

POLYTRICHLOROSILYLSTYRENES

**POLYTRICHLOROSILYLSTYRENES: EXPLOITING THE β -EFFECT
FOR POLYMER SYNTHESIS.**

By

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vii
ABSTRACT	viii
INTRODUCTION	1
1.1 Relative bond strengths	1
1.2 Relative electronegativity	2
1.2.1 Cleavage of silicon-oxygen and silicon-carbon bonds	3
1.3 <i>d</i> -Orbitals	6
1.4 The β -effect	6
1.5 Ab initio calculation	11
1.6 Electrophilic substitution	11
1.6.1 Stereospecificity in electrophilic substitution reactions of vinyl silanes	13
1.7 Electrophilic substitution with other classes of silanes	15
1.7.1 Stereochemistry	17
1.8 Factors influencing the β -effect of silicon	18
1.8.1 Effect of coordination state of Si on β -effect	18
1.8.2 Effect of ligands on Si on β -effect	20
1.9 Addition of electrophiles	24
1.9.1 Friedel-Crafts acylation	24
1.9.2 Friedel-Crafts alkylation	24
RESULTS AND DISCUSSION	26
2.1 Synthesis of the starting materials	26
2.2 Addition of proton to β -trichlorosilylstyrene	28
2.2.1 Lewis acids as proton source	29
2.2.2 Brønstedt acids as proton source	31
2.2.3 Triflic acid as a protonic acid	33
2.3 Oligomerization of β -trichlorosilylstyrene	33
2.4 Structure of the oligomers	34
2.5 Mechanism of oligomerization	37
2.6 Modification of the basic reaction	40
2.6.1 Oligomerization of β -dichloromethylsilylstyrene	40
2.7 Methoxylation of oligomeric chlorosilylstyrenes	42
2.8 Stereochemistry	43
2.9 Degree of polymerization (DP)	45
2.9.1 Effect of reaction conditions on DP	45
2.10 Attempted polymerization with other catalysts	47
2.10.1 Using $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$	47
2.10.2 Free radical polymerization	48
2.11 Copolymerization of styrene with β -trichlorosilylstyrene	49
CONCLUSION	50
EXPERIMENTAL	51
3.1 General remarks	51

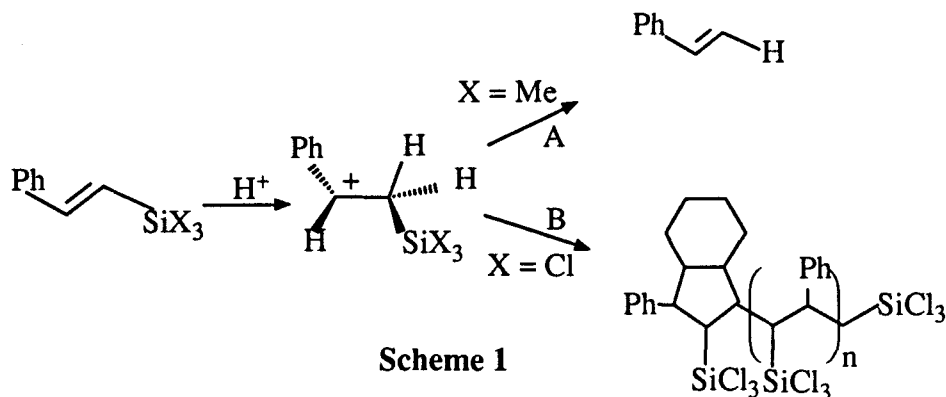
3.2	Hydrosilylation of phenyl acetylene	52
3.3	Polymerization of silylstyrenes	53
3.4	Permethylation of silylstyrene polymer	53
3.5	Separation of permethylated polymer	54
3.5.1	Separation of permethylated β -trichlorosilylstyrene polymer	54
3.5.2	Separation of permethylated β -dichlorosilylmethyl -silylstyrene polymer	55
3.6	Polymerization of β -trichlorosilylstyrene under different reaction conditions	56
3.6.1	Polymerization at different temperatures	56
3.6.2	Polymerization at different monomer concentrations	56
3.6.3	Polymerization using different solvents	57
3.6.4	Polymerization using different catalyst concentrations	58
3.7	Attempted radical polymerizations	58
3.7.1	Using di- <i>t</i> -butyl peroxide	58
3.7.2	Using 2,2'-azo bis isobutyronitrile (AIBN)	58
3.8	Other attempted cationic polymerizations	58
3.8.1	Using tetrafluoroboric acid [HBF ₄ .(OCH ₃) ₂]	59
3.8.2	Using [Pd(CH ₃ CN) ₄](BF ₄) ₂	59
3.9	Methoxylation of silylstyrenes	59
3.10	Attempted polymerization of β -trimethoxysilylstyrene	60
3.11	Methoxylation of β -trichlorosilylstyrene oligomers	60
3.12	Copolymerization of β -trichlorosilylstyrene with styrene	60
3.13	Permethylation of the copolymer	60
REFERENCES		61

LIST OF TABLES

	Page
Table 1. Approximate bond dissociation energies (D) and bond lengths (r) for Si-X and C-X	1
Table 2. Relative electronegativity	2
Table 3. Electron releasing effect of the Me₃Si-C moiety	3
Table 4. Comparison of <i>syn/anti</i> ratio of group electronegativity	23

ABSTRACT

Trimethylsilylstyrenes undergo protodesilylation (Scheme 1, path A), *via* the β -silyl carbonium ion under acidic conditions. In contrast, the corresponding trichlorosilyl substituted compound was found to undergo an oligomerization reaction (Scheme 1, path B) with triflic acid as the catalyst.



The β -effect [$(\sigma\text{-p})\pi$ overlap] may play a significant role in the weakening of the silicon-carbon bond and thus promote the cleavage process, as is observed in scheme 1, path A. Introduction of electronegative chloro groups on silicon weakens the β -effect and hence the silyl leaving group ability, resulting in oligomerization of the styrene (Scheme 1, path B).

In this oligomerization reaction, chain termination by an internal Friedel-Crafts reaction competes with the chain propagation. As a result, indane terminated low molecular weight oligomers are formed. The case is similar to β -methylchlorosilylstyrene, with the only difference that here *ca.* 20% desilylation has occurred, again reflecting the fact that subtle changes in the β -effect can influence the course of electrophilic reactions.

Introduction

The use of silicon containing materials in organic chemistry has dramatically increased over the last 20 years. An overview of the field of organosilicon chemistry would show that in the last several decades the commercial synthesis of organosilicon products has increased substantially, both in annual production and also in the increasing variety of compounds produced. This increase in the number of commercially available carbon-functional organosilicon compounds and their polymers (silicone polymers) is most remarkable and is occurring because new applications are continually being found for these compounds.

Silicon's utility in organic synthesis depends on three main factors: its relative bond strengths to other elements, its relative electronegativity, and the involvement or lack of involvement of its valence *p* and empty *d* orbitals.

1.1 Relative bond strengths

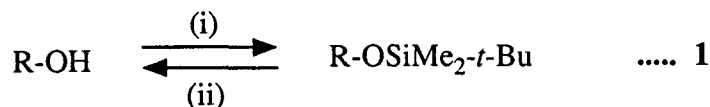
Table 1 indicates the approximate dissociation energies for Si-X and C-X bonds^(1,2).

Table 1. Approximate bond dissociation energies (*D*) and bond lengths (*r*) for Si-X and C-X.

Bond	<i>D</i> /kJ mol ⁻¹	<i>r</i> /nm	Bond	<i>D</i> /kJ mol ⁻¹	<i>r</i> /nm
Si-C	318	0.189	C-C	334	0.153
Si-H	339	0.148	C-H	420	0.109
Si-O	531	0.163	C-O	340	0.141
Si-S	293	0.214	C-S	313	0.180
Si-N	320	0.174	C-N	335	0.147
Si-F	807	0.160	C-F	452	0.139
Si-Cl	471	0.205	C-Cl	335	0.178
Si-Br	403	0.221	C-Br	268	0.194
Si-I	322	0.244	C-I	213	0.214

The energies given in Table 1 are those for the homolytic fission. So these values do not give the

actual picture of the normal mode of behaviour, which is heterolytic fission. But still certain significant generalities can be drawn. In particular, silicon's bonds to oxygen and fluorine are stronger than the corresponding bonds between carbon and these elements; at the same time its bonds to carbon and hydrogen are weaker. An application of these effects can be seen in the extensive use of silyl groups, especially the *t*-butyldimethylsilyl group, to protect hydroxy groups⁽³⁾ (Equation 1); it is easy to form an O-Si bond, but also easy to cleave it using the formation of an Si-F



(i) *t*-BuMe₂SiCl, imidazole, DMF, 35°C, 10h.

(ii) Bu₄N⁺F⁻, THF, 25°C, 40 min.

bond as the driving force.

1.2 Relative electronegativity

Regardless of the scale used, silicon always appears markedly more electropositive than carbon (Table 2), resulting in

Table 2. Relative electronegativity⁽⁴⁾

H	B	C	N	O	F
2.79	1.84	2.35	3.1	3.5	4.0
	Al	Si	P	S	Cl
	1.4	1.64	2.1	2.5	2.8
		Ge	As	Se	Br
		1.69	1.99	2.4	2.52

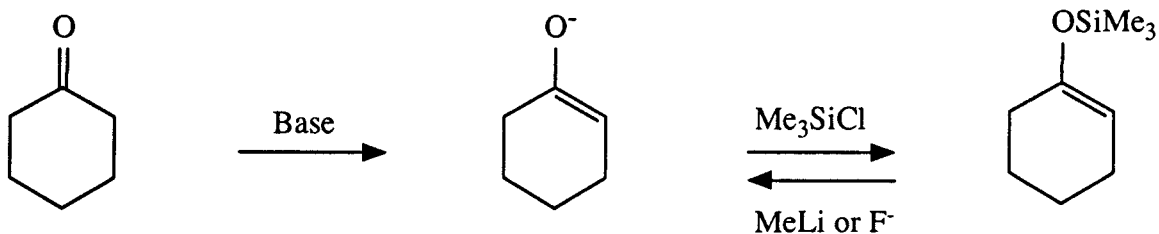
polarization of silicon-carbon bonds in the sense Si^{δ+}-C^{δ-}, and for nucleophilic attack to occur at silicon. Silicon bond polarization must be seen in perspective, however. Silicon's bond to carbon,

for example, while certainly polarized, is only weakly so when compared with those of other organometallic compounds. In general, organosilicon compounds can be handled readily, without the necessity for inert atmospheres or moisture exclusion (except for the halides). Indeed, this is one of the great benefits of organosilicon compounds. Carbon-silicon bonds can withstand a wide variety of reaction conditions and reagents, although they have a latent lability. Reactions such as catalytic hydrogenation, hydroboration, hydroalumination, alcohol halogenation and free radical halogenation, alcohol oxidation and reduction, epoxidation, base induced and organometallic nucleophilic addition reactions have all been performed on carbon-silicon compounds without C-Si bond cleavage⁽³⁾ (provided you have tetra alkyl Si).

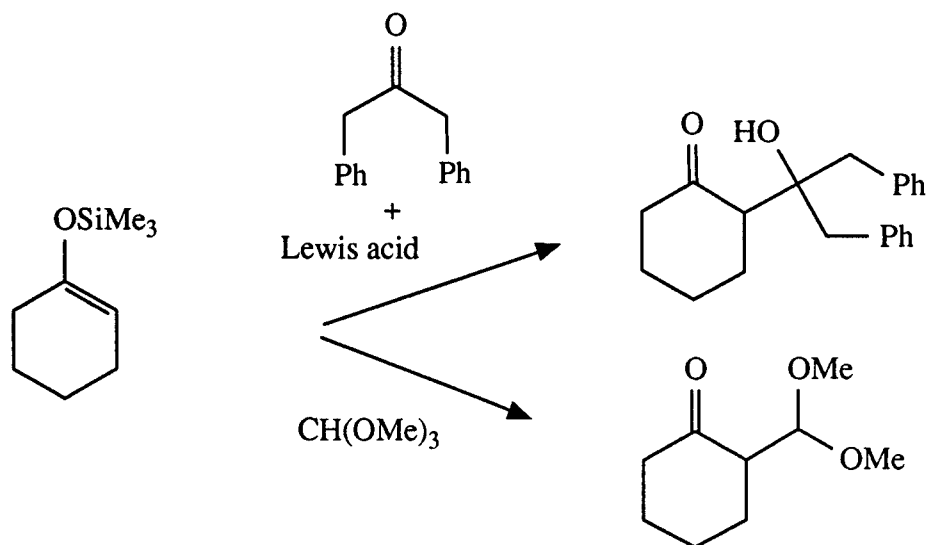
1.2.1 Cleavage of Silicon-Oxygen and Silicon-Carbon bonds

Since O-H bonds formally dissociate in the same direction, $O^{\delta-}H^{\delta+}$, as do O-Si bonds, $O^{\delta-}Si^{\delta+}$, a good indication of the likely behaviour of a Si-O bond can be predicted by consideration of an analogous O-H bond. In the case of oxygen-silicon compounds, the silyl group functions as a substitute for the proton of an alcohol or enol. Like a proton, a silyl group is easy to put on and take off, yet the Si-O bond is slower to break than the corresponding O-H bond. Therefore, the silyl group is like a nonlabile proton, in silicon-oxygen chemistry.

Silyl enol ethers, for example, act as the most easily made derivatives of enols; they can be used either as the precursors of enolates (Scheme 2(a)) or in their own right as versatile carbon nucleophiles (Scheme 2(b)), duplicating and extending much of the enolate chemistry.

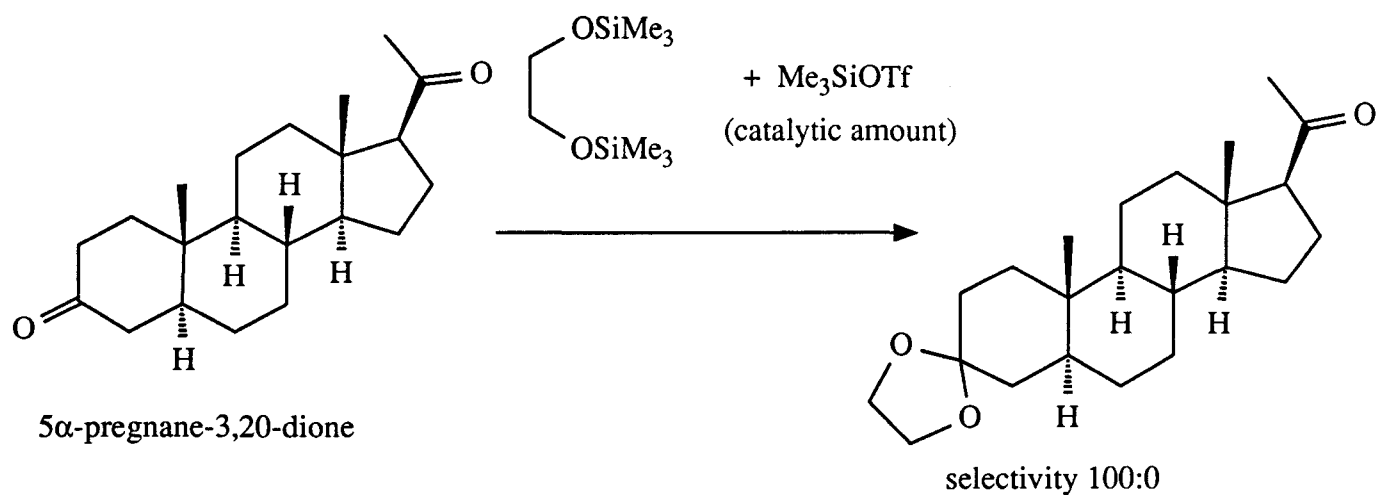


Scheme 2(a)



Scheme 2 (b)

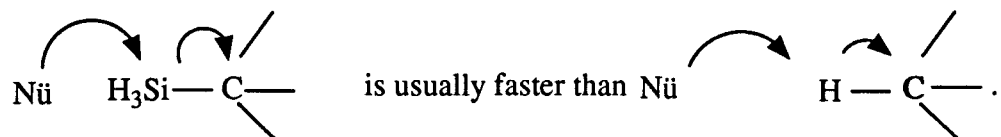
Hwu and his co-workers⁽⁵⁾ have shown that Me₃Si⁺ can be regarded as a "bulky proton". Trimethylsilyltrifluoromethane sulfonate and 1,2-bis[(trimethylsilyl)oxy] ethane (BTSE), the so called "bulky proton" containing reagents can be used to ketalize or acetalize compounds containing two nonconjugated carbonyl groups or one nonconjugated and one α,β -unsaturated carbonyl groups to give with high selectivity, monodioxolanes bearing the ketal or acetal function at the less sterically hindered site (Scheme 3).



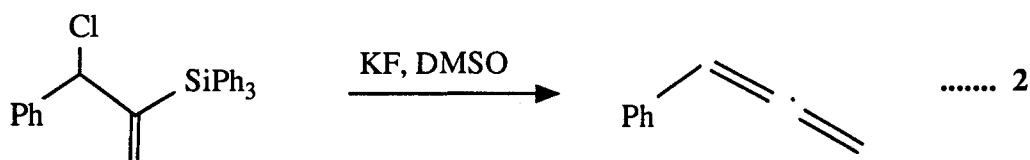
Scheme 3

In much of the chemistry of compounds having a silicon-carbon bond, the silyl group again

functions as a substitute for a proton. But this time, the silicon-carbon bond usually breaks more easily than the corresponding hydrogen-carbon bond (in the presence of oxygen or halogen nucleophiles/bases).

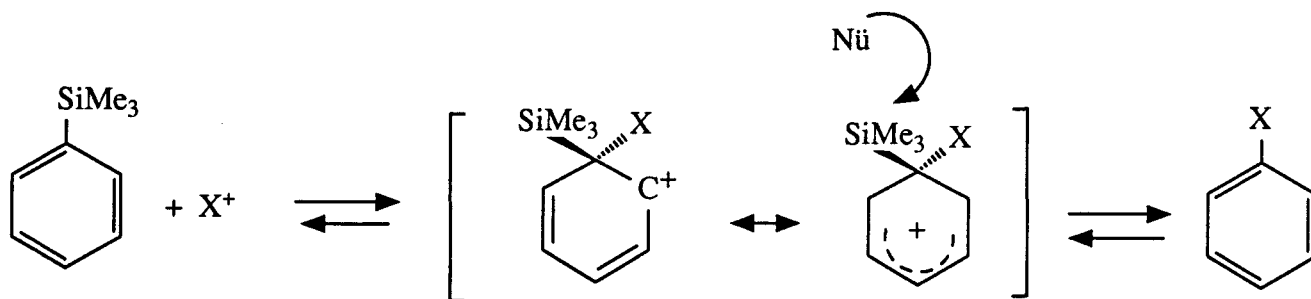


Thus, Chan and his co-workers⁽⁶⁾ have used the β -elimination of haloalkylsilanes to give allenes and allene oxides (Equation 2). On carbon, therefore, a silyl group far from being like a rather feeble



proton, as it is on oxygen, is better thought of as a sort of superproton⁽⁷⁾.

A more potent example of this is the reaction of arylsilanes with electrophiles. Just as Ar-H bonds are cleaved by electrophiles such as Br_2 , so are Ar-Si bonds. Eaborn and others^(1a,8) have shown that such cleavages occur by the same mechanism (Scheme 4) as that of electrophilic aromatic substitution.



Scheme 4

Electrophilic attack occurs at the ring carbon carrying the silyl group, i.e., at the ipso position, because of the stabilization offered to an adjacent carbonium ion by the carbon-silicon bond (the β -effect, which will be discussed in detail later). This additional stabilization can be seen in the observation that aryltrimethylsilanes undergo protodesilylation 10^4 times faster than do the parent arenes undergo hydrogen exchange. Similarly, phenyltriethylsilane is hydrolysed by dilute aqueous

acid to benzene 10^4 times more rapidly than the all-carbon analogue, *t*-heptylbenzene, is hydrolysed.

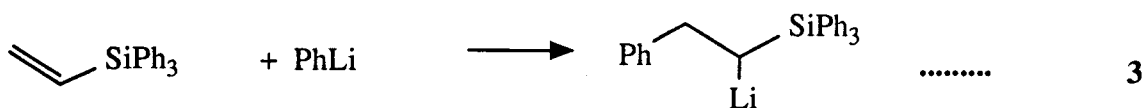
1.3 *d*-Orbitals

Organic compounds of silicon are normally tetravalent, with silicon making sp^3 -hybridized bonds. This is in spite of silicon differing from carbon in having vacant *d*-orbitals, with the outer electronic configuration $3s^23p^23d^0$. Certain physical and chemical properties of organosilicon compounds raise the question of possible involvement of these vacant *d*-orbitals. The three main areas of interest which involve possible *d*-orbital participation are the formation of additional σ -bonds, the stabilization of reaction intermediates and transition states, and the formation of internal π -bonds.

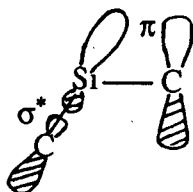
One of the best studied examples of octet expansion is the hexafluorosilicate ion, SiF_6^{2-} ; an X-ray crystallographic analysis⁽⁹⁾ revealed that the six fluorine atoms are arranged octahedrally about silicon, implying $3sp^3d^2$ -hybrid bonds. Sommer's studies⁽¹⁰⁾ on chiral silicon compounds have shown that S_N2 reactions at silicon are often extremely fast, and often proceed with retention of stereochemistry. It is reasonable to propose that the involvement of *d*-orbitals will lower both those transition state energies involved in frontal attack (resulting in retention via a pentacoordinate intermediate) and those involved in backside attack (resulting in inversion); these observations are at least consistent with *d*-orbitals taking part in transition state development.

