Soln.) : singlet τ 6·3 (intensity 1) complex multiplet τ 8·4 - 9·6 (intensity 29). The I.R. spectrum of the alcohol showed characteristic carbon-deuterium absorptions at 2180 cm^{-1} and 2080 cm^{-1}. (Found $C_2H_2D_2$ 12·0% Calc. for $C_{14}H_{32}OSi$ 11·48%).

Thionyl chloride or phosporus tribromide was added dropwise, in excess, to (2-hydroxy-2,2-d_2)tri-n-butylsilane at 0° and after the addition was complete the N.M.R. spectra of the resulting solution was recorded at 35°. These spectra indicate that the resulting material contained 60% (2-haloethyl-2,2d_2)tri-n-butylsilane and 40% (2-haloethyl-1,1d_2)tri-n-butylsilane.

3. The effect of lanthanide shift reagents on the N.M.R. spectra of (2-hydroxyethyl)tri-n-butylsilane and (2-hydroxyethyl-2,2-d_2)tri-n-butylsilane.

The lanthanide shift reagents $Eu(fod)_3$ and $Dy(dpm)_3$ were added to CCl_4 solutions of compounds as follows:

$Bu_3SiCH_2CH_2OH$	$Eu(fod)_3$
$Bu_3SiCH_2CD_2OH$	$Dy(dpm)_3$
$Bu_3SiCH_2CD_2OH$	$Eu(fod)_3$
$Bu_3SiCH_2CD_2OH + PBr_3$	+ $Eu(fod)_3$

The N.M.R. of the resulting solutions were recorded and the spectra shown in figure 3, pages 54,55. The spectra could not be interpreted.

4. The attempted trapping of the 2-(tri-n-butylsilyl)ethyl cation by the silane hydride transfer.

Technical grade methylene chloride was purified as described by Vogel[132] and the distilled product stored over molecular sieves. Trifluoroacetic acid (ex Koch-Light) was used without further purification.

(2-hydroxyethyl)tri-n-butylsilane was prepared as previously described.

Triisopropylsilane was prepared according to the method of Nametkin.[127] Yield 57%; b.p. 60°/10 mm. (Lit. 84 - 86°/35 mm.). N.M.R. (CCl_4 Soln.) : singlet τ 6·65 (intensity 1) singlet τ 9·0 (intensity 21).

Ethyltri-n-butylsilane was prepared following the method of Topchiev.[133] Yield 65%; b.p. 110°/5mm. (Lit. 95 - 96°/2 mm.) N.M.R. (CCl_4 Soln.) : complex multiplet τ 8·4 - 9·6. The conditions employed are similar to those of Carey and Tremper. The reaction was carried out as follows:

Trifluoroacetic acid (0·80g., 0·0070 mole.) was added to a mixture of (2-hydroxyethyl)tri-n-butylsilane (0·756g., 0·0035 mole.) and triisopropylsilane (0·664g., 0·0042 mole.) in methylene chloride (alcohol/solvent 8% W/V) at - 15°. This temperature was maintained for 30 minutes, after which the reaction was quenched with sodium carbonate and the products analysed.

The reaction was repeated at R.T.

Identification of Products.

This was achieved by the combined use of G.L.C., N.M.R. and I.R. analyses. A mixture of authentic samples of ethyltri-n-butylsilane and triisopropylsilane was readily separable at 200° although (2-hydroxyethyl)tri-n-butylsilane and 2-(tri-n-butylsilyl)ethyl trifluoroacetate had greater retention times at this temperature and were observed as broadish peaks.

G.L.C. analysis of the reaction of the alcohol at - 15° indicated that no reaction had taken place. However, analysis of the reaction at R.T. indicated that ethyltri-n-butylsilane had been formed. The only other product detected in the reaction was 2-(tri-n-butylsilyl)ethyl trifluoroacetate and this was identified from the I.R., N.M.R. and mass spectrum. I.R. : strong absorption 1780 cm^{-1} (cf Carey and Tremper - trifluoroacetate compounds 1780 cm^{-1}); N.M.R. (CCl_4 Soln.) : τ 5·6 (intensity 2), complex region τ 8·4 - 9·6 (intensity 29).
(Lit.[79] RCH_2OCOCF_3, methylene protons τ 5·5 - 5·8).

