THE ROLES OF LIGANDS ON SILICON

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By

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ABSTRACT

This thesis presents a study of the roles of ligands on silicon in two parts.

In Part A, the relationship between the β-effect - the ability of a silyl group to stabilize a carbocation β to silicon, and the electron-withdrawing ability of the ligands on silicon was examined. The bromination of a series of (E)-β-silylstyrenes was chosen as a way to quantify the β-stabilization. The degree of *syn*-addition of bromine to (E)-β-silylstyrene was used as a measure of the stabilizing ability of the silyl group.

The bromination of a series of four (E)-β-silylstyrenes was investigated [ligands on silicon: $(SiMe_3O)_3$; $(CH_3COO)_3$; $(CCl_3COO)_3$; $(CF_3COO)_3$]. It was found that the degree of *syn*-addition decreases as the silyl group electronegativity increases. Combined with the results previously obtained in our lab, two linear relationships between the degree of *syn*-addition and the silyl group electronegativity were observed in two groups of (E)-β-silylstyrenes [Group A, ligands on silicon: $Me_{3-n}X_n$, n = 1-3, X = Cl, F and $(MeO)_3$; $(Me_3SiO)_3$ and Group B, $(CH_3COO)_3$; $(CCl_3COO)_3$; $(CF_3COO)_3$; $(p\text{-}MeOPhO)_3$; $(PhO)_3$; $(p\text{-}ClPhO)_3$]. The degree of *syn*-addition was found to be more sensitive towards the group electronegativity for compounds in Group B. It was also found that, as the group electronegativity increases, the α-SiCH ^1H and ^{29}Si NMR chemical shifts of compounds in Group A decrease. In contrast, the α-SiCH ^1H and ^{29}Si NMR chemical shifts of compounds in Group B tend to increase.

In Part B, a series of hydrosilanes were studied and their reactivities in iodination were found to be in the order: $CH_3SiH(OEt)_2$ > PMHS > CH_3SiHCl_2.

The behavior of these organosilicon compounds is discussed in terms of the structural features of the silyl groups - the ligands on silicon.

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Part A

GENERAL INTRODUCTION

Silicon chemistry has attracted increasingly the attention of organic chemists owing to its unusual behaviors in chemistry. We have chosen to investigate some of these effects of silicon, focussing in particular on the roles played by the ligands on silicon.

In the first part of this thesis (Part A), the role of ligands on silicon in the β-effect is described. In the second part (Part B), the reactivity of several hydrosilanes is examined as a consequence of the other ligands on silicon. In each of these sections, a separate introduction, results, discussion and conclusion will be presented.

CHAPTER 1

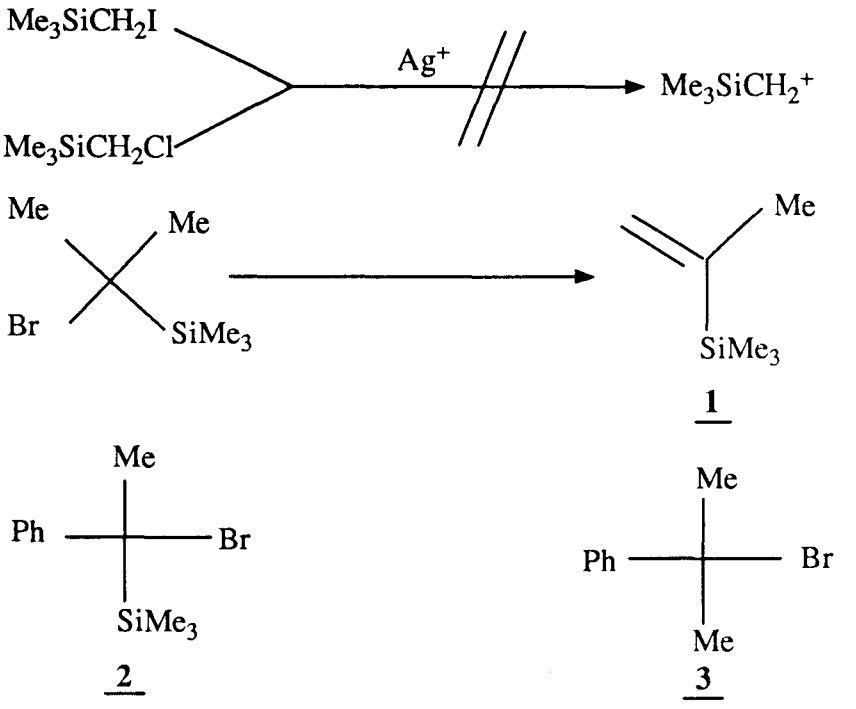
INTRODUCTION

1.1 The β-Silicon Effect[1]

In the past few decades, the explosive growth of use of silicon reagents in organic synthesis is a consequence of certain "unusual properties"[2] of this element. One of the most profound properties is the β-effect - the ability of silicon to stabilize and to promote the generation of a carbonium ion in the β-position.

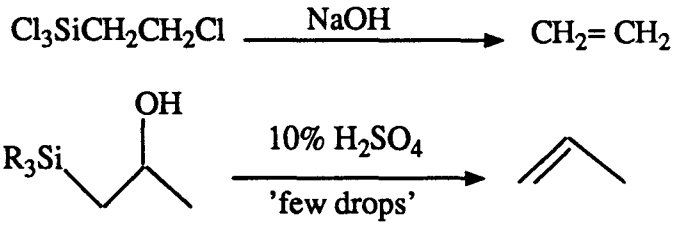
In early studies, it was found that reactions which involve carbonium ion formation or development α to silicon are disfavored, whereas carbonium ion formation or development β to silicon is encouraged. For example, halogenoalkyltrialkylsilanes[3a] are very unreactive under SN1 conditions: neither chloromethyl- nor iodomethyltrimethylsilane[3b] reacts with silver(I) ions; solvolysis[3c] of 2-bromo-2-(trimethylsilyl)propane gives only the vinylsilane **1** by what is believed to be an E2 process; the bromide **2** has been reported[3d] to be 110 times less reactive towards aqueous acetone at 50°C than is the bromide **3** at 0°C (Scheme 1-1):

Scheme 1-1



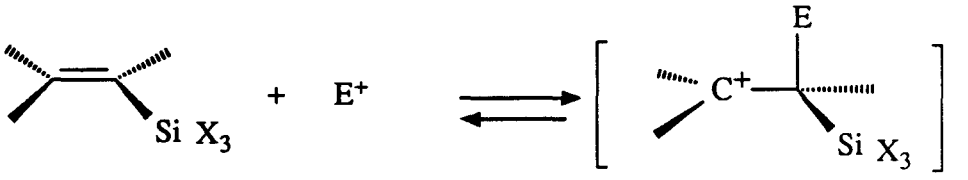
On the other hand, many aliphatic β-functionalized organosilanes exhibit abnormally high reactivity. In 1946, Sommer and Whitmore reported[4a] that β-chloroethyltrichlorosilane was so reactive towards attack by base that it could be titrated with alkali producing ethane. They also found[4b] that 2-hydroxypropyltrialkylsilanes underwent rapid conversion into propene on treatment with dilute sulfuric acid (Scheme 1-2):

Scheme 1-2

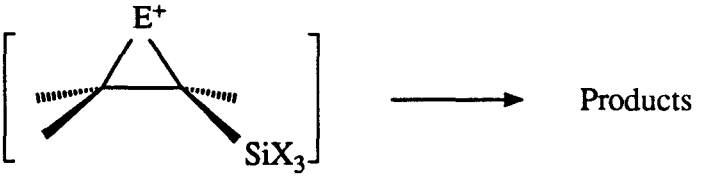


The β-effect has also been invoked mechanistically in most of the reactions in which electrophilic attacks on aryl-, vinyl-, allyl-, allenyl-, alkynyl, propargylsilanes and so on are involved[5]. Electrophilic attacks on these functional groups can often be controlled by the presence of a silyl moiety in the starting materials. Typically, in these reactions, the silyl group encourages the electrophiles to attack at the site which will generate a carbonium ion β to the silicon atom (Scheme 1-3):

Scheme 1-3

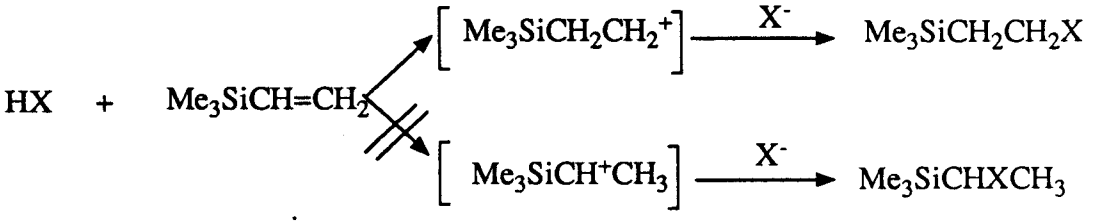


or:



An example is the *anti*-Markovnikov addition of hydrogen halides to vinylsilanes[6]. The β-cation is definitely preferred over the α-cation owing to the directing influence of the silyl group (Scheme 1-4):

Scheme 1-4



This phenomenon has been commonly ascribed to (σ-p)π overlap between the bonding σ-level of the C-Si bond with the adjacent empty p-orbital of the carbonium ion[1,5] (Figure 1-1). The proposed involvement of the Si-C linkage can be understood by consideration of the high degree of polarization of the $Si^{\delta+}$-$C^{\delta-}$ bond owing to the greater electronegativity of carbon (electronegativity of Pauling's scale[7]: C, 2.5; Si, 1.8). This ensures a high coefficient on carbon and results in an enhanced ability of the C-Si σ orbital to stabilize an adjacent electron-poor center by orbital overlap. In addition, and perhaps of more importance, the Si-C bonding orbital is higher in energy than an H-C or C-C bonding orbital, and the energy match with the empty p orbital is therefore better. The above factors make the hyperconjugation of the Si-C bond with the empty p orbital more efficient and greater overall lowering of energy than would be obtained from similar C-C or C-H bond hyperconjugation.

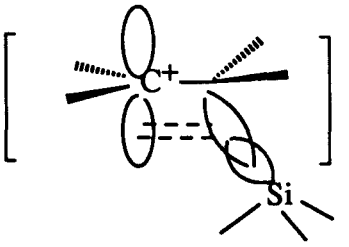
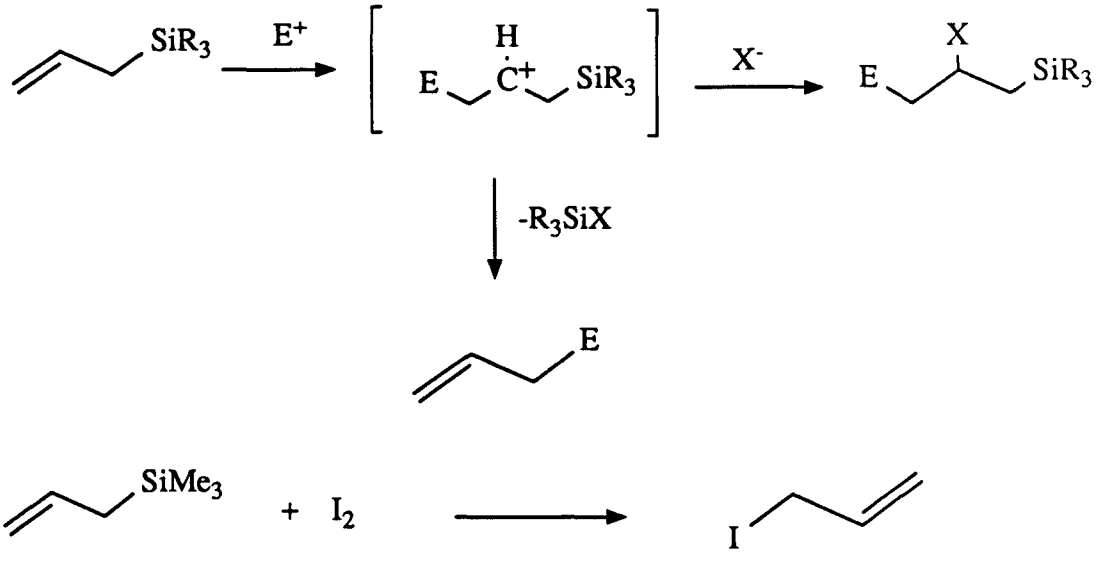


Figure 1-1

1.2 Reactions Involving β-Effect

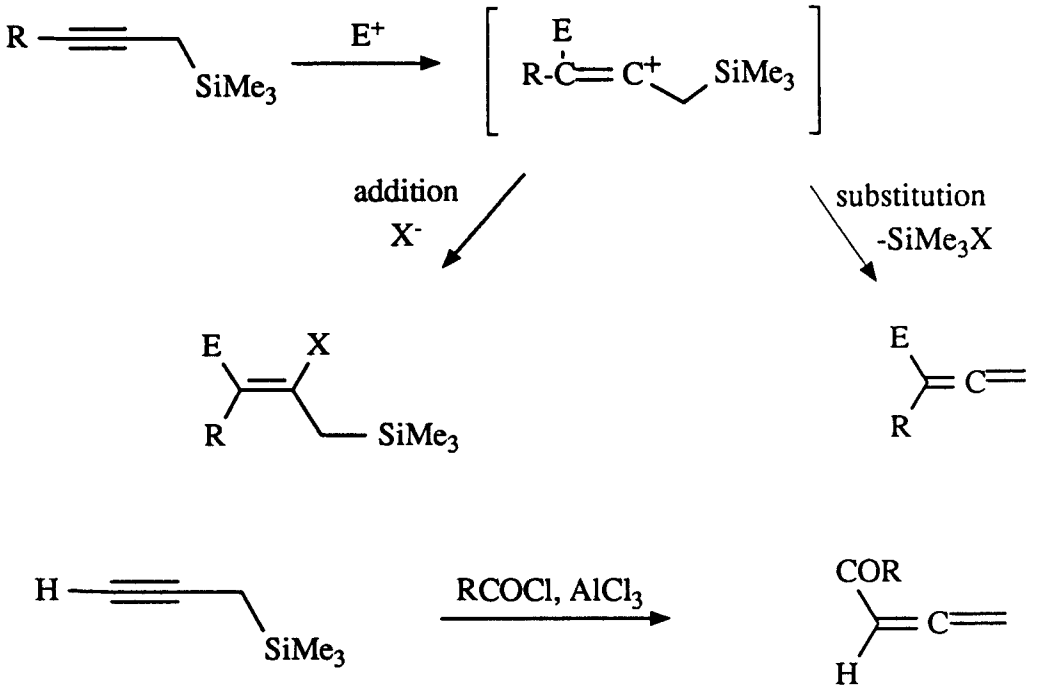
There are many reactions involving the β-effect. For example, allylsilanes usually undergo electrophilic addition or substitution via the intermediacy of β-silylcarbonium ions[8] (Scheme 1-5):

Scheme 1-5



Propargylsilanes will also undergo additions to give the β-silylcarbonium ions. This then reacts further to give either addition or substitution[9] products (Scheme 1-6):

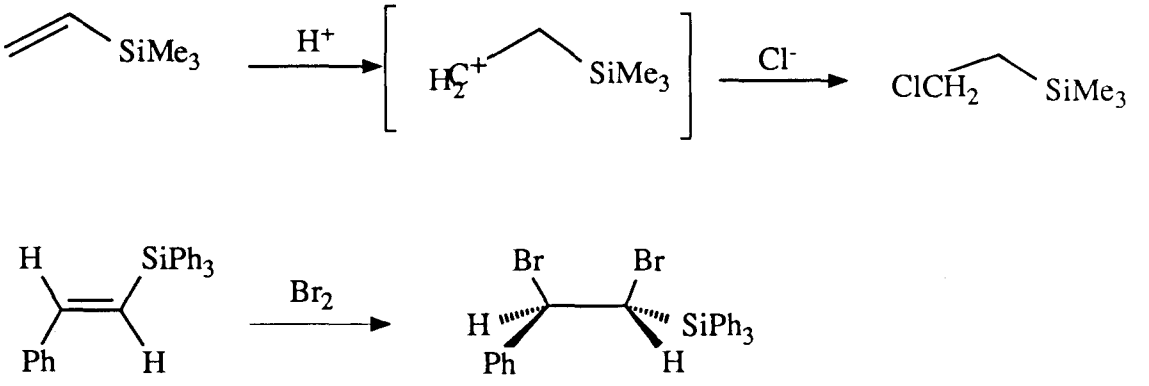
Scheme 1-6



As with most other electrophilic reactions of organosilicon compounds, however, elimination tends to dominate over addition. This may possibly result from (p-σ)π conjugation between the Si-C bond and the developing positive charge in the transition state (Figure 1-1) which may play a significant part in the weakening of the Si-C bond and thus promote the cleavage process which is so frequently encountered in the reactions of β-functionalized organosilanes[1a].

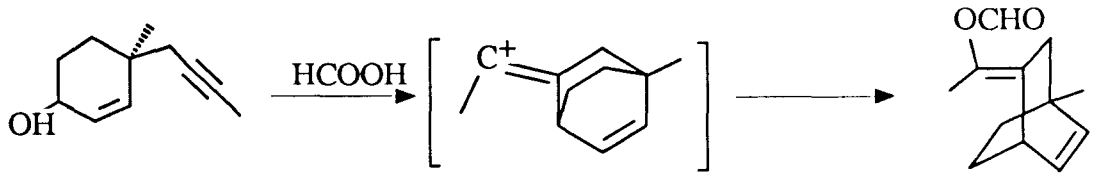
Vinylsilanes can also react readily with a variety of electrophiles and under certain conditions, addition products are sometimes observed[10,11] (Scheme 1-7):

Scheme 1-7



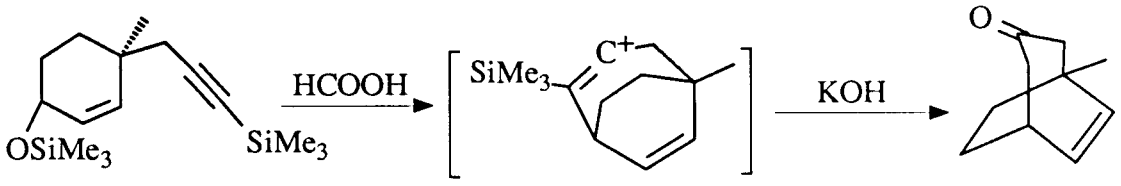
There are many reactions involving silyl group activating and directing effects which promote β-carbonium intermediates and have been used in organic synthesis[5]. For example, intramolecular cyclization of alkenes can be achieved by π cyclization of the type shown in the following equation (Scheme 1-8), which involves electrophilic attack at a triple bond[12]:

Scheme 1-8



Replacing the terminal methyl group by a trimethylsilyl group gives a different product[13](Scheme 1-9). This can be attributed to two major factors: the formation of a carbonium ion β to silicon and the poor stabilization of α-silylcarbonium ion[1,5].

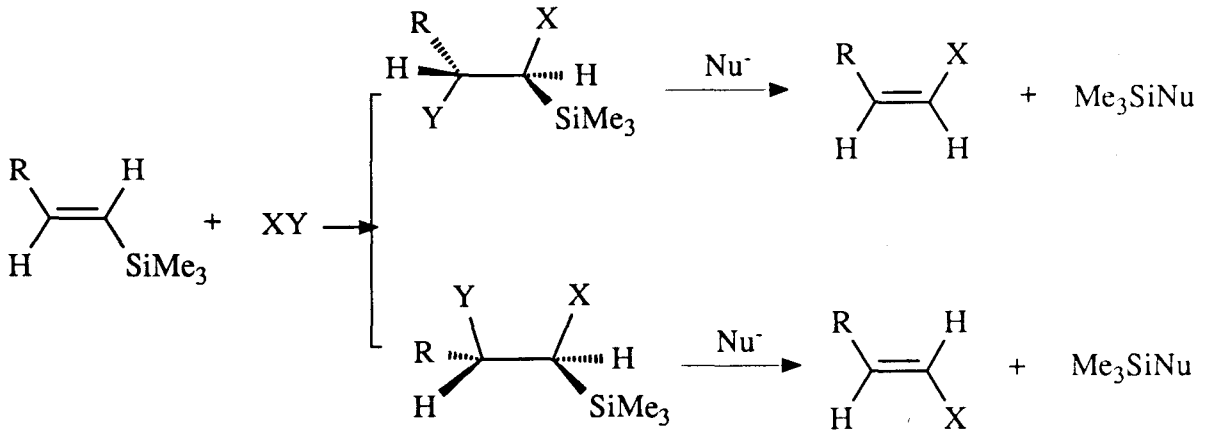
Scheme 1-9



Johnson has employed a similar strategy of using the ethynylsilane group as an effective terminal group in his elegant polyolefin cyclizations[14].

Vinylsilanes can also be used as intermediates to the stereoselective synthesis of vinyl halides. The carbon-carbon double bonds are readily cleaved by various electrophiles in a regio- and stereoselective manner. Halogen cleavage reactions have provided especially efficient methods for the stereoselective synthesis of (E)- and (Z)-alkenyl halides[15,16]. The stereoselectivity has been known to be dependent upon the nature of the reagent and the structure of the alkenyl group, as seen from the literature data summarized[17] in Scheme 1-10. Therefore, by choosing appropriate reaction conditions, one can obtain the vinyl halide with desired geometry.

Scheme 1-10



INVERSION: R = alkyl; XY = Cl_2; Br_2; ICl; I_2/AgO_2COCF_3

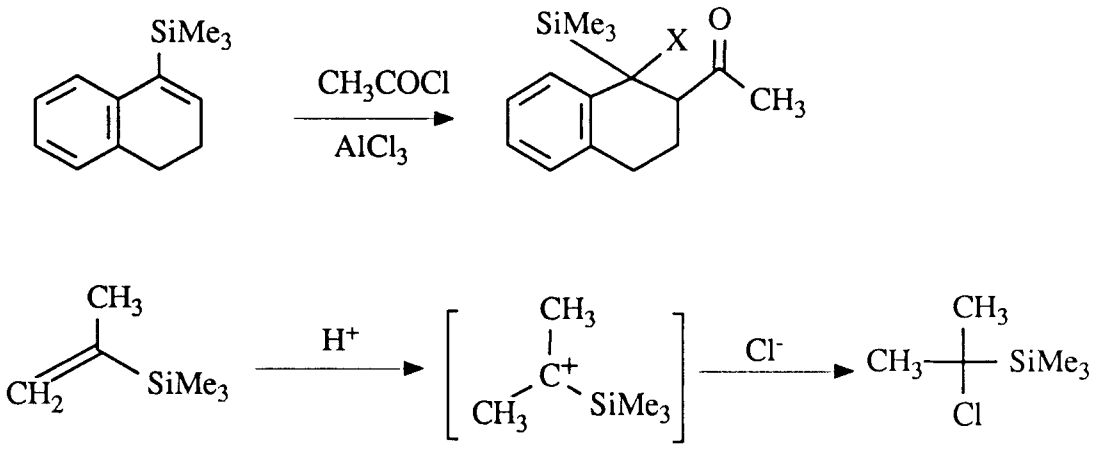
RETENTION: R = alkyl; XY = I_2, $BrCN/AlCl_3$

R = Ph; XY = Br_2

1.3 The Study of the β-Effect

From theoretical point of view, many quantitative studies on β-effect have been carried out[18]. It has been found that the directing influence of trimethylsilyl group is smaller than that of an α-phenyl group[18], the directing influence of two methyl groups is also stronger than that of trimethylsilyl group[9], as are shown by the following reactions (Scheme 1-11):

Scheme 1-11



From further reaction rate[19] and charge transfer spectral data[20], values for the Hammett *para*-substitution constants have been derived (Table 1-1). Those data showed that the electron-releasing effect of a $Me_3Si\text{-}CH_2$ group lies somewhere between that of a methyl and of a methoxy group, being roughly comparable with that of an acetamido group.

Table 1-1 Some Hammett *para*-Substitution Constants, σ^*_p for *p*-RC_6H_4-

substituent R	σ^*_p from reaction rates	σ^*_p from charge-transfer spectra
Me	-0.31	
Et	-0.58	-0.25
$Me_3Si\text{-}CH_2$	-0.54	-0.62
CH_3CONH	-0.58	-0.60
$(Me_3Si)_2CH$	-0.62	
MeO	-0.78	-0.74

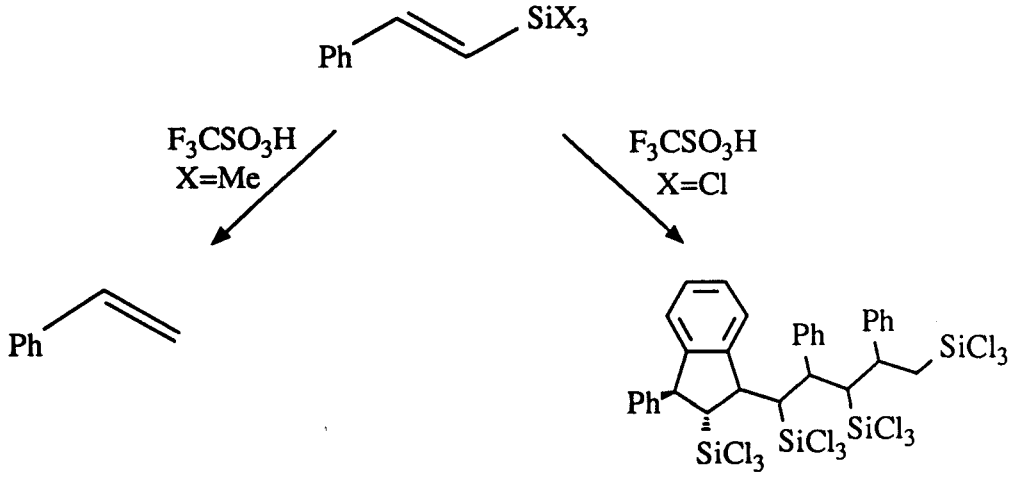
Besides, the ligands on silicon also play very important roles in determining the reactivity as well as other properties of organosilicon compounds. This is also true for the β-effect.

Hayashi studied the electrophilic substitution reactions of optically active allylfluorosilanes[21]. He found that trimethyl- and dimethylfluoroallylsilanes have a pronounced influence on σ-π conjugative interaction between the carbon-silicon bond

and the olefin π system which increases the electron density on the olefin. In contrast, the σ-π conjugation on the olefin is less important in the methyldifluoroallylsilane and is not a factor in the trifluoroallylsilane. The order seems to be consistent with electronic nature of fluorosilyl group.

Brook compared[22] the reactivities of chloro- and methylsilylstyrenes towards cationic conditions. He found that β-(trimethylsilyl)styrene undergoes loss of the silyl group under acidic conditions, the corresponding trichlorosilyl-substituted compound undergoes oligomerization (Scheme 1-12):

Scheme 1-12



Tamao also conducted detailed investigations on the stereochemical dependence on silyl groups by examining the halogenolysis of trimethyl-, trifluorovinylsilanes and pentafluorosilicates. His results indicated[17] that the stereochemical outcome is also dependent upon the silyl group of the vinylsilanes - the ligands on silicon.

