THE BETA EFFECT IN ALKYLSILANES.

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Susan Bratt
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SUMMARY.

It was suggested to us that compounds of the type $XCH_2SiR_2CH_2CH_2Y$ might show interesting chemical and biological activity due to them possessing both an alpha group and a beta group. The aim of this research was to discover whether or not the alpha and beta effects interact with each other, and if so whether interaction is via steric or electronic effects.

A series of compounds were made with a constant chloromethyl alpha function and varying beta functions (hydroxy, methoxy and chloro groups); plus a second series of trimethylsilyl substituted silanes with the same variety of beta functions were synthesised.

The stereochemistry of the products was investigated by analysis of NMR spectra and of dipole moment data. It was found that the β-chloro-substituted compounds possessed restricted rotation. The methoxy- and hydroxy-substituted compounds which displayed more or less simple triplets, appear to possess free rotation; the smaller sized hydroxy and methoxy groups seemingly no great barrier to rotation. Similarly, compounds possessing larger alpha alkyl groups appeared also to possess restricted rotation, it was concluded that for the compounds possessing large alpha or a large beta functions steric effects dominate.

The kinetics of the solvolysis reaction were studied. β-functional alkylsilanes commonly undergo solvolysis by unimolecular elimination at remarkably enhanced rates. The β-hydroxy- and β-methoxy-substituted chloroethyl derivatives reacted substantially slower that their trimethylsilyl analogues, due to the electronegative chlorine pulling electrons into the Si-C bond. For compounds possessing an electronegative substitutent alpha to silicon it seems it is the electronic effects act to inhibit the beta effect.

2-Chloroethylchloromethyldimethylsilane initially appeared not to react solvolytically, however NMR analysis of the solvolysis products indicated that a reaction did occur but by an as yet unknown mechanism. For compounds with an α-electronegative substituent in conjunction with a large β–function it was concluded both steric and electronic effects are important.

Key Words: Solvolysis Reaction; alpha- and beta-functional alkylsilanes; NMR; Dipole Moments.

To David

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LIST OF ABBREVIATIONS.

α_o	Molecular Polarisability
Ar	Aromatic
ax	Axial
br	Broad
cps	cycles/sec
d (NMR)	Doublet
δ	Chemical Shift / ppm
ε	Dielectric Constant
eq	Equatorial
J (NMR)	Coupling Constant
LDA	Lithium Diisopropylamide
m (IR)	Medium
m (NMR)	Multiplet
μ	Dipole Moment
pd	Potential Difference
q (NMR)	Quartet
s (IR)	Strong
s (NMR)	Singlet
THF	Tetrahydrofuran
TFE	1,1,1-Trifluoroethanol
TMEDA	N,N,N',N',Tetramethylethylenediamine
t (NMR)	Triplet
-ve (NMR)	Negative Peak
+ve (NMR)	Positive Peak
v/v	Volume / Volume
w (IR)	Weak
w/v	Weight / Volume

"To accomplish great things we must not only act, but also dream,
Not only plan, but also believe."

Anatole France

Chapter 1

INTRODUCTION.

1. INTRODUCTION.

1.1 THE BETA EFFECT.

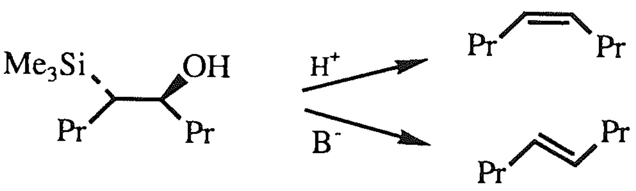
1.1.1 Introduction.

The unusual chemical and physical behaviour of the beta-functional alkylsilanes has been the subject of many investigations. Much progress has been made in determining the factors responsible for much of the anomolous behaviour but some aspects of β-functional activity have still not been resolved, in particular some controversy exists regarding the mode of β-carbonium ion stabilisation by silicon.

It was in 1937 that the remarkable reactivity of the β-halogenosilanes was originally noted by Ushakov and Itenberg[1]. Subsequently, in 1946 Sommer, Whitmore[2,3] and their co-workers remarked upon the high reactivity of β-substituted silanes compared to the α- and γ-substituted compounds[4]. The reactions of β-halogenosilanes were investigated by a number of groups who found that reactions occurred with heat, aluminium chloride[5], basic reagents[3,6] and Grignard reagents[7], to give almost exclusively elimination products.

$$R_3SiCH_2CH_2X \longrightarrow CH_2{=}CH_2 \quad + \quad R_3SiX \tag{1.1}$$

Other workers found that the β-hydroxyalkyltrialkylsilanes behaved in a similar fashion, undergoing elimination under both acidic[8], and basic conditions[9,10] to yield olefin. Hudrlik and Peterson[11] observed that the stereochemistry of the reaction was determined by the choice of conditions; reaction with acid gave the *cis* isomer and reaction with base the *trans* isomer, so that from a single precursor either *cis* or *trans* olefin could be prepared (eqt 1.2):



(1.2)

Other compounds possessing a nucleofugal group on the β-carbon atom generally undergo similar fragmentation reactions, unlike the corresponding γ-substituted compounds which show no such inclination. Silicon containing β–carbonyl compounds, for example, the β-ketosilanes[12] R_3SiCH_2COR and esters[13] of the type $R_3SiCH_2CO_2R$ are readily cleaved by nucleophilic and electrophilic reagents:

$$Me_3SiCH_2COOC_2H_5 + C_2H_5OH \longrightarrow Me_3SiOC_2H_5 + CH_3COOC_2H_5 \qquad (1.3)$$

β-Cyano groups[14] also behave in this manner:

$$Me_3SiCH_2CN + H_2O \longrightarrow Me_3SiOH + CH_3CN \qquad (1.4)$$

The allylsilanes, $R_3SiCH_2CH=CH_2$ and the benzylsilanes, $R_3SiCH_2C_6H_5$ also show unusual reactivity.[15,16] The anomalously high reactivity of the β-alkenylsilanes was first noticed by Petrov and Mironov[15]. They observed that the addition of HBr to allyltrimethylsilane was instantaneous at -70°C, whereas, even at room temperature, the addition to vinyltrimethylsilane and but-3-enyl-trimethylsilane was slow.

In the 1950's Nesmeyanov[198] noted certain distinct features associated with the allylsilanes which included a high reactivity to electrophilic reagents and a low reactivity towards nucleophilic reagents. Sommer, Tyler and Whitmore[17] first studied the addition of hydrogen halides to allylsilanes, they discovered that the additions of HI and HBr (eqt 1.5) were always in accordance with Markovnikov's rule even in the presence of peroxide.

$$Me_3SiCH_2CH{=}CH_2 \; + \; HBr \longrightarrow Me_3SiCH_2CHBrCH_3 \qquad (1.5)$$

1.1.2 Modes of β-Functional Reactivity.

Various factors and effects have been invoked to explain the exceptional reactivity of β-functional silane derivatives, namely;

i) Inductive effects

ii) $(p\text{-}d)_\pi$ bonding

iii) $(p\text{-}d)_\sigma$ bonding

iv) C-Si hyperconjugation

v) A combination of these effects.

1.1.2.1 The Inductive Effect.

The strong electron donating, +I effect of the R_3SiC- moiety has been evaluated by a number of methods. The rates of hydrogen exchange have been measured[18] for a series of [1-3H] acetylenes of the type $YC{\equiv}C^3H$. For these reactions an increase in rate of reaction signifies electron withdrawal and a decrease in rate, electron donation. Trialkylsilylmethyl compounds $R_3SiCH_2C{\equiv}C^3H$ were found to react at half the rate of their carbon analogues and so it can be seen that the R_3SiCH_2- group donates electrons much more effectively than an R_3CCH_2-.

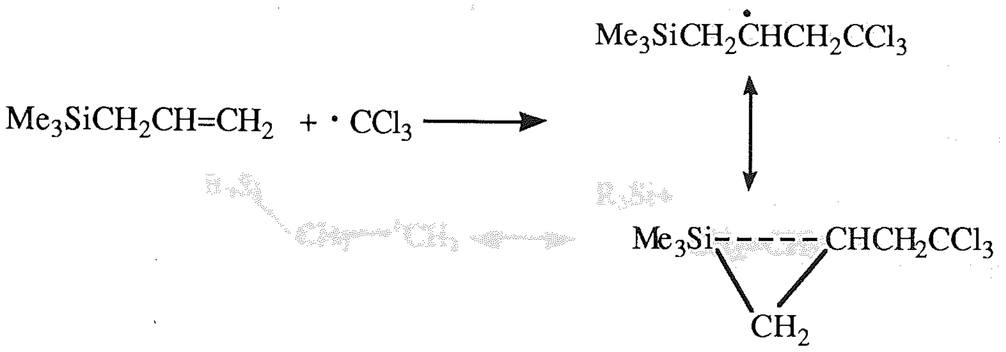
The Taft σ^*-substitution constant[19] is a constant dependent upon the polar effect of a substituent group relative to a methyl group. It is analogous to the Hammett substituent constant but it is of a different nature and origin. This constant is found to increase with increasing electronegativity of the substituent. The Taft σ^*-substitution constant[19] for the Me_3SiCH_2- group has been calculated from the ionisation constant of the acid[20]; Me_3SiCH_2COOH and also from the rate of hydrolysis of the ester[19]; $Me_3SiCH_2CO_2CH_2CH_3$ and found to be -0.26, as compared to -0.165 for the Me_3CCH_2- group and -0.30 for the Me_3C- group. From these results it can be seen that the trimethylsilylmethyl group has a Taft substitution constant comparable to a *t*-butyl system.

Walton[21] used cleavage reactions with aqueous methanolic-perchloric acid of the *meta*- and *para*-substituted aryl systems; *m*- and *p*-$(Me_3MCH_2)C_6H_4SiMe_3$ to obtain a measure of the relative electron releasing power of the trimethylsilyl moiety compared with the *t*-butyl group. Compared with the parent compound $C_6H_5SiMe_3$, the *meta*-*t*-butyl- and the *meta*-trimethylsilmethylene- substituted compounds had relative reactivities of 4.05 and 6.2 respectively, whereas the *para*-substituted compounds had relative reactivities of 20.7 and 330 for the *t*-butyl substituent and the trimethylsilmethylene substituent respectively. The very slight increase in rates for the *meta*-substituted compounds was attributed to hyperconjugation in opposition to the inductive effect. Whereas the massive enhancement by the trimethylsilmethylene group when substituted in the *para* position is a measure of the strong electron donating power of this group.

1.1.2.2 $(p\text{-}d)_\pi$ bonding, $(p\text{-}d)_\sigma$ bonding and C-Si hyperconjugation.

In addition to the inductive effect other modes of stabilisation have been suggested to explain the unusual behaviour of the β-functional alkylsilanes.

For example $(p\text{-}d)_\pi$ bonding has been used to explain the high reactivity of allyltrimethylsilane to undergo radical reactions:[22]



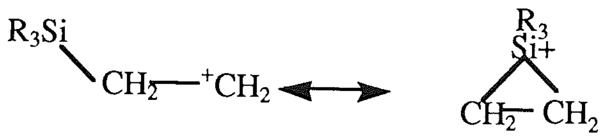
(1.6)

Whereas their high reactivity towards electrophilic reagents has been explained by C-Si hyperconjugation:

$$Me_3SiCH_2CH{=}CH_2 \longleftrightarrow Me_3\overset{+}{Si} \quad CH_2{=}CH\overset{-}{C}H_2 \qquad (1.7)$$

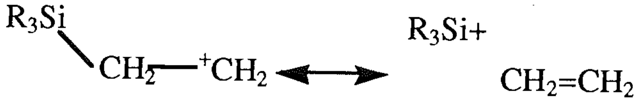
The high reactivity of β-functional silanes and their tendency to eliminate is most often explained by the stabilisation of the beta carbonium ion that is formed by either $(p\text{-}d)_\sigma$ bonding or C-Si hyperconjugation.

$(p\text{-}d)_\sigma$ bonding is the neighbouring group participation of silicon on the beta carbon, the β-carbonium ion is stabilised through formation of a cyclic siliconium ion, this is a non-vertical process:



(1.8)

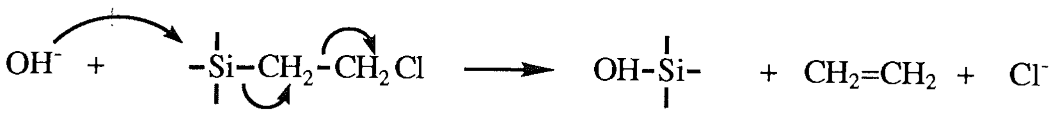
Alternatively, the stabilisation of the β–carbonium ion is often attributed to C-Si hyperconjugation, which is a vertical process:



(1.9)

1.1.3 The Elimination Reaction.

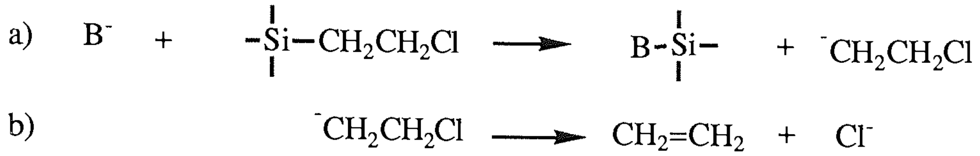
The first mechanistic studies of the elimination reactions of the β-functional organosilanes were carried out by Sommer and co-workers[7]. They examined the base-catalysed elimination reactions of β-chloroethyltrichlorosilane and β-chloro-*n*-propyltrichlorosilane. Initially they proposed a mechanism analogous to the E_2 mechanism[23] assuming initial nucleophilic attack of hydroxyl on silicon:



(1.10)

Later, Sommer elaborated on this proposal, suggesting a mechanism similar to the E_{1cb}

process[5] shown below (equation 1.11), but with an irreversible step a, and steps a and b being effectively simultaneous. They attributed the rapidity of these reactions to the "electron-release from silicon to electronically deficient beta carbon"[5]



$$\text{a)}\quad B^- + -\overset{|}{\underset{|}{Si}}-CH_2CH_2Cl \longrightarrow B-\overset{|}{\underset{|}{Si}}- + {}^-CH_2CH_2Cl$$

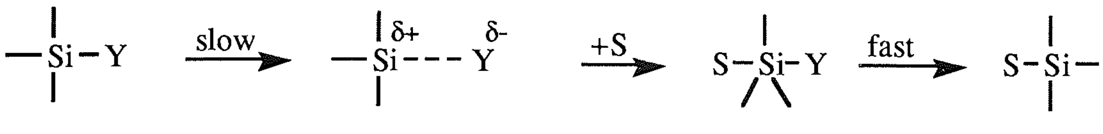
$$\text{b)}\quad {}^-CH_2CH_2Cl \longrightarrow CH_2{=}CH_2 + Cl^-$$

(1.11)

In 1961 Sommer and Baughman[24] examined the kinetics of the solvolysis of 2-chloroethyltrimethylsilane, $Me_3SiCH_2CH_2Cl$. They found that at 30°C, in aqueous ethanol of varying composition over 50% to 80% v/v, the solvolysis followed a first order rate law which could be correlated by the Grunwald-Winstein equation[25],

$$\log k/k_o = mY, \qquad (1.12)$$

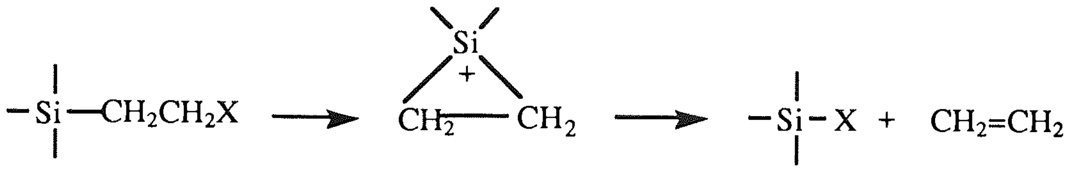
This yielded an m value of 1.02, indicating the reaction to be as ionic in character as the solvolysis of *t*-butyl chloride. They observed that the rate was independent of the nucleophilicity of the solvent, but was dependent upon its ionising power and inferred that the rate controlling transition state must involve strong participation of electron-release from silicon without simultaneous nucleophilic attack at the silicon atom by solvent. In conclusion they proposed a new mechanism which they named "the limiting siliconium ion" mechanism, as shown below (eqt 1.13), where S represents the solvent and Y is the chloroethyl substituent:



$$-\overset{|}{\underset{|}{Si}}-Y \xrightarrow{\text{slow}} -\overset{|\,\delta+}{\underset{|}{Si}}---\overset{\delta-}{Y} \xrightarrow{+S} S-\overset{|}{\underset{/\backslash}{Si}}-Y \xrightarrow{\text{fast}} S-\overset{|}{\underset{|}{Si}}-$$

(1.13)

Baughman[26] later opposed this view, proposing instead a silacyclopropenium type intermediate, with rate determining cleavage of the carbon-halogen bond, assisted by the silicon group:



(1.14)

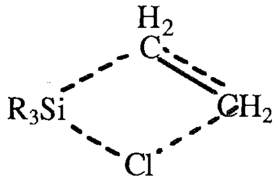
This proposal was based on evidence from entropies of activation and the effect of change of electron density on silicon, measured by the Hammett ρ factor[27].

Examination of the effect of substitution of the bromine for chlorine, which resulted in a seventeen fold increase in the base-catalysed rate, prompted Baughman to reject the siliconium ion theory. He stated that the rate-determining destruction of a pentacovalent silicon intermediate was not a feasible mechanism due to the fact that there appeared to be considerable carbon-halogen bond stretching in the rate determining transition state.

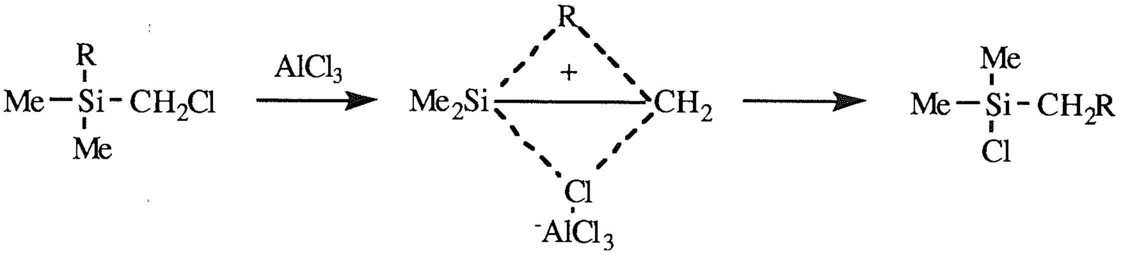
Bott, Eaborn and Rushton[28] also criticised the limiting siliconium ion mechanism. They observed that compounds such as $Me_3SiC{\equiv}CPh$ showed lower base-catalysed solvolytic activity than β-$Me_3SiCH_2CH_2Cl$, yet the former would be expected to form much more stable carbanions and therefore be expected to have a higher reactivity.

Earlier work on the gas phase decompositions of β-halogenosilanes[29,30] and the tendency for intramolecular transfer of halogen from carbon to silicon had indicated a four-centred intermediate for such reactions:

Fig 1.1 4-Centred Intermediate Indicated in Gas Phase Decompositions:



Bott *et al*[28] suggested that the unimolecular solvolysis of a β-halogenoalkylsilane was related to its thermal decomposition and to the tendency for intramolecular transfer of halogen from carbon to silicon. So they proposed instead a four-centred unimolecular process, shown below in equation 1.15. A mechanism that could be consistent with Sommer and Baughman's earlier results,[24] provided that there was sufficient charge separation in the transition state.

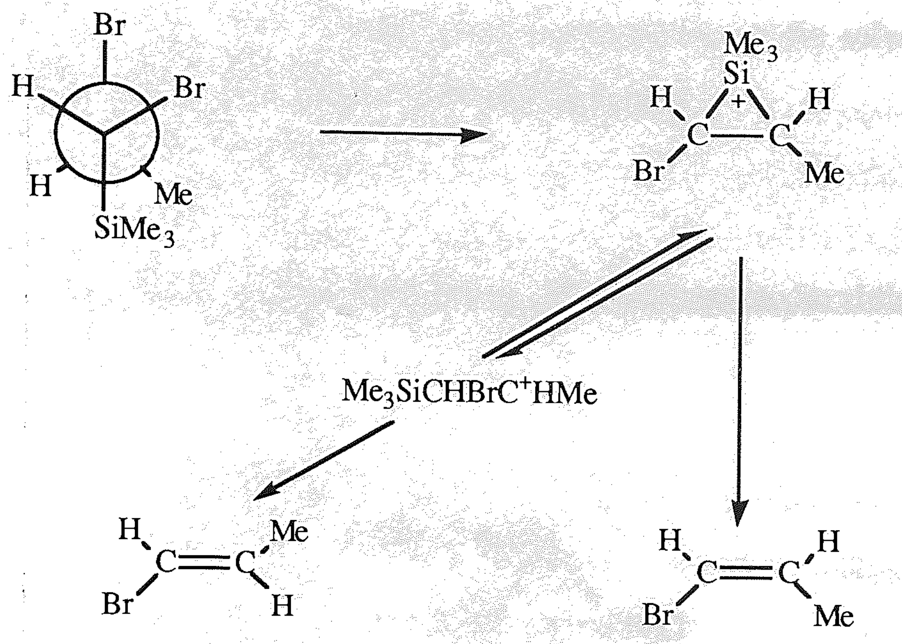


(1.15)

Sommer[31] studied the effects, both polar and steric, of different substituents on the rates of solvolysis of compounds with the general formula $R'R_2SiCH_2CH_2X$ in 70% ethanol at 50°C, where R or R' = Me, Et, i-Pr and Ar, and X = Cl or OH. Using the rate constants for the two arylsilanes he calculated the Hammett ρ factor[27,32] as -2.15 for the ethanolysis of $ArMe_2SiCH_2CH_2Cl$ and -1.85 for the acidic hydrolysis of $ArMe_2SiCH_2CH_2OH$. These results indicate that the solvolysis reaction is promoted by electron donating groups and that there is an increase of positive charge on the aryl groups and hence on the silicon in the transition state. From calculations of the Taft E_s[19] he concluded that the steric factors were most likely due to hindrance to solvation of a developing cationic charge at the silicon atom. These results of Sommer's are consistant with both the siliconium ion mechanism and with rate determined cleavage of the carbon-halogen bond to form a β–carbocation.

Studies carried out by Jarvie *et al*[33,34,16] finally elucidated the mechanism of the reaction. The solvolysis of *erythro*-1,2-dibromopropyltrimethylsilane, in aqueous ethanol at 20°C, resulted in a predominantly *trans*-elimination yielding *cis*-1-bromopropene. This evidence is in disagreement with the limiting siliconium ion theory as the non-stabilised carbanion would not be expected to retain its configuration. As the *trans*-elimination is only possible when the halogen and Me_3Si- electrofuge are antiperiplanar to each other, these results supported the rejection of the four-centred syn-elimination mechanism. This had been previously invalidated due to the observation that the rate of solvolysis was dependent upon the ionising power of the solvent and not upon its nucleophilicity.[24] Although the stereochemistry appeared to indicate a concerted E_2 mechanism, previously described solvent effects require an E_1-type mechanism with rate determining carbon-halogen cleavage. The mechanism suggested by Jarvie incorporating all of the evidence available was one based on the E_1 mechanism but involving stabilisation of the carbocation by neighbouring group participation, $(p\text{-}d)_\sigma$ bonding. This mechanism stems from one originally postulated by Cram[35] and is similar to those proposed by Baughman[26], Kreevoy and Kowitt.[36]

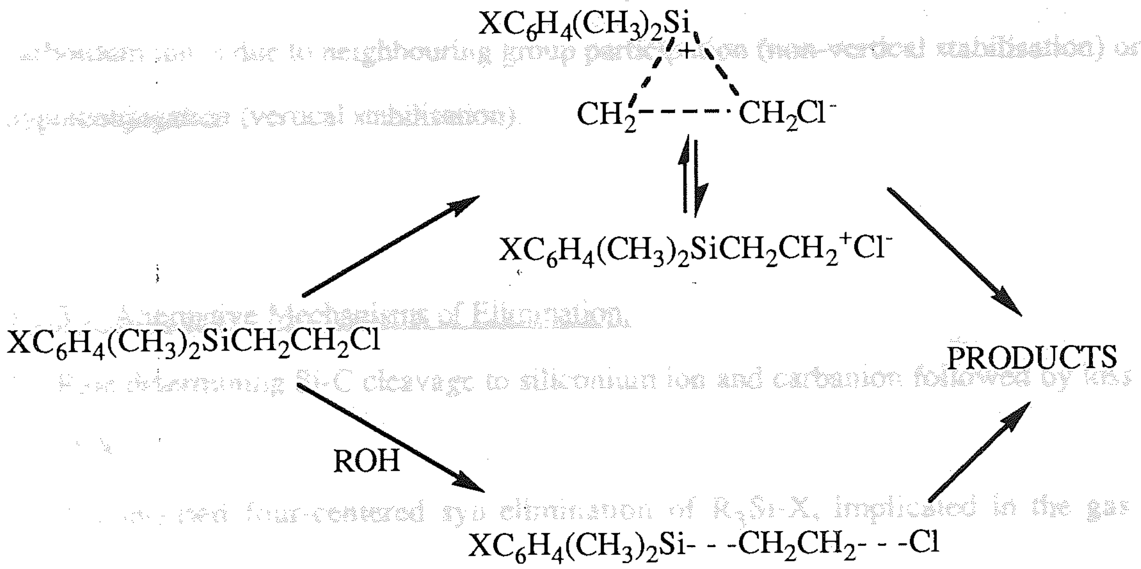
Scheme 1.1 Mechanism of Solvolysis of 1,2-Dibromopropytrimethyl-Silane.



They suggested that the mechanism consisted of initial carbon-halogen cleavage, with the reaction then following two competitive pathways. The first, involving silicon participation as a cyclic siliconium intermediate, yielding *trans*-elimination. The second involving a classical carbonium ion resulting in non-stereospecific elimination, the proportion of which increases in the more highly ionic solvents which provide a greater stabilisation to the carbonium ion. This would account for the small amount of *trans*-propene that was observed.

A modification to the mechanism proposed by Jarvie *et al* was subsequently proposed by Vencl and co-workers,[37] who studied the solvolysis of 2-chloroethylaryl-substituted dimethylsilanes in aqueous ethanolic and methanolic media. They suggested that the mechanism consisted of two independent paths, both proceeding via initial rate determining cleavage of the β-carbon-halogen bond. Of the two routes, the first consisted of internal nucleophilic displacement, giving the previously described three membered siliconium ion and the second was solvent-assisted cleavage, with the proportion of this increasing with increasing nucleophilicity of the solvent and increasing electronegativity of the substituent on the aryl group.

Scheme 1.2 Mechanism of Solvolysis of 2-Chloroethylaryldimethyl Silanes.



where R = H or Alkyl

Jarvie *et al* continued their studies into the elimination reactions with an investigation into secondary deuterium isotope effects on the rates of solvolysis of $Me_3SiCH_2CD_2Br$, Me_3SiCHD,CH_2Br and $(CD_3)_2MeSiCH_2CH_2Br$[38]. The results of which suggested initial carbon-halogen bond cleavage, possibly with assistance from the silicon atom, and also that very little Si-C bond breaking occurs in the rate-determining step. They also found in preparing their compounds that the reaction of $Me_3SiCH_2CD_2OH$ with PBr_3 resulted in both $Me_3SiCH_2CD_2Br$ and $Me_3SiCD_2CH_2Br$, showing that rearrangement had occurred. A result consistent with their theory of a cyclic silicon-bridged ion. Eaborn and co-workers[39] expanded on this and found that the solvolysis of $Me_3SiCH_2CD_2Br$ in aqueous methanol is accompanied by rearrangement to $Me_3SiCD_2CH_2Br$. Due to a lack of $Me_3SiCHDCHDBr$ production they inferred that migration of hydrogen was not responsible and concluded that rearrangement was due to a reversible isolation of the carbon-halogen bond, they too favoured the cyclic siliconium ion.

Since that time there has been some controversy about whether the stabilisation of the carbonium ion is due to neighbouring group participation (non-vertical stabilisation) or hyperconjugation (vertical stabilisation).

1.1.3.1 Alternative Mechanisms of Elimination.

1. Rate determining Si-C cleavage to siliconium ion and carbanion followed by loss of X^-.
2. A concerted four-centered syn-elimination of R_3Si-X, implicated in the gas phase.
3. Rate determining attack of solvent or base on silicon, E_2-like.
4. Rate determining attack by solvent or base on C-X bond, S_N2-like.
5. Rate determining cleavage of C-X bond to form a carbocation, E_1 mechanism.

To date the majority of evidence seems to point in favour of rate determining cleavage of the C-X bond to form a carbocation; the E_1 mechanism. For this mechanism two main processes of silicon interaction, responsible for the dramatic rate enhancements, have been proposed $(p\text{-}d)_\sigma$ bonding, ie neighbouring group participation and C-Si hyperconjugation

1.1.4 Vertical and Non-Vertical Stabilisation Processes.

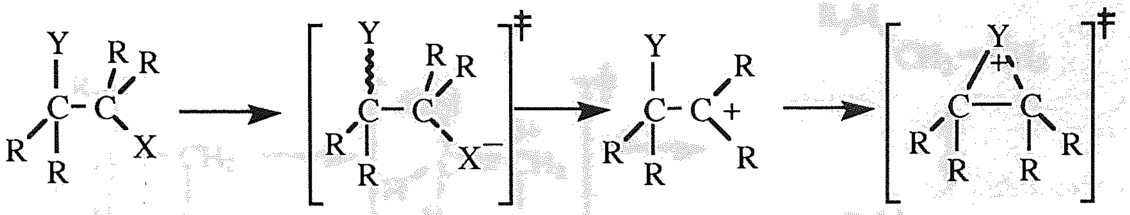
One of the modes of interaction capable of stabilising a beta carbonium ion is a non-vertical process leading to the formation of a three-membered cyclic siliconium ion by internal neighbouring group participation. A second possibility is that of vertical stabilisation with interaction by silicon through hyperconjugation without any accompanying nuclear movement. Both processes may betray larger rate enhancements than expected due to the possibility of assistance to stabilisation of the beta positive charge by the inductive effect of silicon.

1.1.4.1 Non-Vertical Stabilisation.

Non-vertical stabilisation has long been recognised as a mechanism of carbonium ion stabilisation in the reactions of compounds possessing beta nucleophilic groups such as $-O^-$, $-SR$, NR_2[40]. This type of stabilisation involves movement of the nucleophilic Y group to the C+ to form a three-membered ring (Scheme 1.3). A requirement of this type of stabilisation is an antiperiplanar stereochemistry between the internal nucleophile and the leaving group.

Elimination reactions involving neighbouring group participation often display accelerated rates of reaction. Such kinetic enhancement is observed in the reactions leading to the production of epoxides, halonium ions and other similar species. The rate enhancement and stereospecificity associated with the reactions of β–alkylsilanes which lead to the production of a carbocation have often been explained in terms of non-vertical stabilisation.[37-39]

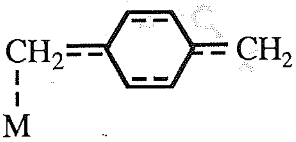
Scheme 1.3 The Development and Stabilisation of a Carbonium Ion by Non-Vertical Stabilisation:



1.1.4.2 Vertical Stabilisation.

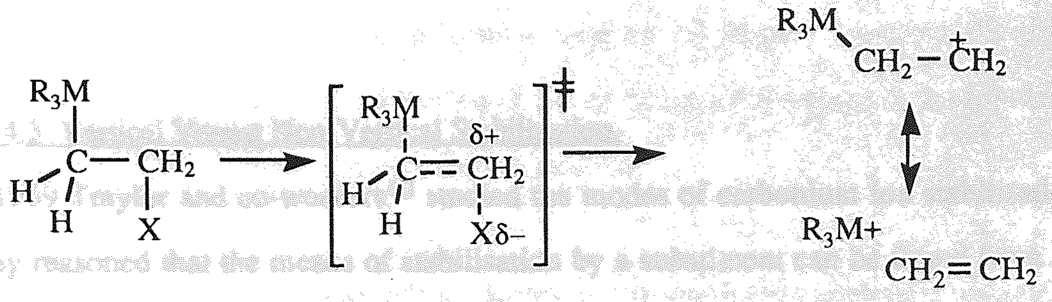
The alternative possibility of vertical stabilisation by hyperconjugation was first suggested for metalloid atoms, such as silicon, in 1948[198]. In 1967 Hanstein and Traylor[41] reported on the strong electron donating effect of the M-CH_2 group via hyperconjugation and its transmittance through a phenylene group, resulting in the structure shown below (fig 1.2):

Fig 1.2 Transmittance of Hyperconjugation Through a Phenylene Group



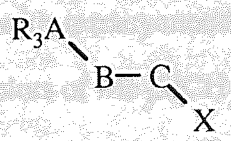
This type of stabilisation leads to a carbon-carbon double bond and a positive charge on silicon, which is more suited to carry a positive charge that either carbon or hydrogen:

Scheme 1.4 The Development and Stabilisation of a Carbonium Ion by Vertical Stabilisation :



There are several conditions to be met for optimal vertical stabilisation[42-44]. In the system shown below (fig 1.3) where X is the leaving group and C is to carry the positive charge, the stabilisation is optimised by; low electronegativity of A, inductive donation by R and no competing R-A conjugation. Low bending and stretching force constants of A-B, a strong B=C double bond, planarity of the ABCX unit and an antiperiplanar arrangement.

Fig 1.3 Example of a Hypothetical System:



The antiperiplanar arrangement of ABCX provides that the silyl and leaving group have bonds parallel to the C-C bond[43]. The synperiplanar arrangement does allow weak hyperconjugation but it is not as favourable as the antiperiplanar.

Hyperconjugation is an electronic vertical process which requires no change in geometry. It has a great ability to stabilise a developing carbocation and is capable, like the former non-vertical process, of explaining both the rate enhancement and the stereochemistry of the reactions of β-functional organosilanes.