5. Reaction of sterically hindered (2-bromoethyl)trialkylsilanes with magnesium.

(2-Bromoethyl)diisopropylmethylsilane (1·95g., 0·0082 mole.) in diethyl ether (9·0 ml.) was added dropwise to magnesium metal (0·60g., 0·025g. atom) in diethyl ether (3·0 ml.) under an atmosphere of nitrogen. Ethylene dibromide (2 drops) was added to try and initiate the reaction and stirring under reflux conditions was continued for one hour. The resulting mixture was hydrolysed with dilute hydrochloric acid (10% V/V) and washed with sodium bicarbonate and water. The organic phase was dried over magnesium sulphate and evaporation gave a liquid. Analysis of the resulting liquid indicated that the starting material had been recovered.

(2-Bromoethyl)triisopropylsilane (2·17g., 0·0082 mole) in diethyl ether (9·0 ml.) was added dropwise to magnesium metal (0·60g., 0·025g. atom) and the reaction carried out as outlined above. Analysis of the resulting material indicated that the starting material had been recovered.

(2-Bromoethyl)tri-n-propylsilane (2·17g., 0·0082 mole) in diethyl ether (9·0 ml.) was added dropwise to magnesium metal (0·60g., 0·025g. atom) and the reaction carried out as previously described. Analysis of the resulting material indicated that fragmentation had taken place. Separation on a silica gel column using benzene or benzene/ether as eluent afforded hydroxytri-n-propylsilane 72%; N.M.R. (CCl_4 Soln.) : singlet τ 5·8 (intensity 1) complex multiplet τ 8·4 - 8·9 (intensity 6) triplet τ 8·9 - 9·3 (intensity 6) complex multiplet τ 9·3 - 9·7 (intensity 9) and hexa-n-propyldisiloxane 16%; N.M.R. (CCl_4 Soln.) : complex region τ 8·4 - 9·7; I.R. (heat liquid) : Si-o-Si absorption 1050 cm^{-1}.

(2-Bromoethyl)tri-n-butylsilane (2·52g., 0·0082 mole.) in 9·0 ml diethyl ether was added dropwise to magnesium metal (0·60g., 0·025g. atom) in diethyl ether and the reaction carried out as described previously. Separation on a silica gel column and subsequent analysis indicated that ethyltri-n-butylsilane (60%) and hydroxytri-n-butylsilane (21%) had been produced. The I.R. and N.M.R. spectra of these compounds were identical to authentic spectra of ethyltri-n-butylsilane and hydroxytri-n-butylsilane.

The reaction between (2-bromoethyl)tri-n-butylsilane and magnesium in ether was repeated. When the reaction was completed, denterium oxide (10·0g., 0·5 mole.) was added dropwise and the resulting mixture stirred for 30 minutes. (The deuterium oxide was supplied by Koch-Light, purity 99·75%). The organic phase was dried over magnesium sulphate. The products were separated on a silica gel column. Examination of the I.R. and mass spectra indicated that less than 10% deuterium incorporation had taken place (estimated from intensities).

6. Reaction of (2-bromoethyl)tri-n-propylsilane and (2-bromoethyl)tri-n-butylsilane with aluminium chloride.

The reaction was carried out as described by Sommer.[41] (2-Bromoethyl)-

tri-n-butylsilane (4·9g., 0·016 mole.) was added dropwise to aluminium chloride (0.4g.) in pentane (5 ml.). The reaction mixture was stirred for one hour. Evolution of gas was observed and the mixture changed from colourless to red. Analysis indicated that the mixture consisted of approximately 50/50 tri-n-butylbromosilane and tri-n-butylchlorosilane; N.M.R. (CCl_4 Soln.) : complex multiplets τ 8·4 - 8·9 and τ 9·0 - 9·5.