1.4 Objectives of the Present Study

The above observations and others suggest that the properties of a silyl group are dependent upon the ligands on silicon atom. This is particularly obvious when a silyl group is involved in stabilizing a carbocation. However, few studies have systematically focused on examining the role played by ligands on silicon in the β-effect in a quantitative manner. To this end, we decided to examine a series of silyl groups with different ligands on silicon and tried to correlate the β-effect with the group electronegativity of the silyl group.

As mentioned before, the β-effect is invoked mechanistically in the electrophilic additions to carbon-carbon double bonds of allyl-, allenyl-, vinyl-, propargyl-, acetylenic- and arylsilanes and so on. We chose to study an electrophilic addition, the bromination of vinylsilanes as a way to quantify the effect of different ligands on silicon in the stabilization of a β-carbocation. The reasons we chose to study this reaction are the following: i) in many other reactions mentioned above, substitution usually dominates over addition, i.e., the addition products tends to undergo elimination to give substitution products; ii) the substitution process is usually stereoselective, the stereoselectivity of the process, the retention or inversion of the olefin geometry depends on the nature of the electrophile, the counterion, the medium and the leaving ability of the silyl group[17]. Although we can use the same electrophile,

counterion, and medium, different silyl groups, which have different leaving ability, will complicate our study. However, addition reactions avoid this situation. Finally, bromination of vinylsilanes can give addition products as was shown earlier and the bromination of olefins has been well-studied[23].

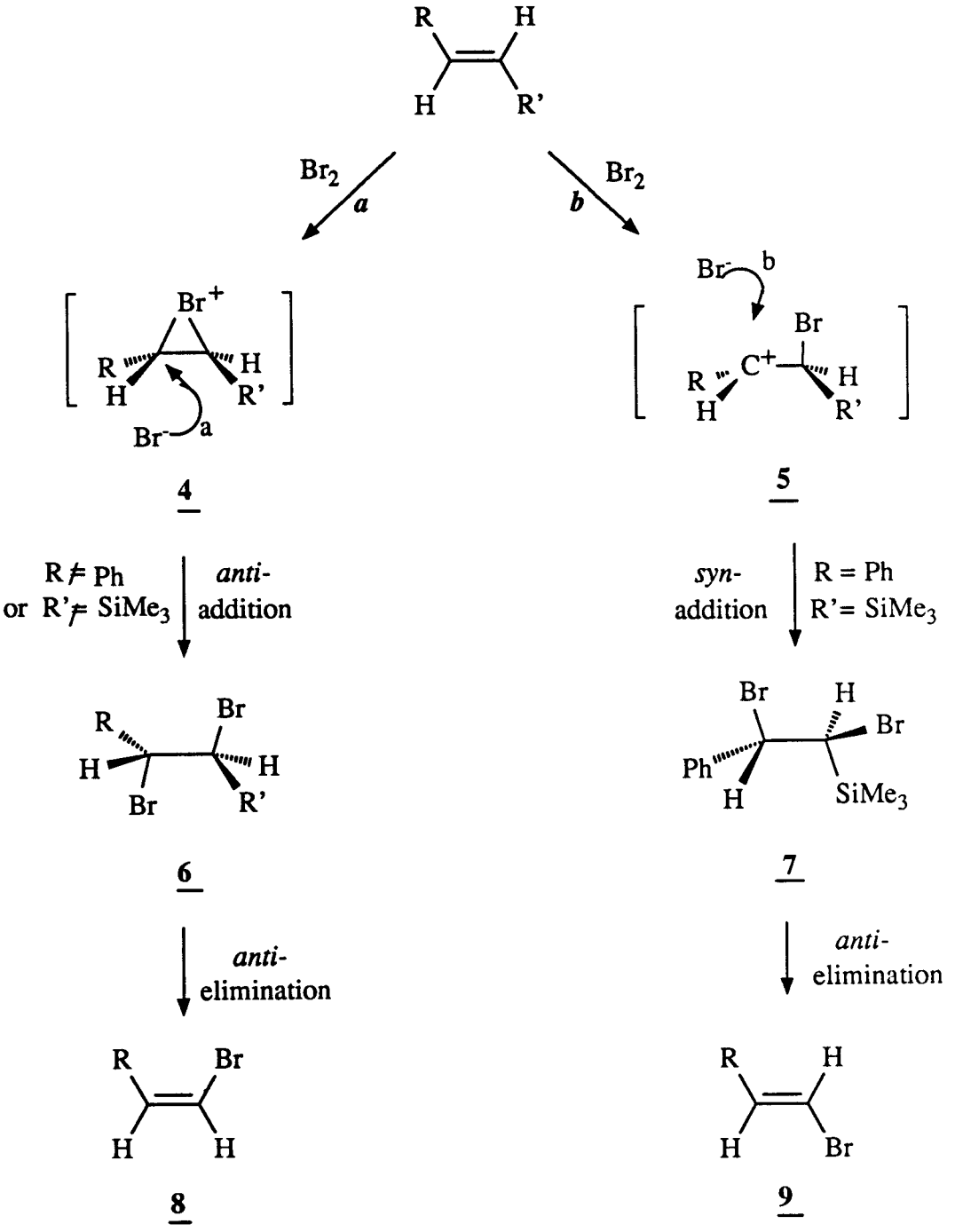
It is widely accepted that the electrophilic addition of bromine to olefin proceeds stereoselectively following the pathway *a* (Scheme 1-13) in an *anti*-addition fashion[23] by the attack of bromide on the cyclic bromonium ion intermediate 4 giving product 6. This, after *anti*-elimination, will result in (Z)-bromoalkene 8.

However, in the case of the bromination of vinylsilanes, different results were observed. In early 1950's Sommer and his coworkers found[10] that the addition of bromine to (E)-β-(trimethylsilyl)styrene followed by elimination led to the formation of (E)-bromostyrene with overall retention of configuration. Weber and Koenig studied[24] the same reaction and isolated the dibromo-adduct and elimination product, (E)-β-bromostyrene. They found that both steps occurred stereoselectively. Thus, the reaction had to proceed through either a *syn*-addition/*anti*-elimination or an *anti*-addition/*syn*-elimination sequence. Later on, Brook and his coworkers studied[11] the x-ray crystal structure of the dibromo-adduct of an analogous compound β-(triphenylsilyl)styrene and found that addition of the bromine takes place in a *syn*-addition fashion. Thus the elimination has to be through an *anti*-fashion as is the usual case.

We know that in most cases, *anti*-addition, as for alkenes in general, is often the course of the reaction, especially when halonium ions are involved[5], but why did *syn*-addition occur in the case of the bromination of β-(trimethylsilyl)styrene?

This observation has been rationalized as follows[24,25] (Scheme 1-13): upon the addition of electrophile Br^+, the reaction can go on through two competitive pathways, *a*

Scheme 1-13


R
H
H
R'
Br2
a
Br2
b
Br+
R
H
H
R'
Br-
a
Br-
b
Br
R
C+
H
H
R'
4
5
R ≠ Ph
or R' ≠ SiMe3
anti-
addition
syn-
addition
R = Ph
R'= SiMe3
R
Br
H
H
Br
R'
Br
H
Ph
H
Br
SiMe3
6
7
anti-
elimination
anti-
elimination
R
Br
H
H
R
H
H
Br
8
9

and *b*. Which pathway will be the dominant one will depend on whether bromonium bridging or hyperconjugative (the β-effect of silyl group plus other stabilizing effects) stabilization of the β-carbonium ion is greater. The cyclic bromonium ion 4 will follow route *a*: *anti*-addition of the bromide followed by *anti*-elimination giving overall the the substitution product 8 with inversion of configuration; the carbonium ion 5 will follow route *b*: *syn*-addition of the bromide followed by *anti*-elimination giving overall the substitution product 9 with retention of configuration.

In the case of β-silylstyrene, R is a phenyl group. The combination of β-effect stabilization of the silyl group and the hyperconjugative stabilization by the phenyl ring promotes the formation of open carbonium ion 5. *syn*-Addition will result from the attack by bromide on 5, a β-silyl carbocation, because of the proximity of the nucleophile to the *syn*-face of the molecule and lower steric hindrance (*anti* to the β-silyl group).

In other cases, pathway *a* overwhelms pathway *b*. The outcome led by *anti*-addition/ *anti*-elimination pathway will be observed giving overall substitution with inversion of configuration.

In this reaction mechanism, the steps generating the intermediates 4 and 5 are rate determining processes and should be slow transitions. The nucleophilic bromide anions's attacks to 4 and 5 are generally considered to be fast processes[23], thus the ratio of the *syn*-addition/*anti*-addition products 7/6 will approximately be equal to the ratio of the two reaction intermediates, 4 and 5. This ratio is determined by the relative stability of 4 and 5. Therefore, the ratio of 7/6 can be used directly as a quantitative measure of the stability of 4 and 5. More importantly, this will reflect the stabilizing effect of the silyl group - the β-effect.

Previous studies showed that with only the phenyl group providing stabilization, the bromination of methylstyrene gives a mixture of 5:95 *syn-/anti*-addition products[26]. This result indicates that the reaction mainly follows pathway *a*, bromide attacks the bromonium ion **4** from the backside. In the case of β-(trimethylsilyl)styrene, however, with the further stabilization contributed by the trimethylsilyl group, the β-effect, the pathway *b* is followed giving 100% *syn*-addition[24]; bromide attacks the carbonium ion **5**, which is stabilized by both trimethylsilyl and phenyl groups.

With other things being equal, by changing only the ligands on silicon, we would expect to see the change of the ratio of **5/4** and thus the change of the ratio of *syn-/anti*-addition product **9/8**. This change should be a reflection in the change of degree of the β-effect provided by the silyl group in stabilizing the carbonium ion **5**. As a silyl group becomes increasingly electron-withdrawing, by putting more electron-withdrawing groups on silicon, bromonium ion **4** should be increasingly favored and therefore, so should the *anti*-addition product **6**. Thus, the ratio of *syn-/anti*-addition products should be a measure of magnitude of the β-effect of different silyl groups.

Previous studies on the bromination of a series of (E)-β-silylstyrenes in our lab[27] showed that the degree of the *syn*-addition is linearly related to the electronegativity of the silyl group. We did further studies on a series of (E)-β-(triacyloxysilyl)styrenes and (E)-β-[tris(trimethylsiloxy)silyl]styrene to broaden our knowledge on the relationship between the degree of the β-effect and the ligands on silicon atom. We would like to present our observations on this subject in the following chapters of this thesis.

CHAPTER 2

RESULTS

2.1. Preparation of (E)-β-Silylstyrenes 11-14 and Their Precursor 10

A total of four (E)-β-silylstyrenes were prepared for the purpose of the bromination study. (E)-β-(Trichlorosilyl)styrene **10** was synthesized as the precursor for the four (E)-β-silylstyrenes **11-14**. Their structures appear in Table 2-1. All the compounds, **11-14** (including their dibromo-adducts), were characterized using ^{1}H, ^{13}C, ^{29}Si NMR, IR and mass spectroscopy. For detailed experimental procedures and spectral data, please consult the experimental section (Chapter 6) of this thesis.

2.1.1 The Precursor (E)-β-(Trichlorosilyl)styrene 10

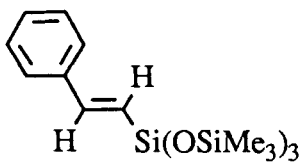
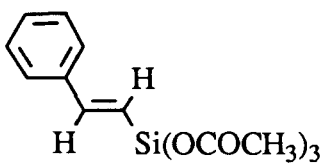
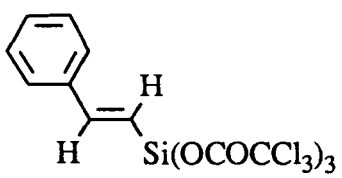
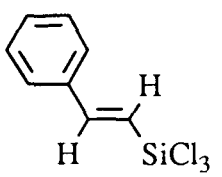
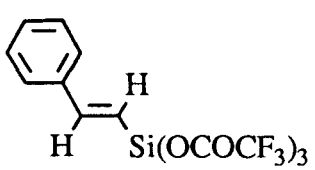
The first step in our study of the four (E)-β-silylstyrenes surveyed, involved the preparation of the precursor 10. The (E)-β-(trichlorosilyl)styrene was prepared by the hydrosilylation[28] of phenylacetylene using hexachloroplatinic acid (0.1 M H_2PtCl_6 in *iso*-propanol), Speier's catalyst[29]. This reaction is stereoselective and the ^{1}H NMR spectra showed that 100% stereochemically pure E isomer was obtained.

2.1.2. (E)-β-Silylstyrenes 11-14

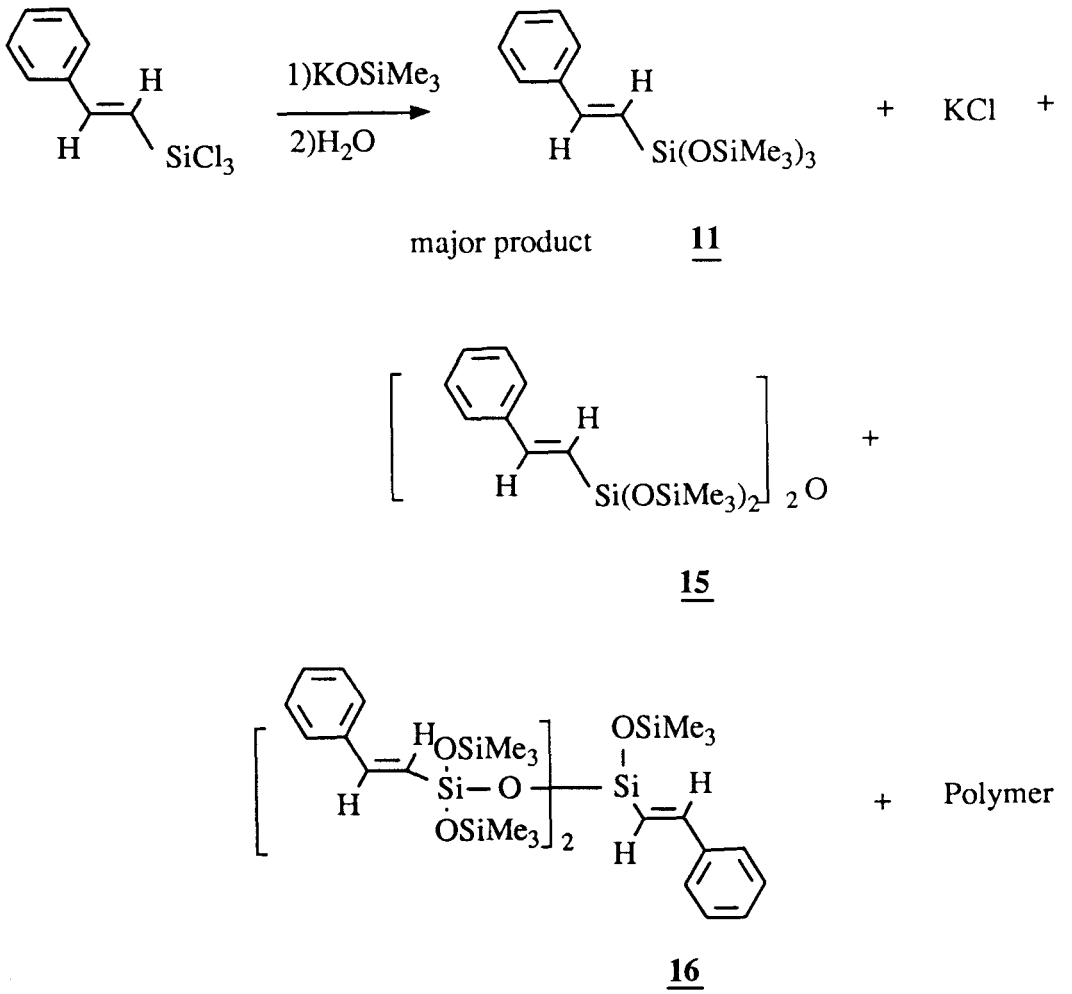
The (E)-β-[tris(trimethylsiloxy)silyl]styrene **11** was synthesized[30] by the reaction of potassium trimethylsilanolate with **10** (Scheme 2-1). In addition to the desired product, some high molecular weight compounds, such as compounds **15** and **16** as well as polymer were also obtained in the reaction mixture. The (E)-β-(triacyloxysilyl)styrenes

Table 2-1

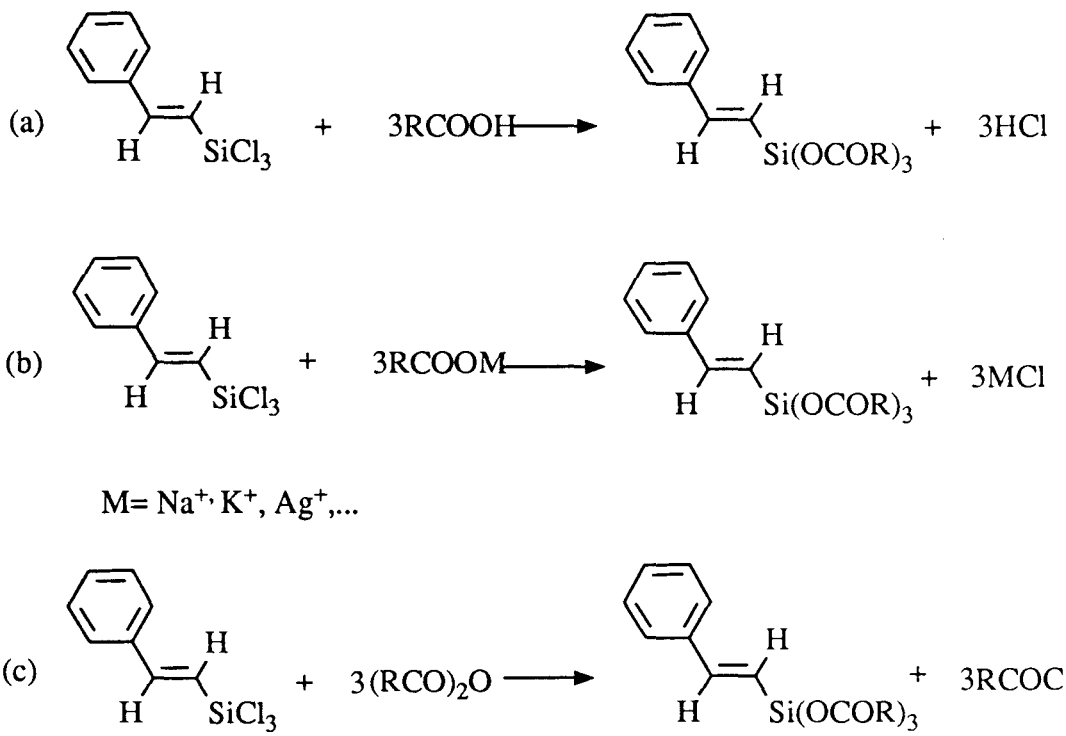
(E)-β-Silylstyrenes Studied and Their Precursor

(E)-β-silylstyrene	precursor
 **11**	
 **12**	
 **13**	 **10**
 **14**	

Scheme 2-1

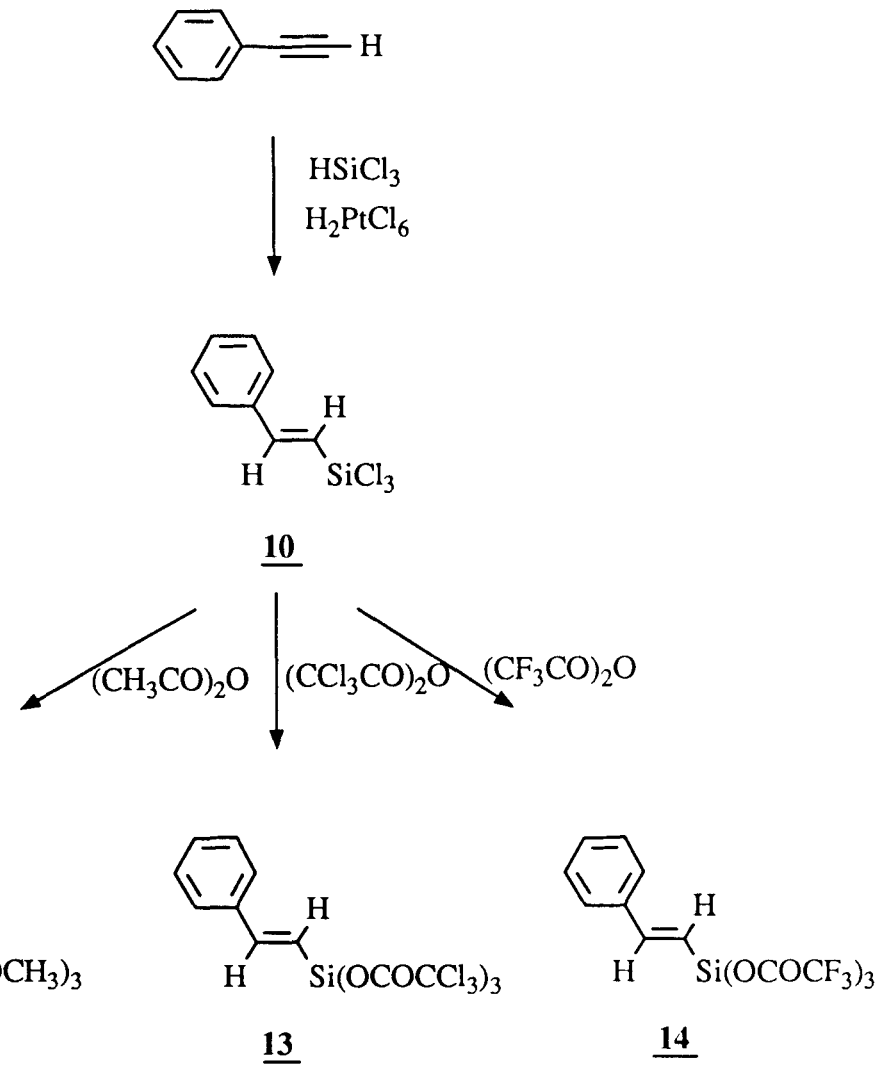

1)KOSiMe3
2)H2O
SiCl3
Si(OSiMe3)3
+ KCl +
major product
11
Si(OSiMe3)2
2O
+
15
OSiMe3
Si—O
OSiMe3
2
Si
+ Polymer
16

11-**14** were obtained from the (E)-β-(trichlorosilyl)styrene **10** by the conversion of chloride to the corresponding carboxylate groups. There are, in general, three methods which can be used for this conversion[31-34]:



In method (a), hydrogen chloride is generated in the process of the reaction and may react with the carbon-carbon double bond of the starting material. This will complicate the desired reaction. In method (b), the purification of the product will suffer from the difficulty of separating the product from the salt formed. Method (c), however, is a convenient way to synthesis compounds **11**-**14**. The by-product, acetyl chloride, usually has lower boiling point than the desired product and can be easily removed by distillation. Therefore, the best way, from the above analysis and also our experience is the method (c) and was chosen for this purpose (Scheme 2-2).

Scheme 2-2


H
HSiCl3
H2PtCl6
H
H
SiCl3
10
(CH3CO)2O
(CCl3CO)2O
(CF3CO)2O
H
H
Si(OCOCH3)3
12
H
H
Si(OCOCCl3)3
13
H
H
Si(OCOCF3)3
14

2.2 Bromination of (E)-β-silylstyrenes 11-14 and Elimination of Dibromo-adducts 11s-14s and 11a-14a

2.2.1 Bromination of Compounds 11-14

The bromination process was conducted with strict temperature control in order to ensure that the reaction was taking place under kinetic control. In a typical run, a precooled bromine solution (-78°C, acetone/dry ice bath) was added to a cooled (-78°C) solution of the (E)-β-silylstyrene in carbon disulfide. The ratios of the two addition products 11s-14s and 11a-14a produced respectively through *syn*- and *anti*-addition, were determined in the crude mixture by the integration of the α-SiCH proton signals in the ^{1}H NMR and correlated with the peak intensity in the ^{13}C NMR and ^{29}Si NMR, respectively. The results are given in Table 2-2.

Table 2-2 Comparison of *syn*-/*anti*-Addition Ratio to Group Electronegativity

vinyl compd	ligands on Si	products	ratio *syn:anti*	ratio E:Z	group EN[a]	$^{1}H^{b}$ chem. shift
11	Me_3SiO	11s:11a	88:12	100:0	2.20	5.99
12	CH_3COO	12s:12a	33:67	40:60	2.34	6.31
13	Cl_3COO	13s:13a	25:75	27:73	2.35	6.37
14	CF_3COO	14s:14a	10:90	16:84	2.36	6.29

[a] electronegativity of silyl group of Mullay's scale[35].

[b] in the ^{1}H NMR of the α-SiCH proton.

To examine the temperature effect towards bromination, a room temperature solution of bromine in carbon disulfide (instead of a cooled one), was added to a cooled (-78°C) solution of the (E)-β-silylstyrene in carbon disulfide. The results (Table 2-3) are completely different from that in Table 2-2, which indicates the importance of strict temperature control during the bromination process.