1.1.4.3 Vertical Versus Non-Vertical Stabilisation.

In 1969 Traylor and co-workers[40] studied the modes of carbonium ion stabilisation. They reasoned that the means of stabilisation by a substituent can be found from the effect of that substituent on a reaction of a known stabilisation process. The stabilising effect on a positively charged transition state by a substituent can be measured by the Hammett linear free energy relationships[27] of *meta*- and *para*-substituted benzene compounds. These can be used to measure a substituent's ability to stabilise excited states from charge transfer, a known vertical process. Reactions of *para*-substituted benzene derivatives having stabilisation from electron donation have a substituent constant σ_p^+.

Traylor *et al*[40] explained that if σ_p^+ obtained from a reaction were the same as that obtained from the charge transfer spectra then it can be concluded that the reaction proceeds via a vertical process. They looked at the σ_p^+ of Me_3SiCH_2- as derived from reaction rates[45] and found that it correlated with the σ_p^+ as determined by the charge transfer spectra of Me_3SiCH_2Ph with tetracyanoethylene, a known vertical process. By analysis of the charge transfer plots of $Me_3SiCH_2CH_2Ph$, where the insertion of the methylene group would destroy the conjugative effect, they concluded that the vertical stabilisation is due to hyperconjugation and not induction. Their results indicated that the electron releasing effect of the Me_3SiCH_2- group is on a par to an acetamido group, CH_3CONH, and considerably higher than that of a methyl group.

Bassindale, Eaborn and co-workers[46,189] reached a similar conclusion from studies of the effect of Me_3SiCH_2-, $(Me_3Si)_2CH$- and $(Me_3Si)_3C$- groups on the rate of electrophilic attack at the *meta* and *para* positions of an aromatic ring and on the ^{19}F chemical shifts in *p*-XC_6H_4-^{19}F compounds[46]. Due to the non-progressive increase in the overall electron release from successive replacements of the Me_3Si- group the authors concluded that inductive influences were not of primary importance in these systems. They attributed the stabilisation of a beta carbocation formed in the solvolysis of $R_3SiCH_2CH_2Cl$ compounds to hyperconjugation.

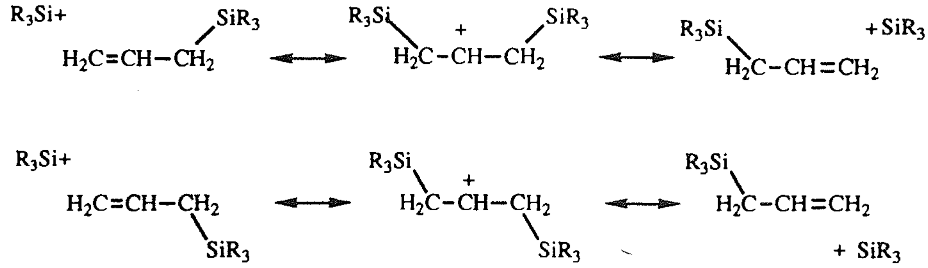
Pitt[47] carried out further studies of the electronic spectra of charge transfer complexes of a series of silyl- and germyl-substituted indanes with tetracyanoethylene; concentrating on the dependence of substituent effects on the position of substitution and on bond lengths. He suggested that hyperconjugation may be the major factor in determining ground state electronic properties, but intimated that the non-vertical $(p\text{-}d)_\sigma$ bonding, ie neighbouring group participation, could play an important role in the excited state.

Reynolds and Bassindale[48] studied the effects of the group IV substituted $(CH_3)_3MCH_2$- and -$M(CH_3)_3$ substituted aromatic derivatives on ^1H and ^{13}C NMR chemical shifts. These studies provided additional evidence that electron release from a polar C-M bond to a phenylic π-electron system is by $\sigma-\pi$ hyperconjugation in $(CH_3)_3MCH_2$- substituted systems. The electron donating properties of -$M(CH_3)_3$ systems are a composite effect made up of electron donating inductive effects and electron withdrawing resonance effects.

Further evidence for hyperconjugative stabilisation of β-silyl carbonium ions was provided by Davis and Jacocks.[49] They studied the rates of acid-catalysed solvolysis of a series of β–hydroxy-substituted compounds. They observed the effect of methyl substituents at the carbinol from a study of the compounds: $Me_3SiCH_2CH_2OH$,

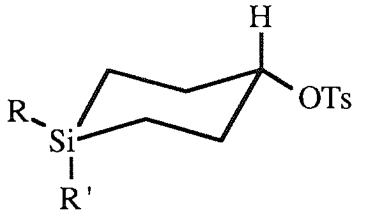
$Me_3SiCH_2CHOHCH_3$, $Me_3SiCH_2C(CH_3)_2OH$ and the effect of the silyl group as compared to the methyl group was obtained from the compound $(Me_3SiCH_2)_2CHOH$. The α CH_3/H ratio was found to be $10^{3.3}$ for both primary/secondary and secondary/tertiary. The replacement of hydrogen with the second trimethylsilyl group resulted in a relative increase in the rate of $10^{5.92}$. These results show two important features; firstly the α CH_3/H ratio of $10^{3.3}$ is of a comparable magnitude to $10^{4.7}$ for *t*-butyl chloride in ethanol, indicating a similar, high degree of carbonium ion character in the transition state, and secondly the addition of the second trimethylsilyl group caused an increase of six orders of magnitude. If the process involved were non-vertical stabilisation this evidence would require that both trimethylsilyl groups be bridged to their full extent, a condition that is sterically unfavourable as well as necessitating a six-coordinated central carbon. However, both the stereoelectronic and coordinate needs for hyperconjugation of the two groups would not be unfavourable, with either of the structures below allowing all of the required conditions to be met:

Fig 1.4 Possible Structures Facilitating Hyperconjugation:



The elimination reactions of the β-functional alkylsilanes have been proven to favour the antiperiplanar arrangement.[11,33,34] In acyclic systems, where anti and gauche isomers are in equilibrium, the compounds are free to assume the most favourable conformation in the transition state. However contributions from less favourable conformations would have the effect of diluting the overall rate, resulting in a lower observed rate of reaction. The implications of sterically altering a molecules freedom of movement are indicated in several instances. The rate enhancement obtained from the direct solvolysis of $Me_3SiCH_2CH_2X$ compared with the carbon analogue $CH_3CH_2CH_2X$ was 10^6-10^7, whereas the electrophilic addition of R^+ to $Me_3SiCH_2CH=CH_2$ compared to $CH_3CH=CH_2$ gave a rate ratio of 30,700 lower than that observed in the former case, with transition state differences being thought responsible. In the case of $Me_3SiCH_2CH=CH_2$, replacement of the $SiMe_3$ by $SiPh_3$ reduced reactivity by a factor of 60, $SiCl_3$ inhibited the reaction and $Si(hexyl)_3$ was found to accelarate the rate of reaction by a factor of three[50]. Washburne and Chawala[51] studied the solvolysis reactions of 4,4-disubstituted,4-silacyclohexyl tosylates in which the silicon atom is conformationally constrained gauche to the leaving group; as shown below in figure 1.5:

Fig 1.5 4,4-Disubstituted, 4-Silacyclohexyl Tosylates.

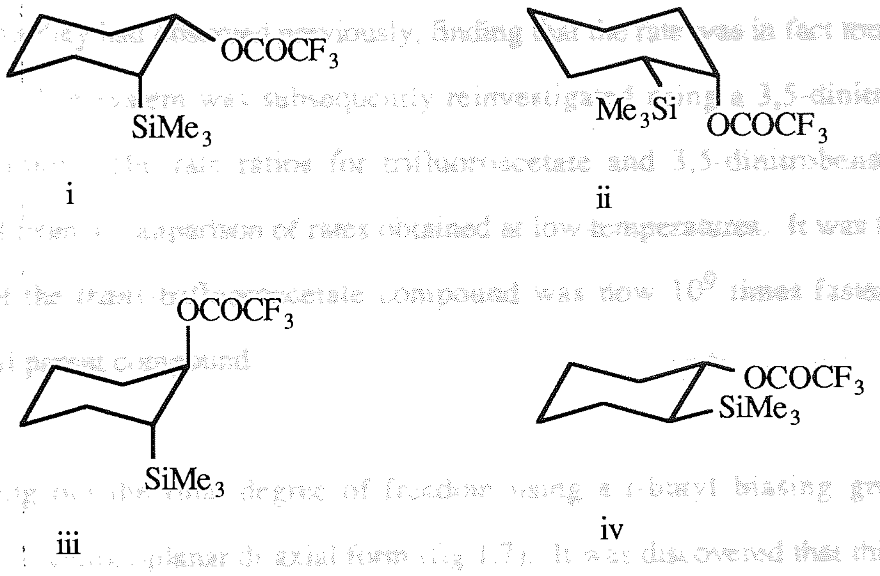


R/R' = Me / Me
= Me / Ph
= Ph / Me

This system is able to provide an indication of the kinetic enhancement in an alternative geometry to the antiperiplanar. In this system non-vertical participation is prevented and vertical participation is greatly reduced. The rate of solvolysis was found to be 3-5 times more rapid that the analogous carbon system. It is possible that the observed small rate increase could be attributed to inductive effects, unfortunately no evidence was obtained to establish whether the solvolysis was S_N1 in character. Six-membered rings tend to solvolyse by the S_N2 reaction so it is possible that the comparison of rates in this manner is misleading.

In recent years detailed studies have been carried out by Lambert[52] with the aim of resolving the vertical versus non-vertical stabilisation controversy. Lambert and Finzel[52,53] investigated the solvolysis of 2-trimethylsilylcyclohexyltrifluoroacetate, (fig 1.6)

Fig 1.6 2-Trimethylsilylcyclohexyltrifluoroacetate:



Both vertical and non vertical participation require an antiperiplanar arrangement of silicon and the leaving group, this is only possible in the *trans* molecule which has the anti di-axial form (fig 1.6 iii) which is in equilibrium with the gauche di-equatorial (fig 1.6 iv). Whereas the inductive effect can operate in all of the forms, and so any enhancement of rates in the *cis* molecule (fig 1.6 i & ii) can be attributed to the inductive effect, as neither the vertical nor the non-vertical modes of stabilisation are possible. In order to minimise solvent interactions the solvolyses were carried out in the low nucleophilic 97% aqueous 1,1,1-trifluoroethanol (TFE) and in all cases the only product of solvolysis is cyclohexene. They assigned to the unsubstituted cyclohexyl system a relative rate of 1 and reported the *cis* isomer as having a relative rate of 3.35 x 10^4 and the *trans* isomer a relative rate of 2.47 x 10^6. They found that as the *cis* conformer solvolysed 4 orders of magnitude faster than the parent cyclohexyltrifluoroacetate this could be attributed to inductive effects and the *trans* isomer which solvolysed 75 times more rapidly than the *cis* represented the non-inductive participation, either by vertical or non-vertical processes.

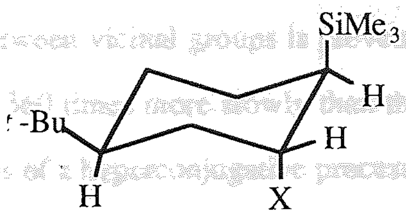
Lambert and co-workers[52,54] reinvestigated these systems several years later. They found that the *trans*-2-trimethylsilylcyclohexyltrifluoroacetate reacted much more rapidly than they had observed previously, finding that the rate was in fact too fast to be measured. The system was subsequently reinvestigated using a 3,5-dinitrobenzene leaving group. The rate ratios for trifluoroacetate and 3,5-dinitrobenzene were calculated from a comparison of rates obtained at low temperatures. It was found that the rate of the *trans*-trifluoroacetate compound was now 10^9 times faster than the cyclohexyl parent compound.

By freezing out the final degree of freedom using a *t*-butyl biasing group, they obtained the antiperiplanar di-axial form (fig 1.7). It was discovered that this resulted in a rate enhancement of 10^{12} compared with the cyclohexyl parent compound; a figure representing the full kinetic enhancement by an antiperiplanar β-silyl group in the production of positive charge on carbon.

The molecularities of the reactions were obtained using the method of Raber and Harris[55,194]. They found that the cyclohexyltrifluoroacetate solvolysed by the K_s (S_N2) mechanism, whereas the silicon containing systems solvolysed by the K_c (S_N1) mechanism, indicating that even an entirely gauche trimethylsilyl group was capable of profoundly changing the mechanism.

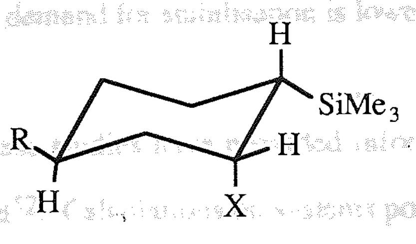
Fig 1.7 5-*t*-Butyl-2-trimethylsilylcyclohexyltrifluoroacetate:

(Biased Antiperiplanar)



The unbiased *cis* substrate, where R= H, and the biased *cis* substrate when R= *t*-Bu, (illustrated in figure 1.8 below) both solvolysed about 4x10^4 times faster than cyclohexyl trifluoroacetate. As non vertical stabilisation is not possible with this geometry, but hyperconjugation from weak overlap is possible, this would suggest that the mode of silicon interaction is via a vertical process.

Fig 1.8 *Cis*-Substituted 2-Trimethylsilylcyclohexyltrifluoroacetate:



On this assumption Lambert *et al*[54] attempted to calculate the acceleration due to the hyperconjugative component and the inductive component from a study of the hydrogen/deuterium secondary kinetic isotope effects. From the rate data of the two biased *t*-butyl systems the 10^{12} overall accelaration was calculated to consist of a 10^{10} hyperconjugative component with 10^2 contribution from the inductive effect. Following on from this they undertook a similar study on the five membered rings[56] *cis*- and *trans*-2-(trimethylsilyl)cyclopentyl trifluoroacetate in which the 180° antiperiplanar geometry between vicinal groups is prevented. They found that the *cis* substrate solvolysed about 360 times more slowly than the *trans*, results which are in support of their assumptions of a hyperconjugative process.

In the gas phase, due to the absence of solvent and associated solvent effects, the mechanisms of reactions can be considerably different. Studies by Davidson *et al*[29,30,57,58] on the kinetics of gas phase thermal decompositions of β-halogenoalkylsilanes and those by Musker and Larson[59] on the thermal decomposition of the *cis*- and *trans*-2-trimethylsilylcyclohexylmethylethers indicated the intramolecular formation of a four-centred transition state.

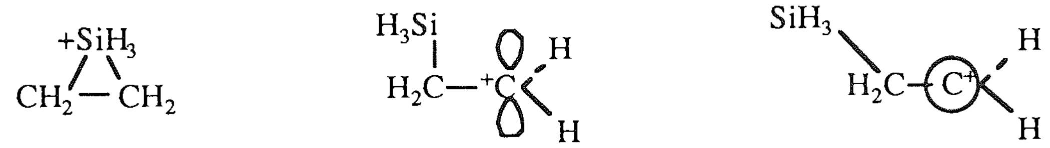
The actual value of the beta effect has been measured by a variety of means. Li and Stone[60] studied the mass spectrometry of the association of trimethylsilylium with alkenes. They found the value of the beta effect in a primary system to be 48.4 kcal mol^{-1} and for secondary ions the value was found to be 28 kcal mol^{-1}, showing the effect to be lower when the demand for stabilisation is lowered.

Various theoretical gas phase studies have provided information as to the origin and magnitude of the beta effect[52]. Calculations on systems possessing primary carbonium ions were done by Jorgenson and co-workers[61,62]. For the isodesmic reaction shown below:

$$H_3SiCH_2CH_2^+ + CH_4 \longrightarrow H_3SiCH_2CH_3 + CH_3^+ \qquad (1.16)$$

they considered three structures[61] shown in figure 1.9:

Fig 1.9 Possible Structures for Ethylene Cations:



I cyclic bridged

II unbridged aligned

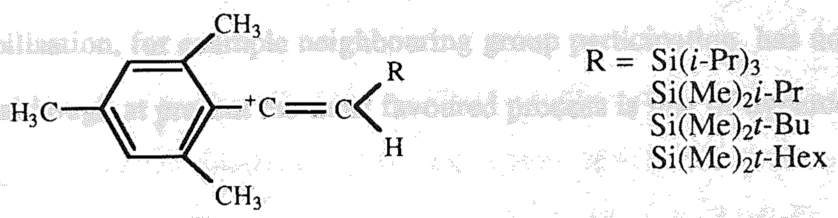
III unbridged unaligned

They found that of the three structures the cyclic form (I) has the greatest stabilisation of 74.4 kcal mol^{-1} followed by the aligned structure (II) with a stabilisation of 72.0 kcal mol^{-1}, this structure has the empty *p* orbital aligned for overlap with the C-Si bond. The unaligned structure (III) which has orthoganol non-overlapping orbitals has a stabilisation of 42.4 kcal mol^{-1}. A comparison of the silyl systems with analogous hydrogen systems $H\text{-}CH_2CH_2^+$ found that the bridged form is 2.4 kcal mol^{-1} more stable than hydrogen and the unaligned silyl-containing structure more stable by 8.9 kcal mol^{-1}, values indicative of the inductive stabilisation of silicon. The aligned conformation was stabilised by 38 kcal mol^{-1} which is a measure of the contribution from all sources. Although from Lambert's studies the value of the stabilisation was found to be 18 kcal mol^{-1}, the differences can be accounted for by the lack of stabilisation from solvent in the gas phase which results in an increased demand for stabilisation by silicon.

Ibrahim and Jorgenson[62] also studied secondary and tertiary systems for the same isodesmic reaction. They found that the unbridged form offered the most stabilisation of 22.1 kcal mol^{-1}, a figure that is in agreement with Lambert's experimental observations[54]. Both secondary and tertiary structures were stabilised less than the primary system as would be expected due to the lower demand for stabilisation from the silicon.

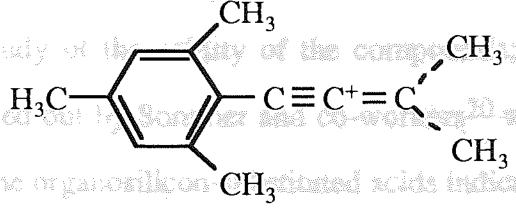
Recently, experimental proof of the β-silyl group's ability of hyperconjugative stabilisation was provided by Siehl and Kaufmann[63]. They studied the ^{13}C NMR spectroscopic characterisation of 1-arylvinyl cations bearing varying β-substituents including alkyl, alkenyl and silyl groups in order to allow a comparison of charge distribution and provide information on the stabilising effect of β-silyl groups in such compounds.

Fig 1.10: β-Silyl-Substituted 1-Arylvinyl Systems:



In β-silyl-substituted 1-arylvinyl compounds of the type shown above (fig 1.10) they found that carbon-silicon hyperconjugation was more efficient than either C-H or C-C hyperconjugation. Finding that it had a similar efficiency in delocalising the positive charge as the 1-mesistylallenyl cation, (fig 1.11), which possesses both α-aryl stabilisation and β-allyl resonance stabilisation:

Fig 1.11 The 1-Mesistylallenyl Cation:



This demonstrates the β-carbon-silicon hyperconjugative stabilisation from the interaction of the β-C-Si σ-bond with the vacant *p* orbital on C^+ to be as effective on charge delocalisation as β- π-conjugation in mesitylallenyl.

There seems no doubt that the mechanism accompanying β-elimination is one involving rate determining C-X cleavage in polar medium, however, whether stabilisation of the resulting carbocation is by a vertical process, such as hyperconjugation or by non-vertical stabilisation, for example neighbouring group participation, has not yet been elucidated, although at present the most favoured process is that of hyperconjugative stabilisation.

1.2 THE ALPHA EFFECT.

1.2.1 Introduction.

Trialkylsilyl-substituents are remarkable in that they are capable of both donating and accepting electrons. In addition to the ability to stabilise a beta carbocation they also act so as to stabilise an alpha carbanion whilst having a destabilising effect upon an alpha carbonium ion.

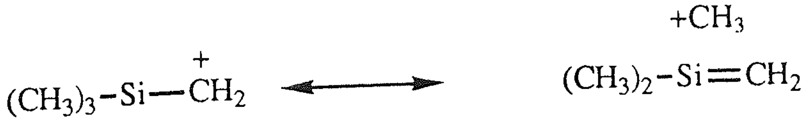
The electron donating power of the R_3Si- moiety as compared to the R_3C- has been demonstrated via a study of the acidity of the compounds; $Me_3SiCH_2CO_2H$ and $Me_3CCH_2CO_2H$ carried out by Sommer and co-workers[20] who found that the acid-weakening effects of the organosilicon-substituted acids indicated a positive inductive effect of electron release from silicon. Because of silicon's greater +I effect with respect to carbon it would be expected to stabilise an adjacent carbocation, however due to opposition by $(p\text{-}d)_\pi$ bonding when silicon is directly attached to an atom with lone pairs or an unsaturated group, usually it is only at the beta position that the strong +I effect is observed.

1.2.2 The Alpha Halogenosilanes.

In 1946 Sommer *et al*[2,3] from a study of the reactivities of carbon-chlorine bonds alpha, beta and gamma to silicon first came upon evidence of the destabilising effect of a trialkylsilyl moiety upon an alpha carbonium ion. They discovered that the α-substituted compounds, trichloro(1-chloroethyl)silane; $Cl_3SiCHClCH_3$ and trichloro(1-chloropropyl)silane; $Cl_3SiCHClCH_2CH_3$ when titrated with dilute alkali yielded a reaction of the Si-Cl bonds only, with the C-Cl bonds unreacted. In contrast, the β-substituted 2-chloroethyl-, 2-chloropropyl- and (2-chloro-*t*-butyl)trichloro- silanes[6] gave a complete reaction on titration with dilute alkali, showing the C-Cl bonds to have reacted as completely as the Si-Cl bonds. They concluded that the silicon inhibited nucleophilic activity at the alpha carbon. The γ-substituted compounds were found to have a reactivity in between that of the α- and β-substituted compounds, having a similar reactivity to the α-substituted compounds in titrimetric analysis, but more reactive when treated with ethanolic potassium hydroxide.

In 1971, in independent studies Eaborn[64], Cartledge[65] and co-workers provided similar explanations for the alpha destabilising effect. Cook, Eaborn and Walton[64], compared the rates of solvolysis of the chlorides and bromides in 90% aqueous acetone or 80% aqueous ethanol, and found that Me_3SiCMe_2X are very slow to react, compared with the carbon compounds Me_3CX and Me_3CCMe_2X, which react rapidly by a S_N1 mechanism. They concluded that the Me_3Si- group was less able to stabilise an adjacent carbonium ion due to electronic effects, and suggested that the absence of hyperconjugation, in the form shown below (fig 1.12), could be responsible for the poor reactivity.

Fig 1.12 Si=C/C$^+$ Hyperconjugation:

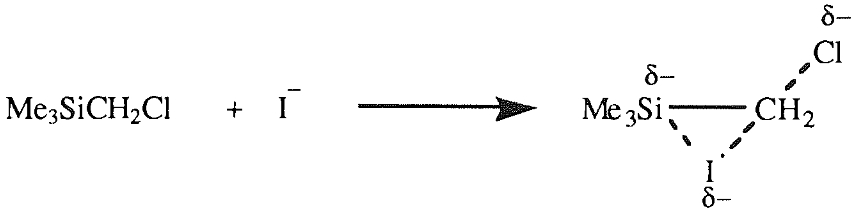


$$(CH_3)_3\text{-Si}-\overset{+}{C}H_2 \longleftrightarrow (CH_3)_2\text{-}\overset{+CH_3}{Si}=CH_2$$

Cartledge and Jones[65] studied the solvolyses of 2-bromo-2-trimethylsilylpropane and its carbon analogue 2-bromo-2,3,3-trimethylbutane. They discovered that the silyl-substituted compound reacted 38 000 times more slowly than the carbon analogue. After consideration of other possible destabilising effects they too concluded that the unexpected lower rate was due to the absence of stabilisation by hyperconjugation from the trimethylsilyl group to the α-carbonium ion, due to silicon's inability to form a silicon-carbon multiple bond. This conclusion was re-enforced by a study by Boye and Post[66] who noticed a decrease in the alpha effect when the α-carbocation was stabilised by an adjacent methyl group.

Eaborn and co-workers[64] reported that the compound $PhMe(Me_3Si)CBr$ reacted with 90% aqueous acetone, at 50°C, 110 times more slowly than $PhMe_2CBr$ at 0°C. Although it might be thought that this system could be stabilised by hyperconjugation, they suggested that the steric interaction between the Me_3Si- and the phenyl group prevents the benzene ring from becoming co-planar with the bonds to the carbonium ion centre and so reduces the stabilisation by hyperconjugation.

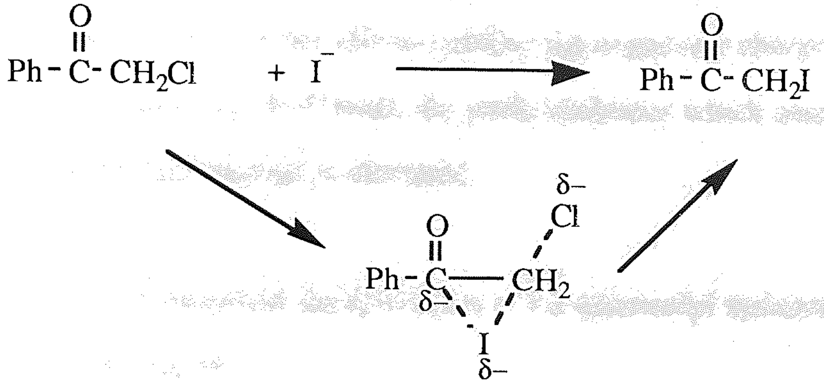
In contrast to the α-halogensilanes relative unreactivity in S_N1 type reactions, S_N2 type reactions are enhanced. In 1946 Whitmore and Sommer[67] observed the enhanced reactivity of silico-neopentyl chloride, Me_3SiCH_2Cl, which reacts with an iodide ion in acetone two million times faster than its carbon analogue, Me_3CCH_2Cl. The S_N2 mechanism is especially good due, it is suggested,[68,69] to silicon's ability to accept electrons into its *d* orbitals allowing the incoming iodide ion to interact with silicon as well as with the carbon. Thus the transition state is stabilised by structures such as that shown in equation 1.17:



(1.17)

This is an analogous situation to that suggested to explain the high reactivity of phenacyl halides.[70] For example, in their reactions with iodide ions the phenacyl chloride $Ph(CO)CH_2Cl$ and the chloride $PhCH_2CH_2Cl$ have relative reactivities of 10^5 and 1 respectively.

Scheme 1.5 The Reaction Of Phenacyl Halides With Iodide Ions:

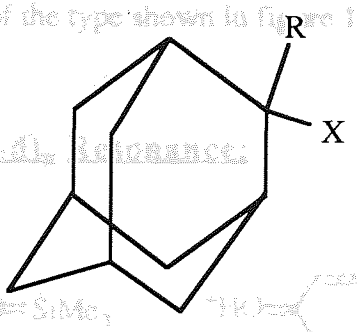


Recently Apeloig and co-workers[71] investigated the solvolysis of the silyl analogues $(CH_3)_3SiCH_2X$, where X = tosylate, *p*-$OSO_2C_6H_4CH_3$ or triflate, OSO_2CF_3. They discovered a dramatic change of mechanism compared with the neopentyl compounds. The triflate substituted silyl analogue solvolysed in absolute ethanol at -20°C without rearrangement, yielding $(CH_3)_3SiCH_2OCH_2CH_3$ exclusively compared with the neopentyl tosylate which yielded 92% rearrangement. From theoretical calculations they were able to dismiss the formation of a free carbocation, which if formed should have undergone rearrangement to a siliconium ion.

Apeloig *et al* observed that in 60% v/v aqueous ethanol at 25°C, the silyl analogue with X = triflate, the silyl analogue with X = tosylate and the carbon analogue reacted with relative rates of 957, 1830 and 1 respectively. In contrast, in the less nucleophilic solvent of 97% trifluoroethanol (TFE) the usual alpha destabilising effect, whereby the silicon-substituted compound is slower than the carbon analogue, is observed. This is explained as being due to the S_N2 type reaction being quenched in favour of the S_N1 mechanism, confirming the bimolecular nature of the solvolyses of silyl-neopentyl systems. From their calculations the authors attributed the destabilising effect of silyl groups, compared with alkyl groups, to weaker hyperconjugation and electrostatic repulsion between adjacent cationic carbon and silicon. They suggested also that the enhancement of S_N2 reactions resulted primarily due to silicon being a better σ-acceptor than carbon and thus better able to stabilise the negatively charged transition state and because of the longer Si-C bond, the steric hindrance which usually inhibits S_N2 reactions in neopentyl systems is alleviated.

Apeloig and Stanger[72] examined the solvolyses of *t*-2-adamantyl systems where the S_N2 mechanism is prevented:

Fig 1.13 Tertiary 2-Silyladamantyl Systems:



They discovered that for R = $SiMe_3$ excellent first order kinetics was followed in both 80% aqueous ethanol and 97% aqueous trifluoroethanol solvents. In 80% ethanol at $25^{o}C$ the methyl-substituted system and the trimethylsilyl systems solvolysed at relative rates of 2.18 : 1, whereas in TFE they solvolysed at relative rates of 0.93 : 1, the very low solvent effects confirming the K_c (S_N1) mechanism. The trimethylsilyl-substituted system was found to react 3.6×10^5 times slower than the *t*-butyl-substituted system. In the same publication the authors carried out *ab initio* calculations concluding that the α-silyl-substituted compounds were destabilised by 6-8 $kcalmol^{-1}$ relative to the methyl-substituted compound and stabilised by 12-14 $kcalmol^{-1}$ compared with the hydrogen-substituted compound.

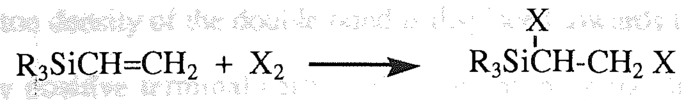
1.2.3 Vinyl and Aryl Silanes.

When an R_3Si- group is directly linked to a π-electron system it can behave as an electron acceptor, stabilising an electron excess on an adjacent carbon atom. In 1953 Benkeser and Krysiak[73] studied the electronic influence of the trimethylsilyl group on the aromatic nucleus. They discovered that trimethylsilyl-substituted aniline and dimethylaniline were less basic than the unsubstituted aniline and that *p*-trimethylsilyl-substitution in phenols increased the acidity relative to phenol. They attributed these effects to $(\pi-d)_\pi$ resonance of the type shown in figure 1.14:

Fig 1.14 Examples of $(\pi\text{-d})_\pi$ Resonance:

The electron attracting effect of the trialkylsilyl-substitutent manifests itself in the electrophilic addition reactions of vinylsilanes.

Halogens add to vinylsilanes to form the corresponding α, β-dihaloalkylsilanes (eqt 1.18). These additions are slower than the addition of halogens to analogous ethenes.



$$R_3SiCH{=}CH_2 + X_2 \longrightarrow R_3Si\overset{X}{C}H\text{-}CH_2\,X \qquad (1.18)$$

The addition reactions of hydrogen halides to vinylsilanes are less vigorous than their reactions with halogen and than the addition of hydrogen halides to both their carbon analogues and allylsilanes. For example, hydrogen bromide does not add to vinyltrimethylsilane without a peroxide catalyst, however with benzoyl peroxide the β-bromoethyltrimethylsilane is formed in 70% yield[74] (eqt 1.19). Sommer and co-workers[74] reported that the additions of HBr, HI and HCl to vinylsilanes were exclusively anti-Markovnikov.

$$Me_3SiCH{=}CH_2 + HBr \xrightarrow{peroxide} Me_3SiCH_2CH_2Br \qquad (1.19)$$

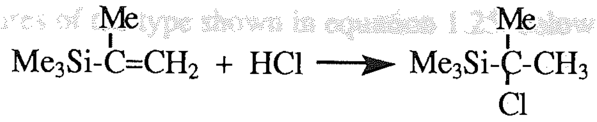
Both the addition of hydrogen bromide to triethylvinylsilane[75] and the aluminium chloride-catalysed addition of hydrogen chloride to vinyltrichlorosilane[76] (eqt 1.20) proceed in an anti-Markovnikov fashion to yield the β-chloroethyl- substituted silanes. Although electronegative chlorine atoms at silicon retard the addition reactions compared with alkyl groups.[15]

$$Cl_3SiCH{=}CH_2 + HCl \xrightarrow{AlCl_3} Cl_3SiCH_2CH_2Cl \qquad (1.20)$$

These non-Markovnikov additions indicate a non-inductive electronic effect of the trimethylsilyl moiety when attatched to a vinyl group. Mironov suggested $(p\text{-}d)_\pi$ conjugation of the Si -C and the C=C bonds[15] to explain the reactivity and direction of addition.

$$Me_3Si\text{-}CH{=}CH_2 \longleftrightarrow Me_3\overset{-}{Si}{=}CH\text{-}\overset{+}{C}H_2 \qquad (1.21)$$

The electon density of the double bond is displaced towards the alpha carbon, causing a relatively positive terminal carbon, thus determining the direction of the addition of hydrogen halide. Although this effect results in extremely unusual chemical reactivity it is weak enough to be reversed by the presence of a single α–methyl-substituent. For example, while isopropenyltrimethylsilane does not react with hydrogen chloride gas, the reaction with concentrated hydrochloric acid gave the α-chloroisopropyltrimethylsilane[74]. The Markovnikov nature of the addition to the α-methyl-substituted compound demonstrates the ease with which this effect can be opposed:



$$Me_3Si\text{-}\overset{Me}{C}{=}CH_2 + HCl \longrightarrow Me_3Si\text{-}\underset{Cl}{\overset{Me}{C}}\text{-}CH_3 \quad (1.22)$$

This and additional evidence obtained from the intramolecular rearrangement of isopropenyltrimethylsilane with concentrated sulphuric acid led Sommer *et al*[74] to conclude that the non-conductive electronic effect being small, could be attributed to a very limited conjugative ability of the trimethylsilyl group.