The reaction was repeated with (2-bromoethyl)tri-n-propylsilane (4·24g. 0·016 mole.). Analysis indicated that the mixture consisted of approximately 50/50 tri-n-propylbromosilane and tri-n-propylchlorosilane; N.M.R. (CCl_4 Soln.) : complex multiplets τ 8·3 - 8·9 and τ 8·9 - 9·4.

E. REACTIONS OF CHLOROMETHYLTRI-n-BUTYLSILANE

Ethanol was dried by the method of Lund and Bjerrum.[134] Sodium metal was purchased from Hopkin and Williams Limited and Aluminium Chloride from B.D.H.

Chloromethyltrichlorosilane was prepared by the method of Jones. Yield 10%, b.p. 119°.

Chloromethyltri-n-butylsilane was prepared by the addition of butylmagnesium bromide (0·75 mole.) in dry diethyl ether (330 ml.) to a stirred solution of chloromethyltrichlorosilane (0·2 mole.) in dry diethyl ether (40 ml.). After the addition, the reaction mixture was heated under reflux for 8 hours and subsequently hydrolysed. The organic layer was dried over magnesium sulphate. Fractionation afforded two products in 1 : 3 ratio.

a) Yield 7·28g., 17%, b.p. 70 - 71°/1mm. (Lit.,[135] b.p. 117 - 118 /17mm.) N.M.R. (CCl_4 Soln.) complex multiplet τ 8·4 - 9·6 (intensity 27) singlet τ 9·9 (intensity 3). This compound was identified as methyltri-n-butylsilane.

b) Yield 23·82g., 48%, b.p. 103 - 105°/1mm. N.M.R. (CCl_4 Soln.) singlet τ 7·2 (intensity 2) complex multiplet τ 8·4 - 9·6 (intensity 27). This compound is chloromethyltri-n-butylsilane.

Reaction of chloromethyltri-n-butylsilane with sodium metal in ethanol.

A mixture of chloromethyltri-n-butylsilane (1·24g., 0·005 mole.) and sodium metal (1·2g., 0·05 mole.) in ethanol (45 ml.) was stirred and heated under reflux until all the sodium metal had dissolved ($\simeq$ 45 minutes). Light petroleum (30 - 40°) was added and the reaction mixture was hydrolysed with water and dilute hydrochloric acid. The aqueous layer was extracted several times with light petroleum and diethyl ether. The combined light petroleum and ether extracts were washed with water and dried over magnesium sulphate. Evaporation of the solvents yielded methyltri-n-butylsilane (71%). N.M.R. (CCl_4) complex multiplet τ 8·4 - 9·6 (intensity 27) singlet τ 9·9 (intensity 3) together with a trace of starting material.

Reaction of Chloromethyltri-n-butylsilane with Sodium ethoxide.

Chloromethyltri-n-butylsilane (1·24g., 0·005 mole.) was added to a solution of sodium ethoxide (sodium 1·2g., 0·05 mole. in ethanol 30 ml.) in ethanol (20 ml.). The reaction mixture was refluxed for three days. Light petroleum (B.p. 30 - 40°) was then added to the cooled mixture and the latter subsequently hydrolysed with water and dilute hydrochloric acid. The aqueous layer was extracted several times with light petroleum and diethyl ether. The organic phase was dried over magnesium sulphate. Evaporation of the solvent and subsequent separation on silica gel column with petroleum ether/benzene as eluent yielded 20% ethoxymethyltri-n-butylsilane. N.M.R. (CCl_4 Soln.) quartet τ 6·5 - 6·6 (intensity 2) singlet τ 6·7 (intensity 2) complex multiplet τ 8·4 - 9·6 (intensity 30) and 68% chloromethyltri-n-butylsilane.

Reaction of chloromethyltri-n-butylsilane with aluminium chloride.

Conditions similar to those of Sommer[92] were employed.