Table 2-3 Temperature Effect on the Ratio of *syn*-/*anti*-Addition in the Bromination of Compounds 11-14

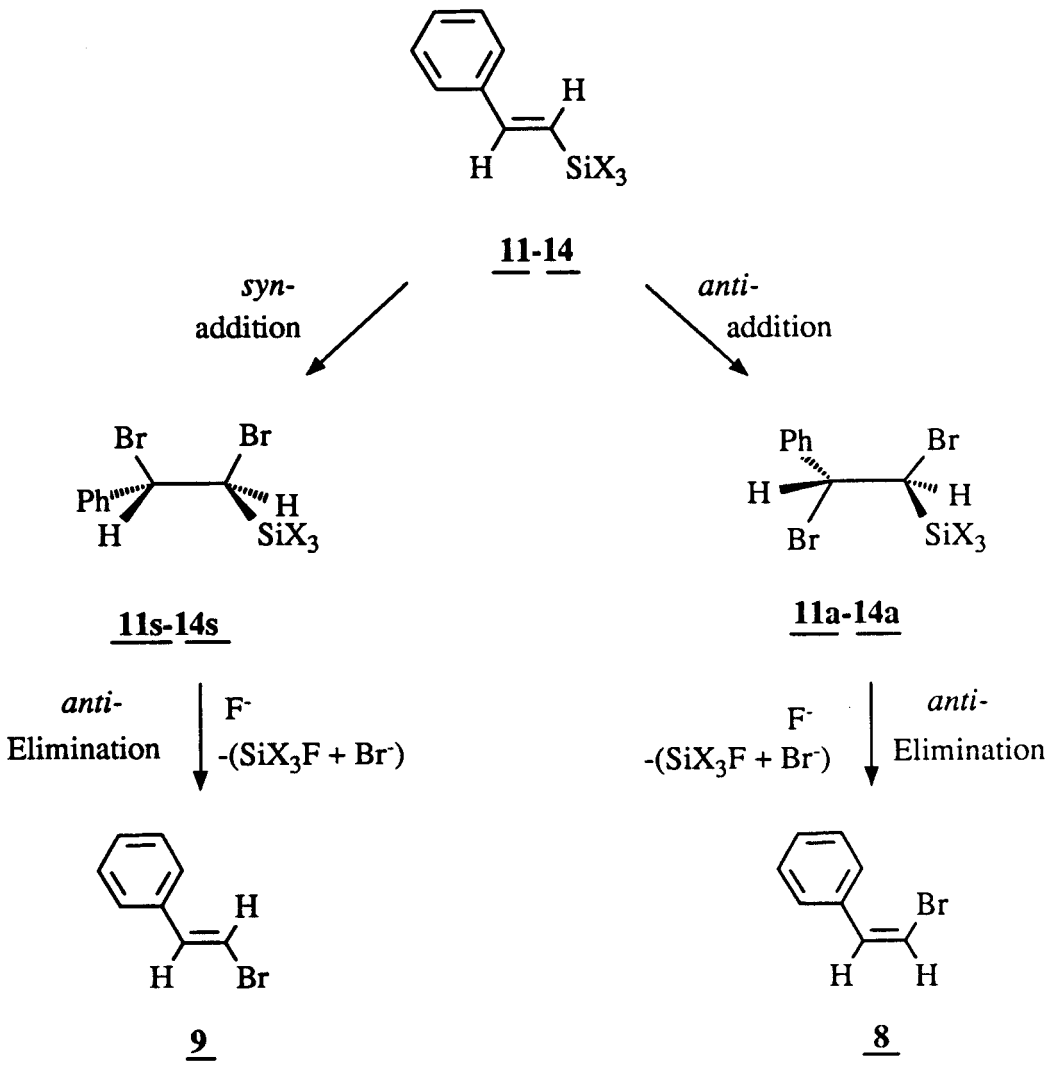
vinyl compd	lingands on Si	products	ratio *syn:anti*
11	Me_3SiO	**11s:11a**	40:60
12	CH_3COO	**12s:12a**	69:31
13	CCl_3COO	**13s:13a**	39:61
14	CF_3COO	**14s:14a**	28:72

2.2.2 Elimination of the Dibromo-adducts 11s-14s and 11a-14a

To further establish the relative geometries of compounds **11s**-**14s** and **11a**-**14a**, the fluoride induced elimination reactions (desilylation)[36] were used to convert these dibromo-adducts to the known (Z)- and (E)-β-bromostyrenes **8** and **9**.

The elimination was performed in $CDCl_3$ using n-Bu_4NF (TBAF) and the ratio of

Scheme 2-3

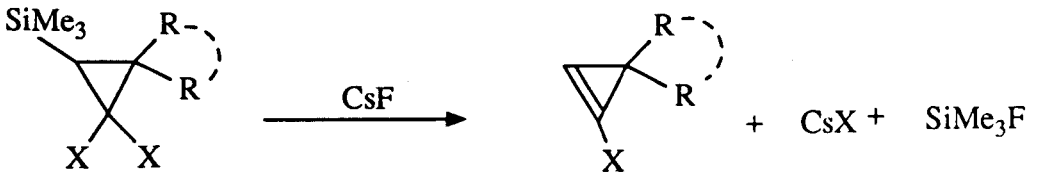

H
H
SiX3
11-14
syn-
addition
anti-
addition
Br
Br
Ph
H
H
SiX3
Ph
Br
H
H
Br
SiX3
11s-14s
11a-14a
anti-
Elimination
F-
-(SiX3F + Br-)
F-
-(SiX3F + Br-)
anti-
Elimination
H
H
Br
Br
H
H
9
8

compounds **8** and **9** was determined by integration of the ^{1}H NMR spectra and by comparison with the ^{1}H NMR spectra of a commercial sample (Aldrich) of (Z)- and (E)-β-bromostyrene (Table 2-2).

We assume that only the *anti*-elimination mechanism is operating in above elimination reactions as is generally the case[11,25] (see also the discussion in Chapter 3). Thus, we can infer that the (E)-β-bromostyrene results from *syn*-addition products **11s**-**14s** and (Z)-β-bromostyrene results from *anti*-addition products **11a**-**14a** (Scheme 2-3). Therefore, the ratio of *syn*-/*anti*-addition products should be, in principle, equal to the ratio of (E)-/(Z)-β-bromostyrene. The results in Table 2-2 show very good correlation between the two ratios. The slight difference observed will be discussed in the discussion section (Chapter 3).

Fluoride ion-promoted 1,2-elimination of a 1,2-halogenosilane is a powerful method for generation of alkenes, especially for strained alkenes. One of the example is shown in the synthesis of halogenocyclopropenes[37] (Scheme 2-4):

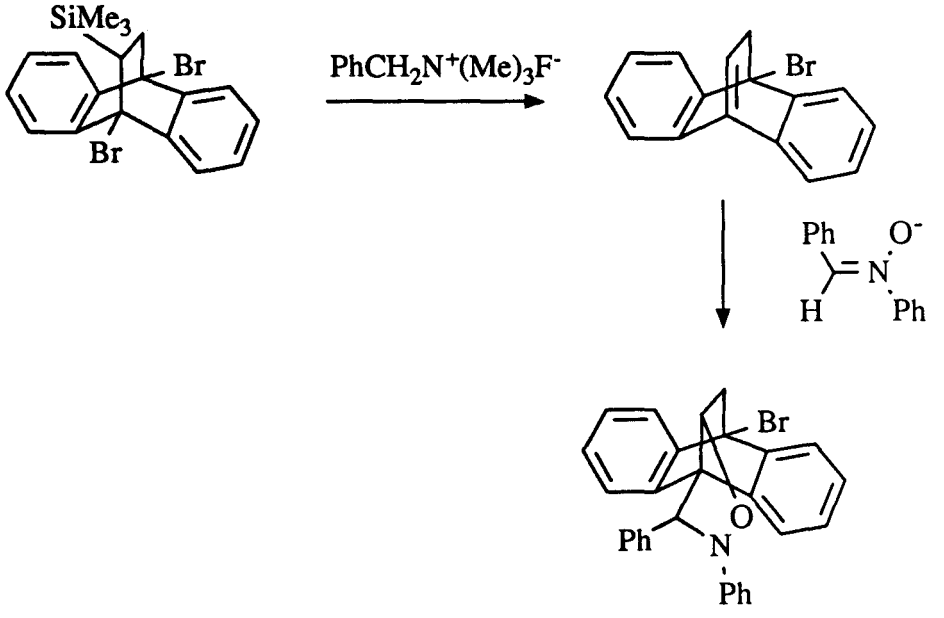
Scheme 2-4



The advantage in above reaction is that the reagent, alkali fluoride, and the products, alkali halide and trimethylsilyl fluoride, are generally neutral and relatively inert to most other functionalities. A further application of this philosophy is seen in

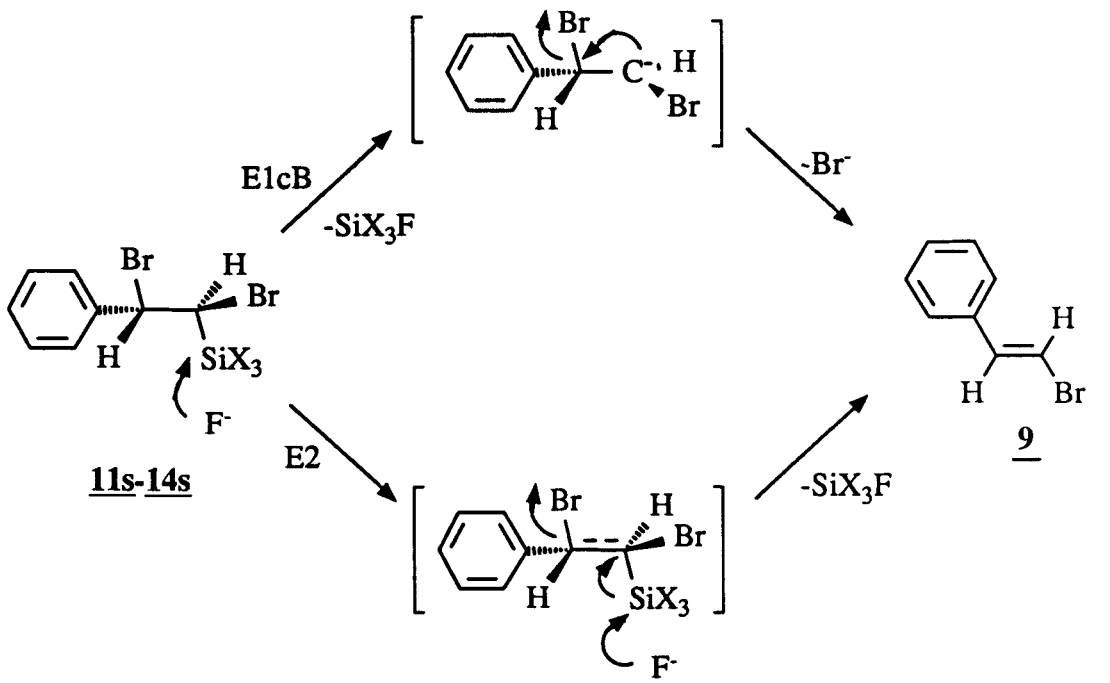
the transient preparation of the strained bridged alkene[38] (Scheme 2-5):

Scheme 2-5



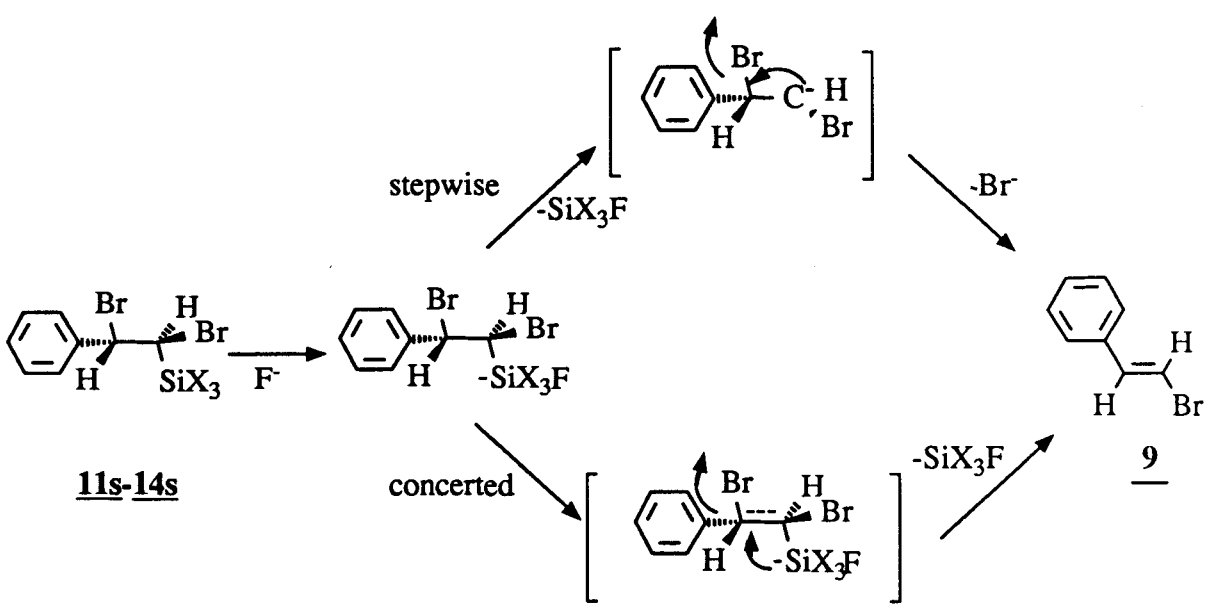
The above examples show that the fluoride-induced elimination provides a remarkable mild, relatively non-basic condition for the preparation of alkene. The mechanism of this type of reactions tends to be E1cB type[39]. The mechanism in our case, however, is not clear. It may take place through either an E1cB or E2 mechanism or somewhere in between. Fluoride, which has a very strong affinity towards silicon, will preferentially attack silicon to promote its leaving, which leads to E1cB mechanism; bromide, on the other hand, is also a very good leaving group and the resulting cation will be stabilized by the adjacent phenyl ring (Scheme 2-6, only the elimination of *syn*-addition products **11s**-**14s** is shown. The elimination of *anti*-addition products **11a**-**14a** will generate correspondingly (Z)-isomer, compound **8**).

Scheme 2-6



Another possibility is that the elimination reaction proceeds through an intermediate similar to that of E1cB via *penta*-coordination at silicon (Scheme 2-7):

Scheme 2-7



It is difficult to predict which mechanism is the predominant one unless further experimental data are given.

CHAPTER 3
DISCUSSION

3.1 The Origin of β-Effect

To study the β-effect, it is important to understand its origin. However, despite the widespread and rapidly growing use of silicon reagents in organic synthesis[40], the effect of silyl group on stability of common reactive intermediates is not fully understood. Even the qualitative description of the origin of the β-effect had been controversial until recently.

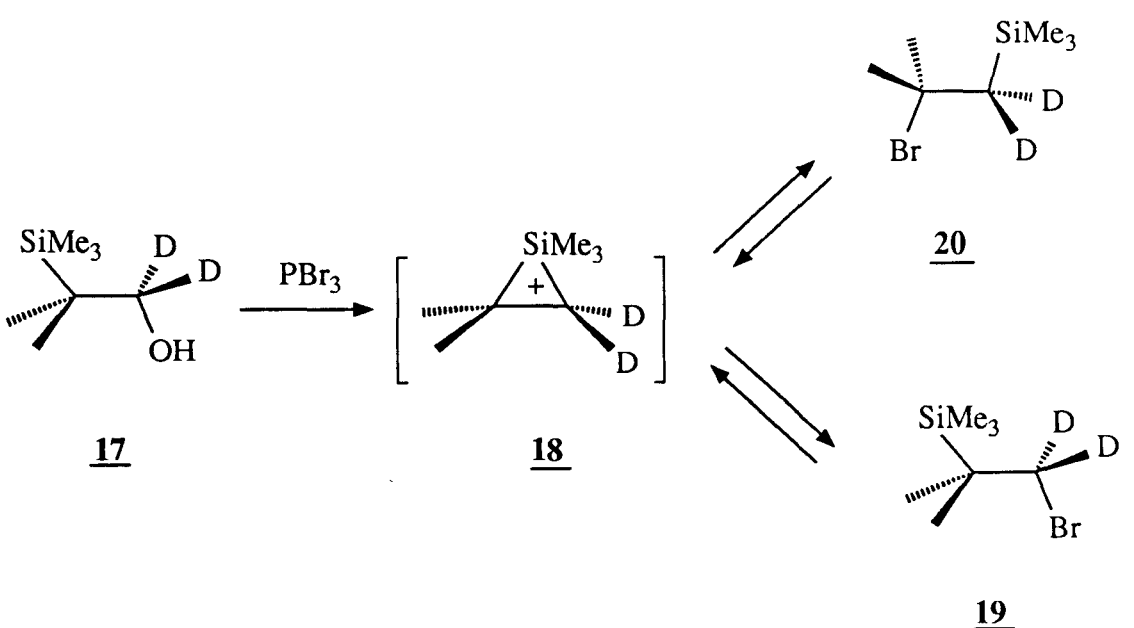
The electronic effect of a silyl group can be roughly divided into four components[5]: (a) inductive effects; (b) field effects; (c) (p-d)π bonding and (d) hyperconjugative effects. In any particular property of a silicon compound or intermediate, the total electronic effect of the silyl group is a combination to a greater or lesser degree, of those effects, and the particular contribution of one or another effect can not always be readily separated from other effects. This is also true in the case of β-effect. In the study of β-effect, hyperconjugative and inductive effects are the major factors generally considered.

The inductive effect of electropositive silicon is not usually considered to be responsible for the unusual β-stabilization since the silyl group is not effective in stabilizing a carbonium ion at the α-position where the inductive effect should operate to a greater extent[1,3]. In fact, early solvolysis work and various other chemical evidence showed that α-silyl groups are less stabilizing than α-alkyl groups towards incipient carbonium ion centers[41]. For example, Cartledge[41c] found that $(CH_3)_3CC(CH_3)_2Br$ solvolyzed

$3.8X10^3$ times faster than its silicon analogue, $(CH_3)_3SiC(CH_3)_2Br$; Fleming also reported that the trimethylsilyl group exerts little directing influence on regioselectivity of cycloaddition reactions[42].

The neighboring group participation stabilizing influence has also been considered in the β-effect. An interesting example of the formation and reaction of a β-silyl-carbonium ion was reported independently by Eaborn[43] and Jarvie[44]. Reaction of the dideuterio-β-hydroxysilane **17** with phosphorous(III) bromide gave the directly substituted bromide, **19**, together with the rearranged bromide **20** (Scheme 3-1):

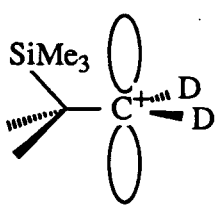
Scheme 3-1



17 **18** **20** **19**

The results were interpreted in terms of anchimeric assistance, by Me_3Si, to give the bridged intermediate **18**. A possible alternative explanation is that the open-chain,

hyperconjugative stabilized carbonium, 21, is formed, but rapidly undergoes facile 1,2-silyl-migration between the two carbon atoms before being trapped by bromide ion[45](Figure 3-1):

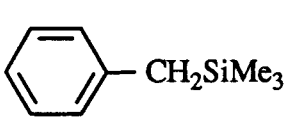
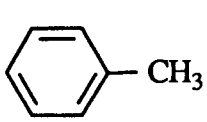
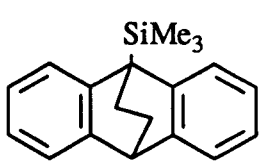
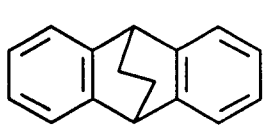


21

Figure 3-1

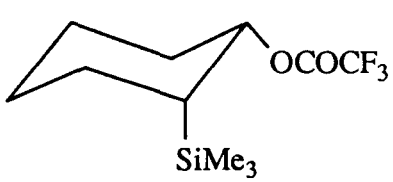
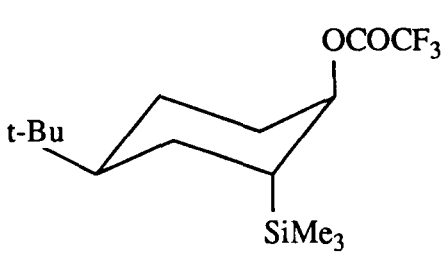
However, data from charge transfer spectra[20a,46] of a range of benzylic organometallics with tetracyanoethene showed that vertical (p-σ)π hyperconjugation is preferred over the alternative of neighbouring nucleophilic participation to account for features in the charge transfer spectra. Hyperconjugation, like all forms of π-conjugation, requires coplanarity of the interacting σ-bond and axis of the electron deficient p-orbital (Figure 1-1). The charge transfer spectral data with tetracyanoethene support the geometrical requirement for σ-p overlap (Table 3-1).

Table 3-1 Charge Transfer Maxima for Compounds 22-25

			
22	23	24	25
λ_{max}(TCNE) 486nm	411nm	424nm	424nm

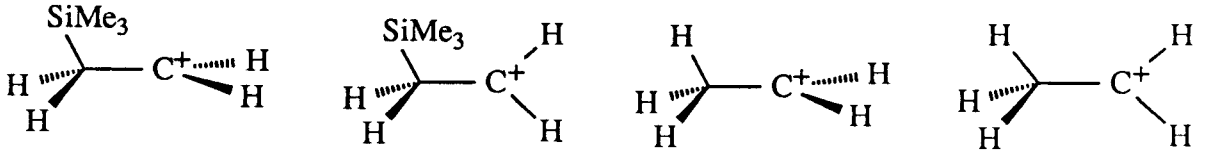
Silanes 22 and 23 have very different charge transfer maxima. 22 has a charge transfer maximum at longer wavelength indicating that group Me_3SiCH_2- has a better hyperconjugation with the phenyl ring than that the methyl group. However, silane 24, in which the Si-C bond cannot overlap with π-orbital of the phenyl ring, has a charge transfer spectrum that is negligibly different from that of the unsubstituted compound 25. This is also further evidence which shows that the β-effect is not mainly inductive and does depend on overlap.

Table 3-2 Kinetic Data of Solvolysis of Substituted Cyclohexanes

substituted cyclohexane	k_{rel}
 **26**	1
 **27**	3.3×10^4
 **28**	10^{12}

Lambert[47] reported his studies on substituted cyclohexanes in an attempt to quantify and elucidate the β-effect on trimethylsilyl group. The experimental results (Table 3-2) showed that the solvolysis of **26** and **27** in 97% CF_3COOH gave cyclohexene as the only product, molecule **28**, in which trimethylsilyl is frozen into the antiperiplanar (diaxial) relationship with respect to the leaving group, reacts about 10^{12} times faster than the non-silylated cyclohexyl trifluoroacetate **26**. In this arrangement, hyperconjugation should be maximized. Thus, the C-Si bond may provide the largest rate acceleration by this arrangement yet attributed to hyperconjugation for an organosilane. Using theory developed for isotope effect analysis permits decomposition of the overall acceleration for *trans*-compound **28** into a hyperconjugative factor of about 10^{10} and an inductive factor of 10^2. The *cis*-compound **27** (60° dihedral angle) solvolyzed 3.3×10^4 times faster than the reference compound **26**. This factor is composed of essentially equal hyperconjugative factor (10^2) and inductive factor (10^2).

Jorgensen and coworkers[48] explored the origin of β-silyl stabilization through *ab initio* calculations at the MP3/6-31G* level. The energies of **29** and **30** were calculated and compared with the ethyl carbonium ions **31** and **32** (figure 3-2). Hyperconjugation is not possible in **30** and **32**, but Si-C and H-C hyperconjugation is allowed for **29** and **31**. A comparison of the energies of the various species allowed the calculated stabilization by inductive and polarization effects to be disentangled from the hyperconjugation effect.



29 **30** **31** **32**

Figure 3-2

The results showed **30** to be more stable than the ethyl cation **32** by 8.9 kcal/mol^{-1}, taken to be a measure of the inductive and polarization stabilization by β-silicon. The comparison of **29** and **31** gave the more dramatic result that **29** was more stable than **31** by 38.0 kcal/mol. The hyperconjugative stabilization of a β-silylcarbonium ion can therefore be estimated as 29.1 kcal/mol, in qualitative agreement with the commonly accepted argument.

The above review on recent studies of the β-effect shows that there is increasingly experimental evidence supporting the argument that the origin of the β-effect can be attributed to the (σ-p)π hyperconjugative stabilization and this idea has become more and more commonly accepted. Therefore, we think it is reasonable to consider (σ-p)π hyperconjugative stabilization as the dominant factor in the β-effect stabilization.

3.2 The Methodology of Our Study

As we discussed above, the β-effect is attributed to the (σ-p)π hyperconjugative stabilization - the stabilizing interaction between the C-Si bond and the empty p_π orbital of the carbonium ion. This is then dominated by two important factors[1,5]: first and the most important one is the polarization and second, the orientation of the stabilizing bond. Owing to silicon's lower electronegativity than carbon, the C-Si bond is polarized and has a relative high coefficient on carbon: $C^{\delta-}$-$Si^{\delta+}$. The negative charge on the α-carbon can give a more effective hyperconjugation in stabilizing a cation. Placing the ligands on silicon atom with more electronegative groups will result in diminishing the polarization of the C-Si bond, and thus the β-effect of the silyl group. Therefore, group electronegativity would be a good measure of the degree of the polarization of the Si-C bond. The group electronegativity of Mullay's scale[35] is used for this purpose. The orientation of the Si-C bond also affects the degree of β-

hyperconjugation and controls the stereochemical outcome. This will be discussed later in detail.

In the introduction, the mechanism of bromination of (E)-β-silylstyrene has been discussed (Scheme 1-13). It has been concluded that the ratio of *syn*-/*anti*-addition products **7**/**6** will approximately be equal to the ratio of two reaction intermediates: **5**/**4**, therefore, this ratio can be used as measure of the relative stability of the two carbonium ions, **5** and **4**, and thus the β-effect. The addition products ratio **7**/**6** can be conveniently determined by the integration of ^{1}H NMR of α-SiCH signals (the coupling constant of the *syn*-addition products is found usually larger than that of the *anti*-additon products). To confirm the assignment of the *syn*- and *anti*-additon products, these addition products were converted to the known (Z)- and (E)-β-bromostyrenes by the elimination reaction. With those data in hand, we could then plot the *syn*-addition ratio versus group electronegativity and correlate the β-effect with the electron-withdrawing ability of the ligands on silicon.

3.3 Results and Discussion

Previous studies in our group[27] showed that there exists a linear relationship between the degree of *syn*-addition in the bromination of a series of (E)-β-silylstyrenes [ligands on silicon: Me_3, Me_2Cl, Me_2F, $MeCl_2$, Cl_3, MeF_2, F_3, $(MeO)_3$] and group electronegativity (Figure 3-3). The exceptional behavior of (trimethylsilyl)styrene was explained by the limit of the scale chosen (100% *syn*-addition). The points for other three compounds, ligands on silicon: $(PhO)_3$, $(p\text{-}MeOPhO)_3$, $(p\text{-}ClPhO)_3$ also deviate considerably from the correlation line as can be seen in Figure 3-3.