1.2.4 Stabilisation of α–Carbanions

Silicon's ability to accept electrons is often strong enough to stabilise an α-carbanion. Cason and Brooks[94,95] were the first to observe nucleophilic addition to a vinyl silane. These reactions often proceed with excellent yields, for example, triphenylvinylsilane gives a 67% yield with *n*-butyllithium, and a yield of 84% with phenyllithium.

$$Ph_3Si\cdot CH{=}CH_2 \quad + \; RLi \longrightarrow \overset{Li^+}{Ph_3Si\cdot \bar{C}H{-}CH_2R} \quad (1.23)$$

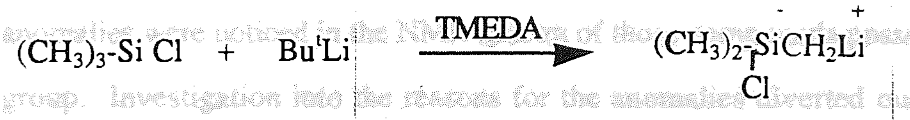
The stabilisation of α-anions is also manifest in the relative ease of proton abstraction alpha to silicon in a variety of functionalised organosilanes. Using a strong base a proton can be removed from even tetramethylsilane. Bases commonly used are alkyl lithiums in the presence of TMEDA or LDA.

$$(CH_3)_4\text{-Si} \quad + \quad Bu^tLi \xrightarrow{\text{TMEDA}} (CH_3)_3\text{-Si}\overset{-}{C}H_2\overset{+}{Li} \qquad (1.24)$$

Such reactions are possible due to the stabilisation of the anions by contributions from resonance structures of the type shown in equation 1.25, below:

$$R_3Si\text{-}\overline{CH_2} \longleftrightarrow R_3\overline{Si}{=}CH_2 \qquad (1.25)$$

The reaction of tetramethylsilane with TMEDA and *t*-butyl lithium although possible is reasonably slow with a resulting 40% yield after four days. Yields are highest when additional carbanion-stabilising groups are present. With the presence of an electronegative substituent on silicon the reaction is much more successful, for example, the reaction of chlorotrimethylsilane with *t*-butyl lithium and TMEDA goes to completion in just one minute.



$$(CH_3)_3\text{-Si Cl} \quad + \quad Bu^tLi \xrightarrow{\text{TMEDA}} (CH_3)_2\text{-}\underset{Cl}{Si}\overset{-}{C}H_2\overset{+}{Li} \qquad (1.26)$$

1.3 AIMS AND SCOPES.

It was suggested[77] to us that compounds of the type $XCH_2Si(CH_3)_2CH_2CH_2Y$ might show interesting chemical and biological activity due to them possessing both an alpha group and a beta group. It was hoped that any information regarding the magnitude and origin of interaction between alpha and beta moieties in silicon systems would help in furthering our understanding of the mechanisms predominant in organosilicon chemistry and ultimately enable its full exploitation in modern organic synthesis.

The aim of this research was to discover whether or not the alpha and beta effects interact with each other, and if so whether interaction is due to steric factors or via electronic transmission through the silicon atom. In order to elucidate this a series of compounds were made with a constant chloromethyl α-function and varying β-functions (hydrogen, hydroxy, methoxy and chloro groups). For comparison a second series of compounds were synthesised with an alpha trimethylsilyl group and the same variety of beta functions. A program of kinetic analysis of solvolysis rates was planned to obtain information on the effect of the different alpha and beta groups on reactivity.

In the course of confirming the structures of the compounds synthesised, certain anomalies were noticed in the NMR spectra of those compounds possessing a β-chloro group. Investigation into the reasons for the anomalies diverted our attention away from the original plan onto a detailed study of NMR conformational effects in our systems. This was of particular interest in the light of the recent reports of highly accelerated rates of solvolysis in restricted β-functional cyclic silane systems[52] The possibility of similar restrictions of conformation in our acyclic systems was one to be considered. Dipole moment studies on the β-chloro substituted compounds were carried out in order to complete the conformational information on our systems.

Chapter 2:

The Solvolysis Reaction.

2. THE SOLVOLYSIS REACTION.

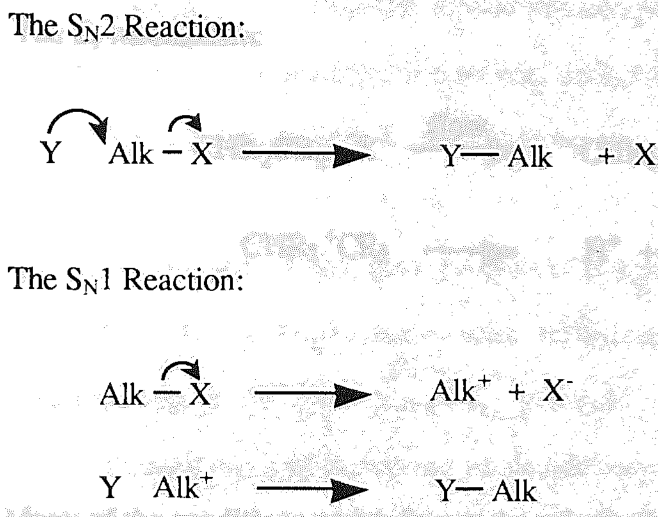
2.1 INTRODUCTION.

Solvolysis is extremely important in organic chemistry. The mechanism of solvolysis has been extensively investigated by numerous methods including kinetic, stereochemical and product analysis studies and to a lesser extent isotope effects and the effect of change of substituent and solvolytic media.[78,79] Hughes, Ingold and Patel[80] first introduced the terms $S_N1$and S_N2 and Hughes and Ingold[23] later reviewed the information available on the mechanism and kinetics of elimination reactions, particularly those reactions which have come to be known as solvolysis reactions. In 1962 Streitweiser[79] published an extensive review of the solvolysis reaction in his book entitled "Solvolytic Displacement Reactions", which discussed the mechanistic postulates and also included a comprehensive overview of the factors influencing the solvolysis reaction.

2.1.1 Solvolysis Reaction Mechanisms.

The term solvolysis is applied to those reactions involving nucleophilic attack by solvent on a substrate. Substrates can react solvolytically by a number of pathways. It is possible for the reaction product to be that of nucleophilic substitution[80,81] either via a bimolecular mechanism, where nucleophilic attack of the solvent assists the cleavage of the leaving group; the S_N2 mechanism (substitution nucleophilic bimolecular) or via a two stage unimolecular reaction; the S_N1 mechanism (substitution nucleophilic unimolecular). In the latter case, the initial and rate determining step is the heterolytic fission of the carbon and the electron attracting leaving group. This leaves a carbonium ion, which is then subsequently attacked by the solvent.

Scheme 2.1 The Two Types of Nucleophilic Substitution Reaction:



The second type of reaction occurring under solvolytic conditions is the elimination reaction[23]. Again, there are two limiting mechanisms; the first, a bimolecular mechanism involves nucleophilic attack by solvent to extract a β–proton whilst an electron attracting group simultaneously separates in possession of an extra electron; the E_2 mechanism (elimination bimolecular). The second is a two step unimolecular mechanism which proceeds via the same first rate determining formation of a carbonium ion as S_N1-type reactions. This is followed by the subsequent loss of a proton from that carbonium ion to the solvent; the E_1 mechanism (elimination unimolecular).

Scheme 2.2 The Two Types of Elimination Reaction:

The E_2 mechanism:

$$Y + \quad H-CR_2-CR_2-X \longrightarrow YH + CR_2{=}CR_2 + X^-$$

The E_1 mechanism:

$$CHR_2CR_2-X \xrightarrow{\text{slow}} CHR_2{}^+CR_2 + X^-$$

$$CHR_2{}^+CR_2 \longrightarrow H^+ + CR_2{=}CR_2$$

Many of the conditions which favour the substitution reaction also promote elimination and thus it is common for the S_N1 reaction to be accompanied by the E_1 reaction and similarly the S_N2 reaction to be accompanied by the E_2 reaction.

It was pointed out[80] that these processes were not considered to be in isolation and that they probably are in fact extremes of a graded range, with varying degrees of collaboration by the reagent in the process of expelling the substitutent that is to be replaced.

2.1.2 Definitions of Mechanisms of Solvolysis.

The term K_s is used frequently to describe solvolytic processes in which there is nucleophilic solvent assistance[82-85] toward both carbon and hydrogen, so both S_N2 and E_2 mechanisms are included in the K_s designation. Solvolysis reactions proceeding by a unimolecular rate determining step are also of two mechanistic types, S_N1 and E_1 and these are designated K_c processes. The designation K_Δ has been assigned to those processes in which unimolecuar ionisation is assisted by neighbouring group participation.[86,195-197] It is frequently observed that neighbouring group assisted and nucleophilic solvent assisted processes are competitive. Solvolyses in which there is no nucleophilic solvent assistance have been described as "limited" solvolyses and include both K_c and K_Δ processes.

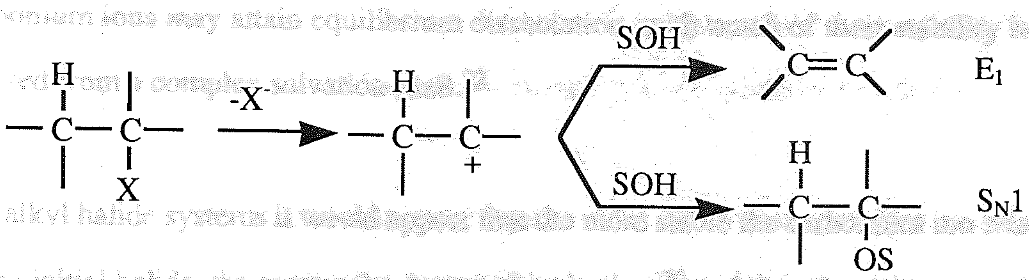
It has been pointed out that the solvolysis of β-substituted alkylsilanes is believed to be of a unimolecular (K_c) nature, with stabilisation from hyperconjugation or by neighbouring group assistance; a K_Δ process. Although it has been intimated that under circumstances of increasing nucleophilicity of the solvent media a bimolecular mechanism could play a role[37,87,88]. (see section 2.3: the S_N1/S_N2 spectrum)

2.2 K_c PROCESSES.

The general unimolecular mechanism was first suggested in 1935 by Hughes and Ingold *et al*[81]. They proposed that the reaction involves the rate determining heterolysis of an electron attracting group, resulting in the formation of a carbonium ion, which subsequently undergoes either substitution or elimination to form olefin, as seen in scheme 2.3.

The unimolecular reaction follows first order kinetics, the rate determining step is ionisation to produce a carbonium ion and so it is not surprising that those compounds which produce stable carbonium ions will solvolyse via the S_N1 or E_1 mechanisms.

Scheme 2.3 S_N1 and E_1 Solvolyses:



2.2.1 Elimination to Olefin: The E_1 Reaction.

When the carbonium ion formed in the initial ionisation step possesses a beta hydrogen, elimination of proton to form olefin is possible. For those reactions proceeding via S_N1/E_1 type unimolecular ionisation the proportion of solvolysis products and elimination products will be independent of the nature of the leaving group, as will be the proportions of isomeric olefins formed from elimination.

The substitution and elimination reactions are usually in competition with each other, however it is usual, due to the weakness of the carbon-silicon bond for elimination to be the usual process in β–silicon bearing systems.[89,90]

The unimolecular elimination mechanism[23] was first established for alkyl chlorides and bromides and later for sulphonium salts. These reactions normally exhibit first order kinetics, however deviations from first order kinetics due to salt effects and the reversibility of the rate determining stage have been observed in the case of alkyl halides.

The two unimolecular mechanisms S_N1 and E_1 have a common slow step resulting in the formation of a carbonium ion. The C-X bond fission passes beyond the transition state without intervention by any specific reagent. The fate of the less stable carbonium ions is determined when the receeding X group is still very close. More stable carbonium ions may attain equilibrium dissociation, with much of their stability being derived from a complex solvation shell.[23]

For alkyl halide systems it would appear that the more stable the carbonium ion relative to the initial halide, the greater the degree of ionisation,[79] and thus the greater reactivity towards unimolecular solvolysis. The order of carbonium ion stability, based on energy data derived from gas phase reactions of carbonium ions[79] has been revealed to be tertiary > secondary > primary > methyl. This stability order is reflected in the solvolysis rates of alkyl halides. For example, in 80% aqueous ethanol at 55°C, the relative rates of solvolysis of methyl, ethyl and isopropyl bromides are 2.51, 1.00 and 1.7 respectively, compared with a relative rate of 8600 for *t*-butyl bromide, a remarkable rate enhancement which is in marked contrast to its relative inactivity in S_N2 reactions[79]. A phenyl group is roughly as effective in stabilising a carbonium ion as are two methyl groups[91] with *t*-butyl chloride and α–phenylethyl chloride having similar reactivities.

In any unimolecular reaction the rate of reaction will be strongly dependent upon the leaving group, in that it is this that is cleaved in the initial rate determining step. From studies of alkyl halides the order of reactivity seems to be F < Cl < Br < I < benzenesulfonate.[63]

2.2.2 The Grunwald-Winstein Equation.

In 1948 Grunwald and Winstein devised a method to assess the measure of a substrate's susceptibility to ionisation. The correlation of rates of unimolecular solvolyses using the Grunwald-Winstein equation[25] has proved to be a very useful tool to deduce the liklihood of a substrate to solvolyse via a unimolecular mechanism.

A solvent's ability to solvate ions may be termed as its "ionising power". The rate determining ionisation step of a unimolecular mechanism is dependent upon the ionising power of the solvent.[25] A measure of a solvent's ionising power is given by the rate of solvolysis of an alkyl halide which reacts by preliminary ionisation in that solvent.

Grunwald and Winstein assigned a definite number, Y, as a quantitative measure of a solvent's ionising power, which they defined as the log of the rate of solvolysis of *t*-butyl chloride (their chosen model unimolecular substrate) in that solvent relative to the rate of solvolysis of *t*-butyl chloride in 80% aqueous ethanol. They found that for a wide range of compounds the logarithms of the solvolysis rates give linear correlation in Y, which can be expressed by the equation:

$$\log k = mY + \log k_o \qquad (2.1)$$

The gradient, m, gives a measure of the susceptibility of the substrate to the ionising power of the solvent, relative to *t*-butyl chloride. This simple relationship between rate of reaction and Y values enabled the arrangement of solvents in a relative order and provided a useful means of correlating unimolecular solvolysis rates, allowing certain deductions to be made regarding the unimolecular rates and the fraction of solvolysis by unimolecular mechanism.

Sommer and Baughman[24] studied the solvolysis, in 50-80% aqueous ethanol, of 2-chloroethyltrimethylsilane, $Me_3SiCH_2CH_2Cl$. They observed that the rate of reaction was not dependent upon the nucleophilicity of the solvent but on its ionising power, and that the substrate had an m value of 1.02. These results indicate that the 2-chloroethyltrimethylsilane is as susceptible to ionisation as *t*-butyl chloride; and that the β-chloro silane is likely to solvolyse by a route similar to that of *t*-butyl chloride, which all the evidence indicates to be a unimolecular mechanism.

2.3 THE S_N1/S_N2 SPECTRUM.

Hughes and Ingold *et al*[80,81] concluded that it is unlikely that reactions proceed via either S_N1 or S_N2 mechanisms solely. It is more likely that the mechanisms are merged with intermediate mechanisms rather than a superposition of extremes, this is probably also true for the elimination reactions.[23]

Grunwald and Winstein used their equation for the correlation of unimolecular solvolysis rates to obtain a formal expression for nucleophilically solvent assisted (K_s) processes:[92]

$$\log (k/k_o) = lN + mY \qquad (2.2)$$

where l is a measure of the response to solvent nucleophilicity, N, and m is the response to the solvent ionising power, Y.

It was expected that for *t*-butyl chloride the values would be; l = 0 and m = 1, ie that it was a limiting S_N1 reaction.

Extensive studies using the Grunwald-Winstein equation for correlation of solvents based on the solvolyses of *t*-butyl chloride revealed a dispersion in correlations applied to limiting K_c substrates possessing leaving groups other than chlorine[87]. It was also found that *t*-butyl chloride behaves anomalously in certain fluorinated solvents because of ion pair partitioning effects. These observations raised questions as to the suitability of *t*-butyl chloride as a model substrate.

Schadt *et al*[87] proposed a revised scale of solvent ionising power derived from tosylate data, using 2-adamantyl tosylate as the model for unimolecular solvolysis. Using the complete Grunwald-Winstein equation (eqt 2.2) they found that the fit of data for primary and secondary tosylates was improved considerably by the inclusion of the term for solvent nucleophilicity, implying that the solvent is kinetically significant not only in the solvolysis of primary tosylates but also for secondary tosylates. It had been previously assumed that the acetolysis of secondary tosylates was via S_N1 or limiting mechanisms. They found from minimum estimates of nucleophilic solvent assistance that rate ratios of at least 470 : 1 may be due to nucleophilic solvent assistance in acetolysis of 2-propyltosylate and that more hindered cyclic structures appeared to be less strongly, but still substantially, nucleophilically assisted. They concluded that the role of the solvent as a kinetically significant nucleophile had previously been underestimated, and introduced the term S_N2(intermediate) to describe those mechanisms which appear to have a reaction intermediate as well as nucleophilic solvent assistance, ie those mechanisms which appear to be an intermediate between the S_N1 and S_N2 processes.

The introduction of the possibility of an S_N2(intermediate) mechanism coupled with the conflicting evidence as to the suitability of *t*-butyl chloride as a model substrate for S_N1 solvolyses prompted Bentley and Carter[88] to re-examine the mechanism of the solvolysis of *t*-butyl chloride and to establish a revised scale of solvent ionising power based on the solvolyses of 1-adamantyl chloride. A systematic study of various model compounds with a tosylate leaving group found them to be insensitive to solvent nucleophilicities. The authors' requirement for a chloride structurally similar to those tosylates examined, in conjunction with other considerations led them to their choice of 1-adamantyl chloride as the model S_N1 substrate. They studied its solvolysis in a range of solvents having a wide variety of ionising powers and nucleophilicities, enabling them to define a scale of solvent ionising power for chlorides. 1-adamantyl chloride is a particularly good substrate for defining a scale of solvent ionising power for chlorides as it is not capable of undergoing elimination or rear sided nucleophilic attack. It was found that a plot of the logarithms of the solvolysis rates for *t*-butyl chloride versus 1-adamantyl chloride was almost linear with aqueous, alcoholic and weakly acidic media (which are known to be relatively nucleophilic) whereas significant deviations were observed for their solvolyses in less nucleophilic media (eg trifluoroethanol). These results emphasised the anomalous behaviour of the solvolyses of *t*-butyl halides and provided evidence of the sensitivity of the solvolyses of *t*-butyl halides to solvent nucleophilicity. From consideration of all of the evidence they proposed that the solvolyses of *t*-butyl halides occurred with nucleophilic solvent assistance accompanying heterolysis of carbon-halogen bond.

Assuming that S_N1 solvolysis rates parallel carbocation stabilities[88] (as derived from equilibria between long lived cations) one would expect that the rates of S_N1 solvolyses of *t*-butyl halides should be lower than those for S_N1 solvolyses of 1-adamantyl chlorides. Bentley and Carter's studies[88] found that in reality *t*-butyl chloride reacts 10^3 times faster than 1-adamantyl chloride in 80% ethanol/water but only 3 times faster in 97% hexafluoroisopropylalcohol/water. They attributed this rate enhancement to nucleophilic solvent assistance in the more nucleophilic solvent. From the new Y scales of solvent ionising power based on the solvolyses of 1-adamantyl halides, they correlated the solvolysis data for *t*-butyl halides in a wide range of solvents using the Grunwald-Winstein equation for K_s processes (equation 2.2). They found that the value for l (the measure of the response to solvent nucelophilicity) for *t*-butyl halides showed that it was in fact significantly sensitive to solvent nucleophilicity. Thus they had established a quantitative link between classical studies on the correlation of solvolysis rates and contemporary studies of stable carbocations.

Most of the evidence detailed above[87,88] seems indicative of a lack of suitability of the traditional Y values (based on *t*-butyl chloride) being used for the correlation of solvolysis rates. However, Kevill *et al*[93] pointed out that for measurements of solvolysis rates in the lower nucleophilic media only minor changes result from using the different Y scales based on the original *t*-butyl chloride and on the adamantyl halides and tosylates.

2.3.1 Raber and Harris' Ethanol-TFE Method.

The different sensitivities of substrates reacting by K_c and K_s mechanisms to solvent nucleophilicity prompted Raber and Harris *et al*[55] to devise a method for determining the involvement of solvent nucleophile in solvolysis reactions.

Aqueous 1,1,1-trifluoroethanol (TFE) and ethanol are very different solvent systems. Ethanol and water are both highly nucleophilic, however water has a much greater ionising power, so for aqueous ethanolic systems an increase in ethanol concentration will decrease the ionising power, with no essential change of nucleophilicity. In contrast both TFE and water are highly ionising solvents but water is far more nucleophilic than TFE. Consequently an increase in TFE content has little effect on the solvent mixture's ionising power but it does significantly decrease the nucleophilicity.

Due to the lower nucleophilicity of aqueous TFE compared with aqueous ethanol; solvolysis reactions proceeding without nucleophilic solvent assistance and those proceeding with nucleophilic solvent assistance show very different responses when the solvent system is changed from aqueous ethanol to aqueous trifluoroethanol.

A model unimolecular substrate should show a negligible response to solvent nucleophilicity, N (l~0) and a large response to ionising power Y (m~1); whereas a bimolecular substrate should show a large response to solvent nucleophility (l~1) and only a moderate response to ionising power (m~0.5).

A bimolecular reagent in TFE should display a large rate response to an increase in the amount of water content due to the increased nucleophilic component. In contrast it should show only a slight change in rate response with increased water content in aqueous ethanolic systems, due to only modest changes in ionising power. Whereas a unimolecular substrate should be independent of nucleophilicity in both solvent systems. This should be apparent by the lack of significant rate differences in aqueous TFE of different compositions. The dependence upon solvent ionising power is evident in the dramatic changes in the rates of solvolysis that accompany changes in aqueous ethanol composition, radically changing the ionising power.

Raber and Harris[55,194] developed a method, which they described as the "ethanol-TFE method", to demonstrate the differing responses of bimolecular and unimolecular substrates to the solvent media. They reasoned that the logarithmic plots of rate constants for solvolysis in aqueous TFE and aqueous ethanol for a unimolecular substrate against the corresponding rate constants for a model unimolecular substrate should result in a single straight line for both the aqueous ethanol and the aqueous TFE solvents. For bimolecular substrates a single line should not be adequately able to correlate the data obtained in the two different solvent media. Raber *et al* developed this theory by constructing logarithmic plots for the solvolytic rate constants of known substrates in aqueous TFE and aqueous ethanol as a function of the rate constants for 1-adamantyl bromide, their chosen model unimolecular substrate.

This method of determination of the involvement of solvent nucleophile in solvolysis reactions has proved to be very useful in the determination of a reaction's molecularity.[194] However the authors[55] do accede that this method is not 'fool proof' and does have some inadequacies which would suggest its use only in conjunction with other mechanistic evidence.

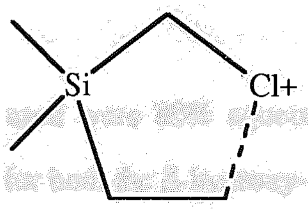
2.4 COMPARISON OF THE SOLVOLYSES OF TRIMETHYL AND CHLOROMETHYL SILANE DERIVATIVES.

2.4.1 Introduction

The main impetus behind this research was the suggestion that compounds of the type $XCH_2R_2SiCH_2CH_2Y$ might show interesting chemical and/or biological activity due to interaction of the alpha and beta functions. In order to establish whether or not the alpha and beta effects are interactive, compounds with a constant chloromethyl alpha group and a variety of beta groups based on the general formula given above, where X is a chloro atom and R a methyl group, were synthesised. The variety of beta functions (=Y) selected for this study were hydroxy, methoxy and chloro groups. For comparison a second series of trimethylsilyl derivatives with the same variety of beta functions were synthesised. The relative β-effect activity of both series of compounds was then assessed from their relative rates of solvolysis.

Any enhancement in chemical reactivity due to interaction of the alpha and beta functions, could be electronic in origin, due to the through silicon effect of X on Y and vice-versa. There is also the possibility that the solvolysis reactions of the α-chloromethyl-substituted systems are even greater enhanced by neighbouring group participative interaction of the α-chloro group at the developing positive charge on the β-carbon. Such interaction would give the most favoured neighbouring group system, a five atom cyclic transition state (fig 2.2) which could have profound effect on the rate of the solvolysis reaction.

Fig 2.1 Cyclic Transition State for the Solvolysis of α-Chloromethyl Derivatives:



2.4.2 Measurement of Rates of Solvolysis for Silyl Systems.

It has been pointed out previously that the solvolysis of β-substituted alkyl silanes usually proceeds via unimolecular elimination with the production of ethene gas.

$$R_3SiCH_2CH_2X \xrightarrow{ROH/H_2O} R_3SiOH + CH_2{=}CH_2 + HX \qquad (2.3)$$

The volume of ethene gas evolved as a function of time is proportional to the quantity of silane reacting and hence provides a means of measuring the rate of solvolysis.

Assuming a first order reaction[96] the rate of reaction for the solvolysis of β-substituted alkyl silanes can be obtained from the expression:

$$\log (a-x) = \log a - \frac{k_r t}{2.303} \qquad (2.4)$$

Where:

a - total volume of ethene evolved

x - volume of ethene at time, t

The reaction rate, k_r, can be calculated from the gradient of a plot of $\log_{10}(a-x)$ versus time.

The standard solvent systems used were 80% aqueous ethanolic media for the β-chloro-substituted systems and, for both the β-hydroxy- and the β-methoxy-substituted systems 5M H_2SO_4 in 50% aqueous methanol. The solvolyses were all carried out at 30°C.

2.4.3 Solvolysis of the β-Hydroxy- and β-Methoxy-Substituted Systems.

The trimethyl derivatives; $Me_3SiCH_2CH_2OH$ and $Me_3SiCH_2CH_2OMe$ both reacted rapidly at rates of 1.84×10^{-3} sec^{-1} and 7.23×10^{-4} sec^{-1} respectively, under the standard solvolysis conditions of 5 M H_2SO_4/ 50% aqueous methanol at 30°C. Such rapid rates are in agreement with those observed previously for other silanes of similar structure.[31]

Table 2.1: Solvolysis Rates of $RMe_2SiCH_2CH_2X$ in 5M H_2SO_4/50% aq MeOH at 30°C:

R	X	k(sec^{-1})
Me	OH	1.84×10^{-3}
Me	OMe	7.23×10^{-4}
$ClCH_2$	OH	3.15×10^{-4}
$ClCH_2$	OMe	3.97×10^{-5}

The α-chloromethyldimethylsilyl derivatives; $ClCH_2Me_2SiCH_2CH_2OH$ and $ClCH_2Me_2SiCH_2CH_2OCH_3$ reacted noticeably slower (3.15×10^{-4} and 3.97×10^{-5} sec^{-1} respectively) than their trimethyl analogues (1.84×10^{-3} and 7.23×10^{-4} sec^{-1} respectively). This slight reduction in solvolytic activity can be satisfactorily explained by the electronegative nature of the chloromethyl moiety inductively pulling electrons into the carbon-silicon bond, thus strengthening it. The solvolyses of these compounds have shown no dramatic enhancement or reduction in reactivity that might have been expected were there any interaction between the alpha (chloromethyl) and beta (hydroxy/methoxy) functions.

2.4.4 Solvolysis of the β-Chloroethyl Substituted Systems.

2.4.4.1 2-Chloroethylchloromethyldimethylsilane.

In contrast to the unremarkable nature of the solvolyses of the 2-hydroxyethyl- and 2-methoxyethyl-substituted systems, the 2-chloroethylchloromethyldimethylsilane did show anomalous behaviour in that it appeared not to react solvolytically. There was no measurable evolution of ethene gas under the standard solvolytic conditions of 80% aqueous ethanol and 30°C even after fourteen days. Absence of ethene production prevailed despite the use of more highly ionising media of 60 and 70% aqueous ethanol and 70, 90 and 100% aqueous trifluoroethanol and an increased working temperature of 50°C. The use of scaled-up quantities of 2 g which would be expected to yield over 260 cm^3 of ethene, still resulted in no evidence of ethene.

This result is extraordinary, in that not only is an anticipated enhancement of rates due to possible alpha and beta group interaction not met but in fact totally the opposite occurs, instead there is a total inhibition of usual beta effect activity. A slight reduction in rate would be understandable because of the electron withdrawing effects of the α-chloromethyl group, as observed previously for the β-methoxyethyl- and β-hydroxyethyl-substituted chloromethyldimethylsilanes. However, such electronic effects would be no where near sufficient to account for the apparent total lack of reactivity of this compound.

It is surprising that a chlorine on an alpha carbon should have such an enormous influence on the reactivity of these systems. Since there appeared to be no reaction then it was understandably of interest to examine the reaction mixture, to see whether the starting material had reacted. A 2 g quantity of starting material, 2-chloroethyl chloromethyldimethylsilane was added to 100 ml of 70% aqueous ethanol. The reaction flask was connected to a gas manometer to monitor ethene evolution. After twenty four hours, and no evidence of ethene production, the water was removed from the mixture with anhydrous magnesium sulphate and the majority of ethanol removed by distillation. Analysis by NMR of the remaining product mixture revealed a mixture of the starting material, $ClCH_2Me_2SiCH_2CH_2Cl$, the siloxane $ClCH_2Me_2SiOSiMe_2CH_2Cl$ and the substitution product $ClCH_2SiMe_2CH_2CH_2OH$ in the ratio of 7 : 2 : 1 (approximately). The same reaction and work-up procedure was repeated, instead allowing the reaction to proceed for five days. This significantly altered the product ratios to 1 : 1 : 1 of starting material, siloxane and substitution product respectively.

Since the siloxane, $ClCH_2Me_2SiOSiMe_2CH_2Cl$, was a product of the reaction, cleavage of the silicon-carbon bond must have occurred. The associated lack of ethene formation would suggest that the most plausible reaction mechanism would be nucleophilic attack at the silicon. The expected products from that reaction would be the siloxane and ethyl chloride:

$$ClCH_2Me_2SiCH_2CH_2Cl + H_2O \longrightarrow ClCH_2Me_2SiOH + CH_3CH_2Cl$$

$$2\,ClCH_2Me_2SiOH \longrightarrow ClCH_2Me_2SiOSiMe_2CH_2Cl \tag{2.5}$$

If ethyl chloride is a product of the solvolysis of 2-chloroethylchloromethyldimethylsilane, due to its solubility in aqueous ethanol (the solvent medium) it would not be expected to collect in the gas manometer, and so it might be hoped that its presence could be detected in the NMR spectra of the product mixture. Subsequent analysis of the product mixture by NMR (prior to distillation to remove the ethanol solvent) did not show the presence of any ethyl chloride. Unfortunately the proton

NMR chemical shifts of the methyl and methylene groups for the ethanol and ethyl chloride are very close, and so it is most probable that the ethanol solvent would obscure the presence of ethyl chloride.

In an attempt to overcome these problems and establish the presence of ethyl chloride, the solvolysis was repeated using 70% aqueous trifluoroethanol as the reaction medium. The presence of ethyl chloride would clearly be seen from analysis of the NMR spectra, as in the proton NMR spectra of a mixture of ethyl chloride and trifluoroethanol both components are easily distinguishable. 2 g of 2-chloroethylchloromethyldimethylsilane in 70% aqueous trifluoroethanol at 30°C was allowed to react for fourteen days. After which time the equipment was attached to an acetone cold trap and flushed through with nitrogen gas. It was hoped that any ethyl chloride formed would be carried over with the nitrogen and be collected in the acetone cold trap for easy identification. Analysis of the contents of the acetone cold trap did not provide any evidence of the production of ethyl chloride. A sample of the reaction mixture was then analysed by NMR spectroscopy in an attempt to identify the presence of ethyl chloride, but again no ethyl chloride was detected. The reaction mixture was then treated as before, with the removal of water and the majority of solvent. Subsequent analysis of the treated reaction mixture revealed the siloxane and β-hydroxyethylchloromethyldimethylsilane in a 1:1 ratio.

2.4.4.2 2-Chloroethyltrimethylsilane.

Since it appeared that 2-chloroethylchloromethyldimethylsilane did not react solvolytically by the S_N1 mechanism as expected, it caused us to question the mechanism for the solvolysis of 2-chloroethyltrimethylsilane, which had previously been assumed to react by the S_N1 mechanism[24]. In order to see whether or not solvent nucleophilicity was important and in fact if S_N2(intermediate)[87] would be a more apt term to describe the mechanism, it was decided to investigate the solvolysis reaction of 2-chloroethyltrimethylsilane in a variety of solvent media of different ionising powers and nucleophilicities.

Table 2.2 **Solvolysis Rates of $Me_3SiCH_2CH_2Cl$ in Various Solvent Media at 30°C:**

Solvent Media (aq)	k (sec^{-1})
70% EtOH	1.74×10^{-4}
80% EtOH	6.26×10^{-5}
70% TFE	2.12×10^{-3}
100% TFE	2.29×10^{-3}

A rate of 6.26×10^{-5} sec^{-1} is observed for the solvolysis of 2-chloroethyltrimethylsilane in the standard solvent media of 80% aqueous ethanol at 30°C. This is of the order expected for this compound and unlike its chloromethyl analogue it is displaying entirely normal beta effect activity. It is interesting to note that this value as found by our experiment is within experimental error of the value 6.1×10^{-5} sec^{-1} as reported by Sommer[24] in 1961.

Analysis of solvolysis rates undertaken in a variety of solvent media gave results which are in support of the belief of the solvolysis of 2-chloroethyltrimethylsilane proceding via unimolecular ionisation. There is a considerable decrease in solvolysis rate for the

2-chloroethyltrimethylsilane from 1.74 x 10^{-4} sec^{-1} to 6.26 x 10^{-5} sec^{-1} when the solvent system is changed from 70% aqueous ethanol to the less ionising 80% aqueous ethanol. In contrast the reaction rate remains more or less constant in aqueous TFE over a concentration range of 70% to 100% (2.12 x 10^{-3} sec^{-1} and 2.29 x 10^{-3} respectively). Such constancy of rates, despite the substantial difference in solvent nucleophilicity is indicative of the reaction proceeding via a unimolecular mechanism. A theory that would account for the observed increase in rate from 1.74 x 10^{-4} sec^{-1} to 2.12 x 10^{-3} which corresponds to the change from 80% aqueous ethanol to the more highly ionising 80% aqueous TFE.