1.4 The β -effect

Silicon has been found to stabilize a negative charge α - to it and a positive charge β - to it. The former one is called the α -effect and the latter one is the β -effect of silicon. This means that silyl substituents behave in a dichotomous manner, showing the properties of both electron donor and acceptor groups. One of the best examples to illustrate the α -effect is the organometallic addition to vinylsilanes⁽²⁾ (Equation 3).



The proposed mechanism for this α -effect is $(\sigma^*-p)\pi$ back donation (Scheme 5).



Scheme 5

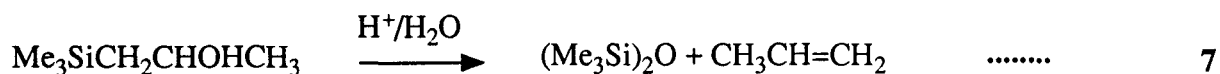
The polarization of C-Si bond in the direction $\text{C}^{\delta-}\text{-Si}^{\delta+}$ ensures a relatively high coefficient on Si in the σ^* level, which enhances the stabilizing effect of such overlaps.

However, due to the synthetic utility and versatility, much more work in organosilicon chemistry has been done in the area of β -functional organosilicon compounds. The exceptional reactivity of the β -halogenoalkylsilanes $\text{R}_3\text{SiCH}_2\text{CH}_2\text{X}$ was originally noted by Ushakov and Itenberg⁽¹¹⁾; subsequently Sommer, Whitmore and their coworkers^(12,13) showed that the β -halogenoalkylsilanes are generally much more reactive than either the α - or γ -substituted compounds towards heat, basic reagents, aluminum chloride and Grignard reagents. The general reaction involved with all of these reagents is elimination of silyl halide and the formation of an olefin (Equation 4-6).



Likewise the β -hydroxyalkyltrialkylsilanes $\text{R}_3\text{SiCH}_2\text{CH}_2\text{OH}$ undergo decomposition with evolution of olefin when treated with dilute acid⁽¹⁴⁾(Equation 7).

The β -ketosilanes⁽¹⁵⁾ $\text{R}_3\text{SiCH}_2\text{COR}'$ and esters⁽¹⁶⁾ of the type $\text{R}_3\text{SiCH}_2\text{COOR}'$ are readily cleaved by nucleophilic and electrophilic reagents (Equation 8 and 9).



Cyano groups have much the same effect as carbonyl groups in promoting cleavage of the silicon carbon bond⁽¹⁷⁾(Equation 10).



Similarly, allylsilanes, $\text{R}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ and benzyl silanes $\text{R}_3\text{SiCH}_2\text{-C}_6\text{H}_5$ show high reactivity towards electrophilic reagents⁽⁸⁾.

The strong electron releasing effect of the $\text{Me}_3\text{Si-C}$ moiety can also be seen in the relative strengthening of aliphatic amine bases^(18,19) and the weakening of carboxylic acids⁽²⁰⁾(Table 3).

Table 3. Electron releasing effect of the $\text{Me}_3\text{Si-C}$ moiety

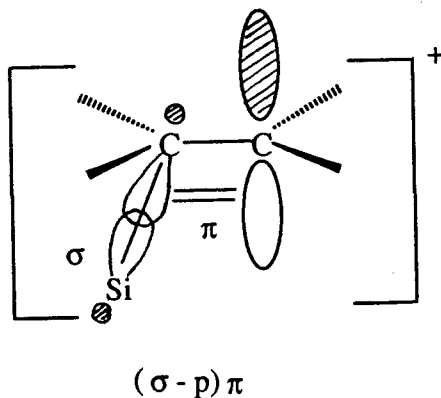
Silicon species	pK _a at 25°C	Carbon species	pK _a at 25°C
$\text{Me}_3\text{Si-CH}_2\text{NH}_2$	10.96	$\text{Me}_3\text{C-CH}_2\text{NH}_2$	10.21
$\text{Me}_3\text{Si-CH}_2\text{COOH}$	5.22	$\text{Me}_3\text{C-CH}_2\text{COOH}$	5.0

All these observations led to an interest in the behaviour of β -functional organosilicon compounds and their abnormal properties have been explained in terms of, (i) inductive effects; (ii) 1,3, and 1,4 interactions between unshared pairs on heteroatom substituents and the vacant silicon *d*-orbitals [*(p-d)* σ bonding]; (iii) the carbon-silicon hyperconjugation; and (iv) various combinations

of these. In recent years it has become more common to attribute any abnormal properties of β -functional organosilicon compounds to $(\sigma-p)\pi$ conjugation.

It was originally suggested by Nesmeyanov⁽²¹⁾ that metal-carbon hyperconjugation might strongly influence the reactivity and properties of organometallic compounds. Subsequently Eaborn⁽²²⁾ proposed that silicon-carbon hyperconjugation might account for the observed properties of β -functional organosilicon compounds. Bock and Alt⁽²³⁾ have provided considerable support for Eaborn's original proposal.

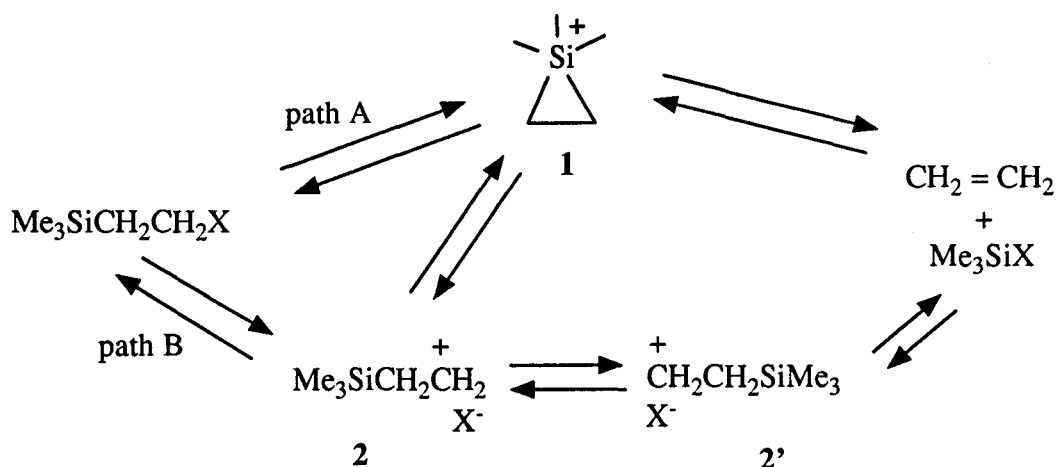
This proposed $(\sigma-p)\pi$ hyperconjugation occurs by the overlap of the bonding σ level of the C-Si bond (which will have a relatively high coefficient on carbon owing to its greater electronegativity) with the adjacent empty p orbital of the carbonium ion (Scheme 6); owing to the higher energy of the C-Si bond, there is a better energy match, and therefore greater overall lowering in energy for this π overlap than that would be obtained from similar C-C or C-H σ bond hyperconjugation.



Scheme 6

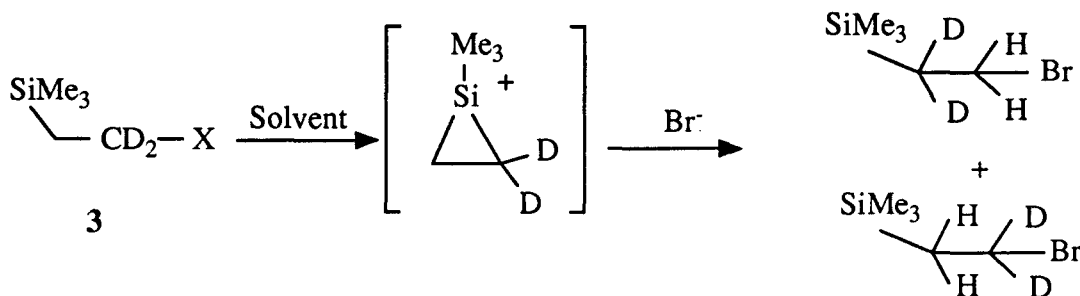
The β -elimination reactions of β -functional organosilicon compounds are well studied and the interesting role of Si appears to parallel that of unsaturated or lone-pairs bearing substituents in achimeric assistance⁽²⁴⁾. Scheme 7 depicts two mechanistic possibilities.

In path A, silicon serves as a true internal nucleophile, engaging in nonvertical participation, to form the siliconium (pentavalent) intermediate **1**. In path B, silicon provides stabilization of the β -positive charge without nuclear movement (vertical stabilization) by means of hyperconjugation. In addition, since silicon is electropositive with respect to carbon, the Me_3Si group can stabilize



Scheme 7

either pathway in Scheme 7 via induction. Eaborn⁽²⁵⁾ has shown that in the case of deuterated silane **3** the deuterium is scrambled between α - and β -position in the recovered β -bromosilanes (Scheme 8) which supports path A in Scheme 7.

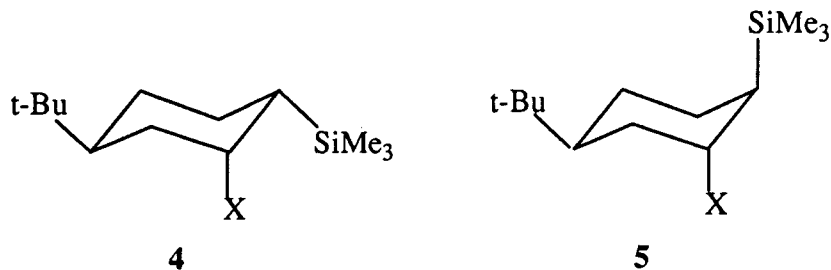


Scheme 8

Even though Lambert *et al*'s⁽²⁶⁾ studies on solvolysis reactions showed that solvent dependence of the rate and of the stereoselectivity favours both siliconium ion **1** and carbonium ion **2** as intermediates, hyperconjugation seems to be the most widely accepted description for β -effect over anchimeric assistance. Very recently, Li and Stone⁽²⁷⁾ based their studies on the enthalpies of binding of ethene and substituted ethenes to Me_3Si^+ . Their work has shown that a changeover takes place from the bridged structure (siliconium ion **1**), for ethylene, to the more classical open structure (carbenium ion **2**) for the substituted alkenes.

1.5 Ab initio calculation

Ab initio calculations of the β -silicon effect on carbonium ions have been done by Jorgensen *et al*⁽²⁸⁾. Their ab initio molecular orbital calculations shows that the influence of a β -SiH₃ group is pronounced for the cations providing 22.1 and 15.9 kcal/mol stabilization for the secondary and tertiary alkyl species relative to hydrogen, while the corresponding stabilization energies for a β -methyl substituent are 6.6 and 5.0 kcal/mol. The β -effect is predominantly due to Si-C hyperconjugation and is correspondingly conformation dependent, which is evident from the fact that for the secondary cyclopropyl cations, the β -silicon effect is diminished to 17.5 kcal/mole due to the less optimal orbital alignment. Inductive and polarization effects represent a relatively minor contribution to the overall β -stabilization. Lambert's solvolytic data⁽²⁴⁾ for **4** and **5** show this orientational effect conclusively. They found that **5** reacts 10¹² times faster than

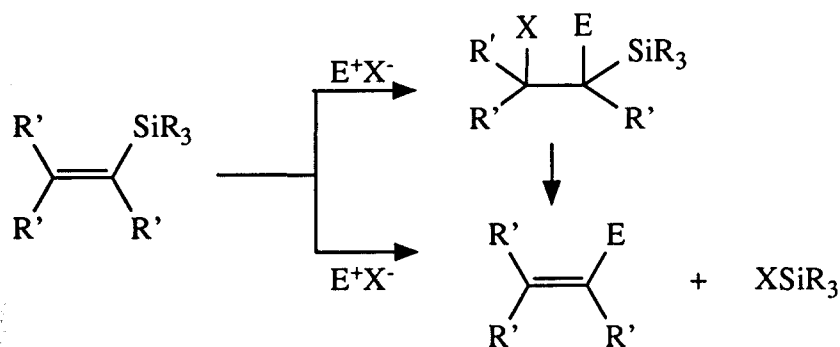


cyclohexyltrifluoroacetate and **4**, 10⁴ times faster. From their analyses, Lambert *et al* concluded that hyperconjugation is responsible for 10¹⁰ of the 10¹² acceleration for **5** and 10² of the 10⁴ for **4**, while both solvolyses benefit by a factor of 10² from induction. The difference in activation energies for the solvolyses of **5** and cyclohexyltrifluoroacetate was calculated to be 18 kcal/mol. The small discrepancy between theory and experiment can be attributed to the detailed differences between the system and conditions that have been studied.

1.6 Electrophilic Substitution

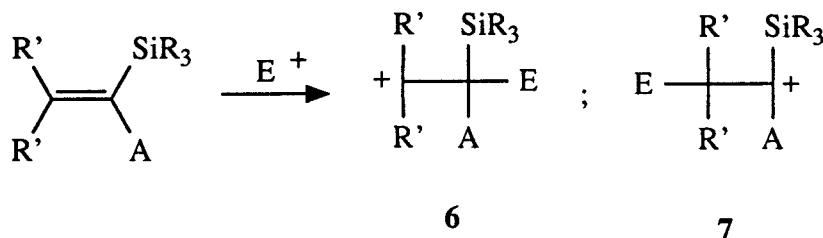
In the reaction of electrophiles with vinylsilanes, addition to the double bond and substitution are both possible (Scheme 9).

The addition product can subsequently undergo elimination either thermally or on treatment with a good nucleophile for silicon, such as fluoride ion; the overall reaction is then again substitution.



Scheme 9

The presence of silicon often directs the attack of the electrophile to the atom to which the silicon is bound, perhaps by the way of the intermediate **6** (scheme 10).

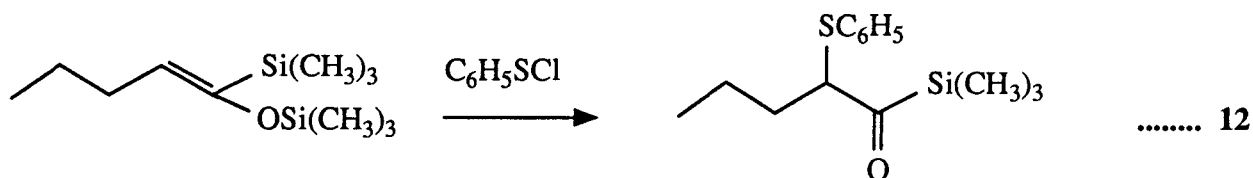
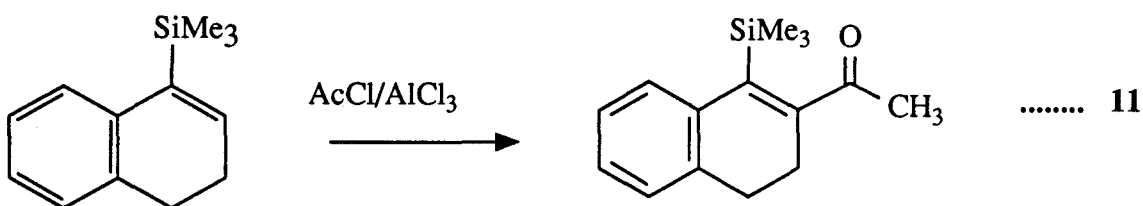
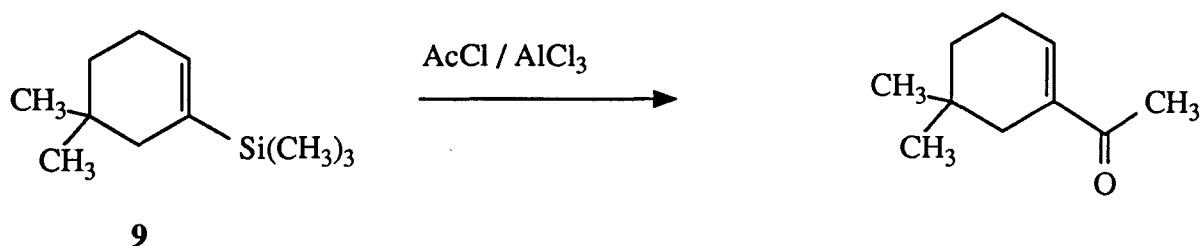
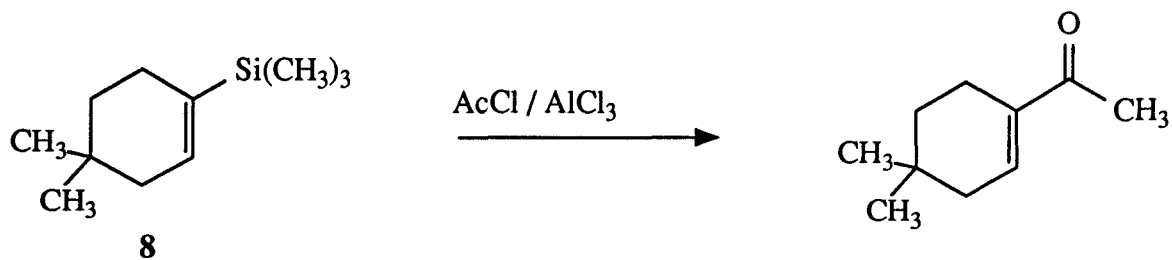


Scheme 10

The formation of such a cation instead of the isomeric cation **7** is due to the stabilizing ability of the neighbouring Si-C bond (β -effect). It is possible that the $(\sigma\text{-}\rho)\pi$ overlap (β -effect) may play a significant part in the weakening of the silicon-carbon bond and thus promote the cleavage processes leading to substitution products rather than addition in most of the cases. Thus, other things remaining the same, an electrophile will attack an alkenylsilane at the site where the silicon is placed, as illustrated by the reactions of the isomeric silanes **8** and **9**⁽²⁹⁾.

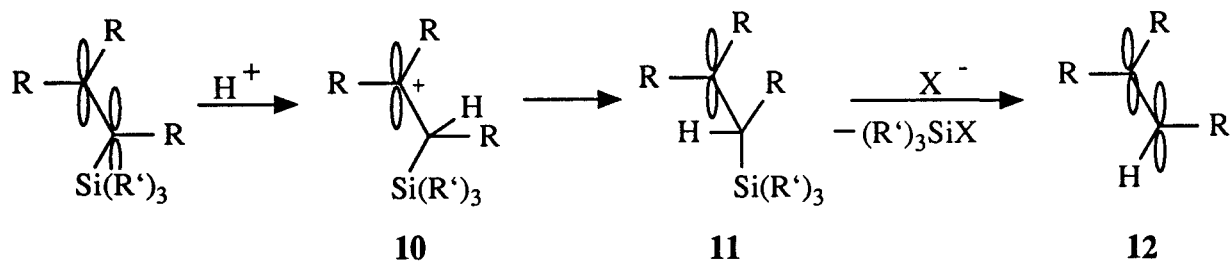
However, if the alkenylsilane has an additional group A (A in **7**) which can stabilize the cationic intermediate **7** better than silicon stabilizes the intermediate **6**, then the direction of electrophilic attack will be determined by the group A and not by the silyl group. This is the case when A is a phenyl group or a trimethylsiloxy group⁽³⁰⁾(Equation 11 and 12).