The results of present studies on a series of (E)-β-(triacyloxysilyl)styrenes [ligands on silicon: $(CH_3COO)_3$, $(CCl_3COO)_3$, $(CF_3COO)_3$] and

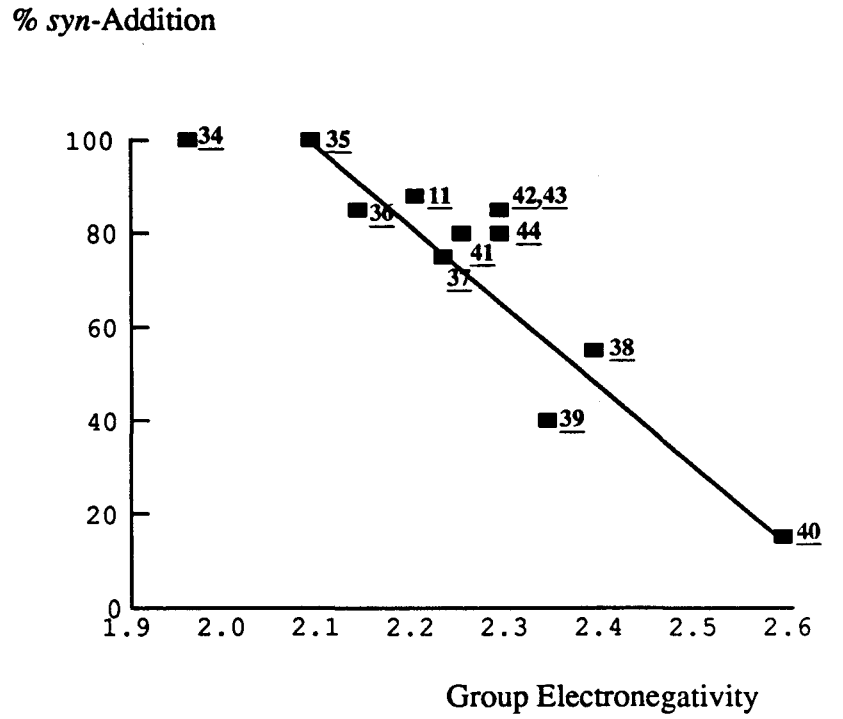
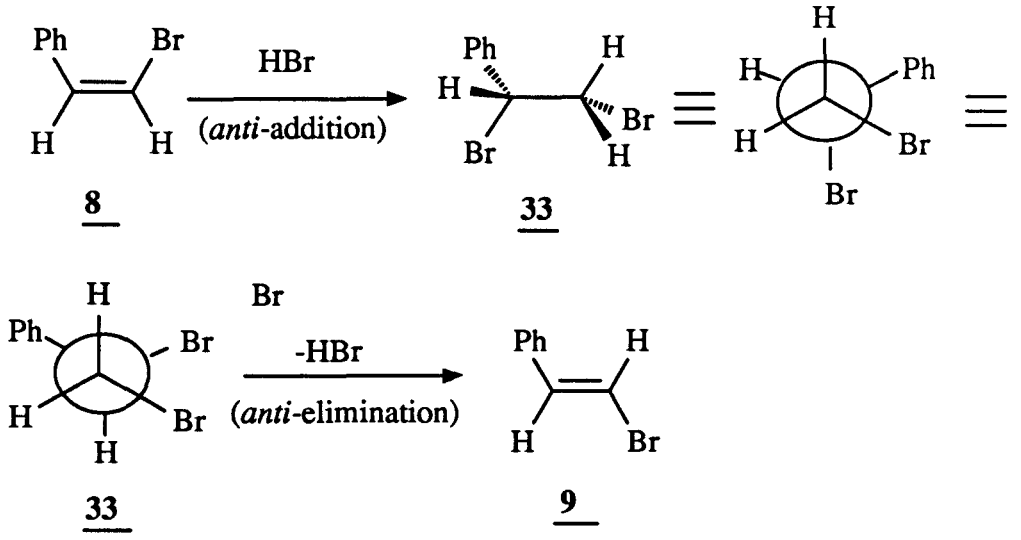


Figure 3-3 Plot of Group Electronegativity *versus* % *syn*-Addition of Bromine

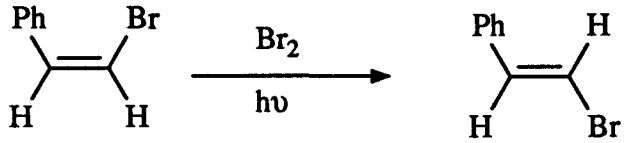
PhCH=CHSiXYZ, SiXYZ = $SiMe_3$ **34**; $SiMe_2Cl$ **35**; $SiMe_2F$ **36**; $SiMeCl_2$ **37**; $SiCl_3$ **38**; $SiMeF_2$ **39**; SiF_3 **40**; $Si(OMe)_3$ **41**; $Si(OPhOMe\text{-}p)_3$ **42**, $Si(OPh)_3$ **43**; $Si(OPhCl\text{-}p)_3$ **44**.

(E)-β-[tris(trimethylsiloxy)silyl]styrene [ligand on silicon: $(Me_3SiO)_3$] are shown in Table 2-2. From the table we can see that the two dibromo-adducts from *syn*- and *anti*-addition correlated reasonably well with the ratio of (E)-/(Z)-β-bromostyrenes resulting from the elimination. The slight discrepancies, always in favor of the *trans*-isomer - (E)-β-bromostyrene can be explained by the known propensity of the *cis*-isomer to undergo isomerization to the thermodynamically more stable *trans*-geometry[25]. This conversion can be attributed to the presence of a small amount of HBr (from bromine) or excess of bromine in the reaction solution. HBr can easily add to the double bond of (Z)-β-bromostyrene in an *anti*-fashion giving compound 33. Compound 33 can then undergo further *anti*-elimination generating the more stable (E)-isomer, 9. In the presence of light, the excess bromine can also induce the isomerization of compound 8 to compound 9[16]. These processes can be illustrated by the following equations (Scheme 3-2):

Scheme 3-2:



or in the presence of light :



8 9

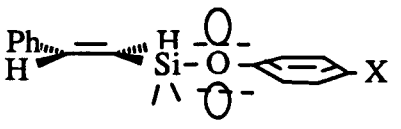
The relationship between the degree of *syn*-addition with group electronegativity follows the earlier results[28]: the more electronegative the silyl group, the lower the ratio of the *syn-/anti*-addition products as expected owing to the fact that the higher the electronegativity of the silyl group, the lower the polarization of the $Si^{\delta+}$-$C^{\delta-}$ bond, the lower the β-stabilization, and thus the lower the proportion of the *syn*-addition products.

Bromination of vinylsilanes is a process involving electrophilic addition to a double bond. The richer the electron density in the double bond is, the easier the electrophilic addition[49]will be. As the ligands on silicon become more and more electronegative, the electron density of the double bond will be diminished, and so will the reactivity of the double bond. In the bromination of (E)-β-(triacyloxysilyl)styrenes and [tris(trimethylsiloxy)silyl]styrene, we observed this effect. The bromination reaction became sluggish as the ligands on silicon become more electronegative. For example, after 1.1 equivalent Br_2 was added at -78°C for 15 minutes, 100% (E)-β-(triacyloxysilyl)styrene 12 was brominated. However, in the case of (E)-β-[tris(trifluoroacyloxy)silyl]styrene 14, only about 50% of the starting material was brominated as can be detected from their ^1H NMR spectra.

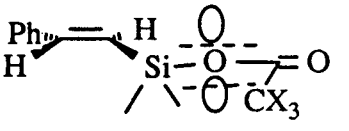
In an attempt to examine the temperature effect, a room temperature solution of bromine in CS_2 was added to a cooled solution (-78°C) of the (triacyloxysilyl)styrenes

(compounds **11**-**14**) in CS_2, the results are shown in Table 2-3. The ratios of *syn*-/*anti*-addition products show no correlation with the group electronegativity of the silyl groups. This could result from the addition of room temperature bromine solution, which would cause a rise in reaction temperature during bromination. At higher reaction temperature, the reaction may no longer be under kinetic control. Thus, the ratio of *syn*-/*anti*-addition will no longer be a measure of the relative stability of the intermediates, **5** and **4**. At intermediate temperature, thermodynamic consideration may affect the product ratio.

The ratio of the *syn*-addition *versus* silyl group electronegativity was plotted. To our surprise, two different classes of silyl groups are observed (Figure 3-4): [tris(trimethylsiloxy)silyl]styrene **11** falls in the same line as with [halo(methyl)silyl]styrenes and (trialkoxysilyl)styrenes (line A). In contrast, the three (triacyloxysilyl)styrenes **12**-**14** fall in the same group as the three (triphenoxysilyl)styrenes **42**-**44** giving a very good linear correlation (line B). Compounds in this group all have one structural feature in common - they all have a π system in their silyl groups (Figure 3-5). Compounds on line A do not have π system in their silyl groups.



X = H
OMe
Cl



X = H
Cl
F

Figure 3-5

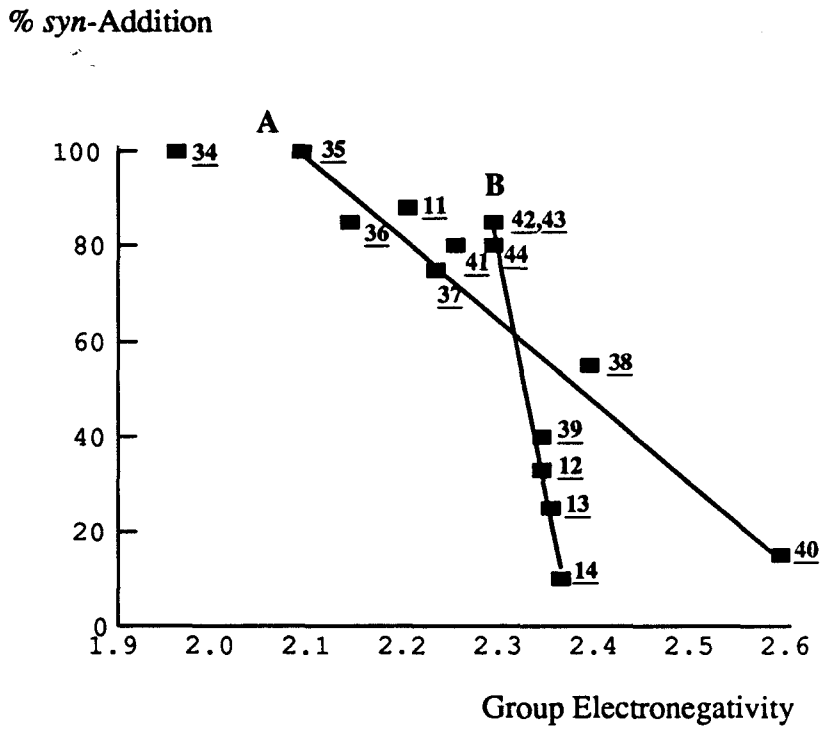


Figure 3-4 Plot of Group Electronegativity *versus* % *syn*-Addition of Bromine

PhCH=CHSiXYZ, SiXYZ = $Si(OSiMe_3)_3$ **11**; $Si(OCOCH_3)_3$ **12**; $Si(OCOCCl_3)_3$ **13**; $Si(OCOCF_3)_3$ **14**.

From the above plot (Figure 3-4), it is quite obvious that the slopes of two lines, which are composed of two classes of compounds are quite different. Line B formed by compounds 12-14 and 42-44 (with π systems in their silyl groups) has a steeper slope than that of Line A formed by compounds 11 and 34-41. The difference observed might indicate a different effect was operating during the bromination process in the two systems. The different effect, if it exists, must be determined by the difference in the structures of the two groups of compounds. For example, compounds 12-14 and 42-44, on line B, all have π systems in their silyl groups. Upon the formation of a carbocation, these π systems can interact directly with the empty p-orbital (figure 3-6).

These interactions will not be possible for the compounds on line A (compounds 11 and 41 are the exceptions).

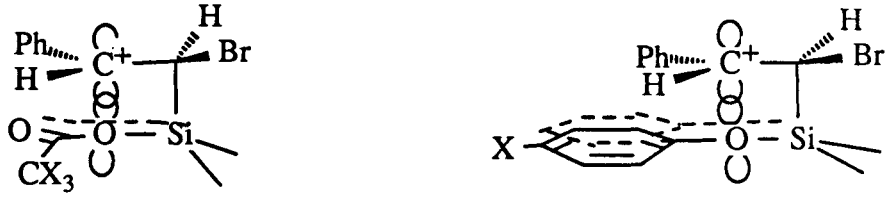


Figure 3-6

Upon examining of the α-SiCH ^{1}H NMR and ^{29}Si NMR chemical shifts of the two groups, it will be noticed that quite different relationships exist: in group A (Table 3-3) (compounds without Si-O bond and π system in their silyl groups), the α-SiCH ^{1}H NMR and the ^{29}Si NMR chemical shifts decrease as silyl group electronegativity increases. In group

Table 3-3 Comparison of Group Electronegativity, *syn*-Addition Ratio with ^{1}H and ^{29}Si NMR Chemical Shifts

group A

vinyl compd	lingands on silicon	GN[b]	*% syn*	^{1}H[c] chem. shift	^{29}Si chem. shift
34[a]	Me_3	1.96	100	6.36	-6.58
35[a]	Me_2Cl	2.09	100	6.34	18.76
36[a]	Me_2F	2.14	85	6.29	20.19
37[a]	$MeCl_2$	2.23	75	6.24	17.43
38[a]	Cl_3	2.39	55	6.21	-2.51
39[a]	MeF_2	2.34	40	6.11	-11.07
40[a]	F_3	2.59	15	5.97	-71.4

[a] data from previous studies in our lab, see ref. 27.

[b] group electronegativity of Mullay's scale.

[c] ^{1}H NMR of the α-SiCH proton.

Table 3-4 Comparison of Group Electronegativity, *syn*-Addition Ratio with ^{1}H and ^{29}Si NMR Chemical Shifts

group B

vinyl compd	ligands on silicon	GN[b]	*%syn*	^{1}H[c] chem. shift	^{29}Si chem. shift
11	$(Me_3SiO)_3$	2.20	88	5.99	-77.33
41[a]	$(MeO)_3$	2.25	80	5.99	-53.70
42[a]	(*p*-MeOPhO)$_3$	2.29	85	6.29	-68.56
43[a]	$(PhO)_3$	2.29	85	6.34	-69.03
44[a]	(*p*-ClPhO)$_3$	2.29	80	6.24	-68.23
12	$(CH_3COO)_3$	2.34	33	6.31	-59.86
13	$(CCl_3COO)_3$	2.35	25	6.37	-56.58
14	$(CF_3COO)_3$	2.36	10	6.29	-56.46

[a,b,c] see the footnotes on Table 3-3.

B [compounds with i) Si-O bond adjacent to α-carbon and ii) π systems in their silyl groups*], however, (although there are some irregular cases), the trend is just opposite: as the *syn*-addition ratio decreases (or group electronegativity increases), the α-SiCH ^{1}H and ^{29}Si NMR chemical shifts increase (Table 3-4). Such differences might be a reflection of internal structural difference between the two groups. However, as the factors which can influence the value of chemical shifts are complicated, the above observations should be dealt with care.

Another common structural feature in Compounds **11**-**14** and **41**-**44** is that they all contain Si-O bond in their silyl groups. This bond is extremely strong and polar, and has high (50%) ionic character[1,3]. This bond can be described as the sum of an Si-O σ-bond and O(n)-Si(σ^*) interaction with π-character[50] [or a (p-d)π interaction[51]]. Such unusual properties of this bond may bring unusual behavior to those compounds. However, Mullay's group electronegativity equation does not include a term to describe the O(n)-Si(σ^*) [or (p-d)π bonding] interaction. Therefore deviation may be caused simply by the insufficiently sophisticated group electronegativity model for the compounds containing Si-O bonds (group B).

In the previous section, only electronic effects - bridging or hyperconjugation, have been discussed in the stereoselectivity of bromination of styrylsilanes (the *syn*-addition ratio). In fact, the steric bulk of the silyl groups may also be an factor to contribute to stereoselective outcome. Although substantial hyperconjugation can be observed when the angle between the Si-C bond and p-orbital is constrained to 60°[47], the maximum hyperconjugation is obtained when the C-Si bond and the empty p-orbital are coplanar[47,52]. The conformations in which silyl groups can give maximum hyperconjugation stabilization can be formed by either 60° or 120° C-C bond rotation (Scheme 3-3). The conformation

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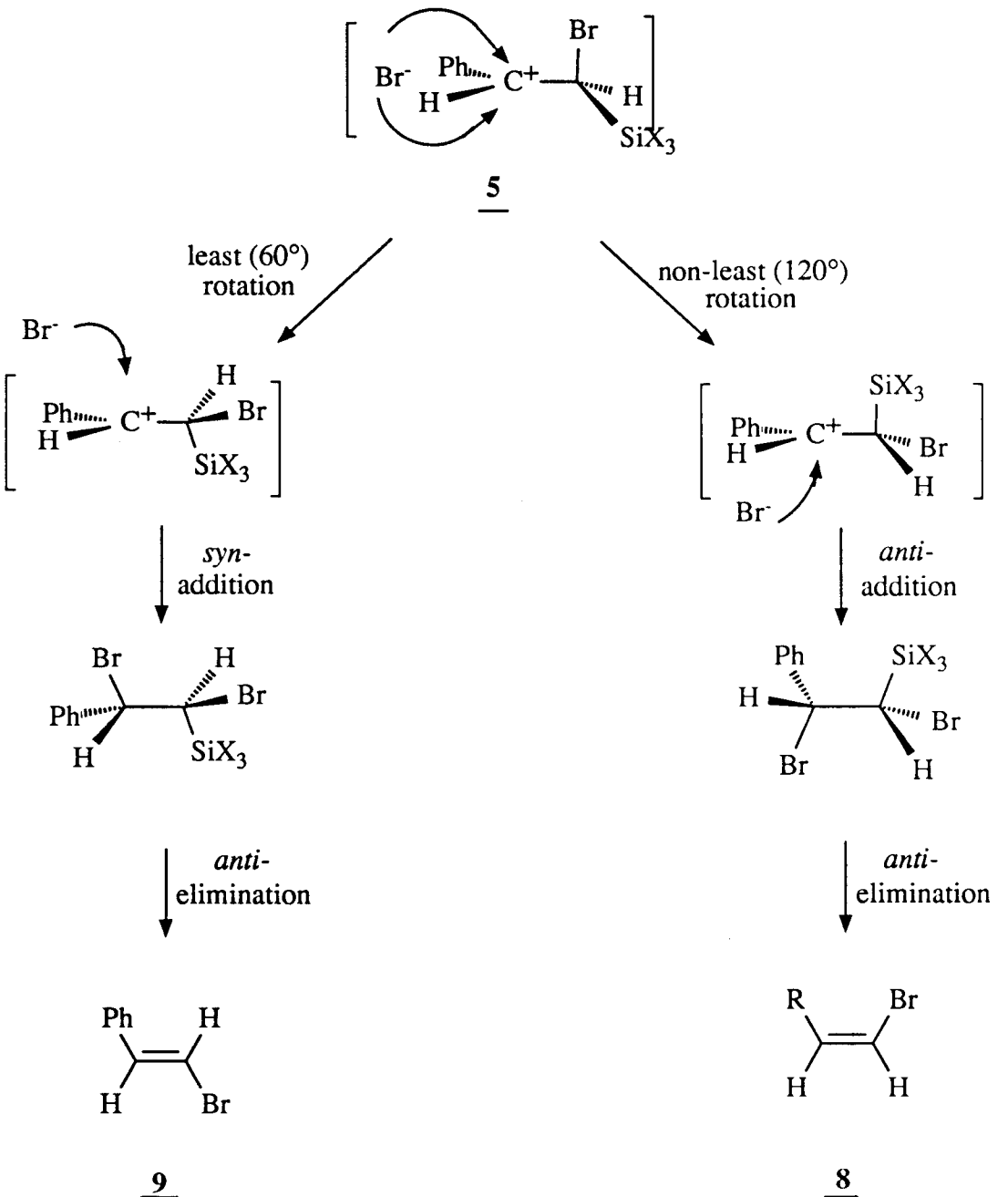
*Note: *Compounds* **11** *and* **41** *are the exceptions.*

Scheme 3-3


Br
Br⁻ Ph C⁺
H
H
SiX3
5
least (60°) rotation
non-least (120°) rotation
Br⁻
H
Ph C⁺ Br
H
SiX3
SiX3
Ph C⁺ Br
H
Br⁻
H
syn- addition
anti- addition
Br H
Ph Br
H SiX3
Ph SiX3
H Br
Br H
anti- elimination
anti- elimination
Ph H
H Br
R Br
H H
9
8

formed by the least nuclear motion - 60° rotation should be favored over the conformation formed by the 120°rotation for several reasons. First, there is an unfavorable interaction between bromide and the ortho-proton on the phenyl ring during 120° rotation. Second, during the 120° rotation, the molecule has to pass through a conformation in which the C-Si bond is orthogonal to the vacant p-orbital which will result in an initial destabilization of the developing carbonium ion. Finally, during a 60°, but not a 120° rotation, the bromide should be closest to the *syn*-face of the molecule. The rate of diffusion of the bromide is expected to be slower compared to the rate of molecular internal motion.

Therefore, *syn*-addition will result from attack by the bromide on the conformation formed by 60° rotation to the *syn*-face of the molecule because of the proximity of the nucleophile to the *syn*-face and lower steric hindrance. The bulkier the silyl group, the more effectively does the silyl group block the *anti*-face of the molecule, the higher the *syn*-addition products will be resulted. On the other hand, the compounds with less bulky silyl groups may give a lower degree of *syn*-addition than predicted from the group electronegativity. Thus, the steric bulk of the silyl group should play a certain role in the stereochemical outcome. While the above argument is reasonable in principle, an obvious deviation caused by steric factors was not observed.

Although many structural differences have been observed between the two classes of compounds, a logical connection between their structures and behaviors, can not, at present stage, be established. Further work needs to be done before a mechanism can be offered as an explanation for the above observations.

A.3.4 Concluding Remarks

The results of the bromination of a series of (E)-β-silylstyrenes have showed that the magnitude of the β-effect is directly related to the electron-withdrawing ability of the ligands on the silicon atom. A linear relationship exists between the *syn*-addition ratio and group electronegativity of silyl group. The more electronegative the ligands on silicon, the less the *syn*-addition products and thus the less the β-effect of the silyl group.

While the above statement holds true, however, two major different classes of silyl groups were also observed. The results of bromination of compounds with these two different classes of silyl groups showed different linear relationships between group electronegativity and the *syn*-addition ratio. The structural features of the two classes of compounds are quite different: compounds on line A are [halo(methyl)silyl]styrenes, (trimethoxysilyl)styrene and [tris(trimethylsiloxy)silyl]styrene. The structural feature of this class of compounds is that they do not have π system in their silyl groups. Compounds on line B are (triphenoxysilyl)styrenes and (triacyloxysilyl)styrenes. They all contain π systems in their silyl groups (Figure 3-5).

Another distinct structural difference between those two classes of compounds is that compounds on line B all contain Si-O bonds, while compounds on line A do not {trimethoxy- and [tris(trimethylsiloxy)silyl]styrenes are the exceptions}.

The slopes of the two lines, A and B, are also quite different. Line B formed by compounds with π system in their silyl groups [(triphenoxysilyl)styrenes and (triacyloxysilyl)styrenes] has a steeper slope, which means that a small change of the group electronegativity of the silyl group will result in a considerable change in the degree of the *syn*-addition ratio. In this class of compounds, the *syn*-addition ratio is more sensitive towards the electron-withdrawing ability of the ligands on silicon. In

another class of compounds {halo(methyl)-, trimethoxy-, and [tris(trimethylsiloxy)-silyl]styrenes}, the *syn*-addition ratio is less sensitive towards the eletron-withdrawing ability of the ligands on silicon.

By comparing the α-SiCH ^{1}H NMR and ^{29}Si NMR chemical shifts with *syn*-addition ratio (or group electronegativity), we observed that different relationships exist in the two classes of compounds. In group A (Table 3-3), as the *syn*-addition ratio decreases, the α-SiCH ^{1}H and ^{29}Si NMR chemical shifts decrease. In group B (Table 3-4), however, as the *syn*-addition ratio decreases, the α-SiCH ^{1}H and ^{29}Si NMR chemical shifts tend to increase. Such a difference might be a reflection of internal structural difference between the two classes of compounds.

Although many distinct differences exist between the two classes, the connection between behavior and structure can not be determined at present stage.

To determine whether the results are relevant to the Si-O bond, a study of compounds with Si-S or Si-N bonds should be undertaken. Further experimental data are needed before any further conclusion can be made on the relationship between behaviors and structure in these two classes of compounds.

Part B

CHAPTER 4

INTRODUCTION

4.1 The Silicon-Hydrogen Bond

Silicon reagents have become increasingly important and widely used in synthetic chemistry. One of the most important categories of silicon compounds is the silanes which contain Si-H bond. This type of compounds is being exploited not only because they have important synthetic utility but also because they are useful in the acquisition of fundamental information concerning reaction mechanisms at silicon[55].

The properties of an organosilicon compound usually depend upon its relative bond strengths to other elements, its relative electronegativity, and the involvement or lack of its valence p- and empty d-orbitals. The Si-H bond strength and the electronegativity for Si and H are listed in Table 4-1 and Table 4-2, respectively, and compared with the C-H bond.

Table 4-1 Approximate Bond Dissociation Energies[1a]

Si-H (Me_3Si-H)	339 kcal/mol	C-H	420 kcal/mol

Table 4-2 Electronegativity of Pauling's Scale[7]

Si:	1.8	H:	2.1	C:	2.5

From the above data, it can be seen that Si-H bond is weaker than the C-H bond and

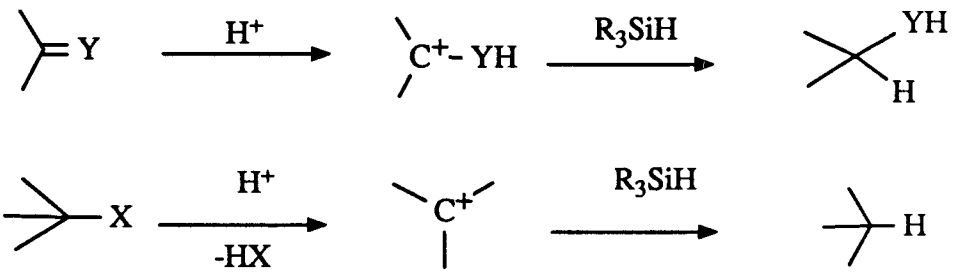
the directions of polarization of the two bonds are opposite: $Si^{\delta+}$-$H^{\delta-}$, $C^{\delta-}$-$H^{\delta+}$. Because hydrogen is more electronegative than silicon, the Si-H bond is polarized in the direction that hydrogen is more electron-rich. This feature makes the Si-H bond a potential source of hydride and therefore a reducing reagent under appropriate conditions[1].

4.2 Hydrosilanes as Reducing Reagents

Although silanes have been studies extensively, the most important property of silanes is probably the addition of the Si-H bond linkage to multiply-bonded substrates. Such addition can be brought about under ionic or catalytic conditions. The former refers to the hydride transfer to a carbonium ions. The term "hydrosilylation" is used to describe the latter - the transition metal-catalysed addition of a hydrosilane to a multiply-bonded system[28].