2.5 CONCLUSIONS.

Both the β-hydroxyethyl- and β-methoxyethyl-substituted trimethylsilyl and chloromethyldimethylsilyl systems displayed entirely normal beta effect activity. The presence of the alpha chloromethyl function had only the slight effect of reducing the observed rate by an amount accountable by the electronegativity of the chlorine pulling the electron density into the Si-C bond and strengthening it. In sharp contrast the replacement of a methyl group by a chloromethyl group in 2-chloroethyltrimethylsilane dramatically alters the solvolytic activity. The presence of the alpha chloromethyl group has the effect of completely inhibiting the normal beta effect activity, whilst simultaneously seeming to facilitate alternative mechanisms. Further work is needed in order to elucidate the exact mechanism by which 2-chloroethylchloromethyldimethylsilane reacts in solvolytic media.

It seems unusual that the profound effect of α-chloro substitution on 2-chloroethyltrimethylsilane is not mirrored in the β-hydroxyethyl- and β-methoxyethyl-substituted systems. However, there have been previous reports of similar discrepancies between the effects of substituents on reactivity observed for β-hydroxyethyl- and β-haloethyl-substituted triphenylsilyl systems. It was reported[97] that 2-bromoethyltriphenylsilane did not react at all solvolytically (only starting material was recovered) even after nine hours of reflux in 90% aqueous acetone or 5 days of reflux in THF/water (50/50). Similarly, 2-chloroethyltriphenylsilane is found to be stable at temperatures below 200°C in solvolytic media.[98] In contrast the β-hydroxyethyltriphenyl systems although generally less reactive than their trimethyl analogues do react[99] by the normal pathways and eliminate alkene. Another reaction worthy of comment is the solvolysis of 2-bromopropyltriphenylsilane which does react solvolytically although not by the ususal route. It does not eliminate propene, instead, the reaction product is that of substitution; the 2-hydroxypropyltriphenylsilane.[97]

Chapter 3

N.M.R CONFORMATIONAL ANALYSIS.

3. N.M.R. CONFORMATIONAL ANALYSIS.

3.1 INTRODUCTION.

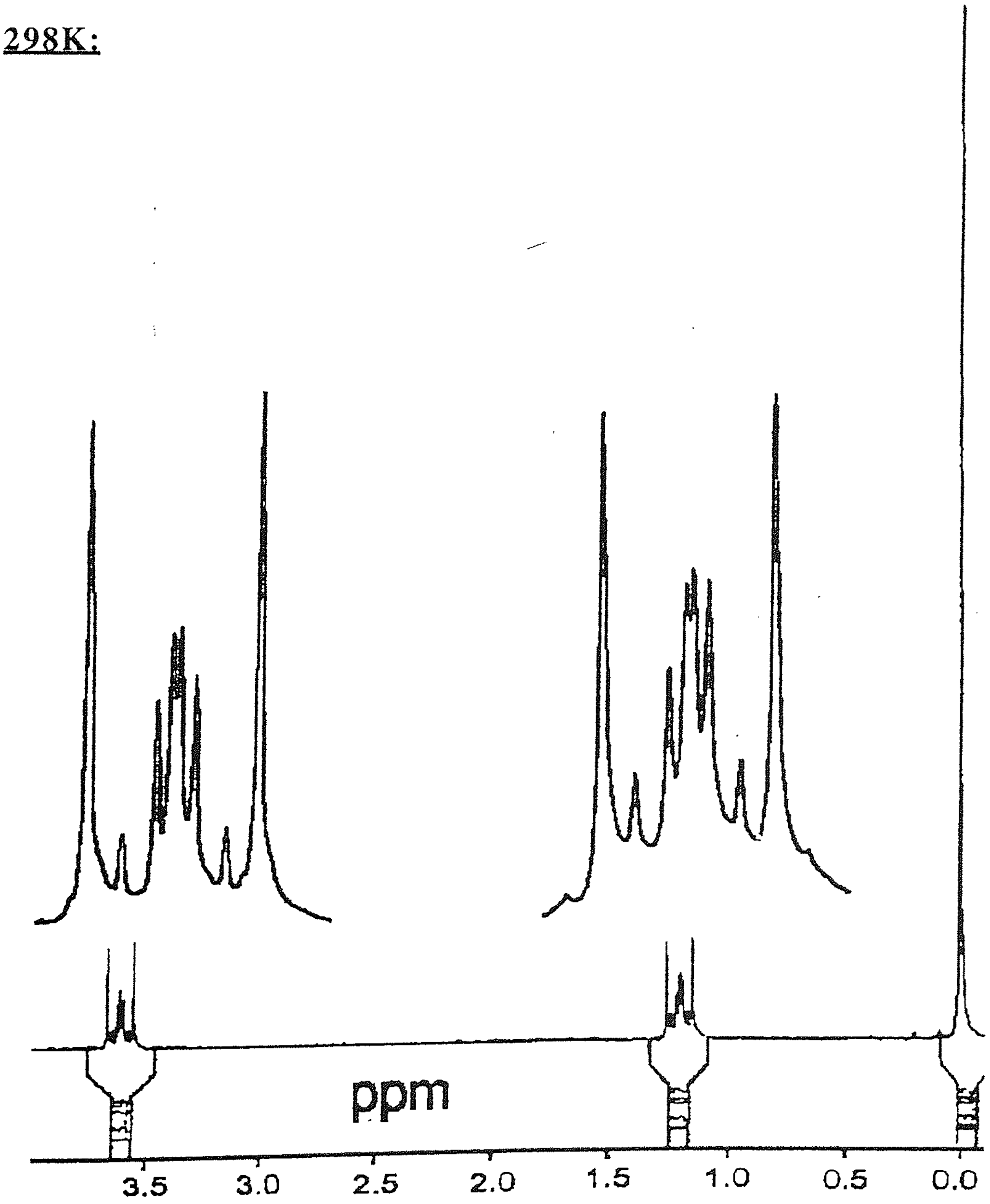
It was during the course of confirming the structure of the compounds synthesised for solvolytic analysis that anomalies were noticed in some of the proton NMR spectra, in particular in the spectra of the β-chloroethyl-substituted compounds. Given the surprising lack of reactivity of 2-chloroethylchloromethyldimethylsilane it was clearly of interest to investigate the cause of the abnormalities in these spectra. In particular, it was hoped that the NMR analysis could give information as to conformational preferences within these systems, which could go some way to providing a possible explanation for their unusual reactivity. As a result the original course of this project was somewhat diverted in the pursuit of conformational information by investigation of the NMR spectra.

Nuclear Magnetic Resonance Spectroscopy is one of the most powerful tools used by organic chemists in structure determination as well as being useful in the investigation of many properties such as isomerism, tautomeric equilibria and reaction rates. It is even possible from the correlation of substituent induced chemical shifts with charge densities to deduce mechanisms of transmission of electronic substituent effects such as field effects, resonance or π polarisation effects.[100,101]

Although most modern organic and physical texts cover this subject the original texts[102-105] of the 1950's and 60's by the pioneers of this technique still remain amongst the most useful and relevant sources of reference.

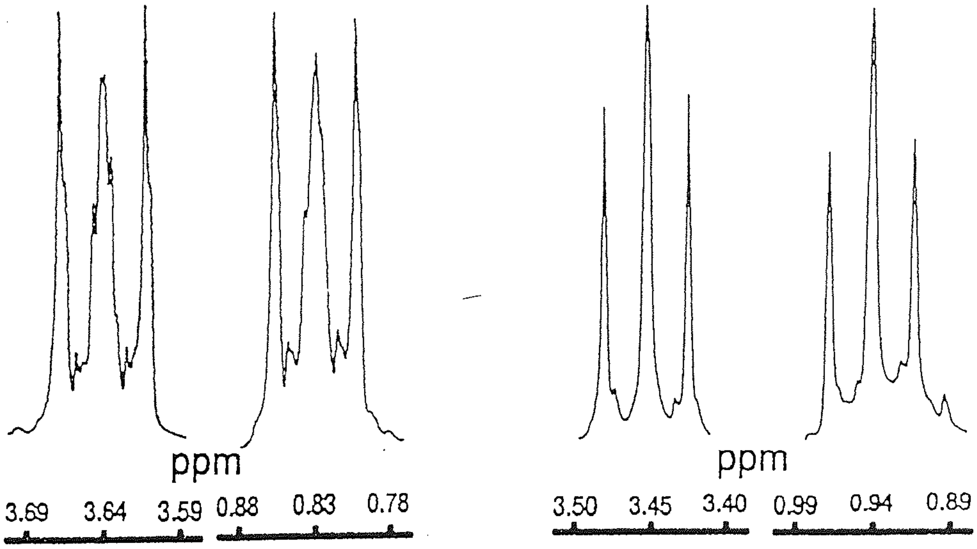
It was explained earlier in this chapter that whilst confirming the structure of the silanes synthesised it was noticed that the proton NMR spectra of the β-chloroethyl-substituted compounds; $Me_3SiCH_2CH_2Cl$ and $ClCH_2Me_2SiCH_2CH_2Cl$ showed unusual complex splitting patterns for the sil-methylene and the chloromethylene protons and not the simple first order triplets that would be expected for such systems in which the chemical shift differences are of the order of 2.0-3.0ppm.[106-107] These abnormalities can clearly be seen in the spectrum (fig 3.1) of 2-chloroethyltrimethylsilane.

Fig 3.1 Proton NMR Spectrum of 2-Chloroethyltrimethylsilane at 298K:



Analysis of the oxygenated β-hydroxyethyl- and β-methoxyethyl-substituted systems $R_3SiCH_2CH_2OR'$ showed splitting patterns much closer to the typical first order patterns as can be seen in figure 3.2 below.

Fig 3.2 Proton NMR Methylene Absorptions of 2-Hydroxyethyltrimethylsilane (A) and 2-Methoxyethyltrimethylsilane (B) at 298K:



A

2-hydroxyethyltrimethylsilane

B

2-methoxyethyltrimethylsilane

It would be expected that the conformationally mobile open chain β-silyl systems $R_3SiCH_2CH_2X$ would exist as a mixture of gauche and anti forms. A possible explanation for the difference in the methylene proton splitting patterns for the halogen- and oxygen-substituted compounds is that the larger halogen in the beta position reduces rotation about the carbon-carbon bond resulting in differences in confomer distributions in the different systems. A detailed theoretical analysis of the splitting patterns has been carried out and spectra obtained at various temperatures for a variety of compounds possessing the general structure $R_3SiCH_2CH_2Y$, with a view to obtaining additional information on conformational distributions in these systems.

3.2 NMR THEORY

3.2.1 Systems of Notation.

In 1957 Bernstein, Pople and Schneider[108] first suggested the universal system of notation for describing systems of nuclear spins in molecules and in 1969 a slightly modified version of their system was presented in a publication by Feeny and Sutcliffe.[103] In this system non-equivalent nuclei of the same species whose chemical shift differences are comparable to the spin coupling constant between them are designated A, B, C..etc. For a second group of non-equivalent nuclei in the same molecule with a large chemical shift separating them from the previous group of nuclei, which amongst themselves have chemical shifts comparable to their coupling are designated X, Y, Z. By the same principle a third intermediate group would be denoted by P, Q, R. Thus, vinyl fluoride CH_2=CHF is referred to as an ABCX system.

These different groups could be of the same species with chemical shift differences large compared to the coupling between groups or they could represent different nuclear species. Nuclei which are magnetically equivalent are referred to by the same symbol with the number of nuclei having the same symbol indicated by a suffix, for example; Cl_2CH-CH_2Cl is an AX_2 system. Nuclei which show chemical shift equivalence but are not magnetically equivalent are described by the same letter but are distinguished from each other by primes. Molecules in which two B nuclei have the same chemical shift but couple to different extents with a nuclei A are designated as ABB' systems.

This is illustrated in the case of 1,1-difluoroethylene, $CF_2=CH_2$ this is described as an AA'XX' system, as there are two pairs of symmetrically equivalent nuclei which are not magnetically equivalent due to the two hydrogen nuclei coupling with each individual fluorine nucleus to a different extent.

3.2.2 The AA'XX' System.

In all of the silanes studied it is the sil-methylene and β-substituted methylene peaks that are of immediate interest. By the standard notation these would be designated as A_2X_2 systems.

The theory for A_2X_2 systems was first given by McConnel, McLean and Reilly[109] with an analysis of the spectrum of 1,1-difluoroethylene. They developed a systematic, quantum mechanical proceedure for the analysis of multiplet splittings and intensities in terms of chemical shifts and coupling constants. These systems consist of four nuclei (two pairs) of spin 1/2 with the two pairs having a large chemical shift or being of different species. Cases in which the members of each pair of nuclei are equivalent in chemical shift but not magnetically equivalent constitute an AA'XX' system.

If $J_{AX} = J_{AX'}$ the system would be designated A_2X_2. Strict AA'XX' spectra are given by pairs of nuclei of different species for example $F_2C=CH_2$. However, certain species with large values of υ_A-υ_X approximate AA'XX' systems very closely.

Fig 3.3 The AA'XX' System Applied to the β-Functional Alkylsilane (I) and the Coupling Constants Associated (II)

I II

This system is characterised by six coupling constants, however the symmetry of the molecule results in $J_{AX} = J_{A'X'}$ and $J_{AX'} = J_{A'X}$ thus reducing the effective number of different spin coupling constants to four, (fig 3.3). The A and X parts of the spectrum are identical.

For convenience the following quantities can be defined:

$$\begin{aligned} K &= JAA' + JXX' \\ L &= JAX - JAX' \\ M &= JAA' - JXX' \\ N &= JAX + JAX' \qquad (3.1) \end{aligned}$$

The relative line intensities can be expressed by the following quantities:

$$\begin{aligned} \theta_s &= 0.5 \operatorname{Cos}^{-1} [\, K/(K^2 + L^2)^{1/2} \,] \\ \theta_a &= 0.5 \operatorname{Cos}^{-1} [\, M/(M^2 + L^2)^{1/2} \,] \qquad (3.2) \end{aligned}$$

The line positions and relative intensities for the AA'XX' case can be seen from Table

3.1, below.

The entire AA'XX' spectrum contains 24 lines; 12 are the A transitions and 12 are the X transitions, but as the X spectrum is identical to that of the A only the 12 transitions of the A (or X) spectrum need be considered. These 12 transitions are symmetric about υ_A. However only 10 lines can be observed as transitions 1 and 2 and transitions 3 and 4 are degenerate.

Table 3.1 The Transitions of an AA'XX' System[110]:

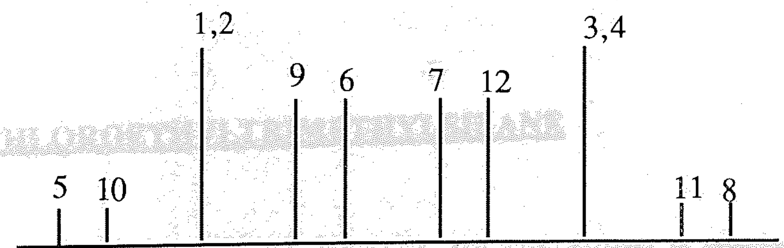
Transition	Position relative to υ_A or υ_X (Hertz)	Relative Intensity
1	0.5 N	1
2	0.5 N	1
3	-0.5 N	1
4	-0.5 N	1
5	$0.5\ K + 1/2(K^2 + L^2)^{1/2}$	$\sin^2\theta_s$
6	$-0.5\ K + 1/2(K^2 + L^2)^{1/2}$	$\cos^2\theta_s$
7	$0.5\ K - 1/2(K^2 + L^2)^{1/2}$	$\cos^2\theta_s$
8	$-0.5\ K - 1/2(K^2 + L^2)^{1/2}$	$\sin^2\theta_s$
9	$0.5\ M + 1/2(M^2 + L^2)^{1/2}$	$\sin^2\theta_a$
10	$-0.5\ M + 1/2(M^2 + L^2)^{1/2}$	$\cos^2\theta_a$
11	$0.5\ M - 1/2(M^2 + L^2)^{1/2}$	$\cos^2\theta_a$
12	$-0.5\ M - 1/2(M^2 + L^2)^{1/2}$	$\sin^2\theta_a$

The A spectrum will contain:

1. A strong doublet, centered about υ_A, from 1, 2 and 3, 4 whose separation equals N = JAX + JAX'
2. Lines 5, 6, 7 and 8 form a quartet centered on υ_A
3. Lines 9, 10, 11 and 12 form a quartet centered on υ_A
4. The separation of lines 5 and 6 (and 7 and 8) gives K
5. The separation of lines 9 and 10 (and 11 and 12) gives M
6. The value of L may be obtained from the value of K and from the difference between lines 5 and 7 (or 6 and 8) $= (K^2 + L^2)^{1/2}$ and from the value of M and the difference between lines 9 and 11 (and 10 and 12) $= (M^2 + L^2)^{1/2}$

Fig 3.4 Typical A (or X) Spectrum for an AA'XX' System

with JAX >> JAX' >0 and JXX'>>JAA>0 (redrawn from reference 110)



Of the two symmetrical quartets it is not possible to decide which quartet is 5, 6, 7 and 8, and which should be assigned 9, 10,11, and 12 and thus it is not possible to differentiate between K and M. Since in the expressions of the transitions from which K, M and L are derived the quantities appear as their squares, their relative signs can not be determined. Although four coupling constants can be found one can not distinguish between $J_{AA'}$ and $J_{XX'}$ or between J_{AX} and $J_{AX'}$. However prior knowledge of the effect of geometry on coupling constants of related compounds does make it possible to assign individual coupling constants.

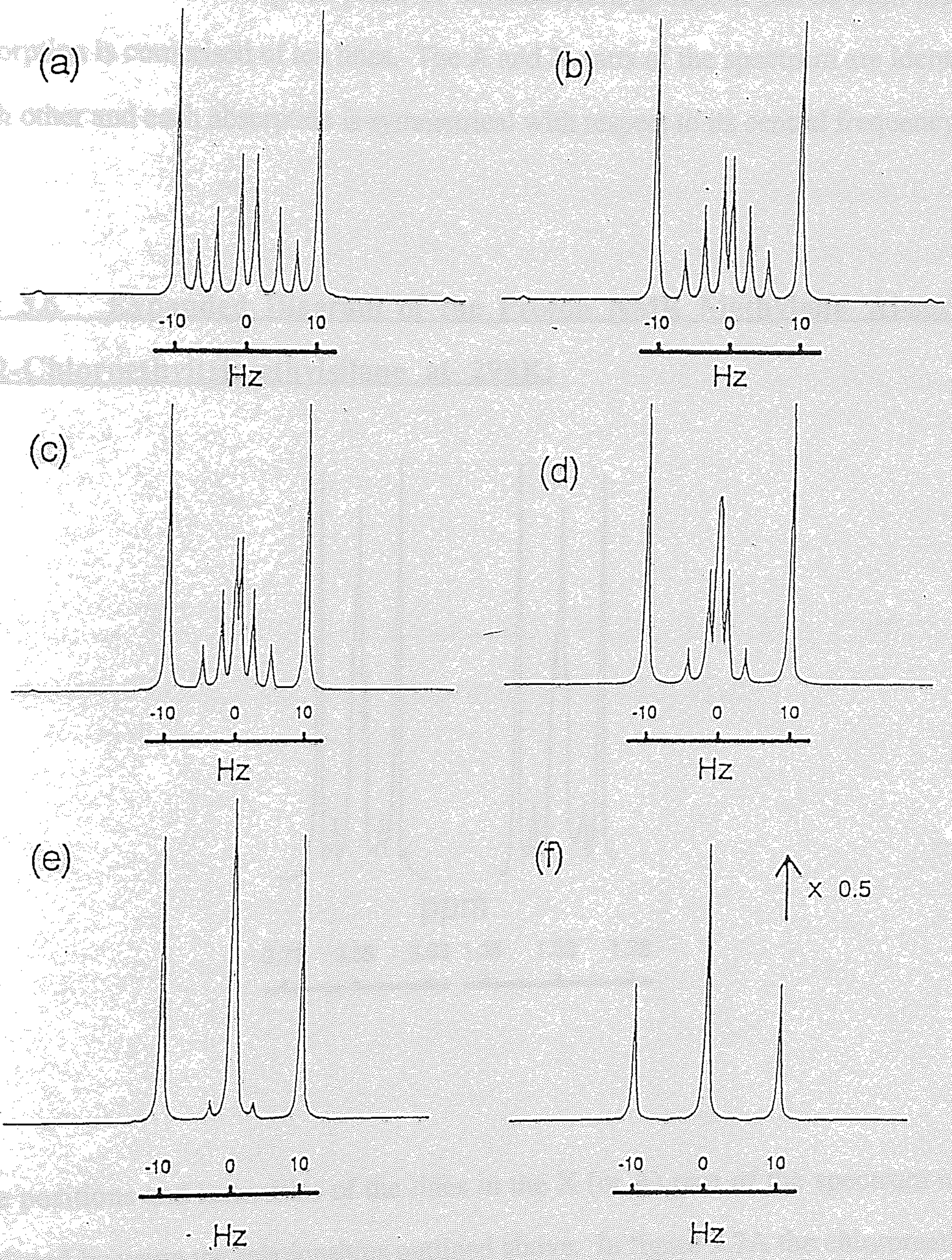
In a system of free rotation $J_{AX} = J_{AX'}$; a true A_2X_2 case, lines 5, 8, 9 and 12 will have a zero intensity and lines 6, 7, 10 and 11 appear at υ_A (or υ_X) thus forming a simple triplet. There are cases when J_{AX} and $J_{AX'}$ are not equal and yet the A and X parts may still be triplets if $J_{AA'} >> |J_{AX} - J_{AX'}| + J_{XX'}$ and so a simple triplet does not necessarily mean that the two A and X coupling constants are equal. Also it must be remembered that even for highly sterically hindered molecules it is possible for an 'accidental' equivalence of J_{AX} and $J_{AX'}$ coupling constants to give rise to a simple triplet.

The general effects on the A (or X) part of the methylene absorptions of varying the relative values of J_{AX} and $J_{AX'}$ can be seen below in figure 3.5. These simulated spectra can be compared to those obtained experimentally.

3.3 2-CHLOROETHYLTRIMETHYLSILANE

The proton NMR spectrum of 2-chloroethyltrimethylsilane is shown in Figure 3.1. The absorptions at 1.28 ppm, 3.68 ppm and ~0 ppm correspond to the protons of the sil-methylene, chloromethylene and methyl moieties respectively. The spin-spin coupling constant for the protons involved in the silmethylene-chloromethylene interaction is determined to be ~18 Hz, and the difference in their chemical shifts is about 2.4 ppm (720 Hz). These values would normally be expected to give rise to first order triplets, a typical 'free rotation' A_2X_2 system. However, at 298 K it is apparent that the individual methylene absorptions depart markedly from the expected triplets.

Fig 3.5 Theoretical Proton NMR Spectrum of the AA'XX' System Showing the A (or X) Absorption:



Where:

(a) $J_{AX} = 14$ Hz, $J_{AX'} = 4$ Hz

(b) $J_{AX} = 13$ Hz, $J_{AX'} = 5$ Hz

(c) $J_{AX} = 12$ Hz, $J_{AX'} = 6$ Hz

(d) $J_{AX} = 11$ Hz, $J_{AX'} = 7$ Hz

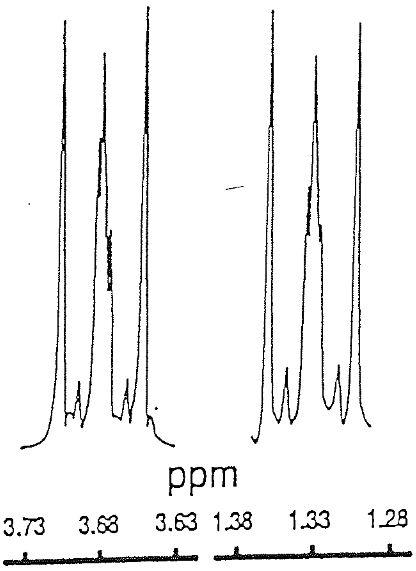
(e) $J_{AX} = 10$ Hz, $J_{AX'} = 8$ Hz

(f) $J_{AX} = 9$ Hz, $J_{AX'} = 9$ Hz

In all cases $J_{AA'} = 14$ Hz and $J_{XX'} = 11$ Hz

Figure 3.6 shows an expanded version of the X part (the chloromethylene fragment) of the observed proton NMR of 2-chloroethyltrimethylsilane. From a detailed examination of the absorption peaks of the methylene groups it can be seen that each absorption is comprised of ten lines. The A and X parts of the spectrum are identical to each other and each absorption is symmetrical with respect to its central frequency.

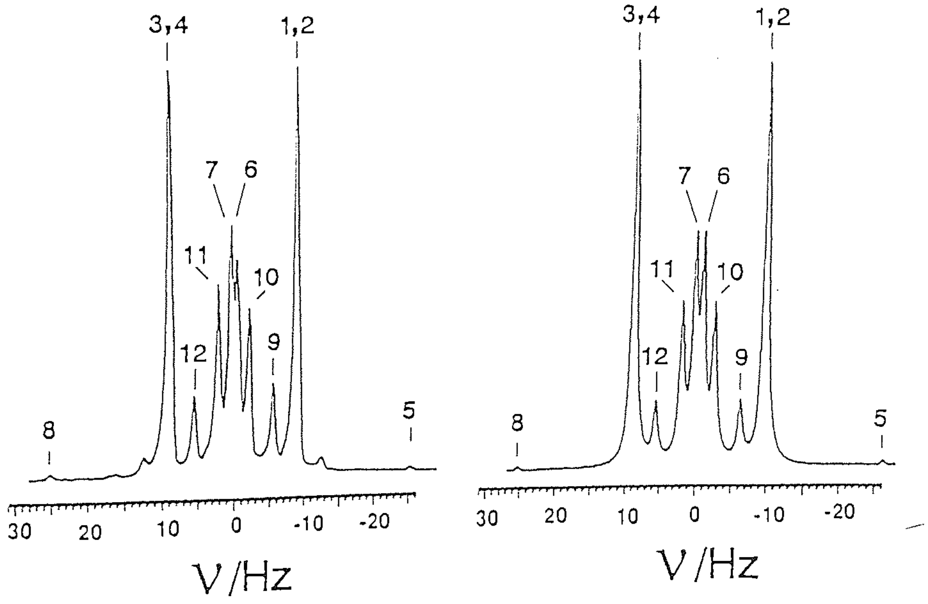
Fig 3.6 Expanded Diagram of the Proton NMR Methylene Absorption of 2-Chloroethyltrimethylsilane at 298K:



The positions and intensities of the lines in the X (or A) part of the spectrum may be analysed by using the relationships outlined above. In figure 3.7A the chloromethylene fragment (the X part) has been further expanded and more closely analysed. The lines in the absorption have been labelled according to the entries shown in Table 3.1 above. Lines 1, 2, 3 and 4 represent the doublet separated by the quantity N. The other lines in the absorption have been labelled to show the quartet associated with the transitions 5, 6, 7 and 8 and the remaining quartet given by transitions 9, 10, 11 and 12.

It is clear from a comparison of the entries in table 3.1 and spectrum A in figure 3.7 below, that all of the possible NMR transitions can be seen for this compound. Direct measurement of line spacings in either the X or A absorptions enables the magnitudes of the parameters K, M and N to be readily deduced by following the procedure previously detailed. Thus for 2-chloroethyltrimethylsilane the parameters K, M and N were found to be 24.4 Hz, 3.5 Hz and 17.9 Hz respectively. The difference between lines 5 and 7 (fig 3.7) gives $(K^2 + L^2)^{1/2}$, which may be used to obtain the modulus of L. The coupling constants were then deduced to be $J_{AA'} = 14$ Hz, $J_{XX'} = 10.5$ Hz, $J_{AX} = 12.5$ Hz and $J_{AX'} = 5.4$ Hz. The signs of J_{AX} and $J_{AX'}$ have been assumed to be positive.

Fig 3.7 The Experimental (A) and Theoretical (B) Proton NMR Methylene Absorption of 2-Chloroethyltrimethylsilane



A

Experimental

B

Theoretical

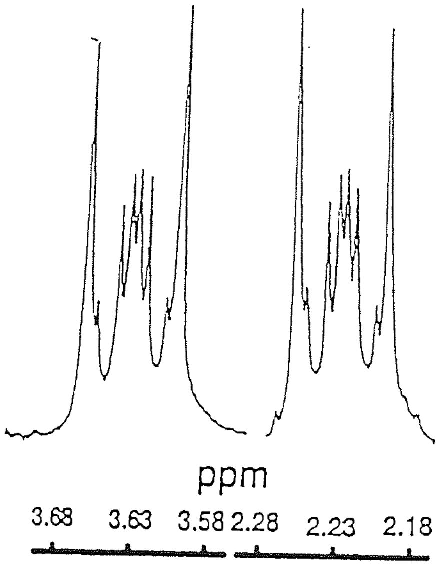
Absorption B, in figure 3.7 above, shows the theoretical absorption of the XX' (or AA') part of the AA'XX' interaction, calculated using the coupling constants obtained from the analysis of the observed absorption peak of 2-chloroethyltrimethylsilane. Comparison of the experimental (A) and theoretical (B) absorptions indicates a fairly close match with respect to line positions and intensities. These results would appear to indicate that the 2-chloroethyltrimethylsilane, at room temperature, has severely restricted rotation about the C-C bond and the molecule appears to be locked in one conformation.

Considering the similarity of the spectra of the 2-chloroethyltrimethylsilane and 2-chloroethylchloromethyldimethylsilane, it would be fair to assume that the latter compound will also possess restricted rotation about the carbon-carbon bond of the ethyl group.

3.3.1 2-Bromoethyltriphenylsilane.

It is interesting also to look at the methylene absorptions of 2-bromoethyltriphenylsilane, which also are of a complex nature (fig 3.8). The large size of the bromine atom and the three phenyl groups will profoundly influence the steric hindrance in this molecule so it is not suprising that this compound appears to exist in the sterically restricted anti form.

Fig 3.8 The Proton NMR Methylene Absorptions of 2-Bromoethyl triphenylsilane at 298K:



3.4 THE β-HYDROXYETHYL-, β-METHOXYETHYL- AND ETHYL-SUBSTITUTED SILYL SYSTEMS.

Figure 3.2 shows the methylene absorptions of the 2-hydroxyethyl- and 2-methoxyethyl-substituted trimethylsilanes. These appear to be very close to first order triplets, seeming to indicate relatively free rotation about the carbon-carbon bond (excepting cases of accidental J_{AX} and $J_{AX'}$ equivalence). The spectra of the β-hydroxyethyl- and β-methoxyethyl-substituted chloromethyldimethylsilanes display similar patterned simple methylene triplets.

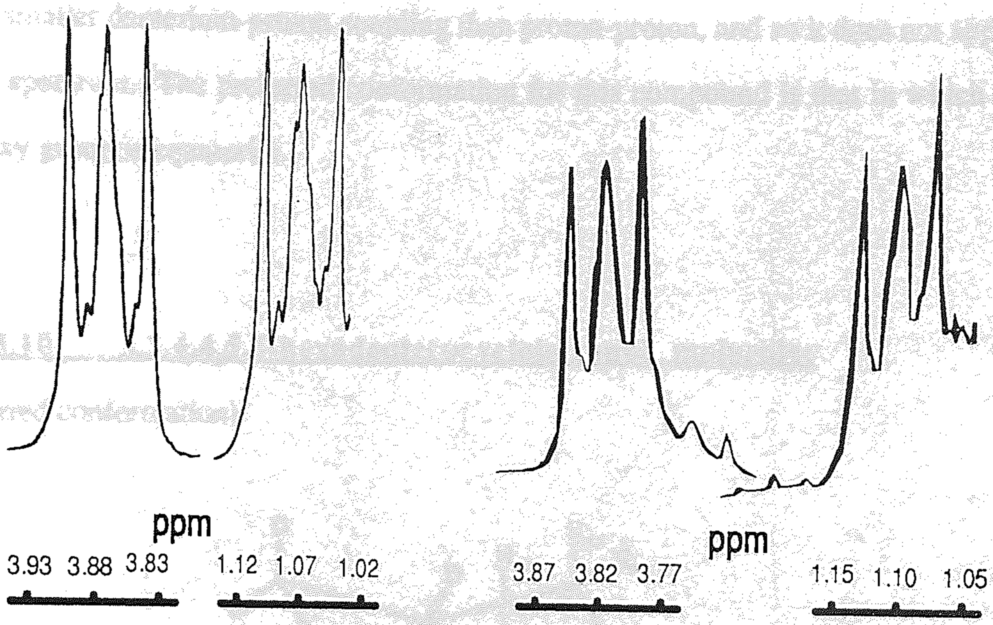
The methylene absorptions of ethyltrimethylsilane[107] which has the smallest X substituent displays typical A_2B_2 spin systems, with distorted intensities and second order splittings due to the relatively small difference in the chemical shifts of the silmethylene and methyl groups.

3.4.1 Triethyl- and Isopropyldimethyl- Substituted 2-Hydroxyethyl-Silanes.

It was apparent from our studies that compounds possessing a relatively small β-function such as the hydroxy and methoxy groups as discussed above, display more or less simple triplets when the groups alpha to silicon are also relatively small, such as trimethyl or chloromethyldimethyl groups. For comparison the spectra of compounds possessing small β-functions but relatively large alpha groups were examined. 2-hydroxyethyltriethylsilane (fig 3.9 I) and 2-hydroxyethylisopropyldimethylsilane (fig 3.9 II) were chosen to represent this type of system. 2-hydroxyethyl*t*-butyl-dimethylsilane was also thought to be a good model to represent this type of system, unfortunately the synthesis of this compound was not successful.

It was discovered that for both compounds the spectra displayed complex methylene absorptions (fig 3.9), similar to those of the β-chloroethyl-substituted systems previously discussed.

Fig 3.9 Proton NMR Methylene Absorptions of 2-Hydroxyethyltriethyl silane (I) and 2-Hydroxyethylisopropyldiethyl silane (II) at 298K:



I

2-hydroxyethyltriethylsilane

II

2-hydroxyethylisopropyldimethylsilane

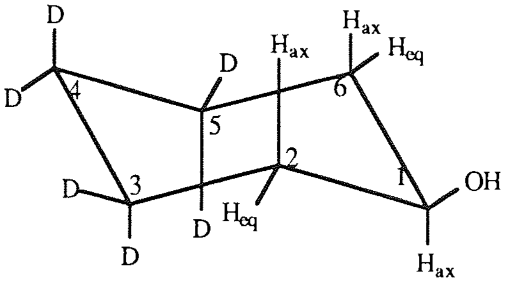
3.5 THE EFFECT OF CONFORMATION ON COUPLING CONSTANTS.