1.6.1 Stereospecificity in electrophilic substitution reactions of vinylsilanes



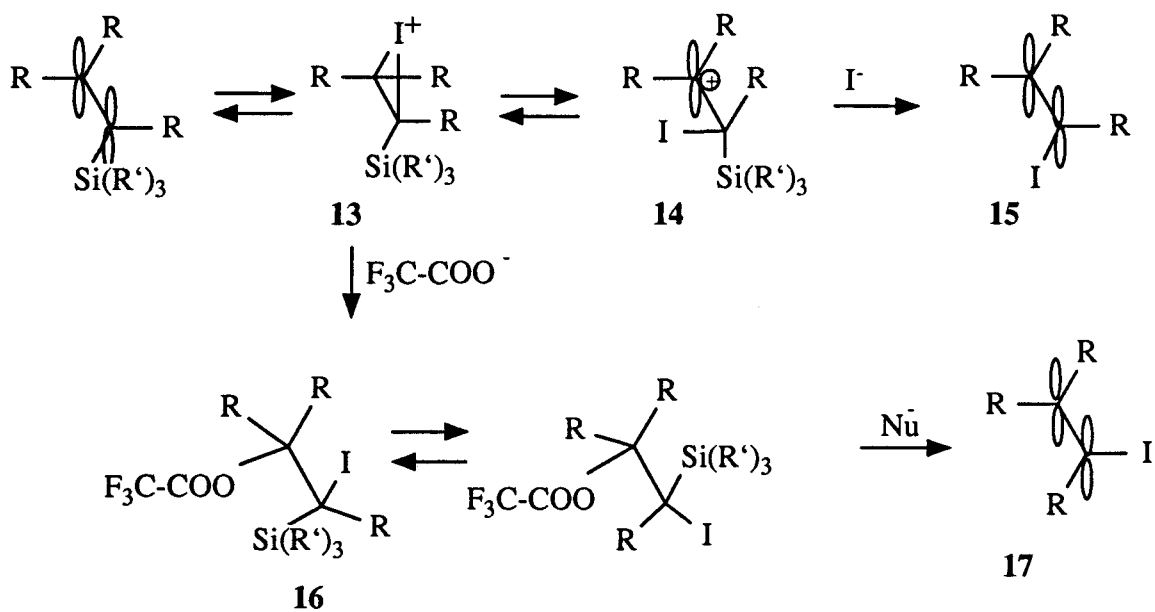
The replacement of the silyl group in an alkenylsilane by an electrophile often takes place stereospecifically. The stereochemical outcome, retention or inversion, depends, however, on the electrophile as well as on the reaction conditions. With a proton as the electrophile, retention of configuration occurs in all cases. The stereospecific nature of the reaction was first demonstrated by Koenig and Weber⁽³¹⁾ who showed that (Z)- and (E)- β -trimethylsilylstyrene were converted to (Z)- and (E)- β -deuterostyrene by deuterium chloride or bromide with complete retention of stereochemistry. A mechanism to account for the retention of stereochemistry was proposed by

Koenig and Weber (Scheme 11). Once the double bond is protonated, the central carbon-carbon bond rotates, **10** \rightarrow **11**, presumably by the shortest path in the direction where the empty *p*-orbital



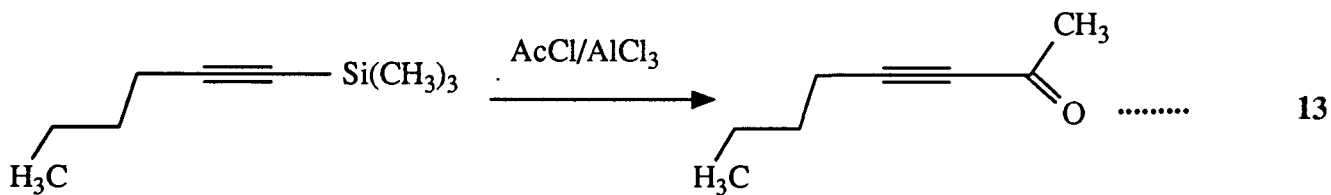
Scheme 11

and the C-Si σ bond are coplanar to each other, which allows the $-\text{Si}(\text{R}')_3$ group to stabilize the incipient β -carbocation (hyperconjugation). If the nucleophile attacks on silicon, **11** \rightarrow **12**, before any further rotation takes place, then the olefin will be formed with retention of configuration. Such a mechanism similarly accounts for the retention of configuration observed for Friedel-Crafts acylation of allenylsilanes to give α,β -unsaturated carbonyl compounds⁽³²⁾. With halogens as electrophiles, the stereochemical results are more complicated (Scheme 12). This is because of the nucleophilicity of the halide ions, and hence their ability to open a bridged halonium ion intermediate. For example, with iodine as the electrophile, the first step may well be the attack of iodine on the double bond to give reversibly the intermediate **13**. Iodide as the only available counterion, is not likely to lead to the unstable diiodo adduct, instead **13** will rotate to give **14**, whereupon elimination can take place to give the iodoalkane **15** with retention of configuration. Thus the stereochemistry with iodine is the same as that of the protodesilylation reaction. If, however, other counter ions such as trifluoroacetate⁽³³⁾ or chloride ions⁽³⁴⁾ are available, then the addition product **16** can be isolated. The formation of **16** is stereospecific with *anti*-addition (and is also site-selective, with nucleophilic attack at the β -carbon, in contrast to the case of epoxysilanes⁽³⁵⁾, where the nucleophile opens the epoxide ring by attack at the α -carbon). This is followed by a stereospecific *anti*-elimination of the trimethylsilyl group and the trifluoroacetate or chloride ion, and the iodoalkene **17** is produced with overall inversion of configuration (this stereospecificity is also discussed later under the section describing the effect of ligands on silicon on β -effect).

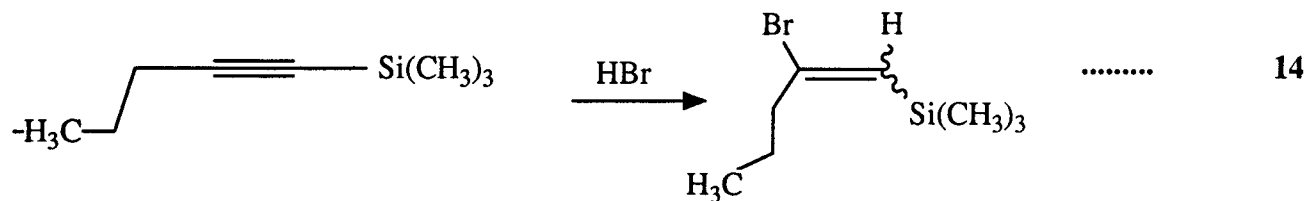


1.7 Electrophilic substitution with other classes of silanes

Alkynylsilanes, like alkenylsilanes, react with electrophiles generally to give substitution⁽³⁶⁾ (Equation 13).



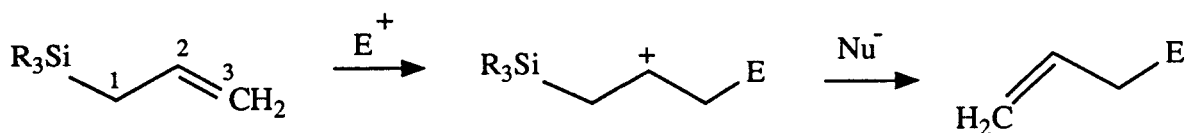
Addition reactions⁽³⁷⁾ are also known (Equation 14).



These adducts do not normally undergo easy β -elimination, but they can be made to do so by

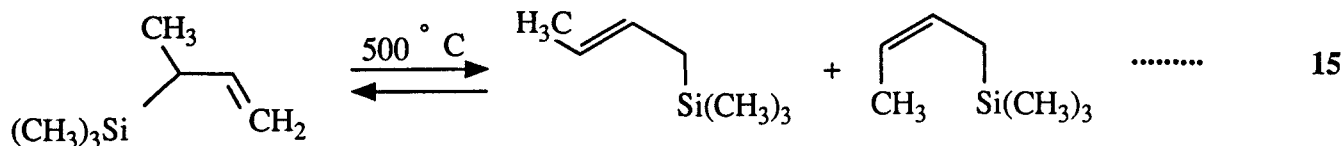
treatment with fluoride ion⁽³⁸⁾.

Allylsilanes react with electrophiles⁽³⁹⁾ in the sequence shown below (Scheme 13). Attack



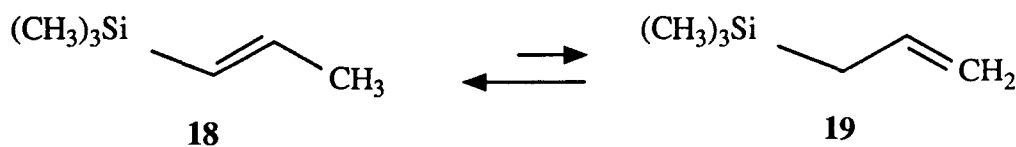
Scheme 13

at C-3 of the allyl system generates a carbocation at C-2 stabilized by the neighbouring silicon-carbon bond (β -effect) and the displacement of silicon is fast. This pattern of reactivity is, of course, the same as that of other allylmetal compounds with electrophiles.⁽⁴⁰⁾ Allylsilanes however, unlike other allylmetal compounds, rearrange only at relatively high temperatures⁽⁴¹⁾ (Equation 15).



For this reason, the reaction of allylsilane with an electrophile is usually regiospecific, giving a single product.

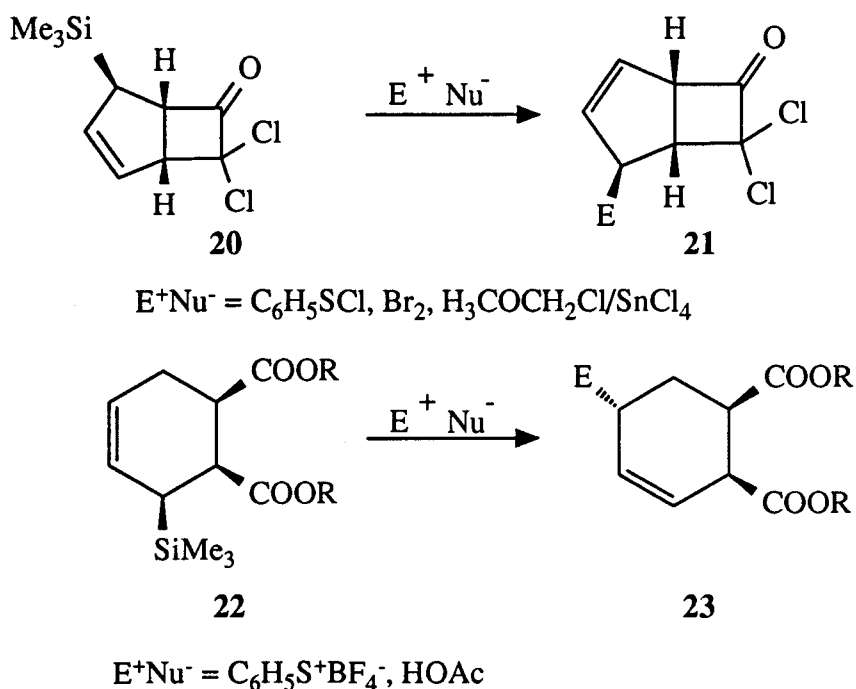
Allylsilanes can be expected to be more reactive than vinylsilanes. The silicon-carbon bond of an allylsilane can overlap with the orbitals of the π -bond; this will raise the energy of the HOMO and hence make the molecule more reactive towards electrophiles. Furthermore this overlap can stabilize the developing positive charge on C-2 (scheme 13); in vinylsilanes the silicon-carbon bond can only stabilize the developing positive charge after a rotation of 90°, as in Scheme 11, **10** \rightarrow **11**. Finally it is known that at equilibrium, the vinylsilane **18** is the major isomer, being about 8 kJmol⁻¹ lower in energy than the corresponding allylsilane **19**⁽⁴¹⁾.



Since protonation of these isomers would give the same intermediate, one would expect the allylsilane to be more reactive. Experimental evidence⁽⁴²⁾ also supports these arguments.

1.7.1 Stereochemistry

Two stereochemical consequences, *syn* and *anti*, are possible for electrophilic substitution of allylsilanes and both have been observed. In the cyclopentenyl system **20**, electrophilic substitution occurred with *syn*-selectivity⁽⁴³⁾, but in the cyclohexenyl system **22**, it occurred with *anti*-selectivity⁽⁴⁴⁾, which is usually observed (Scheme 14).

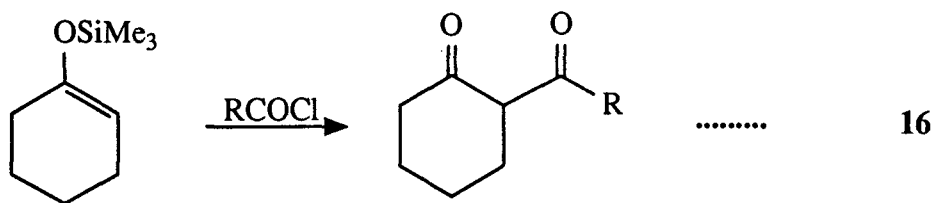


Scheme 14

It seems that the directing effect of the silyl group is not particularly strong, and that the stereochemistry of the reaction can be influenced more by the stereochemical bias of the whole molecule.

Silyl enol ethers also undergo electrophilic substitution reactions which are manifestations of the β -effect. An acetylation reaction⁽⁴⁵⁾ is shown below as an example (Equation 16).

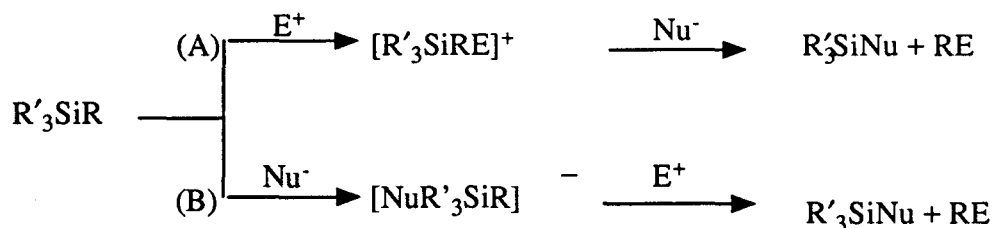
Electrophilic substitution reactions demonstrating the β -effect of silicon have been explored in various other classes of compounds like arylsilanes, benzylsilanes, cyclopropylsilanes, alkylsilanes, silylethers and silylamines, which are outside the scope of this thesis.



1.8 Factors Influencing the β -Effect of Silicon

1.8.1 Effect of Coordination state of Si on β -effect

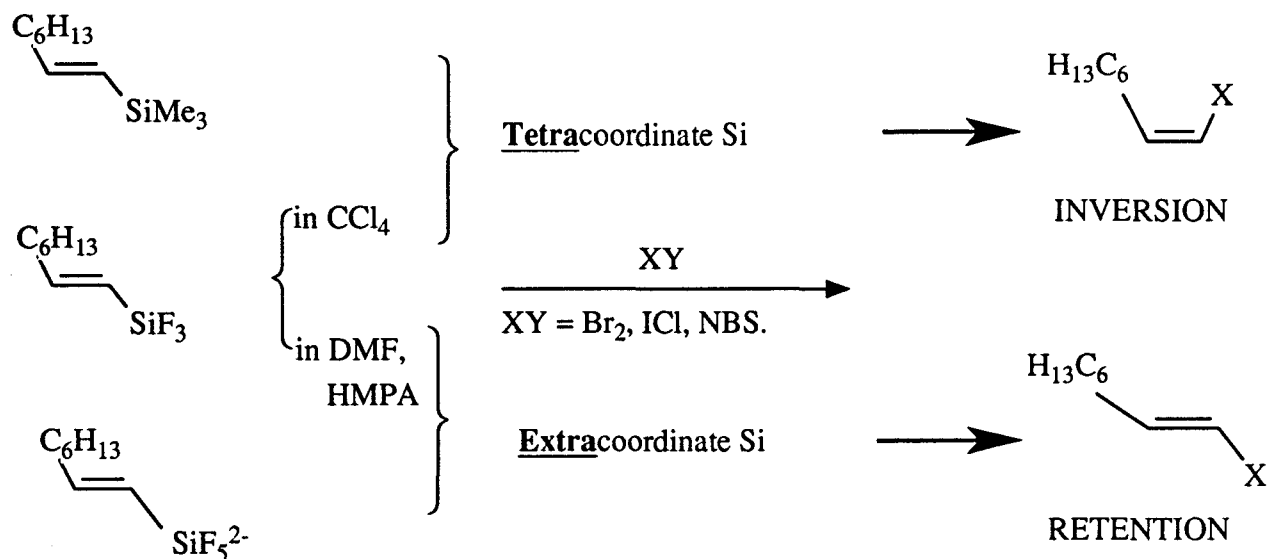
Kumada and his coworkers⁽⁴⁶⁾ have demonstrated that the stereoselectivity of the halogenolysis of alkenylsilanes is greatly dependent upon the nature of the silyl leaving group, especially the coordination state of the silicon. There would be two extreme cases in electrophilic cleavage reactions, depending on the timing of the interaction with an electrophile and a nucleophile, as shown in Scheme 15.



Scheme 15

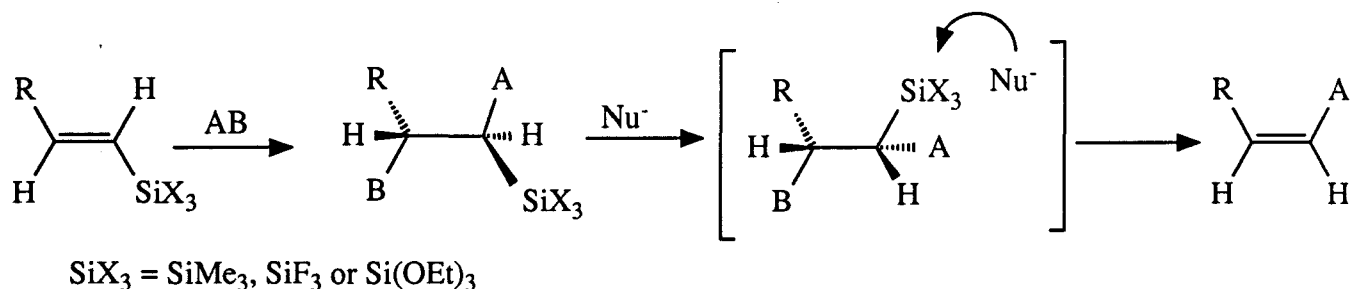
In route A, the presence of electronegative substituents on silicon should diminish the reactivity of the carbon-silicon bond, while in route B, the more electronegative the groups on silicon would be, the easier would be the formation of extracordinate silicon species, and in turn, the more favourable the cleavage reaction. Therefore, route A should be favoured with traditional trimethylsilyl derivatives, while route B should be followed with silafunctional derivatives. There seems to be a good correlation between the stereochemical courses of the halogen cleavage reactions and the coordination states of the silicon center at the stage of attack by electrophiles (Scheme 16).

Thus, while attack on ordinary tetracordinate silicon compounds followed by nucleophilic attack on



Scheme 16

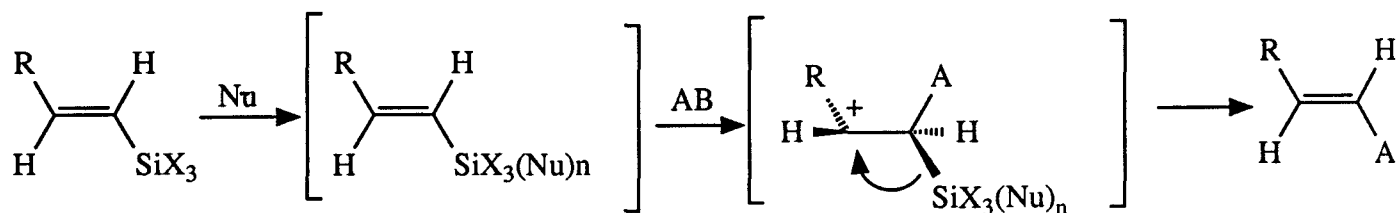
silicon leads to inversion, attack on extracoordinate silicon species results in retention of the olefin geometry. All of the inversion chemistries may be explained by a traditional *trans* addition/*anti* elimination mechanism (Scheme 17).



Scheme 17

All of the retention chemistries of extracoordinate silicon may involve the electrophilic attack on hypervalent silicon species, as shown in Scheme 18. Thus, the attack by a halogen cation on the activated double bond may be followed by cleavage of the activated silicon-carbon bond.

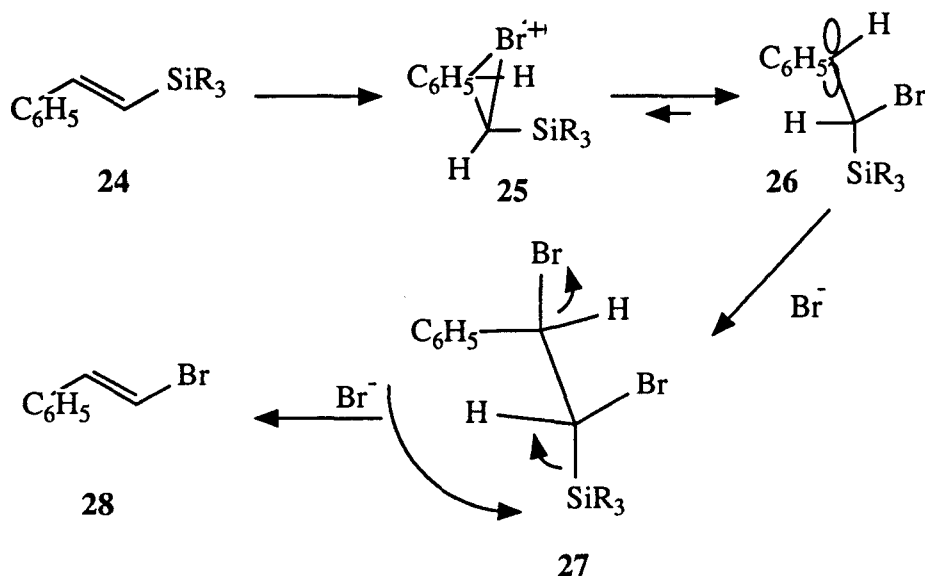
β -Silylstyrenes are a special case: they give retention of stereochemistry with bromine, even though the reaction takes place by the addition-elimination pathway⁽⁴⁷⁾ (Scheme 19). The intermediate adducts of β -triphenylsilylstyrene **24** have been isolated and shown to be the result of *syn*-addition⁽⁴⁸⁾. The overall retention is therefore a result of unusual *syn*-addition, **25** \rightarrow **26**, followed by the usual *anti*-elimination, **27** \rightarrow **28**. A possible explanation of *syn*-addition is that the



$\text{Nu} = \text{F}^-$ and/or donor solvent; $n = 1$ or 2 .

$\text{SiX}_3(\text{Nu})_n = \text{SiF}_5^{2-}$, SiF_4^- or SiF_4^- (solvent).