Chloromethyltri-n-butylsilane (3·72g., 0·015 mole.) and powdered aluminium chloride were heated to approximately 100°. The mixture was filtered and analysis indicated a quantitative recovery of chloromethyltri-n-butylsilane.

F. THE PYROLYSIS OF SILACYCLOBUTANES.

Chloroplatinic acid was purchased from Hopkin and Williams Limited. Magnesium powder (ex.-Fison) was used for the cyclisation of silacyclobutanes.

(3-Bromopropyl)trichlorosilane was obtained using the method of Laane.[136] Yield 105g., 55%, b.p. 200 - 202° (Lit.[136] 202 - 204°). N.M.R. (CCl_4 Soln.) : Triplet τ 6·5 (intensity 2) multiplet τ7·8 (intensity 2) multiplet τ 8·3 (intensity 2).

1,1-dichlorosilacyclobutane was prepared as described by Laane.[136] Yield 35·4g., 62%, b.p. 112 - 114° (Lit.[136] 113 - 114°).

Silacyclobutane was prepared using the method of Laane.[136] Yield 15g., 57%, b.p. 44 - 46° (Lit.[136] 35 - 46°). N.M.R. (CCl_4 Soln.) : multiplet τ 5·3 - 5·6 (intensity 2) quintet τ 7·5 - 8·0 (intensity 2) triplet τ 8·8 - 9·2 (intensity 4) I.R. (neat liquid) : 2140 cm^{-1} Si - H absorption, 927cm^{-1}, 910cm^{-1}, 877cm^{-1} - ring vibrations.

1,1-Dimethylsilacyclobutane was prepared by the addition of methylmagnesium iodide (0·3 mole.) in di-n-butyl ether (130 ml.) to 1,1-dichlorosilacyclobutane (28·2g., 0·2 mole.) in di-n-butyl ether (60 ml.) and the resulting mixture heated under reflux for 3 hours. Fractionation from solvent afforded 1,1-dimethylsilacyclobutane, yield 60%, b.p. 80° (Lit.[137] 80 - 82°) N.M.R. (CCl_4) : quintet τ 7·7 - 8·1 (intensity 2) triplet τ 8·8 - 9·2 (intensity 4) singlet τ9·8 (intensity 6) I.R. (neat liquid) : 930 cm^{-1}, 910cm^{-1}, 880cm^{-1} - ring vibrations.

1,1-Diisopropylsilacyclobutane was prepared by the addition of isopropylmagnesium bromide (0·3 mole.) in tetrahydrofuran (130 ml.) to 1,1-dichlorosilacyclobutane (28·2g., 0·2 mole.) in tetrahydrofuran (60 ml.) and the resulting mixture heated under reflux for 3 hours. The reaction mixture was hydrolysed and after drying over magnesium sulphate and removing the solvent, fractionation afforded 1,1-diisopropylsilacyclobutane, yield 40%, b.p. 75°/5 mm. N.M.R. (CCl_4 Soln.) : quintet τ 7·8 - 8·3 (intensity 2) triplet τ 8·8 - 9·2 (intensity 4) singlet τ 9·0 (intensity 14). I.R. (neat liquid) : 920 cm^{-1}, 910 cm^{-1}, 880 cm^{-1} - ring vibrations.

1,1-Di-n-butylsilacyclobutane was prepared by the addition of butylmagnesium bromide (0·3 mole.) in diethyl ether (130 ml.) to 1,1-dichlorosilacyclobutane (28·2g., 0·2 mole.) in diethyl ether (60 ml.) and the resulting mixture heated under reflux for 3 hours. The reaction mixture was hydrolysed and after drying over magnesium sulphate and removing the solvent, fractionation afforded 1,1-dibutylsilacyclobutane, yield 80%, b.p. 77 - 80°/2·5 mm. N.M.R. (CCl_4 Soln.) : quintet τ 7·7 - 8·1 (intensity 2) complex multiplet τ 8·4 - 9·6 (intensity 22). I.R. (neat liquid): 930 cm^{-1}, 905 cm^{-1}, 885 cm^{-1} - ring vibrations.