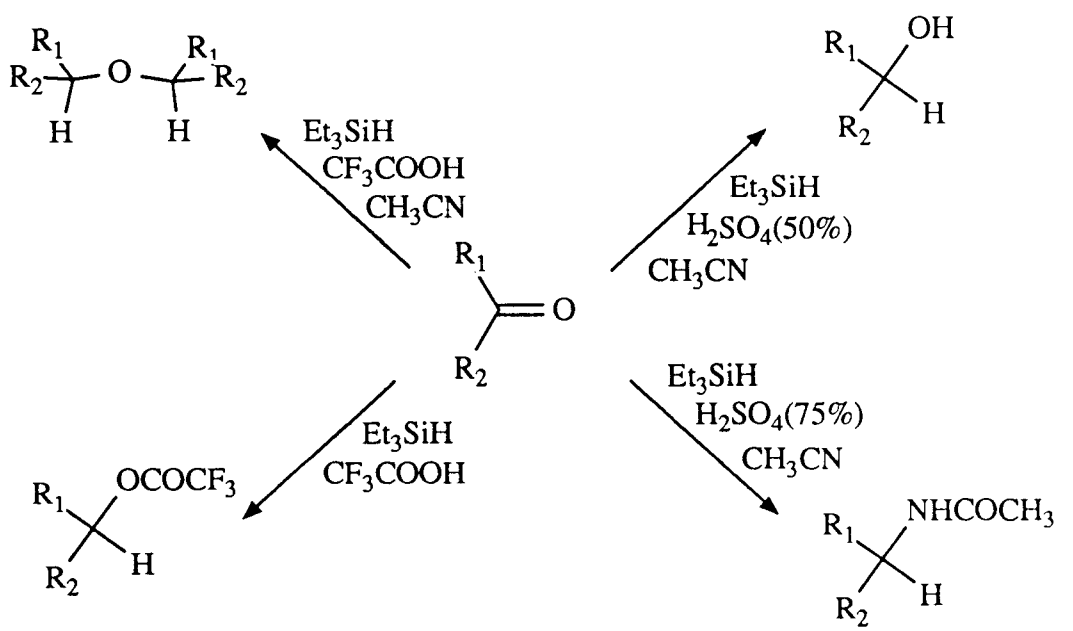
Under "ionic" conditions, silicon hydride (hydrosilane), in common with the similarly polarized boron and aluminium hydrides, can transfer hydride ions to electropositive carbon centers. However, unlike boron and aluminium hydrides, hydrosilanes require additional activation of the carbon center by Lewis or protic acids before such hydride transfer can take place. This process can be illustrated by the following scheme (Scheme 4-1):

Scheme 4-1



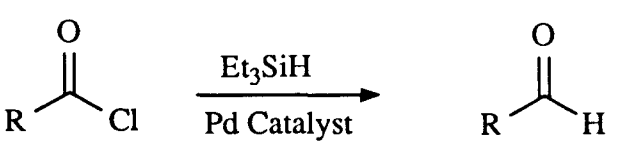
The ionic hydrogenation of aldehydes and ketones can be a most useful process, permitting selective production of alcohols, symmetrical ethers, carboxylate esters, or acetamides. The competitive reactions leading to these species can be manipulated by subtle variation of conditions[56] (Scheme 4-2):

Scheme 4-2



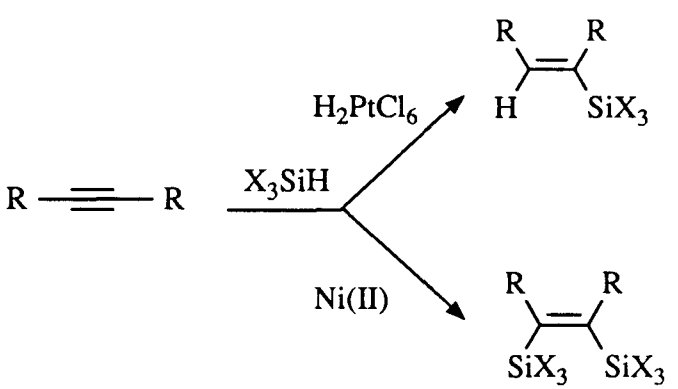
Hydrosilylation is equally important in organic synthesis as it offers[57] not only a method of reduction, such as shown in Scheme 4-3:

Scheme 4-3



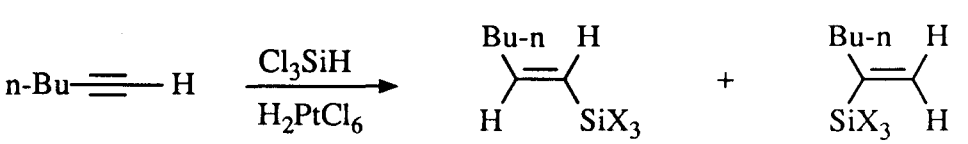
but is also a major route to complex organosilanes such as vinylsilanes. The catalyst most frequently employed in hydrosilylation of alkynes and alkenes is hexachloroplatinic acid. Under such conditions, alkynes undergo *cis*-addition preferencially[58]. Peroxide-initiated addition[58a], on the other hand, gives mainly the products of *trans*-addition, whereas nickel (II) catalyses[59] a stereoselective double *cis*-addition (Scheme 4-4).

Scheme 4-4



Terminal alkynes react with a high degree of regioselectivity with lower reaction temperature[53,60] favoring a greater proportion of the terminal isomer (Scheme 4-5):

Scheme 4-5

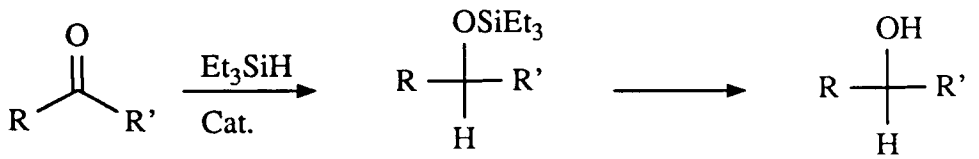


reaction temp. (i) reflex 78 : 22

(ii) 5°C 95 : 5

Silicon hydrides can also add[1] to carbonyl groups of saturated aldehydes and ketones to produce alkoxysilanes. These then can be easily hydrolyzed to alcohols (Scheme 4-6).

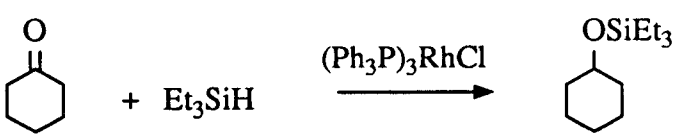
Scheme 4-6



Catalyst = $(Ph_3)_3PhCl$, Rh, et al

A wide variety of catalysts are effective in promoting the reactions, among which tris(triphenylphosphine) rhodium chloride has proved exceptionally active for the hydrosilylation of aliphatic ketones with triethylsilane[61] (Scheme 4-7):

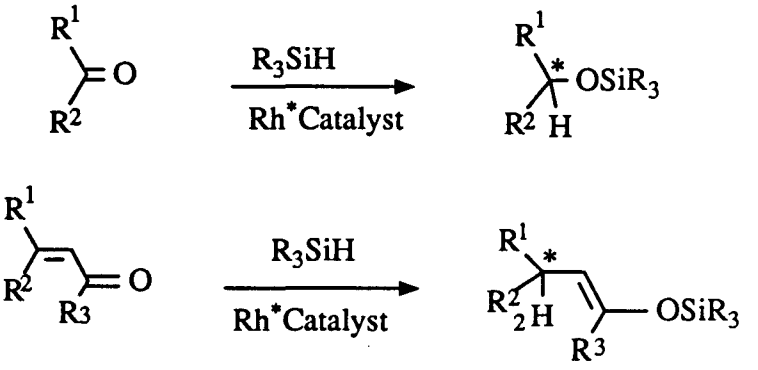
Scheme 4-7



In addition to all those discussed above, the most interesting aspect of silane reduction is that asymmetric hydrosilylation of both saturated and unsaturated carbonyl substrates[62] can be achieved by use of chiral rhodium catalysts, a moderate to high degree

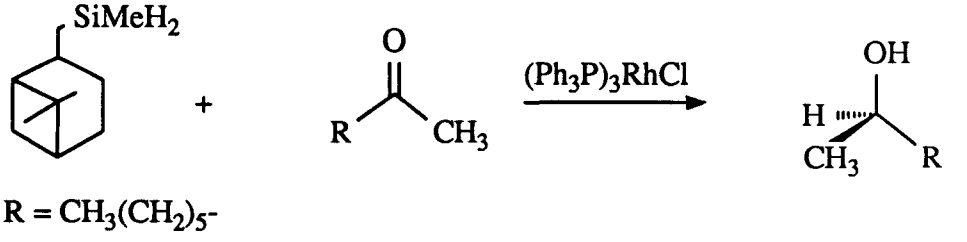
of chirality normally being induced (Scheme 4-8):

Scheme 4-8



Chiral rhodium catalysts related to Wilkinson's catalyst are prepared by substitution of R-(+)-benzylmethylphenylphosphine R(+)BMP or S-(-)-benzylmethylphenyl-phosphine S(-)BMP for triphenylphosphine. The optical yield and configuration of the product alcohol have been reported[63] to be dependent on the structure of the prochiral ketone as well as the silane used. In principal, asymmetric reduction can also be achieved using chiral silanes. Chan studied[64] asymmetrical hydrosilylation of 2-octanone using chiral pinanylmethylsilane. The reduction followed by hydrolysis gave 2-octanol with 25.7% ee (Scheme 4-9).

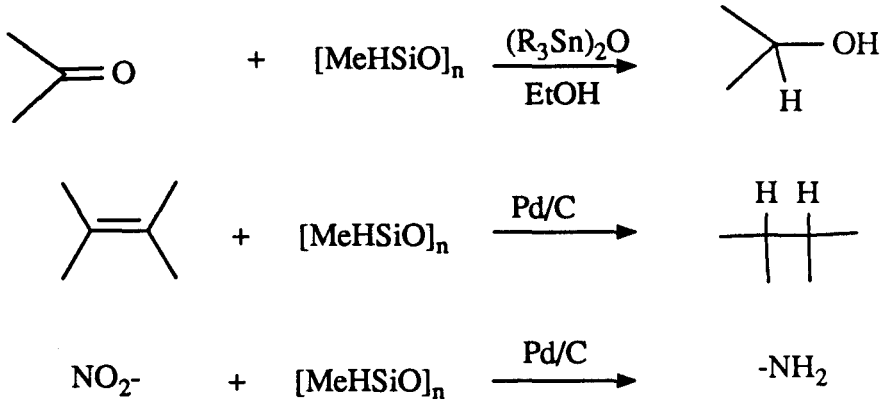
Scheme 4-9



R = $CH_3(CH_2)_5$-

Another interesting case is the study of polymeric silanes as a convenient alternative to the more usual reagents. One such reagent is polymethylhydrosiloxane[65], which is now commercially available. It functions as a mild reagent for selective reduction of aldehydes and ketones to alcohols in the presence of an organic catalyst in a protic solvent. Alkenes and nitro-groups can also be reduced with catalysis by Pd/C. This constitutes a safe, and convenient form of low pressure hydrogenation. In both case, at the end of the reduction, the polymer forms a granular gel during hydrolysis, which can simply be filtered off (Scheme 4-10).

Scheme 4-10



4.3 Ligands on Silicon and Reactivity of Hydrosilanes

Hydrosilanes have been studied not only as useful synthetic reagents but have also been studied for the inherent interest in their the reaction mechanisms.

The properties of Si-H bond are determined by the nature of this bond. Because of

the lower electronegativity than that of hydrogen, Si-H bond is polarized: $Si^{\delta+}$-$H^{\delta-}$. Therefore, silicon is easily attacked by nucleophiles. For example, nucleophilic attack at silicon will result[66] in the substitution of hydrogen gas (Scheme 4-11):

Scheme 4-11

$$R_3SiH + ROH \xrightarrow{^-OH} R_3SiOR + H_2(g)$$

$$Et_3SiH \xrightarrow[Et_2NH]{KNEt_2} Et_3SiNEt_2 + H_2(g)$$

Hydrogen, on the other hand, is readily undergoes electrophilic attack. For example, halogens react rapidly with hydrosilanes[67]. Mechanistic studies showed that this process involves electrophilic attack at hydrogen (Scheme 4-12):

Scheme 4-12

$$Et_3Si\text{-}H \xrightarrow[(X=Cl,Br,I)]{X_2,CCl_4,0°C} Et_3Si\text{-}X$$

It is quite obvious that the extent of polarization of Si-H bonds in hydrosilanes will greatly affect the reactivity of Si-H in these reactions. The polarization of Si-H bond is further determined by the ligands on silicon. For example, the rates of the solvolysis of a series of substituted triarylsilanes, $(R\text{-}C_6H)_4Ph_2SiH$ in aqueous piperidine solution (0.96 M) has been reported[68] as following:

Table 4-3 Effect of Ligands on Silicon at Rates of Base Catalyzed Hydrolysis

$$(R\text{-}C_6H_4)Ph_2SiH + H_2O \xrightarrow{\text{Piperidine}} (R\text{-}C_6H_4)Ph_2SiOH + H_2(g)$$

R	*p*-Cl	H	*m*-Me	*p*-Me	*m*-Me_2N	*p*-MeO	*p*-Me_2N
$10^4k(sec^{-1})$	16.9	3.22	2,75	1.08	0.75	0.89	0.21

The determination of relative rates for the solvolysis of fluoroalkylsilanes $RR'(CH_3)SiH$ in 93.7% ethanol with KOH as catalyst, revealed[69] the predominance of the inductive effects of $CF_3CH_2CH_2$- and $CF_3CF_2CH_2$- groups over the steric effects (Table 4-4):

Table 4-4 Relative Rates for the Solvolysis of Fluoroalkylsilanes in 93.7% Ethanol

$$RR'(CH_3)SiH + EtOH \xrightarrow{^-OH} RR'(CH_3)SiOEt + H_2(g)$$

R	R'	k°_{rel}
$CH_3CH_2CH_2$	CH_3	1.0
$CF_3CH_2CH_2$	CH_3	5.9
CF_3CHFCH_2	CH_3	8.3
$CF_3CF_2CH_2$	CH_3	83
$CF_3CH_2CH_2$	$CF_3CH_2CH_2$	2100

The relative rate constants for basic solvolysis of vinylsilanes were also obtained[70]:

Table 4-5 Relative Rates for Base Catalyzed Solvolysis of Vinylsilanes

$$RR'R''SiH + ROH \xrightarrow{^-OH} RR'R''SiOR + H_2(g)$$

Silane	k°_{rel}
Et_3SiH	1
$(CH_2{=}CH)Et_2SiH$	21
$(CH_2{=}CH)_2EtSiH$	310
$(CH_2{=}CH)_3SiH$	3800

A comparison of the relative rate constants shows that an increase in the rate constant from triethylsilane to trivinylsilane is not constant, indicating a certain influence possibly exerted by (p-d)π interaction of the vinyl groups with the silicon atom.

All the above studies show that in the base catalyzed solvolysis electron-release towards silicon hinders the reaction, as is to be expected for a reaction in which nucleophilic attack on silicon provides the main driving-force. This indicates that in the transition states of base catalyzed solvolysis of hydrosilanes the silicon atom is more negative than in the ground state.

Other studies on hydrosilanes including the acidic catalyzed solvolysis and halogenations have also been carried out and will be discussed in the corresponding

chapter of this thesis.

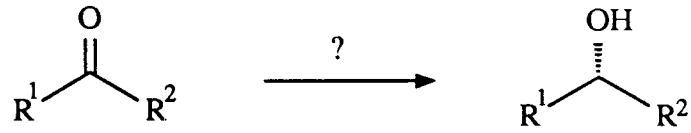
4.4 Objectives of Our Studies

The creation of optical activity is an important problem from both theoretical and practical points of view. For many useful chiral compounds, only one enantiomer is desired, as is the case with pharmaceuticals, food additives, perfumes and so on. Asymmetric reduction of prochiral unsaturated compounds becomes one of the important ways to prepare such compounds. Therefore, synthesis of the asymmetric reducing reagents is becoming increasingly important.

Based on the development discussed in the previous sections, we decided to explore the possibility of synthesizing a novel organosilicon polymeric reducing reagent which has the following features:

(i) It has moderate reducing power to mutiply-bonded organic substrates;

(ii) By introducing chiral centers to the polymer chain, it is hoped to perform asymmetric reduction towards prochiral center, e.g. :



(iii) It also has the advantage of being easily removed from the reaction media.

We studies the methods and conditions of polymerization for making this polymer. The structure of the polymer was studied by ^{29}Si NMR spectroscopy and an iodometric titration method was used to determine the content of Si-H bonds of the polymer.

In order to study the factors which determine the reactivity of silanes, the

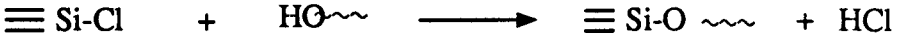
reactivity of a series of hydrosilanes including a model compound of the polymer was examined; their reactivity towards iodination and acidic catalyzed alcoholysis are compared. Different reactivity of hydrosilanes with different ligands on silicon atom were observed.

CHAPTER 5

RESULTS AND DISCUSSION

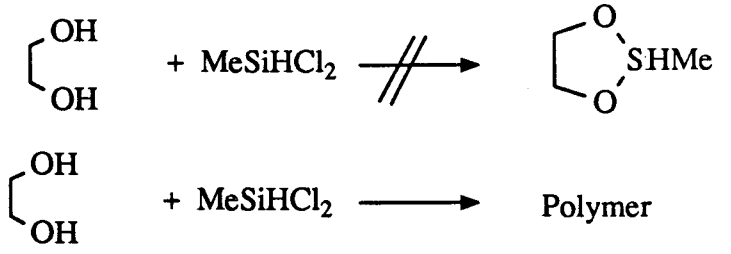
5.1 Glycol-Silicone

One of the fundamental reactions in the preparation of silicones is the reaction between chlorosilanes with molecules bearing hydroxyl groups to form Si-O bond and release HCl[1,3b]:



In the studies of the reaction between ethylene glycol and $MeHSiCl_2$, we found[71] that instead of generating a five membered ring, it gives a gel-like polymer (Scheme 5-1):

Scheme 5-1:

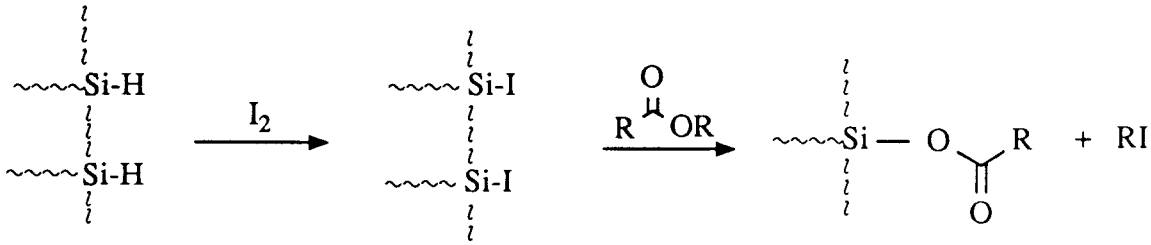


This polymer is of great interest not only because it is easy to prepare, but also because it should be easy to modify. For example, it should be possible to introduce chirality into polymer chain by simply replacing ethylene glycol with a chiral diol.

Furthermore, the Si-H bonds in the polymer are very useful functional groups which can be used as potential hydride resources - reducing reagents or can be converted to

other functionalities. For example, through the reaction with iodine, the Si-H bonds can be converted to Si-I. Trimethylsilyl iodide (TMSI) is known to be a useful reagent for the cleavage of ester, acetal and ether groups under aprotic conditions. Therefore, the possibility of polymer supported versions of TMSI can be explored.

Scheme 5-2:



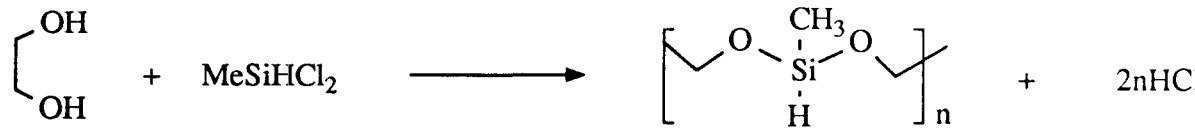
5.1.1 Synthesis

The synthetic procedures of making "glycol-silicone" are simple. The addition of dichloromethylsilane to an equimolar amount of ethylene glycol in CH_2Cl_2 at room temperature will result in a reaction mixture with evolution of gases. After certain reaction time, a gel-like polymer was obtained upon the removal of the solvent.

5.1.2 Structural Studies

The structure of glycol-silcone would be simple if the condensation occurred only through the following reaction (Scheme 5-3):

Scheme 5-3



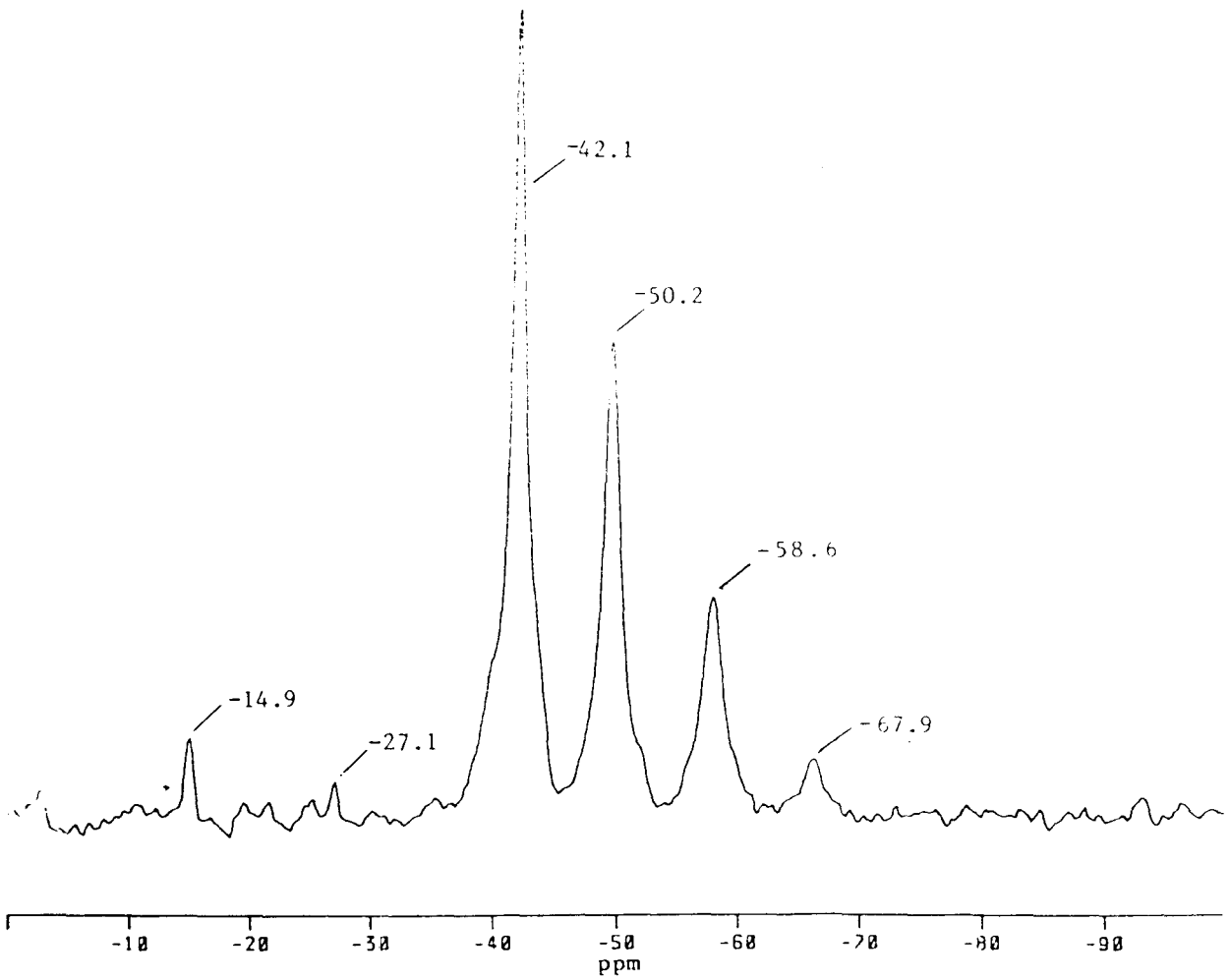


Figure 5-1 ^{29}Si NMR (Solid State MAS) Spectrum of Glycol-Silicone Polymer (Entry 1)

However, ^{29}Si solid state MAS (magic angle spinning) NMR (Figure 5-1) combined with the information from other types of spectroscopy including ^{1}H NMR and IR show that there are several silicon species in the polymer network indicating there are other side reactions as well.

The possible functionally different silicon species which could arise from the reaction are shown in Figure 5-2:

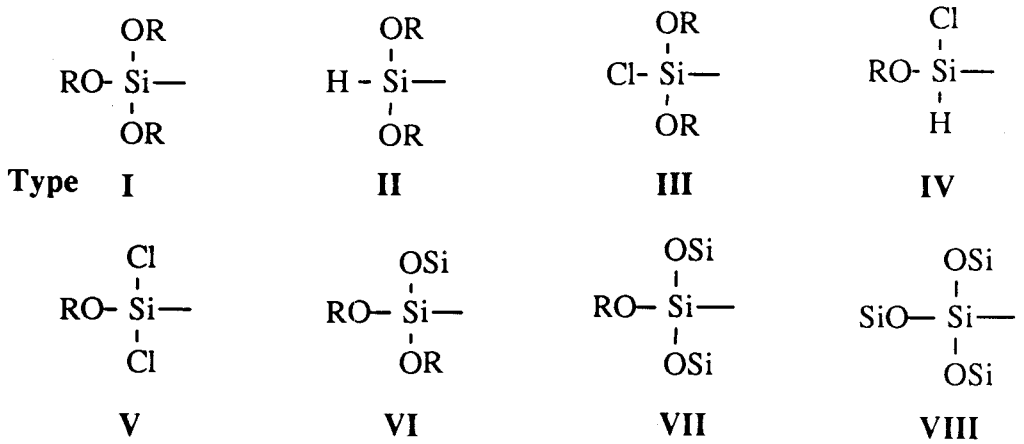


Figure 5-2

To aid in distinguishing these silicon species in the polymer, a variety of structurally related monomeric model compounds were synthesized by the following reactions (Scheme 5-4):

Scheme 5-4:

CH_3SiCl_3 + $HOCH_2CH_2OMe$ ⟶ Product

excess ⟶ $CH_3Si(OCH_2CH_2OMe)_3$ (**45**) + 3HCl

1 : 2 ⟶ $CH_3SiCl(OCH_2CH_2OMe)_2$ (**46**) + 2HCl

1 : 1 ⟶ $CH_3SiCl_2(OCH_2CH_2OMe)$ (**47**) + HCl

CH_3SiHCl_2 + $HOCH_2CH_2OMe$

1 : 2 ⟶ $CH_3SiH(OCH_2CH_2OMe)_2$ (**48**) + 2HCl

1 : 1 ⟶ $CH_3SiHCl(OCH_2CH_2OMe)$ (**49**) + HCl

^{29}Si NMR chemical shift of each compound was then determined (Table 5-1). From these data and combined with known chemical shifts of other polymeric methyl-substituted silicon species, all the ^{29}Si NMR peaks (Figure 5-3, 5-4) of the polymer can be assigned.