Scheme 18



Scheme 19

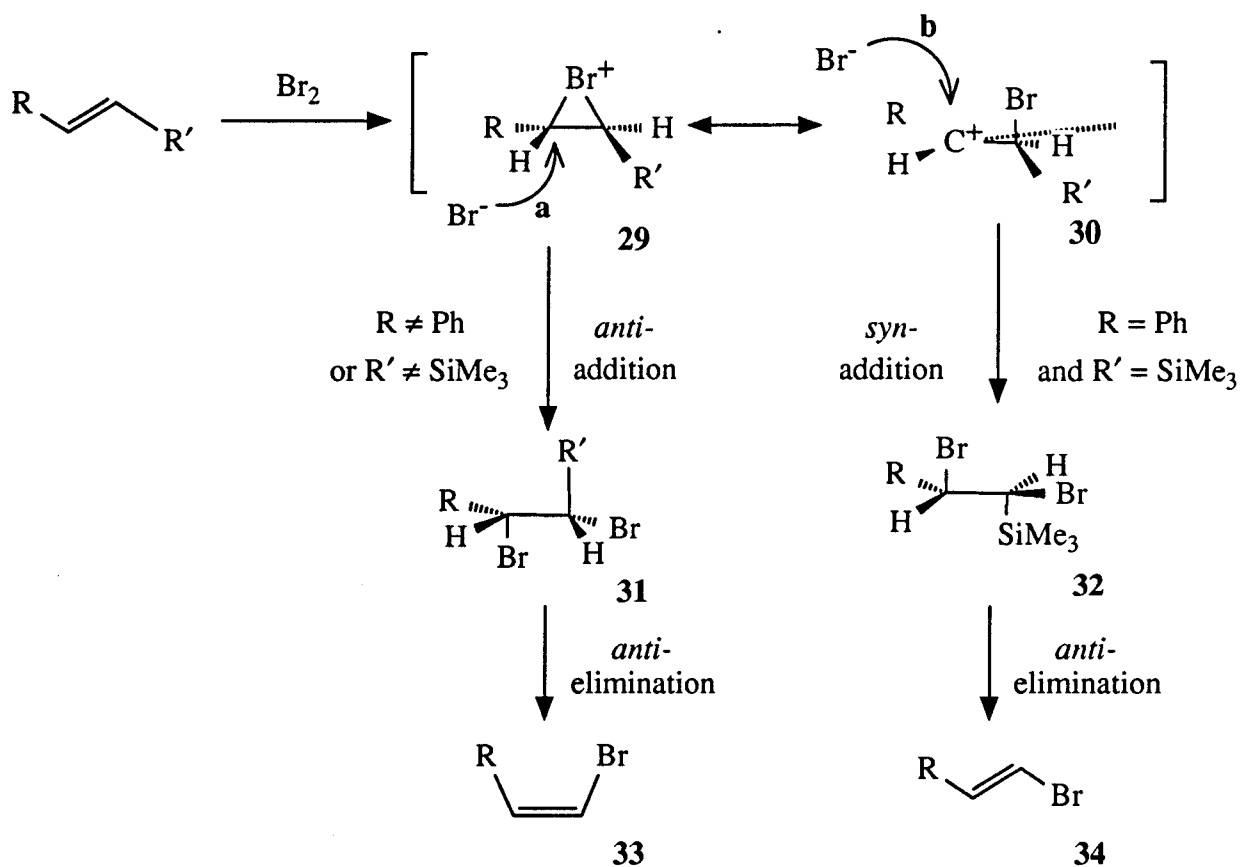
phenyl group stabilizes the intermediate cation so that it is less symmetrical than the usual bridged structure **25** and is therefore more like structure **26**. The bromide ion then adds *anti* to the β -silyl group and hence *syn* to the existing bromine.

1.8.2 Effect of ligands on silicon on β -effect

As we have seen that silicon stabilizes a β -carbocation through $(\sigma\text{-}\rho)\pi$ overlap (hyperconjugation), it is obvious that the ligands on silicon can influence the extent of this stabilization. Fleming and his coworkers have demonstrated that the stabilization of a carbocation

by a phenyl group is more effective than by a β -trimethylsilyl group⁽⁴⁹⁾. However, few studies have directly focused on the role played by the ligands or groups on silicon in the stabilization. Notable are the continuing contributions by the groups of Sakurai, Hayashi, Tamao, Kumada and others in this area, who have examined in some detail the differences between methylsilanes, fluorosilanes and pentafluorosilicates^(46a,50) and more recently mixed halo/amino/alkoxy/alkyl-allylsilanes⁽⁵¹⁾.

More work has been done by Brook and Neuy⁽⁵²⁾ to find the effect of various groups on silicon on the β -effect. They selected the addition of Br_2 to E- β -silylstyrene with various ligands on silicon. In contrast to vinyltrimethylsilanes or other olefins which undergo preferential *anti*-addition of bromine, the addition of Br_2 to E- β -trimethylsilylstyrene occurs *syn* (discussed earlier). In the presence of a strongly stabilizing group, and in this case there are two, the phenyl ring and the silyl group, it is presumed that the bromonium ion **29** can open up to give a carbonium ion **30-a** β -silylcarbocation⁽⁵¹⁾ (Scheme 20). *Syn* addition can result from attack by bromide ion on **30** simply



Scheme 20

because of the proximity of the nucleophile to the *syn*-face of the molecule (vide infra, path b,

Scheme 20). As a first approximation, therefore, it is to be expected that *anti*-addition will result from the reaction of bromide with **29** and *syn*-addition from reaction with **30**. Thus, the ratio of isolated products **31/32** can be directly related to the ratios of the two carbonium ions. In other words, this ratio reflects the stability of the two carbonium ions and thereby, the stabilizing effects of nearby groups, including the β -effect. The primary route for bromide addition is *anti* attack on the bromonium ion **29** (R=Ph, R'=Me, Scheme 20a). This is evidenced from the fact that methylstyrene brominates to give 95% *anti*-product⁽⁵³⁾, where the phenyl group is the only group which provides stabilization. In contrast, trimethylsilylstyrene where there is an additional stabilization from a strong β -effect gives 100% *syn*-addition via reaction of the bromide with the stabilized carbonium ion **30**. Thus, the *syn/anti* addition ratio of this reaction should be a scale with which to measure the degree of the β -effect for different silyl groups. As a silyl group becomes increasingly electron withdrawing, the partition between **29** and **30** (R=ph, R'=SiXYZ, Scheme 20) should increasingly favour **29** and, therefore, formation of the *anti*-product. In all cases the contribution from the phenyl group would be the same.

The ratios of *syn/anti* for various ligands on silicon in the bromination of E- β -silylstyrene are given in Table 4 against the corresponding group electronegativity⁽⁵⁴⁾ of the ligands on silicon. The results show that the higher the group electron withdrawing ability of the ligands on Si and thus the group electronegativity, the higher the *anti*-addition (ie. weaker the β -stabilization effect). In otherwords, electron-donating groups on silicon increase the β -effect.

Table 4. Comparison of *syn/anti* Ratio to Group Electronegativity

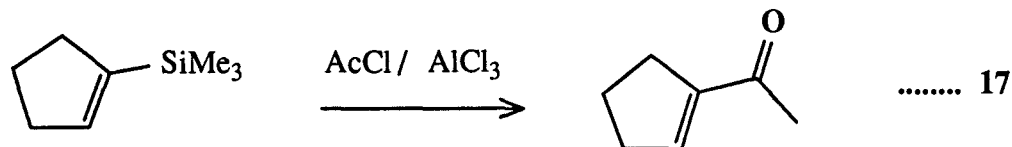
Ligands on Silicon	Ratio <i>syn/anti</i>	Group ⁽⁵⁴⁾ Electronegativity
Me ₃	100/0	2.06
Me ₂ Cl	100/0	2.12
Me ₂ F	85/15	2.18
MeCl ₂	75/25	2.19
Cl ₃	55/45	2.26
MeF ₂	40/60	2.32
F ₃	15/85 ^a	2.47

^a Based on the ratio of bromostyrenes after elimination.

The results of the electrophilic substitution reactions of optically active allylfluorosilanes, (S)-(Z)-MeCH=CHCH(SiF_nMe_{3-n})Ph (n=1-3), with MeCOCl/AlCl₃ and t-BuCl/TiCl₄ carried out by Hayashi and his coworkers^(50b) also proves the above conclusion. Reaction of trimethyl and dimethylfluorosilane compounds proceeded with *anti* stereochemistry to give the corresponding *anti* S_E' products of *S* configuration, while the trifluorosilane gave a low yield of racemic product in acetylation and was unreactive toward *tert*-butylation. Even though *anti* stereochemistry was observed in the S_E' reactions of methyldifluorosilane, the chemical yields were rather low in both acetylation and *tert*-butylation and a significant loss of the enantiomeric purity was observed in the acetylation. These results indicate that σ - π conjugative interaction between the carbon-silicon bond and the olefin π system, which increases the electron density on the olefin and is responsible for the *anti* S_E' reaction, is pronounced in dimethylfluorosilane as well as in the trimethylsilyl analogue. The σ - π conjugation is less important in the methyldifluorosilane and is not a factor in the trifluorosilane. This order seems to be consistent with the electronic nature of the fluorosilyl groups (SiF_nR_{3-n}).

1.9 Addition of electrophiles

Normally, the reaction of electrophiles with vinylsilanes leads to substitution reactions (Equation 17) as discussed earlier.



But previous work in our group⁽⁵⁵⁾ has shown that in some cases addition to the double bond is favoured over substitution.

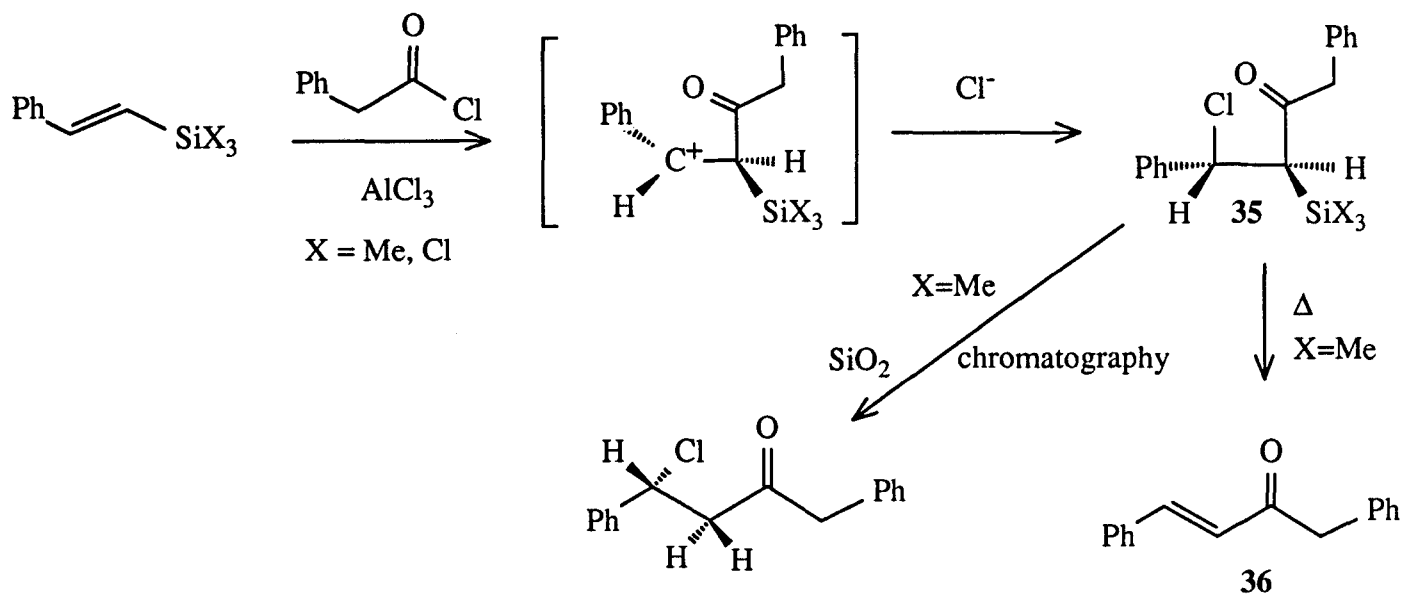
1.9.1 Friedel-Crafts acylation

Friedel-Crafts acylations on (E)- β -trimethyl and (E)- β -trichlorosilylstyrenes using phenylacetylchloride and AlCl_3 gave addition products (Scheme 21). In the case of trimethylsilylstyrene, when the reaction mixture was warmed up, the silyl group was eliminated and the substitution product **36** was identified. In the case of trichlorosilylstyrene, the addition product **35** was identified from the crude ^1H nmr analysis of the reaction product.

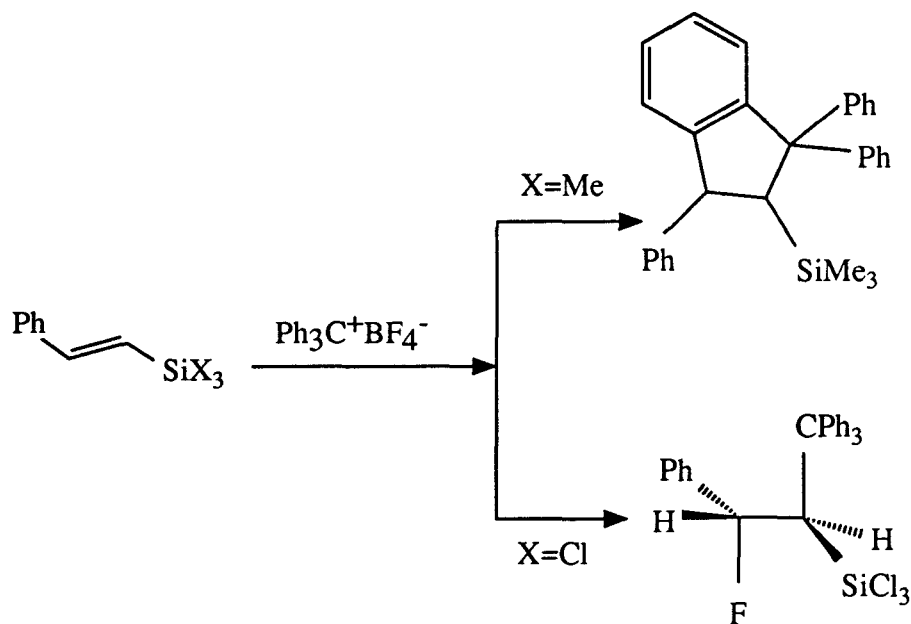
1.9.2 Friedel-Crafts alkylation

(E)- β -Trimethyl and trichlorosilylstyrenes gave two different addition products with triphenylmethyl tetrafluoroborate ($\text{Ph}_3\text{C}^+\text{BF}_4^-$) (Scheme 22). The trimethylsilyl group caused indane formation while the trichlorosilyl group gave a non-indane type addition product containing fluorine.

This observed change from substitution to addition processes upon changing the ligands on silicon from electron donating to electron withdrawing in the carbon based electrophiles prompted us to explore the addition of protons to such species and to see whether addition or substitution was taking place.



Scheme 21



Scheme 22

1.9.3 The Problem

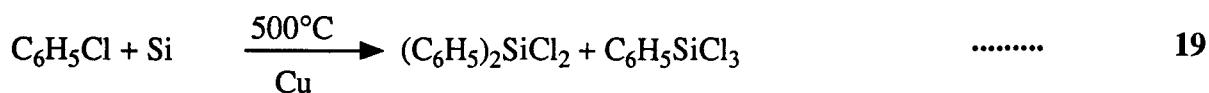
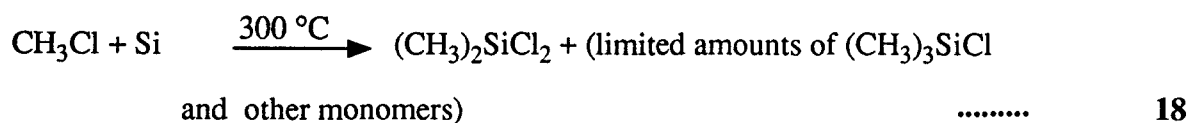
The preceding discussion outlines some of the important aspects of reactivity of organosilicon compounds. As part of an overall effort to examine in particular the β -effect, the study of cationic reactions of β -halosilylstyrenes was initiated. Our goal was to study the reactivity and

relate the observed results to the activating effect provided by the silyl group. The work described in the remainder of this thesis outlines our experimental approach to this problem and the results.

Results and Discussion

2.1 Synthesis of the starting materials

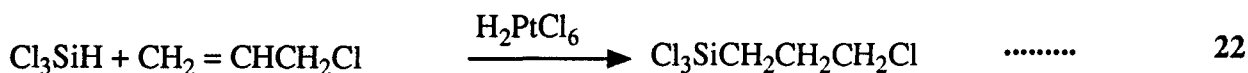
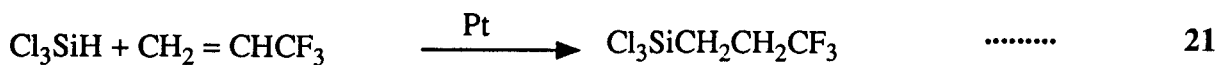
Carbon-functional organosilicon compounds can be produced in several ways, some of which are better applicable to industrial production than others. The direct synthesis from silicon metal and alkylhalogen derivatives, with the exception of CH_3Cl , $\text{CH}_2=\text{CH}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{-Cl}$ (Equation 18 and 19), is not suited for industrial production, due to the fact that the reaction must take place at sufficiently high temperature at which higher alkylhalides decompose, lowering the yield of the product⁽⁵⁶⁾.



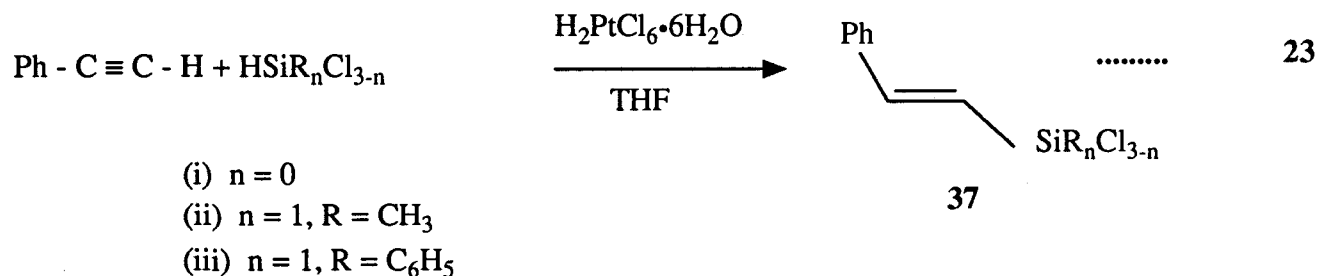
The Grignard synthesis (Equation 20), which is frequently used in the laboratory because of its versatility, is less suitable for commercial production, owing to the use of ether and magnesium.



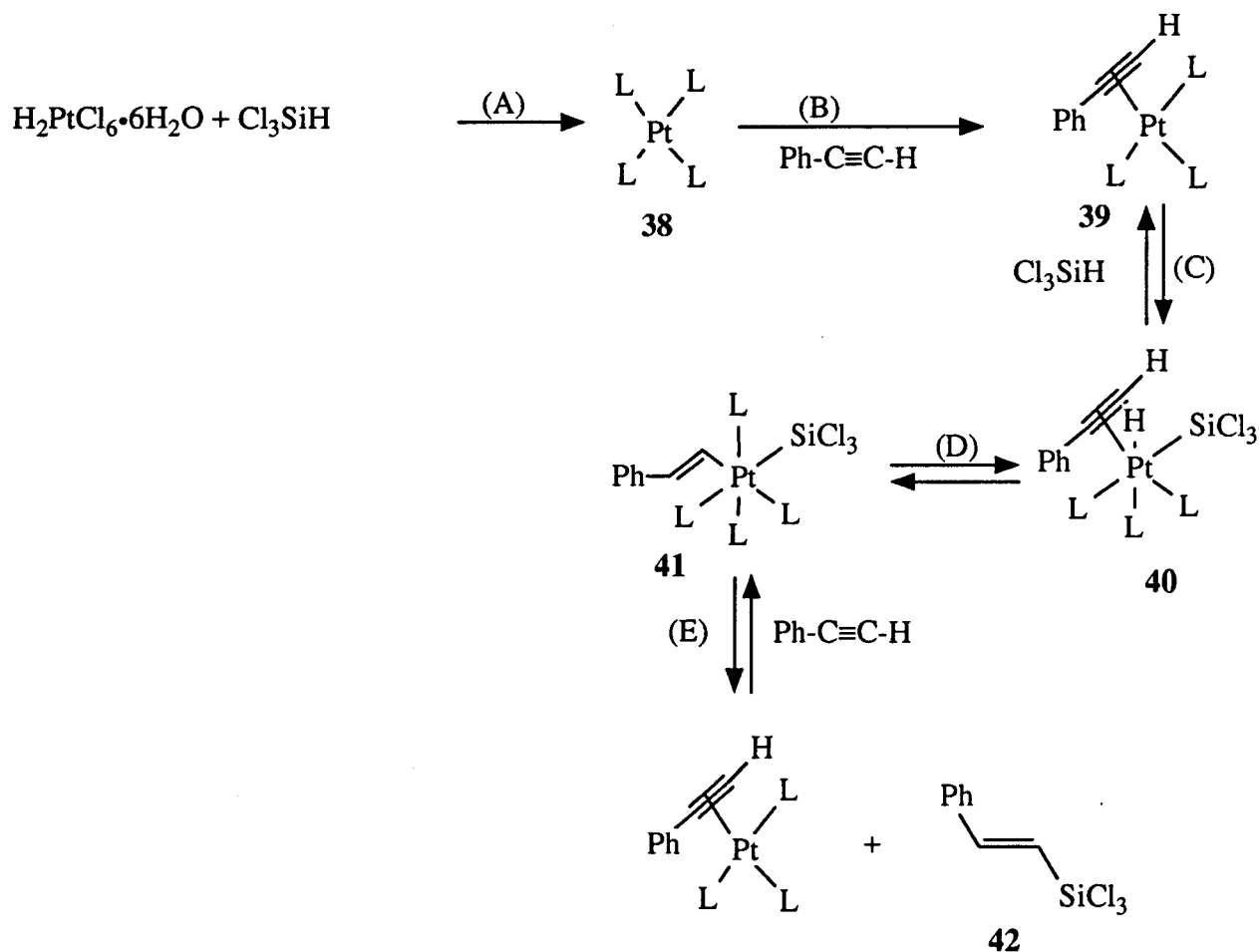
A frequently applied and technologically advantageous process for producing carbon-functional organosilicon compounds is hydrosilylation (Equation 21 and 22), which is a high yielding, reproducible, regio- and stereoselective process^(57,58).