1,1-Diphenylsilacyclobutane was prepared by the method of Nametkin.[136] Yield 65%, b.p. 118 - 120°/0·5 mm. (Lit.[136] 120°/0·5 mm.). N.M.R. (CCl_4 Soln.) multiplet τ 2·3 - 2·8 (intensity 10) quintet τ 7·5 - 7·9 (intensity 2) triplet τ 8·4 - 8·7 (intensity 4). I.R. (neat liquid) : 950 cm^{-1}, 900 cm^{-1}, 850 cm^{-1} - ring vibrations.

The pyrolysis unit previously described was used for all these experiments.

Silacyclobutane was pyrolysed at 560° with the first hot zone of the unit not heated. Examination of the gaseous products indicated 48% of theoretical quantity of ethylene had been liberated. No disilacyclobutane was detected. The polymeric solid deposited in the pyrolysis unit was difficult to analyse as it was found not to be soluble in any of the available solvents.

<u>1,1-Dimethylsilacyclobutane</u> was pyrolysed at 611° with the first hot zone of the unit not heated. Estimation from quantity of ethylene evolved suggests 65% dimerisation to 1,1,3,3-tetramethyl-1,3-disilacyclobutane. N.M.R. (CCl_4 Soln.): singlet τ 9·8 (intensity 12) singlet τ 10·15 (intensity 4) I.R. (neat liquid) 921 cm^{-1} (strong band) cyclic $\mathrm{Si}\overset{\mathrm{CH_2}}{\diagup\quad\diagdown}\mathrm{Si}$.

<u>1,1-Diisopropylsilacyclobutane</u> was pyrolysed at 611° with first hot zone heated to 100°. Analysis of gaseous products indicates a mixture of 57% ethylene and 43% prop-1-ene. Analysis of pyrolysate indicates 47% formation of 1,1,3,3-tetraisopropyl-1,3-disilacyclobutane N.M.R. (CCl_4 Soln.): doublet τ 9·0 (intensity 28) singlet τ 10·2 (intensity 4) I.R. (neat liquid) 920 cm^{-1} (strong band) cyclic $\mathrm{Si}\overset{\mathrm{CH_2}}{\diagup\quad\diagdown}\mathrm{Si}$.

<u>1,1-Di-n-butylsilacyclobutane</u> was pyrolysed at 611° with the first hot zone heated to 100°. Analysis of gaseous products indicates a mixture of 84% ethylene and 16% but-1-ene. Analysis of the pyrolysate indicates 69% formation of 1,1,3,3-tetra-n-butyl-1,3-disilacyclobutane N.M.R. (CCl_4 Soln.) : complex multiplet τ 8·5 - 9·6 (intensity 36) singlet τ 10·15 (intensity 4) I.R. (neat liquid) : 930 cm^{-1} (strong band) cyclic $\mathrm{Si}\overset{\mathrm{CH_2}}{\diagup\quad\diagdown}\mathrm{Si}$.

<u>1,1-Diphenylsilacyclobutane</u> was pyrolysed at 611° with the first hot zone heated to 200°. Under these conditions it was found that 50% polymerization took place. The experiment was repeated heating the first hot zone to 100°. Analysis of gaseous products indicates the presence of 20% benzene and 80% ethylene. Analysis of the pyrolysate indicates the presence of 57% 1,1,3,3-tetraphenyl-1,3-disilacyclobutane, N.M.R. (CCl_4 Soln.) multiplet τ 2·6 - 2·7 (intensity 20) singlet τ 8·95 (intensity 4) I.R. (neat liquid) 940 cm^{-1} (strong band) cyclic $\mathrm{Si}\overset{\mathrm{CH_2}}{\diagup\quad\diagdown}\mathrm{Si}$ and 5% of a solid (m.p. 65°) identified as 1,3-dimethyl-1,1,3,3-tetraphenyldisiloxane. N.M.R. (CCl_4 Soln.): multiplet τ 2·3 - 2·8 (intensity 20) singlet τ 9·5 (intensity 6)

I.R. (neat liquid) : Si-O-Si absorption 1050 cm^{-1}.