Table 5-1 Chemical Shifts of Compound 45-49

compound	**45**	**46**	**47**	**48**	**49**
δ (^{29}Si NMR)	**-42.9**	**-27.7**	**-9.4**	**-14.9**[a]	**-3.1**[a]

[a] data from ref.71

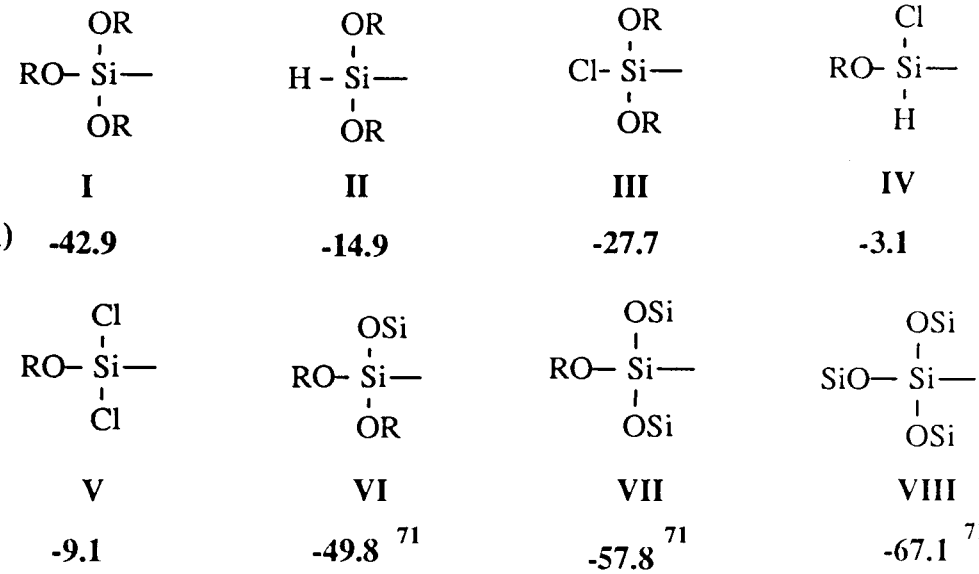


Figure 5-3

From the above ^{29}Si NMR analysis, it can be seen that the polymer is composed primarily of pseudo **T** units*, **I**; alkoxysilane and disiloxane units, **VI** and **VII**, mixed with pseudo **DH** units, **II**; chloroalkoxysilane unit, **III** and T units, **VIII**. However, components related to **IV** and **V** were not observed in ^{29}Si NMR spectra (Figure 5-4).

The above results indicate that the polymer consists not only of the linear glycol-silicone which would be expected to be formed from the condensation of the hydroxyl groups of the ethylene glycol with the Si-Cl bonds (Figure 5-3, Type **II**), but also crosslinked networks. These crosslinks could arise from the reactions of Si-H bonds with

---

*Note: *The repeating unit* Me-Si(-O-)(-O-) *is referred to as a* **D** *unit, while the termination unit* (Me_3SiO) *is referred to as an* **M** *unit. The branch point* O-Si(-O-)(-O-) *and* O-Si(-O-)(-O-) *are referred as* **T** *and* **Q** *groups respectively.*

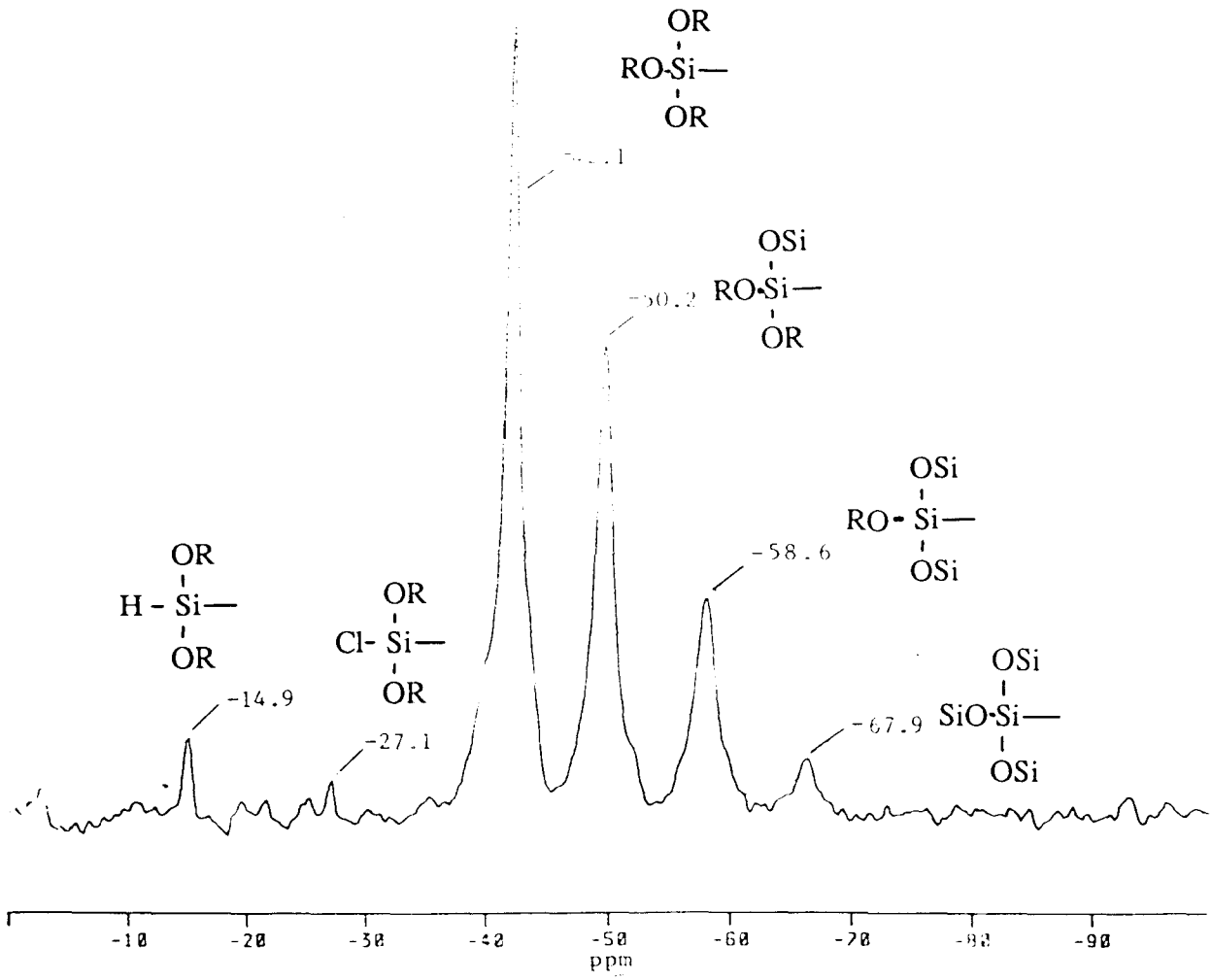
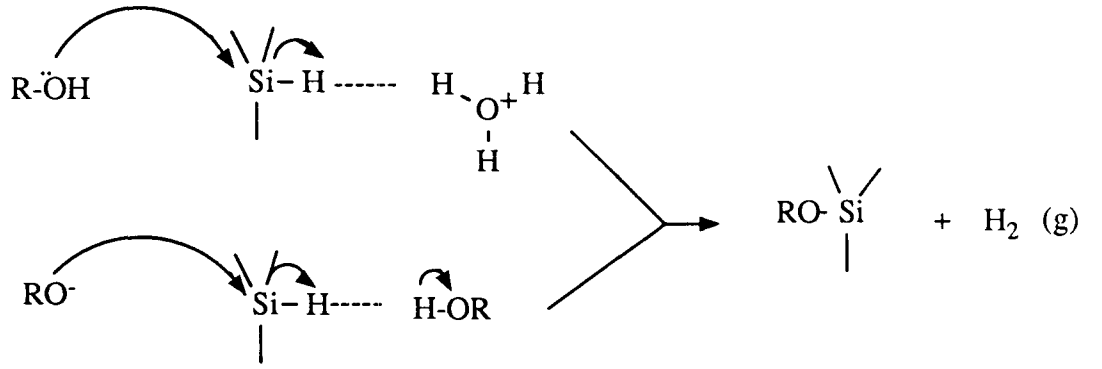


Figure 5-4 Assignments for ^{29}Si NMR (Solid State MAS) Spectrum of Glycol-Silicone Polymer

hydroxyl groups to liberate H_2. These reactions are presumably catalyzed by the condensation by-product - HCl. It is known[1c] that under either acidic or basic conditions, Si-H bonds are readily broken by the attack of hydroxyl groups, although Si-H bonds are relative stable in neutral protic media (Scheme 5-5):

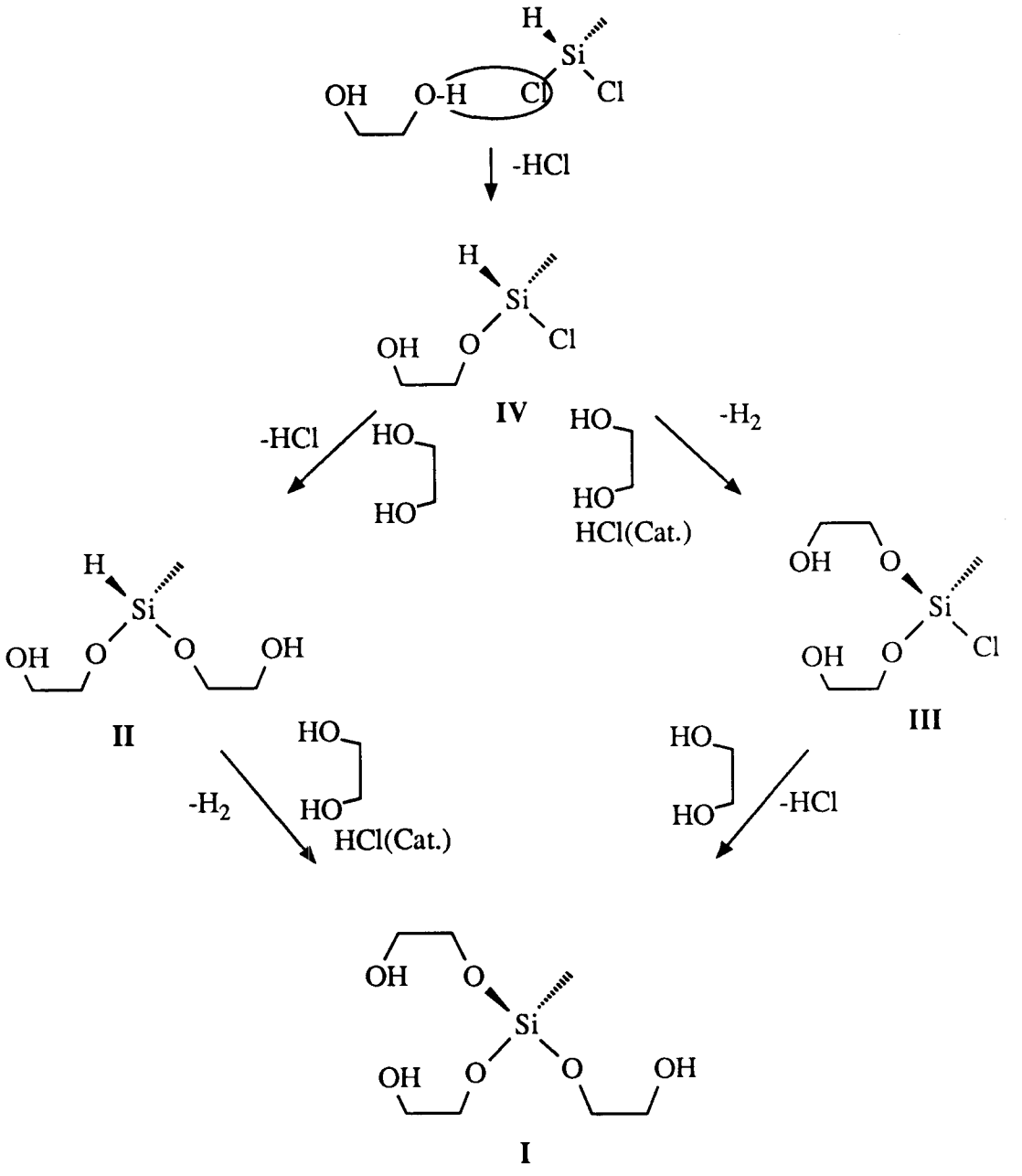
Scheme 5-5



This process is thermodynamically favored with an overall energy difference of about 31 kcal/mol (H-H 104 kcal/mol, Si-O 127 kcal/mol, OH 110 kcal/mol, Si-H 90 kcal/mol)[1a]. It is obvious that the formation of the Si-O bond provides the driving force to make the structure type **I** be the main structure in the polymer matrix.

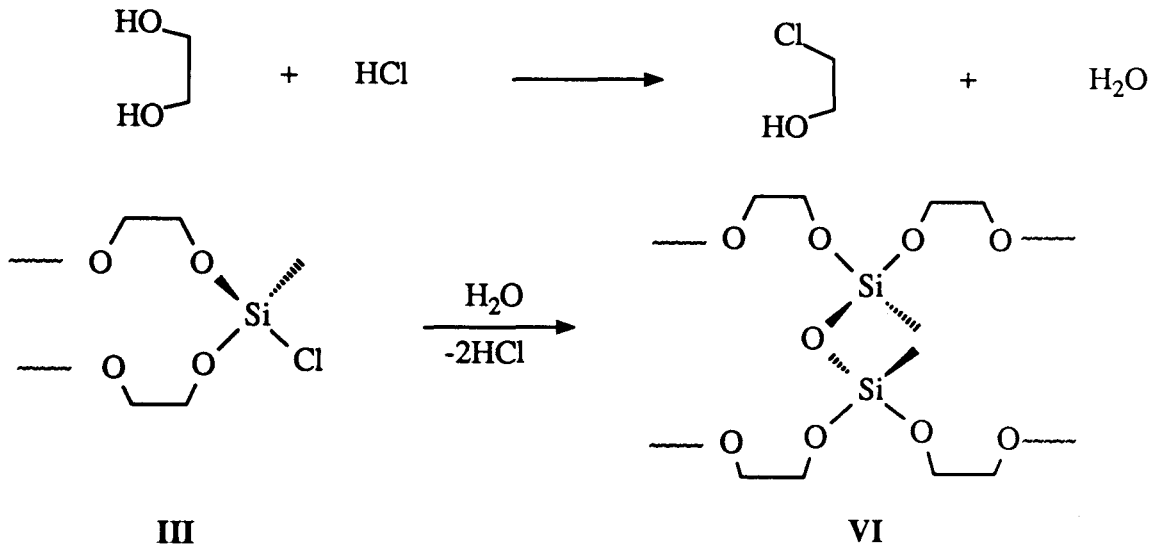
Therefore, type **II** is derived from a normal condensation reaction. This species can react further with ethylene glycol in the presence of HCl resulting in type **I**. **IV**, resulting from monocondensation, can react with ethylene glycol under the catalytic action of HCl to give cleavage of the Si-H bond and the formation of type **III**. Further reaction of type **III** with ethylene glycol also gives type **I** (Scheme 5-6).

Scheme 5-6


H
Si
OH
O-H
Cl
Cl
-HCl
IV
-HCl
HO
HO
HO
HO
HCl(Cat.)
-H2
H
Si
OH
O
O
OH
II
OH
O
Si
OH
O
Cl
III
HO
HO
HCl(Cat.)
-H2
HO
HO
-HCl
OH
O
Si
OH
O
O
OH
I

Another unwanted reaction could be the substitution of hydroxyl group on ethylene glycol by chloride from HCl resulting the generation of H_2O. Under the action of water, type **III** can be hydrolyzed to type **VI**. Similar reactions will lead to components of type **VII** and **VIII** (Scheme 5-7):

Scheme 5-7



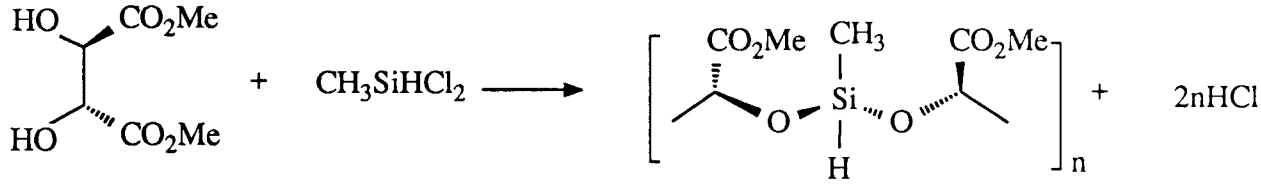
III **VI**

5.2 Synthesis of (2*R*, 3*R*)-Dimethyl Tartrate-Silicone

Although many optically active organosilicon compounds with chirality at silicon are known and could be used in the study of asymmetrical hydrosilylation, the preparation of such optically pure compounds is tedious because of the resolution process. Besides, nucleophilic attacks at silicon take place readily, the racemisation can occur, recovery of such compounds therefore can be difficult. However, studies show that a chiral organosilicon compound with its chirality located at a site remote from silicon can be effective in asymmetrical hydrosilylation[64]. Therefore, it is of high interest to prepare such a kind of compounds from nature occurring, readily available optically active

optically active products. This can be achieved by replacing ethylene glycol with (2*R*, 3*R*)-dimethyl tartrate, chirality can be introduced into the polymer backbone (Scheme 5-8):

Scheme 5-8

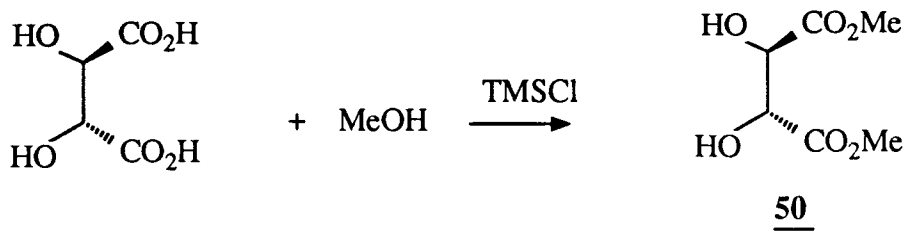


5.2.1 (2*R*, 3*R*)-Dimethyl Tartrate 50

The monomer, (2*R*, 3*R*)-dimethyl tartrate can be easily derived from tartaric acid by esterification. In addition, the starting material (2*R*, 3*R*)-tartaric acid is readily available and inexpensive.

A high yield of dimethyl tartrate was achieved using[72] trimethylchlorosilane (TMSCl) (Scheme 5-9):

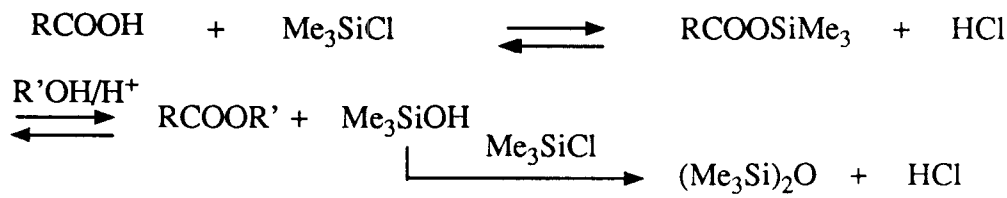
Scheme 5-9



50

The functions of TMSCl in the above reaction are to provide a source of HCl as a catalyst as well as to act as a dehydrating agent, as illustrated by the following processes (Scheme 5-10):

Scheme 5-10



5.2.2 (2*R*, 3*R*)-Dimethyl Tartrate-Silicone

The (2*R*, 3*R*)-dimethyl tartrate-silicone was made in a similar way to that of the glycol-silicone by the reaction in Scheme 5-8. The physical appearance of this polymer is a white solid. It is brittle and can be crushed into fine powder.

5.3 Determination of Si-H Content

An iodometric method[3b] was used to determine the potential reducing power of these polymers.

Hydrosilanes can decolorize iodine by reducing it to iodide . By back-titrating excess iodine with sodium thiosufate, the total Si-H content in the sample can be determined quantitatively (Scheme 5-11):

Scheme 5-11

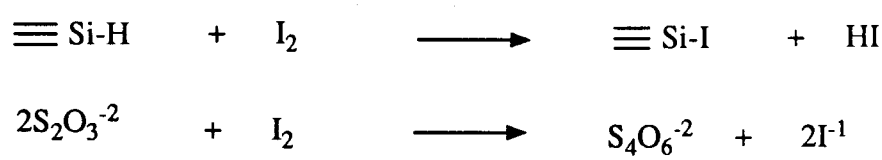


Table 5-2 Relationship Between Si-H Content and Reaction Time & Reaction Temperature

Entry	Temperature (°C)	Polymerization Time (H)	Si-H (mmol/g)	Percentage (%)
1	20	14	1.21	12.6
2	20	48	0.32	3.3
3	20	50.5	0.26	2.7
4	20	68	0.02	0.2
5	20	24	0.55	12.2
6	20	36	0.64	14.1
7	20	48	0.60	13.2
8	20	60	0.37	8.1
9	-23	24	0.40	8.8
10	0	24	0.20	4.4
11	35	24	0.01	0.2

[a] Entry 1-4: glycol-silicone

[b] Entry 5-11: dimethyl tartrate-silicone

The relationship between reaction time, reaction temperature and Si-H content was examined. The titration results are given in Table 5-2.

The above titration results show that longer polymerization time gives lower Si-H content polymer. However, the temperature effect is not very clear; high temperature (above 35°C) obviously does not favor the formation of polymer with high Si-H content.

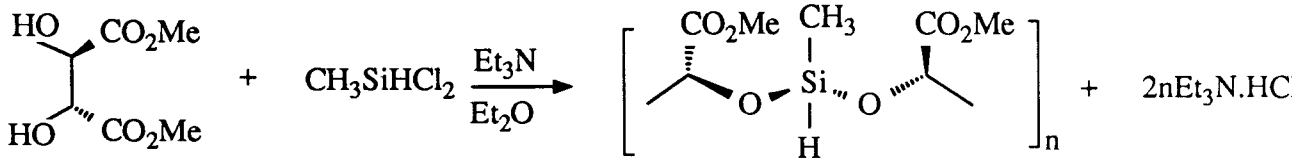
There is also a correlation between the physical "hardness" and Si-H content. High Si-H content materials are compressible gels (e.g., entry 1); whereas low Si-H content material are very hard resins (e.g., entry 11).

The explanations for the above observations are quite obvious. As discussed earlier, the HCl generated during the course of the reaction can act either as catalyst leading to the cleavage of Si-H bond, or as a nucleophile to substitute hydroxyl group in the diol leading to formation of H_2O (Scheme 5-7). The cleavage of Si-H bonds converts the difunctional silane ($MeSiCl_2H$) into trifunctional substrates at the expense of Si-H functionality. The formation of water will result in the formation of the components of type **VI, VII, VIII**. The longer reaction time and high temperature will facilitate the above process resulting in low Si-H content, and therefore highly crosslinked hard polymer.

5.4 High Si-H Content Polymer

The above titration results showed that about 90% of Si-H bonds were lost during the course of the polymerization owing to the HCl produced. Therefore, to achieve high Si-H content polymer, it is important that the HCl be removed from the reaction media immediately after its formation. One of the most commonly used methods is to deactivate HCl using a base such as triethylamine (Scheme 5-12):

Scheme 5-12

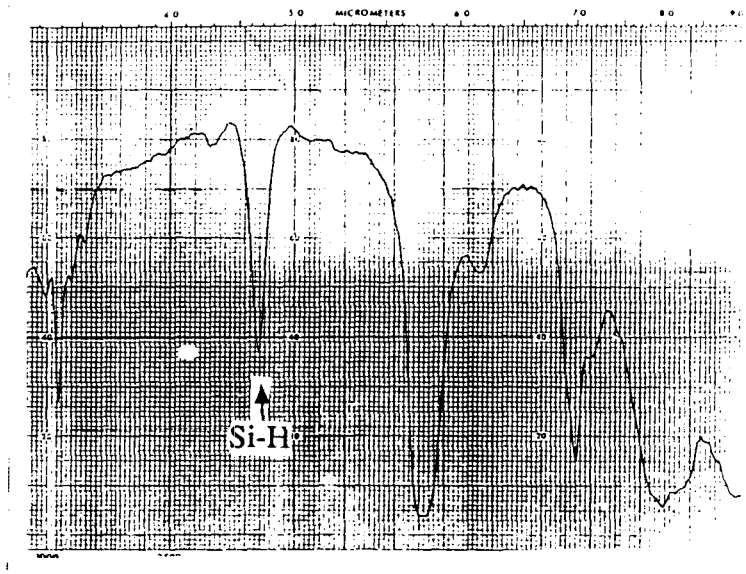


By using triethylamine as an HCl acceptor, the retention of Si-H content has been greatly improved. Titration results showed that the polymer formed under above conditions has about 40% Si-H bond retention (Table 5-3). The polymer obtained by the above reaction is a soft gel. This contrasts with the polymer of lower Si-H content which is hard resin.

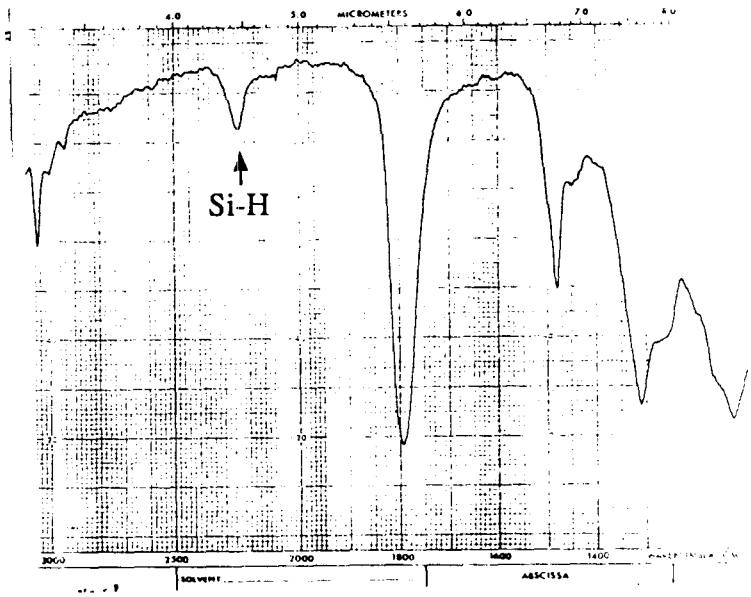
Table 5-3 Titration Result

Entry	Temperature (°C)	Reaction Time (Hour)	Si-H (mmol/g)	Percentage Retention
12	20	4	2.0	44%

The characteristic absorption of Si-H in the IR is in the 2150-2000 cm^{-1} region[73]. The polymer obtained by the above method gives much stronger absorption at 2150 cm^{-1} than the one obtained in the absence of Et_3N (Figure 5-5).



(A)



(B)

IR Spectra of (2R, 3R) Dimethyl tartrate-Silicone [(A) Entry 12; (B) Entyr 6]

Figure 5-5

5.5 Reduction

Having obtained a polymer with moderate Si-H content, the study of carbonyl reduction using it was then explored.

There are a variety of catalysts which are generally used in the hydrosilylation of carbonyls, such as $(Ph_3P)_3PhCl$[74], H_2PtCl_6[54] and bis(dibutylacetoxytin) oxide (BDATO)[65]. These catalysts were used in attempted of reductions of a prochiral ketone - acetophenone. A commercial sample of polymethylhydrosiloxane (PMHS) was also used as a reference. As mentioned in the introduction, PMHS can be used to reduce ketones in the presence of BDATO. The reduction reactions were followed by ^1H NMR and IR. The results are listed in Table 5-4.