For our experiments, the starting materials, chlorosilylstyrenes were synthesised by the hydrosilylation of phenylacetylene (Equation 6).



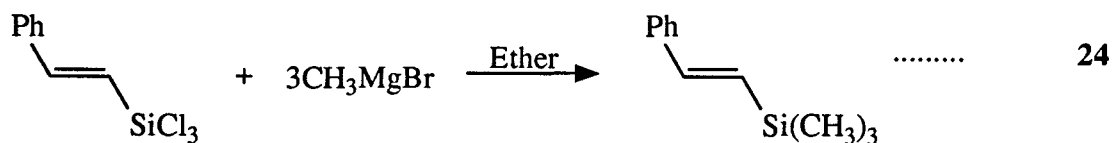
A hydrosilane was added to phenylacetylene under transition metal catalysed conditions; in this case hexachloroplatinic acid, H_2PtCl_6 . Under these conditions the *trans*-terminal alkenylsilane 37 was formed almost exclusively. The postulated mechanism of this reaction is shown in Scheme 23.



(L = unspecified ligand, presumably chlorine, hydrogen, or coordinated solvent)

Scheme 23

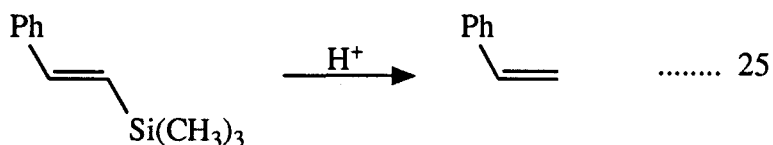
The initial reaction (step A) is the silane reduction of the catalyst d^6 Pt(IV) complex. The resulting d^8 Pt(II) complex **38**, which either contains a weakly held ligand or solvent molecule capable of ready replacement, then coordinates the substrate phenylacetylene (step B). In step C, silane adds oxidatively to **40** providing a d^6 octahedral intermediate which then undergoes a hydrogen and platinum *cis* addition to the alkyne (step D) to give the complex **41**. This complex **41** then reacts with more alkyne giving the hydrosilylation product **42** with retention of configuration at both silicon and carbon. To confirm the structure of the material, it was reacted (capped) with methylmagnesium bromide to give the stable derivative trimethyl-(E)-phenethenylsilane (Equation 24).



The nmr and IR spectra of this product showed that it is a *trans* isomer⁽⁵⁹⁾.

2.2 Addition of proton to β -trichlorosilylstyrene

Normally, the addition of electrophiles to vinylsilanes leads to substitution reactions. The addition of a proton to β -trimethylsilylstyrene is a typical example leading to protiodesilylation⁽⁶⁰⁾(Equation 25).



But, as already stated, previous work in our lab has shown that, in the case of β -trichlorosilylstyrene, addition products are also possible with electrophiles. This prompted us to look into the addition of protons to β -trichlorosilylstyrene. The stronger electron-withdrawing chloro groups on silicon will reduce the ability of the silyl group to stabilize the β -carbonium ion (β -effect) and at the same time it will also reduce its leaving group ability as compared to the β -trimethylsilylstyrene. So with a proton we expect an addition product without desilylation. A

number of acids were used as the proton source. These can be classified into two groups: Lewis acids (or Friedel-Crafts acids) that are contaminated with traces of water or alcohol (co-catalyst), which forms a protonated acid *in situ*, or protonic acids (protonated acids). Prior to the present work (i.e. with protic acids) Lewis acids were examined as a proton source in our lab⁽⁶¹⁾.

2.2.1 Lewis acids as proton source⁽⁶²⁾

Lewis acids are the most important initiating systems for carbocationic polymerization both from the scientific and technological point of view. The great advantage of Lewis acids (Friedel-Crafts systems) over Brønsted acids is their larger kinetic chain length, rendering propagation to high molecular weights possible. Lewis acids by themselves cannot donate protons so they need a co-catalyst like water or alcohol. For example $\text{BF}_3 \cdot \text{O}(\text{Et})_2$ with ethanol forms a protonated acid *in situ* as shown in equation 26. The general mechanism for carbocationic



polymerization involves mainly four steps: (i) initiation, (ii) propagation, (iii) chain transfer, and (iv) termination. In the initiating step, the catalyst/cocatalyst system generates a monomeric cation (M^+) (Equation 27).

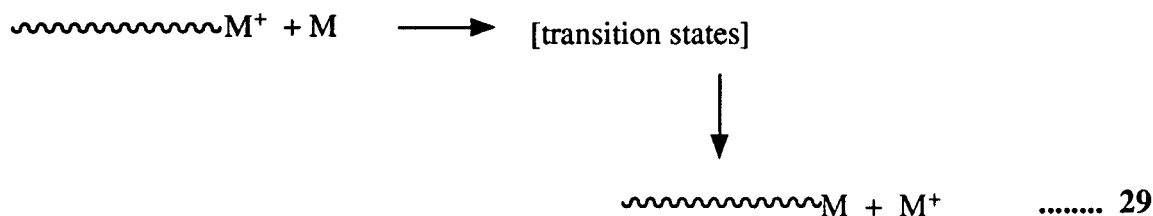


This is followed by the propagation stage where the monomeric cation reacts with a 2nd monomer species, which in turn reacts with a 3rd monomer and so on to give higher molecular weight species (Equation 28).



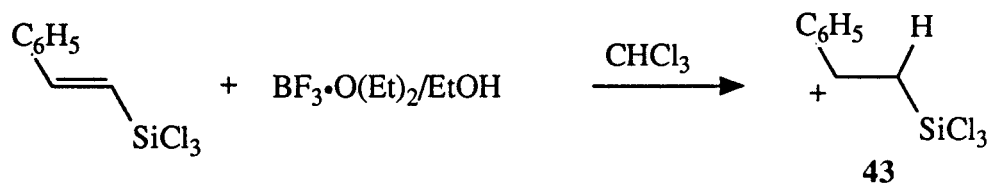
Chain transfer, or charge transfer as it is sometimes called, is the process by which the growing carbonium ion transfers its charge and simultaneously its propagating ability to a monomer either directly or indirectly (Equation 29).

Termination is a chemical reaction in the course of which the propagating ability of the active



polymer end is irreversibly destroyed. This occurs mainly in three ways: (i) collapse of the propagating carbonium ion/counter anion pair or neutralization, (ii) transfer of hydride ions to the chain carrier with simultaneous formation of a stable carbonium ion (which is then unable to propagate), and (iii) deliberate destruction of the chain carrier by purposeful addition of nucleophiles or quenching.

Reaction of β -trichlorosilylstyrene with various Lewis acid/alcohol or water catalyst gave viscous brown liquids which were found to be a mixture of oligomeric materials⁽⁶¹⁾. In the oligomerization of β -trichlorosilylstyrene, the proposed initiation step is shown in scheme 24.

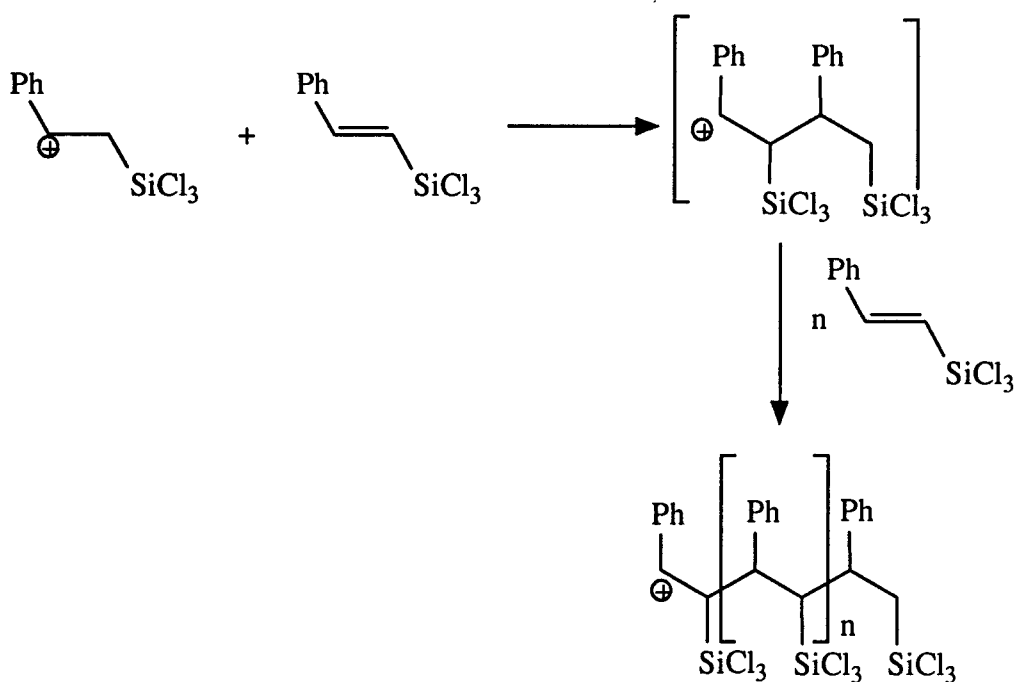


Scheme 24

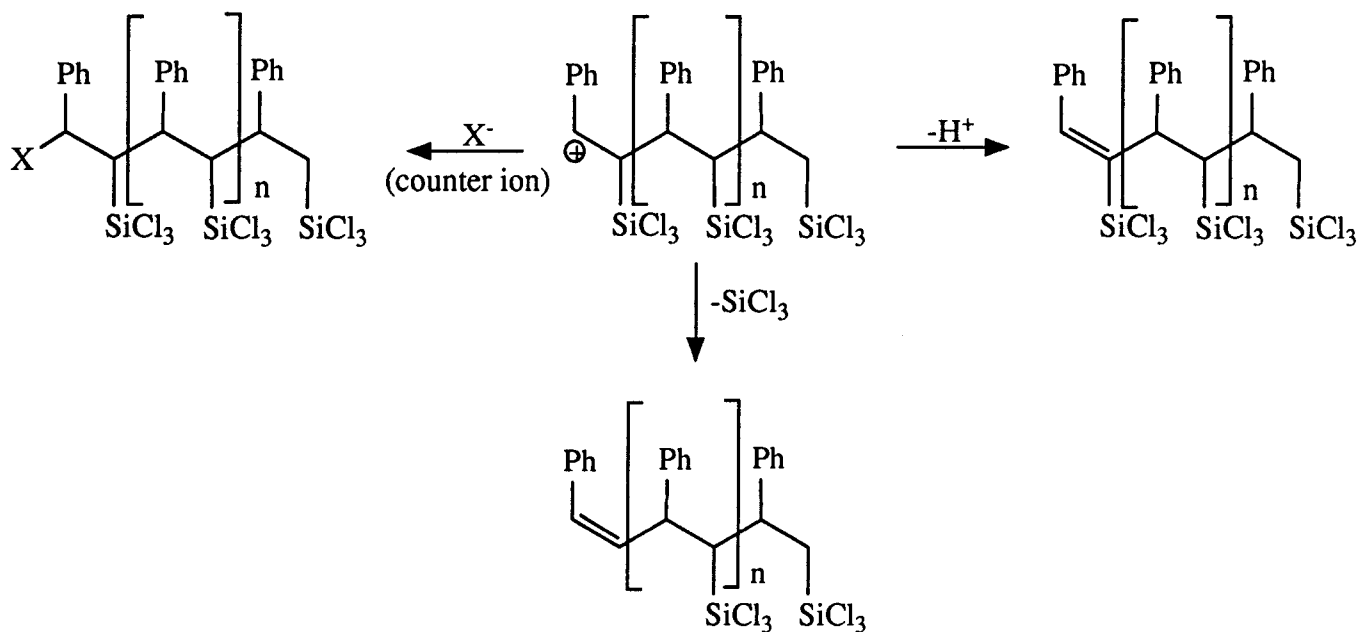
It is known that a silicon atom stabilizes a carbocation in the β -position, so the carbocation **43** is assumed to be formed which is also stabilized by the phenyl group. Once the polymerization process is initiated, the propagation stage begins. The proposed mechanism for propagation is shown in scheme 25.

The exact mechanism of chain transfer and chain termination is not known. However the chain termination could occur by several ways such as: (i) by recombination with the counter ion (e.g. $[\text{BF}_3 \cdot \text{OEt}]^-$), (ii) by loss of a proton, and (iii) by loss of a silyl group (Scheme 26).

A detailed study on the structure of the products or mechanism of the process was not done because of the irreproducibility of the process. A systematic evaluation of the reaction parameters failed to provide a set of reaction conditions which would always lead to oligomers. Therefore, an examination of several protonic acids as proton source was undertaken.



Scheme 25

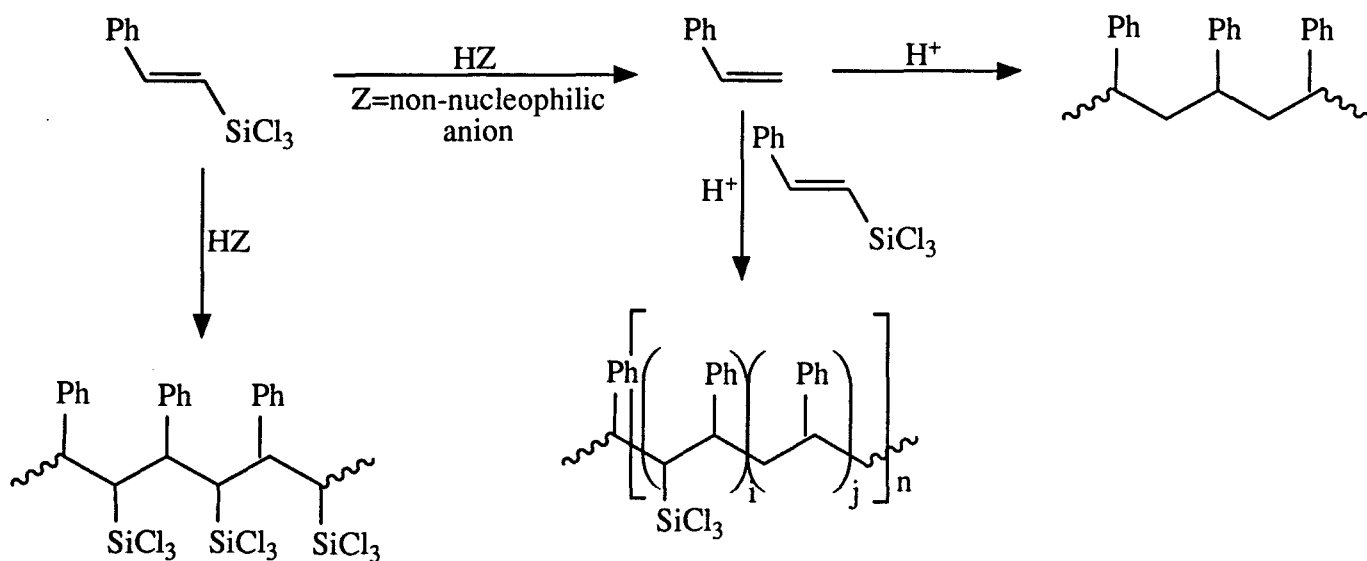


Scheme 26

2.2.2 Protonic acids as proton source

Since Lewis acids, as proton source, were found to be unsuitable, the goal of my project was to examine the reaction of protonic acids with β -trichlorosilylstyrene.

Initially, strong acids such as H_3PO_4 and HBF_4 were examined⁽⁶³⁾. The products could be readily identified using a combination of ^{29}Si , ^{13}C and ^1H nmr. The reaction products included: recovered unreacted starting materials, styrene and polystyrene, and polymers which contained small quantities of pendant silyl groups (from copolymerization of β -trichlorosilylstyrene and styrene) (Scheme 27). The most interesting materials were those in which the silicon groups remain on the product. These were subsequently shown to be oligomeric materials, generally silyl substituted silastyrene oligomers.



Scheme 27

The presence of each of these products can be readily explained. The protodesilylation reaction leading to styrene is well preceded for the trimethylsilyl group. Weber and coworkers has demonstrated that the replacement of silicon with a proton occurs stereospecifically (with retention of double bond configuration) *via* a β -silylcarbocation⁽³¹⁾. Polystyrene presumably results from the cationic polymerization of the styrene produced in the protodesilylation reaction. Similarly, in some cases, small quantities (<10%) of the trichlorosilylstyrene are copolymerized with the styrene under these cationic conditions. Confirmation of the presence of silicon in the latter case is done by conversion of the chloride ligands to methyl groups, which are readily observed in the ^1H nmr. The

degree of polymerization (DP) of these materials was not determined.

2.2.3 Triflic acid as a protonic acid

Subsequently trifluoromethanesulfonic acid, $\text{CF}_3\text{SO}_3\text{H}$, (Triflic acid), one of the strongest acids known was utilized⁽⁶⁴⁾. Somewhat surprisingly, instead of protodesilylation, it was discovered that higher molecular weight materials were formed. Under closer examination by chemical modification and spectroscopic analysis, these materials were shown to be trichlorosilylstyrene oligomers. So far triflic acid is the only one acid which reproducibly produced exclusively the oligomers without the loss of silicon.

Triflic acid has several advantages over other acidic systems^(64a). It is non-oxidising despite the fact that it is one of the strongest acids known. In recent years, a large increase has been seen in its use as a polymerization catalyst. Many aromatic olefins have been polymerized using triflic acid, including styrene, α -methylstyrene, chloro- and methoxy styrenes⁽⁶⁵⁾.

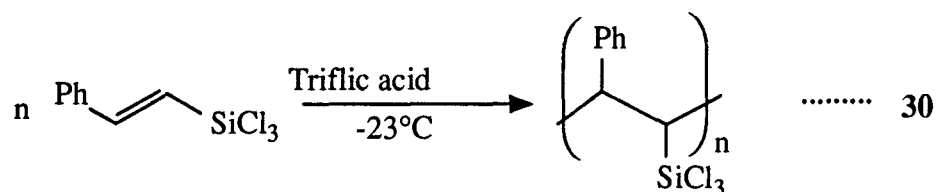
2.3 Oligomerization of β -Trichlorosilylstyrene

To a cooled solution of β -trichlorosilylstyrene in chloroform was added a catalytic amount of triflic acid. The solution suddenly became red orange and was allowed to react for 4-5 hrs. ^1H nmr showed that all starting materials had been consumed. Then, the solvent was removed under low pressure and the moisture sensitive product was methylated with an excess of methylmagnesium bromide in ether. T.L.C. of the product showed that there were 3 fractions. The methylated products were then separated on a flash column using hexane as the eluent. Various spectral analyses including ^1H nmr, ^{13}C nmr, ^{29}Si nmr, MS showed that the first fraction was a dimer; the second fraction, a trimer with traces of tetramer and the third fraction was a mixture of higher molecular weight oligomers. Although an attempt was made to establish the degree of polymerization (DP) of the oligomeric mixture with certainty, it was found to be too low for accurate determination by gel

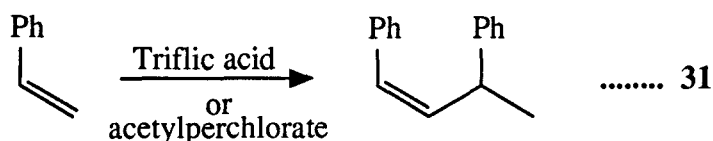
permeation chromatography (GPC) with the available columns (MW<2500 against a polystyrene standard). Mass spectral data shows the presence of a decamer (m.w.=1760) and in light of the GPC data, this appears to be the highest molecular weight material formed.

2.4 Structure of the oligomers

As stated earlier, oligomers bearing one silyl group per monomer unit were reproducibly formed in the oligomerization reaction of β -trichlorosilylstyrene with triflic acid at low temperature (Equation 30).

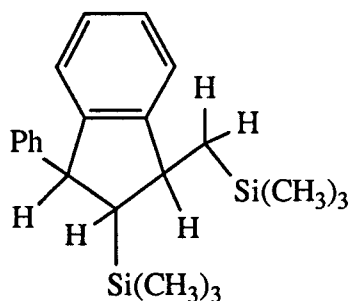


No styrene or polystyrene was observed under the reaction conditions employed. Initially it was anticipated that olefinic protons would be present in the oligomeric product as it was reported that the selective dimerization of styrene with triflic acid or acetyl perchlorate in benzene gives the linear olefinic dimer, 1,3-diphenyl-1-butene⁽⁶⁶⁾(Equation 31).