Although spin-spin coupling constants arise from interactions of nuclei with shared electrons, the signs and magnitude of the coupling constants show a dependence on molecular structure and geometry, ie they are related to the orientation of the coupled nuclei in space. Vicinal couplings, between protons on adjacent atoms, are markedly affected by substituents on the bonded carbons.

The variation of couplings with geometry is illustrated in the spectrum of 3,3,4,4,5,5-hexadeuterocyclohexanol. The replacement of the protons by deuterium effectively simplifies the spectrum[111], as deuterium's smaller magnetogyric ratio, γ, results in a much smaller deuterium-proton coupling than proton-proton, and so it does not appear in the spectrum. The preferred conformation for this compound is that in which the hydroxy group is equatorial.

Fig 3.10 3,3,4,4,5,5-hexadeuterocyclohexanol molecule:

(preferred conformation)



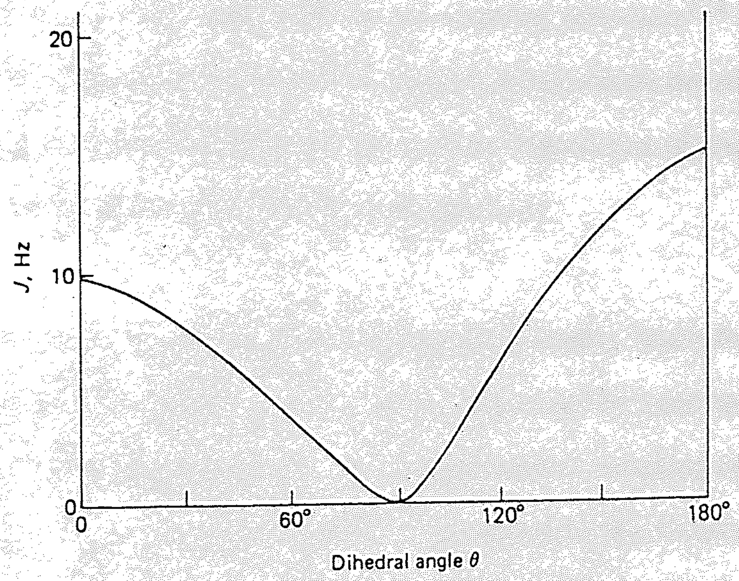
The C-2 and equivalent C-6 protons are the AB part and the C-1 proton the X part of an ABX spectrum; cross-ring couplings are zero. The coupling of the axial C-1 proton to the axial C-2 and C-6 protons is 10.2 Hz yet its coupling to the equatorial C-2 and C-6 protons is only 4.1 Hz. The dihedral angles for $J_{\text{axial-axial}}$ is 180° and for the $J_{\text{axial-equatorial}}$ is 60°. These couplings can be seen to depend upon the dihedral angles between the C-H bonds. Karplus[112-114] established a theoretical relationship between the spin coupling constant and dihedral angle between protons on adjacent carbon atoms. This may be depicted graphically as the Karplus curve (fig 3.11). The coupling constant between two hydrogens reaches a minimum when the dihedral angle, θ, is 90°.

The curve is expressed by the two following equations[112];

$J = 10\cos^2\theta \quad (0^\circ \leq \theta \leq 90^\circ)$

$J = 16\cos^2\theta \quad (90^\circ \leq \theta \leq 180^\circ) \qquad (3.3)$

Fig 3.11 The Karplus Curve[115]:



Similar conclusions were reached by Conroy[116] from a molecular orbital method.

This relationship can be used to provide useful information from absolute values of J. In undistorted cyclohexane rings $J_{ax\text{-}ax}$ is generally large ~ 10-13 Hz whereas $J_{ax\text{-}eq}$, and $J_{eq\text{-}eq}$ tend to be considerably smaller ~ 3-5 Hz.

The magnitude of the vicinal coupling constant can also provide information on the stereochemistry of alkenes[113]. A similar pattern of couplings is found for *cis* and *trans* protons in alkenes. For vinyl chloride J_{cis} = 7.4 Hz and J_{trans} = 14.8 Hz, and for styrene J_{cis} = 10.7 Hz and J_{trans} = 17.5 Hz. Leading to the approximate, yet useful relationship of $J_{trans}/J_{cis} \sim 2$. These observations emphasise the fact that J couplings are transmitted through bonding electrons and not through space, if they were transmitted through space it would be expected that the *cis* (or gauche) protons which are closer together would couple more strongly than the *trans* protons. From the Karplus relationship a similar generalisation as in cyclohexanes can be made which is that in alkenes J_{trans} is large ~ 11-19 Hz and J_{cis} small ~ 5-14 Hz.

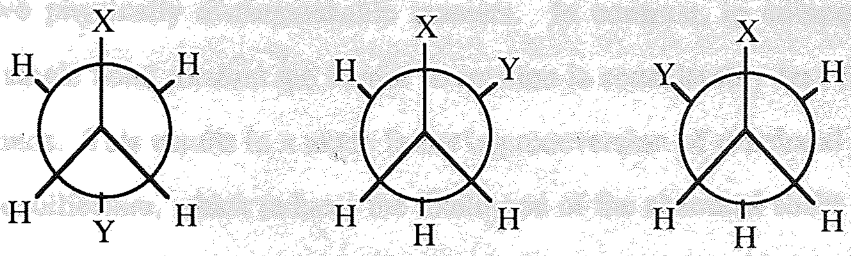
In open chain saturated compounds vicinal coupling constants[114] are influenced by many different factors, none the less the Karplus relationships are still able to provide useful approximations concerning the geometrical dependence of couplings, and hence provide information on a compound's stereochemistry.

For substituted ethanes the observed couplings are generally larger than those predicted from the Karplus relationship and are strongly influenced by substituent effects as well as geometry. For example; ethane has an experimental coupling constant of 8 Hz, a figure notably larger than that of 4.2 Hz[112] predicted by the Karplus equations. It is found that electropositive groups increase vicinal coupling constants whilst nearly all other substituents decrease them.[103,117,118] The dependence on electronegativity is expressed by the equation: $J_{CH_2\text{-}CH_3} = 7.9 - 0.4\ \Delta E_x$, where ΔE_x is the difference in the electronegativities of the substituents. In the case of ethane this relationship gives a theoretical coupling of 7.9 Hz, a figure satisfactorily close to the experimental value of 8 Hz.

The general rule of increasing electronegativity corresponding to decreasing coupling is not without exceptions. Abraham and Gatti[119] found from studies on conformationally restrained systems that for molecules fixed in the *trans* conformation the gauche proton couplings increased with increasing electronegativity. Despite these limitations the Karplus equations can be used to predict general trends of vicinal couplings satisfactorily.

Compounds of the type XCH_2CH_2Y (an A_2X_2 spectra) give two geminal and two vicinal couplings. The prefered confomers for such systems are shown below in figure 3.12;

Fig 3.12 Three Rotational Isomers of 1,2-Disubstituted Ethanes:



I ANTI

II GAUCHE

These confomers will contribute to the average observed coupling in proportion to their mole fractions X_I and X_{II} (for the anti and gauche isomers respectively). Assuming that all J_{gauche} are equal and also that all J_{anti} are equal, the vicinal coupling constants can be found from the equations:

$$J_{AX} = X_I + 0.5\,X_{II}\,(J_g + J_a)$$
$$J'_{AX} = X_I J_a + X_{II} J_g \qquad (3.14)$$

For situations of free rotation when the gauche : anti ratio is 2 (or accidental equivalence of coupling constants) then:

$$J_{AX} = J'_{AX} = 1/3(J_a + 2J_g) \qquad (3.15)$$

resulting in an A_2X_2 spectrum.

3.5.1 The Effect of Restricted Rotation.

The dependence of NMR spectra upon even subtle changes of environment means that NMR spectroscopy can make significant contributions to solving the problems of structural isomerism involving restricted rotation.

In substituted ethenes the high barrier to rotation associated with double bonds gives rise to two physically distinguishable isomers. In contrast, in compounds with hindered single bond rotation the barrier to rotation is considerably less than that of double bonds. This results in a much faster interconversion of rotational isomers in dynamic equilibrium, which reduces the likelihood of the chemical shifts of the two individual isomers being observed and so the NMR spectrum is said to be 'averaged'. That is, the spectrum consists of a superimposition of the spectra of the different forms in equilibria.

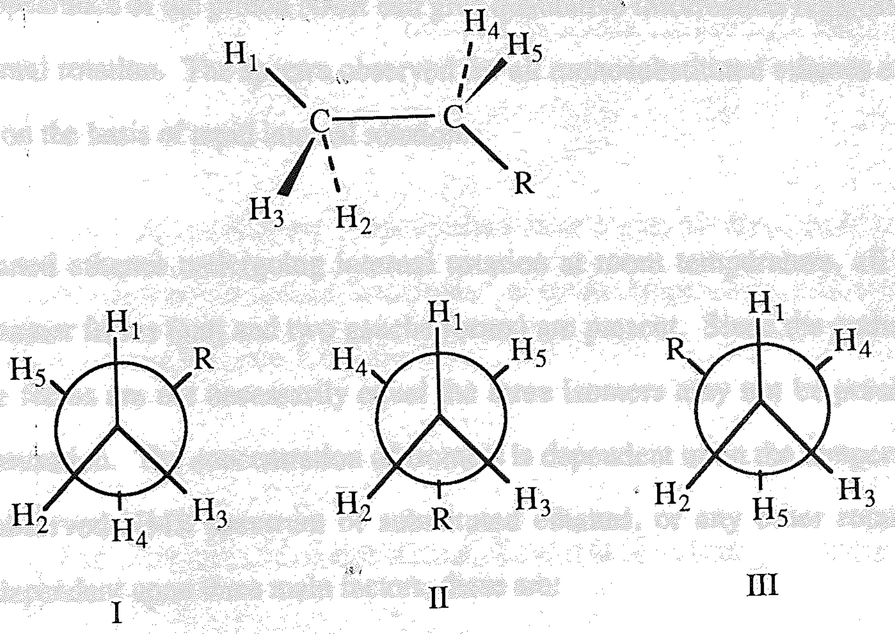
In order for isomers to be distinguishable by NMR the rate of interconversion between two isomers must be less than the chemical shifts (Hz) between the signals from the two isomers.

Pople[102] established a system of classification which arranged the spectra of substituted ethanes according to the possiblities :

1. That between isomers of long lifetime the energy difference is so large that only the most stable is present.
2. There could be a mixture of long-lived isomers in equilibrium, each giving its own NMR spectrum, which results in the observed spectrum being a superposition of the separate isomer spectrum, or
3. Internal rotation may occur rapidly, having the effect of averaging the effective chemical shifts and spin coupling constants.

In order to understand the effects of these different possibilities consider the spectrum of the ethyl group in monosubstituted ethanes CH_3CH_2R, where R is magnetically inactive. Assuming that staggered configurations are more energetically favoured than eclipsed molecules, such a molecule would have three rotational isomers of equal energy and population (fig 3.13).

Fig 3.13 Monosubstituted Ethane and Three of Its Rotational Isomers:



If rotation is slow the observed spectrum will be typical of one structure. Considering form I; if the chemical shifts are large, three types of protons will be apparent in the spectrum; H_4 and H_5; H_2; H_1 and H_3. The resulting spectrum could appear quite complex due to the different number of coupling constants involved. If the rotation was rapid the environment of any proton is averaged over the three possible configurations with equal weighting. This results in the screening constants of H_1, H_2 and H_3 becoming identical. In addition, the spin coupling constants between any methyl proton (H_1, H_2 or H_3) and methylene protons (H_4 or H_5) become equal, so for example: $J_{H_1H_4} = J_{H_1H_5}$.

Hence for rapid rotation the spectrum will be of the type A_2B_3 with all of the AB coupling constants equal. For compounds with a large chemical shift compared to J the observed spectrum will consist of a triplet and a quartet . For compounds with a chemical shift of the same order as the spin coupling constant the spectrum will be of the same pattern but more complicated.

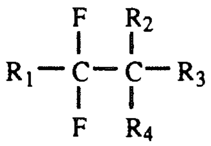
Thus the appearance of the proton NMR can give qualitative information regarding the rate of internal rotation. The spectra observed for all monosubstituted ethanes can be interpreted on the basis of rapid internal rotation.

For substituted ethanes undergoing internal rotation at room temperature, all three prefered rotamer forms (anti and two gauche forms) are present. Since the enthalpies of the three forms are not necessarily equal the three isomers may not be present in equal concentration. The concentration of isomers is dependent upon the temperature. Thus the observed NMR spectrum of substituted ethanes, or any other rotational isomers is dependent upon three main factors, these are:

1. The relative energies of the rotamers.
2. The temperature of the sample.
3. The chemical shifts and coupling constants characteristic of each isomer.

Much has been done to utilise the technique of NMR spectroscopy in the study of conformational equilibria and the rates of conformational interconversion of substituted ethanes. Drysdale and Phillips[120] first used NMR spectroscopy in the analysis of hindered rotation in substituted ethanes. Spectra of the compounds of the type shown below in figure 3.14, possessed absorptions displaying unequivalent fluorine atoms even at temperatures up to 200° C. A result Drysdale *et al* interpreted as restricted rotation.

Fig 3.14 The Variety of Substituted Ethanes Studied by Drysdale and Phillips:[113]

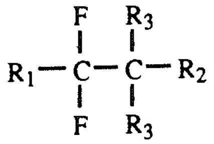


$$\begin{array}{ccccccc} & & F & & R_2 & & \\ & & | & & | & & \\ R_1 & - & C & - & C & - & R_3 \\ & & | & & | & & \\ & & F & & R_4 & & \end{array}$$

	R_1	R_2	R_3	R_4
A	Br	H	Cl	Br
B	Br	F	Cl	Br
C	Br	H	Br	C_6H_5
D	Cl	H	Cl	C_6H_5

In response to this, Nair and Roberts[121] synthesised more highly hindered molecules in the hope of producing stable optical "antipodes" at room temperature, this series of compounds is illustrated in figure 3.15 below:

Fig 3.15 The Variety of Substituted Ethanes Studied by Nair and Roberts:[121]



$$\begin{array}{ccccccc} & & F & & R_3 & & \\ & & | & & | & & \\ R_1 & - & C & - & C & - & R_2 \\ & & | & & | & & \\ & & F & & R_3 & & \end{array}$$

	R_1	R_2	R_3
A	Br	F	Br
B	Br	Br	Cl
C	Br	C_6H_5	Br

Nair and Roberts expectations were not realised as the spectra of this type of compound (fig 3.15) displayed equivalent gem fluorines at temperatures down to -30°C. They pointed out that in compounds of the type shown in figure 3.14, unless the residence times in each conformation are equal, the chemical shift difference between the fluorines (gem) will not average out, whereas in the more symmetrical compounds shown in figure 3.15, rapid rotation will average the chemical shifts. It has been noted that many spectra of 1,2-disubstituted ethanes are of a deceptively simple nature.[122] Many 1,2-disubstituted ethanes give seven line or triplet specta instead of the ten line spectra as a result of J = J', ie L = 0. For ethanes with similar substituents both M and δ are low, giving rise to the ten line spectra. However for two dissimilar substituents, both M and δ are large compared to L and thus give rise to five line or triplet spectra.

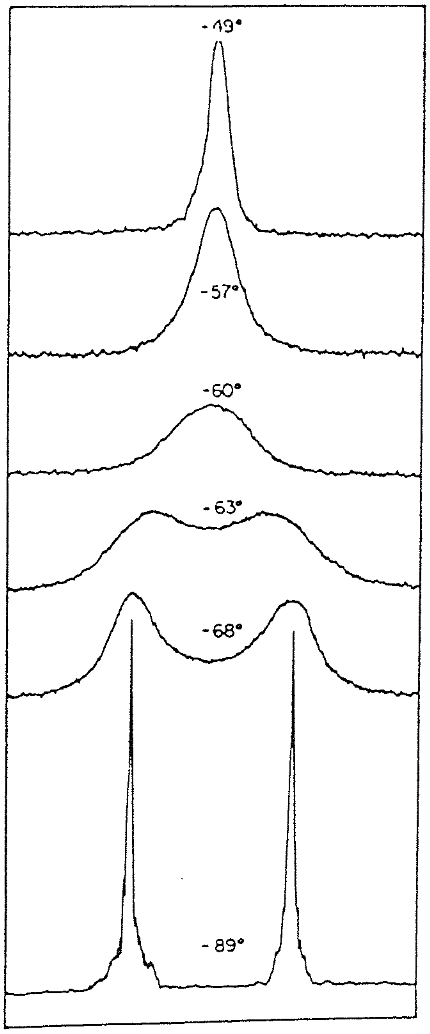
3.6 THE TEMPERATURE DEPENDENCE OF THE NMR SPECTRA.

As explained, molecules often exist in two or more coexisting states, such as different conformations, which are in rapid equilibria with each other. In NMR spectroscopy very marked line broadening, merging the lines may occur even when the conformer lifetimes are as long as 10^{-1} to 10^{-3} sec. For conformers with shorter lifetimes (less than 1 msec) the separate forms will give a single peak and be indistinguishable, that is; the observed absorption is a weighted average of all of the rotational isomers.

Nuclear magnetic resonance spectroscopy is an excellent technique for determining the rates of reactions having half lives in the NMR time scale of about 0.001 to 1 sec. The analysis of the chair-chair interconversion of cyclohexanes provides a typical example. At room temperature the rate of chair-chair interconversion is so fast that only a sharp singlet is observed. This is because NMR spectroscopy measures only the average state of the axial and equatorial hydrogens. At low enough temperatures (< -70°C) the rate of interconversion is so slow, due to the reduction in the energy available for rotation, that two broad bands can be observed. These correspond to the two types of hydrogen (axial and equatorial) within one chair conformation. The absorptions are broad because of coupling between the two types of protons.

This can be clearly seen in the NMR spectrum of cyclohexane-d_{11} (fig 3.16); at -89°C half of the molecules have the proton in the axial position and the other half have an equatorial proton, interconversion is slow. All equatorial hydrogens are equivalent but different from the axial hydrogens, both types of proton have different chemical shifts of δ_{eq} and δ_{ax} respectively, and give rise to two sharp singlets. At temperatures above -49°C rapid chair-chair interconversion gives rise to a singlet with a chemical shift midway between δ_{ax} and δ_{eq}. At intermediate temperatures where the rate of conversion is comparable to the frequency difference a broad band is observed.

Fig 3.16 The Proton NMR Spectrum of Cyclohexane-d_{11} at Different Temperatures:[115]



For most substituted ethanes the rotational barriers are low. Even at temperatures as low as -150°C the observed NMR spectrum is averaged over the preferred conformers in equilibrium. Depending upon the size of the barrier to rotation it is possible in some cases, by reducing the temperature, to slow the interconversion enough to be able to distinguish the different conformers.

For compounds whose confomer populations change with temperature and whose chemical shifts and couplings are different for each confomer, then it is possible to obtain the populations and NMR parameters for each confomer.

Multiple substitution by larger atoms may raise the barrier, causing a freezing out of an individual confomer. For example, difluorotetrachloroethanes[104,123] gives a single peak at room temperature, whereas at low temperatures, below -75° this becomes two peaks corresponding to the anti and gauche isomers. It is possible from analysis of spectra at temperatures below which the exchange is slow to obtain values for the ground state energies of conformations, which when used in the analysis of spectral line shapes in intermediate temperatures it is possible to determine rate constants for various interconversion processes.[124,125]

Generally, if the apparent chemical shifts and coupling constants are temperature dependent, rapid rotation is indicated. Whereas spectra which are independent of temperature and the molecule is such that the form of the spectrum for the rotating molecule is the same as that for one of the isomers the three most likely explanations are:

1. That rotation is highly hindered and so the molecules exist almost entirely as one isomer.
2. The molecules may be rotating rapidly but the energy difference between the

isomeric forms may be so large that one state is much more highly populated than the others.

3. The conformers are separated by very small energy differences so that change in temperature does not appreciably change the relative populations.

Many studies on the temperature dependence of the spectra of substituted ethanes have been carried out. A variety of research groups have used studies of fluorine resonance spectra to establish the presence of rapid rotation in some substituted ethanes. Drysdale and Phillips[120] with $CF_2Cl\text{-}CHClC_6H_5$; Nair and Roberts[121] with $CF_2Br\text{-}CBr_2Cl$ and $CF_2Br\text{-}CBr_2C_6H_5$ both in CS_2 solution. Phillips[126] with $CF_2Br\text{-}CBr_2CN$ in chloroform and $CF_2Br\text{-}CBr(CN)(CH_3)$. All ^{19}F spectra were found to be temperature dependent, suggesting that all of the compounds undergo rapid rotation.

The proton resonance spectrum of 1,2-dibromo-1,1-difluoroethane, which consists of a quartet with close central peaks, separated by δ, has been studied by Graham and Waugh[127]. Due to rapid rotation this spectrum is of an A_2X_2 type. They found that over the temperature range of -54°C to 104°C the quantity δ decreased, confirming their belief that even in cases of very rapid internal rotation evidence of rotational isomerism was still observable.

The energy difference between gauche and anti isomers in 1,2-disubstituted ethanes can be obtained from the temperature dependence of coupling constants. Whitesides *et al*[128] from a study of substituent effects in 1,2-disubstituted ethanes reported a change in the gauche and anti coupling constants in $t\text{-}BuCH_2CH_2SiMe_3$ from 4.0 and 14 Hz at -50°C to 4.3 and 13.2 Hz at 150°C respectively. They interpreted this as being due to the increasing proportion of gauche isomer. Abraham *et al*[119,122] suggested an alternative interpretation of a fixed anti conformation. They explained that an increase in temperature increases torsional vibrations within the molecule which causes a change in coupling for the individual isomers, which are averaged over the torsional motion. So although the average coupling is independent of temperature the couplings of the individual isomers could change appreciably.

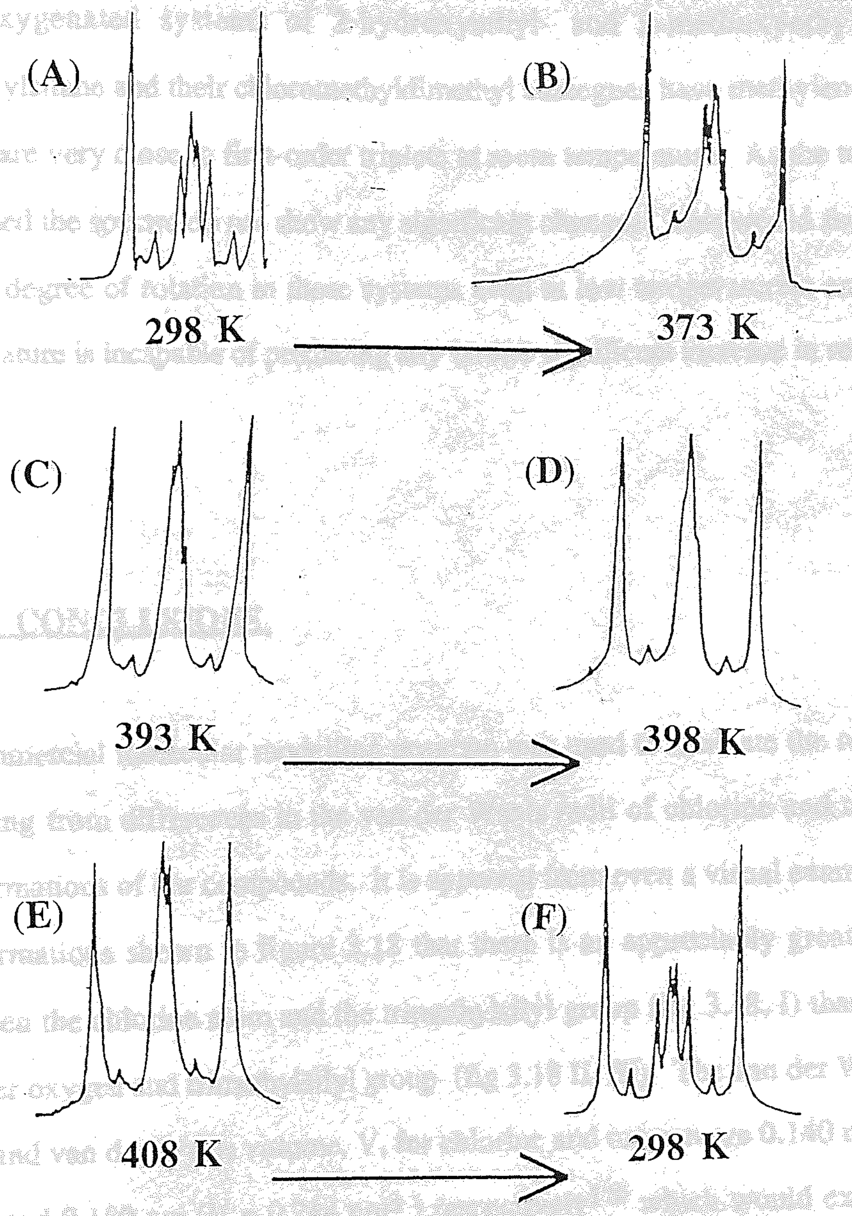
3.6.1 Results of the Temperature Dependent Studies.

Spectra were taken over a range of temperatures and it was found that the spectrum of 2-chloroethyltrimethylsilane; $Me_3SiCH_2CH_2Cl$ did change with temperature (fig 3.17). At room temperature (298K) the spectrum is a ten-line, twelve transition AA'XX' type. For intermediate temperatures (373K-398K) the methylene absorptions are intermediate in shape between the ten-line AA'XX' absorption observed at 'low' temperatures and the 'free-rotation' simple triplet absorption observed at the coalescence temperature. The spectra obtained at higher temperatures more closely resemble first-order triplets (fig 3.17 a-d). Raising the temperature to a sufficiently high value, the coalescence temperature, increases the rate of rotation about the silmethylene-chloromethylene carbon bond so that J_{AX} and $J_{AX'}$ may be considered to be averaged to a single coupling constant.

The spectral changes induced by changes in temperature were found to be entirely reversible (fig 3.17 c.f. e and f).

For 2-chloroethylchloromethyldimethylsilane; $ClCH_2Me_2SiCH_2CH_2Cl$, exactly analogous behaviour to the β-chloroethyl-substituted trimethyl derivative was observed. The methylene absorptions comprised a ten line A_2X_2 spectrum at 298K which became increasingly triplet-like as the temperature was raised above the coalescence temperature. Similarly the changes were reversible.

Fig 3.17 The Proton NMR Methylene Absorptions of 2-Chloroethyltrimethylsilane at Various Temperatures:



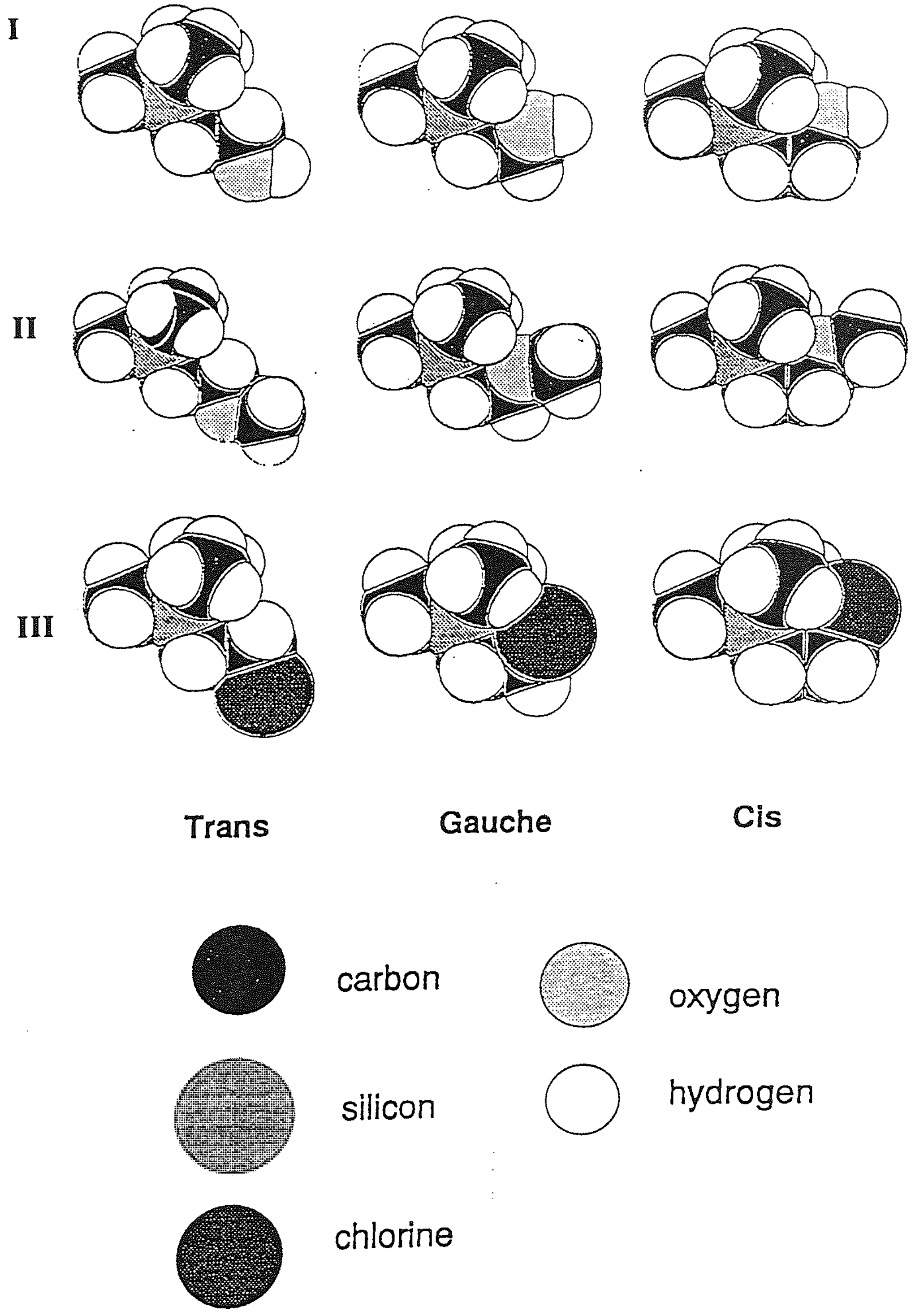
The spectrum of the more heavily substituted and sterically constrained 2-bromoethyltriphenylsilane at room temperature had AA'XX' absorptions very similar to those for the 2-chloroethyltrimethylsilane. Unlike the 2-chloroethyltrimethylsilane however, the spectra for this compound remained constant over the whole range of accessible temperatures (298-408K). It would appear that for this compound there is considerable steric hindrance between the triphenylsilyl- and the bromo-substituent of the ethyl moiety, and the system remains locked in one conformation up to the observed temperature of 408K.

The oxygenated systems of 2-hydroxyethyl- and 2-methoxyethyl-substituted trimethylsilane and their chloromethyldimethyl analogues have methylene absorptions which are very close to first-order triplets at room temperature. As the temperature is increased the spectra do not show any significant changes. This would seem to suggest a high degree of rotation in these systems even at low temperatures; any increase in temperature is incapable of producing any further significant increase in rotation.

3.7 CONCLUSIONS.

A commercial molecular modelling program was used to evaluate the relative effects resulting from differences in the van der Waals radii of chlorine and oxygen on the conformations of our compounds. It is apparent from even a visual examination of the conformations shown in figure 3.18 that there is an appreciably greater interaction between the chlorine atom and the trimethylsilyl group (fig 3.18, I) than between the smaller oxygen and trimethylsilyl group (fig 3.18 II, III). The van der Waals covalent radii and van der Waals volume, V, for chlorine and oxygen are 0.140 nm ($V = 0.115$ nm^3) and 0.180 nm ($V = 0.244$ nm^3) respectively[129] which would explain why the hydroxy and methoxy groups appear to cause significantly less steric hindrance than the chlorine atom.

FIG 3.18 Van der Waals Scale Models Showing The Anti, Gauche and *Cis* Conformations of 2-Hydroxyethyltrimethylsilane (I); 2-Methoxyethyltrimethylsilane (II) and 2-Chloroethyltrimethylsilane (III):



The compounds possessing large groups in the beta position to silicon have so far demonstrated unusual NMR spectra resulting from hindrance to rotation about the carbon-carbon bond. A conclusion which is supported by the temperature dependence of these spectra.

Analysis of silanes with large alkyl substituents alpha to silicon and small beta substituents such as isopropyldimethyl- and triethyl-substituted 2-hydroxyethylsilanes display similar complex patterns for the methylene protons.

It would appear that for the β-functional oxygenated systems there is relatively free rotation in the basic trimethylsilyl systems but as the size of the substituents on silicon increases, the rotation about the C-C bond becomes more restricted and the spectra become more complex. Compounds possessing large groups both alpha and beta to silicon might, in the light of the above information, be expected to show highly complex spectra due to the steric hindrance created by such large groups. These expectations are realised in the spectrum of 2-bromoethyltriphenylsilane, which displays complex splitting, but unlike the systems with large beta but small alpha groups the spectrum does not repond to changes in temperature.

3.7.1 Conformational Preferences in Conjunction with Reactivities of Some β–Functional Silanes.

It would appear that for systems of the type $R_3SiCY_2CZ_2W$ unless R, Y and Z are small there is a strong tendency for such systems to achieve and become locked in a particular conformation. These conformational preferences could account for certain steric and kinetic effects observed in such systems. Both theoretical[62] and observations indicate that steric effects play a major role in determining the high reactivity of beta-functional organosilicon compounds. Lambert's studies[52] on conformationally constrained substituted cyclohexyl systems demonstrated that there was a very large acceleration in the rate of solvolysis for those systems restrained in the antiperiplanar geometry with the silicon and β-carbon *trans* to one another.

Sommer[31] reported on the solvolysis of a variety of β-chloroalkylsilanes in 70 vol % ethanol at 50°C. He observed that the rate of solvolysis decreased with increasing size of the alkyl substituent (table 3.2). He explained this to be as a result of increasing steric hindrance to solvation of the developing positive charge at the silicon atom. Whereas with the β-hydroxyethyl-substituted compounds $R_3SiCH_2CH_2OH$, he found that the rate of acid catalysed solvolysis in 50% methanol at 25°C increased with increasing alkyl substituent size. In both sets of reactions he discovered from calculation of the Hammett reaction constants derived from the rate constants of aryl substituted silanes that both reactions are facilitated by electron donating substituents.