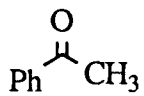
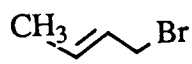
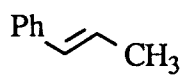
Unfortunately, the reduction turned out to be unsuccessful. In the case of PMHS, only DBATO catalyzed the reduction. The other two catalysts failed to act as catalysts, indicating that some specific hydrosilanes may require specific catalysts to promote the reduction. The absence of reduction may thus be the result of the failure to find an appropriate catalyst for "dimethyl tartrate-silicone".

One interesting case in these experiments was observed when H_2PtCl_6 was used as catalyst. Either in case of PMHS or "dimethyl tartrate-silicone", black precipitates were formed in the reaction solution. In the absence of H_2PtCl_6 or hydrosilanes (PMHS or "dimethyl tartrate-silicone") no black precipitates were observed under identical conditions. This may indicate that Pt(IV) was reduced to Pt(0). This phenomenon was also observed by Speier when he studied[39] hexachloroplatinic acid catalyzed hydrosilylation.

5.6 Reactivity of Hydrosilanes

From the above studies, it has been seen that different silanes may require

Table 5-4 Reduction Results

Substrate	Hydrosilane	Catalyst	Temperature	Solvent	Reduction
	PMHS	DBATO[b]	reflex	EtOH	(+)
	P[a]	"	reflex	EtOH	(-)
	PMHS	"	reflex	THF	(+)
	P	"	reflex	THF	(-)
	PMHS	$(Ph_3P)_3PhCl$[c]	r.t	THF	(-)
	P	"	r.t	THF	(-)
	PMHS	"	reflex	THF	(-)
	PMHS	"	reflex	CH_2Cl_2	(-)
	P	"	reflex	CH_2Cl_2	(-)
	PMHS	H_2PtCl_6[d]	r.t→reflex	THF	(-)
	P	"	"	THF	(-)
	PMHS	"	"	THF	(-)
	PMHS	"	"	THF	(-)

[a] Dimethyl tartrate-silicone

[b] Ref. 65

[c] Ref. 74

[d] Ref. 54

different catalysts for hydrosilylation. This behavior must result from the structure of the silane - the ligands on silicon which also affect the reactivity of Si-H bonds. Therefore, it is of great interest to study the relationship between the reactivity of silanes and the ligands on silicon.

In order to investigate the reactivity of "dimethyl tartrate-silicone", diethoxymethylsilane was used as a model compound in which silicon atom has very similar chemical environment as the silicon in "dimethyl tartrate-silicon".

Diethoxymethylsilane can be synthesized[75] by the following reaction in moderate yield (40-70%) (Scheme 5-13):

Scheme 5-13

$$CH_3SiHCl_2 + 2HC(OEt)_3 \xrightarrow{r.t} \underset{\underline{51}}{CH_3SiH(OEt)_2} + 2EtCl + 2HCOOEt$$

The above reaction has an advantage of the avoidance of HCl production. the conventional method of making silyl ethers uses silicon halide to react directly with corresponding alcohol[1c]:

$$\equiv Si\text{-}Cl + ROH \longrightarrow \equiv Si\text{-}OR + HCl$$

If the silane used also contains an Si-H bond, the yield is usually very low because of the occurrence of the following reaction:

$$\equiv Si\text{-}H + ROH \xrightarrow{HCl} \equiv Si\text{-}OR + H_2\,(g)$$

This is the similar situation as we encountered in the polymerization discussed earlier.

5.6.1 Iodination of Hydrosilanes

The hydrogen atoms of hydrosilanes can be replaced by halogen very readily[67]:

$$\equiv Si\text{-}H + X_2 \longrightarrow \equiv Si\text{-}X + HX$$

This reaction offers a useful route to organosilicon halides, particularly to organosilicon bromides and iodides[55]. For example (Scheme 5-14):

Scheme 5-14

$$PhSiH_3 + Br_2 \longrightarrow PhSiH_2Br$$

$$Et_3SiH + Cl_2 \longrightarrow Et_3SiCl$$

$$Ph_3SiH + Br_2 \longrightarrow Ph_3SiBr$$

$$Et_3SiH + I_2 \longrightarrow Et_3SiI$$

In addition to its synthetic utility, the kinetic study of iodination of triorganosilanes has also been studied in detail.

In the study of the iodination of trialkylsilanes, Eaborn and his coworkers found[76] that: (i) the reaction is a homogeneous and radical-free process; (ii) the steric effect of groups on silicon is small; (iii) triarylsilanes and aryldimethylsilanes are less readily iodinated than trialkylsilanes; and the kinetic reactivities towards iodine are in the

order: Et_3SiH > *n*-Bu_3SiH > *n*-Pr_3SiH >*i*-Pr_3SiH > *i*-Bu_3SiH; (*p*-$MeC_6H_4)_3SiH$ > Ph_3SiH > (*p*-$ClC_6H_4)_3SiH$ > and (*p*-$MeC_6H_4)Me_2SiH$ > $PhMe_2SiH$.

The above observations indicate that electron withdrawing from silicon hinders the reaction, and thus that the silicon atom should be more positive in the transition state than in the ground state. Therefore, electrophilic attack on hydrogen is predominant in this reaction. From detailed kinetic studies, Eaborn proposed the following transition state for iodination reaction:

$$[I^{\delta+}\text{----}I^{\delta-}\text{----}R_3Si^{\delta+}\text{-----}H^{\delta-}\text{---}I^{\delta+}\text{---}I_3{}^{\delta-}]$$

To further examine how ligands on silicon affect the reactivity of Si-H bonds, we chose to study the iodination of following three compounds in $CDCl_3$: (i) diethoxymethyl-silane; (ii) polymethylhydrosiloxane; (iii) dichloromethylsilane. [During iodometric titration, we observed that "dimethyl tartrate-silicone" can decolorize iodine much more quickly than PMHS].

By using proton NMR spectroscopy, the concentration of Si-H versus reaction time can be conveniently measured. The concentration of methyl groups on the silicon atom should remain constant throughout the reaction. However, the concentration of Si-H bonds decreases with reaction time. Thus, by measuring the relative proton signal ratio of [Si-H]/[Si-CH_3] with ^1H NMR, it is possible to determine the rate of the cleavage of Si-H bond.

If the hydrosilanes studied start with the same concentration and are reacted with an equimolar amount of iodine, then the relative reactivity of the hydrosilanes can be compared by simply plotting the ratio of [Si-H]/[Si-CH_3] calculated from ^1H NMR signal

integration *versus* time.

The results of ^1H NMR kinetic study are presented in Table 5-5 and Table 5-6 and were plotted in Figure 5-6 and Figure 5-7.

By comparing the slopes in Figure 5-6 and Figure 5-7, it can obviously be seen that diethoxymethylsilane is much more reactive than PMHS in iodination, and dichloromethylsilane showed hardly any activity towards iodine.

The above observations are consistent with Eaborn's studies. As discussed in Part A, the Si-O bond is polarized in the direction $Si^{\delta+}$-$O^{\delta-}$. However, the lone pair electrons on oxygen can overlap with the empty d (or σ^*) orbital of silicon (or Si-O bond)[51,52]. This back-bonding will decrease the polarity of Si-O bond and increase the electron density on silicon. For example, triphenylsilanol is much more acidic than triphenylmethanol being almost as acidic as phenol[77]. In diethoxymethylsilane, there are two oxygens directly linked to silicon. Therefore, back-donation effect will arise with both of the oxygens to which silicon is bonded. In the PMHS molecule, although each silicon atom connects with two oxygen atoms, each oxygen atom also links with two other silicon atoms. The net effect will be that each silicon atom shares with one oxygen in back-bonding. Therefore, the silicon atom in diethoxymethylsilane should be more electron rich than the silicon atom in PMHS.

Besides electronic effects, there are steric effects although they are small according to Eaborn[76]. It is obvious that the steric effect is much bigger in PMHS than in diethoxymethylsilane. Both the electronic and steric effect make PMHS less reactive than diethoxymethylsilane in the iodination.

The inertness of dichloromethylsilane towards iodine can be explained by the strong electron-withdrawing ability of chloride. The evidence to support this argument comes

Table 5-5 [Si-H]/[Si-CH_3] and Reaction Time in the Iodination for $CH_3SiH(OEt)_2$ and PMHS

$CH_3SiH(OEt)_2 + I_2/CDCl_3$		PMHS + $I_2/CDCl_3$	
Time (min.)	[Si-H]/[Si-CH_3]	Time(min.)	[Si-H]/[Si-CH_3]
0.0	0.30	0.0	0.284
5.0	0.21	10.6	0.274
19.5	0.202	18.5	0.273
25.7	0.190	26.5	0.272
38.6	0.166	50.4	0.272
41.9	0.159	58.1	0.271
54.6	0.155	74.3	0.271
73.9	0.126		

Table 5-6 [Si-H]/[Si-CH_3] and Reaction Time in the Iodination of PMHS and CH_3SiHCl_2

PMHS + I_2/$CDCl_3$		CH_3SiHCl_2 + I_2/$CDCl_3$	
Time (h)	[Si-H]/[Si-CH_3]	Time(h)	[Si-H]/[Si-CH_3]
0.0	0.286	0.0	0.316
0.5	0.271	0.5	0.313
3.5	0.210	3.5	0.312
20.5	0.180	20.5	0.309
26.0	0.175	26.0	0.311
32.0	0.163	32.0	0.309
46.0	0.150	46.0	0.310

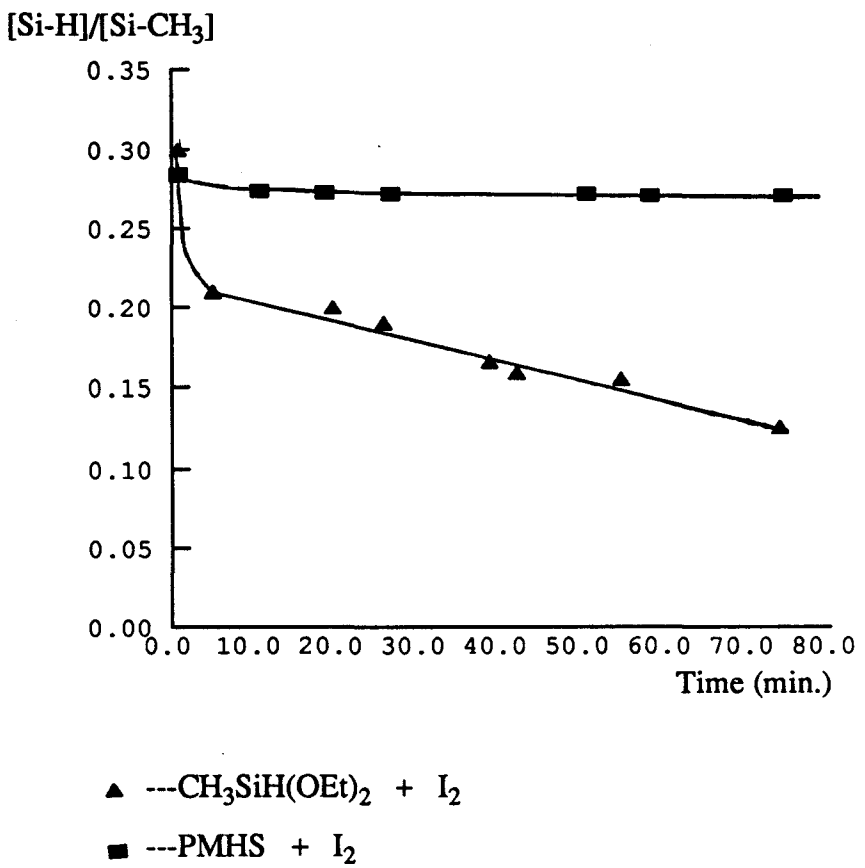


Figure 5-6 Plot of [Si-H]/[Si-CH_3] *versus* Reaction Time (min.)

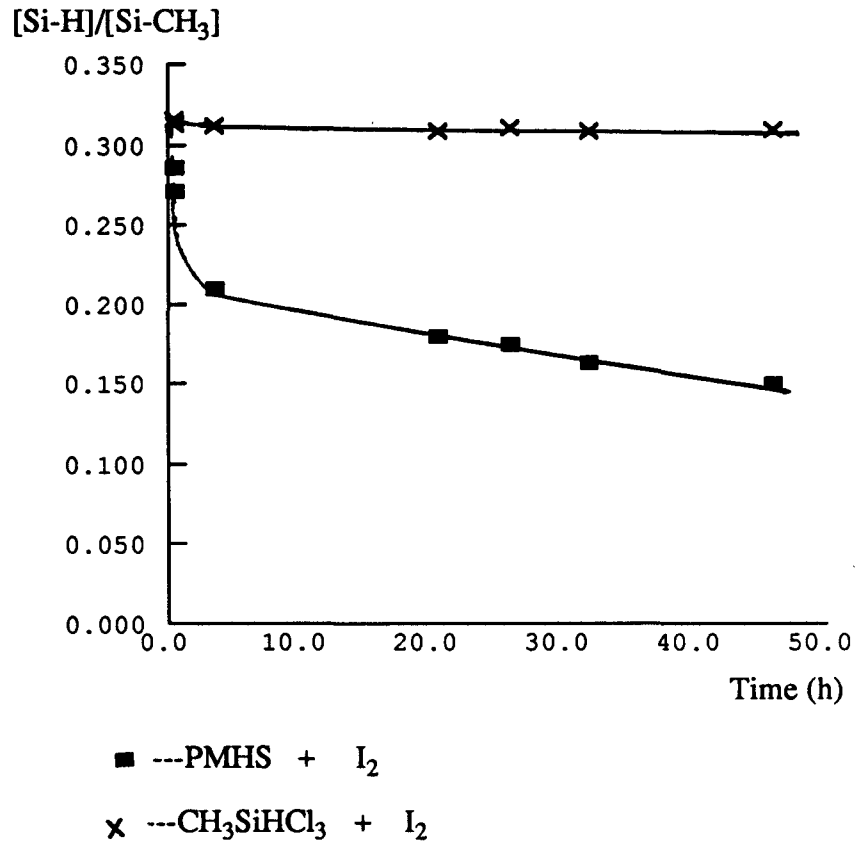
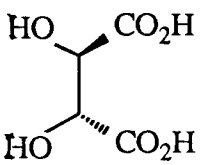


Figure 5-7 Plot of [Si-H]/[Si-CH_3] *versus* Reaction Time (h)

from the the group electronegativity calculation by Mullay[35]. According to his calculation (see also Part A of this thesis), the group electronegativity of -$SiCl_3$ has a value of 2.39; the group electronegativity of -$Si(OMe_3)$ equals 2.25. Thus, the group electronegativity of -$MeSiCl_2$ should be higher than that of -$MeSi(OEt)_2$. The strong electron-withdrawing ability of chloride greatly reduces the electron density on silicon and decreases the reactivity of Si-H bond in iodinaton.

5.6.2 Acid Catalyzed Alcoholysis

During the course of the study of the polymerization of tartaric acid and diethoxymethylsilane, an interesting reaction was observed:



$$+ \quad CH_3SiH(OEt)_2 \xrightarrow{THF} \text{Polymer} \quad + \quad H_2(g) \qquad \text{(i)}$$

The above reaction was a very fast one. After the addition of diethoxymethylsilane, a vigorous evolution of gas was observed and the reaction solution turned into a gel, possibly because the solvent was trapped inside the polymer network. The tartaric acid in above reaction plays roles both as reactant (hydroxyl groups) and catalyst (acid). IR showed that Si-H bond absorption at 2150 cm^{-1}decreases quickly with reaction time. A white precipitate was formed after stirring. The solubility tests show that this precipitate does not dissolve in H_2O, MeOH, CH_2Cl_2 or THF.

When tartaric acid was replaced by equal equivalents of acetic acid and ethanol which bear the same functional groups as tartaric acid, however, no hydrogen evolution was observed:

$$2\,EtOH + 2CH_3COOH + CH_3SiH(OEt)_2 \xrightarrow{THF} \text{No gas evolution!} \quad \text{(ii)}$$

Thus, there may be something unusual which initiated reaction (i). One possible explanation is that tartaric acid and diethoxymethylsilane formed a complex (Figure 5-8) during the transition state. This would lower the activation energy required in the reaction:

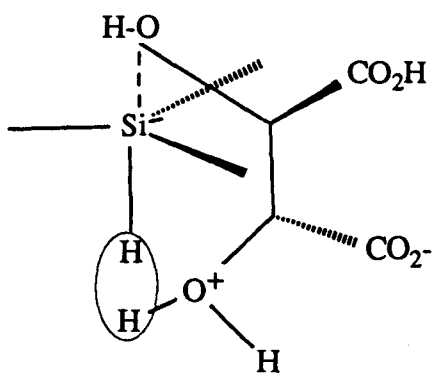


Figure 5-8

However, this penta-coordination is not possible in reaction (ii). An alternative explanation can be the difference of the strength of acidity between tartaric acid and acetic acid.

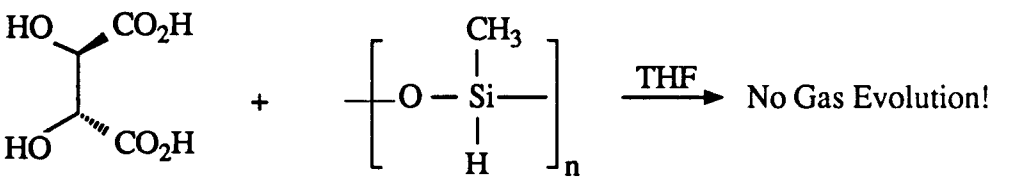
The pK_a values[78] for both acids are listed in Table 5-7. Tartaric acid is about 56 times stronger than acetic acid. Therefore, tartaric acid should be a more effective catalyst than acetic acid.

Table 5-7 pK_a Values of Acetic Acid and (2*R*, 3*R*)-Tartaric Acid

acid	pK_a (25°C)
Acetic acid	4.73
(2*R*, 3*R*)-tartaric acid	2.98 (pK_{a1}), 4.34 (pK_{a2})

Carboxylic acids usually do not react with hydrosilanes in the absence of catalysts[79]. The alcoholysis of hydrosilanes under carboxylic acid catalysis is rather poorly documented in literature.

When diethoxymethylsilane was replaced by PMHS in reaction (i), again, no hydrogen gas was observed:



The above reaction was followed by IR. IR shows that the reaction mixture still possesses strong Si-H absorption after four days.

Eaborn and his coworkers studies[55] the effect of silane structure on the rates of acidic solvolysis of hydrosilanes in 95% EtOH, the data are summarized in Table 5-8

Table 5-8 Acidic Solvolysis of R_3SiH Compounds in 95% EtOH

Relative Rate	30	130	220	180	150
R_3	Ph_3	$(p\text{-}ClC_6H_4)_3$	$(p\text{-}ClC_6H_4)Me_2$	$PhMe_2$	$(p\text{-}MeC_6H_4)Me_2$

They found that electron-release to silicon slightly hinders reaction and electron-acceptor enhances the reaction. Thus, the silicon atom must be more negative in the transition state than in the ground state. In the examination of the isotope effect, they found in dioxane containing 10 percent of water, that the reaction is 2.25 times faster when protium oxide is used than when deuterium oxide is used. This means that an H-O is being broken in the rate-determining step. According to the above observation, a transition state for the reaction was proposed by Eaborn:

$$[H_2O^{\delta+}\text{---}R_3Si^{\delta-}\text{---}H\text{---}H\text{---}OH_2^{\delta+}]$$

In our case, although the electron density at silicon in diethoxymethylsilane molecule may be higher than in PMHS as has already been discussed, the penta-coordination transition state (Figure 5-8), if it exists, must be more sterically demanding. The silicon atom in PMHS has two bulky group, its steric effect may overwhelm its electronic effect.

However, at this time, the above mechanistic discussions are only suggestions, further quantitative study is required in order to elucidate the mechanisms of the above reactions.

5.7 Concluding Remarks:

The synthesis of novel polymeric reducing reagents was attempted and the conditions of polymerization were examined.

^{29}Si NMR results show that ^{29}Si NMR is a useful tool in silicone polymer chemistry for structural studies.

Iodometric titration was also proven a useful method in quantitative determination of Si-H content.

The ^{1}H NMR kinetic study is one of the most convenient ways for kinetic study. The results show that the reactivity in iodination follows the order: $CH_3SiH(OEt)_2$ > PMHS > CH_3SiHCl_2.

In carboxylic acid catalyzed alcoholysis, the reactivities follow the order: $CH_3SiH(OEt)_2$ > PMHS.

The above observations show again that ligands the on silicon play important roles in determining silanes reactivity. Therefore, understanding the relationship between a silane's behaviors and the ligands on silicon will make modifications of silicon reagents with desired properties possible by changing the ligands on silicon.

General Experimental Part

CHAPTER 6

EXPERIMENTAL METHODS

6.1 Instrumental Techniques

^{1}H, ^{13}C NMR spectra were obtained on Bruker WM-200 (200 MHz) and Bruker WM-500 (500 MHz) spectrometers. For preliminary quality checks a Varian EM-390 (90 MHz) was used. Spectra were referenced either with TMS or solvent signals. ^{29}Si NMR spectra were performed on a Bruker WM-250 (250 MHz) spectrometer. Coupling constants J are recorded in Hertz (Hz). The abbreviations: s = singlet, d = doublet, t = triplet, q = quartets, m = multiplet are used in reporting the spectra. All the spectra were run at room temperature.

The ^{1}H NMR kinetic study was performed on a Bruker WM-200 (200 MHz) spectrometer using KINETICS program.

Solid state ^{29}Si NMR spectra were recorded on a Bruker MSL 100 (100 MHz) spectrometer operating with a spinning rate of 4KHz.

Infrared spectra were run on a Perkin-Elmer 283 spectrometer in $CDCl_3$ solution or neat film on a NaCl crystal.

Electron impact (EI) and chemical ionization (CI) mass spectra were recorded at 70 eV with a source temperature ca. 200°C either on a VG Micromass 7070F mass spectrometer equipped with a data system comprised of a PDP8A with VG2000 software or a VG analytical ZAB E mass spectrometer equipped with a VG11-250 data system. High resolution mass spectral (HRMS) data were obtained with the VG-ZAB-E instrument by the EI method.

6.2 Purification of Solvents

Carbon disulfide (CS_2) was prepared by first drying over anhydrous calcium chloride ($CaCl_2$) over night and then the drying reagent was removed by filtration. The carbon disulfide was further purified by distillation under nitrogen atmosphere.

Tetrahydrofuran (THF) and diethyl ether were freshly prepared as needed by distillation under a nitrogen atmosphere from benzophenone/potassium or benzophenone/ sodium.

Anhydrous *iso*-propanol was obtained by distillation under nitrogen after it was dried with sodium over night.

Dichloromethane (CH_2Cl_2) was freshly prepared as needed by distillation under a nitrogen atmosphere from calcium hydride (CaH_2).

6.3 Sources of Materials

Hydrogen hexachloroplatinate(IV) hydrate (H_2PtCl_6, Speier's catalyst) was obtained from Aldrich. A 0.1 M solution of Speier's catalyst was prepared with anhydrous *iso*-propanol. A 1 M solution of n-Bu_4NF (TBAF) in $CDCl_3$ was prepared by removing the THF from a 1 M TBAF solution in THF (from Aldrich) under reduced pressure and diluting the residue with the corresponding volume of $CDCl_3$. The starting material phenylacetylene was obtained from Aldrich or BDH and was purified by simple distillation before use.

$MeSiHCl_2$ was obtained from Dow Corning and was purified by distillation from CaH_2. Ethylene glycol from Fisher was distilled before use. Tartaric acid from Fisher was used without further purification. Ethyl orthoformate was obtained from Aldrich and was purified by distillation prior to use.

6.4 General Experimental Procedures for Part A

Due to the nature of easy hydrolysis of the compounds we dealt with, all work was performed under nitrogen atmosphere, using syringe techniques or in a glove-bag which was continuously purged with dry nitrogen.

6.4.1 Syntheses of Compounds 10-14

6.4.1a. (E)-β-(Trichlorosilyl)styrene 10*

This compound was prepared by the modified method of Benkeser[53]. To a mixture of phenylacetylene (105.7 mmol, 10.8 g) and Speier's catalyst (0.1 M H_2PtCl_6 in iso-propanol, 20 drops), was added $HSiCl_3$ (110.7 mmol, 15 g) within 5 minutes. The resulting mixture was stirred at room temperature under a nitrogen atmosphere for 36 hours. The reaction mixture turned dark brown which upon vacuum distillation gave 23.6 g of a clear colorless liquid (b.p. 85-86°C/4 mm Hg). Yield: 91.5%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.40 (d, 1 H, J = 18.8), 7.41 (d, 1 H J = 18.8), 7.31-7.50 (m, 5 H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 118.83, 127.67, 128.90, 130.49, 135.31, 151.48.

^{29}Si NMR (neat, 49.6 MHz): δ = -2.92

HRMS (M/Z): M^+ calc.: 235.9382; M^+ obs.: 235.9382

IR (neat): υ = 3100, 3080, 3050, 1680, 1580, 1500, 1460, 1340, 1300, 1230, 1205, 1190, 1080, 1035, 990, 840, 825, 740, 690, 610 cm^{-1}

***Note:** *(i) Prolonged reaction time and slightly excess of catalyst and $HSiCl_3$ will*

improve the yield considerably. (ii) Rapid addition of $HSiCl_3$ may cause an explosion and should be avoided.

6.4.1b. (E)-β-(Triacyloxysilyl)styrene 12

The (E)-β-silylstyrene, **12**, was prepared according to the modified method of Andrianov[34]. To (E)-β-(trichlorosilyl)styrene (9.68 mmol, 2.3 g), was injected excess freshly distilled acetic anhydride (15 ml) and the resulting mixture was stirred at room temperature under nitrogen atmosphere for 96 hours. The removal of acetyl chloride and the excess unreacted acetic anhydride by vacuum distillation resulted in a yellow liquid. Further distillation under reduced pressure yielded 2.5 g of a clear colorless liquid (b.p. 240°C at 0.001-0.005 mm Hg) which after standing at room temperature for a period of time, crystallized to give a needle-like crystal (m.p. 33-34°C).

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.18 (s, 9 H), 6.31 (d, 1 H, J = 19.4), 7.43 (d, 1 H, J = 19.4), 7.33-7.49 (m, 5 H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 22.45, 112.59, 127.37, 128.69, 129.89, 136.38, 152.49, 169.28.

^{29}Si NMR (neat, 49.6 MHz): δ = -59.86.

HRMS (M/Z): M^+ calc.: 308.0717, M^+ obs.: 308.0730.

IR (neat): υ = 3480, 3080, 3060, 3030, 2940, 1730-1780, 1610, 1580, 1500,1450, 1430, 1370, 1290, 1260, 1210, 1010, 950, 845, 820, 780, 735, 685, 625, 590 cm^{-1}.