Examination of the oligomeric material obtained from the oligomerization of β -trichlorosilylstyrene with high field ^1H nmr showed that no olefinic protons were present. The IR spectrum of this oligomeric material also confirmed this fact.

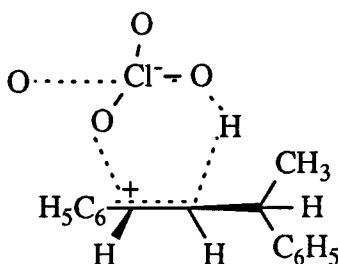
In order to determine the structure of the oligomers, a detailed spectral analysis was done on the three fractions of the methylated product. In the case of the first fraction, the dimer, this analysis was particularly easy. The chemical shifts and the splitting patterns observed in the ^1H nmr are in accordance with the indane terminated cyclic structure 44. ^{13}C nmr, ^{29}Si nmr, MS and nOe studies also favour this structure for the dimer. Subsequent to my work, the structure was confirmed by an



44

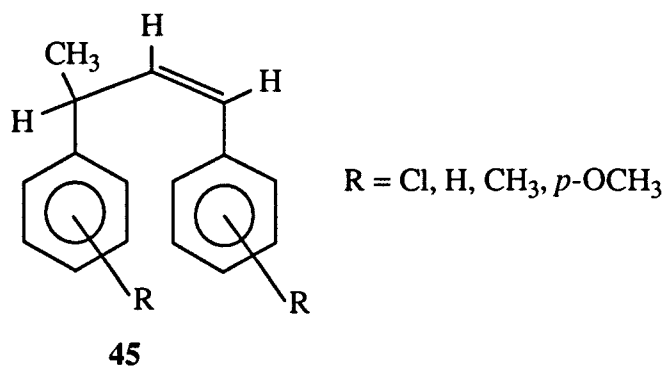
X-ray crystallographic structure determination⁽⁶⁷⁾. The spectroscopic data from the other fractions were also consistent with the indane terminated cyclic structure for the higher oligomers.

As stated earlier, in the selective dimerization of styrene with acetyl perchlorate or triflic acid in benzene, linear olefinic dimers were formed. But at the same time, formation of indane terminated cyclic oligomers were favoured when metal halides were used as the catalyst⁽⁶⁶⁾. The high selectivity for the linear dimer exhibited by the oxo-acids may result from the fact that the oxygen atoms of the counterion derived from them interact strongly with the β -hydrogen of the propagating end to promote its elimination (Scheme 28). On the other hand, counterions derived

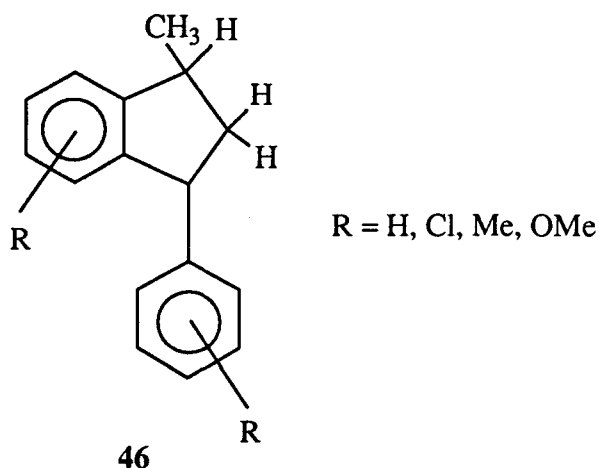


Scheme 28

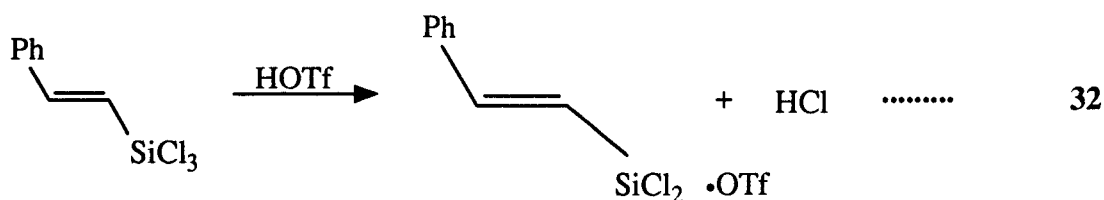
from the metal halides should be reluctant to interact with the β -hydrogen, because of their bulkiness and lack of basic oxygen atoms. This may promote propagation relative to transfer and results in indane terminated higher oligomers. The case is similar with substituted styrenes^(65c). Irrespective of the nature of the substituents, linear unsaturated dimers **45** were produced in good yields with oxoacids in a nonpolar solvent. The high dimer yields for oxoacids, together with the cyclic oligomer formation by metal halides, indicate the importance of strong nucleophilicity of counterions in the dimerization process. On the whole, oxoacids produced the linear unsaturated dimers **45**



predominantly, while metal halides promoted the formation of the cyclic dimers 46.

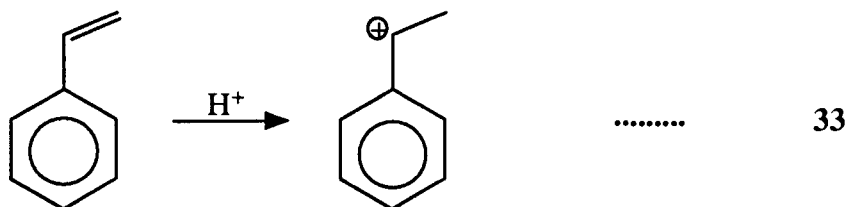


In the case of oligomerization of β -trichlorosilylstyrene, the counterion (triflate ion, CF_3SO_3^-), may be coordinated to the silicon and thus rendered nonnucleophilic and hence is not available to interact with the β -hydrogen of the propagating end. This may explain why indane terminated oligomers are formed in the oligomerization reaction using triflic acid as the catalyst. Support for this suggestion comes from the observation that a relatively large quantity of catalyst (5-10%) was required for the oligomerization reaction. It is conceivable that a ligand exchange reaction is occurring at silicon (Equation 32). This would have the effect of consuming the catalyst; HCl does not initiate polymerization under these conditions⁽⁶⁸⁾.



2.5 Mechanism of the oligomerization

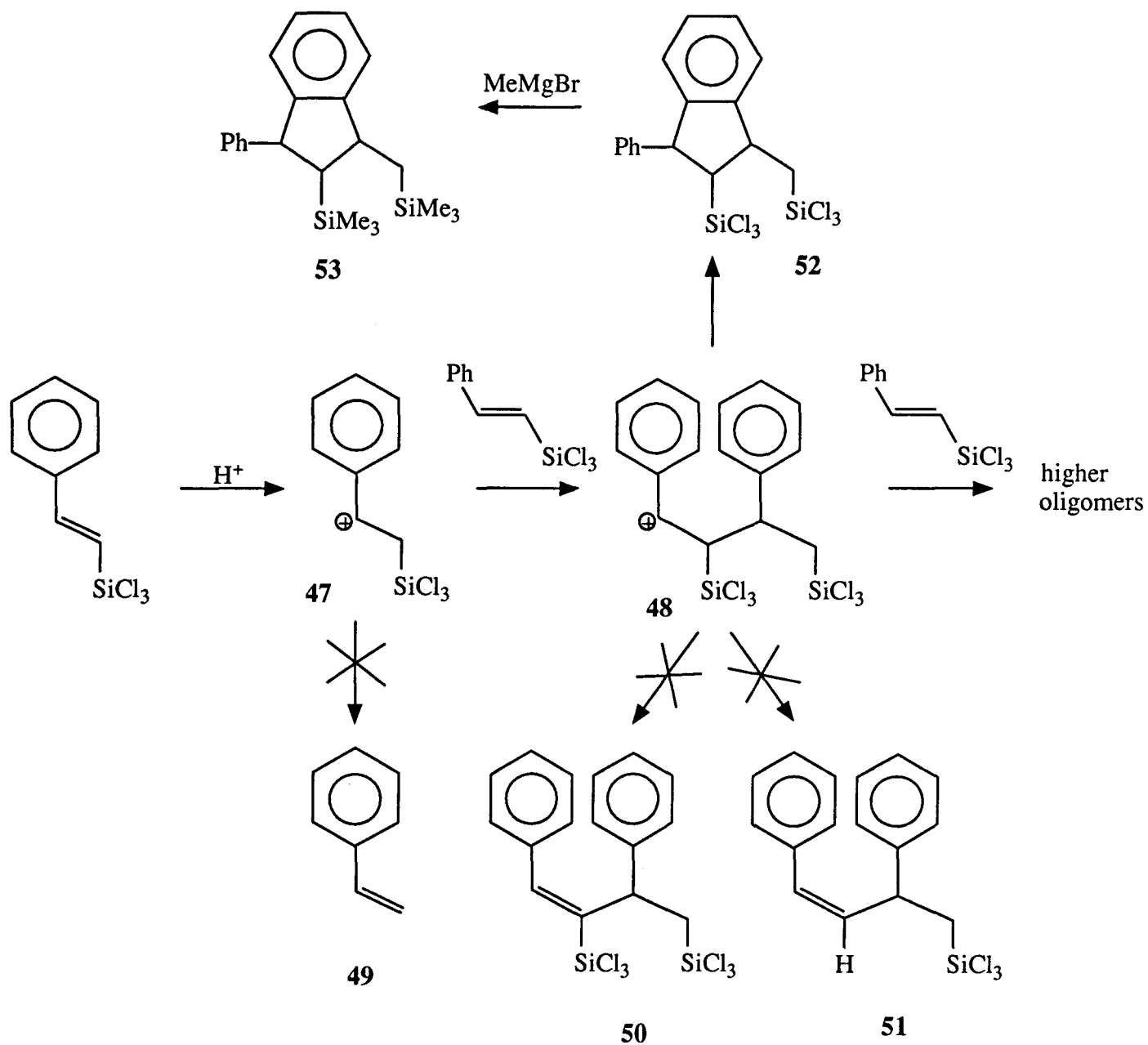
Under cationic conditions styrene is known to undergo protonation at the β -position, where the cation is stabilized by the phenyl ring (Equation 33). Similar is the case with



β -trichlorosilylstyrene, where the cation **47** is doubly favoured as it leads to a carbonium ion stabilized by both the phenyl group and the silyl group (Scheme 29).

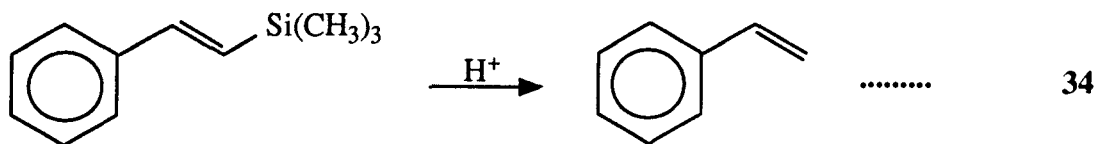
The monomeric cation **47** can undergo loss of a proton to give the starting material or the trichlorosilyl group to give styrene **49**, which is not observed due to poor leaving group ability or can react with the most reactive nucleophile in the media, another monomer molecule, to give the dimeric cation **48** (chain propagation). At this point, a partition between the intermolecular oligomerization process and intramolecular termination takes place. This partition will be affected by mainly two factors: the stability of the cation and the concentration of the monomer. As the reaction proceeds, the monomer concentration will decrease and intramolecular termination will be increasingly favoured.

An obvious concern which arises is the disparity between this reaction and the corresponding polymerization of styrene. It might be expected that the trichlorosilyl group would eliminate, leading to styrene (from the monomeric cation **47**), or vinyl terminated oligomers like **51** from the higher oligomeric cations. That these reactions do not occur can be explained by a combination of the leaving group ability and β -effect of the trichlorosilyl group. We have discussed in the introduction that electronegative groups on silicon weakens its stabilizing effect. It is possible that the $(\sigma\text{-p})\pi$ overlap (β -effect) may play a significant role in the weakening of the silicon-carbon bond and thus promote the cleavage process. Protodesilylation of vinylsilanes⁽⁶⁰⁾ is a good example to



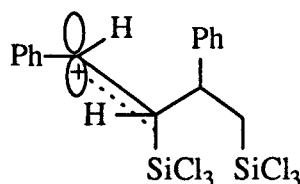
Scheme 29

demonstrate this (Equation 34).



But in our case, the β -stabilization is weaker due to the electronegative chloro groups on silicon, and

hence it will also be a poor leaving group. As a result, no silicon loss is observed in the oligomerization reaction. Again as we discussed in the previous section, the counterion may be coordinated to the silicon and thus is not available to interact with the β -hydrogen of the propagating end. This rules out the chance of proton elimination and hence the formation of oligomers like **50**. This also can be seen from the geometry of the molecule (Scheme 30).



Scheme 30

In order to maximise the hyperconjugative stabilization of the cation, the C-Si bond should be colinear with the empty p-orbital. This conformation prevents the C-H bond from being oriented colinear with the p-orbital, the preferred conformation for elimination.

Three mechanisms can be considered for the termination: E1, E2, and E1cB. In the case of triflic acid initiation, the triflate anion is a sufficiently poor nucleophile that the E1cB mechanism would not be expected to be favoured. The expansion of the co-ordination from 4 to 5 or 6 is known to be relatively facile for silicon atoms bearing electron withdrawing groups such as fluorine or chlorine. Thus, the possibility that triflate adds to the silicon, and expands the co-ordination shell but does not lead to elimination cannot be ruled out. For essentially the same reason, poor nucleophilicity, the E2 mechanism is disfavoured. In the E1 mechanism, the silyl group would formally leave as a positively charged species. The leaving group ability of the trichlorosilyl group is expected to be much worse than the corresponding trimethylsilyl group. In contrast to methyl groups, the electron withdrawing ability of the chlorine ligands would destabilize such a silicenium ion. Thus the monomeric cation **47** is not converted to styrene and the oligomeric cations do not lose silicon to form vinylic oligomers like **51**. Loss of a proton from oligomeric cations to form vinyl terminated oligomers like **50** also does not occur, for reasons described earlier. So instead of such an elimination, an intramolecular Friedel-Crafts reaction preferentially takes place leading to the indane

structure **52**. This type of indane termination reactions are known in the oligomerization of styrene, *p*-methoxy and α -methyl styrenes^(66,65c).

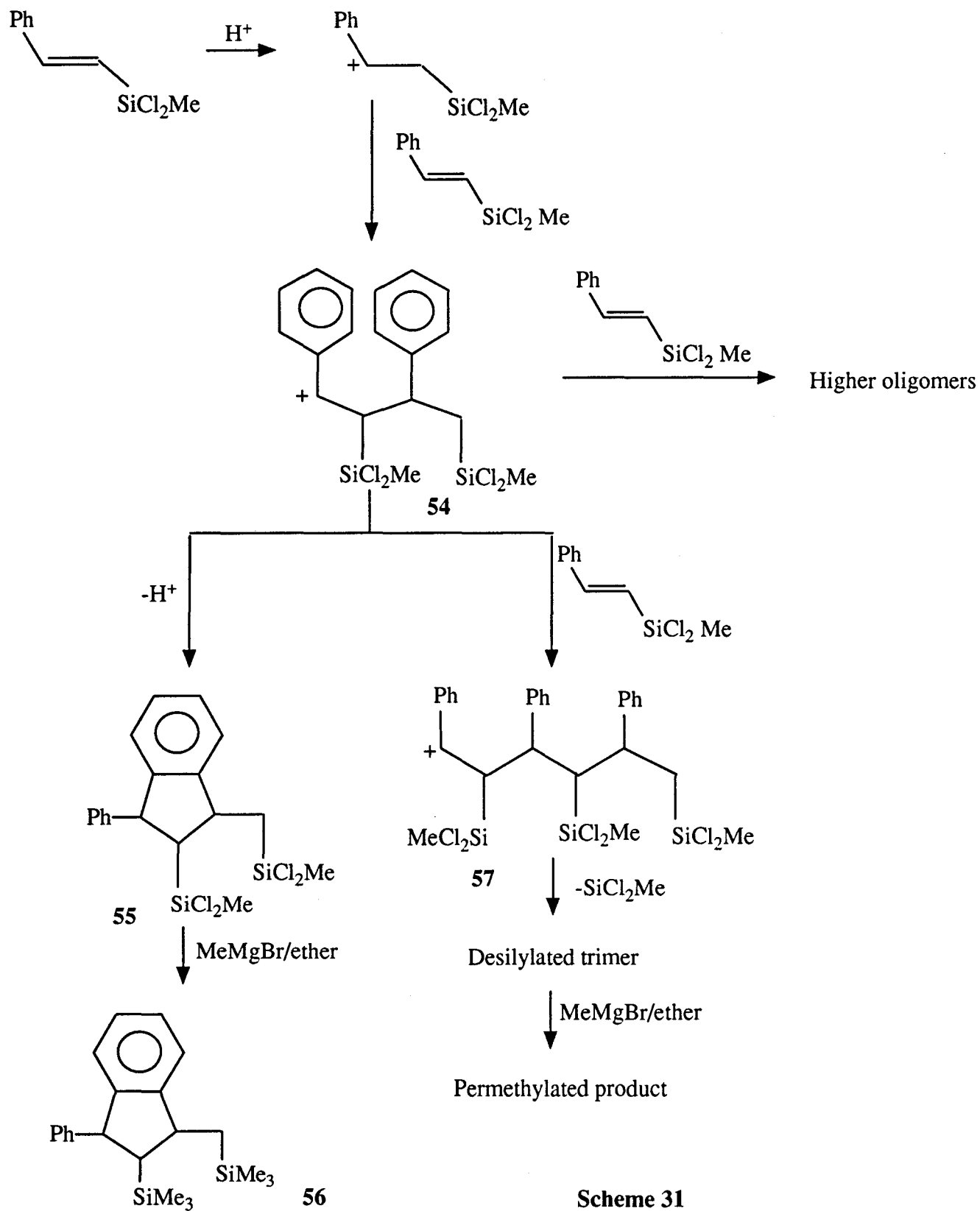
2.6 Modification of the basic reaction

2.6.1 Oligomerization of β -dichloromethylsilylstyrene

In order to examine the extent of the β -effect in the reaction, the oligomerization reaction was attempted with β -dichloromethylsilylstyrene using the same conditions as with β -trichlorosilylstyrene. The oligomeric product was then permethylated using methylmagnesium bromide and separated on a flash column; three fractions were obtained. ^1H nmr, MS and IR were used to identify them.

The first fraction was identified as the dimer **56** (Scheme 31), which was the major product. The second fraction was identified as a desilylated trimer which is presumed to be formed from the cation **57** (the exact structure is not yet known), and the third fraction was found to be a mixture of higher oligomers (up to approximately 10 monomer units). Further evidence for the desilylation was obtained from the ^1H nmr of the crude oligomeric product, where the peak at 1.2 ppm disappeared when the solvent was removed under low pressure. This may be the methyl peak from methylchlorosilyl triflate formed by desilylation.

This reaction shows the effect of leaving group ability of the silyl moiety on the oligomerization reaction. As we replace one of the chlorine ligands on silicon with a methyl group, almost 20% desilylation occurred. But at the same time, the β -effect has also increased, so that a higher degree of polymerization may result as compared to the oligomerization of β -trichlorosilylstyrene. However, we couldn't exactly determine the molecular weight of the highest oligomer for reasons mentioned earlier. But we do know that the percentage of dimer formed decreased from 50%, in the case of β -trichlorosilylstyrene, to 40%, in the case of β -dichloromethylsilylstyrene, under identical conditions. This shows that the β -effect of silicon plays an important role in the oligomerization reaction. However, in the case of



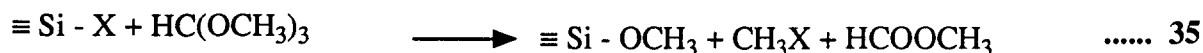
β -trimethylsilylstyrene, the leaving group ability is sufficiently high such that complete

protodesilylation takes place under acidic conditions.

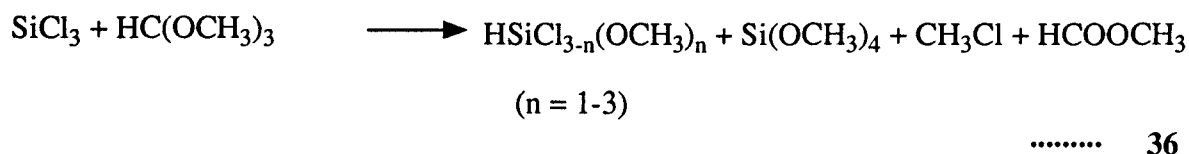
2.7 Methoxylation of oligomeric halosilylstyrene

The main application of these highly silicon functionalized silylstyrene oligomers is in moisture curing surface treatments^(69,70). During this moisture curing, HCl will be liberated which is a health hazard. So we decided to substitute the chlorine ligands with methoxy groups, which during moisture curing will liberate methanol, which is not a health hazard to the same extent.

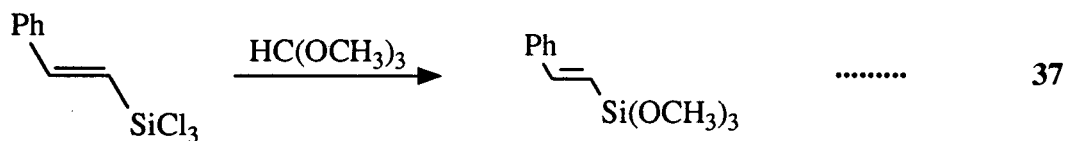
In general, the methoxylation⁽⁷¹⁾ can be done by reacting the halosilane with methyl orthoformate (Equation 35)



In our case methoxylation can be done at three different stages: (1) methoxylate the starting material, the halosilane; or (2) methoxylate the monomer, chlorosilylstyrene; or (3) methoxylate the final oligomer. The first one is not practically feasible, since methoxylation of chlorosilanes (SiHX_3), will lead to the replacement of hydrogen also, along with the formation of partially methoxylated silanes and the required product (Equation 36) and the separation of this mixture is extremely difficult too.