A possible explanation is that for the β–hydroxyethyl-substituted systems, as the size of the substituent increases the population of *trans* conformers increases. However, in the case of the β-chloroethyl-substituted systems, the NMR results seem to indicate that the 2-chloroethyltrimethylsilane is already held in the *trans* conformation and so any further increase in size of substituent at silicon will not result in any increase in the *trans* population. The reduction in rate being explained by the reduction in solvation or solvent substitution at silicon.

Table 3.2 Results of Sommer's Studies[31]:

R_3Si	k/k_o ($R_3SiCH_2CH_2Cl$)	k/k_o ($R_3SiCH_2CH_2OH$)
Me_3Si	1.000	1.00
$EtMe_2Si$	-	1.24
Et_2MeSi	0.955	1.41
Et_3Si	-	1.76
i-$PrMe_2Si$	0.652	-

From our NMR studies we have concluded that 2-bromoethyltriphenylsilane is held rigidly in the preferred conformation for elimination, ie in an antiperiplanar arrangement. However it has been reported[97] that this compound does not react solvolytically, a result somewhat in conflict with the previous findings. Sommer[24] reported the retardation of elimination reactions by electronegative substituents at silicon. He observed that in 70% aqueous ethanol at 50°C $PhMe_2SiCH_2CH_2Cl$ reacted more rapidly than *m*-$CF_3PhMe_2SiCH_2CH_2Cl$. It would appear that when there are electronegative substituents at silicon, electronic effects become more important than the steric factors in determining reactivity.

Chapter 4

DIPOLE MOMENT STUDIES.

4. DIPOLE MOMENT STUDIES.

4.1 INTRODUCTION.

It was established by NMR analysis that rotation about the carbon-carbon bond was restricted to varying degrees in β-functional silanes. Dipole moments, like NMR analysis, can provide information on internal rotation and steric hindrance in molecules. The dipole moment work discussed in this chapter was carried out with a view to obtaining further evidence on the conformational distribution in β-functional silanes and the nature of the restricted rotation about the C-C bond in these systems.

Dipole moment studies have made an important contribution to stereochemical analysis and the determination of resonance and inductive effects. The usefulness of dipole moment studies arises from the intimate relationship between the distribution of electric charge in a molecule and its structure and reactivity. The response of a material to the influence of an electric field is a measurable property and a quantity characteristic of this response is the dielectric constant. The study of the dielectric properties of a material can yield considerable information regarding the molecular structure of the substance.

4.1.1 The Dipole.[130-132]

Molecules can be considered as electrons and nuclei in a state of vibration about fixed points in space, at any given instant the centres of action of positive and negative electrical charges may not be coincident. This results in the molecule possessing a temporary dipole moment which is equal to the product of the charge, q, and the separation distance, d. Experimentally, it is the average dipole moment taken over a definite period of time that is observed. Rigid centro-symmetric molecules have a vanishingly small dipole moment and are thus non-polar molecules. A polar molecule has a finite average (permanent) dipole moment, although the total amounts of positive and negative charge are equal, resulting in the molecule being electrically neutral, the distribution of the two kinds of charge are different. In a molecule, electronic charge, q, is of the order of magnitude 10^{-10} esu and interatomic distance, d, has molecular dimensions 10^{-8} cm (1 Angstrom) and so the dipole moment, μ, is of the order of magnitude of 10^{-18} esu.cm (=1 Debye). The magnitude of the dipole moment is ultimately dependent upon the size and symmetry of the molecule.

The dipole moment is a vector quantity which acts in the direction of the line joining the two charges. In the case of a chemical bond between atoms of different elements the dipole moment normally acts in the direction of the bond, for example HCl is a molecular dipole with the positive end in H.[133] The determination of dipole moments in contributing to the increase of knowledge of structures is made possible because of the relatively simple correlation between the molecular dipole moment and the electric moments of single links within the molecule. The dipole moment of a molecule is the vector sum of all of the individual moments. However, in many molecules one or two of the dipoles are much larger than the others and so a satisfactory approximation may be obtained by disregarding the moments of the others or by treating them as part of the large dipoles.

4.1.2 Geometrical Determination.[130,134-136,190]

Valuable information regarding the symmetry of molecules has been obtained from the study of their dipole moments.[137-139] For example the linear configuration of the carbon dioxide molecule was indicated from its lack of a permanent dipole moment, which was subsequently supported by spectroscopic measurements. In contrast, the presence of a considerable moment in water and ammonium molecules[133] demonstrated these to be non-linear.[140] Dipole moment studies indicated the lack of centro-symmetry in iodine pentafluoride and bromine pentafluoride. These compounds were thought to be trigonal bipyramidal but their respective dipole moments of 2.18 D and 1.51 D showed the impossibility of such structures and indicated a tetragonal pyramidal structure, later confirmed by X-ray measurements[130].

The magnitude of the dipole moment is dependent upon a molecule's configuration and can be used to distinguish structural isomers.[141,191] For example, the structures of disubstituted benzene derivatives may be established from dipole moment data using the principal that the total moment is the vector sum of constituent moments.[142] The *para*-dichlorobenzene would be expected to have zero moment, the *meta* substituted compound to have the lowest non-zero moment and the *ortho* compound to have the highest moment, which is substantiated by the observed values[143] which are 0 D, 1.48 D and 2.27 D respectively. Although it may not be possible to distinguish between two or more structures for a molecule using dipole moment data alone, when used in conjunction with other information the dipole moment may provide support for a particular structural assignment. The geometrical structure of a molecule can be obtained from the calculation of the resultant moment for all of the different molecular models and adopting as correct that model which gives a moment close to that observed.

Information on internal rotation and steric hindrance within a molecule can be obtained from dipole moment measurements.[132,144] Considering the nature of our investigation this aspect of dipole moment studies is of particular interest and importance.

4.2 THE DIELECTRIC CONSTANT.

Both polar and non-polar molecules when in an electric field become polarised by induction in the manner described by Faraday.[132,134] He observed that a charge acquired by a condensor (two parallel plates separated by an insulator) at a given potential difference was dependent upon the material between the plates and that the smallest charge was acquired when a vacuum separated the plate. He observed the relation to be:

$$Q = C'V \tag{4.1}$$

where Q is the charge in Coulombs, on one of the plates, V is the difference of potential between them and C' is a proportionality constant. He noticed that when a material was placed between the plates a different charge, Q', was acquired at the same potential difference. The ratio Q'/Q is termed the dielectric constant, ε, and when combined with the constant $A/4\pi d$ (where A is the area of the plates, cm^2 and d is the distance between the plates, cm) it becomes the quantity termed capacity, C (esu).[145]

Faraday pointed out that although matter is normally electrically neutral it is made up of equal amounts of positive and negative charges. In an electric field, the charges, although not free to move, do undergo small relative displacements. This displacement is polarisation, which generates a field that partially neuteralises the applied field, causing the potential drop across the condensor to be less for a dielectric material than for a vacuum. So we are able to express the dielectric constant relative to a vacuum as unity.

4.2.1 Dielectric Constant Measurement.[135,140,132]

The dielectric constant, which is also known as the specific inductive capacity or the dielectric permittivity, is a fundamental measurement and is usually determined by the measurement of electric capacity. For a parallel plate condensor in a vacuum, if a potential drop, V, is applied across the plates they acquire charges +q and -q per unit area, the capacity per unit area, C_0, is given by equation 4.2:

$$C_0 = q/V \tag{4.2}$$

When the condensor is filled with a non-polar material the electric field polarises the molecules, attracting the positive charges to one end and the negative to the other and so charges of +P and -P per unit area appear at the surface. The condensor holds charge (q + P) per unit area at the applied potential drop, V, and the capacitance is given by:

$$C = (q+P)/V \tag{4.3}$$

The (static) relative permittivity, ε, is given experimentally by the ratio expressed in equation 4.4:

$$\begin{aligned} \varepsilon &= C/C_0 \\ &= (q+P)/q \end{aligned} \tag{4.4}$$

which shows that permittivity is proportional to the polarisability of the molecules. Thus the dielectric constant is a measure of the extent to which a material is polarised by an external field.

In non-polar molecules the polarisability arises from the electric field displacement of the electrons relative to the nucleus, the electronic polarisation, as well as from the displacement of the atomic nuclei relative to one another, the atomic polarisation. The electronic and atomic polarisations are collectively known as the distortion polarisation and the former is usually the greater of the two. For a polar material there is a third contributing process. In the absence of a field the permanent dipole moments are randomly distributed, changing direction constantly because of the thermal motion of molecules. On the application of an electric field the dipole moments align themselves parallel to it. However, because of the thermal motion, in a field of the size normally used for measurement at ordinary temperatures, the departure from the random arrangement is very small. This is orientation polarisation and it is in addition to the distortion polarisation. So polar molecules usually have a higher permittivity than non-polar molecules.

For a typical parallel plate condensor consisting of a pair of plates of area A cm^2 separated by a small gap of distance, d cm, neglecting edge effects, the capacity, C, is given by:

$$C = \frac{\varepsilon A}{4\pi d} \text{ (esu)} = 0.0885.\varepsilon A/d \text{ (pF)} \tag{4.5}$$

ε is the absolute permittivity which is given by the product of the relative permittivity, ε_R and the permittivity of free space ε_o (= 8.854×10^{-12} Fm^{-1}). For measurements of liquids it is usual to take the capacity of the condensor filled with air as C_o, since the dielectric constant of air at 0°C and 760 mm Hg is 1.00058.

In practical terms, simple rearrangement of the basic equation given above can yield an expression for the easy calculation of the dielectric constant of an unknown material. A capacitor when filled with air, a reference material and the unknown material has the capacitances C_{air} C_{ref} and C_{unk} respectively, given by the following expressions:

$$C_{air} = \varepsilon_o A/4\pi d \quad + \quad C_{stray} \dots\dots\dots\dots(4.6)$$

$$C_{ref} = \varepsilon_o \varepsilon_{ref} A/4\pi d \quad + \quad C_{stray} \dots\dots\dots\dots(4.7)$$

$$C_{unk} = \varepsilon_o \varepsilon_{unk} A/4\pi d \quad + \quad C_{stray} \dots\dots\dots\dots(4.8)$$

Where ε_o is the dielectric permittivity of free space and ε_{ref}, ε_{unk} are the relative dielectric permittivity of a reference material (usually toluene) and of the unknown material under investigation respectively. C_{stray} is a term included to account for the stray capacitance present in the leads and connections of the equipment, it will also include edge effects and any stray capacitance in the atmosphere.

Subtraction of equation 4.7 from equation 4.6 yields the following equation (equation 4.9):

$$C_{air} - C_{ref} = \frac{\varepsilon_o A}{4\pi d} \quad [1 - \varepsilon_{ref}] \quad \dots\dots\dots\dots(4.9)$$

Similarly, equation 4.8 subtracted from equation 4.6 gives:

$$C_{air} - C_{unk} = \frac{\varepsilon_o A}{4\pi d} \quad [1 - \varepsilon_{unk}] \quad \dots\dots\dots\dots(4.10)$$

Dividing equation 4.9 by equation 4.10 and multiplying throughout by -1 gives the ratios:

$$\frac{C_{ref} - C_{air}}{C_{unk} - C_{air}} = \frac{[\varepsilon_{ref} - 1]}{[\varepsilon_{unk} - 1]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.11)$$

As zeroing of the digibridge used in measuring the capacitances causes the capacitance of air to be taken as zero, substitution of $C_{air} = 0$ into equation 4.11 reduces the expression to:

$$\frac{C_{ref}}{C_{unk}} = \frac{[\varepsilon_{ref} - 1]}{[\varepsilon_{unk} - 1]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.12)$$

Rearranging this we get:

$$\varepsilon_{unk} = [\varepsilon_{ref} - 1] \frac{C_{unk}}{C_{ref}} + 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots(4.13)$$

By simply substituting all of the known quantities into this final expression (eqt 4.13) we are able to calculate the dielectric constant of the material under investigation.

4.3 CALCULATION OF MOMENT FROM THE DIELECTRIC CONSTANT.

The dipole moment of a molecule is ordinarily obtained from measurements of the dielectric constant of the substance in the gaseous state or in dilute solution in a non-polar solvent.

The statistical relationship between the static dielectric constant, ε, and the molecular dipole moment, μ, was first obtained by Debye in 1912.[131] He expressed the relationship in the form of the familiar Debye equation:

$$(\varepsilon - 1)/(\varepsilon + 2).\ M/d = (4\pi N/3)(\alpha_0 + \mu^2/3kt) \tag{4.14}$$

Where M is the molecular weight, d is the density, N is Avagadro's constant: 6.022×10^{23} mol^{-1}, k is the Boltzmann constant: 1.38×10^{-16} Joules K^{-1} and T is the absolute temperature. α_0 is the molecular polarisability, ie the mean dipole moment induced in a molecule by unit electric field through distortion of the internal states and μ is the permanent dipole moment.

Gas or dilute solution measurements must be used for the calculation of dipole moments from the Debye equation because of the assumption that no local directional forces due to the immediate polar neighbours are acting on the dipoles.

4.3.1 The Guggenheim Equation.

There are a variety of alternative methods[146,147] of handling dielectric constant data in order to obtain dipole moment values, including a variety of adaptations of the original Debye equation. A simplification of the Debye equation was presented by Guggenheim,[142] for use with a dilute solution of a polar solute in a non-polar solvent, it is this method that was chosen for our investigation. The equation as developed by Guggenheim is in the form shown below:

$$\mu^2 = \frac{9kT}{4\pi N} \cdot \frac{3}{(\varepsilon_1 + 2)(n_1^2 + 2)} (\Delta/C)_{C\to 0}$$

Where $\Delta = (\varepsilon_{12} - n_{12}^2) - (\varepsilon_1 - n_1^2)$. (4.15)

ε_{12} and ε_1 are the dielectric constants of the solution and solvent respectively and n_{12} and n_1 are the refractive indices of the solution and solvent respectively.

Since $(\varepsilon_1 - n_1^2)$ must be small compared to $(\varepsilon_{12} - n_{12}^2)$ over the range of concentration it is only necessary to plot $(\varepsilon_{12} - n_{12}^2)$ against the concentration, C mol cm^{-3}, to obtain the slope which gives the value of (Δ/C_0) from the gradient of the curve at $C = 0$. This can then be inserted into equation 4.15 to yield the dipole moment. It must be appreciated that this method of calculating the dipole moment assumes that at any one temperature the refractive index of the solution is equal to that of the solvent.

This is a well known and simple method of calculating the dipole moment. It is a particularly useful method to use if there is a possibility of the dipole moment changing with temperature as the measurements are taken at a constant temperature with varying concentrations. A further advantage of the Guggenheim equation is that the need for accurate density measurements is eliminated. In a large number of cases Δ is a linear function of concentration, most methods of extrapolation yield the same effective dipole moment within the limits of experimental error. However there is the disadvantage that reliable determinations are required at very low concentrations where the difference between solution and solvent permittivity is small and experimental discrimination is correspondingly low.

4.3.2 Results.

Our studies were conducted using the solvents 1,4-dioxane and cyclohexane. The choice of solvent in investigations of this type is very important.[192,193] The ideal solvent would be one which possessed zero dipole moment, had minimum interaction with the solute and is safe to use. Benzene and carbon tetrachloride fulfill the first two requirements but their carcinogenicity prevent their being used. The dipole moments were initially measured in 1,4-dioxane, this solvent has the desired overall zero dipole moment. However, due to 1,4-dioxane's lone pair of electrons it does tend to interact significantly with the solute which could affect the results. The measurements were repeated in cyclohexane, this has the disadvantage that it possesses a small dipole moment but the advantage that it interacts with solute molecules to a lesser degree. It has the further advantages that its dipole moment will change only slightly with temperature and it is relatively safe to use.

In order to observe whether or not there is any significant change of dipole moment with temperature the capacitances of the solutions were measured over a range of 25°-55°C. The results of the dipole moments calculated from the dielectric constants measured experimentally are presented in table 4.1 below:

4.3.3 Discussion of Observed Dipole Moments for β-Functional Chloromethyldimethylsilanes.

The dipole moments of the β-chloroethyl- and β-hydroxyethyl- substituted chloromethyldimethyl silanes observed in 1,4-dioxane are almost identical (2.55 D and 2.54 D respectively), whereas in cyclohexane the observed values are 2.62 D and 2.39 D respectively.

Table 4.1: Experimental Dipole Moments Observed for Compounds Based on the General Formula $XCH_2Si(CH_3)_2CH_2CH_2Y$

X	Y	Solvent	Temperature °C						
			25	30	35	40	45	50	55
Cl	Cl	1,4-dioxane	2.55	2.53	2.53	2.52	2.51	2.51	2.50
		cyclohexane	2.62	2.62	2.62	2.61	2.61	2.60	2.60
Cl	OH	1,4-dioxane	2.54	2.53	2.52	2.52	2.51	2.51	2.50
		cyclohexane	2.39	2.38	2.37	2.36	2.35	2.34	2.32
Cl	OCH_3	cyclohexane	2.48	2.47	2.46	2.45	2.44	2.43	2.42

The relatively large difference in the values for the β-hydroxyethyl- substituted compound in dioxane and cyclohexane (2.54 D and 2.39 D respectively) probably arises from solute-solvent interaction due to hydrogen bonding in the dioxane solvent. This produces a higher apparent solute dipole moment. Dipole moments measured in the gas phase and in solvents such as benzene are lower than those in a hydrogen bonding solvent such as dioxane.[130] It is such interaction with the solvent which complicates the interpretation of the dipole moment values of glycols in dioxane solution.[148]

It would appear from table 4.1 above that there is no change of dipole moment with temperature, or at least any change with temperature is well within experimental error. However, due to the limits imposed by practical considerations it was possible to take measurements only over a very short range of temperatures so the apparent constancy cannot be taken as proof of absence of variation of moment with temperature. The moment variation, if it exists at all in this region is much smaller that that of [149]ethylene chloride which is reported to be 1.37 at 401 K and 1.43 at 436 K.

4.4 THE CALCULATION OF THEORETICAL DIPOLE MOMENTS.

4.4.1 The Group Moment.

The dipole moment is a measure of the electrical asymmetry of a certain section of a molecule, consequently it is affected by the environment of that section and so a change of environment results in a different dipole moment. The dipole itself may influence and be influenced by a second dipole attached to the same atom or immediately adjacent atoms, altering each others' moments by mutual inductive effects. For the majority of compounds, excepting the first few members of a homologous series, dipole moments tend to a constant value with increasing chain length. For straight chain compounds possessing the general formula $C_nH_{2n+1}CH_2Y$ the molecular moment depends only upon the $-CH_2Y$ group which possesses a constant group moment aligned at a certain angle to the rest of the chain. Group moments are component moments of a molecule, they are vector quantities whose direction isn't necessarily coincident with the chemical bond joining the group to the skeleton of the molecule.

Group moments have been determined by chemical evidence and by studies of the changes observed in the overall dipole moment of a compound after the introduction of other polar groups. Once the direction of one group moment is established then the magnitude and direction of others are easily determined and in this manner tables of group moments and their angles have been obtained. Studies of a large variety of compounds have enabled the establishment of a comprehensive log of group moments, the tables of which can be found in many of the texts dealing with dielectric behaviour and dipole moments.[149-152]

It must be remembered that the group moments listed in most tables are relative to the moment of the C-H bond; this is adequate for dipole moment studies on organic molecules. Absolute group moment values can't be established until the moment of C-H is known.

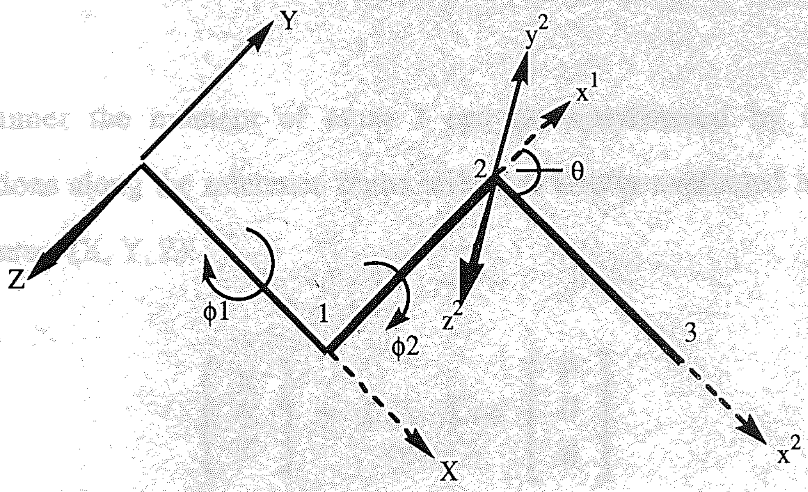
Due to the short range of inductive effects resulting in dipole moments it is practical to use the moment of an ethyl compound for a group attached to an aliphatic chain of greater length than two carbons, as the additional carbons have negligible effects on dipole moments. Group moments facilitate the convenient and practical calculation of theoretical dipole moments and thus assist in the evaluation of structural details.

4.4.2 Calculation of the Dipole Moment from Group Moments.

The simplest method of calculating the dipole moment of a molecule which contains several group moments in fixed positions is to establish a set of reference axes in the molecule and to calculate the component of each group moment along each axis.[153]

A molecule may be idealised as a framework of lines along the valence bonds connecting the atoms. The resultant moment of that molecule may be considered as the vector sum of a series of moments lying along each of these lines. Begining with one end line they are numbered consecutively 1, 2, 3...i.. etc., until the other end line is reached. Each of the i^{th} skeletal bonds can be represented by the x coordinate of a rectangular Cartesian coordinate system. The origin (0, 0, 0) of each coordinate system being centred on a skeletal atom. A 'global' axis, usually the end bond numbered as 1, is selected to which all of the other coordinates can be referred to. At each other atom a local coordinate system can be set up as in figure 4.1:

Fig 4.1 Establishing a Coordinate System:



From the diagram, (fig 4.1) the moment of atom number 3 can be expressed in the coordinate reference frame of atom number 2. As the moment is directed along the bond, the x coordinate is equal to the moment, while both the y and z components are zero. Thus, the dipole moment vector associated with the bond between atoms 2 and 3 may be represented by the vector:

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix}^{3/2} = \begin{bmatrix} \mu \\ 0 \\ 0 \end{bmatrix} \tag{4.16}$$

A transformational matrix containing terms to account for the rotational angles and bond angles of a particular conformation[153] of the molecule can then be used to transform the moment of atom 3, represented in the coordinate reference frame of atom 2, down the chain into the reference frame of 1 by the following equation:

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix}^{3/1} = \underline{T}_{1\text{-}2} \begin{bmatrix} x \\ y \\ z \end{bmatrix}^{3/2} = \underline{T}_{1\text{-}2} \begin{bmatrix} \mu \\ 0 \\ 0 \end{bmatrix} \tag{4.17}$$

In this manner the moment of atom 3 can be transformed by consecutive transformations along the reference frame until it is finally expressed in the global reference frame; (X, Y, Z):

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \underline{T}_{0\text{-}1} \; \underline{T}_{1\text{-}2} \begin{bmatrix} \mu \\ 0 \\ 0 \end{bmatrix} \tag{4.18}$$

By such repeated transformation each electric moment can be referred to a particular set of coordinates which we have called the global coordinates. Once the global coordinates are known it is possible then to obtain the square of the resultant dipole moment for a given conformation from the equation:

$$\mu^2 = X^2 + Y^2 + Z^2 \tag{4.19}$$

and thus the mean square moment is given by:

$$\mu = (X^2 + Y^2 + Z^2)^{1/2} \tag{4.20}$$

For our investigation these calculations were carried out in the manner described above, using a 'QuickBasic' computer program. A copy of the computer program used in this investigation is included in the appendix. It is important to be aware that the computer program used to calculate dipole moments assumes roataional bond angles of 0°, 120° and 240°. Molecular modelling programs show that , for the severely hindered moleculaes, this is not the case[199].

For the purpose of the calculations each silyl molecule was regarded as a short chain of atoms. For example, for the 2-chloroethylchloromethyldimethylsilane molecule, the chain of atoms is numbered in the following manner, shown in figure 4.2:

Fig 4.2 Example of the Numbering System Used in the Calculation of the Dipole Moment Vectors.

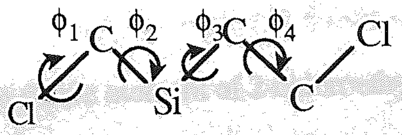
Cl-C-Si-C-C-Cl

i = 1 2 3 4 5

The dipole moment vector associated with the C-Cl bond of the chloromethyl group may be represented by the vector: $\mu_1 = [-2.06, 0, 0]$; and similarly the dipole moment of the C-Cl bond of the chloroethyl group may be represented by the vector: $\mu_5 = [2.06, 0, 0]$; where 2.06 D is the C-Cl group moment.

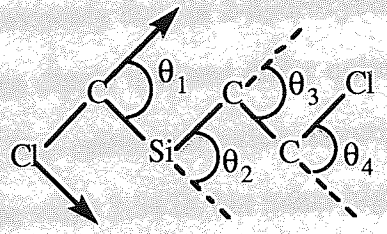
The additional geometrical data required by the program for the calculation of the transformational matrices is defined in the following diagrams, where ϕ_i is the rotational bond angle for bond i, (taken as 0, 120 or 240°):

Fig 4.3 Representation of 2-Chloroethylchloromethyldimethylsilane and Its Rotational Bond Angles:



and θ_i is the bond angle supplement, taken as 70° for a tetrahedral angle:

Fig 4.4 Representation of 2-Chloroethylchloromethyldimethylsilane and Its Bond Angle Supplements:



4.5 THE "FREELY ROTATING" MODEL.

For a fully "freely rotating" system, that is one in which all of the possible conformations are considered as equally probable and thus are equally weighted; the mean dipole moment is obtained from the square root of the sum of the squares of the individual moments for each conformation divided by the total number of conformations possible.[148,153]

The calculations based on this model for our three compounds gave the calculated dipole moment of the 2-chloroethylchloromethyldimethylsilane as 2.89 D, that of the β-hydroxyethyl substituted compound as 2.65 D and a dipole moment of 2.38 D for the β-methoxyethyl substituted compound.

The value calculated for the dipole moment of 2-chloroethylchloromethyldimethylsilane based upon an equal weighting for all conformations gives a value considerably higher than those observed: 2.89 D (calculated) c.f. 2.55 D and 2.62 D (observed in dioxane and cyclohexane respectively). This consistent difference in the calculated and observed values in the two different solvents suggests restricted rotation, as the theoretical value will include an unrealistically high contribution from those conformations of a high dipole moment.

It has been pointed out previously that for 2-hydroxyethylchloromethyldimethylsilane the observed values of the dipole moment differ quite markedly in the dioxane and cyclohexane solvents. The calculated value assuming "free rotation" 2.65 D is comparable to the dioxane value 2.54 D, but rather higher than the cyclohexane value 2.39 D. It may be that for this system as well as solute-solvent interactions there are also some solute-solute interaction and intramolecular hydrogen bonding which could produce a certain degree of restricted rotation.

In the case of the 2-methoxyethylchloromethyldimethylsilane rather unusually the observed dipole moment (2.48 D) is lower than the calculated dipole moment (2.38 D). However, the difference of 0.1 D is an extremely small quantity and these values should be considered a good match. It is fair to assume in this case that the free rotation model is a reasonable model.

4.5.1 Deviations Between the Calculated and the Observed Dipole Moments.

The calculation of molecular dipole moments using the equally weighted model described above, often results in a close correlation with observed values, as is the case for the β-methoxyethyl substituted silane. However there are many examples in which this is not the case; inspection of our results for this model reveals a significant deviation between those values calculated and those observed for the β-chloroethyl and β-hydroxyethyl substituted silanes, with the observed dipole moment being of lower value in all cases. In situations where the structure of the molecule is known and yet the calculated moment deviates considerably from that observed experimentally, analysis of the different values can provide insight into the nature and size of resonance and steric effects in the molecule.

Polar groups in close proximity, as found in 1,1-disubstituted ethenes, induce subsidiary dipoles in each other, such mutual inductive effects alter the effective group moment creating discrepancies in the calculated moments compared with those observed experimentally. This is illustrated with the calculated moment of *ortho*-dichlorobenzene, taking the Cl-(C_6H_5) group moment to be 1.70, this gives a theoretical moment of: 2 x 1.70 cos 30^o = 2.94, whereas the value of the observed moment is 2.51.[154] It is considered to be lower due to the mutual inductive effects of the two C-Cl dipoles. Similarly the moment of *para*-chloronitrobenzene should, in the absence of mutual effects of the two substituents, be 2.51 D. The observed value of 2.78 D[145] has been regarded as either a measure of resonance or inductive interactions.[155] In contrast, excellent agreement exists between the theoretical and the observed moments for the *meta*-substituted compounds where the mutual effects of resonance and dipole-dipole induction are negligible. The analysis of dipole moments provides information on resonance effects. For example, comparing the dipole moments of chlorobenzene with those of the alkyl chlorides[156] reveals the chlorobenzene to have a lower moment which has been attributed to resonance contributions of the type $C=Cl^+$. In such cases the extent of the lowering can be used to calculate contributions of polar structures.[157]

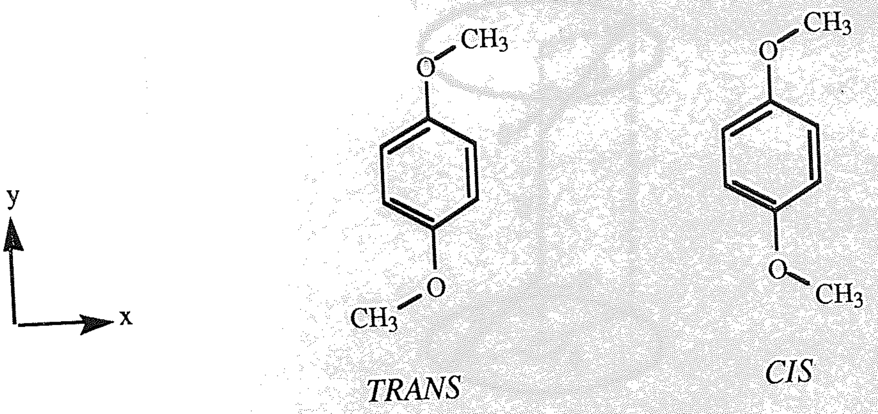
Dipole moment studies can also yield information on internal rotation within molecules. A serious deviation between the observed dipole moment and that calculated under the assumption of free rotation can be indicative of restricted rotation and may be used to calculate the extent of the restriction.[144,158,159]

4.6 DIPOLE MOMENT AND INTERNAL ROTATION.[144,160]

The rotation of groups within a molecule is dependent upon the potential energy barrier between the possible isomers. In a molecule with two isomers separated by a very large potential energy barrier as compared to the thermal energy; each isomer will exist independently of the other, ie they will be separable.

Consider the *para*-dimethoxybenzene molecule.[149] (fig 4.5) The dipole component along the y axis is zero because of the mutual cancellation of the group moments. The component along the x axis is dependent upon the energy barrier restricting rotation about the (aromatic)C-O bond. If the energy barrier is high compared to the thermal energy the methoxy group can adopt one of the two configurations shown below:

Fig 4.5 Two Conformations of the *para*-Dimethoxybenzene Molecule:

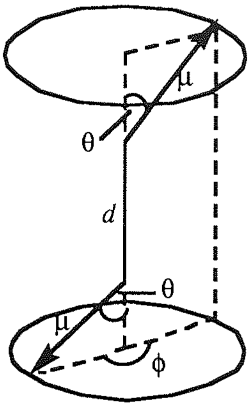


Assuming the configurations to be planar, the *trans* isomer possesses zero dipole moment and the dipole moment of the the *cis* form is given by $2\mu\sin\theta$ where μ is the group moment of methoxy group. If only these two configurations are possible and if they are equally probable then the effective observed moment will be given by:

$$\begin{aligned}\mu^2_{obs} &= 1/2\,0^2 + 1/2(2\mu\sin\theta)^2 \\ &= 2\mu^2\sin^2\theta\end{aligned} \tag{4.21}$$

If the energy barrier restricting rotation is much smaller than the thermal energy, allowing the methoxy groups to rotate freely and independently of each other, a similar result is obtained. Williams[161] made the first approach to this problem by considering it as a case of two equivalent doublets, μ, rotating freely at points d apart and inclined θ^o to the vertical, illustrated below in figure 4.6:

Fig 4.6 Williams' Model for Two Equivalent Rotating Dipole Moments:



If ϕ is the azimuthal angle between the groups at any instant the overall dipole moment at that instant μ', is given by the equation:

$$\mu' = (2\mu^2\sin^2\theta + 2\mu^2\sin^2\theta\cos\phi)^{1/2} \tag{4.22}$$

The mean square corresponding to all possible values of ϕ, which is the value measured experimentally, is given by the integral of the instantaneous moment, μ', between limits of 0 and 2π, which leads to the expression: $\mu^2_{obs} = 2\mu^2\sin^2\theta$ which is identical to the expression previously derived for molecules possessing a high barrier to rotation (equation 4.21). The more general case in which the two moments rotate about axes inclined at an angle can be dealt with similarly.[149] The dipole moment for *para*-dimethoxybenzene calculated in this way is 1.7 D, which is in very good agreement with the observed value[130] of 1.73 D.

In cases when the energy barrier is small compared to the thermal energy, although the potential energies of all the positions are never identical, often the variation of the potential energy with rotation around the bond does not invalidate the use of equation

4.21 as a good approximation.[144]

Theoretically the electronic composition of a carbon-carbon single bond offers little resistance to the mutual rotation of the two atoms about the axis joining their centres. In reality there are other atoms attached to the carbons by what could be polar links, so during one complete rotation there will be a variation in the volume (steric hindrance) and electrostatic interactions. Consequently the molecular potential energy plotted against the angle of rotation will show maxima and minima; when the rotatable parts have resultant dipole moments which are not colinear with the axis of rotation, these maxima or minima will differ among themselves.[149,162]

For the calculation of theoretical dipole moments the expressions containing no temperature terms are applicable only to those, probably non-existant molecules in which a free rotation of groups can occur, in reality such movement is likely to be more or less restricted.[149] This is demonstrated in the case of the polymethylene dibromides and dicyanides,[163] the first members of the series are found to have dipole moments far below the values calculated for free rotation because of repulsion between the terminal groups whereas the nonamethylene and decamethylene derivatives have moments indistinguishable from the free rotation values. However this does not mean that the long chain molecules have complete freedom of rotation around the carbon-carbon bonds instead there are so many possible configurations that the mean moment is indistinguishable from that for free rotation.