6.4.1c. (E)-β-[Tris(trichloroacyloxy)silyl]styrene 13

This compound was prepared in a manner similar to that employed for compound 12 above. A mixture of (E)-β-(trichlorosilyl)styrene (4,5 mmol, 1.08 g) and trichloroacetic anhydride (23.2 mmol, 7.17 g) was added to a round bottomed flask outfitted with a condenser and connected to nitrogen pipeline. The mixture was stirred at room for 96 hours. After distilling off the trichloroacetyl chloride and excess trichloroacetic anhydride under vacuum, a yellow-brown, viscous residue was obtained. Yield: 1.64 g, 58.9%. Due to its moisture sensitivity and ease of polymerization, the product was used without further purification.

^{1}H NMR ($CDCL_3$, 200 MHz): δ = 6.37 (d, 1 H, J = 19.5), 7.71 (d, 1 H, J = 19.5), 7.42-7.61 (m, 5 H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 89.22, 105.85, 127.91, 128.97, 131.35, 135.05, 157.19, 157.55.

^{29}Si NMR ($CDCl_3$, 49.6 MHz): δ = -56.58.

MS (Chemical Ion): $(M + NH_4)^+$: 632(23), 632+2(71), 632+4(94), 632+6(69), 632+8(35), 632+10(13).

IR (neat): υ = 3070, 3040, 1680, 1605, 1478, 1500, 1450, 1300, 1270, 1215, 980, 870, 825, 790, 670 cm^{-1}.

6.4.1d. (E)-β-[Tris(trifluoroacyloxy)silyl]styrene 14

This compound was also prepared in a manner basically similar to that employed for compounds 13. A mixture of (E)-β-(trichlorosilyl)styrene (13 mmol, 3.1 g) and a large excess of trifluoroacetic anhydride (163 mmol, 34.2 g) and anhydrous diethyl ether** (4 ml) was stirred at room temperature under a nitrogen atmosphere for 6 days. Another

portion of trifluoroacetic anhydride (8 ml) was added and the resulting mixture was further stirred at room temperature for 2 days. Upon completion of the reaction, the trifluoroacetic chloride, the excess trifluoroacetic anhydride and diethyl ether were removed by rotary evaporator and a yellow brown liquid was obtained. Subsequent distillation, at reduced pressure gave a colorless liquid (b.p. 150°C at 0.005 mm Hg). Yield: 5.22 g, 85.4%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.29 (d, 1 H, J = 20.0), 7.63 (d, 1 H, J = 20.0), 7.41-7.68 (m, 5 H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 104.80, 113.91 (q, J_{CF} = 285.0 Hz), 128.00, 129.11, 131.72, 134.83, 153.39 (q, J_{CF} = 46.0 Hz), 158.11.

^{29}Si NMR (neat, 49.6 MHz): δ = -56.46.

HRMS(M/S): M^+ calc.: 469.9868; M^+ obs.: 469.9895

IR (neat): υ = 3080, 3060, 3040, 1800, 1610, 1580, 1500, 1450, 1360, 1235, 1170, 1120, 1030, 990, 890, 850, 820, 780, 730, 720, 700, 680 cm^{-1}.

****Note**: *(E)-β-(Trichlorosilyl)styrene and trifluoroacetic anhydride are immiscible. Ether was used so that the reaction could undergo in an homogeneous solution.*

6.4.1e. (E)-β-[Tris(trimethylsiloxy)silyl]styrene 11

The compound, **11**, was prepared using a modified version of the method of Seyferth[30]. A mixture of (E)-β-(trichlorosilyl)styrene (10.3 mmol, 2.46 g) in anhydrous THF (10 ml) was added to a stirred solution of potassium trimethylsilanolate (30.9 mmol, 3.95 g) in anhydrous THF (30 ml) at room temperature under a nitrogen atmosphere. A fairly

exothermic reaction ensued and the speed of the addition was controlled so as to maintain a gentle reflux of the solution. Potassium chloride precipitated during the addition. After the completion of the addition, the reaction mixture was continuously stirred and heated at reflux for 2 hours. The cooled mixture was then hydrolyzed with a 2% HCl aqueous solution (10 ml). The organic layer was washed with distilled water (10 ml) and dried with anhydrous Na_2SO_4. The removal of the THF by rotary evaporator yielded a light yellow liquid. This was distilled by fractionating column under reduced pressure to give a colorless liquid (b.p. 95°C at 0.001 mm Hg). Yield: 40%

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.00 (s, 27 H), 5.99 (d, 1 H, J = 19.0), 6.88 (d, 1 H, J = 19.0), 7.18-7.34 (m, 5 H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 1.80, 122.88, 126.62, 128.28, 128.53, 138.18, 145.99.

^{29}Si NMR (neat, 49.6 MHz): δ = 8.16, -77.4.

HRMS (M/S): M^+, calc.: 398.1587, M^+, obs.: 398.1592

IR (neat): υ = 3060, 3015, 2960, 2900, 1610, 1575, 1490, 1448, 1410, 1330, 1250, 1220, 1195, 1110-1040, 990, 870-830, 792, 750, 730, 682 cm^{-1}

6.4.1f. Compound 15

This compound was a side-product in the preparation of compound **11** and was obtained from the residue in above reaction. It was separated from the residue using alumina (neutral) chromatotron and petroleum ether as eluent. Contacting with alumina for a longer time will result in decomposition of the compound. The compound was completely absorbed by alumina when using alumina column chromatography for the separation.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.00 (s, 36 H), 6.03 (d, 2 H, J = 19.1), 6.94 (d, 2 H, J = 19.1), 7.12-7.30 (m, 10 H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 1.83, 122.48, 126.63, 128.27, 128.50, 138.12, 146.24.

^{29}Si NMR ($CDCl_3$, 49.6 MHz): δ = 8.54, -78.95.

HRMS (M/Z): M^+ calc.: 634.2276, M^+ obs.: 634.2277.

IR (neat): υ = 3080, 3060, 3050, 3000, 2960, 1610, 1575, 1495, 1450, 1415-1400, 1330, 1290, 1250, 1220, 1200, 1130, 1020, 990, 840, 810-790, 750, 730, 685 cm^{-1}

6.4.1g. Compound 16

This compound was also a by-product in the preparation of compound **11** and was separated from the reaction residue by alumina (neutral) chromatotron separation using petroleum ether as eluent. Similar to compound **15**, this compound decomposes when it contacts with alumina for a relative long time. Alumina column chromatography failed to separate the compound.

^{1}HNMR ($CDCl_3$, 200 MHz): δ = 0.00 (s, 45 H), 6.04 (d, 2 H, J = 19.1), 6.08 (d, 1 H, J = 19.2), 6.94 (d, 2 H, J = 19.1), 7.01 (d, 1 H, J = 19.2), 7.12-7.24 (m, 15 H).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 1.88 (two peaks overlapped), 122.15, 122.40, 126.64, 126.68, 128.21, 128.26, 128.43, 128.48, 138.09 (two peaks overlapped), 146.34, 146.51.

^{29}Si NMR ($CDCl_3$, 49.6 MHz): δ = 8.52, -78.78, -80.57.

MS (M/Z): 870 (100, M^+), 855 (85), 792 (10), 766 (28), 754 (12), 724 (14).

IR (neat): υ = 3080, 3075, 3040, 3000, 2970, 2900, 1610, 1575, 1490, 1450, 1415-1400, 1300, 1290, 1250, 1220, 1200, 1140-1010, 990, 890-790, 750, 730, 690, 600 cm^{-1}

6.4.2 Synthesis of Compounds 11s-14s and 11a-14a***

Compounds, **11s-14s** and **11a-14a** were obtained by the bromination of compounds **11-14**. The general bromination procedures for those compounds are as follows: 1 ml of an 0.5 M solution of each (E)-β-silylstyrene compound in carbon disulfide was cooled to -78°C (acetone/dry ice bath) and stirred under nitrogen atmosphere. Then, 1.1 equivalent of a 1 M solution of bromine in carbon disulfide, which was precooled to -78°C, was added in about 30 seconds (1 drop per 2 seconds) using syringe techniques. The resulting reaction mixture was stirred for another 15 minutes at -78°C. Then, it was transferred to an NMR tube and stored in a thermos flask at -78°C before allowing it to warm up to room temperature for recording the NMR spectrum.

Note: *(i) The dibromo-adducts* **12s-14s**, **12a-14a** *can easily decompose and can only survive for a short time at room temperature. In the contrast, the dibromo-adducts,* **11s** *and* **11a**, *are relatively stable and can stay at room temperature for 1-2 days without decomposition. However, at room temperature, compounds* **11s** *and* **11a** *can interconvert from one to the other and their relative ratio can change if they are let to stand at room temperature for a period of time. (ii) According to Seebach's nomenclature* [54], ***11s-14s *can be assigned to the u isomers and* **11a-14a** *to the l isomers respectively.*

6.4.2a. *u/l*-1,2-Dibromo-1-(triacyloxysilyl)-2-phenylethane 12s/12a (*syn*-/*anti*-Addition Bromination Products of Compound 12)

^{1}H NMR (CS_2, 200 MHz): δ = 2,06 (s, 3.0 H, *syn*), 2.30 (s, 6.0 H, *anti*), 4.33 (d, 0.33 H, J = 11.3, *syn*), 4.46(d, 0.67 H, J = 11.4, *anti*), 5.45 (d, 0.67 H, J = 11.4, *anti*),

5.51 (d, 0.33 H, J = 11.3, *syn*), 7.47-7.58 (m, 5 H).

^{13}C NMR (CS_2, 50.3 MHz): δ_{syn} = 21.96, 39.74, 56.60, 128.12, 128.77, 129.08, 140.10, 167.16. δ_{anti} = 22.42, 36.73, 50.13, 128.63, 128.93, 129.12, 139.93, 167.22.

^{29}Si NMR (CS_2, 49.6 MHz): δ_{syn} = -67.06, δ_{anti} = -65.58.

HRMS (M/Z): $(M-Br)^+$ calc.: 386.9894, $(M-Br)^+$ obs.: 386.9837.

6.4.2b. *u/l*-1,2-Dibromo-1-[tris(trichloroacyloxy)silyl]-2-phenylethane 13s/13a (*syn*-/*anti*-Addition Bromination Products of Compound 13)

^{1}H NMR (CS_2, 500 MHz): δ = 4.30 (d, 0.25 H, J = 10.0 *syn*), 4.44 (d, 0.75 H, J = 12.0 *anti*), 5.15 (d, 0.75 H, J = 12.0 *anti*), 5.23 (d, 0.25 H, J = 10.0 *syn*), 7.20-7.40 (m, 5 H).

^{13}C NMR (CS_2, 125.8 MHz): δ_{syn} = 36.50, 54.00, 126.67, 128.68, 129.53, 130.48, 137.67, 156.52. δ_{anti} = 33.58, 48.48, 127.95, 129.42, 129.65, 129.88, 138.27, 156.52.

^{29}Si NMR (CS_2, 49.6 MHz): δ_{syn} = -64.36, δ_{anti} = -62.54.

6.4.2c. *u/l*-1,2-Dibromo-1-[tris(trifluoroacyoxy)silyl]-2-phenylethane 14s/14a (*syn*-/*anti*-Addition Bromination Products of Compound 14)

^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 4.35 (d, 0.1, J = 10.3, *syn*), 4.54 (d, 0.9 H, J = 11.8, *anti*), 5.27 (d, 0.9 H, J = 11.8, *anti*), 5.29 (d, 0.1 H, J = 10.3, *syn*), 7.4-7.8 (m, 5 H).

^{29}Si NMR (CD_2Cl_2, 49.6 MHz): δ_{syn} = -63.36, δ_{anti} = -65.24.

MS (M/Z): $(M-Br)^+$ calc: 549, 549+2, $(M-Br)^+$ obs.: 549, 549+2

IR (neat): υ = 2960, 2150, 1770-1820, 1470-1550, 1360, 1230, 1180, 1110, 950, 900, 860, 750-690, 640 cm^{-1}.

6.4.2d. *u/l*-1,2-Dibromo-1-[tris(trimethylsiloxy)silyl]-2-phenylethane 11s/11a (*syn*-/*anti*-Addition Bromination Products of Compound 11)

^{1}H NMR (CS_2, 500 MHz): δ = 0.00 (s, 27 H), 3.48 (d, 0.88 H, J = 7.7, *syn*), 3.60 (d, 0.12, J = 9.0, *anti*), 5.06 (d, 0.12 H, J = 9.0 *anti*), 5.09 (d, 0.88 H, J = 7.7, *syn*), 7.13-7.34 (m, 5 H).

^{13}C NMR (CS_2, 50.3 MHz): δ_{syn}=1.99, 44.23, 58.00, 128.41, 128.53, 128.66, 140.83. δ_{anti} = 1.99, 42.54, 53.10, 126.88, 128.42, 128.84, 141.16.

^{29}Si NMR (CS_2, 49.6 MHz): δ_{syn} = 9.15, -83.49, δ_{anti} = 9.15, -82.76.

HRMS (M/Z): $(M-Br)^+$ calc.: 477.0771, $(M-Br)^+$ obs.: 477.0776.

IR (neat): υ = 2980, 2150, 1450-1550, 1250, 1030-1100, 900, 840, 750, 730, 690 cm^{-1}.

6.4.3 Elimination Reactions of Compounds 11s-14s and 11a-14a

The dibromo-adducts **11s-14s** and **11a-14a** were converted to (Z)- and (E)-β-bromostyrene, **8** and **9**, by fluoride induced elimination: the CS_2 in the reaction mixture of bromination was removed by rotary evaporator. Then an excess of a 1 M solution of TBAF (n-Bu_4NF) in $CDCl_3$was added. The mixture was stirred at room temperature under nitrogen for 15 minutes, and was transferred using syringe to an NMR tube for recording ^{1}H NMR spectrum. The ratios of **9** to **8** in Table 2-2 were determined by comparing the ^{1}H NMR peaks with those of a commercial sample (Aldrich).

(Z)-β-Bromostyrene **8**/(E)-β-bromostyrene **9**: **^{1}H NMR** ($CDCl_3$, 200 MHz): δ = 6.40 (d, 0.07 H, J = 8.0, Z), 6.73 (d, 0.93 H, J = 14.0, E), 7.08 (d, 0.93 H, J = 14.0, E), 7.63 (d, 0.07 H, J = 8.0, Z), 7.20-7.36 (m, 5 H).

6.5 General Experimental Procedures for Part B

6.5.1 Glycol-Silicone

To a solution of ethylene glycol (6.27 g, 0.1 mol) in CH_2Cl_2 (100 ml) was injected $MeSiHCl_2$ (10.5 ml, 0.1 mol) using a syringe at a speed about 1-2 drops per second under nitrogen atmosphere. The resulting mixture was allowed to stir at room temperature for 14-68 hours. The solvent was removed by rotary evaporator and the white solid material was further dried under vacuum at 4 mm Hg for about 12 hours. Typical recoveries were > 90%.

Entry 1:

^{1}H NMR(CD_3OD, 90 MHz): δ = 0.06-0.08 (m, 3H), 3.59 (s, 4H).

^{29}Si NMR (MAS, peak intensity given in parentheses): δ = -14.9 (6), -27.1 (2), -42.08 (60), -50.16 (35), -58.57 (17), -67.93 (4).

IR (film on NaCl): 3360, 2970, 2880, 2160, 1271, 1118, 1079, 1030, 901, 760 cm^{-1}.

Entry 4:

^{29}Si NMR (MAS): -42.08 (60), -50.16 (48), -58.57 (24), -67.93 (5).

IR (film on NaCl): 3360, 2955, 2880, 1264, 1030, 874, 758 cm^{-1}.

6.5.2 Synthesis of Compounds 45-47

6.5.2a. Compound 45

To an excess of 2-methoxyethanol (30.4 g, 0.4 mol) was added methyltrichlorosilane (15.0 g, 0.1 mol) at room temperature under nitrogen atmosphere. Heat was released during

the addition and a water-bath was used to keep the reaction temperature below 40°C. The resulting mixture was then heated gently for 5 hours and stirred at room temperature over night. A colorless liquid was resulted upon vacuum distillation (b.p. 109-110°C/3mm Hg). Yield: 18.0 g, 79%.

^{1}H NMR ($CDCl_3$, 90 MHz): δ = 0.03 (s, 3 H), 3,25 (s, 9 H), 3.37 (t, 6 H, J = 5.0), 3.79 (t, 6H, J = 5.0).

^{29}Si NMR (neat, 49.6 MHz): δ = -42.9.

MS: 253 (5, M-CH_3)$^+$, 193 (100), 162 (3), 149 (11), 135 (9), 105 (82), 91 (12), 75 (15).

IR (film on NaCl): 2980, 2940, 2880, 2825, 2735, 1458, 1402, 1372, 1335, 1295, 1266, 1201, 1130, 1090, 1027, 970, 843, 821, 787 cm^{-1}.

6.5.2b. Compound 46

To methyltrichlorosilane (15.0 g, 0.1 mol) was added 2-methoxyethanol (15.2 g, 0.2 mol) at a speed of about 1-2 drops per second at room temperature under nitrogen atmosphere. The resulting mixture was heated gently for 3.5 hours and then stirred at room temperature over night. A colorless liquid was isolated by distillation under reduced pressure (b.p 69-70°C). Yield: 15.0 g, 66%.

^{1}H NMR ($CDCl_3$, 90 MHz): δ = 0.45 (s, 3 H), 3,27 (s, 6H), 3.40 (t, 4 H, J = 5.0), 3.85 (t, 2 H, J = 5.0).

^{29}Si NMR (neat, 49.6 MHz): δ = -27.73.

MS: 193 (100, M$^+$-Cl), 153 (22), 105 (80), 75 (15).

IR (film on NaCl): 2990, 2890, 2830, 2730, 1459, 1405, 1372, 1337, 1298, 1270, 1202, 1130, 1070, 965, 846, 783 cm^{-1}.

6.5.2c. Compound 47

To methyltrichlorosilane (22.4 g, 0.15 mol) was added 2-methoxyethanol (11.4 g, 0.15 mol) at room temperature under nitrogen atmosphere. After completion of the addition, the reaction mixture was heated gently for 4 hour and then stirred at room temperature over night. A colorless liquid was obtained by vacuum distillation (b.p 35-36°C at 4 mm Hg). Yield: 20.0 g, 71%.

^{1}H NMR ($CDCl_3$, 90 MHz):δ = 0.73 (s, 3H), 3.33 (s, 3 H), 3.47 (t, 2 H, J = 5.0), 3.97 (t, 2 H, J = 5.0).

^{29}Si NMR (neat, 49.6 MHz): δ = -9.41.

MS: 188 (18, M^+), 173 (12), 153 (18), 143 (139), 129 (24), 115 (63), 113 (100).

IR (film on NaCl): 2920, 2890, 2825, 2725, 1458, 1406, 1371, 1293, 1270, 1250, 1201, 1140, 1090, 1028, 973, 892, 779, 720 cm^{-1}.

6.5.3 (2*R*, 3*R*)-Dimethyl Tartrate-Silicone

6.5.3a. (2*R*, 3*R*)-Dimethyl Tartrate 50

This compound was prepared according to the method of Brook[72]. The tartaric acid (30 g, 0.2 mol) was dissolved in methanol (150 ml). Chlorotrimethylsilane (47.7 g, 0.44 mol) was added to above mixture under a nitrogen atmosphere. The mixture was then stirred overnight at room temperature. The excess methanol was removed by rotary evaporator, and the crude product was distilled under reduced pressure giving a colorless viscous liquid

(b.p 140°C at 4 mm Hg) which crystallized at room temperature after a period of time. Yield: 30.2 g, 85%.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 5.52 (s,2 H), 5.76 (s, 6H), 6.49 (s, 2H).

^{13}C NMR ($CDCl_3$, 50.3 NMR): δ = 53.03, 72.12, 175.0.

MS (CI): 196 [100, $(M+NH_4)^+$], 179 [5, (M+1)].

IR: 3550, 3020, 1970, 1900, 1760-1730, 1440, 1310-1230, 1120-1090, 975, 890, 875, 825, 790, 690, 590 cm^{-1}.

6.5.3b. (2*R*, 3*R*)-Dimethyl Tartrate-Silicon (Method A)

To a solution of (2*R*, 3*R*)-dimethyl tartrate (8.9 g, 0.05 mol) in CH_2Cl_2 (100 ml) was injected $MeSiHCl_2$ (5.25 ml, 0.05 mol) at a speed about 1-2 drops per second under nitrogen atmosphere. The mixture was allowed to stir at room temperature for 24-48 hours. The solvent was removed by rotary evaporator. The resulting white solid material was dried further under reduced pressure at 4 mm Hg for 12 hours. Recoveries were > 90%.

Entry 6:

^{1}H NMR ($CDCl_3$, 200 MHz):δ = 0.49-0.87 (m, 3 H), 3.78 (s, 6 H), 4.77-5.27 (m,2 H).

^{29}Si NMR (CH_2Cl_2, 49.6 MHz): δ = -8.18, -22.14, -27.12, -41.62, -46.29.

IR: 3500, 2960, 2150, 1750, 1440, 1300-1200, 1150-1000, 910, 800-770, 700 cm^{-1}.

Entry 8:

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.48-0.77 (m, 3H), 3.78 (s, 6 H), 4.60-5.26 (m, 2 H).

^{29}Si NMR (CH_2Cl_2, 49.6 MHz): δ = -21.58, -26.99, -41.29, -45.82, -49.53.

IR: 3500, 2800, 2250, 2150, 1750, 1440, 1300-1200, 1150-1020, 910, 800, 730, 700 cm^{-1}.

6.5.3c. (2*R*, 3*R*)-Dimethyl Tartrate-Silicone (Method B)

(2*R*, 3*R*)-dimehtyl tartrate (3.0 g, 16.8 mmol)was dissolved in diethyl ether (60 ml). CH_3SiHCl_2 (1.94 g, 16.8 mmol)was injected to the solution under a nitrogen atmosphere. After the complete addition of CH_3SiHCl_2, triethylamine (3.41 g, 33.6 mmol) was added. Triethylamine hydrogen chloride salt precipitated instantly as triethylamine was added.

The mixture was stirred at room temperature under a nitrogen atmosphere for four hours. The salt was then removed by filtration and solvent was removed by rotary evaporator. The resulting white gel-like polymer was further dried under vacuum at 4 mm Hg over night.

Entry 12:

IR: 3500, 3010, 2960, 2920, 2860, 2195, 1720, 1440, 1355, 1280, 1120, 1000, 900, 770, 740, 700 cm^{-1}.

6.5.4 Determination of Si-H Content Using Iodometric Titration****

To an erlenmeyer flask the polymeric material (about 1.0000 g) and iodine (about 0.3000 g) were quickly weighed out. CH_2Cl_2 (15 ml) was added to dissolve the polymeric material and iodine. The erlenmeyer flask was quickly stoppered with a glass stopper and was left in the dark over night. The stopper and the wall of the erlenmeyer flask were carefully washed with methanol. The resulting solution was titrated with $Na_2S_2O_3$ aqueous solution. The end-point was established by the disappearance of the color of iodine.

****Note: *(i) $Na_2S_2O_3$ solution was prepared by $Na_2S_2O_3.5H_2O$ in distilled water. The concentration of the solution was calculated directly by the weigh of $Na_2S_2O_3.5H_2O$ without*

further standardization. (ii) The concentration of $Na_2S_2O_3$ solution was control between 0.03000 to 0.04000 N. (iii) Two parallel samples were titrated each time and mean value of the two titration results was used. (iv) Methanol was used to aid to establish the end point.

6.5.5 Iodination of Hydrosilanes - Kinetic Study By ^1H NMR

6.5.5a. Synthesis of Diethoxymethylsilane 51

This compound was prepared by the modified method of Shorr[75]. To the freshly distilled ethyl orthoformate (20.4 g, 0.138 mol) was added dichloromethylsilane (7.9 g, 0.069 mol) at a speed of 2-3 drops per second at room temperature under nitrogen atmosphere. Heat was released during the addition. A water-bath was used to maintain the reaction temperature below 40°C. The resulting mixture was stirred overnight and was distilled with a fractionating column. A colorless liquid was obtained (b.p. 94-100°C). Yield: 7.0 g, 75%.

^1H NMR ($CDCl_3$,200 MHz): δ = 0.17 (, 3 H, J = 1.7), 1.18 (t, 6 H, J = 8.3), 3.77 (q, 4 H, J = 8.3), 4.53 (q, 1 H, J = 1.7).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = -3.19, 18.21, 59.10.

MS: 134(M^+, 100), 120(73), 90(68), 77(28), 61(40).

IR: 2970, 2880, 2120, 1440, 1380, 1250, 1050-1150, 940, 870, 810, 760 cm^{-1}.

6.5.5b. Iodination of Hydrosilanes - Kinetic Study By ^1H NMR

To an NMR tube, a 0.5 ml solution of 0.4 M PMHS in $CDCl_3$ was injected under nitrogen atmosphere followed by the injection of 0.5 ml of 0.4 M iodine solution in $CDCl_3$. A stop watch started to record the the time when the above two began to mix. The NMR tube was put in a Bruker WM-200 (200 MHz) spectrometer and the ^1H NMR spectra were recorded at time

interval of about 90 seconds using the Kinetic program.

The kinetic studies of $CH_3SiH(OEt)_2$ and CH_3SiHCl_2 towards iodination were conducted under the same conditions using 0.4 M $CH_3Si(OEt)_2$ and 0.4 M CH_3SiHCl_2 in $CDCl_3$ respectively.

6.5.6 Acid Catalyzed Alcoholysis

Tartaric acid (0.30 g, 2 mmol) was dissolved in 10 ml THF. Diethoxymethylsilane (0.27 g, 2 mmol) was injected under nitrogen atmosphere at room temperature. Gas evolution from the above mixture occurred within 5 minutes after the addition of diethoxymethylsilane. The solution turned into a gel-like polymer. After about one hour, white polymeric material precipitated from the solution.

The solubility of white precipitate was tested with a variety of solvents. It did not dissolve in H_2O, MeOH, CH_2Cl_2, $CHCl_3$ or THF. The IR spectra show no absorption at 2280-2080 cm^{-1} region. A good quality IR spectrum was not obtained [IR (KBr pellet): 3500, 1750, 1270, 1130, 1080, 1020, 860, 780 cm^{-1}].

The cleavage of Si-H bond was followed by IR spectrometer. The solution of diethoxymethylsilane in THF was checked by IR at the very beginning. A strong absorption at 2150 cm^{-1} was observed. The reaction was followed by IR. The IR spectra show that the longer the reaction time, the weaker the absorption at 2150 cm^{-1} (relative intensity compared with other peaks). After two hours, the absorption at 2150 cm^{-1} had disappeared.

The above reaction was repeated under same conditions with PMHS (0.12 g, 2 mmol). No evolution of gas or white precipitate was observed. IR spectra were taken at reaction time about 10 minutes and reaction time about four days. Both spectra show strong absorption at 2150 cm^{-1}

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