The second one, methoxylation of the monomer, can be done easily (Equation 37). However, the

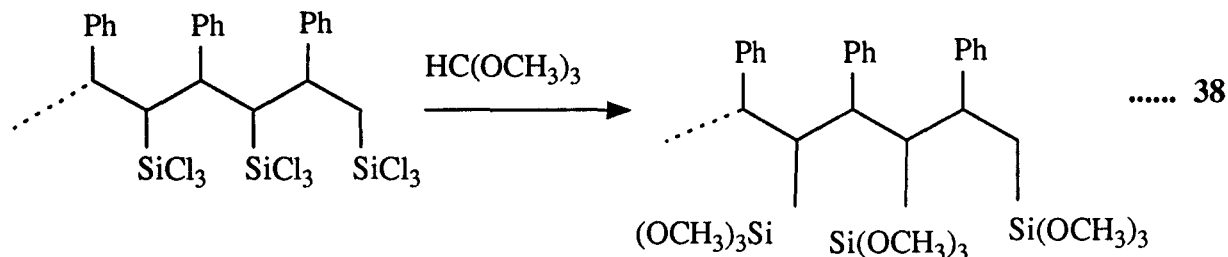


58

problem is that this methoxysilylstyrene **58** doesn't polymerize with triflic acid catalyst. Probably it is undergoing a protodesilylation reaction as occurs with trimethylsilylstyrene. No detailed analysis was done to establish this fact. It is known that the β -effect of silicon is directly related to the

electron-withdrawing ability of the ligands. But it was shown by Brook and Neuy⁽⁵²⁾ that this relationship breaks down in the case of alkoxy and phenoxy silanes. In spite of the high electronegativity of these ligands, a very high β -stabilization is observed in these cases, for reasons which are not yet clear. This may explain why trimethoxysilylstyrene doesn't polymerize with triflic acid.

The only choice left was the methoxylation of the oligomers. Reaction of the oligomeric



mixture, obtained by the oligomerization of β -trichlorosilylstyrene, with excess of methylorthoformate gave the methoxy derivative as shown in Equation 38.

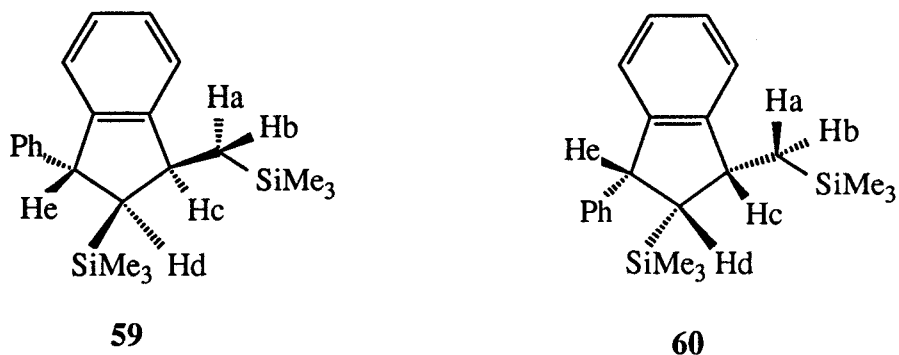
2.8 Stereochemistry

When we examined the high resolution ^1H nmr of the methylated dimers from β -trichloro **53** and β -dichloromethyl **56**-silylstyrenes, we found to our surprise that each was a mixture of two diastereomers. In the case of methylated β -trichlorosilylstyrene dimer **53**, the major diastereomer was identified using high resolution ^1H nmr.

The coupling constant data shows that the protons on the indane ring, H_e and H_d are *trans* to each other and H_d and H_c are *cis* to each other as shown in the structure **59**. This stereochemistry was then confirmed by nOe studies.

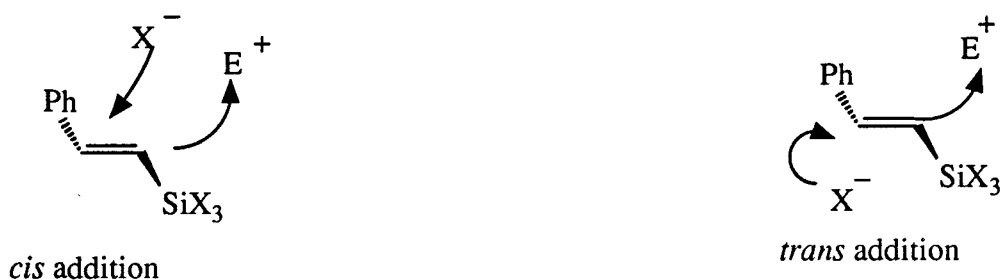
In the second case, i.e. methylated β -dichloromethylsilylstyrene dimer **56**, the major diastereomer was identified by high resolution ^1H nmr and nOe studies as **60**, where all the indane ring protons (H_e , H_d and H_c) are *cis* to each other.

From the coupling constants of the minor components, it was also found that the minor



diastereomer in the first case was identical to the major diastereomer in the second case **60** and that in the second case it was identical to the major diastereomer in the first case **59**.

It is obvious that the β -effect of silicon has an effect in controlling the stereochemistry. We don't know exactly whether the addition is *cis* or *trans* (Scheme 32). This may be studied by using deuterated triflic acid as the catalyst.



Scheme 32

Once the monomeric cation is formed, this undergoes a nucleophilic attack by a second monomer molecule forming a dimeric cation as discussed in the previous section (scheme 29 & 31).

This addition can take place in two stereochemical pathways: (i) *like* addition (*Si* face - *Si* face or *Re* face - *Re* face addition), and (ii) *unlike* addition (*Si* face - *Re* face or *Re* face - *Si* face addition). Model studies show that a *like* addition in both cases will lead to a *trans* relationship between H_c and H_d and an *unlike* addition leads to a *cis* relationship between H_c and H_d (structures **59** and **60**). Since the spectral studies suggest that H_c and H_d are *cis* to each other in both cases, we believe that in both cases it is an *unlike* addition. Now this dimeric cation undergoes termination by indane ring formation. This ring forming termination step can be under kinetic control or

thermodynamic control. In the case of the dichloromethylsilyl derivative, the β -effect is more predominant such that as soon as the dimeric cation is formed, it rotates in the direction to get maximum stabilization for the cation (i.e. the empty p orbital and $-\text{SiMeCl}_2$ group are colinear). This cation then undergoes termination by indane ring formation giving rise to a *cis* relationship between H_e and H_d (structure **60**). But in the case of trichlorosilyl derivative, the β -effect is so weak that as soon as the dimeric cation is formed, it undergoes the termination under kinetic control, giving rise to a *trans* relationship between H_e and H_d (structure **59**). This proposed theory may explain the observed stereochemistry.

2.9 Degree of polymerization (DP)

Few polymers are based upon vinylsilanes. Although trichloro-, trimethyl-, and trimethoxy-vinylsilanes may be radically polymerized to give high polymers⁽⁷²⁾, more highly substituted polymer chains have not been produced by the direct polymerization of vinylsilanes. One notable exception is the recent work of Weber and Chan who demonstrated that silylated butadienes can be polymerized⁽⁷³⁾. The difficulty in preparing highly substituted polymers is, of course, a problem that is not only limited to vinylsilanes; the polymerization of 1,2 - disubstituted olefins is normally extremely difficult⁽⁷³⁾. Thus, when a procedure is found which allows such polymerization to occur, it is of interest from a mechanistic standpoint and also with respect to the properties of materials that can be prepared under cationic conditions. The oligomerization of β -trichlorosilylstyrene leads only to low molecular weight oligomers. In the following section we describe the attempts that we made to increase the DP.

2.9.1 Effect of reaction conditions on oligomerization process

It is well known that cationic polymerization is favoured by low temperature. In our attempt to increase the degree of polymerization (DP), we did the reaction at very low temperature (-78°C).

But to our surprise we found that the results remained unchanged on going from -24°C to -78°C .

We then looked into the effect of monomer concentration on DP. Once the dimeric cation is formed, then a partition between the intermolecular oligomerization processes and intramolecular termination takes place. As stated earlier, this partition will be affected by mainly two factors: the stability of the cation and the concentration of the monomer. The higher the stability of the cation the greater will be the DP. This is clear by the fact that the amount of dimer formed in the case of β -dichloromethylsilyl derivative is less than that in the case of β -trichlorosilyl derivative. Of course, the stability of the cation can't be increased beyond a certain extent by employing the β -effect, since the leaving group ability of the silyl moiety will also increase, which may result in desilylation. This is what we observed in the oligomerization of β -dichloromethylsilylstyrene. Almost 20% desilylation has occurred in this case. This happens because the $(\sigma\text{-p})\pi$ overlap (β -effect) will weaken the C-Si bond and thus promote the cleavage processes (e.g. electrophilic substitution reactions of vinylsilanes, see introduction for more details).

As expected it was found that under very dilute conditions (8.5 mmol/L) the dimer was formed almost exclusively and the amount of dimer decreased to 50% of the total by increasing the concentration to 4.2 mol/L. Further increasing the concentration to a point of bulk polymerization didn't improve the DP. This shows that even in bulk polymerization, the chain transfer is very fast.

Then we looked into the effect of catalyst concentration on DP. Decreasing the catalyst concentration from 10 mole % to 5 mole % didn't change the DP appreciably; it only helped to slow down the rate of the reaction. A concentration less than 5 mole % led to an incomplete reaction. We also did the reaction in three different solvents: hexane, chloroform and methylene chloride, to see whether the solvent polarity will alter the DP. But it was found that the reaction was essentially the same in all three different solvents.

All these data show that it is not possible to increase the DP without changing the nature of the monomer or we may have to find some other catalytic species for the polymerization. Probably by blocking the ortho positions of the phenyl ring in the starting material we may be able to increase the DP since it will prevent the chain transfer (or termination) by the intramolecular Friedel-Crafts

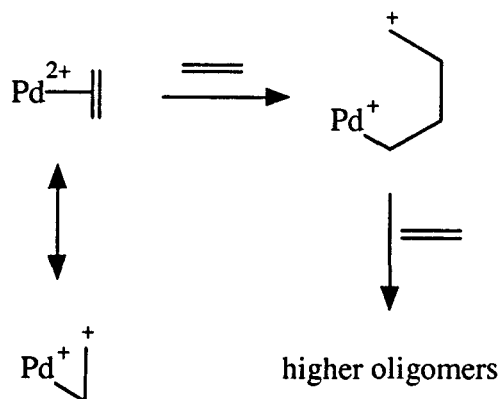
reaction. Another obvious choice is to go to a less stable cation, i.e. using the β -trifluorosilylstyrene monomer. Perhaps this could give a higher molecular weight polymer. Clearly, more work has to be done in this area before coming to a concrete conclusion. We then looked into the choice of using other catalytic species for the polymerization.

2.10 Attempted polymerization with other possible catalysts

2.10.1 Using tetrakis(acetonitrile)palladium(II)-bis-(tetrafluoroborate) catalyst

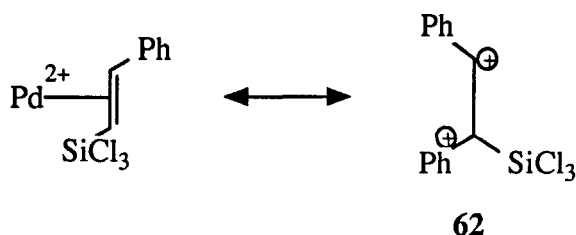
An important requirement of homogeneous transition metal catalysts is that they should have the ability to create vacant coordination sites by dissociation of weakly held ligands. Transition metal cations solvated in weakly coordinating solvents and having non-coordinating counteranions would be expected to meet this criterion. Tetrakis(acetonitrile)palladium(II)-bis (tetrafluoroborate), $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (**61**), belongs to this category. This cationic Pd(II) compound is a versatile catalyst for the polymerization of a wide range of acetylenes and olefins under relatively mild conditions⁽⁷⁴⁾. It is found to catalyze the polymerization of $\text{H}-\text{C}\equiv\text{C}-\text{R}$ ($\text{R}=\text{Ph}$, $-\text{COOMe}$), styrene, α -methylstyrene, 1,3-cyclohexadiene, norbornylene, and norbornadiene under very mild conditions. A possible mechanism for the catalytic polymerization of olefins by this cationic Pd(II) compound would be one which involves direct nucleophilic attack on a coordinated olefin by a second olefin (Scheme 33).

Nucleophilic attack on olefins bound to transition metal centers is a well documented phenomenon⁽⁷⁵⁾, and in view of the strongly electrophilic nature of **61**, participation of even weak nucleophiles such as olefins in a similar reaction step seems feasible. The resulting palladium bound carbonium ion species can further react with olefins to produce higher oligomers. In light of this catalytic property of **61** we thought it is worth attempting the polymerization of β -trichlorosilylstyrene using **61**. Coordination of cationic Pd(II) species to β -trichlorosilylstyrene should give a Pd bound carbonium ion species **62** which is stabilized by the phenyl group and the



Scheme 33

silicon (Scheme 34). This in turn may lead to polymerization⁽²¹⁾.

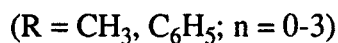
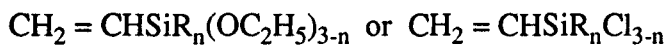


Scheme 34

Compound **61** was synthesized through the interaction of palladium metal with 2 equivalents of nitrosyl tetrafluoroborate in acetonitrile⁽⁷⁶⁾. A catalytic amount of this was then allowed to react with β -trichlorosilylstyrene in CH_3CN . Unfortunately no reaction was observed. Only starting materials were recovered. It is not that surprising due to the fact that it is very difficult to polymerize 1,2-disubstituted olefins.

2.10.2 Free radical polymerization

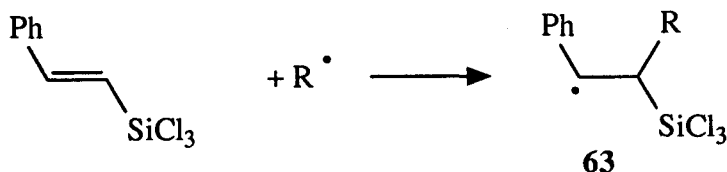
It has been reported⁽⁷⁷⁾ that, in general, vinylsilane compounds of the type:



do not undergo homopolymerization or form homopolymers of relatively low molecular weight.

Bailey *et al*⁽⁷²⁾ has reported the polymerization of vinyltriethoxysilane using di-tert-butylperoxide as the catalyst. It gave clear, colourless, viscous liquid polymers of 3000 to 8000 molecular weight.

In the case of β -trichlorosilylstyrene, the expected intermediate radical **63** is much more stable than simple vinylsilanes because of the resonance stabilization by the phenyl group (scheme



Scheme 35

35). So we examined the reaction of β -trichlorosilylstyrene with radical initiators AIBN and di-*tert*-butylperoxide at elevated temperatures. Here again only starting materials were recovered in both cases.

2.11 Copolymerization of styrene with β -trichlorosilylstyrene

Low molecular weight oligomers are of little use as far as polymeric applications are concerned. Since all our attempts to increase the DP failed, we examined the copolymerization of styrene and β -trichlorosilylstyrene. Copolymers of trimethylsilylstyrene (where the silyl group is on the ring) with chloromethylstyrene have been developed by Suzuki *et al*⁽⁷⁸⁾ as the top imaging layer resist in a bi-layer resist system. A number of other vinylsilicone-organic vinyl copolymers have been previously described by several investigators⁽⁷⁹⁾. So we decided to proceed with the copolymerization of β -trichlorosilylstyrene with styrene. We selected two catalysts for this purpose: (i) the cationic Pd(II) compound $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$, and (ii) triflic acid, $\text{CF}_3\text{SO}_3\text{H}$. We have discussed the catalytic activity and preparation of the Pd(II) compound **61** in the section 2.10.1. Addition of catalytic amount of this catalyst **61** to a mixture of styrene and β -trichlorosilylstyrene in acetonitrile gave only the starting materials; no polymerization occurred. But in the second case, upon addition of catalytic amount of triflic acid to a cooled (-23°C) mixture of styrene and β -trichlorosilylstyrene in a 50:50 ratio gave a highly viscous liquid. The nmr showed no vinyl proton peak. This product was then methylated using methylmagnesium bromide and separated on a flash column. Four fractions were obtained. The first three were negligibly small. So analysis was

done only on the 4th fraction. From the proton nmr of this fraction, comparing the ratio of methyl protons to aromatic protons, it was calculated that in the copolymer β -trichlorosilylstyrene and styrene are in the ratio 0.8:1. More work is underway to establish the nature of this copolymer and to control this copolymerization reaction.

Conclusion

It is known that trimethylsilylstyrene undergoes protodesilylation under acidic conditions. But we found that the corresponding β -trichlorosilyl compound undergoes oligomerization with triflic acid and triflic acid is the only acid known so far which can catalyze such an oligomerization. The β -effect plays a significant role in the weakening of the silicon-carbon bond and thus promotes the cleavage process in the case of trimethylsilylstyrene. But the presence of electronegative chloride groups on silicon weakens the β -effect and hence the leaving group ability of the silyl group. Thus, in the case of β -trichlorosilylstyrene, instead of protodesilylation, oligomerization takes place under acidic conditions. The importance of the β -effect and leaving group ability is also evidenced from the oligomerization reaction of β -dichloromethylsilylstyrene where partial protodesilylation is also observed.

In the polymerization reaction of β -trichlorosilylstyrene with triflic acid, only low molecular weight polymers are formed. This is because the chain termination by an internal Friedel-Crafts reaction resulting in indane terminated oligomers, is much faster than the chain propagation reaction. As far as polymeric applications are considered, these low molecular weight, functionalized silicon polymers are of limited use. Our attempts to increase the degree of polymerization didn't succeed. The highest molecular weight that we obtained is that of a decamer. So we tried the copolymerization of β -trichlorosilylstyrene with styrene which was successful. More work is underway to establish the nature of this copolymerization reaction.

Experimental

3.1 General Remarks

All reactions were carried out in a dry nitrogen atmosphere using syringe techniques, unless otherwise stated. For polymerization reactions, -15°C , -23°C and -78°C were obtained by using $\text{NH}_4\text{Cl}/\text{ice}$, CO_2/CCl_4 and $\text{CO}_2/\text{acetone}$ cooling baths, respectively. All reagents used were either from new bottles or were freshly distilled. Chloroform-*d* (CDCl_3 , min. isotopic purity 99.8 atom% D), purchased from Merck Frosst Canada Inc. was used without further purification. Methylene chloride (CH_2Cl_2), diethyl ether and tetrahydrofuran (THF) were purified by distillation from anhydrous calcium hydride, sodium/benzophenone and potassium/benzophenone, respectively. For flash column chromatography, silica gel (230-400 mesh) obtained from Merck, was used. All boiling points are uncorrected.

Analytical instrumentation: IR spectra were recorded on a Perkin-Elmer model 283 spectrophotometer. ^1H nmr spectra were recorded on either a Varian EM-390 (90 MHz) spectrometer or a Bruker AM-500 (500 MHz) spectrometer. Unless otherwise stated the reported spectra were recorded at 90 MHz. Chemical shifts are given in parts per million (ppm) with the tetramethylsilane (TMS) signal at 0.0 ppm as the internal standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants (J) are given in Hz. A Bruker WM 250 spectrometer was used for recording ^{13}C (broad band decoupled) and ^{29}Si (DEPT in decoupled mode) spectra. Mass spectra were recorded on either a VG 7070-F or a VG ZAB-E spectrometer (70 ev, electron impact, resolution ≈ 1000). Chloroform-*d* was used as the solvent in the sample preparation for all of the spectrometric analysis.

3.2 Hydrosilylation of Phenylacetylene

General Procedure

To a solution of phenylacetylene in THF was added chlorosilane and hexachloroplatinic acid (0.1 M in isopropanol). The solution was stirred for 20 - 24 hrs. and distilled under reduced pressure. The product was isolated as a clear, colorless, slightly viscous liquid.

β -Trichlorosilylstyrene: Phenylacetylene (8.3 mL, 75.0 mmol), trichlorosilane (11.2 mL, 110.0 mmol), H_2PtCl_6 (0.2 mL, *ca.* 0.02 mmol), THF (10 mL). yield: 16.8 gms, 95%; b.p. 89-91°C/1.3 Torr; ^1H nmr: δ = 6.40 (d, 1H, J=19 Hz), 7.40 (d, 1H, J=19 Hz), 7.50 (m, 5H, aromatic); ^{29}Si nmr: δ = -2.14; MS: m/z = 238 (37), 236 (37), 201 (17), 165 (7), 103 (100), 77(8); IR (KBr): ν = 3080, 3060, 3030, 1670, 1630, 1600, 1570, 1490, 1445, 1330, 1190, 1175, 1020, 980, 740 cm^{-1} .