4.6.1 Internal Rotation Hindered by a Single Energy Barrier.

When the energy barrier to rotation between two isomers is comparable to the thermal energy, as far as the relative orientations of the two dipoles are concerned, those rotational positions which give a high dipole moment are made improbable by high potential energies.[164] This has a two-fold effect of lowering the observed dipole moment compared to that calculated for free rotation, as well as causing an increase of apparent resultant moment with rising temperature, due to the increasing population of the higher levels which give higher moments.

Much of the information regarding the methods used for the calculations of dipole moments in molecules possessing hindered rotation was obtained from investigation of the 1,2-dichloroethane molecule. Meyer[162] was the first to create an expression containing a temperature dependent factor to account for the potential energy of a system due to dipole-dipole interactions; the limiting value being in the case of free rotation when the equation reduces to that derived by Williams[161] (eqt 4.21). Smyth, Dornte and Wilson[164] considered the forces determining the configuration to be electrostatic in nature and extended the treatment of Meyer to include the H-C dipole moment. They derived an expression for the mutual potential energy of two dipoles corresponding to any value of the azimuthal angle. For a particular azimuthal angle (ie, a particular conformation) this expression was applied to the nine pairs of dipoles in the molecule, the sum of which gave the total energy for that conformation. They obtained the relative number of molecules in the different levels from the Maxwell-Boltzmann equation. Due to the variation of potential energy with the azimuthal angle they concluded that an increase in dipole moment with rising temperature was to be expected due to the increase in the proportion of molecules in the higher levels where the greater oscillation gives a greater moment. Sturtevant[165] arrived at the same conclusions from a study on the diacetyl molecule.

More extensive treatments of the relationship between the temperature dependence of the effective dipole moment of a molecule and the interaction of its polar groups have been carried out. These have taken into account the forces arising from van der Waals attraction and steric repulsion in addition to the electrostatic forces. These investigations resulted in essentially the same conclusions being made as in the previous investigations.[166,167]

The assumption of a single minimum potential function has facilitated the calculation of the height of the potential barrier restricting rotation. Lewis and Smyth[168] investigated the succinonitrile molecule in the hope that the large dipoles of the cyanide groups would make the single potential barrier a less crude approximation. They accounted for all of the factors known to affect the total potential energy; the potential due to exchange energy giving rise to steric repulsion, the van der Waals attraction energy, dipole-dipole repulsion energy. They also accounted for the dipole induction energy; which is the lowering of each cyano moment by inductive action of the other, this is often neglected in such calculations. They were able to calculate the height of the potential barrier restricting rotation in very close agreement to that found experimentally.

4.6.2 Multiple Potential Energy Barriers.

It has been shown that the assumption of a single potential barrier restricting rotation facilitates the representation of the temperature variation of the dipole moments of some molecules. It has also enabled the height of the potential barrier to be calculated which resulted in values of the same magnitude as those obtained by other methods.

To assume restricted rotation about a single bond to be primarily due to a single potential barrier is useful as a rough approximation for many molecules. However, the inadequacy of this model is illustrated by the low value of 1.36 D observed for the moment of 1,1,2,2-tetrachloroethane, compared with the value of 1.8 D calculated for free rotation, in conjunction with an absence of variation of the moment over a temperature range of 35°C. Smyth and McAlpine[149] calculated the internal energies of this molecule, generating an approximate potential energy curve. This showed three deep minima, two corresponding to the gauche isomers which were 0.36 kcal higher in energy than the one corresponding to the anti conformation. The molecules were treated as being distributed among the three potential energy troughs, with the distribution calculated by the Boltzmann equation. This gave a calculated moment very close to the observed value and indicated that any variation with temperature would be extremely small, well within experimental error.

Thomas and Gwinn[169] extended this study and measured the change of dipole moment over a range of 138°C, finding still no change in temperature they inferred that the different conformations are of very similar energy. They estimated the difference in energy between the anti and the gauche isomers to be 0 +/- 2 kcalmol^{-1}. They reasoned that the stabilisation of the gauche form, due to the relief of steric repulsions through distortion of the bond angles, could be sufficient enough to overcome the electrostatic energy which favours the anti form, resulting in the two being of comparable energy. This theory is borne out by evidence from a molecular level. Replacement of one of the chlorine atoms by a fluorine atom in 1,2-dichloroethane results in an increase in mean moment and decreases its dependence upon temperature. This is easily explained by the smaller size of the fluorine atom which reduces the steric repulsion between the two polar atoms. This reduces the heights of the maxima in the potential energy curves consequently reducing the difference, ΔE, between the potential minima of the two gauche configurations and that of the anti configuration. The resultant increase of the proportion of the molecules in the gauche configuration being responsible for the observed increase in the dipole moment and its decreased temperature sensitivity.[170]

A similar example was provided by Oriani and Smyth[171] who reported on the higher moment and lower temperature dependence of 1,2-dichloropropane compared with 1,2-dichloroethane in which the replacement of a hydrogen by a methyl group evidently lowers ΔE.

In compounds such as 1,1,2,2-tetrachloroethane, the dipole moment depends upon the distribution of the molecules amongst the potential energy troughs. As this distribution depends upon the differences between the minimum potential energy levels and not upon the heights of the potential barriers, the barrier height cannot simply be determined as in the case of the single barrier curve.

Accordingly, for nearly all compounds in which the rotation of polar groups can in theory take place two possibilities may be stated:

1) That there are a pair or more of stable isomers with potential barriers between them high enough to ensure that there are few molecules in intermediate configurations but not so great as to allow the separation of isomers or;
2) that all of the molecules have a single type of configuration in each case but that these are in a state of vibration about the form of least energy

Both views have been investigated by Bloom and Sutton,[172] they favoured the second theory and produced an equation which demonstrated how the dipole moments of molecules with two rotatable polar halves can be represented in terms of restricted rotation about a *trans* position.

4.7 THE COULOMBIC MODEL.

It has been explained that it is unrealistic to imagine that all possible conformations of a molecule will be of equal probability. One simple means of obtaining information on the contributions made by each conformation towards the mean dipole moment is to encorporate a weighting system based on the electrostatic energies of the possible conformations, ie by developing a Coulombic model.[173] Such a Coulombic model can be used to obtain information on the most predominant conformations in a system. Since it appeared from the NMR analysis that there was hindered rotation about the C-C bond in the β-functional organosilanes it was assumed that rotation about the carbon-carbon bond is fixed antiperiplanar, so that the overall number of possible conformations to be considered was reduced.

4.7.1 Coulomb's Law.

Coulombs law of force[145,174] describes simple electrostatic theory, which is expressed by the equation:

$$F = q_1 q_2 / 4\pi\varepsilon_r\varepsilon_0 d^2 \tag{4.23}$$

where F is the force in Newtons, between the charges q_1 and q_2 coulombs, separated by distance, d, meters and ε_r and ε_0 are the relative dielectric constant and the permittivity of free space respectively.

So the electrostatic energy of a molecule possessing a pair of dipoles, E_{12} (Joules), can be found from the equation:

$$E_{12} = \frac{q_1 q_2}{r_{12}} \cdot \frac{1}{4\pi\varepsilon_o\varepsilon_r} \qquad (4.24)$$

Where q_1 and q_2 are the partial charges and r_{12} is the distance between those partial charges.

4.7.1.1 Calculation of Partial Charges.

The partial charge is given by the relation:

$$q = \mu/d \qquad (4.25)$$

where q is the partial charge in coulombs, μ is the bond moment expressed in coulomb meters, and d, is the distance between the charges, in meters.

For a carbon-chlorine bond the distance, d, between the charges is 0.177×10^{-9} m and the bond moment, μ, is 2.06×10^{-18} esu cm.[152] As 1×10^{-18} esu cm = 3.3357×10^{-12} Cm then the bond moment expressed in coulomb meters is 6.87×10^{-30} Cm. As $q = \mu/d$ (eqt 4.25), then substituting in the above values gives a partial charge, q of 0.3882×10^{-19} C for the carbon-chlorine bond.

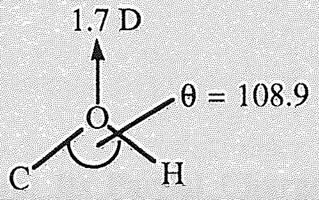
So a carbon-chlorine bond can be considered as having a charge of $+0.3882 \times 10^{-19}$ C centered at the carbon atom and a charge of -0.3882×10^{-19} C centered at the chlorine atom.

For the β–hydroxyethyl- and β–methoxyethyl- substituted chloromethyldimethylsilanes, as the dipole is not along the direction of the bond, the bond moment must first be calculated from the expression below (eqt 4.26). Where m is the group moment and θ is the bond angle.

$$\mu = \frac{m}{2\cos\theta/2} \qquad (4.26)$$

For the β–hydroxyethyl substituted compound the C-O-H group moment ($m_{C\text{-}O\text{-}H}$) is 1.7 D,[152] and the C-O-H bond angle is 108.9°.

Fig 4.7 The C-O-H Group: Its Group Moment and Bond Angles.

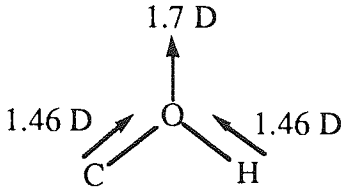


These values for the hydroxy group can be substituted into equation 4.26 to give the individual bond moments, μ:

$$\mu = 1.7 / 2 \cos 54.45 = 1.46\ \text{D} \qquad (4.27)$$

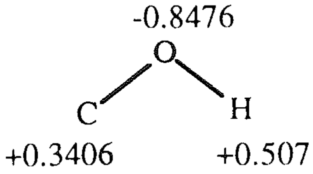
So there is a moment along the carbon-oxygen bond ($\mu_{C\text{-}O}$) of 1.46 D in the direction of the oxygen and also one of 1.46 D from the hydrogen to the oxygen ($\mu_{O\text{-}H}$) shown below in figure 4.8:

Fig 4.8 The C-O-H Group: Its Bond Moments.



The distance between the charges is 0.143 x 10^{-9} m and 0.096 x 10^{-9} m for the C-O bond and the O-H bond respectively. Substitution of these intercharge distances and the bond moments detailed above (after multiplying by the conversion factor of 3.3357 x 10^{-12} Cm) into equation 4.25 for the calculation of partial charges gives a partial charge of +0.3406 at the carbon atom, -0.8476 at the oxygen atom and +0.507 at the hydrogen atom, all in units of 10^{-19} C.

Fig 4.9 The C-O-H Group: Its Partial Charges.



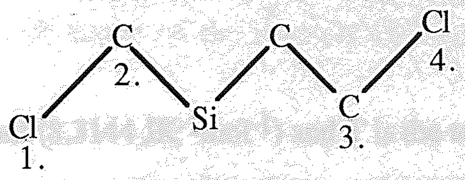
(units of 10^{-19}C)

Similar treatment of the methoxy substituted ethylene group, using a group moment of 1.23 D; C-O-CH_3 bond angle of 110° and a C-O intercharge distance of 0.143 x 10^{-9} m[152] gave partial charges of +0.25 at both of the carbons and -0.5 at the oxygen atom, again in units of 10^{-19} C.

4.7.1.2 Calculation of Electrostatic Energy.

For any molecule an arbitrary charge numbering scheme can be applied. For example, the 2-chloroethylchloromethyldimethylsilane molecule can be numbered in the following way:

Fig 4.10 The Numbering Scheme Adopted in the Calculation of Electrostatic Energies:



The energy of interaction between each pair of charges, 1 and 3; 1 and 4; 2 and 3; and 2 and 4 is calculated using equation 4.24 and then these individual energies summed to give the electrostatic energy of that conformation (eqt 4.28). Multiplication of this energy by Avagadro's number gives the energy for a mole amount.

$$E_{conf} = E_{13} + E_{14} + E_{23} + E_{24} \tag{4.28}$$

4.7.2 Application of a Statistical Weighting Factor.

When the energy of every conformation being considered has been calculated, that of lowest energy is selected, E_{min}. This minimum energy is then subtracted from the electrostatic energy of the other conformations, E_{conf}:

$$E_{conf} - E_{min} = \Delta E \tag{4.29}$$

To give the difference in energy between a conformation and that conformation of least energy, ΔE, which when substituted into the Boltzmann equation;

$$e^{-\Delta E/RT} = \sigma \tag{4.30}$$

where R is the gas constant (8.3144 $JK^{-1}mol^{-1}$) and T is the temperature (298 K) gives σ, the statistical weighting value for that conformation.[173]

The statistical weight of a conformation, σ, is multiplied by the square of the moment calculated for that conformation, this product is then summed for all of the conformations; $\Sigma\, \sigma\mu^2$. This quantity when divided by the sum of all of the statistical weights yields the square of the dipole moment:

$$\mu^2 = \Sigma\, \sigma\mu^2 / \Sigma\, \sigma \tag{4.31}$$

the square root of which gives the mean squared dipole moment:

$$\sqrt{\mu^2} = (\Sigma\, \sigma\mu^2 / \Sigma\, \sigma)^{1/2} \tag{4.32}$$

Because the exact value of the relative dielectric constant is not known the calculations were carried out for a range of assumed relative dielectric constants from 1 to 5.

Although most solvents have a relative dielectric constant around 2, this enabled a wider range of moments to be considered and also enabled us to demonstrate the effect that a variation of relative dielectric constant would have.

4.7.3 Results from the Coulombic Model.

Table 4.2 Dipole Moments Obtained from the Coulombic Model

For Compounds Based on the Formula $ClCH_2Si(CH_3)_2CH_2CH_2X$

X	ε_R				
	1	2	3	4	5
Cl	3.06	2.91	2.86	2.83	2.82
OH	2.47	2.53	2.55	-	2.56
OCH_3	2.28	2.31	-	-	2.32

Although the dielectric constant and its sensitivity to solvent concentration for these molecules is not known, it is apparent from these results that changing the dielectric constant does not significantly alter the value of the dipole moment calculated by this model. The degree of difference of the results calculated over the range of dielectric constants used, give dipole moment differences that would be within experimental error.

4.8 N.M.R. WEIGHTED MODEL.

Another model was considered which took into account the proportion of molecules with the carbon-carbon bond in an anti position and those with the same bond fixed in a gauche position, with all other positions being considered as equally weighted. This information was obtained from the N.M.R. analysis of the β-functional systems.

The sum of the square of the moment for each conformation with the C-C bond fixed anti was averaged over the total number of such conformations to yield μ_a^2. Similarly, the dipole moment for a molecule in which the carbon-carbon bond is fixed in a gauche position, μ_g^2, was obtained from the sum of the square of the individual dipole moments for each conformation divided by the number of such conformations. These quantities μ_a^2 and μ_g^2 are then multiplied by their respective proportions, the products of which are then summed and the square root taken to yield the overall molecular dipole moment.

The N.M.R. analysis indicated that for both the β-methoxyethyl and the β-hydroxyethyl substituted compounds the two types of bond orientation are present in roughly equal amounts; so for these compounds there would be no difference in the values of the theoretical dipole moments calculated via this model and the model which assumed "free rotation".

4.8.1. The 2-Chloroethylchloromethyldimethylsilane

In contrast to the β-hydroxyethyl and β-methoxyethyl derivatives the NMR spectra indicated that in the 2-chloroethylchloromethyldimethylsilane 80% of the molecules possess a carbon-carbon bond in the anti position (as calculated by the Karplus relationship[199]). The square of the dipole moment calculated assuming the carbon-carbon bond to be anti, μ_a^2 was 7.57 (μ_a = 2.75 D) and that for a fixed gauche carbon-carbon bond, μ_g^2 was 8.77 (μ_g = 2.96 D). Assuming 80% of the molecules to possess the anti conformation the resultant dipole moment can be calculated using the proceedure outlined above:

$$<\mu^2> = 0.8 \times 7.57 + 0.2 \times 8.77$$
$$<\mu^2> = 7.81$$
$$\mu = 2.79 \text{ D} \qquad (4.33)$$

This treatment has effectively lowered the calculated moment by 0.1 D from the "free rotation" model (2.89 D). More significant lowering would not be expected because this treatment does not include any terms to account for hindrance to rotation about any bonds other than the carbon-carbon bond nor does it take into account any electrostatic considerations as did the previous Coulombic model.

4.9 DISCUSSION OF RESULTS.

Table 4.3 Observed and Theoretical Results: from all Models Considered.

X	Observed Moments (D)		Calculated Moment (D) from "free rotation" model	Calculated Moment (D) from coulombic model ε		Calculated Moment (D) from NMR weighted model
	dioxane	cyclohexane		2	3	
Cl	2.55	2.65	2.89	2.91	2.86	2.79
OH	2.54	2.39	2.65	2.53	2.55	2.65
OCH_3	-	2.48	2.38	2.31	2.32 (ε = 5)	2.38

It has been mentioned previously that the values of 2.55 D and 2.62 D obtained for the β-chloroethyl substituted silane in dioxane and cyclohexane respectively are the same within experimental error. In the case of the β-hydroxyethyl substituted compound interactions with the dioxane solvent gave a significantly higher value of the dipole moment in dioxane than in cyclohexane (2.54 D and 2.39 D respectively). Since no data was collected for the β-methoxyethyl substituted compound in dioxane it seems reasonable to limit further discussion to a comparison of the cyclohexane data with the data obtained theoretically. However the dioxane results must not be entirely disregarded.

Two factors could be responsible for the lack of observed dipole moment variation with temperature: firstly, the limited range of temperature used and secondly, a reduction in the sensitivity of the dipole moments to temperature due to the presence of multiple potential energy troughs. This latter factor could also be responsible for the deviation between the observed dipole moment and the dipole moments calculated assuming free rotation.

It has been shown that the molecules are most likely distributed amongst a small number of potential energy troughs (section 4.6.2) which occur as rotation takes place around each bond. A state of completely free rotation would correspond to an equal distribution among an infinite number of such troughs. The departure of the observed moment from the value calculated for such an equal distribution is indicative of restriction to rotation.[149]

For the Coulombic model, dielectric constant values over a range of 1 to 5 were assigned to the systems, although we have shown that changing the dielectric constant does not significantly affect the results. In the light of this, the following discussion has been limited to those values of dipole moment calculated using an assumed dielectric constant of 2.

This model yielded a calculated value of 2.91 D (ε=2) for the β-chloroethyl substituted compound which is very similar to that obtained from the "free rotation" model (2.89 D). Whereas the calculated value for the β-hydroxy compound (2.53 D for ε=2) was lower than that obtained for the "free rotation" model (2.65 D) and a good deal closer to the experimentally observed value, particularly to that observed in dioxane (2.54 D in dioxane and 2.39 D in cyclohexane). In contrast, when this treatment was applied to the β–methoxyethyl substituted silane it produced a larger discrepancy between the calculated (2.31 D for ε=2) and the observed (2.48 D) values than did the "free rotation" model (2.38 D)

These results would suggest that the Coulombic model is not a particularly suitable model for our systems. This is probably due to a number of factors. In the case of this model at this level of investigation it is impractical to calculate the weightings and dipole moment contributions for each conformation. Hence many assumptions of symmetry within the molecules have to be made, including the restriction of the carbon-carbon bond in the anti position, as indicated in the NMR results. Since it would appear that there is relatively free rotation in the β–methoxyethyl substituted silane perhaps it is not then suprising that the coulombic model, which assumes an anti carbon-carbon bond, does not produce a comparable value.

It has been pointed out previously that there are many forces in play other than electrostatic forces which determine the distribution of conformations in these systems. The Coulombic model only takes into account the energy due to electrostatic interactions and neglects all steric forces (van der Waals attraction, repulsion and dipole induction energy). Considering the relatively short chain length and the large size of the α-chlorine atom in all of our compounds, it is not unreasonable to expect that there would be considerable contributions from van der Waal repulsive forces. None of our models have taken into consideration the presence of the two methyl groups on the silicon atom. Although consideration of electrostatic energies only gives useful indications[144] it can not do full justice due to the complexity of forces involved, as our results would seem to indicate.

Previous dipole moment studies of the 1,2-dichloroethane molecule provide support for our observations on the inadequacies of a model which neglects steric forces. Altar[166] observed that electrostatic forces were not of primary importance in dichloroethane, the dominating forces were van der Waals attraction and repulsion, with a considerable part of the repulsive energy attributed to the Cl-Cl steric repulsion. Similar studies led Lennard-Jones and Pike to come to the same conclusions.[167] Further studies by Smyth and McAlpine[149] and Thomas and Gwinn[169] of the dipoles moments of a series of trimethylene chloride and bromide[163] compounds found that the dipole repulsive energy appeared to be less important than the steric repulsive energy.

Although there seems an overwhelming case for the over-riding importance of steric effects within short chain molecules in our particular systems the larger size of the silicon must be borne in mind, as in similar studies previously, the majority of compounds possess an all carbon backbone. The effect of the size of the central atom is illustrated in a publication by Lewis and Smyth.[175] They calculated the dipole moments for trialkyl borates and triphenyl phosphite. They reported that strong steric repulsion between the alkyl groups in the borates lowered their moments to less than half the value calculated assuming free rotation and included terms to account for electronic effects from any double bond character. In contrast they found an excellent agreement between the observed values and those calculated in the same manner for the triphenyl phosphite. It is evident that steric repulsion among the alkyl groups reduces the stabilisation of the high moment configurations. The larger size of the central atom in triphenyl phosphite evidently reduces the repulsion so that the moment is not lowered below that calculated for free rotation.

The last model examined in our study was the NMR weighted model. It would appear from the NMR spectra that the β-hydroxyethyl and β-methoxyethyl compounds possess more or less equal weighting for the anti and gauche conformations. The NMR weighted model gave dipole moments exactly the same as the "free rotation" model gave (2.65 D and 2.38 D for the β-hydroxyethyl and the β-methoxyethyl respectively). The NMR model for the β-chloroethyl- substituted compound worked on the assumption that 80% of the molecules had the C-C bond fixed in the anti position. This method gave a calculated dipole moment of 2.79 D, which is actually not too far from the observed value of 2.62 D, and it is considerably lower than either of the values obtained from the "free rotation" and the Coulombic models (2.89 D and 2.91 D respectively). Although it does not take into account numerous factors; including other steric and electronic effects and disregards any bonds other than the carbon-carbon ethyl bond, it would appear to be the most successful model for the 2-chloroethylchloromethyldimethylsilane.

4.10 CONCLUSIONS.

This work has strongly indicated that the 2-chloroethylchloromethyldimethylsilane possesses restricted rotation about the carbon-carbon bond. As the NMR model gave the best fit of calculated with observed dipole moments, this result is consistent with the high degree of restriction to rotation suggested by the NMR analysis of this compound.

2-methoxyethylchloromethyldimethylsilane is indicated by this investigation to possess more or less free rotation, a second result in support of the conclusions based upon the

NMR analysis.

Unfortunately, due to the complications arising from the possibility of intra- and in particular inter-molecular hydrogen bonding in the 2-hydroxyethylchloromethyldimethylsilane it has not been possible to derive any significant conclusions concerning the dipole moment results obtained for this compound.

This comparative study of the observed and theoretically calculated dipole moments appear to essentially support the conclusions arrived at from the NMR analysis.

Chapter 5

CONCLUSIONS.

5. CONCLUSIONS.

The original aim of this project was to discover whether or not in alpha and beta functionalised silanes the two functions interacted, and if so to investigate the magnitude and origin of the interaction.

A variety of silanes were prepared with a constant chloromethyl alpha function and chloro, hydroxy and methoxy beta functions. For a standard of comparison, trimethylsilyl derivatives were synthesised with the same variety of beta functions.

The relative reactivity of these compounds was then analysed by kinetic measurements on the solvolysis reaction. In beta-functional silicon systems solvolysis is most often accompanied by elimination of ethene, the rates of solvolysis were calculated from measurements of the volume of ethene evolved with time. It was found that all of the trimethylsilyl derivatives displayed normal high solvolytic activity. The β-hydroxyethyl- and β-methoxyethyl-substituted chloromethyldimethylsilyl derivatives solvolysed slightly slower than their trimethylsilyl counterparts but this again is entirely normal behaviour, with the reduction in rate being accounted for by the more electronegative alpha function, inductively strengthening the Si-C bond.

In sharp contrast to these results came the results of the solvolytic analysis of the 2-chloroethylchloromethyldimethylsilane which did not eliminate ethene under a variety, of what are usually considered to be, optimum solvolytic conditions. This prompted an investigation into the products of the solvolysis of this compound by NMR analysis. The solvolysis was carried out using the usual solvolysis apparatus, with the standard solvolytic medium for varying lengths of time. The NMR spectra revealed the starting material, 2-chloroethylchloromethyldimethylsilane to react to give siloxane and 2-

hydroxyethylchloromethyldimethylsilane. With the former being produced at a faster rate than the latter. After a twenty four hour period the solvolysis products were the starting material, the siloxane $ClCH_2Me_2SiOSIMe_2CH_2Cl$ and the β-substitution product in a ratio of 7 : 2 : 1, respectively. After a five day period this ratio had changed to become 1 : 1 : 1 respectively. By carrying out the solvolysis in the more nucleophilic solvolytic media of aqueous 1,1,1-trfluoroethanol for the longer reaction time of fourteen days the ratio of products changed to 1 : 1 of siloxane and β-hydroxyethyl-substituted silane respectively. The presence of siloxane has been taken to indicate that some silicon-carbon cleavage occurs due, it would seem to nucleophilic attack at the silicon. However, as we pointed out , a product expected of this type of reaction would be ethyl chloride, considering the total lack of ethene production. Our experiments were unable to establish the presence of ethyl chloride. We have established that the solvolysis of 2-chloroethylchloromethyldimethylsilane does react by an alternative mechanism. Because of the lack of sufficient information on this system and its solvolysis we have been unable to propose a viable alternative mechanism which can take into account all the information we have so far obtained.

NMR spectra were obtained for the purpose of confirming the structures of silanes synthesised for the solvolytic analyses. It was during this routine analysis that certain abnormalities were noticed in some of the spectra. It was observed that whilst the β-methoxyethyl- and the β-hydroxyethyl-substituted compounds gave normal looking NMR spectra, the spectra of the β-chloroethyl-substituted compounds were extremely unusual. Close examination of the methylene triplets of the β-chloroethyl-substituted compounds revealed them to be made up of upto ten close lines, with the outer lines larger than the inner. On a casual glance they appeared to be inverted triplets. Subsequent analysis of these triplets, comparing simulated computer-generated spectra with those obtained experimentally indicated that in the beta-chloro-substituted silanes the carbon-carbon bond appeared to be held in the anti configuration for 80% of the molecules and the gauche configuration for the remaining 20% of the molecules. It seemed fair to assume that the difference between the β-chloroethyl and β-oxygenated (hydroxy or methoxy) systems was one of size, the larger β-chlorine atom being responsible for the hindrance to rotation.

Because of the implication that a large beta function was capable of significant steric hindrance resulting in a fixed anti conformation, in an attempt to provide supporting evidence for this theory the spectra were obtained for 2-bromoethyltriphenylsilane. These spectra also were found to display complex methylene absorptions because, it is assumed, of restricted rotation, due to the large β-bromo group.

The possibility of large beta functions causing significant restriction to rotation about the carbon-carbon bond, raised the question of whether a large alpha function could have the same effect. In order to elucidate this 2-hydroxyethyltriethylsilane and 2-hydroxyethylisopropyldimethylsilane were synthesised and analysed. Both displayed unusual complex methylene absorptions. It was concluded that molecules possessing large alpha or beta functions would possess restricted rotation and be held predominantly in the anti configuration.

In an attempt to provide evidence to support the conclusions from the NMR analysis, the dipole moments of the chloromethyl derivatives were analysed. The dipole moments were calculated from the capacitances measured experimentally. Several theoretical models were developed to try to match theroetical dipole moments with the experimental values. It was found that for the 2-chloroethylchloromethyldimethysilane the closest match was obtained from the model using conformational information derived from the NMR analysis, ie that the C-C bond was held 80% anti and 20% gauche. The β-methoxyethyl-substituted compound had a closest match with the free rotation model, which gave results the same as the NMR based model. So these results are also in agreement with the NMR analysis. The results of the β-hydroxyethyl-substituted compound, which contradicted any expectations, were believed to be complicated due to intra- and inter-molecular hydrogen bonding. As a result no firm conclusion was made based upon the dipole moment information on this compound.

It may be possible to correlate the unusual activity of the 2-chloroethylchloromethyldimethylsilane with the findings of restricted rotation in compounds with a large beta function. Perhaps the resultant anti configuration predominant in these systems, due to restricted rotation about the carbon-carbon bond, is such that it facilitates the formation of a five-membered ring stabilised by neighbouring group participation of the α-chloro atom on the developing beta carbonium ion. Such stabilisation could promote a second, competing and preferential mechanism for the nucleophilic attack by solvent.

Chapter 6:

MATERIALS AND METHODS.

6. MATERIALS AND METHODS.

6.1 REAGENTS.

All reagents were used as supplied unless otherwise stated. Dry ether and THF were obtained by drying over sodium wire, and dry pyridine by drying over KOH.

6.1.1 Silane Synthesis.

Table 6.1: Materials for Silane Synthesis:

COMPOUND	R.M.M.	SUPPLIER
t-Butyldimethylchlorosilane	150.73	Aldrich
Carbon tetrachloride	153.82	Fisons
Chlorochloromethyldimethylsilane	143.09	Dow Corning, Petrarch
chloroisopropyldimethylsilane	135.69	Petrarch
Diethyl ether (Ether)	74.12	Fisons
Ethanol	46.07	BDH
Ethyl magnesium chloride (2M solution in diethylether)	88.83	Aldrich
Hydrochloric acid	36.46	Fisons
Magnesium sulphate, anhydrous	120.37	Aldrich, BDH, Fisons

Mercuric acetate	318.68	Aldrich
Methanol	32.04	Shell
Nitrogen	28.02	BOC
Pyridine	79.10	Fisons
Sodium	22.99	BDH
Sodium borohydride	37.83	Aldrich
Sodium chloride	58.44	Aldrich
Sodium hydroxide	40.00	Fisons
Sulphuric acid	98.08	Fisons
Tetrahydrofuran (THF)	72.11	Fisons
Thionyl chloride	118.97	Aldrich
Triethylsilylchloride	150.73	Petrarch
1,1,1-Trifluoroethanol (TFE)	100.04	Aldrich
Trimethylvinylsilane	100.24	Aldrich
Vinyl magnesium bromide (1M solution in THF)	131.27	Aldrich

6.2 EXPERIMENTAL METHODS.

6.2.1 Silane Synthesis.

6.2.1.1 2-hydroxyethyltrimethylsilane.

The β-hydroxyethyl-substituted silane was prepared following the method detailed by Brown and Geoghegan[176]. Mercuric acetate (112g, 0.35mol) was dissolved in 350ml of distilled water and then 350ml of THF added, yielding an opaque yellow solution.

To this was added trimethylvinylsilane (31g, 0.31mol). The resulting solution was stirred for one minute until decolourisation occured, stirring was continued for a further ten minutes. After which time 350ml of 3M aqueous sodium hydroxide was added followed by 350ml of 0.5M sodium borohydride in 3M aqueous sodium hydroxide solution. Finally diethylether (750ml) was added and the mixture stirred for one hour, resulting in a black solution of suspended mercury. This was saturated with sodium chloride, the organic phase separated, washed with a saturated sodium chloride solution and then dried over anhydrous magnesium sulphate. The solvents were removed on the rotary evaporator. Distillation yielded the pure product 28.27g (77%). bp 52^{o}C/ 2.5mm Hg; Lit bp 61^{o}/19mm Hg[177]

I.R.(cm^{-1}; KBr): 3350(s); 2960(m); 2925(m); 2890(m); 1420(w); 1250(s); 850(m);

^{1}H N.M.R. (δ; $CDCl_3$): -0.15 (s, 9H; Si-$(CH_3)_3$); 0.79 (t, 2H; Si-CH_2), 3.51 (t, 2H; CH_2-OH); 3.78 (s, 1H; -OH)

^{13}C N.M.R. (δ; $CDCl_3$): -2.09 (+ve; Si-CH_3); 22.9 (-ve; CH_2-Si); 58.4 (-ve; CH_2-OH)

6.2.1.2 2-chloroethyltrimethylsilane.

A mixture of 2-hydroxyethyltrimethylsilane (9.5g, 0.08mol), prepared by the method outlined above in section.6.2.1.1, 150mls dry ether, and dry pyridine (3.2ml, 0.04mol) was cooled to 0^{o}C and a mixture of thionyl chloride (5.9ml, 0.08mol) and 50ml dry ether was added dropwise. The solution was allowed to warm to room temperature, stirred for 24 hours and then refluxed for one hour. After cooling, the white pyridinium chloride crystals were filtered off and washed thoroughly with dry ether. The washes were combined with the filtrate and the solvents removed. 6.7g (61%) product was distilled at 39°/2mm.

I.R.(cm^{-1}; KBr): 2900(s); 2980(m); 1426(s); 1260(s); 847(s)

^1H N.M.R. (δ; $CDCl_3$): -0.03 (s, 9H; Si-$(CH_3)_3$); 1.15 (t, 2H; Si-CH_2); 3.66 (t, 2H; CH_2-Cl)

^{13}C N.M.R. (δ; $CDCl_3$): -1.78 (+ve; Si-CH_3); 20.7 (-ve; CH_2-Si); 43.2 (-ve; CH_2-Cl)

^{29}Si N.M.R. (δ; $CDCl_3$): 0.303

6.2.1.3 2-methoxyethyltrimethylsilane.