Pyrolysis of 1,1-di-n-butylsilacyclobutane and 1,1-diphenylsilacyclobutane with oct-1-ene.

1,1-Di-n-butylsilacyclobutane (0·4g., 0·0022 mole.) was pyrolysed with Oct-1-ene (0·739g., 0·0066 mole.) at 611°. Examination of the resulting pyrolysate indicates the presence of 10% disilacyclobutane together with starting material.

1,1-Diphenylsilacyclobutane (0·458g., 0·0022 mole.) was pyrolysed with Oct-1-ene (0·739g., 0·0066 mole.). Examination of the resulting pyrolysate indicates the presence of 10% disilacyclobutane together with starting material.

Pyrolysis of 1,1-di-n-butylsilacyclobutane with benzaldehyde.

1,1-Di-n-butylsilacyclobutane (0·4g., 0·0022 mole.) was pyrolysed at 611° with benzaldehyde (0·665g., 0·0066 mole.). G.L.C. indicates the presence of benzene (10%) and styrene (50%) as well as small amounts of disilacyclobutane and starting material. The siloxane was not identified as a mass determination was not available.

Pyrolysis of 1,1-di-n-butylsilacyclobutane with pentan-2-one.

1.1-di-n-butylsilacyclobutane (0·4g., 0·0022 mole) was pyrolysed at 611° with pentan-2-one (0 567g., 0 0066 mole.). 1,3-Dimethyl-1,1,3,3-tetra-n-butyldisiloxane was obtained as the major product together with small amounts of starting material and disilacyclobutane. N.M.R. (CCl_4 Soln) complex multiplet τ 8·4 - 9·6. I.R. (neat liquid): Si-O-Si absorption 1050 cm^{-1}.

Pyrolysis of 1,1-di-n-butylsilacyclobutane and 1,1-diphenylsilacyclobutane with heptanal.

1,1-Di-n-butylsilacyclobutane (0·4g., 0·0022 mole.) was pyrolysed at 611° with heptanal (0·753g., 0·0066 mole.). Examination of the pyrolysate indicates the presence of Oct-1-ene (4%) established by

G.L.C., together with 1,3-dimethyl-1,1,3,3-tetra-n-butylsilane (major product) and small amounts of starting material and disilacyclobutane. The siloxane was identified as in the previous experiment.

1,1-Diphenylsilacyclobutane (0·458g., 0·0022 mole.) was pyrolysed at 611° with heptanal (0·753g., 0·0066 mole.). Examination of the pyrolysate indicates the presence of ($<1\%$) Oct-1-ene established by G.L.C., together with 1,3-dimethyl-1,1,3,3-tetraphenylsilane (major product) and small amounts of starting material and disilacyclobutane. $(Ph_2SiCH_3)_2O$ - m.p. 65 . N.M.R. (CCl_4 Soln.) : multiplet τ 2·3 - 2·8 (intensity 20) singlet τ 9·5 (intensity 6). I.R. (neat liquid) : Si-O-Si absorption 1050 cm^{-1}.

Pyrolysis of 1,1,di-n-butylsilacyclobutane and 1,1-diphenylsilacyclobutane with cyclohexanone.

1,1-Di-n-butylsilacyclobutane (0·4g., 0·0022 mole.) was pyrolysed at 611° with cyclohexanone (0·68g., 0·0066 mole.). Examination of the reaction products indicates the presence of methylenecyclohexane (6%) and cyclohexene (4%) established by G.L.C. The siloxane formed in this reaction was not identified as a mass determination was not available.

1,1-Diphenylsilacyclobutane (0·458g., 0·0022 mole.) was pyrolysed at 611° with cyclohexanone (0·68g., 0·0066 mole.). Examination of the reaction products indicates the presence of methylenecyclohexane (5%) and cyclohexene (4%). The siloxane formed in this reaction was not identified as a mass determination was not available.

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