β -Methyldichlorosilylstyrene: phenylacetylene (8.3 mL, 75.0 mmol), methyldichlorosilane (11.5 mL, 110.0 mmol), H_2PtCl_6 (0.2 mL, *ca.* 0.02 mmol), THF (10 mL). yield 14.85 g, 92%; b.p. 64-66°C/2 Torr; ^1H nmr: δ = 0.9 (s, 3H), 6.35 (d, 1H, J=19 Hz), 7.3 (d, J=19 Hz), 7.4 (m, 5H, aromatic); ^{29}Si nmr: δ = 17.8; MS: m/z = 220 (14), 219 (11), 218 (69), 217 (16), 216 (100), 203 (24), 201 (35), 181 (14), 167 (38), 165 (98), 118 (21), 103 (70), 102 (26), 77 (27), 63 (17); IR (KBr): ν = 3060, 3025, 2240, 1600, 1570, 1490, 1020, 975, 815, 775, 720 cm^{-1} .

β -Phenyldichlorosilylstyrene: phenylacetylene (1.8 mL, 16.4 mmol), phenyldichlorosilane (2.0 mL, 13.7 mmol), H_2PtCl_6 (1 drop, *ca.* 0.005 mmol), THF (2 mL). Yield: 3.06 g, 80%; b.p. 158°C/3 Torr. ^1H nmr: δ = 6.6 (d, 1H, J=19 Hz), 7.5 (m, 11H). MS: m/z = 278 (M^+), 243, 180 (100), 165, 102, 77.

Note: In the hydrosilylation reaction there is an induction period to start the reaction after the addition of the catalyst chloroplatinic acid. This induction period can last for a relatively long time (\approx 3 -4 hrs.) followed by a very fast exothermic reaction which is dangerous when large amounts of reagents are employed. Attaching a water condenser to the reaction flask and keeping the reaction flask in a water bath are recommended measures to reduce the likelihood

of this potentially dangerous situation.

3.3 Polymerization of silylstyrenes

General Procedure

A solution of the silylstyrene in chloroform-*d* (50%, V/V) was cooled to -23°C, to which triflic acid (10 mol%) was added. Upon addition of triflic acid, the solution immediately turned red orange. It was then kept stirred for 4 - 5 hrs, then allowed to warm up to the room temperature and the solvent was removed by rotary evaporation, the resulting mixture being dark red orange and highly viscous. Alternatively the triflic acid can be removed by adding triethyl amine.

β -Trichlorosilylstyrene polymer: β -trichlorosilylstyrene (2.68g, 11.3 mmol); triflic acid (0.1 mL, 1.13 mmol). ^1H nmr: δ = 1.6-2.7(m); 3.9-4.8(m); 7.2(m). ^{29}Si nmr: δ = 10.48, 9.82. ^{13}C nmr: δ = 25 - 55 (m), 120 -130 (m), 140 -150 (m). IR(KBr): ν = 3060, 3020, 2900, 1590, 1480, 1440, 1270, 1230, 1175, 1015, 725, 680, 570 cm^{-1} .

β -Dichloromethylsilylstyrene polymer: β -dichloromethylsilylstyrene (2.45g, 11.3 mmol), triflic acid (0.1 mL, 1.13 mmol). ^1H nmr: δ = 0.3(s); 0.65(s); 0.7-4.5(m); 7.4(m, aromatic).

β -phenyldichlorosilylstyrene polymer: β -Phenyldichlorosilylstyrene (3.15g, 11.3 mmol); triflic acid (0.1 mL, 1.13 mmol). ^1H nmr: δ = 1.5 (m), 4.25 (m), 7.3(m).

3.4 Permethylation of silylstyrene polymer

General procedure:

To a cooled (0°C) solution of the polymer in anhydrous diethyl ether(10 mL) was added an excess of methylmagnesium bromide. The mixture was stirred overnight at which time it contained a thick white precipitate, was transferred to a separatory funnel and \approx 20 mL of water was added. Two

clear colorless layers were obtained. The bottom aqueous layer was separated out and washed with ether (2×10 mL). The ether fraction from the combined organic extracts were then dried over anhydrous MgSO_4 and the solvent removed under reduced pressure (20 Torr).

Permethylated β -trichlorosilylstyrene polymer:

β -trichlorosilylstyrene polymer (1 g); methylmagnesium bromide (10 mL, 2.5 M in diethylether).

Yield: 0.7 g, 70%. ^1H nmr: $\delta = 0.0 - 0.2$ (m), 1.0 - 1.5 (m), 1.9 - 2.2 (m), 3.5 - 3.8 (m), 4.5 (d), 7.4

(m, aromatic). Permethylated β -dichloromethylsilylstyrene polymer: β -dichlorosilylstyrene polymer

(1 g); methylmagnesium bromide (7.0 mL, 2.5 M in diethylether). Yield: 0.75 g, 75%. ^1H nmr: $\delta =$

0.1 - 0.6 (m), 1.3 - 1.6 (m), 2.6 (m), 3.8 (d), 5.5 (m), 7.5 (m, aromatic).

3.5 Separation of permethylated polymer

3.5.1 Separation of permethylated β -trichlorosilylstyrene polymer

T. L. C. showed 3 major fractions in the product (solvent - hexane). R_f values: 0.366, 0.233 & 0.166. The three fractions were collected using flash chromatography (hexane as eluent, 1.4 g of the compound was used). The solvents were removed under reduced pressure.

The first fraction was shown to be a dimer. Yield: 0.70 g, 50%. ^1H nmr (500 MHz): $\delta = 0.00$ (s, 9H), 0.14 (s, 9H), 1.03 (dd, 1H, $J = 12.03, 14.33$), 1.14 (dd, 1H, $J = 14.33, 2.95$), 2.0 (dd, 1H, $J = 6.5, 11.49$), 3.63 (ddd, 1H, $J = 2.87, 11.98, 6.48$), 4.5 (d, 1H, $J = 11.48$), 7.12 (m, 9H, aromatic). ^{13}C nmr (CDCl_3): $\delta = 150.4, 149.05, 144.94, 129.12, 128.48, 126.60, 126.28, 125.70, 124.77, 123.62, 51.67, 49.24, 43.29, 21.76, -0.11, -0.72$. ^{29}Si nmr: $\delta = -0.61, 0.39$. MS: $m/z = 352$ (15, M^+), 337 (5), 278 (10), 265 (10), 204 (9), 135 (14), 73 (100). IR (neat): $\nu = 3080, 3060, 2950, 2900, 2860, 1600, 1490, 1470, 1450, 1410, 1260, 1240, 1140, 1025, 990, 925, 870-810, 770, 740, 690, 635, 485 \text{ cm}^{-1}$. Anal. calcd. for the dimer ($\text{C}_{22}\text{H}_{32}\text{Si}_2$), Mol. Wt. 352.67; C 74.92, H 9.15; found: C 74.80, H 9.17.

The second fraction was identified to be the trimer contaminated with traces of tetramer.

Yield: 0.2 g, 15%. ^1H nmr (500 MHz): $\delta = -0.23 - 0.04$ (m, 27H), 0.82 - 1.04 (m, 2H), 1.30 - 1.47 (m, 1H), 1.82 - 1.89 (m, 1H), 3.41 - 3.53 (m, 1H), 4.03 - 4.12 (m, 1H), 4.30 - 4.38 (m, 1H), 7.0 - 7.32 (m, 14H, aromatic). ^{13}C nmr: $\delta = -1.89 - 0.99$ (m), 14.08 (s), 21 - 34 (m), 42 - 52 (m), 122.3 - 129 (m),

142 - 147 (m). ^{29}Si nmr: $\delta = -0.84 - 0.59$ (m). MS: $m/z = 704$ (M^+ , tetramer, 1), 672 (0.5), 617 (0.5), 570 (1), 555 (0.5), 528 (M^+ , trimer, 100), 513 (51), 441 (64), 351 (39), 274 (70), 249 (94), 177 (100). IR (neat): $\nu = 3060, 3020, 2950, 2900, 1600, 1490, 1450, 1410, 1250, 1165, 855, 825, 750, 690, 600, 430 \text{ cm}^{-1}$.

The third fraction was found to be a mixture of higher oligomers. Yield: 0.4 g, 30%.

^1H -nmr, ^{13}C -nmr and ^{29}Si -nmr were used in conjunction with mass spectroscopy to confirm that this fraction was indane terminated oligomers; estimated to be 4 units to 9 units in chain length as evidenced from the mass spectrum. MS: $m/z = 1511$ (9mer $^+$ -73(TMS)), 1335 (8mer $^+$ -73), 1159 (7mer $^+$ -73), 983 (6mer $^+$ -73), 807 (5mer $^+$ -73). GPC confirmed only that the materials were of low molecular weight. ^1H -nmr (250 MHz): $\delta = 0.00$ (m), 0.9 - 2.0 (m), 3.2 - 3.6 (m), 3.9 (m), 4.5 (m), 7.1 (m, aromatic). ^{29}Si -nmr (250 MHz): $\delta = 0.00$ (m), 16.9 (m). ^{13}C -nmr (CDCl_3 , 500 MHz): $\delta = -1.2 - 1.0$ (m), 21.5 - 34 (m), 42 - 52 (m), 122 - 129 (m), 144 - 149 (m).

3.5.2 Separation of permethylated β -dichloromethylsilylstyrene polymer

T.L.C. showed 3 major compounds in the product (solvent - hexane). R_f values: 0.37, 0.35, 0.16. On a flash column, the first two compounds (R_f values 0.37 & 0.35) eluted as a single fraction. This was then separated using a chromatotron.

The first fraction was shown to be a dimer. Yield: 0.32 g, 40%. ^1H nmr (500 MHz): $\delta = -0.05$ (s, 9H), 0.01 (s, 9H), 1.1 (dd, 1H, $J = 6.6, 15.2$), 1.14 (dd, 1H, $J = 15.2, 5.2$), 1.54 (t, 1H, $J = 8.25$), 3.32 (dd, broad, 1H, $J = 6.8, 13.1$), 4.16 (d, 1H, $J = 8.5$), 7.12 (m, 9H, aromatic). ^{13}C nmr: $\delta = -1.83$ (s), 0.29 (s), 25.04 (s), 42.58 (s), 44.99 (s), 53.09 (s), 123 - 129 (m), 146 - 150 (s). MS: $m/z = 352$ (M^+ , 7), 337 (9), 265 (100), 221 (25), 204 (14), 177 (24), 147 (30), 135 (40), 73 (100). IR (KBr): $\nu = 2975, 2240, 1790, 1450, 1370, 1240, 1080, 900, 720, 635 \text{ cm}^{-1}$.

The second fraction was identified as a desilylated trimer by ^1H nmr and mass spectrum. Yield: 0.15 g, 20%. ^1H nmr (250 MHz): $\delta = -0.19$ (s, 9H), -0.004 (s, 9H), 0.9 (d, 2H, $J = 6.45$), 1.16 (m, 2H), 2.55 (dd, 1H, $J = 5.27, 12.25$), 2.95 (m, 1H), 3.18 (dd, 1H, $J = 6.1, 11.7$), 4.35 (d, 1H, $J = 5.3$),

7.1 (m, 14H, aromatic). MS: $m/z = 456 (M^+, 12), 441 (65), 426 (35), 367 (100), 353 (88), 337 (64), 321 (28)$. IR (KBr): $\nu = 3060, 3020, 2975, 2900, 2240, 1590, 1480, 1440, 1400, 1240, 900, 730, 690, 635 \text{ cm}^{-1}$.

The third fraction, we believe based on ^1H nmr, to be a mixture of indane terminated higher oligomers. The exact structure of these oligomers are not known. ^1H nmr: $\delta = 0.0 (m), 1.1 (m), 2.6 (m), 4.3 (m), 7.4 (m)$.

3.6 Polymerization of β -trichlorosilylstyrene under different reaction conditions

3.6.1 Polymerization at different temperatures

The polymerization of β -trichlorosilylstyrene was done at (a) -78°C and at (b) room temperature, keeping the procedure and all other reaction conditions same as in the general procedure. β -Trichlorosilylstyrene (2.68 g, 11.3 mmol); triflic acid (0.1 mL, 1.13 mmol).

(a): ^1H nmr: $\delta = 1.6 - 2.7 (m); 3.9 - 4.8 (m); 7.2 (m)$.

(b): ^1H nmr: $\delta = 1.6 - 2.7 (m); 3.9 - 4.8 (m); 7.2 (m)$.

These products were then permethylated and separated according to the general procedure 3.4 and 3.5. The products and the product ratios were found to be the same as obtained in the general case 3.5.1.

3.6.2 Polymerization at different monomer concentrations

Polymerization of β -trichlorosilylstyrene was done at four different monomer concentrations following the general procedure 3.3.

(i) [Monomer] = 8.43 mmol/L.

β -Trichlorosilylstyrene (0.1 g, 0.422 mmol), chloroform (50 mL), triflic acid (0.01 mL, 0.1 mmol).

^1H nmr after 48 hrs showed the complete disappearance of vinyl protons. ^1H nmr: $\delta = 1.6 - 2.7 (m); 3.9 - 4.8 (m); 7.2 (m)$. The product was then permethylated using methylmagnesium bromide as

discussed in the general procedure 3.4. T.L.C. of the product showed three fractions of which the second and the third fractions were negligibly small. The permethylated product was then separated on a chromatotron to get the major fraction (0.096 g, 96%) using hexane as the solvent. ^1H nmr, ^{29}Si nmr, and IR were done on this fraction and were found to be identical to that of the methylated β -trichlorosilylstyrene dimer.

(ii) [Monomer] = 42.15 mmol/L.

β -Trichlorosilylstyrene (0.1 g, 0.422 mmol), chloroform (10 mL), triflic acid (0.01 mL, 0.1 mmol).

Polymerization procedure is the same as the general procedure 3.3. ^1H nmr of the product: $\delta = 1.6 - 2.7$ (m), $3.9 - 4.8$ (m), 7.2 (m). This product was then permethylated as in the previous case. T.L.C. of the product showed 3 fractions. They were then separated on a chromatotron using hexane as the eluent. The first fraction (.08 g, 80%) was found to be identical to the permethylated β -trichlorosilylstyrene dimer by spectral studies. No analysis was done on the other minor fractions.

(iii) [Monomer] = 4.2 M/L. This experiment is same as the general polymerization experiment 3.3 discussed earlier.

(iv) Bulk polymerization: Polymerization of β -trichlorosilylstyrene was done using triflic acid without a solvent. All other conditions were kept the same as in the general procedure, 3.3.

β -Trichlorosilylstyrene (2.68 g, 11.3 mmol), triflic acid (0.1 mL, 1.13 mmol). The reaction was over in 2 hrs. ^1H nmr: $\delta = 1.6 - 2.7$ (m), $3.9 - 4.8$ (m), 7.2 (m). The product was then permethylated and separated as in the general procedure 3.4 and 3.5 respectively. The products and the product ratios were found to be identical to that obtained in the general case, 3.5.1.

3.6.3 Polymerization using different solvents

The polymerization of β -trichlorosilylstyrene was done in pentane and in dichloromethane employing the same conditions and quantities of the reagents as in the general procedure 3.3. The products were then permethylated and separated as in the general case 3.4 and 3.5 respectively. Analyses of the products showed that the products and the product ratios remained the same as in the

general case 3.5.1 where chloroform was used as the solvent.

3.6.4 Polymerization using different catalyst concentrations

The polymerization reaction of β -trichlorosilylstyrene was repeated with several triflic acid concentrations ; (1) 0.1 mL, 1.13 mmol, 10 mole%; (2) 0.07 mL, 0.79 mmol, 7 mole%; (3) 0.05 mL, 0.56 mmol, 5 mole%; (4) 0.04 mL, 0.45 mmol, 4 mole%; and (5) 0.02 mL, 0.22 mmol, 2 mole%; all other reaction conditions and reagent quantities were kept the same as in the general procedure 3.3. In the first 3 cases permethylation followed by separation as in the general procedure 3.4 and 3.5 respectively showed that the products obtained were identical to that obtained in the general case 3.5.1. In the last two cases, ^1H nmr of the polymerization products showed vinyl peaks even after 24 hrs indicating incomplete polymerization.

3.7 Attempted radical polymerizations

3.7.1 Using di *t*-butylperoxide⁽⁷⁷⁾

Di-*t*-butylperoxide (2 mg, 0.014 mmol, 0.1 wt%) was added to β -trichlorosilylstyrene (2 g, 8.4 mmol) and refluxed for 16 hrs at 140°C under nitrogen atmosphere. ^1H -nmr showed no change for the starting material; no polymerization had occurred.

3.7.2 Using 2,2'-azobisisobutyronitrile (AIBN)

AIBN (50 mg, 0.3 mmol) was added to a solution of β -trichlorosilylstyrene (1 g, 4.2 mmol) in dry chloroform (1 mL) and kept stirred under nitrogen atmosphere at 80°C. ^1H -nmr taken after 6 hrs. and after 24 h. showed no change for the starting material.

3.8 Other attempted cationic polymerizations

3.8.1 Using tetrafluoroboric acid ($\text{HBF}_4 \cdot \text{O}(\text{CH}_3)_2$)

To a cooled (-25°C) solution of β -trichlorosilylstyrene (1 g, 4.2 mmol) in dry chloroform (1 mL) was added $\text{HBF}_4 \cdot \text{O}(\text{CH}_3)_2$ (56 mg, 10 mol%) and kept stirred under nitrogen atmosphere.

^1H -nmr taken after 24 h. showed no change for the starting materials.

3.8.2 Using tetrakis(acetonitrile)palladium(II)bis(tetrafluoroborate) [$\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ ⁽⁷⁴⁾

β -Trichlorosilylstyrene (1 g, 4.2 mmol) was added to a solution of the Pd(II) catalyst (50 mg, 0.11 mmol) in MeCN (10 mL) and stirred at room temperature under nitrogen atmosphere. ^1H -nmr taken after 24 h. showed no polymerization had occurred.

3.9 Methoxylation of silylstyrenes⁽⁷¹⁾

General procedure

Freshly distilled methyl orthoformate was added to silylstyrene followed by dry methanol (5 mL). An exothermic reaction began immediately with the evolution of a gas. A water bath was used to maintain the reaction temperature below 46°C . After stirring for 1 h., it was refluxed for 2 h. and then distilled under reduced pressure.

β -Trimethoxysilylstyrene: β -trichlorosilylstyrene (10 g, 42.1 mmol), methylorthoformate (14 mL, 126.3 mmol). Yield: 8.7 g, 92%; b.p. $78\text{-}80^\circ\text{C}/5$ Torr. ^1H -nmr: $\delta = 3.7$ (s, 9H), 6.2 (d, 1H, $J=19$ Hz), 7.3 (d, 1H, $J=19$ Hz), 7.5 (m, 5H, aromatic). ^{29}Si -nmr: $\delta = -53.34$ IR (KBr): $\nu = 2940, 2830, 1950, 1890, 1750, 1600, 1570, 1485, 1440, 1320, 1280, 1180, 1090, 985, 840, 780, 720, 675, 660, 450$ cm^{-1} . MS: $m/z = 224$ (M^+ , 65), 209 (7), 194 (59), 162 (94), 121 (73), 104 (58), 91 (100), 77 (22).

β -Dimethoxymethylsilylstyrene: β -dichloro methylsilylstyrene (10 g, 46.1 mmol), methyl orthoformate (10.5 mL, 94.9 mmol). Yield: 7 g, 73%; b.p. $75\text{-}77^\circ\text{C}/5$ Torr. ^1H nmr: $\delta = 0.3$ (s, 3H), 3.6 (s, 6H), 6.3 (d, 1H, $J= 19$ Hz), 7.3 (d, 1H, $J= 19$ Hz), 7.5 (m, 5H, aromatic). IR (KBr): $\nu = 2960,$

2940, 2830, 2225, 1600, 1565, 1485, 1440, 1250, 1185, 1080, 985, 900, 820, 765, 730, 680, 635 cm^{-1} . MS: $m/z = 208$ (M^+ , 30), 193 (100), 178 (8), 161 (68), 145 (8), 131 (16), 105 (40), 91 (40), 75 (35).

3.10 Attempted polymerization of β -trimethoxysilylstyrene

To a cooled solution (-23°C) of β -trimethoxysilylstyrene (4 mL, 19.6 mmol) in CDCl_3 (4 mL, 50%, V/V) was added triflic acid (0.3 mL, 3.4 mmol) and kept stirred for 6 h. No polymerization was observed; starting materials were recovered.

The polymerization reaction was also tried with β -dimethoxy methylsilylstyrene monomer under the same conditions and the result was the same; no polymerization occurred.

3.11 Methoxylation of β -trichlorosilylstyrene oligomers

The methoxylation was done as described in the general procedure for methoxylation of halosilylstyrenes.

β -Trichlorosilylstyrene oligomers (1 g), methanol (5 mL), methyl orthoformate (1.5 mL). The product was then rotary evaporated to get a highly viscous liquid. ^1H nmr: $\delta = 1.6 - 2.7$ (m), 3.1 - 3.6 (m), 3.9 - 4.8 (m), 7.2 (m).

3.12 Copolymerization of β -trichlorosilylstyrene with styrene

To a cooled (-23°C) mixture of styrene (1 g, 9.6 mmol) and β -trichlorosilylstyrene (2.3 g, 9.6 mmol) in CDCl_3 (2 mL) was added triflic acid (0.05 mL, 0.6 mmol) and stirred for 3 hrs under nitrogen atmosphere. ^1H nmr: $\delta = 1.0 - 1.6$ (broad), 1.9 - 2.3 (broad), 2.6 (m), 4.2 (broad), 7.2 (broad).

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