The procedure followed here was based upon that detailed by Brown *et al.*[188] Mercuric acetate (57.4g, 0.18mol) was dissolved in 180ml methanol and 180ml THF added, yielding a cream coloured solution. Trimethylvinylsilane (16.7g, 0.167mol) was added and the mixture stirred until it decolourised, between one and 2 minutes. Stirring was continued for a further 15 minutes. Aqueous sodium hydroxide (180ml 3M) was added followed by sodium borohydride solution (180ml 0.5M in 3M aqueous sodium hydroxide). The reaction mixture was stirred for two hours and then saturated with sodium chloride. The organic layer was separated and washed with a saturated solution of sodium chloride. The aqueous layer was extracted with ether (3 x 30ml) and the ether extracts combined with the organic phase and dried over magnesium sulphate. Distillation under reduced pressure[178] at 38°/0.6mm Hg yielded 6.33g (30%) of pure product; Lit bp; 49°/70 mm Hg[179]

I.R.(cm^{-1}; Neat): 2960(s); 2925(m); 2820(m); 1460(w); 1256(s);1110(s); 936(s); 860(s); 845(s)

^{1}H N.M.R. (δ; $CDCl_3$): -0.01 (s, 9H; $Si(CH_3)_3$); 0.85 (t, 2H; Si-CH_2); 3.22 (s, 3H; OCH_3); 3.36 (t, 2H; OCH_3-CH_2)

^{13}C N.M.R. (δ; $CDCl_3$): -1.58 (+ve; Si-CH_3); 17.97 (-ve; CH_2-Si); 57.63 (+ve; CH_3-O); 69.73 (-ve; CH_2-OCH_3)

^{29}Si N.M.R. (δ; $CDCl_3$): 0.04

6.2.1.4 chloromethyldimethylvinylsilane.

This compound was prepared by a method based on those detailed by Rosenberg,[180] and Sommer[181] *et al.* Vinyl magnesium bromide (300ml, 0.3mol), under a nitrogen atmosphere, was added dropwise with stirring to chlorochloromethyldimethylsilane (27.6ml, 0.21mol). On completion of the addition, the mixture was refluxed for 4 hours. After allowing to cool, 70mls of 4M aqueous hydrochloric acid was added and the mixture then extracted with 3 x 50ml ether. After drying the organic extracts over magnesium sulphate for 12 hours the solvents were removed and the product was distilled at 121°C Lit bp 121-122°C[182] giving 24.95g (88%) of product.

I.R.(cm^{-1}; Neat): 3060(s); 3020(m); 2980(s); 2960(m); 1600(m); 1420(s); 1504(s); 1256(s); 1175(w); 1050(s); 960(s); 820(s); 798(s)

^{1}H N.M.R. (δ; $CDCl_3$): 0.07 (s, 6H; Si-$(CH_3)_3$); 2.74 (s, 2H; CH_2-OH);

5.66-5.78 (m; 1H; CH=); 5.96-6.16 (m, 2H; CH_2=)

^{13}C N.M.R. (δ; $CDCl_3$):	-4.7 (+ve; Si-CH_3); 29.6 (-ve; CH_2-Cl); 133.45 (-ve; CH_2=); 135.58 (+ve; CH=)
^{29}Si N.M.R. (δ; $CDCl_3$):	-5.68

6.2.1.5 2-hydroxyethylchloromethyldimethylsilane.

The method for this reaction is given by Wilt *et al*[183].

To a mixture of mercuric acetate (16.6g, 0.052mol) and water (52ml), was added THF (52ml) which yielded a yellow solution. To this mixture was added chloromethydimethylvinylsilane (6.5g, 0.048mol) with stirring, causing decolourisation within one minute. Stirring was continued for a further ten minutes. To the resulting mixture sodium hydroxide solution (52ml, 3M) was added followed by 52ml of 0.5M sodium borohydride in 3M sodium hydroxide solution. Finally 150ml of ether was added and the mixture stirred for one hour and then saturated with sodium chloride. The organic phase was separated, washed with a saturated sodium chloride solution and dried over magnesium sulphate. The solvents were removed by rotary evaporation and the product distilled at 68°C/0.3mmHg, Lit. bp 80°c/0.6mm Hg[183] to yield 5.07g (70%)

I.R.(cm^{-1}; Neat):	3420(s); 2950(s); 2920(s); 2880(s); 1390(m); 1256(s); 1120(m); 1060(m); 880(s);

^{1}H N.M.R. (δ; $CDCl_3$): 0.04 (s, 6H; Si-$(CH_3)_3$); 0.97 (t, 2H; Si-CH_2-CH_2); 2.72 (s, 2H; CH_2-Cl); 3.29 (s, 1H; -OH); 3.65 (t, 2H; CH_2-OH)

^{13}C N.M.R. (δ; $CDCl_3$): -4.63 (+ve; Si-CH_3); 19.7 (-ve; CH_2-CH_2-Si); 30.2 (-ve; Cl-CH_2-Si); 60.4 (-ve; CH_2-OH)

^{29}Si N.M.R. (δ; $CDCl_3$): 2.02

6.2.1.6 2-chloroethylchloromethyldimethylsilane.

To a stirred solution of 2-hydroxyethylchloromethyldimethylsilane (11.9g, 0.078mol) [prepared as detailed in section 6.2.1.5], pyridine (3.15ml, 39mmol) and dry ether (100ml) at 0°C, was added a solution of thionyl chloride (5.7ml, 78mmol) and 60ml dry ether dropwise. When the addition was complete the solution was allowed to warm up to room temperature and stirring was continued for a further 24 hours, the mixture was then refluxed for one hour. After cooling, the white crystals were filtered and washed with 100ml of dry ether. The filtrate and ether washes were then washed with 100ml water. The organic phase was separated and dried over magnesium sulphate. The solvent was removed and the product distilled under vacuum at bp 82°C/1mm Hg to give 10.2g, (77%) Lit bp SE-30 column 115°C.[183]

I.R. (cm^{-1}; KBr): 2950(s); 2920(m); 2890(m); 1390(m); 1280(s); 1250(s); 1160(m); 1030(m); 895(m); 843(s)

^{1}H N.M.R. (δ; $CDCl_3$): 0.07 (s, 6H; Si-$(CH_3)_3$); 1.24 (t, 2H; Si-CH_2-CH_2); 2.71 (s, 2H; CH_2-Cl); 3.6 (t, 2H; Cl-CH_2-CH_2)

^{13}C N.M.R. (δ; $CDCl_3$): -4.67 (+ve; Si-CH_3); 19.9 (-ve; CH_2-CH_2-Si); 29.76 (-ve; CH_2-CH_2-Cl); 41.99 (-ve; CH_2-Cl)

^{29}Si N.M.R. (δ; $CDCl_3$): 2.4

6.2.1.7 2-methoxyethylchloromethyldimethylsilane.

To a solution of mercuric acetate (24g, 0.075mol), 75ml methanol and 75ml of THF was added chloromethyldimethylvinylsilane (9.4g, 0.0695mol) and the mixture stirred for 20 minutes. To the resulting solution 75ml 3M NaOH (aq), 75ml of 0.5M sodium borohydride in 3M sodium hydroxide and 200ml ether was added and stirred for 90 minutes. The mixture was saturated with sodium chloride and the organic phase washed with a saturated solution of sodium chloride and then dried over magnesium sulphate. Removal of the solvents and distillation of the product at bp 68°C/0.3mm Hg yielded 6.8g (60%).

I.R. (cm^{-1}; KBr): 2940(s); 2900(s); 2876(m); 2800(m); 1440(m); 1385(m); 1370(s); 1245(s); 1205(m); 1075(s); 9010(m); 830(s); 750(s)

^{1}H N.M.R. (δ; $CDCl_3$): -0.1 (s, 6H; Si-$(CH_3)_3$); 0.89 (t, 2H; Si-CH_2-CH_2); (s, 2H; CH_2-Cl); 3.14 (s, 3H; -OCH_3); 3.34 (t, 2H; CH_2-OCH_3)

^{13}C N.M.R. (δ; $CDCl_3$): -4.58 (+ve; Si-CH_3); 15.14 (-ve; CH_2-CH_2-Si); 30.21

(-ve; Cl-CH_2-Si); 57.7 (+ve; O-CH_3); 60.93 (-ve; CH_2-OCH_3)

6.2.1.8 chloromethyldimethylethylsilane.

This compound was prepared by the method given by Petrov, Mironov and Pogonkina.[184] A mixture of chlorochloromethyldimethylsilane (11.44g, 0.08mol) and 30ml dry ether was added dropwise, with stirring, to ethyl magnesium chloride solution (0.09mol; 30ml of 2M solution in diethylether) under a nitrogen atmosphere. The resulting mixture was then refluxed for 6 hours. After allowing to cool the mixture was hydrolysed with 75ml 4M hydrochloric acid. The hydrolysed solution was then extracted with 3 x 15ml ether and the organic phase dried over magnesium sulphate to yield 1.5g (13%) product, bp 128°C; Lit bp 127.8°C/757 mm Hg.[185] and 127-8°C/750 mm Hg.[184]

I.R. (cm^{-1}; KBr):	2950(s); 2900(m); 2870(m); 1460(w); 1395(m); 1245(s); 1170(w); 1000(m); 995(m); 845(s); 751(s); 700(m)
^1H N.M.R. (δ; $CDCl_3$):	0.07 (s, 6H; Si-$(CH_3)_2$); 0.61 (q, 2H; Si-CH_2-CH_3); 0.94 (t, 3H; CH_3-CH_2); 2.75 (s,2H; CH_2-Cl))
^{13}C N.M.R. (δ; $CDCl_3$):	-5.3 (+ve; Si-CH_3); 5.3 (-ve; CH_3-CH_2-Si); 6.85 (+ve; SiCH_2-CH_3); 29.77 (-ve; Cl-CH_2-Si);

6.2.1.9 2-hydroxyethyl*t*-butyldimethylsilane.

Vinyl magnesium bromide (200ml, 0.2mol) was added dropwise to a stirred solution of t-butyldimethylchlorosilane (25g, 0.167mol) in 100ml dry tetrahydrofuran in a nirogen atmosphere. The mixture was refluxed for two weeks and after cooling was hydrolysed with 100ml 2M HCl and the organic layer separated. The remaining aqueous layer was extracted with 3 x 50ml ether. The organic layer and extracts were combined and dried over magnesium sulphate. The solvents were removed and the unpurified product (11.6g) was added to a stirred mixture of mercuric acetate (22.33g, 0.07mol), water (70ml) and THF (70ml). This mixture was stirred for 30 minutes and then 70ml 3M aqueous sodium hydroxide solution, 70ml 0.5M sodium borohydride (in 3M aqueous sodium hydroxide) and 150ml ether was added. Stirring was continued for two hours. The resulting mixture was saturated with sodium chloride and the organic phase washed with a saturated solution of sodium chloride and then dried over magnesium sulphate. Removal of the solvents and distillation of the product at 93°C/ 6 mm Hg gave 3.7g (13.8%) product.

The product was too impure to enable any structural assignments to be made from the NMR or IR spectra.

6.2.1.10 2-hydroxyethyltriethylhydroxyethylsilane.

Triethylsilylchloride (15.1ml, 0.09mol) was added dropwise, with stirring to vinyl magnesium bromide (100ml, 0.1mol) under a nitrogen atmosphere. This mixture was refluxed for 48 hours and then hydrolysed with 50ml 2M HCl . After extraction with ether (3 x 25ml), the organic phase was dried over magnesium sulphate. The product, triethylvinylsilane was distilled at 144.5°C Lit bp 143.2/755 mm Hg[177]. to yield 6.6g (51.6%). This was then added to a mixture of mercuric acetate (15.6g, 0.05 mol), 50ml water and 50ml THF and stirred for 15 minutes. Aqueous sodium hydroxide solution (50ml; 3M), 50ml sodium borohydride (0.5M) in 3M sodium hydroxide solution, and 100ml ether were added. Stirring was continued for 90 minutes and then the mixture was saturated with sodium chloride and the organic phase washed with a saturated solution of sodium chloride. After drying the organic layer over magnesium sulphate the solvent was removed and the product 4.2 g, (57%) distilled under vacuum at 120°C/3 mm Hg Lit bp 100°/14mm Hg[177] and 190° at atmospheric pressure[186].

I.R. (cm^{-1}; Neat): 3280(s); 2940(s); 2890(m); 2855(s); 1730(m); 1445(m); 1400(m); 1370(w); 1352(w); 1226(s); 1165(m); 1025(m); 990(s); 845(w); 720(s)

^1H N.M.R. (δ; $CDCl_3$): 0.53 (m, 6H; $Si\text{-}CH_2\text{-}CH_2$); 0.9 (m; 11H;); 1.96 (s, 1H; OH); 3.64 (t, 2H; $CH_2\text{-}OH$).

^1H N.M.R.(δ; $CDCl_3$+ Eufod):0.43 (m; 6H; $Si\text{-}CH_2\text{-}CH_3$); 0.8 (m; 9H; $Si\text{-}CH_2\text{-}CH_3$); 0.9 (t, 2H; $Si\text{-}CH_2\text{-}CH_2$); 1.87 (s, 1H; -OH); 3.62 (t, 2H; $CH_2\text{-}OH$)

^{13}C N.M.R. (δ; $CDCl_3$): 3.66 (-ve; $Si\text{-}CH_2\text{-}CH_2$); 7.14 (+ve; $CH_3\text{-}CH_2$); 17.2; (-ve; $Si\text{-}CH_2\text{-}CH_2$); 59.8 (-ve; $CH_2\text{-}OH$);

6.2.1.11 2-hydroxyethylisopropyldimethylsilane.

To a stirred solution of isopropyldimethylsilylchloride (14.1g, 0.09mol) in 175ml dry THF, under an atmosphere of nitrogen, was added vinyl magnesium bromide (100ml, 0.1mol). This mixture was refluxed for 3 days, allowed to cool and hydrolysed with 100ml of 2M hydrochloric acid. The mixture was then extracted with ether (3 x 30ml), the organic extracts combined and dried over magnesium sulphate. The product was distilled to give 1.8g (0.014 mol) 16% yield of isopropyl dimethylvinylsilane bp 117-118°C. This was added to a mixture of mercuric acetate (4.8g, 0.015mol), 15ml water and 15ml THF. The resulting mixture was stirred for 15 minutes followed by the addition of 15ml 3M aqueous sodium hydroxide, 15ml 0.5M sodium borohydride in 3M aqueous sodium hydroxide and 50ml ether. Stirring was continued for 90 minutes, the mixture was then saturated with sodium chloride and the organic phase washed with a saturated solution of sodium chloride. After drying the organic layer over magnesium sulphate the solvent was removed and the product distilled under reduced pressure to yield 0.82g (40%) bp 72°C/5 mm Hg. Lit bp 82°C/14 mm Hg[177]

I.R. (cm^{-1}; Neat):	3300(s); 2955(s); 2905(m) 2890(m); 1740(m); 1730(m); 1447(m); 1410(m); 1355(w); 1245(s); 1170(w); 1005(s); 845(w); 725(s)
^1H N.M.R. (δ; $CDCl_3$):	-0.13 (s, 6H; Si-$(CH_3)_2$); 0.73 (m,1H; Si-CH-CH_3); 0.91 (d, 6H; CH-$(CH_3)_2$); 1.02 (t, 2H; -Si-CH_2); 3.81 (t, 2H; CH_2-OH); 4.2 (s, 1H; -OH)
^{13}C N.M.R. (δ; $CDCl_3$):	-5.6 (+ve; Si-CH_3); 14.28 (+ve; CH-Si); 17.16 (+ve; CH-CH_3); 18.65 (-ve; CH_2-Si); 59.15 (-ve; CH_2-OH)

6.2.1.12 2-bromoethyltriphenylsilane.

This compound was used without further purification as supplied by a previous member of this research group.[187] It had been prepared in 82% yield, m.p.142-144°C, Lit mp 144°C[177].

^{1}H N.M.R. (δ; $CDCl_3$): 2.23 (m; 2H; $SiCH_2$); 3.63 (m; 2H; CH_2Br); 7.52 (m,15H; $-C_6H_5$).

6.2.2 Solvolysis Reactions of 2-Chloroethylchloromethyldimethylsilane

The apparent lack of solvolytic activity of the 2-chloroethylchloromethyldimethylsilane, prompted a more indepth investigation into the solvolysis of this compound. The solvolysis was carried out under a number of different conditions and subsequent analysis of the solvolytic mixture by NMR was undertaken. All of the following solvolyses were carried out using exactly the same equipment as was used for the kinetic measurements in order to confirm the lack of ethene production (see section 6.2.4.2).

6.2.2.1 Solvolysis Reaction - 1.

2-chloroethylchloromethyldimethylsilane (2g, 0.012mol) was added to the solvolytic medium of 50ml of 70% aqueous ethanol at room temperature with stirring. After twenty four hours no observed change in the manometer level led us to assume that no ethene had been produced. The reaction mixture was then dried over anhydrous magnesium sulphate. This was repeated several times, diluting with dry ether as necessary, to ensure a thorough drying. The majority of the solvents were then removed on the rotary evaporator. The product mixture was then analysed by NMR, this showed the presence of three chloromethyldimethylsilane species. Two of these were obviously the starting material, $ClCH_2Si(CH_3)_2CH_2CH_2Cl$ and the siloxane $ClCH_2(CH_3)_2SiOSi(CH_2)_3CH_2Cl$ the third species was considered to be the 2-hydroxyethylchloromethyldimethylsilane $ClCH_2Si(CH_3)_2CH_2CH_2OH$, whose methylene triplets were obscured by the triplets of the starting material. The relative ratio of these compounds was calculated to be 7 : 2 : 1 of the starting material, the siloxane and the β-hydroxyethyl derivative respectively.

^{1}H N.M.R. (δ; $CDCl_3$):	3.65-3.71 (m; 18H; β-CH_2OH & β-CH_2Cl); 2.79 (s; 14H; $ClCH_2$-$SiCH_2CH_2Cl$); 2.77 (s; 2H; $ClCH_2$-$SiCH_2CH_2OH$); 2.72 (s; 8H; $ClCH_2$-SiO); 1.357 (t; 18H; $SiCH_2CH_2OH$ & $SiCH_2CH_2Cl$); 0.856 (m; impurity); 0.233 (s; 6H; $(CH_3)_2$-$SiCH_2CH_2OH$); 0.195 (s; 24 H; $(CH_3)_2$-SiO); 0.157 (s; 42H; $(CH_2)_3$-$SiCH_2CH_2Cl$)
^{13}C N.M.R. (δ; $CDCl_3$):	-4.88 (+ve; CH_3); -2.30 (+ve; CH_3); -1.74 (+ve; CH_3); 19.44 (-ve; CH_2); 24.06 (-ve; CH_2); 28.98 (-ve; CH_2); 29.31 (-ve; CH_2); 29.64 (-ve; CH_2); 36.69 (-ve; CH_2); 41.99 (-ve; CH_2);

6.2.2.2 Solvolysis Reaction - 2.

2-chloroethylchloromethyldimethylsilane (2g, 0.012mol) was added to the solvolysis solution of 70% aqueous ethanol in the solvolysis flask, equilibrated at 30°C. This mixture was stirred for five days, after which time no evidence of ethene gas production had been observed. The solvolysis flask was separated form the apparatus and the mixture thoroughly dried using anhydrous magnesium sulphate. The solvents were removed by distillation and the product mixture analysed by NMR. The proton NMR spectrum showed three different silicon species present. These were found to be the starting material, the siloxane $ClCH_2(CH_3)_2SiOSi(CH_3)_2CH_2Cl$ and the β-hydroxyethyl-substituted chloromethyldimethylsilane, $ClCH_2(CH_3)_2SiCH_2CH_2OH$ as was found in the above experiment (section 6.2.2.1). The relative ratio of these were found to be 1 : 1 : 1 respectively. Unlike in the above spectrum the methylene triplets of the β-hydroxyethyl derivative were clearly observable.

^{1}H N.M.R. (δ; $CDCl_3$):	; 0.01 (s; 6H; CH_3Si-βCl); 0.046 (s; 6H; CH_3Si-βOH); 0.058 (s; 12H; CH_3Si-O); 1.02 (t; solvent impurity); 1.15 (t; 2H; $SiCH_2$-β-OH); 1.32 (t; 2H; $SiCH_2$-β-Cl); 1.51 (s; 1H; -OH); 2.58 (s; 4H; $ClCH_2$-SiO); 2.64 (s; 2H; $ClCH_2$-β-OH); 2.67 (s; 2H; $ClCH_2$-Si-β-Cl)); 3.5 (m; solvent impurity); 3.68 (t; 2H; CH_2CH_2OH); 3.76 (t; 2H; CH_2CH_2Cl); 4.11 (s; solvent impurity)
^{13}C N.M.R. (δ; $CDCl_3$):	-4.49 (+ve; CH_3Si-β-Cl); -3.54 (+ve; CH_3Si-β-OH); -1.616 (+ve; CH_3SiO); 15.44 (-ve; CH_2CH_2Cl); 19.84 (-ve; CH_2CH_2OH); 29.76 (-ve; $ClCH_2$-β-Cl); 30.56 (-ve; $ClCH_2$-β-OH); 30.69 (-ve; $ClCH_2SiO$; 65.66 (-ve; β-CH_2OH; 66.76 (-ve; β-CH_2Cl)

6.2.2.3 Solvolysis Reaction - 3.

The same procedure was carried out as detailed in the above section (6.2.2.3) but with a different reaction time, in this experiment the reaction was allowed to proceed for fourteen days instead of only five days. The mixture was thoroughly dried in the same manner as before and removed of all solvents before being analysed by NMR. Unfortunately the sample was severely contaminated by laboratory grease which rendered the NMR spectra unidentifiable and hence no useful information was obtained from this experiment.

6.2.2.4 Solvolysis Reaction - 4.

2-chloroethylchloromethyldimethylsilane (3.6g, 0.021mol) was injected into a stirred solvolysis solution of 70% aqueous 1,1,1-trifluoroethanol, equilibrated at 30°C. After fourteen days there had been no observable ethene production. The solvolysis flask was then attached by one neck to an acetone trap, immersed in liquid nitrogen and through the second a dry nitrogen bleed was introduced. The system was then flushed through with dry nitrogen in an attempt to flush any ethyl chloride present into the acetone trap. The trap contents were subsequently analysed to reveal only acetone present. The solvolysis mixture was then dried thoroughly over anhydrous magnesium sulphate and the majority of solvents carefully distilled off. The product residue was analysed by NMR. It was discovered that there was no longer any starting material present and the siloxane and 2-hydroxyethylchloromethyldimethylsilane were observed in a ratio of 1 : 1.

^{1}H N.M.R. (δ; $CDCl_3$): ; 0.07 (s; 6H; CH_3Si-βOH); 0.144 (s; 12H; CH_3Si-O); 1.12 (t; 2H; $SiCH_2$-β-OH); 1.96 (s; 1H; -OH); 2.68 (s; 4H; $ClCH_2$-SiO); 2.72 (s; 2H; $ClCH_2$-β-OH); 3.49 (t; 2H; CH_2CH_2OH); 3.8 (m; solvent impurity); 4.86 (s; solvent impurity)

^{13}C N.M.R. (δ; $CDCl_3$): -5.6 (+ve; CH_3Si-β-OH); -2.37 (+ve; CH_3SiO); 13.83 (+ve; impurity); 18.22 (-ve; CH_2CH_2OH); 29.68 (-ve; $ClCH_2$-β-OH); 30.42 (-ve; $ClCH_2SiO$); 65.79 (-ve; β-CH_2OH)

6.2.3 Methods of Analysis.

6.2.3.1 Infra-Red Spectroscopy.

All Infra-Red spectra were recorded on either a Nicolet 510 Fourier Transform Infrared Spectrometer or a Perkin Elmer 1710 Fourier Transform Infrared Spectrometer. Solid samples were prepared as KBr discs and liquids as thin films between sodium chloride plates.

6.2.3.2 Nuclear Magnetic Resonance Spectroscopy.

All Nuclear Magnetic Resonance spectra were recorded on a Bruker AC 300 MHz spectrometer. ^{13}C spectra were recorded as either APT (Attached Proton Test) or DEPT (Distortionless Enhanced Polarisation Transfer) spectra. The spectra were recorded at 25°C in $CDCl_3$ unless otherwise stated. The temperature studies were carried out in deuteriated xylene (*p*-xylene-*d10*).

6.2.4 Measurement of the Physical Properties of the Silanes.

6.2.4.1 Capacitance Measurements.

All capacitances were measured on a Genrad 1689 Precision RLC Digibridge, which was attached to a 30ml water-jacketed glass dielectric cell.

The compound under investigation was made up into 5, 4, 3, 2 and 1% v/v solutions in the chosen solvent (either 1,4 dioxane or cyclohexane). The capacitance was measured for the empty dielectric cell and at this point the digibridge was zeroed. The solution under investigation was then poured to fill the water-jacketed glass dielectric cell and allowed to equilibrate at the chosen temperature. For this experiment the selected working temperatures were 25 to 55^oC through 5^oC increments. Once the solution had settled at the chosen temperature the capacitance (pF) was read off from the digibridge. At all times great care was necessary in avoiding any disturbance to the leads and digibridge to minimise errors in the readings due to stray capacitance.

6.2.4.2 Kinetic Measurements (procedure for solvolytic analysis).

The solvolytic activity of the silanes was monitered via evolution of ethene gas with time. Two standard solvent media were used 70% aqueous ethanol and 5M H_2SO_4 in 50% aqueous methanol. For the study of the β-chloroethyl silane derivatives a variety of concentrations of aqueous ethanolic and aqueous 1,1,1-trifluoroethanol solvent media were used.

The apparatus for the measurement of the volume of ethene gas evolved is detailed below: A water manometer (total volume 250mls, 100cm^3 scale) was linked via a polypropylene tube (8 mm diameter) to one of the necks of a two-necked flat bottomed 200ml water jacketed vessel. 100 mls of the chosen solvent media and a magnetic flea were introduced through the second neck into the solvolysis vessel. The vessel was then closed to the atmosphere by sealing off the second neck with a suba-seal. The solvent was then stirred with a magnetic flea, and allowed to equilibrate at 30^oC (the standard temperature chosen). The manometer level was read prior to the introduction of the silane. The silane was introduced into the solvent system by injection through the suba-sealed second neck of the vessel. Immediately upon injection of the silane the volume level of the manometer was taken and then read again at regular intervals with time until no discernable change could be observed.

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APPENDIX

Quick Basic Computer Program for the Calculation of Dipole Moments of Polymer Conformations (assuming rotational bond angles of 0°, 120° & 240°):

```
DECLARE SUB MATMUL (A(), B(), C(), AI%, AJ%, BJ%)
DECLARE SUB EQUATE (A(), B(),  AII%, AJJ%)

10   REM DIPOLE MOMENT OF POLYMER CONFORMATIONS
20   DIM TO(3, 3), T120(3, 3), T240(3, 3)

25   DIM E3(3, 3), TPROD(3, 3), TB(3, 3), TEMP(3, 3)
30   DIM VEC(20, 3)

50   REM  INITIALISATION
60   RAD = .0174533#  'conversion factor for degrees to radians
200  REM  FILL THE TRANSFORMATION MATRICES
210  REM  T0, T120 AND T240

230  THETA = 70.5 * RAD: PHI = 0: CT = COS(THETA): ST = SIN(THETA): REM
232  SP = SIN(0):  CP = COS(0)
240  T0(1, 1) = CT:          T0(1, 2) = ST:            T0(1, 3) = 0
250  T0(2, 1) = ST * CP:     T0(2, 2) = -CT * CP:      T0(2, 3) = SP
260  T0(3, 1) = ST * SP:     T0(3, 2) = -CT * SP:      T0(3, 3) = -CP

270  PHI = 120 * RAD:     SP = SIN(PHI):        CP = COS(PHI)
280  T120(1, 1) = CT:          T120(1, 2) = ST:           T120(1, 3) = 0
290  T120(2, 1) = ST * CP:     T120(2, 2) = -CT * CP:     T120(2, 3) = SP
300  T120(3, 1) = ST * SP:     T120(3, 2) = -CT * SP:     T120(3, 3) = -CP

310  PHI = 240 * RAD:     SP = SIN(PHI):        CP = COS(PHI)
320  T240(1, 1) = CT:          T240(1, 2) = ST:           T240(1, 3) = 0
330  T240(2, 1) = ST * CP:     T240(2, 2) = -CT * CP:     T240(2, 3) = SP
340  T240(3, 1) = ST * SP:     T240(3, 2) = -CT * SP:     T240(3, 3) = -CP
350  REM

360  REM  FILL IDENTITY MATRIX E3
370  FOR I = 1 TO 3
380  FOR J = 1 TO 3
390  E3(I, J) = 0
400  NEXT J:  NEXT I
410  FOR I = 1 TO 3: E3(I, I) = 1: NEXT I

490  CLS
```

```
500  PRINT "NUMBER OF SKELETAL BONDS   ";
510  INPUT NB

520  CLS
530  PRINT
540  PRINT "INPUT X,Y,Z COMPONENTS OF VECTOR FOR ";
550  PRINT
560  FOR I = 1 TO NB
570  PRINT "BOND  ";  I;:INPUT"  (X,Y,Z <RETURN.)"; VEC(I, 1), VEC(I, 2),
     VEC(I, 3)
580  NEXT I

590  REM
600  CLS : PRINT : PRINT "BOND ROTATIONAL ANGLES" : PRINT
610  PRINT "INPUT BOND ROTATIONAL ANGLE (0, 120 OR 240 ONLY) FOR
     ": PRINT
620  FOR I = 2 TO NB - 1
630  PRINT "BOND "; I; "    ";  :  INPUT PHI%(I)
640  NEXT I
642  PHI%(1) = 0

650  XT =VEC(1, 1):  YT = VEC(1, 2):  ZT =VEC(1, 3)

710  REM  FORM SERIAL PRPDUCTS OF TRANSFORMATION
720  REM  MATRICES & CALC. NEW VECTORS IN THE
730  REM  COORDINATE SYSTEM OF BOND 1

760  CALL EQUATE(TEMP(), E3(), 3, 3):  REM TEMP() = IDENTITY

775  REM
780  FOR II = 1 TO NB - 1
782  K = II + 1
785  'ASSIGN TRANSFORMATION MATRIX TO TB, I.E., TB()=
T0,T120,T240()
790  IF PHI%(II) = 0 THEN CALL EQUATE(TB(), T0(), 3, 3):  GOTO 1000
800  IF PHI%(II) = 120 THEN CALL EQUATE(TB(),T120(),3,3):  GOTO 1000

1000 CALL MATMUL(TEMP(), TB(), TPROD(), 3, 3, 3):
       REM TPROD()=TEMP()*TB()

1010 X = TPROD(1,1)*VEC(K,1)+TPROD(1,2)*VEC(K,2)+
         TPROD(1,3)*VEC(K,3)
```

```
1020  Y = TPROD(2,1)*VEC(K,1)+TPROD(2,2)*VEC(K,2)+
          TPROD(2,3)*VEC(K,3)
1030  Z = TPROD(3,1)*VEC(K,1)+TPROD(3,2)*VEC(K,2)+
          TPROD(3,3)*VEC(K,3)
1040  XT = XT + X:  YT = YT +Y:  ZT = ZT +Z  'UPDATE VECTOR
COMPONENTS
1050  CALL EQUATE(TEMP(), TPROD(), 3, 3): 'UPDATE TEMP,
TEMP()=TPROD()
1055  NEXT II
1060  U = SQR(XT * XT + YT * YT + ZT * ZT): 'CALCULATE DIPOLE
MOMENT

1070  REM
1080  REM PRINT  THE  RESULTS
1090  CLS
1100  PRINT "DIPOLE MOMENT OF POLYMER CONFORMATION"
1110  PRINT "& COMPONENTS EXPRESSED IN COORDINATE"
1120  PRINT "SYSTEM OF THE FIRST BOND IN THE CHAIN"
1130
1140  PRINT "FOR THE CONFORMATION":  PRINT
1150  FOR I = 1 TO NB
1160  IF PHI%(I) = 0 THEN PRINT "T "; : GOTO 1190
1170  IF PHI%(I) = 120 THEN PRINT "G "; : GOTO 1190
1180  PRINT "G' "; :
1190  NEXT I
1200  PRINT:  PRINT
1210  PRINT "THE DIPOLE MOMENT IS ";
1220  PRINT INT(1000*U)/1000;"  DEBYES (";  (1000*U*3.3357)/1000;"=
          Coulomb metre)":  PRINT
1230  PRINT :  PRINT " Components of molecular dipole moment are:-":  PRINT
1231  PRINT "X= "; INT(1000*XT)/1000;" D "; TAB(30); INT(1000*XT)/1000
          * 3.3357; " x 10-30 Cm"
1232  PRINT "Y= "; INT(1000*YT)/1000;" D "; TAB(30); INT(1000*YT)/1000
          * 3.3357; " x 10-30 Cm"
1234  PRINT "Z= "; INT(1000*ZT)/1000;" D "; TAB(30); INT(1000*ZT)/1000
          * 3.3357; " x 10-30 Cm"

1240  PRINT "  PRESS A KEY TO CONTINUE";
1250  K$ = INKEY$:  IF K$ = "" THEN 1250
1260  CLS
1270  PRINT " RESET ROTATIONAL BOND ANGLE ? (Y/N)";
1280  K$ = INKEY$:  IF K$ = "" THEN 1280
1290  IF  K$ = "Y" OR K$ = "y" THEN GOTO 600
```

```
1295  IF  K$ = "N" OR K$ = "n" THEN GOTO 1320
1300  GOTO 1280
1310  PRINT
1320  CLS
1325  PRINT " NEW CHAIN LENGTH ? (Y/N) ";
1330  K$ = INKEY$:  IF K$ = "" THEN 1330
1340  IF  K$ = "Y" OR K$ = "y" THEN GOTO 490
1350  IF  K$ = "N" OR K$ = "n" THEN END
1355  GOTO 1330
1360  CLS
1370  END

SUB  EQUATE  (A(), B(), AII%, AJJ%)
'
'A MATRIX SUBROUTINE TO EQUATE ONE MATRIX TO ANOTHER
'
FOR I = 1 TO AII%
        FOR J = 1 TO AJJ%
                A(I, J) = B(I, J)
        NEXT J
NEXT I

END SUB

SUB  MATMUL  (A(), B(), C(), AI%, AJ%, BJ%)
'
' Performs  the  matrix  multiplication
'
'                    C = A x B
'
'where  A  is  a  matrix  of  NROW%  rows  and  NCOL%  columns
'where  B  is  a  matrix  of  NROW%  rows  and  NCOL%  columns
FOR I = 1 TO AI%
        FOR K = 1 TO BJ%
                CIK = 0
                FOR J = 1 TO AJ%
                        CIK = CIK + A(I, J) * B(J, K)
                NEXT J
                C(I, K) = CIK
        NEXT K
NEXT I
END SUB
```